Frozen Density Embedding Theory based computer simulations of electronic structure in condensed phase

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Abstract

This dissertation concerns numerical simulations of electronic properties (ESR and UV/Vis absorption) of molecules embedded in non-covalently bound environments (hydrogen-bonded clusters and mimics of protein active centers). The applied simulation methods are based on Frozen-Density Embedding Theory (FDET) and involve additional approximations concerning the choice of the frozen density and more technical factors. The applicability of these approximations was studied in view of the investigated spectroscopic properties. The simulations led to the demonstration that the observed cooperativity in the spectral shifts of 7-cis-hydroxyquinoline in hydrogen-bonded clusters, originate from mutual electronic induction of the molecules in the environment rather than from structural rearrangements in the environment. Concerning methodological developments, the computational protocols were developed for FDET calculations, which were shown to lead to equivalent results to the ones obtained form more costly conventional calculations: a) high-end wave-function based methods in the case of spectral shifts and b) conventional Kohn-Sham [...]
Frozen Density Embedding Theory Based Computer Simulations of Electronic Structure in Condensed Phase

THÈSE

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Le Doyen, Jean-Marc TRISCONE

N.B.- La thèse doit porter la déclaration précédente et remplir les conditions énumérées dans les "Informations relatives aux thèses de doctorat à l'Université de Genève".
To my parents Ioannis and Theodosia
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List of Publications


Notre travail sur les applications des méthodes basées sur la théorie “Frozen-Density Embedding Theory” (FDET) [1], à l’étude des propriétés dépendantes de la structure électronique (propriétés de l’absorption UV et de la Spectroscopie de Résonance Paramagnétique Électronique (RPE)). La FDET est une théorie basée sur la théorie de la fonctionnelle de la densité. La FDET emploie le potentiel d’enrobage orbitale-libre (appelé aussi le potentiel de la FDET; en anglais: “orbital-free embedding potential”) qui permet aux molécules de ressentir la présence de leur environnement. Pour une description détaillée regarder le Chapitre 3.

L’accent a été mis sur deux questions principales. La première est l’origine de la coopérativité des liaisons hydrogènes dans le cas des décalages de l’énergie d’excitation optique d’un chromophore en raison de son environnement en phase gazeuse. Les effets de la coopérativité des liaisons hydrogène sont importantes. On sait qu’elles influent les propriétés de l’état fondamental (décalage vers le rouge de la bande infrarouge). Pour des énergies d’excitation optique, les données expérimentales indiquent que l’insertion d’une molécule de liaison dans le milieu de la chaîne qui est liée par une liaison d’hydrogène au chromophore cis-7-hydroxyquinoline en phase gazeuse, provoque un décalage vers le rouge de l’ordre de 400 cm\(^{-1}\) des énergies d’excitation optique [2]. Il s’agit d’un effet important étant donné que la présence de l’environnement résulte à un changement total de 2200 cm\(^{-1}\). L’origine de l’effet, si elle est de nature géométrique ou électronique, ne peut pas être étudiée expérimentalement. En revanche, une expérience appropriée conçue théoriquement permet un tel examen. Une telle expérience a été menée en utilisant une méthode basée sur la FDET, (Chapitre 5) et les résultats indiquent fortement que l’effet coopératif est dû à l’induction électrostatique mutuelle des membres de la chaîne formée des molécules liées par liaisons d’hydrogène et non en raison de changements dans la géométrie. Il est noté que l’effet de la modification de la géométrie en raison de l’ajout de la molécule de liaison provoque un décalage vers le bleu de l’énergie d’excitation optique, mais l’effet global est dans la direction opposée. En outre, l’effet électronique devrait être plus pertinent dans les cas où les chaînes des liaisons hydrogènes sont soumises à des contraintes stériques, par exemple dans les bio-molécules. Les décalages calculés des énergies d’excitation verticales sur lesquelles les conclusions ci-dessus sont fondées, sont en bon accord avec les données expérimentales disponibles. Une comparaison totalement théorique des décalages verticaux des énergies d’excitation optique calculées avec des méthodes basées sur la FDET et des résultats de qualité de référence théorique pour la propriété de la structure électronique est également essentielle pour la consolidation de notre compréhension de la coopérativité. Une telle comparaison est devenue possible lorsque les données de référence réalisées avec “Equation-of-Motion Coupled-Cluster”, ont été mis à notre
disposition par le groupe de recherche du Prof. Piecuch de l’University of Michigan State et c’est pourquoi cette étude (Chapître 6 Partie II) suit chronologiquement notre travail original. On conclut que l’emploi des deux méthodes de calcul conduit aux résultats comparables. Ce fait renforce notre confiance dans notre compréhension de l’origine de la coopérativité des liaisons hydrogène. Il convient de noter que tous les résultats obtenus avec les méthodes basées sur la FDET, dépendent de la densité de l’environnement et des approximations impliquées dans l’expression du potentiel de la FDET. Cette dépendance change quand différentes propriétés de la structure électronique sont étudiées. Pour le cas des décalages spectraux, l’influence du premier facteur a été étudiée (Chapître 6) et il a été constaté que, pour une meilleure précision, pour les liaisons hydrogène, des complexes non-chargés, la densité de l’environnement doit être calculée avec la théorie de la fonctionnelle de la densité, des Kohn et Sham, sans la relaxation (Chapître 6). L’une des approximations précitées qui pourraient influer sur les résultats est celle sur la partie énergie cinétique du potentiel de la FDET et il a été dans le but de se concentrer sur son rôle. Nous avons étudié comment les conclusions de l’évaluation comparative mentionnée ci-dessus, sont affectées par l’utilisation de l’approximation récemment mis au point (Non-Decomposable Second Derivatives (NDSD)), qui prend en compte le comportement asymptotique du potentiel près des noyaux dans l’environnement. Notre analyse indique que l’effet de l’approximation sur les déplacements calculés de la propriété notamment spectroscopiques (énergie d’excitation verticale) est négligeable (Chapître 7). Ce fait vient renforcer notre conviction dans la reproduction des données de référence fiables avec des méthodes basées sur la FDET pour le cas des décalages spectraux. Pour la modélisation multi-niveau, la complexité de l’expression du potentiel d’enrobage est directement liée au coût de calcul des méthodes qui l’emploient. Il faut garder à l’esprit que la qualité de l’expression du potentiel affecte la qualité de toute étude de la structure électronique et non pas seulement l’énergie totale. Une des questions ouvertes avant le début de notre travail et la seconde zone d’intérêt de cette thèse, a été l’effet de négliger la répulsion de Pauli du potentiel enrobage et l’emploi d’une expression seulement électronostatique. Il y a des indications dans la littérature qui montrent que les termes non-électrostatiques sont nécessaires [3]. Lors de la préparation de cette thèse, nous avons fait une démonstration systématique de l’importance du rôle de la répulsion de Pauli et les avantages résultant d’en tenir compte, même sous forme approximative. Nous avons étudié deux propriétés spectroscopiques, l’énergie d’excitation verticale et la valeur iso-g de la spectroscopie RPE et en particulier dans leurs décalages en raison de la présence de l’environnement. Pour le cas du décalage de la valeur iso-g, il est montré que l’expression qui ne comprend que les termes coulombic pour le potentiel d’enrobage ne peut pas capturer le bon sens de l’effet et est également associée une instabilité numérique. En revanche l’utilisation du potentiel de la FDET, qui tient compte approximativement de la répulsion de Pauli, conduit une identification correcte de l’effet et la stabilité numérique (Chapître 8). Pour le cas des décalages des énergies d’excitation verticales, l’emploi d’un potentiel coulombic conduit à des résultats erronés, sauf si les calculs sont effectués avec un ensemble de base de petite taille (i.e. les ensembles de base STO-SZ et STO-DZ du logiciel ADF). En revanche, les données produites en employant le potentiel de la FDET ont un comportement stable numériquement (Chapître 9). Cette observation doit être ajoutée à l’intervention précédente sur son exactitude. Cette dernière analyse complète la troisième partie de cette thèse qui a souligné la nécessité de prendre en compte la répulsion de Pauli pour la modélisation de la structure électronique. En conclusion, les travaux menés au cours de notre recherche doctorale, soulignent
l’origine électronique de la coopérativité des liaisons hydrogène. En outre, cette thèse fournir des preuves convaincantes qui montrent que des méthodes basées sur la FDET devraient être le choix idéal pour le calcul des décalages des énergies d’excitation verticales et l’iso-g de la spectroscopie RPE. Ce choix est fait sur la base de la précision, la stabilité numérique des données et l’efficacité de calcul par rapport aux autres méthodes.
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Introduction

“Quantum Mechanics ... underlies nearly all of modern science and technology” (Stephen Hawking, A brief History of Time, 1988, Bantam, chap.4).

Quantum mechanics describes what classical Newtonian mechanics can not, phenomena in the atomic scale. The central mathematical object is the wave function that determines all of the physical properties of the system. To each physical observable corresponds one quantum mechanical operator, which upon application to the wave function gives the probabilistic result(s) for the observable at the particular state of the system. The accuracy of the theory is remarkable. The gyromagnetic ratio of the electron has been calculated with relativistic quantum field theory and the disagreement with experiment is smaller than one part per million (theoretical result reported in Ref. [4]; experimental result reported in Ref. [5]).

When relativity is not taken into account, the time-dependent Schrödinger equation describes the state of a system and its evolution in time [6]. Unfortunately solving analytically this equation is impossible for most systems and the path of approximate methods needs to be followed. P. M. Dirac acknowledged very early the need for approximate methods: “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of complex atomic systems without too much computation” (P.A.M. Dirac, Proceedings of the Royal Society, 123A, 1929, 714).

Two major nonempirical strategies have been developed since 1929 to provide approximate solutions to the Schrödinger equation. The first is the ab initio (i.e. from the beginning in Latin; a term that signals that fundamental principles are the basis) wave-function-based methods that involve the exact Hamiltonian and approximate wave function. The accuracy of certain representatives of the aforementioned school of methods [7] is of reference level. Unfortunately the computational cost is such that these methods are only applicable to small systems. A second nonempirical approach, Kohn-Sham Density-Functional Theory [8], that is founded on the Hohenberg and Kohn theorems [9], has been developed in the middle 60’s. The key object is the wavefunction corresponding to a fictitious non-interacting reference system. Even though Kohn-Sham Density-Functional Theory is exact, the analytical expression of the quantity (the exchange-correlation functional) is not known for the moment and in practice approximations that often rely on empirical parameters are employed. The accuracy of Kohn-Sham Density-Functional Theory [7] is in many cases very satisfactory and the computational cost relatively low (much lower than high level ab
initio wave function methods). These two facts lead to its intense use by the Physical and Chemical community.

Unfortunately Kohn-Sham Density-Functional Theory can not usually be applied to questions of the influence of the environment of molecules on their electronic structure properties. This is because again the computational cost becomes prohibitive. The role of the environment is important. It can affect the electronic structure properties of the core (embedded) molecule like the Electron Paramagnetic Resonance spectroscopy hyperfine coupling constants and g-values, the ligand-field splittings of f-levels in lanthanide impurities, Nuclear Magnetic Resonance spectroscopy shieldings, dipole and quadrupole moments, electronic excitation energies and frequency-dependent polarizabilities, and the reaction rates of chemical and biochemical reactions. Usually the core molecule is modelled using quantum-mechanical descriptors and the environment with classical mechanics [10]. This is the philosophy of computationally efficient quantum mechanics/molecular mechanics methods, the accuracy of which is in many cases unsatisfactory and in addition empirical, system-dependent parameters are usually involved. Frozen-Density Embedding Theory by Wesołowski and Warshel [1] makes possible the modelling of the effects of the environment in a nonempirical, accurate and computationally inexpensive way. It is founded on a quantum mechanical expression that has as key mathematical object the orbital-free embedding potential. It is orbital free because for a given positions and charges of the nuclei of the environment, the embedding potential is uniquely defined by the pair of two electron densities, that of the embedded system and that of its environment. The first of the two densities is expressed by Kohn-Sham orbitals or multi-determinantal wavefunction or one-electron density matrices, all quantum mechanical objects. The density of the environment, which is a well defined quantity in all scales, can be taken from expressions valid on any scale and of course from experiment. This makes Frozen-Density Embedding Theory suitable for multi-level modelling. The analytical expression of the embedding potential is not known except for a few analytically solvable cases and it needs to be approximated. It is the quality of the density of the environment and of the approximations that define the accuracy of the Frozen-Density Embedding Theory approach. The motivation for the work on this thesis is twofold: a) to apply Frozen-Density Embedding Theory on a physical chemistry question and make a systematic investigation of the factors that can affect the results produced and b) to better understand the role of the intermolecular Pauli repulsion in multilevel computer simulations of electronic structure by studying model systems.

The structure of the thesis is as follows: Part I provides a brief overview of the various quantum-mechanical formalisms on which the numerical methods used in this thesis are based. In Parts II-III, the original research which is the foundation of this thesis is described. In the first chapter of Part II, interpretation of UV-absorption spectroscopic data of hydrogen bonded clusters in gas phase using Frozen-Density Embedding Theory and the cooperative effect of hydrogen-bonded chains in the environment of a $\pi \rightarrow \pi^*$ chromophore (cis-7-hydroxyquinoline), are discussed. The origin of the cooperativity is a very interesting physical chemistry question (it is the reason for the increase of hydrogen bond strength) and considering the size of the complexes, it is appropriate that Frozen-Density Embedding Theory to be applied for the investigation. In the second chapter of Part II, the high accuracy and low computational cost of the Frozen-Density Embedding Theory approach for the theoretical predictions of spectroscopic data (shifts of vertical excitation energies) is presented. This is an essential demonstration of the quality of Frozen-Density Embedding Theory and comes to be added to previous work involving comparison with experiment. It is also a detailed
investigation of most factors that can affect (this varies depending on the electronic structure property under study) the embedding results. The materialization of this study became possible only when the reference theoretical data, which are associated with heavy computational cost, became available to us by the research group of Pr. Piecuch of the Michigan State University. The results produced by calculations involving Frozen-Density Embedding Theory, depend among other factors, on the approximation for the kinetic energy-dependent part of the orbital-free embedding potential. How the results for UV-spectroscopic data are affected by the employment of the most recently developed approximation (Non-Decomposable Second Derivatives) is presented in the Chapter 7 and completes the study of Chapter 6. In Part III, an investigation of the importance of taking into account the intermolecular Pauli repulsion in multi-level computer simulations of electronic structure properties of hydrogen bonded complexes, is described. This is a desired study because the neglect of the Pauli repulsion is associated with the most commonly used embedding approach [11] (Coulombic-only embedding) and also with a decrease of both computational cost and accuracy. This relation and a systematic demonstration of the pitfalls associated with Coulombic-only embedding is of interest to the computational chemistry community. The focus of Chapter 8 is on shifts of the Electron Paramagnetic Resonance Spectroscopy iso-g and of Chapter 9 on shifts of the first vertical excitation energy. Separate studies for each property are conducted as the importance of Pauli repulsion is property-dependent. In addition, in Chapter 8, the choice of the electron density of the environment is also studied and thus the Parts II and III of this thesis provide a complete analysis of the most factors that can influence the quality of Frozen-Density Embedding Theory based studies of embedded systems. The summary and conclusions of this work follow.
Part I.
Theory: Methods and Observables
General introduction to Part I:

Part I of this thesis aspires to provide a short description of the key elements of the theories used for the original research of the author described in Parts II and III. Chapters 1 and 2 deal with ground- and excited-state Density-Functional Theory respectively. The third Chapter presents Frozen-Density Embedding Theory and the Part closes with some points on Electron Paramagnetic Resonance spectroscopy and theoretical predictions of its iso-g property. Hartree atomic units (a.u.) (i.e. $\hbar = 1$) are used throughout.
Chapter 1: Ground State Density-Functional Theory

1.1 Hohenberg-Kohn theorems

Density-Functional Theory (DFT) based methods make possible the approximate description of many electron systems based on a physical observable, the electron density \( \rho \), which compared to the wave-function is a much less complex mathematical object, as it has three dimensions in place of \( 4N \) (where \( N \) is the number of the electrons; one dimension is associated with the spin) and it is well defined in all scales.

\[
\rho(\vec{r}) = \int \ldots |\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, \sigma_1, \sigma_2, \ldots, \sigma_N)|^2 d\vec{r}_2 \ldots d\vec{r}_N d\sigma_1 \ldots d\sigma_N, \tag{1.1}
\]

where \( \vec{r} \) is position vector and \( N \) stands for number of electrons.

In the DFT framework the nuclei are treated as fixed - Born-Oppenheimer approximation assumed -. The electrons interact with each other and with an external potential \( v_{\text{ext}} \), which for the case of the uniform electron gas, is the uniformly distributed positive charge, and for a molecule, it is the attraction to the nuclei (it must be clarified that there is no mathematical restriction about what \( v_{\text{ext}} \) can be). The legitimacy of DFT is based in the two Hohenberg-Kohn theorems. The first is an existence theorem. It states that “the density \( \rho_0(\vec{r}) \) corresponding to a non-degenerate ground state specifies the external potential \( v_{\text{ext}}(\vec{r}) \) up to a constant” [9]. The one-to-one mapping between the \( v_{\text{ext}} \) and \( \rho \) does not assure that such a mapping exists for every density. In reality it exists only for a special and relatively small class of electron densities which are called (\( v \)-representable) and the conditions that need to be satisfied for \( v \)-representability remain unknown. If the \( v \)-representable electron density corresponds to a non-degenerate ground state and is given from a Hamiltonian that neglects repulsion between electrons, it is called “noninteracting pure-state \( v \)-representable”. A reformulation by Levy [12], the “Levy constrained search formulation”, removes the requirement for \( v \)-representability and introduces the \( N \)-representability condition which is much weaker. A density satisfies this condition if it satisfies [13]:

\[
\rho(\vec{r}) \geq 0, \quad \int \rho(\vec{r}) = N, \quad \int |\nabla \rho(\vec{r})|^2 < \infty. \tag{1.2}
\]

Any density that can be obtained by an anti-symmetric wave function belongs to this class. “Levy constrained search” removes also the Hohenberg-Kohn ground state non degeneracy requirement as only one set of degenerate wave functions, the one corresponding to the ground state electron density, is chosen. The “constraint-search” two step minimization formula is as follows:

\[
E_0 = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V} + \hat{V}_{\text{ext}} | \Psi \rangle = \min_{\rho} \left\{ \min_{\Psi} \left[ \langle \Psi | \hat{T} + \hat{V} + \int v_{\text{ext}}(\vec{r}) \rho(\vec{r}) d\vec{r} \right] \right\} = \min_{\rho} F_L[\rho] + \int v_{\text{ext}}(\vec{r}) \rho(\vec{r}) d\vec{r} = \min_{\rho} E[\rho]. \tag{1.3}
\]
1.2. Kohn-Sham Density-Functional Theory

... where \( \hat{T} \) is the kinetic energy operator, \( \hat{V} \) is the electron-electron interaction operator and \( \hat{V}_{\text{ext}} \) is the operator corresponding to the attraction of the electrons to the positive charges.

The inner minimization in the second line searches for all wave functions that give \( \rho \). The outer minimization releases this requirement. If \( \rho \) is \((\nu\text{-representable})\) \( F_{\nu}[\rho] = F_{HK}[\rho] \).

Much more information can be extracted from the electron density \([14]\). Integration of \( \rho \) over all space gives the total number of electrons:

\[
N = \int \rho(\vec{r})d\vec{r}.
\] (1.4)

Additionally, at the local maxima of \( \rho \), which are cusps, the nuclei are found. The atomic number \( Z \) of each nucleus can be calculated using the Kato cusp condition \([15]\):

\[
\frac{\partial \bar{\rho}(r_A)}{\partial r_A} \bigg|_{r_A=0} = -2Z_A \rho(r_A).
\] (1.5)

As the Hamiltonian of the Schrödinger equation depends on external potential and the total number of electrons, the ground state electron density defines the Hamiltonian, which determines all states (ground state and excited states). A total energy expression depending explicitly on the electron density, i.e., a functional of the density, \( E_{\nu}[\rho] \), exists generally and this is assured by the first Hohenberg-Kohn theorem. For \((\nu\text{-representable})\) electron densities Hohenberg-Kohn introduced the \( F_{HK}[\rho] \) functional which is system-independent:

\[
F_{HK}[\rho] = E_{\nu}[\rho] - \int v_{\text{ext}}(\vec{r})\rho(\vec{r})d\vec{r}.
\] (1.6)

An indication about how to predict \( \rho_0(\vec{r}) \) is given by the second Hohenberg-Kohn theorem, which states that for a trial density, that satisfies the conditions:

\[
\rho \geq 0, \quad N = \int \rho(\vec{r})d\vec{r},
\] (1.7)

the total energy functional corresponds to an energy higher or equal to the true ground state energy. Thus candidate \( \rho \)s that give relatively lower energy are approaching more the correct one.

1.2 Kohn-Sham Density-Functional Theory

The Hohenberg-Kohn theorems do not indicate a method to calculate the total energy in a relatively computationally less expensive way than the wave function based methods, because at the end, the Schrödinger equation needs to be solved and the difficulty originating in the electron-electron interaction term in the correct Hamiltonian to be faced. Kohn and Sham \([8]\) proposed as a starting point, a Hamiltonian for a non-interacting system of electrons to be used instead of the true Hamiltonian. A fictitious system of non-interacting electrons that has the same density as the true, interacting system has the same total energy. Also the position and charges of the nuclei are identical. The total energy expression is:
\[ E_{KS}[p] = T_s[p] + J[p] + E_{xc}[p] + \int v_{ext}(\vec{r})\rho(\vec{r})d\vec{r}, \]

where \( T_s[p] \) is the kinetic energy of the non-interacting system, \( J[p] \) is the classical expression for the electron-electron repulsion, \( E_{xc}[p] \) is the so-called “exchange-correlation” functional that includes the correction for the classical self-interaction energy and the difference in kinetic energy between the fictitious non-interacting system and the real, interacting one (see below).

In Kohn-Sham DFT, orthonormal one-electron functions \( \phi_i \) (Kohn-Sham orbitals) are employed. The electron density is given by:

\[ \rho(\vec{r}) = \sum_{i=1}^{N} |\phi_i[p](\vec{r})|^2, \]

\( T_s[p] \), the kinetic energy of the non-interacting system, is described exactly:

\[ T_s[p] = \sum_{i=1}^{N} \langle \phi_i[p](\vec{r}) | -\frac{1}{2} \nabla^2 | \phi_i[p](\vec{r}) \rangle, \]

where \( \phi_i[p](\vec{r}) \) are the orbitals that minimize the expectation value of the kinetic energy operator for the non-interacting wavefunction yielding \( \rho \):

\[ \langle \phi_i[p](\vec{r}) | -\frac{1}{2} \nabla^2 | \phi_i[p](\vec{r}) \rangle \]

for a given electron density \( \rho \) that obeys Eq. (1.10).

Additionally, the analytical form of \( J[p] \) is known:

\[ J[p] = \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}d\vec{r}', \]

\( E_{xc}[p] \) is a much more complicated object. It is defined as:


where \( T[p] \) and \( V[p] \) are the kinetic energy and the electron-electron interaction functionals for the true system. The exact expression for the exchange-correlation functional remains elusive and intensive research continues to take place for its determination. In practical calculations \( E_{xc}[p] \) needs to be approximated. The most simple approximation is the Local Spin Density approximation (LSDA) [8] in which the exchange-correlation energy density at a given point in space is calculated from the electron density at this given point. The generalized gradient approximation introduces first derivatives of the density (GGA). The complexity of the approximations increases with the meta-GGA class that adds second derivatives of the density or terms that depend on the kinetic energy density. Hyper-GGA involves the exact exchange energy density. Exact exchange and correlation obtained from Perturbation Theory are to some extent combined in another class of approximations. The five levels of complexity in the approximation of \( E_{xc}[p] \), a Jacob’s Ladder are comprehensively discussed in Ref. [16]. The Kohn-Sham, one electron equation is:

\[ \left( -\frac{1}{2} \nabla^2 + v_{eff}^{KS}[p](\vec{r}) \right) \Phi_i(\vec{r}) = \epsilon_i \Phi_i(\vec{r}), \]

where

\[ v_{eff}^{KS}[p](\vec{r}) = \sum_{i=1}^{N_{ext}} \frac{Z_i}{|\vec{r} - \vec{R}_i|} + \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|}d\vec{r}' + \frac{\delta E_{xc}[p]}{\delta \rho(\vec{r})}, \]
is the Kohn-Sham effective potential. For the derivation of Eqs. (1.14) and (1.15) the additional assumption, that the functional derivatives exist has been made. The N one electron Kohn-Sham equations are solved in a self-consistent way because \( v_{\text{eff}}^{\text{KS}} \) depends on \( \rho(r) \) though the exchange-correlation potential \( \delta E_{\text{xc}}[\rho] \) and \( \int \frac{\rho(r')}{|r-r'|} dr' \). One starts with “guessed” \( \phi \)s (and thus a “guessed” electron density), calculates the effective potential and then solves the Kohn-Sham equations and finds new \( \phi \)s. The process is repeated until convergence is reached.
Chapter 2: Linear-Response Time-Dependent Density-Functional Theory

In 1984 Runge and Gross extended the Hohenberg-Kohn theorems to the time-independent case [17]. This extension is not further discussed in this part as the focus is on Linear-Response Time-Dependent Density-Functional Theory (LR-TDDFT) that was employed for the research associated with this thesis.

For a small time-dependent external perturbation $v_{\text{appl}}(t)$, that does not change significantly the ground state electronic structure of the system, the LR-TDDFT can be applied [18]. In this case only the linear response of the system is analyzed.

We start from the spin-unrestricted time-dependent Kohn-Sham equations in the adiabatic approximation (i.e. $\frac{\delta E_{\text{XC}}[\rho^\alpha, \rho^\beta]}{\delta \rho^\alpha}$ depends on time only through the time-variation of $\rho$):

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}, t) + \int \frac{\rho(\vec{r}', t)}{\vert \vec{r} - \vec{r}' \vert} d\vec{r}' + \frac{\delta E_{\text{XC}}[\rho^\alpha, \rho^\beta]}{\delta \rho^\alpha} \right] \psi_\sigma(\vec{r}, t) = i \frac{\partial}{\partial t} \psi_\sigma(\vec{r}, t), \quad (2.1)$$

where $\sigma$ is the spin coordinate, $\rho^\alpha$ is the density of the spin up electrons and $\rho^\beta$ the density of the spin down electrons, $\psi_\sigma(\vec{r}, t)$ are the Kohn-Sham spin-orbitals.

The total electron density is given by:

$$\rho_\sigma = \sum_i f^\alpha_i |\psi^\alpha_i(\vec{r}, t)|^2, \quad (2.2)$$

where $f^\alpha_i$ is the occupation number of the $i$-th spin-orbital.

It is convenient to use the Fourier transform $v_{\text{appl}}(\omega)$ (where $\omega = 2\pi v$ is the radial frequency and $v$ is the temporal frequency) of $v_{\text{appl}}(t)$ from the time domain to the frequency domain:

$$v_{\text{appl}}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp[-i\omega t] v_{\text{appl}}(\omega) d\omega, \quad (2.3)$$

The small change of the electron density $\delta \rho_\sigma(\vec{r}, \omega)$ due to the perturbation, can be expressed for the case of the linear response approximation using the Kohn-Sham spin-orbitals calculated in the absence of perturbation:

$$\delta \rho_\sigma(\vec{r}, \omega) = \sum_{\tau} \sum_{ij} \psi_i(\vec{r}) \delta P_{j\tau}(\omega) \psi_j^*(\vec{r}), \quad (2.4)$$

where $\sigma = \alpha, \beta$, $\tau = \alpha, \beta$, $\delta P_{j\tau}(\omega)$ is the time-dependent linear-response of the coefficients matrix and $i, j$ run over all occupied and unoccupied spin-orbitals.
The effect of $v_{\text{appl}}(t)$ to the components of Eq. (2.1) is as follows:

$$v_{\text{ext}}(\vec{r}, t) \rightarrow v_{\text{ext}}(\vec{r}, t) + v_{\text{appl}}(t),$$

Eq. (2.5)
as $\rho_{\sigma}(\vec{r}, t) \rightarrow \rho_{\sigma}(\vec{r}, t) + \delta \rho_{\sigma}(\vec{r}, t)$

$$
\int \frac{p(\vec{r}, t)}{|\vec{r'} - \vec{r}|} d\vec{r'} \rightarrow \int \frac{p(\vec{r}, t)}{|\vec{r'} - \vec{r}|} d\vec{r'} + \int \frac{\delta p(\vec{r}, t)}{|\vec{r'} - \vec{r}|} d\vec{r'},
$$

Eq. (2.6)
and

$$
\frac{\delta E_{\text{XC}}[p^\alpha, p^\beta]}{\delta \rho_{\sigma}} \approx \frac{\delta E_{\text{XC}}[p^\alpha, p^\beta]}{\delta \rho_{\sigma}} + \sum_{\tau=\alpha, \beta} \int \frac{\delta^2 E_{\text{XC}}[p^\alpha, p^\beta]}{\delta \rho_{\sigma}(\vec{r}) \delta \rho_{\tau}(\vec{r}')} \delta \rho_{\tau}(\vec{r}') d\vec{r}'.
$$

Eq. (2.8)

In the above expression the adiabatic approximation is assumed i.e. the right hand side terms of Eq. (2.8) depends on time only through the time-variation of $\rho$.

We move directly to the expression linking $\delta P_{ij\sigma}$ to the properties of the system:

$$
\delta P_{ij\sigma}(\omega) = \frac{f_{j\sigma} - f_{i\sigma}}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma})} \left[ v_{\text{appl},ij\sigma}(\omega) + \sum_{\beta\ell} K_{ij\sigma,\beta\ell} \delta P_{\beta\ell}(\omega) \right].
$$

Eq. (2.9)

where $K$ is the coupling matrix that describes the linear response of the coulomb and exchange-correlation parts of the effective Kohn-Sham potential to the changes of $\rho$ due to the perturbation and is given by the following equation:

$$
K_{ij\sigma,\beta\ell} = \int \int \psi_{i\sigma}(\vec{r}) \psi_{j\sigma}(\vec{r}) \frac{1}{|\vec{r'} - \vec{r}|} \psi_{\beta\ell}(\vec{r'}) \psi_{\beta\ell}(\vec{r'}) d\vec{r} d\vec{r'} + \int \int \psi_{i\sigma}(\vec{r}) \psi_{j\sigma}(\vec{r}) \frac{\delta^2 E_{\text{XC}}[p^\alpha, p^\beta]}{\delta \rho_{\sigma}(\vec{r}) \delta \rho_{\tau}(\vec{r}')} \psi_{\tau\ell}(\vec{r}) \psi_{\tau\ell}(\vec{r'}) d\vec{r} d\vec{r'}. \quad (2.10)
$$

Eq. (2.9) provides a link between the assumed linear response of a given system with a given small time-dependent perturbation $v_{\text{appl}}$ by employing properties of the unperturbed system (the spin-orbitals and the second derivatives of the exchange-correlation functional with respect to the electron density).

For a particular perturbation caused by a time-dependent electric field $\vec{E}$ in the $z$-axis, the induced electric dipole along a given axis $u$ (where $u=x, y, z$) is:

$$
\delta \mu_u(\omega) = -\sum_{ij\sigma} u_{ij\sigma} \delta P_{ij\sigma}(\omega). \quad (2.11)
$$

The dynamic frequency dependent polarizability $\alpha$ is given by the following equation:

$$
\alpha_{uc}(\omega) = -2 \sum_{ij\sigma} u_{ij\sigma} \frac{\text{Re} \delta P_{ij\sigma}(\omega)}{\epsilon_c(\omega)}. \quad (2.12)
$$
where $\text{Re}\delta \hat{P}_{i\sigma}(t)$ is the Fourier transform of the real part of $\delta \hat{P}_{i\sigma}(t)$. After solving Eq. (2.9) and separating the real part we take the following expression for the dynamic polarizability:

$$
\alpha_{\text{d}}(\omega) = 2\mu^2 \hat{S}^{-\frac{1}{2}} \left[ \hat{\Omega} - \omega^2 \hat{I} \right]^{-1} \hat{S}^{-\frac{1}{2}} \omega,
$$

where $\hat{I}$ is the identity matrix. The matrix $\hat{S}$ is defined as:

$$
S_{ij\sigma,kl\tau} = \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} \left( \varepsilon_{k\tau}^{(f)} - \varepsilon_{l\tau}^{(f)} \right) \left( \varepsilon_{l\tau}^{(f)} - \varepsilon_{k\tau}^{((f))} \right).
$$

Using the above expression $\alpha_{\text{d}}$ can be calculated for any frequency $\omega$. There exist some $(\omega)$ for which the matrix $\hat{\Omega} - \omega^2 \hat{I}$ becomes singular. These values of $(\omega)$ combined with the sum-over-states (SOS) theorem of optical physics lead to the following expression for $\bar{\alpha}$:

$$
\bar{\alpha}(\omega) = \frac{1}{3} \sum_{i=1}^{3} \alpha_{ii}(\omega) = \frac{1}{\omega^2 - \omega^2},
$$

where $\alpha_{ii}$ is the trace of the tensor $\alpha$, the poles $\omega_f = E_f - E_0$ are the vertical excitation energies and the residues $f^2 = \frac{2}{3} (E_f - E_0) \left( |\langle \psi_0 \xi \psi_f \rangle|^2 + |\langle \psi_0 \eta \psi_f \rangle|^2 + |\langle \psi_0 \zeta \psi_f \rangle|^2 \right)$ are the oscillator strengths. Consequently, if accurate excitation energies and oscillator strengths were available, we would be able to calculate the mean polarizability. In practice it is easier to calculate the polarizability directly and use Eq. (2.16) to calculate excitation energies and oscillator strengths. Casida showed [18] that by comparing the formula for the dynamic polarizability with the SOS expression for the mean polarizability, the excitation energies and oscillator strengths can be taken from the following pseudoeigenvalue equation (in which the eigenvalues are the excitation energies and the eigenvectors the oscillator strengths):

$$
\hat{\Omega} F_i = \omega_f^2 F_i.
$$

LR-TDDFT is applied with reasonable success to closed-shell systems. There are strong indications in the literature that the quality of the results obtained with LR-TDDFT decreases as the size of the system under study increases [19–23]. In addition, “density transfer excitations” are underestimated, high-energy diffuse states appear often artificially not bound and explicit many-electron excitations can not be included successfully (see Ref. [24]). LR-TDDFT can also be applied to open-shell systems, as it can be formulated to allow fractional occupancies and different orbitals for different spin. The aforementioned application is associated with both successes and failures (see Ref. [25]).
Chapter 3: Frozen-Density Embedding Theory (FDET)

Note: Due to the format of this thesis the presentation of the Frozen-Density Embedding Theory (FDET) is included in this Chapter and also in the “Methods Section” of the reprint of the publication: “Fradelos, G.; Lutz, J.J.; Wesolowski, T.A.; Piecuch, P.; Włoch, M. Embedding vs supermolecular strategies in evaluating the hydrogen-bonding-induced shifts of excitation energies J. Chem. Theory Comput., 2011 7, 1647 (Chapter 6)”. The author emphasizes that at the time of the preparation of the aforementioned article, the need for a detailed presentation of FDET as part of a publication (book chapters were already available) was apparent and this work satisfied it.

3.1 Ground State

The Frozen-Density Embedding Theory (FDET) [1, 26–29] provides basic equations for the variational treatment of a quantum-mechanical subsystem embedded in a given electronic density. Various FDET-based approaches [1, 28–38], differing in the way the environment density is generated, the choice made for the approximations for the relevant density functionals, or the choice for the quantum-mechanical descriptors for the embedded subsystem, are in use today. Below we outline the basic elements of the FDET methodology.

- **Basic variables.** The total system $AB$, consisting of a molecule or an aggregate of molecules of interest, $A$, embedded in the environment $B$ created by the other molecule(s) is characterized by two types of densities. The first one is the density of the embedded molecule(s), $\rho_A(\vec{r})$, which is typically represented using one of the following auxiliary quantities: (i) the occupied orbitals of a non-interacting reference system $\{\phi_i^{(A)}(\vec{r}), i = 1, \ldots, N_A\}$ [1], (ii) the occupied and unoccupied orbitals of a non-interacting reference system [26], (iii) the interacting wavefunction [28], or (iv) the one-particle density matrix [29]. The second one is the density of the environment, $\rho_B(\vec{r})$, which is frozen for a given electronic problem (“frozen density”) (see Figure (3.1)).

---

1A special note goes to the notation used for the orbital-free embedding potential of FDET: $v^{\text{eff}}_{\text{emb}}[\rho_A, \rho_B; \vec{r}]$ (see text). The notation intends to show that the potential contains terms that are functionals or bifunctionals of the electron densities but also a term that depends only on the position. This notation appeared in numerous publications in the past and is adopted in this thesis as well to avoid confusion. A notation of the type: $v^{\text{eff}}_{\text{emb}}[\rho_A, \rho_B](\vec{r})$ is suitable for the $v^{\text{emb}}_{\text{eff}}[\rho_A, \rho_B](\vec{r})$ term of the orbital-free embedding potential (see text) that is indeed a bi-functional of the two electron densities.
Figure 3.1: Electron densities of the core subsystem ($\rho_A$) and the environment ($\rho_B$)

- **Constrained search.** The optimum density $\rho_A(\vec{r})$ of the system $A$ embedded in the environment $B$, represented by the frozen density $\rho_B(\vec{r})$ satisfying

$$\int \rho_B(\vec{r}) d\vec{r} = N_B,$$

is obtained by performing the following constrained search:

$$E_A^{\text{emb}}[\rho_B] = \min_{\rho \geq \rho_B} E_{\text{HK}}[\rho] = \min_{\rho_A} E_{\text{HK}}[\rho_A + \rho_B],$$

subject to the condition

$$\int \rho(\vec{r}) d\vec{r} = N_A + N_B$$

or

$$\int \rho_A(\vec{r}) d\vec{r} = N_A,$$

where $E_{\text{HK}}[\rho]$ in Eq. (3.2) is the Hohenberg-Kohn energy functional defined in the Levy constrained search).

- **Constrained search by modifying the external potential.** In practice, the search for the optimum density $\rho_A$, defined by Eq. (3.3), is conducted by solving the following equation:

$$\left[ \hat{H}_0 + \hat{V}_{\text{emb}} \right] |\Psi_{\text{emb}}\rangle = E_{\text{emb}} |\Psi_{\text{emb}}\rangle,$$

in which $\hat{H}_0^{(A)}$ is the environment-free Hamiltonian of the isolated system $A$ and $\hat{V}_{\text{emb}} = \sum_{i=1}^{N_A} v_{\text{emb}}(\vec{r}_i)$, where $v_{\text{emb}}(\vec{r})$ has the form of a local embedding potential.
3.1. Ground State

\( v_{emb}^{eff} (\vec{r}) \), determined by the pair of densities \( \rho_A (\vec{r}) \) and \( \rho_B (\vec{r}) \) and designated by \( v_{emb}^{eff} [\rho_A, \rho_B ; \vec{r}] \).

- **Orbital-free embedding potential.** As shown earlier [28], the relationship between the local potential \( v_{emb}^{eff} [\rho_A, \rho_B ; \vec{r}] \) (the notation \( v_{emb}^{eff} [\rho_A, \rho_B ; \vec{r}] \) intends to show that the potential contains terms that are functionals or bifunctionals of the electron densities but also a term that depends only on the position. This notation appeared in numerous publications in the past and is adopted in this thesis as well, to avoid confusion.) and densities \( \rho_A (\vec{r}) \) and \( \rho_B (\vec{r}) \) depends on the quantum-mechanical descriptors that are used as the auxiliary quantities for defining \( \rho_A (\vec{r}) \). If we use the orbitals of a non-interacting reference system, the wavefunction of the full configuration interaction form, or the one-particle density matrix as the descriptors to define \( \rho_A (\vec{r}) \), the local, orbital-free, embedding potential reads as follows:

\[
\varepsilon_{\text{emb}}^{eff} [\rho_A, \rho_B ; \vec{r}] = \varepsilon_{\text{ext}}^B (\vec{r}) + \int \frac{\rho_B (\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + \varepsilon_{\text{xc}}^{\text{nad}} [\rho_A, \rho_B] (\vec{r}) + \varepsilon_{\text{eff}}^{\text{mad}} [\rho_A, \rho_B] (\vec{r}),
\]

(3.6)

where

\[
\varepsilon_{\text{xc}}^{\text{mad}} [\rho_A, \rho_B] (\vec{r}) = \frac{\delta E_{\text{xc}} [\rho]}{\delta \rho (\vec{r})} \bigg|_{\rho=\rho_A+\rho_B} - \frac{\delta E_{\text{xc}} [\rho]}{\delta \rho (\vec{r})} \bigg|_{\rho=\rho_A}
\]

(3.7)

and

\[
\varepsilon_{\text{eff}}^{\text{mad}} [\rho_A, \rho_B] (\vec{r}) = \frac{\delta T_e [\rho]}{\delta \rho (\vec{r})} \bigg|_{\rho=\rho_A+\rho_B} - \frac{\delta T_e [\rho]}{\delta \rho (\vec{r})} \bigg|_{\rho=\rho_A}
\]

(3.8)

As we can see, the above equation for \( v_{emb}^{eff} [\rho_A, \rho_B ; \vec{r}] \) involves the external and Coulomb potentials due to the environment \( B \), and the \( \varepsilon_{\text{xc}}^{\text{mad}} [\rho_A, \rho_B] (\vec{r}) \) and \( \varepsilon_{\text{eff}}^{\text{mad}} [\rho_A, \rho_B] (\vec{r}) \) components that arise from the nonadditivities of the exchange-correlation and kinetic energy functionals of the Kohn-Sham formulation [8] of DFT [9], \( E_{\text{xc}} [\rho] \) and \( T_e [\rho] \), respectively.

- **Kohn-Sham equations with constrained electronic density.** Once \( v_{emb}^{eff} [\rho_A, \rho_B ; \vec{r}] \) is defined, as in Eq. (3.6), and if we use a non-interacting reference system to perform the constrained search given by Eq. (3.2), the corresponding orbitals \( \phi_i^A \), \( i = 1, \ldots, N_A \), of the system \( A \) embedded in the environment \( B \) are obtained from the following Kohn-Sham-like equations [cf. Eqs. (20) and (21) in Ref. [1]]:

\[
\left[ -\frac{1}{2} \nabla^2 + \varepsilon_{\text{KS}}^{eff} [\rho_A; \vec{r}] + v_{emb}^{eff} [\rho_A, \rho_B; \vec{r}] \right] \phi_i^A = \varepsilon_i^{(A)} \phi_i^A,
\]

(3.9)

where \( \varepsilon_{\text{KS}}^{eff} [\rho_A; \vec{r}] \) is the usual expression for the potential of the Kohn-Sham DFT for the isolated system \( A \). The orbitals \( \phi_i^A \) and the corresponding orbital energies \( \varepsilon_i^{(A)} \) are calculated by solving Eq. (3.9).

- **Choice of the electron density of the environment (\( \rho_B \)).** As opposed to the supermolecular Density-Functional Theory approaches, the electron density of the environment (\( \rho_B \)) is an input quantity for Eq. (3.9) of FDET and a choice must to be made by the user of the method about how it will be obtained (for this purpose Kohn-Sham DFT, subsystem formulation of DFT (SDFT), statistical methods [39] and other methods can be employed). It needs to be noted that \( \rho_B \)
depends on the Physical Chemistry of the system under study and that the various calculated electronic structure dependent properties can be affected in a different way by the choice of $\rho_B$ (see relevant discussions in Parts II and III of this thesis).

The effectiveness of methods based on Eq. (3.9), with $v^{eff}_{emb}[\rho_A, \rho_B; \vec{r}]$ determined using Eq. (3.6), in the calculations of changes in the electronic structure arising due to the interactions between the embedded system and its environment was demonstrated in a number of applications, including vertical excitation energies [26, 40], ESR hyperfine coupling constants [41, 42], ligand-field splittings of f-levels in lanthanide impurities [43], NMR shieldings [44], and dipole and quadrupole moments, and electronic excitation energies and frequency dependent polarizabilities [45]. The FDET strategy, as summarized above, is expected to calculate: i) the shifts in the vertical excitation energy corresponding to the $\pi \rightarrow \pi^*$ transition in the cis-7HQ system due to its environment in a reasonable manner [19] and the work presented in Chapters 6 and 7, verifies if this is indeed the case by comparing the results of the FDET and $\delta$-CR-EOMCC(2,3)-based EOMCC calculations and ii) the shifts of the iso-g of Electron Paramagnetic Resonance (EPR) Spectroscopy of a radical due to its environment (see Chapter 8 for comparison with Kohn-Sham reference data). The applicability, or even better the expected accuracy, of FDET based methods for a specific electron density depending property can not be determined a priori and individual studies need to be made for each property. The electron density of the environment is an important factor (it is demonstrated in Chapters 6 and 7 that non-relaxed electron density of the environment is associated with more reliable calculated shifts of vertical excitation energies results but relaxed density is associated with systematically reliable calculated shifts of the iso-g of biliverdin (Chapter 8) that merits special investigations. It must be added, that the available approximations for the kinetic energy dependent parts of the orbital-free embedding potential, limits for the moment FDET involving studies to non-covalently interacting subsystems.

In this context, it is useful to mention two other approaches related to FDET that aim at the description of a system consisting of subsystems, including the situation of a molecule or a molecular complex embedded in an environment which interests us here, namely, the subsystem formulation of DFT (SDFT) [46,47] and the recently developed partition DFT (PDFT) [48]. In analogy to FDET, in the SDFT approach the charge of each subsystem is assumed to be an integer, whereas PDFT allows for fractional subsystem charges. In the exact limit, both SDFT and PDFT lead to the exact ground-state electronic density and energy of the total system under investigation, providing an alternative to the conventional supermolecular Kohn-Sham framework. This should be contrasted with the FDET approach, which does not target the exact ground-state electronic density of the total system $AB$, but, rather, the density of subsystem $A$ that minimizes the Hohenberg-Kohn energy functional of the total system, $E_{HK}[\rho_A + \rho_B]$, using a fixed form of the environment density $\rho_B$ in the presence of constraints (Eqs. (3.1),(3.2),(3.3),(3.4)). Thus, FDET may lead to the same total ground-state density as SDFT, Kohn-Sham DFT, or PDFT, but only when the specific set of additional assumptions and constraints is employed [27]. In any other case FDET can only give the upper bound to the exact ground-state energy of the total system $AB$,

$$E^{(A)}_{emb}[\rho_B] \geq E^{(AB)}.$$  

(3.10)

Indeed, in the case of the total system $AB$ consisting of two subsystems $A$ and $B$, where $A$ is a molecular system embedded in the environment $B$, the SDFT approach searches
for the pure-state, non-interacting, \( v\)-representable subsystem densities \( \rho_A \) and \( \rho_B \) that minimize the Hohenberg-Kohn energy functional \( E_{HK}[\rho_A + \rho_B] \):

\[
E^{(AB)} = \min_{\rho_A, \rho_B} E_{HK}[\rho_A + \rho_B], \tag{3.11}
\]

subject to the constraints given by Eqs. (3.1), (3.4):

where \( E_{HK}[\rho] \) in Eq. (3.2) is the usual Hohenberg-Kohn energy functional.

Thus, the sufficient condition for reaching the exact ground-state density of the total system \( AB \), \( \rho_{AB} \), in SDFT is the decomposability of \( \rho_{AB} \) into a sum of two pure-state, non-interacting, \( v\)-representable densities \( \rho_A \) and \( \rho_B \) representing subsystems \( A \) and \( B \) consisting of the integer numbers of electrons, \( N_A \) and \( N_B \), respectively (see the discussion in Ref. 27). The FDET approach does not search for the exact ground-state density \( \rho_{AB} \) of the total system \( AB \). It uses the variational principle described by Eq. (3.2) to find the density which minimizes the total ground-state energy in presence of the constraint

\[
\rho \geq \rho_B, \tag{3.12}
\]

with the subsystem density \( \rho_B \) given in advance (see also Eq. (3.2)). As a result, the total density obtained with FDET is not equal to the exact ground-state density \( \rho_{AB} \) except for one specific case where the difference between \( \rho_{AB}(\vec{r}) \) and the assumed density \( \rho_B(\vec{r}) \) is representable using one of the aforementioned auxiliary descriptors, such as orbitals of the non-interacting reference system [1], interacting wavefunction [28], or one particle-density matrix [29]. Although there are differences between SDFT and FDET, as pointed out above, both methodologies have a lot in common as well. In particular, any computer implementation of the FDET approach can easily be converted into the SDFT algorithm. For example, as shown in the original numerical studies based on SDFT concerning atoms in solids [46,47] and in the recent implementation of SDFT for molecular liquids [49], in the SDFT approach one has to solve a system of coupled Kohn-Sham equations, which is similar to the system represented by Eq. (3.9). One of the most efficient schemes for solving such systems is the “freeze-and-thaw” iterative procedure introduced in Ref. 50. The “freeze-and-thaw” algorithm was exploited in a number of SDFT studies, including those reported in Refs. 51–53, and the same algorithm is used in the present work to carry out the FDET calculations for the hydrogen-bonded complexes of the cis-7HQ system. The “freeze-and-thaw” scheme for solving the coupled Kohn-Sham-like equations of FDET and SDFT was previously used by in the methodological studies on approximations to the bi-functional of the non-additive kinetic energy potential \( v^{\text{rad}}[\rho_A, \rho_B](\vec{r}) \) (see, e.g., Refs. 33, 54, 55) and in the preparatory stages for the large-scale FDET simulations, in which the search defined by Eq. (3.2) is initially performed for smaller model systems in order to establish the adequacy of the simplified form of \( \rho_B(\vec{r}) \) to be used in the subsequent calculations for the target large system. We also demonstrated that the “freeze-and-thaw” procedure for solving the coupled Kohn-Sham-like equations of the type of Eq. (3.9) can be performed simultaneously with displacing nuclear positions, accelerating the SDFT-based geometry optimizations [56]. Finally, it should be noted that the relaxation of the environment density \( \rho_B \) during the SDFT “freeze-and-thaw” iterations is accompanied by errors which are introduced by the approximations to the bi-functional of the non-additive kinetic energy potential \( v^{\text{rad}}[\rho_A, \rho_B](\vec{r}) \), Eq. (3.8), and which can artificially be enhanced by the relaxation of \( \rho_B \). Thus, when the expected polarization effects are small, the relaxation of \( \rho_B \) during the SDFT iterations should be avoided. This problem does not enter the non-relaxed FDET considerations, in
which one fixes the form of \( \rho_B \) prior to FDET iterations, and this is demonstrated in the results presented in Chapter 6 of Part II. On the other hand, one needs to be aware of the fact that if the electronic polarization effects are strong or if the goal is to obtain embedding potentials that mimic supramolecular TDDFT calculations, one should use the fully relaxed “freeze-and-thaw” iterations to optimize both components of the total electronic density \( \rho_{AB} \), i.e., \( \rho_A \) and \( \rho_B \), not just \( \rho_A \). Indeed, as shown in Chapter 6 of Part II, the FDET results for the spectral shifts in the cis-7HQ chromophore induced by complexation, in which \( \rho_B \) is allowed to relax, are quite close to the results of supramolecular TDDFT calculations, even though the latter results are generally poor and far from the EOMCC benchmark values and the corresponding experimental data. The fact that the relaxed FDET calculations lead to a considerably worse description of the complexation-induced shifts in cis-7HQ than the non-relaxed ones has several reasons. One of them is the aforementioned problem of the errors introduced by the approximation used to represent the exact ground-state density of the isolated species \( B \) by the density obtained with the carefully validated wavefunction theory is very important. It is stressed that this kind of investigation needs to be done only once for each type of system (for example, for non-charged hydrogen-bonded complexes as those examined in the work described in Chapters 6 and 7) and the conclusions are expected to guide larger scale subsequent investigations. The main objective of the study described in Chapters 6 and 7 is to demonstrate that when the polarization of the environment is small, as is the case when the weakly bound complexes of the cis-
3.2. Extension of LR-TDDFT to FDET

Frozen-Density Embedding Theory (FDET) has been extended to LR-TDDFT [57]. For complexes in which the excitations are localized on the embedded system and for the cases where environment and core system do not absorb in the same frequency range, it is a reasonable approximation to assume that the response of the environment is negligible. This approximation is termed neglect of dynamic response of environment (NDRE) (the approximation was introduced in Ref. [30]).

The only modification is in the exchange-correlation response kernel, in which terms arising from the orbital-free embedding potential are added. For the case of the adiabatic approximation:

$$f_{\text{total}}(\vec{r}, \vec{r}') = f_{\text{free}}(\vec{r}, \vec{r}') + f_{\text{emb}}(\vec{r}, \vec{r}')$$

(3.13)

In the adiabatic-NDRE combined approximations $f_{\text{emb}}$ is given by the following expression:

$$f_{\text{emb}}(\vec{r}, \vec{r}') = \frac{\delta^2 E_{\text{xc}}[\rho](\vec{r})}{\delta \rho(\vec{r}) \delta \rho(\vec{r}')} - \frac{\delta^2 E_{\text{xc}}[\rho_A](\vec{r})}{\delta \rho_A(\vec{r}) \delta \rho_A(\vec{r}')} + \frac{\delta^2 T_{\text{nad}}[\rho_A, \rho_B](\vec{r})}{\delta \rho_A(\vec{r}) \delta \rho_A(\vec{r}')}$$

(3.14)

The kinetic energy component is taken from the Thomas-Fermi expression for the kinetic energy of the uniform electron gas [58, 59].

A computational method in which the NDRE approximation is not employed has been developed by Neugebauer [60, 61], based on the LR-TDDFT generalization of the FDET approach [57]. It involves Sub-System Density-Functional Theory, and allows for selection of couplings between excitations on different subsystems.

Main advantages of the extension of LR-TDDFT to FDET is the direct access to excitations localised on the core sub-system and the lack of phenomena of deterioration of the quality of the results for relatively larger systems (see relevant discussion in Part II of this thesis).
Chapter 4: Theoretical predictions of Electron Paramagnetic Resonance Spectroscopy data

4.1 EPR

Electron Paramagnetic Resonance spectroscopy is used for the study of radicals (it is inapplicable for spin-compensated molecules) [62, 63]. The sample may be in any phase but difficulties arise in the case of the gas phase. The experiment is based on the resonant absorption of radiation of frequency $\nu$ by the unpaired electron(s). The microwave absorption spectrum, has the magnetic field on the $x$-axis and the energy on the $y$-axis and is obtained while the magnetic field is changed (usually in the region of 0.3 T) and the frequency is fixed. The $g$-value of the radical defines the center of the spectrum. $g$ is a tensorial quantity but for rapidly tumbling molecules in solution the isotropic $g$-value, iso-$g = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$, is of interest. The resonance condition in terms of the $g$-value for an unpaired electron in a radical is (written using symbols without specifying the system of units):

$$h \nu = g \mu_B B$$

Where $h$ is Planck’s constant, $\nu$ is the operating frequency of the spectrometer ($\nu = \frac{1}{T}$ where $T$ is the period), $g$ is the $g$-value, $\mu_B$ is the Bohr magneton and $B$ is the magnitude of the magnetic field at which the center of the spectrum occurs [63]. Eq. (4.1) in hartree atomic units (i.e. $\hbar = 1$) is written:

$$4\pi \nu = gB$$

4.2 Theoretical calculations

The accurate calculation of the $g$-factor requires the employment of the Dirac equation which provides a relativistic description of spin-$\frac{1}{2}$ particles [64]. Because of the difficulty of solving the Dirac equation approximate equations have been developed for its solution. The zeroth-order of the regular expansion of the Dirac equation leads to the zeroth-order regular approximation (ZORA) [65–68]. The regular expansion is not divergent even for a Coulombic potential. In the case that only a time-independent electric field is present, the ZORA equation for one electron is [69]:

$$\left[ V + \vec{\sigma} \cdot \vec{p} \frac{e^2}{2c^2 - V} \vec{\sigma} \cdot \vec{p} \right] \psi^{ZORA} = E^{ZORA} \psi^{ZORA}$$

(4.3)
Where $\vec{\sigma}$ is the vector of the Pauli spin matrices, $\vec{p}$ is the momentum operator, $E$ is the orbital energy of the electron and $c$ is the velocity of light, $V$ is the potential, $\Psi$ is the wave-function for an interacting system of electrons. An approximation of the ZORA equation (for a non interacting system of electrons) can be achieved by using the effective Kohn-Sham potential and employing nonrelativistic approximants for the exchange-correlation potential [69]. Supposing that the ground level of a system with odd number of electrons is doubly degenerate (Kramers doublet) in the absence of magnetic field, the $g$-tensor can be calculated using First-Order Perturbation Theory and the two degenerate aforementioned two spinors, which are eigenfunctions of the ZORA hamiltonian in the presence of electric field only (equations 6,13,20 and 32-47 in Ref. [69]). Gauge including atomic orbitals (GIAOs [70, 71]) are used to solve the gauge dependence problem due to the incompleteness of the basis set. This ZORA and Kohn-Sham Density-Functional Theory based method gives reasonably accurate results [69] and is implemented in ADF2009 [72].

The $g$-tensor of an embedded molecule can be evaluated using the method discussed above in the embedding framework, by adding to the effective Kohn-Sham potential for the embedded molecule, the orbital-free embedding potential [1] or the coulombic only embedding potential. This is implemented in ADF2009. The reasonable accuracy of the results for the case of the orbital-free embedding potential was demonstrated for small complexes in the past [42]. During the work done for this thesis, both aforementioned embedding potentials were used for the first time, for the study of average sized systems (Chapter 8).
Part II.
Modeling spectroscopic properties of hydrogen bonded clusters in gas phase with Frozen Density Embedding Theory
General introduction to Part II:

Part II of this thesis focuses on the physical chemistry question of the origin of the cooperativity of the hydrogen bonded chains which are hydrogen bonded to the 7-cis-hydroxyquinoline chromophore (Chapter 5) and on the effect of two factors (the choice of the electron density of the environment ($\rho_B$) (Chapter 6) and the approximations for the exchange-correlation (Chapter 6) and kinetic energy terms (Chapter 7) appearing in the Frozen-Density Embedding Theory (FDET) equations) on the shifts of excitation energies calculated using FDET based methods. It should not be forgotten that the various factors that can affect the FDET results, need to be studied for each electronic structure-dependent property at least once for each category of systems (for example non-charged hydrogen-bonded complexes). 1 The latter term is less common. The format of the thesis (original scientific papers and substantial additional material) does not allow for full homogenization of the terminology. Introductions are provided for each individual Chapter.

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1We would like to clarify that the terms approximation and approximant are used interchangeably in this thesis
Introduction to Chapter 5:

This chapter is based on the publication:


The purpose of this article is the investigation of the physical chemistry question of the nature of the cooperative effect of hydrogen-bonded chains in the environment of a π → π* chromophore (cis-7-hydroxyquinoline). A computational experiment involving FDET facilitated the insights. The main conclusion is that the origin of the cooperativity is electronic and not geometrical. This conclusion relies on the satisfactory reproduction of experimental results, the incremental shifts of the first excitation energy of the chromophore due to the addition of the third linker to the hydrogen bonded chain, by FDET based methods. It is emphasized in this thesis that the calculated vertical (and not adiabatic that would make full physical sense), shifts of excitation energies are compared to experimental data. The author stresses that the attempt to take into account all physical effects is not always successful when approximate equations are employed and can actually lead to worsening of the results due to introduction of errors greater than the neglect of a certain physical effect. Arguments about the advantages and disadvantages of the vertical excitations picture are given in Ref. [2]. An important observation based on the Table 1 of Ref. [2] is that the standard deviation of the reported vertical excitation energies (calculated with supermolecular Time-Dependent Density-Functional Theory (TDDFT)) is 50 % smaller than the adiabatic excitation energies. The focus of our work are shifts of shifts of excitation energies and not excitation energies and based on Tables 1 and 2 of Ref. [2] the vertical excitation picture is associated with smaller average absolute deviation from the experimental data for the complexes involved in our study. It must also be taken into account that the calculation of the adiabatic excitation energies is about 50 times more costly than the vertical excitation energies for the studied systems Ref. [2]. An additional point is that for the preparation of the first set of geometries discussed in the publication we employed the implementation of a method (it involves Subsystem Density-Functional Theory (SDFT) that is closely related to FDET; see Ref. [53] for details) that does not allow for excited states optimization. For this work we used two sets of geometries one produced with SDFT based methods and one produced with Density-Functional Theory (DFT) based methods, in order to analyse the effect of the geometry to the calculated results. This study, in which relaxed electron density of the environment (ρB) was input for the FDET equations, took place before the study described in Chapter 6, which depended on the availability of the reference data and lead to the conclusion that the optimum choice is non-relaxed ρB for calculation of shifts (it is stressed that “non-relaxed ρB” means that the mutual induction of the molecules of the environment was taken into account but the mutual induction of environment and embedded subsystem is not considered). Taking into account the fact that the electronic effect is substantial and that for the work described in Chapter 5 shifts of shifts were computed that compare well with the experimental data (see discussion above for the unphysical but computationally valid nature of the comparison), the conclusion of Chapter 5 are seen as reliable.

Finally, it is clarified that the author of this thesis contributed to the publication by: i) calculating the local minima with the SDFT based method, ii) producing the FDET
results, and iii) participating in the analysis of the results (experimental theoretical) and formulation of the conclusions. A reprint of the article follows.
Laser resonant two-photon ionization UV spectra provide clear evidence that the effect of increasing the length of the hydrogen-bonded chain consisting of molecules such as NH₃, H₂O, or CH₃OH on the π → π⁺ excitations of cis-7-hydroxyquinoline (cis-7HQ) is strongly cooperative [Thut et al. J. Phys. Chem. A 2008, 112, 5566.] A theoretical analysis of the experimental data is provided to identify the origin of this cooperativity for four chains. The computational method to determine the changes of the electronic structure of a molecule due to interactions with its environment uses the nonempirical expression for the embedding potential [Wesolowski; Warshel J. Phys. Chem. 1993, 97, 8050.] It is concluded that the electronic coupling between the molecules at the ends of the chain, which are hydrogen-bonded to cis-7HQ, plays a crucial role in this cooperativity.

Introduction

The nonpairwise interactions between hydrogen-bonded molecules, which are referred to frequently also as cooperativity or nonadditivity, manifest themselves experimentally in various ways (for a general overview of this phenomenon in water clusters, see ref 1). In hydrogen-bonded networks, the increase of the size results usually in the increase of the strength of individual hydrogen bonds and of the proton-donor bond length accompanied by shortening of the donor–acceptor distance. As a consequence, the red shift of the O–H (or N–H) infrared stretching band increases with the increase of the size of the hydrogen-bonded network or chain.²⁻³ These effects are fully corroborated by quantum mechanical calculations of linear chains of simple hydrogen-bonded molecules such as HCN, HF, and cyanoacetylene as well as water clusters.⁸⁻¹³ Chains or wires of hydrogen-bonded H₂O and NH₃ molecules have been the objects of our research¹⁵,¹⁶ due to their possible role in the excited-state hydrogen atom-transfer processes in biological systems.¹⁴,¹⁵ In ref 16, we study the hydrogen-bonded chains comprising several small molecules, which are attached to the probe chromophore cis-7-hydroxyquinoline (cis-7HQ), which provides a single H-bond acceptor (N) and a single H-bond donor (OH) site, leading to the formation of H-bonded wires of variable length (see Figure 1).

Both experiment and computer modeling for cis-7HQ in various nanosolvent environments comprising molecules that do not absorb in the near-UV show that the spectral shifts of the π → π⁺ excitations localized in cis-7HQ increase with the length of the hydrogen-bonded chain of molecules in the environment.²⁸ An overall picture emerges from these studies according to which (i) the interactions with a single hydrogen-
The cooperative effect of hydrogen-bonded chains

Hydrogen-Bonded Chains in a $\pi \rightarrow \pi^*$ Chromophore

Figure 1. A hydrogen-bonded chain cluster (A···B···C) bound to cis-7-hydroxyquinoline (A = NH$_2$, B = H$_2$O, C = NH$_3$). In this work, A and C denote the H-bonded molecules that interact with the OH donor and N acceptor sites of cis-7-hydroxyquinoline, respectively.

Bonded ligand gives rise to about half of the electronic spectral shift as compared to interactions with two ligands, one attached to the N-site and the other to the OH site and (ii) the addition to the total spectral shift is the following: for cis-7HQ as well as the intermolecular degrees of freedom.

- The contribution to the spectral shift resulting from the modification of the electronic structure of the ligands A and C following the insertion of the linker molecule (B) into the cis-7HQ + AC system, without any changes in geometry. This term, denoted by $\delta \nu_{el-coop}$, arises from the electronic coupling between the two ends of the hydrogen-bonded chain. The numerical value of $\delta \nu_{el-coop}$ cannot be obtained from either experiment or direct theoretical calculations. It is defined as the remainder obtained from subtracting $\delta \nu_{geom}$ the two contributions $\delta \nu_{ABC}$ and $\delta \nu_{geom}$

$$
\delta \nu_{el-coop} = \delta \nu_{B} - \delta \nu_{AC} - \delta \nu_{geom}
$$

In the present work, the relative importance of the above three contributions is investigated. The experimental data do not allow one to address this issue directly. We turn, therefore, to the theoretical analysis because it allows one to decompose the calculated values of $\delta \nu_{B}$.

Orbital-Free Embedding Computations of the Spectral Shifts

The key quantity of interest in this work is the spectral shift induced by the interactions between the chromophore and the molecules hydrogen-bonded to it. The spectral shift is thus a difference between the excitation energies calculated for the same chromophore but for a varying number of molecules in the environment (zero to three in our case). The shifts are rather small (1000 cm$^{-1}$ is just 0.12 eV). Even within the vertical excitation picture of the considered absorption processes, obtaining such shifts from theoretical calculations represents a challenge. Routine application of the “supermolecule strategy”, that is, obtaining the shifts as the differences between the excitation energies calculated for the complex and those for the free chromophore, is far from straightforward and prone to various pitfalls. For organic chromophores, the intrinsic accuracy of the electronic excitation energies derived via the linear response time-dependent DFT strategy (LR-TDDFT) is of the same order of magnitude as the spectral shifts considered in the present work. The quality of the shift calculated as a difference of two excitation energies obtained from LR-TDDFT hinges on the assumption that the errors in the excitation energy for the isolated chromophore and that for the chromophore in the complex are the same (or strongly correlated). Unfortunately, for clusters involving organic chromophores and solvent molecules, such a cancellation cannot be assumed. In fact, the opposite has been observed; increasing the size of the cluster leads to the appearance of artificial excitations of no physical meaning. Moreover, it is known that the accuracy of the excitation energies derived from the LR-TDDFT methods in common use nowadays deteriorates with the size of the investigated system. The established wavefunction-based methods of quantum chemistry have the potential to reach the desired accuracy level for each of the two components of the spectral shift, that is, the excitation energy for the isolated chromophore and that of the chromophore in the complex. They can be used, in principle, without assuming that the errors are correlated. Using such methods is, however, not practical due to the computational effort needed to obtain the total energies (ground and excited state) at the equilibrium
introduced a computational method in which selected coupled excitations are taken into account and demonstrated cases where NDRE is not adequate. (The NDRE calculations are referred to as FDEu, that is, frozen density embedding uncoupled, in ref 27). For the systems considered in this work, we do not consider coupling between excitations in 7HQ and in the hydrogen-bonded chains because they absorb in different spectral regions.

Below, we outline only the key elements of the applied computational protocol. The relaxed two ground-state densities, that is, that of the chromophore (7HQ) and that of its environment (ligands), are obtained from a coupled set of one-electron equations (eqs 20 and 21 of ref 17). The freeze-and-thaw procedure is used for this purpose. The orbitals in each set (occupied and nonoccupied) are localized in the respective subsystems (monomer expansion of electron densities referred to as KS CED(m) in ref 28), which is the default option in ADF2008 and which is described in detail in ref 28. Such a restriction on variational calculations is adequate in the absence of covalent bonds between subsystems and/or charge-transfer between subsystems. These sets of orbitals are used in subsequent LR-TDDFT calculations in a different way. Whereas the ones corresponding to the chromophore are used in the general framework of LR-TDDFT calculations with the response kernel modified to reflect the kinetic energy component of the effective potential, the relaxed orbitals (occupied) corresponding to the environment are used only to derive the electron density of the environment and not contribute to the dynamic response of the system (NDRE approximation).

The applied monomer expansion of electron densities localizes the dynamic response of the chromophore which lies at the origin of the desired elimination of spurious electronic excitations involving the environment (see the relevant discussion in ref 36). The excitation energies were calculated using the ADF2008 code with the following control parameters: Slater-type atomic orbitals (TZ2P), integration parameter 6.0, the GGA-Y approximation for the nonadditive kinetic-energy-dependent part of the embedding potential, the PW91 approximant for the exchange-correlation-dependent part of the total orbital-free embedding potential, and the SAOP potential for the part of the total potential representing the exchange-correlation potential of the embedded subsystem. The eigenvectors of the response matrix in LR-TDDFT calculations were obtained using a tough convergence criteria (TOLERANCE 1e-10).

The ground-state equilibrium geometry for the investigated complexes is obtained following the computational protocol described in detail in ref 26, in which local density approximation as applied for all needed functionals and potentials and the ground-state energy and density of the system is obtained from fully variational freeze-and-thaw calculations. A representative sample of benchmark results is provided in ref 26 and
TABLE 2: Contributions to the Spectral Shift Effect of Inserting the Linker Molecule (B in Figure 1) into the H-Bonded Chain Consisting of cis-7-Hydroxyquinoline and the Ligand Molecules (A and C), From the Linker in the Absence of Other Chain Members (δδν_{el-coop}), Structural Changes Accompanying Inserting the Linker (δδν_{geom}), and Electronic Cooperativity of the Chain (δδν_{el-coop})

<table>
<thead>
<tr>
<th>ligands</th>
<th>δδν_{geom}</th>
<th>δδν_{el-coop}</th>
<th>δδν_{geom}</th>
<th>δδν_{el-coop}</th>
<th>δδν_{geom}</th>
<th>δδν_{el-coop}</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₂</td>
<td></td>
<td>−315</td>
<td></td>
<td></td>
<td>285</td>
<td>298</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>−281</td>
<td></td>
<td></td>
<td>358</td>
<td>325</td>
</tr>
<tr>
<td>CH₃OH</td>
<td></td>
<td>384</td>
<td></td>
<td></td>
<td>285</td>
<td>309</td>
</tr>
<tr>
<td>NH₂</td>
<td></td>
<td>−281</td>
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<tr>
<td>H₂O</td>
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<tr>
<td>CH₃OH</td>
<td></td>
<td>384</td>
<td></td>
<td></td>
<td>285</td>
<td>309</td>
</tr>
</tbody>
</table>

* Geometries from ref 16. The shifts of the π → π* excitations are given in [cm⁻¹]. Reference 16.

Results and Discussion

Table 1 collects the numerical values of δδν_{AC} as the overall accuracy of the calculated shifts is rather good (see columns 4 and 5 in Table 1). The maximum difference between δδν_{AC} derived from the spectroscopic measurements and that from the applied computational protocol is 125 cm⁻¹. Such a discrepancy is rather small in view of the following factors: the vertical differences in interpretation of experimental data; the chosen approximations for the density functional for the exchange-correlation and nonadditive kinetic energy contribution to the energy and to the effective potential needed in the determination of the equilibrium geometry; the chosen approximations for the density functional for the exchange-correlation and nonadditive kinetic energy contribution to the energy, to the effective potential, and to the response kernel and neglect of dynamic response of the environment in the determination of the vertical excitation energies; and other technical details such as basis sets, grids, solver of the Kohn–Sham and Casida equations, and so forth.

The overall good accuracy of the calculated values of δδν_{AC} justifies a more detailed analysis of contributions to this quantity defined in the Introduction. The electronic cooperativity and the direct effect of the linker contribute to δδν_{AC} and both contributions always have a negative sign. Despite the fact that the linker does not interact directly with the chromophore in any of the complexes considered, its contribution (δδν_{el-coop}) in Table 1 is negligible. The contribution arising from the geometry relaxation always has a sign that is opposite to that of the spectral shift. All three contributions are considerable, and none appears to be dominant. It is interesting to note that the spectral shift contributions due to the inserted linker (δδν_{el-coop}) and that due to the geometrical relaxation following introduction of the linker (δδν_{geom}) are opposite in sign. The relative importance of various contributions to δδν_{AC} is similar in all four considered hydrogen-bonded chains. Obviously, the numerical values reported in Table 1 depend on the geometry of the two- or three-member chains, which are taken from computations and not from experiment. It is interesting, therefore, to verify whether the obtained picture concerning the relative importance of various contributions to δδν_{AC} is general, that is, not specific for the considered geometries. To this end, δδν_{AC} as well as its components were recalculated using other methods to derive equilibrium geometries. For instance, for geometries optimized using the DFT-based method reported in ref 16, the corresponding spectral shifts are collected in Table 2 and show essentially the same trends. It is worthwhile to note that the overall agreement between δδν_{AC} derived from experiment and that from calculations is slightly worse for this set of geometries.

The significant role of the electronic coupling between the two ends of the chain reflected in the magnitude of δδν_{el-coop} defined in eq 2 calls for further analysis of its origin. In the language of commonly used decomposition schemes for the intramolecular interaction energy, δδν_{el-coop} can be expected to originate from the nonadditivity of the induction and dispersion contributions. The analysis of the dipole moment of the chain indicates that the effect of induced dipoles on δδν_{el-coop} is significant. For instance, the total dipole moment of the NH₃ chain is 4.7 D, whereas the sum of the dipole moment of the 2(NH₃) chain (AC) and that of the linker NH₃B is 2.9 D. The induced dipole moment arising from interactions between AC and B components of the chain is thus 2.0 D (i.e., about 38% of the total dipole moment of the three-membered chain). The induced dipole moments of the other three systems are collected in Table 3 showing similar trends.

It is well-known that the cooperativity of hydrogen-bonded chains affects the ground-state properties and leads to strengthening of the hydrogen bond as the chain elongates. It is worthwhile, therefore, to supplement the analysis of the cooperativity of hydrogen-bonded chains made for the excited state with a similar analysis for a ground-state property. The total energies at the considered geometries are also available and allow one to address the issue of cooperativity in interactions between cis-7HQ and the molecules hydrogen-bonded to it. The cooperative contributions to the interaction energy due to the insertion of the linker evaluated using our method are collected...
The symbol $\delta E$ (interaction energy) replaces $E$ in the definitions of the discussed quantities and in the table. The electronic cooperativity provides a significant contribution to the energy of the interaction between the chain and the cis-7HQ molecule. Although the linker does not interact directly with cis-7HQ via a hydrogen bond, the electronic cooperativity provides additional stabilization of the system by an energy amount exceeding that of one additional hydrogen bond of the N–H$^+$···N type (about 5 kcal/mol or more). The electronic cooperativity of the hydrogen-bonding chains appears, therefore, to be the major factor in both ground- and excited-state properties of such systems.

Turning back to the LR-TDDFT results, we note that this strategy provides as the direct result the vertical excitation energies and the oscillator strengths of corresponding electronic transitions without, however, constructing the excited-state wave function. Nevertheless, eigenvectors of the response matrix evaluated in LR-TDDFT originate frequently from a contribution of only one pair of orbitals (one occupied and one unoccupied). In such a case, it is worthwhile to use such a pair in labeling. Moreover, in such cases, the difference between eigenvalues of the corresponding orbitals provides a useful simple estimate of the excitation energy. In the considered case, one pair of orbitals (HOMO and LUMO) provides the dominant contribution to the eigenvector (as much as 90%). These orbitals have $\pi$ character. Consequently, we focused on the analysis of these two orbitals. The orbital energies for the considered systems are collected in Table 5. The HOMO–LUMO gap in all of the complexes and clusters always decreases relative to the HOMO–LUMO gap of the isolated cis-7HQ chromophore. The magnitude of the decrease is between −1.4 and −8.2% and increases with the number of solvent molecules. Interestingly, solvation always destabilizes the HOMO relative to that of the isolated cis-7HQ (typically by −0.7 to −4.7%). The effect of solvation on the LUMO is not systematic; both increases and decreases are found. The shifts of the LUMO are about half that of the HOMO. As far as the shapes of these orbitals are concerned, they are not noticeably affected by the interactions with the environment (data not shown).

### Conclusions

The recently reported laser resonant two-photon ionization UV spectra of small clusters comprising the cis-7-hydroxyquinoline molecule and other molecules capable of hydrogen bonding provide a new manifestation of the hydrogen-bond cooperativity. The insertion of a linker molecule in the middle of the hydrogen-bonded chain affects significantly the optical excitation energies of cis-7-hydroxyquinoline. This effect, which can be measured experimentally and which is denoted by $\delta \delta \nu^\text{cis}$, is not negligible. Its magnitude is on the order of 400 cm$^{-1}$, whereas the entire effect of the environment on these excitations is smaller than 2200 cm$^{-1}$. Such manifestation of hydrogen-bonding cooperativity could be expected in view of the known effects of the hydrogen-bonding cooperativity on ground-state properties, for example, the additional infrared band red shift of the donor asymmetric stretching vibration and the additional increase of the hydrogen-bond strength. Since the hydrogen-bond donor and acceptor properties of either end of the chain are strengthened, the effect of these groups on orbitals (occupied and unoccupied Kohn–Sham orbitals, and consequently the properties derived from them) of the chromophore can be expected also to be reinforced.

In the present work, we investigate the origin of $\delta \delta \nu^\text{cis}$ by evaluating the components of its computational counterpart $\delta \delta \nu^\text{cis}$ for the four investigated systems, $\delta \delta \nu^\text{cis}$ is close to the experimental value, and an important contribution to this quantity originates from the electronic coupling between the ends of the chain, which is enhanced by the presence of the linker. The importance of this electronic contribution seems to be a general feature of the considered chains. The changes of the geometry accompanying the insertion of the linker into the chain decrease the magnitude of the spectral shift, whereas the electronic cooperativity increases it. The fact that the observed cooperative effect correlates well with its electronic component in all considered systems and for two sets of similar but not identical geometries indicates that the electronic coupling reflected in the magnitude of the $\delta \delta \nu^\text{el-coop}$ defined in eq 2 should be considered an important factor also in cases where the geometry of the chain can be subject to some steric constraints, as is the case in biomolecules.

### Acknowledgment

T.W. and S.L. acknowledge the support of Swiss National Science Foundation (Projects 200020-116760, 200020-124817/1, and 200020-113798).

### Supporting Information Available

Cartesian coordinates of the considered complexes, equilibrium geometries from TABLE 5: Environment-Induced Shifts of the Orbital Energies (in eV)$^a$

<table>
<thead>
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<th>ligands</th>
<th>$\Delta E_{\text{cis}}$</th>
<th>$\Delta E_{\text{cis}}$</th>
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</thead>
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<tr>
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<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
<tr>
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<tr>
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<td>H$_2$O$^+$</td>
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</tr>
<tr>
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<td>NH$_5$</td>
<td>NH$_6$</td>
<td>NH$_7$</td>
</tr>
</tbody>
</table>

$^a$ For the isolated cis-7HQ molecule, the orbital energies are $E_{\text{HOMO}}$ (cis-7HQ) = −9.737 eV, $E_{\text{LUMO}}$ (cis-7HQ) = −6.435 eV, and $E_{\text{HOMO}}$ (cis-7HQ$^\text{cis}$) = −3.802 eV, $^b$ NH$_3$ geometry, $^c$ CH$_3$OH geometry, $^d$ CH$_3$OH$^+$ geometry, $^e$ CH$_3$OH$^+$ geometry.
The cooperative effect of hydrogenbonded chains

subsystem DFT calculations (freeze-and-thaw), and the equilibrium DFT(B3LYP) geometries used in ref 16 and in this work for reference purposes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


JP906483Z.
Chapter 6 is based on the publication:


The purpose of this work is the better understanding of several factors that can influence the quality of the shifts of vertical excitation energy calculated by employing methods based on Frozen-Density Embedding Theory (FDET). Vertical excitation energy shifts due to formation of weakly bound complexes with environment molecules, are computed with supermolecular methods based on the Equation-Of-Motion Coupled-Cluster (EOMCC) which is the reference, and the Time-Dependent Density-Functional Theory (TDDFT) and also with FDET based methods that, as already stressed in Chapter 5, follow the embedding strategy. The main conclusion is that “non-relaxed electron density of the environment” (\(\rho_B\)) -and no “relaxed \(\rho_B\)”,- leads to the best reproduction of EOMCC results. This fact is very interesting considering that FDET is much less computationally expensive than EOMCC. A clear explanation of why non-relaxed \(\rho_B\) is the optimum input quantity for FDET when shifts of vertical excitation energies is not found yet. The most plausible qualitative explanation according to the author of the thesis, is that the relaxation of \(\rho_B\), which attempts to take into account the polarization of \(\rho_B\) by the electron density of chromophore and vice versa, allows for the amplified introduction of two types of errors. It is noted that for the “relaxation of the electron densities”, coupled one electron equations are solved and an infinite number of pairs of electron densities corresponding to the embedded subsystem and the environment is mathematically justified for the case of exact equations (i.e. without approximations) (see subsequent article). The first type of errors mentioned above is due to the fact that the Kohn-Sham Density-Functional Theory type methods, that employ semilocal approximations to the exchange-correlation energy, used in this work, are known to not be very accurate in the description of molecular polarizabilities. The second type is due to the inaccuracy of the approximation of the kinetic energy component of the orbital-free embedding potential of FDET. Errors related to the two aforementioned sources are allowed to manifest themselves to a relatively higher degree when solving a coupled system of Kohn-Sham-like equations defining the FDET approach and involving the electron densities of the two subsystems. These errors could be more important than the errors associated with the neglect of the polarization. A secondary conclusion of this work is that employment of relaxed \(\rho_B\) leads to better reproduction of supermolecular TDDFT results, perhaps due to the greater presence of the common to the two methods molecular polarizabilities related error mentioned above. It was known from previous studies that for the case of ground state energies, the approximation for the non-additive kinetic energy term appearing
in the FDET equations (in short \( \nu_{\text{nad}} \)). In FDET calculations in which supermolecular expansion of the basis set is employed and the density of the environment is relaxed, \( \nu_{\text{nad}} \) is the only reason for differences between FDET and supermolecular KS-DFT calculated ground state energies—we ignore in this argument differences related to the implementation of the relevant equations—is of sufficient accuracy and when relaxed \( \rho_B \) is employed in the calculations, FDET and supermolecular KS-DFT results are very similar. For excited state energies the adequacy of the aforementioned approximation was unknown. Our work indicates that the approximation is satisfactory also for excited state energies. That said, the fact that two additional approximations (compared with the ground state case) are involved (Neglect of the Dynamic Response of the Environment (NDRE) and extra terms in the exchange correlation response kernel arising from the embedding potential of FDET) and potential error compensation is again suspected, does not allow for a comprehensive explanation of why this the case. The supermolecular TDDFT results which were produced without employing range-separated hybrid [73] (RSH) density functionals (it would be interesting to combine the FDET based methods described in the article, with RSH), as expected, do not reproduce well the reference data. The FDET results produced with relaxed \( \rho_B \), even though they deteriorate with the increase of the size of the system, they continue to compare much better with the EOMCC results than the supermolecular TDDFT results do. In addition, the choice of the approximation for the exchange-correlation potentials and the computational basis set do not seem to affect considerably the behavior of the FDET and supermolecular TDDFT based methods and the main findings are not altered. The comparison with experimental data makes partial physical sense (but this can prove beneficial; see discussion above) because we are restricted in the vertical excitation energies picture. That said, it is observed in Tables 1 and 2 of Ref. [2] that the shifts of the vertical excitation energies (calculated with supermolecular Time-Dependent Density-Functional Theory (TDDFT)) reproduce better the experimental results than the adiabatic excitation energies (i.e. the excitation energies associated with the vibrational ground states of the system). A deeper understanding of this phenomenon is desirable and would be the focus of future work, as would be studies of the accuracy of adiabatic supermolecular TDDFT (reported in [2]), the increase of the calculated excited-state relaxation energy (reported in [2]). The author of this thesis acknowledges the fact that the addition of triples to the EOMCC based methods leads to near-coincidence of calculated vertical excitation energies and adiabatic excitation energies, which is not expected and the matter should be further investigated. Thorough analysis of the article after its publication lead to the identification of the confusion that can be generated by the presentation of the aforementioned “near-coincidence” as a positive element and probably the absolute excitation energies calculated with EOMCC are not as accurate as initially thought. It is stressed that the essence of this work is the comparison of calculated vertical excitation energies computed with different methods taking for granted that the EOMCC are of reference quality and any comparison with experimental results is of secondary importance. The achievement is the demonstration that FDET based methods with non-relaxed \( \rho_B \) can systematically reproduce reference quality results (for hydrogen binded uncharged complexes) which are much more computationally taxing. This opens the way for the study of large systems.

Finally, it is clarified that the author of this thesis contributed to the publication by: i) calculating the local minima of the complexes with a second-order Møller-Plesset Perturbation theory (MP2) [74] based method, ii) producing the FDET and supermolecular TDDFT results, and iii) participating in the analysis of all theoretical
results (with a lesser focus on the differences of the wavefunction based ones) and formulation of the conclusions. A reprint of the article follows. An error that appears in this publication is acknowledged by the author of this thesis. Wherever it appears, “maxima of the absorption band” should be replaced by “electronic origins of the absorption band”. It must be noted that this error does not appear in the subsequent publication that is the subject of Chapter 7 and relates closely to the work described herein. As a footnote, for the term “size-intensivity” the reader is directed to the Ref. [75] from where we quote “We use size extensive and size intensive in analogy with thermodynamics where an extensive property scales with the size of the system and an intensive property is independent of the size of the system.”
Embedding vs Supermolecular Strategies in Evaluating the Hydrogen-Bonding-Induced Shifts of Excitation Energies

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ABSTRACT: Shifts in the excitation energy of the organic chromophore, cis-7-hydroxyquinoline (cis-7HQ), corresponding to the \( \pi \rightarrow \pi^* \) transition in cis-7HQ and induced by the complexation with a variety of small hydrogen-bonded molecules, obtained with the frozen-density embedding theory (FDET), are compared with the results of the supermolecular equation-of-motion coupled-cluster (EOMCC) calculations with singles, doubles, and noniterative triples, which provide the reference theoretical data, the supermolecular time-dependent density functional theory (TDDFT) calculations, and experimental spectra. Unlike in the supermolecular EOMCC and TDDFT cases, where each complexation-induced spectral shift is evaluated by performing two separate calculations, one for the complex and another one for the isolated chromophore, the FDET shifts are evaluated as the differences of the excitation energies determined for the same many-electron system, representing the chromophore fragment with two different effective potentials. By considering eight complexes of cis-7HQ with up to three small hydrogen-bonded molecules, it is shown that the spectral shifts resulting from the FDET calculations employing nonrelaxed environment densities and their EOMCC reference counterparts are in excellent agreement with one another, whereas the analogous shifts obtained with the supermolecular TDDFT method do not agree with the EOMCC reference data. The average absolute deviation between the complexation-induced shifts, which can be as large, in absolute value, as about 2000 cm\(^{-1}\), obtained using the nonrelaxed FDET and supermolecular EOMCC approaches that represent two entirely different computational strategies, is only about 100 cm\(^{-1}\), i.e., on the same order as the accuracy of the EOMCC calculations. This should be contrasted with the supermolecular TDDFT calculations, which produce the excitation energy shifts that differ from those resulting from the reference EOMCC calculations by about 700 cm\(^{-1}\) on average.

Among the discussed issues are the choice of the electronic density defining the environment with which the chromophore interacts, which is one of the key components of FDET considerations, the basis set dependence of the FDET, supermolecular TDDFT, and EOMCC results, the usefulness of the monomer vs supermolecular basis expansions in FDET considerations, and the role of approximations that are used to define the exchange-correlation potentials in FDET and supermolecular TDDFT calculations.

1. INTRODUCTION

Accurately predicting the effect of a hydrogen-bonded environment on the electronic structure of embedded molecules represents a challenge for computational chemistry. In spite of being relatively weak, noncovalent interactions with the environment, such as hydrogen bonds, can qualitatively affect the electronic structure and properties of the embedded molecules. Among such properties, electronic excitation energies are of great interest in view of the common use of organic chromophores as probes in various environments. Typically, hydrogen bonding results in shifts in the positions of the maxima of the absorption and emission bands anywhere between a few hundred and about 3000 cm\(^{-1}\). Thus, in order to be able to use computer modeling for the interpretation of experimental data, the intrinsic errors of the calculated shifts must be very small, on the order of 100 cm\(^{-1}\) or less.

Unfortunately, the brute force application of the supermolecular strategy to an evaluation of the excitation energy shifts due to the formation of weakly bound complexes with environment molecules, in which one determines the shift as a difference between the excitation energy for a given electronic transition in the complex and the analogous excitation energy characterizing the isolated chromophore, has a limited range of applicability. The supermolecular approach hinges on a condition that many of the existing quantum chemistry approaches struggle with, namely, the ability of a given electronic structure method to provide an accurate and well-balanced description of excitation energies in systems that have different sizes, which in the specific case of spectral shifts induced by complexation are the total system consisting of the chromophore and environment molecules and the system representing the isolated chromophore. All \( \text{Ab initio} \) methods based on the equation-of-motion (EOM) \( 6^{-20} \) or linear-response \( 21^{-25} \) coupled-cluster (CC) \( 26^{-28} \) theories (cf. refs 23–25 for selected reviews), including, among many schemes proposed to date, the basic EOMCC approach with singles and doubles (EOMCCSD) \( 29^{-31} \) and the suitably modified variant of the completely renormalized (CR) EOMCC theory with singles, doubles, and noniterative triples, abbreviated as \( \delta \)-CR-EOMCC(2,3), which is based on the CR-CC(2,3) \( 32^{-35} \) and CR-EOMCC(2,3) \( 36^{-39} \)
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methods and which is used in the present study to provide the reference data, or the closely related EOMCCSD(T) and EOMCCSD(T) approximations, satisfy this condition, since they provide an accurate and systematically improvable description of the electronic excitations in molecular systems and satisfy the important property of size-intensitivity,65,66 but their applicability is limited to relatively small molecular problems due to the CPU steps that typically scale as \( \mathcal{O}(N^6) \) with the system size.11. In recent years, progress has been made toward extending the EOMCC and response CC methods to larger molecules through the use of local correlation techniques34-37 and code parallelization, combined, in analogy to the widely used QM/MM techniques, with molecular mechanics,38-42 and we hope to be able to extend our own, recently developed, local correlation cluster-in-molecule CC algorithms43-45 to excited states as well, but in spite of these advances, none of the resulting approaches is as practical, as far as computer costs are concerned, as methods based on the time-dependent density functional theory (TDDFT). Unfortunately, the existing TDDBFT approaches, although easily applicable to large molecular systems due to low computer costs, are often not accurate enough to guarantee a robust description of the complexation-induced spectral shifts in weakly bound complexes when the supermolecular approach is employed, due to their well-known difficulties with describing dispersion and charge-transfer interactions, and other intrinsic errors.

Methods employing the embedding strategy, including those based on the frozen-density embedding theory (FDET)47-50 that interests us in this work, provide an alternative strategy to the supermolecular approach for evaluating the excitation energy shifts. In embedding methods, of both empirical (QM/MM, for instance) and FDET types, the energy shifts. In embedding methods, of both empirical (QM/MM, for instance) and FDET types, the energy shifts. In embedding methods, of both empirical (QM/MM, for instance) and FDET types, the energy shifts. In embedding methods, of both empirical (QM/MM, for instance) and FDET types, the energy shifts.

\[ \Delta(\hat{O}) = \langle \Psi^{(A)}_{\text{emb}} | \hat{O} | \Psi^{(A)}_{\text{emb}} \rangle - \langle \Psi^{(A)}_{\text{emb}} | \hat{O} | \Psi^{(A)}_{\text{emb}} \rangle \]  

\[ \text{i.e., by using the many-electron wave functions } | \Psi^{(A)}_{\text{emb}} \rangle \text{ and } | \Psi^{(A)}_{\text{emb}} \rangle \text{ that represent two different physical states of system } A \text{ corresponding to the same number of electrons, the state of the isolated chromophore } A \text{ and the state of } A \text{ embedded in the environment } B. \text{ This has two immediate advantages over the supermolecular approach. First, the embedding strategy does not require the explicit consideration of the total } (N_A + N_B) \text{ electron system consisting of the interacting complex of chromophore and environment. This may lead to a significant cost reduction in the computer effort in applications involving larger environments. Second, by determining the complexation-induced shift } \Delta(\hat{O}) \text{ using the wave functions } | \Psi^{(A)}_{\text{emb}} \rangle \text{ and } | \Psi^{(A)}_{\text{emb}} \rangle \text{ corresponding to the same number of electrons, the errors due to approximations used to solve the } N_A \text{-electron problem represented by eqs 2 and 4 largely cancel out, as we do not have to worry too much about the possible dependence of the error on the system size. In the calculations of the shifts in excitation energies using the size-intensive EOMCC methods, one does not have to worry about the size dependence of the error resulting from the calculations either, but the supermolecular EOMCC approach requires an explicit consideration of the } (N_A + N_B) \text{-electron system consisting of the chromophore and environment, which may lead to a significant cost increase when } N_B \text{ is larger.}

The above description implies that the accuracy of the complexation-induced shifts obtained in embedding calculations largely depends on the quality of the embedding operator \( \tilde{V}^{(A)}_{\text{emb}} \) or the underlying one-electron potential \( v_{\text{emb}}(\vec{r}) \) that defines it. Thus, when compared with the supermolecular approach, the challenge is moved from assuring the cancellation of errors in approximate solutions of two Schrödinger equations for systems that differ in the number of electrons to developing a suitable form of the embedding potential that can accurately describe the state of the chromophore in the weakly bound complex with environment. As already mentioned above, the practical advantage of the embedding strategy (provided a sufficiently accurate approximation for the embedding potential is employed) is the fact that it can be used for much larger systems than the supermolecular one and can even be applied in multiscale molecular simulations.

As formally demonstrated in our previous studies,47-50 the embedding operator can be represented in terms of a local potential \( v_{\text{emb}}(\vec{r}) \) (orbital-free embedding potential), which is determined by the pair of electron densities, \( \rho_A \) and \( \rho_B \), describing the embedding system \( A \) and constructed using the \( | \Psi^{(A)}_{\text{emb}} \rangle \) wave function, and \( \rho_B \) representing the electron density of the environment \( B. \) Unfortunately, except for some analytically solvable systems,54 the precise dependence of \( v_{\text{emb}}(\vec{r}) \) on \( \rho_A \) and \( \rho_B \) is not known. Only its electrostatic component is known exactly. The nonelectrostatic component, which arises from the nonadditivity of the density functionals for the exchange-correlation and kinetic energies, must be approximated or reconstructed, either analytically (if possible)54 or numerically.55-57 In the case of the hydrogen-bonded environments that interest us in this study, the electrostatic component of the exact embedding potential can be expected to dominate and the overall accuracy of the environment-induced changes of the electronic structure of embedded
species can be expected to be accurately described. Indeed, a number of our previous studies\(^{58,59}\) show that the currently known approximants to the relevant functional representations of \(v_{\text{emb}}(\tau)\) in terms of \(\rho_H\) and \(\rho_B\) are adequate.

Our past examinations of the formal and practical aspects of the FDET methodology have largely focused on model systems or direct comparisons with experimental results. Analytically solvable model systems (see ref S4) are especially important, since, as pointed out above, they enable one to develop ideas about the dependence of the embedding potential \(v_{\text{emb}}(\tau)\) on densities \(\rho_H\) and \(\rho_B\) but real many-electron systems may be quite different than models. A comparison with experimental results is clearly the ultimate goal of any modeling technique, and FDET is no different in this regard, but it often happens that experiments have their own error bars and their proper interpretation may require additional considerations and the incorporation of physical effects that are not included in the purely electronic structure calculations. This study offers an alternative way of testing the FDET techniques. Thus, the main objective of the present work is to make a direct comparison of the benchmark results obtained in the high-level, supermolecular, wave function-based EOMCC calculations, using the aforementioned size-intensive modification of the CR-EOMCC(2,3) method,\(^{29,30}\) designated as \(\delta\)-CR-EOMCC(2,3), with those produced by the embedding-theory-based FDET approach\(^{47–50}\) and the supermolecular TDDFT methodology. To this end, we obtain the \(\delta\)-CR-EOMCC(2,3)-based shifts in the vertical excitation energy corresponding to the \(\pi\rightarrow\pi^*\) transition in the organic chromophore, cis-7-hydroxyquinoline (cis-7HQ), induced by formation of hydrogen-bonded complexes with eight different environments defined by the water, ammonia, methanol, and formic acid molecules and their selected aggregates consisting of up to three molecules, for which, as shown in this work, reliable EOMCC data can be generated and which were previously examined using laser resonant two-photon UV spectroscopy.\(^{5,59}\) and we use the resulting reference shift values to assess the quality of the analogous spectral shifts obtained in the FDET and supermolecular TDDFT calculations.

Having access to accurate reference EOMCC data enables us to explore various aspects of the FDET methodology and approximations imposed within. For example, in addition to the approximations used for the nonelectrostatic component of the embedding potential \(v_{\text{emb}}(\tau)\), the FDET techniques exploit various forms of the electron density of the environment \(\rho_E\). Since \(\rho_E\) is an assumed quantity in the FDET considerations, its choice may critically affect the calculated environment-induced shifts in observables.\(^{50,51}\) The dependence of the FDET values of the shifts in the excitation energies of cis-7HQ induced by the complexation with hydrogen-bonded molecules on the form of \(\rho_E\) represents one of the most important aspects of the present study. Among other issues discussed in this work are the basis set dependence of the FDET, supermolecular TDDFT, and EOMCC results, the usefulness of the monomer vs supermolecular basis expansions in the FDET calculations, and the role of approximations that are used to define the exchange-correlation potentials in the FDET and supermolecular TDDFT calculations.

Although the main focus of this work is a comparison of the embedding-theory-based FDET and supermolecular TDDFT results with the high-level \(\textit{ab initio}\) EOMCC data to demonstrate the advantages of the FDET approach over the conventional supermolecular TDDFT methodology in a realistic application, a comparison of the theoretical shifts with the corresponding experimental data\(^{5,59}\) is discussed as well. The gas-phase complexes examined in this paper have been intensely studied, both experimentally and theoretically, since some of these complexes, particularly the larger ones, can be viewed as models of proton-transferring chains in biomolecular systems.\(^{52}\)

## 2. METHODS

As explained in the Introduction, the main goal of this study is a comparison of the shifts in the excitation energy corresponding to the \(\pi\rightarrow\pi^*\) transition in the cis-7HQ system, induced by the formation of hydrogen-bonded complexes of cis-7HQ with a number of small molecules, resulting from the embedding-theory-based FDET approach and supermolecular TDDFT calculations, with those obtained with the EOMCC-based \(\delta\)-CR-EOMCC(2,3) scheme that provides the theoretical reference data. This section provides basic information about the electronic structure theories exploited in this work. Since the supermolecular TDDFT approach is a well-established methodology, our description focuses on the FDET and EOMCC methods used in our calculations.

### 2.1. Frozen-Density Embedding Theory

The FDET formalism\(^{47–50,63}\) provides basic equations for the variational treatment of a quantum-mechanical subsystem embedded in a given electronic density. Various FDET-based approaches developed by us\(^{47–50,58,64}\) and others,\(^{53–56}\) differing in the way the environment density is generated, the choice made for the approximants for the relevant density functionals, or the choice for the quantum-mechanical descriptors for the embedded subsystem, are in use today. Below, we outline the basic elements of the FDET methodology.

#### 1. Basic Variables

The total system AB, consisting of a molecule or an aggregate of molecules of interest, \(\Lambda\), embedded in the environment \(B\) created by the other molecule(s), is characterized by two types of densities. The first one is the density of the embedded molecule(s), \(\rho_A(\tau)\), which is typically represented using one of the following auxiliary quantities: (i) the occupied orbitals of a noninteracting reference system \(\{\phi_{\Lambda i}(\tau)\}, i = 1, \ldots, N_{\Lambda i}\) of the occupied and unoccupied orbitals of a noninteracting reference system,\(^{53–56}\) (ii) the interacting wave function,\(^{65}\) or (iv) the one-particle density matrix.\(^{59}\) The second one is the density of the environment, \(\rho_B(\tau)\), which is fixed for a given electronic problem (“frozen density”).

#### 2. Constrained Search

The optimum density \(\rho_A(\tau)\) of the system \(A\) embedded in the environment \(B\), represented by the fixed density \(\rho_B(\tau)\) satisfying

$$\int \rho_A(\tau) \, d\tau = N_A$$

is obtained by performing the following constrained search:

$$E_{\text{emb}}[\rho_A] = \min_{\rho \geq \rho_A} E_{\text{EOMCC}}[\rho] = \min_{\rho \geq \rho_A} E_{\text{EOMCC}}[\rho_A + \rho_B]$$

subject to the conditions

$$\int \rho(\tau) \, d\tau = N_A + N_B$$

and

$$\int \rho_A(\tau) \, d\tau = N_A$$

The dependence of the FDET values of the shifts in the excitation energy of cis-7HQ induced by the complexation with hydrogen-bonded molecules on the form of \(\rho_E\) represents one of the most important aspects of the present study. Among other issues discussed in this work are the basis set dependence of the FDET, supermolecular TDDFT, and EOMCC results, the usefulness of the monomer vs supermolecular basis expansions in the FDET calculations, and the role of approximations that are used to define the exchange-correlation potentials in the FDET and supermolecular TDDFT calculations.
where $E_{HK}[\rho]$ in eq 7 is the usual Hohenberg–Kohn energy functional.

3. Constrained Search by Modifying the External Potential. In practice, the search for the optimum density $\rho_0$ defined by eq 7, is conducted by solving eq 4, in which $H^{\text{eff}}$ is the environment-free Hamiltonian of the isolated system $A$ and $V^{\text{emb}}(\vec{r}) = \sum_{\alpha,B} v_{\text{emb}}(\vec{r}, \vec{r}_\alpha)$, where $v_{\text{emb}}(\vec{r})$ has the form of a local, orbital-free, embedding potential $v_{\text{emb}}(\vec{r}, \vec{r}_\alpha)$, determined by the pair of densities $\rho_\alpha(\vec{r})$ and $\rho_\beta(\vec{r})$ and designated by $v_{\text{emb}}[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})]$.

4. Orbital-Free Embedding Potential. As shown earlier, the relationship between the local potential $v_{\text{emb}}[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})]$ and densities $\rho_\alpha(\vec{r})$ and $\rho_\beta(\vec{r})$ depends on the quantum-mechanical descriptors that are used as the auxiliary quantities for defining $\rho_\alpha(\vec{r})$. If we use the orbitals of a noninteracting reference system, the wave function of the full configuration interaction form, or the one-electron density matrix as the descriptors to define $\rho_\alpha(\vec{r})$, the local, orbital-free, embedding potential reads as follows:

$$v_{\text{emb}}[\rho_\alpha, \rho_\beta; \vec{r}] = v_{\text{emb}}(\vec{r}) + \int \rho_{\text{ext}}(\vec{r}) \Phi(\vec{r}) \, d\vec{r},$$

where

$$v_{\text{emb}}[\rho_\alpha, \rho_\beta](\vec{r}) = \frac{\delta E_{\text{ext}}[\rho]}{\delta \rho_{\rho_\alpha} - \delta \rho_{\rho_\beta}} \bigg|_{\rho = \rho_\alpha, \rho_\beta}$$

and

$$v_{\text{emb}}[\rho_\alpha, \rho_\beta](\vec{r}) = \frac{\delta T_{\text{ext}}[\rho]}{\delta \rho_{\rho_\alpha} - \delta \rho_{\rho_\beta}} \bigg|_{\rho = \rho_\alpha, \rho_\beta}$$

As we can see, the above equation for $v_{\text{emb}}[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})]$ involves the external and Coulomb potentials due to the environment $B$ and the $v_{\text{emb}}[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})]$ and $v_{\text{emb}}[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})]$ components that arise from the nonadditivities of the exchange–correlation and kinetic energy functionals of the Kohn–Sham formulation of DFT, $E_{\text{KS}}[\rho]$ and $T_{\text{KS}}[\rho]$, respectively.

5. Kohn–Sham Equations with Constrained Electronic Density. Once $v_{\text{emb}}[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})]$ is defined, as in eq 10, and if we use a noninteracting reference system to perform the constrained search given by eq 7, the corresponding orbitals $\phi_i^{(\alpha)}$, $i = 1, \ldots, N_\alpha$, of the system $A$ embedded in the environment $B$ are obtained from the following Kohn–Sham-like equations [cf. eqs 20 and 21 in our earlier work]:

$$\left[ \frac{1}{2} \nabla^2 + v_{\text{KS}}^{(\alpha)}[\rho_\alpha; \vec{r}] + v_{\text{emb}}^{(\alpha)}[\rho_\alpha, \rho_\beta; \vec{r}] \right] \phi_i^{(\alpha)} = \epsilon_i^{(\alpha)} \phi_i^{(\alpha)}$$

where $v_{\text{KS}}^{(\alpha)}[\rho_\alpha; \vec{r}]$ is the usual expression for the potential of the Kohn–Sham DFT for the isolated system $A$. After obtaining the orbitals $\phi_i^{(\alpha)}$ and the corresponding orbital energies $\epsilon_i^{(\alpha)}$ by solving eq 13, we proceed to the determination of the ground- and excited-state energies and properties, which in this case describe the system $A$ embedded in the environment $B$, in a usual manner, using standard techniques of DFT or TDDFT.

The effectiveness of methods based on eq 13, with $v_{\text{emb}}[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})]$ determined using eq 10, in the calculations of changes in the electronic structure arising due to the interactions between the embedded system and its environment was demonstrated in a number of applications, including vertical excitation energies,58,59 ESR hyperfine coupling constants,76–79 ligand-field splittings of $f$ levels in lanthanide impurities,60 NMR shieldings,61 dipole and quadrupole moments, and electronic excitation energies and frequency-dependent polarizabilities.80

The FDET strategy, as summarized above, is expected to calculate the shifts in the vertical excitation energy corresponding to the $\pi \rightarrow \pi^*$ transition in the cis-7HQ system due to its environment in a reasonable manner,72 and the present paper verifies this if indeed the case by comparing the results of the FDET and $\delta$-CR-EOMCC(2,3)-based EOMCC calculations.

In this context, it is useful to mention two other approaches related to FDET that aim at the description of a system consisting of subsystems, including the description of a molecule or a molecular complex embedded in an environment which interests us here, namely, the subsystem formulation of DFT (SDFT)56,77 and the recently developed partition DFT (PDFT).88 In analogy to FDET, in the SDFT approach, the charge of each subsystem is assumed to be an integer, whereas PDFT allows for fractional subsystem charges. In the exact limit, both SDFT and PDFT lead to the exact ground-state electronic density and energy of the total system under investigation, providing an alternative to the conventional supermolecular Kohn–Sham framework. This should be contrasted with the FDET approach, which does not target the exact ground-state electronic density of the total system AB but, rather, the density of subsystem $A$ that minimizes the Hohenberg–Kohn energy functional of the total system, $E_{\text{HK}}[\rho_A + \rho_B]$, using a fixed form of the environment density $\rho_B$ in the presence of constraints, as in eqs 6–9. Thus, FDET may lead to the same total ground-state density as SDFT, Kohn–Sham DFT, or PDFT, but only when the specific set of additional assumptions and constraints is employed.88 Indeed, in the case of the total system AB consisting of two subsystems $A$ and $B$, where $A$ is a molecular system embedded in environment $B$, the SDFT approach searches for the true, noninteracting, $\nu$-representable subsystem densities $\rho_A$ and $\rho_B$ that minimize the Hohenberg–Kohn energy functional $E_{\text{HK}}[\rho_A + \rho_B]$ subject to the constraints given by eqs 6–9. Thus, the sufficient condition for reaching the exact ground-state density of the total system AB, $\rho_{AB}$, in SDFT is the decomposability of $\rho_{AB}$ into a sum of two pure-state, noninteracting, $\nu$-representable densities $\rho_A$ and $\rho_B$ representing subsystems $A$ and $B$ consisting of the integer numbers of electrons, $N_A$ and $N_B$ respectively (see the discussion in ref 48). The FDET approach does not search for the exact ground-state density $\rho_{AB}$ of the total system AB. It uses the variational principle described by eq 7 to find the density, which minimizes the total ground-state energy in the presence of the constraint

$$\rho \geq \rho_B$$

with the subsystem density $\rho_B$ given in advance. As a result, the total density obtained with FDET is not equal to the exact ground-state density $\rho_{AB}$ except for one specific case where the difference between $\rho_{\text{FDET}}(\vec{r})$ and the assumed density $\rho_B(\vec{r})$ is representable using one of the aforementioned auxiliary descriptors, including orbitals of the noninteracting reference systems58,76 interacting wave function,49 or one particle-density matrix.80 Thus, by the virtue of the Hohenberg–Kohn theorem, unless
\( \rho_0(\vec{r}) \) is representable using the above auxiliary descriptors, the FDET approach can only give the upper bound to the exact ground-state energy of the total system \( AB \),
\[
E^{(4)}_{\text{opt}}(\rho_0) \geq E^{(AB)}(\vec{r})
\]  
(16)

Although there are differences between SDFT and FDET, as pointed out above, both methodologies have a lot in common as well. In particular, any computer implementation of the FDET approach can easily be converted into the SDFT algorithm. For example, as shown in the original numerical studies based on SDFT concerning atoms in solids and the recent implementation of SDFT for molecular liquids, \( \delta \) in the SDFT approach one has to solve a system of coupled Kohn–Sham equations, which is similar to the system represented by eq 13. One of the most efficient schemes for solving such systems is the “freeze-and-thaw” iterative procedure introduced in ref 80. The “freeze-and-thaw” algorithm was exploited in a number of SDFT studies, including those reported in refs 81–83, and the same algorithm is used in the present work to carry out the FDET calculations for the hydrogen-bonded complexes of the cis-7HQ system. The “freeze-and-thaw” scheme for solving the coupled Kohn–Sham–like equations of FDET and SDFT was previously used by us in the methodological studies on approximands to the functional of the nonadditive kinetic energy potential \( v_{\text{kin}}(\rho_0) \) (see, e.g., refs 64, 84, and 85) and in the preparatory stages for the large-scale FDET simulations, in which the search defined by eq 7 is performed initially for smaller model systems in order to establish the adequacy of the simplified form of \( \rho_0(\vec{r}) \) to be used in the subsequent calculations for the target large system. We also demonstrated that the “freeze-and-thaw” procedure for solving the coupled Kohn–Sham–like equations of the type seen in eq 13 can be performed simultaneously with displacing nuclear positions, accelerating the SDFT-based geometry optimizations.

Finally, it should be noted that the relaxation of the environment density \( \rho_0 \) during the SDFT “freeze-and-thaw” iterations is accompanied by errors which are introduced by the approximant to the functional of the nonadditive kinetic energy potential \( v_{\text{kin}}(\rho_0) \), eq 12, and which can artificially be enhanced by the relaxation of \( \rho_0 \). Thus, when the expected polarization effects are small, the relaxation of \( \rho_0 \) during the SDFT iterations should be avoided, and the results presented in section 4 clearly show this. This problem does not enter the nonrelaxed FDET considerations, in which one fixes the form of \( \rho_0 \) prior to FDET iterations. On the other hand, one needs to be aware of the fact that the electronic polarization effects are strong or if the goal is to obtain embedding potentials that mimic supermolecular TD-DFT calculations, one should use the fully relaxed “freeze-and-thaw” iterations to optimize both components of the total electronic density \( \rho_{AB} \), i.e., \( \rho_A \) and \( \rho_B \) not just \( \rho_0 \). Indeed, as shown in section 4, the FDET results for the spectral shifts in the cis-7HQ chromophore induced by complexation, in which \( \rho_0 \) is allowed to relax, are quite close to the results of supermolecular TD-DFT calculations, even though the latter results are generally poor and far from the EOMCC benchmark values and the corresponding experimental data. The fact that the relaxed FDET calculations lead to a considerably worse description of the complexation-induced shifts in cis-7HQ than the nonrelaxed ones has several reasons. One of them is the aforementioned problem of the errors introduced by the approximants used to represent \( v_{\text{kin}}^{(A)}(\rho_A, \rho_B)(\vec{r}) \), which penalize the overlap between \( \rho_A \) and \( \rho_B \). Another is the realization of the fact that the relaxation of \( \rho_B \) in the FDET considerations is not necessarily the same as the physical effect of the electronic polarization of the environment \( B \) by subsystem \( A \), i.e., one cannot expect automatic improvements in the results of the FDET calculations when \( \rho_B \) is allowed to relax, particularly when the polarization effects are small. The relaxation of the environment density \( \rho_B \) within the FDET framework is related to a complex notion of the pure-state noninteracting \( \text{v-representability of the target subsystem density} \), which does not automatically translate into the physical polarization of \( B \) by \( A \). Indeed, let \( \rho_{B,\text{rel}} \) designate the exact ground-state density of the isolated species \( B \) and let \( \rho_{B,\text{rel}} \) be a particular choice of \( \rho_B \) used in FDET. If \( \rho_{B,\text{rel}} \) is chosen in such a way that the density difference \( \rho_B \equiv \rho_{B,\text{rel}} - \rho_{B,\text{ref}} \) where \( \rho_{B,\text{rel}} \) represents the exact ground-state density of the total system \( AB \), is pure-state \( \text{v-representable}, \) we can obtain this \( \rho_B \) by solving the Kohn–Sham system given by eq 10. Most likely, there is an infinite number of densities \( \rho_{B,\text{rel}} \) that lead to the pure-state \( \text{v-representable} \rho_B \). Each one of them will result in a different solution for \( \rho_{B,\text{ref}} \) and, what is more important here, in a different relaxation, as measured by the difference \( \Delta \rho_B \equiv \rho_{B,\text{rel}} - \rho_{B,\text{ref}} \). In particular, if \( \rho_{B,\text{ref}} \) is one of the densities \( \rho_{B,\text{rel}} \) that guarantees the pure-state noninteracting \( \text{v-representability of } \rho_B \), there is no physical relaxation at all (\( \Delta \rho_B = 0 \), and the “freeze-and-thaw” calculations are not needed, regardless of whether the physical polarization of \( B \) by \( A \) is significant or not. It is also worth mentioning that although the pure-state noninteracting \( \text{v-representability of } \rho_B \) cannot be a priori assured, there are strong indications from the recent studies of exactly solvable systems that even if the \( N \)-representable density \( \rho_B \) associated with a given \( \rho_{B,\text{rel}} \) is not pure-state \( \text{v-representable}, \) it can be approached arbitrarily closely by a solution of eq 13 obtained with a suitably chosen smooth embedding potential. All of this demonstrates that the connection between the mathematical (in practice, numerical) relaxation of \( \rho_B \) in the FDET considerations and the physical polarization of the environment \( B \) by subsystem \( A \) is far from obvious. For this reason, comparing the results of the nonrelaxed and relaxed FDET calculations with the independent high-level \textit{ab initio} data obtained with the carefully validated wave function theory is very important. The main objective of the present study is to demonstrate that when the polarization of the environment is small, as is the case when the weakly bound complexes of the cis-7HQ molecule are examined, one is better off by using a simplified FDET procedure in which the relaxation of the \( \text{a priori} \) determined environment density \( \rho_B \) is neglected, as this leads to a considerably better agreement with the results of the converged EOMCC calculations and the experiment.

### 2.2. Equation-of-Motion Coupled-Cluster Calculations

The main goal of the present work is to compare the shifts in the \( \pi \rightarrow \pi^* \) excitation energy of the cis-7HQ system, induced by the complexation of cis-7HQ with small hydrogen bonded molecules, obtained with the FDET approach, with the results of the supermolecular EOMCC calculations with singles, doubles, and noniterative triples, exploiting the size-intensive modification of the CR-EOMCC(2,3) approach, abbreviated as \( \delta \)-CR-EOMCC(2,3), which is used to provide the required reference theoretical data. The basic idea of the EOMCC formalism is the following wave function ansatz:

\[
\Psi_{\text{OMCC}} = R_{\text{num}} e^{i\Phi}
\]
(17)
where $|\Psi_0\rangle$ is the ground ($\mu = 0$) or excited ($\mu > 0$) state, $\Phi$ is the reference determinant, which usually is the Hartree–Fock state [in all of the EOMCC calculations reported in this work, the restricted Hartree–Fock (RHF) configuration], and $R_{\mu}$ is the linear excitation operator which generates the excited-state wave functions $|\Psi_{\mu}\rangle$ from the CC ground state $|\Psi_0\rangle = e^{\Phi}$.

Here and elsewhere in this article, we use a convention in which the $\mu = 0$ excitation operator $R_{\mu=0}$ is defined as a unit operator, $R_{\mu=0} = 1$, to incorporate the ground- and excited-state cases within a single set of formulas. The $T$ operator entering the above definitions is the usual cluster operator of the ground-state CC theory, which is typically obtained by truncating the corresponding many-body expansion

$$T = \sum_{n=1}^{N} T_n$$

where

$$T_n = \sum_{i_1 < \ldots < i_n} \sum_{\alpha_1,\ldots,\alpha_n,\beta_1,\ldots,\beta_n} \langle \Phi_{i_1\alpha_1}^{\alpha_1} \cdots \Phi_{i_n\beta_n}^{\beta_n} | d_{\alpha_1}^{\dagger} \cdots d_{\alpha_n}^{\dagger} (d_{\beta_1}^{\dagger} \cdots d_{\beta_n}^{\dagger}) | \Phi \rangle$$

is the $n$-body component of $T$, at some, preferably low, excitation level $M < N$, and by solving the nonlinear system of equations for cluster amplitudes $\Phi_{i_1\alpha_1}^{\alpha_1} \cdots \Phi_{i_n\beta_n}^{\beta_n}$ with $n \leq M$, which define the truncated form of $T$, designated as $T^{(M)}$, resulting from the substitution of the CC wave function ansatz into the electronic Schrödinger equation and the projection of the resulting equation on the excited determinants $|\Phi_{i_1\alpha_1}^{\alpha_1} \cdots \Phi_{i_n\beta_n}^{\beta_n}\rangle$ that correspond to the many-body components $T_n$ included in $T^{(M)}$. Here and elsewhere in this article, we use a standard notation in which $i_1,\ldots, i_n$ or $i_{1},\ldots, i_{n}$ and $\alpha_1,\ldots, \alpha_n$ or $\alpha_{1},\ldots, \alpha_{n}$ are the occupied and unoccupied spin–orbitals, respectively, and $d^{\dagger}$ ($a^{\dagger}$) designates the usual creation (annihilation) operator. Once the ground-state operator $T$ and the corresponding ground-state CC energy $E_0$ are determined, one obtains the many-body components

$$R_{\mu n} = \sum_{i_1 < \ldots < i_n} \sum_{\alpha_1,\ldots,\alpha_n,\beta_1,\ldots,\beta_n} \langle \Phi_{i_1\alpha_1}^{\alpha_1} \cdots \Phi_{i_n\beta_n}^{\beta_n} | d_{\alpha_1}^{\dagger} \cdots d_{\alpha_n}^{\dagger} a^{\dagger} \cdots a^{\dagger} | \Phi \rangle$$

of the linear excitation operator

$$R_{\mu} = R_{\mu,0} + \sum_{n=1}^{N} R_{\mu,n}$$

which is typically truncated at the same excitation level $M$ as the cluster operator $T$, and the corresponding vertical excitation energies

$$\omega_{\mu} = E_{\mu} - E_0$$

by solving the EOMCC eigenvalue problem involving the similarity-transformed Hamiltonian $H^{(M)} = e^{-i\Phi} H e^{i\Phi}$ in the subspace of the $N$-electron Hilbert space spanned by the excited determinants $|\Phi_{i_1\alpha_1}^{\alpha_1} \cdots \Phi_{i_n\beta_n}^{\beta_n}\rangle$ that correspond to the many-body components $R_{\mu n}$ included in $R_{\mu}$.

The basic EOMCC approximation, in which $M = 2$, so that $T \approx T^{(2)} = T_1 + T_2$ and $R_{\mu} \approx R^{(2)} = R_{\mu,1} + R_{\mu,2}$ defining the EOMCCSD approach, in which one diagonalizes the similarity-transformed Hamiltonian of CCSD, $H^{(2)} = e^{-i\Phi} H e^{i\Phi}$, in the space spanned by singly and doubly excited determinants $|\Phi_{i_1}^{\alpha_1} \rangle$ and $|\Phi_{i_1}^{\beta_1} \rangle$, and its linear-response CCSD counterpart, have been successful in describing excited states dominated by one-electron transitions, but this success does not automatically extend to the more complicated, more multireference excited electronic states, such as those characterized by a significant two-electron excitation nature (cf. refs 29, 30, 87–93 for examples). There also are cases of excited states dominated by singles, where the EOMCCSD theory level may be insufficient to obtain high-quality results. In this context of the present work, we expect the EOMCC theory to provide accurate reference data for the FDET and TDDFT calculations, it is important to examine if the EOMCC results used by us are reasonably well converged with the truncations in $T$ and $R_{\mu}$. Ideally, one would like to perform the full EOMCCSD, (EOMCC with singles, doubles, and triples) calculations and compare them with the corresponding EOMCCSD results to see if the latter results are accurate enough. Unfortunately, it is virtually impossible to carry out the full EOMCCSD calculations for the cis-7HQ system and its complexes investigated in this work due to a steep increase of the CPU time and storage requirements characterizing the EOMCCSD approach that scale as $n_{\mu}^2 n_{\mu}^2$ and $n_{\mu}^2 n_{\mu}^2$ with the numbers of occupied and unoccupied orbitals, $n_{\mu}$ and $n_{\mu}$, respectively, as opposed to the $n_{\mu}^2 n_{\mu}^2$ CPU time and $n_{\mu}^2 n_{\mu}^2$ storage requirements of EOMCCSD. Thus, one has to resort to one of the approximate treatments of triple excitations in EOMCC that replace the prohibitively expensive iterative CPU steps of EOMCCSD that scale as $1^\infty$ with the system size. $1^\infty$ to the more manageable $1^2$–$1^3$ steps.

A large number of approximate EOMCCSDT approaches and their linear-response analogs have been proposed to date. The noniterative EOMCC methods, in which one adds corrections due to triples to the EOMCCSD energies, such as EOM-CC(2)PT(2) and its size-intensive EOM-CCSD(2) analog, CC, and the related N-EOMCCSD(T) approach, including the spin-flip variant of the CR-EOMCC(2,3) approach of refs 29 and 30 considered in ref 107, are particularly promising in this regard, since they represent computational black boxes similar to those of the popular CCSD(T) ground-state approach or its CR-CC(2,3) extension. All of the above methods greatly reduce the computer costs of full EOMCCSDT calculations, while improving the EOMCCSD results. The improvements are particularly significant for the excited states characterized by significant double-excitation components, but they are often non-negligible for states dominated by one-electron transitions. For example, the most promising EOM-CCSD(2), CC, N-EOMCCSD(T), CR-EOMCCSD(T), and CR-EOMCCSD(2,3) approaches are characterized by the iterative $n_{\mu}^2 n_{\mu}^2$ steps of EOMCCSD and the noniterative $n_{\mu}^2 n_{\mu}^2$ steps needed to construct the triples corrections to the EOMCCSD energies, while eliminating the need for storing the $n_{\mu}^2 n_{\mu}^2$ steps needed to construct the triples corrections to the EOMCCSD energies. In this paper, we focus on the size-intensive modification of the CR-EOMCC(2,3) method of refs 29 and 30 and the related CR-EOMCC(2,3) approach implemented in this work. The CR-EOMCC(2,3) approach and the underlying ground-state CR-CC(2,3) approximation are examples of the renormalized CC/EOMCC schemes, which are based on the idea of adding the a posteriori, noniterative, and state-specific corrections.
\[ \delta_n \text{ due to higher-order excitations, neglected in the conventional CC/EOMCC calculations defined by some truncation level } M, \text{ such as CCSD or EOMCCSD, to the corresponding CC/EOMCC energies. The formal basis for deriving the computationally manageable expressions for } \delta_n \text{ is provided by one of the forms } 26(25,28)^{10^9} \text{ of the expansion describing the difference between the full CI and CC/EOMCC energies in terms of the generalized moments of the CC/EOMCC equations characterizing the truncated CC/EOMCC method we want to correct. If we are interested in correcting the results of the CC/EOMCC calculations truncated at } M\text{-tuple excitations, the moments that enter the expressions for the relevant energy corrections } \delta_n \text{ are defined as projections of the CC/EOMCC equations with } T \text{ and } R_\mu \text{ truncated at } M\text{-body components on the excitated determinants } [\Phi^\mu_{\delta(M)^{\alpha \beta}}]_n, \text{ with } n > M \text{ that are disregarded in the conventional CC/EOMCC considerations, i.e.}
\]

\[ \delta_n = \sum_{M=n+1}^{\infty} \sum_{\mu=1}^{M} \rho_{\mu a, a}^\delta \rho_{\mu b, b}^\delta [\Phi^\mu_{\delta(M)^{\alpha \beta}}]_n (\Phi^\mu_{\delta(M)^{\alpha \beta}}) \Phi (23) \]

\[ [R_\mu^{(M)}] \text{ in eq 23 is the } R_\mu \text{ operator truncated at the } M\text{-body component } R_\mu (M). \text{ All of the resulting moment expansions of the full CI energy of the } \mu \text{th electronic state can be cast into the generic form}
\]

\[ \delta_n = \sum_{M=n+1}^{\infty} \sum_{\mu=1}^{M} \rho_{\mu a, a}^\delta \rho_{\mu b, b}^\delta [\Phi^\mu_{\delta(M)^{\alpha \beta}}]_n (\Phi^\mu_{\delta(M)^{\alpha \beta}}) \Phi (24) \]

\[ \text{with } N_{\mu, n} \text{ representing the highest value of } n \text{ for which } \rho_{\mu a, a}^\delta \rho_{\mu b, b}^\delta [\Phi^\mu_{\delta(M)^{\alpha \beta}}]_n (\Phi^\mu_{\delta(M)^{\alpha \beta}}) \Phi \text{ is still nonzero, and is the only essential difference between various approximations based on eq 24 is in the way one handles the coefficients } \rho_{\mu a, a}^\delta \rho_{\mu b, b}^\delta [\Phi^\mu_{\delta(M)^{\alpha \beta}}]_n (\Phi^\mu_{\delta(M)^{\alpha \beta}}) \Phi. \]

\[ \text{In the specific case of the CR-EOMCC(2,3) approach that interests us here, one calculates the energies of the ground and excited states as}
\]

\[ E_\mu = E_\mu^{(\text{CCSD})} + \sum_{i < j < k < l} \rho_{i \mu, j \mu} \rho_{k \mu, l \mu} [\Phi^\mu_{\mu(M)^{\alpha \beta}}]_{ijkl} (\Phi^\mu_{\mu(M)^{\alpha \beta}})_{ijkl} (25) \]

\[ \text{where } E_\mu^{(\text{CCSD})} \text{ are the CCSD } (\mu = 0) \text{ and EOMCCSD } (\mu > 0) \text{ energies, } \rho_{i \mu, j \mu} (2) \text{ are the moments of the CCSD/EOMCCSD equations corresponding to triple excitations, which are defined by eq 23 in which } M = 2, \text{ and } \rho_{i \mu, j \mu} \text{ are the deexcitation amplitudes that one can calculate using the quasi-perturbative expressions shown in refs 29 and 30. The } \rho_{i \mu, j \mu} \text{ amplitudes used in the CR-EOMCC(2,3) considerations are expressed in terms of the one- and two-body components of the deexcitation operator defining the left EOMCCSD eigenstate,} \]

\[ \text{the one-body, two-body, and—in the full implementation of the CR-EOMCC(2,3) defining variant } D \text{ of it designated as CR-EOMCC(2,3),D} \text{—selected three-body components of the similarity-transformed Hamiltonian of CCSD, } H_{12}^{(2)} \text{. The latter components enter the Epstein—Nesbet-like denominator for triple defining the } \rho_{i \mu, j \mu} \text{ amplitudes in the CR-EOMCC(2,3),D approach. In the simplified variant } A \text{ of the CR-EOMCC(2,3), abbreviated as CR-EOMCC(2,3),A and equivalent to the EOM-CC(2),PT(2) method of ref 100, one replaces the Epstein—Nesbet-like denominator defining } \rho_{i \mu, j \mu} \text{ which in variant } D \text{ of CR-EOMCC(2,3),D is calculated as } o_{\mu \delta}^{(\text{CCSD})} = \left( \left( \Phi^\mu_{\delta(M)^{\alpha \beta}} \right)^2 \right)_{ijkl} (\Phi^\mu_{\delta(M)^{\alpha \beta}})_{ijkl} (\Phi^\mu_{\delta(M)^{\alpha \beta}})_{ijkl} (2) \text{, where } o_{\mu \delta}^{(\text{CCSD})} \text{ is the EOMCCSD excitation energy and } H_{12}^{(2)} \text{ is the } n\text{-body component of } H_{12} \text{, by the simplified form of it, which represents the Møller—Plesset-like denominator for triple excitations, } o_{\mu \delta}^{(\text{CCSD})} = (\omega_\delta + \omega_\delta + \omega_\delta - \omega_\delta - \omega_\delta - \omega_\delta). \text{ The differences between variants } A \text{ and } D \text{ are substantial, in favor of CR-EOMCC(2,3),D, when the excited states of interest are dominated by two-electron transitions. When the excited states in question are dominated by one-electron transitions, as is the case when we examine the } \pi \rightarrow \pi^* \text{ excitations in cis-7HQ and its complexes, the CR-EOMCC(2,3),A and CR-EOMCC(2,3),D approaches provide similar results. We refer the reader to the original work on the CR-EOMCC(2,3) approach and its variants}^{29,30} \text{ for further details. The similarity of the CR-EOMCC(2,3),A and CR-EOMCC(2,3),D excitation energies for the cis-7HQ system and its hydrogen-bonded complexes examined in this study is shown in section 4.1.}

\[ \text{Before discussing the computational details of the FDET, TD-DFT, and EOMCC calculations reported in this work, we must explain how one obtains the desired } \delta \text{-CR-EOMCC(2,3) results. As shown in refs 30 and 31, although the ground-state CR-CC(2,3),D energy and its CR-CC(2,3),A analog, which is equivalent to the CCSD(2) approach of ref 112, are size extensive, being ideally suited for examining the weakly bound complexes involving larger molecules,}^{32-40} \text{ such as those studied in this work, their excited state CR-EOMCC(2,3),D and CR-EOMCC(2,3),A or EOM-CC(2)PT(2)} \text{ analogs do not satisfy the property of size intensity satisfied by EOMCCSD,}^{43,45} \text{i.e., the vertical excitation energy of a noninteracting system } A + B \text{, in which fragment } A \text{ is excited, resulting from the CR-EOMCC(2,3) or EOM-CC(2)PT(2) calculations, is not the same as that obtained for the isolated system } A. \text{ Although the departure from strict size intensity in the CR-EOMCC calculations of vertical and adiabatic excitation energies is in many cases of relatively minor significance when compared to other sources of errors,}^{41} \text{ this may be a more serious issue when examining the shifts in the excitation energy due to the formation of weakly bound complexes. The lack of size intensity of the CR-EOMCC(2,3),D and EOM-CC(2)PT(2) excitation energies can be traced back to the presence of the size-extensive contribution}
\]

\[ \beta_{\mu} = \sum_{i < j < k < l} \left( r_{\mu i, j \mu} r_{\mu k, l \mu} - r_{\mu i, k \mu} r_{\mu j, l \mu} \right) (26) \]

\[ \text{in the vertical excitation energy}
\]

\[ o_{\mu \delta}^{(\text{CR-EOMCC(2,3)})} = E_{\mu \delta}^{(\text{CR-EOMCC(2,3)})} - E_0^{(\text{CR-CC(2,3)})} (27) \]

\[ \text{Indeed, using the above equations for the CR-EOMCC(2,3) energies, particularly eq 25, we can decompose the CR-EOMCC(2,3) excitation energy as follows:}^{30,31}
\]

\[ o_{\mu \delta}^{(\text{CR-EOMCC(2,3)})} = o_{\mu \delta}^{(\text{CCSD})} + \mu_\delta + \beta_{\mu} (28) \]

\[ \text{Here, } o_{\mu \delta}^{(\text{CCSD})} \text{ is the vertical excitation energy of EOMCCSD,}
\]

\[ \mu_\delta = \sum_{i < j < k < l} \left( r_{\mu i, j \mu} r_{\mu k, l \mu} - r_{\mu i, k \mu} r_{\mu j, l \mu} \right) (29) \]

\[ \text{where } \left( r_{\mu i, j \mu} r_{\mu k, l \mu} - r_{\mu i, k \mu} r_{\mu j, l \mu} \right) = \left( \Phi^\mu_{\delta(M)^{\alpha \beta}} \right)^2 \left( (R_{\mu i} + R_{\mu j}) \right) (\Phi^\mu_{\delta(M)^{\alpha \beta}}) \text{ is the contribution to the triply excited moment } \rho_{i \mu, j \mu} (2) \text{ of EOMCCSD due to the one- and two-body components of } R_{\mu i} \text{ and } R_{\mu j} \text{ is the quantity defined by eq 26. Since the EOMCCSD approach is rigorously size intensive and, as shown in ref 31, the } \mu_\delta \text{ term is size intensive as well, the } \left( o_{\mu \delta}^{(\text{CCSD})} + \mu_\delta (2,3) \right) \text{ part of the
CR-EOMCC(2,3) excitation energy $\omega_{\mu}^{(\text{CR-EOMCC}(2,3))}$ is a size-intensive quantity. Unfortunately, the $\beta_\mu$ term defined by eq 26, being a size-extensive contribution that does not cancel out, grows with the size of the system,\textsuperscript{30,31} destroying the size intensivity of $\omega_{\mu}^{(\text{CR-EOMCC}(2,3))}$. In order to address this concern and following the discussion in refs 30 and 31 in this work, we have implemented the rigorously size-intensive variant of CR-EOMCC(2,3), designated as $\delta$-CR-EOMCC(2,3), by neglecting the problematic $\beta_\mu$ term in eq 28 and redefining the excitation energy as follows:

$$\omega_{\mu}^{(\delta\text{-CR-EOMCC}(2,3))} = \omega_{\mu}^{(\text{CCSD})} + \alpha_{\mu}$$  \hspace{1cm} (30)

with $\alpha_{\mu}$ given by eq 29. The resulting $\delta$-CR-EOMCC(2,3) approach provides a size-intensive description of the excitation energies and, by defining the total energy of a given electronic state $\mu$, $\varepsilon_{\mu}$, as a sum of the size-extensive ground-state CR-CC(2,3) energy and size-intensive excitation energy $\omega_{\mu}^{(\delta\text{-CR-EOMCC}(2,3))}$, eq 30, so that

$$\varepsilon_{\mu} = \varepsilon_{\mu}^{(\text{CCSD})} + \sum_{i<j<k} f_{\mu \nu \beta \gamma} \delta_{\mu \nu \beta \gamma} (2)$$

$$+ \sum_{i<j<k} f_{\mu \nu \beta \gamma} \Phi_{\mu \nu \beta \gamma} (2)$$  \hspace{1cm} (31)

the size extensive description of state $\mu$, assuming that the electronic excitation in AB is either in A or in B, but not in both fragments simultaneously (cf. refs 16, 33, and 92). Again, as in the regular CR-EOMCC(2,3) approach, we can distinguish between the full variant $\delta$ of $\delta$-CR-EOMCC(2,3) and its various approximations, including variant A. The $\delta$-CR-EOMCC(2,3),A method is equivalent to the EOMCCSD(2)\textsubscript{F} approach of ref 31 and, if we limit ourselves to the vertical excitation energies only, to the EOMCCSD(1) approach of ref 32. As shown in section 4.1, variants A and D provide nearly identical results for the vertical excitation energies in the cis-7HQ chromophore and its complexes, corresponding to the lowest $\pi \rightarrow \pi^*$ transition, which seem to be in good agreement with the experimental data reported in refs 5 and 69.

3. COMPUTATIONAL DETAILS

In order to examine the performance of the FDET approach and to demonstrate its advantages when compared with the results of supermolecular TDDFT calculations, both benchmarked against the high-level EOMCC data of $\delta$-CR-EOMCC(2,3) quality, we have investigated the shifts in the vertical excitation energy $\omega_{\pi \rightarrow \pi^*}$ corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ chromophore induced by the formation of hydrogen-bonded complexes shown in Figure 1, which were previously examined using laser resonant two-photon UV spectroscopy.\textsuperscript{113} The eight complexes considered in this work include the cis-7HQ$\cdot\cdot\cdot$B systems, where B represents one of the following environments: a single water molecule, a single ammonia molecule, a water dimer, a single molecule of methanol, a single molecule of formic acid, a trimer consisting of ammonia and two water molecules, a trimer consisting of ammonia, water, and ammonia, and a trimer consisting of two ammonia and one water molecules (see Figure 1). For each cis-7HQ$\cdot\cdot\cdot$B complex and for each electronic structure employed in this study, the corresponding environment-induced shift $\Delta \omega_{\pi \rightarrow \pi^*}$ was calculated as a difference between the value of $\omega_{\pi \rightarrow \pi^*}$ characterizing the complex and that obtained for the isolated cis-7HQ molecule, using the nuclear geometries of cis-7HQ$\cdot\cdot\cdot$B and cis-7HQ optimized in the second-order Moller–Plesset perturbation theory (MP2)\textsuperscript{115} calculations employing the aug-cc-pVTZ basis set.\textsuperscript{114,115} The optimizations of nuclear geometries of the cis-7HQ and cis-7HQ$\cdot\cdot\cdot$B systems were performed using the analytic gradients of MP2 available in the Gaussian 03 package.\textsuperscript{116} As in all other post-Hartree–Fock wave function calculations discussed in this article, the lowest-energy core molecular orbitals (MOs) correlating with the 1s shells of the C, N, and O atoms were frozen in these optimizations.

Once the nuclear geometries of the cis-7HQ and cis-7HQ$\cdot\cdot\cdot$B systems were determined, we performed the desired FDET and supermolecular TDDFT and EOMCC calculations of the vertical excitation energies $\Delta \omega_{\pi \rightarrow \pi^*}$ and the environment-induced shifts $\Delta \omega_{\pi \rightarrow \pi^*}$. The most essential information about these calculations, including basis sets, key algorithmic details, and computer codes used to perform them, is provided below.

3.1. Reference EOMCC Calculations. In order to establish the reference EOMCC values of the environment-induced shifts $\Delta \omega_{\pi \rightarrow \pi^*}$, we performed a series of EOMCCSD calculations for the cis-7HQ$\cdot\cdot\cdot$B$\cdot\cdot\cdot$H$_2$O$\cdot\cdot\cdot$NH$_3$ and 7HQ$\cdot\cdot\cdot$B$\cdot\cdot\cdot$NH$_3$ systems using five different basis sets, including 6-31+G(d),\textsuperscript{117–119} 6-31+G(dp),\textsuperscript{117–119} 6-311+G(d,p),\textsuperscript{117–119} aug-cc-pVDZ,\textsuperscript{114,115} and the [5s3p2d/3s2p] basis of Sadlej,\textsuperscript{121} designated as POL, followed by the EOMCCSD and $\delta$-CR-EOMCC(2,3) computations for all eight cis-7HQ$\cdot\cdot\cdot$B complexes examined in this work using the largest basis sets that we could afford, namely,
6-311+G(d) in the EOMCCSD case and 6-31+G(d) in the case of the \( \delta \)-CR-EOMCC(2,3) approach. The main purpose of all of these calculations was to examine the stability of the final EOMCC values of the \( \Delta \omega_{x-y} \) shifts, recommended for use in benchmarking the FDET and supermolecular TDDFT data, with respect to the choice of the basis set and higher-order correlation effects neglected in EOMCCSD, but included in \( \delta \)-CR-EOMCC(2,3). As explained in section 4.1, the final EOMCC values of the vertical excitation energies \( \omega_{x-y} \) that are used in this paper to benchmark the FDET and supermolecular TDDFT methods were obtained using the composite approach, in which we augment the EOMCCSD/6-311+G(d) results by the triplets corrections to EOMCCSD energies extracted from the \( \delta \)-CR-EOMCC(2,3)/6-31+G(d) calculations, as in the following formula:

\[
\omega_{x-y} (\text{EOMCC}) = \omega_{x-y} (\text{EOMCCSD/6-311+G(d)}) + (\omega_{x-y} (\delta \text{-CR-EOMCC(2,3)/6-31+G(d)}) - \omega_{x-y} (\text{EOMCCSD/6-31+G(d)}))
\] (32)

All of the EOMCC calculations reported in this work were carried out with the programs developed at Michigan State University described, for example, in refs 26, 30, 91, and 92, that part of the GAMESS package. 122, 123 In order to obtain the final \( \delta \)-CR-EOMCC(2,3) results, we had to modify the previously developed 158, 159 CR-CC(2,3)/CR-EOMCC(2,3) GAMESS routines, since we had to replace the vertical excitation energy of CR-EOMCC(2,3) given by eq 28 with its size-intensive \( \delta \)-CR-EOMCC(2,3) counterpart defined by eq 30. Thanks to this effort, the present GAMESS code enables the calculations of the three different types of triplets corrections to EOMCCSD energies, including CR-EOMCCSD(T) 124, 125, 126, 127 CR-EOMCC-CC(2,3), 128 and \( \delta \)-CR-EOMCC(2,3), as defined by eqs 30 and 31. The corresponding ground-state CCSD calculations, which precede the determination of the left CCSD and right left EOMCCSD eigenstates that enter the formulas for the triplets corrections of \( \delta \)-CR-EOMCC(2,3) and the steps needed to compute the triplets corrections of the ground-state CR-CC(2,3) and excited-state CR-EOMCC(2,3) and \( \delta \)-CR-EOMCC(2,3) approaches, were performed with the routines described in ref 124, which form part of the GAMESS as well. The RHF orbitals were employed throughout, and as pointed out above, the lowest-energy core MOs that correlate with the 1s shells of the non-hydrogen atoms were frozen in the CCSD, EOMCCSD, and \( \delta \)-CR-EOMCC(2,3) calculations. The CCSD/EOMCCSD energies were converged to 10^{-7} Hartree. We refer the reader to refs 26, 30, 91, and 92 for further details of the GAMESS computer codes and algorithms exploited in this work.

3.2. FDET and Supermolecular TDDFT Calculations. All of the FDET and supermolecular TDDFT calculations reported in this article were performed using the linear-response TDDFT routines available in the ADP2009.01 code. 125 In particular, the FDET calculations followed the general protocol introduced in ref 58 in which the occupied and unoccupied orbitals for the embedded chromophore that are obtained by solving the Kohn–Sham-like system defined by eq 13 are subsequently used within the linear-response TDDFT framework 46 to obtain excitation energies.

In order to examine the effect of the basis set on the complexation-induced shifts \( \Delta \omega_{x-y} \), three STO-type basis sets 126 were employed in the FDET and supermolecular TDDFT calculations: STO DZP (double-\( \zeta \) basis with one set of polarization functions), STO TZ2P (triple-\( \zeta \) basis with two sets of polarization functions), and STO ATZ2P, which includes all TZ2P functions plus one set of diffuse s-STO and p-STO functions.

The environment density \( \rho_v \) used in the FDET calculations was either nonrelaxed, i.e., constructed using the ground-state electronic density of the environment obtained by solving the conventional Kohn–Sham equations for the environment molecules in the absence of the chromophore, or relaxed, i.e., obtained with the aforementioned “freeze-and-thaw” procedure. 46 We also examined two types of basis expansions to represent the occupied and unoccupied orbitals of the chromophore \( A \) embedded in the environment \( B \) and densities \( \rho_v \) and \( \rho_s \) in the FDET calculations. In the supermolecular expansion approach, all atomic centers of the total system \( AB \) were used to represent the orbitals and densities. In the monomer-expansion FDET calculations, the orbitals of the chromophore \( A \) embedded in \( B \) and the corresponding density \( \rho_v \) were represented using the atomic centers of \( A \), whereas the environment density \( \rho_s \) was represented using the atomic centers of \( B \) (see refs 80 and 126 for further information).

The monomer-expansion technique using nonrelaxed \( \rho_v \), which is the recommended variant of FDET for the type of applications reported in this article, relies on the approximations, referred to as the Neglect of Dynamic Response of the Environment (NDRE), in which we assume that the dynamic response of the whole system \( AB \) to the process of electronic excitation is limited to chromophore \( A \) and that the coupling between the excitations in the embedded system and in its environment can be neglected. A comparison of the excitation-induced shifts \( \Delta \omega_{x-y} \) in the cis-7HQ•••B systems resulting from the FDET and EOMCC calculations, discussed in the next section, clearly shows that such coupling can indeed be neglected, as the spectral overlap between cis-7HQ and the environment molecules bound to it is negligible. The NDRE approximation and the monomer-expansion-based FDET approach that results from it are very effective in eliminating spurious electronic excitations involving the environment (see the discussion in ref 52). If the coupling between the excitations in the embedded system and in its environment could not be neglected, we would have to rely on the more general formalism introduced in ref 127 (for the additional discussion of the importance of such couplings in FDET calculations, see ref 128).

In both the FDET and supermolecular TDDFT calculations, we used the SAOP scheme 126 to approximate the relevant exchange-correlation potential contributions for the isolated and embedded chromophore (the FDET case) and for the total system (the supermolecular TDDFT case). The nonadditive kinetic energy potential \( v_{\text{kin}}^{\text{eff}}(\rho_s \rho_v) [\pi] \), eq 12, that forms part of the local, orbital-free embedding potential \( v_{\text{tot}}^{\text{eff}}(\rho_s \rho_v) [\pi] \), eq 10, used in the FDET calculations was approximated using the generalized gradient approximation (GGA97), 126 whereas the nonadditive exchange-correlation component of \( v_{\text{tot}}^{\text{eff}}(\rho_s \rho_v) [\pi] \), eq 11, was approximated using the Perdew–Wang (PW91) functional. We also performed calculations in which the nonadditive kinetic energy potential \( v_{\text{kin}}^{\text{eff}}(\rho_s \rho_v) [\pi] \) was approximated with the help of the recently developed NDS approximant, 44 which takes into account the exact conditions that become relevant for the proper behavior of \( v_{\text{kin}}^{\text{eff}}(\rho_s \rho_v) [\pi] \) in the vicinity of nuclei, but we do not show these results in this article, since they are very similar to those obtained with GGA97. Because of the small energy differences that define the spectral shifts examined in this work, we used
Table 2. Vertical Excitation Energies (in cm⁻¹) Obtained with the EOMCCSD Approach Corresponding to the Lowest \( \pi \rightarrow \pi^* \) Transition in the cis-7HQ Chromophore and Its Complexes with the Water and Ammonia Molecules

<table>
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<tr>
<th>basis set</th>
<th>7HQ</th>
<th>7HQ ( \cdots ) H₂O</th>
<th>7HQ ( \cdots ) NH₃</th>
<th>( \Delta \omega_{\pi \rightarrow \pi^*} )</th>
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</thead>
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<td>3496</td>
<td>−528</td>
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<td>6-311+G(d)</td>
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<td>34500</td>
<td>34263</td>
<td>−546</td>
</tr>
<tr>
<td>aug-cc-pVDZ</td>
<td>34707</td>
<td>34182</td>
<td>33923</td>
<td>−525</td>
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<tr>
<td>POL</td>
<td>34596</td>
<td>34077</td>
<td>33819</td>
<td>−519</td>
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</table>

Table 2. Vertical Excitation Energies \( \omega_{\pi \rightarrow \pi^*} \) and the Environment-Induced Shifts \( \Delta \omega_{\pi \rightarrow \pi^*} \) (in cm⁻¹) Obtained with the EOMCCSD/6-31 + G(d), EOMCCSD/6-311 + G(d), \( \delta \)-CR-EOMCC(2,3),A, and \( \delta \)-CR-EOMCC(2,3),D Approaches, and Their Composite EOMCC,A and EOMCC,D Analogs Defined by eq 32, Corresponding to the Lowest \( \pi \rightarrow \pi^* \) Transition in the cis-7HQ Chromophore and Its Various Complexes

<table>
<thead>
<tr>
<th>environment</th>
<th>EOMCCSD/6-31 + G(d)</th>
<th>EOMCCSD/6-311 + G(d)</th>
<th>( \delta )-CR-EOMCC(2,3),A/6-31 + G(d)</th>
<th>( \delta )-CR-EOMCC(2,3),D/6-31 + G(d)</th>
<th>EOMCC,D¹</th>
<th>EOMCC,A²</th>
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</thead>
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<tr>
<td>none</td>
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<td>35046</td>
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<tr>
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<td>34500</td>
<td>30558</td>
<td>30199</td>
<td>30415</td>
<td>30056</td>
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<tr>
<td>NH₃</td>
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<td>34263</td>
<td>30291</td>
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<td>30157</td>
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<td>33699</td>
<td>29700</td>
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<td>29532</td>
<td>29210</td>
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<tr>
<td>HCOOH</td>
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<td>34095</td>
<td>30717</td>
<td>30428</td>
<td>30582</td>
<td>30293</td>
</tr>
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<td>29717</td>
<td>29355</td>
<td>29863</td>
<td>29008</td>
</tr>
<tr>
<td>NH₂−H₂O−NH₃</td>
<td>33542</td>
<td>33585</td>
<td>29355</td>
<td>29035</td>
<td>29177</td>
<td>28879</td>
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<tr>
<td>NH₂−NH₃−H₂O</td>
<td>33302</td>
<td>33156</td>
<td>29088</td>
<td>28612</td>
<td>28922</td>
<td>28646</td>
</tr>
</tbody>
</table>

\( \Delta \omega_{\pi \rightarrow \pi^*} \) for various environments:

- H₂O: −528, −546, −544, −512, −562, −530, −590
- NH₃: −775, −783, −812, −789, −820, −797, −905
- CH₃OH: −1304, −1347, −1403, −1333, −1446, −1376, −1637
- CH₃OH: −341, −351, −386, −283, −396, −292, −467
- HCOOH: −666, −675, −734, −655, −743, −664, −1014
- NH₂−H₂O−H₂O: −1790, −1828, −1932, −1847, −1969, −1855, −2490
- NH₂−H₂O−NH₃: −1629, −1661, −1748, −1675, −1780, −1707, −2136
- NH₂−NH₃−H₂O: −1869, −1910, −2014, −1899, −2055, −1940, −2482

⁴ Defined by eq 32, in which variant A of CR-EOMCC(2,3) is employed.
⁵ Defined by eq 32, in which variant D of CR-EOMCC(2,3) is employed.

The results of our FDET, supermolecular TDDFT, and EOMCC calculations for the shifts in the vertical excitation energy \( \omega_{\pi \rightarrow \pi^*} \) corresponding to the lowest \( \pi \rightarrow \pi^* \) transition in the cis-7HQ chromophore induced by the formation of the eight complexes shown in Figure 1 are summarized in Tables 1—8 and Figures 2—5. We begin our discussion with the analysis of the EOMCCSD and \( \delta \)-CR-EOMCC(2,3) calculations aimed at establishing the reference EOMCC values for benchmarking purposes. The comparison of the FDET shifts \( \Delta \omega_{\pi \rightarrow \pi^*} \) with the reference EOMCC, supermolecular TDDFT, and experimental data is presented immediately afterward. Among the key discussed aspects are the basis set dependence of the FDET and supermolecular TDDFT results, the issues created by relaxing the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi^*} \) resulting from the EOMCCSD calculations on the basis set. In Table 1, we compare the results of the EOMCCSD calculations obtained with the

4. RESULTS AND DISCUSSION

The results of our FDET, supermolecular TDDFT, and EOMCC calculations for the shifts in the vertical excitation energy \( \omega_{\pi \rightarrow \pi^*} \) corresponding to the lowest \( \pi \rightarrow \pi^* \) transition in the cis-7HQ chromophore induced by the formation of the eight complexes shown in Figure 1 are summarized in Tables 1—8 and Figures 2—5. We begin our discussion with the analysis of the EOMCCSD and \( \delta \)-CR-EOMCC(2,3) calculations aimed at establishing the reference EOMCC values for benchmarking purposes. The comparison of the FDET shifts \( \Delta \omega_{\pi \rightarrow \pi^*} \) with the reference EOMCC, supermolecular TDDFT, and experimental data is presented immediately afterward. Among the key discussed aspects are the basis set dependence of the FDET and supermolecular TDDFT results, the issues created by relaxing the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi^*} \) resulting from the EOMCCSD calculations on the basis set. In Table 1, we compare the results of the EOMCCSD calculations obtained with the
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Table 3. Comparison of the Environment-Induced Shifts $\Delta \omega_{\pi^{*} \rightarrow \pi}$ (in cm$^{-1}$) of the Vertical Excitation Energy Corresponding to the Lowest $\pi^{*} \rightarrow \pi^{\*}$ Transition in the cis-7HQ Chromophore Resulting from the Monomer-Expansion-Based FDET and Supermolecular TDDFT Calculations Using the STO ATZ2P Basis Set with the Reference EOMCC,A Data

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<th>FDET</th>
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</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>-562</td>
<td>-944</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>-820</td>
<td>-1222</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>-1446</td>
<td>-2280</td>
</tr>
<tr>
<td>HCOOH</td>
<td>-396</td>
<td>-805</td>
</tr>
<tr>
<td>CH$_3$N$_2$OH-H$_2$O</td>
<td>-1969</td>
<td>-2838</td>
</tr>
<tr>
<td>NH$_3$-H$_2$O-NH$_3$</td>
<td>-1780</td>
<td>-2594</td>
</tr>
<tr>
<td>NH$_3$-H$_2$O-H$_2$O</td>
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<td>-2899</td>
</tr>
<tr>
<td>Av. dev. from EOMCC,A</td>
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<td>-673</td>
</tr>
<tr>
<td>Av. abs. dev. from EOMCC,A</td>
<td>0</td>
<td>104</td>
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</tbody>
</table>

Table 4. Environment-Induced Shifts $\Delta \omega_{\pi^{*} \rightarrow \pi}$ (in cm$^{-1}$) of the Vertical Excitation Energy Corresponding to the Lowest $\pi^{*} \rightarrow \pi^{\*}$ Transition in the cis-7HQ Chromophore Resulting from the Supermolecular Expansion-Based FDET and Supermolecular TDDFT Calculations Using the STO ATZ2P Basis Set, along with the Average Errors Relative to the Reference EOMCC,A Data

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Table 5. Environment-Induced Shifts $\Delta \omega_{\pi^{*} \rightarrow \pi}$ (in cm$^{-1}$) of the Vertical Excitation Energy Corresponding to the Lowest $\pi^{*} \rightarrow \pi^{\*}$ Transition in the cis-7HQ Chromophore Resulting from the Monomer-Expansion-Based FDET and Supermolecular TDDFT Calculations Using the STO TZ2P Basis Set, along with the Average Errors Relative to the Reference EOMCC,A Data

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<td>113</td>
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Table 6. Environment-Induced Shifts $\Delta \omega_{\pi^{*} \rightarrow \pi}$ (in cm$^{-1}$) of the Vertical Excitation Energy Corresponding to the Lowest $\pi^{*} \rightarrow \pi^{\*}$ Transition in the cis-7HQ Chromophore Resulting from the Monomer-Expansion-Based FDET and Supermolecular TDDFT Calculations Using the STO DZP Basis Set, along with the Average Errors Relative to the Reference EOMCC,A Data

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<td>115</td>
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6-31+G(d), 6-31++G(dp), 6-311+G(d), aug-cc-pVDZ, and POL basis sets for the two smallest complexes, 7HQ: $\cdot$ $\cdot$ $\cdot$ NH$_3$ and 7HQ: $\cdot$ $\cdot$ $\cdot$ CH$_3$O, for which we could afford the largest number of computations. The results in Table 1 indicate that although the vertical excitation energies $\omega_{\pi^{*} \rightarrow \pi^{\*}}$ in the bare cis-7HQ system and its complexes with the water and ammonia molecules vary with the basis set (for the basis sets tested here by as much as about 600 cm$^{-1}$), the environment-induced shifts $\Delta \omega_{\pi^{*} \rightarrow \pi^{\*}}$ are almost insensitive to the basis set choice. Although we were unable to perform a similarly thorough analysis for the remaining complexes due to prohibitive computer costs, we were able to obtain the EOMCCSD $\omega_{\pi^{*} \rightarrow \pi^{\*}}$ and $\Delta \omega_{\pi^{*} \rightarrow \pi^{\*}}$ values for all of the complexes examined in this study using the 6-31+G(d) and 6-311+G(d) basis sets. As shown in Table 2, the differences between the EOMCCSD/6-31+G(d) and EOMCCSD/6-311+G(d) values of the environment-induced shifts $\Delta \omega_{\pi^{*} \rightarrow \pi^{\*}}$ remain small for all complexes of interest, ranging from 8 cm$^{-1}$ in the 7HQ: $\cdot$ $\cdot$ $\cdot$ NH$_3$ case to 43 cm$^{-1}$ in the case of 7HQ: $\cdot$ $\cdot$ $\cdot$ (H$_2$O)$_2$, or 1–3%. Thus, we can conclude that the choice of the basis set, although important for obtaining the converged $\omega_{\pi^{*} \rightarrow \pi^{\*}}$ values, is of relatively little significance when the environment-induced shifts in the vertical excitation energy corresponding to the lowest $\pi^{\*} \rightarrow \pi^{\*}$ transition in the cis-7HQ chromophore are considered.

Although the EOMCCSD approach is known to provide an accurate description of excited states dominated by one-electron transitions, such as the $\pi^{*} \rightarrow \pi^{\*}$ transition in cis-7HQ and its complexes, there have been cases of similar states reported in the literature, where the EOMCCSD level has not been sufficient to obtain high-quality results.

Moreover, our interest in this study is in the small energy differences defining the
Table 7. Dependence of the Vertical Excitation Energy Corresponding to the Lowest $\sigma \rightarrow \pi^*$ Transition in cis-7HQ
Resulting from the Supermolecular TDDFT Calculations Using the STO TZ2P Basis Set (in cm$^{-1}$) on the Position of
Ghost Functions

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</tr>
<tr>
<td>(NH$_3$–NH$_2$–H$_2$O)</td>
<td>30454</td>
</tr>
</tbody>
</table>

Table 8. Effect of the Approximation Used for the Exchange-Correlation Energy Functional on the Environment-Induced Shifts $\Delta\omega_{\pi^*-\sigma^*}$ (in cm$^{-1}$) of the Vertical Excitation Energy Corresponding to the Lowest $\sigma \rightarrow \pi^*$ Transition in the cis-7HQ Chromophore Calculated Using the FDET and Supermolecular TDDFT Methodologies and the STO ATZ2P Basis Set

<table>
<thead>
<tr>
<th>environment</th>
<th>FDET$^a$</th>
<th>supermolecular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PW91$^b$</td>
<td>LDA$^b$</td>
</tr>
<tr>
<td>2H$_2$O</td>
<td>–1767</td>
<td>–1756</td>
</tr>
<tr>
<td>av. dev. from</td>
<td>–149</td>
<td>–139</td>
</tr>
<tr>
<td>EOMCCA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>av. abs. dev. from</td>
<td>149</td>
<td>140</td>
</tr>
</tbody>
</table>

$^a$ In FDET calculations, PW91, LDA, and SAOP refer to three different approximations for the exchange-correlation potential evaluated at the chromophore density $\rho_0$. The nonadditive contributions to the orbital-free embedding potential use the same approximants in all cases (PW91 for exchange-correlation and GGA97 for the kinetic energy). The FDET calculations use the nonrelaxed environment density $\rho_0$ and the monomer basis expansion. $^b$ Ref 136. $^c$ Ref 135. $^d$ Ref 129.

environment-induced shifts $\Delta\omega_{\pi^*-\sigma^*}$, which may be sensitive to the higher-order correlation effects neglected in the EOMCCSD calculations. For this reason, we also examined the effect of triples corrections to EOMCCSD energies on the calculated $\omega_{\pi^*-\sigma^*}$ and $\Delta\omega_{\pi^*-\sigma^*}$ values by performing the $\delta$-CR-EOMCC(2,3) calculations with the 6-31+G(d) basis set. The results of these calculations, shown in Table 2, indicate that triple excitations have a significant effect on the vertical excitation energies $\omega_{\pi^*-\sigma^*}$, reducing the 4000–5000 cm$^{-1}$ differences between the EOMCCSD and experimental data to no more than about 800 cm$^{-1}$, when the $\delta$-CR-EOMCC(2,3)/A/6-31+G(d) calculations are performed, and no more than about 500 cm$^{-1}$ when the $\delta$-CR-EOMCC(2,3)/D/6-31+G(d) approach is employed, while bringing the $\Delta\omega_{\pi^*-\sigma^*}$ values closer to the experimentally observed shifts when compared with EOMCCSD. Although the differences between the $\delta$-CR-EOMCC(2,3) and EOMCCSD values of the environment-induced shifts $\Delta\omega_{\pi^*-\sigma^*}$ resulting from the calculations with the 6-31+G(d) basis set do not exceed 15–16% of the EOMCCSD values, triples corrections improve the EOMCCSD results and, as such, are useful for the generation of the reference EOMCC data.

Ideally, one would like to perform the $\delta$-CR-EOMCC(2,3) calculations for basis sets larger than 6-31+G(d), such as 6-311+G(d), but complexes of cis-7HQ examined in this study

Figure 2. The dependence of the environment-induced shifts $\Delta\omega_{\pi^*-\sigma^*}$ of the vertical excitation energy corresponding to the lowest $\sigma \rightarrow \pi^*$ transition in the cis-7HQ chromophore on the STO-type basis set used in the FDET calculations employing the monomer (m) and supermolecular (s) expansions and nonrelaxed $\rho_0$, and a comparison of the resulting FDET shifts with the reference EOMCC/A data.

Figure 3. The dependence of the environment-induced shifts $\Delta\omega_{\pi^*-\sigma^*}$ of the vertical excitation energy corresponding to the lowest $\sigma \rightarrow \pi^*$ transition in the cis-7HQ chromophore on the type of the frozen electron density $\rho_0$ used in the FDET calculations employing the STO ATZ2P basis set and the monomer (m) and supermolecular (s) expansions, and a comparison of the resulting shifts with the reference EOMCC/A and supermolecular TDDFT data.
ωEOMCC,D approaches provide vertical excitation energies triples corrections to EOMCCSD energies extracted from the photon ionization UV spectroscopy. Kohn on the form of the exchange-correlation functional of the electron transitions in the cis-7HQ chromophore and resulting from the FDET data and considering the fact that the triples corrections to the vertical excitation energy corresponding to the lowest π → π* transition in the cis-7HQ system and 668 cm⁻¹ in the case of the bare cis-7HQ system and 668 cm⁻¹ in the case of the NH₂-H₂O-H₂O complex, never exceeding 2% of the experimental excitation energies. The EOMCC,D approach, which adds the triples correction obtained in the δ-CR-EOMCC(2,3),D/6-311+G(d) calculation to the EOMCCSD/6-311+G(d) energy, gives errors in the calculated excitation energies σ → π*-relativetoexperimentalresultsrangebetween17 cm⁻¹ in the case of the 7HQ···(NH₂−H₂O) complex and 361 cm⁻¹ for 7HQ···(NH₂−H₂O−H₂O), or no more than 1% of the experimental values. These results should be compared to the much larger differences between the EOMCCSD/6-311+G(d) and experimental excitation energies that range between 14 and 17%. The complexity-induced spectral shifts Δωσ→π* resulting from the EOMCC,A and EOMCC,D calculations agree with their experimental counterparts to within 5–27% or 15% on average in the case of EOMCC,A and 10–37% or 22% on average in the EOMCC,D case. The EOMCC,D approach, while bringing the excitation energies σ → π*-to a much closer agreement with experimental results than the EOMCCSD/6-311+G(d) calculations, does not offer improvements in the calculated shifts Δωσ→π*. The composite EOMCC,A approach provides additional small improvements in the calculated Δωσ→π* values, reducing the 7–33% errors relative to experiment obtained in the EOMCCSD/6-311+G(d) calculations to 5–27%. For this reason, we consider the EOMCC,A values of the spectral shifts Δωσ→π* as the theoretical reference values for assessing the quality of the FDET and supermolecular TDDFT calculations, although the use of EOMCC,D would not change any of our main conclusions.

Clearly, a comparison of the purely electronic EOMCC and experimental data discussed above has limitations, since we would have to examine the effect of nuclear motion on the calculated EOMCCSD and δ-CR-EOMCC(2,3) excitation energies and use basis sets larger than 6-31+G(d) in the δ-CR-EOMCC(2,3) calculations to make more definitive statements, which we cannot do at this time within the EOMCC framework due to the size of systems examined in this work. To overcome this difficulty, we could try to combine the EOMCC and TDDFT or FDET data, using TDDFT or FDET to examine the role of nuclear geometries and vibrational motions and δ-CR-EOMCC(2,3) to provide electronic excitation energies. The problem is that this would defeat the main purpose of the present study, in which we want to objectively compare the purely electronic FDET and supermolecular TDDFT results for the complexity-induced spectral shifts Δωσ→π* with the corresponding, also purely electronic, EOMCC data, using the best EOMCC approach we can afford and using the same nuclear geometries in all calculations. Thus, although there are limitations in our EOMCC calculations when compared with experimental results which the present study cannot completely overcome, we believe that the EOMCC,A results obtained by combining the EOMCCSD/6-311+G(d) excitation energies with the triples corrections extracted from the δ-CR-EOMCC(2,3),A/6-31+G(d) calculations, as in eq 32, are of sufficiently high quality to allow us to assess the quality of the FDET and supermolecular TDDFT methods in applications involving the environment-induced spectral shifts in complexes of cis-7HQ.
4.2. A Comparison of the Excitation Energy Shifts from the FDET Calculations Using Nonrelaxed Environment Densities with the Reference EOMCC Data. As shown in Table 2 and in agreement with the experimental data, the excitation energy shifts $\Delta \omega_{\pi \rightarrow \pi'}$ for the hydrogen-bonded 7HQ···B complexes examined in this work resulting from the EOMCC calculations are always negative. Although this is not a strict rule, the magnitude of $\Delta \omega_{\pi \rightarrow \pi'}$ correlates, to a large extent, with the size of the hydrogen-bonded environment $B$ in the cis-7HQ···B complex. According to the reference EOMCCA calculations, the shifts in the vertical excitation energy $\omega_{\pi \rightarrow \pi'}$ corresponding to the lowest $\pi \rightarrow \pi'$ transition in the cis-7HQ chromophore vary from $-396$ to $-820$ cm$^{-1}$ in the case of the smaller 7HQ···B complexes involving the CH$_3$OH, H$_2$O, HCOOH, and NH$_3$ monomers, through $-1446$ cm$^{-1}$ in the case of the 7HQ···(H$_2$O)$_2$ complex involving the water dimer, to $-1780$ to $-2055$ cm$^{-1}$ in the case of the largest 7HQ···B systems involving the (NH$_3$·H$_2$O·NH$_3$)$_3$, (NH$_3$·H$_2$O·H$_2$O), and (NH$_3$·NH$_3$·H$_2$O) trimers. It is interesting to examine how well the FDET and supermolecular TDFT calculations reproduce these data.

We begin our discussion by assessing the quality of the FDET results employing the nonrelaxed density $\rho_b$ which is obtained by solving the Kohn–Sham equations for the environment molecule(s) in the absence of the cis-7HQ chromophore, with a focus on the results obtained with the monomer basis expansions to represent the chromophore density $\rho_B$ and the environment density $\rho_b$. As shown in section 3.2, the combined use of the nonrelaxed environment density $\rho_b$ and monomer expansions in the FDET calculations relies on the simplifying assumptions that the response of system $AB$ to the process of electronic excitation is limited to chromophore $A$, that the coupling between the excitations in the embedded system and its environment can be neglected, and that the polarization of the environment molecules by the chromophore is of no importance. The supermolecular EOMCC calculations performed in this work do not rely on any of these assumptions, so a comparison of the FDET results employing the nonrelaxed density $\rho_b$ and monomer expansions of $\rho_A$ and $\rho_B$ with the EOMCC data is particularly interesting.

As shown in Table 3 and Figure 2, the overall agreement of the monomer-expansion-based FDET/ATZ2P data using the nonrelaxed $\rho_b$ with the reference EOMCCA data is excellent. The absolute values of the deviations between the $\Delta \omega_{\pi \rightarrow \pi'}$ values resulting from the nonrelaxed, monomer-expansion-based FDET/ATZ2P and supermolecular EOMCCA calculations range from 4 cm$^{-1}$ in the case of the 7HQ···NH$_3$ complex, where the EOMCCA shift is $-820$ cm$^{-1}$, to $229$ cm$^{-1}$ in the case of the 7HQ···HCOOH system, where the EOMCCA result for $\Delta \omega_{\pi \rightarrow \pi'}$ is $-743$ cm$^{-1}$. The mean signed and unsigned errors in the nonrelaxed, monomer-expansion-based FDET/ATZ2P results for the environment-induced shifts $\Delta \omega_{\pi \rightarrow \pi'}$ relative to the EOMCCA reference data are $-36$ and $104$ cm$^{-1}$, respectively, or 11%, if we average the individual relative errors. On the basis of the analysis of the EOMCCSD and $\delta$-CR-EOMCC(2,3) calculations presented in section 4.1, the deviations between the nonrelaxed, monomer-expansion-based FDET/ATZ2P and reference EOMCCA data shown in Table 3 and Figure 2 are well within the accuracy of the EOMCC calculations, indicating the excellent performance of the nonrelaxed FDET approach.

Remarkably, the nonrelaxed, monomer-expansion-based FDET values of the $\Delta \omega_{\pi \rightarrow \pi'}$ shifts do not vary with the basis set (see Table 3–6), allowing us to obtain reasonably well converged results with the relatively small basis sets, such as STO DZP (cf. Table 6). Moreover, although we prefer to use the monomer expansion within the FDET approach, where the orbitals of the chromophore $A$ and the corresponding density $\rho_A$ are represented using the atomic centers of $A$, whereas the environment density $\rho_b$ is represented using the atomic centers of $B$, the use of the supermolecular expansion within the FDET methodology employing the nonrelaxed $\rho_b$ does not seem to change the calculated shift values. For example, as a comparison of the results shown in Tables 3 and 6 demonstrates, the average deviation from EOMCCA characterizing the nonrelaxed, monomer-expansion-based FDET calculations using the smallest STO DZP basis set, of $115$ cm$^{-1}$, is virtually identical to the analogous average deviation characterizing the nonrelaxed, supermolecular-expansion-based FDET calculations using the largest STO ATZ2P basis ($108$ cm$^{-1}$). It is also worth mentioning that the quality of the shifts calculated with the FDET approach using the nonrelaxed environment density $\rho_b$ does not diminish with or significantly depend on the size of the environment. For example, the absolute value of the difference between the $\Delta \omega_{\pi \rightarrow \pi'}$ values resulting from the nonrelaxed, monomer-expansion-based FDET/ATZ2P and supermolecular EOMCCA calculations for the smallest 7HQ···H$_2$O complex is $83$ cm$^{-1}$ or $15\%$. The analogous difference characterizing the considerably larger 7HQ···3 3 3 complex is $11$ cm$^{-1}$ or $1\%$.

All of the above observations show that the FDET approach employing the nonrelaxed environment densities $\rho_b$ including its simplest, monomer-expansion-based variant, is as accurate in describing complexation-induced shifts as the high-level EOMCC approach with singles, doubles, and noniterative triples, represented here by the composite EOMCCA approximation. The FDET results with relaxed densities $\rho_b$ are discussed next.

4.3. The Dependence of the FDET Shifts on the Choice of $\rho_b$. By determining the environment density $\rho_b$ in the absence of the chromophore, the nonrelaxed FDET model examined in section 4.2 ignores the complexation-induced changes in the electronic density of the environment, such as polarization of the environment molecule(s) by the chromophore. Furthermore, the use of monomer basis expansions to represent the chromophore density $\rho_A$ and the environment density $\rho_b$ does not allow for a penetration of the region of space occupied by the chromophore by the electronic density of the environment or for a penetration of space occupied by the environment by the electronic density of the chromophore. These simplifying assumptions make the nonrelaxed, monomer-expansion-based FDET approach computationally very attractive, as the costs of such calculations are defined by the size of the chromophore only. However, they represent an arbitrary choice, permitting the question of whether relaxing the environment density $\rho_b$ in the presence of the chromophore would help the FDET results.

As explained in section 3.2, for a given choice of approximants for the functionals used in the FDET calculations, one can optimize the environment density $\rho_b$, adjusting it to the density of the chromophore $\rho_A$ when solving the Kohn–Sham system for the chromophore $A$ embedded in the environment $B$ defined by eq 13, by exploiting the “freeze-and-thaw” procedure. One might think that such relaxed FDET calculations should be more accurate than the nonrelaxed ones in which $\rho_b$ is not adjusted, since relaxation of $\rho_b$ takes into account the effect of electronic polarization of the environment by the chromophore. Unfortunately, this is not necessarily the case
because of the inaccuracies in describing the nonadditive kinetic energy potential $\psi_{\text{kin}}(\mathbf{r}_f, \mathbf{r}_h)$, eq 12, that couples the two densities and that enters eq 13, especially when the full, supermolecular set of atomic orbitals, including those centered on A and those centered on B, is used to represent the chromophore density $\rho_A$ and the environment density $\rho_B$. It is usually impossible to $a$ priori determine which effect is numerically more important in a molecular system of interest, the neglect of the electronic polarization of the environment by the chromophore or the errors produced by the approximations used to define the $\psi_{\text{kin}}(\mathbf{r}_f, \mathbf{r}_h)$ potential. In order to perform this issue, we performed the FDET calculations in which the environment density $\rho_B$ was relaxed in the iterative process of solving eq 13 for the orbitals of the cis-7HQ chromophore.

As shown in Tables 3–6 and Figure 3, the relaxation of the environment density $\rho_B$ in the FDET calculations for each of the eight complexes examined in this study substantially worsens the results for the $\Delta \omega_{\pi-\pi}$ shifts when compared with the EOMCCA reference data. The differences between the $\Delta \omega_{\pi-\pi}$ values resulting from the relaxed FDET calculations using the STO ATZ2P basis set and the corresponding EOMCCA data, in absolute value, from 185 cm$^{-1}$ in the case of the 7HQ···NH$_3$ complex, where the EOMCCA shift is $-820$ cm$^{-1}$, to 569 cm$^{-1}$ in the case of the 7HQ···HCOOH system, where the EOMCCA result for $\Delta \omega_{\pi-\pi}$ is $-743$ cm$^{-1}$. These are much larger differences when compared with the corresponding nonrelaxed FDET calculations, which, as pointed out in section 4.2, give substantially smaller differences with the EOMCCA data that range from 4 to 229 cm$^{-1}$ when the same set is used. As shown in Table 3, the mean signed and unsigned errors in the relaxed FDET/ATZ2P results for the environment-induced shifts $\Delta \omega_{\pi-\pi}$ relative to the EOMCCA reference data are $-366$ and $366$ cm$^{-1}$, respectively, or, if we average the individual relative errors, 37%. This should be contrasted with the mean signed error of $-36$ cm$^{-1}$, mean unsigned error of 104 cm$^{-1}$, and average relative error of 11% in the analogous nonrelaxed FDET calculations. In some cases, the effect of relaxing $\rho_B$ in the FDET calculations on the calculated $\Delta \omega_{\pi-\pi}$ shifts is enormous, e.g., 546 cm$^{-1}$ in the 7HQ··· (NH$_3$–NH$_3$–H$_2$O) case. As in the case of the FDET calculations using the nonrelaxed densities $\rho_B$, neither the type of the basis expansion used to represent densities $\rho_A$ and $\rho_B$ (monomer or supermolecular) nor the computational basis set used in the calculations affect the above observations (see Tables 3–6), although the use of the supermolecular expansion to represent $\rho_A$ and $\rho_B$ in the context of the relaxed FDET calculations with the STO ATZ2P basis set seems to worsen the results, increasing the mean unsigned error in the calculated $\Delta \omega_{\pi-\pi}$ values relative to EOMCCA from 366 cm$^{-1}$ in the monomer-expansion case to 486 cm$^{-1}$, when the supermolecular expansion is employed (cf. the results in Tables 3 and 4), bringing the relaxed FDET results closer to the supermolecular TDDFT data (cf. the discussion below).

The substantial increase in the differences between the FDET and EOMCCA shift values due to the relaxation of the environment densities $\rho_B$ may be related to the fact that the Kohn–Sham-type methods applying semilocal approximants to the exchange-correlation energy used in this work tend to overestimate molecular polarizabilities in organic molecules.\textsuperscript{112,113} The exaggerated polarizability values would certainly lead to the overestimated chromophore polarization effects that could result in the artificially enhanced effects of relaxation of environment densities on the calculated $\Delta \omega_{\pi-\pi}$ values observed in our calculations. We must remember though that this argument, although reasonable here, may not be generally applicable, since going to the left-hand side of the periodic table shows that the same functionals underestimate polarizabilities.\textsuperscript{114,115}

It is worth pointing out that the result of the “freeze-and-thaw” FDET calculations employing the complete supermolecular expansion to represent the $\rho_A$ and $\rho_B$ densities, in which the environment density $\rho_B$ is allowed to relax when solving eq 13 for the orbitals of A, represents the variational limit for a given approximant to the nonadditive kinetic energy potential $\psi_{\text{kin}}(\mathbf{r}_f, \mathbf{r}_h)$. If such an approximant was exact and if the same approximant were used to represent all of the exchange-correlation contributions in both supermolecular TDDFT and FDET calculations, the total electron density obtained in the relaxed “freeze-and-thaw” FDET calculations and its analog obtained in the supermolecular TDDFT calculations would be identical (see ref 48 and the references therein).

This explains why the results of the relaxed FDET calculations using the supermolecular basis expansions to represent the $\rho_A$ and $\rho_B$ densities and their supermolecular TDDFT analogs shown in Table 4 and Figure 3 are so similar. Indeed, by relaxing the $\rho_A$ and $\rho_B$ densities simultaneously and by allowing them to penetrate both subsystems A and B when solving eq 13, we produce the situation in which the differences between the supermolecular and embedding strategies for calculating the $\Delta \omega_{\pi-\pi}$ shifts become small. We must remember though that by relaxing the environment densities in the FDET approach or by performing the supermolecular TDDFT calculations with the functionals that are certainly imperfect, we introduce new errors, such as the inadequacy of the representation of the nonadditive kinetic energy potential $\psi_{\text{kin}}(\mathbf{r}_f, \mathbf{r}_h)$ in the FDET calculations that may be significantly enhanced when $\rho_B$ is relaxed or the difficulties with maintaining a balanced treatment of the chromophore and its complex with the environment within the supermolecular TDDFT framework. These are the reasons why the nonrelaxed FDET approach may represent a better computational strategy in determining the excitation energy shifts in weakly bound systems of the type of complexes examined in this work, when compared with the relaxed FDET and supermolecular TDDFT methodologies, as the results in Tables 3–6 and Figures 2–5 clearly illustrate.

4.4 A Comparison of the Excitation Energy Shifts from the Supermolecular TDDFT Calculations with the Nonrelaxed FDET and Reference EOMCC Data. As already alluded to above, the excitation energy shifts in the eight complexes of cis-7HQ examined in this study resulting from the supermolecular TDDFT calculations are a lot less accurate than their FDET counterparts employing the nonrelaxed environment densities, when both types of calculations are compared with the reference EOMCCA data. They are also less accurate than the FDET results obtained with the relaxed environment densities, although, as pointed out at the end of section 4.3, the differences between the $\Delta \omega_{\pi-\pi}$ shift values obtained in the supermolecular TDDFT and relaxed FDET calculations are smaller than the analogous differences between the results of the supermolecular TDDFT and nonrelaxed FDET calculations. Indeed, as shown in Table 3 (cf., also, Figure 3), the differences between the $\Delta \omega_{\pi-\pi}$ shift values obtained in the supermolecular TDDFT calculations using the STO ATZ2P basis set and their reference EOMCCA counterparts range, in absolute value, from 382 cm$^{-1}$ in the case of the 7HQ···HCOOH complex, where the EOMCCA shift
shown in Table 7, the π values resulting from the supermolecular TDDFT calculations is 6 times bigger than the analogous error characterizing the nonrelaxed, monomer-expansion-based FDET/ATZ2P calculations. The basis set superposition error (BSSE), which could potentially be a part of the errors, 65%. These clearly are much larger differences when compared with the corresponding nonrelaxed, monomer-expansion-based FDET calculations that give the 4–229 cm\(^{-1}\) deviations from the EOMCC,A data and the differences, which are about twice as large as those characterizing the relaxed, monomer-expansion-based FDET approach. The 65% average relative error characterizing the Δω\(_{\pi\pi}\) values resulting from the supermolecular TDDFT/ATZ2P calculations is 6 times bigger than the analogous error characterizing the nonrelaxed, monomer-expansion-based FDET/ATZ2P calculations. On the basis of the analysis of the EOMCC calculations performed in this work presented in section 4.1, the differences between the supermolecular TDDFT and reference EOMCC,A data are well outside the accuracy of the EOMCC calculations for the Δω\(_{\pi\pi}\) shifts, indicating the poor performance of the supermolecular TDDFT approach. Unlike in the FDET case, the differences between the supermolecular TDDFT and EOMCC,A Δω\(_{\pi\pi}\) values increase with the size of the environment bound to the cis-7HQ chromophore. This indicates the difficulties with obtaining the balanced description of excitation energies in systems that have different sizes in the supermolecular TDDFT calculations, which are not present in the FDET and EOMCC calculations.

The large inaccuracies in the supermolecular TDDFT results might be due to various reasons. One possibility might be the basis set superposition error (BSSE), which could potentially be well pronounced due to the difficulties the supermolecular TDDFT approach has with obtaining a balanced description of excitation energies in systems that have different sizes, but, as shown in Table 7, the π → π\(^*\) excitation energy in the isolated cis-7HQ system is barely affected by the position of ghost basis functions centered on the atoms of environment molecules. Another possibility might be a particular choice of the approximation used to determine the exchange-correlation potential contributions in the TDDFT calculations (the SAOP scheme\(^{126}\)). To investigate this issue, we performed additional supermolecular TDDFT calculations using two other treatments of the exchange-correlation contributions, namely, the local density approximation (LDA)\(^{120}\) and the PW91 functional,\(^{136}\) which is a representative functional from the GGA family. The results of these additional calculations are shown in Table 8 and Figure 4. It is quite clear that the use of the LDA and PW91 functionals to treat the exchange-correlation contributions does not help the supermolecular TDDFT results, making them, in fact, even less accurate than in the SAOP case. Interestingly, the use of the LDA and PW91 functionals in the nonrelaxed FDET calculations has a small effect on these calculations, increasing the mean unsigned errors relative to EOMCC,A characterizing the SAOP-based nonrelaxed, monomer-expansion-based FDET/ATZ2P calculations of 104 cm\(^{-1}\) to 140 cm\(^{-1}\) in the LDA case and 149 cm\(^{-1}\) in the PW91 case. This makes us believe that the primary reason for the poor performance of the supermolecular TDDFT approach is the difficulty with obtaining a balanced description of excitation energies in systems that have different sizes in the supermolecular TDDFT calculations, which are not present in the size-intensive FDET and EOMCC calculations and which are only enhanced in the supermolecular TDDFT calculations by incorrect asymptotic behavior of the LDA and PW91 (GGA) potentials, critical for the determination of the relatively small spectral shifts in weakly bound molecular clusters. This is yet another argument in favor of the embedding strategy represented here by the FDET approach, which is much less sensitive to the asymptotic behavior of the exchange-correlation potentials.

4.5. A Comparison of the Excitation Energy Shifts from the FDET Calculations Using Nonrelaxed Environment Densities with the Experimental Data. Although the main goal of this work is to compare the FDET and supermolecular TDDFT values of the vertical excitation energy shifts characterizing the hydrogen-bonded complexes of the cis-7HQ system with the corresponding EOMCC,A data, all obtained using the same nuclear geometries, it is useful to comment on the quality of the shifts resulting from our best FDET calculations employing the nonrelaxed environment densities, when compared with the available experimental data.\(^3\) In analogy to the EOMCC,A results discussed in section 4.1, a comparison of the purely electronic FDET and experimental data discussed above has limitations, since one cannot measure vertical excitation energies obtained in the FDET calculations in a direct manner. The experimental shifts reported in ref 5 that we refer to in this work correspond to the complexation-induced shifts in the maxima of the π → π\(^*\) absorption band in the cis-7HQ chromophore. Thus, although the experimental shifts reported in ref 5 are closely related to the theoretical shifts obtained in this study, the two types of quantities differ because of the following factors: (i) the maxima of the absorption bands characterizing the isolated cis-7HQ system and its complexes may not occur between the same vibrational levels as a result of the geometry relaxation in the excited states of the cis-7HQ:···B complexes when compared to the corresponding ground electronic states, and (ii) the MP2/ aug-cc-pVTZ geometries of cis-7HQ and its complexes used in this work, although probably quite reasonable, are not the experimental geometries. All of these factors certainly contribute to the deviations between the theoretical shifts calculated in this study and their experimental counterparts reported in ref 5.

On the other hand, the careful EOMCC calculations reported in this work which, as analyzed in section 4.1, closely follow the experimental excitation energies corresponding to the lowest π → π\(^*\) transition in the cis-7HQ and cis-7HQ:···B systems, particularly when the EOMCC,A and EOMCC,B approaches corrected for triple excitations are employed (see Table 2), seem to indicate that all of the above factors, although important, lead to a relatively small overall effect. It is, therefore, interesting to compare our best FDET results for the excitation energy shifts Δω\(_{\pi\pi}\), obtained in the nonrelaxed, monomer-expansion-based FDET calculations employing the STO ATZ2P basis set, given in Table 3, which are in excellent agreement with the reference EOMCC,A data, with the experimentally derived shifts reported in ref 5 and listed in Table 2. This comparison is shown in Figure 5. As one can see by inspecting Tables 2 and 3 and Figure 5, the Δω\(_{\pi\pi}\) values obtained in the nonrelaxed, monomer-expansion-based FDET/ATZ2P calculations are in very good agreement with the shifts in the experimental UV absorption spectra. The mean unsigned error in the Δω\(_{\pi\pi}\) values resulting from the nonrelaxed, monomer-expansion-based FDET/ATZ2P calculations, relative to the spectral shifts observed in experiment, is 222 cm\(^{-1}\), in excellent agreement with the EOMCC,A approach, which gives 244 cm\(^{-1}\). The analogous mean unsigned error characterizing the supermolecular TDDFT calculations is twice as large (429 cm\(^{-1}\), demonstrating once
again the advantages of the embedding vs supermolecular strategy within the TDDFT framework. It is clearly very encouraging that the nonrelaxed FDET approach, which can be applied to large molecular systems, can provide shifts in the excitation energy corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ system due to the formation of hydrogen-bonded complexes involving cis-7HQ and a variety of small molecules that can compete with the results of the considerably more expensive EOMCC calculations.

5. SUMMARY AND CONCLUSIONS

We used the embedding FDET approach to determine the shifts in the excitation energy corresponding to the lowest $\pi \rightarrow \pi^*$ transition in cis-7-hydroxyquinoline (cis-7HQ), induced by the formation of hydrogen-bonded complexes of cis-7HQ with a number of small molecules, and compared the resulting shift values with the reference EOMCC data and the analogous shifts obtained in the conventional supermolecular TDDFT calculations. The main difference between the embedding strategy, represented in the present study by the FDET method, and the conventional supermolecular approach is in the fact that in the former case one evaluates the excitation energy shifts induced by the interactions of the chromophore with its molecular environment as the differences of the excitation energies of the same many-electron system, representing the chromophore fragment with two different effective potentials, whereas in the latter case one has to perform calculations for two systems that differ in the number of electrons, the complex formed by the chromophore and its molecular environment, and the isolated chromophore.

By considering eight complexes of cis-7HQ with up to three small hydrogen-bonded molecules, we demonstrated that the spectral shifts resulting from the FDET calculations with the a priori determined nonrelaxed environment densities are in excellent agreement with the reference EOMCC data obtained in the supermolecular, rigorously size-intensive EOMCC calculations with singles, doubles, and noniterative triples, whereas the analogous shifts obtained with the supermolecular TDDFT approach are far from those obtained with EOMCC. The nonrelaxed FDET calculations provide shifts that agree with their EOMCC analogs to within about 100 cm$^{-1}$ or 10% on average, where the absolute values of the excitation energy shifts in the complexes of cis-7HQ examined in this study resulting from the EOMCC calculations range between about 500 and 2000 cm$^{-1}$. As shown in the present study, the accuracy of the FDET shift calculations employing nonrelaxed environment densities is on the order of the accuracy of the high-level EOMCC calculations. This should be contrasted with the excitation energy shifts obtained with the supermolecular TDDFT approach, which differ from the reference EOMCC values reported in this work by about 700 cm$^{-1}$ or 65% on average and which are well outside the accuracy of the EOMCC calculations. We demonstrated that none of the above findings are significantly affected by the type of basis expansion used in the FDET calculations (monomer or supermolecular), by the computational basis set used in the FDET and supermolecular TDDFT calculations, or by the approximations applied to the exchange-correlation potentials in the FDET and supermolecular TDDFT calculations, although better approximations for the exchange-correlation potential would help the supermolecular TDDFT approach. One of the key findings of the present study is the fact that the FDET methodology, particularly the nonrelaxed form of it, works well even with the functionals that are characterized by the relatively poor long-range behavior, offering results that are competitive with the high-level EOMCC approaches.

We demonstrated that the relaxation of the environment density in the FDET calculations worsens the quality of the calculated spectral shifts, although the shifts resulting from the relaxed FDET calculations are typically somewhat more accurate than those obtained with the supermolecular TDDFT approach. Among the reasons that may contribute to the worsening of the results obtained with the FDET approach using relaxed environment densities are the difficulties the Kohn–Sham-type methods applying semilocal approximants to the exchange-correlation energy, used in this work, have with describing molecular polarizabilities and the inadequacies in representing the nonadditive kinetic energy potential in the FDET considerations that may be significantly enhanced when the environment density is allowed to relax when solving a coupled system of Kohn–Sham-like equations defining the FDET approach and involving the chromophore and environment densities. Our calculations strongly suggest that at least in the applications involving shifts in the electronic spectrum due to the formation of weakly bound complexes, where the electronic excitation is localized on the absorbing chromophore, the neglect of the electronic polarization of the environment by the chromophore, implicitly assumed in the FDET calculations using nonrelaxed environment densities, is of much lesser significance than the errors that result from the approximations used to define the nonadditive kinetic energy potential, which can be quite substantial. On the basis of a direct comparison of the FDET results obtained with nonrelaxed and relaxed environment densities, the nonrelaxed FDET approach is a preferred strategy for the embedding calculations if the polarization of the environment by the chromophore is small, as is the case when the weakly bound complexes of cis-7HQ are examined. On the other hand, if one is interested in generating results that are similar to those obtained with the supermolecular TDDFT methodology, relaxing environment density in the FDET calculations may be more appropriate. We demonstrated that the fully relaxed FDET calculations are capable of producing spectral shifts that are quite close to the results of the supermolecular TDDFT calculations, even though both sets of calculations led to results that are quite far from the benchmark EOMCC and experimental data.

As shown in our study, the FDET approach with nonrelaxed environment densities represents a robust computational methodology, which works much better than the FDET methods with relaxed densities and supermolecular TDDFT schemes and which can provide complexation-induced spectral shifts that can compete with the high-quality ab initio data resulting from EOMCC calculations, as long as one can neglect the polarization of the environment by the chromophore. This is very encouraging from the point of view of spectroscopic applications involving large weakly bound molecular complexes, since the FDET approach with nonrelaxed environment densities is less expensive than its relaxed and supermolecular TDDFT counterparts, not to mention the EOMCC methods. In the FDET calculations employing nonrelaxed environment densities, one obtains these densities only once and a priori by solving the ground-state Kohn–Sham equations for the environment molecule(s) in the absence of the absorbing chromophore. This should be contrasted with the relaxed FDET calculations, where
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the environment density is allowed to vary during the Kohn–Sham-like calculations for the orbitals of the chromophore embedded in the environment, and with the supermolecular TDDFT and EOMCC calculations, where one has to consider larger many-electron systems corresponding to the chromophore complexes that do not have to be considered in the FDET calculations. The latter is challenging for the supermolecular TDDFT approaches, since they have difficulties with balancing accuracies involving systems of different sizes, and for methods based on the EOMCC theory, which can balance these accuracies, but are often prohibitively expensive.

Although the main focus of this study was the comparison of the FDET and supermolecular TDDFT results for the complexation-induced shifts in the excitation energy corresponding to the lowest \(\pi \rightarrow \pi^*\) transition in cis-7HQ with the EOMCC data, we also compared the FDET, supermolecular TDDFT, and reference EOMCC shift values with the experimental shifts reported in ref 5. Although, as explained in the previous sections, such comparison has obvious limitations due to the neglect of the effect of nuclear motion on photoabsorption spectra in our purely electronic calculations, the spectral shifts obtained with the FDET approach using nonrelaxed environment densities and those obtained with the EOMCC methodology agree with the experimental shifts quite well, whereas the supermolecular TDDFT calculations produce once again very large errors. This confirms the superiority of the FDET strategy when compared with the conventional supermolecular TDDFT approach in applications involving complexation-induced spectral shifts.

ASSOCIATED CONTENT

Supporting Information. The nuclear geometries of the cis-7HQ molecule and its complexes examined in this study along with the vertical excitation energies \(\omega_0 \rightarrow \omega_i\) resulting from the FDET and supermolecular TDDFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org/.

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REFERENCES

(1) Tanner, C.; Manca, C.; Leutwyler, S. Science 2003, 302, 1736.
(23) Gauss, J. In Encyclopedia of Computational Chemistry; Schleyer, P.R., Eds.; Wiley: Chichester, U.K., 1998; Vol. 1
Embedding vs supermolecular strategies


Introduction to Chapter 7:

This chapter is based on the publication:


The objective of this work is to investigate the effect of the approximation for the kinetic energy depending part \( v^{nad}[\rho_A, \rho_B](r) \) of the orbital-free embedding potential of Frozen-Density Embedding Theory (FDET), to the accuracy of the shifts of vertical excitation energies calculated with FDET based methods. Shifts of vertical excitation energies calculated with FDET based methods involving non-relaxed electron density of the environment \( \rho_B \) and two approximations for the \( v^{nad}[\rho_A, \rho_B](r) \) (GGA97 and NDSD), are comparison data produced by employing supermolecular Equation-of-Motion Coupled-Cluster (EOMCC) and Time-Dependent Density-Functional Theory (TDDFT) based methods. This study is closely associated with the work described in Chapter 6. The main outcome of this study is that the FDET based results associated with the GGA97 or the NDSD approximations are almost identical. This conclusion needs to be combined with the conclusions of the previous Chapter. The picture that emerges is that FDET based methods involving non-relaxed \( \rho_B \), when employed for the calculation of shifts of vertical excitation energies of non-charged hydrogen bonded complexes, show very little sensitivity to system independent factors like the basis set and the approximations involved in the FDET equations and reference data are systematically reproduced. This is a very useful insight that would lead to accelerated progress of investigations focusing on large systems. The author acknowledges that the explanation of the behavior of FDET as due to fortunate compensation of errors (see introduction of Chapter 6) is not fully satisfactory. The complexity of the question is high and future studies on this topic are planned. At this point it is noted the comments made for the supermolecular TDDFT in the introduction of the previous Chapter apply here as the reported data are identical and included in the publication for completeness. Finally, it is clarified that the author of this thesis contributed to the publication in the same manner as for the work described in Chapter 6 (see introduction to Chapter 6).
Shifts in Excitation Energies Induced by Hydrogen Bonding: A Comparison of the Embedding and Supermolecular Time-Dependent Density Functional Theory Calculations with the Equation-of-Motion Coupled-Cluster Results

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Abstract Shifts in the $\pi \rightarrow \pi^*$ excitation energy of the cis-7-hydroxyquinoline chromophore induced by hydrogen bonding with small molecules, obtained with the frozen-density embedding theory (FDET), are compared with the results of the high-level equation-of-motion coupled-cluster (EOMCC) calculations with singles, doubles, and noniterative triples, which provide the reference ab initio data, the supermolecular time-dependent density functional theory (TDDFT) calculations, and the available experimental data. It is demonstrated that the spectral shifts resulting from the FDET calculations employing nonrelaxed environment densities and their EOMCC counterparts are in excellent agreement with one another, whereas the analogous shifts obtained with the supermolecular TDDFT approach do not agree with the EOMCC reference data. Among the discussed issues are the effects of higher-order correlations on the excitation energies and complexation-induced excitation energy shifts resulting from the EOMCC calculations, and the choice of the approximants that represent the nonadditive kinetic energy contributions to the embedding potential of FDET.

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1 Introduction

Noncovalent interactions, such as hydrogen bonds, can qualitatively affect the electronic structure and properties of molecules embedded in molecular environments. Among such properties, electronic excitation energies are of particular interest because of the wide use of organic chromophores as probes in various environments [1–4]. Typically, hydrogen bonding results in shifts in the positions of absorption and emission bands anywhere between a few hundred and about 3000 cm\(^{-1}\) [5]. This means that if one is to use computer modeling for interpretation of experimental data, the errors of the calculated shifts must be very small, on the order of 100 cm\(^{-1}\) or less.

Unfortunately, the brute force application of the conventional supermolecular approach to evaluate the excitation energy shifts induced by hydrogen bonding with environment molecules, in which one determines the shift as a difference of two large numbers representing the excitation energy for a given electronic transition in the complex and the analogous excitation energy characterizing the isolated chromophore, encounters several challenges. For example, the supermolecular approach relies on the ability of a given electronic structure method to provide an accurate and well-balanced description of excitation energies in systems that have different sizes, which in the specific case of spectral shifts induced by complexation are the total system consisting of the chromophore and environment molecules and the system representing the isolated chromophore. In great many cases, particularly when the low-level quantum-chemistry methods are exploited and larger molecules are examined, this condition is difficult to satisfy. \textit{Ab initio} methods based on the equation-of-motion (EOM) [6–10] or linear-response [11–16] coupled-cluster (CC) [17–22] theories (cf. Refs. [23–25] for selected reviews), including, among several schemes proposed to date, the basic EOMCC approach with singles and doubles (EOM-CCSD) [7–9] and the so-called \(\delta\)-CR-EOMCC(2,3) method, which represents a suitably modified variant of the completely renormalized (CR) EOMCC theory with singles, doubles, and noniterative triples based on the CR-CC(2,3) [26–28] and CR-EOMCC(2,3) [29–31] approximations and which is used in the present work to provide the reference data, or the related EOMCCSD(2)\(_T\) [32] and EOMCCSD(T) [33] approximations, satisfy this condition, since they provide an accurate and systematically improvable description of the electronic excitations in molecular systems and satisfy the key property of size-intensivity [16, 34], but their applicability is limited to smaller molecular problems due to the CPU steps that typically scale as \(N^6 - N^7\) with the system size \(N\). Significant advances have been made in recent years toward extending the EOMCC and response CC methods to larger molecules through code parallelization and the use of local correlation methodologies [35–38], combined, in analogy to QM/MM techniques, with molecular mechanics [39–43], but none of the resulting approaches is as practical, as far as computer costs are concerned, as methods based on the time-dependent density functional theory (TDDFT) [44]. Unfortunately, the existing TDDFT approaches, although applicable to large molecular systems due to low computer costs, are not always accurate enough to guarantee a robust description of the complexation-induced spectral shifts in weakly
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bound complexes when the supermolecular approach is employed due to their difficulties with describing dispersion and charge-transfer interactions, and other intrinsic errors. It is, for example, unclear if the existing practical implementations of the TDDFT methodology satisfy the aforementioned condition of size intensivity, which is critical for obtaining a well-balanced description of electronic excitations in molecules that differ in size, and accurate values of the spectral shifts. In a size-intensive approach, the vertical excitation energy of a noninteracting system \( A + B \), in which fragment \( A \) is excited, is the same as that obtained for the isolated system \( A \). The aforementioned EOMCCSD, \( \delta \)-CR-EOMCC(2,3), EOMCCSD(2) \( \gamma \), and EOMCCSD(T) methods are size intensive, but, based on the results presented in this study, the widely used TDDFT approximations may violate this property.

Methods employing the embedding strategy, including those based on the frozen-density embedding theory (FDET) [45–48] that interests us in this work, provide an alternative strategy to the supermolecular approach for evaluating the excitation energy shifts. In all embedding methods, of both empirical (e.g., QM/MM) and FDET types, the effect of the environment on the molecular properties of interest is not treated explicitly, but, rather, through the use of the suitably designed embedding potential. Thus, instead of solving the electronic Schrödinger equation for the total \( (N_A + N_B) \)-electron system \( AB \) consisting of the \( N_A \)-electron molecule \( A \) and \( N_B \)-electron environment \( B \), i.e.,

\[
\hat{H}^{(AB)} |\Psi^{(AB)}\rangle = E^{(AB)} |\Psi^{(AB)}\rangle,
\]

where \( \hat{H}^{(AB)} \) is the Hamiltonian of the total system \( AB \), and the electronic Schrödinger equation for the isolated molecule \( A \),

\[
\hat{H}^{(A)} |\Psi^{(A)}\rangle = E^{(A)} |\Psi^{(A)}\rangle,
\]

where \( \hat{H}^{(A)} \) is the Hamiltonian of molecule \( A \) in the absence of environment, and then calculating the shift in an observable of interest associated with an operator \( \hat{O} \) by forming the difference of the expectation values of \( \hat{O} \) computed for systems \( AB \) and \( A \) that have different numbers of electrons,

\[
\Delta \langle \hat{O} \rangle = \langle \Psi^{(AB)} | \hat{O} |\Psi^{(AB)}\rangle - \langle \Psi^{(A)} | \hat{O} |\Psi^{(A)}\rangle,
\]

as one does in supermolecular calculations, one solves two eigenvalue problems characterized by the same number of electrons, namely, Eq. (2) and

\[
\left[ \hat{H}^{(A)} + \hat{V}_{\text{emb}}^{(A)} \right] |\Psi_{\text{emb}}^{(A)}\rangle = E_{\text{emb}}^{(A)} |\Psi_{\text{emb}}^{(A)}\rangle,
\]

where \( |\Psi_{\text{emb}}^{(A)}\rangle \) is the auxiliary \( N_A \)-electron wavefunction describing the effective state of molecule \( A \) in the presence of environment \( B \) and \( \hat{V}_{\text{emb}}^{(A)} = \sum_{i=1}^{N_A} v_{\text{emb}}(r_i) \) is the suitable embedding operator defined in terms of the effective one-electron potential \( v_{\text{emb}}(r) \). As a result, the complexation-induced shift in an observable represented by the \( \hat{O} \) operator is evaluated in the embedding strategy as
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\[ \Delta (\hat{O}) = \langle \Psi_{\text{emb}}^{(A)} | \hat{O} | \Psi_{\text{emb}}^{(A)} \rangle - \langle \Psi^{(A)} | \hat{O} | \Psi^{(A)} \rangle, \tag{5} \]

i.e., by using the many-electron wavefunctions \( |\Psi^{(A)}\rangle \) and \( |\Psi_{\text{emb}}^{(A)}\rangle \) that represent two different physical states of system \( A \) corresponding to the same number of electrons, the state of the isolated molecule \( A \) and the state of \( A \) embedded in the environment \( B \). This has two advantages over the conventional supermolecular approach. First, the embedding strategy does not require the explicit consideration of the total \((N_A + N_B)\)-electron system consisting of the complex of the molecule of interest and its environment, which leads to a significant cost reduction in the computer effort, particularly in applications involving larger environments. Indeed, it has already been demonstrated that FDET can be applied in large-scale multi-scale molecular simulations [46,49–51]. Second, by determining the complexation-induced shift \( \Delta (\hat{O}) \) using the wavefunctions \( |\Psi^{(A)}\rangle \) and \( |\Psi_{\text{emb}}^{(A)}\rangle \) that correspond to the same number of electrons, the errors due to approximations used to solve the \( N_A \)-electron problems represented by Eqs. (2) and (4) largely cancel out as we do not have to be concerned about the possible dependence of the error in the calculated \( \Delta (\hat{O}) \) value on the system size. In the calculations of the shifts in excitation energies using the size-intensive EOMCC methods, one does not have to worry about it either, but the supermolecular EOMCC approach requires an explicit consideration of the \((N_A + N_B)\)-electron system consisting of the chromophore and environment, which may lead to a significant cost increase when \( N_B \) is larger. By representing systems \( A \) and \( AB \) as two quantum-mechanical states of \( A \) with a fixed number of electrons \( N_A \) that correspond to the state of the isolated molecule \( A \) and the state of \( A \) perturbed by the environment \( B \), we can effectively enforce the condition of size intensity of excitation energies in the embedding approaches.

Clearly, the accuracy of the complexation-induced shifts obtained in the embedding calculations largely depends on the quality of the embedding operator \( \hat{V}_{\text{emb}}^{(A)} \). Thus, when compared with the supermolecular approach, the challenge is moved from assuring the cancellation of errors in approximate solutions of two Schrödinger equations for systems that differ in the number of electrons to developing the appropriate form of \( \hat{V}_{\text{emb}}^{(A)} \) that can accurately describe the state of the chromophore in the weakly bound complex with environment. According to the FDET formalism [45–48], the embedding operator \( \hat{V}_{\text{emb}}^{(A)} \) can be represented in terms of a local potential \( v_{\text{emb}}(r) \) (orbital-free embedding potential), which is determined by the pair of electron densities, \( \rho_A \) describing the embedded system \( A \) and constructed using the \( |\Psi_{\text{emb}}^{(A)}\rangle \) wavefunction, and \( \rho_B \) representing the electron density of the environment \( B \). Unfortunately, except for a small number of analytically solvable problems [52], the precise dependence of \( v_{\text{emb}}(r) \) on \( \rho_A \) and \( \rho_B \) is not known. Only its electrostatic component is known exactly. The nonelectrostatic component, which arises from the nonadditivity of the density functionals for the exchange-correlation and kinetic energies, must be approximated or reconstructed, either analytically (if possible) [52] or numerically [53–55]. In the case of hydrogen-bonded environments that interest us in this work, the electrostatic component of the exact embedding potential is expected to dominate and the overall accuracy of the environment-induced changes of
the electronic structure of embedded species should be quite high. Indeed, a number of earlier studies \([56, 57]\) demonstrate that the currently known approximants to the relevant functional representations of \(v_{\text{emb}}(r)\) in terms of \(\rho_A\) and \(\rho_B\) are adequate. Still, it is instructive to examine how the FDET results depend on the approximants that are used to represent the nonelectrostatic components of \(v_{\text{emb}}(r)\), such as the nonadditive kinetic energy potential.

Our previous studies of the methodological and practical aspects of the FDET approach have largely focused on the analytically solvable model systems and direct comparisons with experiment. The exactly solvable model systems are certainly important, since they may provide useful information about the analytic dependence of the embedding potential \(v_{\text{emb}}(r)\) on densities \(\rho_A\) and \(\rho_B\), but one has to keep in mind that real molecular systems may be quite different from such models. A comparison with the experimental data is clearly the final goal of any computational technique, and the FDET approach is no different in this regard, but we also have to remember that experiments have their own error bars and their interpretation may require the incorporation of physical effects that are not included in the purely electronic structure calculations. For these reasons, the present study chooses an alternative way of examining the performance of the FDET methodology in which we make a direct comparison of the benchmark results obtained in the high-level, wavefunction-based EOMCC calculations, using the aforementioned size-intensive modification of the CR-EOMCC(2,3) method \([29–31]\), designated as \(\delta\)-CR-EOMCC(2,3), with those produced by the embedding-theory-based FDET approach \([45–48]\) and the supermolecular TDDFT methodology. In order to address this objective, we first obtain the \(\delta\)-CR-EOMCC(2,3)-based shifts in the vertical excitation energy corresponding to the \(\pi \rightarrow \pi^*\) transition in the cis-7-hydroxyquinoline (cis-7HQ) chromophore, induced by formation of hydrogen-bonded complexes with eight different environments defined by the water, ammonia, methanol, and formic acid molecules, and their aggregates consisting of up to three molecules, for which, as demonstrated in this study, reliable EOMCC data can be obtained and which were previously examined using the laser resonant two-photon UV spectroscopy \([5, 57]\). Then, we use the resulting EOMCC reference shift values to assess the quality of the analogous spectral shifts obtained in the FDET and supermolecular TDDFT calculations. By having access to the highly accurate reference EOMCC data, we can explore various aspects of the FDET methodology and approximations imposed within. One such aspect is the possible dependence of the shifts in the excitation energy of cis-7HQ induced by the complexation with hydrogen-bonded molecules on the approximations used for one of the nonelectrostatic components of the embedding potential \(v_{\text{emb}}(r)\) resulting from the nonadditivity of density functionals for the kinetic energy. We examine this issue by performing two sets of the FDET calculations, one in which the nonadditive kinetic energy potential entering the definition of \(v_{\text{emb}}(r)\) is approximated using the generalized gradient approximation (GGA97) \([58]\), and another one in which the nonadditive kinetic energy component of \(v_{\text{emb}}(r)\) is approximated with the help of the recently developed NDSD approximant \([59]\) that incorporates the exact conditions relevant for the proper behavior of this component of \(v_{\text{emb}}(r)\) in the vicinity of nuclei. Other aspects of the FDET considerations, such
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as the role of approximations that are used to define the exchange-correlation potentials in the FDET (and supermolecular TDDFT) calculations, the usefulness of the monomer vs supermolecular basis expansions in the FDET calculations, the basis set dependence of the FDET results, and the effect of the form of the electronic density of the environment on the FDET results, will be discussed elsewhere [60].

Although our main goal is a direct comparison of the embedding-theory-based FDET and supermolecular TDDFT results with the high-level ab initio EOMCC data, which demonstrates the advantages of the FDET approach over the supermolecular TDDFT methodology in a realistic application, a comparison of the calculated shifts with the corresponding experimental data [5,57] is discussed as well. The gas-phase complexes of the cis-7HQ chromophore are of great interest, since some of them, particularly the larger ones, can be regarded as models of proton-transferring chains in biomolecular systems [1,61].

2 Methods

This section describes the electronic structure methods used in the present study. Since the supermolecular TDDFT approach is an established methodology, we focus on the FDET and EOMCC schemes exploited in our calculations.

2.1 Frozen-Density Embedding Theory

The FDET formalism [45–48,52,56,59] (cf., also, Refs. [62–66]), provides basic equations for the variational treatment of a quantum-mechanical subsystem embedded in a given electronic density. In order to introduce the FDET-based computational methods for describing the molecular system A embedded in the environment B created by some other molecule(s), one introduces two types of electronic densities to represent the total system AB. The first one is the density of the subsystem A defined by embedded molecule(s), \( \rho_A(r) \), which is typically represented using one of the following auxiliary quantities: (i) the occupied orbitals of a noninteracting reference system \( \{ \phi^{(i)}_i(r), i = 1, \ldots, N_A \} \) [45], (ii) the occupied and unoccupied orbitals of a noninteracting reference system [56], (iii) the interacting wavefunction [47], or (iv) the one-particle density matrix [48]. The second one is the density of the subsystem B describing the environment, \( \rho_B(r) \), which is fixed for a given electronic problem (“frozen density”). The optimum density \( \rho_A^*(r) \) of the system A embedded in the environment B, represented by the fixed density \( \rho_B(r) \) satisfying

\[
\int \rho_B(r) dr = N_B, \tag{6}
\]

is obtained by performing the following constrained search:
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\[ E_{emb}^{(A)}[\rho_B] = \min_{\rho_B} E_{HK}[\rho] = \min_{\rho_A} E_{HK}[\rho_A + \rho_B], \]  

(7)

subject to the conditions

\[ \int \rho(r) dr = N_A + N_B \]  

(8)

and

\[ \int \rho_A(r) dr = N_A. \]  

(9)

where \( E_{HK}[\rho] \) in Eq. (7) is the usual Hohenberg-Kohn energy functional.

In practice, the search for the optimum density \( \rho_A \), defined by Eq. (7), is performed by exploiting the Kohn-Sham formulation [67] of DFT [68] to solve Eq. (4), in which \( \hat{H}^{(A)} \) is the environment-free Hamiltonian of the isolated system \( A \) and \( \hat{V}_{emb} = \sum_{i} V_{emb}(\mathbf{r}_i) \) is the potential energy operator describing the effect of environment \( B \) on system \( A \), where \( \hat{V}_{emb}(\mathbf{r}) \) has the form of a local, orbital-free, embedding potential \( \epsilon_{\text{emb}}^{\text{eff}}(\mathbf{r}) \), determined by the pair of densities \( \rho_A(\mathbf{r}) \) and \( \rho_B(\mathbf{r}) \) and designated by \( v_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B; \mathbf{r}] \). As shown in our earlier work [45, 47, 48], the relationship between \( v_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B; \mathbf{r}] \) and densities \( \rho_A(\mathbf{r}) \) and \( \rho_B(\mathbf{r}) \) depends on the quantum-mechanical descriptors that are used as the auxiliary quantities for representing \( \rho_A(\mathbf{r}) \). If we use the orbitals of a noninteracting reference system, the wavefunction of the full configuration interaction (CI) form, or the one-particle density matrix as the descriptors to define \( \rho_A(\mathbf{r}) \), the local, orbital-free, embedding potential \( v_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B; \mathbf{r}] \) can be given the following form:

\[ v_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B; \mathbf{r}] = v_{\text{ci}}^{\text{eff}}(\mathbf{r}) + \int \rho_B(\mathbf{r}) \frac{\rho_B(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + v_{\text{corr}}^{\text{eff}}[\rho_A, \rho_B](\mathbf{r}) + v_{\text{xc}}^{\text{eff}}[\rho_A, \rho_B](\mathbf{r}), \]  

(10)

where

\[ v_{\text{corr}}^{\text{eff}}[\rho_A, \rho_B](\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \bigg|_{\rho = \rho_A + \rho_B} - \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \bigg|_{\rho = \rho_A}, \]  

(11)

and

\[ v_{\text{xc}}^{\text{eff}}[\rho_A, \rho_B](\mathbf{r}) = \frac{\delta T_{\text{xc}}[\rho]}{\delta \rho} \bigg|_{\rho = \rho_A + \rho_B} - \frac{\delta T_{\text{xc}}[\rho]}{\delta \rho} \bigg|_{\rho = \rho_A}. \]  

(12)

As one can see, \( v_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B; \mathbf{r}] \) involves the external and Coulomb potentials due to the environment \( B \), and the \( v_{\text{corr}}^{\text{eff}}[\rho_A, \rho_B](\mathbf{r}) \) and \( v_{\text{xc}}^{\text{eff}}[\rho_A, \rho_B](\mathbf{r}) \) components that arise from the nonadditivities of the exchange-correlation and kinetic energy functionals of the Kohn-Sham DFT, \( E_{\text{xc}}[\rho] \) and \( T_{\text{xc}}[\rho] \), respectively.

Once \( v_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B; \mathbf{r}] \) is defined, as in Eq. (10), and if we use a noninteracting reference system to conduct the constrained search given by Eq. (7), the orbitals \( \phi_i^{(A)} \), \( i = 1, \ldots, N_A \), of the system \( A \) embedded in the environment \( B \) are determined by solving the Kohn-Sham-like equations [cf. Eqs. (20) and (21) in Ref. [45]]

\[ \left[ -\frac{1}{2} \nabla^2 + v_{KS}^{\text{eff}}[\rho_A; \mathbf{r}] + v_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B; \mathbf{r}] \right] \phi_i^{(A)} = \epsilon_i^{(A)} \phi_i^{(A)}. \]  

(13)
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where \( v^{eff}_{KS}[\rho_A; \mathbf{r}] \) is the usual expression for the potential of the Kohn-Sham DFT for the isolated system \( A \). After obtaining the orbitals \( \phi_i^{(A)} \) and the corresponding orbital energies \( \epsilon_i^{(A)} \), we calculate the ground- and excited-state energies and properties other than energy, which in this case describe the system \( A \) embedded in the environment \( B \), in a usual manner, using standard algorithms of DFT or TDDFT.

It may be worth mentioning that there are two other approaches related to FDET that aim at the description of a system consisting of subsystems, including the situation of a molecule embedded in an environment which interests us here, namely, the subsystem formulation of DFT (SDFT) \([69, 70]\) and the recently developed partition DFT (PDFT) \([71]\). There are, however, differences between the SDFT and PDFT methods on the one hand and the FDET formalism on the other hand. Indeed, in the exact limit, both SDFT and PDFT lead to the exact ground-state electronic density and energy of the total system under investigation, providing an alternative to the conventional supermolecular Kohn-Sham framework. This should be contrasted with FDET, which does not target the exact ground-state electronic density of the total system \( AB \), but, rather, the density of subsystem \( A \) that minimizes the Hohenberg-Kohn energy functional of the total system, \( E_{\text{HK}}[\rho_A + \rho_B] \), using a fixed form of the environment density \( \rho_B \) given in advance in the presence of constraints, as in Eqs. (6)–(9). Thus, FDET may lead to the same total ground-state density as SDFT, Kohn-Sham DFT, or PDFT, but only when the specific set of additional assumptions and constraints is employed \([46]\). Otherwise, it can only give the upper bound to the exact ground-state energy of the total system \( AB \), \( E_{\text{SDFT}}^{(A)}[\rho_B] \geq E^{(AB)} \) (see Refs. \([45–48, 60]\) and references cited therein for further information).

The effectiveness of FDET methods based on Eq. (13), with \( v_{\text{eff}}^{(A)}[\rho_A, \rho_B; \mathbf{r}] \) determined using Eq. (10), in the calculations of changes in the electronic structure due to the interactions between the embedded system and its environment was demonstrated in a number of applications, including excitation energies \([56, 57, 72]\), ESR hyperfine coupling constants \([73, 74]\), ligand-field splittings of \( f \)-levels in lanthanide impurities \([75]\), NMR shieldings \([76]\), and multipole moments and frequency dependent polarizabilities \([72]\). Based on these positive experiences, the FDET approach is expected to provide accurate values of the complexation-induced shifts in the vertical excitation energy corresponding to the \( \pi \rightarrow \pi^* \) transition in the cis-7HQ chromophore, and the present study demonstrates that this is indeed the case by comparing the FDET and \( \delta\text{-CR-EOMCC(2,3)} \)-based EOMCC results.

### 2.2 Equation-of-Motion Coupled-Cluster Calculations

The basic idea of the EOMCC theory is the following wavefunction ansatz for the excited-state wavefunctions \(|\Psi_\mu\rangle\) \([6–9]\) (cf. Refs. \([10, 23, 25, 30]\) for reviews):

\[
|\Psi_\mu\rangle = R_\mu |\Psi_0\rangle,
\]

(14)

where the linear excitation operator \( R_\mu \) generates \(|\Psi_\mu\rangle\) from the CC ground state.
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\[ |\Psi_0\rangle = e^T |\Phi\rangle, \]

with \( T \) representing the cluster operator and \(|\Phi\rangle\) the reference determinant [in all of the EOMCC calculations discussed in this work, the restricted Hartree-Fock (RHF) configuration]. Throughout this paper, we use a convention in which we allow index \( \mu \) in Eq. (14) to become zero by defining the \( \mu = 0 \) operator \( R_\mu \) as a unit operator, \( R_{\mu=0} = 1 \), so that we can incorporate the ground- and excited-state cases corresponding to \( \mu = 0 \) and \( \mu > 0 \), respectively, within a single set of formulas.

The cluster operator \( T \) in Eq. (15) is typically obtained by truncating the corresponding many-body expansion

\[ T = \sum_{n=1}^{N} T_n, \]

where

\[ T_n = \sum_{i_1 < \cdots < i_n} t_{i_1\cdots i_n}^{\mu=0} \cdots a_{i_n}^\dagger \cdots a_{i_1} \]

is the \( n \)-body component of \( T \) and \( N \) is the number of correlated electrons in a system, at some, preferably low, excitation level \( M < N \), and by solving the nonlinear system of equations for cluster amplitudes \( t_{i_1\cdots i_n}^{\mu=0} \) with \( n \leq M \), which define the truncated form of \( T \), designated as \( T^{(M)} \), that results from projecting the electronic Schrödinger equation on the excited determinants \( |\Phi_\mu^{M}\rangle \) which correspond to the many-body components \( T_n \) included in \( T^{(M)} \). Once \( T \) and the corresponding ground-state CC energy \( E_0 \) are determined, one obtains the many-body components

\[ R_{\mu,n} = \sum_{i_1 < \cdots < i_n} r_{\mu,i_1\cdots i_n}^{\mu=0} \cdots a_{i_n}^\dagger \cdots a_{i_1} \]

of the linear excitation operator

\[ R_\mu = r_{\mu,0} 1 + \sum_{n=0}^{N} R_{\mu,n}, \]

which is usually truncated at the same excitation level \( M \) as \( T \), and the corresponding vertical excitation energies

\[ \omega_\mu = E_\mu - E_0, \]

by diagonalizing the similarity-transformed Hamiltonian \( \tilde{H}^{(M)} = e^{-T^{(M)} H} e^{T^{(M)}} \) in the subspace of the \( N \)-electron Hilbert space spanned by the excited determinants \( |\Phi_\mu^{M}\rangle \) that correspond to the many-body components \( R_{\mu,n} \) included in \( R_\mu \).

The basic EOMCCSD approach [7–9], in which \( M = 2 \), so that \( T \approx T^{(2)} = T_1 + T_2 \) and \( R_\mu \approx R_\mu^{(2)} = r_{\mu,0} 1 + R_{\mu,1} + R_{\mu,2} \) (in general, \( R_\mu^{(M)} \) designates the \( \mu \)-body operator truncated at the \( M \)-body component \( R_{\mu,M} \), in which one diagonalizes the similarity-transformed Hamiltonian of CCSD, \( \tilde{H}^{(2)} = e^{-T^{(2)} H} e^{T^{(2)}} \), in the space spanned by singly and doubly excited determinants, \(|\Phi_{1}^{(2)}\rangle\) and \(|\Phi_{2}^{(2)}\rangle\), respectively,
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and its linear-response CCSD counterpart [15,16] have been successful in describing excited states dominated by one-electron transitions, but this success does not extend to the more complicated excited states, such as those characterized by a significant two-electron excitation nature (cf. Refs. [29–31, 77–83] for examples). There also are cases of excited states dominated by one-electron transitions, particularly when larger molecular systems are examined, where the EOMCCSD theory level is not sufficiently accurate, producing errors in the computed excitation energies on the order of 0.3–0.5 eV [84, 85]. Thus, particularly in the context of this study, where the molecular systems of interest are not small and where we expect the EOMCC theory to provide accurate reference data for the FDET and TDDFT calculations of the relatively small spectral shifts induced by the formation of weakly bound complexes, it is important to examine if the EOMCC results used by us as a reference are reasonably well converged with respect to the truncations in the $T$ and $R_p$ operators. Ideally, one would like to perform the full EOMCCSDT (EOMCC with singles, doubles, and triples) calculations [86–88] and compare them with the corresponding EOMCCSD results to examine this. Unfortunately, it is not possible to carry out the full EOMCCSDT calculations for the cis-7HQ system and its complexes investigated in this work due to a steep increase of the CPU time and storage requirements characterizing the EOMCCSDT approach that scale as $n_o^4n_u^4$ and $\sim n_o^2n_u^2$ with the numbers of occupied and unoccupied orbitals, $n_o$ and $n_u$, respectively, as compared to the $n_o^2n_u^2$ CPU time and $\sim n_o^2n_u^2$ storage requirements of EOMCCSD. One has to resort to an approximate treatment of triple excitations in the EOMCC theory that replaces the prohibitively expensive iterative CPU steps of full EOMCCSDT that scale as $A^6$ with the system size $A$ to the more manageable, $A^6 - A^7$, steps.

A large number of approximate EOMCCSDT approaches and their linear-response analogs have been developed to date [29–33, 77–79, 81, 82, 86, 87, 89–96]. The noniterative EOMCC methods, in which one adds corrections due to triples to the EOMCCSD energies, such as, for example, EOM-CCSD(2)$_T$ [32], CCSDR3 [92,93], EOMCCSD(T) [33], CR-EOMCCSD(T) [77,78,81,82], N-EOMCCSD(T) [96], and CR-EOMCC(2,3) [29–31], are particularly promising, since they represent computational black boxes similar to those of the widely used ground-state CCSD(T) approach [97] and its CCSD(T) predecessor [98], or their CC-CSD(T) [77, 78, 99, 100], CR-CC(2,3) [26–28], CCSD(2)$_T$ [90, 101–103], and CCSD(T)$_A$ [104–106] analogs (cf. Refs. [107, 108] for related work). All of the above methods greatly reduce the computer costs of full EOMCCSDT calculations, while improving the EOMCCSD results. For example, the aforementioned EOMCCSD(2)$_T$, CCSDR3, EOMCCSD(T), CR-EOMCCSD(T), N-EOMCCSD(T), and CR-EOMCC(2,3) approaches are characterized by the iterative $n_o^3n_u^3$ steps of EOMCCSD and the noniterative $n_o^2n_u^2$ steps needed to construct the triples corrections to the EOMCCSD energies, while eliminating the need for storing the $\sim n_o^2n_u^2$ triply excited amplitudes defining the $T$ and $R_p$ operators. This makes these methods applicable to much larger problems than those that can be handled by full EOMCCSDT, including the complexes of cis-7HQ examined in the present study.

As mentioned in the Introduction, our focus in this work is on the size-intensive modification of the CR-EOMCC(2,3) method of Refs. [29–31], defining the
\( \delta \)-CR-EOMCC(2,3) approach. The CR-EOMCC(2,3) scheme and the underlying ground-state CR-CC(2,3) approximation [26–28] are examples of the renormalized CC/EOMCC schemes, which are based on the idea of adding the \emph{a posteriori}, non-iterative, and state-specific corrections \( \delta \) due to higher-order excitations, neglected in the conventional CC/EOMCC calculations defined by some truncation level \( M \), such as CCSD or EOMCCSD, to the corresponding CC/EOMCC energies. The formal basis for deriving the computationally tractable expressions for corrections \( \delta \) is provided by the moment expansions which describe the differences between the full CI and CC/EOMCC energies [26, 27, 77–79, 99, 109–112]. If we are interested in correcting the energies \( E_\mu(M) \) obtained in the CC/EOMCC calculations truncated at \( M \)-tuple excitations, the CC/EOMCC moments that enter the expressions for the corresponding corrections \( \delta \) are defined as projections of the CC/EOMCC equations with \( T \) and \( R_{\mu} \) truncated at the \( M \)-body components \( T_M \) and \( R_{\mu,M} \), respectively, on the excited determinants \( |\Phi_{n_1, \ldots, n_n}\rangle \) with \( n > M \) that are disregarded in the conventional CC/EOMCC calculations, i.e.,

\[
\mathcal{M}_{\mu, n_1 \ldots n_n}^{\mu_1 \ldots \mu_n}(M) = \langle \Phi_{n_1, \ldots, n_n}^{\mu_1, \ldots, \mu_n} | (\hat{H}^{(M)} R_{\mu}^{(M)}) | \Phi \rangle.
\]

All of the resulting moment expansions of the corrections \( \delta \) that define the differences between the full CI energies \( E_\mu \) and the corresponding CC/EOMCC energies \( E_\mu(M) \), developed to date [26, 27, 77–79, 99, 109–112], can be written as

\[
\delta_\mu \equiv E_\mu(M) - E_\mu = \sum_{n=M+1}^{N_{\mu,M}} \sum_{\mu_1 < \cdots < \mu_n} \ell_{\mu_1 \ldots \mu_n}^{n_1 \ldots n_n} \mathcal{M}_{\mu, n_1 \ldots n_n}^{\mu_1 \ldots \mu_n}(M),
\]

where \( N_{\mu,M} \) represents the highest value of the many-body rank \( n \) for which \( \mathcal{M}_{\mu, n_1 \ldots n_n}(M) \) is still nonzero (in the CCSD/EOMCCSD \( M = 2 \) case, \( N_{\mu,M} = 6 \) when \( \mu = 0 \) and 8 when \( \mu > 0 \)). The only essential difference between various approximations based on Eq. (22) is in the way one handles the \( \ell_{\mu_1 \ldots \mu_n}^{n_1 \ldots n_n} \) coefficients. Equation (22) can be obtained by considering the asymmetric energy expression [26, 27, 77–79, 109] \( E_\mu = \langle \Phi_\mu | \hat{H} R_{\mu}^{(M)} e^{T(M)} | \Phi \rangle / \langle \Phi_\mu | R_{\mu}^{(M)} e^{T(M)} | \Phi \rangle \), which gives the exact, full CI, energy \( E_\mu \), independent of the truncation level \( M \) in \( T^{(M)} \) and \( R_{\mu}^{(M)} \), if \( |\Phi_\mu\rangle \) is the full CI bra state \( |\Psi_\mu\rangle \). When \( |\Psi_\mu\rangle \) is represented as \( |\Phi \rangle \mathcal{Z}_\mu e^{-\mathcal{L}(M)} \), where \( \mathcal{L}_\mu \) is a suitably defined deexcitation operator satisfying \( \langle \Phi | \mathcal{L}_\mu | R_{\mu}^{(M)} | \Phi \rangle = 1 \), the \( \ell_{\mu_1 \ldots \mu_n}^{n_1 \ldots n_n} \) coefficients in Eq. (22) have a meaning of amplitudes defining \( \mathcal{Z}_\mu \) [26, 27]. In that case, the asymmetric energy expression \( E_\mu \) gives the formula for the exact energy in the form \( E_\mu = \langle \Phi | \mathcal{Z}_\mu \mathcal{L}_\mu R_{\mu}^{(M)} | \Phi \rangle \), which becomes equivalent to the conventional CC energy functional [25] (used, for example, to derive the CCSD(T) \( \lambda \) approach [104–106]) when \( \mu = 0 \) and \( M = N \), and which directly leads to Eq. (22) for the \( \delta_\mu \) correction after subtracting the CC/EOMCC energy \( E_\mu(M) \) from \( E_\mu \) and performing straightforward analysis [26, 27].

In the specific case of the CR-EOMCC(2,3) approach that interests us here, which corresponds to setting \( M \) in Eq. (22) at 2 and considering only the \( n = 3 \)
term in the resulting moment expansion for $\delta_\mu$, one calculates the energies of the ground and excited states as

$$E_\mu = E_\mu^{(\text{CCSD})} + \sum_{i<j<k<x,y} \rho_{\mu,ijk} \mathcal{M}_{\mu,abc}(2),$$

(23)

where $E_\mu^{(\text{CCSD})} \equiv E_\mu^{(2)}$ are the CCSD ($\mu = 0$) and EOMCCSD ($\mu > 0$) energies, $\mathcal{M}_{\mu,abc}(2)$ are the moments of the CCSD/EOMCCSD equations corresponding to triple excitations, which are defined by Eq. (21) in which $M = 2$, and $\rho_{\mu,ijk}$ are the deexcitation amplitudes that one can calculate using the quasi-perturbative expressions presented in Refs. [29,31]. The $\rho_{\mu,ijk}$ amplitudes used in the CR-EOMCC(2,3) considerations are expressed in terms of the one- and two-body components of the deexcitation operator defining the left eigenstate of EOMCCSD [9], and the one-body, two-body, and – in the full implementation of CR-EOMCC(2,3) defining variant D of it designated as CR-EOMCC(2,3),D – selected three-body components of the similarity-transformed Hamiltonian of CCSD, $\tilde{H}^{(2)}$. In particular, the one-, two-, and three-body components of $\tilde{H}^{(2)}$ enter the Epstein-Nesbet-like denominator for triple excitations which defines the $\rho_{\mu,ijk}$ amplitudes in the CR-EOMCC(2,3),D approach. In variant A of CR-EOMCC(2,3), abbreviated as CR-EOMCC(2,3),A and equivalent to the EOM-CC(2)PT(2) method of Ref. [90], one replaces the Epstein-Nesbet-like denominator defining the $\rho_{\mu,ijk}$ amplitudes, which in variant D of CR-EOMCC(2,3) is calculated as $\rho_{\mu}^{(\text{CCSD})} \equiv \langle \Phi_{\mu,ijk} | \tilde{H}^{(2)} | \Phi_{\mu,ijk} \rangle$, where $\rho_{\mu}^{(\text{CCSD})}$ is the CCSD excitation energy and $\tilde{H}^{(2)}$ is the $n$-body component of $\tilde{H}^{(2)}$, by the simplified form of it which represents the Møller-Plesset-like denominator for triple excitations, $\rho_{\mu}^{(\text{CCSD})} = \langle \Phi_{\mu} | \tilde{H}^{(2)} | \Phi_{\mu} \rangle$, where $\rho_{\mu}^{(\text{CCSD})}$ is the Møller-Plesset-like denominator for triple excitations.

We now explain how to obtain the desired size-intensive $\delta$-CR-EOMCC(2,3) results within the CR-EOMCC(2,3) framework. As demonstrated in Refs. [31,32], although the ground-state CR-CC(2,3),D method and its CR-CC(2,3),A counterpart, which is equivalent to the CCSD(T) approach of Ref. [101], are size extensive, being perfectly suited for examining weakly bound complexes involving larger molecules [113,114], such as those studied in this work, their excited state CR-EOMCC(2,3),D and CR-EOMCC(2,3),A [or EOM-CC(2)PT(2)] analogs violate the property of size intensivity discussed in the Introduction and satisfied by EOMCCSD [16,34]. Although the departure from strict size intensivity in the CR-EOMCC calculations of vertical and adiabatic excitation energies is in many cases
of minor significance when compared to other sources of errors [82], this may be a more serious issue when examining the shifts in the excitation energy due to formation of weakly bound complexes. The lack of size intensity of the CR-EOMCC(2,3) and EOM-CC(2)PT(2) approaches can be traced back to the presence of the contribution

\[ \beta_\mu = \sum_{i<j<k,a,b,c} \left( r_{i,j} \rho_{i,j,k} - \rho_{i,j,k} \right) \gamma^{i,j,k}_{\mu,abc}(2) \quad (24) \]

in the corresponding vertical excitation energies

\[ \omega^{(C-R-EOMCC(2,3))}_\mu = E^{(C-R-EOMCC(2,3))}_\mu - E^{(CR-CC(2,3))}_0, \quad (25) \]

which is, as shown in Ref. [32], size extensive (cf. the \( E^{(T_0)}_\mu - E^{(T_0)}_0 \) term in Eq. (17) of Ref. [32]; see, also, Ref. [31] for additional remarks). Indeed, using the above equations for the CR-EOMCC(2,3) energies, particularly Eq. (23), we can decompose the CR-EOMCC(2,3) excitation energy \( \omega^{(C-R-EOMCC(2,3))}_\mu \) and its EOMCC(2)PT(2) analog as follows [31, 32]:

\[ \omega^{(C-R-EOMCC(2,3))}_\mu = \omega^{(CCSD)}_\mu + \alpha_\mu + \beta_\mu. \quad (26) \]

Here, \( \omega^{(CCSD)}_\mu \) is the vertical excitation energy of EOMCCSD,

\[ \alpha_\mu = \sum_{i<j<k,a,b,c} \rho_{i,j,k} \gamma^{i,j,k}_{\mu,abc}(2), \quad (27) \]

with \( \gamma^{i,j,k}_{\mu,abc}(2) = \langle \Phi | H^{(2)}(R_{\mu,1} + R_{\mu,2}) | \Phi \rangle \) representing the contribution to the triply excited moment \( \gamma^{i,j,k}_{\mu,abc}(2) \) of EOMCCSD due to the one- and two-body components of \( R^{(2)}_{\mu} \), and \( \beta_\mu \) is defined by Eq. (24). Since the EOMCCSD approach is size intensive and, as shown in Ref. [32], the \( \alpha_\mu \) term, Eq. (27), is size intensive as well (cf. the \( \omega^{(T_1)}_\mu + \omega^{(T_2)}_\mu \) contribution in Eq. (17) of Ref. [32]), the \( [\omega^{(CCSD)}_\mu + \alpha_\mu(2,3)] \) part of the CR-EOMCC(2,3) excitation energy \( \omega^{(C-R-EOMCC(2,3))}_\mu \) is a size-intensive quantity. Unfortunately, the \( \beta_\mu \) term defined by Eq. (24), being a size-extensive contribution, grows with the system size [31, 32], destroying the size intensity of \( \omega^{(C-R-EOMCC(2,3))}_\mu \). In order to address this concern, in this work we have implemented the rigorously size-intensive variant of CR-EOMCC(2,3), designated as \( \delta-CR-EOMCC(2,3) \), by neglecting the problematic \( \beta_\mu \) term in Eq. (26) and redefining the vertical excitation energy in the following manner [31, 32]:

\[ \omega^{(\delta-CR-EOMCC(2,3))}_\mu = \omega^{(CCSD)}_\mu + \alpha_\mu, \quad (28) \]

with \( \alpha_\mu \) given by Eq. (27). The \( \delta-CR-EOMCC(2,3) \) method provides a size-intensive description of the excitation energies and, by defining the total energy \( E_\mu \) of a given electronic state \( \mu \) as a sum of the size-extensive ground-state CR-CC(2,3)
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energy and size-intensive excitation energy $\Delta \omega(\delta$-CR-EOMCC$^{(2,3)})$, Eq. (28), so that

$$E_{\mu} = E_{\mu}^{(\text{CR-CC}(2,3))} + \Delta \omega(\delta$-CR-EOMCC$^{(2,3)})$$

$$= E_{\mu}^{(\text{CCSD})} + \sum_{i<j<k} \rho_{ij}^{abc} \sum_{\mu} \omega_{ijkl}^{abc}(2) + \sum_{i<j<k} \rho_{ij}^{abc} \sum_{ACD} \omega_{ijkl}^{abc}(2),$$

the size-extensive description of state $\mu$, assuming that the electronic excitation in $AB$ is localized on either $A$ or in $B$, but not on both fragments simultaneously (cf. Refs. [16, 34, 82] for a detailed analysis). As in the case of CR-EOMCC$^{(2,3)}$, we can distinguish between the full variant $D$ of $\omega(\delta$-CR-EOMCC$^{(2,3)})$, designated as $\delta$-CR-EOMCC$^{(2,3),D}$, and its various approximations, including variant $A$. The $\delta$-CR-EOMCC$^{(2,3),A}$ method is equivalent to the EOMCC$^{(2,3),D}$ approach of Ref. [32] and, if we limit ourselves to the vertical excitation energies only, to the EOMCCSD(T) approach of Ref. [33]. The latter connection is worth commenting on. The EOMCCSD(T) method of Ref. [33] and its various EOMCCSD(T)-like analogs [33, 91] are based on the idea of directly correcting the EOMCCSD excitation energies rather than determining the total energies first and forming the excitation energies afterwards, as described above. This has an advantage in the fact that the resulting triples corrections, such as those defining EOMCCSD(T), are immediately size intensive. Unfortunately, they are not robust enough in applications involving excited-state potential energy surfaces along bond breaking coordinates (see, e.g., Ref. [81]). The CR-EOMCC$^{(2,3)}$ approach, which is used to design the $\delta$-CR-EOMCC$^{(2,3)}$ method, and its CR-EOMCCSD(T) predecessor [77, 78, 81], as well as their EOM-CC$^{(2,3),PT(2)}$-based analogs [32], in which one corrects the total CCSD and EOMCCSD energies first and computes the excitation energies later, are very useful in calculations of ground- and excited-state potential energy surfaces (see Refs. [78, 81]; cf., also, Ref. [32]), but one has to take extra steps to eliminate terms violating the property of size intensity that cannot be ignored in applications reported in this work. As shown in Section 3.1, the size-intensivity-corrected $\delta$-CR-EOMCC$^{(2,3),A}$ and $\delta$-CR-EOMCC$^{(2,3),D}$ methods provide very similar $\pi \rightarrow \pi^*$ excitation energies in the cis-7HQ chromophore and its complexes, which also are in good agreement with the experimental data reported in Refs. [5, 57].

### 2.3 The Remaining Computational Details

In order to examine the performance of the FDET approach and to demonstrate its advantages when compared with the supermolecular TDDFT calculations, both benchmarked against the high-level EOMCC data, we have investigated the shifts $\Delta \omega_{\pi \rightarrow \pi}$ in the vertical excitation energy $\omega_{\pi \rightarrow \pi}$ corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ chromophore induced by the formation of hydrogen-bonded complexes shown in Fig. 1. The eight complexes considered in this study, which were examined experimentally using the laser resonant two-photon UV spectroscopy [5, 57], include the cis-7HQ $\cdots B$ systems, where $B$ represents one of the
following environments: a single water molecule, a single ammonia molecule, a water dimer, a single molecule of methanol, a single molecule of formic acid, a trimer consisting of ammonia and two water molecules, a trimer consisting of ammonia, water, and ammonia, and a trimer consisting of two ammonia and one water molecules (cf. Fig. 1). For each cis-7HQ···B complex and for each electronic structure approach used in this study, the corresponding environment-induced shift $\Delta \omega_{e-\pi^*}$ was determined as a difference between the value of $\omega_{e-\pi^*}$ characterizing the complex and that obtained for the isolated cis-7HQ molecule. The relevant nuclear geometries of the cis-7HQ···B and cis-7HQ systems were optimized in the second-order Møller-Plesset perturbation theory (MP2) [115] calculations employing the aug-cc-pVTZ basis set [116,117], using the analytic MP2 gradients available in Gaussian(R) 03 [118]. As in all other post-Hartree-Fock wavefunction calculations discussed in this paper, the core molecular orbitals (MOs) correlating with the 1s shells of the C, N, and O atoms were frozen in these optimizations.

Once the nuclear geometries of the cis-7HQ and cis-7HQ···B systems were obtained, we performed the desired FDET and supermolecular TDDFT and EOMCC calculations of the vertical excitation energies $\Delta \omega_{e-\pi^*}$ and the complexation-induced shifts $\Delta \omega_{e-\pi^*}$. First, in order to establish the reference EOMCC values of the environment-induced shifts $\Delta \omega_{e-\pi^*}$, we carried out a series of EOMCCSD calculations for the cis-7HQ, 7HQ···H$_2$O, and 7HQ···NH$_3$ systems using five different basis sets, including 6-31+G(d) [119–121], 6-311+G(d) [121,122], aug-cc-pVDZ [116,117], and the [5s3p2d3s2p] basis of Sadlej [123], designated as POL, followed by the complete set of EOMCCSD and $\delta$-CR-EOMCCSD(2,3) computations using the largest basis sets we could afford for all eight cis-7HQ···B complexes investigated in this work, which were 6-311+G(d) in the EOMCCSD case and 6-31+G(d) in the case of the $\delta$-CR-EOMCCSD(2,3) approach. The main objective of these initial calculations was to determine the stability of the final EOMCC values of the $\Delta \omega_{e-\pi^*}$ shifts recommended for the use in benchmarking the FDET and supermolecular TDDFT data with respect to the basis set choice and the role of the higher-order correlation effects neglected in EOMCCSD, but included in $\delta$-CR-EOMCCSD(2,3). All of the EOMCC calculations reported in this work were carried out with the programs developed at Michigan State University described, for example, in Refs. [26,31,81,82], that form part of the GAMESS package [124,125]. In order to obtain the final $\delta$-CR-EOMCCSD(2,3) results, as defined by Eqs. (28) and (29), we modified the previously developed [26,31] CR-CC(2,3)/CR-EOMCC(2,3) GAMESS routines in a suitable manner. The corresponding ground-state CCSD calculations, which precede the determination of the left CCSD and right left EOMCCSD eigenstates that enter the formulas for the triples corrections of $\delta$-CR-EOMCC(2,3) and the steps needed to compute the triples corrections of the ground-state CR-CC(2,3) and excited-state CR-EOMCC(2,3) and $\delta$-CR-EOMCC(2,3) approaches, were performed with the routines described in Ref. [126], which form part of GAMESS as well. The RHF orbitals were employed throughout and, as pointed out above, the core MOs that correlate with the 1s shells of the nonhydrogen atoms were frozen in the CCSD, EOMCCSD, and $\delta$-CR-EOMCCSD(2,3) calculations. The CCSD/EOMCCSD ener-
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gies were converged to $10^{-7}$ Hartree. Further details of the EOMCC computer codes and algorithms exploited in this work can be found in Refs. [26, 31, 81, 82].

Once the reference EOMCC data were established, we moved to the FDET and supermolecular TDDFT calculations, which were performed using the linear-response TDDFT routines available in the ADF2009.01 code [127]. The FDET calculations followed the protocol described in Ref. [56], in which the occupied and unoccupied orbitals of the embedded chromophore that are obtained by solving the Kohn-Sham-like system defined by Eq. (13) are subsequently used within the linear-response TDDFT framework [44] to obtain excitation energies. All of the FDET and supermolecular TDDFT calculations were performed using the STO ATZ2P basis set [127], which is a STO-type triple-zeta basis with two sets of polarization functions, augmented with one set of diffuse s-STO and p-STO functions. As shown in a separate study [60], the results of the FDET and supermolecular TDDFT calculations using the STO ATZ2P basis set can be viewed as converged with respect to the basis set choice. Because of the small energy differences that define the spectral shifts examined in this work, we used tight convergence criteria when solving the Kohn-Sham and linear-response TDDFT equations ($10^{-10}$ Hartree).

The environment density $\rho_B$ used in the FDET calculations reported in this work was nonrelaxed, i.e., we used the ground-state electronic density of the environment obtained by solving the conventional Kohn-Sham equations for the environment molecules in the absence of the chromophore. Moreover, we exploited the so-called monomer-expansion FDET technique, in which the orbitals of the chromophore $A$ embedded in $B$ and the corresponding density $\rho_A$ are represented using the atomic centers of $A$, whereas the environment density $\rho_B$ and the corresponding orbitals of $B$ are represented using the atomic centers of $B$ (see Refs. [58, 128] for further information). The monomer-expansion FDET technique using nonrelaxed $\rho_B$, which is the recommended variant of FDET for the type of applications reported in this work, relies on the approximation, referred to as the Neglect of Dynamic Response of the Environment (NDRE), in which we assume that the dynamic response of the whole system $AB$ to the process of electronic excitation is limited to chromophore $A$ and that the coupling between the excitations in the embedded system and in its environment can be neglected. The NDRE approximation and the monomer-expansion-based FDET approach that results from it are very effective in eliminating spurious electronic excitations involving the environment [50]. The effect of the relaxation of the electronic density of the environment $\rho_B$ in the presence of the chromophore $A$ and the usefulness of the monomer vs supermolecular basis expansions in the FDET calculations will be discussed in a separate study [60].

In both the FDET and supermolecular TDDFT calculations, we used the SAOP scheme [129] to approximate the relevant exchange-correlation potential contributions. To examine the possible dependence of the complexation-induced shifts in the excitation energy of the cis-7HQ chromophore on the approximations exploited for one of the nonelectrostatic components of the embedding potential $\psi_{\text{eff}}[\rho_A, \rho_B; \mathbf{r}]$, Eq. (10), used in the FDET calculations, resulting from the nonadditivity of density functionals for the kinetic energy, the nonadditive kinetic energy potential $\psi_{\text{eff}}[\rho_A, \rho_B; \mathbf{r}]$, Eq. (12), that forms part of $\psi_{\text{eff}}[\rho_A, \rho_B; \mathbf{r}]$ was deter-
mined using two different approximations, namely, GGA97 [58] and NDSD [59]. Let us recall that the latter approximant incorporates the exact conditions that are relevant for the proper behavior of \( v^{\text{adh}}(\rho_A, \rho_B)(\mathbf{r}) \) in the vicinity of nuclei. The nonadditive exchange-correlation component of \( v^{\text{exc}}(\rho_A, \rho_B)(\mathbf{r}) \), represented by the \( v^{\text{exc}}(\rho_A, \rho_B)(\mathbf{r}) \) potential, Eq. (11), was approximated using the Perdew-Wang (PW91) functional [130]. Other treatments of the exchange-correlation contributions in FDET and supermolecular TDDFT calculations for the cis-7HQ system and its hydrogen-bonded complexes will be examined elsewhere [60], where we will show that the spectral shifts obtained with the nonrelaxed FDET approach are almost insensitive to the choice of functionals used in the calculations.

3 Results and Discussion

The results of our FDET, supermolecular TDDFT, and EOMCC calculations for the shifts in the vertical excitation energy \( \omega_{\pi \rightarrow \pi^*} \) corresponding to the lowest \( \pi \rightarrow \pi^* \) transition in the cis-7HQ chromophore induced by the formation of the eight complexes shown in Fig. 1 are summarized in Tables 1 and 2, and Fig. 2. We begin our discussion with the analysis of the EOMCCSD and \( \delta \)-CR-EOMCC(2,3) calculations aimed at establishing the reference EOMCC values.

3.1 Reference EOMCC Results

In order to determine the level of EOMCC theory that would be suitable for serving as a reference for the FDET and supermolecular TDDFT calculations, we first examine the dependence of the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi^*} \) resulting from the EOMCCSD calculations on the basis set. We first compare the EOMCCSD results for the two smallest complexes, 7HQ .. ·H2O and 7HQ .. ·NH3, for which we could afford the largest number of computations, including the 6-31+G(d), 6-311+G(d), aug-cc-pVDZ, and POL basis sets. The results in Table 1 indicate that although the vertical excitation energies \( \omega_{\pi \rightarrow \pi^*} \) in the bare cis-7HQ system and its complexes with the water and ammonia molecules vary with the basis set (for the four basis sets tested here by as much as about 600 cm\(^{-1}\)), the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi^*} \) are almost insensitive to the basis set choice. Although we could not perform a similarly thorough analysis for the remaining six complexes due to prohibitive computer costs of the EOMCCSD calculations with the aug-cc-pVDZ and POL basis sets, we were able to obtain the EOMCCSD \( \omega_{\pi \rightarrow \pi^*} \) and \( \Delta \omega_{\pi \rightarrow \pi^*} \) values for all eight complexes examined in this study using the 6-31+G(d) and 6-311+G(d) bases. As shown in Table 1, the differences between the EOMCCSD/6-31+G(d) and EOMCCSD/6-311+G(d) values of the \( \Delta \omega_{\pi \rightarrow \pi^*} \) shifts remain small for all complexes of interest, ranging from 8 cm\(^{-1}\) in the 7HQ .. ·NH3 case to 43 cm\(^{-1}\) in the case of 7HQ .. ·(H2O)\(_2\), or 1–3 %. We conclude that the choice of the basis
set, although important for obtaining the converged \( \omega_{\pi \rightarrow \pi'} \) values, is of almost no importance when the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi'} \) are considered.

Although the EOMCCSD approach is known to provide an accurate description of excited states dominated by one-electron transitions, such as the \( \pi \rightarrow \pi' \) transition in cis-7HQ and its complexes, there have been cases of similar states reported in the literature, where the EOMCCSD level has not been sufficient to obtain high-quality results [84, 85]. Moreover, the small energy differences defining the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi'} \) may be sensitive to the higher-order correlation effects neglected in the EOMCCSD calculations. For these reasons, we also examined the effect of triple excitations on the \( \omega_{\pi \rightarrow \pi'} \) and \( \Delta \omega_{\pi \rightarrow \pi'} \) values by performing the \( \delta\text{-CR-EOMCC}(2,3) \) calculations with the 6-31+G(d) basis set. As shown in Table 1, triple excitations have a significant effect on the vertical excitation energies \( \omega_{\pi \rightarrow \pi'} \), reducing the 4000-5000 cm\(^{-1}\) differences between the EOMCCSD and experimental data to no more than about 800 cm\(^{-1}\), when the \( \delta\text{-CR-EOMCC}(2,3),\text{A/6-31+G(d)} \) calculations are performed, and no more than about 500 cm\(^{-1}\) when the \( \delta\text{-CR-EOMCC}(2,3),\text{D/6-31+G(d)} \) approach is employed, while bringing the \( \Delta \omega_{\pi \rightarrow \pi'} \) values closer to the experimentally observed shifts when compared with the EOMCCSD data. Although the differences between the \( \delta\text{-CR-EOMCC}(2,3) \) and EOMCCSD values of the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi'} \) resulting from the calculations with the 6-31+G(d) basis set do not exceed 15–16 % of the EOMCCSD values, triples corrections improve the EOMCCSD results and, as such, are useful for generating the reference EOMCC data.

It would be great if we could perform the \( \delta\text{-CR-EOMCC}(2,3) \) calculations using basis sets larger than 6-31+G(d), such as 6-311+G(d), but the hydrogen-bonded complexes of cis-7HQ examined in this study are too large for performing such calculations on our computers. In the absence of the \( \delta\text{-CR-EOMCC}(2,3) \) larger basis set data and considering the fact that the triples corrections to the \( \Delta \omega_{\pi \rightarrow \pi'} \) shifts are relatively small when compared to their EOMCCSD values, we have decided to combine the EOMCCSD/6-311+G(d) results with the triples corrections to the EOMCCSD energies extracted from the \( \delta\text{-CR-EOMCC}(2,3),\text{X/6-31+G(d)} \) (\( X = \text{A, D} \)) calculations, using the formula

\[
\omega_{\pi \rightarrow \pi'} (\text{EOMCC, } X) = \omega_{\pi \rightarrow \pi'} (\text{EOMCCSD/6-311+G(d)}) + \left[ \omega_{\pi \rightarrow \pi'} (\delta\text{-CR-EOMCC}(2,3),\text{X/6-31+G(d)}) - \omega_{\pi \rightarrow \pi'} (\text{EOMCCSD/6-31+G(d)}) \right],
\]

where \( X = \text{A or D} \). As shown in Table 1, the resulting composite EOMCC,A and EOMCC,D approaches provide vertical excitation energies \( \omega_{\pi \rightarrow \pi'} \) that are in excellent agreement with the experimental excitation energies, while offering further improvements in the environment-induced shifts \( \Delta \omega_{\pi \rightarrow \pi'} \) when compared with the EOMCCSD/6-311+G(d) and \( \delta\text{-CR-EOMCC}(2,3)/6-31+G(d) \) calculations. Indeed, the EOMCC,A approach, which adds the triples correction extracted from the \( \delta\text{-CR-EOMCC}(2,3),\text{A/6-31+G(d)} \) calculation to the EOMCCSD/6-311+G(d) energy, gives errors in the calculated excitation energies \( \omega_{\pi \rightarrow \pi'} \) relative to experiment that range between 147 cm\(^{-1}\) in the case of the bare cis-7HQ system and 668
cm$^{-1}$ in the case of the 7HQ$\cdots$·(NH$_3$·H$_2$O·H$_2$O) complex, never exceeding 2 % of the experimental excitation energies. The EOMCC,D approach, which adds the triples correction obtained in the $\delta$-CR-EOMCC(2,3),D/6-31+G(d) calculation to the EOMCCSD/6-311+G(d) energy, gives errors in the calculated $\Delta \omega_{\pi \rightarrow \pi^*}$ values relative to experiment that range between 17 cm$^{-1}$ in the case of the 7HQ$\cdots$·(H$_2$O)$_2$ complex and 361 cm$^{-1}$ for 7HQ$\cdots$·(NH$_3$·H$_2$O·H$_2$O), or no more than 1 % of the experimental values. These results should be compared to the much larger differences between the EOMCCSD/6-311+G(d) and experimental excitation energies that range between 14 and 17 %. The complexation-induced spectral shifts $\Delta \omega_{\pi \rightarrow \pi^*}$ resulting from the EOMCC,A and EOMCC,D calculations agree with their experimental counterparts to within 5–27 % or 15 % on average in the case of EOMCC,A and 10–37 % or 22 % on average in the EOMCC,D case. In other words, the EOMCC,D approach, while bringing the excitation energies $\omega_{\pi \rightarrow \pi^*}$ to a much closer agreement with experiment than the EOMCCSD/6-311+G(d) calculations, does not offer improvements in the calculated $\Delta \omega_{\pi \rightarrow \pi^*}$ values. The composite EOMCC,A approach provides additional small improvements in the calculated $\Delta \omega_{\pi \rightarrow \pi^*}$ shifts, reducing the 7–33 % errors relative to experiment resulting from the EOMCCSD/6-311+G(d) calculations to 5–27 %. Based on these observations, we consider the EOMCC,A values of the spectral shifts $\Delta \omega_{\pi \rightarrow \pi^*}$ as the theoretical reference values for assessing the quality of the FDET and supermolecular TDDFT calculations, although the use of EOMCC,D would not change any of our main conclusions. Clearly, a comparison of the purely electronic EOMCC and experimental data discussed above has limitations, since we would have to investigate the effect of nuclear motion on the EOMCCSD and $\delta$-CR-EOMCC(2,3) excitation energies and use basis sets larger than 6-31+G(d) in the $\delta$-CR-EOMCC(2,3) calculations to make more definitive statements. We believe, however, that the EOMCC,A results obtained by combining the EOMCCSD/6-311+G(d) excitation energies with the triples corrections extracted from the $\delta$-CR-EOMCC(2,3),A/6-31+G(d) calculations, as in Eq. (30), are of sufficiently high quality to allow us to assess the quality of the FDET and supermolecular TDDFT results in applications involving the environment-induced spectral shifts in complexes of cis-7HQ, which are discussed next.

### 3.2 A Comparison of the Excitation Energy Shifts from the FDET and Supermolecular TDDFT Calculations with the Reference EOMCC Data

In agreement with the experimental data reported in Ref. [5], the excitation energy shifts $\Delta \omega_{\pi \rightarrow \pi^*}$ for the hydrogen-bonded 7HQ$\cdots$·$B$ complexes investigated in this work resulting from the EOMCC calculations are always negative and the magnitude of $\Delta \omega_{\pi \rightarrow \pi^*}$ correlates to a large extent, with the size of the hydrogen-bonded environment $B$ in the cis-7HQ$\cdots$·$B$ complex (see Table 1). In particular, according to the reference EOMCC,A calculations, the shifts in the vertical excitation energy $\omega_{\pi \rightarrow \pi^*}$ corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ chromophore
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vary from (-396)--(-820) cm\(^{-1}\) in the case of the smaller 7HQ--\(\cdots\)B complexes involving the CH\(_3\)OH, H\(_2\)O, HCOOH, and NH\(_3\) monomers, through -1446 cm\(^{-1}\) in the case of the 7HQ--\(\cdots\)(H\(_2\)O)\(_2\) complex, to (-1780)--(-2055) cm\(^{-1}\) in the case of the largest 7HQ--\(\cdots\)B systems involving the (NH\(_3\)-H\(_2\)O-NH\(_3\)), (NH\(_3\)-H\(_2\)O-H\(_2\)O), and (NH\(_3\)-NH\(_3\)-H\(_2\)O) trimers. It is interesting to examine how well the FDET and supermolecular TDDFT calculations reproduce these data.

As shown in Table 2 and Fig. 2, the overall agreement of the monomer-expansion-based FDET/ATZ2P data employing the nonrelaxed environment densities \(\rho_\text{E}\) with the reference EOMCC,A results is excellent, independent of the approximant used to determine the nonadditive kinetic energy potential \(\nu_{\text{nad}}^{\text{eff}}(\rho_\text{A}, \rho_\text{B}; \mathbf{r})\) that forms part of the embedding potential \(\nu_{\text{emb}}^{\text{eff}}(\rho_\text{A}, \rho_\text{B}; \mathbf{r})\). The absolute values of the deviations between the \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) values resulting from the FDET calculations employing the GGA97 approximant to represent \(\nu_{\text{nad}}^{\text{eff}}(\rho_\text{A}, \rho_\text{B}; \mathbf{r})\) and the corresponding supermolecular EOMCC,A calculations range from 4 cm\(^{-1}\) in the case of the 7HQ--\(\cdots\)NH\(_3\) complex, where the EOMCC,A shift is -820 cm\(^{-1}\), to 229 cm\(^{-1}\) in the case of the 7HQ--\(\cdots\)HCOOH system, where the EOMCC,A result for \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) is -743 cm\(^{-1}\). The mean signed and unsigned errors in the FDET results for the environment-induced shifts \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) obtained with the \(\nu_{\text{nad}}^{\text{eff}}(\rho_\text{A}, \rho_\text{B}; \mathbf{r})\) potential approximated with GGA97 relative to the EOMCC,A reference data are -36 and 104 cm\(^{-1}\), respectively, or 11 %, if we average the individual relative errors. The use of the NDSD approximant to represent \(\nu_{\text{nad}}^{\text{eff}}(\rho_\text{A}, \rho_\text{B}; \mathbf{r})\) has virtually no effect on the FDET \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) values, producing errors relative to EOMCC,A that range, in absolute value, between 29 cm\(^{-1}\) for the 7HQ--\(\cdots\)NH\(_3\) complex and 209 cm\(^{-1}\) for the 7HQ--\(\cdots\)HCOOH system, or the mean signed and unsigned errors of -51 and 105 cm\(^{-1}\), respectively (again, 11 %, if we average the individual relative errors). Based on the analysis of the EOMCCSD and \(\delta\)-CR-EOMCC(2,3) calculations presented in Section 3.1, the deviations between the nonrelaxed, monomer-expansion-based FDET/ATZ2P and reference EOMCC,A data shown in Table 2 and Fig. 2 are well within the accuracy of the EOMCC calculations, independent of the approximant used to represent the nonadditive kinetic energy potential \(\nu_{\text{nad}}^{\text{eff}}(\rho_\text{A}, \rho_\text{B}; \mathbf{r})\).

The performance of the FDET method has to be contrasted with the supermolecular TDDFT calculations, which are a lot less accurate than their FDET counterparts, when both types of calculations are compared with the reference EOMCC,A \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) values. Indeed, as shown in Table 2 (see also, Fig. 2), the differences between the \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) shift values obtained in the supermolecular TDDFT calculations using the STO ATZ2P basis set and their reference EOMCC,A counterparts range, in absolute value, from 382 cm\(^{-1}\) in the case of the 7HQ--\(\cdots\)H\(_2\)O complex, where the EOMCC,A shift is -562 cm\(^{-1}\), to 869 cm\(^{-1}\) in the case of the 7HQ--\(\cdots\)(NH\(_3\)-H\(_2\)O-H\(_2\)O) system, where the EOMCC,A \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) value is -1969 cm\(^{-1}\). The mean unsigned error in the supermolecular TDDFT/ATZ2P values of the \(\Delta \omega_{\pi \cdots \pi}^{\text{eff}}\) shifts relative to EOMCC,A is 673 cm\(^{-1}\) or, if we average the individual relative errors, 65 %. Obviously, these are much larger differences when compared with the corresponding nonrelaxed, monomer-expansion-based FDET calculations that give the 4–229 cm\(^{-1}\) deviations from the EOMCC,A data when the GGA97 approximant is used to represent the nonadditive kinetic energy potential.
$v^\text{NDSD}_i[ρ_1, ρ_2](r)$ and the 29–209 cm$^{-1}$ deviations from the EOMCC.A $\Delta ω_{π→π^*}$ values when the NDSD approximant is employed to construct $v^\text{NDSD}_i[ρ_1, ρ_2](r)$. The 65 % average relative error characterizing the $\Delta ω_{π→π^*}$ shift values resulting from the supermolecular TDDFT/ATZ2P calculations is six times larger than the analogous error characterizing the FDET calculations. Based on the analysis of the EOMCC calculations presented in Section 3.1, the differences between the supermolecular TDDFT and reference EOMCC.A data are well outside the accuracy of the EOMCC calculations for the $\Delta ω_{π→π^*}$ shifts, indicating the poor performance of the supermolecular TDDFT approach. Unlike in the FDET case, the differences between the supermolecular TDDFT and EOMCC.A $\Delta ω_{π→π^*}$ values increase with the size of the environment bound to the cis-7HQ chromophore. This indicates the difficulties with obtaining the balanced description of excitation energies in systems that have different sizes in the supermolecular TDDFT calculations, which are not present in the FDET and EOMCC calculations. Based on our numerical results, it is not entirely unlikely that the supermolecular TDDFT approach is not size intensive. All of the EOMCC approximations employed in this work, including the composite EOMCC.A approach, are rigorously size intensive. The FDET methodology offers a size intensive description of the complexation-induced spectral shifts by design.

3.3 A Comparison of the FDET and Supermolecular TDDFT Excitation Energy Shifts with the Experimental Data

Finally, it is instructive to comment on the quality of the shifts resulting from the FDET and supermolecular TDDFT calculations in the context of the available experimental information [5]. In analogy to the EOMCC.A results discussed in Section 3.1, a comparison of the purely electronic FDET or supermolecular TDDFT and experimental data has limitations, since one cannot measure vertical excitation energies obtained in the FDET and supermolecular TDDFT calculations in a direct manner. The experimental shifts reported in Ref. [5] correspond to the complexation-induced shifts in the position of the $\theta^0_{\pi} \pi \rightarrow π^*$ transition in the cis-7HQ absorption band in the cis-7HQ chromophore. Thus, although the experimental shifts obtained in Ref. [5] are closely related to the theoretical shifts obtained in this study, the two types of quantities differ because of the following factors: (i) the geometry relaxation in the excited states of the cis-7HQ and cis-7HQ···B systems when compared to the corresponding ground electronic states, and (ii) the the MP2/aug-cc-pVTZ geometries of cis-7HQ and its complexes employed in this work, although probably reasonable, are not the experimental geometries. All of these factors certainly contribute to the deviations between the theoretical shifts calculated in this study and their experimental counterparts reported in Ref. [5]. On the other hand, the careful EOMCC calculations reported in this work which, as pointed out in Section 3.1, closely follow the experimental excitation energies corresponding to the lowest $\pi \rightarrow π^*$ transition in the cis-7HQ and cis-7HQ···B systems, particularly when the EOMCC.A and EOMCC.D approaches corrected for triple excitations are employed, indicate
that the above factors, although important, lead to a relatively small overall effect. It is, therefore, interesting to compare our FDET and supermolecular TDDFT results for the excitation energy shifts $\Delta \omega_{\pi \rightarrow \pi^*}$, given in Table 2, with the experimentally derived shifts reported in Ref. [5] and listed in Table 1.

This comparison is shown in Fig. 2. As one can see by inspecting Tables 1 and 2, and Fig. 2, the $\Delta \omega_{\pi \rightarrow \pi^*}$ values obtained in the nonrelaxed, monomer-expansion-based FDET/ATZ2P calculations are in good agreement with the shifts in the experimental UV absorption spectra. The mean unsigned error in the $\Delta \omega_{\pi \rightarrow \pi^*}$ values resulting from the FDET calculations employing the GGA97 approximant to represent the nonadditive kinetic energy potential $v_{\text{add}}[\rho_A, \rho_B](r)$, relative to the spectral shifts observed in experiment, is 222 cm$^{-1}$, in excellent agreement with the EOMCC.A approach which gives 244 cm$^{-1}$. The analogous mean unsigned error resulting from the FDET calculations employing the NDSD approximant to represent $v_{\text{add}}[\rho_A, \rho_B](r)$ is very similar (216 cm$^{-1}$). For comparison, the mean unsigned error in the $\Delta \omega_{\pi \rightarrow \pi^*}$ values resulting from the supermolecular TDDFT/ATZ2P calculations, relative to the experimental spectral shifts, is twice as large (429 cm$^{-1}$), demonstrating once again the advantages of the embedding vs supermolecular strategy within the TDDFT framework. It is very encouraging to observe that the FDET approach, which can be applied to large molecular systems, is capable of providing shifts in the excitation energy corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ system due to formation of hydrogen-bonded complexes that can compete with the results of the considerably more expensive EOMCC calculations and that are a lot better than the supermolecular TDDFT results.

4 Summary and Concluding Remarks

We used the embedding FDET approach to determine the shifts in the excitation energy corresponding to the lowest $\pi \rightarrow \pi^*$ transition in cis-7-hydroxyquinoline (cis-7HQ), induced by the formation of hydrogen-bonded complexes of cis-7HQ with a number of small molecules, and compared the resulting shift values with the reference EOMCC data and the analogous shifts obtained in the conventional supermolecular TDDFT calculations. The main difference between the embedding strategy exploited in the FDET formalism and the conventional supermolecular approach is in the fact that in the former case one evaluates the excitation energy shifts induced by the interactions of the chromophore with its molecular environment as the differences of the excitation energies of the same many-electron system, representing the chromophore fragment with two different effective potentials, whereas in the latter case one has to perform calculations for two systems that differ in the number of electrons, the complex formed by the chromophore and its molecular environment and the isolated chromophore.

By considering eight complexes of cis-7HQ with up to three small hydrogen-bonded molecules, we demonstrated that the spectral shifts resulting from the FDET calculations with the $a$ priori determined nonrelaxed environment densities are in
excellent agreement with the reference EOMCC data obtained in the size-intensive EOMCC calculations with singles, doubles, and noniterative triples, whereas the analogous shifts obtained with the supermolecular TDDFT approach are far from those obtained with EOMCC. The nonrelaxed FDET calculations provide shifts that agree with their EOMCC analogs to within about 100 cm$^{-1}$ or 10\% on average, where the absolute values of the excitation energy shifts in the complexes of cis-7HQ examined in this study resulting from the EOMCC calculations range between about 500 and 2000 cm$^{-1}$. As shown in the present study, the accuracy of the FDET shift calculations employing nonrelaxed environment densities is on the order of the accuracy of the high-level EOMCC calculations. This should be contrasted with the excitation energy shifts obtained with the supermolecular TDDFT approach, which differ from the reference EOMCC values by about 700 cm$^{-1}$ or 65\% on average and which are well outside the accuracy of the EOMCC calculations. We demonstrated that none of the above findings are affected by the type of approximant used to represent the non-additive kinetic energy potential $v^{\text{kin}}_{\text{neq}}(\rho_A, \rho_B)(\mathbf{r})$ that forms part of the local, orbital-free, embedding potential $v^{\text{eff}}_{\text{emb}}(\rho_A, \rho_B; \mathbf{r})$ employed in the FDET calculations. Two such approximants, GGA97 and NDSD, were examined, giving the virtually identical FDET spectral shift values.

Although the main focus of the present study was the comparison of the FDET and supermolecular TDDFT results for the complexation-induced shifts in the excitation energy corresponding to the lowest $\pi \rightarrow \pi^*$ transition in cis-7HQ with the EOMCC data, we also compared the FDET, supermolecular TDDFT, and reference EOMCC shift values with the experimental shifts reported in Ref. [5]. Although such a comparison has limitations due to the neglect of the effect of nuclear motion on photoabsorption spectra in purely electronic calculations performed in this work, the spectral shifts obtained with the FDET approach using nonrelaxed environment densities and those obtained with the EOMCC methodology agree with the experimental shifts quite well, whereas the supermolecular TDDFT calculations produce very large errors. This reinforces the superiority of the FDET strategy when compared with the conventional supermolecular TDDFT approach in applications involving complexation-induced spectral shifts.

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References

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17. F. Coester, Nucl. Phys. 7, 421 (1958)
Shfits in Excitation Energies Induced by Hydrogen Bonding


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115. C. Møller, M.S. Plesset. Phys. Rev. 46, 618 (1934)
Table 1 The vertical excitation energies $\omega_{\pi \rightarrow \pi^*}$ and the environment-induced shifts $\Delta \omega_{\pi \rightarrow \pi^*}$ (in cm$^{-1}$) obtained with the EOMCCSD/6-31+G(d), EOMCCSD/6-311+G(d), $\delta$-CR-EOMCC(2,3), A/6-31+G(d), and $\delta$-CR-EOMCC(2,3), D/6-31+G(d) approaches, and their composite EOMCC,A and EOMCC,D analogs defined by Eq. (30), corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ chromophore and its various complexes.

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<th>EOMCCSD/6-311+G(d)</th>
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* Defined by Eq. (30), in which variant A of CR-EOMCC(2,3) is employed. ** Defined by Eq. (30), in which variant D of CR-EOMCC(2,3) is employed. Obtained with the laser resonant two-photon ionization UV spectroscopy by examining the shifts in the origin of the $S_0 \rightarrow S_1$ absorption band [5].
Table 2 A comparison of the environment-induced shifts $\Delta \omega_{\pi \rightarrow \pi^*}$ (in cm$^{-1}$) of the vertical excitation energy corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ chromophore that result from the monomer-expansion-based FDET calculations employing the nonrelaxed environment densities $\rho_B$, the PW91 approximant for the nonadditive exchange-correlation contribution $v_{\text{ex}}^{\text{opt}}[\rho_A, \rho_B](r)$ to the embedding potential $v_{\text{emb}}^{\text{opt}}[\rho_A, \rho_B; r]$, and the GGA97 and NDSD approximants for the nonadditive kinetic energy contribution $v_{\text{kin}}^{\text{opt}}[\rho_A, \rho_B](r)$ to $v_{\text{emb}}^{\text{opt}}[\rho_A, \rho_B; r]$, with the results of the supermolecular TDDFT calculations (all using the SAOP approximant for the exchange-correlation potential and the STO-6G basis set) and the reference EOM-CC data
Fig. 1 The hydrogen-bonded complexes of the cis-7HQ molecule examined in the present study
Nonadditive kinetic energy terms

Fig. 2 A comparison of the environment-induced shifts $\Delta \omega_{\pi \rightarrow \pi^*}$ of the vertical excitation energy corresponding to the lowest $\pi \rightarrow \pi^*$ transition in the cis-7HQ chromophore and resulting from the monomer-expansion-based DFT/GGA97 and DFT/NDSD calculations with nonrelaxed-$\rho_{0}$ and the supermolecular TDDFT calculations (all using the STO-6GZP basis set), with the reference supermolecular EOMCC$_{\alpha}$ data and the experimental shifts in the origin of the $S_{0} \rightarrow S_{1}$ absorption band induced by complex formation [5]
Part III.
The importance of taking into account the Pauli repulsion in multi-level computer simulations of electronic structure properties of hydrogen bonded complexes
General introduction to Part III:

In multi-scale simulations of electronic structure dependent properties the computational cost of the applied methods is a critical factor. Often, simple coulombic-only embedding potentials -the Pauli repulsion is completely neglected- are employed in studies of embedded molecules [11, 76–83] for a pragmatic decrease of the computational effort. This simplification which involves the neglect of Pauli repulsion, is linked to lack of accuracy, numerical instability and unreliability. The intensity of this phenomenon depends on the studied electronic structure depending property and on the system. For this reason individual studies for each property and category of systems (for example charged, non-covalently bonded molecules) are required. The importance of taking into account the Pauli repulsion (even approximately) in theoretical studies is demonstrated in this thesis, for the case of the iso-g of Electron Paramagnetic Resonance (EPR) (Chapter 8) -for combinations of charged/uncharged hydrogen bonded molecules- and the first vertical excitation energy (Chapter 9) -for uncharged hydrogen bonded molecules-, by investigations involving the orbital-free embedding potential ($v_{\text{emb}}^{\text{eff}}$) of Frozen-Density Embedding Theory (FDET). It should stressed at this point that FDET is an exact theory and Pauli repulsion is taken into account exactly but the methods based on FDET involve approximations for the non-Coulombic terms and this is why it is mentioned that “Pauli repulsion is taken into account approximately”. The work described in the Part III is linked to that of Part II as it provides further justification for the choice of employing the $v_{\text{emb}}^{\text{eff}}$ -and not a coulombic-only embedding potential- for the study of the cooperativity of hydrogen-bonded chains (Chapter 5) and studying the approximations (system dependent and system independent) associated with the $v_{\text{emb}}^{\text{eff}}$ (Chapters 6 and 7). In contrast with the conclusions of Chapters 6 and 7 where a non-relaxed electron density of the environment ($\rho_B$) was proven to be ideal input for the FDET equations when excitation energies are to be calculated, the work presented in Chapter 8 indicated that for the study of the iso-g value, relaxation of $\rho_B$ is required (especially when the system is negatively charged). It should also be kept in mind that for successful employment of FDET based methods, an initial study of the approximations involved needs to take place for each investigated molecular property for a particular type of systems (for example a radical embedded in a non-charged environment) is required. The work described in this Part moves in this line by complementing Part II and by providing valuable understanding for the study of EPR parameters.
Introduction to Chapter 8:

This chapter is based on the publication:


The main objective of this paper is to investigate the need of taking into account Pauli repulsion in embedding calculations of the shift of the iso-g value of Electron Paramagnetic Resonance (EPR) of a radical due to its environment. It should be emphasized that respecting fermionic statistics in embedding calculations is associated with increased computational cost. The secondary objective is the study of the effect that the choice for the electron density of the environment ($\rho_B$) has on the calculated results. It should not be forgotten that this type of study is an absolute requirement before large scale investigations of biomolecules (and any considerable study involving proteins would be “large scale”) involving Frozen-Density Embedding Theory (FDET).

We have chosen to study the complex biliverdin-PCYA, where biliverdin is the radical (interesting due to special photoabsorption properties) and PCYA is the protein that surrounds it. We did not put emphasis in creating a realistic model of the complex -this would be the subject of future work- and this is not a pitfall because the intention is to make comparisons between the results produced by employing computational methods based on supermolecular Density-Functional Theory (DFT) -which plays the role of the reference method in this study-, FDET and coulombic-only embedding, and not to analyse the reproduction of experimental data. For this reason the model included only a few, uncharged amino acids, chosen based on their proximity to the radical and biliverdin in several protonation states. The main conclusion is that Pauli repulsion related terms that appear in the orbital-free embedding potential of FDET are absolutely necessary in embedding calculation of shifts of iso-g, both for variational stability and accuracy reasons. It is emphasized that the coulombic-only embedding based method considered in this publication failed to capture the direction of the effect in most cases when non-relaxed $\rho_B$ was employed, presented variational stability problems that made the calculation impossible when the basis set was expanded to the environment (for both the relaxed and non-relaxed $\rho_B$ cases) and overall lead to worse reproduction of the supermolecular DFT results compared to FDET based methods. The secondary conclusion is that $\rho_B$ needs to be relaxed (see comments on the relaxation in “Introduction to Chapter 5”) for systematically satisfactory reproduction -i.e. overall smaller deviation- of reference supermolecular DFT data for all considered protonation states (that are associated with different charges) of biliverdin. It is reminded that also for the case of shifts of vertical excitation energies (see Chapter 6) non-relaxed $\rho_B$ leads to smaller overall deviation between FDET and supermolecular DFT results. It is noted that for the calculation of iso-g, a method based on the Zeroth Order Regular Approximation (ZORA) to the Dirac equation (see article for reference) was employed. The ZORA potential was approximated in embedding calculations, by the effective Kohn-Sham potential for the radical, to which an embedding potential (either the orbital-free embedding potential of FDET or the coulombic-only embedding potential) was added in order for the effect of the environment to the electron density of biliverdin to be taken into account. In supermolecular calculations an effective Kohn-Sham potential for the whole system was employed in the ZORA expressions.

Finally it is clarified that the author of this thesis contributed to the publication by:
The importance of Pauli repulsion for the calculation of Iso-g

i) creating the model of the protein-radical complex based on the crystal structure ii) optimizing the position of the hydrogens a Density-Functional Theory (DFT) based method, iii) producing the FDET and coulombic-only embedding results, and iv) participating in the analysis of the results (experimental theoretical) and formulation of the conclusions. A reprint of the article follows.
The Importance of Going beyond Coulombic Potential in Embedding Calculations for Molecular Properties: The Case of Iso-G for Biliverdin in Protein-Like Environment

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Abstract: The importance of the nonelectrostatic component of the embedding potential is investigated by comparing the complexation induced shifts of the iso-g obtained in embedding calculations to its supermolecular counterparts. The analyses are made in view of such multilevel simulations, for which supermolecular strategy is either impractical or impossible, such as the planned simulations for the whole enzyme ferredoxin oxidoreductase. For the biliverdin radical surrounded by a few amino acids, it is shown that the embedding potential comprising only Coulomb terms fails to reproduce even qualitatively the shifts evaluated from supermolecular calculations. The nonelectrostatic component of the exact embedding potential is a bifunctional of two electron densities [Wesolowski and Warshel, J. Phys. Chem. 1993, 97, 8050; Wesolowski, Phys. Rev. A 2008, 77, 012504]. Therefore we analyze in detail both the quality of the approximant for the bifunctional and the importance of the choice of the electron densities at which it is evaluated in practical calculations.

Introduction

Multilevel techniques in numerical simulation apply the embedding potential to couple the subsystem described at the quantum mechanical level with its environment described using simpler descriptors. If the quantum mechanical treatment of the whole system under investigation is impractical or impossible, then such techniques are the only options available. Such approaches are frequently referred as quantum mechanical/molecular mechanical (QM/MM) and are widely applied in simulation of biomolecules, materials, liquids, solids, and interfaces, for instance. The embedding potential, i.e., the potential added to the potential in the environment-free case, \( v_0(r) \), is commonly represented by the electrostatic potential (atomic units are applied in all the equations given in the present work):

\[
\begin{align*}
\upsilon_{\text{emb Coulomb}}(\rho_A, \rho_B; \vec{r}) &= \upsilon_{\text{ex}}(\vec{r}) + \int \frac{\rho_B(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}' \\
&= \upsilon_{\text{ex}}(\vec{r}) + \sum_{\text{centers}} \frac{Q_{\text{c}}}{|\vec{r}' - \vec{r}|} d\vec{r}'
\end{align*}
\]

The convention used in eq 1 indicating that the embedding potential is a functional of the two electron densities \( \rho_A \) (the electron density of the embedded system) and \( \rho_B \) (the electron density of the environment) and is used for the sake of the subsequent discussions. Note that the embedding potential given in eq 1 does not depend on \( \rho_B \), i.e., the electron density of the embedded system. In practice, the second term representing the classical Coulomb electron–electron repulsion is evaluated using truncated polycenter multipole expansion. Especially simple is the case of the expansion truncated to monopoles, which leads to a very efficient computational method where the nuclear and monopole expansion charges can be bunched together giving rise to a set of distributed effective charges.

The potential given in eq 1 does not take into account the nonelectrostatic effects on the electronic structure of the embedded species which arise from the Pauli exclusion principle (see ref 9 for discussion of this issue in a model system). If such effects cannot be neglected, then the straightforward solution is to add to the electrostatic potential a nonlocal component consisting of projection operators (or simplified molecular pseudopotentials), which hinges on...
the availability of the orbitals for the environment. In multilevel simulations, such as QM/MM, etc., especially if the target is not a property directly related to the electronic structure but to the potential energy surface, the nonelectrostatic component of the exact embedding potential is frequently neglected, resulting in an inexpensive computational approach. In such a case, the deficiencies of electrostatic-only embedding potentials can be corrected by special terms added to the final expression for the total energy.\textsuperscript{11–15} Such corrections are, however, strongly system and method dependent as pointed out by several authors. For instance, the authors of a recent review state that, “QM/MM calculations are not yet black-box procedures,” and the authors of ref \textsuperscript{17} conclude that “...the need to partition the complete system into regions treated at different levels of theory, and to allow these regions to interact, creates two significant problems. First is the treatment of the QM/MM boundary, as it is often necessary to place this boundary across covalent bonds. Second is the parameterization of the hybrid system Hamiltonian.” Several authors reported problems, such as excess polarization of the embedded subsystem by the environment, when the embedding potential comprises only electrostatic terms.\textsuperscript{18–20} Specific numerical problems arising from neglecting nonelectrostatic terms in the embedding potential, especially if the basis set used to construct embedded orbitals extends into the environment, were also reported.\textsuperscript{21–23} In numerical simulations aiming at obtaining properties of embedded systems, which are other than ground-state energy, the large basis sets are frequently indispensable. Therefore, the quality of the calculated values depends directly on the accuracy of the used embedding potential. The pragmatic solution made for the ground-state energy, i.e., as adding a correction term directly to the energy, is less straightforward for other observables. To correct errors for such quantities, the cure must be applied to the embedding potential, as it determines the quality of the calculated electronic structure.

The frozen-density embedding theory (FDET)\textsuperscript{24–28} provides a formal basis for computational methods (besides our own work see also other representative papers)\textsuperscript{29–33} in which both the energy as well as the electronic properties are evaluated in a self-consistent manner. Below, we outline the basic elements of the frozen-density embedding theory:

- **Basic variables.** The total investigated system is characterized by two quantities: the density $\rho_\Lambda(\vec{r})$, which for a given electronic problem is a frozen function, and the density $\rho_0(\vec{r})$, which is represented using auxiliary quantities, such as occupied orbitals of noninteracting reference system $\{\phi_i^\Lambda(\vec{r})\}$,\textsuperscript{24} occupied and unoccupied orbitals of noninteracting reference system,\textsuperscript{25} interacting wave function,\textsuperscript{27} or one-particle density matrix.\textsuperscript{28}

- **Constrained search.** The density $\rho_\Lambda(\vec{r})$ is obtained by performing the following search:

  \begin{equation}
  E_{\text{emb}}[\rho_\Lambda, \rho_0] = \min_{\rho_\Lambda \geq 0} E^{\text{H}}[\rho_\Lambda + \rho_0] \text{ for } \int \rho_\Lambda(\vec{r}) d\vec{r} = N_\Lambda \\
  = \min_{\rho_0 \geq 0} E^{\text{H}}[\rho_0] \text{ for } \int \rho_0(\vec{r}) d\vec{r} = N_0
  \end{equation}

- **Performing the constrained search by modifying the external potential.** The search is conducted in practice by solving the following equation:

  \begin{equation}
  (\widetilde{H}_e + \widetilde{\nu}_{\text{emb}})\psi = E_{\text{emb}}\psi
  \end{equation}

where $\widetilde{H}_e$ is the environment-free Hamiltonian, and the $\widetilde{\nu}_{\text{emb}}(\vec{r})$ has the form of a local potential, which is determined by the pair of densities $\rho_\Lambda(\vec{r})$ and $\rho_0(\vec{r})$, hence orbital-free embedding.

- ** Orbital-free embedding potential.** The form of the dependence of the embedding potential on the densities $\rho_\Lambda(\vec{r})$ and $\rho_0(\vec{r})$ depends on what QM descriptor is used as the auxiliary quantity for $\rho_\Lambda(\vec{r})$ and is given in respective publications.\textsuperscript{24, 25, 28} For the following descriptors: orbitals of noninteracting reference system, a wave function of the full configuration interaction form, and one-particle density matrix, the orbital-free embedding potential reads:

  \begin{equation}
  v_{\text{emb}}^{\text{orb}}[\rho_\Lambda, \rho_0; \vec{r}] = v_{\text{emb}}^{\text{orb}}(\vec{r}) + \int \frac{\rho_\Lambda(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' + \frac{\delta E_{\text{emb}}[\rho]}{\delta \rho} \bigg|_{\rho = \rho_\Lambda, \rho_0} - \frac{\delta E_{\text{emb}}[\rho]}{\delta \rho} \bigg|_{\rho = \rho_\Lambda, \rho_0} - \frac{\delta T[\rho]}{\delta \rho} \bigg|_{\rho = \rho_\Lambda, \rho_0} \tag{4}
  \end{equation}

The correspondence given in eq 4 involves density functionals known in the Kohn–Sham formulation\textsuperscript{34} of density functional theory,\textsuperscript{35} the functional of the exchange–correlation energy ($E_{\text{xc}}[\rho]$), and the functional of the kinetic energy in a noninteracting system ($T[\rho]$). The pair of functional derivatives of the functional $T[\rho]$ arises from nonadditivity of this functional and represents a potential denoted as $v_{\text{emb}}^{\text{orb}}[\rho_\Lambda, \rho_0; \vec{r}]$ in the present work.

In this context, it is useful to relate the frozen-density embedding theory to the subsystem formulation of density functional theory (SDFT)\textsuperscript{36, 37} and to the recently developed partition density functional theory (PDFT).\textsuperscript{38} Both SDFT and PDFT lead to the exact ground-state electron density and the energy of the whole investigated system an alternative way to the conventional Kohn–Sham framework. In SDFT, the charges of each subsystem are assumed to be integral (similarly as in FDET), whereas fractional charges of subsystems are allowed in PDFT. The FDET targets not the ground-state electron density of the total system but the density minimizing the Hohenberg–Kohn energy functional for the total system with the presence of constraints. FDET, therefore, can lead to the same total ground-state density as SDFT and Kohn–Sham DFT or PDFT, only when for particular constraints\textsuperscript{39} (see also below). In the case of two subsystems, SDFT is based on the following variational principle:

\begin{equation}
E_v = \min_{\rho_\Lambda \geq 0, \rho_0 \geq 0} E^{\text{H}}[\rho_\Lambda + \rho_0] \\
\text{for } \int \rho_\Lambda(\vec{r}) d\vec{r} = N_\Lambda, \int \rho_0(\vec{r}) d\vec{r} = N_0
\end{equation}

where the search is performed among subsystem densities which are pure-state noninteracting $\nu$-representable. The sufficient condition for reaching the exact ground-state
density in SDFT is that it can be decomposed as a sum of two pure-state noninteracting $\nu$-representable densities comprising an integer number of electrons $N_A$ and $N_B$ (see the discussions in ref 26). FDET does not target the ground-state of the total system but the density, which minimizes the total ground-state energy in presence of the following constraint:

$$\rho \geq \rho_B$$

(6)

which is given in advance.

The total density obtained in FDET (eq 2 is, therefore, not equal to the exact ground-state density except for a particular case, i.e., when the difference between $\rho_B(\vec{r})$ and the assumed $\rho_B(\vec{r})$ is representable using one of the auxiliary descriptors mentioned above: orbitals of the noninteracting reference system, interacting wave function, or one particle density matrix. On the virtue of Hohenberg–Kohn theorems, FDET can lead only to the upper bound of the ground-state energy:

$$E_{\text{coal}}[\rho_B] \geq E_\text{so}$$

(7)

Any numerical implementation of FDET can be easily converted to methods solving coupled Kohn–Sham–like equations in SDFT. In fact, the first numerical implementation of SDFT applicable for molecular systems used the “freeze-and-thaw” cycle, which was applied in a number of subsequent studies (see for instance refs 40–42). In the original numerical studies based on SDFT concerning atoms in solids and in the recent numerical implementation of SDFT for molecular liquids, the coupled Kohn–Sham equations are solved simultaneously. We have also shown recently that the “freeze-and-thaw” cycle can be performed simultaneously with displacing nuclear position accelerating the SDFT-based geometry optimization. The “freeze-and-thaw” cycle to solve the coupled Kohn–Sham like equations is used by us in methodological studies on approximants to the noninteracting reference system. Using any quantum chemical approach, the macroscale, it is even possible to generate the ground-state energy: for smaller model systems in order to establish the search given in eq 2, the corresponding orbitals ($\phi^A_i$) are obtained from the following Kohn–Sham–like equations (eqs 20–21 in ref 24):

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho_A, \vec{r}] + v_{\text{emb}}[\rho_A, \rho_B, \vec{r}] \right] \phi^A_i = \epsilon_i^A \phi^A_i,$$

$$i = 1, N^A$$

(8)

where $v_{\text{emb}}[\rho_A, \rho_B; \vec{r}]$ is given in eq 4.

The effectiveness of methods based on eq 8 for the studying changes in the electronic structure arising due to the interactions between the embedded system and its environment was demonstrated for: vertical excitation energies, electron spin resonance (ESR) hyperfine coupling constants, ligand-field splittings of $f$-levels in lanthanide impurities, NMR shieldings, dipole and quadrupole moments, electronic excitation energies, and frequency dependent polarizabilities.

In multilevel simulations based on FDET, $\rho_B$ is an assumed quantity, which can obtained following various approaches. Since the electron density is a well-defined quantity also in the macroscopic regime, it is even possible to generate $\rho_B$ without using any quantum chemical approach. A natural choice for $\rho_B$ is to use Kohn–Sham equations to generate it for the isolated environment and to use it for generating the embedding potential. Such procedure does not take into account the electronic polarization of the environment by the embedded subsystem. For this reason such density and embedding potential are labeled as nonrelaxed. If the “freeze-and-thaw” procedure is used to generate $\rho_B$, which together with the optimal $\rho_A$ minimizes the energy of the whole system, then the corresponding quantities are labeled as relaxed.

Our own numerical experience concerning the applicability of eq 1 in embedding calculations shows invariably that it leads frequently to qualitatively wrong or erratic results, especially if other properties than energy are investigated (for a representative study see ref 50). The secondary aim of this study is the analysis of the errors in calculated environment-induced shifts of iso-g for an embedded radical molecule. The g-tensor is an important parameter of ESR spectroscopy, and its analysis is used as a supplementary tool to elucidate the protonation state of a radical in the enzyme’s active center. The protein provides both the steric constraints affecting the geometry of the radical as well as the electronic environment (long-range electrostatic as well as short-range Pauli repulsion), which affect the observed g-tensor. Modeling g-tensor must take a proper account of these two types of effects, and the FDET methods are especially designed to study the electronic effects (for a representative study see ref 50). The secondary aim of this study is the analysis of the errors in calculated environment-induced shifts of iso-g which can be attributed to the use of approximate density functional for the nonadditive kinetic potential $v_{\text{coal}}[\rho_A, \rho_B]$, i.e., the last two terms in eq 4.

We have chosen to study a model system consisting of the biliverdin IXa radical (BV) and a few amino acids of the protein phycocyanobilin (PCYA) representing the nearest neighbors of BV in the BV–PCYA complex. The g-tensor of BV has extremely small anisotropy. It should be noted that conventional ESR cannot resolve the components of g-tensors with very small anisotropy (as those of organic
radicals), but recent developments in high-field ESR allow one to determine the components of even such g-tensors and to use them in the interpretation of biochemical data.\(^\text{57}\) It is known that PCYA catalyzes the reduction of BV to PCYA, the precursor of biliprotein chromophores found in phycobilisomes. The present work represents the preparatory stage of the project aimed at studying the whole protein–radical complex by means of multilevel type of simulations based on FDET. Two numerical model related issues: the adequacy of the used approximant for the bifunctional of the nonrelativistic components of the embedding potential and the adequacy of the choice for \(\rho_n\) are, therefore, at the focus of the present work.

In order to obtain the absolute values of iso-g as and the environment induced shifts of this quantity \([\Delta \text{iso-g} = \text{iso-g(BV + environment)} - \text{iso-g(BV)}]\), the calculations based on either embedding or supermolecular strategy are feasible for the investigated model system, which is rather small. The possible advantages of using the FDET-based embedding calculations over the supermolecular ones lie not only in reducing the computational costs. If the shifts arise from nonbonding interactions between the embedded molecule and its environment, then the quality of the shifts obtained from FDET strategy can be expected to be better than their supermolecular counterparts for the reasons addressed in more detail below. The quality of the results obtained in both the Kohn–Sham and the embedding calculations depend on such common factors as: (a) the molecular model of the real system (size of the model and coordinates of atoms not available from experiments), (b) the approximant for the exchange–correlation functional, (c) the treatment of relativistic effects (the spin–orbit coupling in particular), and (d) the basis set. As far as the environment induced shifts are concerned, however, their quality in supermolecular and embedding calculations is determined by different factors. In the supermolecular case, the shift is the difference between values obtained from two independent Kohn–Sham calculations. As a result, the errors in iso-g might cumulate or cancel. In the embedding case, the calculated shift arises from the addition of the embedding potential to the effective potential corresponding to the system without any environment. The errors in the shifts are, therefore, determined mainly by the quality of the embedding potential given in eq 4. Due to its first-principles based origin, the quality of the embedding potential used in practice is determined by only two factors: the chosen frozen electron density \(\rho_0\) and the used approximant for the nonadditive kinetic potential (the last two terms in eq 4). The importance of the first factor can be easily monitored by performing the “freeze-and-thaw” calculations on model systems. Concerning the orbital-free embedding potential expressed as the functional of \(\rho_0\) and \(\rho_n\), its medium- and long-range part is known exactly (electrostatics) and can be expected to dominate if the embedded molecule is surrounded by noncovalently bound polar molecules. Since the errors in the shifts of the properties related directly to the electronic structure, i.e., to the embedded orbitals and their energies, are determined only by the accuracy of the approximants to the nonadditive kinetic and exchange–correlation potentials, one can expect that, whenever the environment includes polar or charged molecules represented exactly in the orbital-free embedding potential given in eq 4, the shifts obtained from FDET-based calculations surpass in accuracy the ones derived using their supermolecular counterparts.

The model environment of BV considered in the present work is the same as the one investigated earlier in the study aimed at determination of the protonation state of PCYA–bound BV,\(^\text{57}\) where the supermolecular calculations were used to interpret experimental data. We use the same model for different purposes: (a) to explore the possibility of replacing supermolecular calculations by embedding ones for these types of analyses and (b) to determine the necessary conditions (choice of the frozen density, number of centers to expand the embedded orbitals using atomic bases, possibility to neglect nonrelativistic components of the exact orbital-free embedding potential) for the optimal embedding calculations, i.e., ensuring the smallest of the deviations from the supermolecular results at the largest reduction of the computational efforts.

**Computational Details**

The three considered protonation states denoted with \(\alpha\text{ACD}^\circ\), \(\alpha\text{ACD}\), \(\alpha\text{C}\) are shown in Figure 1. In the label, a big letter indicates a protonated nitrogen site in the pyrrole ring (A, B, C, or D), a Greek letter (\(\alpha\) or \(\delta\)) denotes a protonated carbonyl oxygen site, and the + or − denote the charge of the embedded species.

Two cluster models of the environment of the PCYA–bound BV shown in Figure 2 are considered: the smaller (EHD) and the larger (EHDFQ) (the amino acids are referred to with commonly used one letter codes). The EHDQ cluster comprises amino acids: GLU76, HIS88, ASP105, TYR212, and GLN216 in their neutral form taken from the 2DIE structure deposited in the Protein Data Bank (PDB).\(^\text{58}\) The EHD cluster comprises GLU76, HIS88, and ASP105 (all polar). These three amino acids are chosen because of their proximity to the carbonyl oxygen atoms on the pyrrole rings. All of them are capable of hydrogen bonding to the protonated BV and are thus critical for determining the locations of protons in BV. They are expected to affect the g-tensor of the protein-bound BV. The amino acids of the EHD cluster are also believed to be essential in catalysis as proton donors.\(^\text{59}\) Concerning the larger cluster (EHDFQ), it comprises additionally to two polar amino acids TYR212 and GLN216. They are near the \(\alpha\) carbonyl oxygen atom of the pyrrole ring and far from the \(\delta\) carbonyl oxygen atom.

The position of the hydrogen atoms, which is not available in the PDB structure, was generated initially using “Accelrys DS Visualizer suite”\(^\text{60}\) and subsequently refined using the nonrelativistic Kohn–Sham LDA calculations, with the STO-type triple-\(\zeta\) with polarization functions basis sets (TZP label in the ADF version 2009.01 basis set library). The Cartesian coordinates are provided in the Supporting Information.

The g-tensor, the main property investigated in the present work, is related to the magnetic moment of an electron as:

\[
\mu = -g\beta S
\]

where \(S\) is the electron spin, and \(\beta\) the bohr magneton. The \(g\)-value depends on the particular magnetic species under consideration.\(^\text{65}\) The principal components of
the g-tensor together with the hyperfine tensor $A$ specify the positions and the splittings of the lines in ESR spectra, depending on the direction of the magnetic field relative to the molecular axis. The spectral anisotropy is completely specified by three $g$-values ($g_{xx}$, $g_{yy}$, $g_{zz}$) and three hyperfine constants ($A_{xx}$, $A_{yy}$, $A_{zz}$). The isotropic $g$-value (iso-$g$), which is discussed throughout the present work, is the average of the principal $g$-values: iso-$g = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$.

In this study, the molecular $g$-values are calculated based on the solutions of the relativistic Kohn-Sham equations in the “spin-orbit coupling containing zeroth order regular approximation (ZORA) to the Dirac equation”. In ZORA, the spin–orbit coupling interaction (which is for many systems the most important factor for shifting the g-tensor components away from the free-electron value $g_e$) and other relativistic effects are taken into account variationally. The spin-restricted version of the spin–orbit including ZORA calculations, which is computationally less expensive than the spin-unrestricted version and thus more attractive for the study of average and big sized systems, was used. The method introduced in ref 70 combining ZORA with a single-orbital reference technique to deal with gauge dependency for open-shell doublet systems was applied. The Becke–Perdew exchange–correlation functional is used in both supermolecular and embedding calculations. This choice is motivated by its reported reliability in the calculation of the ESR parameters.

The recently developed approximant to the nonadditive kinetic energy bifunctional (NDSD), which satisfies the uniform electron gas limit and the asymptotic form of the exact bifunctional for the nonadditive kinetic potential at $F_A \rightarrow 0$ and $\int \rho_B d\vec{r} = 2$, was used. It takes the following form:

$$\tilde{T}_r^{\text{nonadd(NDSD)}}[\rho_A, \rho_B] = \frac{3}{10} (3\pi^2)^{2/3} \int ((\rho_A + \rho_B)^{5/3} - \rho_A^{5/3} - \rho_B^{5/3}) d\vec{r} + \int f(\rho_B, \nabla \rho_B) \cdot \rho_A(\vec{r}) \cdot \nu_{j}^{\text{lim}}[\rho_B(\vec{r})] d\vec{r}$$

(9)

$$f(\rho_B, \nabla \rho_B) = \left(\exp(\lambda(\rho_B + s^\text{min}_B)) + 1\right)^{-1} \times \left(1 - \left(\exp(\lambda(-\rho_B + s^\text{max}_B)) + 1\right)^{-1}\right) \times \left(\exp(\lambda(-\rho_B + s^\text{max}_B)) + 1\right)^{-1}$$

(11)

and where: $s_B = (\int \nabla \rho_B) / ((2(3\pi^2)^{1/3}) \rho_B^{3/2})$, $s^\text{min}_B = 0.3$, $s^\text{max}_B = 0.9$, $\rho_B^{\text{min}} = 0.7$, and $\lambda = 500$. 

Figure 1. (a) The six positions in the BV IXa radical that can be protonated: $\alpha$, $\delta$, A, B, C, and D. The three considered protonation states: (b) $\alpha$ACD$\delta^+$, (c) ACD$\delta^+$, and (d) ACD$^-$. 

Figure 2. BV IXa in the $\alpha$ACD$\delta^+$ protonation state (for the convention, see Figure 1) in ferredoxin oxidoreductase represented by five amino acids: GLU76, HIS88, ASP105, TYR212, and GLN216.
The STO-type DZP(ZORA) basis set from the ADF version 2009.01 package’s basis set library,⁷⁴ that comprises a valence double-ζ basis set with one set of polarization functions, is used in the evaluation of g-tensor in both embedding and supermolecular calculations. All reported calculations are performed using the ADF version 2009.01 package.⁷⁴ Considering the atomic basis sets, it is important to point out a different significance of the choice of the number of centers used to construct molecular orbitals in supermolecular and in embedding calculations. In the supermolecular calculations, the number of centers is rarely considered an issue as they coincide with the positions of nuclei, except for some particular types of calculations. For instance, the “ghosts” are used commonly to evaluate the basis set superposition error by means of the counterpoise procedure.⁶⁴ In embedding calculations, it is natural to restrict the of centers of atomic basis sets to the nuclei of the embedded species. This is one of the sources of great computational savings in the embedding strategy after all. Addition of atomic sets localized in the environment might, however, significantly affect the numerical results of the embedding calculations.⁴⁵,⁴⁶,⁶²,⁶³ Since eq 8 is based on variational principle (eq 2), any additional basis functions used to construct the embedded orbitals can only bring the results closer to the variational limit. The supermolecular expansion is, therefore, used, as a standard in development/testing approximants for $\psi_{\text{full}}^{\text{mol}}(\rho, \rho_b)$.⁴⁵,⁶⁴ The use of full set of atomic centers, i.e., that in the embedded system and in the environment, is, however, not practical for large-scale simulations but is frequently applied in the preliminary stage of a simulations to choose the minimal size of the basis set and the centers assuring numerical stability for the results.⁶⁵ In the present work, the considered systems are rather small and both variants of embedding calculations are feasible. They are referred to as monomer and supermolecular expansion, respectively.

Finally, it is important to underline that to investigate the possibility of replacing the supermolecular calculations by the embedding ones using the considered embedding potentials, it is crucial that the embedding results and their supermolecular counterparts are obtained using the same: type of atomic basis sets, centers of the atomic basis sets, numerical grid, approximant for the exchange–correlation potential, and the external potential (geometry of the cluster). The particular choices for made for these quantities is of secondary importance from the point of view of the comparisons made in this work as long as the common parameters are the same in supermolecular and embedding calculations. The comparisons between the embedding and supermolecular results are made for several systems (various protonation states of BV and sizes of the environment) to ensure that the results are not accidental and to cover various possible interaction modes of a radical molecule with a protein. Nevertheless, some choices were made arbitrarily such as that for the approximant for the exchange–correlation potential, the choice of the protonation state of the amino acids, and the basis set used in most of the analysis. It is also important to underline that despite the fact that the investigated models are constructed based on the BV–PCYA

### Results and Discussions

Throughout the results section, the environment induced shifts of the iso-$g$ obtained from the embedding calculations are compared with the shifts obtained from the supermolecular strategy. The absolute or relative value of the difference $\Delta$iso-$g$ = iso-$g^{\text{supermolecule}} -$ iso-$g^{\text{embedding}}$ is used in all discussions concerning the accuracy of various embedding potentials considered in the present work. Note that the difference $\Delta$iso-$g$ is equal to the difference between the absolute values of iso-$g$ calculated in supermolecular and embedding strategies (iso-$g$ = iso-$g^{\text{supermolecular}} -$ iso-$g^{\text{embedding}}$).

Table 1 collects the iso-$g$ and $\Delta$iso-$g$ values obtained using nonrelaxed $\rho_b$ for the three protonation states of BV in various environments. The reference Kohn–Sham results are also given for comparison. In three among four investigated systems, eq 1 leads to quantitatively wrong shifts (results obtained with monomer expansion). The situation is even worse when supermolecular expansion is used. The order of orbital levels is wrong, and no self-consistent solutions of eq 8 can be obtained. The situation is greatly improved if the full embedding potential given in eq 4 is used. The results of supermolecular and monomer expansion are quite similar.

<table>
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<tr>
<th>method</th>
<th>environment</th>
<th>protonation state of BV</th>
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<th>$\Delta$iso-$g$ (ppm)</th>
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Table 1. Iso-$g$ and $\Delta$iso-$g$ = iso-$g$(BV + Environment) – iso-$g$(BV) of BV in Various Environments Calculated With Eqs 1 and 4 and Nonrelaxed Density of the Environment⁶⁴

Kohn–Sham results for the isolated and complexed BV are also given for reference. *STO-type DZP(ZORA) basis set was used. **Monomer basis set. *Self-consistent cycle did not converge.
in all cases. The complexation induced shifts obtained from embedding calculations with eq 4 reproduce qualitatively the reference values from supermolecular calculations in three considered cases but lead to qualitatively wrong shifts for ACD$^-$. According to the discussion in the Introduction, these discrepancies might originate from the choice of $\rho_0$ or from the fact that an approximated functional was used for $v_{\text{EHD}}^{\text{iso-g}}[\rho_0, \rho_B]$. We note, however, that for embedded species which are electrically neutral, the agreement between the reference data and the shifts from the embedding calculations using the potential given in eq 4 is the best (156 vs 192 ppm). This indicates that the lack of relaxation might lie at the origin of the large discrepancies in the other cases.

To investigate this interpretation, the shifts were evaluated using the relaxed $\rho_0$ which is obtained in the "freeze-and-thaw" procedure. They are collected in Table 2 which parallels Table 1. The relaxed $\rho_0$ takes into account the electronic polarization of the environment by the embedded species and corresponds to the variational minimum of the total energy functional expressed using the applied approximated density functionals (SDFT). On the practical side, we notice that the "freeze-and-thaw" procedure converges rapidly and that the shifts do not change noticeably after completion of just one cycle (data not shown). Let us start with the worst case analyzed previously, i.e., ACD$^-$. Indeed, the qualitatively wrong complexation induced shift obtained in the absence of relaxation (+89 vs −78 ppm reference value) becomes negative (−164 ppm). The embedding potential of eq 4 leads to the correct direction of the effect but overestimates its magnitude. Removal of the basis functions localized in the environment brings the numerical result even closer to the supermolecular reference (−124 ppm). Similarly as in the nonrelaxed $\rho_0$ case, the differences between the shifts obtained with monomer and supermolecular basis sets are significantly smaller than the magnitudes of the shifts. The situation is quite different if the electrostatic-only (eq 1) embedding potential is used. Similarly as in the previously considered nonrelaxed case, it can be noticed that the electrostatic-only embedding potential cannot be applied with supermolecular basis sets. The results obtained using the monomer expansion with the electrostatic-only embedding potential (the situation most closely resembling the typical QM/MM computational protocol) are reasonable, but they are systematically worse than the ones obtained using the full embedding potential.

As far as the basis set effect on the obtained complexation induced shifts is concerned, it is worthwhile to notice that the two previously considered choices for the basis sets (monomer or supermolecular expansion) represent two extremes in practical calculations. Most of the QM/MM calculations do not employ the basis sets localized in the environment. From the practical point of view, however, it is more useful to analyze the numerical stability of the shifts obtained from embedding calculations if only the monomer expansion is considered but the atomic basis sets change. The following section addresses this issue for one case: BV in the "ACD0" protonation state in the EHD environment.

We start with noticing that, the complexation induced shifts of iso-g obtained from supermolecular calculations are not affected by the change of the basis set significantly (see Table 3). The basis set superposition error on iso-g obtained from the supermolecular strategy is negligible reaching 3 ppm at most (data not shown). Embedding calculations using Coulombic embedding potential appear to be very sensitive to the choice of the basis set. With the monomer expansion, the shifts equal to 35 and 23 ppm for STO-DZ and STO-DZP, respectively. These values represent less than 50% of the reference shifts (72 or 75 ppm). Reducing the size of the basis set on each atom in the supermolecular expansion

### Table 2. Iso-g and Δiso-g = iso-g(BV + Environment) − iso-g(BV) of BV in Various Environments Calculated with Eqs 1 and 4 and Relaxed Density of the Environment

<table>
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<th>Δiso-g (ppm)</th>
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<td>EHD</td>
<td>ACD$^\delta$</td>
<td>2.004572 0</td>
<td></td>
</tr>
<tr>
<td>Kohn−Sham</td>
<td>EHD</td>
<td>ACD$^\delta$</td>
<td>2.004494 −78</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Kohn-Sham results for the isolated and complexed BV are also given for reference. $^b$ STO-type DZP(ZORA) basis set was used. $^c$ Monomer basis set. $^d$ Supermolecular basis set. $^e$ Self-consistent cycle did not converge.

### Table 3. Basis Set Dependence of iso-g and Δiso-g = iso-g(BV + EHD) − iso-g(BV) Obtained in Embedding Calculations and Supermolecular (Kohn−Sham) Calculations

<table>
<thead>
<tr>
<th>method</th>
<th>basis set</th>
<th>iso-g (ppm)</th>
<th>Δiso-g (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kohn−Sham</td>
<td>STO(DZ)</td>
<td>2.002959 72</td>
<td></td>
</tr>
<tr>
<td>Kohn−Sham</td>
<td>STO(DZP)</td>
<td>2.002928 75</td>
<td></td>
</tr>
<tr>
<td>embedding: eq 1</td>
<td>STO(DZ)</td>
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<td></td>
</tr>
<tr>
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<td>STO(DZP)</td>
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<td></td>
</tr>
<tr>
<td>embedding: eq 1</td>
<td>STO(DZP+ghosts)</td>
<td>2.002929 35</td>
<td></td>
</tr>
<tr>
<td>embedding: eq 1</td>
<td>STO(DZP+ghosts)</td>
<td>2.002938 51</td>
<td></td>
</tr>
<tr>
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<td>STO(DZP)</td>
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<td></td>
</tr>
<tr>
<td>embedding: eq 1</td>
<td>STO(DZP+ghosts)</td>
<td>2.002946 59</td>
<td></td>
</tr>
<tr>
<td>embedding: eq 1</td>
<td>STO(DZP+ghosts)</td>
<td>2.002938 51</td>
<td></td>
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<tr>
<td>embedding: eq 1</td>
<td>STO(DZP+ghosts)</td>
<td>2.002919 66</td>
<td></td>
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<tr>
<td>embedding: eq 1</td>
<td>STO(DZP+ghosts)</td>
<td>2.002919 66</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ STO-type DZP(ZORA) basis set was used. $^b$ Results for BV in the aACD0 protonation state. $^c$ Nonrelaxed pp. $^d$ Relaxed pp.
form STO-DZP to STO-DZ does not bring solution to the problem of the lack of convergence in the electrostatic-only embedding case.

The shifts obtained from embedding calculations with the full embedding potential are significantly more stable numerically and closer to the reference. With the monomer expansion the corresponding shifts are 72 and 66 ppm, which are also very close to the corresponding supermolecular reference (72 and 75 ppm for STO–DZ and STO–DZP, respectively). Moreover, adding the centers localized in the environment does not affect the obtained shifts significantly. The shifts obtained with four considered sets of basis functions are scattered between 66 and 72 ppm.

The numerical results discussed so far show invariably that the full embedding potential is indispensable for obtaining numerically stable values of complexation induced shifts. However, an important factor in embedding calculations applying the potential given in eq 4 is the choice of the electron density \( \rho_0 \). Performing the full “freeze-and-thaw” procedure (SDFT) is not practical in the case of large environments, and a nature of multilevel simulations is that additional approximations are introduced for \( \rho_0 \), as in methods based on FDET. In the following part, we focus on the ACD\(^+\) case, where nonrelaxed electron density was shown to be a very inappropriate choice for \( \rho_0 \), as it leads to a wrong sign of the complexation induced shift of iso-g. Moreover, the difference between the results obtained using the monomolecular and supermolecular expansion in embedding calculations was the largest as well as the effect of relaxation was also the largest in magnitude. We notice that opposite to other complexes considered in the present work, the embedded system was charged, and it was charged negatively. This suggests attribution of the failure of nonrelaxed embedding calculations to the neglect of electronic polarization and to the role of charge transfer between the embedded radical and the environment or even some covalent character of the bonding between the embedded species and its environment. The analysis of the complexation induced dipole moments in this systems supports the attribution of the failure of nonrelaxed \( \rho_0 \) embedding calculations to the missing electronic polarization (see Table 3). To support this interpretation of the inadequacy of choosing nonrelaxed \( \rho_0 \) for negatively charged environment of BV, the complexation induced dipole moments collected in Table 4 are analyzed below. The complexation induced shifts are the smallest (2.93 D) if both the embedded species and the environment are not charged, i.e., for ACD\(^-\). In this case, the embedding calculations reproduce quite reasonably the complexation induction increase of the dipole moment (2.46 vs 2.93 D) but only if relaxation is taken into account. It is worthwhile to notice that despite such under performance in reproducing the complexation induced dipole moments in the absence of relaxation, the shifts of iso-g were very accurately reproduced (153 vs 192 ppm see Table 1) even if nonrelaxed \( \rho_0 \) is used in embedding calculations. This indicates that the quality of the embedding potential does not affect all properties of the embedded species in the same way. The choice of the simplified method to obtain \( \rho_0 \) in large scale simulations using eq 4 must, therefore, be subject of dedicated studies depending on the system and the investigated property. Interestingly, the complexation induced dipole moments are only slightly larger for the two cases of cationic embedded species is (3.07 and 3.94 D). Turning back to the ACD\(^+\) case, where the choice of nonrelaxed \( \rho_0 \) was qualitatively wrong for evaluation of \( \Delta \)iso-g, we notice that the complexation induced dipole moment is, indeed, the largest (7.10 D), and effect of the relaxation of \( \rho_0 \) on the calculated dipole moment is the largest.

### Conclusions

The applicability of the embedding strategy as an alternative to supermolecular calculations was investigated using a small model system comprising BV and a few amino acids of the PCYA protein. The numerical results indicate clearly that the nonelectrostatic components of the embedding potential are indispensable. Without a nonelectrostatic component of the exact embedding potential, the results of embedding calculations are not reliable as the effect of the environment on the investigated property (shift of iso-g) is described erratically (strong dependence of the results on the basis sets) and even qualitatively wrong. The magnitude of the change in iso-g resulting from changing the protonation state of the radical can be significant as estimated in this work and in the work by Stoll et al.\(^{57}\) (a few hundreds of ppm). Such effects on iso-g are significantly larger in magnitude than the differences between supermolecular and embedding results. Even larger effects on the magnitude of iso-g can be expected to rise from the effect of protein on the conformation of the radical. Both supermolecular or embedding strategies can be, therefore, used to target these larger effects. The present work indicates that if the nonelectrostatic terms are taken into account by approximate density functionals, then the embedding strategy can be considered as a numerically efficient alternative. It is important to underline that neither supermolecular nor embedding calculations are likely to be used for interpretations of very small effects, such as the shift of iso-g of BV resulting from protein mutations which do not exceed 15 ppm.\(^{57}\) The effect is too small to be reliably predicted by any type of calculations at least for the mutants for which the data is available.
Iso-G for Biliverdin

Concerning practical calculations based on the frozen-density embedding theory,\textsuperscript{24-28} the analytic form of the nonelectrostatic components of the exact embedding potential is unfortunately not known. Approximants must be used instead. The present work shows that the currently known approximants to these terms perform quite reasonably. The embedding calculations can reproduce the 50–90\% of the reference shifts obtained using the supermolecular strategy. The fact that the shifts are not perfectly reproduced indicates that further improvements of the approximants for the kinetic energy-dependent component of the embedding potential are needed. The present work provides also important hints for setting up a large-scale multilevel simulation based on FDET. For the neutral and cationic amino acids interacting with BV, using the nonpolarized electron density to evaluate the orbital-free embedding potential is a reasonable approximation. For negatively charged amino acids, however, the electronic polarization of the environment by the embedded molecule must be taken into account. We underline that the embedding calculations using the orbital-free embedding potential lead to results which are numerically robust and do not vary significantly with the basis sets, even if additional basis sets centered on atoms in the environment are used in construction of embedded orbitals.

Finally, we stress that the practical recommendations and conclusions emerging from the present studies concerning: weak basis set dependence, negligible effect of atomic basis sets localized in the environment, reasonably good approximation of neglecting electronic polarization of neutral and cationic amino acids in the environment, adequacy of the NDSD approximant for the nonadditive kinetic energy were drawn based on the analyses of shifts of the iso-g. Investigation of other properties, the quality of which is directly linked to the accuracy of the used embedding potential, might lead to different recommendations. For instance, the relative errors (deviation from the reference supermolecular results) in the complexation induced dipole moments obtained from embedding calculations do not correlate well with the errors in the iso-g shifts despite the fact that both errors are determined by the quality of the used orbital-free embedding potential. According to our numerical experience, the complexation induced dipole moments are very sensitive to the variations in the embedding potential. This is one of the reasons we use induced dipoles in the methodological studies aimed at development or validation of approximants for the nonadditive kinetic potential.\textsuperscript{45–47}

Acknowledgment. This work was supported by the grant 200020-124817 from the Fonds National Suisse de la Recherche Scientifique.

Supporting Information Available: Cartesian coordinates are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References

Introduction to Chapter 9:

This chapter is based on the publication:


The main objective of this article is to investigate the need of taking into account Pauli repulsion, in embedding calculations of the shift of the first vertical excitation energy of a chromophore due to its environment. For this purpose, the aforementioned property was calculated by employing the embedding approach (both coulombic-only and Frozen-Density Embedding Theory (FDET) with non-relaxed electron density of the environment) for several complexes, involving the 7-cis-hydroxyquinoline chromophore hydrogen-bonded to one to three hydrogen-bonded small molecules. The main conclusion is that Pauli repulsion needs to be taken into account (as is the case in the orbital-free embedding potential of FDET) for reliable calculation of shifts of vertical excitation energies. This finding is in accord with the conclusion of Chapter 8 for a different property (iso-g of EPR). Coulombic-only embedding reproduces FDET based results, which are known to deviate very little from reference quality Equation-of-Motion Coupled-Cluster based data (see Chapters 6 and 7), only when a small basis set is employed. It must be noted, that even the accuracy of FDET results, suffers to some extent from the small basis set and consequently coulombic-only embedding based methods can not prove sufficiently satisfactory for calculations of shifts of vertical excitation energies. In addition, it is demonstrated that coulombic-only embedding, in contrast with FDET based embedding the omnipresent numerical stability of which is not affected by the choice of the basis set, is associated with great variational instability (in many cases the Self-Consistent-Field (SCF) procedure did not converge) and completely artificial results when average and large basis sets are used in the calculations. This is interesting, as scientific work relying on coulombic-only embedding for evaluation of excitation energies, keeps appearing in the literature. The findings described in this article indicate that coulombic-only embedding should be employed only coupled with carefully selected (perhaps with “trial and error”) small basis sets and remains associated with lower accuracy compared with FDET based embedding. It is in order to stress at this point, that the message generated from the Part III of this thesis is that FDET based methods are reliable (unpleasant surprises like “not convergence of the SCF procedure” were not observed) and accurate and that the tuning of this accuracy hinges primarily on the choice of the electron density of the environment.

Finally it is clarified that the author of this thesis contributed to the publication by:

i) calculating the local minima with the Subsystem Density-Functional Theory (DFT)
based method, ii) producing the FDET and electrostatic embedding results, and iii) participating in the analysis of the results (experimental theoretical) and formulation of the conclusions. A preprint of the article follows.
Importance of the Intermolecular Pauli Repulsion in Embedding Calculations for Molecular Properties: The Case of Excitation Energies for a Chromophore in Hydrogen-Bonded Environments

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ABSTRACT: In embedding methods such as those labeled commonly as QM/MM, the embedding operator is frequently approximated by the electrostatic potential generated by nuclei and electrons in the environment. Such approximation is especially useful in studies of the potential energy surface of embedded species. The effect on energy of neglecting the non-Coulombic component of the embedding operator is corrected a posteriori. The present work investigates applicability of such approximation in evaluation of electronic excitation energy, the accuracy of which depends directly on that of the embedding potential. For several model systems involving cis-7-hydroxyquinoline hydrogen-bonded to small molecules, we demonstrate that such truncation of the embedding operator leads to numerically unstable results upon increasing the size of the atomic basis sets. Approximating the non-Coulombic component of the embedding potential using the expression derived in Frozen-Density Embedding Theory ([Wesolowski and Warshel, J. Phys. Chem. 1993, 97, 8050] and subsequent works) by means of even a simple bifunctional dependent on the electron density of the chromophore and its hydrogen-bonded environment, restores the numerical stability of the excitation energies that reach a physically meaningful limit for large basis sets.

INTRODUCTION

Embedding methods are commonly used in numerical simulations for large polyatomic systems such as biomolecules, materials, solvated molecules, etc. In the case of the Schrödinger equation in Born–Oppenheimer approximation, the principal idea behind the embedding strategy consists of simplifying the basic descriptor of the system: from the $N^e$-electron function ($\Psi^{N_e}$) to a simpler object - the $N^e$-electron function ($\Psi^{N_e}$) where $N_e < N_{tot}$. We will refer to such $\Psi^{N_e}$ as embedded wave function ($\Psi^{emb}$). If $N^e$ denotes the number of electrons of the embedded system in the absence of any environment and $H_0$ is the corresponding Hamiltonian, $\Psi^{emb}$ is obtained by solving the following equation:

$$ (H_0 + \hat{V}_{emb})\Psi^{emb} = E_{emb}\Psi^{emb} \tag{1} $$

where $\hat{V}_{emb}$ is an operator representing the effect of the environment on the embedded wave function (embedding operator). Many methods are used in practice differing in the strategy to construct $\hat{V}_{emb}$. By construction, embedding methods must involve subjective choice of the system into its component. If $N_{A} \ll N_{tot}$, the computational efforts needed to solve eq 1 is significantly smaller than that needed to solve the corresponding Schrödinger equation for the whole system:

$$ \hat{H}_{tot}\Psi^{N_{tot}} = E_{tot}\Psi^{N_{tot}} \tag{2} $$

The embedding methods allow, therefore, for reduction of computational costs without sacrificing accuracy. All quantities evaluated from eq 1 depend on the choice made for the embedding operator and $H_0$. In particular, if the environment induced shifts of any evaluated quantity depend critically on the quality of the approximations for the embedding operator.

Frequently, $\hat{V}_{emb}$ is approximated by means of the electrostatic potential generated by the nuclei in the environment ($\nu_{nucl}(r)$) and the potential generated by the classical distribution ($\rho_{cl}(r)$). The above generic form of the embedding operator is usually further simplified by using multcenter multipole expansion of the electrostatic potential including (or not) the polarization of the environment by the embedded species. Such potential takes into account the dominant factor influencing the electronic structure of a species embedded in an environment generating strong electrostatic field (ionic solids, polar liquids, for instance) but does not take into account the fermionic statistics of electrons. It is, nevertheless, frequently used. For instance, Shaik et al.\textsuperscript{2} write about such

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approximation, “Electronic embedding is the standard choice in current QM/MM studies of enzymes.”, in the review published last year. Truncating the embedding operator in the electronic Schrödinger equation to its Coulombic component will be referred to as Coulombic-only approximation in this work. The Coulombic-only approximation is known to be very adequate in studies targeting the potential energy surface of embedded species as indicated by the aforementioned citation from the review by Shaik et al. and countless reported instances of the QM/MM simulations using the Coulombic-only approximation. The origin of the success of the Coulombic-only approximation lies in the fact that the contributions to the conformational energy resulting from quantum-mechanical origin can be added as a posteriori corrections to the total energy. Such corrections have clear interpretation in the theory of intermolecular interactions and take the form of simple pair potentials which can be derived either from first-principles or involve system-dependent parameters (see the review by Shaik et al. for instance). It is worthwhile to note also that the Coulombic-only approximation is usually applied in combination with highly localized basis sets (see the aforementioned review article by Shaik et al.). When plane waves or basis sets extending to the environment are used, flaws of this approximation are revealed that lead to a qualitatively wrong distribution of charge density between the embedded species and the environment. For other observables than the energy, the a posteriori correction of errors resulting from the Coulombic-only approximation is less straightforward. For each observable associated with a given operator other than electronic Hamiltonian, a priori correction would involve parametrizing its expectation value. Several authors clearly indicated the need of going beyond the Coulombic-only approximation and proposed methods in which the Coulombic-only embedding potential is supplemented by either local/nonlocal pseudopotentials or dumping factors for electrostatic interactions as part of the embedding operator. Despite this accumulated numerical evidence of indispensability of taking into account the non-Coulombic part of the embedding operator, the Coulombic-only approximation is still in use even in simulations targeting excitation energies. Interestingly, the reported excitation energies obtained using the Coulombic-only approximations are frequently very good. We attribute this to the use of basis sets localized in the embedded chromophore in such cases. The basis sets used in such calculations do not allow for fully variational exploration of the potential far from the chromophore, that is, where the Coulombic-only approximation is least adequate. The present work provides a systematic analysis of the limits of applicability of the Coulombic-only approximation to the embedding potential and its ability to yield convergent results with increasing size of the basis sets. The cis-7-hydroxyquinoline molecule (cis-7HQ) in different environments was chosen for studying this approximation. Eight environments consisting of 1–3 small hydrogen-bonded molecules: water, ammonia, and methanol (see Figure 1) were considered. The structural and spectroscopic properties of the investigated complexes are well understood, owing to spectroscopic data obtained in molecular beams and theoretical calculations.

In both aforementioned strategies to treat non-Coulombic component of the embedding operator involving pseudopotentials or dumping factors, this component is represented in a system-dependent manner. Frozen-Density Embedding Theory (FDET), on the other hand, provides a system-independent expression for the non-Coulombic component of the embedding operator expressed as local potential. The system dependency is the result of the fact that this potential is shown to be a bifunctional depending on a pair of electron densities: that of the embedded species (ρ*) and that of the environment (ρe). If  and  define (i) the noninteracting reference system (Kohn–Sham case), (ii) the full Configuration Interaction case, or (iii) the system defined by one-particle density matrix, the embedding potential of FDET takes the following form:

$$V_{emb}^{eff} = \frac{\delta E_{xc}}{\delta \rho} + \int \frac{\delta \rho(\rho', r')}{\delta \rho} \delta r' dr'$$

$$+ \delta E_{H} - \delta E_{H}^{\rho*} + \delta E_{H}^{\rho_e}$$

$$+ \frac{\delta \rho(\rho', r')}{\delta \rho} \delta r' dr'$$

$$- \frac{\delta \rho(\rho', r')}{\delta \rho} \delta r' dr'$$

Figure 1. Hydrogen-bonded complexes of the cis-7HQ molecule studied in the present work.
where the nonadditive bifunctionals are defined as $X_{i\alpha}[\rho_{\alpha}]-X[\rho_{\alpha}] = \rho_{\alpha}\cdot[p_{\alpha} + p_{B}], \quad X[\rho_{\alpha}] = \rho_{\alpha}
abla(p_{\alpha})\cdot\rho_{\alpha} - \rho_{\alpha}
abla(p_{\alpha})\cdot\rho_{B}$, with $X[\rho_{\alpha}]$ denoting the density functional for either the exchange-correlation or noninteracting kinetic energy ($E_{kin}[\rho]$ and $T_{kin}[\rho]$, respectively). Note that the notation used in eq 4, $\phi_{\alpha}(\rho_{\alpha}\cdot\rho_{B})$ and not $\phi_{\alpha}(\rho_{\alpha}\cdot\rho_{B})[\tau]\phi_{\alpha}(\tau)$, reflects the fact that the whole FDET embedding potential, opposite to its non-Coulombic components, is not the bifunctional of $\rho_{\alpha}$ and $\rho_{B}$ because it comprises the $\rho_{\alpha}\cdot\rho_{B}$ independent part ($\phi_{\alpha}(\tau)$).

For embedding a system described by an interacting Hamiltonian and the wave function of truncated Configuration Interaction form, the embedding functional comprises also an additional term assuring the self-consistency between energy and embedded wave function which depends on the number of determinants used to construct the embedded wave function. Various computational methods based on FDET differing in (i) the approximations for the bifunctional for the non-Coulombic part of the embedding operator, (ii) the choice for $H_0$, (iii) approximation for $\rho_{B}$ and (iv) additional approximations used in obtaining various observables from the embedded function, have been developed by us (see ref 26 for a recent example) and others.27–33

The second objective of the study is the analysis of the numerical stability of shifts in the excitation energies derived using the full potential given in eq 4, in which the exact bifunctionals are replaced by their approximate counterparts. The used approximate bifunctionals and the choice for $\rho_{B}$ in eq 4 were demonstrated to lead to the hydrogen-bonding induced shifts in the considered chromophore, which are equivalent to the results of benchmark wave function based ones (see ref 34). The Coulombic-only approximation can be seen as an even more drastic approximation to the exact embedding potential given in eq 4 in which all nonadditive bifunctionals are simply neglected. In particular, our own studies showed that the FDET based calculations using the same approximations as the ones applied in the present work provide highly accurate hydrogen-bonding induced shifts of the lowest excitation energies. In a sample of several similar complexes partially overlapping with the ones analyzed in the present work, it was shown that FDET-based shifts are comparable in accuracy to the Equation-of-Motion Coupled Cluster results of the benchmark quality.6,35 We note also that a similar study on the adequacy for evaluation of the environment induced changes of an other property (g-tensor) of both the full potential given in eq 4 and its truncated Coulombic-only approximation was recently reported,46 where it was shown that taking into account the non-Coulombic component of the embedding operator is indispensable.

**Computational Details**

The calculations of the electronic excitations and their shifts follow the general framework of Linear-Response Time-Dependent Density Functional Theory in its original version for the isolated chromophore or its embedding version introduced in ref 5 for the chromophore in the complex. The embedded orbitals and their levels were obtained from the Kohn–Sham DFT for Constrained Electron Density [cf., eq 20 and 21 in our original work21]:

$$\left[ -\frac{1}{2} \nabla^2 + v_{xc}[\rho_{\alpha}] ; \tau \right] + v_{emb}[\rho_{\alpha}, \rho_{B}; \tau] \phi_{\alpha} = \epsilon_{\alpha} \phi_{\alpha} \tag{S}$$

where $\phi_{\alpha}(\rho_{\alpha})$ is the usual expression for the potential of the Kohn–Sham DFT for the isolated system $A$, where $A$ refers to the chromophore, whereas $B$ refers to the environment throughout the present work. For each case, the Kohn–Sham ground-state electron density of the molecules in the environment in the absence of the chromophore was used as $\rho_{B}$. The excitation energy of the embedded chromophore was calculated by replacing the Kohn–Sham effective potential in the LR-TDDFT equations39 by the effective potential in eq 5 evaluated at the same $\rho_{B}$. Such treatment of $\rho_{B}$ defines an additional approximation in LR-TDDFT (neglect of dynamic response of the environment, NDRE approximation in short). The adequacy of NDRE depends on the system under investigation. NDRE cannot be used if the absorption spectra of the embedded species and the molecules in the environment overlap, as comprehensively demonstrated by Neugebauer.27 The formalism introduced by Casida and Wesolowski38 generalizing in the ground-state subsystem formulation of DFT39,40 for excited states, makes it possible to go beyond NDRE. This formalism has not been fully implemented numerically so far. Its simplified version, however, allowing for coupling between selected excitations in different chromophores, was developed by Neugebauer.27 Because the electronic spectra of the environment molecules and the chromophore are separated, NDRE is applicable here.

The geometries of each complex were obtained using the method based on the subsystem formulation of DFT (the code deMon2k-KSCE41, which is based on the code deMon2k)42 applying local density approximation for all relevant bifunctionals and functionals implemented in the deMon2k code (see ref 43 for details). The geometries are provided in the Supporting Information.

The relevant equations of FDET and its LR-TDDFT extension in NDRE approximation have been originally implemented into ADF code by Wesolowski.2 The improved implementation in ADF2009.01 version43 was used in the present work.

The density $\rho_{B}$ was obtained from Kohn–Sham calculations using the SAOP48 exchange-correlation potential and the STO-TZ2P basis set (triple-$\zeta$ basis with two sets of polarization functions) from the ADF2009.01 database. The following approximations were used in the embedding potential: for the exchange-correlation depended part, the Perdew–Wang (PW91) functional49 and for the kinetic energy depended part the recently developed NDSD bifunctional,55 which takes into account the exact conditions that become relevant for the proper behavior of $\nabla^{n+}[\rho_{\alpha}\rho_{B}][\tau]$ in the vicinity of nuclei, whereas the SAOP potential was used for the exchange-correlation component of $\rho_{\alpha}^{\prime}[\rho_{\alpha}][\tau]$ in eq 5.

For the chromophore, the following basis sets defined in the ADF2009.01 database were used: STO-SZ (single-$\zeta$ basis), STO-DZ (double-$\zeta$ basis), STO-ATZP (triple-$\zeta$ basis with one set of polarization functions and one set of diffuse s-STO and p-STO functions), and STO-ATZP+g (where gh stands for ghosts and indicates that the STO-ATZP atomic functions were used not only for the atomic centers of the chromophore, but also at atoms in the environment).

Throughout this work, $\Delta\omega$ denotes the environment induced shift in the vertical excitation energy for the lowest excitation cis-7HQ ($\Delta\omega = \omega_{emb} - \omega_{Isolated}$), $\Delta\omega_{HOOE}$ denotes the corresponding shift in the energy of the highest occupied embedded orbital (HOOE) compared to the energy of the highest occupied molecular orbital (HOMO) of the isolated chromophore, $\Delta\omega_{HOOE} = \epsilon_{emb}^{HOOE} - \epsilon_{HOOE}^{HOOE}$, and $\Delta\omega_{HOOE}$ denotes the shift of the energy of the lowest unoccupied embedded...
is complexation induced shift of the Energy (Δε, in eV), and Shift of the Lowest Unoccupied Embedded Orbital Energy (Δε_{LUEO}, in eV)\(^a\).

<table>
<thead>
<tr>
<th>basis set</th>
<th>Δω</th>
<th>Δδ^{HOEO}</th>
<th>Δδ^{LUEO}</th>
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<tbody>
<tr>
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<td>STO-DZ</td>
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<td>STO-ATZP+gh</td>
<td>−658</td>
<td>0.340</td>
<td>0.271</td>
</tr>
</tbody>
</table>

\(^a\) The experimental complexation induced shift of the \(S_n \rightarrow S_1\) excitation is −590 cm\(^{-1}\).20

Table 2. Basis Set Dependence of the FDET Results for cis-7-Hydroxyquinoline Hydrogen Bonded to Two \(H_2O\) Molecules Obtained with Coulombic-Only (eq 3) and Full (eq 5) Embedding Potentials: Shift of the Lowest Excitation (Δω, in cm\(^{-1}\)), Shift of the Highest Occupied Embedded Orbital Energy (Δδ^{HOEO}, in eV), and Shift of the Lowest Unoccupied Embedded Orbital Energy (Δδ^{LUEO}, in eV)\(^a\).

<table>
<thead>
<tr>
<th>basis set</th>
<th>Δω</th>
<th>Δδ^{HOEO}</th>
<th>Δδ^{LUEO}</th>
</tr>
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<tbody>
<tr>
<td>STO-SZ</td>
<td>2285</td>
<td>0.039</td>
<td>−0.048</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>−1710</td>
<td>0.074</td>
<td>−0.114</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>−8535</td>
<td>−0.030</td>
<td>−0.596</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>−658</td>
<td>0.340</td>
<td>0.271</td>
</tr>
<tr>
<td>Full Embedding Potential</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>2184</td>
<td>0.078</td>
<td>−0.019</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>−1703</td>
<td>0.166</td>
<td>−0.022</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>−1626</td>
<td>0.148</td>
<td>−0.026</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>−1629</td>
<td>0.144</td>
<td>−0.030</td>
</tr>
</tbody>
</table>

\(^a\) Unfilled fields denote lack of convergent solutions. The experimental complexation induced shift of the \(S_n \rightarrow S_1\) excitation is −1637 cm\(^{-1}\).20

orbital (LUEO) compared to the energy of the lowest unoccupied molecular orbital (LUMO) of the isolated chromophore, \(Δδ^{LUEO} = ε^{LUEO} - ε^{LUMO}\). The shifts of the excitation energies and orbital energies were evaluated as differences of the corresponding quantities evaluated with and without the environment at the unchanged geometry of the chromophore.

RESULTS AND DISCUSSION

We start with the results obtained with the full embedding potential given in eq 4. For cis-7HQ···\(H_2O\), which is the smallest complex investigated here, Δω changes sign from +129 cm\(^{-1}\) to −922 cm\(^{-1}\) upon increasing the basis set from STO-SZ to the STO-DZ (see Table 1). The addition of diffused functions to the monomer basis set (STO-ATZP) results in a noticeable effect on the shift reducing it to −621 cm\(^{-1}\). The addition of more centers to the STO-ATZP basis set by including ghosts (STO-ATZP+gh) localized in the environment, which is the \(H_2O\) molecule in this case, affect further the shift but the effect is significantly smaller (less than 40 cm\(^{-1}\)). Note that the energy of the lowest excitation in isolated cis-7HQ varies within the 80 cm\(^{-1}\) range if additional ghost centers carrying the STO-ATZP basis sets are used (see Table 9). Except for the STO-SZ basis case, the lowest excitation obtained from LR-TD-DFT calculations involves mainly the highest occupied and lowest unoccupied embedded orbitals, each of them being of the \(τ\) character (\(τ \rightarrow τ^*\) transition).

The above trends in the dependence of the excitation energy on the basis set are reflected also in the shifts in orbital energies (Δε). \(Δδ^{LUEO}\) becomes more positive when one goes from STO-SZ basis set to the STO-DZ basis set (from 0.237 to 0.470 eV), then much more negative (0.348 eV for STO-ATZP) and finally slightly more negative (0.340 eV for STO-ATZP+gh). Almost the same pattern is observed for the \(Δε^{LUEO}\). The relative numerical stability of the \(Δδ^{HOEO}\) and \(Δδ^{LUEO}\) obtained with the larger than STO-SZ basis sets is reflected also in the shape of the frontier orbitals. Figures 4 and 5 show that the shape of the embedded frontier orbitals obtained with the STO-DZ, STO-ATZP, and STO-ATZP+gh basis sets is basically indistinguishable. For the cis-7HQ···\(H_2O\) complex, similar tendencies in the basis set dependency of Δω and Δδ^{HOEO} occur. The magnitudes of the shifts calculated for each considered basis set are, however, larger, reflecting thus the stronger interactions with the chromophore (two hydrogen bonds linking the chromophore with the environment). The analysis of Tables 1–8 collecting the results for all the complexes investigated in this work reveals several common tendencies in the basis set dependency of the analyzed quantities if obtained with the full embedding potential. The self-consistent procedure to obtain embedded orbitals (solving eq 5) and the Davidson procedure20 to
Table 4. Basis Set Dependence of the FDET Results for cis-7-Hydroxyquinoline Hydrogen Bonded to Two NH₃ Molecules Obtained with Coulombic-Only (eq 3) and Full (eq 5) Embedding Potentials: Shift of the Lowest Excitation ($\Delta \omega$, in cm⁻¹), Shift of the Highest Occupied Embedded Orbital Energy ($\Delta \omega^{HOEO}$ in eV), and Shift of the Lowest Unoccupied Embedded Orbital Energy ($\Delta \omega^{LUEO}$ in eV)\(^a\)

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\Delta \omega$</th>
<th>$\Delta \omega^{HOEO}$</th>
<th>$\Delta \omega^{LUEO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic-Only</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>2351</td>
<td>0.295</td>
<td>0.215</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-1554</td>
<td>0.324</td>
<td>0.153</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-18325</td>
<td>0.142</td>
<td>-1.634</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>2140</td>
<td>0.365</td>
<td>0.261</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-1609</td>
<td>0.415</td>
<td>0.238</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-1517</td>
<td>0.399</td>
<td>0.237</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>-1477</td>
<td>0.402</td>
<td>0.243</td>
</tr>
</tbody>
</table>

\(^a\)Unfilled fields denote lack of convergent solutions. The experimental complication induced shift of the $S_0 \rightarrow S_1$ excitation is $-1715$ cm⁻¹.

Table 5. Basis Set Dependence of the FDET Results for cis-7-Hydroxyquinoline Hydrogen Bonded to Three NH₃ Molecules Obtained with Coulombic-Only (eq 3) and Full (eq 5) Embedding Potentials: Shift of the Lowest Excitation ($\Delta \omega$, in cm⁻¹), Shift of the Highest Occupied Embedded Orbital Energy ($\Delta \omega^{HOEO}$ in eV), and Shift of the Lowest Unoccupied Embedded Orbital Energy ($\Delta \omega^{LUEO}$ in eV)\(^a\)

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\Delta \omega$</th>
<th>$\Delta \omega^{HOEO}$</th>
<th>$\Delta \omega^{LUEO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic-Only</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>2089</td>
<td>0.351</td>
<td>0.237</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-1791</td>
<td>0.367</td>
<td>0.171</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-24997</td>
<td>0.189</td>
<td>-2.414</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>-28324</td>
<td>-16.277</td>
<td>-19.542</td>
</tr>
<tr>
<td>Full</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>1824</td>
<td>0.434</td>
<td>0.290</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-1833</td>
<td>0.455</td>
<td>0.253</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-1681</td>
<td>0.433</td>
<td>0.253</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>-1664</td>
<td>0.440</td>
<td>0.261</td>
</tr>
</tbody>
</table>

\(^a\)Unfilled fields denote lack of convergent solutions. The experimental complication induced shift of the $S_0 \rightarrow S_1$ excitation is $-2030$ cm⁻¹.

solve the Casida equations\(^4\) always converge (see Tables 1—8). The numerical values of $\Delta \omega$, $\Delta \omega^{HOEO}$, and $\Delta \omega^{LUEO}$ seem to stabilize with the increase of the basis set. In fact, adding the basis sets localized in the environment (making the results prone to any inaccuracies in the embedding potential) results in a very small (usually less than 40 cm⁻¹) numerical effect (see the STO-ATZP or STO-ATZP+gh results collected in Tables 1—8). The good numerical stability of the calculated shifts reflects the variational origin of the applied FDET-based calculations. It is worthwhile to underline that the shifts in the vertical excitation energies obtained with the two largest basis sets considered are in good agreement with the closely related experimental quantities, the complication induced shifts of the origin of the $S_0 \rightarrow S_1$ excitation collected in Table 10.

To investigate the importance of the non-Coulombic component of the orbital-free embedding potential, we turn now our attention to the results obtained with the truncated embedding potential (Coulombic-only embedding). The situation changes qualitatively compared to the discussed previously full potential.

Table 6. Basis Set Dependence of the FDET Results for cis-7-Hydroxyquinoline Hydrogen Bonded to Two CH₃OH Molecules Obtained with Coulombic-Only (eq 3) and Full (eq 5) Embedding Potentials: Shift of the Lowest Excitation ($\Delta \omega$, in cm⁻¹), Shift of the Highest Occupied Embedded Orbital Energy ($\Delta \omega^{HOEO}$ in eV), and Shift of the Lowest Unoccupied Embedded Orbital Energy ($\Delta \omega^{LUEO}$ in eV)\(^a\)

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\Delta \omega$</th>
<th>$\Delta \omega^{HOEO}$</th>
<th>$\Delta \omega^{LUEO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic-Only</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>2155</td>
<td>0.111</td>
<td>0.010</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-1824</td>
<td>0.142</td>
<td>-0.058</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-16291</td>
<td>0.031</td>
<td>-1.456</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>-27053</td>
<td>-22.290</td>
<td>-25.424</td>
</tr>
<tr>
<td>Full</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>2048</td>
<td>0.151</td>
<td>0.040</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-1819</td>
<td>0.235</td>
<td>0.035</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-1734</td>
<td>0.216</td>
<td>0.031</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>-1727</td>
<td>0.223</td>
<td>0.039</td>
</tr>
</tbody>
</table>

\(^a\)Unfilled fields denote lack of convergent solutions. The experimental complication induced shift of the $S_0 \rightarrow S_1$ excitation is $-1868$ cm⁻¹.

Table 7. Basis Set Dependence of the FDET Results for cis-7-Hydroxyquinoline Hydrogen Bonded to Three CH₃OH Molecules Obtained with Coulombic-Only (eq 3) and Full (eq 5) Embedding Potentials: Shift of the Lowest Excitation ($\Delta \omega$, in cm⁻¹), Shift of the Highest Occupied Embedded Orbital Energy ($\Delta \omega^{HOEO}$ in eV), and Shift of the Lowest Unoccupied Embedded Orbital Energy ($\Delta \omega^{LUEO}$ in eV)\(^a\)

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\Delta \omega$</th>
<th>$\Delta \omega^{HOEO}$</th>
<th>$\Delta \omega^{LUEO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic-Only</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>1894</td>
<td>0.137</td>
<td>0.000</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-2114</td>
<td>0.148</td>
<td>-0.082</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-27053</td>
<td>-22.290</td>
<td>-25.424</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Full</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>1670</td>
<td>0.209</td>
<td>0.047</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>-2063</td>
<td>0.248</td>
<td>0.021</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>-1890</td>
<td>0.230</td>
<td>0.029</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>-1920</td>
<td>0.226</td>
<td>0.021</td>
</tr>
</tbody>
</table>

\(^a\)Unfilled fields denote lack of convergent solutions. The experimental complication induced shift of the $S_0 \rightarrow S_1$ excitation is $-2329$ cm⁻¹.
The shifts collected in Tables 1–8 seem to depend strongly on the basis set. Let us start with the complex cis-7HQ· · ·(H$_2$O) and the results obtained with the two smallest basis sets (STO-SZ and STO-DZ). For STO-SZ, similarly as in the previously discussed full-potential case, not the lowest but the second-lowest transition obtained from LR-TDDFT calculations has the $\pi\rightarrow\pi^*$ character. For STO-DZ, similarly as in full potential calculations the lowest excitation is, indeed, a $\pi\rightarrow\pi^*$ transition. The shifts in the excitation energies calculated with the full and with the truncated (Coulombic-only) embedding potential agree quite reasonably (see Table 1) of the smallest basis sets are used. For instance, $\Delta\omega$ also changes sign from +108 to −858 cm$^{-1}$ (the corresponding full embedding potential results are 129 and −922 cm$^{-1}$). $\Delta\epsilon^{HOMO}$ becomes much more positive and increases from 0.225 to 0.434 eV (the corresponding full potential

Table 8. Basis Set Dependence of the FDET Results for cis-7-Hydroxquinoline Hydrogen Bonded to One H$_2$O and Two NH$_3$ Molecules Obtained with Coulombic-Only (eq 3) and Full (eq 5) Embedding Potentials: Shift of the Lowest Excitation ($\Delta\omega$, in cm$^{-1}$), Shift of the Highest Occupied Embedded Orbital Energy ($\Delta\epsilon^{HOMO}$ in eV), and Shift of the Lowest Unoccupied Embedded Orbital Energy ($\Delta\epsilon^{LUMO}$ in eV)$^a$

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\Delta\omega$</th>
<th>$\Delta\epsilon^{HOMO}$</th>
<th>$\Delta\epsilon^{LUMO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic-Only Embedding Potential</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>1953</td>
<td>0.326</td>
<td>0.196</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>−1964</td>
<td>0.337</td>
<td>0.123</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>−28123</td>
<td>−16.203</td>
<td>−19.244</td>
</tr>
<tr>
<td>Full Embedding Potential</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO-SZ</td>
<td>1688</td>
<td>0.409</td>
<td>0.249</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>−1991</td>
<td>0.429</td>
<td>0.221</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>−1800</td>
<td>0.404</td>
<td>0.209</td>
</tr>
<tr>
<td>STO-ATZP+gh</td>
<td>−1844</td>
<td>0.410</td>
<td>0.216</td>
</tr>
</tbody>
</table>

$^a$Unfilled fields denote lack of convergent solutions. The experimental complexation induced shift of the $S_0\rightarrow S_1$ excitation is −1780 cm$^{-1}$.

Table 9. Lowest Vertical Excitation Energy $\omega$ (in cm$^{-1}$) in Isolated cis-7-Hydroxquinoline, the Energy of the Highest Occupied Orbital $\epsilon^{HOMO}$ (in eV), and the Energy of the Lowest Unoccupied Orbital $\epsilon^{LUMO}$ (in eV) Evaluated with Different Basis Sets in LR-TDDFT Calculations

<table>
<thead>
<tr>
<th>basis set</th>
<th>$\omega$</th>
<th>$\epsilon^{HOMO}$</th>
<th>$\epsilon^{LUMO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO-DZ</td>
<td>29770</td>
<td>−7.404</td>
<td>−3.952</td>
</tr>
<tr>
<td>STO-DZ</td>
<td>31633</td>
<td>−10.232</td>
<td>−6.834</td>
</tr>
<tr>
<td>STO-ATZP</td>
<td>30700</td>
<td>−9.712</td>
<td>−6.411</td>
</tr>
<tr>
<td>STO-ATZP+gh (H$_2$O)</td>
<td>30709</td>
<td>−9.721</td>
<td>−6.419</td>
</tr>
<tr>
<td>STO-ATZP+gh ((H$_2$O)$_2$)</td>
<td>30722</td>
<td>−9.719</td>
<td>−6.417</td>
</tr>
<tr>
<td>STO-ATZP+gh ((H$_2$O)$_3$)</td>
<td>30632</td>
<td>−9.699</td>
<td>−6.403</td>
</tr>
<tr>
<td>STO-ATZP+gh ((NH$_3$)$_2$)</td>
<td>30737</td>
<td>−9.705</td>
<td>−6.400</td>
</tr>
<tr>
<td>STO-ATZP+gh ((NH$_3$)$_3$)</td>
<td>30742</td>
<td>−9.704</td>
<td>−6.399</td>
</tr>
<tr>
<td>STO-ATZP+gh ((CH$_3$OH)$_2$)</td>
<td>30661</td>
<td>−9.664</td>
<td>−6.368</td>
</tr>
<tr>
<td>STO-ATZP+gh ((NH$_3$−H$_2$O−NH$_3$)</td>
<td>30663</td>
<td>−9.687</td>
<td>−6.390</td>
</tr>
</tbody>
</table>
Table 10. Experimental Environment-Induced Shifts of the $S_n \rightarrow S_1$ Excitation ($\Delta \omega_{S_n \rightarrow S_1}^{env}$ in cm$^{-1}$) in cis-7-Hydroxyquinoline$^{20}$

<table>
<thead>
<tr>
<th>environment</th>
<th>$\Delta \omega_{S_n \rightarrow S_1}^{env}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>-590</td>
</tr>
<tr>
<td>$\left(H_2O\right)_2$</td>
<td>-1637</td>
</tr>
<tr>
<td>$\left(H_2O\right)_3$</td>
<td>-2060</td>
</tr>
<tr>
<td>$\left(NH_3\right)_2$</td>
<td>-1715</td>
</tr>
<tr>
<td>$\left(NH_3\right)_3$</td>
<td>-2030</td>
</tr>
<tr>
<td>$\left(CH(OH)\right)_2$</td>
<td>-1868</td>
</tr>
<tr>
<td>$\left(CH(OH)\right)_3$</td>
<td>-2329</td>
</tr>
<tr>
<td>$NH_3-H_2O-NH_3$</td>
<td>-1780</td>
</tr>
</tbody>
</table>

The results obtained with the Coulombic-only embedding potentials also agree quite well. The shifts $\Delta \omega$ calculated with the STO-SZ, STO-DZ basis sets are 2285 and $\sim 1710$ cm$^{-1}$ in the Coulombic-only embedding potential case and the corresponding full-potential results are 2184 and $\sim 1703$ cm$^{-1}$, respectively. For the remaining complexes, similar observations can be made concerning the similarity between the full embedding potential and the Coulombic-only embedding potential results obtained with the two smallest basis sets (see Tables 1–8).

The use of the largest basis sets (STO-ATZP and STO-ATZP+gh) reveals, however, a completely different picture concerning the applicability of the Coulombic-only embedding potential. For cis-7HQ$\cdots\cdot\cdot\cdot\left(H_2O\right)_2$ and STO-ATZP, the shift as large as $-12999$ cm$^{-1}$ is obviously erroneous. It is 1 order of magnitude larger than either the corresponding ab initio reference value of the vertical excitation energy shift ($-562$ cm$^{-1}$)33 obtained from high-level wave function based calculations or the shift of the $S_1 \rightarrow S_2$ transition (see Table 2), the results obtained with the Coulombic-only and full embedding potentials also agree quite well. The shifts $\Delta \omega$ calculated with the STO-SZ, STO-DZ basis sets are 2285 and $\sim 1710$ cm$^{-1}$ in the Coulombic-only embedding potential case and the corresponding full-potential results are 2184 and $\sim 1703$ cm$^{-1}$, respectively. For the remaining complexes, similar observations can be made concerning the similarity between the full embedding potential and the Coulombic-only embedding potential results obtained with the two smallest basis sets (see Tables 1–8).

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CONCLUSIONS

In all investigated cases, the Coulombic-only embedding potential was shown to lead to numerically unstable excitation energies. Not taking into account the Pauli exclusion principle in the embedding potential leads to erratic results if the size of the basis set increases. Such instabilities are similar to those observed in the case of environment-induced shifts in g-tensor reported elsewhere. In the recent literature, however, studies of optical properties applying the Coulombic-only approximation to the embedding potential have reported. Usually, rather small basis sets are used, and the dependency of the results is rarely studied in detail. The present results show clearly that, in the presence of the approximated embedding potential, the convergence of the excitation energy shifts with the basis sets is governed by its own rules. Especially, extra caution is required if the Coulombic-only approximation to the embedding potential is applied. The problem of numerical instability of the results obtained with Coulombic-only approximation might be less severe, though, if the exact Coulomb potential considered in the present work is approximated by means of net point charges. For all complexes, the lowest excitations evaluated with the basis set, which are localized in the environment, occur in the shape of the frontier orbitals upon addition of the functions into the embedding potential are reported. For other systems, similar global changes in the optical properties applying the Coulombic-only approximation to the embedding potential given in eq 4. We note that the issue of the necessity of the Davidson procedure failed to converge.

REFERENCES

Conclusions of the thesis

In this dissertation is described our work on applications of Frozen-Density Embedding Theory [1] based computational methods, to the study of the cooperativity of hydrogen-bonded chains and the electronic structure depended, UV-absorption and electron paramagnetic resonance spectroscopic properties of embedded molecules. Firstly, the origin of the hydrogen-bonding cooperativity in the case of shifts of the optical excitation energies of a chromophore due to its environment in gas phase, is investigated. Hydrogen-bonding cooperativity effects are important. It is known that they affect ground state properties and it is the reason for example for the additional infrared band redshift of the donor asymmetric stretching vibration and the additional increase of the hydrogen-bond strength. For optical excitation energies, experimental data indicate that the insertion of a linker molecule in the middle of the hydrogen-bonded chain which is hydrogen-bonded to the cis-7-hydroxyquinoline chromophore in gas phase, causes a red shift of the order of 400 cm$^{-1}$ of the optical excitation energies [2]. This is a substantial effect considering that the presence of the environment results to a shift that is smaller than 2200 cm$^{-1}$. The origin of the effect, if it is geometric or electronic in nature, can not be investigated experimentally. In contrast a suitably designed theoretical experiment allows for such examination. Such an experiment was conducted using a Frozen-Density Embedding Theory based computational method, (Chapter 5 Part II) and the findings point strongly that the cooperative effect is due to mutual electrostatic induction of the members of the hydrogen bonded chain and not due to changes in the geometry. It is noted that the effect of the change of the geometry due to the addition of the linker molecule causes a blue shift of the optical excitation energy but the overall effect is in the opposite direction. Furthermore, the electronic effect is expected to be more relevant in cases that hydrogen bonded chains are subject to steric constraints, for example in biomolecules. The calculated shifts of the vertical excitation energies on which the aforementioned conclusions are based, agree well with the available experimental data. A fully theoretical comparison of the shifts of the vertical optical excitation energies calculated with Frozen-Density Embedding Theory and reference quality theoretical results for the same electronic structure property is essential for the consolidation of our understanding of the cooperativity. Such comparison became possible when the reference data produced with the Equation-of-Motion Coupled-Cluster method, became available to us by the research group of Pr. Piecuch of the Michigan State University and this is why this study (Chapter 6 Part II) follows chronologically our original work. It is concluded that the employment of the two computational methods leads to comparable results. The demonstrated reliability of the Frozen-Density Embedding Theory based method, reinforces our confidence in our understanding of the origin of the hydrogen-bonding cooperativity. It should be noted that all that the results produced with Frozen-Density Embedding Theory based
methods depend on the density of the environment and on the approximations involved in the expression for the orbital-free embedding potential. This dependence changes to some extent when different electronic structure properties are studied. For the case of spectral shifts, the influence of the first factor was studied (Chapter 6 Part II) and it was found that for best accuracy, for hydrogen bonded, non-charged complexes, the density of the environment needs to be calculated with Kohn-Sham Density-Functional Theory without relaxation (Chapter 6 Part II). One of the aforementioned approximations that could affect the results is the one for the kinetic energy-dependent part of the orbital-free embedding potential and it was in order to focus on its role. We investigated how the findings of the benchmarking mentioned above, are affected by the use of the recently developed (Non-Decomposable Second Derivatives) to the non-additive kinetic energy bi-functional, which takes into account the exact property of the aforementioned bi-functional, derived by Lastra et al. The imposed exact property is more relevant for the nuclei in the environment. Our analysis indicates that the effect of the choice of the approximation on the calculated shifts of the particular spectroscopic property (vertical excitation energy) is negligible (Chapter 7 Part II). This fact further solidifies our belief in the reliable reproduction of reference data with Frozen-Density Embedding Theory for the case of spectral shifts.

For multi-level modelling, the complexity of the expression for the embedding potential is directly linked to the computational cost of the methods employing it. It should be kept in mind that the quality of the expression for the potential, affects the quality of any studies of the electronic structure and not only the total energy. One of the open questions before the start of our work and the second area of focus of this thesis, was the effect of neglecting the Pauli repulsion terms of the embedding potential and the employment of an electrostatic only expression which is the most commonly adopted strategy [11]. There are indications in the literature that the non-electrostatic terms are needed [3]. During the preparation of this thesis we made a systematic demonstration of the important role of Pauli repulsion and the benefits resulting from taking it into account even in approximate form and of the dangers associated with associated with Coulombic-only embedding. We studied two spectroscopic properties, first vertical excitation energy and the iso-g value of the Electron Paramagnetic Resonance Spectroscopy and in particular in their shifts due to the presence of the environment. For the case of the shift of the iso-g value, it is shown that the expression that comprises only Coulombic terms for the embedding potential can not in many cases capture the correct direction of the effect, it never reproduces satisfactorily the reference data and is associated with numerical instability. In contrast the use of the orbital-free embedding potential, that takes into account the Pauli repulsion approximately, leads to correct identification of the effect in most cases, good agreement with the reference results and numerical stability (Chapter 8 Part III). For the case of shifts of vertical excitation energies, the employment of a Coulombic only embedding potential leads to erroneous results except if the relevant calculations involve a small basis set. In contrast, the data produced involving the orbital-free embedding potential of Frozen-Density Embedding Theory have a numerically stable behavior that is basis set-independent (Chapter 9 Part III). This is to be added to the previous remarks on its accuracy. This last analysis completes the third Part of this thesis that emphasized the necessity of taking into account the the Pauli repulsion when modelling the electronic structure of molecules and also demonstrated the need for relaxation of the electron density of the environment when the iso-g value of EPR is investigated with Frozen-Density Embedding Theory based method.

In conclusion, the work conducted during our doctoral research, points strongly to-
Towards an electronic origin of the cooperativity of hydrogen bonded chains. In addition, this thesis provides convincing evidence that Frozen-Density Embedding Theory based methods should be the ideal choice for the calculation of shifts of the vertical excitation energies and electron paramagnetic resonance iso-g of medium sized and large hydrogen bonded complexes. This is on the basis of accuracy, numerical stability of the data and computational efficiency compared to embedding methods that neglect Pauli repulsion and supermolecular Linear-Response Time-Dependent Density-Functional Theory based methods which are the main competitive approaches.

**Future work**

This thesis demonstrates the suitability of Frozen-Density Embedding Theory based methods for the calculation of vertical excitation energies and the iso-g of Electron Paramagnetic Resonance. Understanding is provided about the effect of the electron density of the environment, the approximations appearing in the Frozen-Density Embedding Theory expressions and the Pauli repulsion terms, on the calculated spectroscopic properties. The electronic origin of the hydrogen-bonding cooperativity for shifts of optical excitation energies of a chromophore due to its environment in gas phase, is also explained. Our work makes possible the decision for future major computer simulations of the electronic structure research work employing Frozen-Density Embedding Theory and not Coulombic-only embedding approaches (as we systematically exposed their limitations in Part III), to be taken with confidence. In the short future, we plan to focus on large clusters and further investigate hydrogen-bonding cooperativity, by employing Frozen-Density Embedding Theory based methods. We shall also investigate Electron Paramagnetic Resonance spectroscopic properties of embedded radicals in considerably large models of proteins, as our thesis made visible that such very interesting studies can be materialized, without investing time on the preparation of an empirical set of parameters and with *a priori* knowledge of the reliability and good numerical behaviour of the results. Given the similarities between Nuclear Magnetic and Electron Paramagnetic Resonance spectroscopic observables, an equivalent study for the former would be desirable future research.
Conclusions of the thesis
References


REFERENCES


