Kohn-Sham equations with constrained electron density: an iterative evaluation of the ground-state electron density of interacting molecules

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Reference


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Kohn–Sham equations with constrained electron density: an iterative evaluation of the ground-state electron density of interacting molecules

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Abstract

A new method for calculating the ground state electron density of interacting molecules is presented. The supermolecule electron density is obtained using an iterative procedure. At each step the electron density of one molecule is calculated using previously introduced Kohn–Sham equations with constrained electron density. These equations contain terms representing the coupling between constrained and non-constrained electron densities. The coupling terms also involve a new functional, namely the non-additive kinetic energy functional that is not present in the original Kohn–Sham method. Its first-principles analytical form is not yet known. We examine the analytical form of this functional derived from Thomas–Fermi theory. The electron density obtained is compared with that calculated using the original Kohn–Sham method applied to the supermolecule. Good agreement has been found for a broad range of electron density overlaps.

1. Introduction

The formalism of density functional theory (DFT) uses the electron density as a basic variable. The electron density, in contrast to the wavefunction that is the variable in standard Hartree–Fock and similar approaches, can be the subject of straightforward physical approximations. One possible approximation consists of constraining the total electron density by freezing a fraction of it [1,2]. In this formalism, the electron density that minimizes the total electronic energy is represented as a sum of frozen and non-frozen electron densities. The non-frozen electron density is deduced from equations that are similar to the ones of the original Kohn–Sham theory [3] but which contain terms describing the coupling between the frozen and the non-frozen electron densities (see Ref. [1] for the derivation),

\[(F_0 + F_1) \Psi_i = \epsilon \Psi_i, \quad i = 1, N,\]

where, \(\Psi_i \ (i = 1, N)\) are molecular orbitals, and the operators \(F_0\) and \(F_1\) are defined as

\[F_0 = -\frac{1}{2} \nabla^2 + V(R) + \int \frac{\rho_1(R')}{|R - R'|} dR' + V_{xc}[\rho_1(R)]\]

and

\[F_1 = \int \frac{\rho_2(R')}{|R - R'|} dR' + V_{xc}[\rho_1(R) + \rho_2(R)] - V_{xc}[\rho_1(R)] + \frac{\delta T_{\text{add}}[\rho_1, \rho_2]}{\delta \rho_1}.\]
$V(R)$ is the external potential, $\rho_1$ is the non-frozen electron density equal to $\sum_{i=1}^{N_x} \psi_i^{*} \psi_i$, $\rho_2$ is the frozen electron density, $V_{xc}$ is the exchange–correlation potential, and $\delta T_{\text{add}}^{\phi}[\rho_1, \rho_2] / \delta \rho_1$ is the functional derivative of the non-additive kinetic energy functional [1, 4], which is defined in the following decomposition of the kinetic energy:

$$T_{\xi} [\rho_1 + \rho_2] = T_{\xi} [\rho_1] + T_{\xi} [\rho_2] + T_{\xi}^{\text{add}} [\rho_1, \rho_2].$$

(4)

where $T_{\xi}$ denotes the kinetic energy in a reference system of non-interacting [3] electrons. Atomic units are used in all equations throughout the text. Eqs. (1)–(4) will be referred to as Kohn–Sham equations with constrained electron density (KSCED) further in the text.

The operator $F_0$ can be easily identified as the Kohn–Sham–Fock Hamiltonian in the original Kohn–Sham equations for electron density $\rho_1$ in the absence of frozen electron density. The operator $F_1$ contains terms representing the coupling between electron densities $\rho_1$ and $\rho_2$. These terms include: the Coulomb repulsion, the contribution of the frozen electron density to the exchange–correlation potential, and the functional derivative of the non-additive kinetic energy functional. The Hohenberg–Kohn theorem and the Kohn–Sham formalism define both exchange–correlation as well as kinetic energy functionals but their first-principles analytical forms have not yet been proposed. Whereas there are accurate parametrizations of the exchange–correlation functional reported in the literature (for a review see Ref. [5]), much less has been done with respect to the kinetic energy functional [6]. Actually the kinetic energy functional is not explicitly used in the Kohn–Sham method, where an accurate expression for the kinetic energy in a reference system of non-interacting electrons is used ($T_{\xi} [\rho]$). In the Kohn–Sham equations with constrained electron density (KSCED), the additional functional ($T_{\xi}^{\text{add}} [\rho_1, \rho_2]$) is used for evaluation of only a small fraction of the total kinetic energy (see Eq. (4)).

The evaluation of electron density $\rho_1$ using Eq. (1) requires significantly less computational effort than corresponding calculations for the supermolecule electron density ($\rho^{\text{sm}}$ where sm indicates the supermolecule) using the original Kohn–Sham equations for the whole system. Indeed, the ratio of the number of electrons described by the frozen electron density to the total number of electrons determines the exact computer time saving. The electron density $\rho_1$ that is obtained using Eq. (1) depends on the frozen electron density $\rho_2$. There are many possible ways to calculate $\rho_2$. One of the simplest ones is to perform original Kohn–Sham calculations for the isolated molecular fragment(s) corresponding to $\rho_2$ and to use the electron density obtained in this way as a frozen electron density in Eqs. (1)–(4). We used this approach in our previous applications of the KSCED [1, 2]. However, this way of obtaining the frozen electron density $\rho_2$ severely limits the range of possible applications of the KSCED. In this Letter, we address the problem of the difficulties of calculating $\rho_2$ in cases where the assumption of freezing it is no longer valid. One such problem is the calculation of the potential energy surface (PES) of two interacting molecules forming a weak chemical bond. In this case a natural choice for $\rho_1$ is the electron density of one molecule and for $\rho_2$ the electron density of the other. In the general case, both $\rho_1$ and $\rho_2$ change when taking different conformations of the molecular complex. Consequently, it is necessary to use different frozen electron densities $\rho_2$ for different conformations. We propose a solution to this difficulty by allowing

<table>
<thead>
<tr>
<th>ITERATION STEP</th>
<th>$\rho_1$</th>
<th>$\rho_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\rho_1^{(0)} = \rho_{\text{PHCN}}$</td>
<td>$\rho_2 = 0$</td>
</tr>
<tr>
<td>1</td>
<td>$\rho_1^{(1)} = \rho_{\text{H2}}$</td>
<td>$\rho_2 = \rho_1^{(0)}$</td>
</tr>
<tr>
<td>2</td>
<td>$\rho_1^{(2)} = \rho_{\text{PHCN}}$</td>
<td>$\rho_2 = \rho_1^{(1)}$</td>
</tr>
<tr>
<td>3</td>
<td>$\rho_1^{(3)} = \rho_{\text{H2}}$</td>
<td>$\rho_2 = \rho_1^{(2)}$</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>N</td>
<td>$\rho_1^{(N)} = \rho_{\text{H2}}$</td>
<td>$\rho_2 = \rho_1^{(N-1)}$</td>
</tr>
</tbody>
</table>

Fig. 1. Scheme of the iterative evaluation of the supermolecule electron density. Each iteration requires one evaluation of Eq. (1) (see text).
the frozen electron density to relax in a series of successive iterations (see Fig. 1). We start by choosing the electron density of one molecule as \( \rho_1 \). This density is calculated using Eq. (1) and initial values of the electron density \( \rho_2 \). In the next iteration step, we replace \( \rho_1 \) by \( \rho_2 \) in Eq. (1). We use the electron density \( \rho_1 \) from the previous iteration as the frozen electron density \( \rho_2 \). This procedure is repeated until self-consistency is achieved. The final total electron density is obtained as a sum of final densities \( \rho_1 \) and \( \rho_2 \). This procedure makes it possible to calculate the total electron density of a given conformation using a number of evaluations of Eq. (1) instead of solving the Kohn–Sham equation for the whole system (supermolecule).

The two approaches should lead to the same electron density if the terms representing the coupling between electron densities \( \rho_1 \) and \( \rho_2 \) in Eq. (3) are accurate. If the analytical form of the exchange–correlation functional used in the supermolecule Kohn–Sham equations is the same as the one used in Eqs. (1)–(3), the only term that may lead to the differences in the final densities is the last one in Eq. (3) i.e. the functional derivative of the non-additive kinetic energy functional. Consequently, the examination of the differences between the electron density obtained with the supermolecule Kohn–Sham approach (\( \rho_{\text{sm}} \)) and the electron density obtained at the end of our iteration procedure (\( \rho_1 + \rho_2 \)) might be used to address the issue of the accuracy of the non-additive kinetic energy functional.

We have selected two molecules, \( \text{H}_2 \) and NCH, as a test case for our model. This choice was motivated by the fact that \( \text{H}_2 \)–NCH is a relatively small molecular system in which a weak chemical bond may be formed at small intermolecular distances; in addition, it is a system where polarization effects at intermediate distances are significant. The PES of this complex should, therefore, represent a good test case for our method.

2. Computational details

The resolution of Eqs. (1)–(3) was implemented into the program deMon [7]. The non-additive kinetic energy functional was derived from Thomas–Fermi theory (see Eqs. (25) and (26) in Ref. [1]. Its analytical form is written

\[
T_\text{s}^{\text{add}}[\rho_1, \rho_2] = T_\text{TF}^{\text{add}}[\rho_1, \rho_2] \\
= 2.87 \int \left[ \frac{(\rho_1 + \rho_2)^{5/3} - (\rho_1)^{5/3}}{(\rho_2)^{5/3}} \right] \mathrm{d}R. \tag{5}
\]

The total kinetic energy at each iteration step shown in Fig. 1 has been calculated using Eq. (4) which combines both analytically calculated kinetic energies \( T_\text{TF}[\rho_1] \) and \( T_\text{TF}[\rho_2] \) as well as the non-additive kinetic energy functional \( T_\text{s}^{\text{add}}[\rho_1, \rho_2] \). The 6-31G* orbital basis set for orbitals and the following auxiliary basis sets [7]: \( \text{C}(5, 2; 5, 2), \text{O}(5, 2; 5, 2), \) and \( \text{H}(5, 1; 5, 1) \) have been used. The local density approximation (LDA) with the VWN [8] correlation functional was applied in both supermolecule Kohn–Sham calculations as well as in KSCEF evaluations. The initial electron density in the iterative procedure shown in Fig. 1 corresponds to that of the isolated NCH molecule. The iterative procedure (Fig. 1) was terminated with the same convergence criterion (10^{-6} hartree) as that of the SCF procedure. All calculations with Eqs. (1)–(4) have been made using the supermolecule grid and supermolecule basis sets. The supermolecule Kohn–Sham results were corrected for the basis set superposition error (BSSE) using the procedure of Boys and Bernardi [9]. A cross section through the PES of the complex has been studied. In all the conformations investigated, the \( \text{H}_2 \) and HCN molecules are assumed to form a linear complex. Its geometry is defined by a variable intermolecular distance \( R \) (equals the distance from the N atom to the center of the \( \text{H}_2 \) molecule) and rigid conformations of both \( \text{H}_2 \) as well as HCN molecules \( R_{\text{HH}} = 0.74 \, \text{Å}, \ R_{\text{CH}} = 1.10 \, \text{Å}, \ R_{\text{CN}} = 1.16 \, \text{Å}. \)

3. Results and discussion

3.1. The potential energy curve

The total energy obtained using the Kohn–Sham supermolecule calculations together with the one using the iterative procedure shown in Fig. 1 is pre-
presented in Fig. 2. The intermolecular distances between $H_2$ and NCH molecules ranged from 1.95 to 5 Å. The iterative procedure ($\rho_1$, $\rho_2$) converged usually after about 10 iterations. It is seen in Fig. 2 that both curves are similar. The BSSE corrected interaction energy at the minimum of the potential energy curve is $-1.387$ kcal/mol according to supermolecule DFT calculations and $-1.349$ kcal/mol by the present method. The corresponding intermolecular distances calculated at the energy minimum are: 2.88 and 2.81 Å, respectively. Both energy curves are almost identical for intermolecular distances larger than the energy minimum. However, the difference between the two curves is larger for shorter intermolecular distances, where the relative contribution of the non-additive kinetic energy functional increases.

3.2. The non-additive kinetic energy functional

The iterative resolution of Eqs. (1)-(3) according to the scheme of Fig. 1 leads to a final electron density whose kinetic energy was calculated according to Eqs. (4) and (5). The corresponding kinetic energy was also evaluated analytically using supermolecule Kohn-Sham equations. The kinetic energies obtained using both methods are similar for the intermolecular distances considered. Instead of displaying them directly we present the differences of their analytical components $(T_s[\rho^{sm}] - (T_s[\rho_1] + T_s[\rho_2]))$ as well as the integrated values of the non-additive kinetic energy functional $T^{nadd}_s[\rho_1, \rho_2]$ in Fig. 3. It is seen that Eq. (5) provides a good approximation for the true $T^{nadd}_s[\rho_1, \rho_2]$ functional at various intermolecular distances. The differences between the two curves increase with decreasing intermolecular distance where the overlap between frozen and non-frozen electron densities increases. This allows one naturally to conclude that Eq. (4) provides a less accurate approximation for the non-additive kinetic energy functional when the overlap between densities $\rho_1$ and $\rho_2$ increases. We also found that modifying the multiplicative constant in Eq. (4) does not lead to a better agreement between the supermolecule Kohn-Sham electron density ($\rho^{sm}$) and the electron density obtained at the end of the iteration procedure ($\rho_1 + \rho_2$).

More elaborate formulae for the non-additive kinetic energy functional are clearly needed for cases where there is a large overlap between frozen and non-frozen electron densities. The most promising ones are those that also involve gradient dependent terms (see Eq. (28) in Ref. [1]).

3.3. The convergence of iterations

We have discussed so far the electron density obtained at the end of the iterative procedure shown
in Fig. 1. In this section we present results obtained using a non-iterative resolution of the KSCED that is similar to the one used in our previous reports [1,2]. We used the isolated NCH electron density as $\rho_2$ in Eqs. (1)–(4) and calculated the electron density $\rho_1$ corresponding to the bound H$_2$ molecule. The potential energy curve calculated in this way is presented in Fig. 4. It is seen that the non-iteratively calculated energies are higher than those obtained at the end of the iteration procedure. The minimum of the total energy is shifted towards shorter intermolecular distances.

Similar non-iterative calculations have been performed with the electron density of HCN used as $\rho_1$ and the electron density of an isolated H$_2$ molecule used as $\rho_2$. We note even larger deviations from the results obtained at the end of the iteration procedure. These results illustrate the fact that the electron density of the H$_2$ molecule is more perturbed than the electron density of the HCN molecule when the system forms a weak chemical bond.

4. Conclusions

We have presented a new type of application of the previously introduced formalism of solving Kohn–Sham equations with partially frozen electron density (KSCED). An iterative approach leading to the removal of constraints imposed on the total electron density is proposed. The ground state potential energy surface of the linear complex H$_2$...NCH calculated using this approach is similar to the one obtained with the original Kohn–Sham equations. It is found that, even in the case where the electron density is significantly modified upon forming a weak chemical bond, a small number of iterations is needed to evaluate the supermolecule electron density at a good level of approximation. This procedure is computationally advantageous over supermolecule calculations since Eqs. (1)–(3) need to be solved for smaller system than the whole complex. It is worthwhile stressing here that throughout the whole computational procedure the total electron density is represented as a sum of two components which can be identified as individual electron densities of molecules forming the complex. Many possible applications of this feature of our formalism may be foreseen, in particular for the modeling of large molecular systems where the supermolecule treatment is not feasible.

It is worthwhile pointing out at this stage that our procedure resembles the ‘divide and conquer’ approach by Yang [10]. Similarly, we divide the system into fragments (two in our case) and solve separately the eigenvalue problems for each subsystem. The coupling between the two subsystems involves the Coulomb interaction in both approaches but instead of the requirements of equalising the chemical potential in the Yang approach we introduce a new functional, namely the non-additive kinetic energy functional. As our results indicate, the proposed form of this functional proves to be accurate for intermediate molecular distances. This functional uses only fundamental constants without empirical parameters.

Finally, the approximation of the total kinetic energy using formulae derived from Thomas–Fermi theory is reasonably accurate; however, further developments are needed, especially in the case of a large overlap between the two electron densities of interacting fragments.

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