The basis set effect on the results of the minimization of the total energy bifunctional \( E[\rho_A, \rho_B] \)

DULAK, Marcin, WESOLOWSKI, Tomasz Adam

Abstract

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Reference

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The Basis Set Effect on the Results of the Minimization of the Total Energy Bifunctional $E[\rho_A, \rho_B]$

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ABSTRACT: The basis set effect on the results of the minimization of the total energy bifunctional $E[\rho_A, \rho_B]$ approximated at the local density approximation level is analyzed for several weak intermolecular complexes. The considered complexes formed by hydrocarbons at the equilibrium geometry were previously studied by means of the same formalism using large decontracted basis sets consisting of Gaussian-type atomic orbitals limited to s-, p-, and d-functions. In this work, we use our two new computer implementations of the formalism to analyze the basis set effects accompanying changing the basis sets from Gaussian-type orbitals to Slater-type orbitals and including f-functions. We show that the interaction energies, their components, and the energies of the highest occupied molecular orbital converge within a range of 0.07 kcal/mol, 0.08 kcal/mol, and 0.06 eV, respectively. © 2004 Wiley Periodicals, Inc. Int J Quantum Chem 101: 543–549, 2005

Key words: basis sets; total energy bifunctional; orbital-free embedding; weak intermolecular complexes

1. Introduction

The most widely used practical route to perform the minimization of the ground-state energy functional ($E^{HK}[\rho]$) defined in Hohenberg–Kohn theorems [1] is based on Kohn–Sham equations [2]. The kinetic energy functional $T[\rho]$, which is one of the biggest components of $E^{HK}[\rho]$, can be split into its major component—the kinetic energy of the noninteracting reference system ($T_s[\rho]$)—and the remaining small part ($T_c[\rho]$). In the Kohn–Sham formalism, evaluation of the kinetic energy as an explicit functional of electron density ($T_s[\rho]$) is avoided owing to the use of its orbital-dependent equivalent. As a result, only a small fraction of the total energy known as the exchange-correlation functional ($E_{xc}[\rho]$) needs to be approximated. An alternative route to minimize $E^{HK}[\rho]$ is
based on the hybrid representation of $T_s[\rho]$ introduced by Cortona to study solids [3]:

$$T_s[\rho] = T_s[\rho_1 + \rho_2 + \ldots + \rho_N] = \sum_{j=1}^{N}(T_s[\rho_j]) + T_s^{\text{nad}}[\rho_1, \rho_2, \ldots, \rho_N], \quad (1)$$

where, $\rho_1, \rho_2, \ldots, \rho_N$ are electron densities of $N$ subsystems each comprising an integer number of electrons. In the case of two subsystems, denoted as $A$ and $B$, the total energy bifunctional takes the following form:

$$E[\rho_A, \rho_B] = T_s[\rho_A] + T_s[\rho_B] + T_s^{\text{nad}}[\rho_A, \rho_B]$$

$$+ \frac{1}{2} \int \frac{(\rho_A(r') + \rho_B(r'))(\rho_A(r) + \rho_B(r))}{|r' - r|} dr' dr + \int \nu(r)(\rho_A(r) + \rho_B(r)) dr + E_{\text{xc}}[\rho_A + \rho_B], \quad (2)$$

where $\nu(r)$ is the external potential and $E_{\text{xc}}[\rho]$ is the exchange-correlation functional defined in the Kohn–Sham formalism. The ground-state energy and density can be derived by performing double minimization of $E[\rho_A, \rho_B]$: 

$$\min_{\rho_A \rightarrow \rho_A^{\text{min}}} \min_{\rho_B \rightarrow \rho_B^{\text{min}}} E[\rho_A, \rho_B]. \quad (3)$$

The bifunctional $E[\rho_A, \rho_B]$ is also a key element in the orbital-free embedding formalism introduced by Wesolowski and Warshel [4]. In various practical embedding approaches labeled as QM/MM, QM/MD, hybrid methods, etc., one uses a coupling term to represent the interactions between the subsystem described at quantum mechanical level and the subsystem described at a lower level. In such methods, the effect of the microscopic environment on the subsystem investigated at quantum mechanical level is described by means of an embedding potential also called QM/MM coupling term.

As shown in Ref. [4], the electron density of an embedded subsystem ($\rho_A$) in a given microscopic environment described by the electron density ($\rho_B$) can be derived via partial minimization of $E[\rho_A, \rho_B]$:

$$\min_{\rho_A \rightarrow \rho_A^{\text{min}}} E[\rho_A, \rho_B]. \quad (4)$$

which leads to the Kohn–Sham-like equations for one-electron orbitals used to construct $\rho_A$ [4] (referred to in this work as Kohn–Sham equations with constrained electron density, KSCEF). The effective potential in KSCEF can be expressed as a sum of two components, one describing the effective potential for the isolated subsystem $\rho_A$ and the other part representing the embedding effective potential which is expressed exactly using the universal functionals of density functional theory [4]:

$$V_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B, r] = \sum_{N_B} Z_{N_B} \frac{\rho_B(r')}{|r - r'|} + \int \frac{\rho_A(r')}{|r' - r|} dr'$$

$$+ \frac{\delta E_{\text{xc}}[\rho_A + \rho_B]}{\delta \rho_A} + \frac{\delta E_{\text{xc}}[\rho_B]}{\delta \rho_B} + \frac{\delta T_s^{\text{nad}}[\rho_A, \rho_B]}{\delta \rho_A}, \quad (5)$$

where the first term shows the explicit form of the contributions of the atomic nuclei to the effective potential.

It is worth noting that the whole effective potential that determines $\rho_A$ for a frozen $\rho_B$ is very similar to that in the Kohn–Sham equations. They differ only by the presence of the $\delta T_s^{\text{nad}}[\rho_A, \rho_B]/\delta \rho_A$ term, which results from restricting the variations of the whole $\rho$ to $\rho_A$. In this work, we refer to $E[\rho_A, \rho_B]$ and $V_{\text{emb}}^{\text{eff}}[\rho_A, \rho_B, r]$ as the KSCEF energy and the KSCEF effective embedding potential, respectively.

In practice, to perform either double or single minimization of $E[\rho_A, \rho_B]$, not only a good approximation for $E_{\text{xc}}[\rho]$ is needed (as in conventional Kohn–Sham calculations), but also an adequate approximation for $T_s^{\text{nad}}[\rho_A, \rho_B]$. Note that evaluation of the terms $T_s[\rho_A]$ and $T_s[\rho_B]$ can be done without any additional approximations upon introducing two sets of Kohn–Sham-like orbitals to construct $\rho_A$ and $\rho_B$.

An obvious first choice to approximate $E_{\text{xc}}[\rho]$ and $T_s^{\text{nad}}[\rho_A, \rho_B]$ is local density approximation (LDA). In LDA, $E_{\text{xc}}[\rho]$ is approximated by a functional combining Dirac’s exchange functional [5] and the Vosko–Wilk–Nusair [6] parametrization of the electron-density dependence of the correlation energy obtained by Ceperley and Alder [7] for the uniform electron gas, and $T_s^{\text{nad(LDA)}}[\rho_A, \rho_B]$ is derived from Thomas-Fermi theory [8, 9] and reads:

$$T_s^{\text{nad(LDA)}}[\rho_A, \rho_B] = C_T \int (\rho_A + \rho_B)^{5/3} - \frac{5}{3} \rho_A^{5/3} - \frac{5}{3} \rho_B^{5/3} dr,$$
where \( C_{TF} = 3/10(3\pi^2)^{2/3} \). We denote the resulting approximate bifunctional as \( E_{\text{LDA}}^{\text{LDA}}[\rho_A, \rho_B] \). LDA was used in our earlier works [4, 10, 11]. The use of LDA to all relevant functionals has the significant advantage that both \( E_A[\rho] \) and \( T_A[\rho] \) use the same approximation to the one-particle density matrix. Unfortunately, LDA is not sufficiently accurate, as shown comprehensively in our recent report [12]. The functionals depending on the gradient of the electron density offer a straightforward route to improve upon \( E_{\text{LDA}}^{\text{LDA}}[\rho_A, \rho_B] \).

Our dedicated search for the best approximation to \( T_s^{\text{ad}}[\rho_A, \rho_B] \) [13–15] led us to the gradient-dependent approximation to \( T_s^{\text{ad}}[\rho_A, \rho_B] \) of the generalized gradient approximation (GGA) form [14]. Together with the conjoint approximation to \( E_{\text{xc}}[\rho] \) derived by Perdew and Wang [17], this approximation leads to a good description of such pairs of electron densities where \( \rho_A \) and \( \rho_B \) do not overlap significantly [12].

This work concerns practical aspects related to the minimization of \( E[\rho_A, \rho_B] \), namely, the dependence of the results on the choice of the atomic basis sets used to construct \( \rho_A \) and \( \rho_B \). We exploit the new possibilities offered by our recent implementation of a procedure to minimize \( E[\rho_A, \rho_B] \) into a more universal computer code (deMon 2002 [18]), allowing us to use also Gaussian-type orbitals (GTO) of the f-type in the basis sets. Moreover, some results presented in this work are compared with those derived from yet another implementation of our method into the ADF computer code [19], which applies Slater-type functions (STO) of benchmark quality. The main issues specific to these new computer implementations are outlined in Section II.

The basis set effect on the results derived from the minimization of \( E[\rho_A, \rho_B] \), is important for various reasons. Because of the qualitatively different shape of the orbital-free embedding effective potential compared to the effective potential in conventional Kohn–Sham calculations,* one cannot exclude the possibility of a very different basis set dependence in these two methods. The results reported previously [23–25] obtained using large basis sets limited to s–d functions indicate that the interaction energies derived from double minimization of \( E[\rho_A, \rho_B] \) converge rather fast with the size of the basis sets. In this work, the comparisons are made more systematically for a larger set of intermolecular complexes to estimate the error bars on the interaction energies reported in our previous work [12]. Distinguishing the effects of the applied basis sets from the effects resulting from the fact that our use of approximate functionals is crucial for our undergoing work on improvements of the approximations to \( E[\rho_A, \rho_B] \). Moreover, the estimation of the magnitude of the effects resulting from incompleteness of the basis sets is useful for the application of this formalism to larger systems.

II. Computational Details

A. KEY ELEMENTS OF IMPLEMENTATION OF ORBITAL-FREE EMBEDDING POTENTIAL INTO deMon 2002

- GTO basis sets comprising s-, p-, d- and f-functions;
- Automatic generation of auxiliary basis set (s–g functions) for fitting;
- Coulomb integrals calculated using the expression

\[
J = \int \frac{\rho_A(r)\rho_B(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \int \frac{\tilde{\rho}_A(r)\tilde{\rho}_B(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'
\]

\[
+ \int \frac{\rho_A(r)\tilde{\rho}_B(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \int \frac{\tilde{\rho}_A(r)\tilde{\rho}_B(r)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (7)
\]

where \( \tilde{\rho} \) denotes the fitted electron density;

- Pruned (75, 302) grid of G94/DFT [21, 22];
- Exact (not fitted) density used for the calculation of \( E_{\text{xc}}[\rho] \) and \( T_s^{\text{ad}}[\rho_A, \rho_B] \).

B. KEY ELEMENTS OF IMPLEMENTATION OF ORBITAL-FREE EMBEDDING POTENTIAL INTO ADF

- Slater-type atomic orbitals [20];
- Grid corresponding to the integration accuracy criterion (Integration 6.0) [19];
- Exact (not fitted) \( \rho_A \) and fitted \( \rho_B \) in the expressions relevant to KSCED energy and effective potential;
- \( T_s^{\text{ad}}[\rho_A, \rho_B] \) evaluated using the formula

\[
T_s^{\text{ad}}[\rho_A, \rho_B] = T_s^{\text{ad}}[\tilde{\rho}_A, \tilde{\rho}_B] + T_s^{\text{ad}}[\rho_A, \tilde{\rho}_B] - T_s^{\text{ad}}[\tilde{\rho}_A, \tilde{\rho}_B], \quad (8)
\]

*See Figure 8 in Ref. [16] showing the dependence of the non-additive kinetic energy density on the position in several weakly bound intermolecular complexes.
where \( \tilde{\rho} \) denotes the fitted electron density.

### C. MOLECULES AND GEOMETRIES

The intermolecular complexes chosen for this study form a subset of the complexes analyzed previously [12]. They are formed by hydrocarbons and form a representative sample covering the whole range of interaction energies in the original set. The geometry of each considered complex corresponds to the equilibrium structures derived from high-level benchmark ab initio calculations (see Ref. [12] for details).

### D. BASIS SETS

The applied GTO basis sets are distributed with the deMon 2002 package [18]. For compactness, they are labeled in this work with single letters (A–F) according to the scheme: A, DZVP; B, TZVP; C, TZVP-FIP1; D, TZVP-FIP2; E, IGLO-III; F, TZ-ANO; G, the basis set developed by Partridge limited to s–d functions. F is the largest GTO basis set used in our new numerical implementation of the KSCED formalism (deMon 2002). G is the largest GTO basis set available in our previous numerical implementation of the KSCED formalism (deMon-KSCED) [13]. In the ADF implementation, we used the STO basis set developed by Chong and collaborators [20] for use in benchmark calculations (basis set QZ4P, labeled H in this work).

### III. Results

#### A. INTERACTION ENERGIES

In this section, we consider the interaction energies derived from minimization of \( E_{\text{LDA}}^{\left[\rho_A, \rho_B\right]} \) (Table I). The “best two” basis sets (F and G) leads to very similar interaction energies. For these basis sets, the maximum deviations amount to 0.07 kcal/mol (\( \text{C}_6\text{H}_6-\text{C}_2\text{H}_2 \)). As expected, the use of basis set A leads to the largest maximum deviation 0.2 kcal/mol (\( \text{C}_6\text{H}_6-\text{C}_2\text{H}_2 \)) from the results derived using either the F or G basis set. Increasing the basis set from DZVP to TZVP (compare the basis set A and B results) reduces this deviation significantly (the maximum deviation for basis set B is 0.09 kcal/mol for \( \text{C}_6\text{H}_6-\text{C}_2\text{H}_2 \)). Adding f-functions to the basis sets (compare basis sets C and D) does not lead to any significant effect (0.03 kcal/mol for \( \text{C}_6\text{H}_6-\text{C}_2\text{H}_6 \)). Adding the diffuse functions to the basis sets (compare basis sets B and C) is more important, as it leads to energetic effects up to 0.06 kcal/mol (for \( \text{C}_2\text{H}_2-\text{C}_2\text{H}_2 \)).

#### B. CONTRIBUTION TO THE INTERACTION ENERGIES DUE TO APPROXIMATE FUNCTIONALS \( E_{\text{XC}}^{\text{LDA}} \) AND \( T_{\text{AD}}^{\text{LDA}}[\rho_A, \rho_B] \)

In this and the following sections, the results derived using all the considered GTO basis sets are supplemented by those derived using STO basis sets. We start with the analysis of the effect of the basis set on the contribution to the interaction energy calculated using approximate functionals. This

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**TABLE I**

Results of \( \min_{\rho_A} \min_{\rho_B} E[\rho_A, \rho_B] \) obtained using various basis sets: interaction energies (kcal/mol).

<table>
<thead>
<tr>
<th>Complex</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_4-\text{CH}_4 )</td>
<td>0.63</td>
<td>0.60</td>
<td>0.61</td>
<td>0.62</td>
<td>0.62</td>
<td>0.61</td>
<td>0.64</td>
</tr>
<tr>
<td>( \text{CH}_4-\text{CH}_4 )</td>
<td>0.37</td>
<td>0.40</td>
<td>0.41</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>0.46</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6-\text{CH}_4 )</td>
<td>0.49</td>
<td>0.51</td>
<td>0.52</td>
<td>0.53</td>
<td>0.52</td>
<td>0.53</td>
<td>0.52</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6-\text{C}_2\text{H}_4 )</td>
<td>1.08</td>
<td>1.05</td>
<td>1.08</td>
<td>1.09</td>
<td>1.06</td>
<td>1.07</td>
<td>1.06</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6-\text{CH}_4 )</td>
<td>0.72</td>
<td>0.68</td>
<td>0.69</td>
<td>0.70</td>
<td>0.71</td>
<td>0.70</td>
<td>0.73</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2-\text{C}_2\text{H}_2 )</td>
<td>1.78</td>
<td>1.66</td>
<td>1.72</td>
<td>1.74</td>
<td>1.69</td>
<td>1.72</td>
<td>1.72</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6-\text{CH}_4 )</td>
<td>0.43</td>
<td>0.42</td>
<td>0.44</td>
<td>0.47</td>
<td>0.47</td>
<td>0.48</td>
<td>0.42</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6-\text{C}_2\text{H}_6 )</td>
<td>0.62</td>
<td>0.66</td>
<td>0.68</td>
<td>0.70</td>
<td>0.68</td>
<td>0.69</td>
<td>0.72</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6-\text{C}_2\text{H}_4 )</td>
<td>0.86</td>
<td>0.78</td>
<td>0.80</td>
<td>0.82</td>
<td>0.82</td>
<td>0.81</td>
<td>0.87</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_6-\text{C}_2\text{H}_2 )</td>
<td>2.07</td>
<td>1.87</td>
<td>1.91</td>
<td>1.92</td>
<td>1.90</td>
<td>1.87</td>
<td>1.94</td>
</tr>
</tbody>
</table>

For description of basis sets A–G, see text.
TABLE II

Results of min_{ρA} min_{ρB} E[ρA, ρB] obtained using various basis sets: \( \Delta E_{xc}[ρA, ρB] + T_{x}^{\text{adm}}[ρA, ρB] \) (kcal/mol).

<table>
<thead>
<tr>
<th>Complex</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_2H_4-CH_4</td>
<td>-0.14</td>
<td>-0.12</td>
<td>-0.12</td>
<td>-0.08</td>
<td>-0.08</td>
<td>-0.07</td>
<td>-0.09</td>
<td>-0.08</td>
</tr>
<tr>
<td>CH_4-CH_4</td>
<td>-0.10</td>
<td>-0.11</td>
<td>-0.13</td>
<td>-0.12</td>
<td>-0.12</td>
<td>-0.08</td>
<td>-0.07</td>
<td>-0.09</td>
</tr>
<tr>
<td>C_2H_2-C_2H_4</td>
<td>-0.13</td>
<td>-0.11</td>
<td>-0.12</td>
<td>-0.12</td>
<td>-0.07</td>
<td>-0.08</td>
<td>-0.08</td>
<td>-0.10</td>
</tr>
<tr>
<td>C_6H_6-C_2H_6</td>
<td>-0.06</td>
<td>0.01</td>
<td>0.05</td>
<td>-0.00</td>
<td>0.03</td>
<td>0.02</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>C_6H_6-C_2H_2</td>
<td>0.14</td>
<td>0.18</td>
<td>0.22</td>
<td>0.19</td>
<td>0.25</td>
<td>0.22</td>
<td>0.21</td>
<td>0.26</td>
</tr>
<tr>
<td>C_2H_2-C_2H_2</td>
<td>0.23</td>
<td>0.25</td>
<td>0.32</td>
<td>0.34</td>
<td>0.30</td>
<td>0.32</td>
<td>0.32</td>
<td>0.31</td>
</tr>
<tr>
<td>C_6H_6-C_2H_6</td>
<td>1.00</td>
<td>0.97</td>
<td>1.04</td>
<td>1.01</td>
<td>1.10</td>
<td>1.03</td>
<td>1.02</td>
<td>1.11</td>
</tr>
<tr>
<td>C_6H_6-C_2H_2</td>
<td>0.14</td>
<td>0.21</td>
<td>0.22</td>
<td>0.20</td>
<td>0.30</td>
<td>0.23</td>
<td>0.26</td>
<td>0.25</td>
</tr>
<tr>
<td>C_6H_6-C_2H_4</td>
<td>0.81</td>
<td>0.82</td>
<td>0.93</td>
<td>0.85</td>
<td>0.88</td>
<td>0.84</td>
<td>0.86</td>
<td>0.91</td>
</tr>
<tr>
<td>C_6H_6-C_2H_2</td>
<td>0.43</td>
<td>0.44</td>
<td>0.56</td>
<td>0.46</td>
<td>0.45</td>
<td>0.39</td>
<td>0.47</td>
<td>0.45</td>
</tr>
</tbody>
</table>

For description of basis sets A–H, see text.

C. ENERGIES OF THE HIGHEST OCCUPIED MOLECULAR ORBITAL (HOMO)

The energy of HOMO provides a sensitive test for the convergence of the KSCED effective potential with the basis set. Moreover, because HOMO is the orbital the extending the farthest from the center of the molecule, its orbital energy could be prone to any inaccuracies in the numerical integration procedure. Tables III and IV collect the HOMO energies of the embedded molecules calculated with various basis sets. The triad of “the best” basis sets (F, G, H) leads to similar results. The maximum deviation between the corresponding values is 0.06 eV (C_6H_6-CH_4). It is important to underscore that the three basis sets were implemented in three various computer codes. Moreover, basis sets F and G consist of GTOs, whereas basis set H consists of STOs. As expected, the orbital energies derived using basis set A deviate significantly more from the above converged values (the differences reach 0.17 eV for C_6H_6-CH_4 and C_6H_6-C_2H_4). Apparently, the

TABLE III

Results of min_{ρA} min_{ρB} E[ρA, ρB] obtained using various basis sets: HOMO orbital energy (eV) of the M1 monomer in the M1 . . . M2 complex.

<table>
<thead>
<tr>
<th>M1–M2</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_2H_4-CH_4</td>
<td>-6.890</td>
<td>-6.974</td>
<td>-6.980</td>
<td>-6.983</td>
<td>-6.986</td>
<td>-7.005</td>
<td>-6.993</td>
<td>-6.984</td>
</tr>
<tr>
<td>C_2H_2-C_2H_4</td>
<td>-8.008</td>
<td>-8.064</td>
<td>-8.071</td>
<td>-8.077</td>
<td>-8.078</td>
<td>-8.081</td>
<td>-8.098</td>
<td>-8.058</td>
</tr>
<tr>
<td>C_6H_6-C_2H_6</td>
<td>-6.891</td>
<td>-6.974</td>
<td>-6.976</td>
<td>-6.979</td>
<td>-6.985</td>
<td>-7.001</td>
<td>-6.993</td>
<td>-6.974</td>
</tr>
<tr>
<td>C_6H_6-C_2H_2</td>
<td>-6.480</td>
<td>-6.558</td>
<td>-6.563</td>
<td>-6.564</td>
<td>-6.556</td>
<td>-6.578</td>
<td>-6.572</td>
<td>-6.544</td>
</tr>
<tr>
<td>C_6H_6-C_2H_1</td>
<td>-6.487</td>
<td>-6.566</td>
<td>-6.572</td>
<td>-6.573</td>
<td>-6.564</td>
<td>-6.586</td>
<td>-6.582</td>
<td>-6.554</td>
</tr>
<tr>
<td>C_6H_6-C_2H_1</td>
<td>-6.531</td>
<td>-6.605</td>
<td>-6.609</td>
<td>-6.609</td>
<td>-6.602</td>
<td>-6.621</td>
<td>-6.615</td>
<td>-6.585</td>
</tr>
<tr>
<td>C_6H_6-C_2H_2</td>
<td>-6.668</td>
<td>-6.727</td>
<td>-6.730</td>
<td>-6.730</td>
<td>-6.725</td>
<td>-6.742</td>
<td>-6.733</td>
<td>-6.707</td>
</tr>
</tbody>
</table>

For description of basis sets A–H, see text.
monomer in the M1

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motivated these studies:

plying LDA allow us to address the key issues that
using basis sets A and B).

in the valence shell (compare the results derived

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TABLE IV
Results of min\(_{\mu_{A}}\) min\(_{\mu_{B}}\) \(E[\mu_{A},\mu_{B}]\) obtained using various basis sets: HOMO orbital energy (eV) of the M2 monomer in the M1 ... M2 complex.

<table>
<thead>
<tr>
<th>M1–M2</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{2})H(</em>{2})-C(<em>{2})H(</em>{2})</td>
<td>−7.091</td>
<td>−7.192</td>
<td>−7.176</td>
<td>−7.176</td>
<td>−7.184</td>
<td>−7.189</td>
<td>−7.190</td>
<td>−7.184</td>
</tr>
<tr>
<td>C(<em>{3})H(</em>{6})-C(<em>{2})H(</em>{2})</td>
<td>−7.709</td>
<td>−7.795</td>
<td>−7.805</td>
<td>−7.812</td>
<td>−7.811</td>
<td>−7.825</td>
<td>−7.863</td>
<td>−7.809</td>
</tr>
<tr>
<td>C(<em>{3})H(</em>{6})-C(<em>{2})H(</em>{4})</td>
<td>−7.607</td>
<td>−7.676</td>
<td>−7.685</td>
<td>−7.691</td>
<td>−7.690</td>
<td>−7.695</td>
<td>−7.708</td>
<td>−7.679</td>
</tr>
<tr>
<td>C(<em>{6})H(</em>{10})-C(<em>{2})H(</em>{4})</td>
<td>−6.935</td>
<td>−7.046</td>
<td>−7.042</td>
<td>−7.047</td>
<td>−7.048</td>
<td>−7.068</td>
<td>−7.093</td>
<td>−7.063</td>
</tr>
</tbody>
</table>

For description of basis sets A–H, see text.

most significant reduction of these deviations follows the addition of an additional set of functions in the valence shell (compare the results derived using basis sets A and B).

IV. Conclusions

The numerical results of KSCED calculations applying LDA allow us to address the key issues that motivated these studies:

- Using a larger basis set (F) than those applied in our previous studies (G) does not lead to any significant changes in the interaction energies. The maximum difference between the KSCED (basis set F) results and KSCED (basis set G) amounts to 0.07 kcal/mol. Because the largest deviations between the KSCED interaction energies reported previously [12] and the ab initio reference data for hydrocarbons amounted up to 1.4 kcal/mol, we can attribute these differences to the approximations to the functionals relevant to the KSCED formalism and not to the fact that the basis set used in our previous calculations was limited to s-, p-, and d-functions.

- DZVP basis sets do not seem well suited for practical calculations. Increasing the basis sets from DZVP to TZVP improves the interaction energies. A sharp improvement in accuracy of the KSCED interaction energies accompanies adding diffuse functions of the s- and d-type. It is worth noting that introduction of GTO of the f-type, not possible in our previous computer implementation, does not lead to any noticeable effect (less than 0.03 kcal/mol).

- The comparisons between the results derived using the largest basis set applying GTOs (TZ-ANO) and STOs (QZ4P) shows that all compared quantities (interaction energies, contributions to the interaction energies, and HOMO orbital energies) converge toward common values if calculated using one of “the best” basis sets implemented in three different computer programs. The largest differences between those quantities are 0.07 kcal/mol for the interaction energies, 0.08 kcal/mol for the sum of nonadditive kinetic and the exchange-correlation contributions to the total energy, and 0.06 eV for HOMO orbital energies.

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References

20. The even-tempered family of basis sets developed by Prof. D. Chong is available at http://www.scm.com.