Application of 25 density functionals to dispersion-bound homomolecular dimers

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Abstract

The ability of 25 density functional theory (DFT) methods to treat Ne 2, Ar 2, (CH 4)2, (C 2H4)2 and three conformations of the benzene dimer was studied. Only PW91, HCH407, and VSXC predict all dimers to be bound. However, VSXC strongly over-binds all of the complexes. The DFTs predict repulsive potential energy surfaces (PES) for parallel benzene at large separations, in contrast to MP2. VSXC, B1B95, BB95, and BB1K, and to a lesser extent OLYP and O3LYP, are sensitive to the size of the integration grid used. When used with standard grids, these methods predict multiple minima on one or more dimer PESs. Crown Copyright © 2004 Published by Elsevier B.V. All rights reserved.

1. Introduction

There is now a plethora of density functional theory (DFTs) methods available. Some of these DFTs have been tested on van der Waals dimers [1–3] but there is no general study that assesses and compares many of these methods for their ability to predict the binding of some simple dispersion-bound complexes. Herein, we report the binding energies and relevant geometry data of Ne 2, Ar 2, and the methane (CH 4) and ethylene (C 2H4) and three conformations of the benzene (C 6H6) dimer obtained using 25 DFT methods. We also discuss the long-range behaviour of the functionals for the dimers studied.

2. Method of calculation

All calculations were performed with the GAUSSIAN-03 suite of programs [4], utilizing 6-31G** [4] basis sets. Geometries of the monomers and dimers were fully optimized with tight convergence criteria and with ultrafine integration grid sizes (99 radial, 590 angular points). Some functionals predicted potential energy surfaces (PESs) with many inflections and/or multiple minima for some dimers. In these cases, grids containing up to 250 radial and 590 angular points were used, although this large grid did not resolve all cases of spurious behaviour.

Binding energies (BE) were computed as the negative of the electronic energy difference between the geometry optimized dimers and monomers without zero-point or counterpoise corrections [5]. Thus, a positive BE reflects a bound dimer and a negative BE represents the energetic separation between a metastable dimer conformer and separated monomers. Additional binding energy calculations were performed with larger basis sets.

Potential energy surfaces were computed using partially constrained monomer geometries. We did not calculate PESs for slipped parallel (C 6H6) 2.

3. Results

Table 1 lists the DFT/6-31G** optimum intramonomer separations for the six dimers. The structures
for the dimers have been reported elsewhere [1 and references therein]: Methane dimer is a staggered, $D_{3d}$ structure and ethylene dimer has a crossed, $D_2d$ structure. Benzene has two nearly degenerate, well-bound conformations, a $C_{2v}$ 'T-shaped' (T) structure and a $C_{2h}$ ‘slipped-parallel’ (SP) structure. The stacked or $D_{6h}$ 'parallel' (P) arrangement of the benzene dimer is a saddle-point. Some of the DFT methods predict dimers to be unbound (indicated with a ‘U’ in the tables).

Table 2 contains the computed BE. Some functionals predict $P-(C_6H_6)_2$ to be metastable. In these cases, the barriers to dissociation are given in brackets.

The data in the tables are roughly organized according to methods which predict dimer binding from strongly bound to completely unbound. The DFT results are compared with high-level correlated ab initio (CCSD(T)) data given at the bottom of the Tables.

PEEs for $Ar_2$ using different integration grids with the VSXC functional are shown in Fig. 1. PEEs for $P-(C_6H_6)_2$ using HF, MP2 and a selection of DFTs are shown in Fig. 2.

4. Discussion

The data in the tables show that only VSXC [6], PW91 [7] and HCTH407 [8] predict all seven dimers to be bound. VSXC predicts smaller intramonomer separations (0.1–0.6 Å too short) and larger binding energies (by factors of 2–11) than those predicted by high-level theory and thus is strongly overbinding. In preliminary calculations with a 'standard' integration grid (75 radial, 302 angular) [4], we found that VSXC predicts deep multiple minima in the PEEs for $Ne_2$, $Ar_2$ and $P-(C_6H_6)_2$. Increasing the grid size to ‘ultrafine’ [4] (99 radial, 590 angular points) eliminated the multiple minima in the $Ar_2$ and $P-(C_6H_6)_2$ PEEs but oscillations in the curves did not disappear unless a very large grid was used (see Fig. 1). The use of an ultrafine grid with VSXC for $Ne_2$ did not result in a PEE with a single minimum. This sensitivity to grid size is a problem common to meta-generalized gradient approximation (MGGA) DFTs used in this study, except TPSS (see below). Users of these functionals should exercise caution.

PW91 and HCTH407 predict reasonable intramonomer separations for all dimers except for $Ne_2$ (which is

### Table 1

<table>
<thead>
<tr>
<th>DFT</th>
<th>Ne$_2$</th>
<th>Ar$_2$</th>
<th>(CH$_4$)$_2$</th>
<th>(C$_2$H$_4$)$_2$</th>
<th>T-(C$_6$H$_6$)$_2$</th>
<th>SP-(C$_6$H$_6$)$_2$</th>
<th>P-(C$_6$H$_6$)$_2$</th>
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<td>3.76</td>
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<td>5.78</td>
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<td>U</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td>U</td>
</tr>
</tbody>
</table>

High level

|          | 3.2$^c$ | 3.8$^c$ | 3.87$^c$ | 3.92$^c$ | 4.89$^d$ | 3.8$^d$ | 3.7$^d$ |

U, complex is unbound.

$^a$ Using an integration grid of 250 radial and 590 angular points.

$^b$ PEEs, generated using ultrafine grids, contain oscillations but tend to become smooth as the size of the integration grid increases.

$^c$ Ref. [1].

$^d$ Ref. [25].
Table 2

Binding energies (kcal/mol) of dispersion-bound compounds predicted using different density functional theory methods with 6-31G** basis sets

<table>
<thead>
<tr>
<th>DFT</th>
<th>Ne₂</th>
<th>Ar₂</th>
<th>(CH₄)₂</th>
<th>(C₂H₆)₂</th>
<th>T-(C₆H₆)₂</th>
<th>SP-(C₆H₆)₂</th>
<th>P-(C₆H₆)₂</th>
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<tbody>
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<td>VSXC⁻</td>
<td>0.49ᵇ</td>
<td>1.15ᵇ</td>
<td>4.33</td>
<td>9.96</td>
<td>8.28</td>
<td>16.95</td>
<td>11.23ᵇ</td>
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<td>0.97</td>
<td>0.36</td>
<td>0.52</td>
<td>1.56</td>
<td>1.65</td>
<td>1.55</td>
<td>0.24ᵇ</td>
</tr>
<tr>
<td>HCTH407</td>
<td>0.76</td>
<td>0.48</td>
<td>0.71</td>
<td>1.53</td>
<td>1.41</td>
<td>1.63</td>
<td>0.67ᵇ</td>
</tr>
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<td>B971</td>
<td>0.58</td>
<td>0.21</td>
<td>0.36</td>
<td>1.46</td>
<td>1.50</td>
<td>1.44</td>
<td>0.11ᵇ</td>
</tr>
<tr>
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<td>0.19</td>
<td>0.29</td>
<td>1.30</td>
<td>1.33</td>
<td>1.27</td>
<td>0.22ᵇ</td>
</tr>
<tr>
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<td>0.25</td>
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<td>0.42ᵇ</td>
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<td>0.73</td>
<td>0.84</td>
<td>0.88</td>
<td>0.24ᵇ</td>
</tr>
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<td>0.04</td>
<td>0.05</td>
<td>0.19</td>
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<td>U</td>
<td>U</td>
<td>U</td>
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</table>

High level  0.07ᶜ  0.26ᶜ  0.49⁵ᶜ  1.15ᶜ  2.74ᵈ  2.78ᵈ  1.81ᵈ

U, complex is unbound.

ᵃ Using an integration grid of 250 radial and 590 angular points.
ᵇ PESs, generated using ultrafine grids, contain oscillations but tend to become smooth as the size of the integration grid increases.
ᶜ Ref. [1].
ᵈ Ref. [25].

Fig. 1. VSXC/6-31G** PESs for the argon dimer using different integration grid sizes.
significantly over-bound by most of the DFTs) and for
SP-(C_6H_6)_2 (which is under-bound by all of the DFTs).
PW91 and HCTH407 do not predict multiple minima or
oscillations on any of the PESs. PW91 and HCTH407
predict that P-(C_6H_6)_2 is repulsive at large separations,
in contrast to the MP2/6-31G** results, a problem
which is common to all of the DFTs, see Fig. 2. The
long-range repulsive behaviour in the P-(C_6H_6)_2 system
is similar to that predicted by HF/6-31G**. Both
HCTH407 and PW91 over-bind Ar_2, (CH_4)_2 and
(C_2H_4)_2 (by up to 2 \times) and under-bind the benzene
dimer conformers (by up to 7 \times). We performed addi-
tional calculations with PW91 and HCTH407 using
6-311+G(2d,2p) basis sets. These calculations predict
larger intramonomer separations (by ca. 0.3 Å) and
generally lower BEs (by 0.4 kcal/mol or less) than the
smaller basis set results. Exceptions to this are the large
basis set PW91 results for the benzene dimers, which are
considerably worse than those obtained with the small
basis set.

Six of the DFTs predict the P-(C_6H_6)_2 dimer to exist in
a metastable minimum with respect to separated mono-
mers and the other dimers to be bound. Of these, B971
[9], PBE [10], B98 [11,12] and HCTH147 [13] predict a
barrier to P-(C_6H_6)_2 dissociation along the ring separa-
tion coordinate to be in the range of 0.1–0.3 kcal/mol.
PBE1PBE [10] and TPSS [14] predict very broad minima
but only very small (0.04 and 0.02 kcal/mol, respectively)
barriers to P-(C_6H_6)_2 dissociation. The BEs for all of
the other dimers, except Ne_2, are lower than those predicted
by PW91 and HCTH407 and by high-level theory. The
structures predicted by these DFTs are varied, with
HCTH147 predicting monomer separations larger than
PW91 by up to 0.4 Å. All six of these DFTs predict smooth
PESs for all of the dimers.

The remainder of the DFTs studied predict one or
more of the dimers to be unbound. OLYP [15,16],
O3LYP [15,16], BH\textsubscript{Hand}HLYP [4,16], MPW1K [17],
MPW1PW91 [2], B972 [18], OPW91 [7,15] and H\textsubscript{TCH}93
[9] predict only P-(C_6H_6)_2 to be unbound. B3LYP
[16,19], B1LYP [20], B3P86 [19,21] and B3PW91 [7,19]
predict Ar_2, (CH_4)_2 and P-(C_6H_6)_2 dimers to be un-
bound. G96LYP [16,22] predicts repulsive PESs for all
seven dimers. These DFTs also predict smooth PESs
for all of the dimers.

The remaining DFTs are meta-GGA functionals:
BB1K [23], B1B95 [24] and BB95 [24] predict PESs with
substantial oscillations and multiple minima, making
them useless for dispersion applications. Increasing the
integration grid size results in smoother but not neces-
sarily single-minimum PESs. The DFTs that predict
PESs with severe oscillations and/or multiple minima
use the same correlation formalism.

5. Conclusions

Twenty-five density functionals were tested with
6-31G** basis sets for their ability to predict equilibrium
parameters for dispersion-bound dimers including Ne_2,
Ar_2, (CH_4)_2, (C_2H_4)_2, and three conformations of ben-
zene. Only three functionals, VSXC, PW91 and
HCTH407 predicted all seven dimers to be bound.
VSXC strongly over-binds all dimers by up to a factor.
of 11, relative to high-level ab initio results, and predicts oscillations and multiple minima in the potential energy surfaces of some dimers. Ultimately, VSXC cannot properly describe the dispersion interactions in the test systems. The most promising functionals for dispersion interactions, PW91 and HCTH407, strongly over-bind Ne₂ (as do all of the DFTs), slightly over-bind Ar₂, (CH₄)₂ and (C₂H₄)₂, and under-bind the benzene dimer conformers. These functionals, and all of the others tested, predict long-range repulsive behaviour in parallel-(C₆H₆)₂ that is similar to Hartree–Fock behaviour and contrary to MP2 results. B971, PBE, B98, PBE1PBE, HCTH147 and TPSS, which may have some utility in calculating geometries of dispersion-bound systems, predict all of the dimers to be bound, with parallel-(C₆H₆)₂ being metastable with respect to benzene monomers. OLYP, O3LYP, BH and HLYP, MPW1K, MPW1PW91, B972, OPW91 and HCTH93 predict one or more of the dimers to be unbound. The meta- generalized gradient approximation functionals BB1K, B1B95 and BB95, like VSXC, predict for most dimers oscillations and multiple minima in the potential energy surfaces that show integration grid size dependence. These functionals, which have the same correlation formalism in common, are not usable for the dispersion-bound dimers tested.

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References