LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2000 issue.

COMMENTS


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In the recent article by Milet et al.,\textsuperscript{1} the authors compare the interaction energies obtained from accurate wave function based approaches to the ones derived from density-functional theory calculations (DFT) for several weakly interacting complexes. The supermolecule calculations at the coupled-cluster single double and noniterative triple excitation [CCSD(T)] level and the symmetry adapted perturbation theory (SAPT) calculations were used to determine the interaction energy at several arbitrary geometries which was then used as a reference for comparison with DFT results. Several approximate exchange-correlation functionals of either the generalized gradient approximation (GGA) form or of the hybrid type were applied.

This comment concerns mostly the GGA functionals applied in Ref. 1. All of them (the ones labeled as BP86, BLYP, and BPW91 in Ref. 1) share the same exchange functional (B88) proposed by Becke.\textsuperscript{2} The B88 functional was shown to be unsuitable for modeling weakly interacting complexes as evidenced by rather unsatisfactory results obtained by many investigators for different weakly interacting complexes (see, for example, Refs. 3–6). These studies revealed that the attraction between weakly bound complexes is either too weak to even be noticeable or else divergences which correlation functional was combined with B88. The set of approximate exchange-correlation functionals applied in Ref. 1 appears, therefore, not to be well suited to address the title question of Ref. 1.

The origin of this deficiency of the B88 functional was analyzed in detail in two recent papers.\textsuperscript{5,6} The main points of these analyses can be summarized as follows:

(i) Following the fact that the electron densities of the molecules forming a van der Waals complex do not overlap significantly, the DFT interaction energies are very sensitive to the way the applied approximate exchange-correlation functional depends on the electron density gradient. For the exchange functionals of the GGA form, the dependence on the density gradient is determined by the enhancement factor \[F(s),\]

where \(s = \sqrt[n]{\rho}\) and \(\rho\) is the electron density.

The enhancement factor of the B88 exchange functional \((F^{\text{B88}})\) assures the correct asymptotic behavior of the exchange energy density. The B88 functional violates, however, a number of other mathematical conditions satisfied by the exact functional. In particular, its divergent behavior at the electron densities (where \(s\) is large) results in violation of the Lieb–Oxford bound, which in its global version reads: \(E_{\gamma}(\rho) = -1.679\int_0^\infty \rho^{3/2}(r) dr\). As discussed by Perdew and collaborators,\textsuperscript{8} the enhancement factor of a GGA exchange functional satisfying the Lieb–Oxford must be bound from above. The divergent behavior of \(F^{\text{B88}}(s)\), leads to less significant energy errors for stronger interactions. The energetics of strongly bound complexes is determined rather by the large density (small \(s\)) regions in the real space at which all GGA exchange functionals behave similarly (see Fig. 3 of Ref. 5 or Fig. 1 of Ref. 6 for instance).

(ii) The two mathematical conditions (asymptotic behavior of the exchange energy density and the Lieb–Oxford bound) cannot be simultaneously satisfied by functionals of the general GGA form. The analyses presented in Refs. 5 and 6 provide, therefore, numerical evidence that, the condition associated with the Lieb–Oxford bound is more important than the condition of the correct asymptotic behavior of the exchange energy density for weakly bound complexes.

The \(F^{\text{B88}}(s)\) not only diverges at small electron densities but also grows with increasing \(s\) faster than other commonly used GGA functionals (PW86\textsuperscript{9} of Perdew and Wang, LG\textsuperscript{10} of Lacks and Gordon, for instance). The enhancement factors of the PW91\textsuperscript{11} functional of Perdew and Wang, its parameter-less variant PBE,\textsuperscript{12} and its new reparametrization by Barone and Adamo (mPW91)\textsuperscript{13} are all bound from above.
The B88 exchange functional appears, therefore, as one of the worst choices among the commonly used GGA functionals to describe the energetics of low electron densities.

To illustrate the above considerations, the results presented for the He⋯CO$_2$ complex in Ref. 1 are supplemented here (Table I) by the ones obtained using two approximate exchange functionals not considered in Ref. 1: (a) the PW91 functional which is nonempirical and can be seen as the B88 functional with the Oxford–Lieb bound built in, (b) the Lacks–Gordon exchange functional which diverges slower than B88 at large $s$ and which similarly to B88 contains some empirical parameters.

As shown in Table I, replacing the B88 exchange functional by PW91 results in a stronger attraction (or weaker repulsion). The PW91PW91 interaction energies agree significantly better with the SAPT ones than the BPW91 interaction energies. The differences between the DFT and the SAPT results are reduced by factor two to four! The PW91PW91 results also approach significantly better the exact interaction energies than the ones obtained using any GGA considered in Ref. 1. The results presented in Ref. 1 obtained by means of the hybrid functionals are significantly better than the GGA considered there. It is important to note, therefore, that the accuracy of the PW91PW91 interaction energies is about the same as that of the B3LYP interaction energies of Ref. 1. The last functional being considered in Ref. 1 to be the best.

The LGP86 results approach even better the SAPT ones. This should not come as a surprise since, unlike PW91, the LG functional was parametrized for weak interactions. The enhancement factor of LG also diverges at large $s$ but it grows with $s$ much slower than B88 resulting in less severe violation of the Lieb–Oxford bound.

Finally, it is important to acknowledge, that the description of the London dispersion forces remains a challenge for density-functional theory (see Ref. 14 for instance). For instance, all semilocal GGA functionals do not lead to any attraction between two spherically symmetric nonoverlap-

$$\begin{array}{cccc}
\theta & 0 \text{ deg} & 30 \text{ deg} & 60 \text{ deg} & 90 \text{ deg} \\
\text{wave function based} & E_{\text{int}}^{\text{SAPT}} & 90.88 & 12.39 & -26.14 & -26.38 \\
\text{approaches} & E_{\text{int}}^{\text{CCSD(T)}} & 93.62 & 15.83 & -24.72 & -25.70 \\
\text{GGA functionals} & E_{\text{int}}^{\text{BPW91}} & 409.24 & 244.66 & 87.84 & 47.01 \\
& (318.4) & (232.3) & (114) & (73.4) \\
& E_{\text{int}}^{\text{BLYP}} & 231.29 & 125.37 & 48.76 & 33.24 \\
& (404.0) & (137.8) & (74.9) & (59.6) \\
\text{hybrid functionals} & E_{\text{int}}^{\text{B3LYP}} & 164.79 & 79.05 & 25.69 & 17.83 \\
& (73.9) & (66.7) & (51.8) & (44.2) \\
& E_{\text{int}}^{\text{PW91PW91}} & 22.2 & -62.3 & -86.1 & -70.4 \\
& (-68.7) & (-74.5) & (-60.0) & (-44.0) \\
& E_{\text{int}}^{\text{SAPT}} & 58.6 & 5.3 & -4.3 & 1.9 \\
& (-32.3) & (-7.1) & (21.8) & (24.5) \\
\end{array}$$

*Reference 1.

$^a$This work; GAUSSIAN 98 code was used (Ref. 15); as the C–He distance is not given in Ref. 1 its value of 3.70 Å is estimated based on the energies in Table V of Ref. 1.

The intermolecular interactions...