van der Waals interactions of the benzene dimer: towards treatment of polycyclic aromatic hydrocarbon dimers

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Although density functional theory (DFT) in principle includes even long-range interactions, standard implementations employ local or semi-local approximations of the interaction energy and fail at describing the van der Waals interactions. We show how to modify a recent density functional that includes van der Waals interactions in planar systems [Phys. Rev. Lett. 91, 126402 (2003)] to also give an approximate interaction description of planar molecules. As a test case we use this modified functional to calculate the binding distance and energy for benzene dimers, with the perspective of treating also larger, flat molecules, such as the polycyclic aromatic hydrocarbons (PAH).

Keywords: van der Waals Interactions; Density Functional Theory; Benzene.

I. INTRODUCTION

The benzene dimer is the prototype for aromatic interactions and has been studied extensively both by theoretical and experimental means. Describing benzene interactions can be regarded as the first step toward describing interactions of polycyclic aromatic hydrocarbons (PAHs). PAHs are planar molecules consisting of several aromatic rings, where the peripheral carbon atoms are covalently bonded to hydrogen atoms. Both benzene and PAHs structurally resemble graphite and exhibit very similar intra- and intermolecular bond lengths, particularly for (stacks of) large PAHs. Like the interactions between the sheets in graphite, the interactions between parallel benzene molecules or layers in PAH stacks are dominated by the weak, nonlocal van der Waals (vdW) interaction. However, the description of the vdW interaction is absent in the traditional implementations of density functional theory (DFT), implementations which have otherwise been very successful in describing dense, hard materials on the atomic scale.

The past few years a number of publications have addressed the problem of consistently extending the common DFT implementations to also include the vdW interaction. For the mutual interactions of planar sheets or surfaces a functional was obtained in Refs. For example, a relatively good estimate of the binding distance between two graphite planes (graphene) was obtained with this planar functional, while the usual generalized gradient approximations (GGA) fail to bind the graphene layers or do so at an unphysical binding distance and energy. Since benzene and PAHs are similar to graphite, the correction to the regular calculations will be significant also in dimers of these molecules.

In this work, we study dimers of benzene (C\textsubscript{6}H\textsubscript{6}) by modifying and approximating the planar nonlocal density functional in order to treat molecules of finite size. We here concentrate on dimers where the molecules are placed directly on top of each other (“AA stacking”). The method we use is developed with the aim of being able to study also PAH molecules, and it is described below. The results for some of the small PAH molecules naphthalene, anthracene, and pyrene (C\textsubscript{10}H\textsubscript{8}, C\textsubscript{14}H\textsubscript{10}, and C\textsubscript{16}H\textsubscript{10}) will be reported in a forthcoming publication.

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II. METHOD

DFT in principle does include even long-range interactions, such as the vdW interactions, but those are a part of the exchange-correlation functional $E_{xc}$ which is approximated in the implementations of DFT. The most commonly used approximations to $E_{xc}$ are the local density approximation (LDA) and the generalized gradient approximation (GGA), both of which are local or semi-local and do not include the vdW interaction. However, GGA (and to some extend LDA) has proven very successful in describing the interactions within dense matter, e.g., within a molecule, and a consistent correction scheme that includes the long-range intermolecular vdW interactions must not change the short-range intramolecular interaction.

A. The graphite interactions

In the vdW correction scheme for planar sheets and surfaces, defined and described in Refs. [13, 15, 16], the exchange energy from GGA is retained, and the correlation energy is determined as a sum of the local correlation (obtained from LDA) and the nonlocal correlation $E_{nl}^c$, which will be described below. For the exchange part the GGA revPBE flavor of Zhang and Yang [20] is chosen because it is fitted to exact exchange for atoms. Thus the (vdW-corrected) total energy is written as

$$E_{vdW-DF} = E_{GGA} - E_{GGA,c} + E_{LDA,c} + E_{nl}^c,$$

where all energy terms are functionals of the electron charge density $n(r)$, and $E_{GGA,c}$ and $E_{LDA,c}$ are the correlation from GGA and LDA, respectively. These energy terms are directly available from our DFT calculations. Our DFT calculations are performed by the plane-wave pseudo-potential based program Dacapo [21].

The nonlocal correlation, per area $A$, for a planar, translationally invariant system such as graphite is given by [13]

$$E_{nl}^c/A = -\lim_{L \to \infty} \int_0^\infty \frac{du}{2\pi} \int \frac{d^2k}{(2\pi)^2} \ln \frac{\phi'(0)}{\phi_0'(0)},$$

where $\phi(z)$ fulfills the differential equation $(\epsilon_k \phi)' = k^2 \epsilon_k^2 \phi$ with boundary conditions $\phi(0) = 0$ and $\phi(L) = 0$, and $\phi_0(z)$ is the vacuum solution. The system is enclosed in a long box of length $L$ along the direction perpendicular to the graphite plane(s). $\epsilon_k$ is the dielectric function of graphite, Fourier-transformed in the plane of the graphite sheet

$$\epsilon_k(z, iu) = 1 + \frac{\omega_p^2(z)}{u^2 + \nu_F^2(z)(k^2 + q_{||}^2)/3 + (k^2 + q_{||}^2)^2/4}.$$  (3)

The plasmon frequency $\omega_p$ is defined by $\omega_p^2(z) = 4\pi n(z)$, the Fermi velocity by $\nu_F(z) = (3\pi^2 n(z))^{1/3}$, $n(z)$ is the planarly averaged electron density varying in the $z$-direction perpendicular to the plane, and $iu$ is the imaginary frequency. We use atomic units unless otherwise noted.

The parameter $q_{||}$ is introduced to compensate for the locality of $\epsilon_k$ in the $z$-direction. The value of $q_{||}$ is materials dependent, and it is found from a separate set of GGA DFT calculations with an applied, static electric field across the graphite layer.

In Figure 1(a) we show the interaction curve of graphene-graphene in the AA stacking according to [13]. These results of graphene in the AA stacking allow us to directly compare to our results of benzene, and later PAHs, also in AA stacking. The binding separation 4.0 Å of graphene (AA) is larger than for graphene in the physically correct AB stacking (3.76 Å), calculated within the same vdW correction scheme [15]. We used the value $q_{||} = 0.756$ in atomic units for a graphene sheet [17].

B. Extending the functional to treat planar molecules

It is a natural next step to modify $E_{nl}^c$ for planar, translational invariant sheets to treat planar, large, but not infinitely extended molecules. The PAH molecules are pieces of graphene, passivated
by hydrogen atoms at the broken carbon-carbon bonds. We would therefore like to introduce appro-\
appropriate approximations in order to apply the functional to planar, large, finite molecules.

The (semi-)local part of the total energy in \( E_{\text{GGA}} - E_{\text{GGA},c} + E_{\text{LDA},c} \), can be determined directly from a usual DFT implementation. Such calculations provide us, besides the energy terms, with a three-dimensional electron density \( n(r) \). In the formalism for \( E_{\text{nl}} \) in \( E \) the density profile \( n(z) \) is assumed translationally invariant along the molecule. For the finite molecules we take \( n(z) = n_{\text{mol}}^{-1} \int dx \, dy \, n(x,y,z) \) where \( n_{\text{mol}} \) is the size of the molecular area that affects the vdW interactions; this area must be estimated.

For carbon-dominated molecules such as benzene and PAH the dominating contribution to the vdW correction comes from the carbon atoms. We thus assume that the dielectric function for the molecules is well described by the functional form \( \epsilon \) with the graphene value \( q_L = 0.756 \) a.u. By comparing the dacapo-calculated static \( (u = 0) \) electric response of the isolated molecule with that found from the model dielectric function \( \epsilon \), with \( A_{\text{mol}} \) as a parameter, we can determine \( A_{\text{mol}} \). For benzene we find that \( A_{\text{mol}} = 51.7 \) \( \text{Å}^2 \) reproduces the static response.

Given the model dielectric function \( \epsilon \) with the parameter \( A_{\text{mol}} \) determined as described above, the calculation of the \( E_{\text{nl}} \) contribution follows from \( E \). The physical analogy of using the molecularly averaged \( n(z) \) in \( E \) is that of molecules moved together such that they each take up the lateral area \( A_{\text{mol}} \). \( E_{\text{nl}} \) for molecules calculated this way therefore somewhat overcounts the vdW interaction by including not only the physically correct interaction of one dimer molecule with its partner, but also the interaction with the partner’s neighbors. Because the vdW attraction falls off with distance this effect decreases as the molecule size increases. The other energy terms of \( E \) are not affected.

We stress that \( A_{\text{mol}} \) is larger than the area of the same amount of carbon atoms in a graphene plane. In our procedure of finding \( A_{\text{mol}} \) we compare the (static) response of a molecule isolated in all three directions. We make sure that our Dacapo-calculated response really does come from an isolated molecule by checking the convergence of the response with increasing lateral unit cell size. The response of the low-density charge distribution region within the molecular plane is thus included in our description, and therefore the vdW interaction of these sheets of close molecules is different than the vdW interaction of two sheets of graphite, even though the molecules are mostly composed of carbon atoms.

With the assumptions introduced above, necessary for applying the vdW planar functional to finite molecules, the quality of the vdW interaction calculations increases with increasing molecular size. We emphasize that in this sense, the benzene molecule is an extreme molecule, and we do not expect full quantitative agreement of our results with full-powered quantum-chemistry calculations \( \text{DFT} \) or with results in our new (more costly) general-geometry formulation of the vdW-DF \( \text{DFT} \).

III. RESULTS

We here present the results of applying the modified vdW functional to the benzene dimer in the AA stacking. The first step is to determine the structure of the isolated molecule, the static response to an applied electric field, the (semi-)local energy contributions to the dimer binding, and the electron density of the dimer. This step is carried out in a standard DFT program. The second step is to calculate the nonlocal correlation energy contribution, \( E_{\text{nl}} \), with the approximations discussed above.

The standard DFT calculations were performed with the plane-wave pseudopotential code Dacapo \( \text{DFT} \) with periodic boundary conditions. We performed the self-consistent calculations (before adding \( E_{\text{nl}} \)) using the revPBE GGA functional. The choice of unit cell size involves a trade-off between manageable calculations on the one hand, and large lateral and vertical separations between periodically repeated images of the molecules (or dimers) on the other hand. When deciding on the unit cell size we also benefit from the short-range nature of the traditional DFT-Implementations. In our calculations we used a hexagonal unit cell of size \( (17.112 \text{ Å}, 17.112 \text{ Å}, 26 \text{ Å}) \).

In the plane-wave code the number of plane waves is determined by a cutoff in the plane-wave energy. A preliminary analysis showed a cutoff at 450 eV to be sufficient. However, as we discuss below, there is a small energy difference between dimers within the same unit cell at very large separation and two isolated molecules in two separate unit cells. This offset depends on the plane-wave cutoff in a non-trivial way. We emphasize that the offset in the total energy difference is unrelated to \( E_{\text{nl}} \).
FIG. 1: Energy curves for graphene and benzene dimers in the AA stacking as a function of separation distance. Panel (a) shows the graphene-graphene interaction, panel (b) shows the benzene-benzene interaction. The dashed lines are the self-consistently determined revPBE total energies, the dotted lines show the $E_{\text{nl}}$ correction, and the solid lines show the $E_{\text{vdW-DF}}$ total energy curves obtained according to Eq. (1). The circles on the $E_{\text{vdW-DF}}$ curves indicate the calculations performed.

A. Benzene-benzene interaction energy

The benzene dimer interaction is calculated by fixing the relative atomic positions within of each of the two molecules of the dimer and varying the distance between them, while keeping the size of the unit cell constant. Figure 1(b) shows the total-energy curves for benzene: the revPBE curve (which shows no binding at all), the nonlocal correlation $E_{\text{nl}}$, and the full $E_{\text{vdW-DF}}$ that includes nonlocal correlation. The reference energy is the benzene dimer at large (11 Å) separation.

We find in vdW-DF the binding energy 100 meV at the distance 4.1 Å. These results are in agreement with our results for the AA stacked graphene dimer as we expect the binding distance there to be similar to that of the benzene dimer and PAH dimers in the AA stacking. Both the benzene separation distance and interaction energy are in reasonable, although not perfect agreement with experiments and other calculations. For instance, Refs. [2, 4, 5] report calculating binding separations of around 3.8 Å and binding energies in the range of 64–92 meV. As mentioned earlier, we expect the quality of our results to improve for larger molecules.

As previously mentioned, no binding arises in the revPBE flavor of GGA. We note that GGA Perdew-Wang 91 (PW91) [22] calculations (not shown) exhibit an unphysically small binding energy of the benzene dimer (12 meV) at separation 4.7 Å. However, this PW91 binding arises from the unphysical interactions mediated by the exchange contribution in the manner previously documented for graphite [15].
B. Discussion of the energy reference level

During the course of this benzene and PAH study we encountered a technical problem in determining an appropriate reference level for our (traditional) total energy calculations based on GGA.

All dimer energies presented in this paper, whether revPBE or vdW-DF energies, are given with reference to the energy of two molecules far apart. Thus the energies that we report, and which we for now generally denote $E_{\text{diff}}$, are total energy differences given by

$$E_{\text{diff}}(d) = E_{\text{tot}}(d) - E_{\text{ref}}$$

where $E_{\text{tot}}(d)$ is the total energy of the dimer determined at separation $d$, and $E_{\text{ref}}$ is the energy of two molecules far apart. This applies both to the benzene molecules and the graphite sheets. The reference level $E_{\text{ref}}$ can be calculated either by removing one molecule to find half the reference energy, or by keeping both molecules within the unit cell and moving them “far apart” within the box. In both cases, we make sure that the periodic cell is sufficiently large that the molecule does not interact (electrostatically) with its periodic images. In our underlying GGA-DFT calculations it turned out that these two seemingly equivalent ways of determining $E_{\text{ref}}$ lead to two slightly different results. Numerically, the difference is more significant for the benzene molecules than for graphene.

In Fig. 1(b) we report curves of interaction energies of dimers with increasing separation. The natural choice of reference energy $E_{\text{ref}}$ is therefore the dimer with the two molecules “far apart”, by which we mean 11–12 Å separation in boxes of length of 24–26 Å. However, the problem merits an analysis.

In Figure 2 we show the difference in reference energies $\delta E_{\text{ref}}$ — defined as the energy of a pair of molecules “far apart” subtracted by the energy of two separate molecules — as a function of the charge-density cutoff. In Dacapo, besides the plane-wave energy cutoff for the wave functions, it is possible to set a different (larger) cutoff for the charge density, to enhance the description of the charge density at the price of only a modest increase in the calculational size. Most of the calculations in Figure 2 use a larger charge-density cutoff than the wave-function cutoff. In order to analyze $\delta E_{\text{ref}}$ also for large charge-density cutoffs we carried out a number of calculations in a unit cell with reduced lateral size (10 Å).

A few immediate conclusions can be drawn on the basis of Figure 2. By comparing the single-cutoff and the double-cutoff results at charge-density cutoff 500 eV and 550 eV we find that the quality of the wave-function description does not affect $\delta E_{\text{ref}}$. We see this in Figure 2 by the collapsed data points (indicated by arrows) for the revPBE total energy, but it is true also for the exchange and the correlation parts of the energy, as well as for PW91 (not shown). This indicates that the (noninteracting) kinetic part of the total energy, which is calculated from the wave functions, does not contribute to $\delta E_{\text{ref}}$.

In contrast, $\delta E_{\text{ref}}$ depends non-trivially on the charge-density cutoff. It is not clear that a very high cutoff value will yield good results, rather, $\delta E_{\text{ref}}$ seems to oscillate with charge-density cutoff. By comparing the results for the usual box size with the small-box results we further notice that $\delta E_{\text{ref}}$ decreases with the amount of low-density (vacuum) region in the box. $\delta E_{\text{ref}}$ thus seems to be mainly affected by contributions from the low-density regions. A major part of $\delta E_{\text{ref}}$ comes from the exchange part of the total energy. Not shown in the figure are $\delta E_{\text{ref}}$ for the PW91 total energy and for correlation (revPBE and PW91). These energies all give a finite, but smaller value of $\delta E_{\text{ref}}$. Unfortunately the problems are worse exactly for the revPBE-GGA that enters our subsequent vdW-DF calculations in 4.

Besides the ever-present risk of undetected programming errors, we speculate on three possible origins for the finite $\delta E_{\text{ref}}$ that affects our underlying GGA-DFT calculations: (i) numerical instabilities and formal inaccuracies arising from the implementation of the exchange-correlation approximation; (ii) the mixing of different exchange-correlation approximations for creation of pseudopotentials and use in calculations; and (iii) the use and/or implementation of ultrasoft pseudopotentials. The possibility of formal problems in the exchange-correlation term borrows some support from the work by Lacks and Gordon in 1993. PW91 exchange, and a number of other exchange approximations, were shown to give values of $|\delta E_{\text{ref}}|$ for noble gas dimers far exceeding those from exact exchange. The deviation arises from contributions in the low-density, large-gradient regions of space, which is precisely the regions that dominate our system. If this will turn out to be the origin.
of at least a part of the offset $\delta E_{\text{ref}}$, it is not too surprising that this does not seem to be perceived as a general problem, since GGA and most present-day DFT codes have been implemented and tested mostly on dense systems with less vacuum.

We might worry that using a mix of exchange-correlation approximations in the pseudo-potential and in the energy calculations could lead to unwanted effects. Our calculations within traditional DFT were carried out with Vanderbilt ultrasoft pseudopotentials [25], originally created within the PW91 flavor of the GGA functional, and the energy and the charge density were self-consistently determined within revPBE. However, we carried out a set of calculations for the graphene-graphene system, where the offset is much less in size, that showed this mixing to not be the cause of the offset. The calculations of $\delta E_{\text{ref}}$ were carried out with all combinations of pseudopotentials (revPBE, PW91, PBE [26]), self-consistently determined charge density (revPBE, PW91, PBE), and energy extracted (revPBE, PW91, PBE, RPBE [27], LDA, as well as all exchange and correlation contributions). In all cases, the major part of the offset arises from the exchange part of the energy, whereas the offset on the GGA and LDA correlation is generally almost an order of magnitude smaller.

We cannot, within this study, test whether the use of ultrasoft pseudopotentials contributes to $\delta E_{\text{ref}}$. This issue requires controlled comparison of results from different codes and choice of pseudopotentials and will be addressed in a forthcoming investigation.

In addition to the tests mentioned above, we also tested that the exact position of the monomer with respect to the Fast-Fourier-Transform grid does not matter on the scale of energy differences considered here. Further, we speculated that $\delta E_{\text{ref}}$ might be due to numerical errors arising when very small charge-density values are left out in the calculation of the energies, but by changing the limit of the smallest charge-density values included we found this to be irrelevant to $\delta E_{\text{ref}}$.

IV. CONCLUSIONS

We have presented a modification of an existing planar-system van-der-Waals DFT functional to approximately treat also large but finite planar molecules. We use the modified functional for the benzene dimer as an example, with the prospect of applying it to polycyclic aromatic hydrocarbon...
molecules. We have characterized a problem in traditional implementations of DFT for molecular systems with large volumes of low charge density. This problem motivates further investigations. The modified vdW functional presented is a step towards being able to treat sparse matter systems consistently within DFT.

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