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Prediction of Dispersion Forces: Is There a Problem?

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We discuss the ability of a number of standard and non-standard computational techniques to reproduce dispersion forces, using examples from the literature as well as some new examples. We conclude that there are still some cases where standard methods are not so far successful. There are some promising directions under study, however.

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I. Introduction

This paper considers the present state of the art in predicting dispersion (van der Waals, vdW) forces. Stronger forces such as covalent and ionic interactions often mask these relatively weak attractive forces. Dispersion forces are undoubtedly important, however, for rare-gas chemistry and in many soft-matter situations such as protein folding and polymer cohesion. They are also suspected to be important in the energetics of hydrogen intercalation in graphenes including carbon nanotubes and intercalated graphite, with potential implications for a clean energy economy. We will argue that, although satisfactory practical methods exist for many cases, there remain important problems involving dispersion forces for which no quantitatively reliable predictive method has yet been demonstrated. There are promising leads, however, and these will also be discussed.

The emphasis here is on approaches derived from recent developments in the physics community, but which could have relevance for chemistry also.

In a common point of view, dispersion forces arise from the mutual dynamic polarization of the electronic clouds of two or more condensed-matter systems. They are perhaps most familiar in the context of the interaction between closed-shell atoms separated by a distance R , where the dispersion force contributes a long-ranged attractive tail in the interatomic force law, with an effective potential of form

$$V(R) = -C_6 R^{-6}. \quad (1)$$

Here C_6 is termed the Hamaker constant for the particular pair of atoms or molecules. In contrast to the electrostatic forces which arise when one or more of the systems possess a permanent electric moment, dispersion forces require no such moment but have their origin in the transient moments caused by zero-point quantal (or possibly in some cases

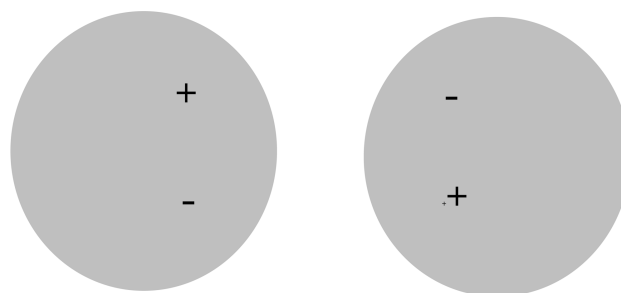


Fig. 1. Origin of dispersion forces.

thermal) fluctuations. In the simplest picture of two finite well-separated systems such as a pair of atoms (see Fig. 1), the fluctuations generate a spontaneous, transient dipole moment on atom No. 1. This dipole causes an electric field of order R^{-3} at the second atom, and this induces a dipole on atom No. 2, again depending on R^{-3} . A field of order $R^{-3} \cdot R^{-3} = R^{-6}$ is thus created back at the first atom, and the interaction energy between this field and the original transient dipole is also of order R^{-6} . Although this energy arises from transient processes, it is of second order in the fluctuating dipole, and so does not average to zero. More detailed versions of this qualitative argument (see reference 1 for example) lead to approximate expressions for the Hamaker constant in equation (1) such as

$$C_6 \approx A_1 A_2 \hbar \omega_0$$

where $A_{1,2}$ are the dipolar electric polarizabilities of the two atoms, and ω_0 is a characteristic oscillation frequency of the atoms.

Another way to view the above mechanism is to notice that the dipolar fluctuations on the two systems are correlated. In the language of electron density functional

theory, this means that the vdW interaction between distant systems is due to a very long-ranged correlation hole, quite different in form from the uniform-gas hole. It is therefore unsurprising that the local density approximation misses the long-ranged tail of the vdW interaction.

II. Quantitative Methods for Calculating Distant vdW Interactions—Finite Systems

(a) Exact Asymptotic Formulae

As suggested by the above argument, where two actions of the Coulomb interaction were involved, the dispersion interaction between two finite well-separated systems is given exactly, to leading order in $1/R$, by a suitable form of *second-order* perturbation theory (not the same as Moeller–Plesset perturbation theory, however: see below). A prerequisite for this treatment is that there is no overlap of the electronic clouds so that two electrons can be regarded as distinguishable if they are located on the two different systems. Exchange effects between the two systems are thereby ignored. Under these circumstances, the part of the Coulomb interaction V_{12} acting between the two systems can be unambiguously defined. The formulae below are obtained by treating V_{12} as a second-order perturbation (in contrast to Moeller–Plesset perturbation theory, for example, which treats *all* interelectron Coulomb interactions beyond Hartree–Fock as the perturbation). By this approach one can arrive at a number of apparently different (but equivalent) expressions for the dispersion interaction. In quantum chemistry texts^[2,3] and reviews^[4] one finds expressions involving exact electronic states and energies of the isolated atoms or molecules, while Zaremba and Kohn^[5] gave the following exact expression for the second order dispersion energy:

$$E^{(2)} = -\frac{\hbar}{2\pi} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}'_1 d\mathbf{r}'_2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{e^2}{|\mathbf{r}'_1 - \mathbf{r}'_2|} \times \int_0^\infty \chi^{(1)}(\mathbf{r}_1, \mathbf{r}'_1, iu) \chi^{(2)}(\mathbf{r}_2, \mathbf{r}'_2, iu) du. \quad (2)$$

Here, $\chi^{(1)}$ and $\chi^{(2)}$ are the spatially non-local density–density responses of the two separate systems (atoms/molecules). The expression (2) may appear to be of $O(R^{-2})$ as the separation R between the systems approaches infinity. This appearance is deceptive, however, because the density–density responses have to satisfy the charge neutrality and constant potential conditions

$$\int \chi(\vec{r}, \vec{r}', iu) d\vec{r}' = \int \chi(\vec{r}, \vec{r}', iu) d\vec{r} = 0$$

These conditions are automatically satisfied^[1] if one writes the density–density responses as the gradient of non-local dynamic polarizability tensors α ,^[6]

$$\chi(\vec{r}, \vec{r}', iu) = -\frac{1}{e^2} \partial_{r_i} \partial_{r'_j} \alpha_{ij}(\vec{r}, \vec{r}', iu) \quad (3)$$

provided that α vanishes at the system's edges, or at infinity. Using integration by parts, one obtains from (2) and (3)

$$E^{(2)} = -\frac{\hbar}{2\pi} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}'_1 d\vec{r}'_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|^3} \frac{1}{|\vec{r}'_1 - \vec{r}'_2|^3} \times \sum_{ijkl=1}^3 t_{ik}(\vec{r}_{12}) t_{jl}(\vec{r}'_{12}) \int_0^\infty \alpha_{ij}^{(1)}(\vec{r}_1, \vec{r}'_1, iu) \alpha_{kl}^{(2)}(\vec{r}_2, \vec{r}'_2, iu) du \quad (4)$$

$$\approx -\frac{\hbar}{2\pi R^6} \sum_{ijkl=1}^3 t_{ik}(\vec{R}) t_{jl}(\vec{R}) \int_0^\infty A_{ij}^{(1)}(iu) A_{ij}^{(2)}(iu) du \text{ as } R \rightarrow \infty \quad (5)$$

where

$$t_{ij}(R) = \frac{3\vec{R}_i \vec{R}_j - \delta_{ij} |\vec{R}|^2}{R^2}, \quad A_{ij}(iu) = \int d\vec{r} d\vec{r}' \alpha_{ij}(\vec{r}, \vec{r}', iu).$$

From (5) it is clear that the dispersion energy $E^{(2)}$ is of $O(R^{-6})$ at large separations, and that $E^{(2)}$ depends, in general, on the orientation of the two systems as embodied in the principal axes of the net dipole polarizability tensors $A^{(1)}$, $A^{(2)}$. For isotropic polarizabilities we have $A_{ij} = \delta_{ij} A$, and then we obtain the familiar formula

$$E^{(2)} = -C_6/R^6, \quad C_6 = \frac{3\hbar}{\pi} \int A^{(1)}(iu) A^{(2)}(iu) du. \quad (6)$$

For non-overlapping electronic systems one can go further within perturbation theory with respect to the inter-system Coulomb interaction. For example, by going to third order, one finds an interaction between three separated systems, which cannot be expressed as the pairwise sum of R^{-6} Hamaker terms such as (5) or (6). At large separations and spherical systems the leading (dipolar) contribution to this third-order term has the Axilrod–Teller form^[7]

$$E^{(3)vdW} \approx \frac{C_9}{R_{12}^3 R_{23}^3 R_{13}^3} \quad (7)$$

where C_9 contains some angular dependence.

For more closely spaced, but still not overlapping, electronic densities, one can go beyond the dipolar expressions such as (5) by making a multipolar expansion of the coulomb potential in (4). The chemical literature contains many papers whose results are equivalent to an expansion of the pair interaction (4) in terms of multipole polarizabilities of the two separate systems. A summary of this approach can be found in the review by Jeziorski et al.^[4]

(b) Numerically Exact Evaluation of R^{-6} Hamaker Term

As can be seen from (5), calculation of the Hamaker constant for a pair of systems can be achieved by computation of the net dipole polarizability A of each system for all frequencies. Equivalently, more direct perturbative expressions require a wide range of excited-state energies and dipole matrix

elements of each system. For atomic or small molecular systems, standard quantum-chemical packages are able to perform these tasks quite well. Methods of time-dependent density functional theory are also becoming popular for such purposes.^[8–14]

As the molecules become larger, however, even these methods become cumbersome. Some attempts have, therefore, been made to simplify the evaluation of Hamaker constants along the lines of static, but spatially non-local, density functionals. An older approach for a pair of many-atom systems was to perform pairwise addition of atomic R^{-6} Hamaker contributions. These approaches for the asymptotic vdW interaction are discussed in the following two sections.

(c) Approximations to the Zaremba–Kohn Formula, Leading to Non-Local Asymptotic vdW Density Functionals

Conventional Local-Density and Generalized Gradient approximations miss the asymptotic van der Waals interaction completely. Simple non-local density functionals can be obtained, however. In the present context, the easiest way^[15] to obtain formulae of this type is to approximate the exact asymptotic formula (4) by making a local uniform gas-based approximation

$$\alpha_{ij}(\vec{r}, \vec{r}', iu) \approx \frac{n(\vec{r})}{m[\omega_p^2(\vec{r}) + u^2]} \delta^3(\vec{r} - \vec{r}') \quad (8)$$

where $n(\vec{r})$ is the ground-state electron density and

$$\omega_p(\vec{r}) = \sqrt{4\pi n(\vec{r})e^2/m} \quad (9)$$

is the local plasma frequency. Equations (4) and (8) lead, after some algebra,^[15] to a highly non-local density functional

$$E^{(2)} \approx -\frac{3\hbar e^{1/2}}{4(4\pi)^{3/2} m^{1/2}} \int_a d\vec{r}_1 \int_b d\vec{r}_2 \frac{1}{r_{12}^6} \frac{\sqrt{n_a(\vec{r}_1)n_b(\vec{r}_2)}}{(\sqrt{n_a(\vec{r}_1)} + \sqrt{n_b(\vec{r}_2)})}. \quad (10)$$

Rapcewicz and Ashcroft,^[7] using a different argument, had earlier obtained a formula similar to (10), and found that it gave reasonable results for atomic Hamaker constants, but only if a cutoff was applied in the low-density tails where the reduced density gradient exceeds the local Thomas–Fermi screening wavenumber. Andersson et al.^[16] modified the Ashcroft–Rapcewicz formulae and by these means were the first to obtain the result (10). Once again reasonable results for atoms were obtained provided that the Rapcewicz–Ashcroft cutoff was applied. Otherwise the Hamaker constants were severely overestimated. Hult et al.^[17] tried the same approach for larger systems including metal surfaces. They found that the Rapcewicz–Ashcroft cutoff was not appropriate, which is somewhat puzzling

since the Rapcewicz–Ashcroft cutoff argument, involving electron-gas screening considerations, would appear more appropriate for electron-gas-like jellium surfaces than for atoms where the cutoff is in fact successful. Hult et al.^[17] further found that reasonable results could be obtained, instead, by taking static response properties (image plane) from a more microscopic calculation, then using this information to make a model of the dynamic response. A similar approach was also applied to atoms,^[18] where the use of a cutoff was once more avoided by using the static dipolar polarisability as input. The present authors recently^[19] attempted to use an exact sum rule to avoid both cutoffs and the use of prior static response calculations. While this approach shows some promise for static polarizabilities, further refinement is needed to make it work with a useful degree of generality.

(d) Pairwise Addition of R^{-6} Atomic Contributions—Counter Examples

The exact approaches based on (2) (or equivalent methods) become unwieldy when applied to the Hamaker constant between systems containing many atoms. It has, therefore, been common in the past (see for example references in Mahanty and Ninham^[20]), and indeed is still common in biochemical modelling^[21] to add separate energy contributions of form $C_{ab}^{(ab)}/R_{ab}^6$ for each pair of atoms, where atom a is in the first subsystem and atom b is in the second. In current biochemical modelling packages the $1/R^6$ term is frequently introduced as part of a pairwise Lennard–Jones potential $V_{ab}(R_{ab}) = A_{ab}(x^{-12} - x^{-6})$, where $x = R_{ab}/\sigma_{ab}$ is a scaled separation parameter. The short-ranged repulsive x^{-12} contribution has no basis in microscopic theory, so that any fit to the interaction between nearby parts of large systems must be regarded as purely empirical. The attractive x^{-6} term does have a physical basis, representing an additive pairwise Hamaker term which is indeed the correct form between two isolated atoms at large separation R , to leading order in $1/R$.

For multi-atom systems, however, this pairwise addition of atomic interactions is not strictly correct to leading order in $1/R$, even at large separations. The reason is basically that the mutual dynamic polarization phenomenon applies not only to pairs of atoms but also to triplets (see the Axilrod–Teller formula, equation (7)) and to higher groupings. To see that the triplet atomic energy terms affect

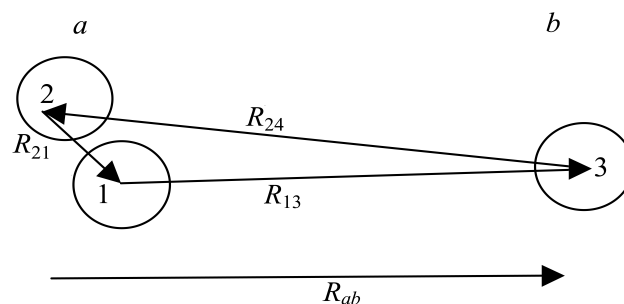


Fig. 2. Counter-example to additivity of C_6R^{-6} energies.

the leading Hamaker $1/R^6$ coefficient C_6 between multi-atom groups, consider the somewhat idealized situation shown in Figure 2. Atoms 1, 2 and 3 are all spherical closed-shell atoms of the same species. System a consists of atoms 1 and 2 in close (but not overlapping) proximity, held (artificially) at a constant separation R^{12} . System b consists of atom 3, which is separated from the centre of mass of system a by a distance R . We imagine varying the distance R while holding R_{12} constant. Including the pairwise terms from equation (6) and the triplet terms from equation (7) we find the part of the interaction involving both system a and system b is

$$E^{(2+3)} = \frac{C_6}{R_{13}^6} + \frac{C_6}{R_{23}^6} + \frac{C_9}{R_{12}^3 R_{13}^3 R_{23}^3}.$$

At large distances $R \rightarrow \infty$ we have $R_{13} \approx R$ and $R_{23} \approx R$ so that the leading interaction between molecules a and b is

$$E^{(2+3)} = \frac{C_6^{(ab)}}{R^6}, C_6^{(ab)} = 2C_6 + \frac{C_9}{R_{12}^3}. \quad (11)$$

Notice that R_{12} is a fixed quantity independent of R as long as molecule a retains its shape. Assuming only pairwise interactions we would obtain only the first term $C_6^{(ab)} = 2C_6$ instead of the full result (11). Thus the pairwise summation method does not even give the correct results to leading order in $1/R$. For any particular class of systems (e.g. proteins) one can perhaps compensate for this partially by using an empirical atomic coefficient C_6 rather than the correct one derived for isolated atoms.

Clearly if there were three atoms in molecule a , then quadruplet vdW interactions between four atoms simultaneously would also contribute to $C_6^{(ab)}$. What has failed in the pairwise summation approach is that the mutual polarisation between a given pair of atoms, one in system a and one in system b , is affected by consequent polarization of the other atoms in each system. Consider for example two thick insulating slabs of atomic solid of infinite surface area, separated by distance D . The pairwise summation method yields an attractive vdW energy with the correct D^{-2} distance dependence, but with the wrong coefficient. An extreme case of this cooperative phenomenon occurs when systems a and b are thin metallic films or quantum well electron gases of thickness L . Then pairwise summation of atomic $1/R^6$ interactions fails spectacularly, giving a vdW energy of form $E = KD^{-4}$, where $D \gg L$ is the distance between the parallel slabs of metal. By treating the problem in terms of coupled two-dimensional plasmons as is appropriate to metallic systems (see below) one finds that the correct distance dependence of the vdW energy is in fact of the form $E = K'D^{-5/2}$, so that both the power law and the coefficient are wrong within pair summation theory. This discrepancy is due not only to massively mutual polarization, but also to the fact that electrons can flow freely from atom to atom inside each metal film, a phenomenon not envisaged in the derivation of an assumed $1/R^6$ interatomic vdW energy.

III. Quantitative Methods for Calculating Distant vdW Interactions: Infinite Systems

(a) Zaremba–Kohn Formula

The perturbative formula (2) is correct in the distant non-overlapping limit, for two finite systems. It is also correct for a combination of one infinite and one finite system, such as a molecule near a metal surface. It breaks down, however, for certain cases where both systems are infinite, for example two parallel metal surfaces. There, contrary to the assumptions used in obtaining (2), the Coulomb interaction between the two systems cannot be treated as a perturbation, basically because an infinite number of image reflections of the field are involved. In these cases other methods can be used, however. Perhaps the simplest of these is the coupled-plasmon approach in a hydrodynamic approximation.

(b) Coupled Plasmon Approach

In its simplest (zero-temperature) form, the coupled plasmon theory equates the separation-dependent part of the inter-system energy to the (finite) separation-dependent part of the (infinite) zero point energy of the plasmons of the combined system:

$$\Delta E = \frac{\hbar}{2} \sum_j \Delta \omega_p^{(j)}. \quad (12)$$

Here the $\{\omega_p^{(j)}\}$ are the set of electron plasmon frequencies of the combined, Coulomb-coupled systems. $\Delta \omega_p^{(j)}$ is the change in the j th plasmon frequency due to a change in relative positions of the interacting subsystems, and ΔE is the corresponding change in the total ground-state energy. While (12) seems very plausible, it concentrates on collective zero-point motions and neglects single-particle like motions.

To derive (12) we can start from an exact but highly formal expression for the ground-state electronic correlation energy of an arbitrary system, which will also be useful in discussing other approaches below. This expression, known as the adiabatic connection–fluctuation dissipation^[22] theorem, can be written as follows:

$$E_{xc} = -\frac{\hbar}{2\pi} \int_0^1 d\lambda \int d^3r d^3r' \frac{e^2}{|\vec{r} - \vec{r}'|} \left[\int_0^\infty \chi_\lambda(\vec{r}, \vec{r}', \omega = is) ds - \delta^3(\vec{r} - \vec{r}') n(\vec{r}) \right] \quad (13)$$

$$E_c = -\frac{\hbar}{2\pi} \int_0^1 d\lambda \int d^3r d^3r' \frac{e^2}{|\vec{r} - \vec{r}'|} \left[\int_0^\infty ds (\chi_\lambda(\vec{r}, \vec{r}', \omega = is) - \chi_0(\vec{r}, \vec{r}', \omega = is)) \right] \quad (14)$$

Equation (13) follows by combining the adiabatic connection formula^[23,24] (ACF) with the zero-temperature fluctuation-dissipation theorem (FDT). The physical meaning of (13) is discussed, for example, in Chapters 1 and 4 of a recent Proceedings volume.^[25] In (13), $\chi_\lambda(\vec{r}, \vec{r}', \omega = is)$ is the imaginary frequency Kubo density–density response

function of the whole system, with an additional external potential $V_\lambda(\vec{r})$ added so as to maintain the true ($\lambda = 1$) ground-state density $n(\vec{r})$ in the presence of a modified electron–electron interaction $\lambda V_{coul} \equiv \lambda e^2/|\vec{r} - \vec{r}'|$. The $\lambda = 0$ response χ_0 is thus the Kohn–Sham density–density response: i.e. it is the response of independent Fermions moving in the ground-state Kohn–Sham potential $V_{KS}(\vec{r})$, the latter being the one-particle potential required to produce the true interacting ground-state density when acting on independent Fermions.

The interacting response χ_λ and the bare response χ_0 in (13) are related by the exact Dyson-like screening equation^[10]

$$\chi_\lambda = \chi_0 + \chi_0 * (\lambda V_{coul} + f_{xc,\lambda}) * \chi_\lambda. \quad (15)$$

Here $\chi_\lambda \equiv \chi_\lambda(\vec{r}, \vec{r}', \omega = is)$, and is the exchange–correlation kernel of the inhomogeneous system. The spatial convolution of two functions has been denoted $(a*b)(\vec{r}, \vec{r}') = \int a(\vec{r}, \vec{r}_1) b(\vec{r}_1, \vec{r}') d^3 r_1$. While f_{xc} is not known for inhomogeneous systems, some information is available for the uniform electron gas.^[10,11,26] The state of the art for weakly inhomogeneous systems is the tensor xc kernel \mathbf{f}_{xc} of Vignale and Kohn.^[27] We do not use this here because it is valid only for $\omega \gg v_F q$, where v_F is the local Fermi wavenumber and q is the wavenumber of the perturbation: by contrast the ACF/FDT (equation (13)) requires an integral over all frequencies ω .

It is interesting to note^[28] that the Zaremba–Kohn formula (2) can be derived from (13) by expanding the screening equation (15) to first order in the inter-system Coulomb potential, assuming that $f_{xc,\lambda}$ is short-ranged and proportional to λ . Another approach^[29] has been given, also using perturbation expansion of (15) but treating the entire Coulomb interaction as a perturbation, more akin to Moeller–Plesset perturbation theory.

If (15) is expanded to third order in the Coulomb interactions between three systems, then results of the Axilrod–Teller type (see equation (7)) can be obtained.

The Random Phase Approximation (RPA) is obtained by neglecting $f_{xc,\lambda}$ in (15). Within the RPA one can evaluate the coupling constant integral in $\int d\lambda$ in (13), leading to a logarithm in which χ_λ is evaluated at the physical interaction strength $\lambda = 1$. The interacting response function $\chi_{\lambda=1}$ has poles at the plasmon (collective electron oscillation) frequencies $\omega_p^{(j)}$. Ignoring the branch cuts which must also be present when $\chi_{\lambda=1}$ is calculated microscopically, one can then also perform the integral over imaginary frequency $\int ds$ in (13) by using a theorem which relates logarithmic integrals to a sum of poles minus a sum of zeros (or to a differences sums of poles: see for example equation 1.75 of Mahanty and Ninham^[20]). This then leads to (12).

(c) Coupled Plasmon Approach in the Hydrodynamic Approximation

For well-separated, large non-overlapping metallic systems such as a pair of metal surfaces, a tractable approximation to

(12) is obtained by evaluating the plasmon frequencies $\omega_p^{(j)}$ by electron hydrodynamics. This type of approach has been extensively explored.^[30,31] Two examples are given now, the first of which is a relatively new development.

(i) Two-Dimensional Nondispersive Hydrodynamic Electron Gas Model

In this hydrodynamic model we consider two thin metal slabs, each of which is treated as a two-dimensional (2-D) electron gas (egas) of areal electron number density N_s . The bare in-plane response of each electron gas is modeled by the displacement $\vec{x}(\vec{r}_\parallel, \omega) = \vec{\nabla}_\parallel V(\vec{r}_\parallel)/(m \omega^2)$ of free electrons at position \vec{r}_\parallel in the plane, to a total effective electric field $\vec{E}_\parallel(\vec{r}_\parallel) = e^{-1} \vec{\nabla}_\parallel V$. The first neglected term in this approximation is a pressure force proportional to a density gradient, so that we have a long-wavelength or low- q theory. The density perturbation is then $n(\vec{r}_\parallel) = -N_s \vec{\nabla}_\parallel \vec{x}$. Fourier transforming in the plane we obtain a density perturbation $n(q_\parallel, \omega) = \chi_0^{2D}(q_\parallel, \omega) V(q_\parallel, \omega)$ where

$$\chi_0^{2D}(q_\parallel, \omega) = \frac{N_s q_\parallel^2}{m \omega^2}.$$

When two egases ‘1’ and ‘2’ are separated by distance D each gas responds to a total dynamic mean field including contributions from its own density distortion and that in the other gas. The unforced dynamics are then described by the equations

$$n_1 = \chi_0^{2D} \left(\frac{2\pi e^2}{q_\parallel} n_1 + \frac{2\pi e^2 e^{-q_\parallel D}}{q_\parallel} n_2 \right) \quad (16)$$

$$n_2 = \chi_0^{2D} \left(\frac{e^2}{2\pi q_\parallel} n_2 + \frac{2\pi e^2 e^{-q_\parallel D}}{q_\parallel} n_1 \right). \quad (17)$$

The eigen-frequencies ω_\pm obtained from these equations are given by

$$\omega_\pm^2(q_\parallel, D) = \omega_{2D}^2(q_\parallel) \left[1 \pm \exp(-q_\parallel D) \right] \quad (18)$$

where

$$\omega_{2D}(q_\parallel) = \sqrt{\frac{2\pi N_s e^2 q_\parallel}{m}}$$

is the 2-D plasma frequency. Note that $\omega_+(q_\parallel, D \rightarrow \infty) = \omega_-(q_\parallel, D \rightarrow \infty) = \omega_{2D}(q_\parallel)$.

The cross-correlation energy of the egases is obtained as the difference of zero-point energies between separation D and separation ∞

$$\begin{aligned}
E_c^{cross} &= \frac{\hbar}{2} \frac{A}{(2\pi)^2} \int_0^\infty 2\pi q_{\parallel} dq_{\parallel} \\
&\quad \left[\omega_+(q_{\parallel}, D) + \omega_-(q_{\parallel}, D) - 2\omega_{2D}(q_{\parallel}) \right] \\
E_c^{cross}/A &= \frac{\hbar}{2} (2\pi)^{-1} \sqrt{\frac{2\pi N_s e^2}{m}} \int_0^\infty q_{\parallel}^{3/2} dq_{\parallel} \\
&\quad \left[\sqrt{1 + \exp(-q_{\parallel} D)} + \sqrt{1 - \exp(-q_{\parallel} D)} - 2 \right] \\
&= \frac{\hbar}{4\pi} \sqrt{\frac{2\pi e^2 N_s}{m}} D^{-5/2} \\
&\quad \int_0^\infty x^{3/2} \left(\sqrt{1 + \exp(-x)} + \sqrt{1 - \exp(-x)} - 2 \right) dx \\
&= -1.256_2 \times 10^{-2} \hbar \sqrt{\frac{e^2 N_s}{m}} D^{-5/2} \quad (19)
\end{aligned}$$

This result agrees with the appropriate limit of microscopic RPA calculations for a pair of 2-D electron gases, as quoted by Sernelius and Bjork.^[32]

(ii) *Hydrodynamic Model: Non-dispersive Semi-Infinite Jellia*

In this model we consider two very *thick* metal slabs, in contrast to the previous calculation which treated the limit of zero thickness. A positive background of three-dimensional (3-D) charge density en_0 is taken to occupy two half-spaces, $z < -D/2$ and $z > D/2$. In each halfspace we once again neglect the electron gas pressure, yielding a plasma dielectric function $\epsilon = 1 - \frac{\omega_p^2}{\omega^2}$, where $\omega_p = \sqrt{(4\pi n_0 e^2/m)}$ is the bulk (3-D) plasma frequency. Matching fields at the boundaries, we obtain plasmons with a density perturbation of form $f(z)\exp(i[q_{\parallel|x} + q_{\parallel|y}, y])$ and a dispersion

$$\omega_{\pm}^2 = \omega_p^2 \frac{1 \pm e^{-q_{\parallel} D}}{2}.$$

This is a well-known model, and the sum of zero-point energies gives the following for the separation-dependent part of the energy per unit area:

$$\begin{aligned}
E_c^{cross}/A &= \frac{\hbar}{4\pi} \frac{\omega_p}{\sqrt{2}} D^{-2} \\
&\quad \int_0^\infty x \left(\sqrt{1 + e^{-x}} + \sqrt{1 - e^{-x}} - 2 \right) dx, \quad x \equiv q_{\parallel} D \\
&= -5.522_8 \times 10^{-3} \frac{\hbar \omega_p}{\sqrt{2}} D^{-2} \quad (20)
\end{aligned}$$

Results for two insulating surfaces can be obtained by similar methods involving a macroscopic description of the dielectric response ϵ of the materials involved: see, for example, p. 47 of Mahanty and Ninham.^[20]

(d) *Summary of Methods for a Well-Separated System*

Prediction of asymptotic vdW forces between a pair of small well-separated systems presents no fundamental problem, requiring only an accurate calculation of dipolar polarisabilities at a sufficient number of frequencies. For closer but still non-overlapping separations, multipolar response theory can be used.

Large systems of simple geometry can also be handled by macroscopic or hydrodynamic methods, provided that the separation D is great enough.

The situation is different when electronic clouds begin to overlap so that exchange phenomena occur and other forms of bonding coexist with vdW effects. Here, there is not a clear-cut distinction between local correlations and the more distant vdW type of correlation. With reference to the title of the present paper, in the following sections we will argue, with some examples, that there is indeed a “problem”: in practice, standard methods are not always satisfactory in these situations, especially for larger systems.

IV. Methods Valid for Overlapped Systems: Seamless vdW Calculations

Approaches which permit correct calculation of distant dispersion (vdW) forces, but which remain valid into the regime of electron density overlap, are sometimes termed *seamless vdW formalisms*.^[14,33] Distant van der Waals interactions clearly represent a correlation phenomenon. Of course correlation can also be significant in overlapped regimes, and in these cases there is probably no fully clear-cut distinction between dispersion interactions and those from other forms of correlation. An interesting case is that of *aurophilic interactions*, which involve shortening of Au–Au distances between the metal cores in inorganic and organic gold complexes, when correlation is taken into account subsequent to a HF calculation. In the context of aurophilic interactions, Pykko^[34] has suggested that dispersion correlations should shorten bonds whereas other forms of correlation may lengthen them. In the discussion of rare-gas dimers that we will present below, we will attempt to introduce a qualitative picture that distinguishes the correlations responsible for dispersion forces (see particularly Fig. 6).

We now discuss in turn the suitability of some standard (and some not-yet-standard) methods for seamless vdW calculations.

(a) *Configuration Interaction (CI)*

This method^[3,2] minimizes the total energy over a trial wavefunction that is a coherent sum of the ground-state Hartree–Fock determinant and a finite number of excited determinants. These determinants can contain one promoted electron (*singles*), two promoted electrons (*doubles*), etc. CI calculations are limited in practice to small systems, but they

are certainly capable of reproducing the vdW interaction. For example, in order to achieve a non-zero vdW interaction between two non-overlapping atoms, one needs to consider at least doubles excitations, in which one creates a coherent mixture of ground and excited state on one atom, simultaneously with a similar mixture on the other. This method is typically implemented using localised atomic bases, though these often have to be supplemented with diffuse functions in order to reproduce the highly polarizable outer orbitals. When the atoms are brought together, counterpoise basis sets typically have to be used to avoid achieving different accuracies at different interatomic spacings. Otherwise, extra unphysical effects occur in the variational energy when the atoms overlap, because the two localized bases share the same spatial region, with effects similar to a finer spatial grid. This *basis set superposition error* is not unique to the CI approach but is common to all methods relying on *total* energies derived from atom-centred basis sets, within a supermolecule approach where both interacting subsystems are treated together.

To get the full Hamaker constant for two distant molecules from the super-molecule CI approach, one will need to account for dynamic internal screening within each molecule. This presumably requires a treatment beyond the doubles level, with consequent high computational cost.

Full CI (i.e. a treatment beyond doubles) has been applied^[35] to a He₂ dimer near the van der Waals equilibrium separation R_0 . Good agreement was obtained with Coupled Cluster Singles-Doubles-Triples (CCSD(T)) theory. The CI calculation gave a weaker binding energy (31 μ Hartree) than a Quantum Monte Carlo calculation^[36] (34.8 μ Hartree). This discrepancy was largely removed by an approximate extrapolation to basis set saturation in the CI calculation.

It is not clear whether the CI results extend to large enough separations to identify the C_6 coefficient accurately.

(b) Moeller–Plesset Perturbation Theory

Moeller–Plesset (MP) perturbation theory^[3,4] treats all electron–electron interactions (beyond the Hartree–Fock level) as a perturbation. Second-order Moeller–Plesset theory (MP2) is routinely available in commercial quantum chemistry packages. Higher-order versions are available in some packages, at very significant computational cost for systems of more than a few electrons.

(i) MP Theory and the Asymptotic vdW Limit ($R \rightarrow 1$)

Because the asymptotic vdW interaction between finite systems is derivable from a type of second-order Coulomb perturbation theory (see above), supermolecule MP2 theory is indeed able to produce distant vdW pair interactions of the correct R^{-6} form (1). The MP2 value of the Hamaker constant C_6 in equation (1) is not, in general, accurate, however. It is of the correct form given in (6) or more generally (5), but it contains the *bare* polarizabilities $A^{(0)}$ of the subsystems rather than the correct interacting values A : only the latter include dynamic electron–electron interactions inside each subsystem (dynamic intra-atom screening). The reason for this discrepancy is that the

second-order perturbation approach leading to the exact asymptotic results (5), (6) treats only the Coulomb interaction V_{12} between the two subsystems as a perturbation: the dynamic coulomb interactions V_{11} , V_{22} inside each subsystem are assumed to be treated exactly. Because they treat *all* dynamic electron–electron interactions on an equal footing as a perturbation, finite-order MP calculations cannot give the exact answer for the Hamaker constant. In particular, supermolecule MP2 theory has already “used up” both orders of perturbation theory in describing the basic intersystem vdW interaction, leaving no room (within the separation-dependent energy term) for perturbations within each subsystem. The review article by Jeziorski et al.^[4] also stresses the need for inclusion of correlations *within* vdW-interacting fragments, and not only between them.

In practice the difference between A and $A^{(0)}$ can be fairly small for some smaller atoms, especially those with closed n-shells, or with one electron in excess of such a relatively rigid full-shell core. That is, one electron in excess a full n-shell yields a polarisability differing little from the bare quantity. The reason is basically one of forbidden self-interaction:^[37,38] a single electron, added over the relatively inert closed shell, cannot polarize itself and hence cannot correlate with itself. For example, using a time-dependent density functional formalism that is free of spurious orbital self-interaction, we found,^[39] for He, Li, Ne and Na, that the bare dipolar polarizabilities $A^{(0)}$ differ from the interacting ones, A , by only a few percent. The same was true for the $C_6^{(0)}$ and C_6 coefficients obtained from equation (6). For such cases, MP2 can be expected to give a fairly accurate account of the distant part of the dispersion interaction, provided adequate basis sets are used.

For Be, Mg and Zn, on the other hand, we found that the bare polarizability over-estimates the true value by 100% or more at low frequency, and the C_6 coefficient is similarly strongly affected by dynamic intra-atom interactions. This is because of strong mutual polarization/correlation between the two loosely-bound outer electrons. For these atoms, and for large polarizable finite systems in general, the MP2 overestimation of C_6 can be quite significant. Thus, for example, we do not expect MP2 to give a good account of the distant interaction between two benzene rings. See also the following section for discussion of the benzene dimer near the equilibrium separation.

At any rate, being a total-energy method, the MPx supermolecule approach for dispersion energies at large separations depends on small differences of large numbers. If implemented in the normal fashion with a local basis, this method will also require the usual correction for basis set superposition error.

(ii) MP Theory for Closely Adjacent Systems

Although we have just argued that MP2 does not, in general, give the correct strength for the asymptotic dispersion force at large separations, this in itself does not necessarily imply that MP2 results will be poor at small separations near the equilibrium molecular bond distance.

There is, however, evidence that fourth-order Moeller–Plesset theory (MP4), or higher, is needed, for accurate reproduction of the force between two rare-gas atoms, near the minimum-energy separation. MP2 was found by Woon^[35] to produce qualitatively reasonable, but quite inaccurate results, for the rare-gas dimers He₂, Ne₂ and Ar₂. Now He₂ and Ne₂ are systems where we expect the distant vdW interaction to be reasonably well reproduced by MP2, as discussed in the previous paragraph, but the work of Woon shows that, even in these cases, MP2 is not reliable at *short* distance.

MP2 has also been used recently to investigate the correlation aspects of the force between benzene rings^[40,41] and finite planar graphene fragments,^[42] both near their equilibrium separations. The MP2 results were found^[43,44] to be inadequate when compared with CCSDT calculations. Even MP4 did not produce the correct energetic ordering of rival weakly bound benzene dimer structures. For the case of larger graphitic fragments, Ruuska et al.^[42] gave MP2 results and considered that MP4 and CCSDT calculations would not be feasible at present. The relatively large spatial extent of the π_z cloud on each graphene subsystem suggests that MP2 will be inadequate also for large intermolecular separations because of dynamic intramolecular screening, which will lead to a large difference between the bare and interacting polarizabilities.

Hence we feel that further study of these issues is required, especially if one is interested in ‘stretched’ bonds and graphitic systems.

(iii) MP2 for Large Metallic Systems

As noted above, for infinite systems such as parallel metal surfaces, Coulomb perturbation theory fails significantly, so any perturbative method including MP2 (or even MP4) can be expected to give qualitatively wrong predictions for vdW effects. We expect that ‘stretched’ graphite and intercalated graphene systems are likely to fall within this category.

(c) More Sophisticated Perturbation Theory: Symmetry-Adapted Perturbation Theory, etc.

Rather than considering the small dispersion component of a large total energy (as in direct supermolecule MP or CI approaches) it can be advantageous to treat the interaction between the subsystems separately. In overlapped situations this cannot be done by assuming electrons on different subsystems are distinguishable, however. Otherwise exchange effects are missed, and indeed, the simplest perturbation theory described above for non-overlapping systems diverges when overlap is present. What is needed is an approach that still distinguishes subsystems and singles out their cross-interaction, but in which the correct Pauli antisymmetry of the many-body wavefunction under particle-label interchange is preserved. Approaches which project out states with incorrect exchange symmetry have been termed *symmetry-adapted perturbation theory* and have been reviewed extensively by Jeziorski et al.^[4] This approach seems to have had considerable success for small to moderate-sized molecules, but will presumably fail for

problems such as parallel metal surfaces where Coulomb perturbation theory is inappropriate. Chapter 14 of McWeeny’s 1989 book^[2] discusses a somewhat related approach.

(d) Monte Carlo (MC) Approaches

(i) Variational Monte Carlo Calculations

These typically estimate the ground-state energy by statistical sampling of the energy integral $\langle \Psi | \hat{H} | \Psi \rangle$ over a many-body trial wavefunction of Jastrow form:

$$|\Psi\rangle = \prod_{i,j} f(\vec{r}_i, \vec{r}_j) \text{Det}(\{\phi_k\}) \quad (21)$$

A wavefunction of this form, with a simple short-ranged trial Jastrow function f , does not exhibit the correct long-ranged correlation physics leading to the vdW interaction. It is perhaps possible to achieve the correct physics by using a pair factor f with a long-ranged vdW part, which will have to be specific to the particular geometry at hand. Perhaps the form of the Jastrow factor could be motivated from RPA-type pair distributions (see below). The authors are not aware of any such Jastrow-vdW calculations on large systems, however.

(ii) Diffusion Monte Carlo Calculations

These calculations sample imaginary-time Schrodinger evolution under the interacting many-electron Hamiltonian, typically starting from a Jastrow wavefunction of the form (21). Apart from statistical sampling errors and the Fermion sign problem, this method should converge to the exact many-body ground-state, which of course contains all vdW effects. These calculations are limited to finite electron numbers, requiring careful scaling and noise analysis when applied to larger systems. The authors are unaware of any such calculations specifically demonstrating the van der Waals interaction between large electronic systems. In order to describe the dispersion energy, they would of course necessarily involve small differences of large energies.

(iii) Green Function Monte Carlo

This type of approach re-expresses the many-electron Schrodinger equation as an integral equation using a Green function approach. The integral equation is solved by an iterative method, using Monte-carlo importance sampling based on a given initial trial many-body wavefunction, usually of Jastrow variational form. Like diffusion Monte Carlo methods, this approach will in principle give exact answers subject to noise limitations. Anderson et al.^[36] used this method to compute the binding energy curve of the He₂ dimer, obtaining a binding energy of 11.01 ± 0.1 K = 34.8 μ Hartrees at a separation of 5.6 au. This is to be compared with about 34 μ Hartrees estimated by Woon^[35] from the basis-set saturation limit of his full CI calculations.

(e) Random Phase Approximation (RPA) and Related Time Dependent Density Functional Methods

The RPA is equivalent to the summation of an infinite subset of perturbation terms (ring diagrams). In the present context,

it consists of neglect of the exchange-correlation kernel $f_{xc,\lambda}$ in the dynamic screening equation (15). The bare response function χ_0 corresponds to a single open loop in diagrammatic perturbation theory. Iterative solution of the screening integral equation (15) (with $f_{xc} = 0$) produces all possible closed ring diagrams with open loops joined by Coulomb lines. This amounts to a mean-field (correlationless) approximation for the finite-frequency interacting density response function χ_λ . A substantial level of correlation energy is nevertheless generated when the interacting χ_λ^{RPA} is used in the Adiabatic Connection-Fluctuation Dissipation formula (13) to calculate the ground-state energy E_{xc} . In particular, an approximation to the vdW (dispersion) energy is included in this RPA correlation energy. Specifically, it has been shown,^[28] by expanding the screening equation (15) to first order in the inter-subsystem part V_{12} of the Coulomb interaction, that the RPA correlation energy contains essentially the Zaremba–Kohn^[5] formula (2) which gives the asymptotic vdW energy as discussed above.

However, the susceptibilities χ_1, χ_2 appear as the RPA versions rather than the exact interacting susceptibilities that appear in the true Zaremba–Kohn formula. (This is to be compared with the MP2 approach in which χ_1 and χ_2 appear as the bare versions.) In the distant limit, this means that the RPA versions of the subsystem dipolar polarizabilities A will appear in the Hamaker constant formulae (6), (5).

A major advantage of the RPA approach is that it is not limited to cases where at least one subsystem is small (unlike perturbation theory in V_{12}) nor is it limited to cases without overlap. To obtain the correct Hamaker constant for pairs of finite systems, one needs to supplement the RPA equations with a non-zero exchange-correlation kernel $f_{xc} \neq 0$, thus implementing the time-dependent density functional formalism,^[9,10] (see equation (15)). If the kernel is realistic enough to predict an accurate frequency-dependent dipolar polarizability of each subsystem, then the RPA + f_{xc} formalism provides a seamless vdW theory with the correct distant Hamaker limit. There is a substantial literature concerning the calculation of atomic and cluster polarizabilities by TDDFT.^[39,45–52]

It is important to note that the full RPA equations include exchange energy between the two subsystems, and therefore covalent bonds, for example, will be described in a seamless fashion, in addition to any vdW bonds. Specifically, if the bare ($\lambda = 0$) density response is used in the Adiabatic connection formula (13), the exact (non-local) DFT exchange energy of the combined systems is recovered. The correlation energy is introduced, in addition to exchange, by going from the bare to the interacting response function χ . Some higher-order exchange diagrams (exchange-correlation cross terms) are neglected in the RPA, but can be treated approximately by inclusion of a suitable approximate exchange-correlation kernel $f_{xc,\lambda}$ in the screening equation (15).

The full implementation of the RPA energy equations ((13) and (15) with $f_{xc,\lambda} = 0$), while trivial for the uniform electron gas for which the RPA approach was originally

developed,^[53] is numerically demanding for inhomogeneous systems. Although solution of the RPA screening equation (15) has been commonplace, e.g. for the computation of plasmon or other collective oscillation frequencies, the extensive integration over the resulting interacting susceptibility, as in equation (15), has rarely been attempted for inhomogeneous electronic systems. Recently, however, the full RPA equations have been used to find the surface energy of jellium^[54] and the vdW interaction between jellium slabs.^[33] Both of these calculations were genuinely inhomogeneous treatments, in that the smooth self-consistent decay of the electron density at the jellium edge was fully accounted for. The infinite planar jellium slab geometry is a rather special case in the van der Waals context. One can show,^[33,55] using a form of the f-sum rule, that the coefficients C_4 and $C_{5/2}$ are unaffected by the inclusion of any short-ranged xc kernel in the screening equation (15). These coefficients are defined by the asymptotic vdW energy formulae $-C_2 D^{-2}$ for two jellium half-spaces, and $-C_{5/2} D^{-5/2}$ for two 2-D electron gases (the same results as obtained above from hydrodynamic arguments). This insensitivity to f_{xc} has been numerically verified by including an “energy-optimized” xc kernel^[56] within the full RPA equations. As predicted by the f-sum rule, for jellium slab geometry the same distant attractive interaction is obtained as with the pure RPA calculation.^[33] Perhaps more surprisingly, the results were very close to RPA results even when the electron gases in the two slabs were completely overlapped. This suggests that a pure RPA calculation is an accurate, seamless, vdW formalism for this type of geometry. It is clear from the discussion above, however, that inclusion of a nonzero kernel f_{xc} is required for other geometries such as for atoms and molecules, where the f-sum rule alone does not prescribe the asymptotic interaction. The energy-optimized kernel^[56] is a promising computationally efficient approach here, but for small systems it will probably need to be generalized to include a dynamic orbital self-interaction correction. Very recently,^[57] the RPA correlation energy approach (without the xc kernel f_{xc}) has been applied to small molecules.

These considerations suggest that RPA + f_{xc} is one of the most promising formalisms for seamless vdW calculations for larger systems, but it is numerically very demanding as presented above in the frequency domain.^[33] Recently, Kohn et al.^[14] have suggested a potentially efficient real-space, imaginary-time approach to the solution of RPA-like screening problems in vdW situations. To date, however, this method has apparently not been demonstrated in practice for large systems. It has been suggested by Yan et al.^[58] that existing coupled-cluster codes might be a convenient way to implement RPA-like schemes.

(f) Ground-State Density Functional Theory

This is perhaps the most controversial formalism with regard to van der Waals forces. The commonly used Kohn–Sham Local Density Approximation^[59] (LDA) and the various Generalized Gradient Approximations^[60–63] (GGA) are very popular for solid-state (and some molecular) calculations,

because they are computationally less demanding than the other schemes discussed above in the present section. It is well-known, however, that they entirely miss the dispersion energy in the limit of large separations, because they cannot account for correlations between distant electrons when these differ from those of a uniform or near-uniform electron gas.

A clean counter-example to the validity of LDA/GGA can be set up by considering two neutral planar jellium slabs each of thickness L , separated by a region with infinitely high potential and finite thickness D . Imagine that the separation between the slabs is increased by ΔD , by moving the right-hand slab rightwards by ΔD , while the thickness of the infinite barrier is also increased by ΔD . The barrier completely prevents electrons moving between the two slabs, but does not prevent the Coulomb interaction between electrons in the two slabs. Within the LDA (or any theory using only a finite number of local density derivatives), it is easily seen that the two cases have identical ground-state energies and identical density profiles except that the right-hand electron density is moved to the right by ΔD , in the second case. Thus local-gradient theories give no dependence of the ground-state energy on the slab separation D . This assumes that the ground-state density is uniform in the directions parallel to the slab faces, so that the Hartree field at the second slab, due to the first slab, is zero and does not change when the separation is increased. (A departure from this would constitute a symmetry-breaking phase transition to a corrugated ground state. That unlikely situation would involve static multipole–multipole interactions, but these are, in any case, not the dispersion interaction.) By contrast, theories such as RPA or coupled-plasmon hydrodynamics show that in this situation the infinite barrier does not suppress the usual dispersion energy, which depends on the net slab separation as D^{-2} if $L \gg D$ and^[32,33] as $D^{-5/2}$ if $D \gg L$. Thus the LDA/GGA has missed the dispersion energy altogether.

(g) Ground-state DFT Approach: Large Metallic Systems

A concrete and quite informative example of the failure of the LDA in a planar vdW situation was provided by the full RPA calculation of Dobson and Wang,^[33] which involved two slabs of positive background of thickness $L = 5$ au with the background edges separated by distance D : D was varied from zero to 12 au. Here there was no artificial infinite barrier, unlike the idealized counter-example quoted above, and the smooth ground-state density was calculated self-consistently (in the LDA) at all separations down to $D = 0$ where the slabs are in contact forming a metallic bond. As shown in Figure 3, the LDA gives a poor approximation to the separation-dependent total correlation energy $E_c(D)$ at all separations. In particular, as expected from the idealized example above, the LDA misses the dispersion energy altogether at large separations $D \geq 5$ au. It is informative, however, to study the separation-dependent part, $E_g(D)$, of the total ground-state energy, shown for the first time in Figure 4. The total energy for the LDA case (dashed line) is calculated using the LDA for exchange as well as for correlation. The

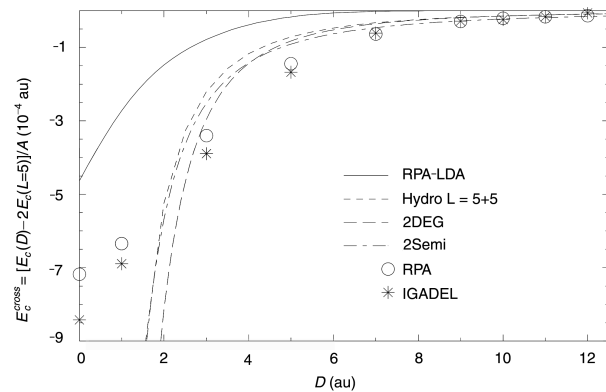


Fig. 3. Cross-correlation energy per unit area between two jellium slabs with 3-D electron density so that $r_s = 2.07$ and positive background thickness $L = 5$ au. $D(\text{au})$ is the separation between the near edges of the positive backgrounds. Unbroken line: LDA using RPA uniform-gas e_c . Circles: full RPA. Asterisks: seamless vdW functional: Dashed lines: hydrodynamic approximations. From reference 33.

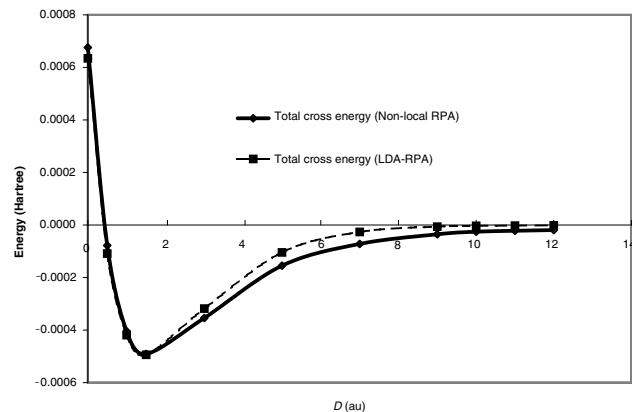


Fig. 4. Separation dependent part of the total energy per unit area, for two jellium slabs as in Fig. 3.

exchange energy component for the full RPA case (solid line) was calculated as the full non-local Fock energy using the ground-state Kohn–Sham-LDA wavefunctions. The LDA total energy still lacks the distant vdW dispersion contribution at large separations, as expected. For overlapped cases $D \leq 2$ au, however, the error in the local correlation energy is largely compensated by an opposite error in the local exchange energy, as often occurs within the LDA. As a result, the metallic bonding region up to the potential energy minimum is quite accurately described by the LDA. (It is worth noting that the well-known failure of the standard jellium model to be in mechanical equilibrium at a surface^[64,65] means that the minimum of the total energy curve does not lie at $D = 0$.) Thus for our particular parameters at least, the LDA is quite adequate to describe the metallic bond near the equilibrium separation, but fails to produce the vdW interaction when the subsystems are pulled further apart. The jellium slab calculation also sheds some light on the proposition that one should correct LDA calculations simply by adding a vdW dispersion energy obtained from some other scheme. This procedure can, of course, give good

results in the asymptotic region of distant vdW attraction where the LDA gives essentially zero interaction and the correction gives the whole of the energy. The same procedure gives very poor results, however, near the equilibrium separation in our example of jellium slabs. For reasons discussed in the previous paragraph, at equilibrium the edges of the jellium positive background are still separated by about $1\frac{1}{2}$ au. It is therefore quite feasible to calculate a finite dispersion energy from the sum of plasmon zero-point energies within a hydrodynamic model which is known to yield the vdW dispersion attraction at large separations. The energy data from an appropriate hydrodynamic calculation is shown in Figure 3, denoted by the short-dashed curve labeled ‘Hydro $L = 5 + 5$ ’. This annotation ‘ $5 + 5$ ’ indicates that each of the two jellia in the hydrodynamic model had finite thickness 5 au. Since the electron densities don’t overlap in the hydrodynamic model, all correlations that it introduces are ‘distant’ correlation and there is certainly no exchange. Therefore one might have hoped to add the correlation energy from this calculation to the LDA results (on the grounds that the LDA might be expected to describe only the short-ranged part of the correlations). In fact, however, the LDA calculation alone does include longer-ranged correlations, but only those of the uniform electron gas. As it happens, this (together with the local exchange approximation) gives the correct energy near equilibrium, and the hydrodynamic correction from Figure 3 would massively (and incorrectly) change the energy and equilibrium separation. While one could criticize the use of non-dispersive hydrodynamics in this example, it is hard to imagine any reasonably simple calculation of the distant correlations that gives the necessary zero value of the energy correction near equilibrium separation. This example highlights the need for a non-arbitrary way to ‘saturate’ asymptotic vdW energy formulae at short distances, where they diverge, in order to add them to energy calculations of the local density type.

A possible general solution to this difficulty was suggested by Kohn et al.^[14] They gave a more sophisticated way to isolate the long-ranged vdW contributions from the local-density contributions, by splitting the bare electron-electron Coulomb potential into long-ranged and short-ranged parts from the outset, writing $V_{coulomb} = V_{lr} + V_{sr}$. Once the cutoff distance between short and long-ranged parts has been decided, the theory gives an exact expression for the correlation energy in which the parts E_{lr} and E_{sr} , due to V_{lr} and V_{sr} respectively, are cleanly separated. E_{sr} can be reasonably approximated in the LDA or GGA, but the polarization energy $E_{lr}(\equiv E_{pol})$ is intended to be treated by an RPA-like scheme of time-dependent density functional theory. To date, it seems there are no practical implementations of this Kohn–Meir–Makarov scheme for specific large overlapped systems, despite their suggestion of an efficient imaginary-time implementation of the RPA-like correlation energy formula involved in E_{pol} .

Another less idealized metallic case is that of bulk graphite, which can be regarded as consisting of largely inert covalent sp^2 bonded x - y planes of electrons, with out-of-plane π_z orbitals forming an essentially metallic near-2-D

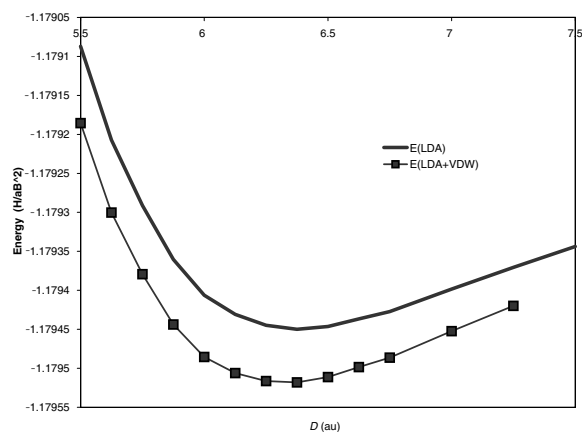


Fig. 5. Energy versus interplanar lattice spacing for bulk AA graphite, in LDA and with a van der Waals correction.

electron gas layer on each graphene slab. Here we have not so far performed a full RPA calculation, but we can make the following estimates starting from self-consistent LDA ground-state calculations by Arellano et al.^[66] For pure bulk graphite (BB form), Arellano et al. computed the LDA ground-state energy as a function of distance D between the graphene planes. The energy minimum is at $D = D_0 = 6.275$ au, which is within 1% of the experimental number 6.34 au. Now we estimate the additional dispersion energy of a pair of graphene planes at the same separation, an energy presumably missed by an LDA calculation, in a naive interpretation. For an order-of-magnitude estimate, we treat each graphene layer as a 2-D electron gas and, therefore, use equation (19) to estimate the vdW energy and hence the extra vdW force attracting two adjacent layers. Using the stiffness constant d^2E/dD^2 from the LDA calculation, we estimate that the vdW attraction causes a change in the equilibrium separation D_0 of only $\Delta D_0 = -0.05$ au. This is indeed less than 1% of the LDA interlayer distance, which tends to support the conclusion that the LDA adequately describes the essentially metallic interplanar bond near the equilibrium interplanar spacing. We give results for the AA form of graphite in Figure 5. Of course, the example of jellium slabs treated above shows that one cannot, in fact, simply add the vdW attraction in this fashion, but that the small numbers obtained for graphite tend to support the validity of the LDA results nevertheless. (We could have made the hydrodynamic vdW correction larger by giving the metallic layers finite thickness, however. On the other hand, the unusual semi-metallic band structure of isolated graphene planes suggests that treating each graphene plane as a normal electron gas may overestimate the response functions and hence the vdW interaction. This all suggests that a full RPA correlation energy calculation including the actual graphite band structure could be a very interesting exercise.)

It is possible that the LDA works well here for the same reason that it does so in the previous jellium-slab example, namely that we are dealing with a metallic bond between graphene layers. Band structure calculations for graphite^[67,68] do show a weak overlap of electronic valence

and conduction Bloch bands, due to allowed hopping of electrons between layers. The band overlap is absent for a single graphene plane at zero temperature, which is a zero-gap insulator. The ground-state electronic density shows^[68] that the proximity of the graphene planes causes a small displacement of electronic charge into the interlayer region, where it is relatively uniformly distributed. This metallic bonding explanation is speculative, however. The bond is certainly only very weakly metallic in the z (interplanar) direction, if at all.

For parallel metallic slabs the distant vdW interaction is relatively strong because of the highly polarizable character of macroscopic electron gases. Nevertheless, the conclusion from our limited tests on jellia and graphite described above, is that even the LDA does a good job of the total metallic energy in overlapped situations near to the equilibrium spacing. This is certainly not the case when layers are separated significantly beyond the equilibrium spacing, however.

(h) Ground-State DFT Approach: Large Polarizable Non-Metallic System

Next we turn to large, polarizable but non-metallic systems. Montenari et al.^[69] investigated the binding of polyethylene within the LDA and various GGAs. They computed the energy as a function of inter-chain separation D . They found that the LDA gave a value of D that was 9% smaller than experiment. The Becke–Perdew gradient functional was found not to bind the chains at all, but the Perdew–Burke–Ernzerhof gradient functional gave a D value 12% greater than experiment. Full quantitative agreement thus still seems elusive.

(i) Ground-State DFT Approach: Small Highly Polarizable Systems

Next consider a fairly small but rather polarizable system, benzene. Meier and Sprik^[70] found that the LDA gives reasonable binding energy and equilibrium separation for the benzene dimer, a result which they felt was fortuitous. (We wonder, however, if this might not once more be regarded as a kind of metallic bond akin to the graphite case, so that the success of LDA may not be totally fortuitous). The hybrid BLYP functional gave reasonable results only when supplemented by an explicit empirical vdW term. Our experience described above for metals suggests the need for caution when adding such terms. CCSDT results^[43,44] have shown that MP2 is poor for this system, so it is all the more remarkable that LDA does well here. One might speculate that even small finite parallel graphene fragments are exhibiting the weak metallic interplanar bonding suggested above for the infinite-area case (graphite). To try and understand this better, it might be worth exploring Time Dependent Density Functional Theory fluctuation-dissipation methods for the correlation energy for this system, as these methods should give a balanced treatment of all forms of bonding. The Kohn–Meir–Makarov scheme^[14] might also be appropriate here.

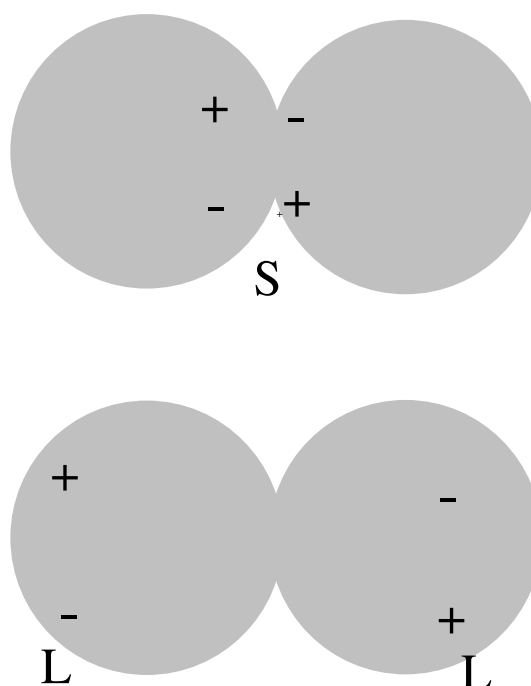


Fig. 6. Short-ranged and longer-ranged correlations in a dimer of large rare gas atoms (qualitative).

(j) Ground-State DFT Approach: Small Weakly Polarizable Systems

As an example of small weakly polarizable systems, we turn to Nobel gas dimers, for which there is negligible ionic or covalent interaction. Here it seems both short-ranged and longer-ranged vdW-style correlations might be important near the equilibrium separation. Consider two closed-shell atoms in fairly close proximity as shown schematically in Figure 6. The symbols marked ‘S’ represent charge fluctuations that correlate over a fairly short range comparable to the local screening length, and that might reasonably resemble the short-ranged correlations in a slightly inhomogeneous electron gas (i.e. they may be captured by a GGA (but probably not an LDA) calculation). The symbols marked ‘L’ represent more distant vdW-style charge correlations, which owe their character to the combined edge inhomogeneities at the outer boundaries of the two atoms, and which are not reproduced within a local or local-gradient approach. To see how this idea is borne out in specific calculations we consider several recent density functional calculations on rare-gas dimers. These are very delicate supermolecule calculations, aimed at a small attractive component of the total energy.

Peres–Jorda and Becke^[71] used a real-space mesh to avoid basis-set superposition error. They studied He_2 , Ne_2 , Ar_2 , HeNe , HeAr and NeAr . They found that the LDA severely over binds while the Becke88x–Perdew91c gradient functional did not bind. Some hybrid functionals gave mixed results. Thus none of the then-popular gradient density functionals gave a satisfactory account of the binding. They used a common LDA ground-state density for evaluation of

all the energy functionals, which may have influenced their results.

It was emphasized by Zhang et al.^[72] that a large part of the difference between functionals is due to their different treatments of exchange (rather than just of correlation, as one might have expected for vdW calculations). They found that the PBE GGA and Becke86x-PW91c gradient density functionals did give reasonably good results for the bond lengths and binding energies. They did not consider any cases of two large, polarizable rare gases such as Ar₂ or Kr₂, however, so perhaps they were considering cases where correlations of type L (see Fig. 6) are unimportant.

Patton and Pederson^[73] noted the importance of minimizing the energy with respect to electron density for each separate functional, rather than using a common electron density for evaluation of all the functionals. They took great care with convergence with respect to basis sets and other numerical considerations. They included also the larger noble gas pairs, e.g. Kr₂, not considered by Zhang et al. They found that the PW91^[74] and PBE^[62] gradient functionals gave reasonable binding energies and bond lengths (i.e., with small absolute error). These are small energies, however, and closer inspection shows that PBE underestimates the binding by a factor of two in the larger, more polarisable systems (Ar₂, Kr₂, ArKr), while it overestimates it for the smaller systems. PW91 overestimates the binding by a factor of 5–10 for the smaller dimers. The harmonic vibrational frequencies are off by apparently random factors varying from 1/2 to 2. Thus none of the functionals tested was quantitatively adequate over the whole range of dimers of large and small noble atoms. We surmise that some of this may be due to the increasing importance of the more distant correlations (labelled ‘L’ in Fig. 6), as one moves to the larger, more polarizable noble gases. This is perhaps borne out by the finding of Patton and Pederson that an asymptotic, non-overlapping formula of the form C_6R^{-6} produced a large fraction of the observed binding energies when evaluated at the equilibrium separation. It also highlights the difficulty in distinguishing distant van der Waals correlations from local ones in any meaningful way.

In all of these papers the LDA was found to cause the rare gas atoms to overlap too much, thereby causing a large exchange energy, and a binding that is much too strong. At first this may seem counter-intuitive, as one imagines that the true binding is due to correlation between dynamic dipolar charge fluctuations on the two atoms. It is clear, however, that the strong LDA binding comes from a quite different pseudo-covalent mechanism in which exchange is very important.

The conclusion seems to be that there is indeed still a problem in predicting the energy curves of rare-gas dimers in the slightly overlapping region near the van der Waals minimum, using any standard ground-state density-functional theory.

(k) Empirical Force Fields

This is a large subject, which we do not attempt to review here. Undoubtedly for very big (e.g. biological) systems this

is currently the only practical approach^[21,75] for inclusion of dispersion forces. As discussed above, one cannot in general simply add an asymptotic vdW potential to a short ranged one, and optimization of the constants in (say) a 6–12 potential is necessarily a compromise. The recent work of Kohn, Meir and Makarov (1998), though proposed by those authors for use with a numerically-intensive time-dependent density functional approach, may well be the basis for a non-empirical short-ranged saturation of a simple asymptotic vdW interaction when added to a short-ranged LDA term.

V. Summary

This paper has addressed the question ‘is there a problem with *ab initio* prediction of van der Waals (dispersion) forces?’. The conclusion has been a qualified ‘yes’. The least contentious case is prediction of the distant van der Waals attraction between two small non-overlapping electronic systems. For example, prediction of the Hamaker constant C_6 in the pairwise vdW attraction (equation (1)) requires only the evaluation of the dipolar polarizabilities of the two participating molecules at a range of frequencies (equation (6) and (5)). Time-dependent density functional calculations can do a reasonable job here.^[14] Alternatively, knowledge of a sufficient number of energies and dipole transition matrix elements of a range of excited states of each molecule will suffice^[3] to find C_6 . These can be computed with standard quantum chemical codes implementing, for example, the configuration interaction approach. When the molecules are closer, but not overlapping, one needs to consider multipole polarizabilities as well, or one can sum all multipoles by using the Zaremba–Kohn^[5] formula (2) which requires a knowledge of the point-by-point response function $\chi(\vec{r}, \vec{r}, \omega)$ rather than just its dipole moment. Simplified density-based formulae are also available, such as equation (10). These are typically of modest accuracy and require either a semi-empirical cutoff or the input of static polarizability data. Recent attempts to remove the need for a cutoff, by the application of exact constraints,^[19] have so far met with limited success, producing relatively good polarizabilities at low and high imaginary frequency u , but becoming inaccurate at intermediate u .

The common practice of adding C_6/R^6 contributions between each pair of atoms in a larger system is not accurate in general, and can give qualitatively wrong results in some cases such as metal surfaces. Nevertheless this approach is still commonplace in force-field models for predicting protein conformation. Its adequacy in these cases requires further investigation.

The biggest problems in predicting dispersion forces arise when systems begin to overlap so that other forms of bonding compete. Several common many-body techniques, represented in commercially-available software, can obtain the basic vdW attraction phenomenon, and yet remain reasonably accurate under overlap conditions (i.e. they give a ‘seamless’ description of vdW). They all have drawbacks, however.

Moeller–Plesset perturbation theory, applied with an adequate basis set, includes a form of the distant vdW

interaction, even at the MP2 level. The results from MP2 are, however, equivalent to an approximate form of equation (4) with the true interacting polarizabilities $A^{(1)}$, $A^{(2)}$ replaced by bare ones. This inaccuracy is expected to be worst for large, highly polarizable atoms or molecules. MP4 should improve the situation, but no finite order of MP perturbation theory can give the exact Hamaker vdW coefficient. At least MP3 is required to obtain a non-zero value for the three-atom Axilrod–Teller interaction (7). MP theory is expected to be inadequate for the vdW attraction in large planar metallic systems, where Coulomb perturbation theory is known to fail. MP2 is also known to give poor results for rare-gas dimers and the benzene dimer. Even MP4 disagrees with coupled cluster calculations for prediction of the lowest-energy conformation of the benzene dimer.

Symmetry-adapted perturbation theory^[4] may well be the best approach for small molecules, but like all methods dealing with many-electron wavefunctions, it will become prohibitive for large systems.

CI methods, assuming adequate basis sets, should produce a Hamaker style vdW interaction already at the ‘doubles’ level of excited determinant. Once again, higher levels of excitation (triples, ...) are probably required to provide accurate C_6R^{-6} behaviour for molecular pairs, for the same reason as in the MP2 approach. Triples are clearly the minimum requirement for the three-molecule Axilrod–Teller interaction. CI methods are currently considered impractical for calculations on larger systems with significant vdW energy contributions, such as interacting graphene fragments.

Variational **Monte Carlo approaches** will not yield the distant vdW interaction if the simplest short-ranged Jastrow factor is used. In view of the basic coupled-charge-fluctuation nature of vdW interactions, a longer-ranged coupled-plasmon type of Jastrow factor might be successful, but would probably need to be tailored to the specific vdW geometry at hand. The **diffusion Monte Carlo** approach should, in principle, contain all of the dispersion energy, but it remains to be seen whether these relatively weak effects are accessible in practice for complex systems.

Green function Monte Carlo calculations have been successful for the He dimer, but it is not clear whether they will be feasible for larger systems of interest.

Ground-state density functional theory (DFT) is popular for atomic and solid-state calculations because it is computationally less costly than the schemes described above. Unfortunately the usual local (LDA) and local-gradient (GGA) approximations fail to obtain the distant vdW interaction. For closer separations with overlap of electron density, the situation is less clear because there is no sharp demarcation between local correlations and longer-ranged vdW correlations. The following cases, in which vdW forces are potentially significant, were discussed above:

- **Metallic bonds.** Here vdW forces can be relatively large because metals contain highly polarisable electrons. Despite missing these forces completely at large separation, even the standard LDA gave accurate ground-state energies near the metallic-bonding energy minimum, in two test cases.

- **Polymers** often show non-covalent, non-ionic inter-chain bonding in which dispersion forces are important because the chains are highly polarizable. Monteneri et al.^[69] found that the LDA failed to bind the polymer chains in bulk polyethylene. Various GGAs gave mixed results, one not binding at all, another overestimating the interchain spacing by about the same degree that the LDA underestimates it.

- **Small polarizable molecules** such as benzene may exhibit vdW influences in their binding. Meier and Sprik^[70] investigated the binding of the benzene dimer and found that the LDA did (fortuitously?) well but the popular B3LYP hybrid functional required supplementation.

- **For closed-shell atoms**, despite the relatively small electronic polarizability, the weak vdW forces are important because conventional covalent and ionic bonding are absent. Several authors studied rare-gas dimers within LDA and GGAs. The LDA gives unrealistic results, systematically overbinding and underestimating the bond length. Gradient functionals do somewhat better but often give binding energies and vibrational frequencies that are out by factors of two or more. The problem is worse for large than for small rare gas dimers. This might indicate the importance of quite long-ranged vdW correlations involving electrons at the outer surfaces of the larger rare gas monomers.

Random Phase Approximation (RPA) and related time-dependent density functional methods produce correlation energy by the adiabatic connection-fluctuation dissipation theorem, equation (13). This is a very promising, but not yet widely programmed, approach for seamless vdW calculations. Here, an interacting density–density response function is calculated and then integrated over two position variables, and also over frequency and coupling strength, to yield a non-trivial ground-state correlation energy. It has been shown^[28] that the pure RPA equations yield, for a pair of well-separated finite systems, the correct form C_6R^{-6} for the vdW energy. The Hamaker constant C_6 is also of the correct form as in Equation (4) except that the RPA polarisabilities A of the fragments appear in place of the true polarisabilities. The time-dependent DFT formalism^[10] allows one to generalize this approach beyond the RPA without significant extra computation. RPA calculations of H_2 and Be_2 have recently been reported.^[57] Pure RPA and also TDDFT calculation of the seamless interaction of two metallic slabs has also been achieved,^[33] but the numerical approach used there is cumbersome for systems of more general geometry. Recent suggestions^[14] for a real-time, real-space implementation look promising. There have also been proposals^[28,33] for non-local density-based approximations to seamless RPA-style schemes.

In summary, there are a number of van der Waals situations, typically those involving larger systems such as graphite or graphene fragments, in regimes where dispersion forces and other types of force coexist, for which it has not been demonstrated that any of the existing many-body predictive methods is adequate in practice. Various computationally intensive methods seem promising for these situations, but it may be some time before one has non-empirical force laws that are simple enough to treat very

large problems involving (e.g.) stretched (intercalated) graphite, protein folding^[75] or general polymer energetics.^[69]

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