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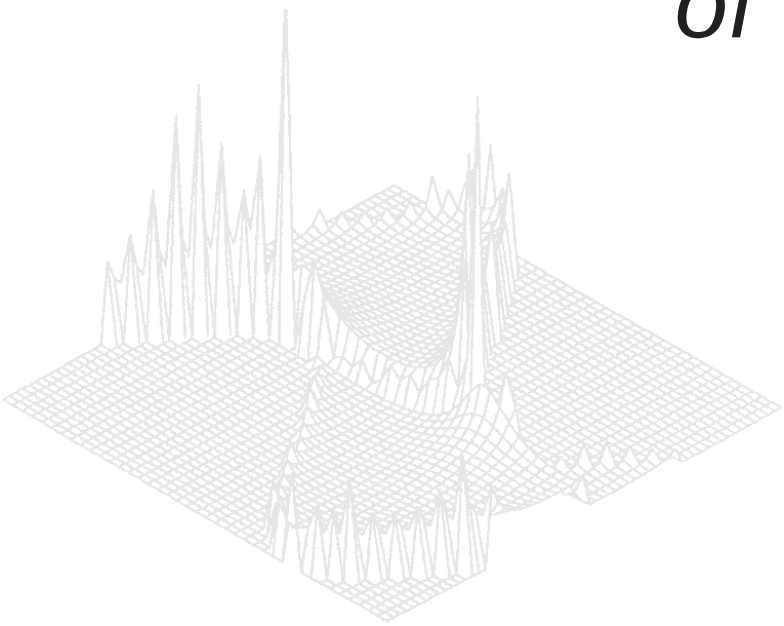

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A Novel Constraint for the Simplified Description of Dispersion Forces*

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Abstract

We propose a novel use of an exact constraint in the construction of simple approximations for response functions of interacting many-electron systems. Within its simplest local version, the resulting theory gives improved approximations for static atomic dipolar polarisabilities without the direct use of wavefunctions or semi-empirical cutoffs. It leads to correct van der Waals energies between distant planar systems, but over-corrects existing cutoff theories for the van der Waals C_6 coefficient for atoms. It is argued that a nonlocal-response version of the constrained theory will do better.

1. Introduction

Dispersion or van der Waals (vdW) forces, though weak compared with other types of intermolecular interaction, can play a crucial role in soft-matter and biophysical situations; for example, in the folding of proteins. An accurate *ab initio* description of these forces requires the inclusion of a long-ranged, geometry-dependent part of the electronic correlation energy, corresponding to the 'vdW hole' in the electronic pair distribution. Because dispersion forces are typically strongest in very large systems for which standard quantum chemical energy calculations are impractical, one would naturally think of trying density functional methods. Unfortunately, the usual local and local-gradient functionals miss the long-ranged vdW interaction, although some gradient functionals have been found to give quite a good account of the vdW interaction between small rare-gas atoms near their equilibrium separation (Zhang *et al.* 1997). For this it is only necessary to describe the relatively short-ranged correlations between the neighbouring parts of the two electronic clouds, and this is achieved quite well by the PBE functional (Perdew *et al.* 1996) among others. The R^{-6} interaction between distant rare gas atoms is wholly absent in the PBE and other generalised gradient functionals, however. Moreover, the gradient functionals do not perform particularly well for the larger, more polarisable rare gases even near the equilibrium separation (Patton and Pederson 1997), possibly because correlation between more distant parts of the atoms is important. For chain-folding problems in large chemical and biological systems, the long-ranged part governing interactions between non-contacting regions of the chains is even more important, so that there is a need for a simple but nonlocal functional to provide reliable energy surfaces.

The present paper addresses this problem via approximations for the dynamic density–density response function $\chi(\vec{r}, \vec{r}\,', \omega)$ or related tensor response functions. The philoso-

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phy of this approach is as follows. The ground-state correlation energy depends on the nontrivial part of the ground-state electron pair distribution, which describes how electrons avoid one another in the ground state. The avoidance between electrons in different parts of a pair of separated systems gives rise to the van der Waals interaction.

This phenomenon can also be thought of in terms of transient fluctuations: if a zero-point fluctuation in electron density produces a dipole moment on one subsystem, this induces an opposing moment on the other system, and the Coulomb interaction between these temporary charges gives a negative fluctuation (i.e. correlation) contribution to the ground-state energy.

This way of viewing the van der Waals phenomenon leads naturally to the involvement of response functions which describe the process whereby a fluctuation in one region induces a response elsewhere. Several alternative nonlocal response functions contain the necessary information: the nonlocal tensor conductivity $\boldsymbol{\sigma}(\vec{r}, \vec{r}', \omega)$, the dynamical tensor polarisability $\boldsymbol{\alpha}(\vec{r}, \vec{r}', \omega)$, and the scalar density–density response function $\chi(\vec{r}, \vec{r}', \omega)$. The van der Waals correlation energy is mathematically related to these response functions through the fluctuation–dissipation theorem. This theorem is needed because the response functions describe how the system responds to *specified external* fields, whereas in the vdW process we are concerned with response to *spontaneous internal fluctuations*.

The accurate calculation of any one of these response functions is a many-body problem with no closed exact solution, though evidence is emerging that the random phase approximation (RPA) may be an adequate approximation for vdW purposes, in many circumstances. While it is now possible (Pitarke and Eguiluz 1998; Dobson and Wang 1999) to carry such RPA calculations through in full for large systems of very simple geometry such as metal slabs and possibly small molecules also, such a calculation would be daunting in the extreme for cases of practical interest such as folded proteins. The present paper therefore concerns approximation schemes for the RPA (or higher) response functions, intended to make this approach tractable for large systems of chemical and biological interest.

A direct approximation for the full interacting response functions based on the local ground state density can be shown (Dobson *et al.* 1998) to yield the ordinary LDA energy, which misses the long-ranged van der Waals interaction. Nevertheless, local approximations can in principle yield sensible results. What is required is to recognise that the calculation of the interacting response can be broken into two parts:

- Step 1: calculation of the independent-particle response
- Step 2: screening of the independent response to produce the interacting response, a process which involves the long-ranged Coulomb interaction.

The first step is amenable to local approximations in the van der Waals context, while the second is not because of the long range of the Coulomb potential. The second step is, however, amenable to perturbation theory in many (but not all) cases. The purpose of the present work is to discuss a new approach in the generation of quasi-local approximations for Step 1. The paper is organised as follows.

In Section 2 we give basic equations which provide formally exact, and also perturbative, expressions for the ground-state correlation energy including the vdW energy.

In Section 3 we discuss some previous approaches and approximation schemes. The 'seamless' theories satisfactorily describe vdW forces between two systems at all separations right down to intimate contact. By contrast the asymptotic theories are valid only for non-overlapping systems, but provide much simpler approximations than the seamless approaches. The response and correlation properties of the uniform electron gas can be

used to guide these theories, but in the case of small systems they still require quite drastic semi-empirical cutoffs. They typically give gross overestimates of the vdW force without such cutoffs.

In Section 4 we propose an additional exact constraint in order to 'tie down' the electronic response of finite systems, a phenomenon clearly lacking in the uniform-gas model. This replaces the somewhat arbitrary cutoffs of the simplest, most numerically tractable, existing vdW theories.

In Section 5 we discuss the performance of a highly simplified version of the new constrained, cutoff-free theory. Its properties for the asymptotic van der Waals interaction between planar systems appear good. It gives improved static dipole polarisabilities for many atoms, compared with existing cutoff theories. The values of the van der Waals C_6 coefficient are over-corrected, however.

2. Basic Formulae

(2a) Ground State

The Kohn–Sham (1965) formulation of density functional theory shows that there is a one-particle Kohn–Sham (KS) potential $V_{KS}(\vec{r})$ such that the true ground-state electronic number density $n(\vec{r})$ is reproduced by a set of effective one-body Kohn–Sham orbitals ϕ_j:

$$n(\vec{r}) = \sum_j f_j \phi_j^*(\vec{r})\phi_j(\vec{r}),$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(\vec{r})\right)\phi_j(\vec{r}) = \varepsilon_j \phi_j(\vec{r}).$$

Here f_j is the Fermi occupation factor and ε_j is the KS eigenvalue.

The KS potential is a unique functional of the ground-state density, but the form of this functional is unknown in general. For the remainder of this paper we will assume that $V_{KS}(\vec{r})$, $n(\vec{r})$ and $\{\phi_j(\vec{r})\}$ are given sufficiently accurately by currently popular formalisms such as the local density approximation or the generalised gradient approximation. For small finite systems we will also need orbital self-interaction corrections (SIC) in the ground state, resulting in an effective potential V_j^{eff} which can exhibit orbital dependence beyond the KS format:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_j^{eff}(\vec{r})\right)\phi_j(\vec{r}) = \varepsilon_j \phi_j(\vec{r}).$$

In atoms and other small systems, this refinement is essential in order to obtain the correct asymptotic form of orbitals and potentials far from the nucleus of a neutral atom, where an electron 'sees' an effective Coulomb field due to a net charge $+|e|$, caused by the exclusion of its own charge as a source. By contrast, the standard local approximations include the electron's own charge as a source of potential, resulting in artificially weak binding. This is important in the present context because the low-density outer tails of the orbitals contribute strongly to the polarisabilities which we will be using to generate the vdW interaction. In practice we have used the Perdew–Zunger (1981) form of V_j^{eff}, in

which one starts with the local density approximation (LDA) but then subtracts the contribution of each orbital j to its own effective potential. Ideally one would use the optimised effective potential (OEP) method (Li *et al.* 1993) in which all orbitals feel the same potential, but self-interaction correction is nevertheless achieved. Unfortunately, programs for this approach are readily available only for the pure exchange case, so we preferred the Perdew–Zunger method which easily accommodates correlation as well as exchange.

The ground-state density- and orbital-functional formalisms mentioned above are used because, unlike more standard many-body methods such as the configuration interaction (CI) approach, they remain tractable for large systems. None of them, however, correctly describes the long-ranged part of the vdW interaction. The present work aims to produce relatively simple formalisms which use the ground-state density and effective potential as input, but nevertheless yield a correlation energy including the long ranged vdW interaction (as well as the portion of the correlation energy already covered by the above-mentioned local methods).

One could argue that it is inconsistent to use ground-state properties from the above standard formalisms as input to our new functionals. Certainly, it would be ideal to use optimised ground-state density, orbitals and potentials emerging from the new formalism itself. However, this distinction is a higher-order effect compared with the basic reproduction of the distant vdW interaction by our formalism, a property entirely lacking in the standard density functional methods. Furthermore, experience has shown that approximate densities from the standard methods are usually rather accurate.

(2b) Dynamic Response Functions (Generalised Susceptibilities)

The density–density response function $\chi_\lambda(\vec{r}, \vec{r}\,', \omega)$ is defined as the linear change in electron density at position $\vec{r}$, due to a small time-oscillating variation in external potential localised at point $\vec{r}\,'$. If the change in potential is not localised but extends over all points $\vec{r}\,'$, then by linearity the density change at $\vec{r}$ is

$$\delta n(\vec{r},t) = \exp(-i\omega t) \int \chi_\lambda(\vec{r},\vec{r}\,',\omega)\delta V^{ext}(\vec{r}\,',\omega)d\vec{r}\,' \tag{1}$$

to first order in the external potential $\delta V^{ext}(\vec{r}, \omega)\exp(-i\omega t)$. The subscript λ refers to a problem in which the electron–electron interaction has been reduced by a factor λ lying between 0 and 1, so that the pair potential is

$$U_\lambda(\vec{r},\vec{r}\,') = \lambda e^2 \left|\vec{r} - \vec{r}\,'\right|^{-1}.$$

The introduction of the factor λ is useful in obtaining the kinetic part of the ground-state correlation energy: see Section 2*e* below. Following standard practice we define the $\lambda \neq 1$ problem to be one in which an external potential $V_\lambda(\vec{r})$ is applied so as to maintain the ground-state density at the fully interacting value, so that $n_\lambda(\vec{r}) = n_{\lambda=1}(\vec{r})$.

For an interacting ($\lambda \neq 0$) inhomogeneous many-electron system, the exact calculation of χ_λ is an insoluble many-body problem. Fortunately (Gross and Kohn 1985) the task can be broken into two parts: calculation of the independent-particle response $\chi_0 \equiv \chi^{KS}$, followed by dynamic screening to produce the interacting response χ_λ.

Linear response functions other than the scalar χ_λ will also prove useful. The interacting current–current response tensor $\chi_{ik,\lambda}$ is the response of the current density $\vec{j}(\vec{r})$ to a small externally-applied vector potential $\vec{A}^{ext}(\vec{r}\,')\exp(-i\omega t)$:

$$j_i(\vec{r},t) = \exp(-i\omega t)\int \chi_{ik,\lambda}(\vec{r},\vec{r}\,',\omega)A_k^{ext}(\vec{r}\,')d\vec{r}\,', \tag{2}$$

where the Einstein summation convention is assumed on the index k. In a gauge where the scalar potential is zero, the small external electric field is

$$\vec{E}^{ext} = -i\omega\vec{A}^{ext}. \tag{3}$$

We may also define an electronic displacement vector $\vec{p}$ such that

$$\vec{j} = \frac{d\vec{p}}{dt} = -i\omega\vec{p}. \tag{4}$$

Then

$$\vec{p}(\vec{r},t) = \exp(-i\omega t)\int \alpha_{jk,\lambda}(\vec{r},\vec{r}\,',\omega)E_k^{ext}(\vec{r}\,')d\vec{r}\,', \tag{5}$$

where α is the dynamic polarisability tensor given by $\boldsymbol{\alpha} = -\omega^{-2}\boldsymbol{\chi}$.

By use of the continuity equation with (3) (see Dobson *et al.* 1998 where α is denoted by $\bar{\mathbf{A}}$), one recovers the scalar density–density response from the dynamic polarisability tensor:

$$\chi_\lambda(\vec{r},\vec{r}\,',\omega) = \frac{-1}{e^2}\frac{\partial^2}{\partial r_j \partial r_k}\alpha_{jk,\lambda}(\vec{r},\vec{r}\,',\omega). \tag{6}$$

The relation (6) can be useful (Dobson and Dinte 1996) when making simple direct approximations for response functions. In particular, for finite systems by charge conservation we must have $\int \chi_\lambda(\vec{r},\ \vec{r}\,',\omega)d\vec{r} = 0$, and furthermore $\int \chi_\lambda(\vec{r},\ \vec{r}\,',\omega)\,d\vec{r}\,' = 0$ because a constant potential produces no force. These conditions for α_λ are guaranteed if we make direct approximations for α_λ, and then use (6), provided that our approximation for α_λ vanishes at infinity. For this reason the approximation schemes outlined in Sections 3 and 4 are couched in terms of the dynamic polarisability $\boldsymbol{\alpha}_\lambda$ rather than directly in terms of the density–density response χ_λ.

(2c) Independent-particle (Kohn–Sham, KS) Response

The KS response of a many-body system is the $\lambda = 0$ response: that is, the response of electrons with no mutual Coulomb repulsion, but experiencing an external potential $V_{\lambda=0} \equiv V^{KS}(\vec{r})$ such that the true interacting ground-state density is maintained. From one-electron perturbation theory one obtains the exact result

$$\chi_0(\vec{r},\vec{r}\,',\omega) = \sum_{,j,k}\frac{(f_j - f_k)}{\varepsilon_j - \varepsilon_k - \hbar\omega}\phi_j(\vec{r})\phi_k(\vec{r})\phi_k(\vec{r}\,')\phi_j(\vec{r}\,') \tag{7}$$

where $\{\phi_k\}$,$\{\varepsilon_k\}$ are the (real) eigenfunctions and eigenvalues of $V^{KS}(\vec{r})$, and f_i is the Fermi occupation factor. Equation (7) is readily computed for small or geometrically simple systems, but one of our aims is to find approximations for χ_{KS} that are simple enough to be carried through for large systems of arbitrary geometry. This means in practice that one prefers not to use the Kohn–Sham eigenfunctions directly when approximating χ_0.

Like χ_λ, the interacting response functions $\chi_{jk,\lambda}$ and $\alpha_{jk,\lambda}$ introduced above also have their Kohn–Sham versions $\chi_{jk,0}$ and $\alpha_{jk,0}$. In particular, from (6) we get

$$\chi_0(\vec{r},\vec{r}',\omega) = \frac{-1}{e^2}\frac{\partial^2}{\partial r_j \partial r_k}\alpha_{jk,\lambda=0}(\vec{r},\vec{r}',\omega). \tag{8}$$

2d Dynamic Screening Equation

The interacting response χ_λ as defined in (1) is related to the KS response (7) by the Dyson-like screening equation (Gross and Kohn 1985):

$$\chi_\lambda(\vec{r},\vec{r}',\omega) = \chi_0(\vec{r},\vec{r}',\omega) + \int Q(\vec{r},\vec{r}'',\omega)\chi_\lambda(\vec{r}'',\vec{r}',\omega)d\vec{r}'', \tag{9}$$

$$Q(\vec{r},\vec{r}'',\omega) = \int \chi_0(\vec{r},\vec{r}_1,\omega)[\lambda e^2 |\vec{r}_1 - \vec{r}''|^{-1} + f_{xc\lambda}(\vec{r}_1,\vec{r}'',\omega)]d\vec{r}_1. \tag{10}$$

These equations are exact, but the exchange-correlation kernel f_{xc} of an inhomogeneous interacting system is not known precisely. Setting $f_{xc} = 0$ gives the usual random phase approximation (RPA), and various non-zero approximations are also available for f_{xc}. The kernel Q is long-ranged in space even when χ_0 is not, because of the long range of the Coulomb potential in (10). This leads $\chi_{\lambda\neq 0}$ to be long-ranged via equation (9). Specifically, $\chi_{\lambda\neq 0}$ has a long-ranged van der Waals part connecting two isolated fragments of matter, even though χ_0 has no such part because independent electrons cannot move between the isolated fragments. This last property has been termed the 'no-flow condition' for χ_0 (Dobson *et al.* 1998). These observations are the basis for using locally-based approximations for χ_0 in constructing a 'seamless' vdW energy functional (Dobson 1994*a*; Dobson *et al.* 1998; Dobson and Wang 1999). Solving (or suitably approximating) equation (9) then introduces a vdW tail into the response function. The final step in obtaining a vdW energy functional is to use the long-ranged interacting response with the fluctuation–dissipation theorem to produce a long-ranged van der Waals correlation energy. This step is explained in the following two sections.

(2e) Adiabatic Connection and Fluctuation–Dissipation Theorems

For a general inhomogeneous system of Coulomb-interacting electrons, the ground-state correlation energy can be written exactly as

$$E^c = \tfrac{1}{2}\int_0^1 d\lambda \int d\vec{r} \int d\vec{r}' \frac{e^2}{|\vec{r}-\vec{r}'|}(-\hbar\pi^{-1})\int_0^\infty (\chi_\lambda(\vec{r},\vec{r}',iu) - \chi_0(\vec{r},\vec{r}',iu))du. \tag{11}$$

The frequency integral implements the zero-temperature fluctuation–dissipation theorem, which relates fluctuations (correlations) in the quantum ground state to the linear response

χ_λ to external perturbations. The formula (11) has the appearance of a potential energy due to correlation, but the integration over Coulomb coupling strength λ implements the adiabatic connection formula (Langreth and Perdew 1975; Gunnarsson and Lundqvist 1976) which allows zero-point kinetic energy of correlation to be included also.

In (11), the response χ_λ is that of a system of electrons with pair interaction $\lambda e^2|\vec{r}-\vec{r}\,'|$, moving in an external potential $V_\lambda(\vec{r})$ chosen so that the physical ($\lambda = 1$) ground-state electron number density $n(\vec{r})$ is the ground-state density at each particular λ. This implies that

$$V_{\lambda=1} = V^{ext}, \quad V_{\lambda=0} = V^{KS}\,.$$

Kohn, Meir and Makarov (KMM) (1998) have derived a variant of (11) in which the bare Coulomb potential is split into a long-ranged part and a short-ranged part, so that

$$\frac{e^2}{|\vec{r}-\vec{r}\,'|} = U_{sr}(|\vec{r}-\vec{r}\,'|) + U_{lr}(|\vec{r}-\vec{r}\,'|).$$

Only the long-ranged part plays a direct role in the long-ranged part of the vdW interaction. By replacing U_{lr} by λU_{lr} to produce a total bare electron–electron interaction $\tilde{U}_\lambda$, and then switching on λ from 0 to 1, KMM obtained an exact exchange-correlation energy formula in the form $E_{xc} = E_{xc}^{(sr)} - \frac{1}{2}U_{lr}(0) + E^{pol}$. Here $E_{xc}^{(sr)}$ is the exchange-correlation energy with only U_{sr} present, and the 'polarisation energy' is given by

$$E^{pol} = \tfrac{1}{2}\int_0^1 d\lambda \int d\vec{r} \int d\vec{r}\,' U^{lr}(|\vec{r}-\vec{r}\,'|)\{-\hbar\pi^{-1}\}\int_0^\infty \mathrm{Im}\tilde{\chi}_\lambda(\vec{r},\vec{r}\,',\omega)d\omega. \qquad (12)$$

Here $\tilde{\chi}_\lambda$ is calculated from the screening equation (9) with $\tilde{U}_\lambda$ in place of $\lambda e^2|\vec{r}-\vec{r}\,'|^{-1}$. For vdW applications, $E_{xc}^{(sr)}$ can be evaluated by an LDA. KMM also proposed a time-domain method of evaluating E^{pol}. In this approach two steps of the present approach were rolled into one set of time-dependent Schrödinger solutions: (i) evaluating χ_0 and (ii) screening it to produce $\tilde{\chi}_\lambda$. This is a very accurate method, but for large systems it requires a large number of wavefunctions to be included. There are also some mixed methods (Lein *et al.* 1999) involving wavefunctions plus some simplifying assumptions. Here we will be seeking formulae which approximate the van der Waals correlation energy without summation over wavefunctions, in order to accommodate large systems in a simple fashion.

(2f) Perturbative vdW Energy Expression for Small Non-overlapping Systems

Consider two finite systems 'a' and 'b' with negligible overlap of ground-state electron density, so that electrons in the two subsystems may be considered distinguishable. Then the screening equation (9) may be solved by performing perturbation theory with respect to the part of the Coulomb interaction $V_{ab}^{\mathrm{Coulomb}}$ which couples the two systems (Dobson 1994*a*). This gives a second-order correlation energy

$$E^{(2)} = -\frac{\hbar}{2\pi}\int_a d\vec{r}_1 d\vec{r}_1{}' \int_b d\vec{r}_2 d\vec{r}_2{}' \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\frac{e^2}{|\vec{r}_1{}' - \vec{r}_2{}'|}$$
$$\times \int_0^\infty \chi_{a,\lambda=1}(\vec{r}_1, \vec{r}_1{}', iu)\chi_{b,\lambda=1}(\vec{r}_2, \vec{r}_2{}', iu)du. \tag{13}$$

Notice that there is now no integration over λ: the way in which the λ integration goes away in the perturbation treatment is not straightforward and is treated in detail for the RPA case in Dobson (1994*a*). The same proof also applies when f_{xc} is assumed to be local and proportional to λ. The formula (13) can also be obtained by direct perturbation theory on many-body wavefunctions (Zaremba and Kohn 1976). Here χ_a includes the electron–electron interaction amongst the electrons within system *a* to all orders at full coupling strength $\lambda = 1$, and similarly for χ_b. Equation (13) does however represent a second-order perturbation result in terms of the inter-system interaction V_{ab}^{Coulomb}.

When the distance *R* between the systems greatly exceeds the size of either, (13) can be expanded in powers of *R*. The leading term is obtained by writing χ_a in terms of a polarisability, $\chi_a(\vec{r}, \vec{r}\,', \omega) = -e^{-2}\partial_i\partial_j'\alpha_{ij}^{(a)}(\vec{r}, \vec{r}\,', \omega)$, then integrating by parts. This gives

$$E^{(2)} \approx -R^{-6}\frac{\hbar}{2\pi}\sum_{ijkl=1}^{3} C_{ijkl}(R)W_{ik}(R)W_{jl}(R), \tag{14}$$

where

$$W_{ik}(R) = \delta_{ik} - 3R_iR_k/R^2,$$

$$C_{ijkl} = \int_0^\infty A_{ij}^{(a)}(iu)A_{kl}^{(b)}(iu)du$$

and the dipole polarisability of system *b* is

$$A_{kl}^{(b)}(iu) = \int_{V_b} \alpha_{kl}^{(b)}(\vec{r}_1, \vec{r}_2{}', \omega)d\vec{r}_1 d\vec{r}_2. \tag{15}$$

For a spherically symmetric system, $A_{ij}(\omega) = A(\omega)\delta_{ik}$ and (14) gives the familiar result

$$E^{(2)} \approx -C_6R^{-6}, \quad C_6 = \frac{3\hbar}{\pi}\int_0^\infty A^{(a)}(iu)A^{(b)}(iu)du. \tag{16}$$

The dipole polarisability *A* of small systems such as spherical atoms can of course be calculated quite accurately from a number of many-body techniques, and also from time-dependent density functional methods. We will use this information to test simplified van der Waals energy functionals which are sufficiently tractable numerically to be applied in more complex situations.

3. Existing Approximate vdW Functionals

(3a) Seamless van der Waals Functionals

The term 'seamless' refers to a correlation energy formula which remains valid when interacting systems approach and overlap, as well as correctly giving the asymptotic vdW energy when the systems are well separated. The random phase approximation (RPA) falls into this class, as do modifications of the RPA which make local approximations for f_{xc} (rather than setting it to zero as in the RPA). The KMM approach outlined above is an efficient procedure for implementing such RPA-like formulae without approximation. For large, complex systems one would like something simpler, based more directly on the density and not requiring the calculation of excited wavefunctions. Such formulae can be derived in principle by simplified uniform-gas-based approximations for χ_0, followed by solution of a screening equation. This approach has had some success for large systems (Dobson and Wang 1999) but tends to overestimate the interaction between small systems such as atoms.

(3b) Existing Asymptotic Functionals for Well-separated Systems

The exact second-order perturbation result (13) has been used (Dobson and Dinte 1996) to generate a very simple but highly nonlocal density functional for the distant vdW interaction between finite systems. The idea was to approximate the density–density response functions χ_a and χ_b in (13) using only the ground-state electron density $n(\vec{r})$ as input. The approximation proposed by Dobson and Dinte can be expressed as follows. In the simplest hydrodynamic model with neglect of the zero-point pressure, the polarisability of a *homogeneous* electron gas is

$$\alpha_{jk}(\vec{q},\omega) \approx \delta_{jk}\frac{n_0}{m[\omega^2-\omega_P^2(n_0)]}, \tag{17}$$

where n_0 is the uniform electron number density and $\omega_P(n_0) = (4\pi n_0 e^2/m)^{1/2}$ is the plasma frequency. The space Fourier transform of (17) is

$$\alpha_{jk}(\vec{r}-\vec{r}',\omega) \approx \delta_{jk}\frac{n_0}{m[\omega^2-\omega_P^2(n_0)]}\delta^3(\vec{r}-\vec{r}') \tag{18}$$

and the simplest generalisation to an inhomogeneous system is

$$\alpha_{jk}(\vec{r},\vec{r}',\omega) \approx \delta_{jk}\frac{n(\vec{r})}{m[\omega^2-\omega_P^2(n(\vec{r}))]}\delta^3(\vec{r}-\vec{r}'), \tag{19}$$

where $n(\vec{r})$ is the inhomogeneous ground-state electronic number density. Using (6) we obtain

$$\chi(\vec{r},\vec{r}',\omega) \approx -\frac{1}{e^2}\nabla_r\cdot\nabla_{r'}\left(\frac{n(\vec{r})}{m[\omega^2-\omega_P^2(n(\vec{r}))]}\delta^3(\vec{r}-\vec{r}')\right). \tag{20}$$

Substituting (20) into (13), using integration by parts in the space integrations and performing the imaginary frequency integral analytically, we find a simple and explicit but highly nonlocal density functional for the van der Waals interaction:

$$E^{(2)} \approx -\frac{3\hbar e^{1/2}}{4(4\pi)^{3/2}m^{1/2}} \int_a d\mathbf{r}_1 \int_b d\mathbf{r}_2 \frac{1}{r_{12}^6} \frac{\sqrt{n_a(\mathbf{r}_1)n_b(\mathbf{r}_2)}}{(\sqrt{n_a(\mathbf{r}_1)} + \sqrt{n_b(\mathbf{r}_2)})}. \tag{21}$$

An approximation similar to (21) was earlier obtained via quite different arguments by Rapcewicz and Ashcroft (1991), who evaluated it for atoms and found a substantial overestimation of the vdW interaction. For atoms, they were able to cure this problem in large part by cutting off the space integrations in the outer tails wherever the wavenumber representing the spatial variation of the density sufficiently exceeds the local Thomas–Fermi screening wavenumber. Specifically they set their integrand to zero whenever

$$\frac{\nabla n}{6n} > \sqrt{4me^2}(n/9\pi)^{1/6}. \tag{22}$$

For the fully spin-polarised case the cutoff

$$\frac{\nabla n}{6n} > \sqrt{2me^2}(2n/9\pi)^{1/6} \tag{23}$$

was proposed by Andersson *et al.* (1998). Andersson *et al.* (1996) modified the Rapcewicz–Ashcroft formula slightly in order to accommodate some known limits, and obtained exactly the formula (21) proposed by Dobson and Dinte on different grounds. Once again, Andersson *et al.* found that considering the simplicity of the formula (21), it gave surprisingly good answers for the distant vdW interaction between atoms, but only when used in conjunction with the cutoff (22). The cutoff is intended to express the fact that atomic electron gases respond less readily than the homogeneous electron gas, in the tails where their density is highly inhomogeneous. Unfortunately, the same cutoff does not appear so suitable for use in systems with large spatial extent.

4. Simple vdW Energy Functionals without Empirical Cutoffs

The purpose of the present paper is to explore ways to avoid the use of semi-empirical cutoffs in simple asymptotic vdW formulae. The essential physics of our approach is straightforward: a major reason for reduced response in small systems is that their electrons are tied down (pinned) by the same confining potential which causes the system to have finite size. Thus, particularly at low driving frequency and long wavelength where inertial confinement is ineffective, the lack of pinning in a homogeneous electron gas makes that system a very poor model for the response of a finite or confined system. This vague idea is transformed into a precise constraint on response functions, by using a force theorem described in the following subsection.

(4a) Force Theorem

By viewing the ground state from a moving reference frame undergoing rigid simple harmonic motion of small amplitude, one derives (see the Appendix) the following exact

constraint relating the dynamic polarisability α to the ground-state electron density $n(\vec{r})$ and the static confining potential V_λ:

$$\int d\vec{r}_2 \alpha_{ij,\lambda}(\vec{r}_1,\vec{r}_2,\omega)\left(\frac{\partial^2}{\partial r_{2I}\partial r_{2j}}V_\lambda(\vec{r}_2) - m\omega^2\delta_{jI}\right) = e^2\delta_{iI}n(\vec{r}_1). \tag{24}$$

Here V_λ is the effective external potential required to maintain the true ($\lambda = 1$) ground-state density in the presence of a pair interaction $\lambda e^2|\vec{r} - \vec{r}\,'|$. There are two cases where fairly accurate values of V_λ are typically available. The first case is $\lambda = 0$ for which $V_{\lambda=0}$ is the Kohn–Sham potential V^{KS}, obtainable numerically to reasonable accuracy from a number of density functional theory packages, while $\alpha_{\lambda=0}$ is the bare or Kohn–Sham response. The other case is $\lambda = 1$ for which $V_{\lambda=1}$ is the bare external confining potential V^{ext} and $\alpha_{\lambda=0}$ is the interacting polarisability. For these cases (24) represents a practically useful constraint, as we shall see. The theorem (24) is essentially that derived for the tensor χ_{ij} (see equation 2) by Vignale and Kohn (1996). In Vignale and Kohn the theorems were used to help identify necessary properties of the tensor exchange-correlation kernel $\mathbf{f}_{xc}$ in time-dependent density functional theory. When $\mathbf{f}_{xc}$ is neglected in time-dependent DFT (giving the full RPA theory), satisfaction of (24) is automatic. Similarly, it can be shown (Dobson and Le 2000) that satisfaction of these force equations is automatic in electron hydrodynamics provided that the pressure force per unit volume is correctly written as a space gradient. Then the net self-force on a system due to pressure vanishes: that is, the pressure term satisfies conservation of momentum. If we attempt to write the response function down directly, however, without solving theories such as the RPA or hydrodynamics, then (24) becomes a significant constraint, and this is the approach we will explore here.

(4b) vdW Implications of the Force Theorem for Systems of Infinite Area

One interesting property of the force theorem (24) for $\lambda = 0$ relates to planar geometry, that is to a pair of parallel jellium metal slabs of finite thickness L, or of infinite thickness, separated by distance D. The zero-temperature van der Waals energy of these systems is known (Sernelius and Björk 1998; Dobson and Wang 1999) to be proportional to $D^{-5/2}$ when $D \gg \lambda_{TF}, L$, and proportional to D^{-2} when $D \gg \lambda_{TF}$ and $L \to \infty$. We have evidence (Dobson and Wang 2000) that *any* approximation for α_0 which satisfies (24) for $\lambda = 0$ leads to these correct asymptotic vdW forces, after using (8) to obtain χ_0, solving (9) for χ_λ with any short-ranged $f_{xc,\lambda}$, and substituting into (11) to obtain the correlation energy. This is true even for very trivial approximations for α_0, such as the space delta-function discussed below, though there the Kohn–Meir–Makarov long-ranged pair potential (see equation 12) should be used to avoid a contact divergence where $\vec{r} = \vec{r}\,'$. These good properties are not maintained if we apply the force theorem (24) directly to the interacting $\alpha_{\lambda\neq 0}$, thus obtaining χ_λ without solving the screening equation. In these systems with infinite area, in order to obtain the correct long-ranged vdW behaviour, it is necessary to solve the screening equation fully in the appropriate geometry. Perturbation in the inter-slab Coulomb potential is not sufficient: that is, (13) cannot be used to replace the solution of (9). The details of the seamless vdW functional arising from these considerations for slab geometry will be given elsewhere (Dobson and Wang 2000). The present paper will concentrate on small non-overlapping systems such as atoms, where the perturbative result

(13) reduces the prediction of vdW forces to computation of the dynamic response of each atom separately: see equations (14)–(16).

(4c) Local Approximation for α_λ with Force-theorem Constraint

The principal result of the present paper is that the sum rule (24) is sufficient to determine the response completely, if we assume, as in the asymptotic theories outlined in Section 3*b* above, that the polarisability is local in space, so that

$$\alpha_{ij,\lambda}(\vec{r}_1,\vec{r}_2,\omega) = \delta(\vec{r}_1-\vec{r}_2)a_{ij,\lambda}(\vec{r}_1) \ . \tag{25}$$

Putting (25) into the constraint (24) we find

$$a_{ij,\lambda}(\vec{r}) = -e^2[\mathbf{B}^{-1}]_{ij}n(\vec{r}), \tag{26}$$

where

$$B_{ij}(\vec{r}) = -\frac{\partial^2 V_\lambda}{\partial r_i \partial r_j} + m\omega^2\delta_{ij}. \tag{27}$$

Note that there was no need to appeal to properties of the homogeneous electron gas: the assumption (25) of spatial locality, plus the exact force sum rule (24), are sufficient to determine α_λ completely.

Defining $V_{ij,\lambda}(\vec{r}) = \partial 2V_\lambda/\partial r_i \partial r_j$ (a symmetric curvature tensor or Hooke's law force-constant tensor at the point $\vec{r}$), we can diagonalise $V_{ij,\lambda}$ at each space point $\vec{r}$:

$$V_{ij,\lambda}(\vec{r}) = m\sum_n \xi_i^{*(n)}(\vec{r})\xi_j^{(n)}(\vec{r})\Lambda^{(n)}(\vec{r}),$$

where m is the electron mass. The eigenvalues $\Lambda^{(n)}(\vec{r}) = \omega^{(n)2}(\vec{r})$ can be thought of as the squares of harmonic frequencies $\omega^{(n)}$ matched to the local curvature of the potential, but note that $\lambda^{(n)}$ may be negative. The matrix $\boldsymbol{B}$ can then be inverted in general to give

$$\alpha_{ij,\lambda}(\vec{r}_1,\vec{r}_2,\omega) = \delta(\vec{r}_1-\vec{r}_2)\sum_n \xi_i^{*(n)}(\vec{r})\xi_j^{(n)}(\vec{r})\frac{1}{m[\omega^{(n)2}(\vec{r})-\omega^2]}. \tag{28}$$

Here $\vec{\zeta}^{(n)}$ and $\omega^{(n)}$ both depend on the coupling strength λ, but for notational simplicity this dependence has not been shown explicitly in (28). Equation (28) can be used to obtain the dipolar polarisability as in equations (14)–(16). The spherical case is studied below.

(4d) Polarisability α_λ of Spherical System with Local Force-theorem Ansatz

For spherical (or sphericalised) atoms the confining potential is a function of radius only $[V_\lambda(\vec{r}) \equiv V_\lambda(r)]$, and then (27) becomes

$$\begin{aligned} B_{ij}(\vec{r}) &= -\frac{\partial^2 V_\lambda}{\partial r_i \partial r_j} + m\omega^2\delta_{ij} \\ &= -\frac{r^2\delta_{ij} - r_i r_j}{r^3}\, V_\lambda{}'(r) - \frac{r_i r_j}{r^2} V_{\lambda k}{}''(r) + m\omega^2\delta_{ij}. \end{aligned}$$

This can be written in the usual polar coordinates (r, θ, ϕ) as

$$\begin{aligned}\mathbf{B}(\vec{r}) &= m\omega^2\mathbf{I} - \vec{\nabla}\vec{\nabla}V_\lambda(r)\\ &= m\omega^2\mathbf{I} - V_\lambda{}''(r)\hat{r}\hat{r} - \frac{1}{r}V_\lambda{}'(r)[\mathbf{I}-\hat{r}\hat{r}]\\ &= [m\omega^2 - V_\lambda{}''(r)]\hat{r}\hat{r} + \left(m\omega^2 - \frac{1}{r}V_\lambda{}'(r)\right)[\hat{\theta}\hat{\theta}+\hat{\phi}\hat{\phi}],\end{aligned}$$

where $\hat{r}$, $\hat{\theta}$, $\hat{\phi}$ are the usual unit vectors and we have noted that $\hat{r}\,\hat{r}+\hat{\theta}\,\hat{\theta}+\hat{\phi}\,\hat{\phi} = \mathbf{I}$. Thus the tensor $\mathbf{B}(\vec{r})$ is diagonal in the orthonormal basis $(\hat{r}, \hat{\theta}, \hat{\phi}) \equiv (\vec{\xi}^{(1)}, \vec{\xi}^{(2)}, \vec{\xi}^{(3)})$ and so can be inverted immediately (see equation 28). Then (25) and (26) give for a spherical system

$$\alpha_\lambda(\vec{r},\vec{r}',\omega) = e^2 n(r)\delta(\vec{r}-\vec{r}')\left(\frac{1}{V_\lambda{}''(r) - m\omega^2}\hat{r}\hat{r} + \frac{1}{\frac{1}{r}V_\lambda{}'(r) - m\omega^2}[\hat{\theta}\hat{\theta}+\hat{\phi}\hat{\phi}]\right), \quad (29)$$

where

$$V_{\lambda=0}(\vec{r}) = V^{KS}(\vec{r}), \quad V_{\lambda=1}(\vec{r}) = V^{ext}(\vec{r}).$$

(4e) Dipole Polarisability of Spherical System with Local Force-theorem Ansatz for α_λ

For a spherical system (29) and (15) give a dipole polarisability

$$\begin{aligned}\mathbf{A}_\lambda(\omega) = e^2\int r^2 dr n(r)\Bigg(&\frac{1}{V_\lambda{}''(r) - m\omega^2}\int d^2\Omega\hat{r}\hat{r}\\ &+ \frac{1}{\frac{1}{r}V_\lambda{}'(r) - m\omega^2}\int d^2\Omega(\mathbf{I}-\hat{r}\hat{r})\Bigg),\end{aligned}$$

where

$$\int d^2\Omega \equiv \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta).$$

Using

$$\int \mathbf{I}d^2\Omega = 4\pi\mathbf{I}, \quad \int \hat{r}\hat{r}d^2\Omega = \frac{4\pi}{3}\mathbf{I},$$

we obtain the dipole polarisability of a spherical system as

$$\mathbf{A}_\lambda(\omega) = \frac{4\pi e^2}{3}\mathbf{I}\int_0^\infty dr r^2 n(r)\left([V_\lambda{}''(r) - m\omega^2]^{-1} + 2\left(\frac{1}{r}V_\lambda{}'(r) - m\omega^2\right)^{-1}\right). \quad (30)$$

For $\omega = 0$ this becomes

$$\mathbf{A}_\lambda(\omega=0) = e^2\frac{4\pi}{3}\mathbf{I}\int_0^\infty dr r^2 n(r)\left([V_\lambda{}''(r)]^{-1} + 2r[V_\lambda{}'(r)]^{-1}\right), \quad (31)$$

while at high frequency V_λ'' and $r^{-1}V_\lambda'$ are negligible beside $m\omega^2$, so that

$$\begin{aligned}\mathbf{A}_\lambda(\omega\to\infty) &\sim \frac{4\pi e^2}{3}\frac{-1}{m\omega^2}\mathbf{I}\int_0^\infty dr r^2 n(\vec{r})[1+2]\\ &= \frac{-e^2}{m\omega^2}\mathbf{I}\int_0^\infty dr 4\pi r^2 n(\vec{r}) = \frac{-e^2}{m\omega^2}\mathbf{I}\int_0^\infty n(\vec{r})d^3r\\ &= \frac{-e^2}{m\omega^2}N\mathbf{I}. \end{aligned} \tag{32}$$

This is the response of N free electrons, as required by a version of the f-sum rule.

(4f) Test on Hooke's Atom (Parabolic Quantum Dot)

Hooke's atom is a simple model of N electrons confined by an isotropic harmonic external potential, $V^{ext}(\vec{r}) = \frac{1}{2}m\omega_0^2 r^2$, and interacting amongst themselves via the usual Coulomb potential. For this system the harmonic potential theorem (HPT) (extended generalised Kohn theorem, Dobson 1994*b*) shows that, under the action of an oscillating spatially uniform electric field $\vec{E}_0\cos(\omega t)$, the ground-state density $n(\vec{r})$ moves rigidly with simple harmonic motion, yielding a density $n(\vec{r} - \vec{R}(t))$, where $\vec{R}(t) = -e\vec{E}_0 m^{-}[\omega^2 - \omega_0^2]^{-1}\cos(\omega t)$. This gives a dipole moment

$$\vec{P} = -Ne\vec{R}(t) = Ne^2\vec{E}_0 m^{-1}[\omega^2 - \omega_0^2]^{-1}\cos(\omega t).$$

The dynamic interacting dipole polarisability of Hooke's atom is thus exactly

$$\mathbf{A}^{\text{Hooke}}(\omega) = Ne^2 m^{-1}[\omega^2 - \omega_0^2]^{-1}\mathbf{I}.$$

We now show that our constrained local approximation (30) for $\lambda = 1$ reproduces this exact result. For this case, $V_{\lambda=1}(r) = V^{ext}(r) = \frac{1}{2}m\omega_0^2 r^2$, so that (30) becomes

$$\begin{aligned}\mathbf{A}_{\lambda=1}(\omega) &= \frac{4\pi e^2}{3}\mathbf{I}\int_0^\infty dr r^2 n(r)\left([m\omega_0^2 - m\omega^2]^{-1} + 2[m\omega_0^2 - m\omega^2]^{-1}\right)\\ &= \mathbf{I}\int_0^\infty dr\frac{4\pi}{3}r^2 n(r)(1+2)dr e^2 m^{-1}[\omega_0^2 - \omega^2]^{-1}\\ &= \mathbf{I}\int_0^\infty n(r)4\pi r^2 dr e^2 m^{-1}[\omega_0^2 - \omega^2]^{-1} = Ne^2 m^{-1}[\omega^2 - \omega_0^2]^{-1}\mathbf{I}\text{: QED.}\end{aligned}$$

It is also readily shown that the present theory gives the exact dipole polarisability of *anisotropic* Hooke's atoms at all frequencies.

(4g) Dipole Polarisablity of Regular Atoms

We have also applied our formula (30) to regular atoms. In finite charge-neutral systems such as these it is important to obtain the density and Kohn–Sham potential from a self-interaction-corrected (SIC) formalism. This is because, in the local density approximation (LDA) (Kohn and Sham 1965) and related formalisms, the unphysical repulsion of the electron in each orbital from its own orbital charge density causes $V_{KS}(\vec{r})$ to lack the correct $-e^2/r$ behaviour at large distance r from the nucleus (Perdew and Zunger 1981). The outer orbitals are strongly affected, and hence so is the density in the outer region

where most of the polarisability is generated. We used an atomic code written by H. B. Shore and J. H. Rose, implementing the Perdew–Zunger (1981) LDA–SIC scheme. In place of the unknown exact (and therefore automatically SIC) KS potential, we used a density-weighted combination of SIC potentials from the various orbitals i:

$$V_{\lambda=0}(\vec{r}) = \left(\sum_{i\ occ} V_i^{eff} n_i(\vec{r}) \right) / n(\vec{r}). \tag{33}$$

Very similar results were also obtained using, for all orbitals, the V_i from the last occupied SIC orbital.

So far the static dipole polarisability has been investigated in detail using (31). Table 1 shows atomic dipole polarisabilities in units of 10^{-24} cm^3 (Gaussian cgs units). Note that 10^{-24} cm^3 ≡ 6.7487 Hartree units.

For the elements from H to Na, the static polarisability data from Table 1 is also plotted in Figs 1 and 2. Fig. 1 shows the weakly polarisable elements (those with a full or nearly

Table 1. Static dipolar polarisabilities of atoms

Units are 10^{-24} cm^3 (Gaussian cgs). Column 2: accurate values of the interacting polarisability from Chemical Rubber Company Tables (CRC 1995). Column 3: predicted interacting polarisabilities from the $\lambda = 1$ version of equation (31). Column 4: predicted bare polarisabilities from the $\lambda = 0$ version of equation (31), using orthogonalised SIC density and orbital-averaged potential from (33) (results in brackets used the SIC potential V_j of the last occupied orbital). Column 5: predicted interacting polarisabilities from existing cutoff local theory, equations (21) and (22) (results in brackets used spin-polarised cutoff, equation 23)

Atom	$A_{\lambda=1}^{exact}(\omega = 0)$ CRC (1995)	$A_{\lambda=1}^{force\ thm}(\omega = 0$ Eq. (31)	$A_{\lambda=1}^{force\ thm}(\omega = 0)$ Eq. (31) $V_{\lambda=0}$ from (33) (Brackets: $V_{i\ max}$)		$A_{\lambda=1}^{cutoff}(\omega = 0)$ Eq. (19), cutoff as in (22) (Brackets: cutoff from 23)	
H	0.666793	0.556	0.556	[0.555]	1.55	(0.714)
He	0.204956	0.1406	0.2505	[0.250]	0.28638	(0.10467)
Li	24.3±2%	4.614	6.8927	[7.05]	27.67	(18.245)
Be	5.6±2%	1.1283	3.7747	[3.78]	9.093	
B	3.03±2%	0.6873	2.4785	[2.47]	5.022	
C	1.76±2%	0.41789	1.6310	[1.79]	3.089	
N	1.1±2%	0.27138	1.1394	[1.309]	1.755	
O	0.802±2%	0.1982	0.9248	[0.953]	1.136	
F	0.557	0.1446	0.72927	[0.751]	0.743	
Ne	0.3956±0.1%	0.1082	0.5825	[0.586]	0.499	
Na	24.08±0.4%	0.76156	7.8466	[8.004]	32.14	(9.324)
Mg	10.6±2%	0.6485	6.178	[6.240]	15.45	
. . .						
Kr	2.4844±0.05%	0.1832	2.9241	[2.973]		
Rb	47.3±2%	0.54199	15.8443	[16.72]		
Sr	27.6±8%	0.57171	14.985	[15.15]		
. . .						
U	24.9±6%	0.3504	18.1503			

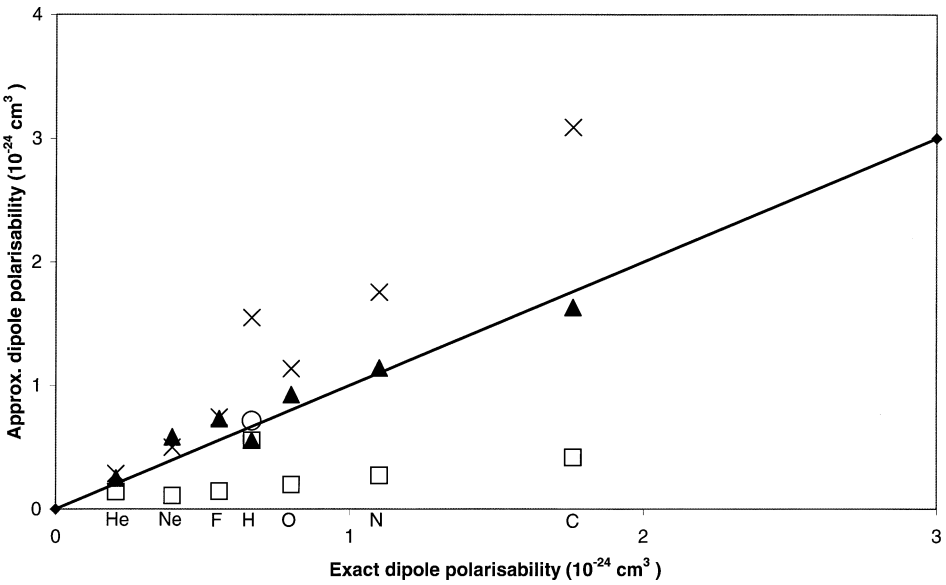

Fig. 1. Dipole polarisabilities of weakly polarisable atoms, in units of 10^{-24} cm^3 (Gaussian cgs). The horizontal axis orders elements by their interacting dipole polarisability from experiment or accurate theory (CRC 1995). The vertical axis shows approximate polarisabilities for various theories. Solid line: accurate results from CRC (1995). Solid triangles: bare or Kohn–Sham values from equation (31) with $\lambda = 0$. Open squares: interacting values from (31) with $\lambda = 1$. Crosses: existing cutoff theory (spin unpolarised) from equations (19) and (22). Open circle: existing cutoff theory (spin polarised) from equations (19) and (23) (shown only for hydrogen since inclusion of spin polarisation does not appear to improve the other monovalent cases).

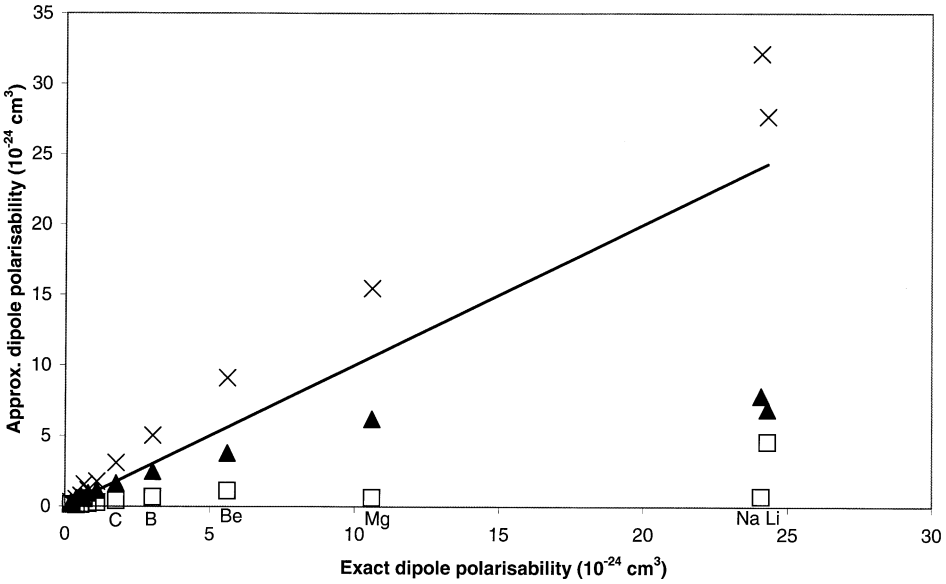

Fig. 2. Dipole polarisabilities as in Fig. 1, but including highly polarisable atoms. The congested part of this figure is shown more clearly in Fig. 1.

full outer shell). Here the exact interacting polarisability (solid line) is quite well reproduced by the bare polarisability from the local force-theorem formula (31) with $\lambda = 0$ (solid triangles). For these systems, the new formula does somewhat better than the previous local formula (21) with the cutoff (22) (crosses). [Without the cutoff the previous theory (20) gives an infinite polarisability at zero frequency.] Since Coulomb screening of perturbations is weak in these tightly-bound systems, it is not surprising that an approximate theory for the *bare* response gives results close to the *interacting* response. It seems at first paradoxical, however, that the dipole polarisability is seriously underestimated (open squares) by the local-force-theorem approximation (31), applied directly for the interacting response $\alpha_{\lambda=1}$. Since the force theorem is exact, the local assumption (25) would therefore seem to be less accurate for the interacting response $\alpha_{\lambda=1}$ than for the bare response $\alpha_{\lambda=0}$, in these systems. While the screening of a given bare response does not greatly affect the dipole moment $\int \alpha_\lambda d\vec{r} d\vec{r}'$ in tightly bound systems, the extra nonlocality introduced into α by screening evidently does make a large difference in the application of the force theorem (24), where α_λ is integrated with a rapidly varying function $\vec{\nabla}\vec{\nabla}V_\lambda$. The notion that a local approximation is better for a bare than for an interacting polarisability is certainly in line with the philosophy of Dobson (1994*a*), Dobson and Wang (1999) and Dobson *et al.* (1998).

Fig. 2 plots the approximation (31) and other approximations as for Fig. 1, but for a range of more highly polarisable atoms with only one or two electrons present in the outer shell. For the divalent metals Be and Mg, our new approximation (31) for the bare response (solid triangles) gets only about two-thirds of the exact interacting result, slightly better than the older local theory given by (18) and (22) which overestimates by 50% or more. Only for the alkali metals Na and Li does the new theory do worse than the old, giving only about one-third of the correct polarisability. In these cases there is a near-degeneracy between the outer s orbital and a dipole-allowed excited p orbital, resulting in a very large dipole polarisability because of a small energy denominator in equation (7). With such an orbital-specific mechanism in force, it is unsurprising that a crude local theory does poorly.

Once more, it is evident in Fig. 2 that the local-force-theorem approximation based on the *interacting* response gives a severely under-estimated polarisability (open squares).

(4h) Dipole Response of Atoms at Finite Frequency: vdW C_6 Coefficient

We have already noted that the high-frequency response is correct in our new theory based on the force theorem (see equation 32), and we found in the previous section that the zero-frequency response for atoms is typically comparable to or better than that from the older local theory, except for alkali metal atoms. One might therefore imagine that the response would be a good approximation at all finite complex frequencies. This is too much to ask of such a simple theory, however, because the exact response must have poles on the real frequency axis corresponding to discrete atomic excitation frequencies which are not present in the approximate theory. This in itself is not a problem for calculation of the vdW interaction, because one can use analyticity to write the asymptotic vdW interaction as an integral of the dipolar polarisability over imaginary frequencies, $\omega = is$. On the imaginary frequency axis the exact susceptibility α is a real, smooth function of s: it is guaranteed to lack singularities on the imaginary axis because causality ensures it is analytic in the upper half frequency plane. In this connection the approximation (30) has a serious problem, because $V''(r)$ is typically negative for atoms, so that α has poles on the imaginary

frequency axis [as well as poles on the real axis from the $r^{-1}V'(r)$ term]. These poles on the imaginary axis correspond to a lack of causality which can be traced back to the local assumption made in equation (25), and its effect in the force sum rule (24). Because of the poles just described, one cannot in practice perform a numerical integral over imaginary frequency to obtain the vdW C_6 coefficient. Instead, one can integrate along (for example) a contour at 45° to the real frequency axis, where there are no poles. Our preliminary results for this process have been disappointing, with predicted C_6 values only about half of the true answer, even for atoms where the new theory gave a good estimate of the static polarisability. The details will be described elsewhere when complete.

5. Summary and Discussion

In the context of van der Waals interactions, we have proposed a new approach using constrained approximations for dynamic response functions of inhomogeneous many-electron systems. The exact constraint used was the force theorem (24) for the dynamic polarisability $\alpha(\vec{r}, \vec{r}\,', \omega)$. We outlined several paths to simplified vdW energy calculations via approximations for response functions, in which the constraint could be useful. First we have given a brief discussion of the application of the force theorem in 'seamless' vdW theory, valid for vdW-interacting systems at all separations, where the new constraint automatically imposes the correct asymptotic vdW behaviour for distant parallel jellium slabs. Our main emphasis, however, was on the simplified perturbative calculation of vdW effects for finite well-separated systems. For the case of atoms, the correct results are of course known from existing, more computationally intensive methods, providing a test of our theory.

The simplest existing approximate theory for such cases (Rapcewicz and Ashcroft 1991; Dobson and Dinte 1997; Andersson *et al.* 1996) assumed a local form for α, based on the long-wavelength response of a uniform electron gas (see equations 19 and 21). If applied verbatim to small bound systems such as atoms, this approach gives very poor results including a divergent static dipolar polarisability, and grossly over-estimated vdW attraction. With use of a semi-empirical cutoff (Rapcewicz and Ashcroft 1991; Andersson *et al.* 1996, 1998) in the low-density regions, however, the existing approach was found to give reasonable vdW C_6 coefficients for a range of systems, with some tendency to over-estimation.

The principal aim of the present work was to remove the need for semi-empirical cutoffs, while maintaining the simplicity of a local theory. We found that, with the local assumption (25), the force theorem (24) was sufficient to determine the polarisability $\alpha_\lambda(\vec{r}, \vec{r}\,', \omega)$ completely, without the need for cutoffs or even the use of the response properties of a uniform electron gas (see equation 28). For the first twelve elements H–Mg, the resulting function α_λ was used to compute the dipolar polarisability $\boldsymbol{A}_\lambda$ (equations 30 and 31), from which the van der Waals coefficient C_6 can also be obtained via (16). Two versions of this theory were tested.

The first ($\lambda = 0$) version of the theory expresses $\alpha_{\lambda=0}$ directly in terms of the ground-state density and the static Kohn–Sham potential (see equation 15). This theory gave reasonable values for $\boldsymbol{A}(\omega = 0)$, slightly better than the previous theory with cutoff, for the weakly polarisable atoms (see Fig. 1). For the alkali metals, however, the new theory gives only about one-third of the correct polarisability (see Fig. 2). These metals owe their very high polarisability to a near-degeneracy of s- and p-orbitals, an effect probably not systematically reproducible in a simple, non-wavefunction approach.

In contrast, for $\lambda = 1$, the new theory severely underestimated the static dipole polarisability of most atoms. Since the force theorem is exact, the nonlocality of the Coulomb screening effects in the interacting polarisability $\alpha_{\lambda=1}$ must be the culprit, invalidating the local approximation in the context of the force theorem. Fortunately, the interacting dipole polarisability $\boldsymbol{A}_{\lambda=1}$ is close to the KS polarisability $\boldsymbol{A}_{\lambda=0}$ for most atoms. (For atoms with substantially full outer shells, the binding is tight and the polarisability and screening are small, while for the monovalent elements the most polarisable outer electron cannot screen itself (SIC effect). It is mainly for the divalent atoms that screening strongly affects the overall dipolar polarisability. The same argument, implying minimal effects of screening, cannot be made in the context of the force theorem, where α is integrated with a strongly varying function $\vec{\nabla}\vec{\nabla}V^{ext}$ (there the nonlocality introduced by the screening term can override its small size).

Thus, fortunately, our $\lambda = 0$, $\omega = 0$ theory can be used for most atoms, at the level of accuracy of these very simple theories.

In order to predict van der Waals forces, it is necessary to know $\boldsymbol{A}(\omega)$ for finite as well as zero frequency ω (see equations 14 and 16). Here our simplest force-constrained theory did not do so well, underestimating the vdW C_6 coefficient in our initial tests, despite its relatively good low-frequency and high-frequency properties. The problem appears to be related to a lack of causality arising from imaginary pinning eigenfrequencies $\omega^{(n)}$ (negative principal values of the curvature tensor $\vec{\nabla}\vec{\nabla}V^{KS}$) in equation (28). We believe that a simple nonlocal theory might do better, by averaging over regions of negative and positive curvature: in some sense the latter must predominate if the system is overall bound. In this context, it is noteworthy that the kinetic pressure of the electron gas has been ignored, both in the relatively successful cutoff vdW theory (equations 19 and 22), and also in our new theory. The pressure leads to dispersion of the plasmon pole in equation (18), and to a corresponding space nonlocality in the polarisability tensor $\alpha_\lambda(\vec{r}, \vec{r}\,', \omega)$. Information from the homogeneous electron gas, not used in the local α_0 form of the present theory, can be inserted into the formalism at this level. We are currently investigating this.

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Appendix: Derivation of Force Theorem for α

Consider a fictitious system with reduced pair interaction $U_\lambda = \lambda e^2/|\vec{r} - \vec{r}\,'|$ in an external one-electron potential $V_\lambda(\vec{r})$. For $\lambda = 1$, we have the true Coulomb problem and $V_{\lambda=1}$ is defined to be the true external potential $V^{ext}(\vec{r})$, giving the true ground-state density $n(\vec{r})$. For each $\lambda < 1$, $V_\lambda(\vec{r})$ is *defined* so that the ground-state density with U_λ and V_λ is still the true ground-state density $n(\vec{r})$. For $\lambda = 0$ we have independent electrons, for which the external potential producing $n(\vec{r})$ is V_{KS}, by definition of the Kohn-Sham (1965) potential $V_{KS}(\vec{r})$. Thus, we have

$$V_{\lambda=1} = V^{ext}, \quad V_{\lambda=0} = V_{KS}, \quad n_\lambda(\vec{r}) \equiv n(\vec{r})\,\forall\lambda. \tag{34}$$

This construction of V_λ is the standard one for implementation of the exact adiabatic connection formula (11). The external electric field corresponding to the external potential V_λ is

$$\vec{E}_\lambda(\vec{r}) = e^{-1}\vec{\nabla}V_\lambda(\vec{r}). \tag{35}$$

Now view the fictitious system, in its ground state $|\,\psi_\lambda\,\rangle$, from a (non-rotating, non-relativistic) frame whose moving origin O' is at position

$$\vec{X}(t) = \vec{X}\cos(\omega t)$$

relative to the original stationary frame. In this frame the position coordinate is $\vec{r}\,' = \vec{r} - \vec{X}(t)$, so that $\vec{r} = \vec{r}\,' + \vec{X}(t)$. The density function in the moving frame is

$$n'(\vec{r}',t) = n(\vec{r}) = n(\vec{r}' + \vec{X}(t)) = n(\vec{r}') + \vec{X}(t).\vec{\nabla}n(\vec{r}') \text{ to linear order.} \tag{36}$$

The external field seen in the accelerated frame includes a fictitious or inertial component:

$$\begin{aligned}\vec{E}_\lambda{}' &= \vec{E}_\lambda(\vec{r}) + (-e)^{-1}\left(-m\frac{d^2}{dt^2}\vec{X}(t)\right)\\ &= \vec{E}_\lambda(\vec{r}' + \vec{X}(t)) - me^{-1}\omega^2\cos(\omega t)\vec{X}\\ &= \vec{E}_\lambda(\vec{r}') + (\vec{X}(t).\vec{\nabla})\vec{E}_\lambda(\vec{r}') - me^{-1}\omega^2\cos(\omega t)\vec{X},\end{aligned} \tag{37}$$

where linearisation in $\vec{X}$ is used in the last line.

Thus, the accelerated observer sees a zeroth order confining external field $\vec{E}_\lambda(\vec{r}\,')$ the same as the stationary observer, and a linearised additional external driving field

$$\delta\vec{E}_\lambda{}' = \cos(\omega t)[(\vec{X}.\vec{\nabla}')\vec{E}_\lambda(\vec{r}') - me^{-1}\omega^2\vec{X}], \tag{38}$$

where linearisation in $\vec{X}$ was used to replace $\vec{\nabla}$ by $\vec{\nabla}'$.

Since the accelerated observer is simply viewing the rest-frame ground state, he sees a rigid displacement of the ground state with velocity $-d\vec{X}/dt = \omega\sin(\omega t)\vec{X}$ and hence from (36) an electric current density

$$\begin{aligned}\vec{j}' &= -en(\vec{r}' + \vec{X}\cos(\omega t))(\omega\vec{X}\sin(\omega t))\\ &= -en(\vec{r}')\vec{X}\omega\sin(\omega t)\end{aligned} \tag{39}$$

to linear order in $\vec{X}$. Therefore, from (4), by time-integrating (39),

$$\delta\vec{p}' = en(\vec{r}')X\cos(\omega t). \tag{40}$$

Since $\vec{r}$ and $\vec{r}'$ differ only by the space-independent displacement $\vec{X}(t)$, the electron–electron interaction in the accelerated frame is $U_\lambda'(\vec{r}_1{}', \vec{r}_2{}') = \lambda e^2/|\vec{r}_1 - \vec{r}_2| = \lambda e^2/|\vec{r}_1{}' - \vec{r}_2{}'|$, of the same form as in the rest frame. Indeed all effects of the acceleration, including the fictitous force in equation (37), are accounted for by the linearised external driving field (38).

The field $\delta\vec{E}'$ (equation 38) and polarisation $\delta\vec{p}'$ (equation 40) are seen in the accelerated frame as small departures about an equilibrium described by $n(\vec{r}\,')$, $E_\lambda(\vec{r}\,') = -\vec{\nabla}'V_\lambda(\vec{r}\,')$. They must therefore be related by the corresponding polarisability $\alpha_\lambda(\vec{r}_1, \vec{r}_2{}', \omega = is)$, the same function as for the rest frame. Thus, from the definition (5),

$$\int d\vec{r}_2\alpha_\lambda(\vec{r}_1{}', \vec{r}_2{}', is)[(\vec{X}.\vec{\nabla}')\vec{E}_\lambda(\vec{r}_2{}') - me^{-1}\omega^2\vec{X}]\cos(\omega t) = e\vec{X}\cos(\omega t)n(\vec{r}_1{}'). \tag{41}$$

This must hold for arbitrary vectors $\vec{X}$. [Since (41) is already linearised $\vec{X}$ does not need to be small.] Thus we can choose $X_k = \delta_{Ik}$ for I arbitrary. Then, using the Einstein summation convention and renaming dummy position variables, we have

$$\int d\vec{x}\alpha_{ij,\lambda}(\vec{r},\vec{x},\omega)\left(\frac{\partial}{\partial x_I}\vec{E}_{j,\lambda}(\vec{x}) - me^{-1}\omega^2\delta_{jI}\right) = e\delta_{iI}n(\vec{r}) \tag{42}$$

or, using (35)

$$\int d\vec{x}\alpha_{ij,\lambda}(\vec{r},\vec{x},\omega)\left(\frac{\partial^2}{\partial x_I\,\partial x_j}V_\lambda(\vec{x}) - m\omega^2\delta_{jI}\right) = e^2\delta_{iI}n(\vec{r}). \tag{43}$$

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