

## van der Waals Energies in Density Functional Theory

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In principle, density functional theory yields the correct ground-state densities and energies of electronic systems under the action of a static external potential. However, traditional approximations fail to include van der Waals energies between separated systems. This paper proposes a practical procedure for remedying this difficulty. Our method allows seamless calculations between small and large intersystem distances. The asymptotic H-He and He-He interactions are calculated as a first illustration, with very accurate results. [S0031-9007(98)05991-2]

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Density functional theory (DFT) [1–3] has become a useful tool for calculating ground-state energies and density distributions of atoms, molecules, and solids, particularly of systems consisting of *many* atoms. The simplest approximation for practical purposes is the local-density approximation (LDA) [2], based on the properties of the uniform electron gas. The so-called generalized gradient approximations (GGA) are important refinements of the LDA [3].

In principle, DFT yields the exact ground-state energy, including long-range van der Waals (vdW) energies, very important in organic chemistry and elsewhere. However, the commonly used LDA and GGA, designed for nonuniform electron gases, fail to capture the essence of vdW energies. The latter reflect correlated motions of electrons due to the Coulomb interactions between distant, even nonoverlapping atoms, molecules, and solids. Thus a new strategy is needed.

Here we propose a first-principles approach, which contains the following ingredients: (i) The density distribution,  $n(r)$ , is approximated by the LDA or GGA. (ii) The Coulomb interaction is divided into short and long-range parts, of which only the latter contributes to vdW energies. (iii) The contribution of the long-range interactions to the energy is expressed by the so-called adiabatic connection formula [see Eq. (3) below]. (iv) This expression is transformed into the time domain, avoiding the need to solve a self-consistent equation for the density-density response function. As an illustration we calculate the asymptotic vdW interaction between two helium atoms and between hydrogen and helium atoms, with excellent results. The method allows seamless calculation of the interaction of two subsystems, e.g., an atom and a surface, from small to large separations. Our work was carried out independently and differs substantially from recently published work by Andersson *et al.* [4] and by Hult *et al.* [5], which depend critically on a fitting parameter.

Since the vdW energies are due to the long range of the electron-electron interaction,  $U(r) = 1/r$ , we may separate this interaction, as a preliminary step, into short- and long-range parts,

$$U(r) = U_{\text{sr}}(r) + U_{\text{lr}}(r). \quad (1)$$

For example, we can choose  $U_{\text{sr}}(r) \equiv e^{-\kappa r}/r$ , with a suitably chosen value of  $\kappa$ . The calculated total energy is, in principle, independent of the choice of  $\kappa$ , in practice—with appropriate approximations—nearly so. (This separation is not a necessity. The theory can also be developed with  $\kappa = \infty$ , i.e.,  $U_{\text{lr}} = U$  and  $U_{\text{sr}} = 0$ .)

We now write the Hamiltonian as a function of a coupling constant  $\lambda$  that “turns on”  $U_{\text{lr}}$ , such that the physical Hamiltonian operator corresponds to  $\lambda = 1$ :

$$\mathcal{H}(\lambda) = T + V_\lambda + U_\lambda, \quad 0 \leq \lambda \leq 1, \quad (2)$$

where  $T$  is the kinetic energy,  $U_\lambda \equiv U_{\text{sr}} + \lambda U_{\text{lr}}$ , and the external potential  $V_\lambda$  is chosen such that the ground-state density  $n_\lambda(r)$  of  $\mathcal{H}(\lambda)$  equals the exact physical density  $n_{\lambda=1}(r)$  for all  $\lambda$  [6]. Note that for  $\lambda = 0$ , the interaction is entirely short range and that, for  $\lambda = 1$ ,  $V_{\lambda=1} = V_{\text{ext}}$ . We denote the ground-state energy of  $\mathcal{H}(\lambda)$  by  $E(\lambda)$ . Then the ground-state energy of the physical system,  $E \equiv E(1)$ , is given by

$$\begin{aligned} E &= E(0) + \int_0^1 d\lambda \frac{dE}{d\lambda} \\ &= E(0) + \int_0^1 d\lambda \left[ \frac{dV_\lambda(r)}{d\lambda} n(r) + \langle U_{\text{lr}} \rangle_\lambda \right] \\ &= E(0) + \int dr [V_{\text{ext}}(r) - V_0(r)] n(r) \\ &\quad + \frac{1}{2} \int dr dr' U_{\text{lr}}(r - r') \\ &\quad \times \left[ \int_0^1 \langle \hat{n}(r) \hat{n}(r') \rangle_\lambda d\lambda - n(r) \delta(r - r') \right], \quad (3) \end{aligned}$$

where  $\hat{n}$  is the density operator and  $\langle \dots \rangle_\lambda$  means expectation value in the ground state of  $\mathcal{H}(\lambda)$ ;  $V_0(r)$ , defined above, eventually drops out [see Eq. (5)].

From DFT, using  $U_{\lambda=0} = U_{\text{sr}}$ ,  $E(0)$  is given by

$$E(0) = T_s[n(r)] + \int dr V_0(r)n(r) + \frac{1}{2} \int dr dr' U_{\text{sr}}(r - r')n(r)n(r') + E_{\text{xc}}^{\text{sr}}[n(r)], \quad (4)$$

where  $T_s[n(r)]$  is the noninteracting kinetic energy functional and  $E_{\text{xc}}^{\text{sr}}[n(r)]$  is the exchange-correlation energy corresponding to density  $n(r)$  and the interaction  $U_{\text{sr}}$ .

Substituting (4) into (3) we find, after simple manipulations, the exact result:

$$E = T_s[n(r)] + \int dr V_{\text{ext}}(r)n(r) + \frac{1}{2} \int dr dr' U(r - r')n(r)n(r') + E_{\text{xc}}^{\text{sr}}[n(r)] - \frac{1}{2} U_{\text{lr}}(0)N + E_{\text{pol}}[n(r)], \quad (5)$$

where  $N$  is the number of electrons and

$$E_{\text{pol}} \equiv \frac{1}{2} \int dr dr' U_{\text{lr}}(r - r') \times \int_0^1 d\lambda [\hat{n}(r) - n(r)][\hat{n}(r') - n(r')]_\lambda. \quad (6)$$

$E_{\text{pol}}$  includes the long-range vdW energies.

To calculate the first four terms in Eq. (5) we use traditional methods. Experience [3] has shown that the density  $n(r)$  may be calculated to a very good approximation by the LDA with the full  $U(r)$ . Such a calculation also automatically yields an approximate  $T_s[n(r)]$ ,

$$T_s[n] = \sum_{j=1}^N \epsilon_j - \int v_{\text{KS}}(r)n(r)dr, \quad (7)$$

where  $v_{\text{KS}}$  is the Kohn-Sham (KS) effective potential that reproduces  $n(r)$ , and the  $\epsilon_j$  are the single-particle energies available from the LDA calculation.  $E_{\text{xc}}^{\text{sr}}[n(r)]$  is available in the LDA [7].

By means of the fluctuation-dissipation theorem we can express the integral in Eq. (6) in terms of the imaginary part of the retarded linear susceptibility  $\chi$  [8],

$$\langle [\hat{n}(r) - n(r)][\hat{n}(r') - n(r')] \rangle_\lambda = -\frac{1}{\pi} \int_0^\infty \text{Im} \chi(r, r'; \omega, \lambda), \quad (8)$$

giving

$$E_{\text{pol}} = - \int dr dr' U_{\text{lr}}(r - r') \times \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{2\pi} \text{Im} \chi(r, r'; \omega, \lambda), \quad (9)$$

where  $\chi$  is defined, as usual, as follows: Let  $V_1(r, \omega)e^{-i\omega t}$  be a small perturbing potential, acting on the ground state of  $\mathcal{H}(\lambda)$ , and producing a density response  $n_1(r, \omega, \lambda)e^{-i\omega t}$ . Then  $\chi$  is defined by

$$n_1(r, \omega, \lambda) = \int dr' \chi(r, r'; \omega, \lambda) V_1(r', \omega). \quad (10)$$

With simple approximations for  $\chi$  (Hartree or better)  $E_{\text{pol}}$  includes long-range vdW energies. For  $\lambda = 1$ , methods used to evaluate  $\chi(r, r'; \omega, \lambda)$  have been discussed in the past [9,10], and can be formally carried over to  $\lambda < 1$ .  $\chi$  is the solution of the integral equation:

$$\chi(r, r'; \omega, \lambda) = \chi_{\text{KS}}(r, r'; \omega) + \int dr'' dr''' \chi_{\text{KS}}(r, r''; \omega) \times [U(r'' - r''') + f_{\text{xc}}(r'', r'''; \omega, \lambda)] \times \chi(r''', r'; \omega, \lambda), \quad (11)$$

where  $\chi_{\text{KS}}(r, r'; \omega)$  is the response function of the corresponding noninteracting Kohn-Sham system, and  $f_{\text{xc}}$  describes exchange and correlation effects [see Eq. (6) of Ref. [10]].

However, except for systems of very high symmetry, such as spherical atoms, the self-consistent solution of (11) is computationally very forbidding. Here we propose an equivalent but much less cumbersome procedure, which avoids the solution of a self-consistent integral equation for each value of  $\lambda$  and of  $\omega$ . We note that  $\chi(r, r'; \omega, \lambda)$  is the Fourier transform,  $\chi(r, r'; \omega, \lambda) = \int dt \chi(r, r'; t, \lambda)e^{i\omega t}$ , of the *time-dependent* response function,  $\chi(r, r'; t, \lambda)$ , defined as follows:

$$n_1(r, t, \lambda) = \int dr' dt' \chi(r, r'; t - t', \lambda) V_1(r', t'), \quad (12)$$

where  $V_1(r', t)$  and  $n_1(r, t, \lambda)$  are, respectively, external perturbing potential and density response. Equation (9) can be rewritten as

$$E_{\text{pol}} = -\frac{1}{2\pi} \int dr dr' U_{\text{lr}}(r - r') \times \int_0^1 d\lambda \int_0^\infty \frac{dt}{t} \chi(r, r'; t, \lambda). \quad (13)$$

Following Gross and Kohn [10], we can replace the density response of the physical system to the external perturbing potential by the response of the ( $\lambda$ -independent) KS system to an effective potential  $V_1^{\text{eff}}$ ,

$$n_1(r, t, \lambda) = \int dr' dt' \chi_{\text{KS}}(r, r'; t - t', \lambda) V_1^{\text{eff}}(r', t', \lambda), \quad (14)$$

$$V_1^{\text{eff}}(r', t', \lambda) \equiv V_1(r', t') + \int dr'' U_\lambda(r' - r'') \times n_1(r'', t, \lambda) + V_{1,\text{xc}}(r', t', \lambda). \quad (15)$$

$V_{1,\text{xc}}(r', t', \lambda)$  is defined by Eqs. (14) and (15). Thus  $\chi(r, r'; t, \lambda)$  is the density response of the noninteracting

KS system at time  $t$  to the  $V_1^{\text{eff}}(r', t', \lambda)$  at any time  $t'$  ( $0 \leq t' \leq t$ ), induced by an external potential  $V_1(r'', t') = \delta(r'' - r)\delta(t)$ .

To complete this procedure we need a practical approximation for  $V_{1,\text{xc}}$ , for which, following Ref. [9], we set

$$V_{1,\text{xc}}(r', t', \lambda) = \frac{\partial V_{\text{xc}}(n, \lambda)}{\partial n} \Big|_{n_0(r')} n_1(r', t', \lambda), \quad (16)$$

where  $n_0$  is the unperturbed density and  $V_{\text{xc}}$  is the static exchange-correlation potential in the LDA. Here, in addition to the usual approximation of the LDA, the frequency dependence (or retardation) of  $V_{\text{xc}}$  is neglected.

The evaluation of  $\chi$  now requires the calculation of the evolution of the noninteracting KS system under the action of  $V_1^{\text{eff}}(r', t', \lambda)$ . At this point it is convenient to change from the coordinate representation to an orthonormal basis,  $f_n(r)$ , and use the notation

$$F(r) = \sum_{m=1}^{\infty} F_m f_m(r), \text{ etc.} \quad (17)$$

Thus Eq. (12) becomes

$$n_{1,m}(t, \lambda) = \int_0^{\infty} dt' \sum_{m'} \chi_{\text{KS},mm'}(t - t'; \lambda) V_{1,m'}^{\text{eff}}(t', \lambda). \quad (18)$$

The following steps need to be carried out for each value of  $\lambda$ : (i) At time  $t = 0^-$  the KS system is given by the determinant  $(N)^{-1} \text{Det}[\phi_1 \phi_2 \cdots \phi_N]$  of the occupied KS orbitals  $\phi_j$ . (ii) At time  $0^+$ , after the action of a small external perturbation,  $V(r) = \alpha f_m(r)\delta(t)$  ( $\alpha$  small), each of the KS orbitals is changed,  $\phi_j(r, t) \rightarrow \phi_j(r, t) - i\alpha f_m(r)\phi_j(r, t)$ . [Effects of the *finite* unperturbed KS Hamiltonian and of the induced parts of  $V^{\text{eff}}$  in the *infinitesimal* interval ( $0^-, 0^+$ ) are negligible.] (iii) For  $t > 0^+$  we integrate the time-dependent Schrödinger equation for each  $\phi_j$  in a stepwise fashion, evaluating the first-order induced density  $\alpha n_{1,m}(r, t) = \sum_j |\phi_j(r, t)|^2 - n_0(r)$  at each time step, to be able to compute the induced parts of  $V_1^{\text{eff}}$  [Eq. (15)], which depend on  $n_{1,m}(r, t)$ . Writing, for each  $m$  and  $\lambda$ ,  $\phi_j = \phi_{0j} + \alpha \phi_{1j}$ , one has

$$i \frac{\partial \phi_{1j}}{\partial t} = \mathcal{H}_0 \phi_{1j} + V_1^{\text{eff}} \phi_{0j}, \quad (19)$$

where  $\mathcal{H}_0$  is the unperturbed,  $\lambda$ -independent KS Hamiltonian and  $V_1^{\text{eff}}$  is defined in Eq. (15), with  $n_1(r, t) = 2 \sum_j \text{Re}[\phi_{0j}^* \phi_{1j}]$ . (iv) The projection of  $n_{1,m}$  on  $f_{m'}$  gives  $\chi_{mm'}(t)$ ,

$$\chi_{mm'}(t) = (f_{m'}, n_{1,m}(t)). \quad (20)$$

From Eq. (13), we obtain

$$E_{\text{pol}} = -\frac{1}{2\pi} \int_0^{\infty} \frac{dt}{t} \int_0^1 d\lambda \sum_{m,m'} \chi_{mm'}(t, \lambda) U_{1r:mm'}. \quad (21)$$

In practice, the  $\lambda$  integration is replaced by a finite sum.

As a simple example of this general procedure, we now apply it to the calculation of the asymptotic vdW

interaction of a pair of spherically symmetric atoms. We denote the atoms by  $A$  and  $B$ , their nuclear coordinates by  $R_A$  and  $R_B$  (taken to be on the  $z$  axis), and write  $R = |R_A - R_B|$ . We take  $R \gg a_A + a_B$ , the sum of the atomic radii and  $R^{-1} \ll \kappa \ll a_{A,B}^{-1}$ . The asymptotic vdW interaction is obtained from those parts of  $E_{\text{pol}}$  [Eq. (6)] in which  $r$  and  $r'$  are in different atoms. Take  $r$  to be in  $A$  and  $r'$  in  $B$ . Since  $\kappa \ll a_{A,B}^{-1}$ ,  $U_{1r}$  can be treated as a small perturbation, giving to first order

$$\chi(r, r'; \omega, \lambda) = \lambda \int dr_1 dr_2 U_{1r}(r_1 - r_2) \times \chi_A(r, r_1; \omega) \chi_B(r_2, r'; \omega), \quad (22)$$

where  $\chi_{A,B}$  are the responses of the isolated atoms  $A$  or  $B$ . The integration over  $\lambda$  is now trivial. Lastly, we expand  $U_{1r}(r - r')$  in  $1/R$  and obtain the final expression,  $E_{\text{vdW}} = -C_6/R^6$ ,

$$C_6 = \frac{3}{\pi} \text{Im} \int_0^{\infty} d\omega \chi_A^{zz}(\omega) \chi_B^{zz}(\omega) = \frac{3}{\pi} \int_0^{\infty} dt_1 \int_0^{\infty} dt_2 \frac{\chi_A^{zz}(t_1) \chi_B^{zz}(t_2)}{t_1 + t_2}. \quad (23)$$

In the above,  $\chi^{zz}$  is defined as the  $z$  component of the density response to a perturbation in the  $z$  direction,  $\chi^{zz} = \int dr_1 dr_2 \chi(r_1, r_2) z_1 z_2$ . The first form is well known [11], the second is its Fourier transform into the time domain.

We have calculated the time-dependent response for the helium atom in DFT as follows. We begin with the exact  $V_{\text{xc}}(r)$  [12], which reproduces the exact ground-state density  $n_0(r)$  (known from highly accurate independent calculations), and the corresponding exact KS orbital  $\phi_0$  and energy  $\epsilon_0$ . We take  $V_1(r, t) \equiv -\alpha z \delta(t)$ . At time  $t = 0^+$  the wave function will be

$$\phi(r, t = 0^+) = \phi_0(r) - i\alpha z \phi_0(r), \quad (24)$$

a combination of  $s$  and  $p$  functions. For  $t > 0$ , we solve the time-dependent Schrödinger equation for  $\phi(r, t) \equiv \phi_0(r, t) + \alpha \phi_1(r, t)$ , with the initial condition (24). Linearizing in  $\alpha$  gives the following equation for  $\phi_1$ :

$$i \frac{\partial \phi_1(r, t)}{\partial t} = \mathcal{H}_0 \phi_1(r, t) + \mathcal{H}_1(t) \phi_0(r, t), \quad (25)$$

$$\phi_1(r, 0^+) = -ir \phi_0(r),$$

where  $\phi_0(r, t) = e^{-i\epsilon_0 t} \phi_0(r)$ ,  $\mathcal{H}_0$  is the KS unperturbed helium Hamiltonian,

$$\mathcal{H}_1(t) = \int dr' \frac{n_1(r', t)}{|r - r'|} + \frac{\partial V_{\text{xc}}}{\partial n} \Big|_{n_0(r)} n_1(r, t), \quad (26)$$

and  $n_1(r, t) = 4 \text{Re}[\phi_0(r, t) \phi_1^*(r, t)]$ .  $V_{\text{xc}}$  was calculated using the parametrization of Vosko *et al.* [13]. Equations (25) and (26) were solved by stepwise integration in time. The time evolution from  $t$  to  $t + \Delta t$  was carried out by the fast Fourier transform method as used in Ref. [14]. Since at each instant  $\phi_1$  evolves under the action of the

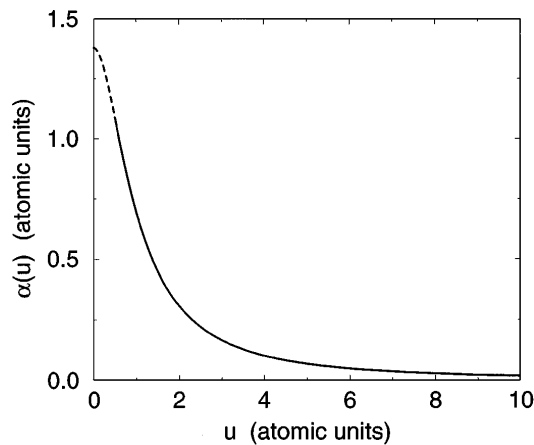


FIG. 1. The imaginary-frequency susceptibility  $\alpha(u)$  for helium (solid line: direct evaluation; dashed line: extrapolation).

total effective potential, the resulting response function  $\chi(t)$  [and, if desired, the corresponding  $\chi(\omega)$ ] is automatically self-consistent *without the need to first solve a self-consistent integral equation*, as is the case in the direct evaluation of  $\chi(\omega)$  [see Eq. (11)].

In practice, the direct evaluation of the time integral in (23) is inconvenient because  $\chi(t)$  oscillates with undiminishing amplitude at large  $t$ . However, it has been noted [11] that, if we define  $\alpha(u) = \int_0^\infty \chi^{zz}(t) e^{-ut} dt$  [i.e.,  $\alpha(u) = \chi^{zz}(i\omega)$ ], the vdW coefficient  $C_6$  can be written as

$$C_6 = \frac{3}{\pi} \int_0^\infty du \alpha_A(u) \alpha_B(u). \quad (27)$$

For helium,  $\chi(t)$  was calculated up to  $t = 15$  atomic units, which allows accurate calculation of  $\alpha(u)$  for  $u > u_0 = 0.4$ . In the interval  $0 \leq u \leq u_0$ , we represented  $\alpha(u)$  by the expression  $a + b/(1 + cu^2)$ , and fitted  $a, b, c$  to  $\alpha(u)$  and its first two derivatives at  $u = u_0$ . (We checked that the results are insensitive to the exact choice of  $u_0$  or to the choice of the extrapolating function.) Figure 1 shows our  $\alpha(u)$  for He. The correct asymptotic form,  $\alpha(u) \rightarrow 2/u^2$  (the  $f$ -sum rule), is automatically obeyed. The completeness sum rule requires  $\int_0^\infty \alpha(u) du = 2\pi \langle \phi_0 | z^2 | \phi_0 \rangle \approx 2.50$ . Our  $\alpha(u)$  gives 2.33. An independent check on our  $\alpha(u)$  is the static susceptibility  $\alpha(0)$ . The best theoretical value is 1.383 241 [15], while we find 1.38.

Our results for the He-He vdW constant is  $C_6 = 1.45$ , almost identical to the best theoretical value [16] 1.458. For the H-He system we find  $C_6 = 2.81$  compared to the best theoretical value [17] of 2.817.

We feel cautious about the significance of the high accuracy of our results for the He-He and the H-He systems in view of the fact that our calculated  $\alpha(u)$  leads to a 7% error in the completeness sum rule. At the same time, our results demonstrate the soundness and feasibility of our approach. We are optimistic that our approach

will not only give asymptotic van der Waals coefficients, but the *entire* nuclear potential energy function  $\epsilon(R)$ , including vdW energies.

We found that the results are sensitive to the choice of a good KS potential for the unperturbed ground state. Repeating the calculation by replacing the exact  $V_{xc}$  by  $V_{xc}$  in the local-density approximation, the result for  $C_6$  of the He-He system was 1.85, 28% too high. This is qualitatively similar to the experience of Petersilka *et al.* [18] with calculations of excited-state energies.

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