Constraint Satisfaction in Local and Gradient Susceptibility Approximations: Application to a van der Waals Density Functional

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We show how charge conservation and reciprocity can be built into local density or gradient approximations for density-density response functions (susceptibilities). We apply these ideas to derive from first principles a variant of the Rapcewicz-Ashcroft formula for the van der Waals interaction. We also discuss how improved formulas may be obtained.

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Overall, electron density functional theory (DFT) has been gratifyingly successful in approximating the energies of inhomogeneous interacting electronic systems [1,2]. Part of this success is due to the satisfaction of the exchange-correlation (xc) hole normalization condition, often achieved with considerable effort [3]. The usual local density approximation (LDA) [4] and its various gradient extensions [2] do not, however, give an adequate description of dispersion or van der Waals (vdW) forces [5]. The approach to be introduced here both simplifies the problem of achieving hole normalization, and facilitates the derivation of van der Waals functionals.

The difficulty of describing vdW forces in the LDA or gradient approaches is not surprising since these forces depend on correlations between distant density fluctuations, which may be different from those in the uniform or near-uniform electron gas upon which the above approximations are based. Rather general methods have been proposed [6,7] for treating these long-ranged correlations by explicit solution of nonlocal screening equations, while still making the local density approximation for a suitable intermediate quantity. These methods are expected to work well for a wide variety of situations including both overlapping and nonoverlapping electron distributions. Such approaches will usually require substantial computation, however.

We therefore first consider a less ambitious problem, the efficient calculation of the vdW interaction between a pair of nonoverlapping neutral systems, using as input only the ground-state electron densities $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$ of the two systems. Rapcewicz and Ashcroft [8] have already given an expression for this limit of the vdW interaction, using arguments based on Feynman diagrams and three-point functions, plus a conjecture about an appropriate average density computed between two distant points. We will here derive a similar but not identical expression from a straightforward local density approximation for a suitable quantity. The result will depend crucially on satisfaction of some constraints, and the methods used to achieve this should be useful elsewhere.

Consider a pair of nonoverlapping many-electron systems so that electrons in system 1 can be considered distinguishable from those in system 2. Under these circumstances it is well known that second-order perturbation theory in the Coulomb interaction between the two systems yields a good approximation to the van der Waals or dispersion interaction. Zaremba and Kohn [9] reexpressed this second-order energy, without further approximation, in the form

$$E^{(2)} = -\frac{\hbar}{2\pi}\int d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_1'\, d\mathbf{r}_2' \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\frac{e^2}{|\mathbf{r}_1'-\mathbf{r}_2'|} \times \int_0^\infty \chi_1(\mathbf{r}_1,\mathbf{r}_1',iu)\chi_2(\mathbf{r}_2,\mathbf{r}_2',iu)\,du\,. \qquad (1)$$

Here $\chi_1(\mathbf{r},\mathbf{r}',\omega)$ and $\chi_2(\mathbf{r},\mathbf{r}',\omega)$ are the exact density-density response functions (in the Kubo sense) of each separate system in the absence of the other. χ_1 is defined by the linear density response $\delta n_1(\mathbf{r})\exp(ut)$ of the electrons in system 1 to an externally applied electron potential energy perturbation $\delta V^{\text{ext}}(\mathbf{r})\exp(ut)$,

$$\delta n_1(\mathbf{r}) = \int \chi_1(\mathbf{r},\mathbf{r}',iu)\delta V^{\text{ext}}(\mathbf{r}')\,d\mathbf{r}'\,, \qquad (2)$$

and similarly for χ_2. It is important to note that χ_1 includes the electron-electron interaction amongst the electrons of system 1 to all orders, and similarly for χ_2. [Note also that, unlike Ref. [9], we have referred the space arguments of χ_1 and χ_2 in (1) to a common origin.]

To simplify (1), we will approximate χ_1 and χ_2 via a form of local density approximation. That is, we will appeal to a simple model of the density-density response of a homogeneous electron gas, and modify it suitably to approximate the response of the inhomogeneous gas in each system. The simplest such homogeneous response model is a nondispersive form of hydrodynamics in which we eliminate the fluid velocity $\mathbf{v}$ between the linearized continuity equation, Newton's second law (with no pressure term), and Poisson's equation. In Fourier representation, this gives a density perturbation $\delta n(q,\omega) = \chi(q,\omega)\delta V^{\text{ext}}(q,\omega)$ where δV^{ext} is the bare external potential energy and

$$\chi^{\text{hom}}(q\to 0,\omega) = \frac{q^2 n_0}{m[\omega^2-\omega_P^2(n_0)]}\,, \qquad (3)$$

where n_0 is the unperturbed electron number density and $\omega_P^2(n) = 4\pi n e^2/m$. Equation (3) corresponds to a real-space response which is local in the sense of a delta-function second derivative:

$$\chi_{\rm local}^{\rm hom}(\mathbf{r},\mathbf{r}',\omega) = \frac{n_0}{m[\omega_P^2(n_0) - \omega^2]}\nabla^2\delta^3(\mathbf{r}-\mathbf{r}'). \qquad (4)$$

How should we make the corresponding local approximation for an inhomogeneous system, in which the uniform unperturbed density n_0 is replaced by a given inhomogeneous ground state electronic density $n(\mathbf{r})$? For the present application it will be necessary to take into account the following two exact constraints.

(*A*) *Charge conservation:* Because a time-dependent potential perturbation can move electronic charge around but not create or destroy it, we must have

$$\int \chi(\mathbf{r},\mathbf{r}',iu)\,d\mathbf{r} = 0 \text{ for each } \mathbf{r}' \text{ and } u. \qquad (5)$$

(*B*) *Reciprocity:*

$$\chi(\mathbf{r},\mathbf{r}',iu) = \chi(\mathbf{r}',\mathbf{r},-iu) \text{ for real } u. \qquad (6)$$

Equation (6) is readily proved from the general Kubo form for the imaginary-frequency response in terms of the interacting many-body eigenstates. Because of (6), Eq. (5) also holds with the arguments $\mathbf{r}$ and $\mathbf{r}'$ reversed in the susceptibility.

One simple way to ensure (5) is to express χ as a spatial gradient of a function which vanishes at infinity, thus ensuring that χ integrates to zero. Furthermore, the *form*

$$\chi(\mathbf{r},\mathbf{r}',iu) = \nabla_r\cdot\nabla_{r'}F(\mathbf{r},\mathbf{r}',iu), \qquad (7)$$

where F is symmetric in $\mathbf{r}$ and $\mathbf{r}'$ and vanishes at infinity, will guarantee both charge conservation and reciprocity even where F includes density gradient terms. As a first step in implementing these ideas for a general inhomogeneous system, we seek the simplest local density approximation for χ consistent with the lowest-order homogeneous result (4). The form (7) essentially mandates the following choice, if F is to be a scalar:

$$\chi_{\rm local}^{\rm inhom}(\mathbf{r},\mathbf{r}',\omega) = \nabla_r\cdot\nabla_{r'}\left[\frac{1}{m}\frac{n(\mathbf{r})\delta^3(\mathbf{r}-\mathbf{r}')}{\omega^2-\omega_P^2[n(\mathbf{r})]}\right]. \qquad (8)$$

In (8), the large square bracket is F, and it is essential, for charge conservation, that $n(\mathbf{r})$ does not occur outside the differentiations. While the density arguments in (8) appear at first sight to be reciprocity violating because they involve only $\mathbf{r}$ and not $\mathbf{r}'$, they occur right against a delta function and so do not in fact violate reciprocity. Indeed $n(\mathbf{r})$ in (8) could be replaced by, e.g., $[n(\mathbf{r}) + n(\mathbf{r}')]/2$ or $[n(\mathbf{r})n(\mathbf{r}')]^{1/2}$ with no effect on the formula (8), when it is integrated with a further function as in (1) and integrations by parts are performed. The symmetric form of the derivatives in (8) is, however, crucial as we shall see: while the operators ∇_r^2 and $-\nabla_r\cdot\nabla_{r'}$ are equivalent in the uniform case, this is not so for the inhomogeneous case in which only the latter form guarantees reciprocity.

Representing $\nabla_r\cdot\nabla_{r'}$ by $\sum_\mu(\partial/\partial r_\mu)\partial/dr'_\mu$ and applying (8) in (1) to approximate χ_1 in terms of $n_1(\mathbf{r}_1)$ [and also χ_2 in terms of $n_2(\mathbf{r}_2)$], we obtain the approximate vdW energy

$$E^{(2)} = -\frac{\hbar}{2\pi m^2}\int d\mathbf{r}_1\,d\mathbf{r}_1'\,d\mathbf{r}_2\,d\mathbf{r}_2'\,\frac{\partial^2}{\partial r_{1\alpha}\partial r_{2\beta}}\left(\frac{e^2}{|\mathbf{r}_2-\mathbf{r}_1|}\right)\frac{\partial^2}{\partial r'_{1\alpha}\partial r'_{2\beta}}\left(\frac{e^2}{|\mathbf{r}_2'-\mathbf{r}_1'|}\right)$$
$$\times\int_0^\infty\left[\frac{n_1(\mathbf{r}_1)\delta^3(\mathbf{r}_1-\mathbf{r}_1')}{-u^2-\omega_P^2[n_1(\mathbf{r}_1)]}\right]\left[\frac{n_2(\mathbf{r}_2)\delta^3(\mathbf{r}_2-\mathbf{r}_2')}{-u^2-\omega_P^2[n_2(\mathbf{r}_2)]}\right]du.$$

Here we have already integrated by parts on each space variable, and have used the Einstein summation convention in the α and β summations. Performing the second derivatives explicitly on the Coulomb potentials and then using the delta functions to remove two integrations, we have

$$E^{(2)} = -\frac{\hbar e^4}{2\pi m^2}\int d\mathbf{r}_1\,d\mathbf{r}_2\sum_{\alpha,\beta}\left\{\frac{3r_{12\alpha}r_{12\beta}-\delta_{\alpha\beta}r_{12}^2}{r_{12}^5}\right\}^2\int_0^\infty\left[\frac{n_1(\mathbf{r}_1)}{-u^2-\omega_P^2[n_1(\mathbf{r}_1)]}\right]\left[\frac{n_2(\mathbf{r}_2)}{-u^2-\omega_P^2[n_2(\mathbf{r}_2)]}\right]du$$
$$= -\frac{\hbar e^4}{2\pi m^2}\int d\mathbf{r}_1\,d\mathbf{r}_2\,\frac{6}{r_{12}^6}\,n_1(\mathbf{r}_1)n_2(\mathbf{r}_2)\,\frac{\pi/2}{(\omega_1+\omega_2)\omega_1\omega_2} = -\frac{3\hbar}{32\pi^2}\int d\mathbf{r}_1\,d\mathbf{r}_2\,\frac{1}{r_{12}^6}\,\frac{\omega_1\omega_2}{(\omega_1+\omega_2)}, \qquad (9)$$

where $\omega_1 = \omega_{P1} = [4\pi e^2 n_1(\mathbf{r}_1)/m]^{1/2}$ and similarly for ω_2. It is interesting that the integrand in (9) is proportional to the *harmonic mean,* $\omega_1\omega_2/(\omega_1+\omega_2)$, of the two local plasma frequencies.

Equation (9) is our main result. It is basically similar to the Rapcewicz-Ashcroft formula [8] except that one of the three factors of the geometric mean $(\omega_1\omega_2)^{1/2}$ appearing on the denominator in [8] has been replaced by an arithmetic mean in (9). This may make the result less sensitive to a low-density cutoff than the formula of Ref. [8]. A cutoff (e.g., that from [8]) will certainly still be appropriate, however, because the uniform-gas-based ansatz (8) for the response is a serious overestimate in the outer tails of the electronic density. The essential point, though, is that a formula of this type has here been *derived* by a simple local density ansatz which embodies suitable constraints. The satisfaction of charge conservation was essential because, without it, (1) would represent the second-order Coulomb interaction between nonzero charges, and this would not give the correct $\mathbf{r}_{12}^{-6}$ dipole-dipole interaction. The reciprocity constraint is just as vital in the present case: if, in approximating χ_1, (8) had been replaced by an expression of the form $\nabla_1^2 F(\mathbf{r}_1, \mathbf{r}_1')$ instead of $\nabla_1 \cdot \nabla_1' F(\mathbf{r}_1, \mathbf{r}_1')$, then two integrations by parts with respect to $\mathbf{r}_1$ in (1) would have yielded a factor of $\nabla_1^2(|\mathbf{r}_1 - \mathbf{r}_2|^{-1})$ resulting in a delta function which can never be satisfied because the two systems do not overlap. Thus the reciprocity-violating $\nabla_r^2 F(\mathbf{r}, \mathbf{r}')$ form of susceptibility would give a zero vdW interaction.

The form (7) can be put in a more general context. A nonlocal conductivity quantity $\overline{\sigma}$ (related to the fully interacting Kubo current-current response function by $\overline{\sigma} = \chi_{JJ}/i\omega$) can be defined by the linear response of the current density j to an external electric field $\mathbf{E}_{\text{ext}}(\mathbf{r}) \exp(-i\omega t)$:

$$j_\mu(\mathbf{r}, \mathbf{r}', \omega) = \int \sum_\nu \overline{\sigma}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) E_\nu^{\text{ext}}(\mathbf{r}')\, d\mathbf{r}' . \qquad (10)$$

$\overline{\sigma}$ is not identical to the usual conductivity tensor σ, whose definition is similar to (10) but involves the total Hartree field $\mathbf{E}^{\text{tot}}(\mathbf{r}')$ in place of $\mathbf{E}^{\text{ext}}(\mathbf{r}')$.

To relate χ to $\overline{\sigma}$ we note that χ is appropriate only when the external field comes from a scalar potential so that $\mathbf{E}_\nu^{\text{ext}}(\mathbf{r}') = -\nabla_\nu' \delta V^{\text{ext}}(\mathbf{r}')/(-e)$, where $\delta V^{\text{ext}} = -e\Phi^{\text{ext}}$ is the electron potential energy corresponding to the external potential Φ^{ext}. Then, using the continuity equation $-i\omega(-e)\delta n + \nabla_\mu j_\mu = 0$, we obtain the electron density perturbation as $\delta n(\mathbf{r}) \exp(-i\omega t)$ with

$$\delta n(\mathbf{r}) = \left(\frac{-1}{i\omega e}\right) \frac{\partial}{\partial r_\mu} \times \int \overline{\sigma}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) \left(\frac{1}{e} \frac{\partial}{\partial r_\nu'} \delta V^{\text{ext}}(\mathbf{r}')\right) d\mathbf{r}' ,$$

where the Einstein summation convention was used. For a finite system we apply integration by parts (Green's theorem) and, *assuming that the conductivity vanishes when* $\mathbf{r}'$ *goes to infinity*, we obtain the density in the form of Eq. (2) with a susceptibility given by

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = (i\omega e^2)^{-1} \frac{\partial^2}{\partial r_\mu \partial r_\nu'} \overline{\sigma}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) . \qquad (11)$$

In particular, the above conserving local approximation for χ [Eq. (8)] is obtained from (11) by making the interacting local conductivity approximation

$$\overline{\sigma}_{\mu\nu}(\mathbf{r}, \mathbf{r}', \omega) \simeq \delta_{\mu\nu} n(\mathbf{r}) \frac{ie^2\omega}{m} \frac{\delta^3(\mathbf{r} - \mathbf{r}')}{\omega^2 - \omega_P^2[n(\mathbf{r})]} .$$

In general, any approximation for the conductivity quantity $\overline{\sigma}(\mathbf{r}, \mathbf{r}', \omega)$ of a finite inhomogeneous system, provided that $\overline{\sigma}$ is symmetric and vanishes fast enough at infinity, will yield, via (11), a charge-conserving reciprocity-respecting susceptibility. It is therefore not necessary to consider charge conservation explicitly when one begins from the current response. [A possible exception is the case of infinite systems in the limit $\omega \to 0$, in which case (11) may require an additional term whenever the system has a nonzero Drude weight [10].]

In the present context, one may hope to obtain a generalization of the vdW formula (9) by considering the next order in gradients (i.e., inclusion of a pressure or dispersion term) in a hydrodynamic theory of the current-current response, followed by the use of (1) and (11). This approach has some elements in common with the hydrodynamic approach to vdW interactions pursued extensively by Mahanty and Paranjape [11,12]. Care will be required here, however, because it was recently shown [13] that the usual pressure term is not adequate for the long-wavelength dynamic response of inhomogeneous systems when the electron density is allowed to fall off smoothly at the edges. Furthermore, once gradient terms are considered, one should also include a nonzero exchange-correlation kernel f_{xc} along with the bare Coulomb potential in the self-consistent dynamic potential.

Finally it is interesting to enquire how the present constraint considerations might apply to the derivation of vdW energy functionals in circumstances more general than the perturbative nonoverlapping case implied by (1). The exchange-correlation part, $n_{2\text{xc}} = n_2(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}')$, of the pair distribution n_2 can be written in terms of operator fluctuations as

$$n_{2\text{xc}} = \langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle - \delta^3(\mathbf{r} - \mathbf{r}') n(\mathbf{r}) , \qquad (12)$$

and has the normalization property

$$\int n_{2\text{xc}}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r} = -n(\mathbf{r}') . \qquad (13)$$

Upon dividing $n_{2\text{xc}}$ by $n(\mathbf{r}')$ to form the xc hole density n_{xc}, we can express (13) as the familiar condition (see [1]) that the xc hole contains –1 electron. Using (12) we can also express the same fact as

$$\int \langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle\, d\mathbf{r} = 0 \text{ for all } \mathbf{r}'. \qquad (14)$$

Using the zero-temperature fluctuation-dissipation theorem we can express the density fluctuation in terms of a density-density response at imaginary frequency:

$$\langle \delta\hat{n}(\mathbf{r}) \delta\hat{n}(\mathbf{r}') \rangle = -\frac{\hbar}{\pi} \int_0^\infty \chi(\mathbf{r}, \mathbf{r}', \omega = iu)\, du , \qquad (15)$$

where χ is the density-density response function (susceptibility) defined in (2). Substituting into the adiabatic connection formula [1] we obtain an expression for the xc energy of an inhomogeneous system,

$$E^{\mathrm{xc}} = \frac{1}{2}\int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \, \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \times \left\{ -\hbar\pi^{-1}\int_0^\infty \chi(\lambda,\mathbf{r},\mathbf{r}',iu)\,du - n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \right\}, \quad (16)$$

where $\chi(\lambda,\mathbf{r},\mathbf{r}',\omega)$ is the interacting susceptibility defined as in (2) but with a reduced Coulomb interaction $\lambda e^2/r$ between electrons. Comparing (15), (5), and (14) we find that in the context of Eq. (16) *the charge conservation condition (5) for* χ *implies xc hole normalization.* Use of the bare susceptibility $\chi(\lambda = 0,\mathbf{r},\mathbf{r}',iu)$ in (16) yields the exact exchange energy. Subtraction of this exchange energy expression from the above xc energy, substitution of the double-gradient form (7) into (16), and integration by parts with use of $\nabla^2|\mathbf{r}-\mathbf{r}'|^{-1} = -4\pi\delta^3(\mathbf{r}-\mathbf{r}')$ results in

$$E^c = -\frac{1}{2}\int_0^1 d\lambda \int d\mathbf{r}\, 4\pi e^2(\hbar\pi^{-1}) \times \int_0^\infty \{F(\lambda,\mathbf{r},\mathbf{r},iu) - F(\lambda=0,\mathbf{r},\mathbf{r},iu)\}\,du\,. \quad (17)$$

Thus the correlation energy density involves F only at $\mathbf{r} = \mathbf{r}'$, so that reciprocity is not an issue in this form of the correlation energy.

We note that a delta-function approximation for F, such as (8), will *not* suffice for direct substitution into (17) because one would then obtain a singular correlation energy density: the simple delta-function form (8) sufficed in Eq. (1) because much of the physics of correlation had already been done in performing second-order perturbation theory inherent in the derivation of (1). As an example of a form which *does* yield sensible results in (17), we can put $F(\lambda,\mathbf{r},\mathbf{r}',iu) = \epsilon(\lambda,\overline{n}(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|,iu)$. Here $\epsilon(\lambda,n,\mathbf{r},iu)$ is the Fourier transform, with respect to q, of $q^{-2}\chi^{\mathrm{hom}}(\lambda,n,q,iu)$ where $\chi^{\mathrm{hom}}(\lambda,n,q,iu)$ is the interacting susceptibility of the homogeneous electron gas with reduced Coulomb interaction $\lambda e^2/r$; $\overline{n}(\mathbf{r},\mathbf{r}')$ is some average of the densities at $\mathbf{r}$ and $\mathbf{r}'$. For this case one obtains the usual LDA correlation energy from (17). A gradient expansion of the function χ, for a weakly inhomogeneous gas, cut off if necessary in an arbitrary fashion at large separations when generating F, will still automatically result in a normalized correlation hole when substituted into (17).

As a second example, consider approximation of the *bare* inhomogeneous susceptibility $\chi^0(\mathbf{r},\mathbf{r}',iu) = \chi(\lambda = 0,\mathbf{r},\mathbf{r}',iu)$ by $\nabla_r \cdot \nabla_{r'} F^0$ where F^0 is the same as F in the previous paragraph except that the *bare* uniform-gas susceptibility $\chi(\lambda = 0,n,q,iu)$ is used in place of the interacting uniform-gas susceptibility. This is followed by solution of a real-space screening equation [14], using $\chi^0(\mathbf{r},\mathbf{r}',iu)$ as input, to obtain the RPA interacting susceptibility $\chi(\lambda,\mathbf{r},\mathbf{r}',iu)$ of the inhomogeneous system. It can be shown that this χ satisfies charge conservation. Furthermore, for the simplest (but reciprocity-violating) case $\overline{n}(\mathbf{r},\mathbf{r}') = n(\mathbf{r})$ this interacting χ has poles at, e.g., the long-wavelength 2D plasmon mode of a slab of jellium of finite thickness [15] and at the long-wavelength surface plasmon on a jellium half space. When substituted into (16) this χ amounts to a realization, at the RPA level, of the vdW scheme proposed in Ref. [6]: once more it automatically obeys xc hole normalization.

In summary, we have derived a simple density functional (9) for the van der Waals or dispersion interaction between nonoverlapping electronic systems: it is similar but not identical to one proposed by Rapcewicz and Ashcroft [8] on rather different grounds. We achieved this starting from a formula (1) which is exact to second order in the intersystem Coulomb interaction. Our method was to make a local density approximation for a susceptibility. This approximation [Eq. (8)] was constructed for automatic attainment of charge conservation (xc hole normalization) and reciprocity, constraints which were vital in obtaining our result. We have also suggested how this approach may be extended.

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