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Spin-density functionals for the electron correlation energy with automatic freedom from orbital self-interaction

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Abstract. Using two different interpretations of the concept of the Fermi hole curvature, we derive a class of correlation energy expressions for the inhomogeneous interacting electron gas. Their properties include freedom from spurious orbital self-interaction, invariance under unitary transformations among occupied orbitals, correct values in the homogeneous limit, correctly normalized correlation hole, inclusion of kinetic energy (KE) as well as potential energy of correlation, and non-vanishing values for fully spin-polarized systems (in contrast with some similar schemes developed for chemical applications). Minimization of the energy with respect to the orbitals leads to a Euler–Lagrange equation resembling the Hartree–Fock one-electron effective Schrodinger equation, with the addition of a term resembling the KE operator for an inhomogeneous effective mass. For current-carrying states there is a further term involving an effective dynamically induced vector potential. Despite these complications the effective one-electron Hamiltonian is Hermitian, so that the canonical orbitals are orthogonal, in contrast with those of the commonest self-interaction correction scheme.

1. Introduction

The local-density functional (LDF) and local-spin-density functional (LSDF) theories of the non-uniform electron gas [1–3] are widely used for atomic, molecular and solid state calculations but are known to suffer from a spurious interaction of a localized orbital with itself [4, 5]. This spurious self-interaction contributes to difficulties such as the well known ‘band-gap’ problem [6, 7] in the LDF description of the electronic structure of insulators and semiconductors. Such difficulties are largely removed by the computationally convenient expedient of explicitly subtracting a sum of separate Hartree and exchange–correlation (XC) [5] (or correlation [4]) energies. Such schemes will be referred to here as self-interaction correction (SIC) formalisms.

In the SIC scheme of Perdew and Zunger (PZ) [5] the subtraction is done separately for each orbital, which has the advantage of allowing separate effective potentials for the valence and conduction bands, thus helping to alleviate the above-mentioned band-gap problem. This prescription for the SIC has the somewhat disconcerting feature that its predictions are not invariant under a unitary transformation among the occupied orbitals. For example, the spin density generated by a full band of Bloch orbitals is identical with that from a full lattice of the corresponding Wannier

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functions. The PZ prescription, however, gives a non-zero SIC only for the Wannier case. This leads to some difficulties with extended systems and even for the uniform electron gas on which the theory is presumably based [8, 9]. In the PZ scheme there is also a 'slight but annoying' non-orthogonality of the canonical effective one-electron orbitals.

By contrast, Hartree-Fock (HF) theory, while not accounting for correlation, is explicitly free of orbital self-interaction terms, since they cancel between the direct and exchange energy expressions. Furthermore, the HF energy is easily shown to be invariant under any unitary transformation among occupied orbitals (to prove this, one merely notes that the determinantal wavefunction itself has this property). Thus, HF computations retain their freedom from unwanted self-interaction regardless of the basis used for calculation. Also, the HF effective one-electron Hamiltonian, although non-local, is Hermitian so that the canonical orbitals are mutually orthogonal.

It is desirable to retain these positive HF features in a theory which incorporates correlation as well as exchange. A promising class of theories are those which *multiply* the HF pair distribution by a correlating factor. In this vein, the 'closed- and open-shell' theory of Colle and Salvetti [10] is free of orbital self-interaction but does not formally account for the kinetic correlation energy. (The numerical implementation of [10], however, appears to fit a parameter to the known correlation energy of He, which of course does contain a kinetic component and, probably as a result of this, Colle and Salvetti obtain very good correlation energies for small atoms). The Colle-Salvetti correlation hole is normalized only in an approximate and averaged fashion. From the standpoint of magnetic properties of solid state systems a more serious drawback of [10] is that it predicts zero correlation energy for a fully spin-polarized system, in qualitative disagreement with the known properties [11] of the uniform electron gas. Dobson and Rose [12] proposed a somewhat similar theory with proper account of kinetic correlation and of the spin-polarized limit, but this theory was not pursued numerically because it violated correlation hole normalization.

In the SIC scheme of Stoll *et al* [4] the exchange energy is assumed known. LSDF theory is used for the correlation energy, but correlation between electrons of like spin orientations (which of course contains among other contributions the spurious self-interaction) is removed by subtracting the LSDF correlation energies of totally spin-polarized uniform electron gases. Since this theory does not deal with the individual orbitals but rather the total density $n(\mathbf{r}, s)$ of a given spin orientation, it is invariant under a unitary transformation among occupied orbitals. The removal of parallel-spin correlations may be reasonable in atoms and small molecules but it is not reasonable for solid state applications; in the latter case the close spacing of energy levels and correspondingly high polarizability causes stronger correlations, even for like spins where the Pauli principle operates.

The present paper describes a class of functionals with all the desirable formal features just discussed. We start with the exact direct (Hartree) plus exchange Coulomb energy and make a type of local-density approximation for the remaining correlation energy; this can be related to the form of the correlation hole around an electron. The essential ingredient here is a special choice for the spin density $\tilde{n}(\mathbf{r}, s)$ of the fictitious uniform gas whose correlation hole is used to mimic that of an inhomogeneous many-electron system. This choice is based on the notion of 'other' electrons or on explicit 'pair' quantities and is realized mathematically via the 'Fermi hole curvature' [13, 17]. This special choice of \tilde{n} ensures that the correlation energy is free from orbital self-interaction. Once \tilde{n} is chosen, the approach is somewhat similar to the

usual derivation [14, 3] of LSDF theory by consideration of the uniform-gas XC holes for a range of Coulomb interaction strengths λ . Here, however, the full exchange energy is retained, a local-density approximation being made only for the correlation term. The functionals which emerge turn out to be quite similar to those proposed by Becke [15, 16] and by Stoll *et al* [17]. The details of the new functionals are different from these earlier formulae, however, and new physical interpretations are given here which permit generalization in a number of directions. Schrodinger-like Euler-Lagrange equations are also discussed here for the first time for functionals in this class.

We assume for simplicity that all orbitals have a common axis of spin quantization, so that each orbital is either 'up' ($\uparrow, s = \frac{1}{2}$) or 'down' ($\downarrow, s = -\frac{1}{2}$). Before formally constructing the modified spin density $\tilde{n}(\mathbf{r}, s)$ it is useful to consider some limiting cases.

Case (1): For a single spin-up electron in the ground state of an external potential (e.g. the hydrogen atomic ground state) there is of course no correlation hole; there is a zero spin-down density and a zero density of 'other' spin-up electrons in which the single electron can cause a hole. Thus the uniform gas employed in mimicking the correlation hole should have zero spin-up and spin-down densities.

Case (2): Similarly for a two-electron paramagnetic state such as the helium ground state, an electron of either spin 'sees' no density of 'other' electrons of the same spin in which it could cause a hole. Therefore, to mimic the correlation hole around an electron of spin s , we should use a uniform gas with a zero density $\tilde{n}_s = 0$ of spin- s electrons but a non-zero density $n_{-s} = n(\mathbf{r}, -s)$ of the opposite spin, where $n(\mathbf{r}, -s)$ is the true spin density of the inhomogeneous system. Thus we shall be dealing with the hole around an isolated spin- s electron in a gas of electrons of spin $(-s)$.

Case (3): For the lithium ($\uparrow\uparrow\downarrow$) ground state, the best choice of a spin-up density \tilde{n}_\uparrow would be a value less than the local value of $n(\mathbf{r}, \uparrow)$ in the inhomogeneous system; this reflects the fact that there is only one 'other' spin-up electron, and not two.

2. A correlation functional based on the number of 'other' nearby electrons

To generalize the above ideas in a spatially local fashion, we consider a non-interacting reference state $|D\rangle = \det[\varphi_i(\mathbf{r}, s)]$ consisting of the determinant of one-body Kohn-Sham-like or HF-like orthonormal spin orbitals. For this reference state the normal-ordered pair distribution n_2^{NO} defined in general by

$$n_2^{\text{NO}}(\mathbf{r}, s : \mathbf{r}', s') \equiv \langle |\hat{\Psi}^\dagger(\mathbf{r}, s)\hat{\Psi}^\dagger(\mathbf{r}', s')\hat{\Psi}(\mathbf{r}', s')\hat{\Psi}(\mathbf{r}, s)| \rangle \quad (1)$$

takes the value

$$n_{2,D}^{\text{NO}}(\mathbf{r}, s : \mathbf{r}', s') = \sum_{ij \text{ occ}} \varphi_i^*(\mathbf{r}, s)\varphi_j^*(\mathbf{r}', s')[\{\varphi_j(\mathbf{r}', s')\varphi_i(\mathbf{r}, s)\} - \{i \leftrightarrow j\}]. \quad (2)$$

Note that (1) and (2) both vanish when $s = s'$ and $\mathbf{r} = \mathbf{r}'$. The normalization property of (1) and (2) is

$$\int n_2^{\text{NO}}(\mathbf{r}, s : \mathbf{r}', s') d^3r' = (N_{s'} - \delta_{ss'})n(\mathbf{r}, s) \quad (3)$$

where $n(\mathbf{r}, s)$ is the spin density at \mathbf{r} , and N_s is the total number of spin- s electrons. Note that (1), (2) and (3) are all identically zero in a one-electron state.

The probability of finding a spin- s electron at \mathbf{r} and simultaneously 'another' spin- s' electron within radius R of \mathbf{r} is found by integrating (1) or (2) with respect to \mathbf{r}' . We are thus led to define the number of 'other' spin- s' particles within radius R of a given spin- s electron located at \mathbf{r} by

$$N_R(s'|\mathbf{r}, s) = n(\mathbf{r}, s)^{-1} \int \theta(R - |\mathbf{u}|) n_2^{\text{NO}}(\mathbf{r}, s; \mathbf{r} + \mathbf{u}, s') d^3u. \quad (4)$$

As $R \rightarrow \infty$ this approaches $N_{s'} - \delta_{ss'}$, while for $R \rightarrow 0$ a 3D Taylor expansion in the variable u gives

$$N_R(s'|\mathbf{r}, s) \underset{R \rightarrow 0}{\simeq} n(\mathbf{r}, s)^{-1} [(4\pi R^3/3) n_2^{\text{NO}}(\mathbf{r}, s; \mathbf{r}, s') + (2\pi R^5/15) \nabla'^2 n_2^{\text{NO}}(\mathbf{r}, s; \mathbf{r}', s')|_{\mathbf{r}'=\mathbf{r}} + O(R^7)]. \quad (5a)$$

The terms containing even powers of R vanish because of the spherical symmetry of the integration region. Equation (5a) can be evaluated in the reference determinant $|D\rangle$, giving to lowest non-vanishing order in R ,

$$N_R^{\text{ref}}(s'|\mathbf{r}, s) \underset{R \rightarrow 0}{\simeq} \begin{cases} \frac{4\pi R^3}{3} n(\mathbf{r}, s') + O(R^5) & s' \neq s \\ \frac{2\pi R^5}{15 n(\mathbf{r}, s)} \sum_{i,j \text{ occ}} |\varphi_i(\mathbf{r}, s) \nabla \varphi_j(\mathbf{r}, s') - \{i \leftrightarrow j\}|^2 + O(R^7) & s' = s. \end{cases} \quad (5b)$$

The summation on the right-hand side of equation (5b) is the 'Fermi hole curvature' [13] $\nabla'^2 n_2^{\text{NO}}(\mathbf{r}, s; \mathbf{r}', s)|_{\mathbf{r}'=\mathbf{r}}$ evaluated for the reference determinantal state $|D\rangle$. For a uniform electron gas the Kohn-Sham-like orbitals are plane waves, and (5b) becomes (with k_F , the Fermi wavenumber for spin s)

$$N_R^{\text{ref},u}(s'|\mathbf{r}, s) \underset{R \rightarrow 0}{\simeq} \begin{cases} (4\pi R^3/3) n_{s'} + O(R^5) & s \neq s' \\ (4\pi R^5/25) n_s k_{F,s}^2 + O(R^7) & s = s'. \end{cases} \quad (5c)$$

By equating (5c) and (5b) we find the spin density $n_{s'}$ of a uniform gas whose reference state has the same number of 'other' spin- s' electrons in a small neighbourhood of a given spin s at \mathbf{r} , as does the reference state $|D\rangle$ of the inhomogeneous system under study. For unlike spins ($s' = -s$) the R^5 -term is negligible as $R \rightarrow 0$, and we obtain the trivial result $n_{-s} = n(\mathbf{r}, -s)$ reflecting the fact that all electrons of unlike spin are 'other' electrons. For like spins, however, the R^3 -term is identically zero and, matching the R^5 -terms, we obtain the following non-trivial result: to achieve the same number of 'other' nearby electrons as are present in the reference determinant state of the inhomogeneous system, a uniform gas will need to have a spin density $n_s = \bar{n}_A(\mathbf{r}, s)$ where

$$\frac{3}{5} (6\pi^2)^{2/3} \bar{n}_A(\mathbf{r}, s)^{5/3} = n(\mathbf{r}, s)^{-1} \frac{1}{2} \sum_{i,j \text{ occ}} |\varphi_i(\mathbf{r}, s) \nabla \varphi_j(\mathbf{r}, s) - \{i \leftrightarrow j\}|^2 \quad (6a)$$

and

$$n(\mathbf{r}, s) = \sum_{i \in \text{occ}} |\varphi_i(\mathbf{r}, s)|^2. \quad (6b)$$

Note that $\tilde{n}_A(\mathbf{r}, s)$ (equation (6a)) is zero in a one-electron state; there are no 'other' spin- s electrons for that case.

In the spirit of LDF theory, we now approximate the normal-ordered pair distribution of the interacting inhomogeneous system as follows:

$$\begin{aligned} n_2^{\text{NO}}(\mathbf{r}, s : \mathbf{r}', s') &\simeq n_{2,D}^{\text{NO}}(\mathbf{r}, s : \mathbf{r}', s') \\ &+ n(\mathbf{r}, s) g^u(s' | s : |\mathbf{r} - \mathbf{r}'| : \tilde{n}_A(\mathbf{r}, s), n(\mathbf{r}, -s)). \end{aligned} \quad (7)$$

Here the HF-like term $n_{2,D}^{\text{NO}}$ is built from the Kohn-Sham-like orbitals as in equation (2), while the correlation correction is built from the correlation hole

$$g^u(s' | s : \mathbf{r} : n_\uparrow, n_\downarrow) \equiv g^u(s' | s : \mathbf{r} : n_\downarrow, n_\uparrow) \quad (8)$$

in the spin- s' density at \mathbf{r} in a *uniform interacting* spin-polarized electron gas, because of the presence of a spin- s electron at $\mathbf{r} = \mathbf{0}$. In (7), note that the modified density \tilde{n}_A from equation (6a) is required only for the 'like-spin' density of the *uniform* gas; the 'opposite' spin ($-s$) has the regular density $n(\mathbf{r}, -s)$ from equation (6b), as discussed immediately prior to equation (6). The reasonableness of this choice is readily seen from the examples of the H, He and Li ground states discussed above. Alternative choices are discussed in section 6 below.

A Coulomb integration over the approximate pair distribution (7) will give an approximate potential energy contribution to the correlation energy of the inhomogeneous system. To include the kinetic part of the correlation energy, however, we need to replace the Coulomb interaction by $\lambda e^2 / r_{12}$ and then to perform a λ integration while applying a λ -dependent local external potential in order to hold the spin density constant [3, 14]. When this is done, we obtain an approximate expression for the total energy of the inhomogeneous interacting system as a functional of the set of one-body trial orbitals $\{\varphi_i\}$:

$$E \simeq E^{\text{HF}}[\{\varphi_i\}] + E_A^c[\{\varphi_i\}]. \quad (9)$$

Here E^{HF} is the HF (kinetic, external, direct and exchange) energy generated by the $\{\varphi_i\}$, while the first of our new correlation energy functionals is

$$E_A^c = \int d\mathbf{r} \sum_s n(\mathbf{r}, s) \epsilon^u(s, \tilde{n}_A(\mathbf{r}, s), n(\mathbf{r}, -s)). \quad (10)$$

In (10), \tilde{n}_A is the modified density defined in equation (6a), while

$$\epsilon^u(s, n_\uparrow, n_\downarrow) = \frac{1}{2} \sum_{s'} \int d^3r \frac{e^2}{r} \int_0^1 d\lambda g_\lambda^u(s' | s : \mathbf{r} : n_\uparrow, n_\downarrow) \quad (11)$$

is the (kinetic plus potential) correlation energy contribution in a uniform spin-polarized electron gas, arising from the correlation hole around one of the spin- s electrons.

Apart from built-in freedom from spurious orbital self-interaction, the correlation energy functional defined by (10) has a number of other desirable properties which it shares with a second functional, E_B^c , introduced in the following section. These properties are enumerated in section 5, after E_B^c has been defined.

3. A functional based on pair kinetic energy density

A second, alternative correlation functional may be derived by considering not the number of 'other' electrons near a given electron, but rather the density of the *relative* kinetic energy (KE) of *pairs* of electrons at a given position \mathbf{r} . This notion can be made more specific [13] by introducing the *normal-ordered* Wigner pair distribution

$$f_2^{\text{NO}}(\mathbf{r}_1, \mathbf{k}_1, s_1 : \mathbf{r}_2, \mathbf{k}_2, s_2) = (2\pi)^{-6} \int d^3\xi_1 d^3\xi_2 \exp[i(\mathbf{k}_1 \cdot \xi_1 + \mathbf{k}_2 \cdot \xi_2)] \\ \times \langle |\hat{\Psi}^\dagger(\mathbf{r}_1 + \frac{1}{2}\xi_1) \hat{\Psi}^\dagger(\mathbf{r}_2 + \frac{1}{2}\xi_2) \hat{\Psi}(\mathbf{r}_2 - \frac{1}{2}\xi_2) \hat{\Psi}(\mathbf{r}_1 - \frac{1}{2}\xi_1)| \rangle. \quad (12)$$

Within the limits imposed by the uncertainty principle, we may interpret f_2 as the probability density for finding an electron at position \mathbf{r}_1 with momentum $\hbar\mathbf{k}_1$ and spin projection s_1 , and simultaneously a *different* electron at position \mathbf{r}_2 with momentum $\hbar\mathbf{k}_2$ and spin projection s_2 . Thus f_2 is a quantum generalization of the classical pair distribution function and has many corresponding properties. For example, when f_2 is integrated with respect to \mathbf{k}_1 and \mathbf{k}_2 the normal-ordered pair distribution (1) is recovered. If f_2 is integrated with respect to \mathbf{r}_1 and \mathbf{r}_2 the normal-ordered two-body momentum distribution $\langle |\hat{c}_{\mathbf{k}_1}^\dagger \hat{c}_{\mathbf{k}_2}^\dagger \hat{c}_{\mathbf{k}_2} \hat{c}_{\mathbf{k}_1}| \rangle$ is recovered. A less convenient feature of f_2 is that it is not positive definite, which renders less meaningful the interpretation as a probability density. A further feature relative to the present discussion is that f_2 , unlike the pair density n_2^{NO} , does not vanish when $(\mathbf{r}_1, s_1) = (\mathbf{r}_2, s_2)$. This can be understood from the uncertainty principle; specification of \mathbf{k}_1 and \mathbf{k}_2 has rendered \mathbf{r}_1 and \mathbf{r}_2 'fuzzy'.

An expected density (per unit volume squared) of *relative* KE of *pairs* located near \mathbf{r} may be defined by an average over the Wigner distribution:

$$t_2(\mathbf{r}, s_1, s_2) = \frac{1}{2} \int d^3\mathbf{k}_1 d^3\mathbf{k}_2 \frac{\hbar^2}{2m} |\mathbf{k}_1 - \mathbf{k}_2|^2 f_2^{\text{NO}}(\mathbf{r}, \mathbf{k}_1, s_1 : \mathbf{r}, \mathbf{k}_2, s_2) \quad (13)$$

where the factor $\frac{1}{2}$ corrects for double counting under interchange of labels 1 and 2. This quantity is readily evaluated for a single determinantal state, and for like spins it takes a value proportional to the Fermi hole curvature $C(\mathbf{r}, s)$ of equation (5b) (see also [13]):

$$t_2^{\text{HF}}(\mathbf{r}, s, s) = \frac{\hbar^2}{4m} \sum_{i, j \text{ occ}} |\phi_i(\mathbf{r}, s) \nabla \phi_j(\mathbf{r}, s) - \phi_j(\mathbf{r}, s) \nabla \phi_i(\mathbf{r}, s)|^2. \quad (14a)$$

Being an expectation of a pair quantity, equation (14a) naturally vanishes in a one-electron state. Its value for a uniform HF electron gas (built from plane-wave orbitals and having spin densities n_\uparrow and n_\downarrow) is

$$t_{2,u}^{\text{HF}}(s, s) = n_s^2 \frac{2}{5} \epsilon_{F_s} = (\hbar^2/2m) \frac{3}{5} (6\pi^2)^{2/3} n_s^8/3. \quad (14b)$$

Thus, if we have computed the pair KE density $t_2^{\text{HF}}(\mathbf{r}, s, s)$ at point \mathbf{r} for an inhomogeneous system using HF-like orbitals $\{\varphi_i\}$ as in equation (14a), we can find the spin density \tilde{n}_B of a fictitious uniform gas having the same pair KE density in the HF approximation:

$$\tilde{n}_B(\mathbf{r}, s, s) = [\frac{5}{3} (6\pi^2)^{-2/3} (2m/\hbar^2) t_2^{\text{HF}}(\mathbf{r}, s, s)]^{3/8}. \quad (15)$$

This can also be written

$$\frac{3}{5}(6\pi^2)^{2/3}[\tilde{n}_B(\mathbf{r}, s, s)]^{8/3} = \frac{1}{2} \sum_{i,j,\text{occ}} |\phi_i(\mathbf{r}, s) \nabla \phi_j(\mathbf{r}, s) - \phi_j(\mathbf{r}, s) \nabla \phi_i(\mathbf{r}, s)|^2. \quad (16)$$

Here, as for the density \tilde{n}_A defined in the previous section, the result involves the Fermi hole curvature [13] (the summation on the right-hand side of (16)).

The second of our correlation functionals, which we shall call E_B^c , is then

$$E_B^c[\{\varphi_i\}] = \int d\mathbf{r} \sum_s n(\mathbf{r}, s) \epsilon^u(s, \tilde{n}_B(\mathbf{r}, s), n(\mathbf{r}, -s)) \quad (17)$$

where \tilde{n}_B is given by (16) and ϵ^u by (11); the arguments leading to this expression are identical with those leading to our first correlation functional E_A^c (see the discussion prior to equation (9)). Equation (16) is analogous to equation (6a) above except that the true density n in (6a) is replaced by a factor of \tilde{n} in going from (6a) to (16). Thus the effective density \tilde{n}_B in (16) is not as small as the effective density \tilde{n}_A from (6a), in the case of a relatively isolated electron for which the effective densities \tilde{n} are much less than the true density n . Nevertheless \tilde{n}_A and \tilde{n}_B both quite properly vanish for a strictly one-electron problem. A number of other desirable properties also hold for both E_A^c and E_B^c . These are listed in section 5.

4. Euler-Lagrange equations

To implement the present theory using either the functional for scheme A (equations (9) and (10)) or the functional for scheme B (equation (17)), one could follow one of two strategies.

(i) Where SIC effects are expected to be fairly small, one could take the $\{\phi_i\}$ to be self-consistent LSDF or unrestricted Hartree-Fock (UHF) orbitals without minimizing the functionals explicitly. The UHF orbitals may be better in that they already contain important elements of self-interaction correction.

(ii) More accurate answers, especially where orbital self-interaction is important as in semiconductor calculations, will presumably be obtained from orbitals which minimize the respective functionals. The corresponding Euler-Lagrange equations are of modified HF form and will now be derived.

Schemes A and B derived in sections 2 and 3 above both give a total energy of the form

$$E = E^{\text{HF}}[\{\varphi_i\}] + E_C \quad (18a)$$

where

$$E_C = \sum_s \int w_s(C(\mathbf{r}, s), n(\mathbf{r}, s), n(\mathbf{r}, -s)) d^3\mathbf{r}. \quad (18b)$$

Here, for scheme A,

$$w_s(C, n_s, n_{-s}) = n_s \epsilon^u(s, [\alpha C/n_s]^{3/5}, n_{-s}) \quad (19)$$

while, for scheme B,

$$w_s(C, n_s, n_{-s}) = n_s \epsilon^u(s, [\alpha C]^{3/8}, n_{-s}). \quad (20)$$

In (18)–(20), $\alpha = \frac{5}{6}(6\pi^2)^{-2/3}$, $\epsilon^u(s, n_s, n_{-s})$ is the spin-specific correlation hole energy of a uniform polarized electron gas from equation (11), and

$$C(\mathbf{r}, s) = \sum_{i,j \text{ occ}} |\varphi_i(\mathbf{r}, s) \nabla \varphi_j(\mathbf{r}, s) - \{i \leftrightarrow j\}|^2 \quad (21)$$

is the Fermi hole curvature [13] evaluated in the reference determinantal state $|D\rangle = \det\{\varphi_i\}$. After some algebra [18] one can re-express $C(\mathbf{r}, s)$ as

$$C(\mathbf{r}, s) = (4m/\hbar^2)[n(\mathbf{r}, s)t(\mathbf{r}, s) - \hbar^2/8m|\nabla n(\mathbf{r}, s)|^2 - (m/2)|\mathbf{J}(\mathbf{r}, s)|^2] \quad (22)$$

where

$$t(\mathbf{r}, s) = \frac{\hbar^2}{2m} \sum_{i \text{ occ}} |\nabla \varphi_i(\mathbf{r}, s)|^2 \quad (23)$$

is one version of the kinetic energy density of spin- s electrons at \mathbf{r} , and

$$\mathbf{J}(\mathbf{r}, s) = \frac{\hbar i}{2m} \sum_{i \text{ occ}} [\varphi_i(\mathbf{r}, s) \nabla \varphi_i^*(\mathbf{r}, s) - \varphi_i^*(\mathbf{r}, s) \nabla \varphi_i(\mathbf{r}, s)] \quad (24)$$

is the Schrödinger current density of electrons of spin projection s . In a standard calculus-of-variations approach, we consider the change in the correlation energy E_C (equation (18b)) when we make a small change $\delta\varphi_I^*(\mathbf{r}, s)$ in the I th orbital:

$$\begin{aligned} \delta E^c = \sum_s \int & \left[\left(\frac{\partial w_s}{\partial n(\mathbf{r}, s)} + \frac{\partial w_{-s}}{\partial n(\mathbf{r}, s)} \right) \right. \\ & \left. \times \varphi_I(\mathbf{r}, s) \delta\varphi_I^*(\mathbf{r}, s) + \frac{\partial w_s}{\partial C(\mathbf{r}, s)} \delta C(\mathbf{r}, s) \right] d^3\mathbf{r}. \end{aligned}$$

In the last term the change δC in the Fermi hole curvature is, from equations (21)–(24),

$$\begin{aligned} \delta C(\mathbf{r}, s) = 4m\hbar^{-2} t \varphi_I \delta\varphi_I^* + 2n \nabla \varphi_I \cdot \nabla \{\delta\varphi_I^*\} - \nabla n \cdot [\varphi_I \nabla \{\delta\varphi_I^*\} + \nabla \varphi_I \delta\varphi_I^*] \\ - 2m(\hbar i)^{-1} \mathbf{J} \cdot [\nabla \varphi_I \delta\varphi_I^* - \varphi_I \nabla \{\delta\varphi_I^*\}] \end{aligned}$$

where the arguments (\mathbf{r}, s) are understood on n , φ_I , φ_I^* , t and \mathbf{J} . Then after an integration by parts (i.e. use of Green's theorem) on all terms involving $\nabla\{\delta\varphi_I^*\}$ we obtain a result for the total energy change in the form

$$\delta E = \delta E^{\text{HF}} + \delta E^c = \sum_s \int [F_I^{\text{HF}}(\mathbf{r}, s) + F_I^c(\mathbf{r}, s)] \delta\varphi_I^*(\mathbf{r}, s) d^3\mathbf{r}.$$

The orbitals φ which minimize the energy will lead to a zero variation δE for arbitrary variations $\delta\varphi_I^*$ (subject to the constraint of orthonormality, imposed by a set of Lagrange multipliers ϵ_{ij}), giving $F_I^{\text{HF}}(\mathbf{r}, s) + F_I^c(\mathbf{r}, s) - \sum_J \epsilon_{IJ} \varphi_J = 0$. This leads to the following HF-like Euler-Lagrange equation with an additional local correlation potential V^c and two further terms. These are reminiscent of the KE due to an inhomogeneous inverse effective-mass correction $\Delta\rho(\mathbf{r}, s)$, and the interaction with a fictitious vector potential $\mathbf{a}(\mathbf{r}, s)$:

$$\begin{aligned} & \{\hat{H}^{\text{HF}} + V^c(\mathbf{r}, s) + \frac{1}{2}\hat{\mathbf{P}} \cdot \Delta\rho(\mathbf{r}, s)\hat{\mathbf{P}} - \frac{1}{2}[\mathbf{a}(\mathbf{r}, s) \cdot \hat{\mathbf{P}} + \hat{\mathbf{P}} \cdot \mathbf{a}(\mathbf{r}, s)]\}\varphi_i(\mathbf{r}, s) \\ & = \sum_j \epsilon_{ij} \varphi_j(\mathbf{r}, s). \end{aligned} \quad (25a)$$

Here

$$\begin{aligned} V^c(\mathbf{r}, s) & = \partial(w_s + w_{-s})/\partial n(\mathbf{r}, s) \\ & + (4m/\hbar^2)t(\mathbf{r}, s)\partial w_s/\partial C_s + \nabla \cdot [(\partial w_s/\partial C_s)\nabla n(\mathbf{r}, s)] \end{aligned} \quad (25b)$$

$$\mathbf{a}(\mathbf{r}, s) = (4m/\hbar^2)(\partial w_s/\partial C_s)\mathbf{J}(\mathbf{r}, s) \quad (25c)$$

and

$$\Delta\rho(\mathbf{r}, s) = (4/\hbar^2)(\partial w_s/\partial C_s)n(\mathbf{r}, s). \quad (25d)$$

\hat{H}^{HF} is the usual Hartree-Fock effective Hamiltonian

$$\begin{aligned} \hat{H}^{\text{HF}}\varphi_i(\mathbf{r}, s) & = [(2m)^{-1}\hat{\mathbf{P}} \cdot \hat{\mathbf{P}} + V^{\text{ext}}(\mathbf{r})]\varphi_i(\mathbf{r}, s) \\ & + \sum_{j \neq i}^{\text{occ}} e^2 \int \frac{\varphi_i^*(\mathbf{r}', s')[\varphi_i(\mathbf{r}', s')\varphi_j(\mathbf{r}, s) - \varphi_i(\mathbf{r}', s')\varphi_j(\mathbf{r}, s)]}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \end{aligned} \quad (25e)$$

$\hat{\mathbf{P}} = (\hbar/i)\nabla_{\mathbf{r}}$ is the momentum operator, which is understood to act on all other quantities multiplied to its right.

Equation (25a) is not in canonical form, in the sense that the 'energy' (Lagrange multiplier) ϵ_{ij} on the right-hand side is not diagonal, but ϵ can be diagonalized by a unitary transformation. However, a unitary transformation between the $\{\varphi_i\}$ is well known to leave the HF operator invariant in form. It also leaves the rest of the effective Hamiltonian, namely $\Delta\hat{H} = \hat{H}^{\text{total}} - \hat{H}^{\text{HF}}$ on the left-hand side of equation (25a) invariant, because the only quantities in $\Delta\hat{H}$ involving the orbitals are the spin density $n(\mathbf{r}, s)$, the KE density $t(\mathbf{r}, s)$ (equation (23)), the Fermi hole curvature $C(\mathbf{r}, s)$ (equation (22) or (21)) and the Schrödinger current (equation (24)); each is evaluated in the reference determinantal state $|D\rangle = \det\{\varphi_i\}$; but this reference determinant is itself invariant under a unitary transformation among the $\{\varphi_i\}$, so that the non-HF terms on the left-hand side of equation (25a) are indeed invariant. This means that the Euler-Lagrange equations (25a) can be brought by a unitary transformation to the 'canonical' (diagonal) form

$$\{\hat{H}^{\text{HF}} + V^c + \frac{1}{2}\hat{\mathbf{P}} \cdot \Delta\rho\hat{\mathbf{P}} - \frac{1}{2}(\mathbf{a} \cdot \hat{\mathbf{P}} + \hat{\mathbf{P}} \cdot \mathbf{a})\}\varphi_i(\mathbf{r}, s) = \epsilon_i \varphi_i(\mathbf{r}, s) \quad (26)$$

in which the right-hand side does not mix the orbitals, and V^c , α and $\Delta\rho$ are as in equations (25b)–(25d), unmodified. Furthermore, the HF Hamiltonian \hat{H}^{HF} is well known to be Hermitian, and the additional Hamiltonian terms are also readily shown to be Hermitian. The latter follows because the momentum \hat{P} and the real local (multiplicative) operators $\alpha(\mathbf{r}, s)$ and $\Delta\rho(\mathbf{r}, s)$ are Hermitian, and the combinations $\hat{A}\hat{B}\hat{A}$ and $\hat{A}\hat{B} + \hat{B}\hat{A}$ of Hermitian operators \hat{A} and \hat{B} are Hermitian in general. Thus the eigenvalue ϵ_i in (26) is real and the $\{\varphi_i\}$ are orthogonal for unequal ϵ_i . By contrast, this desirable orthogonality is not preserved in the standard PZ [5] LDF SIC formalism, which has otherwise proved very useful.

5. Properties of functionals E_A^c and E_B^c

The correlation functionals E_A^c and E_B^c defined in sections 2 and 3 have the following desirable properties.

(a) *Freedom from orbital self interaction*: for a single orbital i of spin s , both the modified spin density $\tilde{n}_A(\mathbf{r}, s)$ of equation (6a) and the regular spin density $n(\mathbf{r}, -s)$ of equation (6b) vanish; so (10) contains as a factor the correlation energy per particle of a zero-density uniform gas, which is zero. Similarly, for scheme B, \tilde{n}_B (equation (15)) vanishes and hence so does E_B^c (equation (17)).

(b) *Invariance under a unitary transformation among occupied orbitals*: a determinantal state is well known to have this invariance property. Now the spin density $n_A(\mathbf{r}, s)$ and the pair distribution $n_{2,D}^{\text{NO}}$ of equation (2) (from which \tilde{n}_A is constructed via (5a) and (6)) are both expectations over a determinant $|D\rangle$ of orbitals $\{\varphi_i\}$. Thus both n and \tilde{n}_A , and hence the functional E_A^c of equation (10), are similarly invariant. The invariance of the remaining HF part of equation (9) has already been discussed in the introduction. Similar statements hold for E_B^c .

(c) *Formally correct spatially homogeneous limit*: for the uniform spin-polarized gas the modified spin density \tilde{n}_A and \tilde{n}_B (equations (6a) and (15)) equal the true spin density $n(\mathbf{r}, s)$ (equation (6b)), so that E_A^c and E_B^c (equations (10) and (17)) reduce to the correlation energy of the uniform gas. This point is mentioned because the Colle–Salvetti [10] functionals, which are fitted to atomic data, do not give accurate results in the uniform-gas limit.

(d) *Correctly normalized correlation hole*: the approximate correlation hole g introduced in equation (7) has the correct normalization [3], i.e. it yields zero when integrated over \mathbf{r}' for fixed \mathbf{r} . This follows from the corresponding property of the exact uniform-gas hole, plus the fact that the spin-density arguments of g in (7) do not involve \mathbf{r}' . Similar considerations hold for the functional in scheme B.

(e) *Inclusion of kinetic as well as potential correlation energy*: this is ensured by the Feynman λ integration in equation (11). This point is mentioned in contrast with [10].

(f) *Non-zero correlation energy in the fully spin-polarized case*: this point is mentioned here because a related functional [10] vanishes in the fully spin-polarized limit. The present theory, unlike that of [10], should be appropriate for magnetic as well as non-magnetic systems.

(g) *Orthogonality of canonical minimizing orbitals*: this was proved in the previous section. It should be noted that the most widely used SIC scheme, that of PZ, does not have this desirable feature.

Potentially undesirable features of functionals E_A^c and E_B^c include the fact that the equations, numerically speaking, are of HF rather than LDF Kohn–Sham complexity. It should be noted, however, that the self-consistent HF equations for an infinite crystal are now solvable with a standardized computer software package, at least in the spin-restricted case [19], so this may be less of a drawback than it would previously have been. Secondly, it does not appear that the original form of Koopman’s theorem holds for this functional, in contrast with the Dobson–Rose [12] and the pure HF functionals. Thirdly, it seems that, if (despite the lack of Koopman’s theorem) one does make so bold as to interpret the ϵ_i as excitation energies in the present schemes, then the characteristic HF singularity in the $\epsilon(k)$ spectrum will appear at the Fermi surface in extended metallic systems.

6. Comparison with a functional introduced by Becke

Becke [15] has described (and successfully tested on small atoms and molecules) a correlation functional based on the ‘local curvature’ of the HF pair distribution. The second approximation E_B^c described above turns out to be almost identical with Becke’s functional. Thus, Becke’s work can alternatively be interpreted as introducing a uniform gas whose relative KE density (for like-spin pairs in the HF approximation) is equal to that of the non-uniform electronic system at hand.

Becke introduced a modified density $\tilde{\rho}$. To see the equivalence between our $\tilde{n}_B(\mathbf{r}, s)$ and Becke’s $\tilde{\rho}$ we note that, for non-diamagnetic states (i.e. those with zero current density J), equation (22) leads to the following result for the Fermi hole curvature:

$$\begin{aligned} C(\mathbf{r}, s) &\equiv \sum_{i,j \text{ occ}} |\phi_i(\mathbf{r}, s) \nabla \phi_j(\mathbf{r}, s) - \phi_j(\mathbf{r}, s) \nabla \phi_i(\mathbf{r}, s)|^2 \\ &= 2n(\mathbf{r}, s) \sum_{i \text{ occ}} |\nabla \phi_i(\mathbf{r}, s)|^2 - \frac{1}{2} |\nabla n(\mathbf{r}, s)|^2. \end{aligned} \quad (27)$$

Thus equation (16) above becomes identical with equation (15) of Becke [15], showing that our $\tilde{n}_B(\mathbf{r}, s)$ is $\tilde{\rho}_s$ of [15]. The only difference between Becke’s functional and our second functional E_B^c above lies in the way in which the modified density \tilde{n} is inserted into the uniform-gas correlation data. Becke [15] takes the correlation energy between electrons of a given spin orientation (e.g. \uparrow) from a uniform gas which is fully spin polarized (e.g. all \uparrow); good data already exist for such a gas. The correlation energy $E_{\uparrow\downarrow}^{\text{LSD}}$ between unlike spins are taken by Becke to be those of conventional LSD theory, with the like-spin correlation energy removed according to the SIC scheme of Stoll *et al* [4]. Thus, Becke’s correlation functional is, in the present notation,

$$E_{c3} = E_{\uparrow\downarrow}^{\text{LSD}} + \sum_s \int \tilde{n}(\mathbf{r}, s) \epsilon^u(s, \tilde{n}(\mathbf{r}, s), 0) d^3r \quad (28)$$

where ϵ^u is defined in equation (11) and $\tilde{n}(\mathbf{r}, s)$ is \tilde{n}_B from equation (16). By contrast, our equations (17) and (10) require the correlation hole in the density of *each* spin species around (say) a spin-up electron to be that of the corresponding spin species in a uniform gas with a modified spin-up density \tilde{n}_\uparrow but an unmodified spin-down density n_\downarrow . To see the distinction between this prescription and that of Becke we look again at two of the small-atom ground states discussed in the introduction.

(i) First consider the hole around the spin-up electron in helium. since there are no 'other' spin-up electrons, both theories have $\tilde{n}_\uparrow = 0$. Thus, the present theory requires a knowledge of the hole around an isolated 'test' spin-up electron in an otherwise entirely spin-down electron gas; this can be found in principle from a limit as $\tilde{n}_\uparrow \rightarrow 0$ of the corresponding hole in a uniform gas of densities \tilde{n}_\uparrow and n_\downarrow . On the other hand, the hole in Becke's theory (identical in this case with that of Stoll *et al* [4]) is the hole in the spin-down gas around one of the many spin-up electrons in a gas where both spin species have finite densities n_\uparrow and n_\downarrow . In Becke's case there is thus additional screening of the hole in the spin-down density, due to polarization of the excess spin-up electrons. By a RPA or fluctuation-dissipation theorem argument, one might expect that this screening will reduce the up-down correlation energy $E_{\uparrow\downarrow}^{\text{LSD}}$. There is in fact no such additional screening of the hole around the single spin-up electron in a helium atom; so $E_{\uparrow\downarrow}^{\text{LSD}}$ underestimates the correlation in this respect. However, a uniform electron gas is much more polarizable than the electrons in He because the latter have discretely spaced energy levels. Thus, the uniform-gas model substantially overestimates correlation, and the undercorrelation of $\uparrow\downarrow$ pairs inherent in Becke's scheme may actually improve the total correlation energy (compared with our scheme) in the case of small atoms at least. For molecular and solid state systems, one might imagine that it would be preferable to describe the screening more realistically, however, as the discrete-level effects are presumably smaller.

(ii) Next consider the hole around a spin-up electron in Li($1s \uparrow\downarrow, 2s \uparrow$). The uniform-gas hole invoked by equation (11) is the hole around a spin-up electron in a gas of spin densities \tilde{n}_\uparrow and n_\downarrow where $\tilde{n}_\uparrow < n_\uparrow$. This entails a screening of the hole in the spin-up density by the spin-down electrons. In the Becke approach there is no such screening since the hole in the spin-up density is taken from a totally spin-polarized gas of up and down densities \tilde{n}_\uparrow and 0. Similarly equation (11) invokes a hole in the spin-down density which is screened by a reduced density \tilde{n}_\uparrow of spin-up electrons, whereas the LSD hole used in the Becke theory is screened by the full density n_\uparrow . The true situation in Li is that the \uparrow electron causing the hole is not available for screening as it has already been 'localized' in the conditional probability situation envisaged in the definition of a correlation hole. Thus (by this argument at least), one concludes that the screening effects are more accurately treated in the present model than in that of Becke, provided that the effects of finite level spacing are ignored.

To summarize the present comparison, one of the modified electron densities \tilde{n}_B (equation (15)) introduced in the present work is identical with $\tilde{\rho}$ of Becke [15]: the other version, \tilde{n}_A (equation (6a)) tends to be smaller than $\tilde{\rho}$. Once a particular \tilde{n} is chosen, it seems that the present scheme (equations (10) (or (17)) and (11)) for choosing a uniform reference electron gas may give a more realistic description of the screening phenomena than the Becke prescription [15]. This advantage is, however, of little use for small systems for which the uniform-gas model inherently overscreens because of the neglect of finite energy level spacing. On the debit side, the present method requires detailed uniform-gas data concerning the separate holes around the two different spin species in a partially (or fully) spin polarized gas. Such data do not appear to be available in the literature to date, but it should not be too difficult to construct them, at least at the level of a 'RPA plus Wigner interpolation'. The argument just presented suggests that it will be worth pursuing the present type of approach for applications in solid state physics, particularly for

small-gap insulators, for magnetic systems with partially localized orbitals and for metal-insulator transitions. In all these cases, polarizability and screening effects are expected to be more important, and discrete-level effects less so, than they are in the atomic and molecular cases tested by Becke [15].

7. Summary and conclusions

In summary, we have suggested several approximate expressions for the correlation and total energies of an interacting inhomogeneous many-electron system in terms of a set of trial spin orbitals $\{\varphi_i\}$. Specifically equations (10), (6a) and (11) define a correlation functional E_A^c based on the number of 'other' electrons near to a given electron, equations (17), (16) and (11) define a correlation functional E_B^c based on the density of relative KE of electron pairs per unit volume squared, and equations (28), (16) and (11) define a correlation functional E_{c3} similar to the KE-density-based approach just described, but using uniform-gas data in a slightly different way. This turns out to be identical with a functional proposed by Becke [15].

If Becke's approach to the use of uniform-gas data is adopted, then another functional emerges; this is based on the number of 'other' nearby electrons as defined by equations (6a), (11) and (28) (i.e. it is the Becke scheme with $\tilde{n}_A(\mathbf{r}, s)$ rather than $\tilde{n}_B(\mathbf{r}, s)$ in place of $\tilde{n}(\mathbf{r}, s)$ in (28)). This functional was not written out explicitly in the text above but it could be denoted E_D^c .

The same computer programs [15] used to test Becke's functional E_{c3} could presumably be modified rather easily to test the above functional E_B^c on atoms and small molecules. Testing of the functionals E_A^c and E_B^c will not be so easy, because they require detailed data for the spin-polarized uniform electron gas which do not appear to be available as yet in the literature. (For example, in the case of the He ground state, one needs the correlation energy due to deflection of a spin-up electron gas by a single 'test' spin-down electron.) The advantage to be gained by using E_A^c and E_B^c is that they probably describe screening effects more reasonably than E_{c3} and E_D^c do, provided of course that uniform-gas screening is a reasonable approximation for the non-uniform problem under study. This is more likely to be so for solid state problems than for atomic cases. In atomic systems the discrete spacing of the energy levels means that a uniform-gas approximation necessarily overcorrelates, since its continuous energy levels lead to a polarizability which is much too large.

All the functionals introduced in the present work are free of orbital self-interaction in the sense that they give vanishing correlation energy for a single-electron state. They achieve this while maintaining invariance under a unitary transformation among occupied orbitals, unlike the PZ self-interaction correction scheme [5] which has proved useful and practical for solid state calculations except for this non-invariance problem. This feature of the new schemes should be an advantage for electronic band-structure calculations in periodic solids where the requirement to use localized functions in the PZ scheme is at the very least inconvenient. Despite the above improvement with regard to self-interaction the present schemes automatically satisfy the XC hole normalization requirement without the need for explicit integral constraints. This latter feature is shared by the 'average density' scheme of Gunnarsson *et al* [21], although not by their 'weighted-density' approximation [20]. On the debit side, the present schemes require a full UHF energy evaluation for the chosen orbitals before the new correlation functionals can be added to yield an XC energy.

If this is not done, the exact SIC and invariance properties are lost. Functionals of the type proposed here lead via a variational procedure to Euler–Lagrange equations which are Schrödinger-like and involve non-local self-consistent fields which generalize the HF field. Other desirable features of the present class of functionals are listed in section 5 above; one such feature is the orthogonality of the canonical orbitals satisfying the Euler–Lagrange equation. This desirable feature is not shared by the standard PZ LDF SIC scheme.

A functional of the general type proposed here has already been tested with some success [15] for the correlation contribution to dissociation energies of small molecules. HF methods are now practicable for band problems also [19]; so functionals for correlation alone, such as those introduced here, should play a useful role in future studies of solid state systems. Problems which suggest themselves particularly as being sensitive to SIC phenomena include semiconductor band gaps, localization problems involving magnetism, metal–insulator transitions and Wigner crystallization.

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