Exchange and correlation as a functional of the local density of states

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A functional $E_{xc}[\rho(\mathbf{r}, \epsilon)]$ is presented, in which the exchange and correlation energy of an electron gas depends on the local density of occupied states. A simple local parametrization scheme is proposed, entirely from first principles, based on the decomposition of the exchange-correlation hole in scattering states of different relative energies. In its practical Kohn-Sham-like form, the single-electron orbitals become the independent variables, and an explicit formula for the functional derivative is obtained.

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I. INTRODUCTION

Density functional theory\(^1\)\(^2\) (DFT) has become an essential tool in the study and simulation of molecules and condensed systems. Its evolution from the initial local density approximation (LDA) to the generalized gradient approximation\(^3\)\(^-\)\(^5\) (GGA), the mixing of exact exchange\(^6\)\(^-\)\(^7\) and, more recently, to the meta-GGAs\(^8\)\(^-\)\(^9\) has brought a substantial increase in accuracy. However, this evolution is not systematic and the holy grail of “chemical accuracy” (~ 1 Kcal/mole for reaction energies) still appears rather distant. Perhaps more importantly, basic difficulties remain unsolved, specially for strongly correlated and magnetic systems, as well as for excited states. Among the latter, the systematic underestimation of the insulating band gap is particularly troublesome for the simulation of solids.

In this work, I propose a functional for the exchange and correlation energy $E_{xc}$, which might potentially overcome some of these difficulties. Like in the meta-GGAs, its basic ingredient is not just the electron density. Rather, $E_{xc}$ depends on a richer and more informative function, namely the local density of occupied states. Since this function changes much more drastically and transparently than the total density for excited states, the functional can in principle describe these in addition to the ground state. Furthermore, the functional form can be rationalized naturally in terms of electron-electron scattering states, what in principle allows also to parametrize the functional in an entirely ab initio and unambiguous way.

II. DENSITY OF STATES FUNCTIONAL

Let us first define the local density of occupied kinetic-energy states as

$$\rho(\mathbf{r}, \epsilon) = \sum_{i=1}^{N} \int d^3N \mathbf{r} \frac{|\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2}{\delta^3(\mathbf{r}_i - \mathbf{r})} \times \delta(\epsilon_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) - \epsilon)$$  \hspace{1cm} (1)

with

$$\epsilon_i(\mathbf{r}_1, \ldots, \mathbf{r}_N) = -\frac{\hbar^2}{2m_e} \frac{\nabla^2 \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)}{\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)}$$  \hspace{1cm} (2)

where $\Re$ means real part and I will omit spin degrees of freedom to simplify the notation. Notice that the first two moments of $\rho(\mathbf{r}, \epsilon)$,

$$\rho(\mathbf{r}) = \int_{-\infty}^{+\infty} d\epsilon \rho(\mathbf{r}, \epsilon)$$  \hspace{1cm} (3)

and

$$\tau(\mathbf{r}) = \int_{-\infty}^{+\infty} d\epsilon \rho(\mathbf{r}, \epsilon) \epsilon$$  \hspace{1cm} (4)

are the electron and the kinetic energy densities. The former is the functional variable in all DFT’s and the latter is used as an additional auxiliary function in meta-GGAs\(^8\)\(^-\)\(^9\) (with $\rho(\mathbf{r})$ and $\tau(\mathbf{r})$ obtained from a noninteracting wave function, see below). These may thus be considered as particular cases of a more general functional $E[\rho(\mathbf{r}, \epsilon)]$.

Notice that, since the wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ is determined\(^1\) by the electron density $\rho(\mathbf{r})$, the density of states $\rho(\mathbf{r}, \epsilon)$ is also fully determined by $\rho(\mathbf{r})$, and therefore it formally does not add any variational freedom. However, in practice $\rho(\mathbf{r}, \epsilon)$ provides explicitly much more information on the electronic state than $\rho(\mathbf{r})$, and therefore it allows for a more accurate parametrization of the exchange and correlation energies. On this respect, $\rho(\mathbf{r}, \epsilon)$ is a reasonable half way in complexity between $\rho(\mathbf{r})$ and $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Thus, I express the total energy as

$$E[\rho(\mathbf{r}, \epsilon)] = T[\rho(\mathbf{r}, \epsilon)] + U_H[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r}, \epsilon)]$$

$$+ \int d^3 \mathbf{r} \rho(\mathbf{r}) \nu_{ext}(\mathbf{r})$$  \hspace{1cm} (5)

where $T$ is the kinetic energy

$$T[\rho(\mathbf{r}, \epsilon)] = \int d^3 \mathbf{r} \tau(\mathbf{r}),$$  \hspace{1cm} (6)
leads to the Kohn-Sham equations

\[ U_H[\rho(r)] = \int \int d^3r \ d^3r' \frac{e^2\rho(r)\rho(r')}{|r-r'|} \] (7)

\( v_{\text{ext}}(r) \) is the external potential, and \( E_{xc}[\rho(r,\epsilon)] \) is some approximation to the exchange and correlation energy, which includes everything else.

Although Eq. (6) is in principle the total kinetic energy, in practice we will use a density \( \rho(r,\epsilon) \) obtained from a single-determinant wave function \( \Psi_0 \) and therefore \( E_{xc}[\rho(r,\epsilon)] \) must also contain the difference in kinetic energy between \( \Psi_0 \) and the exact wave function. More precisely, let us introduce another functional

\[ E^0[\rho^0(r,\epsilon)] = T[\rho^0(r,\epsilon)] + U_H[\rho(r)] + E_{xc}^0[\rho^0(r,\epsilon)] \]

+ \( \int d^3r \ \rho(r) \ v_{\text{ext}}(r) \) (8)

where

\[ \rho^0(r,\epsilon) = \sum_{\alpha=1}^N |\psi_\alpha(r)|^2 \ \delta(\epsilon_\alpha^0(r) - \epsilon), \]

\[ \epsilon_\alpha^0(r) = -\frac{\hbar^2}{2m_e} \nabla^2 \psi_\alpha(r), \] (10)

and \( \psi_\alpha(r) \) are single-electron, orthonormal, occupied orbitals.

For a given density \( \rho(r) \), the functions \( \rho(r,\epsilon) \) and \( \rho^0(r,\epsilon) \) are different. Furthermore, since the same density \( \rho(r) \) can result from different sets of \( \psi_\alpha(r) \)'s, and therefore from different functions \( \rho^0(r,\epsilon) \), there is an intrinsic indetermination in the functional \( E^0 \). An example of such indetermination is a rotation in the space of occupied orbitals, which leaves invariant \( \rho(r) \) but not \( \rho^0(r,\epsilon) \). The indetermination can be removed by specifying an explicit way of obtaining \( \psi_\alpha(r) \) from \( \rho(r) \). A natural choice is to minimize \( T[\rho^0(r,\epsilon)] \), under the constraint (3). This leads to the Kohn-Sham equations

\[ \left( -\frac{\hbar^2}{2m_e} \nabla^2 + v(r) - \epsilon_\alpha \right) \psi_\alpha(r) = 0 \] (11)

where \( v(r) \) is the Lagrange multiplier associated to the constraint (3), and \( \epsilon_\alpha \) is that associated to the normalization constraint for \( \psi_\alpha \). However, we will simply consider the indetermination in \( \rho^0(r,\epsilon) \) as an additional freedom to achieve a practical and accurate parametrization of \( E^0[\rho^0(r,\epsilon)] \).

In Eqs. (5) and (8), \( E[\rho(r,\epsilon)] \) and \( E^0[\rho^0(r,\epsilon)] \) are formally assumed to be infinite for all functions, \( \rho(r,\epsilon) \) and \( \rho^0(r,\epsilon) \), which cannot be expressed in the forms (1) and (9), respectively. In practice, this condition needs not be dealt with, since we will use the standard Kohn-Sham procedure\(^2\) of minimizing the total energy as a function of \( \psi_\alpha(r) \) rather than of \( \rho^0(r,\epsilon) \). In what follows, I will refer only to \( E_{xc} \) and \( \rho^0(r,\epsilon) \), but I will drop the superscript 0 to simplify the notation.

The advantage of \( \rho(r,\epsilon) \) as a functional variable is that it provides much more explicit information on the system state than \( \rho(r) \). Thus, it naturally leads to an energy and orbital-dependent exchange-correlation potential, much like quasiparticle self energies, thus offering hope of improving the description of excited states and band gaps. Also, since the density of states is very different in localized and extended systems, it offers the possibility to address electron localization and self-interaction problems. In a different context, the relevance of spectral functions in the description of electron localization and strong correlation has been stressed by dynamical mean field theory\(^10\). Finally, the success of meta-GGA functionals in improving atomization energies gives us some confidence that the proposed functional may also improve considerably on formation and reaction energies. On the other hand, it might be suspected that, since the local density of states is much richer in structure than the total density, a functional dependent on it should be also much harder to parametrize. I will show that, at least in principle, this is not the case, and that unambiguous and physically rooted parametrizations of \( E_{xc} \) are possible.

III. FUNCTIONAL FORM

Here I propose the local functional form\(^11\)

\[ E_{xc} = \int d^3r \int_{-\infty}^{+\infty} de \ de' \ K_{xc}(\rho(r),\epsilon,\epsilon') \ \rho(r,\epsilon) \ \rho(r,\epsilon') \] (12)

where the kernel \( K_{xc} \) is an average of the interaction energy between two electrons with wave vectors \( \mathbf{k} \) of fixed size \( k = \sqrt{2m_e}\epsilon/\hbar \) but random direction \( \mathbf{k} \):

\[ K_{xc}(\rho,\epsilon,\epsilon') = \frac{1}{2} \int \frac{d^2k}{4\pi} \int \frac{d^2k'}{4\pi} \ e_{xc}(\rho,|\mathbf{k} - \mathbf{k}'|) \]

\[ = \frac{1}{2} \int dq \ e_{xc}(\rho,\epsilon) \ P(q|\epsilon,\epsilon') \] (13)

where the factor 1/2 corrects double counting and \( P(q|\epsilon,\epsilon') \) is the probability that the two electrons, with kinetic energies \( \epsilon = \hbar^2k^2/2m_e \) and \( \epsilon' = \hbar^2k'^2/2m_e \), have relative momentum \( \hbar|\mathbf{k} - \mathbf{k}'|/2 \):

\[ P(q|\epsilon,\epsilon') = \int \frac{d^2k}{4\pi} \frac{d^2k'}{4\pi} \delta\left(|\mathbf{k} - \mathbf{k}'| - q\right) \]

\[ = \begin{cases} 2q/(kk') & \text{if } |k-k'| < 2q < |k+k'| \\ 0 & \text{otherwise} \end{cases} \] (14)

e_{xc}(\rho,\epsilon) is the energy change of an electron pair, with relative momentum \( \hbar q \), in a homogeneous gas of density \( \rho \) (assumed unpolarized for simplicity), when their antisymmetry is imposed and their interaction potential \( \epsilon^2/r \) is switched on. It may be written as \( e_{xc}(\rho,\epsilon) = e_x(q) + e_c(\rho,\epsilon) \). Expanding the plane waves in spherical
where $P_{\text{effective}}$ interaction potential for the screened Coulomb $V$ and $|j\rangle$ density. Eqs.(18-19) define a problem which derives GGAs from $e_{xc}$.

**IV. FUNCTIONAL DERIVATIVE**

To minimize the total energy or to perform ab initio molecular dynamics, we need the functional derivative $\delta E_{xc}/\delta \psi^*_{\alpha}(r)$. To calculate it, it is convenient to assume that the occupied orbitals $\psi_{\alpha}(r)$, density $\rho(r)$, and density of states $\rho(r, \epsilon)$ are given in a mesh of points $r_i$ and discrete energies $\epsilon$. Their gradients and laplacians can then be calculated as

$$\nabla \rho_i \equiv \nabla \rho(r_i) = \sum_j g_{ij} \rho_j$$

$$\nabla^2 \psi_{i\alpha} \equiv \nabla^2 \psi_{\alpha}(r_i) = \sum_j L_{ij} \psi_{j\alpha}$$

where $\rho_i \equiv \rho(r_i)$, $\psi_{i\alpha} \equiv \psi_{\alpha}(r_i)$, and $g_{ij}, L_{ij}$ are coefficients of some unspecified finite-difference formulas. We can then replace the functional derivatives by ordinary partial derivatives and recover the continuous limit at the end. Using atomic units ($\hbar = e = m_e = 1$) and omitting for brevity the grid increments, $\Delta x^3$ and $\Delta \epsilon$, when replacing the integrals $\int d^3r$ and $\int d\epsilon$ by grid sums, the discretized equations are

$$E_{xc} = \sum_j \sum_{\epsilon \epsilon'} K_{j\epsilon\epsilon'} \rho_{j\epsilon} \rho_{j\epsilon'}$$

where $K_{j\epsilon\epsilon'} \equiv K_{xc}(\rho(r_j), |\nabla \rho(r_j)|, \epsilon, \epsilon')$.

$$\rho_{j\epsilon} = \sum_{\alpha} \psi^*_{j\alpha} \psi_{\alpha \epsilon} \delta_{j\epsilon \alpha}$$

with $\delta_{j\epsilon \alpha}$ a discretized delta function (remember that $\epsilon$ are now discrete energies) like

$$\delta_{j\epsilon \alpha} = \delta(\epsilon_{j\alpha} - \epsilon) = \begin{cases} \frac{1}{\Delta \epsilon} \left(1 - \frac{|\epsilon_{j\alpha} - \epsilon|}{\Delta \epsilon}\right) & \text{if } |\epsilon_{j\alpha} - \epsilon| < \Delta \epsilon \\ 0 & \text{otherwise} \end{cases}$$

which must verify that $\sum_\epsilon \delta_{j\epsilon \alpha} = 1 \ \forall \epsilon_{j\alpha}$, where

$$\epsilon_{j\alpha} = -\Re \nabla^2 \psi_{j\alpha} / 2 \psi_{j\alpha} = -\frac{1}{2} \sum_k L_{jk} \left( \psi^{k\alpha} \psi^{k\alpha}_{j\alpha} + \psi^{k\alpha}_{j\alpha} \psi^{k\alpha}_{j\alpha} \right).$$

I will now consider formally $\psi^*_{j\alpha}$ and $\psi_{j\alpha}$ as independent variables to perform the derivatives

$$\frac{\partial \rho_j}{\partial \psi^*_{j\alpha}} = \delta_{ij} \psi_{j\alpha},$$

the total one-electron effective potential is a constant-force ramp $v(r) = -f \cdot (r - r_0)$. Since a constant force does not affect the relative motion of two equal particles, it is a good approximation to use the same $e_{xc}$ of the homogeneous gas and to modify only the probability $P$ of equation (13) for the Airy gas. To do this, we can use the one-to-one relationship $\rho(r, \nabla \rho(r)) \leftrightarrow (f, r_0)$, making $P$ and $K_{xc}$ dependent on $|\nabla \rho|$ in addition to $\rho$. In fact, this procedure can be used also to derive GGAs and meta-GGAs from $e_{xc}(\rho, q)$. 

**harmonics**

$$e_x(q) = \sum_{l=0}^{\infty} (2l+1) s_l - 1 \int_0^{\infty} dr \ 4 \pi r^2 e^2 / r \ j_l^2(qr)$$

$$= -\frac{\pi}{2q^2}$$

(15)

where the factor $s_l = 1 - (-1)^l/2$ accounts for the antisymmetry of equal-spin electron-pair wavefunctions. $e_c$ may be approximated by

$$e_c(\rho, q) = \sum_{l=0}^{\infty} (2l+1) s_l \int_0^{\infty} dr \ 4 \pi r^2$$

$$\times \left[ \phi_l(\rho, q, r) H_l \phi_l(\rho, q, r) - j_l(qr) H_l j_l(qr) \right],$$

where $H_l = T_l + e^2 / r$ and

$$T_l \equiv -\frac{\hbar^2}{2\mu r} \partial^2 / \partial r^2 + \frac{\hbar^2 l(l+1)}{2\mu r^2},$$

(16)

and $j_l(qr)$ is the solution of the same equation with $V_{\text{int}} = 0$, i.e. a spherical Bessel function. $V_{\text{int}}(\rho, q, r)$ is an effective interaction potential for the screened Coulomb repulsion, designed to reproduce accurately the pair correlation function of the homogeneous electron gas.

$$g(\rho, q, r) = \sum_{l=0}^{\infty} (2l+1) s_l \int_0^{k_F} dq \ P(q|\rho) \ \phi_l^2(\rho, q, r),$$

(19)

where $P(q|\rho)$ is the probability of finding an electron pair with relative momentum $\hbar q$ in a homogeneous gas of density $\rho$. For $q < k_F = (3\pi^2 \rho)^{1/3}$,

$$P(q|\rho) = \int_0^{k_F} dq' \ P(q|\epsilon, \epsilon') \ P(\epsilon|\rho) \ P(\epsilon'|\rho)$$

$$= 24 q^2 / k_F^3 - 36 q^3 / k_F^4 + 12 q^5 / k_F^5$$

(20)

where $P(\epsilon|\rho) = 3k / k_F^3$ is proportional to the free-electron density of states. Eqs.(18-19) define a problem which is presently under very active research. Furthermore, there is a common alternative for $e_c$ in Eq. (16), like using $e^2 / r$ instead of $H_l$ and integrating in the coupling constant of the electron-electron interaction. Therefore, the actual parametrization of $V_{\text{int}}(\rho, q, r)$ and $e_{xc}(\rho, q)$ will be left for a future work.

A problem with the above approach is that, while the local kinetic energies $\epsilon_{\alpha}(r)$ are negative in classically-forbidden regions, they are always positive in a homogeneous gas. This problem may be overcome by using the Airy gas proposed by Kohn and Mattsson in which $\delta(\epsilon_{\alpha} - \epsilon)$ is a discretized delta function (remember that $\epsilon$ are now discrete energies) like

$$\delta_{j\epsilon \alpha} = \delta(\epsilon_{j\alpha} - \epsilon) = \begin{cases} \frac{1}{\Delta \epsilon} \left(1 - \frac{|\epsilon_{j\alpha} - \epsilon|}{\Delta \epsilon}\right) & \text{if } |\epsilon_{j\alpha} - \epsilon| < \Delta \epsilon \\ 0 & \text{otherwise} \end{cases}$$

which must verify that $\sum_\epsilon \delta_{j\epsilon \alpha} = 1 \ \forall \epsilon_{j\alpha}$, where

$$\epsilon_{j\alpha} = -\Re \nabla^2 \psi_{j\alpha} / 2 \psi_{j\alpha} = -\frac{1}{2} \sum_k L_{jk} \left( \psi^{k\alpha} \psi^{k\alpha}_{j\alpha} + \psi^{k\alpha}_{j\alpha} \psi^{k\alpha}_{j\alpha} \right).$$

I will now consider formally $\psi^*_{j\alpha}$ and $\psi_{j\alpha}$ as independent variables to perform the derivatives

$$\frac{\partial \rho_j}{\partial \psi^*_{j\alpha}} = \delta_{ij} \psi_{j\alpha},$$

(27)
where $\delta_{ij}$ is the usual Kronecker delta,

$$
\frac{\partial |\nabla \rho_j|}{\partial \psi_{i\alpha}^*} = \nabla \rho_j g_{ji} |\nabla \rho_j| \psi_{i\alpha},
$$

(28)

$$
\frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} = \frac{-L_{ji}}{4\psi_{j\alpha}^*} + \frac{\delta_{ij}}{4\psi_{j\alpha}^*} \sum_k L_{jk} \psi_{k\alpha}^*,
$$

(29)

$$
\frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} = \delta_{ij} \psi_{j\alpha} \delta_{j\alpha} + \psi_{j\alpha} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} \frac{\partial \rho_{j\alpha}}{\partial \psi_{j\alpha}^*} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*}

+ \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} \frac{\partial \rho_{j\alpha}}{\partial \psi_{j\alpha}^*} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*}

= \left( \delta_{ij} \psi_{j\alpha} \delta_{j\alpha} - \frac{L_{ji}}{4\psi_{j\alpha}^*} \right)

\psi_{j\alpha},
$$

(30)

and

$$
\frac{\partial E_{xc}}{\partial \psi_{i\alpha}^*} = \sum_{j\alpha} \left( \frac{\partial K_{j\alpha\epsilon}}{\partial \rho_j} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} - \frac{\partial K_{j\alpha\epsilon}}{\partial \psi_{j\alpha}^*} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} \right) \rho_{j\alpha} \rho_{j\epsilon'}

+ 2 \sum_{j\alpha} \eta_{j\alpha} \rho_{j\alpha} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*},
$$

(31)

Substituting (27), (28), and (30) into (31) we obtain

$$
\frac{\partial E_{xc}}{\partial \psi_{i\alpha}^*} = \left( u_i + 2 \sum_{\epsilon} \delta_{i\alpha\epsilon} v_{i\epsilon} \right) \psi_{i\alpha}

+ \frac{\psi_{i\alpha}}{2\psi_{i\alpha}^*} \sum_j L_{ij} \psi_{j\alpha} \sum_{\epsilon} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} v_{i\epsilon}

- \frac{1}{2} \sum_j L_{ij} \psi_{j\alpha} \sum_{\epsilon} \frac{\partial \rho_{j\alpha}}{\partial \psi_{i\alpha}^*} v_{i\epsilon},
$$

(32)

I have defined

$$
u_i \equiv \sum_{\epsilon'} \frac{\partial K_{j\epsilon\epsilon'}}{\partial \rho_j} \rho_{j\epsilon} \epsilon' - \sum_j \frac{g_{ji} \nabla \rho_j}{|\nabla \rho_j|} \sum_{\epsilon'} \frac{\partial K_{j\epsilon\epsilon'}}{\partial |\nabla \rho_j|} \rho_{j\epsilon} \epsilon',
$$

(33)

$$
u_{ie} \equiv \sum_{\epsilon'} K_{j\epsilon\epsilon'} \rho_{j\epsilon},
$$

(34)

where I have used that $L_{ji} = L_{ij}$ and $g_{ji} = -g_{ij}$. Returning to the continuous limit,

$$
\frac{\delta E_{xc}}{\delta \psi_{i\alpha}^*}(\mathbf{r}) = \left( u(\mathbf{r}) + 2 \int d\epsilon \delta(\epsilon_\alpha(\mathbf{r}) - \epsilon) v(\mathbf{r}, \epsilon) \right) \psi_\alpha(\mathbf{r})

+ \frac{\psi_\alpha(\mathbf{r}) \nabla^2 \psi_\alpha(\mathbf{r})}{2\psi_\alpha^2(\mathbf{r})} \int d\epsilon \frac{\partial \delta(\epsilon_\alpha(\mathbf{r}) - \epsilon)}{\partial \epsilon_\alpha(\mathbf{r})} v(\mathbf{r}, \epsilon)

- \frac{1}{2} \nabla^2 \left( \psi_\alpha(\mathbf{r}) \int d\epsilon \frac{\partial \delta(\epsilon_\alpha(\mathbf{r}) - \epsilon)}{\partial \epsilon_\alpha(\mathbf{r})} v(\mathbf{r}, \epsilon) \right)

\int \int d\epsilon d\epsilon' \frac{\partial K_{xc}(\mathbf{r}, \epsilon, \epsilon')}{|\nabla \rho(\mathbf{r})|} \rho(\mathbf{r}, \epsilon) \rho(\mathbf{r}, \epsilon')
$$

(35)

$$
u(\mathbf{r}) = \int \int d\epsilon d\epsilon' \frac{\partial K_{xc}(\mathbf{r}, \epsilon, \epsilon')}{|\nabla \rho(\mathbf{r})|} \rho(\mathbf{r}, \epsilon) \rho(\mathbf{r}, \epsilon')

- \nabla \left( \frac{\nabla \rho(\mathbf{r})}{|\nabla \rho(\mathbf{r})|} \right)
$$

(36)

$$
v(\mathbf{r}, \epsilon) = \int d\epsilon' K_{xc}(\mathbf{r}, \epsilon, \epsilon') \rho(\mathbf{r}, \epsilon')
$$

(37)

where I am using the shorthand notation $K_{xc}(\mathbf{r}, \epsilon, \epsilon') = K_{xc}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|, \epsilon, \epsilon')$. Using integration by parts in (35) to integrate out the delta functions

$$
\frac{\delta E_{xc}}{\delta \psi_{i\alpha}^*}(\mathbf{r}) = (u(\mathbf{r}) + 2v(\mathbf{r}, \epsilon_\alpha(\mathbf{r}))) \psi_\alpha(\mathbf{r})

+ \psi_\alpha(\mathbf{r}) \nabla^2 \psi_\alpha(\mathbf{r}) \frac{\partial v(\mathbf{r}, \epsilon_\alpha(\mathbf{r}))}{\partial \epsilon_\alpha(\mathbf{r})}

- \frac{1}{2} \nabla^2 \left( \psi_\alpha(\mathbf{r}) \frac{\partial v(\mathbf{r}, \epsilon_\alpha(\mathbf{r}))}{\partial \epsilon_\alpha(\mathbf{r})} \right).
$$

(38)

In practice, $v(\mathbf{r}, \epsilon_\alpha(\mathbf{r}))$ and its derivative will be interpolated from the values at a number of discrete energies, i.e. $v(\mathbf{r}, \epsilon_\alpha(\mathbf{r})) = \sum \psi_{i\epsilon} c_{\alpha}(\epsilon_\alpha(\mathbf{r}))$, where the interpolation functions $c_{\alpha}$ are determined by, e.g. Lagrange or spline interpolation formulas. Comparison with Eq. (32) shows that the discrete delta values $\delta_{i\alpha\epsilon}$, used to distribute the contribution of state $\alpha$ to $\rho(\mathbf{r}, \epsilon)$, at the discrete energies $\epsilon$, are simply $\delta_{i\alpha\epsilon} = c_{\alpha}(\epsilon_\alpha(\mathbf{r}))$. Thus, for example, Eq. (25) corresponds to a simple linear interpolation for $v(\mathbf{r}, \epsilon_\alpha(\mathbf{r}))$. Though Eqs. (36-38) are considerably more complicated than the functional derivatives in LDA or GGA functionals, the gradients and laplacians can be calculated efficiently using fast Fourier transforms or finite differences, at a quite affordable computational cost.

V. CONCLUSIONS

In conclusion, I have proposed a functional form for the exchange and correlation energy, with the potential to describe more accurately excitation energies and band gaps than the present forms. The basic ideas, embodied in Eq. (12), are that the interaction between two electrons depends on their relative motion, and that the exchange and correlation energy of an electron depends on its kinetic energy. These ideas are physically transparent and intuitively appealing, and therefore they may be expected to allow for significant improvements in the description of the inhomogeneous electron gas.

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One might also add for generality a linear term in \( \rho(r, \epsilon) \), i.e.,

\[
E_{xc} = \int d^3r \int d\epsilon K_1(\rho(r), \epsilon) \rho(r, \epsilon) + \int d^3r \int d\epsilon d\epsilon' K_2(\rho(r), \epsilon, \epsilon') \rho(r, \epsilon) \rho(r, \epsilon').
\]

This allows to incorporate a density-dependent effective mass by making

\[
K_{xc}(\rho(r), \epsilon, \epsilon') = K_2(\rho(r), \epsilon, \epsilon') + K_1(\rho(r), \epsilon) / \rho(r).
\]

However, it is easy to see that using \( K_{xc}(\rho(r), \epsilon, \epsilon') = K_2(\rho(r), \epsilon, \epsilon') + K_1(\rho(r), \epsilon) / \rho(r) \) makes the previous expression equivalent to eqs. (6) and (12).

In a more elaborate formulation, \( V_{int} \) will depend also on the relative spins of the two electrons, as well as on the electron gas polarization.

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