PHYSICAL REVIEW B VOLUME 27, NUMBER 10 15 MAY 1983

General operator ground-state expectation values in the Hohenberg-Kohn-Sham density-functional formalism

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(Received 15 December 1982)

Explicit density functionals are constructed for the ground-state expectation values of arbitrary quantum-mechanical operators in terms of the solutions of the Kohn-Sham self-consistent equations and well-defined correction terms. The one-particle Green function, and consequently quasiparticle excitation energies, and the one-particle density matrix are, for example, expressible in this way. Implications for the practice of electronic structure calculations are discussed.

I. INTRODUCTION

The importance of the Hohenberg-Kohn-Sham density-functional formalism[1–5] stems mainly from the Kohn-Sham self-consistent equations,[2] which provide a rigorous algorithm for the calculation of the ground-state total energy E and the ground-state electronic charge density $\rho(\vec{r})$ of a nonrelativistic electron gas which is subject to a static and local external potential $V_{\text{ext}}(\vec{r})$. Generalizations are possible.[3–5] In atomic units $e^2/2=2m_e=h/2\pi=1$, which will be used throughout, the Kohn-Sham equations[2] with square brackets denoting the functional dependence read

$$\{-\vec{\nabla}^2+V_H[\rho](\vec{r})+V_{\text{ext}}(\vec{r})+V_{\text{xc}}[\rho](\vec{r})\}\phi_i(\vec{r})=\epsilon_i\phi_i(\vec{r}) \,, \quad (1)$$

where V_H is the Hartree potential of the electronic charge density and V_{xc} is the exchange-correlation potential, i.e., the functional derivative of the exchange-correlation energy $E_{\text{xc}}[\rho]$:

$$V_{\text{xc}}[\rho](\vec{r})=\frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\vec{r})} \,. \quad (2)$$

The electronic ground-state charge density is given by

$$\rho(\vec{r})=\sum_i \Theta(\mu-\epsilon_i)\,|\phi_i(\vec{r})|^2 \,, \quad (3)$$

where Θ is the unit step function and μ is the chemical potential determined by the particle-number constraint

$$\sum_i \Theta(\mu-\epsilon_i)=N \,. \quad (4)$$

The total energy may be written

$$E[\rho]=\sum_i \Theta(\mu-\epsilon_i)\epsilon_i - \int \rho(\vec{r})\{\tfrac{1}{2}V_H(\vec{r})+V_{\text{xc}}[\rho](\vec{r})\} \times d\vec{r}+E_{\text{xc}}[\rho] \,. \quad (5)$$

One should keep in mind that Eqs. (1)–(5) rely on the assumption of noninteracting wave function V representability.[6]

In electronic structure calculations the eigenvalues and eigenvectors of the Kohn-Sham equations (1) are often and successfully interpreted as independent-particle wave functions and quasiparticle excitation or orbital energies. However, this practice lacks rigor because the ϕ_i and ϵ_i in (1) are formal variational functions and Lagrange multipliers which have a meaning only for the electronic charge density and the total energy by Eqs. (3) and (5). In Sec. II some light will be shed on the problem by the derivation of a rigorous density functional for the ground-state expectation value of an arbitrary quantum-mechanical operator in terms of the solutions of the Kohn-Sham equations and a well-defined correction term. This is accomplished by a generalization of the Lam-Platzman theorem on electronic momentum densities,[7] employing the construction of the exchange-correlation energy functional by the integration over the Coulomb coupling constant.[8,9] The correction term is analyzed in Sec. III by diagrammatic perturbation theory,[10] which results in another derivation of the theorem. Selected applications in Sec. IV are density matrices and Green functions. Approximations will be discussed in Sec. V, while Sec. VI concentrates on conceptual and practical consequences.

II. FUNCTIONALS

It is a corollary of the Hohenberg-Kohn theorem[1] that the ground-state expectation value of the operator $\hat{o}$

$$\langle \hat{o} \rangle = \langle \Psi_0 | \hat{o} | \Psi_0 \rangle \tag{6}$$

is a functional of the electronic charge density which will be denoted by $O[\rho]$. The Hellmann-Feynman theorem,[11] a fictive interaction,[7,12,13] and the exchange-correlation energy functional as proposed in Refs. 8 and 9 form the ingredients to obtain an explicit expression of $O[\rho]$.

Consider an effective Hamiltonian as a function of the Coulomb coupling constant g (Refs. 8 and 9):

$$H(g) = \sum_i \{ -\vec{\nabla}_i^2 + V_{\rm ext}(\vec{r}_i) + V_{\rm eff}[\rho](\vec{r}_i; g) \} + \sum_{i \neq j} \frac{g}{|\vec{r}_i - \vec{r}_j|} , \tag{7}$$

where $V_{\rm eff}$ is a hypothetical local potential which generates the physical charge density for g between 1 and 0, i.e., the charge density of the ground-state wave function $\Psi_0(g)$ of $H(g)$ equals the charge density corresponding to the physical ground-state wave function. The total energy may then be written as

$$E(g=1) = E(g=0) + \int_0^1 \frac{dg}{g} E_{\rm int}(g) - \int d\vec{r} \rho(\vec{r}) V_{\rm eff}[\rho](\vec{r}, g=0) , \tag{8}$$

where

$$E(g) = \langle \Psi_0(g) | H(g) | \Psi_0(g) \rangle \tag{9}$$

and

$$E_{\rm int}(g) = \left\langle \Psi_0(g) \left| \sum_{i \neq j} \frac{g}{|\vec{r}_i - \vec{r}_j|} \right| \Psi_0(g) \right\rangle , \tag{10}$$

and the exchange-correlation energy is by comparison with (5)

$$E_{\rm xc}[\rho] = \int_0^1 \frac{dg}{g} E_{\rm int}(g) - \int d\vec{r} d\vec{r}' \rho(\vec{r}) \rho(\vec{r}') / |\vec{r} - \vec{r}'| . \tag{11}$$

The effective Hamiltonian is now augmented by the operator $\hat{o}$ via a scalar coupling constant λ:

$$H(\lambda, g) = \sum_i \{ -\vec{\nabla}_i^2 + V_{\rm ext}(\vec{r}_i) + V_{\rm eff}[\rho](\vec{r}_i; \lambda, g) \} + \sum_{i \neq j} \frac{g}{|\vec{r}_i - \vec{r}_j|} + \lambda \hat{o} . \tag{12}$$

$V_{\rm eff}$ is supposed to generate the physical charge density for all relevant values of the parameters λ and g. The total energy is then obtained as a function of λ as

$$E(\lambda, g=1) = E(\lambda, g=0) + \int_0^1 \frac{dg}{g} E_{\rm int}(\lambda, g) + \int d\vec{r} \rho(\vec{r}) \{ V_{\rm eff}[\rho](\vec{r}; \lambda, g=1) - V_{\rm eff}[\rho](\vec{r}; \lambda, g=0) \} . \tag{13}$$

The derivative of the ground-state energy expectation value is, according to the Hellmann-Feynman theorem,[11]

$$\frac{d}{d\lambda} E(\lambda, g) = \langle \Psi_0(\lambda, g) | \frac{d}{d\lambda} H(\lambda, g) | \Psi_0(\lambda, g) \rangle = \langle \Psi_0(\lambda, g) | \hat{o} + \sum_i \left[\frac{d}{d\lambda} V_{\rm eff}[\rho](\vec{r}_i; \lambda, g) \right] | \Psi_0(\lambda, g) \rangle . \tag{14}$$

Substitution of (14) into (13) and taking the limit of λ→0 yields

$$\langle \Psi_0(g=1) | \hat{o} | \Psi_0(g=1) \rangle = \langle \Psi_0(g=0) | \hat{o} | \Psi_0(g=0) \rangle + \frac{d}{d\lambda} \int_0^1 \frac{dg}{g} E_{\rm int}(\lambda, g) \Big|_{\lambda=0} . \tag{15}$$

The left-hand side is identical to the desired ground-state expectation value (6). The first term on the right-hand side is the expectation value of $\hat{o}$ for a system of noninteracting fermions moving in an effective field equal to the sum of the Hartree and exchange-correlation potential as in (1), and will be denoted by $O_0[\rho]$. The static Coulomb energy part in $E_{\rm int}$ is not λ dependent by construction and, from (11) and (15), the central result is established:

$$O[\rho] = O_0[\rho] + \frac{d}{d\lambda} E_{\rm xc}[\rho](\lambda) \Big|_{\lambda=0} . \tag{16}$$

Whereas the original Hohenberg-Kohn theorem[1] requires only N representability of $\rho(\vec{r})$,[14] the existence of the effective ρ-generating potential, i.e., an extended V representability, must be assumed for all relevant λ for Eq. (16) to be valid. The V representability problem of the Kohn-Sham equations comes down to the special case $\lambda = g = 0$. Note that V

representability of ρ for $g=0$ and $\lambda\neq 0$ is a necessary condition for the existence of the partial derivative in Eq. (2.19) of Ref. 7 also.

III. CORRECTION TERM

The correction term as derived above,

$$\Delta O[\rho]=\frac{d}{d\lambda}E_{\text{xc}}[\rho](\lambda)\bigg|_{\lambda=0}\ , \tag{17}$$

gets more transparent if analyzed by diagrammatic perturbation theory.[10] Moreover, this approach provides an alternative derivation of Eq. (16). The system is assumed to be normal and complications concerning the adiabatic hypothesis in the zero-temperature diagrammatic perturbation expansion for inhomogeneous systems,[10,15] which can be resolved by taking the zero-temperature limit of the finite temperature formalism,[15,16] will be ignored. The effective potential V_{eff} is assumed to keep the charge density ρ and the chemical potential μ constant as a function of the parameters λ and g. One-particle operators $\hat{o}$ will be treated only, but the generalization does not give any new insights. For this case the fictive interaction may be absorbed into the one-particle part $h(\lambda,g)$ of the effective Hamiltonian (12):

$$h(\lambda,g)=-\vec{\nabla}^2+V_{\text{ext}}(\vec{r})+V_{\text{eff}}[\rho](\vec{r};\lambda,g)+\lambda\hat{o}\ . \tag{18}$$

The noninteracting one-particle Green function corresponding to (18) is

$$(G_0)_{kk'}(\epsilon;\lambda,g)=\{\epsilon-h(\lambda,g)+i\eta[\Theta(\epsilon-\mu)-\Theta(\mu-\epsilon)]\}^{-1}_{kk'}\ , \tag{19}$$

where η is a positive infinitesimal constant and the subscript kk' denotes matrix elements with respect to a complete orthonormal one-electron basis. The interaction energy

$$E_{\text{int}}(\lambda,g)=\left\langle\Psi_0(\lambda,g)\left|\sum_{i\neq j}\frac{g}{|\vec{r}_i-\vec{r}_j|}\right|\Psi_0(\lambda,g)\right\rangle \tag{20}$$

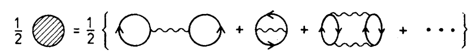
is by the Galitskii-Migdal formula[10,17]

$$E_{\text{int}}(\lambda,g)=\frac{1}{4\pi i}\int d\epsilon\sum_k\sum_{k'}G_{kk'}(\epsilon;\lambda,g)\times(G_0^{-1})_{kk'}(\epsilon;\lambda,g)\ , \tag{21}$$

or simply

$$E_{\text{int}}(\lambda,g)=\tfrac{1}{2}\text{tr}\frac{G(\lambda,g)}{G_0(\lambda,g)}\ . \tag{22}$$

E_{int} is proportional to the sum of all unlinked, unlabeled, and connected diagrams[10]:



, (23)

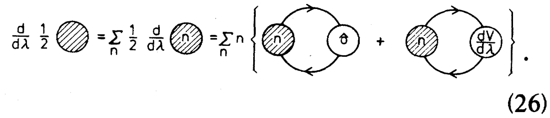
where a line —▸— denotes a noninteracting Green function (19) and ∼∼∼ stands for a Coulomb interaction vertex of strength g. The nth-order diagrams E^n_{int} of (23) contains n vertices and $2n$ lines. Only the latter are λ dependent and all equivalent with respect to differentiation:

$$\frac{d}{d\lambda}G_0(\lambda,g)=G_0^2(\lambda,g)\left[\hat{o}+\frac{dV_{\text{eff}}(\lambda,g)}{d\lambda}\right]\ . \tag{24}$$

The derivative of E_{int} is hence

$$\frac{d}{d\lambda}E_{\text{int}}(\lambda,g)=\sum_n\frac{d}{d\lambda}E^n_{\text{int}}(\lambda,g)=\sum_n n\,\text{tr}\left[G^n(\lambda,g)\left[\hat{o}+\frac{d}{d\lambda}V_{\text{eff}}(\lambda,g)\right]\right]\ , \tag{25}$$

diagrammatically

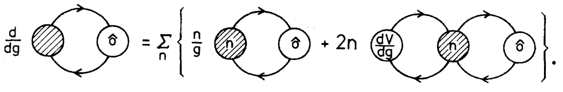


(26)

The expectation value of the operator $\hat{o}$ is in terms of the Green function

$$\langle\Psi_0(\lambda,g)\,|\,\hat{o}\,|\,\Psi_0(\lambda,g)\rangle=\text{tr}[G(\lambda,g)\hat{o}]\ . \tag{27}$$

The derivative of (27) with respect to g is conveniently expressed by diagrams:

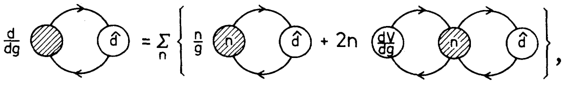


(28)

The two-particle Green function is involved in the second term on the right-hand side. The expectation value of

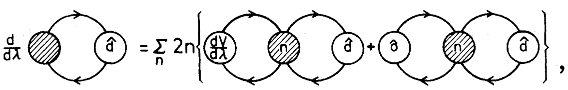
$$\hat{d}=\Psi^\dagger(\vec{r})\Psi(\vec{r})\ , \tag{29}$$

where $\Psi^{\dagger}(\vec{r}),\Psi(\vec{r})$ denote creation and annihilation field operators, is the electronic charge density which does not depend on λ and g, hence



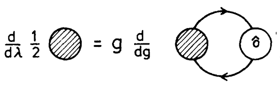
(30)

and



(31)

equal zero. By combining (26), (28), (30), and (31),



(32)

The integration over g is now carried out easily:

$$\frac{d}{d\lambda}E_{\mathrm{xc}}[\rho]\Big|_{\lambda=0}=\int_0^1\frac{dg}{g}\frac{d}{d\lambda}E_{\mathrm{int}}(\lambda,g)\Big|_{\lambda=0}=\mathrm{tr}[G(\lambda=0,g)\hat{o}]\,|_0^1 \tag{33}$$

or

$$\Delta O[\rho]=O[\rho]-O_0[\rho]\,, \tag{34}$$

which is identical to the result of Sec. II.

IV. APPLICATIONS

A. Density matrix

The ground-state N-particle properties are reflected in the N-particle density matrix Γ_N,[18] which apart from a normalization factor may be expressed as the ground-state expectation value of the N-particle density operator $\hat{\gamma}_N$ in position space:

$$\hat{\gamma}_N(\vec{r}_1,\dots,\vec{r}_N;\vec{r}\,'_1,\dots,\vec{r}\,'_N)=\Psi^{\dagger}(\vec{r}_1)\cdots\Psi^{\dagger}(\vec{r}_N)\Psi(\vec{r}\,'_1)\cdots\Psi(\vec{r}\,'_N)\,, \tag{35}$$

and in momentum space:

$$\hat{\gamma}_N(\vec{p}_1,\dots,\vec{p}_N;\vec{p}\,'_1,\dots,\vec{p}\,'_N)=a^{\dagger}_{\vec{p}_1}\cdots a^{\dagger}_{\vec{p}_N}a_{\vec{p}\,'_1}\cdots a_{\vec{p}\,'_N}\,, \tag{36}$$

in the conventional notation for creation and annihilation operators. Equation (16) is a formal density-functional expression for the N-particle density matrix if the operator $\hat{o}$ is substituted by (35) or (36).

The one-particle density matrix is of special interest because it determines important properties as the electronic charge density, the electronic momentum density, and the kinetic energy. The charge density is represented by the diagonal elements of Γ_1 in position space, and the correction term is zero by construction. The Kohn-Sham equation result for the momentum density, i.e., the diagonal elements of Γ_1 in momentum space, must be augmented by a correction term identical to that in Eq. (3.29) of Ref. 7:

$$\Delta\Gamma[\rho](\vec{p},\vec{p})\equiv\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\epsilon_{\vec{p}}}\,. \tag{37}$$

The relevance of the momentum-density correction term for crystalline copper will be discussed in Ref. 19 in more detail (cf. Sec. VI). The kinetic energy contribution of the exchange-correlation energy functional is recovered by a simple integration over the momentum density:

$$\Delta T[\rho]=\int d\vec{p}\,|\vec{p}\,|^2\Delta\Gamma[\rho](\vec{p},\vec{p})\,. \tag{38}$$

The rigorous kinetic energy functional lost in the derivation of the Kohn-Sham equations is thus restored *a posteriori*.

The noninteracting ground-state wave function is necessarily a Slater determinant and not a simple product function because the adiabatic generation of the ground state by turning on the Coulomb interaction conserves the permutational symmetry. Exchange terms reflecting the Fermi hole are thus present in the zero-order term of Γ_2:

$$[\Delta\Gamma_2(\vec{r}_1,\vec{r}_2;\vec{r}\,'_1,\vec{r}\,'_2)]_0=\sum_{i,j}\Theta(\mu-\epsilon_i)\Theta(\mu-\epsilon_j)[\phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\phi_i(\vec{r}\,'_1)\phi_j(\vec{r}\,'_2)-\phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\phi_i(\vec{r}\,'_2)\phi_j(\vec{r}\,'_1)]\,. \tag{39}$$

In general, the zero-order term of all two-particle operators contains an exchange term. An alternative ground-state energy functional to Eq. (5) is obtained, for example, if $\hat{o}$ in (16) is replaced by the Hamiltonian:

$$\begin{aligned}E[\rho]={}&\sum_i\Theta(\mu-\epsilon_i)\epsilon_i-\int d\vec{r}\rho(\vec{r})\{\tfrac{1}{2}V_H[\rho](\vec{r})+V_{\mathrm{xc}}[\rho](\vec{r})\}\\&-\sum_{i,j}\Theta(\mu-\epsilon_i)\Theta(\mu-\epsilon_j)\int d\vec{r}\,d\vec{r}\,'\phi_i^*(\vec{r})\phi_j^*(\vec{r}\,')\phi_j(\vec{r})\phi_i(\vec{r}\,')/|\vec{r}-\vec{r}\,'|+\Delta E[\rho]\,,\end{aligned} \tag{40}$$

which is a generalization of the exact-exchange energy functional in Ref. 2.

B. Green function

Attention will be restricted in the following mainly to the one-particle Green function, but generalization to the N-particle case is accomplished analogously to the density matrices. The causal one-particle Green function is defined as the ground-state expectation value of the time-ordered product of creation and annihilation operators,[10] in position space:

$$\hat{g}(\vec{r},\vec{r}\,';t)=\begin{cases}-i\Psi(\vec{r};t)\Psi^\dagger(\vec{r}\,';0)\ , & t>0\\ i\Psi^\dagger(\vec{r};0)\Psi(\vec{r}\,';t)\ , & t\leq 0\end{cases} \tag{41}$$

and

$$\Psi(\vec{r};t)=e^{iHt}\Psi(\vec{r})e^{-iHt}\ . \tag{42}$$

In the limit $t\to 0^-$, the density operator is recovered. After Fourier transformation into the energy domain the "Green density functional" is, by Eqs. (16) and (41),

$$G[\rho](\vec{r},\vec{r}\,';\epsilon)=G_0[\rho](\vec{r},\vec{r}\,';\epsilon)+\Delta G[\rho](\vec{r},\vec{r}\,';\epsilon)\ . \tag{43}$$

The relevance of the Green function is due to its poles ϵ_p, usually identified as quasi—particle-hole excitations, where the real part defines the energy and the imaginary part the damping.[10] By Eq. (43) it is shown rigorously that the ground-state density-functional theory may be employed for the calculation of excitation properties. The problem of singularities in (43), which do not properly cancel if ΔG is known only approximately, can be cirumvented by replacing (43) by a set of equations for the Green-function poles and its residues:

$$\epsilon_p[\rho]=(\epsilon_p)_0[\rho]+\Delta\epsilon_p[\rho]\ , \tag{44}$$

$$\operatorname{Res}G[\rho](\vec{r},\vec{r}\,';\epsilon_p)=\operatorname{Res}G_0[\rho](\vec{r},\vec{r}\,';\epsilon_p)+\operatorname{Res}\Delta G[\rho](\vec{r},\vec{r}\,';\epsilon_p)\ . \tag{45}$$

The poles of G_0 are real but not equal to the eigenvalues of the Kohn-Sham equations. This is again a consequence of the permutational (anti)symmetry of the noninteracting pseudofermion wave function and the two-particle operators in (42). The poles are found instead at

$$(\epsilon_p)_0[\rho]=\epsilon_i-\int d\vec{r}\,|\phi_i(\vec{r})|^2\{\tfrac{1}{2}V_H[\rho](\vec{r})+V_{\rm xc}[\rho](\vec{r})\}-\sum_j\Theta(\mu-\epsilon_j)\int d\vec{r}\,d\vec{r}\,'\phi_i^*(\vec{r}\,')\phi_j^*(\vec{r})\phi_i(\vec{r}\,')\phi_j(\vec{r})/|\vec{r}-\vec{r}\,'|\ , \tag{46}$$

which includes an exchange term. The correction term $\Delta\epsilon_p$ describes the shift in energy and the damping of the stationary Hartree-Fock-type quasiparticles and will introduce new poles due to collective effects. The residues of G_0 are simply

$$\operatorname{Res}G_0[\rho](\vec{r},\vec{r}\,';\epsilon_p)=\phi_i^*(\vec{r})\phi_i(\vec{r}\,')\ , \tag{47}$$

hence normalized to unity. In general, the correction will introduce a deformation and renormalization.

An important special form of the two-particle Green function is the polarization propagator or dynamical susceptibility, which is closely related to the dielectric function. Following the terminology of Ref. 20, the zeroth-order term for this quantity is a random-phase approximation with exchange in density-functional context.

V. APPROXIMATIONS

Both the exchange-correlation potential $V_{\rm xc}$ and the correlation-correction term ΔO are derivatives of the exchange-correlation energy $E_{\rm xc}$ by Eqs. (2) and (17). It appears consistent to use the same approximate form of $E_{\rm xc}$ for both quantities. By far most band-structure calculations are carried out in the local-density approximation (LDA) to the exchange-correlation energy functional[2]:

$$E_{\rm xc}^{\rm LDA}[\rho]=\int d\vec{r}\,\rho(\vec{r})\epsilon_{\rm xc}(\rho(\vec{r}))\ , \tag{48}$$

where $\epsilon_{\rm xc}(\rho(\vec{r}))$ is the exchange-correlation energy per electron of the homogeneous interacting electron gas as a function of the (local) density $\rho(\vec{r})$. The LDA correction term to the result of the Kohn-Sham equations is thus

$$\Delta O^{\rm LDA}[\rho]=\int d\vec{r}\,\rho(\vec{r})[o_h(\rho(\vec{r}))-o_0(\rho(\vec{r}))]\ . \tag{49}$$

If the expectation values of $\hat{o}$ (per electron) for the homogeneous interacting electron gas $o_h(\rho(\vec{r}))$ and for the homogeneous free-electron gas $o_0(\rho(\vec{r}))$ are available, obtained preferably by the same method as $\epsilon_{\rm xc}$, $\Delta O^{\rm LDA}$ is easily evaluated from the self-consistent electronic charge density which is an output of the Kohn-Sham equations. Note that (49) is identically zero in an exchange-only treatment.

An exact theory of electron correlations must be free of spurious self-interactions,[22] which in the present context can be formulated as

$$\Delta O[\rho_i]=0$$

if

$$\int \rho_i(\vec{r})d\vec{r}=1 \; , \tag{50}$$

which suggests a modification of ΔO^{LDA} in the spirit of the self-interaction-correction (SIC) approach[22]:

$$\Delta O^{\text{SIC}}[\rho]=\Delta O^{\text{LDA}}[\rho]-\sum_i \Theta(\mu-\epsilon_i)\Delta O^{\text{LDA}}[\rho_i] \; , \tag{51}$$

where

$$\rho_i(\vec{r})=|\phi_i(\vec{r})|^2 \; . \tag{52}$$

The combination of a SIC exchange-correlation potential and Eq. (51) guarantees exact results for one-electron systems. Another improvement of ΔO^{LDA} could possibly be achieved taking into account nonlocal effects by the introduction of an effective average $\rho^{AD}(\vec{r})$ over the electron density in the proximity of $\vec{r}$ (Ref. 23):

$$\Delta O^{AD}[\rho]=\int d\vec{r}\rho(\vec{r}) \times[o_h(\rho^{AD}(\vec{r}))-o_0(\rho^{AD}(\vec{r}))] \; . \tag{53}$$

Both (51) and (53) would not introduce additional computational difficulties once the Kohn-Sham equations are solved. Note that (51) and (53) reflect the philosophy but are not identical to the explicit derivatives of the respective exchange-correlation energy functionals. In general, a further improvement of ΔO^{LDA} is expected to be tedious.

VI. DISCUSSION

The above results establish the Hohenberg-Kohn-Sham density-functional formalism[1–5] as a general purpose many-body theory, which can be employed in principle to calculate any ground-state property of an inhomogeneous electron gas except the wave function itself. To some extent excited-state properties are obtainable also via the Green function. As a by-product, the Kohn-Sham exact exchange density functional[2] is derived. In Ref. 2 the exact exchange functional [Eq. (40) in the LDA], furnishes the starting point for the derivation of a set of Hartree-Fock-type self-consistent equations. However, the present result gives a theoretical justification to combine the advantage of the exact exchange formulation as the lack of spurious self-interactions with the computational simplicity of a Hartree-type potential.[24] The well-known deficiencies of the Hartree-Fock method will be present in the zero-order term, but should be canceled by the correlation correction. Excited-state properties from the poles of the Green function as band structures and Fermi surfaces are treated analogously. In contrast to the Kohn-Sham equation eigenvalues,[25,26] Eq. (46) is a rigorous self-interaction free formulation of quasiparticle excitation energies.

The popularity of the Kohn-Sham equations for the calculation of electronic structures stems largely from the apparent success and the computational simplicity of the LDA of the exchange-correlation energy functional. According to Eq. (49), a necessary input for the LDA calculation of a property of the inhomogeneous system is the value of this property for the homogeneous electron gas for an appropriate range of densities. If these data are available,[21] the calculation of ΔO^{LDA} is not difficult and the independent-particle result should be augmented by this term at least for consistency.

The Hohenberg-Kohn-Sham theory is obviously optimized for the calculation of the electronic charge density, because in this case everything unknown is lumped together into a single term V_{xc} which is then approximated. For other properties, however, the introduction of the somewhat artificial correction term which has to be approximated also will increase the uncertainties. Anisotropic correlation effects which are not appropriately described by the Kohn-Sham equations (see, e.g., Refs. 19 and 27–32) do thus not necessarily prove the failure of the approximate potential employed. The experimental momentum density of copper[30] is, for example, not well reproduced by state of the art band-structure calculations.[31,32] There is indeed evidence[19] that it is not the crystal potential but the correction term which is badly described by the LDA. A way out could in this case be provided by the application of the variational principle to an energy functional of the momentum density[33] which would render the correction term obsolete.

ACKNOWLEDGMENTS

I am grateful to Professor H. Dachs for his support. Special thanks are due to Dr. J. R. Schneider for initiating the present work and his continuous and active interest. Helpful discussions with Professor P. Fulde, Professor O. Gunnarson, Professor N. K. Hansen, Dr. J. Redinger, and Dr. G. Stollhoff are acknowledged.

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