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Generalized Kohn-Sham theory for electronic excitations in realistic systems

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Instead of expressing the total energy of an interacting electron system as a functional of the one-particle density as in the Hohenberg-Kohn-Sham theory, we use a conventional approach in determining total energies by forming the expectation value $\langle \mathscr{H} \rangle$ of the N-electron Hamiltonian with the true wave function $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$. We introduce a new concept of partitioning $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ into two components such that the one-particle density is connected with the first component only. If one requires $\langle \mathscr{H} \rangle$ to be stationary against variation of $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, this first component turns out to be one Slater determinant in terms of one-particle states which obey Kohn-Sham—type one-particle equations. Hence, the expression for the one-particle density becomes identical to that of the Kohn-Sham theory. The virtues of the new approach, particularly its capability of describing thermal excitation in solids, optical transitions, etc., are discussed in detail. We also address the so-called gap problem which has recently been an extensively debated subject within the one-particle description of N-electron systems.

I. INTRODUCTION

Despite the considerable success of the theory of Kohn and Sham[1] in quantitatively describing the ground-state properties of N-electron systems, there has as yet been little progress in extending this relatively simple computational scheme to excited states.[2] As has been pointed out by Hedin,[3] it is possible to cast the Dyson equation in the form of an effective one-particle equation. The calculation of excitation energies by self-consistently solving this equation has proved, however, to be extremely demanding in terms of the computational effort involved. Recent attempts made by Louie and associates[4] to calculate the band gaps of Si and Ge have clearly demonstrated that excitation energies can, in fact, very accurately be determined within that scheme. However, the authors had to include in their calculations up to 200 excited bands in order to arrive at sufficiently converged values of the band gaps of these semiconductors.

We undertake in the present paper to tackle the excitation problem of N-electron systems from a completely different angle by trying to retain essential features of the Kohn-Sham theory, but sacrificing the theorem of Hohenberg and Kohn[5] as a guiding principle. Instead, we take advantage of the fact that electronic excitations do not pose a conceptual problem in quantum chemistry where excited states are determined by extremizing the expectation value $\langle \mathscr{H} \rangle$ of the Hamiltonian operator formed with the N-electron wave function. Optical transitions, for example, can very reliably be treated within golden-rule—type calculations involving these stationary states. We use as a starting point a particular form of the total electronic energy E of the N-electron system under study. This expression has been derived by Langreth and Perdew,[6] for example, and reads

$$E=\langle T_0 \rangle + \int \rho(\mathbf{r}) U_{\text{ext}}(\mathbf{r}) d^3r + \langle \overline{U}_{e\text{-}e} \rangle \ , \tag{1}$$

where $\langle T_0 \rangle$ is the kinetic energy of a noninteracting N-electron system having the same one-particle density $\rho(\mathbf{r})$ as the present one. The external potential is denoted by $U_{\text{ext}}(\mathbf{r})$, and $\langle \overline{U}_{e\text{-}e} \rangle$ represents the Coulombic electron-electron interaction energy averaged over the coupling strength λ. The latter ranges from 0 to 1. If one introduces the pair correlation function $g_\lambda(\mathbf{r}',\mathbf{r})$ at coupling strength λ, one may rewrite $\langle \overline{U}_{e\text{-}e} \rangle$ in the form

$$\langle \overline{U}_{e\text{-}e} \rangle = \tfrac{1}{2} \int \int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|} d^3r'\, d^3r - \tfrac{1}{2} \int \int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})\overline{f}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|} d^3r'\, d^3r \ , \tag{2}$$

where the so-called correlation factor $\overline{f}(\mathbf{r}',\mathbf{r})$ is defined[7] by

$$\overline{f}(\mathbf{r}',\mathbf{r}) = 1 - \int_0^1 g_\lambda(\mathbf{r}',\mathbf{r}) d\lambda \ . \tag{3}$$

The one-particle density may be written

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2 \ , \tag{4}$$

where the φ_i's relate to one-particle states of the noninteracting system. Requiring $E[\rho]$ to be stationary against variation of these states, one arrives at Schrödinger-type one-particle equations to be satisfied by the φ_i's. Hence, these states will, in general, form a complete orthonormal set $\{\varphi_i(r)\}$. We may construct a Slater determinant $\phi_0(r_1,r_2,\ldots,r_N)$ from N states out of this set which belong to N consecutive lowest-lying one-particle energies ε_i. By definition, $\phi_0(r_1,r_2,\ldots,r_N)$ is normalized to unity.

The following points concern a particular consequence of the Kohn-Sham theory which has as yet not been discussed in the literature. The total wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ of the interacting system may be expanded in a configuration-interaction (CI) series,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\sum_K c_K\phi_K(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\;, \tag{5}$$

where ϕ_K's denote Slater determinants formed by selecting different subsets of N states $\varphi_i(\mathbf{r})$ out of the complete set $\{\varphi_i(\mathbf{r})\}$.

The above expansion may be rewritten

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)+\tilde{\Psi}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\;, \tag{6}$$

where

$$\tilde{\Psi}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\sum_K \tilde{c}_K\phi_K(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$$

and

$$\tilde{c}_K=\begin{cases}c_K & \text{for } K\neq K_0\;,\\ c_K-1 & \text{for } K=K_0\;.\end{cases}$$

Here, K_0 denotes the configuration referring to $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$. Obviously, $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ and $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ are nonorthogonal to one another. The two-particle density resulting from (6) can be cast in the form

$$\rho_2(\mathbf{r}',\mathbf{r})=\rho_2^{(0)}(\mathbf{r}',\mathbf{r})+\tilde{\rho}_2(\mathbf{r}',\mathbf{r})\;, \tag{7}$$

where $\rho_2^{(0)}(\mathbf{r}',\mathbf{r})$ is the contribution of $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$.

Hence, $\tilde{\rho}_2(\mathbf{r}',\mathbf{r})$ is defined by

$$\tilde{\rho}_2(\mathbf{r}',\mathbf{r})=N(N-1)\int(\phi_0^*\tilde{\Psi}+\phi_0\tilde{\Psi}^*+\tilde{\Psi}\tilde{\Psi}^*)d^3r_3\cdots d^3r_N\,.$$

Because of the general property of $\rho_2(\mathbf{r}',\mathbf{r})$,

$$\int\rho_2(\mathbf{r}',\mathbf{r})d^3r'=(N-1)\rho(\mathbf{r})\;,$$

and since by definition

$$\int\rho_2^{(0)}(\mathbf{r}',\mathbf{r})d^3r'=(N-1)\rho(\mathbf{r})\;, \tag{8}$$

we have

$$\int\tilde{\rho}_2(\mathbf{r}',\mathbf{r})d^3r'=0\quad\text{for all }\mathbf{r}\;. \tag{9}$$

Equations (5)–(9) state an important ground-state property of N-electron systems: It is obviously possible to partition the wave function of the interacting N-electron system into two parts, $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ and $\tilde{\Psi}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)$, such that the two-particle density associated with $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ integrates (apart from a factor $N-1$) to the total one-particle density. By definition, $\rho_2^{(0)}(\mathbf{r}',\mathbf{r})$ contains exchange only, and this is reflected in the occurrence of an exchange hole around $\mathbf{r}$ in the real space of positions $\mathbf{r}'$. Thus, in terms of this picture $\tilde{\rho}_2(\mathbf{r}',\mathbf{r})$ provides the correlation hole around $\mathbf{r}$ and, in addition, a "fine tuning" around the exchange hole connected with the interaction of electrons of like spins. This will become more evident in the following section, where spin-dependent properties of $\rho_2(\mathbf{r}',\mathbf{r})$ will be expressed explicitly.

We have arrived at the conclusion then that all many-body effects beyond the Hartree-Fock–type exchange can be absorbed into a two-particle density which does not contribute to the one-particle density.

The objective of the following section is to show that this subdivision of the total wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ into two parts $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ and $\tilde{\Psi}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ can be generalized by forming $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ from a complete orthonormal set $\{\psi_i(\mathbf{r})\}$ different, in general, from $\{\varphi_i(\mathbf{r})\}$ such that the (correspondingly altered) components $\rho_2^{(0)}(\mathbf{r}',\mathbf{r})$ and $\tilde{\rho}_2(\mathbf{r}',\mathbf{r})$ of the two-particle density retain the decisive properties (8) and (9). The method of generating the orbital set $\{\psi_i(\mathbf{r})\}$ will be based on the requirement that the expectation value of the total N-electron Hamiltonian be stationary against variation of $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ subdivided into two segments according to (6). Since wave functions of this property represent eigenfunctions of the N-electron Schrödinger equation, the results obtained apply to the ground state as well as to any other eigenstate of the N-electron system. Still, the equations defining the orbitals $\psi_i(\mathbf{r})$ will turn out to have the Kohn-Sham form.

In addition, the one-particle density will be given by (4), as before, but with $\psi_i(\mathbf{r})$ standing in place of $\varphi_i(\mathbf{r})$. This applies likewise to the total energy (1), except that the correlation factor $\bar{f}(\mathbf{r}',\mathbf{r})$ has to be replaced by its nonaveraged counterpart $f(\mathbf{r}',\mathbf{r})$ and that there is now an additional kinetic-energy term $\langle\tilde{T}_{e\text{-}e}\rangle$. In an excited state the ψ_i's contained in $\phi_0(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ and E do no longer correspond to a subsequent filling of N one-particle levels ε_i, but rather they refer to an occupancy distribution involving at least one electron-hole pair excitation.

In Sec. III we briefly discuss the problem of finding simple approximations to the correlation factor $f(\mathbf{r}',\mathbf{r})$. Section IV will be devoted to excitations. We shall, in particular, be concerned with thermal excitations in solids and with optical transitions. Energy gaps of semiconductors are known to be severely underestimated within the Kohn-Sham theory if $U_{\mathrm{xc}}(\mathbf{r})$ is approximated by "local" expressions which solely depend on $\rho(\mathbf{r})$. From the point of view consistent with our approach, the energy gap of a semiconductor represents the minimum excitation energy ΔE. It turns out that ΔE consists of two contributions,

$$\Delta E=(\varepsilon_f-\varepsilon_i)+\Delta\;,$$

where the first term (in parentheses) refers to the minimum band-energy difference between occupied and unoccupied bands. This term proves to be only slightly affected by nonlocal corrections to $U_{\mathrm{xc}}(\mathbf{r})$ (see Manghi *et al.*[9] and Hybertsen and Louie[4]). The second term, Δ, is connected with the occurrence of $\langle\tilde{T}_{e\text{-}e}\rangle$. The primary one-particle density change $\Delta\rho(\mathbf{r})$ that occurs in the process of an electronic transition is generally modified by the response of the entire system to the perturbing potential connected with $\Delta\rho(\mathbf{r})$. General experience appears to suggest that metals respond in a way that leaves $\langle\tilde{T}_{e\text{-}e}\rangle$ practically unchanged. The response in insulators and semiconductors will, of course, be severely affected by the presence of an energy gap above the majority of occupied levels. Hence, one may in this case expect a sizable contribution of the change of $\langle\tilde{T}_{e\text{-}e}\rangle$. Sham and Schlüter,[10] and, independently, Perdew and Levy,[11] have discussed the gap problem within the density-functional theory, where ΔE is defined as the difference between the ionization potential I and the affinity energy A of the solid in question. Hence, ΔE can only be determined from total-energy differences between ground states referring to

$N-1$, N, and $N+1$ electrons, respectively. Excitation energies ΔE which would, for example, refer to optical transitions across the direct gap in semiconductors with an indirect gap are not accessible within this approach. Since our treatment rests on the N-electron Schrödinger equation rather than on the ground-state theorem of Hohenberg and Kohn essential to the density-functional theory, excitations are fully accounted for, including, of course, the one of lowest energy which defines the energy gap of non-metallic solids.

In Sec. V we will summarize the relative merits of our approach.

II. GENERALIZATION OF THE KOHN-SHAM THEORY

As indicated in the preceding section, we subdivide the wave function of an interacting N-electron system within an infinitesimal vicinity of an eigenstate $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ into two components,

$$\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)+\tilde{\Psi}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)\,, \tag{10}$$

where $\mathbf{q}_j=(\mathbf{r}_j,s_j)$ is shorthand notation for the real-space coordinate $\mathbf{r}_j$ of the jth particle and its spin orientation $s_j=\pm 1$. We have omitted the subscript 0 of $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ to indicate that this component of the total wave function cannot, at the outset, be expected to be representable by one Slater determinant. As before, $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ and $\tilde{\Psi}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ are chosen such that

$$\rho_2(\mathbf{q}',\mathbf{q})=\rho_2^{(0)}(\mathbf{q}',\mathbf{q})+\tilde{\rho}_2(\mathbf{q}',\mathbf{q})\,, \tag{11}$$

where

$$\rho_2^{(0)}(\mathbf{q}',\mathbf{q})=N(N-1)\int|\phi(\mathbf{q}',\mathbf{q},\mathbf{q}_3,\mathbf{q}_4,\ldots,\mathbf{q}_N)|^2\times d^4q_3\,d^4q_4\cdots d^4q_N \tag{12a}$$

and

$$\tilde{\rho}_2(\mathbf{q}',\mathbf{q})=N(N-1)\int[\phi^*\tilde{\Psi}+\phi\tilde{\Psi}^*+\tilde{\Psi}\tilde{\Psi}^*]\times d^4q_3\,d^4q_4\cdots d^4q_N\,. \tag{12b}$$

Here, $\int\cdots d^4q_j$ stands for real-space integration and spin summation for the jth particle. The spin-dependent one-particle density $\rho_s(\mathbf{r})$ is given by

$$\rho_s(\mathbf{r})=\frac{1}{N-1}\sum_{s'}\int\rho_2^{(0)}(\mathbf{q}',\mathbf{q})d^3r'\,, \tag{12c}$$

and hence

$$\rho(\mathbf{r})=\sum_s\rho_s(\mathbf{r})\,. \tag{12d}$$

As a result of (12c) we have

$$\sum_{s'}\int\tilde{\rho}_2(\mathbf{q}',\mathbf{q})d^3r'=0 \quad \text{for any } \mathbf{r} \text{ and } s\,. \tag{12e}$$

Consequently, $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ must be normalized to unity as before. It will be shown below that the properties (11) and (12a)—(12e) uniquely define the two components $\phi(q_1,q_2,\ldots,q_N)$ and $\Psi(q_1,q_2,\ldots,q_N)$ in any of the eigenstates $\Psi_n(q_1,q_2,\ldots,q_N)$.

We now expand $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ in a CI series,

$$\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\sum_K a_K\phi_K(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)\,, \tag{13}$$

where the ϕ_K's denote Slater determinants formed from a complete orthonormal set $\{\psi_{is}(\mathbf{r})\}$ to be specified later. If we write the N-electron Hamiltonian (in hartree units)

$$\mathscr{H}=\mathscr{H}_0+\tfrac{1}{2}\sum_{\substack{i,j\\(i\neq j)}}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\,, \tag{14a}$$

where

$$\mathscr{H}_0=\sum_{i=1}^{N}[-\tfrac{1}{2}\nabla_i^2+U_{\text{ext}}(\mathbf{r}_i)]\,, \tag{14b}$$

the expectation value of $\mathscr{H}_0$ can be written

$$\langle\mathscr{H}_0\rangle=\sum_{i,j,s}D_{ij}^{(s)}\int\psi_{is}^*(\mathbf{r})[-\tfrac{1}{2}\nabla^2+U_{\text{ext}}(\mathbf{r})]\times\psi_{js}(\mathbf{r})d^3r+\langle\tilde{T}_{e\text{-}e}\rangle\,. \tag{15}$$

Here, $\langle\tilde{T}_{e\text{-}e}\rangle$ stands for the contribution to the kinetic energy not contained in $\phi(q_1,q_2,\ldots,q_N)$, and $D_{ij}^{(s)}$ denotes the elements of the first-order density matrix in the orbital representation with respect to $\{\psi_{is}(\mathbf{r})\}$.

These elements are defined as

$$D_{ij}^{(s)}=\sum_{K=K(i,s)}\;\sum_{L=L(j,s)}a_K^*a_L\,, \tag{16}$$

where the sum runs over all configurations K,L which differ in just one orbital. That is to say, if K contains $\psi_{is}(\mathbf{r})$, then L contains $\psi_{js}(\mathbf{r})$ instead, but agrees in all other orbitals present in K. In writing the contribution of the external potential $U_{\text{ext}}(\mathbf{r})$ to $\langle\mathscr{H}_0\rangle$, we have already made use of

$$\rho_s(\mathbf{r})=\sum_{i,j}D_{ij}^{(s)}\psi_{is}(\mathbf{r})\psi_{js}(\mathbf{r})\,, \tag{17}$$

which follows from (12a), (12c), (13), and (16).

If we expand the total wave function $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ in analogy to (13) using the same basis set, we can define another density matrix whose elements $\Delta_{ij}^{(s)}$ are connected with the expansion coefficients c_K of $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ in complete analogy to (16). The kinetic-energy correction $\langle\tilde{T}_{e\text{-}e}\rangle$ in (15) may therefore be expressed as

$$\langle\tilde{T}_{e\text{-}e}\rangle=\sum_{i,j,s}\tilde{D}_{ij}^{(s)}\int\psi_{is}^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\psi_{js}(\mathbf{r})d^3r\,, \tag{18a}$$

where

$$\tilde{D}_{ij}^{(s)}=\Delta_{ij}^{(s)}-D_{ij}^{(s)}\,. \tag{18b}$$

As a consequence of (17) we have

$$\sum_{i,j}\tilde{D}_{ij}^{(s)}\psi_{is}^*(\mathbf{r})\psi_{js}(\mathbf{r})\equiv 0\,, \tag{18c}$$

which must hold for finite matrix elements $\tilde{D}_{ij}^{(s)}$; otherwise the total wave function and $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ would have identical CI expansions, i.e., $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ would vanish identically.[12]

Since $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ is normalized to unity, we have

$$\sum_K |a_K|^2=1 . \tag{19}$$

Thus, because of (16),

$$n_{is} \leqq 1 , \tag{20a}$$

where

$$n_{is}=D_{ii}^{(s)} \tag{20b}$$

is customarily referred to as occupation number. If one integrates (17) over the real space one obtains

$$\sum_i n_{is}=N_s , \tag{20c}$$

and because of (12d),

$$N=\sum_s N_s . \tag{20d}$$

The electronic interaction energy may be written as

$$\langle U_{e\text{-}e}\rangle=\tfrac{1}{2}\sum_{s',s}\int\int \frac{\rho_2(\mathbf{q}',\mathbf{q})}{|\mathbf{r}'-\mathbf{r}|}d^3r'\,d^3r . \tag{21}$$

Hence,

$$E=\langle \mathscr{H}_0\rangle+\langle U_{e\text{-}e}\rangle \tag{22}$$

represents the expectation value of $\mathscr{H}$.

We consider the CI expansion of the total wave function,

$$\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\sum_K c_K\phi_K(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N) , \tag{23}$$

and subject it to a distortion by replacing $c_K \rightarrow c_K'$ while keeping the set $\{\phi_K\}$ fixed. We give c_K' the form

$$c_K'=c_K+\eta\,\delta c_K ,$$

where η denotes some real parameter.

Hence we have

$$\Psi'(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)+\eta\,\delta\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N) , \tag{24a}$$

where

$$\delta\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\sum_K \delta c_K\,\phi_K(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N) . \tag{24b}$$

The δc_K's are subject to the constraint

$$\sum_K c_K^*\,\delta c_K=0 , \tag{24c}$$

which guarantees norm conservation of $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ to first order in η. If the wave function represents an eigenstate $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, the variation of $\langle\mathscr{H}\rangle$ connected with $\delta\Psi(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_N)$ must have the property

$$\delta\langle\mathscr{H}\rangle=\text{const}\times\eta^2 . \tag{25}$$

We shall in the following show that this requirement can only be met if $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ represents just one Slater determinant in terms of specified orbitals $\{\psi_{is}(\mathbf{r})\}$.

To prove this we first cast the distortion (24b) in a convenient form by expanding it in terms of the complete set of eigenfunctions $\Psi_m(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ which belong to $\mathscr{H}$. We then have

$$\delta\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\sum_{\substack{m\\(m\neq n)}}\alpha_{nm}\Psi_m(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N) ,$$

where $m\neq n$ (i.e., $\alpha_{mm}=0$) ensures norm conservation of $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ to first order in the expansion coefficients α_{nm}. Using (24a) we obtain new first-order densities

$$\rho_s'(\mathbf{r})=\rho_s(\mathbf{r})+\delta\rho_s(\mathbf{r}) ,$$

where $\delta\rho_s(\mathbf{r})$ is given by

$$\delta\rho_s(\mathbf{r})=\eta\sum_{\substack{m\\(m\neq n)}}\alpha_{nm}S_{nms}(\mathbf{r})+\text{c.c.} , \tag{26}$$

which holds to first order in α_{nm}.

The functions $S_{nms}(\mathbf{r})$ are independent of α_{nm} and are defined as

$$S_{nms}(\mathbf{r})=N\int\Psi_n^*(\mathbf{q},\mathbf{q}_2,\mathbf{q}_3,\ldots,\mathbf{q}_N)\Psi_m(\mathbf{q},\mathbf{q}_2,\mathbf{q}_3,\ldots,\mathbf{q}_N)d^4q_2\,d^4q_3\cdots d^4q_N .$$

Likewise we get

$$\delta\rho_2^{(s's)}(\mathbf{r}',\mathbf{r})=\eta\sum_{\substack{m\\(m\neq n)}}\alpha_{nm}S_{nms's}(\mathbf{r}',\mathbf{r})+\text{c.c.} , \tag{27}$$

where we have omitted the index n on the left-hand side to simplify the notation somewhat. The functions on the right-hand side are defined

$$S_{nms's}^{(2)}(\mathbf{r}',\mathbf{r})=N(N-1)\int\Psi_n^*(\mathbf{q}',\mathbf{q},\mathbf{q}_3,\mathbf{q}_4,\ldots,\mathbf{q}_N)\Psi_m(\mathbf{q}',\mathbf{q},\mathbf{q}_3,\mathbf{q}_4,\ldots,\mathbf{q}_N)d^4q_3\,d^4\mathbf{q}_4\cdots d^4q_N .$$

As will be shown in the Appendix, there exists for any $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ a function $\Gamma_n^{(s's)}(\mathbf{r}'',\mathbf{r}',\mathbf{r})$ having the property

$$\int\Gamma_n^{(s's)}(\mathbf{r}'',\mathbf{r}',\mathbf{r})\delta\rho_s(\mathbf{r}'')d^3r''=\delta\rho_2^{(s's)}(\mathbf{r}',\mathbf{r}) . \tag{28}$$

This function is uniquely defined by the complete set of eigenstates associated with $\mathscr{H}$. It is invariant against interchange of $(\mathbf{r}',s')$ and $(\mathbf{r},s)$.

We now introduce a potential

$$U_n^{(s)}(\mathbf{r}'')=\tfrac{1}{2}\sum_{s'}\int\int\frac{\Gamma_n^{(s's)}(\mathbf{r}'',\mathbf{r}',\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'\,d^3r , \tag{29}$$

by means of which the variation of $\langle U_{e\text{-}e} \rangle$,

$$\delta\langle U_{e\text{-}e} \rangle = \tfrac{1}{2} \sum_{s',s} \int \int \frac{\delta\rho_2^{(s's)}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}',\mathbf{r}|} d^3r'\, d^3r \ ,$$

may be written

$$\delta\langle U_{e\text{-}e} \rangle = \sum_{s} \int \delta\rho_s(\mathbf{r}'') U_n^{(s)}(\mathbf{r}'') d^3r'' \ , \tag{30}$$

where we have used (28). As follows from the proof in the Appendix, $U_n^{(s)}(\mathbf{r}'')$ is dependent on the particular N-electron eigenstate. We want to emphasize, however, that it does not depend on any of the one-particle states $\psi_{is}(\mathbf{r})$ and nor does it depend on the one-particle energies ε_{is} to be defined later [see Eq. (34)]. In the parlance of Hartree-Fock theory $U_n^{(s)}(\mathbf{r})$ must hence be referred to as a *local* (energy-independent) potential.

Since we require the subdivision (10) of the total wave function to be possible within an infinitesimal environment of any eigenstate, the respective functions $\Psi'_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ and $\phi'_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ must give identical one-particle densities. This is guaranteed if the associated density matrix elements $\Delta_{ij}^{(s)'}$ and $D_{ij}^{(s)'}$ have the property

$$\Delta_{ij}^{(s)'} = \Delta_{ij}^{(s)} + \delta D_{ij}^{(s)}$$

and

$$D_{ij}^{(s)'} = D_{ij}^{(s)} + \delta D_{ij}^{(s)} \ .$$

Because of (18b) we then have

$$\delta \widetilde{D}_{ij}^{(s)} = 0 \quad \text{for any } i,j \text{ and } s \ ,$$

and hence[16]

$$\delta\langle \widetilde{T}_{e\text{-}e} \rangle = 0 \ .$$

From (15) and (17) we thus obtain (again omitting the index n)

$$\delta\langle \mathscr{H}_0 \rangle = \sum_{i,j,s} \delta D_{ij}^{(s)} \int \psi_{is}^*(\mathbf{r})[-\tfrac{1}{2}\nabla^2 + U_{\text{ext}}(\mathbf{r})] \times \psi_{js}(\mathbf{r}) d^3r \tag{31}$$

and

$$\delta\rho_s(\mathbf{r}) = \sum_{i,j} \delta D_{ij}^{(s)} \psi_{is}^*(\mathbf{r}) \psi_{js}(\mathbf{r}) \ . \tag{32}$$

Hence, because of (30)–(32) the variation of the total energy (22) takes the form

$$\delta E = \sum_{i,j,s} \delta D_{ij}^{(s)} \int \psi_{is}^*(\mathbf{r})[-\tfrac{1}{2}\nabla^2 + U_{\text{ext}}(\mathbf{r}) + U_n^{(s)}(\mathbf{r})] \times \psi_{js}(\mathbf{r}) d^3r \ . \tag{33}$$

If we now specify the functions $\psi_{is}(\mathbf{r})$ by requiring that they satisfy a Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2 + U_{\text{ext}}(\mathbf{r}) + U_n^{(s)}(\mathbf{r})]\psi_{is}(\mathbf{r}) = \varepsilon_{is}\psi_{is}(\mathbf{r}) \ , \tag{34}$$

Eq. (33) attains the simple form

$$\delta E = \sum_{i,s} \varepsilon_{is}\, \delta n_{is} \ . \tag{35a}$$

Since the occupation numbers n_{is} sum up to the total number of electrons [cf. Eqs. (20c) and (20d)], the variation is subject to the constraint

$$\sum_{i,s} \delta n_{is} = 0 \ . \tag{35b}$$

We shall use the latter two equations to prove that the component $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ in (10) represents just one Slater determinant if $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ is an eigenstate.

We start by assuming that $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ has, in fact, the form of a Slater determinant. In that case we have, for the coefficients in the CI expansion (13),

$$a_K = \begin{cases} 1 & \text{for } K = K_0 \ , \\ 0 & \text{for } K \neq K_0 \ . \end{cases} \tag{36}$$

If we now distort the total wave function $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, the associated new a_K's may be written as

$$a_K = \begin{cases} a'_K & \text{for } K = K_0 \quad \text{where } |a'_{K_0}|^2 < 1 \ , \\ \eta\, \delta a_K & \text{for } K \neq K_0 \ . \end{cases}$$

Because of the normalization (19) we have

$$|a'_{K_0}|^2 + \eta^2 \sum_{\substack{K \\ (K \neq K_0)}} |\delta a_K|^2 = 1 \ ,$$

which we rewrite as

$$\delta_{n_0} = -\eta^2 \sum_{\substack{K \\ (K \neq K_0)}} |\delta a_K|^2 \ . \tag{37}$$

The quantity

$$\delta n_0 = |a'_{K_0}|^2 - 1$$

describes a uniform lowering of the occupation numbers referring to all states contained in $\phi_{K_0}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$. According to our assumption (36) on the undistorted form of $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, these occupation numbers are originally all equal to one. On the other hand, there is an increase, δn_{is}, of the occupation number of a formerly occupied state $\psi_{is}(\mathbf{r})$ because—as a result of distorting $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$—it now appears also in configurations $K \neq K_0$ whose coefficients were formerly zero. The net change δn_{is} of the occupation number n_{is} is therefore given by

$$\delta n_{is} = \begin{cases} \delta n_0 + \delta \widetilde{n}_{is} & \text{for formerly occupied states} \ , \\ \delta \widetilde{n}_{is} & \text{for formerly unoccupied states} \ , \end{cases}$$

where

$$\delta \widetilde{n}_{is} = \eta^2 \sum_{\substack{K = (i,s) \\ (K \neq K_0)}} |\delta a_K|^2 \ .$$

Inserting this net change into (35a) and using (37) we are led to

$$\delta E=\eta^2\sum_{K,K'}\beta_{K'K}\delta a_{K'}^*\delta a_K\ , \tag{38a}$$

where

$$\beta_{K'K}=(1-\delta_{K'K_0})\left[\sum_{i,s}\varepsilon_{is}\delta_{K'K(i,s)}-\bar{\varepsilon}N\delta_{K'K}\right]\ , \tag{38b}$$

and

$$\bar{\varepsilon}=\frac{1}{N}\sum_{i,s\,(K_0)}\varepsilon_{is}$$

denotes the arithmetic mean of energies ε_{is} which belong to states $\psi_{is}(\mathbf{r})$ contained in $\phi_{K_0}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$.

We have thus established the validity of (25), which means that (36) describes the contribution $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ to the total wave function in an eigenstate. If the expansion coefficients a_K had been assumed to be all finite, i.e., different from (36), the new coefficients a_K' obtained after distortion of $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ would all have had the form

$$a_K'=a_K+\eta\,\delta a_K\ . \tag{39}$$

Because of (17) and (20b) we then have

$$n_{is}'=\sum_K^{(i,s)}|a_K'|^2\ ,$$

where

$$n_{is}'=n_{is}+\delta n_{is}\ . \tag{40}$$

Hence, in the case considered we obtain, upon insertion of (39) into (40),

$$\delta n_{is}=\eta\sum_K^{(i,s)}(a_K^*\,\delta a_K+\text{c.c.})+\eta^2\sum_K^{(i,s)}\delta a_K^*\,\delta a_K\ .$$

When this is substituted into (35a), we arrive at

$$\begin{aligned}\delta E=\eta\sum_{i,s}\varepsilon_{is}&\left[\sum_K^{(i,s)}a_K^*\,\delta a_K+\text{c.c.}\right]\\&+\eta^2\sum_{i,s}\varepsilon_{is}\sum_K^{(i,s)}\delta a_K^*\delta a_K\ .\end{aligned} \tag{41}$$

On the other hand, we have

$$N=\sum_{i,s}n_{is}\ ;$$

that is,

$$\sum_{i,s}\sum_K^{(i,s)}|a_K|^2=N\ .$$

Since the distortion of $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ has to be performed under the constraint that N be constant, the latter equation leads to

$$\sum_{i,s}\left[\sum_K^{(i,s)}a_K^*\delta a_K+\text{c.c.}\right]=0\ , \tag{42}$$

where the expression in large parentheses is, in general, nonzero. The one-particle energies ε_{is} are, of course, in no way correlated with the δa_K's. Because of (42) we are thus led to

$$\sum_{i,s}\varepsilon_{is}\left[\sum_K^{(i,s)}a_K^*\,\delta a_K+\text{c.c.}\right]\neq 0\ ,$$

which means that the first expression in (41) does not vanish as it should if the wave function considered was an eigenstate.

We may summarize the above results by stating that the decomposition (10) of any eigenstate yields a component $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ which represents just *one* Slater determinant. We denote the latter by $\phi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$:

$$\begin{aligned}\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\phi_n&(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)\\&+\tilde{\Psi}_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)\ .\end{aligned} \tag{43}$$

The spin-dependent one-particle density is thus given by

$$\rho_s(\mathbf{r})=\sum_i|\psi_{is}(\mathbf{r})|^2\ , \tag{44a}$$

so that

$$\rho(\mathbf{r})=\sum_s\rho_s(\mathbf{r})\ . \tag{44b}$$

The sum in (44a) runs over N_s terms.

The above considerations apply to closed-shell—type states. There is no problem, however, in extending our conclusions to multiplet states. In this case one merely has to reinterpret a_{K_0} in (13) as the expansion coefficient in front of a suitably chosen linear combination of Slater determinants,

$$\phi_{K_0}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)=\sum_L\alpha_L\phi_L(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)\ , \tag{45}$$

which ensures the proper symmetry of the multiplet state in question. The above sum runs over a finite set of configurations L and the α_L's are normalized,

$$\sum_L|\alpha_L|^2=1\ . \tag{46}$$

The remaining infinite number of expansion terms in (13), which have to be included at the beginning of the consideration, consist of Slater determinants differing from those contained in (45) by at least one state. Hence, one has, as before,

$$\sum_K|a_K|^2=1\ ,$$

and going through an analogous discussion starting with (36) we are again led to the conclusion that (13) reduces to one term, $\phi_{K_0}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, whose form, however, is now given by (45). The functions $\phi_L(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ under the sum in (45) differ only in those states $\psi_{is}(\mathbf{r})$ which are involved in forming the multiplet state. The associated occupations numbers n_{is} now have fractional values between one and zero because each $|\alpha_L|^2$ is less than unity due to (46). Hence, expression (44a) for $\rho_s(\mathbf{r})$ has to be modified accordingly. For simplicity we shall in the following always refer to the case where $\phi_{K_0}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ is just one Slater determinant.

In order to make our one-particle equations readily comparable with the Kohn-Sham form used in the literature (see, e.g., Krüger *et al.*[15]), we introduce the exchange-correlation energy per particle $\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})$ by setting

$$\int \delta\rho_s(\mathbf{r})U_n^{(s)}(\mathbf{r})d^3r = \int \delta\rho_s(\mathbf{r})U_H(\mathbf{r})d^3r + \int \delta[\rho_s(\mathbf{r})\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})]d^3r \ , \tag{47a}$$

where

$$U_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d^3r' \tag{47b}$$

is the Hartree potential. Equation (47a) can be put in the form

$$\sum_s \int \delta\rho_s(\mathbf{r})U_n^{(s)}(\mathbf{r})d^3r = \int \delta\rho(\mathbf{r})U_H(\mathbf{r})d^3r + \delta\sum_s \int \rho_s(\mathbf{r})\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})d^3r \ ,$$

and hence (30) may be rewritten as

$$\delta\langle U_{e\text{-}e}\rangle = \delta\left[\frac{1}{2}\int\int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'\,d^3r + \sum_s \int \rho_s(\mathbf{r})\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})d^3r\right] , \tag{48}$$

where the term in large parentheses represents an alternative expression for $\langle U_{e\text{-}e}\rangle$. The second term in large parentheses may be referred to as the exchange-correlation energy. To make this evident we introduce the pair correlation functions $g_{s's}(\mathbf{r}',\mathbf{r})$ defined by

$$\rho_2^{(s's)}(\mathbf{r}',\mathbf{r}) = \rho_{s'}(\mathbf{r}')\rho_s(\mathbf{r})g_{s's}(\mathbf{r}',\mathbf{r}) \ . \tag{49}$$

Because of the properties of $\rho_2^{(s's)}(\mathbf{r}',\mathbf{r})$ we have

$$g_{s's}(\mathbf{r}',\mathbf{r}) = g_{ss'}(\mathbf{r},\mathbf{r}') \tag{50a}$$

and

$$g_{ss}(\mathbf{r}',\mathbf{r}) = 0 \quad \text{for all } \mathbf{r}'=\mathbf{r} \text{ and } s=\pm 1 \ . \tag{50b}$$

The latter equation reflects the existence of an exchange hole in the space of positions $\mathbf{r}'$ around $\mathbf{r}$.

If we, further, introduce the correlation factors $f_{s's}(\mathbf{r}',\mathbf{r})$ by setting

$$f_{s's}(\mathbf{r}',\mathbf{r}) = 1 - g_{s's}(\mathbf{r}',\mathbf{r}) \ , \tag{51}$$

the electron-electron interaction energy (21) may be cast in the form

$$\langle U_{e\text{-}e}\rangle = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'\,d^3r - \frac{1}{2}\sum_{s',s}\int\int \frac{\rho_{s'}(\mathbf{r}')\rho_s(\mathbf{r})f_{s's}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'\,d^3r \ , \tag{52}$$

where we have used Eqs. (49) and (51). Upon comparing (52) with the term in large parentheses in (48) we find that the exchange-correlation energy E_{xc} may be expressed as

$$E_{\mathrm{xc}} = \sum_s \int \rho_s(\mathbf{r})\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})d^3r \ , \tag{53a}$$

where the exchange-correlation energy per particle is given by

$$\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r}) = -\frac{1}{2}\sum_{s'}\int \frac{\rho_{s'}(\mathbf{r}')f_{s's}(\mathbf{r}',\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r' \ . \tag{53b}$$

Obviously, the form of (52) is identical with the respective expression (2) of the Kohn-Sham theory, except that (2) contains the correlation factor averaged over the coupling strength λ. Furthermore, if we insert (53b) into (47a) our one-particle equations (34) attain the Kohn-Sham form

$$[-\tfrac{1}{2}\nabla^2 + U_{\mathrm{ext}}(\mathbf{r}) + U_H(\mathbf{r}) + U_{\mathrm{xc}}^{(s)}(\mathbf{r})]\psi_{is}(\mathbf{r}) = \varepsilon_{is}\psi_{is}(\mathbf{r}) \ , \tag{54a}$$

where

$$U_{\mathrm{xc}}^{(s)}(\mathbf{r}) = -\sum_{s'}\int \frac{\rho_{s'}(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}\left[f_{s's}(\mathbf{r}',\mathbf{r}) + \frac{1}{2}\sum_{s''}\frac{\delta f_{s's''}(\mathbf{r}',\mathbf{r})}{\delta\rho_s(\mathbf{r})}\rho_{s''}(\mathbf{r})\right]d^3r' \ . \tag{54b}$$

We want to emphasize again that $U_{\mathrm{xc}}^{(s)}(\mathbf{r})$ is a strictly local potential for any eigenstate $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ under consideration. Furthermore, since $U_n^{(s)}(\mathbf{r})$ depends on the particular eigenstate in question (indicated by the index n), it follows from our definitions (47a), (49), and (51) that $\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})$ and $f_{s's}(\mathbf{r}',\mathbf{r})$ are state dependent also. We omit, however, expressing this property explicitly.

The kinetic-energy correction (18a) can be cast in a more convenient form. If we rewrite (34) as

$$-\frac{1}{2}\nabla^2\psi_{js}(\mathbf{r}) = [\varepsilon_{js} - U_{\mathrm{ext}}(\mathbf{r}) - U_n^{(s)}(\mathbf{r})]\psi_{js}(\mathbf{r}) \ ,$$

and multiply this equation by $\widetilde{D}_{ij}^{(s)}\psi_{is}^*(\mathbf{r})$, we obtain, after real-space integration and summation over all states,

$$\langle \widetilde{T}_{e\text{-}e}\rangle = \sum_{i,s}\widetilde{n}_{is}\varepsilon_{is} \ , \tag{55}$$

where we have used (18c). The occupation-number differences defined by

$$\widetilde{n}_{is} = \Delta_{ii}^{(s)} - n_{is} \tag{56a}$$

have the property

$$\sum_i \widetilde{n}_{is} = 0 \ . \tag{56b}$$

Because of (55) and (56a) and (56b), one can immediately show that $\langle \widetilde{T}_{e\text{-}e}\rangle$ must, in the ground state, always be positive. The latter case is characterized by a consecutive filling of levels ε_{is} up to a highest level ε_{Fs} for either spin orientation. If we multiply (56b) by ε_{Fs}, sum with respect to s, and subtract the result from (55), we obtain

$$\langle \widetilde{T}_{e\text{-}e}\rangle = \sum_{i,s}(\varepsilon_{is} - \varepsilon_{Fs})\widetilde{n}_{is} \ .$$

In the ground state we have

$$\tilde{n}_{is}=\begin{cases}\Delta_{ii}^{(s)}-1\leqq 0 & \text{for levels } \varepsilon_{is}\leqq\varepsilon_{Fs}\ ,\\ \Delta_{ii}^{(s)}>0 & \text{for levels } \varepsilon_{is}>\varepsilon_{Fs}\ .\end{cases}$$

Hence $\langle \tilde{T}_{e\text{-}e}\rangle$ must be positive because all terms under the above sum are non-negative.

We are now in the position to write the total electronic energy of the system in any of the eigenstates,

$$E=\sum_{i,s}\varepsilon_{is}-\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'\,d^3r$$
$$+\sum_{s}\int\rho_s(\mathbf{r})[\varepsilon_{\text{xc}}^{(s)}(\mathbf{r})-U_{\text{xc}}^{(s)}(\mathbf{r})]d^3r+\langle\tilde{T}_{e\text{-}e}\rangle\ , \qquad (57)$$

where we have eliminated expressions containing $-\frac{1}{2}\nabla^2$ by means of (54a). The one-particle density is given by

$$\rho(\mathbf{r})=\sum_{s}\rho_s(\mathbf{r})\ , \qquad (58a)$$

where

$$\rho_s(\mathbf{r})=\sum_{i}|\psi_{is}(\mathbf{r})|^2\ . \qquad (58b)$$

The summation index (i,s) runs over N terms if $\phi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ represents a closed-shell—type state, irrespective of whether it refers to an excited state or to the ground state. We again observe that, apart from the occurrence of $\langle\tilde{T}_{e\text{-}e}\rangle$ in E, expressions (57) and (58a) and (58b) are for non-spin-polarized systems identical to those of the Kohn-Sham theory, except that the latter defines $\varepsilon_{\text{xc}}^{(s)}(\mathbf{r})$ and $U_{\text{xc}}^{(s)}(\mathbf{r})$ by means of the λ-averaged correlation factors (3). Of course, the two alternative approaches cannot lead to different results for E and $\rho(\mathbf{r})$ in the ground state. This case deserves a more detailed discussion.

Equation (54a) and the corresponding Kohn-Sham equations may be interpreted as one-particle equations for noninteracting electrons which move in an external potential,

$$U'_{\text{ext}}(\mathbf{r})=U_{\text{ext}}(\mathbf{r})+U_H(\mathbf{r})+U_{\text{xc}}(\mathbf{r})$$

(here we have dropped the spin index for simplicity.)

Since the one-particle densities emerging from our theory and from that of Kohn and Sham must agree, it follows from invoking the Hohenberg-Kohn theorem that the associated two potentials $U'_{\text{ext}}(\mathbf{r})$ must be identical. If we rewrite (54b) as

$$U_{\text{xc}}(\mathbf{r})=2\varepsilon_{\text{xc}}(\mathbf{r})+\tilde{\varepsilon}_{\text{xc}}(\mathbf{r})\ , \qquad (58c)$$

where $\tilde{\varepsilon}_{\text{xc}}(\mathbf{r})$ is derived from the second term in (54b), the two potentials may be interrelated:

$$\bar{U}'_{\text{ext}}(\mathbf{r})=U'_{\text{ext}}(\mathbf{r})+2[\bar{\varepsilon}_{\text{xc}}(\mathbf{r})-\varepsilon_{\text{xc}}(\mathbf{r})]+[\bar{\tilde{\varepsilon}}_{\text{xc}}(\mathbf{r})-\tilde{\varepsilon}_{\text{xc}}(\mathbf{r})]\ .$$

Here we have characterized the Kohn-Sham quantities by an overbar. Since $\varepsilon_{\text{xc}}(\mathbf{r})$ and $\bar{\varepsilon}_{\text{xc}}(\mathbf{r})$ are certainly not identical, because the latter is connected with the λ-averaged correlation factor, their difference must obviously cancel with the respective difference of $\tilde{\varepsilon}_{\text{xc}}(\mathbf{r})$ and $\bar{\tilde{\varepsilon}}_{\text{xc}}(\mathbf{r})$. On the other hand, the total energies must agree, which means that

$$\langle\tilde{T}_{e\text{-}e}\rangle=\int\rho(\mathbf{r})[\bar{\varepsilon}_{\text{xc}}(\mathbf{r})-\varepsilon_{\text{xc}}(\mathbf{r})]d^3r\ .$$

At first sight, the occurrence of $\langle\tilde{T}_{e\text{-}e}\rangle$ in the present theory appears to introduce an undesirable uncertainty because the occupation-number differences $\tilde{n}_{is}$ contained in the expression (55) for $\langle\tilde{T}_{e\text{-}e}\rangle$ are unknown. However, the total potential energy

$$\langle U\rangle=\langle U_{\text{ext}}\rangle+\langle U_{e\text{-}e}\rangle$$

is completely known once $\rho_s(\mathbf{r})$ and $\varepsilon_{\text{xc}}^{(s)}(\mathbf{r})$ have been calculated by self-consistently solving Eq. (54a) and by using (58b) and (54b). Since $\langle U\rangle$ thus determined refers to the potential energy in an eigenstate, we may invoke the virial theorem, which yields

$$E=\tfrac{1}{2}\langle U\rangle\ .$$

The above scheme provides a one-to-one correspondence between $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ and $\phi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$. Hence, the degeneracy of an energy level E may be determined just by finding the number of different Slater determinants $\phi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ which lead to the same total energy E. In connection with thermal excitations (Sec. IV), the case of near degeneracy will be of importance, where one disregards the relaxation energy between configurations which differ in degenerate one-particle states. It will then be possible to define the entropy of the system and to consistently derive the Fermi distribution function for an ensemble of interacting electrons whose number is fixed.

III. SIMPLE APPROXIMATE FORMS OF THE CORRELATION FACTORS

As a consequence of definitions (49) and (51), $f_{s's}(\mathbf{r}',\mathbf{r})$ has the following properties (cf. e.g., McWeeny[8]):

$$f_{ss}(\mathbf{r},\mathbf{r})=1 \quad \text{for any } \mathbf{r} \text{ and } s\ , \qquad (59a)$$

$$f_{s's}(\mathbf{r}',\mathbf{r})\underset{(=)}{<}1 \quad \text{for any } \mathbf{r}',\mathbf{r} \text{ and } s',s\ , \qquad (59b)$$

where the equality sign in parentheses in (59b) refers to the case described by (59a). Moreover, if the system under study has a finite extension the correlation factors exhibit a well-defined asymptotic behavior:[8]

$$\lim_{|\mathbf{r}'-\mathbf{r}|\to\infty} f_{s's}(\mathbf{r}',\mathbf{r})=\delta_{s's}\frac{1}{N_s}\ , \qquad (59c)$$

where $\mathbf{r}'$ (or alternatively $\mathbf{r}$) is some internal point of the system.

The two-particle density has the property

$$\int\rho_2(\mathbf{q}',\mathbf{q})d^3r'=(N_{s'}-\delta_{s's})\rho_s(\mathbf{r})\ , \qquad (60)$$

which, after summation with respect to s', attains the familiar form (12c),

$$\sum_{s'}\int\rho_2(\mathbf{q}',\mathbf{q})d^3r'=(N-1)\rho_s(\mathbf{r})\ .$$

Substituting (49) into (60) and replacing $g_{s's}(\mathbf{r}',\mathbf{r})$ by means of (51), we arrive at the well-known sum rules

$$\int\rho_s(\mathbf{r}')f_{s's}(\mathbf{r}',\mathbf{r})d^3r=\delta_{s's} \quad \text{for any } \mathbf{r}\ . \qquad (61)$$

In practice, it has proved surprisingly successful to use the following relatively crude approximation to $f_{s's}(\mathbf{r}',\mathbf{r})$:

$$f_{ss}(\mathbf{r}',\mathbf{r})=f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|) \qquad (62a)$$

and

$$f_{s's}(\mathbf{r},\mathbf{r})\equiv 0 \quad \text{for } s'\neq s\ , \qquad (62b)$$

the latter implying the complete neglect of correlation for electrons of unlike spins. The function on the right-hand side of (62a) has to be chosen such as to meet the requirements (59a)–(59c) and (61), which, of course, leave considerable latitude as to the analytical form of $f_{ss}(\mathbf{r}',\mathbf{r})$. Nevertheless, the electronic properties obtained from self-consistently solving Eq. (54a) turn out to be not severely affected by differnet assumptions on the shape of the correlation factor (62a). This has recently been studied in detail by Gollisch *et al.*,[17] who performed their calculations within the present theoretical framework. The conditions (59a)–(59c) and, in particular, the sum rule (61) represent obviously so strong a constraint that the remaining arbitrariness in the choice of $f_{ss}(\mathbf{r}',\mathbf{r})$ has relatively little influence on key quantities such as the total energy or the one-particle density.

Within the above approximation [(62a)], the dependence of $f_{s's}(\mathbf{r}',\mathbf{r})$ on the eigenstate becomes particularly transparent. Since $\rho_s(\mathbf{r})$ depends on the eigenstate in question, the sum rule (61) forces $f_{ss}(\mathbf{r}',\mathbf{r})$ to adjust accordingly.

A possible choice of the analytical form of $f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|)$ is, for example, a Lorentzian,

$$f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|)=\{1+[\,|\mathbf{r}'-\mathbf{r}|/r_s(\mathbf{r})]^2\}^{-1}\ , \qquad (63)$$

which conforms to conditions (59a) and (59c). Its width $r_s(\mathbf{r})$ is, for any $\mathbf{r}$, uniquely determined by the sum rule (61). Another expression of similar properties is due to Gunnarsson and Jones.[18] These authors suggest a non-spin-dependent form of the correlation factor whose usefulness for electronic structure calculations of semiconductors has been tested by several groups.[9,15] The expression put forward by Alonso and Girifalco[19] is identical to that obtained for the homogeneous electron gas, viz.,

$$f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|)=[3j_1(x)/x]^2\ , \qquad (64a)$$

where

$$x=(2/9\pi)^{1/3}\,|\mathbf{r}'-\mathbf{r}|\,/r_s(\mathbf{r})\ , \qquad (64b)$$

and $j_1(x)$ denotes the spherical Bessel function of index 1. If $\rho(\mathbf{r})$ is a constant, r_s represents the familiar Wigner-Seitz radius; otherwise $r_s(\mathbf{r})$ is determined via the sum rule (61). Expression (64a) has been successfully applied to electronic structure calculations on metals by Przybylski and Borstel.[20] The present author and co-workers[13,14] have intensively studied another type of correlation factor which represents expression (63) to the $\frac{5}{2}$ power. The results obtained for a series of free atoms are, by and large, very satisfactory. Apart from the total energies, and first and second ionization potentials, arrived at, there is also a noticeable gain in accuracy regarding the electron affinities and the *s*-*d* transfer energies for transition metals. Moreover, certain types of excited states are well described.[14]

Obviously, all the expressions for $f_{ss}(\mathbf{r}',\mathbf{r})$ that have so far been used in practical calculations suffer from a fundamental deficiency in that they have the common form (62a), which is obviously not symmetric with respect to $\mathbf{r}'$ and $\mathbf{r}$. This conflicts with the general property of $f_{ss}(\mathbf{r}',\mathbf{r})$ as established by (50a) and (51). Curiously, the numerical results appear to indicate that this inconsistency gives rise to only minor effects, which at the present level of approximation are still far from being relevant. On the other hand, the characteristic asymmetry of (62a) renders this class of correlation factors readily accessible to finding the functional derivative $\delta f_s/\delta\rho_s$ (see Gollisch *et al.*[17] and Gunnarsson *et al.*[21]). Once the analytical form of $f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|)$ has been chosen, the expressions

$$P_s(\mathbf{r}',\mathbf{r})=\delta f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|)/\delta r_s(\mathbf{r})$$

and

$$p_s(\mathbf{r})=\int \rho_s(\mathbf{r}')P_s(\mathbf{r}',\mathbf{r})d^3r'$$

are known functions. By employing the sum rule (61) it is easy to show then that $\tilde{\varepsilon}_{xc}^{(s)}(\mathbf{r})$ in (58c) can be cast in the form

$$\tilde{\varepsilon}_{xc}^{(s)}(\mathbf{r})=\int \rho_s(\mathbf{r}')C_s(\mathbf{r}')[f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|)/p_s(\mathbf{r}')]d^3r'\ ,$$

where

$$C_s(\mathbf{r})=-\frac{1}{2}\int \frac{\rho_s(\mathbf{r}')P_s(\mathbf{r}',\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d^3r'\ .$$

Since $\varepsilon_{xc}^{(s)}(\mathbf{r})$ only depends on $f_s(r_s(\mathbf{r}),\ |\mathbf{r}'-\mathbf{r}|)$, the exchange-correlation potential (58c) is obviously completely determined. Potentials thus constructed have the important property that

$$\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} U_{xc}^{(s)}(\mathbf{r})=-1/r \qquad (65)$$

if $\mathbf{r}'$ and $\mathbf{r}=0$ are internal points of an atom, a molecule, or a cluster. The relatively satisfactory results on electron-affinity energies[13] are directly connected with this asymptotic behavior of $U_{xc}^{(s)}(\mathbf{r})$. On the other hand, the long-tail form of $U_{xc}^{(s)}(\mathbf{r})$ is a consequence of the asymptotic behavior of $f_{ss}(\mathbf{r}',\mathbf{r})$. If one inserts (59c) into (54b), one immediately arrives at (65).

It is interesting to consider the analogous case of a metal which fills a semispace with a planar surface perpendicular to the z direction. We again choose $\mathbf{r}'$ to be an internal point and $\mathbf{r}=0$ a point at the surface. If one moves $\mathbf{r}$ along the z direction away from the surface, one may—for sufficiently large distances—use the asymptotic form (59c) for $f_{ss}(\mathbf{r}',\mathbf{r})$. The quantity $\rho_s(\mathbf{r})f_{ss}(\mathbf{r}',\mathbf{r})$, which represents the exchange-hole charge density, becomes proportional, then, to $\rho_s(\mathbf{r}')$, which means that the exchange hole spreads out over the entire metal. Hence, $U_{xc}^{(s)}(\mathbf{r})$ tends, outside the metal, to a constant, and cannot exhibit any image-potential behavior. This clearly reflects the limited applicability of assumption (62b). If we allow $f_{s's}(\mathbf{r}',\mathbf{r})$ for $s'\neq s$ to be finite, the associated correlation hole charge density $\rho_{s'}(\mathbf{r}')f_{s's}(\mathbf{r}',\mathbf{r})$ integrates the zero according to (61), and hence gives rise to a dipolelike contribution to $U_{xc}^{(s)}(\mathbf{r})$, which just constitutes the image potential. This interrelationship between electron correlation and image potential has recently been studied in detail by Mohammed and Sahni.[22] Similar considerations apply to atoms, molecules, and clusters regarding the occurence of an additional term proportional to r^4 emerging from $U_{xc}^{(s)}(\mathbf{r})$.

An approximation to $U_{\mathrm{xc}}^{(s)}(\mathbf{r})$ which is even cruder than that based on (62a) and (62b) consists of the following assumption: If $\rho_s(\mathbf{r}')$ does not vary too strongly within a sphere of radius $r_s(\mathbf{r})$ around $\mathbf{r}$, it will be sufficient to replace it by a first-order Taylor polynomial,

$$\rho_s(\mathbf{r}')=\rho_s(\mathbf{r})+\nabla\rho_s(\mathbf{r})\cdot(\mathbf{r}'-\mathbf{r}) \ . \tag{66}$$

If this is inserted into the sum rule (61) one obtains, by employing (62a) and (62b) and (64a) and (64b),

$$\frac{4\pi}{3}r_s^3(\mathbf{r})\rho_s(\mathbf{r})=1 \ .$$

Using the same approximation in evaluating (54b), one arrives at

$$U_{\mathrm{xc}}^{(s)}(\mathbf{r})=-\tfrac{3}{2}\alpha(3/\pi)^{1/3}[2\rho_s(\mathbf{r})]^{1/3}, \quad \alpha=\tfrac{2}{3} \ . \tag{67}$$

This expression is familiar from the theory of the homogeneous electron gas and is usually referred to as a "local" approximation to $U_{\mathrm{xc}}^{(s)}(\mathbf{r})$ since it depends solely on the local value of ρ_s attained at $\mathbf{r}$. It should be noted that the above derivation explicitly accounts for inhomogeneity which, in fact, is far from being weak in realistic systems. Nevertheless, the gradient term in (66) does not give any contribution within the present approximation. This is one of the major reasons for the unexpected success of the above "local" potential and other forms containing corrections to (67). (Widely used versions of the latter type are due to von Barth and Hedin[23] and to Gunnarsson and Lundqvist.[24])

Clearly, the assumption underlying the above derivation cannot possibly apply to few electron atoms, of which hydrogen represents an extreme example. In these cases $r_s(\mathbf{r})$ is comparable to or larger than the respective atomic radius and (66) can no longer hold. The same can be said regarding the peripheral region of many-electron atoms, molecules, and low-density regions of solids (predominately those with covalent bonds). As soon as the use of (66) is no longer justified, "nonlocal" effects become important, which are reflected in the $(\mathbf{r}',\mathbf{r})$ dependence of the exchange and correlation hole density $\rho_s(\mathbf{r}')f_{s's}(\mathbf{r}';\mathbf{r})$. The actual "nonlocality" of $U_{\mathrm{xc}}^{(s)}(\mathbf{r})$ in the sense defined gives rise to interatomic correlation, which is known to be nonnegligible in many cases. Hence, the plethora of results obtained in the past with the use of local potentials $U_{\mathrm{xc}}^{(s)}(r)$ should generally be taken with some reservation.

IV. EXCITATIONS

As already stated in Sec. II the total energy in any eigenstate is equal to $\frac{1}{2}\langle U\rangle$; that is,

$$E=\tfrac{1}{2}\sum_s \int \rho_s(\mathbf{r})[U_{\mathrm{ext}}(\mathbf{r})+\tfrac{1}{2}U_H(\mathbf{r})+\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})]d^3r \ . \tag{68a}$$

The spin-dependent density is given by

$$\rho_s(\mathbf{r})=\sum_{k=1}^{N_s}|\psi_{ks}(\mathbf{r})|^2 \ . \tag{68b}$$

The ground state is associated with one-particle states $\psi_{ks}(\mathbf{r})$ whose energies ε_{ks} are the N_s lowest consecutive eigenvalues of (54a). In the following we limit ourselves to closed-shell—type states which can be described by a single-configuration wave-function component $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$. We shall use the subscript 0 for quantities referring to the ground state and subscript 1 for denoting excited eigenstates. Excitation energies $\Delta E=E_1-E_0$ for atoms, molecules, and clusters may be obtained by performing standard ΔSCF calculations (SCF denotes self-consistent field) within the framework of Eqs. (54a) and (68a) and (68b). In the case of extended periodic systems the total energies E_0 and E_1 can, of course, no longer be calculated individually. A possible way of directly determining ΔE follows.

The primary charge-density change characterizing the transition is given by

$$\Delta\rho_s(\mathbf{r})=|\psi_{fs}(\mathbf{r})|^2-|\psi_{is}(\mathbf{r})|^2 \ , \tag{69a}$$

where the subscripts f and i refer to the state which is filled or depleted, respectively. For simplicity we disregard transitions involving spin flip. If we recalculate $U_H(\mathbf{r})+U_{\mathrm{xc}}^{(s)}(\mathbf{r})$ for the new charge density,

$$\rho_s'(\mathbf{r})=\rho_s(\mathbf{r})+\Delta\rho_s(\mathbf{r}) \ ,$$

and solve (54a), we obtain new, slightly distorted states $\widetilde{\psi}_{ks}(\mathbf{r})$ and, according to (68b), a new density $\widetilde{\rho}_s(\mathbf{r})$ which is a functional of $\Delta\rho_s(\mathbf{r})$. Hence, the modified change of the charge density is given by

$$\Delta\widetilde{\rho}_s(\mathbf{r})=\Delta\rho_s(\mathbf{r})+\{\widetilde{\rho}_s[\Delta\rho_s(\mathbf{r})]-\rho_s'(\mathbf{r})\} \ .$$

Since the states for $s'\neq s$ change as well, we have, in general, for $s'=\pm 1$,

$$\Delta\widetilde{\rho}_{s'}(\mathbf{r})=\delta_{s's}\Delta\rho_s(\mathbf{r})+\{\widetilde{\rho}_{s'}[\Delta\rho_s(\mathbf{r})]-\rho_{s'}'(\mathbf{r})\} \ , \tag{69b}$$

which, again, is a functional of $\Delta\rho_s(\mathbf{r})$. Within the limits of a linear-response behavior of the electronic system, this functional has the property

$$\Delta\widetilde{\rho}_{s'}[\lambda\Delta\rho_s(\mathbf{r})]=\lambda\Delta\widetilde{\rho}_{s'}[\Delta\rho_s(\mathbf{r})] \ , \tag{70}$$

where λ is some real number.

Using (68a) and (47a) we may cast ΔE in the form

$$\Delta E=\tfrac{1}{2}\sum_{s'}\int_V \Delta\widetilde{\rho}_{s'}(\mathbf{r})U_{s'}(\mathbf{r})d^3r \ , \tag{71a}$$

where

$$U_{s'}(\mathbf{r})=U_{\mathrm{ext}}(\mathbf{r})+U_H(\mathbf{r})+U_{\mathrm{xc}}^{(s')}(\mathbf{r}) \ , \tag{71b}$$

and $\Delta\widetilde{\rho}_{s'}(\mathbf{r})$ is given by (69a) and (69b). In forming ΔE we have used (47a), setting $\delta\rho_s(\mathbf{r})=\Delta\rho_s(\mathbf{r})$. This implies that the change $\Delta f_{s's}(\mathbf{r}',\mathbf{r})$ can be calculated as if it were caused by a change $\Delta\rho_s(\mathbf{r})$ resulting from a variation of the ground-state wave function. We assume this to be approximately true. Hence, $U_{s'}(\mathbf{r})$ refers to the ground state.

Equation (71a) holds to first order in $\Delta\widetilde{\rho}_{s'}(\mathbf{r})$. The integrals on the right-hand side extend over the volume of the crystal under study. The integrands have lattice periodicity, and hence we may rewrite (71a) in the form

$$\Delta E=\tfrac{1}{2}\sum_{s'}\int_\Omega \Delta\widetilde{\rho}_{s'}^{(\Omega)}(\mathbf{r})U_{s'}(\mathbf{r})d^3r \ , \tag{72}$$

where Ω is the volume of the lattice cell and $\Delta\rho_{s'}^{(\Omega)}(\mathbf{r})$ is defined as

$$\Delta\tilde{\rho}_{s'}^{(\Omega)}(\mathbf{r})=N_c\Delta\tilde{\rho}_{s'}(\mathbf{r}) ,$$

with N_c standing for the number of lattice cells.

As long as (70) holds, $\Delta\tilde{\rho}_s^{(\Omega)}(\mathbf{r})$ may be calculated from (69b), where $\Delta\tilde{\rho}_s^{(\Omega)}(\mathbf{r})$ is given according to (69a), but with the states $\psi_{fs}(\mathbf{r})$ and $\psi_{is}(\mathbf{r})$ now renormalized to unity with respect to the lattice cell. Since the magnitude of $\Delta\tilde{\rho}_s^{(\Omega)}(\mathbf{r})$ is of the order of charge-density changes for intra-atomic transitions, there should be no problem in calculating the associated new charge density $\tilde{\rho}_{s'}^{(\Omega)}(\mathbf{r})$ needed to determine $\Delta\tilde{\rho}_{s'}^{(\Omega)}(\mathbf{r})$ in (72). Work in this direction is under way.

In order to find a relation between ΔE and $\varepsilon_f-\varepsilon_i$, we rewrite (71a) using (69b),

$$\Delta E=\tfrac{1}{2}\int_\Omega \Delta\rho_s^{(\Omega)}(\mathbf{r})U_s(\mathbf{r})d^3r+\Delta' , \tag{73a}$$

where

$$\Delta'=\tfrac{1}{2}\sum_{s'}\int_\Omega \{\tilde{\rho}_{s'}[\Delta\rho_s^{(\Omega)}(\mathbf{r})]-\rho_{s'}^{(\Omega)'}(\mathbf{r})\}\,U_{s'}(\mathbf{r})d^3r . \tag{73b}$$

From (54a) and (71b) we have

$$\int_\Omega |\psi_{ks}(\mathbf{r})|^2\,U_s(\mathbf{r})d^3r=\varepsilon_{ks}-T_{ks} , \tag{74}$$

where T_{ks} is the one-particle expectation value of the kinetic energy and $\psi_{ks}(\mathbf{r})$ is normalized to unity with respect to the lattice cell. If we take (74) for $(k,s)=i$ and $(k,s)=f$, form the difference of the two equations, and insert the result into (73a), we obtain

$$E=(\varepsilon_f-\varepsilon_i)+\Delta ,$$

where

$$\Delta=\tfrac{1}{2}\sum_{s'}\int [\Delta\rho_{s'}^{(\mathrm{resp})}(\mathbf{r})-\delta_{s's}\Delta\rho_{s'}^{(\Omega)}(\mathbf{r})]\times U_{s'}(\mathbf{r})d^3r-(T_f-T_i) \tag{75}$$

is the gap correction and

$$\Delta\rho_{s'}^{(\mathrm{resp})}(\mathbf{r})=\{\tilde{\rho}_{s'}[\Delta\rho_s^{(\Omega)}(\mathbf{r})]-\rho_{s'}^{(\Omega)'}(\mathbf{r})\} .$$

Unfortunately, expression (75) is not very illuminating. It appears difficult to understand how the first term can systematically cancel T_f-T_i, which—according to general experience—is approximately true for many metals.

There is an alternative derivation of (75) which takes advantage of (35a). If one wants to integrate this expression for δE over a finite variation of two occupation numbers (n_i and n_f), starting the integration at $E=E_0$ and ending it at the energy E_1 of an excited eigenstate, one is no longer justified in setting $\delta\langle\tilde{T}_{e\text{-}e}\rangle$ equal to zero. We thus have

$$\delta E=\varepsilon_f\,\delta n_f+\varepsilon_i\,\delta n_i+\delta\langle\tilde{T}_{e\text{-}e}\rangle . \tag{76}$$

In an extended system ε_f and ε_i do not depend on a finite variation of the occupation numbers. Moreover, since $n_f+n_i=1$, we have

$$\delta n_i=-\delta n_f .$$

Hence, the integration of (76) with respect to n_f from 0 to 1 yields

$$\Delta E=(\varepsilon_f-\varepsilon_i)+\Delta ,$$

where

$$\Delta=\Delta\langle\tilde{T}_{e\text{-}e}\rangle .$$

This result, together with (75), confirms our previous statement that the kinetic correction reflects the specific way in which a solid responds to the density change $\Delta\rho_s(\mathbf{r})$ occurring in a transition. It should be noticed, however, that $[\tilde{\rho}_{s'}(\mathbf{r})-\rho_{s'}^{(\Omega)'}(\mathbf{r})]$ in (73b) integrates to zero within the lattice cell. The magnitude of its amplitude is therefore not necessarily correlated with the magnitude of Δ'.

Despite the capability of the present theory to describe excitations, the quantitative treatment of optical transitions, for example, is only possible within certain approximations. First of all, it appears that transition rates and related quantities are accessible only by resorting to Fermi's golden rule. Secondly, the associated transition matrix elements M_{fi} require the true wave functions $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ for the respective eigenstates to be known, whereas our scheme only provides their first components, $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$. It appears to be very likely, however, that the matrix elements formed with the true wave function and with the ϕ's, respectively, differ very little. On the other hand, measurements on oscillator strengths involving these matrix elements are usually performed with relatively limited accuracy, so that the errors introduced by approximately forming the matrix elements with the ϕ's may even be smaller than the experimental errors. If the two Slater determinants $\phi_f(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ and $\phi_i(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ differ in the one-particle states $\psi_{fs}(\mathbf{r})$ and $\psi_{is}(\mathbf{r})$, the optical matrix element attains the simple form

$$M_{fi}\propto\int\psi_{fs}^*(\mathbf{r})\mathbf{A}\cdot\nabla\psi_{is}(\mathbf{r})d^3r ,$$

where $\mathbf{A}$ denotes the vector potential of the radiation field. This expression for M_{fi} has, without justification, often been used in the literature (see, e.g., Benbow and Smith[25]). Calculations on the optical absorption of various metals (Mo, W, Pd, and Pt) have successfully been carried out within the above scheme by Eckardt.[26]

We now turn to the problem of thermal excitations in interacting N-electron systems. As already stated in Sec. II degenerate states $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ are characterized by associated Slater determinants $\phi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ which differ in degenerate one-particle states. To simplify the notation we shall, in the following, drop the spin index. Furthermore, we use an index α for a group of degenerate one-particle states and the index i to label the associated one-particle energy. The degeneracy of a one-particle level, ε_i, will be denoted by g_i. As the interaction between the system under study and the heat bath is turned on, transitions into excited states $\Psi_1(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ occur. Slater determinants $\phi_1(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ which differ only in states $\psi_{i\alpha}(\mathbf{r})$ for fixed i will appear with some probability $\bar{n}_i<1$. This refers to an average number $\bar{n}_i g_i$ of occupied degenerate states $\phi_1(\mathbf{q}_1,q_2,\ldots,\mathbf{q}_N)$. Hence, the entropy of the system is given by

$$S=k_B\ln\Gamma , \tag{77a}$$

where

$$\ln\Gamma = \sum_i \ln\Gamma_i \tag{77b}$$

and

$$\Gamma_i = g_i!/(\bar{n}_i g_i)!(g_i - \bar{n}_i g_i)! \ . \tag{77c}$$

The quantity k_B denotes Boltzmann's constant. From (77a)–(77c) we obtain

$$T\,\delta S = -k_B T \sum_i \{\ln(g_i \bar{n}_i) - \ln[g_i(1-\bar{n}_i)]\} g_i\,\delta\bar{n}_i \ , \tag{78a}$$

where T is the temperature of the heat bath.

The variation of the total energy is, according to (35a),

$$\delta\bar{E} = \sum_{i,\alpha} \varepsilon_i\,\delta\bar{n}_{i\alpha} \ . \tag{78b}$$

The occupation numbers $\bar{n}_{i\alpha}$ and $\bar{n}_i$ are connected through

$$\bar{n}_i g_i = \sum_{\alpha=1}^{g_i} \bar{n}_{i\alpha} \ , \tag{79a}$$

where

$$\sum_{i,\alpha} \bar{n}_{i\alpha} = N \ . \tag{79b}$$

Writing $\delta\bar{E}$ in the form (78b) implies that we assume the corresponding variation $\delta\langle \tilde{T}_{e\text{-}e}\rangle$ to be negligibly small, as is approximately true for many metals. Within our theory it is absolutely crucial that the number of particles is a constant. Hence, we have, from (79a) and (79b),

$$\sum_i g_i\,\delta\bar{n}_i = 0 \ . \tag{80}$$

Requiring the free energy $F = \bar{E} - TS$ to attain a minimum under the constraint (80), and using expressions (78a) and (78b), we are led to

$$\sum_i \left[\varepsilon_i + \frac{1}{\beta} \ln \left[\frac{\bar{n}_i}{1-\bar{n}_i} - \mu \right] \right] g_i\,\delta\bar{n}_i = 0 \ ,$$

where

$$\beta = 1/k_B T \ ,$$

and μ denotes a Lagrange multiplier.

Obviously, the expression in large parentheses must vanish, and then rewritten as

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \ . \tag{81}$$

We have thus arrived at the Fermi distribution function for an interacting electron system having a fixed particle number N. It is obvious from our derivation that (78b) constitutes a key equation which can neither be obtained from Kohn-Sham theory nor from the Hartree-Fock approximation. The latter theories deal with occupation numbers which are strictly unity. On the other hand, our derivation crucially depends on the one-to-one correspondence between $\phi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ and $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$; otherwise we would not be able to clearly define the "thermodynamical probability" Γ by use of (77b) and (77c). The above derivation is due to Slater,[27] who justifies the use of Eq. (78b) by heuristic considerations. This applies similarly to Landau's derivation of (81) in his paper on Fermi-liquid theory.[28]

V. SUMMARY

We have shown that an extension of the Kohn-Sham theory to excited states is possible without losing its striking advantages regarding the relatively simple numerical techniques required to solve the relevant one-particle equations. A concomitant virtue of the new approach is that it elucidates the interrelationship between the Kohn-Sham theory and conventional N-electron theory developed primarily in quantum chemistry. It becomes evident from this interrelation that the Slater determinant $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, which within the Kohn-Sham theory merely plays the role of an auxiliary construct, has an important physical meaning: it constitutes an optimized component of the true wave function $\Psi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ carrying maximum information on the one- and two-particle densities which can be absorbed into one Slater determinant. The remaining difference, $\tilde{\Psi}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, between the true wave function and the Kohn-Sham wave function does not contribute to the one-particle density and only provides a fine-tuning around the exchange-hole. [The latter represents a massive structure in the two-particle density which is completely modeled by $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$.] In addition, $\tilde{\Psi}(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ gives rise to the correlation hole, which is, again, a weak structure comparable to the "fine-tuning" structure in the exchange part of the two-particle density. This property of $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, viz., that it contains the key information already in the correct order of magnitude, lends strong support to the (so far unjustified) assumption that transition matrix elements may—to a very good approximation—be calculated by using the functions $\phi(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ for the states involved. Another interesting insight gained by our analysis is that the one-particle energies of the Kohn-Sham theory are not just numerical parameters which are relevant only to technical performance of the self-consistent calculations. These energies appear exactly in the Fermi distribution function, and hence they determine the (phonon-undressed) electronic contribution to the specific heat in metals. On the other hand, it can easily be shown that excitation energies for interband transitions in solids are, in general, not given by the difference of the bands involved. It appears that approximate corrections to these differences are readily accessible.

Since our derivation leads to an exchange-correlation potential which—in contrast to the Kohn-Sham theory—is formed with the original (non-λ-averaged) correlation factor, it will presumably be easier to find ways of systematically improving the present approximations by consulting quantum-chemical calculations on identical systems.

Finally, the present approach lends itself to a relativistic generalization which allows a consistent treatment of spin ordering in the presence of spin-orbit coupling. This extended scheme has successfully been applied to ferromagnetically ordered iron and expanded palladium metal. The results will be published elsewhere.

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APPENDIX

We want to show the existence of the integral kernel $\Gamma_n^{(s',s)}(\mathbf{r}'',\mathbf{r}',\mathbf{r})$ defined by

$$\int \Gamma_n^{(s',s)}(\mathbf{r}'',\mathbf{r}',\mathbf{r})\delta\rho_s(\mathbf{r}'')d^3r''=\delta\rho_2^{(s',s)}(\mathbf{r}',\mathbf{r}) .$$

When we introduce here expressions (26) and (27) for $\delta\rho_s(\mathbf{r})$ and $\delta\rho_2^{(s',s)}(\mathbf{r}',\mathbf{r})$, respectively, and observe that the quantities α_{nm} may be chosen at will, we are led to

$$\int \Gamma_n^{(s',s)}(\mathbf{r}'',\mathbf{r}',\mathbf{r})S_{nms}(\mathbf{r}'')d^3r''=S_{nms's}^{(2)}(\mathbf{r}',\mathbf{r}) . \tag{A1}$$

We expand the right-hand side of this equation in terms of a complete set of functions $\chi_i(\mathbf{r})$ which we may identify with one of the sets $\{\psi_{is}(\mathbf{r})\}$ for $s=\pm1$, each of which will, in general, be complete:

$$S_{nms's}^{(2)}(\mathbf{r}',\mathbf{r})=\sum_{k,l} a_{mn}^{(k,l),(s',s)}\chi_k(\mathbf{r}')\chi_l(\mathbf{r}) .$$

Likewise,

$$\Gamma_n^{(s',s')}(\mathbf{r}'',\mathbf{r}',\mathbf{r})=\sum_{m'}\sum_{k,l} A_{m'n}^{(k,l),(s's)}\chi_k(\mathbf{r}')\chi_l(\mathbf{r})\chi_{m'}(\mathbf{r}'') .$$

Substituting these expansions into (A1), we obtain

$$\sum_{k,l}\left[\sum_{m'} A_{m'n}^{(k,l),(s',s)}M_{mm'n}^{(s)}\right]\chi_k(\mathbf{r}')\chi_l(\mathbf{r}) =\sum_{k,l} a_{mn}^{(k,l),(s',s)}\chi_k(\mathbf{r}')\chi_l(\mathbf{r}) ,$$

where

$$M_{mm'n}^{(s)}=\int S_{nms}(\mathbf{r}'')\chi_{m'}(\mathbf{r}'')d^3r''$$

are known quantities which form a matrix for each n,s given. The above equation requires

$$\sum_{m'} A_{m'n}^{(k,l),(s',s)}M_{mm'n}^{(s)}=a_{mn}^{(k,l),(s',s)} .$$

These linear inhomogeneous equations may be solved for the coefficients $A_{m'n}^{(k,l),(s',s)}$ which determine the integral kernel in question. The matrix defined by the quantities $M_{mm'n}^{(s)}$ is well behaved since the functions $S_{nms}(\mathbf{r})$ represent overlap densities between eigenstates Ψ_n and Ψ_m. Hence, the m-dependent upper bounds of their absolute values will, in general, form a rapidly convergent sequence. The same applies to the m' dependence of $M_{mm'n}^{(s)}$ if the functions $\chi_{m'}(\mathbf{r})$ are ordered according to increasing values of their associated one-particle energies. The existence of a solution to the above infinite system of linear equations is, for the ground state, ensured by the Kohn-Sham theory. Since the principal structure of the matrix $M_{mm'n}^{(s)}$ is not different in an excited state, there must always be a solution to these equations.

It should be noticed that these equations elucidate another important feature of $\Gamma_n^{(s)}(\mathbf{r}'',\mathbf{r}',\mathbf{r})$: The information contained in this function obviously comprises the full set of eigenstates $\Psi_m(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$. Although it is possible to obtain $\varepsilon_{\mathrm{xc}}^{(s)}(\mathbf{r})$ from $\Psi_n(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ alone, $U_{\mathrm{xc}}^{(s)}(\mathbf{r})$ requires the information on the full Hilbert space.

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[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[2] See, e.g., O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976). These authors present a generalization of the Kohn-Sham theory to lowest excited states of each symmetry.

[3] L. Hedin, Phys. Rev. **139**, A796 (1965). The effective one-particle equations given in this paper were independently discussed later by L. J. Sham and W. Kohn, Phys. Rev. **145**, 561 (1966).

[4] M. S. Hybertsen and G. S. Louie, Solid State Commun. **51**, 451 (1984); Phys. Rev. B **30**, 5777 (1984).

[5] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[6] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977). The derivation given by these authors is similar to that of J. Harris and R. O. Jones [J. Phys. F **4**, 1170 (1974)]. The idea of averaging the electronic Coulomb interaction energy over the coupling strength had been discussed before by D. Pines and P. Nozières, in *The Theory of Quantum Fluids I* (Benjamin, New York, 1966), and by C. O. Almbladh (unpublished).

[7] We use a definition for $\mathcal{f}(\mathbf{r}',\mathbf{r})$ which differs in sign from that introduced by McWeeny (Ref. 8).

[8] R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

[9] F. Manghi, G. Riegler, C. M. Bertoni, and G. B. Bachelet, Phys. Rev. B **31**, 3680 (1985).

[10] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[11] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[12] In previous papers by the present author and associates [see Fritsche and Gollisch (Ref. 13) and Fritsche *et al.* (Ref. 14)] it has erroneously been assumed (but not explicitly been stated) that (18c) requires the matrix elements $\tilde{D}_{ij}^{(s)}$ to be zero, as a consequence of which $\langle \tilde{T}_{e\text{-}e}\rangle$ would vanish. Nevertheless, the total-energy expression arrived at in these papers is approximately correct as $\langle \tilde{T}_{e\text{-}e}\rangle$ represents a relatively small contribution to the total energy E. Moreover, the order of magnitude of this contribution compares to that of other errors typical of approximations to $\varepsilon_{\mathrm{xc}}(\mathbf{r})$ and $U_{\mathrm{xc}}(\mathbf{r})$ applied within the Kohn-Sham theory.

[13] L. Fritsche and H. Gollisch, Z. Phys. B **48**, 209 (1982); in *Local Density Approximations in Quantum Chemistry and Solid State Physics* (Plenum, New York, 1984).

[14] L. Fritsche, J. Noffke, and H. Gollisch, J. Phys. B. **17**, 1637 (1984).

[15] P. Krüger, G. Wolfgarten, and J. Pollmann, Solid State Commun. **53**, 885 (1985).

[16] We could alternatively obtain functions $\Psi_n'(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ and $\phi_n'(\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$ by applying an external perturbational potential and by simultaneously enlarging or reducing the coupling strength λ of the electron-electron interaction in a suitable way so that $\delta\langle \tilde{T}_{e\text{-}e}\rangle=0$.

[17] H. Gollisch, J. Cordes, and L. Fritsche (unpublished).

[18] O. Gunnarsson and R. O. Jones, Phys. Scr. **21**, 394 (1980).

[19] J. A. Alonso and L. A. Girifalco, Phys. Rev. B **17**, 3735 (1978).

[20] H. Przybylski and G. Borstel, Solid State Commun. **49**, 317 (1984).

[21] O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B **20**, 3136 (1979).

[22] Abdel-Raouf E. Mohammed and V. Sahni, Phys. Rev. B **31**, 4879 (1985).

[23] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[24] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[25] R. L. Benbow and N. V. Smith, Phys. Rev. B **27**, 3144 (1983).

[26] H. Eckardt, Ph.D. thesis, Technische Universität Clausthal, 1984.

[27] J. C. Slater, in *Advances in Quantum Chemistry*, edited by P. O. Löwdin (Academic, New York, 1972), p. 1.

[28] L. D. Landau, Zh. Eksp. Teor. **30**, 1058 (1956) [Sov. Phys.—JETP **3**, 920 (1956)].