Exact results for the charge and spin densities, exchange-correlation potentials, and density-functional eigenvalues

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We derive asymptotically exact results for the charge and spin densities far away from finite systems (atoms and molecules) and far outside solid surfaces. These results are then used to obtain the correct asymptotic form of the exchange-correlation potential of density-functional (DF) theory and to prove that, for all systems, the eigenvalue of the uppermost occupied DF orbital equals the exact ionization potential. For spin-polarized finite systems we show that the uppermost DF eigenvalue in each spin channel is also given by exact excitation energies.

I. INTRODUCTION

Density-functional (DF) theory as formulated by Hohenberg, Kohn, and Sham[1,2] is, in principle, an exact scheme of the ground-state properties of electronic systems. The main problem within this theory lies in finding adequate approximations for that functional of the particle density that describes the effects of exchange and correlation. Fortunately, even the simplest possible, but widely used, local-density (LD) approximation produces very useful and quantitatively accurate results for the ground-state properties of solids. The great appeal of DF theory lies in the fact that it leads to an effective one-particle scheme, which makes it computationally feasible to treat exchange and correlation effects in quite complicated systems. It has often been stressed in the literature[3] that the resulting one-particle energy eigenvalues are not be identified with excitation energies. Nevertheless, the majority of all photoemission spectra are interpreted in terms of these eigenvalues, as they are obtained by the use of the LD approximation. Therefore, it would clearly be interesting to investigate the limitations of such interpretations. Unfortunately, very little theoretical work has been done towards this end. Only recently, in two review articles,[4,5] has the importance of such research been emphasized. In this context we can clearly identify two issues: (i) the relations between the exact excitation energies and the one-particle eigenvalues of the exact DF theory, and (ii) the effect of the LD approximation on the DF eigenvalues. In the present paper we will address the first issue and will limit ourselves to finite systems, except for an analysis of the effective one-electron potential far outside a solid surface.

We will show here, for the first time, that, for any system, the uppermost occupied DF eigenvalue is identical to the exact ionization potential. Our proof makes use of the fact that the effective one-particle scheme of DF theory gives the exact ground-state charge density, whose behavior far away from the system is, therefore, determined by the highest occupied DF eigenvalue. Quite independently of DF theory, we then derive the same asymptotic form of the density directly from the many-electron Hamiltonian and find an exponential decay with an exponent simply related to the ionization potential.

This allows us to identify the latter with the uppermost occupied DF eigenvalue. The correct exponential decay of the density has been known for some time,[6,7] but the connection to the one-particle eigenvalues has not been made earlier. Our method actually gives the exact asymptotic form of the density matrix. We find this result quite interesting *per se*. For instance, a slight modification of our technique allows us to conclude that most ground-state properties such as the natural orbitals or the density response function have a characteristic decay length far away from the system which is given by the ionization potential.

The asymptotic expansion of the density can be carried out further in order to include terms of higher order in reciprocal distance. This enables us to show for the first time that the exact exchange-correlation potential v_{xc} has the asymptotic form that one would expect from classical arguments. We use a similar technique to show that v_{xc} far outside a solid surface is given by the classical image potential. This result has independently been obtained by Langreth[8] using an entirely different method based on an exact expression for v_{xc} in terms of the pair-correlation function, and by Sham[9] using yet another technique.

In Sec. II we demonstrate the basic ideas by deriving the exact asymptotic form of the density profile, and of v_{xc}, for a finite system with a nondegenerate ground state. In Sec. III we generalize to spin-polarized systems, and show that for systems having a single electron outside closed shells (such as Na), the uppermost DF eigenvalue of the majority-spin channel gives the ionization potential, whereas the uppermost DF eigenvalue of the minority-spin channel gives an excitation energy corresponding to the lowest possible final $(N-1)$-electron state of triplet symmetry. Once the basic ideas have been understood, it is relatively easy to apply them to more complicated cases, such as systems with higher spin and orbital degeneracies. Solid surfaces are considered in Sec. IV, and in Sec. V, finally, we give some concluding remarks.

II. SYSTEMS WITH A NONDEGENERATE N-ELECTRON GROUND STATE

We first introduce a general theoretical and notational framework, and then specialize to finite systems with a

nondegenerate ground state. Throughout this paper we consider nonrelativistic systems without spin-orbit interactions. We write the many-electron Hamiltonian in second-quantized form:

$$H = \int dx\, \psi^\dagger(x)[-\tfrac{1}{2}\nabla^2 + w(x)]\psi(x)$$
$$+ \tfrac{1}{2}\int dx \int dx'\, \psi^\dagger(x)\psi^\dagger(x')v(\mathbf{r}-\mathbf{r}')\psi(x')\psi(x) . \quad (1)$$

In Eq. (1), x is shorthand for a space variable $\mathbf{r}$ and a spin index σ $(\sigma = \pm 1)$, $\int dx = \sum_\sigma \int d^3r$, $\psi(x)$ is the electron-field operator which annihilates an electron of spin σ at the point $\mathbf{r}$, $v(\mathbf{r}) = 1/r$ is the Coulomb interaction, and $w(x)$ is the "external" potential which, in our case, is the spin-independent potential from the nuclei. We use atomic units, i.e., we choose $\hbar = m = e^2/(4\pi\epsilon_0) = 1$.

We also write the spin-density matrix $\gamma(x,x')$ in second-quantized form,

$$\gamma(x,x') = \langle N \mid \psi^\dagger(x')\psi(x) \mid N \rangle , \quad (2)$$

$|N\rangle$ being an N-electron ground state. When $|N\rangle$ is an eigenstate of the spin operators $\mathbf{S}^2$ and S_z, $\gamma(x,x')$ is diagonal in spin indices:

$$\gamma(x,x') = \gamma_\sigma(\mathbf{r},\mathbf{r}')\delta_{\sigma\sigma'} . \quad (3)$$

We let s enumerate the set of $(N-1)$-electron eigenstates $\{\,|N-1,s\rangle\,\}$, and insert these states in Eq. (2) to obtain

$$\gamma(x,x') = \sum_s f_s(x)f_s^*(x') , \quad (4)$$

where

$$f_s(x) = \langle N-1,s \mid \psi(x) \mid N \rangle . \quad (5)$$

The matrix elements $f_s(x)$ are usually termed quasiparticle amplitudes. These amplitudes are the counterparts for an interacting system of the one-electron orbitals in the case of a noninteracting system. They satisfy a Schrödinger-like equation which we now derive. We form the commutator $[\psi(x),H]$ and take matrix elements between the states $|N\rangle$ and $|N-1,s\rangle$. This gives

$$[-\tfrac{1}{2}\nabla^2 + w(x)]f_s(x) + \langle N-1,s \mid \hat{V}_H(\mathbf{r})\psi(x) \mid N \rangle$$
$$= \epsilon_s f_s(x) , \quad (6)$$

where

$$\epsilon_s = E(N) - E(N-1,s)$$

is an exact one-particle excitation energy. In particular, $-\epsilon_0$ is the ionization potential. The operator

$$\hat{V}_H(\mathbf{r}) = \int d^3r'\, v(\mathbf{r}-\mathbf{r}')\hat{\rho}(\mathbf{r}') \quad (7)$$

gives the electrostatic Hartree potential, and

$$\hat{\rho}(\mathbf{r}) = \sum_\sigma \psi^\dagger(x)\psi(x) \equiv \sum_i \delta(\mathbf{r}-\mathbf{r}_i) \quad (8)$$

is the electron-density operator.

For noninteracting systems, $v(\mathbf{r}) = 0$, and Eq. (6) properly reduces to an independent-electron orbital equation. If $|N\rangle$ and $|N-1,s\rangle$ are approximated by Slater determinants, Eq. (6) becomes a Hartree-Fock orbital equation.

We now specialize to finite systems with a nondegenerate N-electron ground state. Since this ground state $(\,|N\rangle\,)$ is a singlet, the $(N-1)$-electron state $\psi(\mathbf{r},\sigma)|N\rangle$ has spin $S = \tfrac{1}{2}$, $M_S = -\sigma/2$. Consequently, we only need to consider states of this spin in our analysis of the quasiparticle amplitudes [Eq. (6)]. We first consider the case when the $(N-1)$-electron ground level only has the obvious twofold spin degeneracy.

For later applications it will prove convenient to subtract the $(N-1)$-electron ground-state average $\langle N-1 \mid \hat{V}_H \mid N-1 \rangle$ from the Hartree potential operator $\hat{V}_H$ in Eq. (6) and write the last term as

$$\langle N-1,s \mid \hat{V}_H(\mathbf{r})\psi(\mathbf{r},\sigma) \mid N \rangle$$
$$= \langle N-1 \mid \hat{V}_H(\mathbf{r}) \mid N-1 \rangle f_s(\mathbf{r},\sigma) + R , \quad (9)$$

where R involves

$$\delta\hat{V}_H(\mathbf{r}) = \hat{V}_H(\mathbf{r}) - \langle N-1 \mid \hat{V}_H(\mathbf{r}) \mid N-1 \rangle .$$

The explicit form of R is

$$R = \int d^3r'\, v(\mathbf{r}-\mathbf{r}')\langle N-1,s \mid \delta\hat{\rho}(\mathbf{r}')\psi(\mathbf{r},\sigma) \mid N \rangle , \quad (10)$$

where

$$\delta\hat{\rho}(\mathbf{r}) = \hat{\rho}(\mathbf{r}) - \langle N-1 \mid \hat{\rho}(\mathbf{r}) \mid N-1 \rangle .$$

The probability of finding an electron far away from a finite system decays exponentially with distance. Thus, we can confine the $\mathbf{r}'$ integration in Eq. (10) to a finite region, which allows us to make a multipole expansion of the Coulomb interaction $v(\mathbf{r}-\mathbf{r}')$. The monopole term vanishes since the state $\psi(\mathbf{r},\sigma)|N\rangle$ contains $N-1$ electrons. The leading-order term is thus the dipole term, and we have

$$R \sim \frac{1}{r^2}\langle N-1,s \mid \hat{\mathbf{r}}\cdot\mathbf{d}\,\psi(\mathbf{r},\sigma) \mid N \rangle$$
$$= \frac{1}{r^2}\sum_{s'}\langle N-1,s \mid \hat{\mathbf{r}}\cdot\mathbf{d} \mid N-1,s'\rangle f_{s'}(\mathbf{r},\sigma) , \quad (11)$$

where

$$\mathbf{d} = \int \mathbf{r}\delta\hat{\rho}(\mathbf{r})d^3r$$

is the dipole-moment operator, and $\hat{\mathbf{r}} = \mathbf{r}/r$ is a unit vector. [The leading-order term will prove sufficient in order to obtain the density to a relative accuracy $O(r^{-4})$.] We insert this into Eq. (6) and find

$$[-\tfrac{1}{2}\nabla^2 + w(\mathbf{r}) + \langle N-1 \mid \hat{V}_H(\mathbf{r}) \mid N-1 \rangle - \epsilon_s]f_s(x)$$
$$+ \frac{1}{r^2}\sum_{s'}D_{ss'}f_{s'}(x) = 0 . \quad (12)$$

In Eq. (12) we have used $D_{ss'}$ as shorthand for the dipole-moment matrix elements,

$$D_{ss'}(\hat{\mathbf{r}}) = \hat{\mathbf{r}}\cdot\langle N-1,s \mid \mathbf{d} \mid N-1,s'\rangle .$$

Without the inhomogeneous term in Eq. (12), the quasiparticle amplitudes $f_s(x)$ would decay as $\exp(-\kappa_s r)$, where

$$\kappa_s = (-2\epsilon_s)^{1/2} . \quad (13)$$

We notice that $\kappa_s > \kappa_0$ when $s \neq 0$, and that $\kappa_0^2/2 = E(N-1) - E(N)$. Thus, without the inhomogeneous term all amplitudes except the ground-state amplitude (f_0) would decay exponentially faster than $\exp(-\kappa_0 r)$ when $r \to \infty$. For an excited-state amplitude f_s, the inhomogeneous term in Eq. (12) contains f_0, and the decay of f_s is instead determined by f_0. Thus, all terms decay as $\exp(-\kappa_0 r)$.

In order to obtain an asymptotically correct equation involving only the ground-state amplitude f_0, we need a leading-order estimate of the excited-state amplitudes f_s. Since these amplitudes decay exponentially as $\exp(-\kappa_0 r)$, we have, to leading order,

$$(-\tfrac{1}{2}\nabla^2 - \epsilon_s)f_s(x) \sim (\epsilon_0 - \epsilon_s)f_s(x) \ .$$

Furthermore, for large r the external potential w from the nuclei and the Hartree potential $\langle N-1 | \hat{V}_H | N-1 \rangle$ can be dropped in comparison with $\epsilon_0 - \epsilon_s$. This gives

$$(\epsilon_s - \epsilon_0)f_s(x) \sim \frac{1}{r^2} \sum_{s'} D_{ss'} f_{s'}(x)$$

$$\sim \frac{1}{r^2} D_{s0} f_0(x), \quad r \to \infty \tag{14}$$

where the terms coming from excited-state amplitudes in the inhomogeneous part can be dropped since we see that these amplitudes are down by a factor r^{-2} relative to the ground-state amplitude f_0. Thus,

$$f_s(x) \sim -\frac{1}{r^2} \frac{D_{s0}}{\omega_s} f_0(x) \ , \tag{15}$$

where

$$\omega_s = E(N-1, s) - E(N-1)$$

is an excitation energy of the $(N-1)$-electron system. Inserting this into Eq. (12) for the ground-state amplitude gives

$$\left[-\tfrac{1}{2}\nabla^2 + w(x) + \langle N-1 | \hat{V}_H(\mathbf{r}) | N-1 \rangle - \frac{1}{2r^4} \sum_{i,j} \hat{r}_i \hat{r}_j \alpha_{ij} \right] f_0(x) = \epsilon_0 f_0(x) \tag{16}$$

to order r^{-4}. We have here expressed the term

$$\frac{1}{r^2} \sum_{s>0} D_{0s} f_s(x) \sim -\frac{1}{r^4} \sum_s \frac{|D_{s0}|^2}{\omega_s} f_0(x)$$

in the static ground-state polarizability of the $(N-1)$-electron system,

$$\alpha_{ij} = 2 \sum_s \frac{\langle N-1 | d_i | N-1, s \rangle \langle N-1, s | d_j | N-1 \rangle}{\omega_s} \ . \tag{17}$$

In the expression above, i and j denote Cartesian components and $\hat{r}_i$ is a component of the unit vector $\hat{\mathbf{r}}$.

For spherically symmetric systems (atoms), $\langle N-1 | \hat{V}_H(\mathbf{r}) | N-1 \rangle$ is, to exponential accuracy, equal to $(N-1)/r$, and α_{ij} is diagonal, $\alpha_{ij} = \alpha \delta_{ij}$. Equation (16) then simplifies to

$$\left[-\tfrac{1}{2}\nabla^2 + \frac{-Z+N-1}{r} - \frac{\alpha}{2r^4} \right] f_0(x) = \epsilon_0 f_0(x) \ .$$

The asymptotic density matrix may now be written. It follows from Eqs. (4) and (15) that

$$\gamma(x,x') = f_0(x)f_0^*(x')[1 + O(r^{-2}r'^{-2})] \ . \tag{18}$$

It is not difficult to see from Eq. (16) that

$$f_0(x) \sim C r^\beta e^{-\kappa_0 r}(1 + A_1 r^{-1} + A_2 r^{-2}$$

$$+ A_3 r^{-3} + A_4 r^{-4} + \cdots) \ , \tag{19}$$

where $\beta = (Z_N - N + 1)/\kappa_0 - 1$ and Z_N is the total charge of all nuclei. The coefficients $A_1 - A_4$ are uniquely determined by the nuclear and Hartree potentials, and by the ground-state polarizability α_{ij} of the $(N-1)$-electron system. (In general, A_i depends on the angular coordinate $\hat{\mathbf{r}}$.)

In the derivation above we assumed that the asymptotic behavior of the right-hand side (rhs) of Eq. (12) is determined by the term which has the slowest decay, i.e., by the term which involves f_0. This involves some considerations concerning mathematical rigor, which will be discussed in more detail in Sec. IV.

The correct exponential decay [i.e., the exponential prefactor in Eq. (19)], was obtained in 1975 by Levy,[6] and later, and independently, by Katriel and Davidson.[7] An approximate result has also been found by Morrell et al.[10]

We now discuss the implications of the above results to DF theory. According to this theory the ground-state energy and spin-dependent density $n(\mathbf{r}, \sigma)$ [$= \gamma(\mathbf{r}\sigma, \mathbf{r}\sigma)$] of the interacting many-electron system are obtained by minimizing the functional

$$E[n,w] = T_0[n] + \tfrac{1}{2} \int d^3r \int d^3r' \rho(\mathbf{r})\rho(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')$$

$$+ E_{xc}[n] + \int dx\, n(x)w(x) \ , \tag{20}$$

with respect to n while keeping the external potential w and the particle number N fixed. Here, the functionals T_0 and E_{xc} give, respectively, the kinetic energy of noninteracting electrons and the exchange-correlation energy, and $\rho(\mathbf{r}) = \sum_\sigma n(\mathbf{r}, \sigma)$ is the electron density. The variations of E_{xc} with spin-dependent density defines the exchange-correlation potential v_{xc} according to

$$\delta E_{xc} = \int dx\, v_{xc}(x)\delta n(x) \ . \tag{21}$$

As is well known, the minimum of $E[n,w]$ is found from the orbital equations[2]

$$[-\tfrac{1}{2}\nabla^2 + w(x) + V_H(\mathbf{r}) + v_{xc}(x)]\varphi_i(x) = e_i\varphi(x) \ , \tag{22}$$

where V_H is the electrostatic Hartree potential from the ground-state electron density ρ,

$$V_H(\mathbf{r}) = \langle N \mid \hat{V}_H(\mathbf{r}) \mid N \rangle \equiv \int d^3r\, v(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') \ ,$$

and $\{e_i\}$ are the DF eigenvalues. We label the orbitals φ_i such that $e_i \le e_{i+1}$. The spin density is obtained from the self-consistent solution of Eq. (22) by summing the contribution from the N lowest DF orbitals,

$$n(x) = \sum_1^N |\varphi_i(x)|^2 \ . \tag{23}$$

We now focus our attention on the density-functional eigenvalues $\{e_i\}$ in Eq. (22). Obviously, a discussion of these eigenvalues would be meaningless unless the zero of potential energy is defined. From Eq. (21) it follows that variations in the density that keep the particle number fixed only defines v_{xc} to within a constant. Here we follow the normal convention and fix this constant by choosing v_{xc} to be zero at infinity.

In contrast to the quasiparticle amplitudes, the decay of the DF orbitals is governed by their respective eigenvalues. Thus, for large r, we may, to exponential accuracy, keep only the contribution from the uppermost orbital, $\varphi_N(x)$, to the density $n(x)$. From the two different expressions for the density in Eqs. (23) and (18), we conclude that

$$\varphi_N(x) = f_0(x)[1 + O(r^{-4})] \ . \tag{24}$$

By comparing the orbital equations for φ_i [Eq. (22)] and for f_0 [Eq. (16)], we further find that

$$e_N = \epsilon_0 \equiv E(N) - E(N-1) \tag{25}$$

and

$$v_{xc}(\mathbf{r}) = \langle N-1 \mid \hat{V}_H(\mathbf{r}) \mid N-1 \rangle - \langle N \mid \hat{V}_H(\mathbf{r}) \mid N \rangle$$
$$- \frac{1}{2r^4} \sum_{i,j} \hat{r}_i \hat{r}_j \alpha_{ij} \tag{26}$$

to order r^{-4} when $r \to \infty$. This concludes our proof for the case when the $(N-1)$-electron ground states form a spin doublet without orbital degeneracies. The polarizability term in v_{xc} is the same as that one would anticipate on the basis of simple classical arguments (see, e.g., Refs. 4 and 5). The first term in Eq. (26) describes the Fermi hole and gives, to leading order,

$$v_{xc} \sim -1/r, \quad r \to \infty \ .$$

For the special case of an atom with orbitally nondegenerate (and thus spherical) N and $(N-1)$-electron ground states, such as Mg and Mg$^+$, v_{xc} assumes the simple form

$$v_{xc} \sim -1/r - \alpha/2r^4, \quad r \to \infty \ . \tag{27}$$

We conclude this section by sketching the theory for the case of orbitally degenerate $(N-1)$-electron ground states. We assume a g-fold orbital degeneracy in addition to the twofold spin degeneracy and write the $(N-1)$-electron ground states with $M_S = -\sigma/2$ as $\mid N-1, 0, \alpha \rangle$ and the corresponding quasiparticle amplitudes as $f_{0\alpha}$. The analysis can be carried out along rather similar lines as before. We find that, to leading order in $1/r$, the excited-state amplitudes are given by

$$f_s(x) \sim -\frac{1}{r^2\omega_s} \sum_1^g D_{s0\alpha} f_{0\alpha}(x) \ .$$

Inserting this expression in the orbital equation for the ground-state amplitudes [cf. Eq. (12)] gives the following $g \times g$ matrix equation for these amplitudes $(f_{0\alpha})$ in place of Eq. (16):

$$[-\tfrac{1}{2}\nabla^2 + w(\mathbf{r}) - \epsilon_0] f_{0\alpha}(x) + \sum_\beta U_{\alpha\beta}(\mathbf{r}) f_{0\beta}(x) \sim 0 \ , \tag{28}$$

where

$$U_{\alpha\beta}(\mathbf{r}) = \left\langle N-1, 0, \alpha \left| \hat{V}_H(\mathbf{r}) - \frac{1}{2r^4} \mathbf{d} \cdot \hat{\mathbf{r}} \frac{1-P}{H-E(N-1)} \mathbf{d} \cdot \hat{\mathbf{r}} \right| N-1, 0, \beta \right\rangle \tag{29}$$

only involves $(N-1)$-electron ground-state matrix elements of the Hartree potential and the static polarizability. [In Eq. (29), P is the projector on the g $(N-1)$-electron ground states with spin $M_S = -\sigma/2$.] As before, Eq. (28) determines the ground-state amplitudes to within a relative accuracy r^{-3} (inclusive). To leading order, $f_{0\alpha}(x) = r^\beta \exp(-\kappa_0 r)$. The asymptotic spin-density matrix is, in this case,

$$\gamma(x,x') = \sum_1^g f_{0\alpha}(x) f_{0\alpha}^*(x')[1 + O(r^{-2}r'^{-2})] \ . \tag{30}$$

Upon comparison with the DF orbital equations, we find that $e_N = \epsilon_0$. We also obtain an asymptotic expression for v_{xc} correct to order r^{-4}. To leading order, $v_{xc} = -1/r$, as in the orbitally nondegenerate case. In Appendix A we give further details on the construction of v_{xc} in this case.

III. FINITE SPIN-POLARIZED SYSTEMS

We now indicate how our results may be generalized to the case of spin-polarized ground states. As an example we consider the case when the N-electron ground states form a spin doublet without any orbital degeneracy. The systems we have in mind have one electron outside closed shells. More general cases, such as systems with higher spin and orbital degeneracies, are readily analyzed along similar lines as the prototypical case considered here.

We quantize the spin along the z direction and study the ground state $\mid N \rangle$ with $M_S = \frac{1}{2}$. From the commutation relations between the electron-field operator and the spin, one finds that the state $\psi(\mathbf{r}, -1) \mid N \rangle$ is a triplet, whereas the state $\psi(\mathbf{r}, 1) \mid N \rangle$ is a mixture of singlet and triplet states with $M_S = 0$. Since the Hartree potential operator $\hat{V}_H(\mathbf{r})$ conserves spin, only triplet states with

$M_S = 1$ are involved in the analysis of Eq. (6) for the quasiparticle amplitudes $f_s(\mathbf{r}, -1)$ for down spin, while both triplet and singlet states enter in the equations for the amplitudes $f_s(\mathbf{r}, +1)$ for up spin. Since we assume that the N-electron ground state has one electron outside closed shells, the $(N-1)$-electron ground state has $S = 0$. Equation (6) for the majority-spin channel $\sigma = 1$ generally involves the $(N-1)$-electron ground state and can be analyzed by the same methods as used above. Since the $(N-1)$-electron ground state is nondegenerate in this case, the asymptotic spin-density matrix $\gamma_+(\mathbf{r}, \mathbf{r}')$ in the majority-spin channel is given by Eqs. (16) and (18). We also find that the uppermost DF eigenvalue e_+ in the majority-spin channel equals the ionization potential,

$$e_+ = E(N) - E(N-1) , \qquad (31)$$

and that $v_{xc}^+(\mathbf{r}) \equiv v_{xc}(\mathbf{r}, 1)$ is given asymptotically by Eq. (26).

The quasiparticle amplitudes $f_s(\mathbf{r}, -1)$ in the minority-spin channel can also be worked out by essentially the same methods as before. Since in this case only $(N-1)$-electron states with $S = M_S = 1$ enter in the analysis, the lowest $(N-1)$-electron *triplet* state plays the same role as the $(N-1)$-electron ground state did in the previous cases. The result of the analysis can just be read off our earlier results in Sec. II [Eqs. (16)–(30)] by replacing the $(N-1)$-electron ground state(s) by the lowest triplet state(s) with $M_S = 1$, and the $(N-1)$-electron ground-state energy $E(N)$ by the lowest triplet energy, $E(N-1, S = 1)$. We thus find that the asymptotic spin-density matrix $\gamma_-(\mathbf{r}, \mathbf{r}')$ is given by the counterparts to Eqs. (28)–(30) or Eqs. (16)–(18) depending on whether the lowest triplet states have orbital degeneracies or not. In particular, we have, to leading order,

$$\gamma_-(\mathbf{r}, \mathbf{r}') \sim (rr')^{\beta^-} \exp[-\kappa^-(r + r')] , \qquad (32)$$

where

$$\kappa^- = \{2[E(N-1, S = 1) - E(N)]\}^{1/2}$$

is given by the lowest triplet energy, and $\beta^- = (Z_{tot} - N + 1)/\kappa^- - 1$.

Upon comparing with the DF orbital equations [cf. Eqs. (22) and (23)], we find that the highest occupied DF eigenvalue e_- in the minority-spin channel is

$$e_- = E(N) - E(N-1, S = 1) . \qquad (33)$$

When the lowest triplet states have no orbital degeneracies, $v_{xc}^-(\mathbf{r}) \equiv v_{xc}(\mathbf{r}, -1)$ is given by the counterpart to Eq. (26),

$$v_{xc}^-(\mathbf{r}) \sim \langle N | \hat{V}_H(\mathbf{r}) | N \rangle - \langle \Phi | \hat{V}_H | \Phi \rangle$$
$$- \frac{1}{2r^4} \sum_{i,j} \hat{r}_i \hat{r}_j \alpha_{ij}^T, \quad r \to \infty \qquad (34)$$

where $| \Phi \rangle$ is an $(N-1)$-electron triplet state corresponding to the lowest possible energy, and α_{ij}^T is the corresponding static polarizability. When the lowest triplet states involve orbital degeneracies, v_{xc}^- may be deduced to order r^{-4} from the counterparts to Eqs. (28)–(30).

In order to illustrate the formal results presented above,

we now discuss the special case of the Na atom and give some numerical results taken from experiment.[11] Let us, e.g., consider the $M_S = \frac{1}{2}$ ground state. The uppermost occupied DF eigenvalue in the majority-spin channel is

$$e_{3s+} = E(11) - E(10) = -5.14 \text{ eV} .$$

Furthermore,

$$v_{xc}^+(\mathbf{r}) \sim -1/r - \alpha/2r^4, \quad r \to \infty$$

α being the ground-state polarizability of the Na$^+$ ion. The lowest triplet state of this ion is the state $| (2p^5 3s)\,^3P \rangle$. Consequently, the highest occupied DF eigenvalue in the minority-spin channel is given by

$$e_{2p-} = E(11) - E[10, (2p^5 3s)\,^3P] = -38.11 \text{ eV} .$$

Since, in this case, the lowest triplet states involve orbital degeneracies, v_{xc} may be found from an analysis analogous to that in Appendix A. The result is

$$v_{xc}^-(r) \sim -\frac{1}{r} + \frac{Q^T}{r^3} - \frac{\alpha^T}{2r^4}, \quad r \to \infty$$

Q^T and α^T being the quadrupole moment and static polarizability, respectively, of the Na$^+$ ion in its lowest triplet state, $| (2p^5 3s)\,^3P \rangle$.

IV. SOLID SURFACES

A. General considerations

We now focus our attention on systems of macroscopic size. For such systems it has been known for a long time[2] that the uppermost occupied DF eigenvalue equals the chemical potential, denoted, in this section, by μ [$\mu \equiv E(N) - E(N-1)$]. We shall derive here the asymptotic form of the density and the exchange-correlation potential v_{xc} far outside a solid surface. The method used above on finite systems, however, cannot be straightforwardly applied to macroscopic systems. In the previous case we could assume that there was a finite difference in energy between the ground level and the lowest excited state. Owing to this property the contribution to the density from excited-state quasiparticle amplitudes is down by a factor r^{-4} relative to the contribution from the ground-level amplitudes at large distances r. This is not the case for systems of macroscopic size.

In order to get a feeling for the behavior of the quasiparticle amplitudes in such systems, we first briefly discuss a noninteracting case. The quasiparticle amplitudes are then the usual one-electron orbitals (φ_s), which (for a short-range surface potential) have an exponential falloff $\sim A \exp(-\kappa_s z)$ determined by their eigenvalues ϵ_s [z is the distance from the surface, A is a constant, and $\kappa_s = (-2\epsilon_s)^{1/2}$]. For a finite system only the highest occupied orbital(s) with eigenvalue μ contributes to the density at far distances and the density falls off as $\exp(-2\kappa_0 z)$ [$\kappa_0 = (-2\mu)^{1/2}$]. For macroscopic (metallic) systems, on the other hand, one readily finds that all states within a thin shell,

$$|\mu - \epsilon_s| < \mu / (\kappa_0 z) , \qquad (35)$$

at the Fermi surface, contribute at far distances, and that the density instead falls off as $z^{-1}\exp(-2\kappa_0 z)$.

Our analysis below will show that, for an interacting system as well, the leading long-range contribution to the density is given by the quasiparticle amplitudes within the same thin shell. However, since all quasiparticle amplitudes are coupled by the long-range Coulomb interaction, quasiparticle amplitudes of lower energies ϵ_s are down only by a power in z^{-1} relative to the Fermi-surface amplitudes.

We now turn to the detailed analysis and assume the system to be semi-infinite and confined to $z < 0$. First, we consider (nonmagnetic) metals and discuss the modification needed to treat semiconductors and insulators at the end of our analysis (Sec. IV E). We introduce the total electrostatic or Coulomb potential of the $(N-1)$-electron system:

$$V_C(\mathbf{r}) = \langle N-1 | \hat{V}_H(\mathbf{r}) | N-1 \rangle + w(\mathbf{r}) , \tag{36}$$

and rewrite the basic Eq. (6) for the quasiparticle amplitudes as

$$[-\tfrac{1}{2}\nabla^2 + V_C(\mathbf{r}) - \epsilon_s]f_s(\mathbf{r},s) + \langle s | \delta\hat{V}_H(\mathbf{r})\psi(\mathbf{r},\sigma) | N \rangle = 0 . \tag{37}$$

When $z \to \infty$ the total electrostatic potential V_C tends exponentially to a constant, which we here choose as our reference energy. For macroscopic systems the exchange potential also tends exponentially to zero,[12] and, consequently, long-range components in the effective DF potential can only originate from correlation or polarization effects. Without the inhomogeneous term in Eq. (37), the decay of the quasiparticle amplitudes would be determined by their respective eigenvalues, as in the case of noninteracting particles, and we would have $f_s(\mathbf{r},\sigma) \sim \exp(-\kappa_s z)$. The inhomogeneous term contains contributions from quasiparticle amplitudes arbitrarily close to the Fermi surface and will therefore decay as $\exp(-\kappa_0 z)$. As a consequence, all quasiparticle amplitudes have the asymptotic large-z behavior,

$$f_s(\mathbf{r},\sigma) \sim g_s e^{-\kappa_s z} + h_s e^{-\kappa_0 z} , \tag{38}$$

where the functions g_s and h_s have a slower than exponential variation with distance. For states with energies away from the Fermi energy, the first term in Eq. (38) can be neglected, as was the case for finite systems. For states with energies close to the Fermi energy, however, a more complicated behavior is to be expected. We handle this situation by introducing a number $a \gg 1$ which can be chosen arbitrarily large, but which then is held fixed in the discussion to follow. We divide the $(N-1)$-electron states into two subspaces, P and $1-P$, with wave numbers smaller and larger than $\kappa_0 + a/z$, respectively. Thus, the subspace P corresponds to energies ϵ_s close to the Fermi energy, $\mu - \omega_0 \le \epsilon_s \le \mu$, where

$$\omega_0 = a\kappa_0/z = -2a\mu/(\kappa_0 z) .$$

The projection operators on the two subspaces defined above are also labeled P and $1-P$, respectively.

B. Quasiparticle amplitudes for states in subspace $1-P$

For amplitudes corresponding to the space $1-P$, we can, for large z, safely approximate $(-\nabla^2/2)f_s(\mathbf{r},\sigma)$ by $(-\kappa_0^2/2)f_s(\mathbf{r},\sigma)$. This gives

$$(\mu - \epsilon_s)f_s(\mathbf{r},\sigma) = -\langle s | \delta\hat{V}_H(\mathbf{r})\psi(\mathbf{r},\sigma) | N \rangle . \tag{39}$$

In this approximation we have dropped terms containing derivatives which are of order $(\kappa_0/z)f_s(\mathbf{r},\sigma)$ or smaller. This is permissible since κ_0/z is small compared to $\mu - \epsilon_s \ge \omega_0 = a\kappa_0/z$. We have also dropped the exponentially small term $V_C(\mathbf{r})$.

Following the case for finite systems we would like to reexpress the rhs of Eq. (39) in terms of quasiparticle amplitudes corresponding to the subspace P. Inserting a complete set of states and using Eq. (39) in the subspace $1-P$, we obtain

$$\langle s | \delta\hat{V}_H(\mathbf{r})\psi(\mathbf{r},\sigma) | N \rangle = \langle s | \delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma) | N \rangle + \left\langle s \left| \delta\hat{V}_H(\mathbf{r})\frac{1-P}{E_0-H}\delta\hat{V}_H(\mathbf{r})\psi(\mathbf{r},\sigma) \right| N \right\rangle ,$$

where $E_0 = E(N-1)$, the ground-state energy of the $(N-1)$-electron system. This procedure can be repeated any number of times. In this way we obtain an expansion of the form

$$\langle s | \delta\hat{V}_H(\mathbf{r})\psi(\mathbf{r},\sigma) | N \rangle = \langle s | \delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma) | N \rangle + \sum_{n \ge 1} \left\langle s \left| \delta\hat{V}_H(\mathbf{r}) \left[\frac{1-P}{E_0-H}\delta\hat{V}_H(\mathbf{r}) \right]^n P\psi(\mathbf{r},\sigma) \right| N \right\rangle . \tag{40}$$

When $z \to \infty$, the projector P approaches the projector on the ground states, and it is not difficult to see that the nth-order term in Eq. (40) gives the nth-order perturbation of a ground state to an external potential,

$$\hat{V}_H(\mathbf{r}) = \int d^3r \, \hat{\rho}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}') ,$$

describing a unit test charge at $\mathbf{r} = (\kappa, y, z)$ outside the metal. When $z \to \infty$, the higher-order contributions to the response become negligible compared to the linear response. Keeping only the first term in Eq. (40), we have the estimate

$$f_s(\mathbf{r},\sigma) = \left\langle s \left| \frac{1}{E_0-H}\delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma) \right| N \right\rangle , \tag{41}$$

which is correct to leading order in z^{-1} for states s in subspace $1-P$.

C. Quasiparticle amplitudes for states with energies near the Fermi energy

We now turn to the quasiparticle amplitudes for states in subspace P and introduce a spectral decomposition of the density matrix $\gamma(x,x')$:

$$A(x,x',\epsilon)=\sum_s \delta(\epsilon-\epsilon_s)f_s(x)f_s^*(x')=\langle N\mid\psi^\dagger(x')\delta(H+\epsilon-E(N))\psi(x)\mid N\rangle\ , \tag{42}$$

where x and x' are space-spin coordinates. Thus,

$$\int_{-\infty}^{\mu}A(x,x',\epsilon)=\gamma(x,x')\ . \tag{43}$$

For nonmagnetic systems, the spectral function A and the density matrix are diagonal in the spin indices and will be written

$$A(x,x',\epsilon)=A(\mathbf{r},\mathbf{r}',\epsilon)\delta_{\sigma\sigma'}$$

and

$$\gamma(x,x')=\gamma(\mathbf{r},\mathbf{r}')\delta_{\sigma\sigma'}\ .$$

We want to derive an equation for A valid far away from the system and for energies very close to the Fermi energy. We start from the equation for the quasiparticle amplitudes [Eq. (37)] and use our asymptotic estimate of the inhomogeneous term in the subspace $1-P$. For large z, we obtain

$$\tfrac{1}{2}(\kappa_s^2-\nabla^2)f_s(\mathbf{r},\sigma)+\left\langle s\left|\delta\hat{V}_H(\mathbf{r})\frac{1-P}{E_0-H}\delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma)\right|N\right\rangle+\langle s\mid\delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma)\mid N\rangle=0\ .$$

We multiply this expression with $f_s^*(\mathbf{r}',\sigma)\delta(\epsilon-\epsilon_s)$, sum over all states s, and obtain

$$\tfrac{1}{2}(\kappa^2-\nabla^2)A(\mathbf{r},\mathbf{r}',\epsilon)+\left\langle N\left|\psi^\dagger(\mathbf{r}',\sigma)\delta(H+\epsilon-E_0-\mu)\delta\hat{V}_H(\mathbf{r})\frac{1-P}{E_0-H}\delta\hat{V}_H(\mathbf{r})\psi(\mathbf{r},\sigma)\right|N\right\rangle-Q(\mathbf{r},\mathbf{r}',\epsilon)=0\ , \tag{44}$$

where

$$Q(\mathbf{r},\mathbf{r}',\epsilon)=-\langle N\mid\psi^\dagger(\mathbf{r}',\sigma)\delta(H+\epsilon-E_0-\mu)\delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma)\mid N\rangle\ , \tag{45}$$

and where $\kappa=(-2\epsilon)^{1/2}$.

In order to estimate the second term in Eq. (44), we can argue as follows. This term is of the form $\langle\Phi\mid M\mid\Psi\rangle$, where

$$M=\delta\hat{V}_H(\mathbf{r})\frac{1-P}{E_0-H}\delta\hat{V}_H(\mathbf{r})\ ,$$

and where

$$\mid\Phi\rangle=\delta(H+\epsilon-E_0-\mu)\psi(\mathbf{r}',\sigma)\mid N\rangle$$

and

$$\mid\Psi\rangle=P\psi(\mathbf{r},\sigma)\mid N\rangle$$

are (unnormalized) $(N-1)$-electron state vectors with energies very close to that of the ground state. From general arguments, it can be shown that such matrix elements of well-behaved operators M are given by

$$\langle\Phi\mid M\mid\Psi\rangle=\langle N-1\mid M\mid N-1\rangle\langle\Phi\mid\Psi\rangle\ . \tag{46}$$

The conditions for the validity of this equation, as well as its relative accuracy, are discussed in detail in Appendix B. Here we just mention that $\langle N-1\mid M\mid N-1\rangle$ should be nonzero, and that the corrections are of the order Δ/μ, where Δ is an upper estimate of the excitation energies contained in the states $\mid\Phi\rangle$ and $\mid\Psi\rangle$. In our case, the states $\mid\Phi\rangle$ and $\mid\Psi\rangle$ have energies which exceed E_0 with,

at most, $\omega_0\sim a/(\kappa_0 z)$. Thus, to leading order, we find that the second term in Eq. (44) is given by

$$\langle N-1\mid M\mid N-1\rangle A(\mathbf{r},\mathbf{r}',\epsilon)\ .$$

In the expectation value

$$\langle N-1\mid M\mid N-1\rangle$$

$$=\left\langle N-1\left|\delta\hat{V}_H(\mathbf{r})\frac{1-P}{E_0-H}\delta\hat{V}_H(\mathbf{r})\right|N-1\right\rangle\ ,$$

we can replace $1-P$ by unity. In order to see this, we note that the rhs of this expression can be written in terms of the charge response function $\mathcal{X}(\mathbf{r},\mathbf{r}',\omega)$, or rather its spectral function $\mathrm{Im}\mathcal{X}$:

$$\langle N-1\mid M\mid N-1\rangle=-\int_{\omega_0}^{\infty}\frac{d\omega}{\pi}\,\mathrm{Im}(v\mathcal{X}v)(\mathbf{r},\mathbf{r},\omega)/\omega\ .$$

In the expression above, $(v\mathcal{X}v)(\mathbf{r},\mathbf{r}',\omega)$ is short for the convolution

$$\int d^3r_1\,d^3r_2\,v(\mathbf{r}-\mathbf{r}_1)\mathcal{X}(\mathbf{r}_1,\mathbf{r}_2,\omega)v(\mathbf{r}_2-\mathbf{r}')\ .$$

Since $\mathrm{Im}\mathcal{X}(\mathbf{r},\mathbf{r}',\omega)$ is linear in ω for small ω,[13,14] we can replace $\omega_0\sim\mu a/(\kappa_0 z)$ by 0 in the lower limit of the integral. The rhs then equals the Kramers-Kronig representation of the static polarizability. To leading order, we thus find

$$\langle N-1 \mid M \mid N-1 \rangle = \tfrac{1}{2}\alpha(\mathbf{r},\mathbf{r}) \equiv \tfrac{1}{2}(v\chi v)(\mathbf{r},\mathbf{r},0) \ . \tag{47}$$

We now turn to the third term, $Q(\mathbf{r},\mathbf{r}',\epsilon)$, in Eq. (44), and notice that this term is of the form $\langle \Phi \mid \delta \hat{V}_H(\mathbf{r}) \mid \Psi \rangle$ [cf. Eq. (45)]. Since, by definition,

$$\langle N-1 \mid \delta \hat{V}_H(\mathbf{r}) \mid N-1 \rangle = 0 \ ,$$

Eq. (46) does not apply and we need a more elaborate scheme to estimate Q. Such a scheme is given in Appendix B, and we find that Q is of order

$$Q(\mathbf{r},\mathbf{r}',\epsilon) \sim z^{-1}[a\gamma_P(\mathbf{r},\mathbf{r})A(\mathbf{r}',\mathbf{r}',\epsilon)]^{1/2} \tag{48}$$

or smaller. Here,

$$\gamma_P(\mathbf{r},\mathbf{r}') = \langle N \mid \psi^\dagger(\mathbf{r}',\sigma)P\psi(\mathbf{r},\sigma) \mid N \rangle$$

is the contribution to the density matrix from states in subspace P.

D. Density matrix and exchange-correlation potential far outside a metal surface

The results of the preceding subsection can be summarized in an asymptotic equation for the spectral density A:

$$\tfrac{1}{2}[-\nabla^2 + \kappa^2 + \alpha(\mathbf{r},\mathbf{r})]A(\mathbf{r},\mathbf{r}',\epsilon) = Q(\mathbf{r},\mathbf{r}',\epsilon) \ . \tag{49}$$

The quantity of $Q(\mathbf{r},\mathbf{r}',\epsilon)$ is defined in Eq. (45) and is estimated in Eq. (48). Equation (49) is valid far outside the surface and within the energy shell

$$\mu \geq \epsilon \geq \mu - \omega_0$$

(for definiteness, we will, in the following, take $z' \geq z$).

We will later show that Eq. (49) is valid also far outside the surface of an insulator or semiconductor, but for the moment we shall assume the system to be metallic. The polarizability $\alpha(\mathbf{r},\mathbf{r}')$, which appears in Eq. (49), gives the induced electrostatic potential at $\mathbf{r}$ due to a unit test charge at $\mathbf{r}'$. When $\mathbf{r}$ and $\mathbf{r}'$ are both well outside the system, macroscopic electrostatics is valid. For metals one readily finds

$$\alpha(\mathbf{r},\mathbf{r}) \sim -(2z)^{-1} \ , \tag{50}$$

and thus the spectral function A fulfills the equation

$$\tfrac{1}{2}\left[\kappa^2 - \nabla^2 - \frac{2\nu\kappa_0}{\kappa z}\right]A(\mathbf{r},\mathbf{r}',\epsilon) = Q(z,z') \ , \tag{51}$$

where we have introduced the parameter

$$\nu = 1/4\kappa_0 \ . \tag{52}$$

(Q can be considered as a function only of z and z' far away from the surface.)

In the absence of the inhomogeneous term Q in Eq. (51), the asymptotically correct solution would be

$$A(\mathbf{r},\mathbf{r}',\epsilon) \sim (zz')^{\nu\kappa_0/\kappa}e^{-\kappa(z+z')} \ , \tag{53}$$

giving a contribution

$$\gamma_P(\mathbf{r},\mathbf{r}') \equiv \int_{\mu-\omega_0}^{\mu} A(\mathbf{r},\mathbf{r}',\epsilon)d\epsilon$$

$$\sim \frac{\kappa_0}{z+z'}A(z,z',\mu)[1+O(z^{-1}\ln z)] \tag{54}$$

to the density matrix. We can, however, show that the presence of the term Q does not change this result for γ_P. Using Eq. (48) we can, for metals, estimate Q as follows:

$$|Q(z,z')| \lesssim z^{-1}[a\gamma_P(z,z)A(z'z',\mu)]^{1/2}$$

$$\sim a^{1/2}z^{-3/2}A(z,z',\mu) \ . \tag{55}$$

This follows from the fact that $A(z,z,\epsilon)/A(z,z,\mu)$ tends to zero when $z \to \infty$ and, thus, $\gamma_P(z,z)$ is at most of the order $z^{-1}A(z,z,\mu)$. When $(\kappa-\kappa_0)z \lesssim 1$, $Q(z,z')$ is down by at least a factor $(a/z)^{1/2}$ compared to $z^{-1}A$, and thus A is given by the homogeneous solution in Eq. (53). The energy integral over the shell $\mu > \epsilon > \mu - \kappa_0/z$ now gives the estimate in Eq. (54). When $(\kappa-\kappa_0)z \gtrsim 1$ and, thus, $\mu - \kappa_0/z \gtrsim \epsilon > \mu - \omega_0$, we can neglect terms of the order $z^{-1}A$ on the left-hand side (lhs) of Eq. (51) and find

$$A(z,z',\epsilon) \sim \frac{1}{\mu-\epsilon}Q(z,z') \ .$$

Consequently, the inhomogeneous contribution to γ_P from this interval is of order $Q(z,z')\ln\omega_0$, which is down by at least a factor $(a/z)^{1/2}\ln z$ compared to the leading-order estimate in Eq. (54).

The arguments given here can actually be placed on a more rigorous footing by directly studying the differential equation (51). This equation is first converted to a first-order equation by making the replacement

$$\kappa^2 - \frac{\partial^2}{\partial z^2} = \left[\kappa - \frac{\partial}{\partial z}\right]\left[\kappa + \frac{\partial}{\partial z}\right] \approx 2\kappa_0\left[\kappa + \frac{\partial}{\partial z}\right] \ .$$

Its solution can then be obtained in closed form, allowing a direct study of the contribution to γ_P.[15]

The remaining contribution γ_{1-P} comes from quasiparticle amplitudes corresponding to eigenvalues $\epsilon_s < \mu - \omega_0$. These can be estimated by our results in Sec. IV B [Eq. (41)], and we find

$$\gamma_{1-P}(z,z') \sim \left\langle N \left| \psi^\dagger(\mathbf{r}',\sigma)P\delta\hat{V}_H(\mathbf{r})\frac{1-P}{(E_0-H)^2}\delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma) \right| N \right\rangle$$

$$\sim \langle N \mid \psi^\dagger(\mathbf{r}',\sigma P\psi(\mathbf{r},\sigma) \mid N \rangle \left\langle N-1 \left| \delta\hat{V}_H(\mathbf{r})\frac{1-P}{(E_0-H)^2}\delta\hat{V}_H(\mathbf{r}) \right| N-1 \right\rangle \ . \tag{56}$$

Here, we have used the analysis in Appendix B to obtain the second asymptotic equality. The first factor in this equation gives, by definition, $\gamma_P(z,z')$, which we analyzed above. We see that the second factor can be written as

$$\int_{\omega_0}^{\infty} d\omega \, \mathrm{Im}(v\chi v)(\mathbf{r},\mathbf{r}',\omega)/\omega^2 \sim (z+z')^{-1}\ln(\mu/\omega_0)$$

$$\sim z^{-1}\ln(a\kappa_0 z) \; ,$$

where we have made use of the low-ω behavior of the response function χ, $\mathrm{Im}\chi(\mathbf{r},\mathbf{r}',\omega)\sim\omega$, and the fact that classical image-charge theory is valid far away from the surface. Thus, γ_{1-P} is smaller than γ_P by at least a factor of the order $z^{-1}\ln(az)$.

In summary, we have found that the density matrix far away from a metal surface is given by

$$\gamma(z,z') \sim [\kappa_0/(z+z')]A(\mathbf{r},\mathbf{r}',\mu) \; , \tag{57}$$

where $A(\mathbf{r},\mathbf{r}',\mu)$ fulfills

$$[-\tfrac{1}{2}\nabla^2 + V_C(\mathbf{r}) + \tfrac{1}{2}\alpha(\mathbf{r},\mathbf{r}) - \mu]A(\mathbf{r},\mathbf{r}',\mu) = 0 \tag{58}$$

to leading order in z^{-1}, and a similar equation in the variable z'. The spectral function A exhibits the asymptotic behavior

$$A(\mathbf{r},\mathbf{r}',\mu) \sim (zz')^{\nu}e^{-\kappa_0(z+z')} \; , \tag{59}$$

where (for metals) $\nu = (4\kappa_0)^{-1}$.

In order for DF theory to correctly reproduce the density profile,

$$\rho(\mathbf{r}) \sim z^{2\nu-1}e^{-2\kappa_0 z}, \quad z \to \infty$$

the DF orbital equations must have the form

$$[-\tfrac{1}{2}\nabla^2 + V_C(\mathbf{r}) + \tfrac{1}{2}\alpha(\mathbf{r},\mathbf{r})]\varphi_k(\mathbf{r},\sigma) = e_k\varphi_k(\mathbf{r},\sigma)$$

far away from the system, and the uppermost occupied eigenvalue must fulfill $e_N = E(N) - E(N-1)$ as in the finite-N case. From the DF orbital equations, we deduce that

$$v_{\mathrm{xc}}(\mathbf{r}) \sim \tfrac{1}{2}\alpha(\mathbf{r},\mathbf{r}) \sim -1/4z, \quad z \to \infty \; . \tag{60}$$

E. Insulator and semiconductor surfaces

We shall discuss here the modifications needed to cover the case of insulators and semiconductors. With regard to the discussion above, the main difference between these and metals is the vanishing state density in the gap. In terms of the spectral function $A(\mathbf{r},\mathbf{r}',\epsilon)$, the one-particle state density $D_\Omega(\epsilon)$ of the volume Ω is defined by

$$D_\Omega(\epsilon) = \frac{2}{\Omega}\int_\Omega d^3r \, A(\mathbf{r},\mathbf{r},\epsilon) \; ,$$

where Ω is a volume of interest, such as the entire solid or the surface region. Our discussion so far relies on having a spectral function which does not vanish outside the solid. Clearly, this cannot be the case for an insulator since $D_\Omega(\epsilon) = 0$ in the gap for any Ω. At the end of this section we will discuss this case in more detail, but first we note that it is somewhat academic. Real insulators always have some impurities which give rise to impurity

states and thus to a nonvanishing density of gap states. Even in the ideal case with absolutely no impurities, there are still surface states in an insulator which again give a continuum of states in the gap. It is uncertain whether or not the surface states can ever be removed by some suitably chosen external potential, and, consequently, for all realistic cases the discussion above carries over to the case of insulators with only minor modifications. One difference is that the polarizability $\alpha(\mathbf{r},\mathbf{r})$ well outside the solid becomes

$$\alpha(\mathbf{r},\mathbf{r}) \sim -\frac{1}{2z}\frac{\epsilon_0-1}{\epsilon_0+1} \tag{61}$$

instead of Eq. (50). Remembering that DF theory is a theory of electrons subject to a time-independent external potential, we notice that ϵ_0 is the static (macroscopic) dielectric constant of only the electrons. As before, Eq. (61) follows from classical macroscopic arguments. Thus we find that the density matrix far away from the surface of an insulator with a nonzero density of impurity or surface states in the gap is given by the same expressions as for metals, Eqs. (57)–(59), provided we use the polarizability relevant for insulator surfaces [Eq. (61)], and the corresponding exponent

$$\nu = \frac{1}{4\kappa_0}\frac{\epsilon_0-1}{\epsilon_0+1} \tag{62}$$

in Eq. (59). By requiring the DF theory to reproduce the density, we again deduce that v_{xc} far outside the system is given by the polarizability,

$$v_{\mathrm{xc}}(\mathbf{r}) \sim \tfrac{1}{2}\alpha(\mathbf{r},\mathbf{r}) \sim -\frac{1}{4z}\frac{\epsilon_0-1}{\epsilon_0+1} \; . \tag{63}$$

It will follow from our analysis below of an ideal insulator that the density far outside a real insulator originates entirely from impurity and/or surface states. Despite this fact, we see in Eq. (63) that v_{xc} outside the surface is insensitive to the presence of surface and impurity states as long as they do not give important contributions to the dielectric response to a test charge far outside the surface.

We now turn to the modifications needed to treat the case of an ideal insulator with no surface or impurity states in the fundamental gap. We shall assume that the valence band is exactly filled in the N-electron ground state $|N\rangle$. In this case the one-particle state density $D_\Omega(\epsilon)$ tends to zero with the excitation energy $\mu-\epsilon$ for any Ω. On physical grounds it is clear that $A(\mathbf{r},\mathbf{r}',\epsilon)$ outside the system tends to zero as the density of one-particle levels, i.e., normally as $(\mu-\epsilon)^{1/2}$ when $\epsilon\to\mu$. Here, we confine ourselves to that case.

Although the density of $(N-1)$-electron levels tends to zero when $\epsilon\to\mu$, it is clear that the inhomogeneous term in Eq. (37) for the quasiparticle amplitudes contains contributions from amplitudes with energies arbitrarily close to μ. This again implies that all amplitudes decay as $\exp(-\kappa_0 z)$ far away from the surface.

Following our previous procedure of dividing the excited states into two groups with energies close to (P) and further away $(1-P)$ from the Fermi energy, we find that our analysis of the quasiparticle amplitudes corresponding

to the group $1-P$ goes through unchanged. Thus, Eq. (41) is still valid, as is our estimate of the contribution γ_{1-P} to the density matrix [see Eq. (56) and following].

To analyze the contribution γ_P to the density matrix corresponding to energies close the Fermi energy, we introduce a renormalized spectral function

$$B(\mathbf{r},\mathbf{r}',\epsilon)=(\mu-\epsilon)^{-1/2}A(\mathbf{r},\mathbf{r}',\epsilon) , \qquad (64)$$

which tends to nonzero values when $\epsilon \to \mu$. Far outside the surface, B only depends on ϵ, z, and z', and fulfills a similar equation as the spectral function A [Eq. (49)], the only difference being that the inhomogeneous term is now $(\mu-\epsilon)^{-1/2}Q(\mathbf{r},\mathbf{r}',\epsilon)$, in place of $Q(\mathbf{r},\mathbf{r}',\epsilon)$. For the perfect insulator we are considering, the low-lying excited $(N-1)$-electron states have one single, stable quasihole in the valence band. As a consequence, there are phase-space restrictions which allow us to improve our earlier estimate of the inhomogeneous term [see Appendix B, Eq. (B12)]:

$$(\mu-\epsilon)^{-1/2}Q(z,z',\epsilon)=O(z^{-3/2}B(z,z',\mu)) .$$

Using this estimate and our methods in Sec. IV D, we verify that the inhomogeneous term in the asymptotic equation for $B(z,z',\epsilon)$ [cf. Eq. (49)] does not influence the density matrix to leading order in z^{-1}. Thus, the density matrix far outside the system is given by

$$\gamma(z,z')=\int_{\mu-\omega_0}^{\mu}d\epsilon(\mu-\epsilon)^{1/2}B(z,z',\epsilon)$$
$$\sim \tfrac{1}{2}(\pi)^{1/2}[\kappa_0/(z+z')]^{3/2}B(z,z',\mu) , \qquad (65)$$

where $B(z,z',\mu)$, fulfills the same asymptotic equation as $A(z,z',\mu)$, Eq. (58). B has the form

$$B(z,z',\mu)\sim(zz')^{\nu}e^{-\kappa_0(z+z')} ,$$

with ν given, as before, by Eq. (62), in terms of the dielectric constant.

The asymptotic density for the ideal insulator,

$$\rho(\mathbf{r})\sim z^{\nu-3/2}e^{-2\kappa_0 z} ,$$

tends to zero more rapidly than the density from the corresponding imperfect insulator with impurity or surface levels in the fundamental gap. We have thus shown that the density far away from an imperfect insulator originates entirely from impurity and/or surface states.

By requiring the DF theory to reproduce the density far outside an ideal insulator, we find the following:

(a) The uppermost occupied DF eigenvalue equals μ.

(b) The exchange-correlation potential is given by Eq. (63) in terms of the polarizability $\alpha(\mathbf{r},\mathbf{r})$ or the macroscopic dielectric constant.

[In order to obtain the last result, (b), we have assumed that the DF energy levels exhibit a fundamental gap.]

Note that whereas the density far outside an ideal insulator is qualitatively different from the density far outside an insulator with surface or impurity states, the exchange-correlation potential is essentially the same.

V. CONCLUDING REMARKS

In this paper we have studied the relations between DF eigenvalues and exact excitation energies. From exact asymptotic results for the spin density far away from a finite system, we have shown that the uppermost DF eigenvalue equals the ionization potential, not only for extended systems like solids, but also for finite systems like atoms. Thus, contrary to what one might expect from Koopmans's theorem, no relaxation correction should be added to the highest DF eigenvalue in order to obtain the difference $E(N)-E(N-1)$ in total energies between the N- and $(N-1)$-electron systems. We have also been able to deduce the asymptotic form of the ground-state potential v_{xc} far away from finite systems, and far outside solid surfaces, from higher-order terms in the asymptotic density profile. For spin-polarized systems we have shown that the uppermost occupied DF eigenvalue in each spin channel gives an exact excitation energy.

Our exact results make it possible to test the accuracy of approximate exchange-correlation potentials, and may also provide some guidance for constructing better approximations. Detailed comparisons between exact results and results obtained from approximate density-functional schemes have been given elsewhere.[16]

APPENDIX A

In this paper we have studied the relations between DF eigenvalues and exact excitation energies. From exact exchange-correlation potential for a simple case where the $(N-1)$-electron ground states involve orbital degeneracies. We consider an atom with a nondegenerate N-electron ground state $|N\rangle$ (^1S) and orbitally and spin-degenerate ground states corresponding to the term ^2L.

We start from Eqs. (28)—(30) derived in Sec. II. The density matrix is the same in both spin channels since $|N\rangle$ has zero spin, and we thus only need to consider one channel, σ. We label the $(N-1)$-electron ground states in the subspace $M_S=-\sigma/2$ as

$$|N-1,0,\alpha\rangle \equiv |LM\rangle ,$$

L and M being the usual angular momentum labels. We perform a multipole expansion of the Hartree potential matrix elements in Eq. (29) and make use of the Wigner-Eckart theorem:

$$\langle LM | \hat{V}_H(\mathbf{r}) | LM'\rangle = \frac{N-1}{r}\delta_{MM'}+\frac{1}{r^3}\frac{\langle LM | 2M-M';LM'\rangle}{\langle L0 | 20;L0\rangle}Y^*_{2,M-M'}(\hat{\mathbf{r}})\langle L0 | \hat{Q}_{20} | L0\rangle ,$$

$\hat{Q}_{2m}$ being the quadrupole-moment operator. Equation (29) also involves a polarizability operator which we term $\hat{\alpha}_{ij}$.

We write this operator in terms of spherical-tensor operators of rank zero ($\hat{a}_0$) and two ($\hat{a}_{2m}$),

$$\sum_{i,j} \hat{r}_i \hat{r}_j \hat{\alpha}_{ij} \equiv \mathbf{d} \cdot \hat{\mathbf{r}} \frac{1-P}{H-E(N-1)} \mathbf{d} \cdot \hat{\mathbf{r}} = \hat{a}_0 + \sum_m Y^*_{2m}(\hat{\mathbf{r}}) \hat{a}_{2m} \ ,$$

form the required matrix elements in Eq. (29), and use the Wigner-Eckart theorem. After adding the Hartree potential matrix elements, we obtain

$$U_{MM'}(\mathbf{r}) \equiv \left\langle LM \left| \hat{V}_H(\mathbf{r}) - \frac{1}{2r^4} \sum_{i,j} \hat{r}_i \hat{r}_j \hat{\alpha}_{ij} \right| LM' \right\rangle$$

$$= \left[\frac{N-1}{r} - \frac{1}{2r^4} \langle L\,0 | \hat{a}_0 | L\,0 \rangle \right] \delta_{MM'} + \frac{\langle LM | 2M-M';M' \rangle}{\langle L\,0 | 20;L\,0 \rangle} \left\langle L\,0 \left| \frac{1}{r^3} \hat{Q}_{20} - \frac{1}{2r^4} \hat{a}_{20} \right| L\,0 \right\rangle Y^*_{2,M-M'}(\hat{\mathbf{r}}) \ .$$

$$(A1)$$

Insert this result in Eq. (28) for the ground-state amplitudes $f_{0\alpha}(\mathbf{r},\sigma) \equiv f_{LM}(\mathbf{r})$, and use the relation

$$f_{LM}(\mathbf{r}) = \langle LM | \psi(\mathbf{r},\sigma) | N \rangle = R(r) Y^*_{LM}(\hat{\mathbf{r}}) \ , \qquad (A2)$$

which follows from the transformation properties of $\psi(\mathbf{r},\sigma)$ under spatial rotations. This gives

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z-N+1}{r} + \frac{Q}{r^3} - \frac{\alpha}{2r^4} - \epsilon_0 \right] f_{LM}(\mathbf{r}) \sim 0 \ ,$$

$$r \to \infty \qquad (A3)$$

where we again have used the Wigner-Eckart theorem. In Eq. (A3),

$$Q = \left[\frac{5}{4\pi} \right]^{1/2} \langle L\,0 | \hat{Q}_{20} | L\,0 \rangle$$

$$= \int d^3r \, (\tfrac{3}{2}z^2 - \tfrac{1}{2}r^2) \langle L\,0 | \hat{\rho}(\mathbf{r}) | L\,0 \rangle \qquad (A4)$$

is the quadrupole moment, and

$$\alpha = \left\langle L\,0 \left| \hat{a}_0 + \left[\frac{5}{4\pi} \right]^{1/2} \hat{a}_{20} \right| L\,0 \right\rangle$$

$$= 2 \left\langle L\,0 \left| p_z \frac{1-P}{H-E(N-1)} p_z \right| L\,0 \right\rangle \qquad (A5)$$

is the polarizability of the $(N-1)$-electron ion in its ground state $|{}^2L;0M_S\rangle$. The asymptotic spin density of the N-electron atom is given by

$$n(\mathbf{r},\sigma) = \sum_M |f_{LM}(\mathbf{r})|^2 = \frac{2L+1}{4\pi} |R(r)|^2 \qquad (A6)$$

to order $\exp(-\kappa_0 r)/r^3$ in terms of the solution to Eq. (A3) [cf. Eq. (30)].

The uppermost $(2L+1)$-degenerate DF orbitals in spin channel σ, φ_{nLM}, fulfill the asymptotic equation

$$\left[-\frac{1}{2}\nabla^2 + \frac{Z-N}{r} + v_{xc}(r) - e_{nL} \right] \varphi_{nLM}(\mathbf{r}) \sim 0 \ .$$

We see that

$$e_{nL} = \epsilon_0 \equiv E(N) - E(N-1)$$

and that

$$v_{xc}(r) \sim -\frac{1}{r} + \frac{Q}{r^3} - \frac{\alpha}{2r^4} \ , \qquad (A7)$$

since these orbitals must give the same asymptotic density as the ground-state amplitudes f_{LM} in Eq. (A6).

APPENDIX B

In this Appendix we shall study matrix elements $\langle \Psi | M | \Phi \rangle$ between many-electron states $|\Phi\rangle$ and $|\Psi\rangle$ with energies very close to the ground-state energy E_0. More specifically, we shall assume that $|\Psi\rangle$ and $|\Phi\rangle$ belong to the subspace (P) corresponding to energies $E < E_0 + \omega_0$. The operator M is assumed to be a macroscopic operator, i.e., it should to be insensitive to the fine-grained structure of the quantum states. In our application, the operator M is either taken as the Hartree potential $\hat{V}_H(\mathbf{r})$ or the polarizability

$$\delta \hat{V}_H(\mathbf{r}) \frac{1-P}{E_0 - H} \delta \hat{V}_H(\mathbf{r})$$

at points $\mathbf{r}$ far outside the system. Owing to the long-range nature of the Coulomb interaction, both these operators are insensitive to variations in charge density over microscopic distances, as required.

We first study the expectation value $\langle \Phi | M | \Phi \rangle$ with respect to a normalizable state $|\Phi\rangle$. Because $|\Phi\rangle$ is close in energy to the ground state ($|0\rangle$), and since M is a macroscopic observable, we expect that

$$\langle \Phi | M | \Phi \rangle = \langle 0 | M | 0 \rangle \langle \Phi | \Phi \rangle \ . \qquad (B1)$$

In order to see this, we note that the validity of thermodynamics requires ensemble averages of macroscopic observables to be insensitive to the fine-grained structure of the ensembles. In particular, in the thermodynamic limit $(N \to \infty)$ all ensembles (ρ) with an energy very close to that of the ground state should give the same ensemble average as the ground-level ensemble, i.e., $\text{Tr}(\rho M) = \langle 0 | M | 0 \rangle$. Thus, Eq. (B1) follows by choosing $\rho = |\Phi\rangle\langle\Phi| / \langle\Phi|\Phi\rangle$.

Yet another physical argument for Eq. (B1) is based on Landau's Fermi-liquid picture:[13] When studying very-

low-lying matrix elements $\langle \Phi | M | \Psi \rangle$ of macroscopic observables M in a normal Fermi system, one may represent the actual interacting system by a fictitious system of noninteracting fermions with properly chosen one-particle energies. It is then not difficult to see that Eq. (B1) holds to within an accuracy ω_0 compared to the Fermi energy μ.

In order to estimate $\langle \Phi | M | \Psi \rangle$, we apply Eq. (B1) to the state $\alpha | \Phi \rangle + \beta | \Psi \rangle$ with arbitrary α and β, and identify the coefficients for α and β. This gives

$$\langle \Psi | M | \Phi \rangle = \langle 0 | M | 0 \rangle \langle \Psi | \Phi \rangle . \tag{B2}$$

We next study the corrections to Eq. (B1) in more detail. We write the correction as

$$R = \langle \Phi | \delta M | \Phi \rangle ,$$

where $\delta M = M - \langle 0 | M | 0 \rangle$. We use Schwarz's inequality and the identity $| \Phi \rangle = P | \Phi \rangle$ to obtain

$$| R | \leq \langle \Phi | \Phi \rangle (\Delta_\Phi)^{1/2} , \tag{B3}$$

where the low-energy fluctuations, Δ_Φ, in M, are defined by

$$\Delta_\Phi = \langle \Phi | \delta M P \delta M | \Phi \rangle / \langle \Phi | \Phi \rangle . \tag{B4}$$

The projector P restricts the phase space to a thin energy shell of thickness ω_0. Simple phase-space arguments would suggest that Δ_Φ is of the order ω_0/μ. However, the Pauli principle imposes additional restrictions and causes the density of particle-hole excitations to tend to zero as ω with the excitation energy ω.[13] (The density of multipair excitations tends to zero even faster.) As a consequence, Δ_Φ is actually of the order $(\omega_0/\mu)^2$, and

$$| R | \sim \langle \Phi | \Phi \rangle \omega_0/\mu . \tag{B5}$$

As an example, we derive Eq. (B5) for the case when $M = \hat{V}_H(\mathbf{r})$ and $\mathbf{r}$ is far outside the system. Let us first assume the validity of Eq. (B1) and replace $| \Phi \rangle$ by $| 0 \rangle$ in Eq. (B4). Since $\langle 0 | 0 \rangle = 1$, we obtain

$$\Delta_0 = \langle 0 | \delta \hat{V}_H(\mathbf{r}) P \delta \hat{V}_H(\mathbf{r}) | 0 \rangle$$
$$= \int_0^{\omega_0} d\omega (vSv)(\mathbf{r},\mathbf{r},\omega) , \tag{B6}$$

where

$$S(\mathbf{r},\mathbf{r}',\omega) = (2\pi)^{-1} \int dt \, e^{i\omega t} \langle 0 | \hat{\rho}(\mathbf{r},t)\hat{\rho}(\mathbf{r}',0) | 0 \rangle \tag{B7}$$

is the dynamical structure factor at zero temperature, and vSv is shorthand for the convolution of S with two Coulomb interactions (v). In metals, the structure factor behaves as $S \sim \omega/\mu$ for small energies ω,[13,14] whereas, for ideal insulators, $S = 0$ when ω is below the threshold for particle-hole excitations. Furthermore, in the ground-state state, the structure factor equals the spectral function of the charge response function χ. As explained in Sec. IV, $(v\chi v)(\mathbf{r},\mathbf{r},\omega) \sim z^{-1}$ far away from a solid surface, and we have

$$\Delta_0 = O((\omega_0/\mu)^2/z) , \tag{B8}$$

giving

$$\langle \Phi | \delta \hat{V}_H(\mathbf{r}) | \Phi \rangle = O(\langle \Phi | \Phi \rangle (\omega_0/\mu) z^{-1/2}) . \tag{B9}$$

Here, the factor ω_0/μ would enter in the estimate of any macroscopic one-electron observable, whereas the factor $z^{-1/2}$ originates from the particular properties of the Hartree potential $\hat{V}_H$.

Let us now argue that our estimate (B7) based on a study of the ground-state fluctuations Δ_0 is not altered if we instead use the fluctuations Δ_Φ. The quantities Δ_0 and Δ_Φ can be considered as macroscopic averages of charge-density fluctuations with respect to two different ensembles, one with zero energy content and one with an energy of the order ω_0. The central quantity of the discussion above is the ground-state structure factor, which now should be replaced by that corresponding to the state $| \Phi \rangle$. We will assume it to be known that such averages are insensitive to details in the ensemble as long as macroscopic quantities such as the mean energy remain the same. Supported by this argument, we will instead consider the structure factor corresponding to the canonical ensemble with a mean energy per particle of order ω_0. In this case the structure factor is proportional to the energy at small energies, as was the case for the structure factor of the ground state, but only down to ω_0. Below this value the canonical structure factor stays approximately constant down to zero energy. This behavior follows from (i) the fluctuation-dissipation theorem[13] which relates the structure factor to the dissipative part $\mathrm{Im}\chi$ of the density-density response function, and (ii) the fact that $\mathrm{Im}\chi$ is proportional to the energy for small energies.[13,14] Consequently, the value of the integral in Eq. (B6) will only change by a numerical factor of order unity if the ground state is replaced by the state $| \Phi \rangle$, and we see that our order-of-magnitude estimates in Eqs. (B8) and (B9) are also valid in this case.

We have so far considered normalizable states ($| \Phi \rangle$ and $| \Psi \rangle$), but we actually need to approximate quantities of the form

$$\langle N | \psi^\dagger(x')\delta(H + \epsilon - E_0 - \mu)MP\psi(x) | N \rangle$$

by the simpler expression

$$\langle N | \psi^\dagger(x')\delta(H + \epsilon - E_0 - \mu)\psi(x) | N \rangle \langle N - 1 | M | N - 1 \rangle$$
$$\equiv A(x,x',\epsilon)\langle N - 1 | M | N - 1 \rangle ,$$

where $\epsilon > \mu - \omega_0$ [cf. Eq. (46)]. [$E_0 = E(N-1)$.] The correction to this,

$$\Delta(\epsilon) = \langle N | \psi^\dagger(x')\delta(H + \epsilon - E_0 - \mu)\delta MP\psi(x) | N \rangle ,$$

cannot be directly estimated by our previous method since $\Delta(\epsilon)$ involves δ-function-normalized state vectors. Instead, we introduce the state vector

$$| \Phi(\epsilon) \rangle = [A(x',x',\epsilon)]^{-1/2}\delta(H + \epsilon - E_0 - \mu)\psi(x') | N \rangle ,$$

and, for brevity, we write

$$| \Psi \rangle = \delta MP\psi(x) | N \rangle .$$

We readily verify that the states $\{ | \Phi(\epsilon) \rangle \}$ are δ-function-normalized,

$$\langle \Phi(\epsilon) | \Phi(\epsilon') \rangle = \delta(\epsilon - \epsilon') .$$

Next, we express $\Delta(\epsilon)$ in terms of $|\Phi(\epsilon)\rangle$, integrate $\Delta^2(\epsilon)$ over an interval ϵ to $\epsilon+\delta\epsilon$,

$$\int_\epsilon^{\epsilon+\delta\epsilon} d\epsilon' \Delta^2(\epsilon') = \int_\epsilon^{\epsilon+\delta\epsilon} d\epsilon' A(x',x',\epsilon')$$
$$\times \langle \Psi | \Phi(\epsilon')\rangle\langle\Phi(\epsilon')|\Psi\rangle,$$

and replace $A(x',x',\epsilon')$ by its maximum value in the interval. The expression obtained in this way becomes larger by replacing the projector

$$P_1 = \int_\epsilon^{\epsilon+\delta\epsilon} d\epsilon' |\Phi(\epsilon')\rangle\langle\Phi(\epsilon')|$$

by the projector

$$P_2 = \int_\epsilon^{\epsilon+\delta\epsilon} d\epsilon' \delta(\epsilon'+H-E_0-\mu).$$

(This follows from the fact that P_2 projects onto all eigenstates of H in the interval ϵ to $\epsilon+\delta\epsilon$, whereas P_1 only projects onto a subclass.) We obtain

$$\int_\epsilon^{\epsilon+\delta\epsilon} d\epsilon' \Delta^2(\epsilon') \leq \max_{\epsilon \leq \epsilon' \leq \epsilon+\delta\epsilon} A(x',x',\epsilon') \int_\epsilon^{\epsilon+\delta\epsilon} d\epsilon' \langle \Psi | \delta(\epsilon'+H-E(N)) | \Psi\rangle .$$

By letting $\delta\epsilon$ tend to zero, we now find an estimate analogous to the estimate (B3) for normalized state vectors,

$$\Delta^2(\epsilon) \leq A(x',x',\epsilon)\langle N | \psi^\dagger(x)P\delta M\delta(H+\epsilon-E_0-\mu)\delta MP\psi(x) | N\rangle . \qquad (B10)$$

The analysis now proceeds as before [cf. Eq. (B4) and following]. Application of Eq. (B1), with $|\Phi\rangle = P\psi(x)|N\rangle$, and M replaced by $\delta M\delta(H+\epsilon-E_0-\mu)\delta M$, gives

$$\Delta^2(\epsilon) \leq A(x',x',\epsilon)\gamma_P(x,x)\langle N | \delta M\delta(H+\epsilon-E_0-\mu)\delta M | N\rangle ,$$

where

$$\gamma_P(x,x') = \langle N | \psi^\dagger(x')P\psi(x) | N\rangle .$$

In the particular case $M = \hat{V}_H(\mathbf{r})$, the last factor is seen to be $(vSv)(\mathbf{r},\mathbf{r},\mu-\epsilon)$. For this quantity we had the estimate

$$(vSv)(\mathbf{r},\mathbf{r},\mu-\epsilon) = O(z^{-1}\omega_0/\mu) .$$

We thus find [cf. Eqs. (44) and (45)]

$$Q(\mathbf{r},\mathbf{r}',\epsilon) = -\langle N | \psi^\dagger(\mathbf{r}',\sigma)\delta(H+\epsilon-E_0-\mu)\delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma) | N\rangle$$
$$= O([A(\mathbf{r}',\mathbf{r}',\epsilon)\gamma_P(\mathbf{r},\mathbf{r})z^{-1}\omega_0/\mu]^{1/2}) . \qquad (B11)$$

In the case of an arbitrary macroscopic observable M, we would have obtained a similar estimate as in Eq. (B11), but without the factor z^{-1}.

In Sec. IV we make the choice

$$\omega_0 = a\kappa_0/z \sim \mu a/(\kappa_0 z) .$$

In this case the rhs of Eq. (B11) becomes

$$O(z^{-1}[aA(\mathbf{r}',\mathbf{r}',\epsilon)\gamma_P(\mathbf{r},\mathbf{r})]^{1/2}) .$$

For the special case of and "ideal insulator," i.e., a system with no many-electron states in a forbidden gap, we need a sharper estimate of $Q(\mathbf{r},\mathbf{r}',\epsilon)$ (cf. Sec. IV E). We assume that the valence band is exactly filled in the N-electron ground state. Then, the low-lying $(N-1)$-electron states have only one single, perfectly stable quasihole and can therefore be labeled by *one single one-electron label* α. This is a very strong restriction with important consequences. We write these states $|N-1,\alpha\rangle$, or simple $|\alpha\rangle$, to distinguish them from a general $(N-1)$-electron state $|N-1,s\rangle$, where s stands for $\sim N \sim 10^{23}$ labels.

The special structure of the low-lying $(N-1)$-electron states gives rise to drastic phase-space restrictions. The density of (many-electron) states $\sum_s \delta(E-E_s+E_0)$ is normally of the order $\exp(N)$. (This follows since the logarithm of the density of states defines the entropy, which is normally of order N.) For a perfect insulator, however, the density of $(N-1)$-electron states is only of order

$$\sum_s \delta(E-E_s+E_0) \equiv \sum_\alpha \delta(\epsilon-\epsilon_\alpha) \sim N(\mu-\epsilon)^{1/2}$$

below the threshold for particle-hole creation. The lhs of Eq. (B11) now becomes

$$Q(\mathbf{r},\mathbf{r}',\epsilon) = -\sum_\alpha \langle N | \psi^\dagger(\mathbf{r}',\sigma | \alpha\rangle\delta(\epsilon-\epsilon_\alpha)$$
$$\times \langle \alpha | \delta\hat{V}_H(\mathbf{r})P\psi(\mathbf{r},\sigma) | N\rangle .$$

From this we see that Q is proportional to the density of $(N-1)$-electron states and thus of order

$$Q(\mathbf{r},\mathbf{r}',\epsilon) = O\left[(\mu-\epsilon)^{1/2}\omega_0^{-3/2} \int_{\mu-\omega_0}^\mu Q(\mathbf{r},\mathbf{r}',\epsilon')d\epsilon'\right] ,$$

where we can estimate that

$$\int_{\mu-\omega_0}^\mu Q(\mathbf{r},\mathbf{r}',\epsilon)d\epsilon = O(\gamma_P(\mathbf{r},\mathbf{r}')(\omega_0/\mu)z^{-1/2})$$

using a slight modification of the method leading to Eq. (B9). Thus,

$$Q(\mathbf{r},\mathbf{r}',\epsilon) = O([(\mu-\epsilon)/(\omega_0 z)]^{1/2}\gamma_P(\mathbf{r},\mathbf{r}')) \qquad (B12)$$

for an ideal insulator with no states in the forbidden gap. With $\omega_0 = a\kappa_0/z$, the rhs of Eq. (B12) is of the order or smaller than $az^{-3/2}B(z,z',\mu)$, in terms of the renormalized spectral density B used in Sec. IV E [cf. Eq. (64)].

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