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Correlation Potentials in a Nonuniform Electron Gas

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A microscopic theory of the correlation operator, directed toward conduction electrons in a metal, is developed. The off-diagonal matrix elements, between electron states $\vec{k}$ and $\vec{k}+\vec{q}$, that arise when the electron density has a modulation of wave vector $\vec{q}$, determine the correlation contribution to band structure. These are computed explicitly. They depend dramatically on $\vec{k}$ (i.e., nonlocal behavior) and on $\vec{q}$. The sum of exchange and correlation operators is also nonlocal, but is less singular than either individually. An alternative division of exchange plus correlation into screened-exchange plus Coulomb-hole operators is made. It is shown that the (often ignored) Coulomb-hole operator is usually much larger than the screened-exchange operator.

I. INTRODUCTION

The contribution of exchange and correlation to one-electron Hamiltonians is a widely debated and important problem. Our attention here is focused on energy-band problems for crystalline solids. The periodic potential that appears in a (one-electron) Schrödinger equation must have contributions from exchange and correlation as well as from the Hartree term.

The exchange operator A^X is often replaced by the Slater $\rho^{1/3}$ approximation,[1]

$$A_S^X = -3e^2(3\rho/8\pi)^{1/3} \ , \qquad (1.1)$$

where $\rho(\vec{r})$ is the local electron density. It has been shown[2] that A_S^X is a very poor approximation to A^X. For band calculations the off-diagonal matrix elements of A^X arising from a spatial modulation of ρ (having, say, wave vector $\vec{q}$) are the most relevant quantities. Not only does $\langle \vec{k}+\vec{q} | A^X | \vec{k} \rangle$ depend markedly on $\vec{k}$, which shows that A^X is severely nonlocal, but it also depends on $\vec{q}$. For some combinations of $\vec{k}$ and $\vec{q}$ it is singular. In contrast Eq. (1.1) leads to off-diagonal matrix elements that are independent of $\vec{k}$ and $\vec{q}$.

Arguments which suggest approximations such as (1.1), or variants[3] of it, are supposedly most reliable for small q. It was therefore surprising to find[2] that the relevant off-diagonal elements of A^X become infinitely large in comparison with those obtained from the approximation (1.1) as $q \to 0$.

The sum of exchange and correlation operators, $A^{XC} \equiv A^X + A^C$, is of paramount physical interest. If A^{XC} is to be well behaved for $q \to 0$, then $\langle \vec{k}+\vec{q} | A^C | \vec{k} \rangle$ must become infinite (and have negative sign) relative to (1.1). This surmise[2] contrasts sharply with a very small and positive value suggested by prior work.[3]

The purpose of this study is to develop a *microscopic* theory of the correlation potential so that the explicit dependence of $\langle \vec{k}+\vec{q} | A^C | \vec{k} \rangle$ on $\vec{k}$ and $\vec{q}$ can be calculated. By combining this with the known[2] behavior of A^X, we determine the $\vec{q}$ dependence and nonlocal behavior of A^{XC}. This is carried out in Secs. II and III. The plasmon model[4] for treating dynamic correlations of electrons is employed. The off-diagonal behavior of A^C and A^{XC} in the $q \to 0$ limit is treated in Sec. IV.

The exchange and correlation operator can be subdivided into screened-exchange and Coulomb-hole operators, $A^{XC} \equiv A^{SX} + A^{CH}$. This alternative subdivision is displayed in Sec. V. We show that screened exchange is generally much less important than the Coulomb-hole potential. This deserves emphasis because the Coulomb-hole potential is often completely ignored. In some calculations its neglect can lead (and has led) to grossly incorrect conclusions.

II. FORMULATION OF CORRELATION OPERATOR

A microscopic theory of the correlation operator depends primarily on the excitation spectrum of the electron system. For a degenerate electron gas, this spectrum consists of plasma and single-particle excitations. The simplifying feature of the plasmon model[4] is the replacement of the entire excitation spectrum by a single effective plasmon frequency spectrum $\omega(q)$ for *all* $\vec{q}$. This is accurate for small q, since the plasma mode exhausts the f-sum rule.[5] For large q, $\omega(q) \sim \hbar q^2/2m$, the center of gravity of the single-particle excitations. The accuracy of the model is assured by requiring the electron-plasmon interaction to exhaust the f-sum rule (for all $\vec{q}$), and by determining $\omega(q)$ so that the model reproduces the correct electron-gas dielectric function.

The model is suitable for calculating quasiparticle energy spectra of states near the Fermi energy. On the other hand, the model would break down for calculations that depend critically on the spectral width of the excitations. The practical utility of the model has been shown in Ref. 4 (hereafter referred to as I) for the case of a uniform electron gas. It will become apparent in what follows that treatment of the nonuniform case would be intractable without the simplified excitation spectrum employed.

For the purpose of developing a suitable perturbation theory, we write the total electron Hamiltonian as

$$H = H_{\mathrm{HF}} + (H - H_{\mathrm{HF}}) \ , \tag{2.1}$$

where H_{HF} is the Hartree-Fock Hamiltonian, and we proceed to apply the plasmon model to the term in parentheses. This term must take account of all interactions associated with charge-density fluctuations from the HF mean. We follow the original development of the model in I but omit much of the detail.

The charge-density operator of the electron system with N electrons in volume Ω is

$$\underline{\rho}(\vec{r}) = e\,\Omega^{-1} \sum_{\vec{p},\vec{k}} c_{\vec{k}+\vec{p}}^{\ \dagger} c_{\vec{k}}\, e^{i\vec{p}\cdot\vec{r}} \ . \tag{2.2}$$

The expectation value $\langle \underline{\rho}(\vec{r}) \rangle$ of the charge density has Fourier components associated with the band structure:

$$\langle \underline{\rho}(\vec{r}) \rangle \equiv \rho_{\mathrm{band}}(\vec{r}) = e\,\Omega^{-1} \sum_{\vec{q}} \rho_{\vec{q}}\, e^{-i\vec{q}\cdot\vec{r}} \ , \tag{2.3}$$

where $\{\vec{q}\}$ are the reciprocal-lattice vectors and $\rho_{\vec{q}}$ are the Fourier coefficients of the ground-state charge density.

The dynamical response of an electron to the instantaneous fluctuations of $\underline{\rho}(\vec{r})$ from its mean (2.3) is the origin of the correlation energy. The fundamental simplification of the plasmon model is the representation of these fluctuations by plasmon operators only:

$$\underline{\rho}(\vec{r}) - \rho_{\mathrm{band}}(\vec{r}) = \sum_{\vec{p}} \lambda_{\vec{p}} (a_{\vec{p}}\, e^{i\vec{p}\cdot\vec{r}} + a_{\vec{p}}^{\ \dagger}\, e^{-i\vec{p}\cdot\vec{r}}) \ , \tag{2.4}$$

where $a_{\vec{p}}$ and $a_{\vec{p}}^{\ \dagger}$ are the plasmon annihilation and creation operators. As in I,[4] the coefficients $\lambda_{\vec{p}}$ are determined from the requirement that the model satisfy the f-sum rule. The sum rule is[6]

$$\sum_n \hbar\,\omega_{n0} \,|\, (\underline{\rho}_{\vec{p}})_{n0} |^2 = N\hbar^2 p^2/2m \ , \tag{2.5}$$

where $\hbar\omega_{n0}$ is the energy difference between the zero-order state and the excited state n. Since the plasmon model assumes only one excitable mode for each $\vec{p}$, Eq. (2.5) reduces to

$$\hbar\,\omega_{\vec{p}}\, \Omega^2 \lambda_{\vec{p}}^2 = N\hbar^2 p^2/2m \ . \tag{2.6}$$

We have used the well-known matrix elements, 0 and 1, of $a_{\vec{p}}$ and $a_{\vec{p}}^{\ \dagger}$, respectively. In the present context (2.6) applies to all $\vec{p}$ except the reciprocal-lattice vectors $\vec{q}$. For the latter, $\rho_{\vec{q}}$ is macroscopic, so the value of $\lambda_{\vec{q}}^2$ is smaller than that given by (2.6) by a factor $\sim N$.

The Coulomb potential experienced by an electron in the electrostatic field of the charge fluctuation (2.4) is determined by a simple application of Poisson's equation. This would be the entire electron-plasmon interaction were it not for exchange and correlation potentials. As shown in I, the latter potentials may be incorporated in the matrix elements $M_{\vec{p}}$ of the electron-plasmon interaction. The correction term $(H - H_{\mathrm{HF}})$ of (2.1) must additionally contain the self-energy of the plasmon excitations. Accordingly,

$$(H - H_{\mathrm{HF}}) = \sum_{\vec{p}} \hbar\, \omega_{\vec{p}}\, a_{\vec{p}}^{\ \dagger} a_{\vec{p}} + \sum_{\vec{p},\vec{k}} M_{\vec{p}}\, c_{\vec{k}+\vec{p}}^{\ \dagger} c_{\vec{k}} (a_{\vec{p}} + a_{-\vec{p}}^{\ \dagger}) \ , \tag{2.7}$$

with

$$M_{\vec{p}} = \frac{4\pi e^2}{p^2}\, \lambda_{\vec{p}}\, [1 - G^{XC}(p/2k_F)] \ . \tag{2.8}$$

G^{XC} is the exchange and correlation contribution to the self-consistent potential. Modern treatments of the electron-gas dielectric function can usually be interpreted as attempts to determine the behavior of G^{XC}. The dielectric function is

$$\epsilon_p = 1 + \frac{Q(p/2k_F)}{1 - G^{XC}(p/2k_F) Q(p/2k_F)} \ , \tag{2.9}$$

where

$$Q(x) = \frac{me^2}{\pi\hbar^2 k_F x^2} \left(\frac{1}{2} + \frac{1 - x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \right) \ . \tag{2.10}$$

In the calculations that follow we shall use the approximate G^{XC} employed in I.

Since the band-electron wave functions are not plane waves, the perturbation (2.7) is not yet in the most useful form. We now assume that the one-electron wave functions of the zero-order state are known. They are linear combinations of plane waves with the wave vectors of the components differing by vectors of the reciprocal lattice. Thus we write the creation and annihilation operators for the band states as

$$b_{\vec{K}}{}^{\dagger}=\sum_{\vec{k}} U_{\vec{K}\vec{k}}\, c_{\vec{k}}{}^{\dagger} \quad , \quad b_{\vec{K}}=\sum_{\vec{k}} U_{\vec{k}\vec{K}}{}^{\dagger} c_{\vec{k}} \quad . \qquad (2.11)$$

(Throughout this paper capital letters will be used to designate positions in the Brillouin zone, and lower case letters will designate the wave vectors of plane-wave components.) U is a unitary matrix, so, using an extended zone scheme, we have

$$c_{\vec{k}}{}^{\dagger}=\sum_{\vec{K}} U_{\vec{k}\vec{K}}{}^{\dagger} b_{\vec{K}}{}^{\dagger} \quad , \quad c_{\vec{k}}=\sum_{\vec{K}} U_{\vec{K}\vec{k}}\, b_{\vec{K}} \quad . \qquad (2.12)$$

On substituting (2.12) and (2.7), the perturbation term is found to be

$$(H-H_{\mathrm{HF}})=\sum_{\vec{p}} \hbar\omega_{\vec{p}}\, a_{\vec{p}}{}^{\dagger} a_{\vec{p}} + \sum_{\vec{p},\vec{k},\vec{K},\vec{K}'} M_{\vec{p}}\, U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}\vec{k}}\, b_{\vec{K}'}{}^{\dagger} b_{\vec{K}}(a_{\vec{p}}+a_{-\vec{p}}{}^{\dagger}) \quad . \qquad (2.13)$$

The second-order energy due to this perturbation is, for this model, the system correlation energy

$$E^{C}=\sum_{\vec{p},\vec{k},\vec{k}',\vec{K},\vec{K}'} |M_{\vec{p}}|^{2} U_{\vec{k}'-\vec{p},\vec{K}}{}^{\dagger} U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'} U_{\vec{K}\vec{k}} \times \frac{1}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}-\hbar\omega_{\vec{p}}}\, n_{\vec{K}}(1-n_{\vec{K}'}) \quad . \qquad (2.14)$$

The energies $\epsilon_{\vec{K}}$ occurring in the denominator of (2.14) are the energy eigenvalues of the band state for which the creation operator is $b_{\vec{K}}{}^{\dagger}$ (see Appendix A). That is, the band wave functions (2.11) and energies to be used in (2.14) are those which are found self-consistently (in a manner analogous to the Hartree-Fock approach) from any of the usually successful band-theory methods, but with the Hartree-Fock Hamiltonian augmented with the one-electron correlation Hamiltonian to be derived below (2.16).

The one-electron correlation energy is

$$\epsilon_{\vec{K}}^{C}=\frac{\partial E^{C}}{\partial n_{\vec{K}}}=\sum_{\vec{p},\vec{k},\vec{k}',\vec{K}} |M_{\vec{p}}|^{2} \quad U_{\vec{k}'-\vec{p},\vec{K}}{}^{\dagger} U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'} U_{\vec{K}\vec{k}} \times\left(\frac{1-n_{\vec{K}'}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}-\hbar\omega_{\vec{p}}}-\frac{n_{\vec{K}'}}{\epsilon_{\vec{K}'}-\epsilon_{\vec{K}}-\hbar\omega_{\vec{p}}}\right)$$

$$=\sum_{\vec{k},\vec{k}'} U_{\vec{k}',\vec{K}}{}^{\dagger} U_{\vec{K},\vec{k}} \langle\vec{k}'|A_{\vec{K}}^{C}|\vec{k}\rangle \quad . \qquad (2.15)$$

This defines the one-particle correlation operator $A_{\vec{K}}^{C}$ for the band state $\vec{K}$. Its matrix elements in a basis of plane-wave states are

$$\langle\vec{k}'|A_{\vec{K}}^{C}|\vec{k}\rangle=\sum_{\vec{K}',\epsilon_{\vec{K}'}>\epsilon_{F}} \sum_{\vec{p}} |M_{\vec{p}}|^{2} \frac{U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'+\vec{p}}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}-\hbar\omega_{\vec{p}}} + \sum_{\vec{K}',\epsilon_{\vec{K}'}<\epsilon_{F}} \sum_{\vec{p}} |M_{\vec{p}}|^{2} \frac{U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'+\vec{p}}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}+\hbar\omega_{\vec{p}}} . \qquad (2.16)$$

For the special case of the uniform electron gas $U_{\vec{k},\vec{K}}=\delta_{\vec{k},\vec{K}}$ and the correlation operator is diagonal. In this case (2.16) reduces to the correlation energy expression derived in I.

The exact matrix elements of the exchange operator $A_{\vec{K}}^{X}$ are also of interest, since a quantity of considerable theoretical interest is the sum of exchange and correlation terms:

$$\langle\vec{k}'|A_{\vec{K}}^{X}|\vec{k}\rangle=-\sum_{\vec{K}',\epsilon_{\vec{K}'}<\epsilon_{F}} \sum_{\vec{p}} \frac{4\pi e^{2}}{\Omega p^{2}} U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'+\vec{p}} \quad . \qquad (2.17)$$

Standard procedures may be used to convert the summations in (2.16) and (2.17) to integrals.

III. APPLICATION TO PERIODICALLY MODULATED ELECTRON GAS

To explicitly display some of the properties of the correlation operator (2.16), we choose to study a special simple system, an electron gas (with the usual rigid neutralizing background charge) to which has been applied a potential of the form $V\cos\vec{q}\cdot\vec{r}$. As emphasized in Sec. II, the electron wave functions should be found self-consistently using the Hartree-Fock Hamiltonian together with the correlation Hamiltonian; self-consistency is usually obtained by iteration. Since it is not our purpose to obtain precision, but rather to display the qualitative behavior of the matrix elements, we make no attempt to achieve self-consistency. Instead, we derive our wave functions from the ansatz that the sum of all potentials (imposed, Coulomb, exchange, and correlation) is itself a local (state-independent) potential $G\cos\vec{q}\cdot\vec{r}$. *A posteriori*, this ansatz is found to be unjustified, so the results displayed must be regarded as only the first step in the iterative march to self-consistency.

With the above ansatz, the Hamiltonian in a basis of plane-wave states takes the infinite tridiagonal form

$$\left(\begin{array}{cccccc} \vdots & \vdots & \vdots & & & \\ G/2 & \frac{1}{2}(\vec{k}-\vec{q})^{2} & G/2 & & & \\ & G/2 & \frac{1}{2}\vec{k}^{2} & G/2 & & \\ & & G/2 & \frac{1}{2}(\vec{k}+\vec{q})^{2} & G/2 & \\ & & & G/2 & \frac{1}{2}(\vec{K}+2\vec{q})^{2} & G/2 \\ & & & \vdots & \vdots & \vdots \end{array}\right) . \qquad (3.1)$$

Provided there is no degeneracy, the Hamiltonian is easily diagonalized by first-order perturbation theory. When a degeneracy exists, all but a 2×2 matrix can be diagonalized similarly; this small matrix can subsequently be diagonalized exactly. The eigenfunctions of (3.1) found using this prescription are

$$\psi_{\vec{K}}(\vec{r})=\frac{1}{\sqrt{2}}\biggl[\left(1+\frac{|\Delta|}{(\Delta^{2}+G^{2})^{1/2}}\right)^{1/2}\left(e^{i\vec{K}\cdot\vec{r}}+\frac{Ge^{i(\vec{K}\pm\vec{q})\cdot\vec{r}}}{K^{2}-(\vec{K}\pm\vec{q})^{2}}\right)$$

$$+\frac{\Delta}{|\Delta|}\frac{G}{|G|}\left(1-\frac{|\Delta|}{(\Delta^2+G^2)^{1/2}}\right)^{1/2}$$

$$\times\left(e^{i(\vec{K}\mp\vec{q})\cdot\vec{r}}+\frac{Ge^{i(\vec{K}\mp 2\vec{q})\cdot\vec{r}}}{(\vec{K}\mp\vec{q})^2-(\vec{K}\mp 2\vec{q})^2}\right)\Bigg] \ ,$$

$$0<|K_z|<\tfrac{3}{2}q$$

with

$$\Delta=\tfrac{1}{2}K^2-\tfrac{1}{2}(\vec{K}\mp\vec{q})^2 \ . \qquad (3.2)$$

The corresponding energy eigenvalues are

$$\epsilon_{\vec{K}}=\tfrac{1}{2}[K^2+q^2+(\Delta/|\Delta|)(\Delta^2+G^2)^{1/2}-(\Delta'^2+G^2)^{1/2}] \ , \qquad (3.3)$$

where

$$\Delta'=\tfrac{1}{2}K^2-\tfrac{1}{2}(\vec{K}\pm\vec{q})^2 \ .$$

The upper (lower) signs should be taken in (3.2) and (3.3) when K_z is positive (negative). If G is vanishingly small, the wave functions (3.2) simplify to

$$\psi_{\vec{K}}(\vec{r})=e^{i\vec{K}\cdot\vec{r}}+\frac{Ge^{i(\vec{K}+\vec{q})\cdot\vec{r}}}{\vec{K}^2-(\vec{K}+\vec{q})^2}+\frac{Ge^{i(\vec{K}-\vec{q})\cdot\vec{r}}}{\vec{K}^2-(\vec{K}-\vec{q})^2} \ . \qquad (3.4)$$

These are the usual perturbation wave functions, and in any case they should be used outside of the range of K_z specified in (3.2).

One further assumption reduces (2.16) to quadrature: The plasmon spectrum to be used is the same as that utilized in I to fit the correlation energy for the uniform electron gas:

$$\omega_{\vec{q}}^2=\omega_P^2\epsilon_p/(\epsilon_p-1) \ . \qquad (3.5)$$

ω_P is the classical plasma frequency $4\pi Ne^2/m\Omega$, and ϵ_p is the static dielectric function (2.9). The choice used in I of $G^{XC}(x)$ in (2.9) is

$$G^{XC}(x)=1.1x^2/(1+10x^2+1.5x^4)^{1/2} \ . \qquad (3.6)$$

The diagonal elements of (2.16) are the correlation corrections to the quasiparticle energy, which to first order in G are the same as those studied in I. Here we are concerned only with the off-diagonal elements $\langle\vec{K}+\vec{q}\,|A_{\vec{K}}^{C}|\vec{K}\rangle$, together with the corresponding exchange matrix elements. A useful datum is the off-diagonal matrix element which would be computed if the Slater potential (1.1) is used for exchange and correlation. If the wave functions (3.4) are used, the charge density ρ is

$$\rho(\vec{r})=\rho_0(1-\rho'\cos\vec{q}\cdot\vec{r}) \ , \qquad (3.7)$$

where

$$\rho_0=k_F^3/3\pi^2 \ , \qquad (3.8)$$

and the fractional charge-density modulation is[2]

$$\rho'=(3G/2\epsilon_F)f(q/2k_F) \ ,$$

$$f(x)=\tfrac{1}{2}+[(1-x^2)/4x]\ln|(1+x)/(1-x)| \ . \qquad (3.9)$$

Then the off-diagonal matrix element of A_S^X is[2]

$$\langle\vec{K}+\vec{q}\,|A_S^X|\vec{K}\rangle=e^2k_F\rho'/4\pi \ . \qquad (3.10)$$

Since the right-hand side of (3.10) is independent of both $\vec{K}$ and $\vec{q}$ (for fixed fractional charge modulation), it is a convenient unit by which to measure the computed correlation and exchange matrix elements, and we term in a "Slater" unit.

By using first-order perturbation theory to derive the wave functions (3.2) and (3.6), we have implicitly supposed an interest only in terms linear in G. Accordingly, it is unnecessary to consider for integration purposes the deviations of the Fermi surface from the spherical shape, since such distortions introduce corrections of order G^2 and higher only.

In Figs. 1(a)–1(h) are displayed the computed off-diagonal matrix elements of correlation, exchange, and their total as a function of the magnitude of the wave vector of the charge-density modulation, for electrons at the following positions in the Fermi sphere; the points P and Q where the $\vec{q}$ axis intersects the Fermi surface, the Fermi-sphere center C, the equatorial position E, two additional axial positions A and B with $|\vec{K}_A|=|\vec{K}_B|=0.5k_F$, and the points G and H where the $\vec{q}$ axis intersects the gap planes, $|\vec{K}_G|=|\vec{K}_H|=\tfrac{1}{2}q$. The exchange curves for the points P, Q, C, and E have been published previously.[2] To facilitate comparison of the curves for the total of exchange and correlation, and to emphasize that for consideration of the importance of features of this total the appropriate scale is a tenth of a Slater unit, the curves for the points P, Q, C, and E are replotted on an expanded scale in Fig. 1(i). In Figs. 2(a)–2(c) the wave vector of the modulation is fixed and the matrix elements for axial electron states are plotted as a function of position on the axis. For the matrix elements of Figs. 1 and 2, the electron density [ρ_0 in (3.8)] was assumed to be that of sodium. The exchange curves of Figs. 1 and 2 are universal functions of density, but the correlation curves are not. (This emphasizes the fact that exchange and correlation have different physical origins—exchange results from a kinematic restriction on the wave functions, correlation derives from dynamic interactions.) Accordingly, in Figs. 3(a)–3(c), the density dependence of the curves for the total of exchange and correlation are displayed for the points P, Q, and C.

Figures 1–3 afford the following general remark about the relationship between the off-diagonal behavior of the exchange and correlation operators. For any feature of an exchange curve, a corresponding feature (with opposite sign) exists in the corresponding correlation curve. For example, if we examine the sequence of curves, Figs. 1(a)–1(e), for the points Q, B, C, A, and P, we note that for

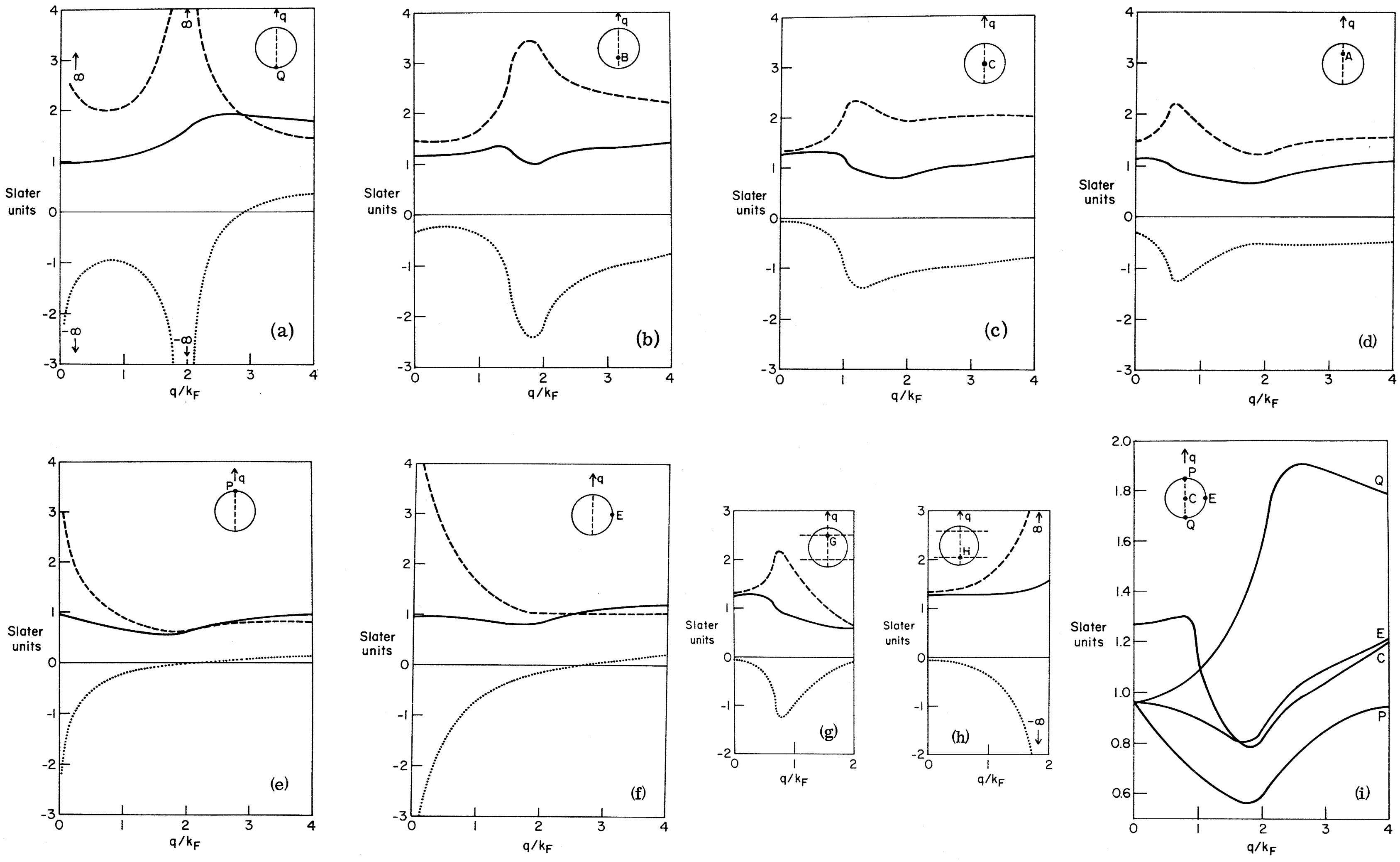


FIG. 1. Off-diagonal matrix elements of exchange (dashed curve), correlation (dotted curve), and the total of exchange and correlation (solid curve) as a function of the wave vector $\vec{q}$ of a periodic charge modulation, for electrons at various positions in the Fermi sphere. The matrix elements are measured in Slater units, which are defined in Eq. (3.10). The electron states for which matrix elements are depicted are (a) Q, on the negative $\vec{q}$ axis at the Fermi surface; (b) B, on the negative $\vec{q}$ axis, midway from sphere center to the Fermi surface; (c) C, the sphere center; (d) A, on the positive $\vec{q}$ axis midway from the center to the Fermi surface; (e) P, on the positive $\vec{q}$ axis at the Fermi surface; (f) E, the equatorial position; (g) G, on the positive $\vec{q}$ axis of the gap plane; (h) H, on the negative $\vec{q}$ axis at the gap plane; (i) Q, C, P, and E as given in Figs. 1(a), 1(c), 1(e), and 1(f).

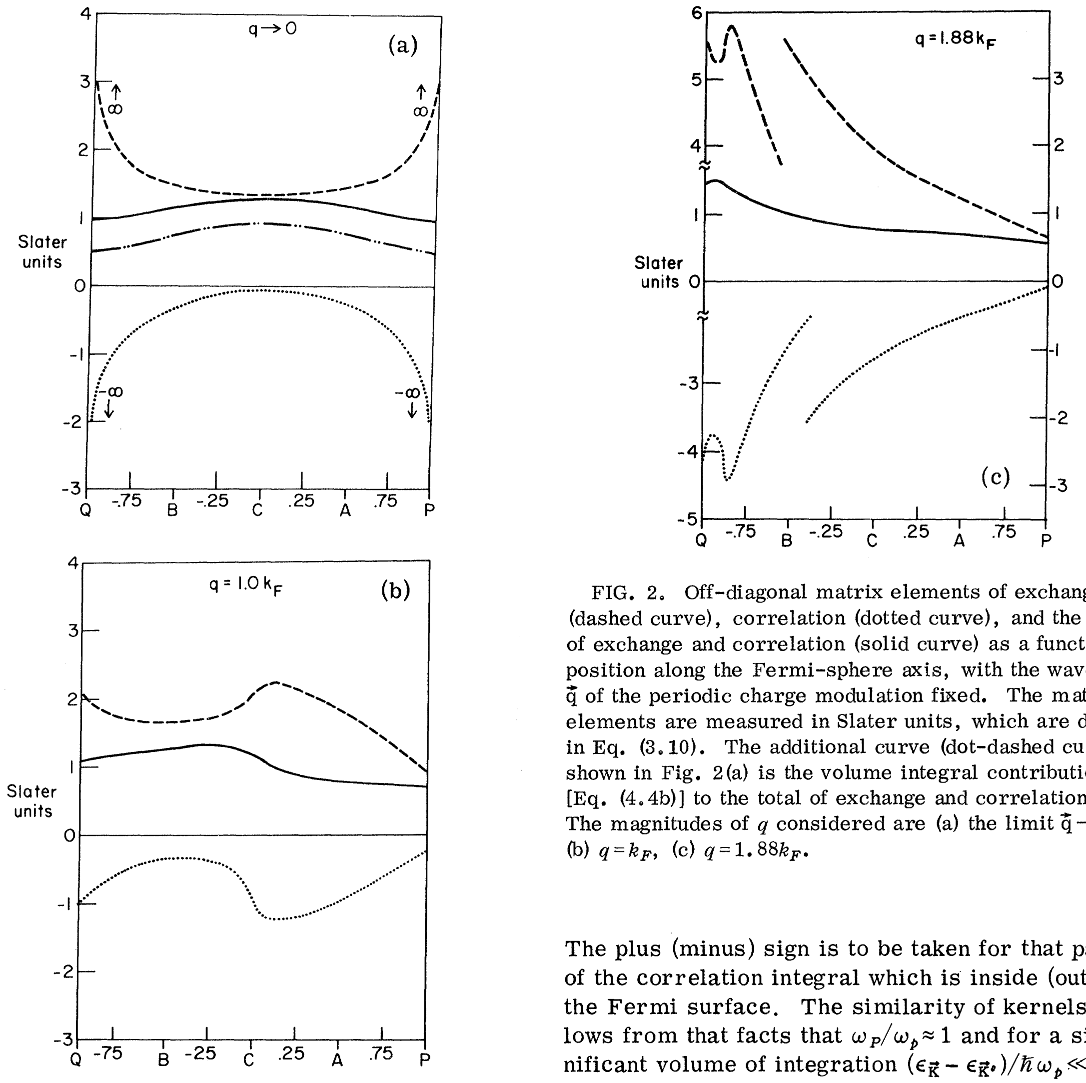


FIG. 2. Off-diagonal matrix elements of exchange (dashed curve), correlation (dotted curve), and the total of exchange and correlation (solid curve) as a function of position along the Fermi-sphere axis, with the wave vector $\vec{q}$ of the periodic charge modulation fixed. The matrix elements are measured in Slater units, which are defined in Eq. (3.10). The additional curve (dot-dashed curve) shown in Fig. 2(a) is the volume integral contribution [Eq. (4.4b)] to the total of exchange and correlation. The magnitudes of q considered are (a) the limit $\vec{q}\rightarrow 0$, (b) $q=k_F$, (c) $q=1.88k_F$.

both exchange and correlation there is a notable feature which starts out as a divergence at $q/k_F=2$ for the point Q, then becomes a hump located at a smaller value of q at B, and continues to move towards smaller values of q as the point of interest moves along the Fermi-sphere axis, finally becoming the divergence at $q\rightarrow 0$ on reaching the Fermi surface at P.

The reason for the similarity of the exchange and correlation curves is that for small and medium plasmon wave vectors, the kernels of the correlation and exchange integrals [(2.16) and (2.17), respectively] are very similar. For $p\approx 0$, the kernels are

$$\text{correlation:}\quad \frac{2\pi e^2}{\Omega p^2}\left(\frac{\omega_P}{\omega_p}\right)^2\left(\frac{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}}{\omega_p}\pm 1\right)^{-1},$$

$$\text{exchange:}\quad -\frac{4\pi e^2}{\Omega p^2} \qquad (3.11)$$

The plus (minus) sign is to be taken for that part of the correlation integral which is inside (outside) the Fermi surface. The similarity of kernels follows from that facts that $\omega_P/\omega_p\approx 1$ and for a significant volume of integration $(\epsilon_{\vec{K}}-\epsilon_{\vec{K}'})/\hbar\omega_p \ll 1$. Note that the exchange and correlation curves for points on the Fermi surface have (logarithmic) divergences, but that the sum of these does not. The divergent contributions to the integrals come from those regions where $p\approx 0$, $\epsilon_{\vec{K}}\approx\epsilon_{\vec{K}'}$. Observing that for a small region around the point of divergence there are equal contributions to the correlation integral from the interior and exterior of the Fermi surface, it is clear that the mutual cancellation of the divergences has occurred only because the plasmon frequency ω_p is, for $p\rightarrow 0$, precisely equal to ω_P, the classical plasma frequency.

Notwithstanding the over-all similarities of the exchange and correlation curves, the presence of the recoil energy in the denominators for correlation does affect both the magnitude and the positioning of extrema, so that the curves for the sum are not smooth but have structure of significant amplitude, typically 0.4 Slater units peak to peak for sodium. Deviations from the Slater value are as much as a factor of 2. Moreover, the curves

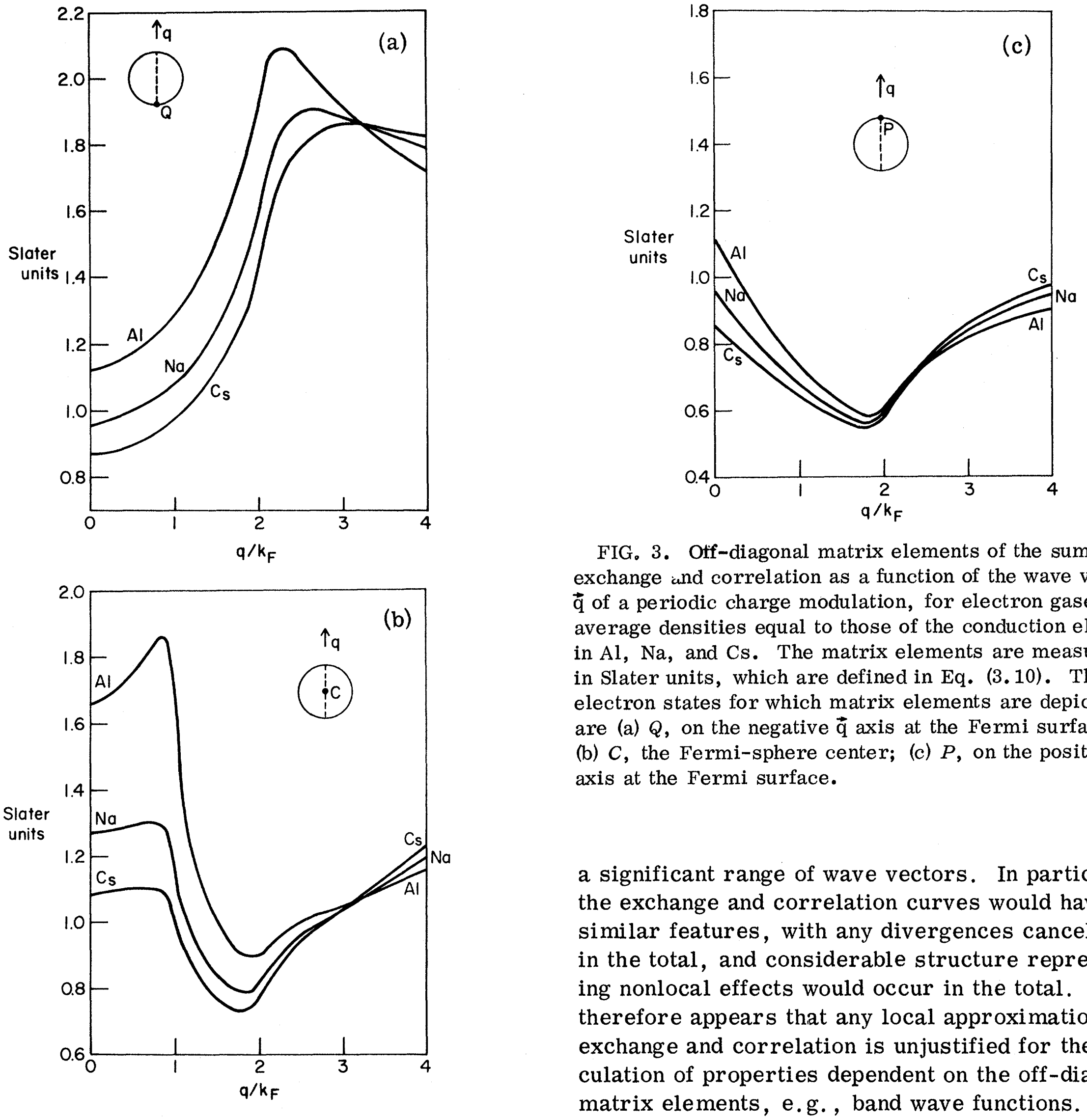


FIG. 3. Off-diagonal matrix elements of the sum of exchange and correlation as a function of the wave vector $\vec{q}$ of a periodic charge modulation, for electron gases with average densities equal to those of the conduction electrons in Al, Na, and Cs. The matrix elements are measured in Slater units, which are defined in Eq. (3.10). The electron states for which matrix elements are depicted are (a) Q, on the negative $\vec{q}$ axis at the Fermi surface; (b) C, the Fermi-sphere center; (c) P, on the positive $\vec{q}$ axis at the Fermi surface.

are highly state dependent. Thus the off-diagonal behavior of the sum of exchange and correlation remains highly nonlocal. The structure of the curves, and thus the influence of nonlocality, is more pronounced at the higher densities.

Although we have treated only a simplified system, similar conclusions would obtain for a real metal, since the plasmon frequency would again be expected to be close to the plasma frequency for a significant range of wave vectors. In particular, the exchange and correlation curves would have similar features, with any divergences canceling in the total, and considerable structure representing nonlocal effects would occur in the total. It therefore appears that any local approximation to exchange and correlation is unjustified for the calculation of properties dependent on the off-diagonal matrix elements, e.g., band wave functions.

IV. $q\to 0$ LIMIT

In order that first-order perturbation theory apply to the calculation of the wave functions (3.2), we see from (3.1) that we must have

$$\left|\tfrac{1}{2}(\vec{k}-\vec{q})^2-\tfrac{1}{2}k^2\right| \gg |G/2| \quad , \tag{4.1}$$

and thus we must have $G/qk_F \ll 1$. Thus, in taking the limit $q\to 0$, we must also have $G\to 0$, so that the appropriate wave functions to use are (3.4). For this situation, (2.16) becomes

$$\langle \vec{K}+\vec{q}|A^C_{\vec{K}}|\vec{K}\rangle_{q\to 0}=\sum_{\vec{K}'}\left(|M_{\vec{K}'-\vec{K}}|^2\frac{U_{\vec{K}',\vec{K}'}^{\dagger}U_{\vec{K}',\vec{K}'+\vec{q}}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}\pm\hbar\omega_{\vec{K}'-\vec{K}}}+|M_{\vec{K}'-\vec{K}-\vec{q}}|^2\frac{U_{\vec{K}'-\vec{q},\vec{K}'}^{\dagger}U_{\vec{K}',\vec{K}'}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}\pm\hbar\omega_{\vec{K}'-\vec{K}-\vec{q}}}\right) . \tag{4.2}$$

After some simple standard manipulations, (4.2) becomes

$$\sum_{\vec{K}'}\{\text{surface 1}\}\,|M_{\vec{K}'-\vec{K}}|^2\frac{U_{\vec{K}',\vec{K}'}^{\dagger}U_{\vec{K}',\vec{K}'+\vec{q}}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}\pm\hbar\omega_{\vec{K}'-\vec{K}}}-\sum_{\vec{K}'}\{\text{surface 2}\}\,|M_{\vec{K}'-\vec{K}}|^2\frac{U_{\vec{K}',\vec{K}'}^{\dagger}U_{\vec{K}',\vec{K}'+\vec{q}}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}\pm\hbar\omega_{\vec{K}'-\vec{K}}}$$

$$+\sum_{\vec{K}'}\{\text{surface 2}\}\,|M_{\vec{K}',\vec{K}'}|^2\,U_{\vec{K}',\vec{K}}^{\dagger}U_{\vec{K}',\vec{K}'+\vec{q}}\left[(\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}\pm\hbar\omega_{\vec{K}'-\vec{K}})^{-1}-(\epsilon_{\vec{K}}-\epsilon_{\vec{K}'+\vec{q}}\pm\hbar\omega_{\vec{K}'-\vec{K}})^{-1}\right]\quad . \tag{4.3}$$

The meaning of the notation used in (4.3) is: For that part of the summation which applies to the interior (exterior) of the surface indicated, the upper (lower) sign should be taken in the denominator. Surface 1 is the Fermi sphere, and surface 2 is an identical surface shifted by $-\vec{q}$.

The summands of the first two summations in (4.3) are identical, so together they represent a single summation over a thin shell at the Fermi surface. With a choice of axes such that $\vec{K}$ is in the plane $\varphi=0$, and the usual conversion of the sums into integrals, these two terms become

$$-\frac{\Omega G}{(2\pi)^3}\int_{-k_F}^{k_F} dK_z'\int_0^{\pi} d\varphi\,|M_{\vec{K}'-\vec{K}}|^2\left(\frac{1}{\epsilon_K-\epsilon_F+\hbar\omega_{\vec{K}'-\vec{K}}}-\frac{1}{\epsilon_K-\epsilon_F-\hbar\omega_{\vec{K}'-\vec{K}}}\right)\quad . \tag{4.4a}$$

$\vec{K}'$ in (4.4a) is restricted to the Fermi surface.

To consider the remaining summation in (4.3), we write the energy denominator as

$$\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}\pm\hbar\omega_{\vec{K}'-\vec{K}}=D\quad . \tag{4.5}$$

Then

$$\epsilon_{\vec{K}}-\epsilon_{\vec{K}'+\vec{q}}\pm\hbar\omega_{\vec{K}'-\vec{K}}=D-\epsilon_{\vec{K}'+\vec{q}}+\epsilon_{\vec{K}'} \tag{4.6}$$

and

$$\frac{1}{D}-\frac{1}{D+\epsilon_{\vec{K}'}-\epsilon_{\vec{K}'+q}}=\frac{1}{D}-\frac{1}{D}\left(1+\frac{\epsilon_{\vec{K}'}-\epsilon_{\vec{K}'+\vec{q}}}{D}\right)^{-1}$$
$$=\frac{\epsilon_{\vec{K}'}-\epsilon_{\vec{K}'+\vec{q}}}{D^2}-\cdots\text{(terms of higher order)}\quad . \tag{4.7}$$

So to first order in G the required term is

$$\sum_{\vec{K}'}\{\text{Fermi surface}\}\,|M_{\vec{K}'-\vec{K}}|^2\,\frac{G}{2D^2}\quad . \tag{4.8}$$

Writing

$$\vec{K}'-\vec{K}=\vec{R}\quad , \tag{4.9}$$

and for this integral choosing the z axis to be parallel to $\vec{K}$, we have

$$D^2=(\tfrac{1}{2}R^2\mp\hbar\omega_R+KR\cos\theta)^2\quad , \tag{4.10}$$

where θ is the angle between $\vec{K}$ and $\vec{R}$. Then the required term is

$$\frac{\frac{1}{2}\Omega G}{(2\pi)^3}\int_{\text{Fermi surface}} d^3R\,\frac{|M_R|^2}{(\frac{1}{2}R^2\mp\hbar\omega_R+KR\cos\theta)^2}\quad . \tag{4.4b}$$

Again the notation is that the upper (lower) sign is to be taken in the denominator for that part of the integration which is interior (exterior) to the Fermi surface. Two of the three integrations in (4.4b) can be performed analytically. Note that because the z axis is chosen to be parallel to $\vec{K}$, this term is isotropic as a function of the direction of $\vec{K}$.

The exchange integral corresponding to (4.4) is

$$\langle\vec{K}+\vec{q}\,|A_{\vec{K}}^{X}|\,\vec{K}\rangle_{q\to 0}=\frac{4\pi e^2G}{(2\pi)^3}\int_{-k_F}^{k_F} dK_z'\int_0^{\pi} d\varphi\,|\vec{K}'-\vec{K}|^{-2}\quad . \tag{4.11}$$

Equation (4.11) can be integrated analytically.

We notice immediately a further distinction between exchange and correlation. Whereas for exchange, the off-diagonal matrix element in the limit $q\to 0$ depends only on the states at the Fermi surface, by virtue of the term (4.4b), for correlation all states contribute. This should be compared with the free-electron gas where the dynamic interactions among electrons produce momentum distributions which differ significantly from the Fermi-Dirac distribution both above and below the Fermi surface, whereas exchange interactions do not. These observations again underscore the inadequacy of a local approximation to exchange and correlation.

In Fig. 2(a) the off-diagonal matrix elements for axial states are displayed. In Appendix B we prove that the $q\to 0$ matrix elements of exchange and correlation for any state $\vec{K}$ depend only on the magnitudes of $\vec{K}$ and k_F. That is, the curves for the line CP may be used to find the matrix elements for any point in the Fermi volume in the limit $q\to 0$. The volume term (4.4b) is also plotted in Fig. 2(a), and it is seen to be a significant contribution for all states.

The present case of $q\to 0$ is useful for illustration of the changes to be expected in further iterations. We initially supposed a total state-independent potential $G(\vec{K})=G(0)$ for the purpose of generating the wave functions. The output $G(\vec{K})$ for $q\to 0$ is found [Fig. 2(a)] to be a monotonically decreasing function of K, and the necessity of iteration is thereby manifest. Recognizing that for a local potential, the total polarization is produced solely by $G(K_F)$, let us fix $G(K_F)$ so that the iterations all refer to the same fractional polarization. If now we use as input a $G(K)$ profile somewhat like Fig. 2(a), since $G(K_F)$ is fixed, there will be no change in the integrals (4.4a) or (4.11), since these are restricted to the Fermi surface. For K on the Fermi surface, the denominator in (4.4b) has its largest value and hence smallest contribution from the region of enhanced G, so although there is some change in the output $G(K_F)$, it will be small. However, it appears that an output curve can easily be obtained which point by point has the same slope as the input curve. Then writing

$$G_{\text{output}}(K) = G_{\text{imposed}}(K) + G_{\text{Hartree}}(K) + G_{\text{ex and corr}}(K) \quad ,$$

thus demanding self-consistency, we are able to compute an output dielectric constant, and from (3.5) a new plasmon spectrum. The choice (3.6) corresponds to an input $G_{\text{ex and corr}}(K_F) = 0.72$ Slater units, which is, as was discussed in I, the Kohn-Sham value. Our output value is (for the electron density of sodium) 0.96 Slater units, somewhat higher than the Kohn-Sham value. [Note, however, that the volume contribution (4.4b), which cannot be present for a local potential model such as that of Kohn and Sham, contributes 50% of this total.] As described above, the process of iteration with a fixed dielectric function may raise this value to, say, 1.0. In this case, the output plasmon spectrum starts out like $[1+0.04 \times (p/2k_F)^2]\omega_p^2$, which is to be compared with the input spectrum which started out like $[1+0.46(p/2k_F)^2]\omega_p^2$. Thus the new plasmon spectrum lies below the old one, and this lowers the total of exchange and correlation on the next cycle of iteration. Eventually we would arrive at a self-consistent plasmon spectrum, dielectric function, and matrix element, with the latter somewhere near the value quoted without the iterations.

Our results for A^{XC} in the $q \to 0$ limit are somewhat larger than one would obtain from the work of Kohn and Sham.[3] However, it is apparent that the latter work is not a theory of a one-electron exchange and correlation operator. This can be seen from the fact that the off-diagonal matrix element of the Kohn-Sham exchange term differs from that of the exact exchange operator by an infinite factor (as $q \to 0$).[2]

V. SCREENED-EXCHANGE AND COULOMB-HOLE POTENTIALS

Since the removal of the divergences due to the exchange potential is one of the more dramatic functions of correlation interactions, approximate incorporation of the correlation potential has often been sought through the use of a screened-exchange potential. Formally we may write the sum of the (exact) exchange and correlation operators as the sum of a screened-exchange operator A^{SX} and a further operator termed the "Coulomb hole,"[7] A^{CH}:

$$A^X + A^C = A^{SX} + A^{CH} \quad . \tag{5.1}$$

The separation of terms indicated by the right-hand side of (5.1) is accomplished by a reallocation of terms between (2.16) and (2.17). Again following the discussion in I, the required matrix elements are

$$\langle \vec{k}' | A_{\vec{K}}^{SX} | \vec{k} \rangle = - \sum_{\vec{K}', \epsilon_{\vec{K}'} < \epsilon_F} \sum_{\vec{p}} U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'+\vec{p}} \times \left(\frac{4\pi e^2}{\Omega p^2} + \frac{|M_{\vec{p}}|^2}{\epsilon_{\vec{K}} - \epsilon_{\vec{K}'} - \hbar\omega_{\vec{p}}} - \frac{|M_{\vec{p}}|^2}{\epsilon_{\vec{K}} - \epsilon_{\vec{K}'} + \hbar\omega_{\vec{p}}} \right) , \tag{5.2}$$

$$\langle \vec{k}' | A_{\vec{K}}^{CH} | \vec{k} \rangle = \sum_{\vec{K}'} \sum_{\vec{p}} |M_{\vec{p}}|^2 \frac{U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'+\vec{p}}}{\epsilon_{\vec{K}} - \epsilon_{\vec{K}'} - \hbar\omega_{\vec{p}}} \quad . \tag{5.3}$$

If, in (5.2), the recoil energies $\epsilon_{\vec{K}} - \epsilon_{\vec{K}'}$ are arbitrarily deleted and the factor $1-G$ of (2.8) is omitted, then the right-hand side of (5.2) ceases to be a dynamically screened-exchange interaction but becomes equal to the exchange interaction screened by the static dielectric function. One further approximation has proved popular, the use of a wave-number–independent screening constant, usually the Thomas-Fermi value.[8] The operator for such an exchange interaction is then

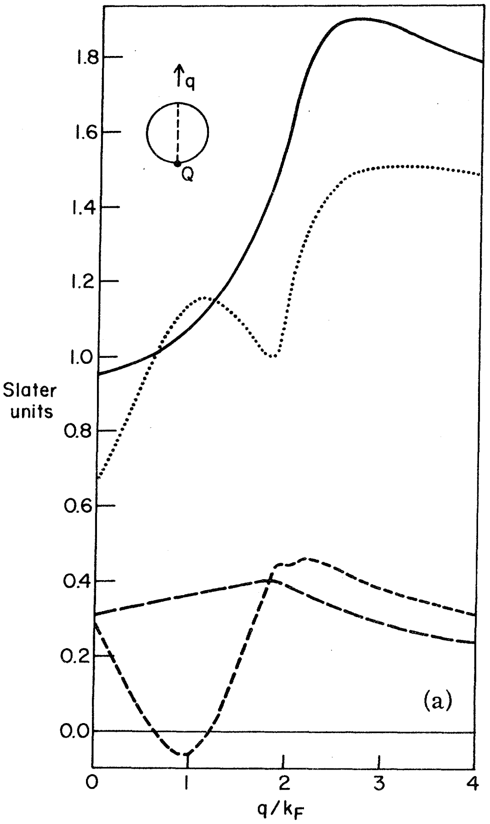
$$\langle \vec{k}' | A_{\vec{K}}^{X\,TF} | \vec{k} \rangle = - \sum_{\vec{K}', \epsilon_{\vec{K}'} < \epsilon_F} \sum_{\vec{p}} U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} \times U_{\vec{K}',\vec{k}'+\vec{p}} \frac{4\pi e^2}{\Omega(p^2+\alpha^2)} \quad , \tag{5.4}$$

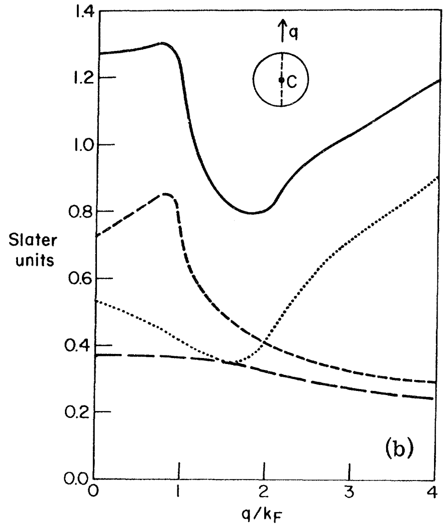
where the Thomas-Fermi screening constant is

$$\alpha^2 = 6\pi N e^2 / \Omega \epsilon_F \quad . \tag{5.5}$$

Equations (5.1)–(5.5) have been applied to the system described in Sec. III for the points Q, C, and P, and the off-diagonal matrix elements are plotted in Figs. 4(a)–4(c). It is seen that screened exchange alone is a very poor approximation to the total of exchange and correlation for the purpose of the calculation of the off-diagonal matrix elements. The matrix elements of A^{SX}, the dynamically screened-exchange operator, typically underestimate the matrix elements of $A^X + A^C$ by a factor of 2–6. Thus the (usually neglected) Coulomb-hole term is, for most $\vec{q}$ and $\vec{K}$, a better approximation to the total than is screened exchange. Static screened exchange is at best a plausible approximation to dynamic screened exchange, but for the particular value of α used [Eq. (5.5)], it represents a further deterioration in the quality of approximation to $A^X + A^C$. If the approximations made in deriving (5.4) from (5.2) are used in (5.3), then (5.3) becomes a constant (independent of $\vec{K}$, but dependent on $\vec{q}$). It should be noted that for a given value of $\vec{q}$, the curves for $A^{X\,TF}$ are not separated from those for $A^C + A^X$ by an amount independent of $\vec{K}$, so that even the consitent use of a static approximation in both Coulomb-hole and screened-exchange terms leaves something to be desired.

We have here considered only the off-diagonal





matrix element. However, the central conclusion reached here coincides with that reached in I by consideration of the diagonal matrix element: In no sense is the use of screened exchange alone an adequate approximation to the sum of exchange and correlation.

VI. SUMMARY

The new information gained by this study is as follows.

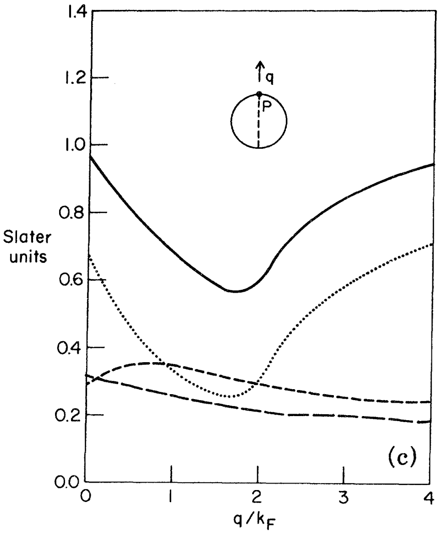


FIG. 4. Off-diagonal matrix elements of static screened exchange [Eq. (5.4), long-dashed curve], dynamic screened exchange [Eq. (5.2), short-dashed curve], Coulomb hole [Eq. (5.3), dotted curve], and the total of exchange and correlation (solid curve), as a function of the wave vector $\vec{q}$ of a periodic charge modulation, for electrons at three positions in the Fermi sphere. The matrix elements are measured in Slater units which are defined in Eq. (3.10). The electron states for which matrix elements are depicted are (a) Q, on the negative $\vec{q}$ axis at the Fermi surface; (b) C, the Fermi-sphere center; (c) P, on the positive $\vec{q}$ axis on the Fermi surface.

(a) A model has been formulated for the one-electron correlation operator. The model has been constrained to satisfy certain physical criteria. It has been found to incorporate the important feature known to exist for the correlation potential—the mutual cancellation between exchange and correlation of divergent matrix elements caused by the long-range components of the Coulomb potential. Note that this means that, in contrast to the common interpretation of previous theory,[3] certain off-diagonal correlation matrix elements for small wave-vector potentials are large and negative (as opposed to small and positive), but this is required to cancel divergent behavior of the exact exchange operator.

(b) The properties of the correlation operator have been illuminated by the explicit display of the off-diagonal matrix elements for a simple illustrative system.

(c) As was expected, correlation has been found to be highly nonlocal. The sum of exchange and correlation has also been found to be quite nonlocal, but significantly less singular than either individually. The departures from the traditional Slater value typically range between a factor of $\frac{1}{2}$ and a factor of 2.

(d) The distinctly different origins of exchange and correlation have again been underscored by the calculation of the off-diagonal matrix elements in the limit $q \to 0$. A volume integral appears for correlation which has no counterpart in the exchange integral. Its origin is the existence for correlation of energies of recoil due to the dynamic interactions. Thus exchange is of kinematic origin, while correlation is a dynamic interaction.

(e) It has been demonstrated that screened exchange alone is a very inadequate substitute for the sum of the exchange and correlation potentials.

There are many situations in solid-state physics where the off-diagonal matrix elements have determining influence on the properties of interest. For static properties, band structures and energy gaps play a major role, and these are necessarily related to the coefficients of admixture of different plane-wave components. The incorporation of exchange in band-structure calculations has most frequently been attempted by the use of some variant of the Slater $\rho^{1/3}$ approximation. A few calculations have been reported in which extraordinary care has been taken to isolate the effects of the $\rho^{1/3}$ approximation so that its applicability may be appraised. For example, orthogonalized-plane-wave (OPW) calculations[9] for Si, Ge, and ZnSe employing up to 230 plane waves produced well-converged energies and charge densities which were in qualitative, but not quantitative agreement with experiment. Since the only approximate feature in an otherwise high-precision calculation was the (local) exchange potential, the authors concluded that it was the cause of the deficiency. Also the calculated x-ray scattering form factors for ferromagnetic iron came into closer agreement with experiment when the local exchange potential was replaced[10] by a more realistic incorporation of exchange and correlation. More recently, Kane[11] has shown that in silicon, it is not possible to simultaneously fit cyclotron effective masses and principal energy gaps using the local exchange approximation. Again the care exercised in the calculations allowed the author to point to the local exchange potential as the deficiency. While the materials treated in these papers do not necessarily fall in the purview of the present method, they do constitute an experimental verification of the conclusion reached here, that the approximation of exchange with a local density model is not soundly based. The present work indicates that the nonlocal exchange and correlation potential can and should be used.

APPENDIX A

In the paragraph following (2.14) it is asserted the the band wave functions and energies to be used in the calculation of the second-order energy (2.14) are those determined in the presence of the perturbation itself. This follows from an application of a variant of Brillouin-Wigner perturbation theory. In the present context this form of perturbation theory requires that we modify (2.1) so that it has the form

$$H = H_{\mathrm{HF}} + H_2 + (H - H_{\mathrm{HF}} - H_2) \quad . \tag{A1}$$

The parenthesized expression in (A1) is regarded as a perturbation on the assumption that the eigenfunctions of $H_{\mathrm{HF}} + H_2$ are known. H_2 in turn is determined by requiring that the second-order energy of the perturbation vanish. Then the second-order energy of $H - H_{\mathrm{HF}}$ is given simply by the expectation value of the operator H_2.

It is clear from (2.13) that we can write

$$H_2 = \sum_{\vec{p}} \hbar \omega_{\vec{p}} a_{\vec{p}}^{\dagger} a_{\vec{p}} + H_{\mathrm{corr}} \equiv H_{pl} + H_{\mathrm{corr}} \quad . \tag{A2}$$

H_{corr} will be found to be the effective correlation operator. In the usual fashion we apply a canonical transformation to (A1) and carry out the expansion to second order:

$$e^{-S} H e^{S} = H + [H, S] + \tfrac{1}{2}[[H, S], S] + \cdots \tag{A3}$$

$$\begin{aligned} &= H_{\mathrm{HF}} + H_2 + [H_{\mathrm{HF}} + H_2, S] + \tfrac{1}{2}[[H_{\mathrm{HF}} + H_2, S], S] + \cdots \\ &\quad + H - H_{\mathrm{HF}} - H_{pl} + [H - H_{\mathrm{HF}} - H_{pl}, S] + \cdots \\ &\quad - H_{\mathrm{corr}} \cdots \quad . \end{aligned} \tag{A4}$$

Following the standard procedure, S is determined by requiring that the first-order terms of (A4) vanish identically:

$$[H_{\mathrm{HF}} + H_2, S] + H - H_{\mathrm{HF}} - H_{pl} = 0 \quad . \tag{A5}$$

From (A5), (A2), and (2.13), we find

$$S = \sum_{\vec{k}, \vec{p}, \vec{K}, \vec{K}'} M_{\vec{p}} U_{\vec{k}+\vec{p}, \vec{K}'}{}^{\dagger} U_{\vec{K}, \vec{k}} \times \left(\frac{b_{\vec{K}'}{}^{\dagger} b_{\vec{K}} a_{\vec{p}}}{\epsilon_{\vec{K}} - \epsilon_{\vec{K}'} + \hbar \omega_{\vec{p}}} + \frac{b_{\vec{K}'}{}^{\dagger} b_{\vec{K}} a_{-\vec{p}}{}^{\dagger}}{\epsilon_{\vec{K}} - \epsilon_{\vec{K}'} - \hbar \omega_{\vec{p}}} \right) \quad . \tag{A6}$$

In deriving (A6) we have assumed that the states for which the creation operators are $b_{\vec{K}}{}^{\dagger}$, are eigenstates of $H_{\mathrm{HF}} + H_2$ with one-electron energy eigenvalues $\epsilon_{\vec{K}}$. On substituting (A5) into (A4), the right-hand side of (A4) becomes

$$H_{\mathrm{HF}} + H_2 + \tfrac{1}{2}[H - H_{\mathrm{HF}} - H_{pl}, S] - H_{\mathrm{corr}} \quad . \tag{A7}$$

Clearly, our goal of finding a suitable H_2 (or H_{corr}) would be reached if we could set

$$\tfrac{1}{2}[H - H_{\mathrm{HF}} - H_{pl}, S] - H_{\mathrm{corr}} = 0 \quad . \tag{A8}$$

However, this condition is too strong. H_{corr} would contain operators which are nondiagonal in the $b_{\vec{K}}{}^{\dagger}$, $b_{\vec{K}}$ representation:

$$\sum_{\vec{p},\vec{k},\vec{k}',\vec{K},\vec{K}_1,\vec{K}_2,\vec{K}_3} |M_{\vec{p}}|^2 U_{\vec{k}'-\vec{p},\vec{K}_3}{}^{\dagger} U_{\vec{k}+\vec{p},\vec{K}_1}{}^{\dagger} U_{\vec{K}_2,\vec{k}'} U_{\vec{K}\vec{k}} b_{\vec{K}_3}$$

$$\times {}^{\dagger} b_{\vec{K}_2} b_{\vec{K}_1} \frac{1}{2}\left(\frac{1}{\epsilon_{\vec{K}_3}-\epsilon_{\vec{K}_2}-\hbar\omega_{\vec{p}}}+\frac{1}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}_1}-\hbar\omega_{\vec{p}}}\right). \tag{A9}$$

This would contradict our requirement that the band states be eigenstates of $H_{\mathrm{HF}}+H_2$. However, all we require is that the expectation value of the left-hand side of (A8) vanish, since this gives the second-order energy, so we simply delete the nondiagonal terms from (A9). We also delete the terms for which $\vec{K}_1=\vec{K}$, $\vec{K}_3=\vec{K}_2$, because for these the only allowed values of $\vec{p}$ are the reciporocal-lattice vectors, and by the comment following (2.6) the square matrix element is smaller by a factor $1/N$ than it is for the terms retained. Thus

$$H_{\mathrm{corr}}=\sum_{\vec{p},\vec{k},\vec{k}',\vec{K},\vec{K}'} |M_{\vec{p}}|^2 U_{\vec{k}'-\vec{p},\vec{K}}{}^{\dagger} U_{\vec{k}+\vec{p},\vec{K}'}{}^{\dagger} U_{\vec{K}',\vec{k}'} U_{\vec{K},\vec{k}}$$

$$\times \frac{b_{\vec{K}}{}^{\dagger} b_{\vec{K}'} b_{\vec{K}'}{}^{\dagger} b_{\vec{K}}}{\epsilon_{\vec{K}}-\epsilon_{\vec{K}'}-\hbar\omega_{\vec{p}}} . \tag{A10}$$

The expectation value of (A10) with respect to the zero-order state gives the correlation energy (2.14), and the energies and wave functions in (2.14) have the meaning claimed for them.

APPENDIX B

Consider a sphere of radius r symmetrically placed inside a cylinder of unit radius. Let ds be any small segment of the surface of the sphere and let dS be the projection of ds on the surface of the cylinder *by lines orthogonal to the axis of the cylinder*. Then each of the integrals (4.4a) and (4.11) is of the form

$$I(\vec{K})=\int dS\, f(|\vec{K}'-\vec{K}|) , \tag{B1}$$

where the point $\vec{K}'$ is contained in ds; the integral extends over all $\vec{K}'$ on the sphere. The locus on the sphere of constant values of the integrand is a circle, the radius of which is independent of the orientation of $\vec{K}$. It follows that the appropriate elemental area ds (a thin circular strip) for fixed f does not depend on the direction of $\vec{K}$. It is also true that the projected area dS is independent of orientation of $\vec{K}$, so that the value of (B1) is dependent only on the magnitudes of $\vec{K}$ and k_F. This suffices to prove that the $q\to 0$ off-diagonal matrix elements of exchange (4.11) are independent of orientation of $\vec{K}$. To prove that the corresponding correlation matrix elements have the same property, we only have to note additionally that by the comment following (4.4b), the volume term (4.4b) is also isotropic.

The proof that the projected area dS is independent of the orientation of $\vec{K}$ is elementary. Let the origins of spherical and cylindrical coordinate axis coincide with the center of the sphere and let the two coordinate systems have a common z axis parallel to the cylinder axis. Consider the four planes $z=z_1$, $z=z_1+\delta z$, $\varphi=\varphi_1$, and $\varphi=\varphi_1+\delta\varphi$. The area on the sphere enclosed by these four planes is

$$\delta s_1=(\rho\delta\varphi)(\delta z/\sin\theta)=r\delta\varphi\delta z=r\delta S_1 , \tag{B2}$$

where δS_1 is the area on the cylinder of the projection of δs_1. Since $\delta s_1/\delta S_1$ is independent of θ and φ, the desired result is proven.

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