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Exchange Potentials in a Nonuniform Electron Gas

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Off-diagonal matrix elements of the exchange operator are computed for a degenerate electron gas having a small sinusoidal density modulation. The extreme nonlocal character of exchange is shown explicitly by its wave-vector dependence. The Slater exchange approximation severely underestimates the off-diagonal action of the exact exchange operator (by a numerical factor approaching ∞ for long-wavelength modulations). Such errors are largely compensated by neglect of the correlation potential.

In recent years there has been considerable debate[1] on how best to approximate the (nonlocal) exchange operator A with a local potential. A frequent choice is the Slater $\rho^{1/3}$ relation

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

where $\rho(\vec{r})$ is the electron density. We believe that an explicit display of the properties of the exact A for a simple case indicates the futility of debate.

Consider a degenerate electron gas having a density

$$\rho(\vec{r}) = \rho_0(1 - p\cos\vec{q}\cdot\vec{r}) . \tag{2}$$

The mean density is $\rho_0 = k_F^3/3\pi^2$, and the fractional modulation p is assumed small. We shall presume that the modulation is caused by a (total) perturbing potential $V\cos\vec{q}\cdot\vec{r}$. Accordingly, the one electron wave functions are

$$\psi_{\vec{k}} \cong e^{i\vec{k}\cdot\vec{r}}[1 + (V/2\Delta_+)e^{i\vec{q}\cdot\vec{r}} + (V/2\Delta_-)e^{-i\vec{q}\cdot\vec{r}}] , \tag{3}$$

where the energy denominators are $\Delta_+(\vec{k}) \equiv E(\vec{k}) - E(\vec{k}+\vec{q})$, etc. We neglect any $\vec{k}$ dependence of V. These wave functions are the ones generally employed, e.g., in the random-phase approximation (RPA), with or without local exchange and correlation corrections. If we take $E(\vec{k}) = \hbar^2k^2/2m$ and sum $|\psi_{\vec{k}}|^2$ over all occupied states, we find the modulation to be

$$p = (3V/2E_F)g(q/2k_F) , \tag{4}$$

where

$$g(x) \equiv \tfrac{1}{2} + [(1-x^2)/4x]\ln|(1+x)/(1-x)|$$

and $E_F = \hbar^2k_F^2/2m$.

The matrix element of the Slater potential is, from (1) and (2), in the *pure-momentum* representation

$$\langle \vec{k}+\vec{q}\,|A_S|\,\vec{k}\rangle \cong e^2 k_F p/4\pi \ . \tag{5}$$

One should observe that, for a given p, this is independent of both $\vec{k}$ and $\vec{q}$.

On the other hand, the exact exchange operator is defined by the transformation it effects on a general function $\varphi(\vec{r})$,

$$A\varphi(\vec{r}) \equiv -\sum_{\vec{k}} \left[\int \psi^*_{\vec{k}}(\vec{s})(e^2/|\vec{r}-\vec{s}|)\varphi(\vec{s})d^3s\right]\psi_{\vec{k}}(\vec{r}) \ . \tag{6}$$

The summation includes all occupied states k with spin parallel to that of $\varphi(\vec{r})$. We insert (3) into (6), eliminate V with the help of (4), and obtain off-diagonal matrix elements in the *pure-momentum* representation

$$\langle \vec{k}+\vec{q}\,|A|\,\vec{k}\rangle \cong -pE_F/3g \times\sum_{\vec{k}'}\left(\frac{4\pi e^2}{|\vec{k}'-\vec{k}|^2\Delta_+(\vec{k}')}+\frac{4\pi e^2}{|\vec{k}'-\vec{k}-\vec{q}|^2\Delta_-(\vec{k}')}\right). \tag{7}$$

In contrast with (5) this depends markedly on both $\vec{k}$ and $\vec{q}$.

The ratio of (7) to (5) is shown (as a function of q) in Fig. 1 for several points in $\vec{k}$ space. The striking (logarithmic) singularity at $q = 2k_F$ for the point Q is the mathematical origin of the spin-density wave-instability theorem.[2] The extreme variation of (7) with $\vec{k}$ and $\vec{q}$ indicates that, for wave-function calculations pertaining to real materials, approximate exchange potentials should be judged empirically.

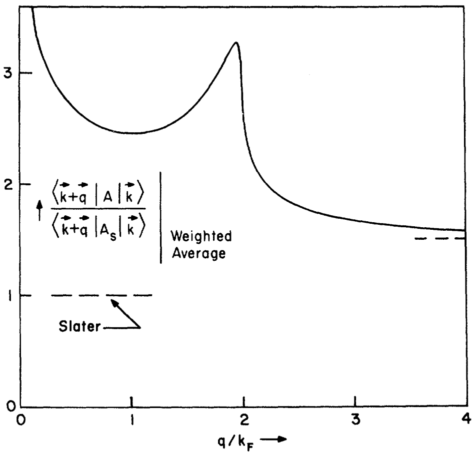

FIG. 1. Matrix elements of the exchange operator A for an electron gas with a small density modulation p cos$\vec{q}\cdot\vec{r}$. The ratio of the exact to the Slater values are shown for $\vec{k}$ at the center C, the equator E, and the poles P and Q of the Fermi sphere. The curves remain the same if the sign of $\vec{q}$ is reversed, except that P and Q are interchanged. Matrix elements of A and A_s are in the pure-momentum representation. All curves for $\vec{k}$ on the Fermi surface between P and the equator will have a singularity at $q = 0$. All curves for $\vec{k}$ on the Fermi surface between Q and the equator will have two singularities: at $q = O$ and at $q = 2|k_z|$. From Eq. (7) it is easy to show analytically that all singularities are logarithmic.

The average of (7) over $\vec{k}$ within the Fermi sphere is not particularly relevant. However, in Fig. 1 it would fall monotonically from the value 2 at $q = 0$ to 1.5 as $q \to \infty$. This latter limit contradicts a previous calculation due to Payne,[3] who concluded that the exchange potential falls rapidly to zero for $q > 2k_F$. The oversight in Payne's work is subtle. He optimized (by a variational calculation) the admixture of $\vec{k}\pm\vec{q}$ components in $\{\psi_{\vec{k}}\}$ caused by an applied sinusoidal perturbation $w(\vec{r})$. The resulting modulation in electron density was misinterpreted by failing to isolate (off-diagonal) exchange contributions from a renormalization of the $w(\vec{r})$ contributions caused by (diagonal) exchange corrections to the energy differences Δ_+ and Δ_-.[4]

The foregoing remarks are relevant to an explanation why the exchange potentials for the points E, P, and Q in Fig. 1 diverge like $\ln(1/q)$ as $q \to 0$. (One might have expected them to approach the Kohn and Sham value $\frac{2}{3}$.) It is well known that the spin susceptibility $\chi(\vec{q})$ is enhanced relative to the Pauli value at $q = 0$. However, if one were to compute $\chi(\vec{q})$ for small (but finite) q by perturbation theory, taking into account only the exchange corrections to $E(\vec{k})$, $\chi(\vec{q})$ would approach 0 as $[\ln(1/q)]^{-1}$. An exchange potential which diverges as $\ln(1/q)$ must be present to compensate this effect. Otherwise the exact (Hartree-Fock) $\chi(\vec{q})$ could not be continuous at $q = 0$.

We observe that the extreme nonlocality of A calls into question the reliability of any local approximation to it, especially in a band calculation where the $\vec{k}$ dependence of the electron wave function and energy is the major question. However, if one insists on replacing A with a local operator, the question arises: What is the most appropriate average (over $\vec{k}$) of $\langle \vec{k}+\vec{q}\,|A|\,\vec{k}\rangle$? The answer depends, of course, on what one ultimately intends to calculate. However, a particularly appealing choice is the following: What is the local operator which, when acting in first-order perturbation, gives rise to the same charge-density modulation that A does? One can show that this is given by the average of Eq. (7) (over occupied $\vec{k}$ states) computed with a $1/\Delta_+(\vec{k})$ weighting function. In other words, it is the average of (7) weighted (algebraically) in proportion to each electron's contribution to p. This weighted average shown in Fig. 2 falls from $\ln(\infty)$ at $q = 0$ to a minimum near $q = k_F$, goes through a sharp maximum near $q = 2k_F$, and approaches 1.5 for large q.

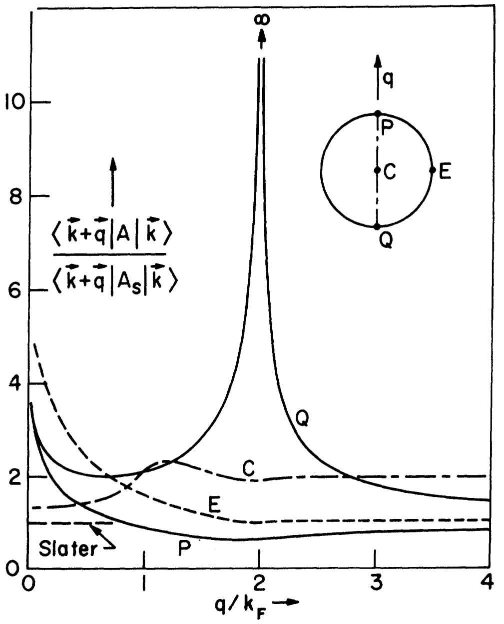

FIG. 2. Weighted average of the exchange operator for an electron gas with a small density modulation. The weighting function employed was proportional to each electron's contribution to the modulation.

The physical consequences of the large exchange potentials, illustrated in Figs. 1 and 2, will of course be moderated by (compensating) correlation potentials. The work of Kohn and Sham[5] has shown that in the small-q limit the sum of the exchange and correlation potentials is slightly larger than $\frac{2}{3}$ of the Slater potential. However, their work seems to suggest that (for $q\to 0$) the exchange potential is $\frac{2}{3}$ of Eq. (1) and that the correlation potential is much smaller and of the same sign. The present work indicates that (for $q\to 0$) the exchange potential approaches $\ln(\infty)$. We conclude, then, that the correlation potential approaches $-\ln(\infty)$ in such a way that the sum of exchange and correlation potentials equals the sum given by Kohn and Sham. It is perhaps academic to argue how a sum is divided into parts, if it is only the sum that matters. However, the physical mechanisms which might enter a (future) microscopic theory of the correlation potential may depend on whether the result to be obtained is small and positive or large and negative. A treatment of the nonlocal properties of correlation is an outstanding theoretical challenge.

Inspection of Figs. 1 and 2 shows that A_S severely underestimates the off-diagonal action of the exact exchange operator. The empirical success of the Slater exchange approximation in energy band calculations can be attributed to compensation of this error by neglect of the correlation potential.

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