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# Investigations of nonlocal exchange and correlation effects in metals via the density-functional formalism*

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The density-functional formalism of Hohenberg, Kohn, and Sham is used to investigate the effects of nonlocal exchange and correlation on the Fermi surface of a simple-cubic metal. The "nonlocal" Fermi surface is obtained by solving the Dyson equation for the quasiparticle states on the Fermi surface with the nonlocal self-energy approximated according to the density-functional scheme in the presence of an external model pseudopotential. This was done by using the corresponding local theory to define a zeroth-order Hamiltonian which provides basis functions to solve the nonlocal eigenvalue problem. It was found that the maximum Fermi-surface distortions obtained from the nonlocal theory were substantially reduced from the local theory, as experiments suggest. The calculations were carried out in the random-phase approximation.

## I. INTRODUCTION

Most first-principles calculations of the Fermi-surface (FS) distortions have been based on local approximations for exchange and correlation effects among the valence electrons. Comparison of such calculations with the experimental FS distortions result in large discrepancies.[1-3] The primary objective of this work is to show by direct calculation with a realistic model that the FS given by a nonlocal many-body theory is significantly different from the corresponding local theory, both treated within the framework of the Hohenberg-Kohn-Sham[4-6] theory of an inhomogeneous electron gas.

The usual starting point for describing a number of interesting properties of the many-body system is to solve for the Green's function[7] $G(\vec{r}, \vec{r}; E)$. In particular it determines the system's single-particle-like excitations, a quantity of central interest in this work.

The Green's function is a solution of the Dyson equation

$$-\left(+\frac{\hbar^2}{2m}\nabla^2+E\right)G(\vec{r},\vec{r}\,';E)+\int d\vec{r}\,''\times\Sigma(\vec{r},\vec{r}\,'';E)G(\vec{r}\,'',\vec{r}\,';E)=-\delta(\vec{r}-\vec{r}\,')\ . \quad (1)$$

Equivalently, in the usual matrix notation Eq. (1) can be written

$$G(E)-G_0(E)\Sigma(E)G(E)=G_0(E)\ , \quad (2)$$

where $G_0(E)$ is the Green's function for the noninteracting homogeneous electron gas, and $\Sigma$ is the so called mass operator.

The same mass operator $\Sigma$ appears also in a Schrödinger type equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r})+\int d\vec{r}\,'\Sigma(\vec{r},\vec{r}\,';E_{\vec{k}})\psi_{\vec{k}}(\vec{r}\,')=E_{\vec{k}}\psi_{\vec{k}}(\vec{r})\ , \quad (3)$$

where $\Sigma$ in Eq. (3) has been specialized to a periodic system. The solutions of this homogeneous equation [i.e., the homogeneous part of Eqs. (1) or (2)] have the meaning of the quasiparticle states $\psi_{\vec{k}}$ and the quasiparticle excitations $E_{\vec{k}}$. The solution of Eq. (3) for $E_{\vec{k}}$ will hence describe the corresponding FS.

In Sec. II we briefly discuss some main features of the "local" Hohenberg-Kohn-Sham[4,5] theory, which is strictly applicable to the calculation of the density $n(\vec{r})$ and the corresponding ground-state energy, but has also been commonly used for the determination of the FS (henceforth referred to as the local FS). Approximate forms for the mass operator $\Sigma$ by use of the density-functional formalism will be discussed in Sec. III, which will be used to calculate the nonlocal FS.

In Sec. IV we formulate a simple, self-consistent procedure, for calculating the local and nonlocal FS and specialize the calculation to the random-phase approximation (RPA). Sec. V consists of results and discussion.

## II. COMMENTS ON THE LOCAL HOHENBERG-KOHN-SHAM THEORY

Suppose we impose on an interacting electron gas an external potential $V_{\text{ext}}(\vec{r})$ which induces a density distribution $n_1(\vec{r})$ [Note $n(\vec{r})=n_0+n_1(\vec{r})$] where $n_0$ is the uniform density. Hohenberg and Kohn[4] have shown that the ground-state energy of such a system can be written as

$$E[n]=\int d\vec{r}\ V_{\text{ext}}(\vec{r})n(\vec{r})+\frac{e^2}{2}\int\frac{d\vec{r}\,d\vec{r}\,'n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}+F[n]\ , \quad (4)$$

where $F[n]$ is a unique functional of $n(\vec{r})$. Furthermore they show that $E[n]$ assumes its minimum value for the correct $n(\vec{r})$.

Kohn and Sham[5] went a step further by noting that in writing

$$F[n] = T_s[n] + E_{xc}[n]\ , \tag{5}$$

(where $T_s[n]$ is the kinetic energy of a noninteracting electron gas of density $\vec{n}(r)$, and $E_{xc}[n]$ is the exchange correlation functional) the density can be determined exactly from one particle-like Schrödinger equation solved self-consistently as follows:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + v_{xc}(\vec{r})\right)\phi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\phi_{\vec{k}}(\vec{r})\ , \tag{6}$$

$$n(\vec{r}) = \sum_{\vec{k}} |\phi_{\vec{k}}(\vec{r})|^2\theta(K_F - |\vec{k}|)\ , \tag{7}$$

$$V(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r})\ , \tag{8}$$

$$V_H(\vec{r}) = e^2\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'\ , \tag{9}$$

and

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n}\ . \tag{10}$$

In Eq. (7) $K_F \equiv K_F(\hat{k})$ is the surface that encloses the correct number of electrons. The surface corresponding to $K_F(\hat{k})$ is determined from the solutions $\epsilon_{\vec{k}}$ of Eq. (6) and will be referred to as the local FS.

At this juncture two remarks are in order:

(a) The $\phi_{\vec{k}}(\vec{r})$ and $\epsilon_{\vec{k}}$ of Eq. (6) do not represent the quasiparticle states or excitation energies. Thus it would be extremely fortuitous for Eq. (6) to give the correct FS [the solution of Eq. (3) will].

(b) The self-consistent soluticns of Eqs. (6) and (7) would give the density $n(\vec{r})$ exactly if $E_{xc}[n]$ were known.

A common approximation for $E_{xc}[n]$ is

$$E_{xc}[n] \approx \int n(\vec{r})\epsilon_{xc}[n(\vec{r})]\,d\vec{r}\ , \tag{11}$$

where $\epsilon_{xc}[n(\vec{r})]$ is the exchange and correlation energy per electron of a uniform electron gas with density $n(\vec{r})$.

From Eqs. (10) and (11),

$$v_{xc}(\vec{r}) \approx \frac{d[n\epsilon_{xc}(n)]}{dn}\ . \tag{12}$$

In this work $v_{xc}(\vec{r})$ will be approximated by Eq. (12) and the corresponding solution $\epsilon_{\vec{k}}$ of Eq. (6) will define our local FS.

As previously mentioned, although formally the $\epsilon_{\vec{k}}$'s of Eq. (6) have no relevance to describing the quasiparticle excitations, the approximation of Eq. (12) does represent a further approximation to the nonlocal $\Sigma$ of Eq. (3) for electrons on the FS (we will return to this point briefly at the end of Sec. III). Equation (6) coupled with Eq. (12) has thus been commonly used in the calculation of band structures and the corresponding FS.

Finally, for completeness, we write two further approximations to $E_{xc}[n]$.

For a large but slowly varying $n_1(\vec{r})$ Hohenberg and Kohn[4] recommended approximating $E_{xc}(n)$ by a gradient expansion, i.e.,

$$E_{xc}(n) \approx \int d\vec{r}\,n(\vec{r})\epsilon_{xc}(n(\vec{r})) + \frac{1}{2}\int g_{(2)}^{(2)}(n)\nabla n\cdot\nabla n\,d\vec{r}\ . \tag{13}$$

For a small but rapidly varying $n_1(\vec{r})$ Kohn and Sham[5] suggested

$$E_{xc}[n] \approx \int d\vec{r}\,n(\vec{r})\epsilon_{xc}(n(\vec{r})) - \frac{1}{2}\iint d\vec{r}\,d\vec{r}\,' \times K_{xc}(\vec{r}-\vec{r}\,', n(\tfrac{1}{2}(\vec{r}+\vec{r}\,')))[n(\vec{r}) - n(\vec{r}\,')]^2\ . \tag{14}$$

Both the coefficients of Eq. (13) and $K_{xc}$ of Eq. (14) can be related to the electron screening function $\Pi(\vec{q})$.[4,5]

The approximations of Eqs. (13) and (14) have been tested in the calculation of cohesive energies (see, e.g., Ma and Brueckner,[8] Herman *et al.*[9] and recently by Sham[10]). Their use for calculating the $\epsilon_{\vec{k}}$'s of Eq. (6) as an attempt to get improved band structures (or FS) is however highly questionable in that Eqs. (13) and (14) have not been shown to result from the localization of Eq. (3), in contrast to Eq. (12), which has (see Sec. III).

## III. APPROXIMATIONS FOR THE SELF-ENERGY OPERATOR

In the previous section we briefly discussed the local theory represented by Eqs. (6) and (7) [coupled with the approximation of Eq. (12)] used in most band-structure calculations. As stressed, the procedure does give the correct density and cohesive energy (if $E_{xc}[n]$ is known), but does not give the correct quasiparticle excitations. To get these one has to solve for the $E_{\vec{k}}$'s of Eq. (3) with the nonlocal mass operator which we will now discuss.

It is useful to exhibit the local and nonlocal components of $\Sigma$ explicitly, i.e.,

$$\Sigma(\vec{r},\vec{r}\,';E) = V(\vec{r})\delta(\vec{r}-\vec{r}\,') + M(\vec{r},\vec{r}\,';E)\ , \tag{15}$$

where $V(\vec{r})$ has been defined in Eq. (8) and $M$ is the self-energy operator whose structural form is given by many-body theory.[11] For an inhomogenous system it is extremely complicated (in fact even for a homogenous system its full form is not known) and some approximate form must be constructed. One way of proceeding is to do the standard graphical calculation[7] of $M$, e.g., some low-order diagrams representing the expansion of $M$ are shown in Fig. 1. The arrows represent the Green's function $G_v(\vec{r},\vec{r}\,';E)$ satisfying the equation

$$\left[-\left(\frac{\hbar^2}{2m}\nabla^2 + E\right) + V(\vec{r})\right]G_v(\vec{r},\vec{r}\,';E) = -\delta(\vec{r}-\vec{r}\,')\ , \tag{16}$$

the wiggly line is the screened electron-electron interaction $W(\vec{r},\vec{r}\,';E)$ whose solution graphically is given by Figs. 2(a) and 2(b).

In principle such a procedure is exact; however,

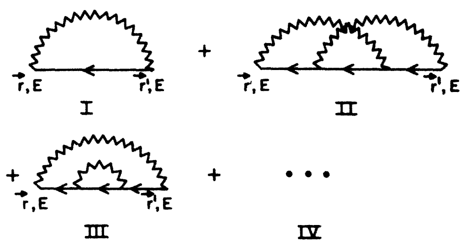

FIG. 1. First few low-order contributions to $M(\vec{r}, \vec{r}'; E)$. The arrows represent the $G_v(\vec{r}, \vec{r}'; E)$ of Eq. (16), and the wiggly lines are the screened electron-electron interactions $W(\vec{r}, \vec{r}'; E)$ shown in Fig. 2.

in practice, even evaluating $M$ in the approximation of Fig. 1-I and II approximated by Fig. 2(b)-I (i.e., the inhomogenous RPA approximation) is a considerable task which has not been done exactly. Kane[12] has attempted such a procedure for the calculation of the band structure of silicon. In this work (as pointed out in the Introduction) both local and nonlocal effects will be treated within the framework of the Hohenberg-Kohn-Sham[4–6] theory. We hence turn to a discussion of $M$ in this context.

We first note that according to the theory of Hohenberg and Kohn[4] $\Sigma$ is a functional of the density $n(\vec{r})$. Sham and Kohn[6] (SK) have exploited this property to suggest a number of approximations for $M$. More recently Hedin and Lundqvist[13] have generalized the SK version of $M$ by introducing a functional of $n$, $\Delta[n]$, into the self energy operator $M_h$ of a uniform interacting electron gas as follows:

$$\Sigma(\vec{r}, \vec{r}'; E) \approx V(\vec{r})\delta(\vec{r}-\vec{r}') + M_h(\vec{r}-\vec{r}'; E - V(\vec{r}_0) + \Delta[n(\vec{r}_0)]; n(\vec{r}_0)) \,, \tag{17}$$

where $n$ is the density at $\vec{r}_0 = \frac{1}{2}(\vec{r}+\vec{r}')$. This choice of form for $\Sigma$ is made so that, with appropriate restrictions on $\Delta[n]$, it satisfies the following conditions:

(i) Equation (3) which is invariant under a constant shift in $V_{\text{ext}}(\vec{r})$ is maintained by Eq. (17).

(ii) For a small and slowly varying $V_{\text{ext}}(\vec{r})$, Eq. (17) is exact.

Condition (i) requires $\Delta[n_0] = 0$ and (ii) requires $\Delta(\vec{q}) \to 0$ as $\vec{q} \to 0$ [see Eq. (24)]. The two forms suggested by SK correspond to:

$$\Delta_a[n] \equiv 0 \,, \tag{18}$$

$$\Delta_b[n] \equiv \mu_h(n(\vec{r}_0)) + V(\vec{r}_0) - \mu \,, \tag{19}$$

(henceforth referred to as "$a$" and "$b$", respectively), where $\mu_h$ is the chemical potential for a uniform gas of density $n$ and $\mu$ is the chemical potential. These forms clearly satisfy the above requirements on $\Delta[n]$.

Before discussing the merits of Eqs. (18) and (19) for $\Delta[n]$, we wish to comment on the introduction of the $\vec{r}_0$ variable in Eq. (17). Although the $\vec{r}_0$ variable evolves naturally in the SK analysis, it in fact has advantages over other possible choices. To see this we write $\Sigma$ to first order in the external potential (Fig. 3), i.e.,

$$\Sigma(\vec{r}, \vec{r}'; E) \approx M_h(\vec{r}-\vec{r}'; E; n_0) + \Sigma^{(1)}(\vec{r}, \vec{r}'; E) \,, \tag{20}$$

where

$$\Sigma^{(1)}(\vec{r},\vec{r}'; E) = -\frac{1}{2}\int \frac{d\vec{q}}{(2\pi)^3}\int \frac{d\vec{p}}{(2\pi)^3}\,\frac{n_1(\vec{q})}{\Pi(\vec{q})}\,e^{i[\vec{p}\cdot(\vec{r}-\vec{r}')+\vec{q}\cdot\vec{r}_0]}\left(\tilde{\Lambda}(\vec{p}+\beta\vec{q}, \vec{q}; E)e^{i\beta\vec{q}\cdot(\vec{r}-\vec{r}')} + \tilde{\Lambda}(\vec{p}-\beta\vec{q}, \vec{q}; E)e^{-i\beta\vec{q}\cdot(\vec{r}-\vec{r}')}\right) \,, \tag{21}$$

and $\tilde{\Lambda}$ is the proper vertex function. To examine the small $\vec{q}$ behavior of the right-hand side of Eq. (21), we note that for small $\vec{q}$

$$\tilde{\Lambda}(\vec{p}+\beta\vec{q}, \vec{q}; E) \approx \tilde{\Lambda}(\vec{p}+\beta\vec{q}, 0; E) + O(\vec{q}^{\,2}) \,. \tag{22}$$

This follows from the integral equation for $\tilde{\Lambda}$ (see Nozières,[14] P. 255) when ${}^0I(\vec{p}, \vec{p}'; \vec{q}) = {}^0I(\vec{p}', \vec{p}; \vec{q})$, which, from time-reversal symmetry, implies that ${}^0I(\vec{p}, \vec{p}'; \vec{q}) = {}^0I(\vec{p}, \vec{p}', -\vec{q})$ and thus $\tilde{\Lambda}(\vec{p}, \vec{q}; E) = \tilde{\Lambda}(\vec{p}, -\vec{q}; E)$. For example, these conditions on ${}^0I$ are satisfied for the self-consistent RPA (see Fig. 4). We also note that this property of $\tilde{\Lambda}$ implies that $\Sigma^{(1)}(\vec{r}, \vec{r}'; E)$ is symmetrical in $\vec{r}$ and $\vec{r}'$.

Equation (21) suggests many symmetrical forms for $\Sigma$ constructed in the spirit of Eq. (17). For example with $\beta = \frac{1}{2}$ in Eq. (21) results in $\Sigma$ of Eq. (17) given by

$$\Sigma(\vec{r}, \vec{r}'; E) \approx \tfrac{1}{2}[V(\vec{r}) + V(\vec{r}')]\delta(\vec{r}-\vec{r}') + \tfrac{1}{2}[M_h(\vec{r}-\vec{r}'; E - V(\vec{r}) + \Delta(\vec{r}); n(\vec{r})) + M_h(\vec{r}-\vec{r}'; E - V(\vec{r}') + \Delta(\vec{r}'); n(\vec{r}'))] \,. \tag{23}$$

However, for $\beta = 0$ (the SK form), it is straightforward to show that Eq. (17) is exact, in linear order of the external potential, to order $\vec{q}^{\,2}$. This can be seen by setting $\beta = 0$ in Eqs. (21) and (22), and expanding Eq. (17) to linear order in the external potential. The difference, $\Delta\Sigma(\vec{r}, \vec{r}'; E)$, of Eqs. (17) and (21) is given by

$$\begin{aligned}\Delta\Sigma(\vec{r}, \vec{r}'; E) = -\int \frac{d\vec{p}}{(2\pi)^3}e^{i\vec{p}\cdot(\vec{r}-\vec{r}')}\int \frac{d\vec{q}}{(2\pi)^3}e^{i\vec{q}\cdot\vec{r}_0}\frac{n_1(\vec{q})}{\Pi(\vec{q})}\Big[&\delta\tilde{\Lambda}(\vec{p}, \vec{q}; E) \\ &+ \frac{\partial M_h(\vec{p}, E; n_0)}{\partial \mu_h}\left(\frac{d\mu_h}{dn_0}\right)\delta\Pi(\vec{q}) - \frac{\partial M_h(\vec{p}, E; n_0)}{\partial E}\,\frac{\Delta(\vec{q})}{V(\vec{q})} + O(q^3)\Big] \,,\end{aligned} \tag{24}$$

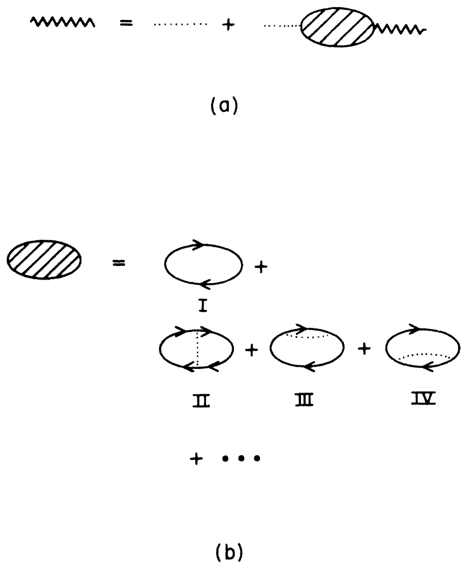

FIG. 2. (a) Integral equation of $W(\vec r, \vec r\,'; E)$; (b) first few low-order contributions to the screening function $\Pi$.

where

$$\delta\tilde\Lambda(\vec p, \vec q; E) \equiv \tilde\Lambda(\vec p, \vec q; E) - \tilde\Lambda(\vec p, 0; E)\ , \tag{25}$$

$$\delta\Pi(\vec q) \equiv \Pi(\vec q) - \Pi(0)\ , \tag{26}$$

$$M_h(\vec r - \vec r\,'; E; n_0) = \int \frac{d\vec p}{(2\pi)^3} M_h(\vec p, E; n_0) e^{i\vec p\cdot(\vec r - \vec r\,')}\ , \tag{27}$$

and $M_h(\vec p, E)$ is the usual self-energy operator in momentum-energy space for a homogeneous electron gas with density $n_0$. In deriving Eq. (24) we have used the Ward identity

$$\lim_{\vec q\to 0}\tilde\Lambda(\vec p, \vec q; E) = 1 - \frac{\partial M_h(\vec p, E; n_0)}{\partial E} - \frac{\partial M_h(\vec p, E; n_0)}{\partial \mu_h} \tag{28}$$

and the compressibility sum rule

$$\lim_{\vec q\to 0}[\Pi(\vec q)]^{-1} = \frac{d\mu_h}{dn_0}\ . \tag{29}$$

From Eqs. (22), (25), and (26) the expression in large square brackets in Eq. (24) is clearly of order $\vec q^{\,2}$ if $\Delta(\vec q) \to 0$ as $\vec q \to 0$. Similar analysis for $\beta \neq 0$ give the resulting $\Sigma$ in Eq. (17) exact to first power in $\vec q$ and linear in the external potential.

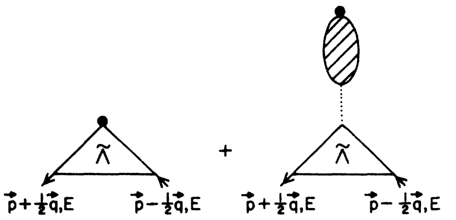

FIG. 3. Self-energy to first order in the external potential $V_{\text{ext}}(\vec r)$, •, in terms of the proper vertex function $\tilde\Lambda$ and the screening function $\Pi$ for a homogeneous electron gas.

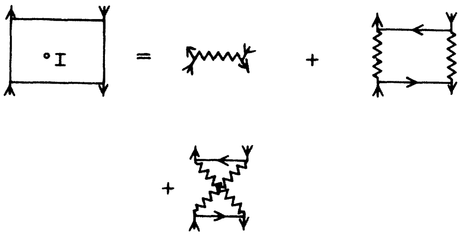

FIG. 4. Irreducible scattering function $^\circ I$ in the self-consistent RPA.

We now return to Eq. (17) to consider forms for $\Delta[n(\vec r_0)]$. We first consider the merits of Eqs. (18) and (19) and then introduce a new form that satisfies the conditions (i) and (ii) above and a density self-consistency condition on the Green's function.

Hedin and Lundqvist[13] have suggested that the form (19) is preferable. Their argument is based on constructing an approximate vertex function by expanding Eq. (17) for $\Sigma$ to first order in $V$, $\Delta$, and $n_1$ and comparing with Eq. (21) ($\beta = 0$). In our notation, for the $\Delta$'s given in Eqs. (18) and (19), the following approximate vertex functions result, respectively:

$$\tilde\Lambda_a(\vec p, \vec q; E) = 1 - \frac{\partial M_h(\vec p, E; n_0)}{\partial E} - \Pi(\vec q)\left(\frac{d\mu_h}{dn_0}\right)\frac{\partial M_h(\vec p, E; n_0)}{\partial \mu_h}\ , \tag{30}$$

$$\tilde\Lambda_b(\vec p, \vec q; E) = 1 - \Pi(\vec q)\frac{d\mu_h}{dn_0} \times\left(\frac{\partial M_h(\vec p, E; n_0)}{\partial E} + \frac{\partial M_h(\vec p, E; n_0)}{\partial \mu_h}\right). \tag{31}$$

Restricting Eqs. (30) and (31) to electrons on the FS (i.e., $|\vec p| = K_0$ and $E = \mu_n$) gives:

$$\tilde\Lambda_a(\vec K_0, \vec q; \mu_h) = Z^{-1}\left[1 - \frac{\Pi(\vec q)}{\Pi(0)}\left(1 - \frac{m}{m^*}\frac{\kappa}{\kappa_0}\right)\right]\ , \tag{32}$$

$$\tilde\Lambda_b(\vec K_0, \vec q; \mu_h) = 1 - \frac{\Pi(\vec q)}{\Pi(0)}\left(1 - Z^{-1}\frac{m}{m^*}\frac{\kappa}{\kappa_0}\right)\ , \tag{33}$$

where $Z^{-1}$ is the renormalization factor $[1 - \partial M_h(\vec p, E; n_0)/\partial E]$ on the FS; $\kappa/\kappa_0$ and $m^*/m$ are the ratios of the compressibility and effective masses on the FS, respectively, of the interacting and noninteracting electron gas which are related to the vertex function through the Ward identity[14]

$$\lim_{\vec q\to 0}\tilde\Lambda(\vec K_0, \vec q; \mu_h) = Z^{-1}\left(\frac{m}{m^*}\right)\left(\frac{\kappa}{\kappa_0}\right)\ .$$

Hedin and Lundqvist note that the choice (b) for $\Delta$ gives the correct large $\vec q$ limit of $\tilde\Lambda(\vec K_0, \vec q; \mu_h)$, i.e., unity [see Eq. (33)]. Furthermore, Watabe and Yashuhara[15] evaluated the vertex function for electrons on the FS and found $\vec{\Lambda}(\vec{K}_0, \vec{q} = 2.28\vec{K}_0; \mu_h) = 1.55$ for $r_s = 4$. Using Eqs. (32) and (33) with $\Pi(\vec{q} = 2.28\vec{K}_0)$ from Geldart and Taylor[16] and the values $Z^{-1} = 1.55$, $m/m^* = 0.94$, $\kappa_0/\kappa = 0.292$ (see Hedin and Lundqvist[17] P. 103) we find $\tilde{\Lambda}_a = 1.95$ and $\tilde{\Lambda}_b = 1.47$, in agreement with Hedin and Lundqvist.[13] From these considerations choice (b) for $\Delta[n]$ appears to be preferable. Thus in the calculations presented in this work the approximate form for $\Sigma(\vec{r}, \vec{r}\,'; E)$ is

$$\Sigma_b(\vec{r}, \vec{r}\,'; E) = V(\vec{r})\delta(\vec{r} - \vec{r}\,') + M_h(\vec{r} - \vec{r}\,'; E - \mu + \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) \, . \tag{34}$$

We also note that this form has the advantage of not having $V(\vec{r}_0)$ as an argument of $M_h$, as occurs with choice (a) and for calculations on the FS $E = \mu$ so that the $E$ dependence is also removed.

There remains the question of the density dependence of $\Sigma$ being adequately accounted for by use of Eq. (34). This can be investigated by introducing a more general form for $\Delta[n(\vec{r}_0)]$ and requiring the Green's function produced by the $\Sigma$ used in Eq. (2) be self-consistent to linear order in $n_1(\vec{r})$. A natural extension of Eq. (19) is

$$\Delta[n(\vec{r}_0)] = \Delta_b[n(\vec{r}_0)] + \int F(\vec{r}_0 - \vec{s}) n_1(\vec{s})\, d\vec{s} \, , \tag{35}$$

and the requirement $\Delta(\vec{q}) \to 0$ as $\vec{q} \to 0$ implies $F(\vec{q}) \to 0$ in this limit. $F(\vec{r}_0 - \vec{s})$ in Eq. (35) is in a way analogous to $K_{xc}$ in Eq. (14) of the local theory and corresponds to a partial infinite sum of gradient terms for the nonlocal problem. The effect of including the $K_{xc}$ term has recently been investigated by Sham.[10] The importance of these nonlocal gradient terms will be reflected in the $\vec{q}$ dependence of $F(\vec{q})$, i.e., an essentially zero $F(\vec{q})$ would indicate that the density dependence is adequately represented by Eq. (34). [Some numerical evidence for the adequacy of Eq. (34) will be presented in Sec. V, where FS distortions obtained by use of Eq. (34) are compared with those obtained by omitting the density dependence in $\Sigma$, i.e., replacing $n(\vec{r}_0)$ by $n_0$.]

The density self-consistency equation on the Green's function may be written as

$$n_1(\vec{q}) = \lim_{\tau \to 0} \mathrm{tr}_p G(\vec{p} + \vec{q}, \vec{p}; E) e^{iE\tau} \, , \tag{36}$$

where

$$G(\vec{r}, \vec{r}\,'; E) = \int \frac{d\vec{p}_1}{(2\pi)^3} \int \frac{d\vec{p}_2}{(2\pi)^3} G(\vec{p}_2, \vec{p}_1; E) e^{i\vec{p}_2 \cdot \vec{r}} e^{-i\vec{p}_1 \cdot \vec{r}\,'} \, , \tag{37}$$

and

$$\mathrm{tr}_p(\cdots) \equiv \int \frac{d\vec{p}\, dE}{i(2\pi)^4} (\cdots) \, . \tag{38}$$

Expanding the Green's function $G$ of Eq. (2) to first order in $n_1$ with $\Sigma$ and $\Delta$ given by Eqs. (17) and (35) and applying Eq. (36) to the resultant gives

$$F(\vec{q}) = \left(1 + \frac{F_3(\vec{q})}{\Pi(\vec{q})} - \frac{F_1(\vec{q}) + F_2(\vec{q})}{\Pi(0)}\right) \Big/ F_1(\vec{q}) \, , \tag{39}$$

where

$$F_1(\vec{q}) = 2\, \mathrm{tr}_p \frac{\partial M_h(\vec{p}, E; n_0)}{\partial E} G_h(\vec{p} + \tfrac{1}{2}\vec{q}, E) G_h(\vec{p} - \tfrac{1}{2}\vec{q}, E) \, , \tag{40}$$

$$F_2(\vec{q}) = 2\, \mathrm{tr}_p \frac{\partial M_h(\vec{p}, E; n_0)}{\partial \mu_h} G_h(\vec{p} + \tfrac{1}{2}\vec{q}, E) G_h(\vec{p} - \tfrac{1}{2}\vec{q}, E) \, , \tag{41}$$

$$F_3(\vec{q}) = 2\, \mathrm{tr}_p G_h(\vec{p} + \tfrac{1}{2}\vec{q}, E) G_h(\vec{p} - \tfrac{1}{2}\vec{q}, E) \, , \tag{42}$$

and $G_h(\vec{p}, E)$ is the exact Green's function in momentum-energy space for a homogeneous electron gas with density $n_0$. With these expressions in Eq. (39) $F(\vec{q}) \to 0$ as $\vec{q} \to 0$.

We end this section by returning to the point raised in Sec. II that $v_{xc}(\vec{r})$ of Eq. (12) is a local approximation to the nonlocal $\hat{M}$ of Eq. (34) with $E = \mu$ (i.e., electrons on the FS). This is achieved by employing a WKB-type argument.[6] Writing

$$\psi_{\vec{k}}(\vec{r}) = A(\vec{r}) e^{i\vec{k}(\vec{r}) \cdot \vec{r}} \tag{43}$$

and then neglecting the $\vec{r}$ dependence of $A(\vec{r})$ and $\vec{k}(\vec{r})$ when $\hat{M}_h$ of Eq. (34) operates on $|\psi_{\vec{k}}\rangle$, we get

$$\hat{M}_h |\psi_k\rangle = M_h(\vec{k}(\vec{r}); E - \mu + \mu_h(n(\vec{r})); n(\vec{r})) |\psi_{\vec{k}}(\vec{r})\rangle \, . \tag{44}$$

To solve for $\vec{k}(\vec{r})$, Sham and Kohn[6] have proposed the approximation

$$\mu = V(\vec{r}) + \mu_h(n(\vec{r})) \, , \tag{45}$$

which is valid for a slowly varying density. Then using Eqs. (3), (43)–(45), and restricting the electrons to the FS (i.e., $E = \mu$) it follows that

$$\hat{M}_h |\psi_{\vec{k}}\rangle = M_h(\vec{k}(\vec{r}); \mu_h(n(\vec{r})); n(\vec{r})) |\psi_{\vec{k}}(\vec{r})\rangle \, , \tag{46}$$

with $k(\vec{r}) = [3\pi^2 n(\vec{r})]^{1/3}$. This local $\hat{M}_h$ is easily seen to be identical to $v_{xc}(\vec{r})$ defined by Eq. (12).

It should be stressed that:

(i) The procedure for localizing $\hat{M}_h$ given by Eqs. (43)–(46) entails many assumptions. It is precisely the purpose of this work to show that they are not valid for describing FS distortions;

(ii) The approximation of Eq. (45) enters the derivation of the local form [Eq. (46)] and is not used in constructing $M_h$ of Eq. (34) [i.e., Eq. (19) is not equivalent to Eq. (45)];

(iii) The local form of $M_h$ [Eq. (46)] has been the one used most often in local FS calculations. In the following chapter it will thus serve as the basis for comparison of local and nonlocal FS.

Finally, the fact that the corresponding local form for $\hat{M}_h$ [i.e., Eq. (46)] is $v_{xc}(\vec{r})$ of Eq. (12), and so can be simultaneously used for calculating the local FS and the appropriate density $n(\vec{r})$, will be utilized in Sec. IV.

## IV. COMPARISON OF LOCAL AND NONLOCAL FS; FORMULATION

We start by emphasizing that our interest is strictly the effect of nonlocality of $M$ on the FS. Thus, we do not wish to investigate the effect of the local Hartree field $V_H(\vec{r})$, nor become involved with complicated self-consistent band-structure calculations. This is achieved as follows: Instead of starting with an external potential $V_{ext}(\vec{r})$ in Eq. (6) or (8) and constructing the corresponding self-consistent density distribution, the process is reversed; i.e., construct the external potential corresponding to a given self-consistent density distribution.[18] In other words, solve the equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_m(\vec{r})\right)\phi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}}\phi_{\vec{k}}(\vec{r}) , \tag{47}$$

where $V_m(\vec{r})$ is some (non-self-consistent) periodic model pseudopotential appropriately chosen and construct the density $n(\vec{r})$ according to Eq. (7). Equation (47) is easily solved since it is not a self-consistent equation and more important from our viewpoint gives the exact density $n(\vec{r})$ to be used in Eqs. (3) and (15). The effect on $\Sigma(\vec{r}, \vec{r}', E)$ of introducing $V_m(\vec{r})$ in Eq. (47) can be obtained by comparing Eqs. (6) and (47) clearly:

$$V(\vec{r}) = V_m(\vec{r}) - v_{xc}(\vec{r}) \tag{48}$$

and hence

$$\Sigma(\vec{r}, \vec{r}'; E) = V_m(\vec{r}')\delta(\vec{r} - \vec{r}') + M(\vec{r}, \vec{r}'; E) - v_{xc}(\vec{r})\delta(\vec{r} - \vec{r}') . \tag{49}$$

[At first sight Eqs. (15) and (49) might appear contradictory to the theorem that $\Sigma$ is a unique functional of $n$. This is however immediately resolved by recalling that $V(\vec{r})$ of Eq. (15) is also a unique functional of $n$[4]. ] Equation (49) has been written in a manner to emphasize the difference in the local theory [i.e., Eq. (47)] and the corresponding nonlocal theory given by substituting Eq. (49) in Eq. (3), i.e.,

$$H_0\psi_{\vec{k}}(\vec{r}) + \hat{V}_p\psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\psi_{\vec{k}}(\vec{r}) , \tag{50}$$

where $H_0$ is the Hamiltonian in Eq. (47) and

$$\hat{V}_p\psi_{\vec{k}}(\vec{r}) \equiv \int d\vec{r}'\,[M(\vec{r}, \vec{r}'; E_{\vec{k}}) - v_{xc}(\vec{r}')\delta(\vec{r} - \vec{r}')]\psi_{\vec{k}}(\vec{r}') , \tag{51}$$

with the interpretation that $\hat{V}_p$ is the perturbation of the local theory and quasiparticle excitations due to the nonlocal character of $M(\vec{r}, \vec{r}'; E)$.

Equation (50), like Eq. (3), is exact, as of course is the density resulting from Eq. (47) and Eq. (7) to be used in $\hat{M}$ and $v_{xc}$. However, because of their complicated forms, $\hat{M}$ and $v_{xc}$ are next approximated by their forms discussed in Secs. II and III. That is, in Eq. (51) we use for $\hat{M}$ its approximate form given in Eq. (34) with $E = \mu$, i.e.,

$$M(\vec{r}, \vec{r}'; E_{\vec{k}}) \approx M_h(\vec{r} - \vec{r}'; \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) , \tag{52}$$

and for $v_{xc}$ its form in Eq. (12) or equivalently Eq. (46).

We are now in a position to define precisely what we mean by FS derived from a local and a nonlocal theory. (a) Solve Eqs. (6) and (7) self-consistently for $\epsilon_{\vec{k}}$ and $n(\vec{r})$ with $v_{xc}(\vec{r})$ given by Eq. (12) or (46). From the $\epsilon_{\vec{k}}$'s of Eq. (7) determine the FS which will be referred to as the local FS. (b) Use the density $n(\vec{r})$ in Eq. (52) to obtain $\hat{M}_h$, which would then be used in Eq. (3) to determine $E_{\vec{k}}$ and the corresponding FS, which we will refer to as the nonlocal FS.

Actually, in the calculation which we present here the self-consistent calculation (a) has been replaced by Eq. (47) and the corresponding $n(\vec{r})$ it produces. The effect of nonlocality is contained in Eqs. (50) and (51), so that if the effect of nonlocality is small then $\hat{V}_p$ of Eq. (51) will not perturb the local FS obtained from Eq. (47).

We wish to repeat that using $v_{xc}(\vec{r})$ of Eqs. (12) or (46) for describing the local FS (i.e., $\epsilon_{\vec{k}}$'s) serves in the above procedure only as a basis of comparison and does not involve any further approximations. However, extending it to the calculation of the density $n(\vec{r})$ does introduce further assumptions in the calculation of the nonlocal FS. Strictly speaking, a proper way to solve for the self-consistent density $n(\vec{r})$, corresponding to $M_h$ of Eq. (34), is to use Eq. (36). However, such a procedure is extremely difficult. Calculating $n(\vec{r})$ via the above procedure [Eqs. (6), (7), and (12)] has been a common approach, and is assumed here to give the appropriate density for $M_h$.

Noting that the model pseudopotential may be written as

$$V_m(\vec{r}) = \sum_{\vec{G}} V_m(\vec{G})e^{i\vec{G}\cdot\vec{r}} , \tag{53}$$

where $\vec{G}$'s are the reciprocal-lattice vectors, the solution for the local problem (Part a) is obtained by expanding the wave function in plane waves

$$\phi_{\nu\vec{k}}(\vec{r}) = \sum_{\vec{G}} A_{\vec{G}}(\nu\vec{k})e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \tag{54}$$

and substituting in Eq. (47). The energies $\epsilon_{\nu\vec{k}}$ and the expansion coefficients $A_{\vec{G}}(\nu\vec{k})$ are calculated in the standard procedure. Note that a band index and reduced zone scheme for $\vec{k}$ has been introduced. In fact (see below), by a special choice of lattice and $V_m$ in the model calculation presented here, this local band-structure calculation is made trivial.

The energies $E_{\vec{k}}$ for the nonlocal problem are obtained by expanding $\psi$ in terms of $\phi_{\nu\vec{k}}(\vec{r})$:

$$\psi_{\lambda\vec{k}}(\vec{r}) = \sum_{\nu} c_\nu(\lambda\vec{k})\phi_{\nu\vec{k}}(\vec{r}) \;, \tag{55}$$

and substituting in Eq. (50). The energies are given by the solution of

$$\mathrm{Det}\left| H_{\nu'\nu}(\vec{k}) - \delta_{\nu'\nu}E_{\vec{k}} \right| = 0 \;, \tag{56}$$

$$H_{\nu'\nu}(\vec{k}) = \delta_{\nu'\nu}\epsilon_{\nu\vec{k}} + \langle \phi_{\nu'\vec{k}} | \hat{V}_p | \phi_{\nu\vec{k}} \rangle \;. \tag{57}$$

The whole nonlocal nature of the problem is now contained in the last term of Eq. (57). To evaluate this term within the approximation of Eqs. (12) and (52), we first note that from Eq. (52)

$$M_h(\vec{r} - \vec{r}\,', \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) = \int \frac{d\vec{p}}{(2\pi)^3} M_h(\vec{p}, \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) e^{i\vec{p}\cdot(\vec{r}-\vec{r}\,')} \;, \tag{58}$$

and the corresponding Fermi vector is

$$k_F(\vec{r}_0) = [3\pi^2 n(\vec{r}_0)]^{1/3} \;. \tag{59}$$

Then, noting that the $\vec{r}_0$ dependence is periodic in the lattice and thus may be expressed as a Fourier series:

$$M_h(\vec{p}, \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) = \sum_{\vec{G}''} M_h(\vec{p}; \vec{G}'') e^{i\vec{G}''\cdot\vec{r}_0} \;, \tag{60}$$

it is straightforward to show that

$$\langle \phi_{\nu' k} | \hat{V}_p | \phi_{\nu k} \rangle = \sum_{\vec{G}',\vec{G}} A^*_{\vec{G}'}(\nu'\vec{k}) A_{\vec{G}}(\nu\vec{k}) \times \left[ M_h\left(\vec{k} + \frac{\vec{G}' + \vec{G}}{2} \;;\; \vec{G}' - \vec{G}\right) - v_{xc}(\vec{G}' - \vec{G}) \right]. \tag{61}$$

Equation (61) is completely general; however, $M_h(\vec{p}, E; n(\vec{r}_0))$ is, in general, very complicated[11] so that we must make a definite approximation for $M_h(\vec{p}, E; n(\vec{r}_0))$. We choose the RPA for Eq. (58) so that

$$M_h(\vec{p}, \mu_h(n(\vec{r}_0)); n(\vec{r}_0)) \approx M_x(\vec{p}; n(\vec{r}_0)) + M_{\mathrm{RPA}}(\vec{p}, \mu_0(n(\vec{r}_0)); n(\vec{r}_0)) \;, \tag{62}$$

where $M_x$ is the Fock exchange:

$$M_x(\vec{p}; n(\vec{r}_0)) = -\frac{e^2 k_F}{\pi}\left[1 + \frac{k_F^2 - p^2}{2pk_F} \ln\left(\frac{k_F + p}{k_F - p}\right)\right]. \tag{63}$$

$M_{\mathrm{RPA}}$ is given by (see, for example, Hedin[7])

$$M_{\mathrm{RPA}}(\vec{p}, \mu_0; n(\vec{r}_0)) = -\frac{e^2 k_F^2}{\pi^2 p}\int_0^\infty \frac{dq}{q}\int_0^\infty dy \times \ln\left(\frac{[1-(p/k_F - 2q)^2]^2 + 16y^2}{[1-(p/k_F + 2q)^2]^2 + 16y^2}\right) \times \left(\frac{1}{\epsilon(q, iy)} - 1\right) \;, \tag{64}$$

and $\mu_0 = \hbar^2 k_F^2/2m$, with $k_F$ defined in Eq. (59).

The consistent approximation for $v_{xc}(r)$, when $M_h$ is approximated by Eqs. (62)–(64), is, according to Eq. (46):

$$v_{xc}(\vec{r}) = M_x(k_F \,; n(\vec{r}_0)) + M_{\mathrm{RPA}}(k_F, \mu_0 \,; n(\vec{r}_0)) \;. \tag{65}$$

This completes the definition of all the quantities entering the nonlocal problem of Eq. (50) through Eq. (61) in the RPA.

To avoid getting into a complicated band-structure calculation, a simple cubic lattice was chosen (cube edge "$a$") and all the Fourier coefficients in Eq. (53) were set equal to zero except for the first nearest neighbors. The resulting pseudopotential is

$$V_m(\vec{r}) = 2V_1\left(\cos\frac{2\pi x}{a} + \cos\frac{2\pi y}{a} + \cos\frac{2\pi z}{a}\right) \tag{66}$$

(the three-dimensional Mathieu potential), which allows Eq. (47) to be separated into three one-dimensional equations, and the calculation of the band structure and wave functions [i.e., $A_{\vec{G}}(\nu\vec{k})$] becomes trivial for the local theory.

## V. COMPARISON OF LOCAL AND NONLOCAL FS; RESULTS AND DISCUSSION

As stressed in Sec. IV, the whole nonlocal nature of the problem is contained in the last term of Eq. (57). We wish to next focus on the numerical aspect of Eq. (61) as it enters Eqs. (56) and (57).

Since the density is the central quantity in the theory we start by giving a brief description of the numerical calculation of $n(\vec{r})$ [see Eq. (7)] given by Eq. (47) with $V_m(\vec{r})$ of Eq. (66), from which the corresponding $M_h(\vec{p}, \vec{G})$ given by Eqs. (62)–(64) is then evaluated. Also, to appreciate dependence of the nonlocal effects for a range of strengths of potential, three cases of $V_1$ will be considered.

The density of Eq. (7) can be written as

$$n(\vec{r}) = \frac{2}{3\pi^3}\int_0^1 dt \int_0^{\pi/2} d\phi \int_0^{K_F^3(t,\phi)} ds\, F(\vec{r}, s, \phi, t) \;, \tag{67}$$

where

$$F(\vec{r}; \vec{k}) = |\chi_{1k_x}(x)\chi_{1k_y}(y)\chi_{1k_z}(z)|^2 \;.$$

$\chi_{\nu_x k_x}$ satisfies the equation

$$\left(\frac{-d^2}{dx^2} + 2V_1 \cos x\right)\chi_{\nu_x k_x}(x) = \epsilon_{\nu_x k_x}\chi_{\nu_x k_x}(x) \;, \tag{68}$$

$$\phi_{\nu\vec{k}}(\vec{r}) = \chi_{\nu_x k_x}(x)\chi_{\nu_y k_y}(y)\chi_{\nu_z k_z}(z) \;, \tag{69}$$

$$\epsilon_{\nu\vec{k}} = \epsilon_{\nu_x k_x} + \epsilon_{\nu_y k_y} + \epsilon_{\nu_z k_z} \;, \tag{70}$$

and $s = k^3$, $t = \cos\theta$ (note units of $2\pi/a = \hbar^2/2m = 1$ have been used). The coordinates of Eq. (67) were chosen since the FS is almost spherical [i.e., $K_F(t, \phi) \simeq$ constant] and the variation from the volume element is eliminated.

The solutions of Eq. (68) are the Mathieu functions, and with these the density is easily evaluated

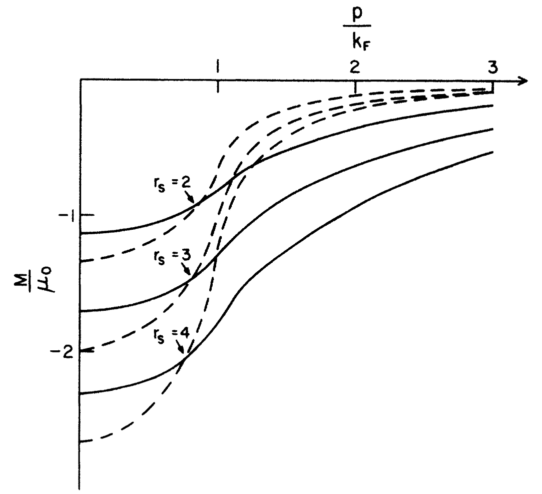

FIG. 5. Self-energy $M_h(\vec{p},\mu_0(r_s);\ n(r_s))$ of Eq. (62). Solid lines, $M_x(\vec{p};n(r_s))$ of Eq. (63); dashed lines, for indicated values of $r_s$. Note that $k_F=1/\alpha r_s$ and $\mu_0=k_F^2$.

numerically from Eq. (67) for an appropriate mesh in $\vec{r}_0$.

The $M_h(\vec{p};\vec{G})$ corresponding to the above density (Eq. 67) is determined in two steps. First we evaluate Eqs. (63) and (64) for a range of $p$ and $r_s$. The Fock part [Eq. (63)] is of course trivial to evaluate and simply requires substituting $k_F=1/\alpha r_s$ [$\alpha=(4/9\pi)^{1/3}$]. $M_{\text{RPA}}(\vec{p};\mu_0(r_s);n(r_s))$ [Eq. (64)] with

$$\epsilon(q,iy)=1+Q(q,iqy)\,, \tag{71}$$

and

$$Q(q,iqy)=\frac{\alpha r_s}{4\pi q^2}\left\{2+\frac{y^2+1-q^2}{2q}\ln\left(\frac{y^2+(1+q)^2}{y^2+(1-q)^2}\right)\right.$$
$$\left.-2y\left[\tan^{-1}\left(\frac{1+q}{y}\right)+\tan^{-1}\left(\frac{1-q}{y}\right)\right]\right\} \tag{72}$$

is done numerically in a straightforward manner, taking advantage of the large $y$ and $q$ behavior of Eqs. (64), (71), and (72) to improve convergence and doing the $q$ integration analytically for small $q$. The $M_h(\vec{p},\ \mu_0(r_s);n(r_s))$ of Eq. (62) for $r_s=2, 3, 4$ as compared to the Fock part, $M_x(\vec{p};n(r_s))$, as a function of $p$ is plotted in Fig. 5. There are several features of these curves that are worth noting. It will become clear in the following that the nonlocal effect on the FS distortion is strongly governed by the range of the self-energy in $\vec{p}$ space (or equivalently $\vec{r}$ space[7]). We wish to note that as expected the full $M_h$, including correlations, is significantly smoother in $p$ space than $M_x$. Hence, calculations which neglect correlations would totally misrepresent the nonlocal effects.

Once the function $M_h(\vec{p},\ \mu_0(r_s);n(r_s))$ is tabulated for an appropriate mesh of $r_s$, then the left side of Eq. (62) is found as a function of $\vec{r}_0$ by finding the $r_s$ corresponding to a specific $\vec{r}_0$ through Eq. (59). The function $M_h(\vec{p};\vec{G})$ is then determined by Fourier transforming the above function in the variable $\vec{r}_0$. This is done numerically using the Fillon[19] method, and we note since the above is periodic in $\vec{r}_0$ the integration is only over a unit cell. The Fourier transform of Eq. (65) [i.e., $v_{xc}(\vec{G})$] is again obtained numerically in the same way.

With the function $M_h(\vec{p};\vec{G})$ and $v_{xc}(\vec{G})$ tabulated for the different strengths of $V_1$, we next evaluate Eq. (61) for a mesh of points $\vec{k}$. The coefficients $A_{\vec{G}}(\nu\vec{k})$ for the corresponding points of $\vec{k}$ are determined from Eqs. (68) and (69) and the sum over $\vec{G}$ and $\vec{G}'$ is performed. Eq. (56) is then solved for the nonlocal energies $E_{\lambda\vec{k}}$ and the corresponding wave functions $\psi_{\lambda\vec{k}}(\vec{r})$ [Eq. (55)] with $\epsilon_{\nu\vec{k}}$ given by Eq. (70).

For each $\hat{k}$ the nonlocal $E_{\lambda\vec{k}}$ is evaluated for three $\vec{k}$'s closely spaced around the unperturbed Fermi sphere, denoted by $K_0$ (the corresponding Fermi energy is $\epsilon_0=\hbar^2K_0^2/2m$). With the above results for $E_{\lambda\vec{k}}$ with $\lambda=1$ (lowest nonlocal band) and $\epsilon_{\nu\vec{k}}$ with $\nu=1$ (lowest local band) the local and nonlocal radial distortions are determined in the usual way by finding a surface of constant energy (i.e., $E=\mu$) which encloses the correct volume in $\vec{k}$ space.

The resulting radial distortions, in the (001) plane, for $V_1/\epsilon_0=\frac{15}{32}$, $\frac{5}{32}$, and $\frac{25}{32}$ and $K_0=0.8\pi/a$ corresponding to the local and nonlocal theories are exhibited in Figs. 6, 7, and 8. As clearly seen the nonlocal effects significantly reduce the radial distortions for the three $V_1$'s.

An interesting feature of the calculation is that while the radial distortions are reduced by more than a factor of 2, the corresponding nonlocal wave functions [Eq. (55) with $\lambda=1$] change much less. In other words, in Eq. (55) for $\lambda=1$, $V_1/\epsilon_0=\frac{15}{32}$, $|C_2(\lambda\vec{k})|\leqslant 0.05$ and $|C_\nu(\lambda\vec{k})|\leqslant 0.01$ for $\nu\geqslant 3$. (We will return to the implication of the above at the end of this section.) We also note that this implies

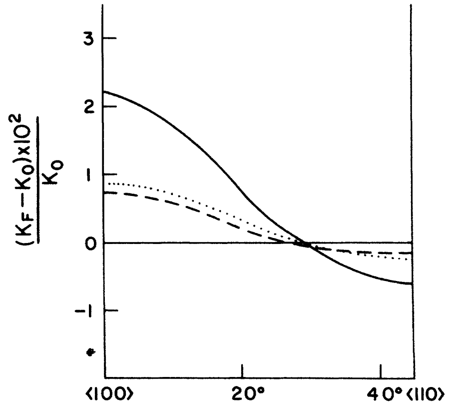

FIG. 6. Radial distortions for $V_1=\frac{15}{32}\epsilon_0$. The solid line is local result, the dash line - - is the nonlocal, and the dotted line ··· is the uniform density approximation.

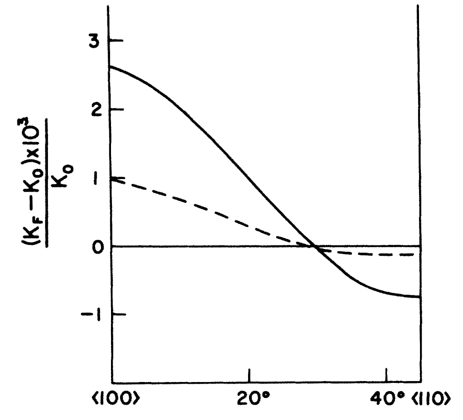

FIG. 7. Radial distortions for $V_1 = \frac{5}{32}\epsilon_0$. See Fig. 6.

that the diagonal matrix element of Eqs. (57) [i.e., $H_{1,1}(\vec{k})$] gives $E_{1\vec{k}}$ to ~90% accuracy. Finally the nonlocal theory increases the energy separation at the FS ($E_{2k} - E_{1k}$) by ~15% over the local theory. We however wish to stress that our calculations have been formally restricted to $E = \mu$ and are not strictly applicable to the calculation of the higher energy state ($E \neq \mu$).

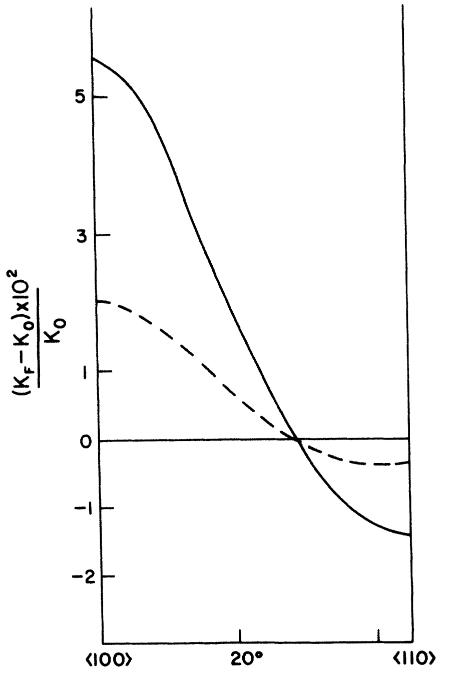

FIG. 8. Radial distortions for $V_1 = \frac{25}{32}\epsilon_0$. See Fig. 6.

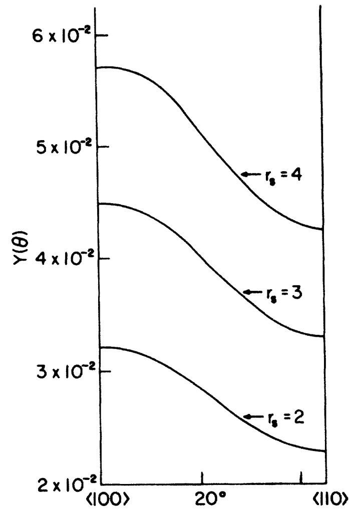

FIG. 9. Uniform density approximation for $\langle \phi_{1\vec{k}}, \hat{V}_P\, \phi_{1\vec{k}} \rangle / \mu_0 \equiv Y(\theta)$, see text, Eq. (77).

Although the $C_\nu(1\vec{k})$, $\nu \geq 2$ are small, in some phenomena the admixture of waves $e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$, $\vec{G} \neq 0$ play a crucial role (e.g., interband optical absorption). Thus it is worthwhile to summarize the changes in two typical examples:

For $\vec{k} = K_0(1, 0, 0)$, [$\vec{G} = (2\pi/a)(-1, 0, 0)$ in the following],

$$\phi_{1\vec{k}}(\vec{r}) \approx 0.94|\vec{k}\rangle + 0.31|\vec{k}+\vec{G}\rangle\,, \tag{73a}$$

$$\phi_{2\vec{k}}(\vec{r}) \approx -0.31|\vec{k}\rangle + 0.94|\vec{k}+\vec{G}\rangle\,, \tag{73b}$$

and $C_1(1\vec{k}) = 0.998$, $C_2(1\vec{k}) = -0.05$. Therefore

$$\psi_{1\vec{k}}(\vec{r}) \approx 0.95|\vec{k}\rangle + 0.26|\vec{k}+\vec{G}\rangle\,, \tag{74}$$

and we see that the coefficient of $|\vec{k}+\vec{G}\rangle$ has been reduced by ~15%. For $\vec{k} = K_0(\frac{1}{2}\sqrt{3}, \frac{1}{2}, 0)$

$$\phi_{1\vec{k}}(\vec{r}) \approx 0.96|\vec{k}\rangle + 0.22|\vec{k}+\vec{G}\rangle\,, \tag{75a}$$

$$\phi_{2\vec{k}}(\vec{r}) \approx -0.22|\vec{k}\rangle + 0.96|\vec{k}+\vec{G}\rangle\,, \tag{75b}$$

and $C_1(1\vec{k}) = 0.999$, $C_2(1\vec{k}) = -0.023$. Therefore,

$$\psi_{1\vec{k}}(\vec{r}) \approx 0.96|\vec{k}\rangle + 0.20|\vec{k}+\vec{G}\rangle\,, \tag{76}$$

a reduction of 10% in the coefficient of $|\vec{k}+\vec{G}\rangle$.

Another question of interest is the importance of including the proper density $n(\vec{r}_0)$ in Eq. (62). To estimate it we replace $n(\vec{r}_0)$ by the mean (uniform) density for $r_s = 3$ in the $V_1 = \frac{15}{32}\epsilon_0$ example. The appropriate $A_{\vec{G}}(\nu\vec{k})$, however, are maintained in evaluating Eq. (61). The consequence, of course, is that only $\vec{G}' = \vec{G}$ enters in $M_h$ and $v_{xc}$ of Eq. (61). The resulting local and nonlocal radial distortions are given in Fig. 6. The maximum density variation, which occurs at the center of the cell, is of the order of 150%. From Fig. 6, it can be seen that the nonlocal effects are well represented by this approximation, (within 15% at the maximum radial distortion). This gives us confidence that nonlocal gradient term effects (e.g., $\Delta[n]$ of Eq.

(35)) will not drastically change our conclusions.

The calculation of the radial distortions are masked by a large number of steps and details. We wish to next produce a qualitative argument for the reduction in the radial distortions due to nonlocal effects.

If we use the uniform density approximation in the left-hand side of Eq. (60) and noting that $M_h(\vec{p}, \mu_h(n_0); n_0)$ is a monotonically decreasing function of $p$, then for $p > K_0$, $M_h(\vec{p}, \mu_h(n_0); n_0) > v_{xc}(n_0)$. Next, recognizing that the effect of $\nu$ and $\nu' > 1$ is small, and then realizing that a major contribution to Eq. (67) comes from the coefficient $A_{\vec{G}}(\nu\vec{k})$ $(\nu = 1)$ for $|\vec{k} - \vec{G}|$ minimum, it is easy to see that for $\vec{k}$ closest to the zone boundary Eq. (61) is greatest (and positive). As $\vec{k}$ moves away from the zone (with $|\vec{k}| = K_0$) it becomes smaller. Such an angular dependence of Eq. (61) added to the local energy $\epsilon_{\nu k}$ $(\nu = 1)$, can be seen to reduce the variation in energy and hence reduce the radial distortions. This effect is shown in Fig. 9, where the function

$$Y(\theta) = \sum_{\vec{G}} |A_{\vec{G}}(1\vec{k})|^2 \, [M_h(\vec{k} + \vec{G}; 0) - v_{xc}(0)]/\mu_0 \, , \quad (77)$$

$G = (2\pi/a)(-1, 0, 0)$ and $(2\pi/a)(0, -1, 0)$, is plotted for $\vec{k}$ in the (001) plane as a function of angle $\theta$ for $r_s = 2$, 3, and 4, $V_1/\epsilon_0 = \frac{15}{32}$. The variation of $Y(\theta)$ is dominated by the changes in $A_{\vec{G}}(1\vec{k})$ as $\vec{k}$ moves away from the zone boundary [see Eqs. (73a) and (75a)]. It corresponds to $\approx 60\%$ of the full angular variation of Eq. (61). It is worth noting that the above argument suggests that the reduction in the radial distortions is not restricted to $M_h$ in the RPA, but will also occur for the full $M_h$, although the amount of reduction could change. It also strongly suggests that the above effect will occur in at least simple monovalent metals. We wish to emphasize that for the actual determination of the size of the effect the above qualitative arguments are not sufficient. A full solution, as discussed earlier, should be carried out.

Finally we wish to note that the calculated changes in the radial distortions in the nonlocal theory are much larger than the changes in the corresponding wave functions. This may have important implications on procedures which attempt to correlate FS data with other phenomena. For example, distortions of the FS are used to determine wave functions in the vicinity of the FS via phase shifts or pseudopotentials. These wave functions are then used to theoretically correlate a number of phenomena. The above suggests that these methods may result in significant inaccuracies.

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