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Effect of nonlocality on the Fermi surface of copper*

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We investigate the effect of the nonlocal nature of the self-energy on the Fermi surface of copper. Results obtained using a simple representation for the nonlocal structure show that this feature has the potential of resolving the discrepancy between first-principles local theory and experiment.

I. INTRODUCTION

The adequacy of the local-potential approximation for the description of elementary excitations in solids has been of interest for many years. An initial investigation of this question was carried out by Kane[1] with emphasis on the band structure of semiconductors. Recently, Rasolt and Vosko[2] (to be referred to as RV) and Rasolt, Nickerson, and Vosko[3] have also investigated the importance of nonlocality with emphasis on simple metals. These authors have treated the exchange and correlation contributions to nonlocality on equal footing. Other works, in simple metals,[4] have focused more on the Hartree-Fock contribution to nonlocality with the correlation contribution included as a correction.

The nonlocality of the potential Σ is exhibited in the following equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_{\vec{k}}(\vec{r})+\int d\vec{r}\,'\,\Sigma(\vec{r},\vec{r}\,',E_{\vec{k}})\Psi_{\vec{k}}(r')=E_{\vec{k}}\Psi_{\vec{k}}(\vec{r}), \tag{1}$$

where Σ has been specialized to a periodic system. This is a Schrödinger-type equation with $\Psi_{\vec{k}}(\vec{r})$ having the meaning of quasiparticle states and $E_{\vec{k}}$ that of quasiparticle excitations.[2,5] Equation (1) corresponds to an equation with nonlocal potential in that Σ depends on a finite difference between $\vec{r}$ and $\vec{r}\,'$ and cannot be approximated by $\Sigma(\vec{r},\vec{r}\,',E) \rightarrow \Sigma(\vec{r},\vec{r}\,',E)\delta(\vec{r}-\vec{r}\,')$. We note that the constant-energy surface described by $E_{\vec{k}}$ which encloses the proper number of electrons[5] will correspond to the experimentally measured Fermi surface (FS).

In this work we wish to extend some of the results of RV from simple to more complex metals, specifically copper. The motivation is the recent thorough FS calculation for copper[6] in which no first-principles local version of Σ was found adequate to reproduce the experimental FS accurately. This work is mainly an attempt to establish whether the nonlocal feature of Σ has the potential, in trend and magnitude, of resolving the above discrepancy between theory and experiment.

The work is divided into three sections. In Sec. II we spherically decompose the structure of Σ in order to study its effect on the FS via the augmented-plane-wave (APW) method. In Sec. III we apply these results to the band structure and FS of copper.

II. SPHERICAL DECOMPOSITION OF Σ

Equation (1) describes rigorously the quasiparticle states and corresponding excitation energies. To further discuss this equation, it is useful to separate Σ into the following terms:

$$\Sigma = V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) + M(\vec{r},\vec{r}\,',E), \tag{2}$$

where $V_{\text{ext}}(\vec{r})$ is the external potential, $V_H(\vec{r})$ is the usual Hartree contribution, and M is the self-energy operator.[7] We note that M is a unique functional of the density[2,5] $n(\vec{r})$, i.e., the density of the system determines, in principle, the form of M. Unfortunately, the structure of M is extremely complex and not known exactly. Thus various procedures for approximating M, or equivalently, for obtaining the quasiparticle excitations in Eq. (1) have been suggested.

A common starting point is to solve Eq. (1) with the Hartree-Fock approximation,[8] i.e.,

$$M(\vec{r},\vec{r}\,',E) \cong e^2\rho(\vec{r},\vec{r}\,')/|\vec{r}-\vec{r}\,'|, \tag{3}$$

where

$$\rho(\vec{r},\vec{r}\,') = \sum_{\vec{k}=\text{occupied}} \Psi_{\vec{k}}(\vec{r})\Psi^*_{\vec{k}}(\vec{r}\,'). \tag{4}$$

The solution of Eqs. (1), (3), and (4) in metallic systems yield a dispersion $E_{\vec{k}}$ which is known to be much too wide and to have an unphysical singularity on the FS. Both of these deficiencies are corrected when correlation is included in M. (Note that while the correlation contributions to the total energy are small, their effect on M is very large and equal in importance to that of exchange.[9]) Thus it is important to treat correlation and exchange contributions to M with equal care. To solve first for the Hartree-Fock excitations and then add the effect of correlation as a correction is likely to misrepresent the nonlocal structure of M.

For simple metals (or equivalently the contribution of the metallic s and p bands) an appealing approach for including correlation in M is that used by RV. In that work, M is approximated by the self-energy operator M_h of a uniform electron gas, i.e.,

$$M \cong M_h[\vec{r}-\vec{r}\,';E-\mu+\mu_h(n(\vec{r}_0));n(\vec{r}_0)], \tag{5}$$

where μ_h is the chemical potential for a uniform electron gas of density n, μ is the chemical potential, and $\vec{r}_0=\frac{1}{2}(\vec{r}+\vec{r}\,')$. The properties satisfied by this M, together with a way to include corrections to Eq. (5), are discussed extensively by RV. It is sufficient to observe that Eq. (5) is the first term of an expansion for the nonlocal M, similar to the first term in the gradient expansion of the local theory. In fact in Sec. III we will further simplify M in replacing the density $n(\vec{r}_0)$ by its uniform value n_0. In addition the correlation contribution will be evaluated within the random-phase approximation (RPA). Then

$$M(\vec{r},\vec{r}\,',E) \cong \int \frac{d\vec{k}}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} M(\vec{k},E,n_0), \tag{6}$$

where

$$M(\vec{k},E,n_0)=M_x(\vec{k},n_0)+M_{\mathrm{RPA}}(\vec{k},E,n_0), \tag{7}$$

$$M_x(\vec{k},n_0)=\frac{-e^2k_F}{\pi}\left[1+\frac{k_F^2-k^2}{2k_Fk}\ln\left(\frac{k_F+k}{k_F-k}\right)\right], \tag{8}$$

$$\begin{aligned} M_{\mathrm{RPA}}(\vec{k},E,n_0)={}&\frac{2e^2k_F^2}{\pi k}\int_0^\infty \frac{dq}{q}\int_{(k/2k_F-q)^2}^{(k/2k_F+q)^2} dx\left(\frac{1}{\mathcal{E}(q,\omega-x)}-1\right)[\Theta(\omega-x)-\Theta(0.25-x)]\\ &-\frac{e^2k_F^2}{\pi^2k}\int_0^\infty \frac{dq}{q}\int_0^\infty dy\,\ln\left[\frac{[\omega-(k/2k_F-q)^2]^2+y^2}{[\omega-(k/2k_F+q)^2]^2+y^2}\right]\left(\frac{1}{\mathcal{E}(q,iy)}-1\right), \end{aligned} \tag{9}$$

$$\mathcal{E}(q,iy)=1+Q(q,iy), \tag{10}$$

$$Q(q,iy)=\frac{\alpha r_s}{4\pi q^2}\left\{2+\left(\frac{y^2/q^2+1-q^2}{2q}\right)\ln\left(\frac{y^2/q^2+(1+q)^2}{y^2/q^2+(1-q)^2}\right)-2y/q\left[\tan^{-1}\left(\frac{1+q}{y/q}\right)+\tan^{-1}\left(\frac{1-q}{y/q}\right)\right]\right\}, \tag{11}$$

and

$$E=\omega 2\hbar^2k_F^2/m,\quad k_F=(3\pi^2n_0)^{1/3},$$

$$\alpha=(4/9\pi)^{1/3},\quad r_sa_0=1/\alpha k_F,\quad a_0=\hbar^2/me^2.$$

In Sec. III the above structure of M will be applied in conjunction with the APW method for states on the FS. This requires a spherical decomposition of M within each unit cell. We end this section by giving the explicit structure of M in spherical coordinates up to angular momentum $l=2$ for E on the FS ($\omega=\frac{1}{4}$). Writing

$$M(\vec{r},\vec{r}\,')=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} Y_{lm}(\theta,\varphi)Y_{lm}^*(\theta',\varphi')M_l(r,r'), \tag{12}$$

where θ and φ are the polar angles of $\vec{r}$ and Y_{lm} are the spherical harmonics. Using Eq. (6) we have

$$M_l(r,r')=\frac{2}{\pi}\int_0^\infty p^2dp\,M(p,\mu_h(n_0),n_0)\,j_l(pr)j_l(pr'). \tag{13}$$

The integration over p can be gotten in closed form. The calculation is straightforward but a bit tedious. The key points are integration by parts followed by proper contour integration using the analytic properties of

$$E_1(z)=\int_1^\infty \frac{e^{-zx}}{x}dx. \tag{14}$$

Below we write down the results for both exchange and correlation for $l=0,1,2$. For exchange

$$M_l^x(r,r')=\frac{-e^2k_F^2}{\pi rr'}(-D_l^++D_l^-), \tag{15}$$

where

$$D_0^\pm=\frac{1}{2}\left[\frac{\sin(\rho_\pm)}{\rho_\pm^2}-\frac{\cos(\rho_\pm)}{\rho_\pm}-\mathrm{Si}(\rho_\pm)\right]; \tag{16}$$

$$D_1^\pm=\frac{1}{\gamma}D_0^\pm+\frac{1}{\gamma\kappa^2}[\mathrm{Si}(\rho_\pm)-\sin(\rho_\pm)]; \tag{17}$$

$$\begin{aligned} D_2^\pm={}&\frac{-3-\gamma^2}{2\gamma^2}D_0^\pm+\frac{3}{\gamma}D_1^\pm\\ &+\frac{3}{2\gamma^2\kappa^4}[\rho^{\pm2}\sin(\rho_\pm)+3\rho^\pm\cos(\rho_\pm)-3\sin(\rho_\pm)]; \end{aligned} \tag{18}$$

and

$$\gamma=\frac{2rr'}{r^2+r'^2};\quad \kappa=k_F(r^2+r'^2)^{1/2};\quad \rho_\pm=k_F\left|r\pm r'\right|;\quad \mathrm{Si}(\rho)=I_mE_1(i\rho)+\tfrac{1}{2}\pi. \tag{19}$$

For correlation

$$M_l^{\mathrm{RPA}}(r,r')=\frac{-e^2k_F^2}{\pi^2rr'}\int_0^\infty\frac{dq}{q}\int_0^\infty dy\left(\frac{1}{\mathcal{E}(q,iy)}-1\right)F_{l,r,r'}(q,y), \tag{20}$$

$$F_{l,r,r'}(q,y)=-C_l^+(a_+,b)+C_l^-(a_+,b)-C_l^+(a_-,b)+C_l^-(a_-,b), \tag{21}$$

where

$$C_0^\pm(a,b)=2I_mE_1[(b+ia)\rho_\pm]; \tag{22}$$

$$C_1^\pm(a,b)=\frac{1}{\gamma}C_0^\pm(a,b)+\frac{2e^{-b\rho_\pm}}{\gamma\kappa^2(a^2+b^2)}\left[\left(-\frac{b\rho_\pm}{\kappa}+\frac{a^2-b^2}{a^2+b^2}\right)\sin(a\rho_\pm)-\left(\frac{a\rho_\pm}{\kappa}+\frac{2ab}{a^2+b^2}\right)\cos(a\rho_\pm)\right]; \tag{23}$$

$$\begin{aligned}C_2^\pm(a,b)=\frac{-3-\gamma^2}{2\gamma^2}C_0^\pm(a,b)+\frac{3}{\gamma}C_1^\pm(a,b)+\frac{3e^{-b\rho_\pm}}{\gamma^2\kappa^4(a^2+b^2)}\Bigg[&\left(b\rho_\pm^3-\frac{3(a^2-b^2)}{a^2+b^2}\rho_\pm^2-\frac{6b(3a^2-b^2)}{(a^2+b^2)^2}\rho_\pm-\frac{6(a^4-6a^2b^2+b^4)}{(a^2+b^2)^3}\right)\sin(a\rho_\pm)\\&+\left(a\rho_\pm^3+\frac{6ab}{a^2+b^2}\rho_\pm^2-\frac{6a(a^2-3b^2)}{(a^2+b^2)^2}\rho_\pm-\frac{24ab(a^2-b^2)}{(a^2+b^2)^3}\right)\cos(a\rho_\pm)\Bigg];\end{aligned} \tag{24}$$

and

$$a_\pm=2q\pm\{0.5[(1+16y^2)^{1/2}+1]\}^{1/2},\quad b=\{0.5[(1+16y^2)^{1/2}-1]\}^{1/2}.$$

Finally,

$$M_l(r,r')=M_l^x(r,r')+M_l^{\mathrm{RPA}}(r,r'). \tag{25}$$

After appropriate transformations, Eqs. (20)–(24) have been integrated numerically for a mesh of r and r'. In Figs. 1–3 we display the forms of $M_l(r,r')$ and $M_l^x(r,r')$ for $l=0,1,2$ with the density corresponding to the 4s electron of copper; $r_s=2.67$. A comparison of $M_l(r,r')$ and $M_l^x(r,r')$ reemphasizes again the importance of treating correlation and exchange contributions to the nonlocal structure of M in metals on equal footing. The $M_l^x(r,r')$ is very wide for all l, as expected from the structure of $M_h(|\vec{r}-\vec{r}'|,\mu_h(n_0),n_0)$.[9] The correlation contribution greatly reduces this width. Nevertheless, from Figs. 1–3 it is clear that a substantial contribution of $M_l(r,r')$ resides outside the muffin-tin [10](MT) radius R_m.

In Sec. III we apply these results to the study of their effect on the band structure and more specifically the FS of copper.

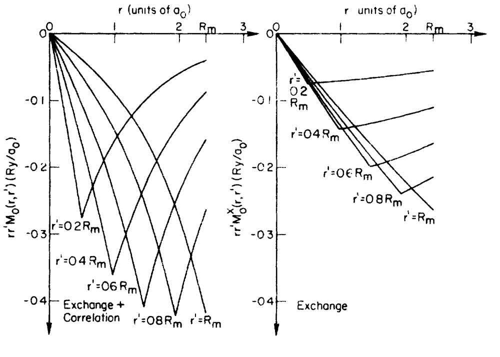

FIG. 1. The $l=0$ component of the angular decomposed nonlocal exchange and correlation potential as a function of r for $r'=0.2$, 0.4, 0.6, 0.8, $1R_m$. The curves are peaked at $r=r'$. $M(r,r')=M(r',r)$. The muffin-tin approximation corresponds to ignoring the contribution of M beyond the muffin-tin radius R_m. The curves on the right are for exchange potential only.

III. APPLICATION TO THE FERMI SURFACE OF COPPER

Owing to the high precision measurements of its FS and its relatively low atomic number, making it nonrelativistic, copper has been for many years a testing ground for theoretical studies of non-

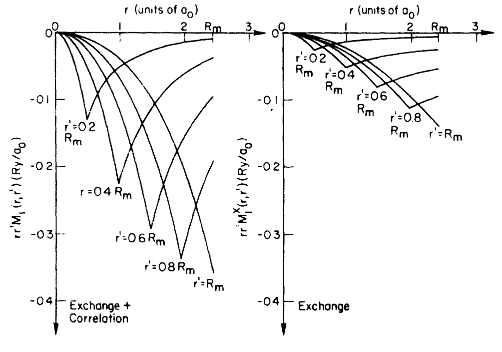

FIG. 2. Same as Fig. 1 with $l=1$.

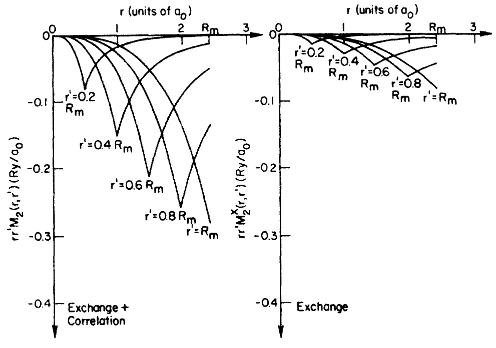

FIG. 3. Same as Fig. 1 with $l=2$.

simple metals. A recent and very extensive study of copper is that of Janak, Williams, and Moruzzi.[6] Since our interest in this section is the FS of copper, we focus on this aspect of their study, although their analysis covers many other features of copper.

The interesting feature of the Janak, Williams, and Moruzzi FS analysis is that all of the local forms for M based on a fundamental theory (e.g., Slater,[11] Kohn and Sham,[5,12] and Hedin and Lundqvist[13]) resulted in discrepancy with the experimental FS. More precisely, the FS neck was 20% too large. They note that a relative shift in energy between a point on the calculated FS along $L \rightarrow W$ and that along $\Gamma \rightarrow X$ of 0.02 Ry would remove this discrepancy.[6] (We note that when these authors chose an *ad hoc* $\alpha = 0.77$ in the "$X\alpha$" local potential these discrepancies were removed.)

Since the calculation of Janak, Williams, and Moruzzi was done within the Korringa-Kohn-Rostoker scheme, they estimated the error introduced through the MT approximation. They further investigated the effect of gradient corrections ($X\alpha\beta$ method) and relativistic corrections, and showed that none of the above is sufficient to explain these discrepancies. These authors conclude that since the electron-gas results do not appear to contain uncertainties of the required magnitude, one should question the adequacy of the local approximation for M. In this section we wish to investigate this possibility in the simplest possible way with the hope of doing a more refined calculation in the future.

The first of our simplifications is to take the Chodorow[14] potential for our local description of the FS of copper. We thus measure the effect of M by adding its contribution to the Chodorow band structure.

The second simplification involves the structure of M. Let us first state the form we chose, and then show that although it is very crude, we still expect it to contain the essential features.

For $M(\vec{r}, \vec{r}', E)$ we chose the uniform electron form of Eq. (5) with $E = \mu$ and constant density n_0 corresponding to the 4s electron of copper and evaluated it within RPA (Sec. II). In other words, in Eqs. (1) and (2),

$$\Sigma \cong V_C(r) + M_h(|\vec{r} - \vec{r}'|, \mu_h(n_0), n_0) - v_{xc}(n_0), \quad (26)$$

where $V_C(r)$ is the Chodorow potential. The potential $V_C(r)$ includes in principle the full electronic density. Since only the contribution from the 4s density to $V_C(r)$ is replaced by a nonlocal structure we remove the corresponding local part $[v_{xc}(n_0) = M(k_F, \mu_h(n_0), n_0).^2]$ in Eq. (26).

RV in a model calculation of simple metals with sizable density variation have set $n(\vec{r}) = n_0$ and found the error on the FS distortions to be relatively small. This suggests that the s,p contributions to M (in copper) can be approximated by $n(\vec{r}) = n_0$ while maintaining the qualitative effect of M on the FS.

The reason for using the density of a single electron can be argued from Fig. 4, where we choose the band structure of copper in the $\Gamma \rightarrow L$ direction (the direction is not important). First we note that the filled d bands (Λ_3) are narrow and

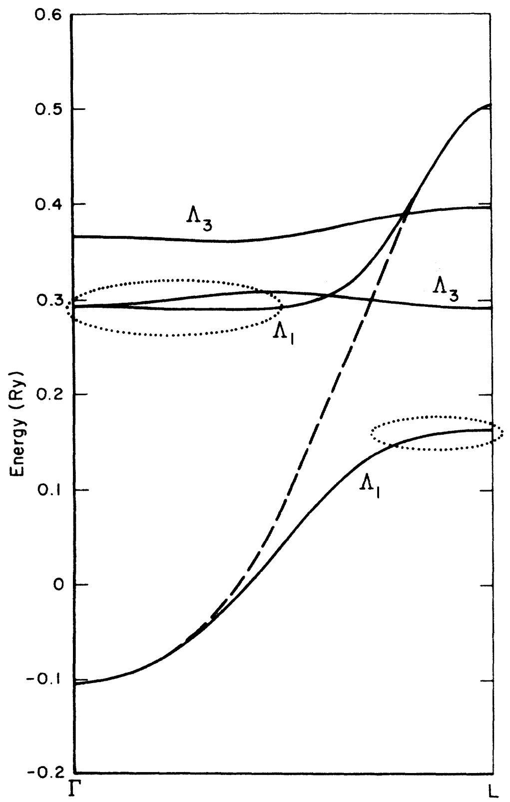

FIG. 4. The band structure of copper along Γ to L direction. The bands Λ_3 are d like. The encircled portions of bands Λ_1 are also d-like. The dashed curve corresponds to the unhybridized s band of copper.

correspond to semilocalized states. The nonlocal structure of M of the uniform electron gas is bound to totally misrepresent their contribution and we are forced to leave them as part of $V_c(r)$.

The two bands Λ_1 have been collapsed into a single s,p band given by the dashed line, the rationale being that in the encircled region the states are highly d like and again are left as part of $V_c(r)$. Away from this region the states become more s,p like and we can include them in M. We make the approximation that the number of these states is equal to one electron.

We next return to Eq. (1) and angularly decompose it within a single unit cell and get the usual radial equation

$$-\frac{\hbar^2}{2m}\frac{d^2P_l(r)}{dr^2}+\left(\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}+V_c(r)-v_{xc}(n_0)\right)P_l(r)$$
$$+\int_0^{R_M}dr'K_l(r,r')P_l(r')=EP_l(r), \quad (27)$$

where

$$K_l(r,r')\equiv rr'M_l(r,r'),\ P_l(r)=rR_l(r), \quad (28)$$

$R_l(r)$ is the radial wave function and l is the angular momentum. We then use the $M_l(r,r')$ (Sec. II) in Eq. (27) and solve the differential-integral equation for $P_l(r)$ by an iterative procedure. The corresponding phase shifts are then used following the APW method to determine the corresponding $E_{\vec{k}}$. The results for the energy difference between the points on the calculated local FS (FS calculated with a local potential) along $L\rightarrow W$ and $\Gamma\rightarrow X$ are tabulated in the first row of Table I. The nonlocal corrections are seen to have the right magnitude and sign for explaining the discrepancy between local theory and experiment.

TABLE I. The relative energy shifts in rydbergs between a point on the calculated local Fermi surface (LFS) along $L\rightarrow W$ and that along $\Gamma\rightarrow X$ for the nonlocal exchange and correlation potential and for the exchange potential only. The first row is calculated by the APW method with the nonlocal potential treated nonperturbatively within the muffin-tin approximation. The last three rows are calculated by first-order perturbation [see Eq. (33)]. The methods employed to determine the coefficients needed in the perturbation correction and the local potential used are those of Refs. 15–17, respectively.

	$E_{\text{LFS}}(L\rightarrow W)-E_{\text{LFS}}(\Gamma\rightarrow X)$ Exchange plus correlation	Exchange
APW – NLMT[a] (Chodorow)	0.018	
Interpolation (Chodorow)	0.022	0.056
APW (Chodorow)	0.015	0.044
EPM[b] (Fong and Cohen)	0.024	

[a] NLMT, nonlocal muffin tin.

[b] EPM, empirical-pseudopotential method.

As noted previously (Sec. II, Figs. 1–3), significant portion of M resides outside the MT radius. To ensure that this contribution (neglected in the MT approximation) does not have drastic effect on the above results (or trends) we have in addition examined the effect of M in a perturbative approach, which does not involve an MT approximation. Within this approach and consistent with neglecting the d contribution to M, we also neglect the d character in s,p bands. The easiest way to concentrate on the s,p bands is to use an interpolation scheme in which the solution of, e.g., the Chodorow potential, is expressed in terms of (s,p) and d contributions separately.

Using, e.g., Mueller's interpolation[15] scheme, we can write

$$|\varphi_{\vec{k}}(\vec{r})\rangle=\sum_{\vec{G}}\alpha_{\vec{k}+\vec{G}}|\phi_{\vec{k}+\vec{G}}\rangle+\sum_n\alpha_n|\phi_{dn}\rangle, \quad (29)$$

where

$$|\phi_{\vec{k}}\rangle=\left(|\vec{k}\rangle-\sum_n M_{dn}(\vec{k})|\phi_{dn}\rangle\right)C_{\vec{k}}^{-1}, \quad (30)$$

$$|C_{k}|^2=1-\sum_n|M_{dn}(\vec{k})|^2, \quad (31)$$

$$M_{dn}(\vec{k})=\langle\phi_{dn}|\vec{k}\rangle. \quad (32)$$

$|k\rangle$ and $|\phi_d\rangle$ are the plane wave and d states, respectively.

Once the secular equation[15] is solved for $\alpha_{\vec{k}+\vec{G}}$ and α_n, we ignore all d-band effects [i.e. set $\alpha_n=0$ and $M_{dn}(k)=0$] and treat the nonlocal term in Eq. (26) via first-order perturbation.[2] The first-order perturbation correction is

$$\Delta E_{\vec{k}}=\sum_{\vec{G}}|\alpha_{\vec{k}+\vec{G}}|^2[M_h(\vec{k}+\vec{G},\mu_h(n_0),n_0)-v_{xc}(n_0)]. \quad (33)$$

Near the high-symmetry points L and X, the d character is small. Thus, we used in addition in Eq. (33) the coefficients $\alpha_{\vec{k}+\vec{G}}$ from the APW solution of the Chodorow potential,[16] and the plane-wave coefficients of the empirical-pseudopotential solution for copper[17] to see if the answer does not depend strongly on the interpolation scheme. The results are tabulated in rows 2–4 in Table I and are seen to give similar results to each other and to that found in the nonperturbative MT solution. In Table I we also tabulate the results using Eq. (33) with M_x alone. As can be seen, the effects are much too large.

Finally we make the following two observations. First it is apparent from Table I that in copper the nonlocal contributions to the FS distortion are relatively small compared to the local contributions resulting, e.g., from $V_C(r)$. Nevertheless, to achieve such nonlocal corrections requires a significant change in the parameter α of the local M from any of its first-principles values.[6] Second, in Ref. 6 the full density was used in the local potential. We have corrected only the 4s contribution to the local potential by a nonlocal one. As discussed above, similar corrections with the density from the localized states included in Eq. (26) will totally misrepresent the true quasiparticle potential. For example, from the HF form for M in Eqs. (3) and (4) it is clear that the difference in $\vec{r}$ and $\vec{r}'$ is confined to the "radius" of the localized states. It is thus likely that for these states a local potential as used, e.g., in Ref. 6 is preferable to a nonlocal version of the form of Eq. (5).

We end by emphasizing that this calculation was done only to illustrate that the nonlocality in M of the s, p electrons has the potential for removing the discrepancy between first-principles local theory and experiment in the FS of copper.[6] Refinements such as putting the density dependence in M, studying an improved form for M (see RV), properly including the d states are being considered. The question of how to include the d contribution to the s, p bands in the structure of M is especially challenging.

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[1] E. O. Kane, Phys. Rev. B **4**, 1910 (1971); **5**, 1493 (1972).

[2] M. Rasolt and S. H. Vosko, Phys. Rev. Lett. **32**, 297 (1974); Phys. Rev. B **10**, 4195 (1974).

[3] M. Rasolt, S. B. Nickerson, and S. H. Vosko, Solid State Commun. **16**, 827 (1975).

[4] D. J. Mickish, A. B. Kunz, and S. T. Pantelides, Phys. Rev. B **10**, 1369 (1974); L. Kumar, H. J. Monkhorst, and F. E. Harris, *ibid.* **9**, 4084 (1974); L. Kumar and H. J. Monkhorst, J. Phys. F **4**, 1135 (1974).

[5] L. J. Sham and W. Kohn, Phys. Rev. **145**, 561 (1966).

[6] J. F. Janak, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **6**, 4367 (1972); **11**, 1522 (1975).

[7] L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23.

[8] D. J. Mickish and A. B. Kunz, J. Phys. C **6**, 1723 (1973); L. Dagens and F. Perrot, Phys. Rev. B **5**, 641 (1972); N. O. Lipari and W. B. Fowler, *ibid.* **2**, 3354 (1970).

[9] L. Hedin, Phys. Rev. **139**, A796 (1965).

[10] The potential has the MT form if it is spherically symmetric within a sphere centered on each ion and inscribed in the unit cell, and it is constant in the region between these spheres. The radius of the sphere is the MT radius.

[11] J. C. Slater, Phys. Rev. **81**, 835 (1951).

[12] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1965); W. Kohn and L. J. Sham, *ibid.* **140**, A1133, (1965).

[13] L. Hedin and S. Lundqvist, J. Phys. C **4**, 2064 (1971).

[14] J. I. Chodorow, Ph.D. thesis (MIT, 1939) (unpublished).

[15] F. M. Mueller, Phys. Rev. **153**, 659 (1967).

[16] G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[17] C. Y. Fong and M. L. Cohen, Phys. Rev. Lett. **24**, 306 (1970).