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Exchange Approximations Used in the Energy-Band Calculations of Metals*

Michael Boring and E. C. Snow
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

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The use of different exchange approximations in the self-consistent energy-band calculations for a metal (Cu) is shown to yield different one-electron eigenvalue spectra. Specifically, when an energy-dependent exchange potential proposed by Liberman was used, the resulting bandwidths (s-p, d) were much wider than those obtained with the $\rho^{1/3}$ exchange operator. Also it is shown that when the energy-dependent exchange operator is screened, as in the Bohm-Pines theory, the resulting bandwidths were considerably narrowed. Although the "$\rho^{1/3}$" operator and the screened-exchange operator yielded similar results, the variation of the screening parameter did not correspond to a variation of the α parameter of the "$\rho^{1/3}$" method. Use of the screened-exchange operator appears to yield a reasonable band structure.

I. INTRODUCTION

This paper concerns, in a pragmatic way, the role of various exchange approximations used in energy-band calculations of transition metals, and the one-electron eigenvalue spectra generated by these exchange operators are considered for three regimes: the isolated atom, the metallic crystal, and the electron gas. Copper was chosen for the energy-band calculations because it typifies the sensistivity of the d bands of the first-row transition metals to the exchange approximation. Since none of the exchange approximations used here in the band calculations has a rigorous theoretical basis, they are compared solely on the basis of the one-electron eigenvalue spectrum which each generated in self-consistent-field calculations. The calculations are relevant mainly to those energy-band-calculational methods in which the choice of the crystal potential is independent of the self-consistency criterion.

II. THEORY

Since Slater[1] derived the local-electron-gas-exchange approximation ($\rho^{1/3}$ or $X\alpha$ method), it has been used successfully in many atomic calculations[2] and in most energy-band calculations. This exchange operator is

$$V_{xs}(r) = -6[(3/8\pi)\rho(r)]^{1/3}\ , \tag{1}$$

where $\rho(r)$ is the (nonuniform) electronic-charge density. From the considerations of Kohn and

Sham[3] and others,[4] this exchange has been generalized to

$$V_x^{\alpha}(r) = \alpha V_{xs}(r)\,. \tag{2}$$

Slater's original value of α is 1, the value obtained by Kohn and Sham[3] is $\frac{2}{3}$, and values of α between these limits have been used in many calculations. The limits of applicability of this potential are the same as for the potential in the Thomas-Fermi statistical theory.[5]

Liberman[6] recently obtained an energy-dependent exchange operator based on similar considerations, i.e.,

$$V_x^L(r) = -8F^L(\eta(E,r))\,V_{xs}(r)\,, \tag{3}$$

where

$$F^L(\eta(E,r)) = \frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\,. \tag{4}$$

(The label L is used in this paper to denote Liberman.) In this expression

$$\eta = \eta(E,r) = k(E,r)/k_F(r),$$

where $k_F(r)$ is the magnitude of the Fermi wave vector appropriate to a free-electron gas of density ρ, and $k(E,r)$ is the magnitude of the wave vector of the electron under consideration. Liberman also gave the following approximations for these vectors:

$$k_F(r) = [3\pi^2\rho(r)]^{1/3}\,, \tag{5}$$

and

$$k(E,r) = [E - V(r)]^{1/2}, \tag{6}$$

where E is the energy eigenvalue (in Ry) of the electron in the state k and $V(r)$ is the total one-electron potential (Coulomb plus exchange). Slater, Wilson, and Wood[7] have applied this exchange approximation to the Cu^+ ion, using a somewhat different prescription for $k_F(r)$, viz.,

$$k_F(r) = [E_F - V_F(r)]^{1/2}, \tag{7}$$

where

$$V_F(r) = V_c(r) - 4V_{xs}(r).$$

The term $4V_{xs}(r)$ is the value of the one-electron exchange potential at the Fermi energy E_F, and $V_c(r)$ is the Coulomb potential. In that paper it was also shown that the functions $F(\eta)$, which were labeled $F(\eta)_{XLSW}$, and which, for convenience, we will label $F^S(\eta)$, are very similar (orbital for orbital) to the equivalent Hartree-Fock (HF) functions for Cu^+,

$$F^{HF}(\eta) = \tfrac{3}{4}[V_{XHF}(\eta,r)/V_{xs}(r)]\,, \tag{8}$$

where $V_{XHF}(\eta,r)$ is the Hartree-Fock exchange operator. Those calculations[6,7] indicate that the energy-dependent exchange approximations, with either $F^S(\eta)$ or $F^L(\eta)$, give an eigenvalue spectrum in isolated atoms that is closer to the HF one-electron spectrum than is the spectrum generated by the $X\alpha$ exchange operator.

The final exchange approximation considered in this paper is a screened-exchange operator derived by Bohm and Pines[8] (BP) for the electron gas (see the Appendix). This exchange operator is given by

$$V_x^{BP}(E,r) = -8F^{BP}(\eta(E,r))V_{xs}(r), \tag{9}$$

where

$$F^{BP}(\eta) = F^L(\eta) - \beta \quad \text{for} \quad k < k_F - k_c \tag{10}$$

and

$$F^{BP}(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{\beta}\right| + \frac{3}{8}\,\frac{(\eta^2-1)}{\eta} - \frac{\beta}{2} + \frac{\beta^2}{8\eta} \quad \text{for } k < k_F - k_c\,. \tag{11}$$

In this expression k_c^{-1} is the BP screening length, $\beta = k_c/k_F$, and the Liberman scheme $[\eta = \eta(E,r)]$ was used to extend this operator into the region of variable charge density. No atomic calculations have been performed with this operator.

Before describing the use of these exchange approximations in energy-band calculations [augmented-plane wave (APW)], we recall their role (plus the kinetic-energy operator) in the electron-gas problem. First, in this situation the Liberman exchange operator becomes the HF operator and generates the HF one-electron eigenvalue spectrum. Second, V_x^{BP} is a screened-exchange operator acting over the interaction range k_c^{-1} and generates a bandwidth only slightly wider than the Hartree bandwidth.[8] Pines has shown that this one-electron eigenvalue spectrum, unlike the HF spectrum, does not have the objectionable feature of a zero density of states at the Fermi surface. Third, the V_x^{α} operator is a constant, different for each value of α, and yields an eigenvalue spectrum having a bandwidth equal to the Hartree bandwidth. Although an α can be found which will make the total energy (using the statistical expression[9]) calculated by the $X\alpha$ method equal to the HF total energy, the role of α as a one-electron exchange operator in the uniform-density case is not consistent with any basis theory (such as Hartree-Fock). Finally, the V_x^L, V_x^{BP}, and V_x^{α} operators are all used in the same spirit in the energy-band calculations, that is, in comparing the results of calculation with experiment.

III. METHOD OF CALCULATION

All of the calculations were performed self-consistently with a "frozen" core ($1s-3p$). These core states were taken to be the same as those determined from a self-consistent $X\alpha(\alpha=\frac{5}{6})$ energy-band calculation in which the core was not frozen. In earlier calculations, although they did not involve energy-dependent exchange potentials, we observed that freezing the core states has little effect on the bandwidths. The band states were determined at 2048 points of the full Brillioun zone (BZ) for the $F(\eta)$ exchange $[F^L(\eta)$ and $F^S(\eta)]$ and at 256 points of the BZ for the screened exchange. The self-consistency criterion required that the eigenvalues of the last iteration agree with those of the previous iteration to within 0.002 Ry.

For each iteration, the following calculation has to be carried out to obtain the Liberman exchange. Because there are two equations involving $\eta(E, r)$, namely,

$$k(E, r) = [E - V_c(r) + 8F(\eta)\, V_{xs}(r)]^{1/2} \tag{12}$$

and

$$\eta(E, r) = k(E, r)/k_F(r), \tag{13}$$

they must be solved simultaneously. This was done by an iterative procedure which was started by arbitrarily choosing a value for η in the first equation and then calculating a new η for the second equation. The criterion for this procedure was that η should differ from the previously calculated η by less than 10^{-6}. This iterative procedure was carried out for each value of E and r. In the screened-exchange calculation, the Liberman $F^L(\eta)$ was obtained by this procedure and then $F^{\mathrm{BP}}(\eta)$ was determined from Eq. (10) or (11). The alternative procedure of determining $F^{\mathrm{BP}}(\eta)$ by arbitrarily choosing a starting value and iterating did not lead to converging process because of the form of $F^{\mathrm{BP}}(\eta)$ and was abandoned.

Two more points should be mentioned in connection with the calculation of $F(\eta)$. First, if $F^S(\eta)$ is calculated, $\eta(E, r)$ is bounded from above and below,[7] i.e.,

$$0 \leq \eta\,(E, r) \leq 1.$$

If the Liberman prescription for $k_F(r)$ is used, however, the $\eta(E, r)$ is only bounded from below:

$$0 \leq \eta(E, r).$$

Second, since values of η greater than 1 do not occur for occupied states in the electron-gas theory, η may either be restricted artificially to be less than 1, or allowed to have values greater than 1, and the results of the calculations are not affected. Both methods were used and the results were found to be insensitive to the restriction. The same was also found to be true of the atomic calculations.[10] On the other hand, in determining $F^S(\eta)$, a value must be chosen for the Fermi energy E_F appearing in the theory. Whether this should be the experimental E_F or the eigenvalue of the last-calculated occupied state is not clear from the theory. We arbitarily chose E_F as the eigenvalue of the last-occupied state.

IV. RESULTS

In Table I, a summary of the results of these self-consistent calculations is given along with photoemissions data[11,12] on Cu and the $X\alpha(\alpha = \frac{5}{6})$ results.[13] In Fig. 1 the $E(k)$ curves are shown along the x direction of the Brillouin zone (BZ) to illustrate the large differences obtained. As shown in the table, the $F^S(\eta)$ calculation gives a d bandwidth nearly twice as wide as that predicted from either the photoemission data or from the $X\alpha$ calculation and an s-p bandwidth nearly twice as wide as that determined from the $X\alpha$ potential. The $F^L(\eta)$ potential gives a d bandwidth about 25% wider than that predicted from the photoemission data or from the $X\alpha$ potential, and an s-p bandwidth 50% wider than the $X\alpha$ result.

The $F^{\mathrm{BP}}(\eta)$ calculations were performed for three values of the screening parameter k_c. Increasing k_c corresponds to decreasing the range of the exchange interaction.[8] From Table I, one sees that the screening has little or no effect on the d bandwidth. On the other hand, the s-p bandwidth decreases significantly with increasing k_c and is only 15% wider than the $X\alpha$ result for the maximum k_c used. Although the relative positions of the s-p and d bands are different for different values of k_c, no pattern is apparent. In Fig. 1 it is shown that the $F^{\mathrm{BP}}(k_c = 0.500k_F)$ results agree more closely with $X\alpha$ results than do those of either the $F^L(\eta)$ or $F^S(\eta)$. This agreement holds throughout the BZ and indicates that the $F^{\mathrm{BP}}(\eta)$ results are in reasonable agreement with Fermi-surface data.[13]

V. CONCLUSIONS

Before drawing any conclusions from the results

TABLE I. Energy differences showing bandwidths (s-p, d) and relative positions of the s-p and d bands (energies in Ry).

Method	Relative position[a]	s-p bandwidth[b]	d bandwidth[c]
		Photoemission data	
Spicer[d]			0.250
Eastman[e]			0.220
		APW self-consistent calculations	
$\rho^{1/3}$, $\alpha = \frac{5}{6}$[f]	0.376	0.796	0.224
$F^S(\eta)$	0.791	1.580	0.395
$F^L(\eta)$	0.476	1.221	0.285
$F^{\mathrm{BP}}(\eta); k_c = 0.010k_F$	0.492	1.207	0.273
$F^{\mathrm{BP}}; k_c = 0.250k_F$	0.554	1.041	0.282
$F^{\mathrm{BP}}; k_c = 0.500k_F$	0.494	0.909	0.282

[a] $E(\Gamma_{25'}) - E(\Gamma_1)$.

[b] $E(X_{4'}) - E(\Gamma_1)$.

[c] $E(X_5) - E(X_1)$.

[d] Reference 11.

[e] Reference 12.

[f] Reference 13.

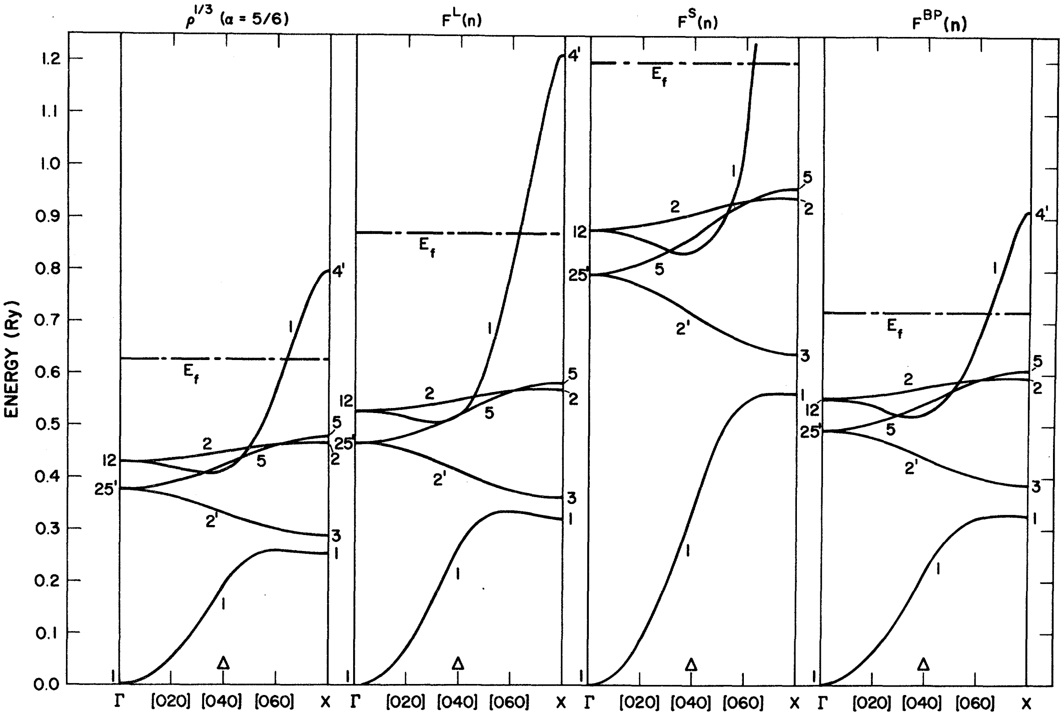

FIG. 1. $E(k)$ curves along the x direction for the four different exchange potentials.

of our calculations, we should mention that other similar attempts to study the effects of exchange, and correlation, in band-structure calculations have been made.[14,15] However, because those studies dealt with crystals in which the sensitivity of the bands to the exchange approximation is different from that of the bands of a transition metal (narrow d bands with an overlapping s-p band), we have not compared the results of those studies with our results.

If the charge density obtained in a band calculation could be easily separated into an atomic part and a free-electron-gas part, then the role of the exchange operators in these regimes could be directly related to the role of the operators in the energy-band problem. Since such separation does not seem possible, we must restrict ourselves to the following conclusions:

(i) The energy-dependent and nonenergy-dependent exchange operators give very different one-electron eigenvalue spectra when used in self-consistent energy-band calculations for transition metals.

(ii) The $X\alpha$ exchange operator and the F^{BP} screened-exchange operator do give similar bandwidths. By decreasing α, a d bandwidth equal to that given by the F^{BP} operator can be obtained, and by increasing k_c of the F^{BP} operator, an s-p bandwidth equal to that given by the $X\alpha$ operator should be obtainable. However, this also points out the different natures of these two exchange operators. A variation of the α parameters in the $X\alpha$ operator affects only the d bandwidth, whereas a variation of the screening length (k_c^{-1}) in the F^{BP} operator affects only the s-p bandwidth.

(iii) The $F^{\mathrm{BP}}(\eta)$ exchange operator gives results that appear to be in as good agreement with experiment as are the $X\alpha$ results, with $\alpha=\frac{5}{6}$. Since the F^{BP} operator requires no arbitrary parameter (k_c can be obtained from the free-electron-gas theory and is 0.586 for a uniform gas of Cu density[16]), it should become a strong contender for use in future energy-band calculations.

(iv) The energy-dependent exchange operators [$F^S(\eta)$ and $F^L(\eta)$] give, for a metal, eigenvalue spectra that are similar to that which would be expected if the true HF exchange were used. These operators widen both the s-p and d bands and thus will probably widen the bands in most metals.

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APPENDIX

In terms of perturbation theory, with $V_c = 0$, the electron-gas self-energy operator is

$$H_i - T_k = V_i, \tag{A1}$$

where V_i is V_{XHF}, or some better approximation to the self-energy of the electrons. For a many-particle Fermion system,[17] the HF eigenvalue spectrum is determined from

$$\epsilon_k^{\mathrm{HF}} = \tau_k + \sum_{l<k_F} (V_{klkl} - V_{lkkl}), \tag{A2}$$

where τ_k is the kinetic energy. For the electron gas, the direct term is cancelled by the positive background and we obtain

$$\epsilon_k^{\mathrm{HF}} = \tau_k - (4/\pi) F(\eta) k_F . \tag{A3}$$

In terms of Feynman diagrams, only the exchange-diagram contributes to the self-energy in this approximation. In the random-phase approximation (RPA), the "polarization diagrams" are summed to all orders for equal momentum transfers q and the self-energy operator becomes

$$V^{\mathrm{RPA}}(q, \omega) = \frac{V_q}{1 + V_q \pi_0(q, \omega)} , \tag{A4}$$

where $V_q = 4\pi e^2/q^2$ and $\pi_0(q, \omega)$ is the polarization part of the diagrams. $\pi_0(q, \omega)$ evaluated for small q and $\omega = 0$ (static limit) yields

$$V^{\mathrm{RPA}}(\text{small } q, 0) = 4\pi e^2/(q^2 + k_c^2), \tag{A5}$$

which is just a screened Coulomb interaction with a screening length k_c^{-1}. This result is also obtained in the BP theory[16,18] and leads to the following one-electron spectrum:

$$\epsilon_k^{\mathrm{HF}}(\text{screened}) = \tau_k - (4/\pi) F^{\mathrm{BP}}(\eta) k_F = \epsilon_k^{\mathrm{BP}}, \tag{A6}$$

where $F^{\mathrm{BP}}(\eta)$ is given by Pines[8] [Eqs. (10) and (11) is the present text]. In terms of diagrams, the exchange diagram has been replaced by a screened-exchange diagram.

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