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## Self-Consistent Energy Bands of Cu via the $X_{\alpha\beta}$ Method\*

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The energy bands of Cu have been calculated self-consistently through use of the improved exchange approximation of Herman, Van Dyke, and Ortenburger (the so-called  $X_{\alpha\beta}$  method). The resulting bands are compared with the self-consistent energy bands calculated by the  $X_{\alpha}$  method with  $\alpha = 1.00$ ,  $\frac{5}{6}$ ,  $0.721$ , and  $\frac{2}{3}$ . The  $X_{\alpha}$  and  $X_{\alpha\beta}$  energy-band widths ( $s$ - $p$ ,  $d$ ) are compared with photoemission data. The differences between the energy-band calculations and the atomic calculations are described. A brief discussion is given of the role of the virial theorem and the variational principle.

### I. INTRODUCTION

Since Herman<sup>1</sup> proposed the improved approximation ( $X_{\alpha\beta}$ ) for the exchange operator, there have been several atomic calculations<sup>2-4</sup> incorporating it. Herman has shown<sup>2</sup> that the total energies of atoms calculated via Hartree-Fock (HF) theory using  $X_{\alpha\beta}$  orbitals are in better agreement with HF total energies (determined from HF orbitals) than are HF total energies calculated from  $X_{\alpha}$  orbitals. It has also been shown that the parameter  $\beta$  (with  $\alpha = \frac{2}{3}$ ) in the  $X_{\alpha\beta}$  method is less sensitive to atomic number ( $z$ ) and the Latter potential shift in atomic systems than is the parameter  $\alpha$  of the  $X_{\alpha}$  scheme.<sup>4</sup> In this paper we present the results of a calculation for which the  $X_{\alpha\beta}$  method was proposed, the energy-band structure of a crystal.

In Sec. II, a discussion is given of the statistical exchange methods ( $X_{\alpha}$  and  $X_{\alpha\beta}$ ), and the difference between  $X_{\alpha\beta}$  calculations in atoms and in crystals is pointed out. In Sec. III, we give the results of a self-consistent calculation of the energy-band structure of Cu using the  $X_{\alpha\beta}$  exchange approximation. In that section we also compare the results of this calculation with the self-consistent energy bands of Cu calculated by the  $X_{\alpha}$  method for

$\alpha = 1.00$ ,  $\frac{5}{6}$ ,  $0.721$ , and  $\frac{2}{3}$ . In Sec. IV the role of the virial theorem and the variational principle in these statistical exchange approximations is discussed.

### II. METHOD

In the  $X_{\alpha}$  method, the local one-electron exchange operator is written as

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

where

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

is the Slater exchange,<sup>5</sup> and  $\rho(r)$  is the electronic charge density of the system. In the  $X_{\alpha}$  method, the constant  $\alpha$  can be determined for a given atom by generating a set of orbitals  $\{\Phi(\alpha)\}$  that minimizes<sup>6</sup> the Hartree-Fock total energy  $E^{\text{HF}}$ , i. e.,

$$\alpha_{\text{min}} \rightarrow \{\Phi(\alpha_{\text{min}})\} \rightarrow E^{\text{HF}}[\Phi(\alpha_{\text{min}})],$$

where  $E^{\text{HF}}[\Phi(\alpha_{\text{min}})]$  is total HF energy calculated with  $X_{\alpha}$  orbitals. Kmetko<sup>7</sup> has obtained in this manner a set of  $\alpha_{\text{min}}$ 's for all the atoms in the Periodic Table. Since  $\frac{2}{3}$  is considered to be the correct value of  $\alpha$  for a nearly homogeneous electron gas,<sup>8</sup> deviations from this value may be con-

sidered as an indication of inhomogeneity of the charge densities of atomic and crystal systems.

In the  $X_{\alpha\beta}$  method, gradient corrections are included in the local one-electron exchange operator as a means of accounting for this inhomogeneity. The local one-electron exchange operator is then written as

$$V_x^{\alpha\beta}(r) = [\alpha + \beta G(r)] V_{xs}(r),$$

where

$$G(r) = \frac{1}{\rho(r)^{2/3}} \left[ \frac{4}{3} \left( \frac{\nabla \rho(r)}{\rho(r)} \right)^2 - \frac{\nabla^2 \rho(r)}{\rho(r)} \right].$$

As Herman has pointed out,<sup>1</sup>  $G(r)$  must be modified at very large and very small values of  $r$  in atomic systems. The small- $r$  correction factor may be omitted if the integration is not carried too close to the nucleus. The omission of this correction has only a minor effect on the results. The blow up of  $G(r)$  at large  $r$  due to the smallness of  $\rho(r)$  cannot be avoided in the atomic-structure computer code, and Herman's convergence factor must be used. Although the large- $r$  convergence factor changes the calculated energies insignificantly, its use leads to one-electron equations that are variationally incorrect. Fortunately, use of this large- $r$  convergence factor is not necessary in the crystal calculations because the charge density remains finite for all  $r$  values within the unit cell.

There are two more comments to be made about  $V_x^{\alpha\beta}(r)$  before describing the results of the energy-band calculation. Slater<sup>9</sup> has pointed out that, although the  $X_{\alpha\beta}$  method gives total energies in good agreement with HF values, the potential used in total energy expression has in its structure that is very "un-Hartree-Fock-like." The second point is that, because  $G(r)$  contains the derivatives of

$\rho(r)$ , which contain information about  $\rho(r)$  at points other than  $r$ ,  $V_x^{\alpha\beta}(r)$  should have some of the non-local features that some of the momentum-dependent exchange operators exhibit.<sup>10</sup>

### III. CALCULATION

The energy-band structure of Cu was determined with the  $V_x^{\alpha\beta}(r)$  exchange operator using the augmented-plane-wave (APW) method.<sup>11</sup> The calculation was performed self-consistently in the following manner. For each iteration, separate calculations were made for the core states (1s, 2s, 2p), the "inner" band states (3s, 3p), and the "valence"-band states (3d, 4s). The core states were computed for the crystal potential (from the previous iteration) using a modified Herman-Skillman atomic program. The inner band states were determined using the APW program at 32 points in the full Brillouin zone, and the valence-band states were similarly calculated at 2048 points. The self-consistency criterion was a maximum energy difference in the one-electron eigenvalues of 0.002 Ry from one iteration to the next. As a check on the method, the  $G(r)$  computed for the crystal charge density was compared with the  $G(r)$  of the Cu atom. These two  $G(r)$ 's did not differ appreciably except at those  $r$  values for which the charge densities differed significantly.

In Table I, the results of the  $X_{\alpha\beta}$  energy-band calculation along with four  $X_{\alpha}$  self-consistent results are given for certain selected energy-level differences. The  $\alpha = 1.00$ ,  $\frac{5}{6}$ , and  $\frac{2}{3}$  results<sup>12</sup> are from Snow's work,<sup>13</sup> and the  $\alpha = 0.721$  results are from Ref. 10. The  $\alpha = 0.721$ <sup>14</sup> calculation was performed because that value was suggested by Slater as optimum for the  $X_{\alpha}$  method.<sup>15</sup> In our earlier work on atoms,<sup>4</sup> we fixed  $\alpha$  and found the  $\beta$  for which the virial theorem was satisfied when the

TABLE I. Energy differences indicating widths and positions of bands.<sup>a</sup>

	Experimental						
	$\Gamma_{25'} - \Gamma_1$	$X_8 - \Gamma_1$	$X_5 - X_1$	$X_{4'} - \Gamma_1$	$E_f - X_5$	$E_F - L_3$	$E_F - L_{2'}$
Spicer (Ref. 16)			0.250		0.147		0.026
Eastman (Ref. 17)			0.220				
Lettington (Ref. 18)					0.147	0.162	
$\alpha$	APW calculations <sup>b</sup>						
1.000	0.278	0.368	0.189	0.793	0.223	0.232	-0.005
$\frac{5}{6}$	0.375	0.477	0.224	0.795	0.149	0.159	0.029
0.721	0.425	0.535	0.245	0.796	0.118	0.129	0.057
$\frac{2}{3}$	0.452	0.565	0.262	0.797	0.111	0.123	0.201
Present <sup>c</sup>	0.454	0.568	0.258	0.797	0.105	0.116	0.074

<sup>a</sup>Energies in rydbergs.

<sup>c</sup> $\alpha = \frac{2}{3}$ ,  $\alpha = 0.0040$ .

<sup>b</sup>Self-consistent nonrelativistic calculations at 2048 points.

HF energies (potential, kinetic, and total) were calculated using  $X_{\alpha\beta}$  orbitals. For  $\alpha = \frac{2}{3}$  and  $\beta = 0.0040$ , the virial theorem was satisfied, and these values we choose as the optimum for the  $X_{\alpha\beta}$  method. In the APW method, we use a muffin-tin potential in which the potential is constant outside the APW radius, and  $G(r)$  vanishes in this region.

Also included in Table I are the photoemission data of Cu.<sup>16-18</sup> As can be seen, the experimental data on the  $d$  bandwidth ( $X_5 - X_1$ ) do not agree, and this is unfortunate because the  $d$  bandwidth is very sensitive to the exchange approximation used in the energy-band calculation. The  $\alpha = 0.721$ ,  $\alpha = \frac{2}{3}$ , and the  $X_{\alpha\beta}$  energy bands give a  $d$  bandwidth that agrees well with Spicer's data.<sup>16</sup> The  $\alpha = \frac{5}{8}$  bands, on the other hand, give a  $d$  bandwidth in agreement with Eastman's data.<sup>17</sup> The only energy bands ruled out by photoemission data on  $d$  bandwidth are those calculated with  $\alpha = 1.00$ . Although the Fermi energy  $E_F$  was determined by a histogram method, it is still accurate enough so that a comparison can be made between the calculated energy differences of the last three columns of Table I ( $E_F - X_5$ ,  $E_F - L_3$ ,  $E_F - L_2$ ) and the experimental data for these differences. Again, the only results that seem to be completely in disagreement with photoemission data are those for  $\alpha = 1.00$ .

The energy differences in the first two columns of Table I ( $\Gamma_{25'} - \Gamma_1$  and  $X_5 - \Gamma_1$ ) give the positions of the  $d$  band relative to the  $s$ - $p$  band and show that these are also sensitive to the exchange approximation. The last energy difference shown in Table I ( $X_4 - \Gamma_1$ ) is the  $s$ - $p$  bandwidth. As can be seen, it is insensitive to the value of  $\alpha$  in the  $X_\alpha$  method. Crudely, this can be explained by the following argument. First, let  $E(\Gamma_1) = E_1$ ,  $E(X_4) = E_2$ , and  $\Phi_1$ ,  $\Phi_2$  be the eigenfunctions corresponding to these eigenvalues. The eigenvalue equations are

$$E_i = \int \Phi_i^* [T_k + V_c(r) + \alpha V_x(r)] \Phi_i d\bar{r},$$

where  $T_k$  is the kinetic-energy operator ( $-\nabla^2$ ),  $V_c(r)$  is the Coulomb-potential operator (electron-nuclear  $V_{ne}$  and electron-electron  $V_{ee}$ ), and  $V_x(r) = V_{xs}(r)$ .

We observe that most of the  $s$  and  $p$  eigenfunctions have their maximum amplitudes in the same region of the unit cell ( $R_1 = 1.30 \leq r \leq 2.4 = R_2$ , a.u.), and that the charge density is rather constant in this region. So, if we look at the energy difference ( $E_1 - E_2$ ) due to exchange operator only, we have

$$(E_1 - E_2)_x \approx \alpha \int \Phi_1^* V_{xs}(r) \Phi_1 d\bar{r} - \alpha \int \Phi_2^* V_{xs}(r) \Phi_2 d\bar{r} = \alpha(I_1 - I_2)$$

and, although  $\Phi_1$  and  $\Phi_2$  have their maximum amplitudes at different  $r$  values (which are also shifted

with different  $\alpha$ 's) but within the range ( $R_1$ ,  $R_2$ ), the flatness of  $V_x(r)$  makes these two integrals roughly equal and we obtain

$$(I_1 - I_2) \approx 0.005 \text{ Ry for all } \alpha.$$

For  $d$  states, it is found that  $V_x(r)$  varies in the range in which most  $d$  orbitals have their maximum amplitudes, and the difference between any two  $d$ -orbital exchange integrals will vary with  $\alpha$  (because of shifting positions of their maximum amplitudes) and will not be small. Hence the  $d$  bands are very sensitive to  $\alpha$ . Now it is easy to explain why  $V_x^{\alpha\beta}(r)$  gives the same  $s$ - $p$  bandwidth as  $V_x^\alpha(r)$ .  $G(r)$ , which depends upon  $\rho(r)$  and its derivative, is flat in the range ( $R_1$ ,  $R_2$ ) of maximum amplitude of  $s$  and  $p$  orbitals, and again the exchange integrals almost cancel. Therefore, we can make the prediction that the  $X_{\alpha\beta}$  calculated  $s$ - $p$  bandwidth will not change (within  $\pm 0.010$ ) when  $\beta$  is changed.

#### IV. STATISTICAL THEORIES

For atomic systems, the parameter  $\alpha$  or  $(\alpha, \beta)$  cannot be determined uniquely in the statistical theories ( $X_\alpha$  and  $X_{\alpha\beta}$ ) by applying the virial theorem or the variational principle to the energy expressions (total, kinetic and potential).<sup>15</sup> As has been shown for the  $X_\alpha$  method, and is also true for the  $X_{\alpha\beta}$  method, the virial theorem is satisfied for any  $\alpha$  (or  $\alpha, \beta$ ),<sup>9</sup> if the statistical energies are calculated. Although  $\alpha = \frac{2}{3}$  is the variational correct result for the nearly uniform electron gas,<sup>8</sup> values of  $\alpha$  different from  $\frac{2}{3}$  may be taken and the variational principle can still be satisfied if the proper relationship is maintained between the statistical total-energy expression and the one-electron eigenvalue equations. To ensure that the one-electron eigenvalue equations are variationally correct for  $V_x^\alpha(r)$  or  $V_x^{\alpha\beta}(r)$  exchange approximations, the total energy expressions must be<sup>19,2</sup>

$$E^\alpha = \int [T_k + V_{ne}(r) + \frac{1}{2}V_{ee}(r) + \frac{3}{4}\alpha V_{xs}(r)] \rho(r) d\bar{r}$$

and

$$E^{\alpha\beta} = \int \{T_k + V_{ne}(r) + \frac{1}{2}V_{ee}(r) + [\alpha + 3\beta G(r)] V_{xs}(r)\} \rho(r) d\bar{r}.$$

Since the total statistical energy is close to a linear functional of  $\alpha(\alpha, \beta)$  and the variational principle is satisfied for each  $\alpha(\alpha, \beta)$ , the statistical theory gives no preferred  $\alpha(\alpha, \beta)$  in atomic systems. It is for this reason that Slater suggested calculating H-F energies as a means of selecting  $\alpha$  or  $\alpha, \beta$  (method discussed in Sec. II and used in this paper) in the isolated atom and then using that  $\alpha(\alpha, \beta)$  in the energy-band calculations.

In using the statistical-energy expressions in

energy-band calculations, as the H-F energies are virtually impossible to calculate, the above equations are used<sup>19</sup> [with an added potential term  $V_m(r)$  for nuclear-nuclear interactions] so as to again satisfy the variational principle. Now the virial theorem, which takes the form<sup>20</sup>

$$PV = \frac{2}{3} E_k + \frac{1}{3} U,$$

where

$$E_k = \int \rho(r) T_k dr,$$

and  $U$  is the total potential energy, must be satisfied. As Ross<sup>20</sup> has shown, only one value of  $\alpha$  ( $\beta$ , with fixed  $\alpha$ ) will give  $P=0$  at the observed experimental lattice constant  $a_0$ , which is unlike atomic systems in which  $P=0$  and the virial theorem is satisfied for any  $\alpha(\beta)$ . Although the virial theorem is again satisfied by all  $\alpha$ 's ( $\alpha, \beta$ 's), the constraint of fixed volume in the crystal calculation yields a unique  $\alpha(\alpha, \beta)$ . Ross has also shown that the virial theorem implies that this value of  $\alpha(\alpha, \beta)$  will yield the experimental lattice constant if the total energy is calculated as a function of lattice parameter and the minimum is obtained.<sup>20</sup> Ross also found that the  $\alpha$  obtained in this manner is very close to the  $\alpha$  obtained using the Slater scheme.<sup>15</sup> This is very comforting because it adds

merit to the Slater scheme which is much simpler than the time-consuming calculations of Ross.

## V. CONCLUSIONS

The main goal of this paper, to show that the  $X_{\alpha\beta}$  method can be applied to energy-band calculations, has been accomplished. Also, it is no more difficult to apply than the  $X_\alpha$  method. The results compare favorably with the  $X_\alpha$  results, and compare as well with photoemission data as do the  $X_\alpha$  results. Perhaps a calculation of the total energy as a function of lattice parameter, such as Ross's calculation, would indicate that one method is better than the other. The desirable feature of the  $X_{\alpha\beta}$  method, that a single  $\beta(\alpha=\frac{2}{3})$  can be used for the whole Periodic Table, cannot, of course, be confirmed by a single calculation.

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