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Comparison of Several Exchange Potentials for Electrons in the Cu^+ Ion*

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Self-consistent calculations of the Cu^+ ion have been carried out using five different methods of approximating the Hartree-Fock exchange. These calculations have been compared with Hartree's Cu^+ calculation to test the accuracy of the various approximations and to interpret their interrelations. The best results were obtained from two quite different methods. The first, suggested by Liberman with modifications which we have introduced, uses a different local exchange potential for each orbital and gives a very good approximation to the Hartree-Fock method, but with considerable computational difficulty. The second amounts to multiplying the local potential proportional to the $\frac{1}{3}$ power of the electronic charge density, suggested by the senior author in 1951, by a constant factor α chosen to minimize the total energy. This second method is much simpler to apply than the first and gives very nearly as good orbitals, as well as a very good total energy, but gives poor one-electron energies for the x-ray levels. The reasons for the different results are discussed. The latter method, which has been empirically arrived at by a number of the workers in the energy-band field, is probably the most useful one for practical calculation.

I. INTRODUCTION

The Hartree-Fock method, which is a version of the self-consistent-field method, is too complicated to use for calculating energy bands in crystals. Consequently, various simplified versions, based on the statistical theory of the atom, have been suggested. They lead to approximately equivalent results, but recent energy-band calculations are sufficiently precise that the small differences between them become of great importance. We shall examine a number of these versions in the present paper, testing them by their application to the Cu^+ ion, and shall come to definite conclusions as to which ones may be best adapted to the energy-band problem.

To formulate these methods in a unified way, we write the Schrödinger equation for a one-electron orbital u_i in an atom in the form

$$(-\nabla^2 + V_C + V_X)u_i = E_i u_i. \qquad (1)$$

We shall use Rydbergs as units of energy, Bohr units as units of distance, so that $-\nabla^2$ is the kinetic energy operator. V_C is the Coulomb potential energy; that is, the potential energy of an electron in the field of the nucleus and of all electrons, including itself, as computed from the total charge density by Poisson's equation. V_X is the correction of V_C arising from the fact that the electron does not act on itself. It is usually referred to as the exchange potential, and the distinction between the various approximations which we shall describe comes from the assumption made about V_X.

First note that if we use the Hartree-Fock equations, so that u_i and E_i are the Hartree-Fock eigenfunctions and eigenvalues, we can compute V_X from the functions by the equation

$$V_{X\mathrm{HF}} = E_i - V_C + (\nabla^2 u_i)/u_i. \qquad (2)$$

Hartree[1] computed these exchange potentials for the various orbitals of Cu^+, from Hartree-Fock calculations that had been made for that ion by Hartree and Hartree. For that reason we chose this ion for the comparisions made in the present paper. Since we shall make considerable use of Hartree's results, we have reproduced in Figs. 1 and 2 the figures from Ref. 1, showing Hartree's calculated $V_{X\mathrm{HF}}$ for the various orbitals in Cu^+. One conspicuous feature of the curves arises from the form of Eq. (2). It is found that $\nabla^2 u_i$ does not have its zeros at exactly the nodes of u_i. Hence, at each node of u_i, the exchange potential $V_{X\mathrm{HF}}$ has a simple pole, becoming asymptotically infinite. The curves are closely related in the way in which each starts to rise at large r, a result of the fact that u_i goes to zero faster than does $\nabla^2 u_i$, in the tail of the wave function.

These phenomena of course do not lead to a divergent expectation value of $V_{X\mathrm{HF}}$, since in finding such an expectation value we integrate $u_i{}^* u_i V_{X\mathrm{HF}}$ over the volume, and the divergence disappears. These divergences are not of fundamental significance. By their nature they come at points where $u_i{}^* u_i V_{X\mathrm{HF}}$ is small, and, as we shall show, one can set up approximate V_X that do not show the singularities found in Figs. 1 and 2, and yet which lead to very nearly the same eigenfunctions and eigenvalues.

The approximations that are made to V_X are based on the theory of the free-electron gas obeying the Fermi statistics. In such a gas, of density ρ, measured in units of electrons per cubic Bohr unit, it is known[2] that the exchange potential is proportional to $\rho^{1/3}$ and to a function of η, the ratio of the momentum of the electron to the momentum at the Fermi energy. Specifically.

$$V_{X\text{gas}} = -8F(\eta)[(3/8\pi)\rho]^{1/3}, \tag{3}$$

$$\text{where } F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| . \tag{4}$$

In the units we are using, a free electron with wave function $\exp ikx$ has a momentum k and a kinetic energy k^2. The Fermi energy is

$$E_F = k_F^2 = (3\pi^2\rho)^{2/3}. \tag{5}$$

In terms of these quantities, the variable η in Eqs. (3) and (4) is

$$\eta = k/k_F. \tag{6}$$

The function $F(\eta)$ equals unity when $\eta = 0$, $\frac{1}{2}$ when $\eta = 1$, zero when $\eta = \infty$. The average value of $F(\eta)$, averaged over all electrons in a Fermi gas at the absolute zero of temperature, is $\frac{3}{4}$.

The simplest approximation to V_X for an atom, based on this free-electron theory, was suggested by the senior author in 1951.[3] It was based on the use of Eq. (3), and ρ was treated as the local charge density at any point inside the atom. Further, for $F(\eta)$ the average value $\frac{3}{4}$ was used. Thus we have the exchange, which we may call V_{XS}, equal to

$$V_{XS} = -6[(3/8\pi)\rho]^{1/3}. \tag{7}$$

The exchange V_{XS} as a function of r is shown by Hartree for Cu$^+$ in Figs. 1 and 2. Hartree also shows a weighted mean of the Hartree-Fock exchanges $V_{X\text{HF}}$, which was proposed in Ref. 3. We see from Figs. 1 and 2 that the statistical exchange V_{XS} agrees quite well with the weighted mean. However, the individual Hartree-Fock exchanges $V_{X\text{HF}}$ for the various orbitals show a good deal of variation, with a spread of at least a factor of 2 at each value of r. It is only natural that the use of an average in place of an exchange that varies from one orbital to another as much as the figures indicate will lead to considerable error in the final results. The exchange V_{XS} has been used in a great many energy-band calculations, and small disagreements between the calculated and experimental energy bands are now being ascribed to uncertainty in the precise value of exchange used. We can well understand these uncertainties, from Figs. 1 and 2, and it is the purpose of the present paper to examine how to reduce or remove them.

An alternative approximation to V_X was suggested by Kohn and Sham,[4] following an earlier treatment by Gaspar.[5] This method is based on use of the variation method: the total energy of the system is computed and is minimized as the charge density is varied. A similar calculation applied to the Thomas-Fermi-Dirac method had been used many years earlier by Lenz and Jensen.[6] This procedure leads to an exchange different from V_{XS} in that it uses the value of $F(\eta)$ found at the Fermi level, namely $\frac{1}{2}$, rather than the average value $\frac{3}{4}$ used in V_{XS}. Thus if we call this exchange $V_{X\text{KSG}}$, we have

$$V_{X\text{KSG}} = -4[(3/8\pi)\rho]^{1/3} = \tfrac{2}{3}V_{XS}. \tag{8}$$

This suggestion of Kohn, Sham, and Gaspar was tested by Cowan *et al.*[7] in 1966. They carried out self-consistent calculations for argon, using the two potentials V_{XS} and $V_{X\text{KSG}}$ as well as the

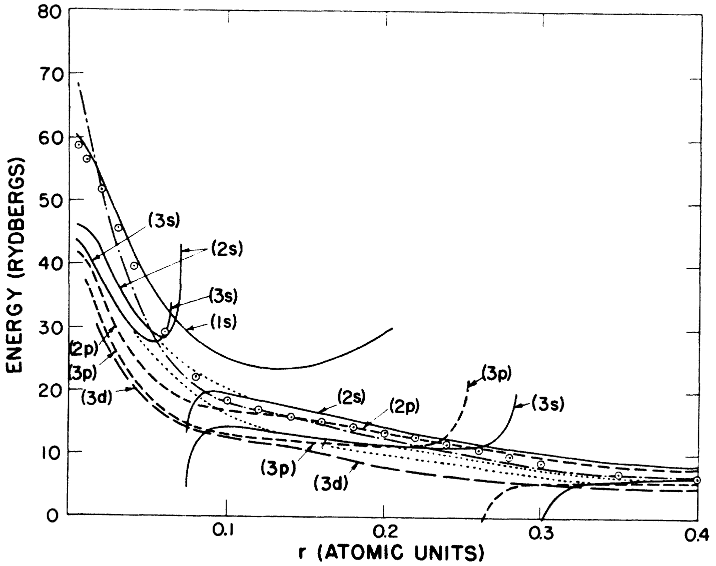

FIG. 1. Absolute value of exchange potential $V_{X\text{HF}}$ for Cu$^+$ computed by Hartree (Ref. 1) for the various orbitals. Ringed points show weighted mean of $V_{X\text{HF}}$. Dot-dash curve shows V_{XS}. Energies in rydbergs.

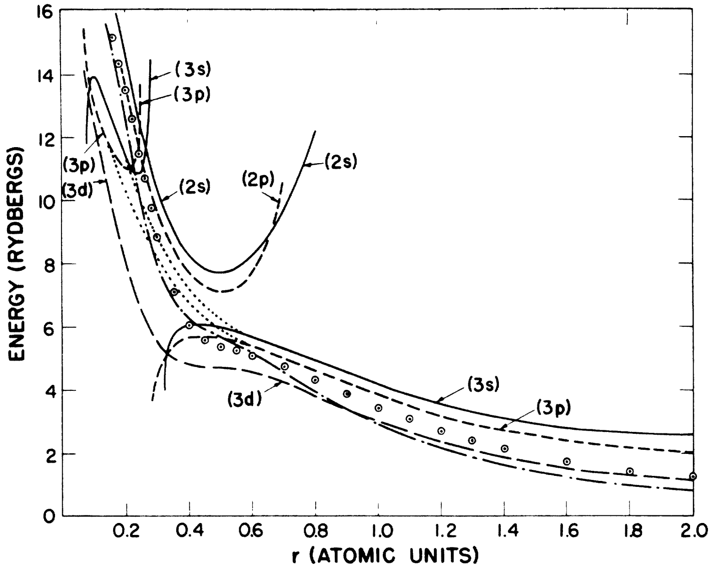

FIG. 2. Same as Fig. 1, different scale.

Hartree-Fock and Hartree values. Their conclusions were that the wave functions u_i given by the KSG exchange agreed more closely with the Hartree-Fock values than did those given by V_{XS}, but the one-electron eigenvalues were not as good as those found with use of V_{XS}. These results have led various people making energy-band calculations to try the effect of using different values of the constant α, chosen to give

$$V_{X\alpha} = \alpha V_{XS}. \tag{9}$$

It has been found in some cases[8] that values of α intermediate between unity, the value for V_{XS}, and $\frac{2}{3}$, the KSG value, give even better results than either of these extremes. Suggestions have also been made by Lindgren, by Berrondo and Goscinski,[9] and by Payne[10] which are similar to varying α to get the best results.

Very recently Liberman[11] made a more elaborate suggestion, which Sham and Kohn[12] have independently proposed. Liberman's thought was the following. The exchange of Eq. (3), depending on η, should properly depend on k the momentum of the electron. Suppose we determine this quantity k as if we were dealing with a free-electron gas and were considering an electron whose kinetic energy is k^2. That is, let us replace Eq. (1) by the free-electron equivalent

$$k^2 + V_C + V_X = E, \quad k = (E - V_C - V_X)^{1/2} \tag{10}$$

and substitute the free-electron gas exchange from Eq. (3) for V_X. Let us then use Eq. (6) for η and Eq. (5) for k_F. Thus we are led to the equation

$$\eta = k/k_F = \{E - V_C + 8F(\eta)[(3/8\pi)\rho]^{1/3}\}^{1/2}(3\pi^2\rho)^{-1/3}. \tag{11}$$

We shall call the resulting exchange X_L. To compute it, we have

$$V_{XL} = -8F(\eta)[(3/8\pi)\rho]^{1/3}, \tag{12}$$

where η is to be determined in terms of ρ and $E - V_C$ from the transcendental Eq. (11). This equation can be solved by an iterative method with the digital computer. Liberman, in Ref. 11, applied his method to argon and mercury, showing that the charge density determined by his method was as good as that obtained from the KSG exchange, and the eigenvalues were in much better agreement with the Hartree-Fock values than were those found either with V_{XS} or V_{XKSG}.

There is one difficulty associated with Liberman's method. If we consider an electron whose energy is just equal to the Fermi energy (a situation which we encounter at the top of the occupied levels in a band calculation), it does not automatically have $\eta = 1$, from Eq. (11). If we take $\eta = 1$, so that $F(\eta) = \frac{1}{2}$, it is clear that we could rewrite Eq. (11) in the form

$$k_F{}^2 = E_F - V_C + 4[(3/8\pi)\rho]^{1/3} = (3\pi^2\rho)^{2/3}. \tag{13}$$

This is a quadratic equation for $\rho^{1/3}$, whose solution is

$$\left(\frac{3}{8\pi}\rho\right)^{1/3} = \frac{[\pi^2(E_F - V_C) + 1]^{1/2} + 1}{2\pi^2}. \tag{14}$$

This equation would be satisfied if ρ were determined from $E_F - V_C$ by the Thomas-Fermi-Dirac method,[13] but it is not exactly satisfied by the actual charge density in an atom. Instead of using the right-hand side of Eq. (13) for $k_F{}^2$ in Eq. (11), we propose using the left-hand side. That is, we propose as an alternative to Eq. (11) that we let

$$\eta=\{E-V_C+8F(\eta)[(3/8\pi)\rho]^{1/3}\}^{1/2}$$

$$\times\{E_F-V_C+4[(3/8\pi)\rho]^{1/3}\}^{-1/2} \qquad (15)$$

which automatically gives $\eta=1$ when $E=E_F$. We shall denote by $V_{X\text{LSW}}$ the exchange found from Eq. (12) if η is determined by Eq. (15). We have programmed this method, as well as the X_{L} method, and shall present results determined by its use.

We have now described the various schemes that we shall compare in the further sections of this paper. Specifically, we have considered the Cu$^+$ ion by using $V_{X\text{L}}$, $V_{X\text{LSW}}$, $V_{X\text{KSG}}$, $V_{X\text{S}}$, and $V_{X\alpha}$ with a value of α equal to 0.77. This value was determined by solving for a number of values of α, and choosing the one that minimized the total energy, which we find for Cu$^+$ to be $\alpha=0.77$. In the $V_{X\text{LSW}}$ calculations, we have arbitrarily set $E_F=0$. The value of E_F may be considered in an isolated atom to be a disposable constant, and the outer orbitals are rather sensitive to the value chosen. We have not yet made an exhaustive study of the best value to use in the present case. We compare the results obtained by the five methods enumerated above with the Hartree-Fock results determined originally by Hartree and Hartree.[14] Those writers did not tabulate the integrals we require for our purpose, but these have been computed by Dr. J. B. Mann.[15] We are much indebted to Dr. Mann for supplying these unpublished results.

II. RESULTS OF THE CALCULATION

In this section we present some results of the calculations outlined in Sec. 1. It would take too much space to present all details. However, we can give a fair idea of the situation by means of several tables modeled after those in the paper of Cowan *et al*. (Ref. 7). In Table I, we give values of 1-electron integrals and 1-electron energies found for each of the cases. In Table II we give values of 2-electron integrals. In Table III we give the total radial charge density as a function of r. For each entry in the tables, we indicate by an asterisk the approximate calculation which is closest to the Hartree-Fock value. A very crude estimate of the accuracy of the various methods is found by adding the number of asterisks

TABLE I. The I integrals,[a] the "binding energies" ϵ,[b] the eigenvalues E,[c] and total energies,[d] for the ground state of Cu$^+$. The exchanges used, $V_{X\text{HF}}$, $V_{X\text{L}}$, $V_{X\text{LSW}}$, $V_{X\text{KSG}}$, $V_{X\alpha}$, and $V_{X\text{S}}$, are described in the text. The values close to Hartree-Fock are starred. Energies in rydbergs. In the calculations for the exchange XLSW, E_F was set equal to zero. In all but the XHF calculations, a modification of the Herman-Skillman program was used. [F. Herman and S. Skillman, Atomic Structure Calculations, (Prentice-Hall, Englewood-Cliffs, New Jersey 1963)]. In these calculations the Latter potential was imposed, as described by Herman and Skillman. The integrals were computed using a modified form of the program described by Zare [R. N. Zare, Report No. 80, Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, 1966, (unpublished)]. This integral program of Zare was designed to be used in conjunction with the Herman-Skillman program.

		$V_{X\text{HF}}$	$V_{X\text{L}}$	$V_{X\text{LSW}}$	$V_{X\text{KSG}}$	$V_{X\alpha}$	$V_{X\text{S}}$
1s	I	−840.700	−840.655	−840.670	−840.642	−840.682*	−840.760
	ϵ	−658.215	−659.080	−658.823	−658.781*	−656.842	−655.763
	E	−658.215	−656.17*	−656.13	−642.27	−644.76	−650.41
2s	I	−206.456	−206.252	−206.178	−206.101	−206.250	−206.573*
	ϵ	−82.256	−82.739	−82.700	−82.775	−82.088*	−80.575
	E	−82.256	−81.81*	−81.65	−77.01	−77.57	−78.88
2p	I	−205.137	−204.918	−204.975	−205.035	−205.216*	−205.603
	ϵ	−71.857	−72.376	−72.322	−72.398	−71.680*	−70.093
	E	−71.857	−71.79	−71.88*	−67.69	−68.31	−69.74
3s	I	−80.066	−80.072	−80.106*	−80.183	−80.325	−80.662
	ϵ	−10.650	−10.789	−10.952	−11.110	−10.754*	−9.991
	E	−10.650	−10.37	−10.41*	−8.840	−8.892	−9.357
3p	I	−75.795	−75.560	−75.888*	−76.159	−76.355	−76.821
	ϵ	−7.284	−7.411	−7.572	−7.729	−7.386*	−6.647
	E	−7.284	−7.078	−7.123*	−5.942	−6.076	−6.431
3d	I	−62.159	−61.677	−61.289	−60.777	−61.792*	−63.932
	ϵ	−1.620	−1.713	−1.843	−1.959	−1.700*	−1.097
	E	−1.620	−1.410	−1.334	−1.131	−1.217	−1.461*
E_{tot}		−3277.46	−3277.33	−3277.36*	−3277.23	−3277.30	−3276.96

[a] $I=(u_i|-\nabla^2-2Z/r|u_i)$.

[b] $\epsilon=(u_i|-\nabla^2-2Z/r|u_i)+\sum_j[(u_iu_j|2/r_{12}|u_iu_j)-(u_iu_j|2/r_{12}|u_ju_i)]$.

[c] E is the eigenvalue of the Schrödinger one-electron equation.

[d] $E_{\text{tot}}=\sum_i(u_i|-\nabla^2-2Z/r|u_i)+\frac{1}{2}\sum_{ij}[(u_iu_j|2/r_{12}|u_iu_j)-(u_iu_j|2/r_{12}|u_ju_i)]$.

for each of the five approximations.

In Table IV we give information bearing on the accuracy of the various approximations, including not merely the total number of asterisks but also the root-mean-square (rms) deviation of the entries in the charge-density table from the Hartree-Fock values and the deviation in the total energy from the Hartree-Fock value. We see that on all counts the exchange $V_{X\mathrm{LSW}}$ gives the best results. It leads to the largest number of asterisks (that is, largest number of entries in Tables I, II, and III in which it is closer to the Hartree-Fock result than is any other), its charge density shows the smallest rms deviation from the Hartree-Fock values, and its total energy is closer to the Hartree-Fock value than that found by any of the other methods. (We have, however, found certain other atoms in which the total energy found by the $X\alpha$ method is slightly lower than that found by the XLSW methods.) The XL method is not far behind. But it is significant that the $X\alpha$ method makes a very good showing and, as we shall point

TABLE II. The F and G integrals[a] for the ground state of Cu^+. The values closest to the Hartree-Fock values are starred. All values are in rydbergs.

	$V_{X\mathrm{HF}}$	$V_{X\mathrm{L}}$	$V_{X\mathrm{LSW}}$	V_{KSG}	$V_{X\alpha}$	$V_{X\mathrm{S}}$
$F^0(1s1s)$	35.531	35.467	35.483	35.460	35.507*	35.610
$F^0(1s2s)$	10.693	10.646	10.635	10.624	10.653	10.717*
$F^0(1s2p)$	12.038	11.990	12.006	12.022*	12.060	12.144
$F^0(1s3s)$	3.647	3.645*	3.657	3.670	3.680	3.704
$F^0(1s3p)$	3.584	3.555	3.596*	3.625	3.638	3.671
$F^0(1s3d)$	2.797	2.764	2.758	2.738	2.793*	2.915
$F^0(2s2s)$	7.615	7.587	7.576	7.563	7.585	7.632*
$F^0(2s2p)$	8.077	8.046	8.042	8.037	8.062*	8.117
$F^0(2s3s)$	3.269	3.266	3.269*	3.275	3.285	3.308
$F^0(2s3p)$	3.187	3.168	3.190*	3.208	3.221	3.251
$F^0(2s3d)$	2.745	2.715	2.705	2.684	2.738*	2.855
$F^0(2p2p)$	8.797	8.761	8.769	8.777	8.808*	8.875
$F^2(2p2p)$	4.162	4.146	4.146	4.147	4.163*	4.198
$F^0(2p3s)$	3.320	3.317	3.322*	3.330	3.340	3.363
$F^0(2p3p)$	3.251	3.231	3.256*	3.277	3.290	3.322
$F^2(2p3p)$	0.638	0.628	0.642*	0.652	0.655	0.661
$F^0(2p3d)$	2.759	2.728	2.720	2.698	2.753*	2.872
$F^2(2p3d)$	0.508	0.496	0.506*	0.503	0.518	0.552
$F^0(3s3s)$	2.492	2.497	2.494	2.493*	2.501	2.521
$F^0(3s3p)$	2.438	2.438*	2.441	2.445	2.455	2.478
$F^0(3s3d)$	2.168	2.158*	2.135	2.115	2.151	2.229
$F^0(3p3p)$	2.389	2.384	2.392*	2.401	2.412	2.439
$F^2(3p3p)$	1.194	1.200	1.195	1.194*	1.201	1.216
$F^0(3p3d)$	2.128	2.115	2.097	2.080	2.117*	2.196
$F^2(3p3d)$	0.987	0.987*	0.961	0.947	0.970	1.018
$F^0(3d3d)$	1.926	1.907*	1.872	1.838	1.891	2.005
$F^2(3d3d)$	0.867	0.861*	0.829	0.806	0.837	0.902
$F^4(3d3d)$	0.535	0.532*	0.509	0.494	0.514	0.557
$G^0(1s2s)$	0.990	0.978	0.979	0.975	0.979	0.989*
$G^1(1s2p)$	2.068	2.048	2.057	2.074*	2.086	2.113
$G^0(1s3s)$	0.128	0.127*	0.131	0.132	0.133	0.134
$G^1(1s3p)$	0.237	0.231	0.242*	0.249	0.250	0.253
$G^2(1s3d)$	0.005	0.004	0.005*	0.005*	0.005*	0.005*
$G^1(2s2p)$	4.634	4.625	4.613	4.603	4.614	4.639*
$G^0(2s3s)$	0.213	0.211*	0.216	0.217	0.217	0.218
$G^1(2s3p)$	0.187	0.182	0. 188*	0.194	0.195	0.196
$G^2(2s3d)$	0.349	0.336	0.352*	0.355	0.367	0.393
$G^1(2p3s)$	0.264	0.262*	0.268	0.271	0.271	0.272
$G^0(2p2p)$	0.243	0.234	0.246*	0.251	0.251	0.253
$G^2(2p3p)$	0.255	0.248	0.258*	0.264	0.265	0.267
$G^1(2p3d)$	0.373	0.360	0.376*	0.376*	0.389	0.416
$G^3(2p3d)$	0.212	0.205	0.214*	0.214*	0.221	0.236
$G^1(3s3p)$	1.616	1.622	1.616*	1.614	1.621	1.637
$G^2(3s3d)$	0.920	0.921*	0.888	0.875	0.897	0.944
$G^1(3p3d)$	1.223	1.222*	1.185	1.168	1.196	1.257
$G^3(3p3d)$	0.736	0.738*	0.713	0.701	0.720	0.759

[a] $F^k(nl\,n'l') = 2\int_0^\infty\int_0^\infty R_{nl}^2(r)R_{n'l'}^2(r')(r_<^k/r_>^{k+1})r^2r'^2\,drd'r$, $G^k(nl\,n'l') = 2\int_0^\infty\int_0^\infty R_{nl}(r)R_{n'l'}(r)R_{nl}(r')R_{n'l'}(r')(r_<^k/r_>^{k+1})r^2r'^2\,drdr'$, where the R_{nl} are normalized radial wave functions and $r_< = \min(r, r')$, $r_> = \max(r, r')$.

TABLE III. Total electronic radial charge density for Cu$^+$ as determined by several schemes. The values closet to Hartree-Fock are starred. All values in a.u.

r	$V_{X\mathrm{HF}}$	$V_{X\mathrm{L}}$	$V_{X\mathrm{LSW}}$	$V_{X\mathrm{KSG}}$	$V_{X\alpha}$	$V_{X\mathrm{S}}$
0.0072	7.142	7.085	7.112	7.117	7.138*	7.186
0.0144	18.854	18.737	18.780	18.788	18.840*	18.959
0.0216	28.093	27.964	28.000	28.000	28.072*	28.234
0.0288	33.275	33.161	33.186	33.180	33.256*	33.427
0.0432	33.421	34.350	34.386	34.385	34.450*	34.598
0.0576	30.798	30.722	30.805*	30.845	30.911	31.061
0.0720	28.109	27.968	28.111*	28.209	28.301	28.509
0.0864	28.029	27.793	27.984*	28.135	28.266	28.565
0.1153	33.151	32.798	32.992	33.173*	33.372	33.821
0.1441	38.511	38.195	38.310	38.429*	38.635	39.099
0.1729	39.917	39.717	39.769	39.789	39.951*	40.315
0.2017	37.404	37.317	37.361	37.298	37.403*	37.636
0.2594	27.547	27.542*	27.693	27.597	27.654	27.786
0.3170	19.995	19.861*	20.167	20.173	20.300	20.593
0.3746	17.578	17.224	17.630*	17.762	18.001	18.551
0.4322	18.539	18.071	18.425	18.623*	18.951	19.702
0.5475	22.148	21.933	21.799	21.907	22.280*	23.119
0.6628	22.387	22.563*	21.993	21.875	22.174	22.832
0.7780	19.603	19.962	19.270	18.971	19.168	19.577*
0.8933	15.778	16.123	15.530*	15.162	15.268	15.460
1.1238	9.156	9.270*	9.037	8.755	8.746	8.667
1.1354	5.158	5.109	5.134*	4.990	4.927	4.734
1.5849	2.984	2.898	3.041	2.988*	2.900	2.668
1.8154	1.790	1.729	1.896	1.913	1.813*	1.575
2.2765	0.6951	0.7012*	0.8153	0.9094	0.8174	0.6205
2.7376	0.2814	0.3075	0.3734	0.4680	0.3986	0.2641*
3.1987	0.1142	0.1367	0.1730	0.2437	0.1969	0.1142*
3.6597	0.0459	0.0603	0.0794	0.1256	0.0964	0.0491*
4.5819	0.0071	0.0112	0.0160	0.0318	0.0221	0.0087*
5.5040	0.0010	0.0020	0.0030	0.0075	0.0048	0.0015*
6.4261	0.0001	0.0003	0.0005	0.0017	0.0010	0.0002*

out in the next section, it has the great advantage of resulting from a single potential rather than from a different exchange for each orbital, as in XL and XLSW. This makes it much easier to compute and results in automatic orthogonality of the orbitals. The XKSG and XS methods, which alone were considered by Cowan *et al*. in Ref. 7, are the poorest of the five.

To show that our results are not in contradiction to those of Cowan *et al*., we include in Table IV a listing of the number of asterisks that would have been found if we had considered only the XKSG and XS entries. When we examine those numbers, and the rms deviation and ΔE total for these two cases, we see that we should have concluded, in agreement with Cowan *et al*., that the XKSG method is much better than the XS. We should, however, note as Cowan *et al.* did, that in the matter of the one-electron eigenvalues, the quantities E of Table I, the XS method gives in every case values in closer agreement with the Hartree-Fock method than does the XKSG method. On the other hand, both the XL and XLSW methods (they are very similar as concerns the one-electron energies)

TABLE IV. Accuracy of various approximation. "Number of asterisks" is the sum from Tables I, II, III. "Number of asterisks considering XKSG, XS only" is the corresponding number which would have been found if only the XKSG and XS calculations had been made. rms deviation is the root-mean-square deviation of charge densities in Table III from the Hartree-Fock value, averaged over the various entries. ΔE total is deviation of total energy from Table I from Hartree-Fock value.

	XL	XLSW	XKSG	$X\alpha$	XS
No. of asterisks	20	28	12	26	15
No. of asterisks considering XKSG and XS only			69		28
rms deviation	0.190	0.149	0.225	0.213	0.445
ΔE total (Ry)	0.13	0.10	0.23	0.16	0.50

are better than the other three methods as far as one-electron energies are concerned in five out of the six cases, as we see from Table I.

III. INTERPRETATION OF THE RESULTS

We have now tabulated a good deal of information concerning the respective merits of the five calculations, but it is interesting to go more deeply into the significance of these results, and try to understand them better. Why, for instance, can a single potential as in the $X\alpha$ method do nearly as well as the separate potentials for each orbital used in the Hartree-Fock, XL, and XLSW methods? It is obviously of great advantage, in energy-band calculations, to have such a single potential, which makes us think very seriously of using the $X\alpha$ potential rather than the much more difficult XLSW method. But why are the one-electron energies found by the $X\alpha$ method in poorer agreement with the Hartree-Fock method? This last point is particularly important, since it is the one-electron energies found as the eigenvalues of the differential equation that are used in finding energy bands.

As a first step in our discussion, we consider the XLSW method, which we have seen gives the closest agreement with the Hartree-Fock method. In Figs. 3 and 4 we show the exchange potentials for the various orbitals, as functions of r, resulting from this method. If we compare these curves with the Hartree-Fock curves from Figs. 1 and 2, we see that there is much resemblance between them. We must disregard the singular behavior of the Hartree-Fock curves around the nodes of u_i, which we mentioned in Sec. 1. The curves of Figs. 3 and 4 resemble smoothed versions of the Hartree-Fock exchange curves, eliminating the singular behavior. This can be seen particularly easily from the 1s, 2p, and 3d orbitals, which have no nodes, and therefore no singularities in the exchange. To show the degree of agreement between the Hartree-Fock and XLSW exchanges in these nodeless cases, we show just these exchanges in Fig. 5, on a different scale from that used in Figs. 3 and 4. It is clear that the XLSW curves form very satisfactory approximations to the Hartree-Fock exchange. The deviations at the largest values of r shown (particularly in the 1s curves) come out in the tail of the wave function, where errors in the potential have merely a slight effect on the rate of exponential decrease of the wave function.

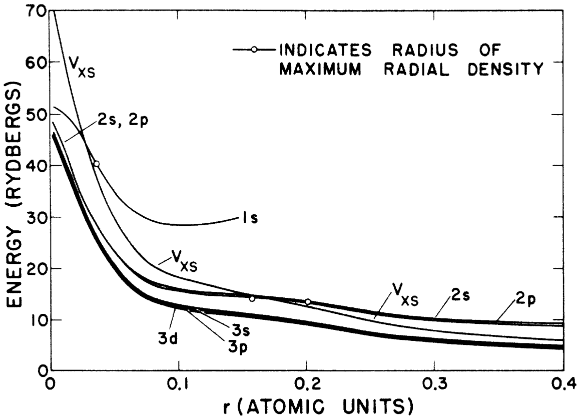

FIG. 3. Absolute value of exchange potential $V_{X\,\mathrm{LSW}}$ for Cu$^+$ for the various orbitals, compared with V_{XS}. Radius of maximum radial charge density is indicated for each $V_{X\,\mathrm{LSW}}$ curve.

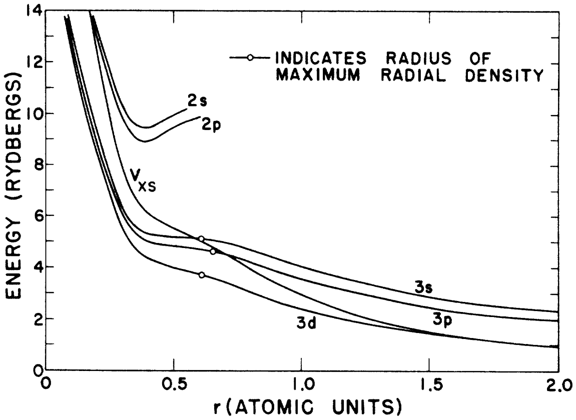

FIG. 4. Same as Fig. 3, different scale.

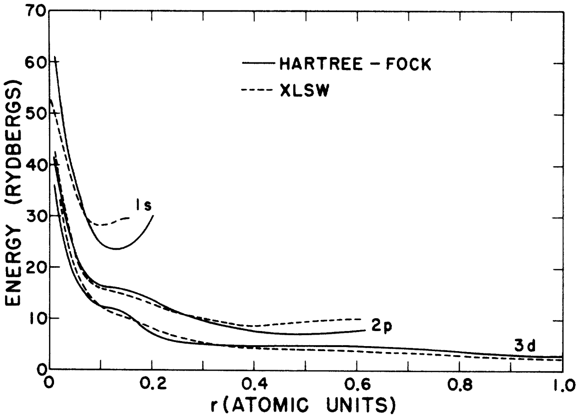

FIG. 5. Hartree-Fock exchange potential $V_{X\mathrm{HF}}$ compared with exchange potential $V_{X\,\mathrm{LSW}}$, for 1s, 2p, 3d orbitals of Cu$^+$.

It is clear from these curves that the reason why the XLSW method works so well is that it really furnishes a very good approximation to the Hartree-Fock exchange. We notice from Figs. 3 and 4 that each of the exchange curves for XLSW lies below the XS exchange for small r, above it for large r. The reason for this is interesting and throws considerable light on the general form of the Hartree-Fock exchange of Figs. 1 and 2. In explanation we give in Fig. 6 a set of curves of η as a function of r, as found in the course of the calculations of the XLSW method. In each case η goes to unity as r goes to zero and falls to zero at a value of r where, as we shall see in a moment, the classical kinetic energy would become zero. The reason for this behavior is easily explained. As r approaches zero, the Coulomb potential energy V_C goes to $-\infty$. Hence both numerator and denominator in Eq. (15), namely

$$\{E - V_C + 8F(\eta)[(3/8\pi)\rho]^{1/3}\}^{1/2}$$

$$\text{and } \{E_F - V_C + 4[(3/8\pi)\rho]^{1/3}\}^{1/2} \tag{16}$$

become infinite and equal, so that their ratio, which is η, approaches unit y. On the other hand, the classical kinetic energy is the square of the first expression of Eq. (16), so that η becomes zero when it is zero. Now we recall that $F(1)=\frac{1}{2}$, $F(0)=1$. Since the exchange XS is computed for the average value of $F(\eta)$, namely $\frac{3}{4}$, we see that as r goes to zero the XLSW exchange must approach $(\frac{1}{2})(\frac{4}{3})=\frac{2}{3}$ times the XS value, while at the point where η goes to zero it must become $\frac{4}{3}$ times the XS value. It is this behavior which we see in the figures.

Beyond the point where η becomes zero, the numerator of Eq. (15) will become pure imaginary, so that this case cannot be shown in Fig. 6. It is easy to extend the value of $F(\eta)$ to this case, by using the expansion

$$F(\eta) = 1 - \frac{\eta^2}{1\times 3} - \frac{\eta^4}{3\times 5} - \frac{\eta^6}{5\times 7} - \cdots, \tag{17}$$

which has a circle of convergence of unity in the complex plane. This expansion shows that for pure imaginary η, we shall have $F(\eta)$ real and greater than unity. Outside the circle of convergence of the expansion of Eq. (17), we may mention the following useful expansion for real η $(\eta > 1)$:

$$F(\eta) = \frac{1}{1\times 3\eta^2} + \frac{1}{3\times 5\eta^4} + \frac{1}{5\times 7\eta^6} + \cdots. \tag{18}$$

We also have the following useful formula for imaginary η $(\eta = iy)$:

$$F(\eta) = \frac{1}{2} + \frac{1+y^2}{4y}\tan^{-1}\left(\frac{2y}{1-y^2}\right). \tag{19}$$

Note that Eqs. (17) and (18) furnish a simple proof of the fact that, for real η,

$$F(\eta) + F(1/\eta) = 1. \tag{20}$$

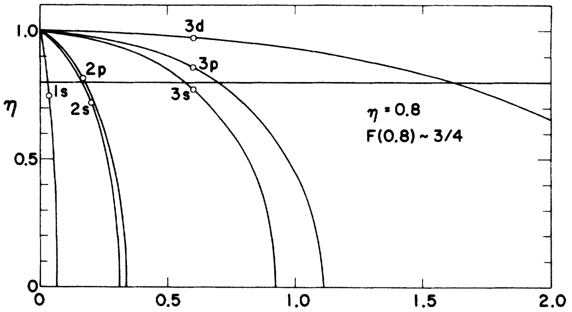

FIG. 6. Parameter η as function of r, XLSW method, for Cu$^+$. Radius of maximum radial charge density is indicated for each curve.

To show the effect of $F(\eta)$ becoming greater than unity, we give in Fig. 7 calculations of $F(\eta)$ as a function of r, for the various orbitals, both for the Hartree-Fock method and the XLSW method. In the Hartree-Fock case, we define $F(\eta)$ as that value, for each orbital and each value of r, which would make the free-electron-gas exchange of Eq. (3) equal to the Hartree-Fock exchange. That is, by using Eqs. (3) and (7), we have

$$F(\eta)_{\mathrm{HF}} = \tfrac{3}{4}\, V_{X\mathrm{HF}}/V_{X\mathrm{S}}. \tag{21}$$

Similarly in the XLSW method we have

$$F(\eta)_{X\mathrm{LSW}} = \tfrac{3}{4}\, V_{X\mathrm{LSW}}/V_{X\mathrm{S}}. \tag{22}$$

It is now clear from Fig. 7 that the Hartree-Fock curves start at $r=0$ approximately at $F(\eta)=\frac{1}{2}$, which as we have noted corresponds to $\eta=1$. On the other hand, for large r, they rise far above $F(\eta)=1$, the value $F(\eta)=1$ coming approximately

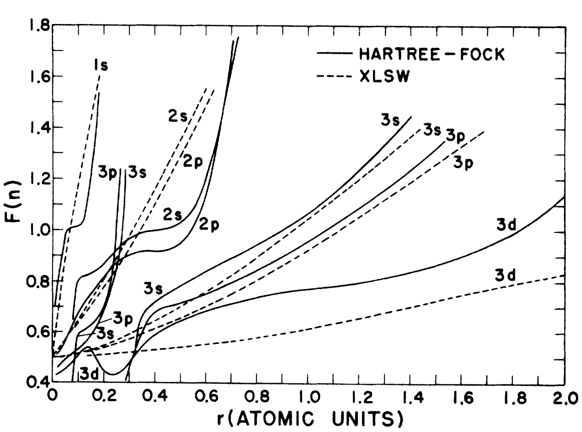

FIG. 7. $F(\eta)$ as function of r, for the various orbitals of Cu$^+$, found by Hartree-Fock and $V_{X\mathrm{LSW}}$ methods.

at the point where the classical kinetic energy equals zero. Thus the Hartree-Fock case shows the sort of behavior discussed in the preceding paragraph for the *X*LSW method.

It should be pointed out that the program that has been used for the present calculations arbitrarily sets $F(\eta) = 1$ for all values of r greater than that for which η becomes zero, so that the calculations of $F(\eta)_{X\text{LSW}}$ follow the curves in Fig. 7 up to $F(\eta) = 1$, and for larger r they give the constant value $F(\eta) = 1$. Clearly this behavior is not mathematically justified, and is not in agreement with the Hartree-Fock case. This situation was not realized when the program was set up. As a temporary expedient, we have extended the curves of $F(\eta)_{X\text{LSW}}$ into the region of negative kinetic energy by solving Eq. (15) in this range by numerical methods, using Eq. (19) for $F(\eta)$. This modification has been made in the graphs shown in Figs. 3 – 5, and 7 – 9, but not in the data given in the Tables. The resulting errors in wave functions come out only in the tails of the wave functions, and we anticipate that, if we later modify the programs to take proper account of the case where $F(\eta)$ is greater than unity, it will result in only very minor modifications in the results in the Tables. The curves for $F(\eta) > 1$, shown in Fig. 7, are in much closer agreement with the Hartree-Fock curves than are those which limit $F(\eta)$ to a maximum value of unity, particularly in the case of the 3*s* and 3*p* orbitals.

For the 3*d* orbital, there is a considerable discrepancy between the Hartree-Fock and *X*LSW methods, which perhaps could be improved by using a different E_F. (We recall that the calculations reported used $E_F = 0$.) This plot of $F(\eta)$ versus r seems to be a particularly useful one for illustrating the way in which each individual potential curve corresponds to a function $F(\eta)$ that varies quite rapidly with r, both in the Hartree-Fock method and in the *X*LSW method, which fairly well reproduces the Hartree-Fock behavior.

We now understand why the *X*LSW exchange potentials, and consequently the Hartree-Fock exchange, do not follow the *X*S exchange. Each exchange potential is numerically less than the *X*S for small r and is greater for large r. As one sees in Figs. 3 and 4, the dividing line between the two cases comes roughly at the radius of maximum radial density of each orbital, so that the *X*S exchange is approximately correct through the part of the orbital where it has its maximum value. This is why the *X*S method works reasonably well on the average and gives fairly good eigenvalues. But the individual exchanges vary less rapidly with r than does the *X*S exchange, which is why the *X*S method does not yield very good orbitals. Let us next inquire why a single exchange potential, namely the $X\alpha$, does so well in approximating to the wave functions, though not to the eigenvalues.

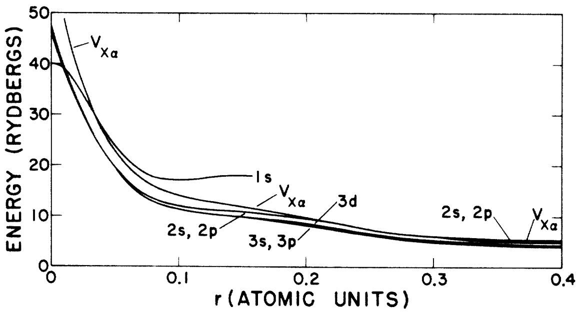

FIG. 8. Absolute value of $V_{X\text{LSW}} - E_{X\text{LSW}} + E_{X\alpha}$ for the various orbitals of Cu$^+$, compared with $V_{X\alpha}$.

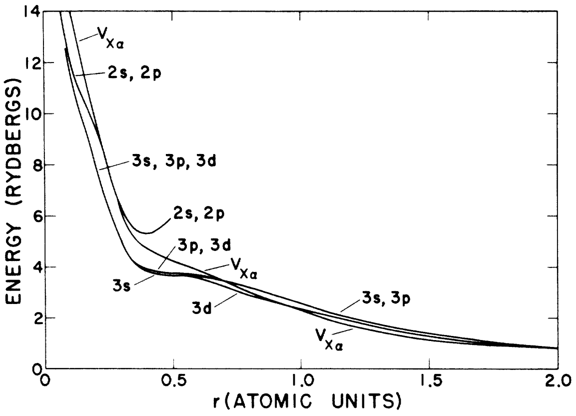

FIG. 9. Same as Fig. 8, different scale.

We cannot expect agreement between the wave functions determined by $X\alpha$ and *X*LSW unless we really solve almost the same Schrödinger equations in the two cases. We must remember that it is only the variation of potential energy with r that is significant in determining the wave functions; an additive constant in the potential energy will merely produce an equal additive constant in the eigenvalue. Now if we multiply the exchange *X*S by the constant α, which we have seen is 0.77 in our case, the variation of $V_{X\alpha}$ will be only 0.77 as much as for V_{XS}. It seems plausible from Figs. 3 and 4 that the resulting variation of $V_{X\alpha}$ with r might be similar to that shown for $V_{X\text{LSW}}$. In other words, the increase of $F(\eta)$ with r, from $\frac{1}{2}$ at $r = 0$ to 1 at the point where the classical kinetic energy goes to zero, and to larger values for larger r, might modify the natural decrease of V_{XS} with r enough so that it would simulate the behavior of $V_{X\alpha}$, and consequently the latter potential might lead to about the same eigenfunctions.

This suggests, in other words, that it might be possible to approximate the magnitude of the *X*LSW exchange, which is

$$8F(\eta)[(3/8\pi)\rho]^{1/3},$$

by the magnitude of the $X\alpha$ potential, which is

$$6\alpha[(3/8\pi)\rho]^{1/3},$$

plus a constant. That is, we might have approximately

$$8F(\eta)[(3/8\pi)\rho]^{1/3} = 6\alpha[(3/8\pi)\rho]^{1/3} + A, \tag{23}$$

where A would be a different constant for each orbital. Then we should replace the Schrödinger equation of the XLSW method, namely

$$\left[-\nabla^2 + V_C - 8F(\eta)\left(\frac{3}{8\pi}\rho\right)^{1/3}\right]u = E_{X\mathrm{LSW}}u, \tag{24}$$

by

$$\left[-\nabla^2 + V_C - 6\alpha\left(\frac{3}{8\pi}\rho\right)^{1/3}\right]u$$

$$= (E_{X\mathrm{LSW}} + A)u = E_{X\alpha}u. \tag{25}$$

If this were possible, we should get identical orbitals by the two methods, but the eigenvalue $E_{X\alpha}$ would be equal to $E_{X\mathrm{LSW}} + A$. Since $E_{X\mathrm{LSW}}$ is known to agree well with the Hartree-Fock energy, this would explain the poorer eigenvalue found by the $X\alpha$ method.

If the assumption of Eq. (23) were satisfied, it would imply that the exchanges $V_{X\mathrm{LSW}}$ for the various orbitals would all equal a common curve,

$$6\alpha[(3/8\pi)\rho]^{1/3},$$

plus constants A which would be different for the various orbitals and equal to $E_{X\alpha} - E_{X\mathrm{LSW}}$. This can be easily tested. We have the curves of $V_{X\mathrm{LSW}}$ in Figs. 3 and 4 and the values of $E_{X\alpha}$ and $E_{X\mathrm{LSW}}$ in Table I. By using this information we show in Figs. 8 and 9 the quantities $V_{X\mathrm{LSW}} - E_{X\mathrm{LSW}} + E_{X\alpha}$ for each orbital, together with the potential $V_{X\alpha}$. We see in fact that the curves are brought much more nearly into coincidence than are the original exchange potentials $V_{X\mathrm{LSW}}$, and the common curve is quite well approximated by $V_{X\alpha}$. The discrepancies in Fig. 9, by which the 1s, 2s, and 2p curves at large r lie above the $V_{X\alpha}$ curve, come out in the tails of the orbitals where they have only a very small effect on the wave functions. This, then, is the explanation of the fact that a single potential $V_{X\alpha} = \alpha V_{XS}$ can furnish a good approximation to the different potentials $V_{X\mathrm{LSW}}$ for the different orbitals, but that it gives incorrect eigenvalues. Since the resulting Schrödinger equations are very similar, and since the single potential $V_{X\alpha}$ will necessarily lead to orthogonal orbitals, we may expect a fairly close approach to orthogonality for the XLSW method. We find in fact that the overlaps with the XLSW method are 0.0014 for (1s/2s), 0.0003 for (1s/3s), 0.0040 for (2s/3s), and 0.0017 for (2p/3p).

Before we leave our calculations, we shall inquire what sort of results we have for the XL method, which we have seen is very nearly as good as XLSW. We illustrate the sort of difference found between XL and XLSW in Fig. 10, in which we show V_X versus r for the 3s orbital, as found by both methods. The XLSW curve of Fig. 10 is identical with that of Fig. 3. The shell structure of the atom introduces oscillations in the value of $V_{X\mathrm{L}}$ computed for the XL method by Eq. (11), which are not found in the XLSW method. These lead to oscillations of exchange that do not seem to improve the agreement with the Hartree-Fock exchange. The only exception to this situation seems to be in the 3d orbital, for which, as we see from Table II, the XL method seems to lead to values of the integrals somewhat closer to the Hartree-Fock values than does the XLSW. It is hard to know whether this is significant or merely the result of an accident, such as a poor choice of E_F in the XLSW method.

IV. DISCUSSION

We have examined five different approximations to the Hartree-Fock exchange in atoms, and have found that one of them, the XLSW method is definitely superior to the others but that it is complicated to program and carry through, since it involves different exchange potentials for each orbital. Nearly as good results are obtained from the $X\alpha$ method, which amounts to multiplying the standard exchange XS by a constant α. In the case of Cu$^+$, we found that the lowest energy of the atom is obtained by setting $\alpha = 0.77$, and the orbitals determined from this simple potential are very nearly as good as those found from the more complicated XLSW exchange. Both of these methods can be programmed for application to energy bands, and E. C. Snow[16] has computed the energy bands for the copper crystal by the XLSW method. The results, however, are disappointing.

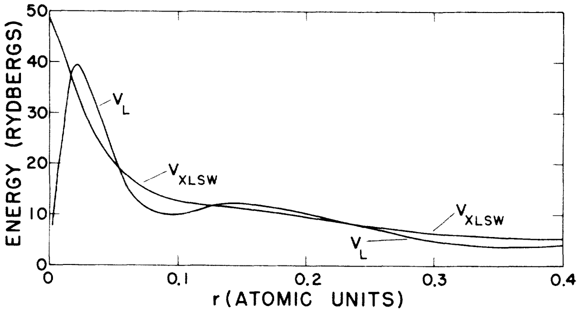

FIG. 10. Absolute value of exchange potentials $V_{X\mathrm{LSW}}$ and $V_{X\mathrm{L}}$ for 3s orbital, Cu$^+$.

The energy bands seem to be further from experiment than those found by Snow[17] using the $X\alpha$ method, in which he got very good results for $\alpha = \frac{5}{6} = 0.833$. It is too early to give an evaluation of this situation, but it suggests that the $X\alpha$ method may prove to be more useful for energy-band calculations than is the XLSW method. However, we must remember that if we use the $X\alpha$ method, the one-electron energies of inner shells must be modified by amounts $E_{X\text{LSW}} - E_{X\alpha}$, pushing the energies of the inner shells down with respect to the Fermi energy.

There is one respect in which our calculation is very specialized; it is carried out for a closed-shell ion Cu^+. Many of the important problems in energy-band work arise from atoms having partially filled shells, such as Fe, Co, and Ni in magnetic crystals. In such cases, an entirely different point comes in: there are often two partially-filled shells that have almost the same orbital energies, like the $3d$ and $4s$ shells in the atoms just named. We can then be in some uncertainty as to which orbitals will be occupied in the ground state of the atom. If we wish to carry out a variational argument, minimizing the energy as is done in Refs. 4, 5, and 6, by varying the charge distribution, we can vary the charge distribution in two quite different ways: by modifying the individual orbitals or by shifting charge from one orbital to the other. The latter possibility leads to very interesting conclusions that have not been sufficiently considered in the literature. Consequently, in a later paper[18] we shall look in detail into this question of variable occupation numbers. We shall find that it leads to very interesting results and throws new light on the validity of the one-electron approximation to the many-electron problem. In particular, it also puts the question of the difference between eigenvalues obtained by the Hartree-Fock method and by the $X\alpha$ method in a new context, and suggests that it has a more fundamental significance than has appeared from our discussion in the present paper.

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