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Wave Functions and Energy Levels for Cu$^+$ as Found by the Slater Approximation to the Hartree-Fock Equations*

GEORGE W. PRATT, JR.
Massachusetts Institute of Technology, Cambridge, Massachusetts

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Results of a self-consistent field calculation using the Slater method are given for Cu$^+$. Wave functions, energies, total radial charge density, $2(2l+1)\cdot(1-Z_{nl})$ functions for the $3p$ and $3d$ electrons, and the $2Z_p(r)$ functions are listed. The corresponding results for the Hartree-Fock method, and in some cases the Hartree method, are given for comparison of the various calculations. The method of integrating the radial wave equation and a method for shortening the self-consistent calculation are included.

INTRODUCTION

THE quantum-mechanical many-body problem as treated by the Hartree method[1] is, for many purposes, somewhat oversimplified. The more accurate Hartree-Fock method,[2] which correctly includes the Pauli principle within the framework of the one-electron approximation, is so complicated to carry out that it has found only a rather restricted use. Slater[3] has shown that a considerable simplification of the Fock equations can be achieved if one uses an average exchange charge density and from this computes an average exchange potential energy. The purpose of this work was to examine the accuracy of Slater's method by applying it to Cu$^+$ which has been investigated by both the Hartree[4] and the Hartree-Fock method.[5]

The average exchange charge density as given by Slater for an atomic system containing an equal number of electrons of each spin is

$$\rho_{\mathrm{Av}}=\frac{-e\sum_{j=1}^{N}\sum_{k=1}^{N} u_j^*(x_1)u_k^*(x_2)u_k(x_1)u_j(x_2)}{\sum_{j=1}^{N} u_j^*(x_2)u_j(x_1)}, \qquad (1)$$

where u_j are orthonormal one-electron functions and the x_i refer to spatial and spin coordinates. In terms of this function the Fock equations are

$$H_1u_i(x_1)+\left\{\sum_{k=1}^{N} e^2\int\frac{u_k^*(x_2)u_k(x_2)}{r_{12}}dx_2\right\}u_i(x_1)$$
$$-\left\{\sum_{k=1}^{N} e^2\int\frac{u_i^*(x_1)u_k^*(x_2)u_k(x_1)u_i(x_2)/r_{12}}{\sum_{i=1}^{N} u_i^*(x_1)u_i(x_1)}dx_2\right\}u_i(x_1)$$
$$=E_iu_i(x_1), \qquad (2)$$

where H_1 is the kinetic energy and the electrostatic energy coming from the electron-nucleus interaction of an electron at X_1. The result of the averaging has been to reduce the Fock equations to the eigenvalue type and to make the exchange term the same for all electrons. It is to be remembered that the Slater method only applies when the total many electron wave function is written as a single determinant.

The Fock equations are still rather complicated to apply, even using the averaged exchange term. In order to further simplify the application of these equations, Slater has used a free electron gas model to calculate the average exchange energy. When this is done, we are enabled to write the Fock equations in the case in which there are an equal number of electrons of each spin, as

$$H_1u_i(x_1)+\left[\sum_{k=1}^{N} e^2\int\frac{u_k^*(x_2)u_k(x_2)}{r_{12}}dx_2\right.$$
$$\left.-3e^2\left\{\frac{3}{8\pi}\sum_{k=1}^{N} u_k^*(x_1)u_k(x_1)\right\}^{\frac{1}{3}}\right]u_i(x_1)=E_iu_i(x_1). \qquad (3)$$

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[1] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89, 111 (1927).

[2] V. Fock, Z. Physik. **61**, 126 (1930).

[3] J. C. Slater, Phys. Rev. **81**, 385 (1951); see also R. Sternheimer, Phys. Rev. **78**, 235 (1950).

[4] D. R. Hartree, Proc. Roy. Soc. (London) **A141**, 282 (1933).

[5] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A157**, 490 (1936).

TABLE I. Trial eigenvalues for $P_{2p}(r)$ for Cu^+ and its corresponding behavior for large r.

E (at. units)	Behavior[a]
−69.489	Wave function went negative at $r=0.890$, slope 0.418
−69.494	Wave function went negative at $r=0.960$, slope 0.246
−69.495	Wave function went negative at $r=1.020$, slope 0.174
−69.496	Wave function had minimum at $r=1.120$, min 0.008956
−69.4955	Wave function went negative at $r=1.080$, slope 0.108
−69.4957	Wave function had minimum at $r=1.240$, min 0.003677

[a] The correct wave function should approach zero through positive values and become zero at about $r=1.30$.

For the case of unbalanced spins only slight modifications of the averaging procedure are required if we use a single determinant as the total wave function. In this case the Fock equations can be expressed as

$$H_1u_i(x_1)+\left[\sum_{k=1}^{N} e^2\int\frac{u_k^*(x_2)u_k(x_2)}{r_{12}}dx_2 -3e^2\left\{\frac{3}{4\pi}\left(\frac{N_\pm}{N}\right)\sum_{k=1}^{N}u_k(x_1)u_k(x_1)\right\}^{\frac{1}{3}}\right]u_i(x_1) =E_iu_i(x_1), \quad (4)$$

where $N_\pm/N$ represents the fraction of electrons of a given spin at a radius r from the nucleus.

The local electron density $\sum_k u_k^*(x)u_k(x)$ can be related through Poisson's equation to the potential set up by the nucleus and all of the electrons. Denoting this potential by $2Z_p/r$, we can express the averaged exchange energy as

$$-\frac{6}{r}\left\{\frac{3}{32\pi^2}\right\}^{\frac{1}{3}}\left\{r^2\frac{d^2Z_p}{dr^2}\right\}^{\frac{1}{3}} \quad (5)$$

in atomic units. It is often very useful to write the $2Z_p(r)$ function and the exchange energy in terms of the radial wave functions $P_{nl}(r)$ where $u_{nl}(x)=[P_{nl}(r)/r]\cdot Y_{l,m}(\theta,\varphi)$. Assuming a spherically symmetric charge distribution, one finds for $2Z_p(r)$ the expression

$$2Z_p(r)=2Z-2\sum_{nl}2(2l+1)\times\left\{\int_0^r P_{nl}^2dr'+r\int_r^\infty\frac{P_{nl}^2}{r'}dr'\right\}, \quad (6)$$

where Z is the atomic number. For the exchange potential energy times r we have

$$z(r)=+6\left(\frac{3}{32\pi^2}\right)^{\frac{1}{3}}\left(r^2\frac{d^2Z_p}{dr^2}\right)^{\frac{1}{3}} =+6\left\{\frac{3}{32\pi^2}\sum_{nl}2(2l+1)rP_{nl}^2(r)\right\}^{\frac{1}{3}}. \quad (7)$$

The radial wave equation may be written as

$$\frac{d^2P_{nl}}{dr^2}+\left[E_{nl}+\frac{2Z_p}{r}+\frac{z(r)}{r}-\frac{l(l+1)}{r^2}\right]P_{nl}=0. \quad (8)$$

This equation leads to the definition of a new function $W(r)$, which is $W(r)=2Z_p(r)+z(r)$. In the actual calculations it was decided to use $W(r)$ to determine the degree of self-consistency.

METHOD OF SOLUTION

Having obtained the radial equation to be solved, let us investigate the method of its solution. This equation must be integrated numerically with trial values of the energy E_{nl}. Because of the fact that it often requires ten or more guesses of E_{nl} before a satisfactory value is found, a rapid and accurate integration method is highly desirable. In customary methods of numerical integration, one makes an estimate of a forward point, or a number of forward points, and then proceeds to improve these points by some sort of iterative scheme. These approaches are cumbersome to use on automatic equipment, especially I.B.M. machines, because of the complex machine programs required and the consequent reduction of the speed of solution. The Noumerov method[6] appears to be the answer to many of these difficulties. The essence of this method is to make a change of dependent variable so that one may find advance points with no iteration required but still have a very small truncation error.

Let the radial one-electron Schrödinger equation be written as

$$d^2P/dr^2=g(r)\cdot P(r), \quad (9)$$

where $g(r)$ is

$$g(r)=-[E+W(r)/r-l(l+1)/r^2]. \quad (10)$$

We now expand P about the point $r=r_n$ in a Taylor's series:

$$P_{n+1}=P_n+hP_n'+\frac{h^2}{2!}P_n''+\frac{h^3}{3!}P_n'''+\frac{h^4}{4!}P_n^{iv}+\cdots, \quad (11)$$

where h is $r_{n+1}-r_n$. Differentiating twice, one finds the expansion for d^2P/dr^2 to be

$$P_{n+1}''=P_n''+hP_n'''+\frac{h^2}{2!}P_n^{iv}+\frac{h^3}{3!}P_n^{v}+\cdots. \quad (12)$$

Let us define a new dependent variable $y(r)$ as

$$y_n(r)=P_n(r)-(h^2/12)P_n''(r). \quad (13)$$

We can write the Taylor's series expansion of $y(r)$ about r_n as

$$y_{n+1}=P_n+hP_n'+\frac{5h^2}{12}P_n''+\frac{h^3}{12}P_n''' -\frac{h^5}{180}P_n^{v}-\frac{h^6}{480}P_n^{vi}+\cdots. \quad (14)$$

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[6] B. Noumerov, Publ. Observ. Astrophys. Cent. Russie **11** (Moscu, 1923); Monthly Not. Roy. Astron. Soc. **84**, 592 (1924).

To obtain y_{n-1} one merely changes the sign of h in the above expression. Thus the second difference in y at r_n is

$$\delta^2 y_n = y_{n+1} - 2y_n + y_{n-1} = h^2 P_n'' - (h^6/240) P_n^{\mathrm{vi}}. \quad (15)$$

Therefore, if one neglects the sixth and higher order terms, we find the very simple relationship

$$\delta^2 y_n = h^2 P_n''. \quad (16)$$

Combining the definition of $y(r)$ with the original differential equation, we see that $y_n(r)$ can be written

$$y_n = P_n - (h^2/12) P_n'' = P_n(1 - g_n h^2/12). \quad (17)$$

We can also express the second difference in y as

$$\delta^2 y_n = h^2 P_n'' = h^2 g_n P_n,$$

which leads to the final expression

$$\delta^2 y_n = \left\{ \frac{h^2 g_n}{1 - g_n h^2/12} \right\} y_n. \quad (19)$$

If we define u_n as

$$u_n = \frac{g_n h^2/12}{1 - (g_n h^2/12)}, \quad (20)$$

our final form is

$$\delta^2 y_n = 12 u_n y_n. \quad (21)$$

The simplicity of solution of this equation is immediately apparent. The truncation error is controlled by the term $(h^6/240)P^{\mathrm{vi}}$, so that by keeping h small this source of error can be readily controlled without using so small an h that the length of calculation becomes troublesome. In this work on Cu$^+$, h was taken as 0.005 from the origin to $r = 0.800$. The interval was 0.010 between $r = 0.800$ and 0.900; 0.020 between $r = 0.900$ and 1.400; 0.040 between $r = 1.400$ and 2.440; 0.080 between $r = 2.44$ and 2.60; 0.160 between $r = 2.60$ and 4.20; 0.320 for all larger values of r.

By choosing the intervals in the above manner the range of $h = 0.005$ covered the values of r in which all wave functions passed through their maxima and minima. The $3d$ wave function had the outermost maximum of all wave functions, and this occurred at approximately $r = 0.480$. Therefore, larger intervals were used in the range of r in which all functions were approaching zero with relatively small slopes.

TABLE II. Radial charge due to the $2p$ wave function corresponding to an eigenvalue of -69.4957.

r (at. units)	$\int_0^r P_{2p}^2 dr$
0.600	0.996929
0.700	0.999496
0.800	0.999856
0.900	0.999989
1.000	0.999998
1.240	1.000000

TABLE III. Comparison of initial and calculated $W(r)$ functions for the first and second cycles.

r	$W^{(0)}$	$W^{(1)}$	$W^{(2)}$	$W^{(3)}$
0.000	58.000	58.000	58.000	58.000
0.090	42.727	42.246	42.353	42.862
0.300	25.240	24.206	24.459	25.849
0.700	11.547	10.649	10.877	12.612
1.400	4.940	4.727	4.779	5.818
2.600	3.051	3.008	3.002	3.611
	First cycle		Second cycle	

The radial equation was integrated outward by the Noumerov method on the I.B.M. 602-A calculating punch computer[7] with trial values of the energy until a "best" eigenvalue was found. The exact eigenvalue will be the one for which the wave function goes to zero with zero slope for sufficiently large r. As the exact eigenvalue is never realized in practice, one must select some standard for an acceptable energy. The criterion used in this work was that the wave function should go through zero at large r with a slope of not more than ± 0.05. As an example of the kind of results obtained, Table I gives some trial eigenvalues for the $2p$ wave function of Cu$^+$ and the behavior of the wave function at large r. The value 69.4957 was selected as the final value of the energy. The charge within a sphere of radius r corresponding to this wave function are shown in Table II. The purpose of determining an energy value to so many figures is only to insure that the corresponding charge density will behave smoothly in the region where the wave function is going to zero.

Having determined all wave functions and energies, one proceeds to recompute the common potential $W(r)/r$ and the $2Z_p$ function. If the initial and final $W(r)$ functions do not agree to within some standard set for the calculation, another cycle must be undertaken. One cannot use the $W(r)$ resulting from previous cycle as the initial function for the next cycle, because the self-consistent procedure is not necessarily convergent. Let us denote the initial $W(r)$ for the first cycle as $W^{(0)}$. This function was obtained from the results of Hartree and Hartree's work on Cu$^+$ as calculated with exchange.[5] The final $W(r)$ as found from the wave functions resulting from the first cycle is denoted by $W^{(1)}$. The initial data for the second cycle will be labeled $W^{(2)}$, and this function was selected intermediate between $W^{(0)}$ and $W^{(1)}$ as follows:

$$W^{(2)} = W^{(0)} + \tfrac{3}{4}(W^{(1)} - W^{(0)}).$$

The method of selection of $W^{(2)}$ used here was merely a rough guess made with the hope of attaining a rapid convergence. It turned out that the factor $\frac{3}{4}$ was rather poor and should have been about 0.40. The function resulting from the second cycle $W^{(3)}$ is shown in Table III. It is clear that the self-consistent process is diverging at the end of the second cycle. One would

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[7] N. A. Lindburger, Proc. Endicott Forum on Sci. Comp. (1948) (unpublished).

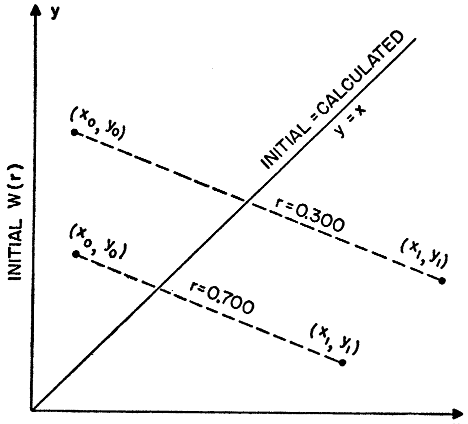

FIG. 1. The graphical estimation of a new $W(r)$ function.

expect that $W^{(3)}$ would lie between $W^{(1)}$ and $W^{(2)}$ if the method were converging.

The following approach was used to correct this divergent character. One can make a plot having the initial value of $W(r)$ for some given r along the ordinate. The derived value of $W(r)$ for that cycle at the same r is plotted along the abscissa. Using the results of the first and second cycles, two points at each value of r can be obtained:

$$(x_0, y_0)=(W^{(1)}, W^{(0)}),$$
$$(x_1, y_1)=(W^{(3)}, W^{(2)}).$$

A line is drawn connecting these points. The intersection of this line with the 45° line determines the new estimate of $W(r)$ at the given value of r. The function so obtained will be denoted by $W^{(4)}$, and it was used as the initial data for the third cycle. This method is illustrated in Fig. 1. The intersection can be obtained analytically as

$$W^{(4)}=\frac{W^{(0)}\{W^{(3)}-W^{(1)}\}-W^{(1)}\{W^{(2)}-W^{(0)}\}}{\{W^{(3)}-W^{(1)}\}-\{W^{(2)}-W^{(0)}\}}. \quad (22)$$

TABLE IV. A comparison of the initial and final $W(r)$ functions for the second and third cycles.

r	$W^{(2)}$	$W^{(3)}$	d_{23}	$W^{(4)}$	$W^{(5)}$	d_{45}
0.02	53.841	53.969	−0.13	53.989	53.890	0.008
0.10	41.108	41.639	−0.53	41.282	41.242	0.04
0.20	31.252	32.265	−1.02	31.599	31.470	0.13
0.26	26.917	28.171	−1.25	27.332	27.181	0.15
0.32	23.351	24.794	−1.44	23.805	23.652	0.15
0.40	19.557	21.180	−1.62	20.003	19.889	0.11
0.50	15.906	17.660	−1.75	16.396	16.246	0.15
0.65	11.903	13.667	−1.77	12.364	12.217	0.14
0.75	9.989	11.675	−1.68	10.406	10.275	0.12
0.90	7.938	9.459	−1.52	8.246	8.193	0.06
1.14	5.963	7.213	−1.25	6.187	6.187	0.00
1.38	4.849	5.901	−1.05	4.987	5.062	−0.07
1.68	···	···	···	4.135	4.248	−0.11
1.72	3.994	4.820	−0.83	···	···	···
2.44	3.116	3.754	−0.63	3.159	3.271	−0.11
3.24	2.666	3.178	−0.51	2.708	2.768	−0.06
	Second cycle			Third cycle		

The function $W^{(4)}$ was calculated by applying this relation at each point $r_{2n}=r_0+2nh$, and Lagrangian interpolation was used to find the values at $r_{2n+1}=r_0+(2n+1)h$.

The result of this method was most satisfactory in that the function $W^{(5)}$ as derived from the third cycle was in very close agreement with $W^{(4)}$. The degree of self-consistency achieved in the third cycle was within the standards set by Hartree. The success of the graphical interpolation is evident from the results shown in Table IV.

RESULTS

The final results of the third cycle of calculations are shown in Tables V through XV. Included in these data are the normalized radial wave functions $P_{nl}(r)$ as found by the Hartree-Fock method[5] and the Slater approximation for Cu$^+$. The total radial charge density is given for the Hartree,[4] Hartree-Fock, and Slater methods. In order to see the differences between the Slater and Hartree-Fock solutions to Cu$^+$ in more detail, a table is included showing the charge outside a sphere of radius r due to the $3p$ and $3d$ electrons, as found by both methods. The inner electrons of Cu$^+$ behave so much like Hartree-Fock electrons that similar tables are not given for them. A table is included showing the electronic energies as determined by the Hartree, Hartree-Fock, and Slater methods. This is accompanied by a table of uncertainties in the energies found in this work. Finally a table is given, showing the $2Z_p(r)$ function resulting from the third cycle and as derived from the Hartree-Fock work on Cu$^+$.

TABLE V. The $1s$ radial wave function P_{1s} as determined by the Hartree-Fock method and by the Slater approximation.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	0.000	0.000	0.120	1.211	1.206
0.005	1.328	1.327	0.140	0.809	0.804
0.010	2.299	2.294	0.160	0.530	0.526
0.015	2.985	2.980	0.180	0.344	0.340
0.020	3.445	3.438	0.200	0.221	0.217
0.025	3.729	3.721	0.220	0.141	0.137
0.030	3.876	3.867	0.240	0.089	0.086
0.035	3.918	3.909	0.260	0.056	0.054
0.040	3.881	3.871	0.280	0.036	0.033
			0.300	0.023	0.020
0.050	3.645	3.636			
0.060	3.290	3.281	0.350	0.007	0.004
0.070	2.890	2.880	0.400	0.002	0.000
0.080	2.488	2.479	0.450	0.001	0.000
0.090	2.110	2.103	0.500	0.000	0.000
0.100	1.769	1.762	0.550	0.000	0.000
			0.600	0.000	0.000

DISCUSSION

Let us inquire about the degree of self-consistency achieved in the work on Cu$^+$. The criterion for self-consistency that Hartree and many others have employed is to demand that the initial and calculated radial charge functions $Z_{nl}(r)$, which are given as $\int_0^r P_{nl}(r)^2dr$, must agree to within a certain tolerance. This is usually of the order of $0.02/2(2l+1)$. Because of the methods used to find a new estimate of $W(r)$ for each cycle, initial $Z_{nl}(r)$ functions were not available to compare with those functions obtained at the end of the cycle in the present calculation. It is possible however, to deduce approximately the deviations in the $Z_{nl}(r)$ functions from the differences between the initial and final $W(r)$ functions. If the relation

$$2(2l+1)Z_{nl}(r)_{\text{final}}=2(2l+1)Z_{nl}(r)_{\text{initial}}+d$$

is assumed for all r and nl, where d is the deviation averaged over all nl and over all r for a cycle, then one can readily show that

$$2Z_p(r)_{\text{final}}=2Z_p(r)_{\text{initial}}-d\sum_{nl}2. \tag{23}$$

TABLE VI. The $2s$ radial wave function P_{2s} as determined by the Hartree-Fock method and by the Slater approximation.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	0.000	0.000	0.200	−2.168	−2.170
0.005	0.407	0.409	0.220	−2.134	−2.134
0.010	0.700	0.702	0.240	−2.050	−2.049
0.015	0.896	0.898	0.260	−1.932	−1.930
0.020	1.011	1.013	0.280	−1.795	−1.791
0.025	1.061	1.062	0.300	−1.646	−1.642
0.030	1.057	1.058			
0.035	1.009	1.009	0.350	−1.270	−1.267
0.040	0.926	0.926	0.400	−0.940	−0.936
			0.450	−0.674	−0.672
0.050	0.686	0.683	0.500	−0.474	−0.472
0.060	0.384	0.379	0.550	−0.328	−0.326
0.070	0.054	0.048	0.600	−0.225	−0.222
0.080	−0.280	−0.287			
0.090	−0.602	−0.609	0.700	−0.104	−0.100
0.100	−0.900	−0.908	0.800	−0.048	−0.044
			0.900	−0.022	−0.018
0.120	−1.403	−1.411	1.000	−0.011	−0.006
0.140	−1.770	−1.777	1.100	−0.004	−0.001
0.160	−2.007	−2.013	1.200	−0.002	0.000
0.180	−2.132	−2.136	1.300	−0.001	0.000

For Cu$^+$ this becomes

$$2Z_p(r)_{\text{final}}=2Z_p(r)_{\text{initial}}-12d. \tag{24}$$

$W(r)$ is given as

$$W(r)=2Z_p+z(r), \tag{25}$$

and we shall neglect the deviation in $z(r)$ in a cycle. Then the deviation in $2Z_p$ will be regarded as the same as that in $W(r)$, although it is probably less. If we set $12d$ equal to the maximum difference in the third cycle, which from Table IV is seen to be -0.15, then the maximum value of the averaged d is -0.0125. This value of d is of the same order of magnitude as that used by Hartree which is usually $d=0.02$.

TABLE VII. The $2p$ radial wave function, P_{2p}, as determined by Hartree-Fock method and by the Slater approximation.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	0.000	0.000	0.220	1.934	1.933
0.005	0.016	0.016	0.240	1.808	1.804
0.010	0.061	0.060	0.260	1.670	1.665
0.015	0.128	0.126	0.280	1.528	1.520
0.020	0.213	0.208	0.300	1.386	1.377
0.025	0.310	0.303			
0.030	0.416	0.409	0.350	1.055	1.045
0.035	0.528	0.523	0.400	0.778	0.769
0.040	0.644	0.640	0.450	0.561	0.553
			0.500	0.398	0.392
0.050	0.877	0.877	0.550	0.279	0.274
0.060	1.103	1.106	0.600	0.195	0.189
0.070	1.312	1.318			
0.080	1.500	1.508	0.700	0.093	0.089
0.090	1.663	1.673	0.800	0.045	0.041
0.100	1.801	1.812	0.900	0.022	0.019
			1.000	0.011	0.008
0.120	2.002	2.013	1.100	0.005	0.004
0.140	2.111	2.121	1.200	0.002	0.003
0.160	2.142	2.150	1.300	0.001	0.000
0.180	2.113	2.119	1.400	0.000	0.000
0.200	2.040	2.042			

One can get a better physical picture of the significance of this degree of consistency by computing the initial $W(r)/r$ function for the fourth cycle and taking the difference between this function, denoted as $W(r)^{(6)}/r$, and the final potential of the third cycle $W(r)^{(5)}/r$ as a perturbing potential. This has been done and the average value has been computed with respect to the $3d$ wave function. The $3d$ function was selected because it is the most sensitive of all the wave functions of Cu$^+$ and because the $3d$ eigenvalue incurred the largest changes from one cycle to another. The average value of the difference over the $3d$ wave function was found to be about 0.05. Therefore, it may be estimated that the $3d$ eigenvalue reported should not differ from

TABLE VIII. The $3s$ radial wave function, P_{3s}, as determined by Hartree-Fock method and by the Slater approximation.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	0.000	0.000	0.350	0.438	0.401
0.005	0.152	0.156	0.400	0.757	0.724
0.010	0.261	0.267	0.450	1.001	0.974
0.015	0.334	0.341	0.500	1.170	1.148
0.020	0.376	0.384	0.550	1.268	1.254
0.025	0.393	0.401	0.600	1.311	1.302
0.030	0.389	0.400			
0.035	0.368	0.383	0.700	1.275	1.276
0.040	0.334	0.353	0.800	1.147	1.154
			0.900	0.983	0.994
0.050	0.238	0.263	1.000	0.817	0.828
0.060	0.119	0.147	1.100	0.663	0.675
0.070	−0.010	−0.020	1.200	0.531	0.542
0.080	−0.139	−0.109	1.300	0.420	0.429
0.090	−0.260	−0.234	1.400	0.329	0.337
0.100	−0.370	−0.345			
			1.600	0.198	0.204
0.120	−0.544	−0.527	1.800	0.117	0.121
0.140	−0.651	−0.644	2.000	0.069	0.070
0.160	−0.692	−0.695	2.200	0.040	0.040
0.180	−0.677	−0.688	2.400	0.023	0.021
0.200	−0.614	−0.632	2.600	0.014	0.009
0.220	−0.515	−0.539	2.800	0.008	0.001
0.240	−0.390	−0.419	3.000	0.004	0.000
0.260	−0.247	−0.279	3.200	0.002	0.000
0.280	−0.094	−0.129	3.400	0.001	0.000
0.300	0.062	0.026	3.600	0.000	0.000

TABLE IX. The $3p$ radial wave function P_{3p} as determined by the Hartree-Fock method and by the Slater approximation.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	0.000	0.000	0.400	−0.804	−0.837
0.005	0.006	0.006	0.450	−0.993	−1.024
0.010	0.022	0.023	0.500	−1.123	−1.149
0.015	0.047	0.047	0.550	−1.200	−1.221
0.020	0.078	0.078	0.600	−1.235	−1.250
0.025	0.113	0.114			
0.030	0.152	0.153	0.700	−1.212	−1.216
0.035	0.193	0.196	0.800	−1.115	−1.109
0.040	0.234	0.239	0.900	−0.986	−0.992
			1.000	−0.848	−0.831
0.050	0.317	0.325	1.100	−0.717	−0.697
0.060	0.395	0.406	1.200	−0.598	−0.577
0.070	0.465	0.478	1.300	−0.494	−0.474
0.080	0.524	0.540	1.400	−0.405	−0.386
0.090	0.572	0.589			
0.100	0.601	0.625	1.600	−0.269	−0.252
			1.800	−0.176	−0.162
0.120	0.642	0.659	2.000	−0.114	−0.103
0.140	0.632	0.646	2.200	−0.073	−0.065
0.160	0.583	0.592	2.400	−0.047	−0.041
0.180	0.503	0.508	2.600	−0.030	−0.026
0.200	0.400	0.399	2.800	−0.019	−0.018
0.220	0.281	0.274	3.000	−0.012	−0.008
0.240	0.152	0.139	3.200	−0.007	−0.005
0.260	0.018	0.001	3.400	−0.004	−0.003
0.280	−0.116	−0.140	3.600	−0.002	−0.001
0.300	−0.249	−0.276	3.800	−0.001	
			4.000		
0.350	−0.554	−0.586			

TABLE X. The $3d$ radial wave function P_{3p} as determined by the Hartree-Fock method and by the Slater approximation.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	0.000	0.000	0.600	0.991	1.032
0.005	0.000	0.000			
0.010	0.000	0.000	0.700	0.978	1.004
0.015	0.001	0.001	0.800	0.937	0.949
0.020	0.002	0.002	0.900	0.882	0.882
0.025	0.003	0.003	1.000	0.821	0.811
0.030	0.005	0.006	1.100	0.759	0.740
0.035	0.008	0.008	1.200	0.698	0.673
0.040	0.011	0.012	1.300	0.639	0.610
			1.400	0.585	0.552
0.050	0.019	0.022			
0.060	0.030	0.035	1.600	0.488	0.450
0.070	0.044	0.050	1.800	0.406	0.367
0.080	0.061	0.069	2.000	0.337	0.298
0.090	0.080	0.090	2.200	0.279	0.242
0.100	0.101	0.114	2.400	0.231	0.197
			2.600	0.191	0.160
0.120	0.149	0.168	2.800	0.158	0.130
0.140	0.203	0.228	3.000	0.130	0.105
0.160	0.261	0.292	3.200	0.107	0.085
0.180	0.321	0.359	3.400	0.088	0.068
0.200	0.382	0.425	3.600	0.072	0.055
0.220	0.442	0.491	3.800	0.059	0.044
0.240	0.501	0.554	4.000	0.049	0.035
0.260	0.557	0.614			
0.280	0.610	0.670	4.500	0.029	0.019
0.300	0.660	0.723	5.000	0.018	0.008
			5.500	0.010	0.002
0.350	0.770	0.834	6.000	0.006	0.000
0.400	0.855	0.918			
0.450	0.917	0.977	7.000	0.002	0.000
0.500	0.958	1.013	8.000	0.001	0.000
0.550	0.981	1.030			

the actual value corresponding to the Slater method by more than 0.05.

By considering the differences between the initial function $W(r)^{(2)}$ for the second cycle and the initial function $W(r)^{(4)}$ for the third cycle, and the differences in the energies found for these cycles, one can make rough estimates of the uncertainties in the energies reported for the third cycle. The $W^{(2)}$, $W^{(4)}$ difference is of the same nature as the $W^{(4)}$, $W^{(6)}$ difference, but is approximately ten times as large. Therefore, one might expect a change in the energies corresponding to a fourth cycle to be about one-tenth of the change in the eigenvalues from the second to third cycle. For example, the $3d$ energy for the second cycle was -0.855 and for the third cycle it was -1.353, a change of about 0.50. According to the above, one might expect the change in the $3d$ energy for a fourth cycle to be about one-tenth of this difference or about 0.05 which is just what the perturbation arguments have indicated. In Table XIV are given the electronic energies and their corresponding uncertainties so determined. These uncertainties are to be interpreted as follows: The actual energy of a given level as determined by the Slater method will be more positive than the reported value by approximately the stated uncertainty.

Let us now examine the behavior of the common potential $W(r)/r$ which results from the free electron gas model of the exchange charge density. This quantity is given as

$$W(r)/r=[2Z_p+z(r)]/r$$

$$=\frac{2Z}{r}-\frac{2}{r}\sum_{nl}2(2l+1)\left\{\int_0^r P_{nl}{}^2dr+r\int_r^\infty\frac{P_{nl}{}^2}{r'}dr'\right\}+\frac{6}{r}\left\{\frac{3}{32\pi^2}\sum_{nl}2(2l+1)rP_{nl}{}^2\right\}^{\frac{1}{3}},\qquad(26)$$

where Z is the atomic number. For large r, $W(r)/r$ approaches $2C/r$, where C is the net charge on the atom or ion being considered. This implies that an electron located outside the charge cloud of a singly ionized atom would move in a potential field of $2/r$ in atomic units. This is quite wrong, for such an electron experiences the field set up by the nuclear charge and $n-1$ electrons. Therefore, such an electron moves in a field which varies as $4/r$. This incorrect behavior arises because the exchange term as found by the free electron approximation goes to zero at large r. We recall that the exchange term not only represents the interaction of an electron with its exchange charge density but also corrects for the fact that an electron does not act on itself.

In the case of Cu^+ one would expect the incorrect behavior of the potential to have the greatest effect on the $3d$ states as they are the most extended. If one examines the table of total radial charge density, Table XI, it is apparent that very little charge lies outside a sphere of radius 1.68. Also the $3d$ electrons spend 92 percent of the time inside a sphere of this radius. One can conclude that almost the entire character of the 3*d* wave function will be determined by the physical properties of the ion which depend on values of r less than 1.68. The quantity $W(r)/r$ at $r=1.68$ is 4.25 and, therefore, only about 8 percent of the time do the outermost electrons move in a potential field which is less than $4/r$. One may surmise, therefore, that the incorrect asymptotic behavior of the total potential function will have only a small effect on the eigenfunctions and corresponding eigenvalues. This appears to be borne out by the results of the calculation.

TABLE XI. The total radial charge density in atomic units, $U(r)=\Sigma_{nl}2(2l+1)P_{nl}(r)^2$, for the Hartree, Hartree-Fock, and the Slater methods.

r	Hartree	Hartree-Fock	Slater	r	Hartree	Hartree-Fock	Slater
0.000	0.00	0.00	0.00	0.500	19.22	20.89	22.184
0.005	3.9	3.9	3.9	0.550	20.53	22.17	23.365
0.010	11.7	11.7	11.7	0.600	21.16	22.74	23.737
0.015	19.7	19.7	19.7				
0.020	26.3	26.3	26.42	0.700	20.45	21.70	22.266
0.025	31.0	31.0	31.05	0.800	18.02	18.89	19.053
0.030	33.7	33.7	33.74	0.900	15.02	15.54	15.422
0.035	34.9	34.9	34.93	1.000	12.17	12.39	12.086
0.040	34.8	34.8	34.90	1.100	9.72	9.72	9.307
				1.200	7.75	7.57	7.114
0.050	32.7	32.8	32.91	1.300	6.21	5.91	5.434
0.060	30.0	30.2	30.30	1.400	5.01	4.62	4.166
0.070	28.1	28.3	28.51				
0.080	27.4	27.7	27.99	1.600	3.37	2.89	2.490
0.090	27.9	28.3	28.69	1.800	2.35	1.86	1.531
0.100	29.4	29.9	30.30	2.000	1.69	1.21	0.963
				2.200	1.24	0.81	0.617
0.120	33.61	34.20	34.655	2.400	0.91	0.55	0.399
0.140	33.61	34.20	34.655	2.600	0.67	0.37	0.261
0.140	37.35	37.96	38.445	2.800	0.50	0.25	0.171
0.160	39.32	39.83	40.328	3.000	0.37	0.17	0.111
0.180	39.23	39.59	40.073	3.200	0.28	0.11	0.072
0.200	37.36	37.62	38.085	3.400	0.20	0.08	0.046
0.220	34.35	34.53	35.009	3.600	0.15	0.05	0.030
0.240	30.81	30.97	31.480	3.800	0.11	0.03	0.019
0.260	27.24	27.43	29.004	4.000	0.08	0.02	0.012
0.280	23.98	24.26	24.930				
0.300	21.26	21.67	22.451	4.500	0.03	0.00	0.004
				5.000	0.01	0.00	0.001
0.350	17.19	18.04	19.106	5.500	0.00	0.00	0.000
0.400	16.48	17.72	18.992	6.000	0.00	0.00	0.000
0.450	17.61	19.13	20.470	6.500	0.00	0.00	0.000

CONCLUSIONS

It is evident from the results presented that the Slater method is a rather accurate approximation of the Hartree-Fock solution to Cu^+. The energies found by the Slater method lie closer to the Hartree than Hartree-Fock values. Only the 1*s* and 3*d* levels show much real difference from the Hartree eigenvalues. The 1*s* energy as found by the Slater method is -649.53, more positive than the Hartree value of -658. This difference is most likely due to the failure of the exchange term to correct for the interaction of the 1*s* electrons with themselves, because the 1*s* electrons are concentrated in a region where the charge density due to the other electrons is quite small. The Slater 3*d* energy of -1.353 is somewhat of an improvement over the Hartree value of -1.195. This result indicates that Slater's exchange correction has not been a source of large error due to its incorrect behavior at large r.

TABLE XII. The charge outside a sphere of radius r due to the 3*p* electrons of Cu^+. This is given as $6(1-Z_{3p})$, and $Z_{3p}(r)$ is $\int_0^r P_{3p}(r)^2dr$.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	6.000	6.000	0.300	5.693	5.679
0.005	6.000	6.000			
0.010	6.000	6.000	0.350	5.641	5.620
0.015	6.000	6.000	0.400	5.500	5.464
0.020	6.000	6.000	0.450	5.254	5.201
0.025	6.000	6.000	0.500	4.945	4.843
0.030	5.999	5.999	0.550	4.507	4.419
0.035	5.998	5.998	0.600	4.061	3.958
0.040	5.997	5.997			
			0.700	3.150	3.033
0.050	5.992	5.992	0.800	2.331	2.216
0.060	5.984	5.984	0.900	1.666	1.564
0.070	5.975	5.972	1.000	1.161	0.999
0.080	5.959	5.956	1.100	0.794	0.725
0.090	5.941	5.937	1.200	0.535	0.482
0.100	5.920	5.915	1.300	0.356	0.317
			1.400	0.235	0.208
0.120	5.873	5.865			
0.140	5.823	5.813	1.600	0.100	0.085
0.160	5.779	5.767	1.800	0.042	0.035
0.180	5.743	5.730	2.000	0.017	0.014
0.200	5.718	5.705	2.200	0.007	0.005
0.220	5.704	5.692	2.400	0.003	0.002
0.240	5.698	5.686	2.600	0.001	0.001
0.260	5.697	5.685	2.800	0.000	0.000
0.280	5.697	5.685	3.000	0.000	0.000

TABLE XIII. The charge outside a sphere of radius r due to the 3*d* electrons of Cu. This is given as $10(1-Z_{3d})$, and $Z_{3d}(r)$ is $\int_0^r P_{3d}(r)^2dr$.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	10.000	10.000	0.350	9.39	9.27
0.005	10.000	10.000	0.400	9.06	8.88
0.010	10.000	10.000	0.450	8.67	8.43
0.015	10.000	10.000	0.500	8.23	7.94
0.020	10.000	10.000	0.550	7.76	7.41
0.025	10.000	10.000	0.600	7.27	6.88
0.030	10.000	10.000			
0.035	10.000	10.000	0.700	6.29	5.84
0.040	10.000	10.000	0.800	5.37	4.88
			0.900	4.54	4.04
0.050	10.000	10.000	1.000	3.82	3.20
0.060	10.000	10.000	1.100	3.19	2.73
0.070	10.000	10.000	1.200	2.66	2.27
0.080	10.000	10.000	1.300	2.21	1.82
0.090	10.000	10.000	1.400	1.84	1.50
0.100	10.000	10.000			
			1.600	1.27	0.98
0.120	9.99	9.99	1.800	0.87	0.65
0.140	9.99	9.99	2.000	0.59	0.42
0.160	9.98	9.97	2.200	0.41	0.28
0.180	9.96	9.95	2.400	0.28	0.18
0.200	9.93	9.92	2.600	0.19	0.12
0.220	9.90	9.88	2.800	0.13	0.10
0.240	9.86	9.82	3.000	0.09	0.06
0.260	9.80	9.76	3.200	0.06	0.03
0.280	9.73	9.67	3.400	0.04	0.02
0.300	9.65	9.56	3.600	0.02	0.01
			3.800	0.01	0.01
			4.000	0.01	0.00

TABLE XIV. The electronic energy levels as determined by the Hartree, Slater, and Hartree-Fock methods for Cu^+ together with the uncertainties in the values found for the Slater method. The unit of energy is the ionization energy of the hydrogen atom, $e^2/2a_0$.

nl	Hartree	Hartree-Fock	Slater	Uncertainty
$1s$	−658	−658.4	−649.5	0.1
$2s$	−78.45	−82.30	−78.92	0.16
$2p$	−69.86	−71.83	−69.50	0.13
$3s$	−8.986	−10.651	−8.822	0.03
$3p$	−6.078	−7.279	−6.279	0.06
$3d$	−1.195	−1.613	−1.353	0.05

From the table of total radial charge density one notes two points. First, the total radial charge density as found by the Slater method is more concentrated about the nucleus than the corresponding Hartree-Fock density, while the Hartree function is more spread out than the Hartree-Fock. Second, the values of this quantity found by the Slater method are more accurate than the Hartree method for large r.

A comparison of the Slater and Hartree-Fock radial wave functions for Cu^+ shows that the $1s$, $2s$, $2p$, and $3s$ functions are nearly the same. The $3p$ and $3d$ wave functions are more pulled in by the Slater method, but are generally within 5 percent of the Hartree-Fock values.

In the case of Cu^+ the total wave function can be written as a single determinant. The Slater approximation of the Fock equations only applies when the total wave function can be expressed in this manner. The simplification of the more general Fock equations and the consequences of incorrectly expressing a total wave function as a single determinant are questions which remain to be investigated.

As a general appraisal of the Slater method as applied to Cu^+ it can be said that it yields wave functions which are an improvement over the Hartree functions. The electronic energy levels are about equal to the Hartree results with poorer values for the innermost electrons and better values for the outermost electrons. The purpose of the Slater method is, of course, to make the task of finding fairly reliable eigenfunctions and eigenvalues easier than that of the Hartree-Fock method in those cases where such a simplification is applicable. In view of the fact that the Slater method requires less work than the Hartree method and is a slight improvement over that method, it appears that the Slater method merits thorough consideration when one is investigating atomic structure. One can also conclude from these results that the Slater method should be of considerable use in the investigation of crystal problems.

TABLE XV. The $2Z_p(r)$ function as determined by the Hartree-Fock method and as found by the Slater method. The product of r times $2Z_p(r)$ is the total electrostatic potential of the atom at a distance r from the nucleus.

r	Hartree-Fock	Slater	r	Hartree-Fock	Slater
0.000	58.00	58.000	0.450	16.00	15.288
0.010	55.35	55.322	0.500	14.13	13.412
0.020	52.92	52.863	0.550	12.47	11.759
0.030	50.75	50.662	0.600	11.01	10.317
0.040	48.80	48.686			
0.050	47.02	46.885	0.700	8.65	8.007
0.060	45.38	45.217	0.800	6.91	6.334
0.070	43.84	43.651	0.900	5.64	5.139
0.080	42.38	42.167	1.000	4.72	4.270
0.090	40.99	40.753	1.100	4.05	3.684
0.100	39.66	39.403	1.200	3.56	3.245
			1.300	3.19	2.935
0.120	37.18	36.886	1.400	2.91	2.740
0.140	34.94	34.597			
0.160	32.91	32.528	1.600	2.55	2.409
0.180	31.07	30.660	1.800	2.34	2.247
0.200	29.42	28.970	2.000	2.21	2.144
0.220	27.91	27.433	2.200	2.13	2.088
0.240	26.54	26.023	2.400	2.08	2.053
0.260	25.26	24.719	2.600	2.05	2.032
0.280	24.07	23.501	2.800	2.03	2.021
0.300	22.95	22.354	3.000	2.02	2.012
			3.200	2.01	2.006
0.350	20.38	19.733	3.400	2.00	2.004
0.400	18.08	17.391			

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