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Representation of the Exchange Terms in Fock's Equations by a Quasi-Potential*

D. R. HARTREE
Cavendish Laboratory, Cambridge, England
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Fock's equations for the (*nl*) wave functions of an atom can be expressed in the form of Schrödinger's equation for a single particle by including in the potential energy a term $\eta(nl;r)$ expressing the "exchange" terms in the equation. As a further approximation, this term can be replaced by some average over the various (*nl*) wave functions. This "exchange" contribution to the potential is evaluated for the (*nl*) wave functions of Cu^+, and an appropriate mean is compared with the "averaged exchange potential," based on the statistical model, suggested by Slater and used by Pratt in calculations for Cu^+. It is found that the range of variation of $\eta(nl;r)$ with (*nl*) is of the order of a factor 2, so that its replacement by an average over (*nl*) is only a rough way of treating exchange effects.

IN the approximation to a many-electron atom expressed by the term "self-consistent field with exchange," the equation for the (*nl*) radial wave function $P(nl;r)$ can be written

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}Y(nl;r)-\epsilon_{nl,\,nl}-\frac{l(l+1)}{r^2}\right]P(nl;r)=X(nl;r), \quad (1)$$

where $r^{-1}Y(nl;r)$ is the potential function used in evaluating that wave function, and $X(nl;r)$ is the "exchange" term for that wave function. These equations, for the set of wave functions of an atomic configuration, are called Fock's equations. In the equation for $P(nl;r)$ the function $r^{-1}Y(nl;r)$ differs from the total potential $r^{-1}Y(r)$ at radius r, first through the omission of the contribution $r^{-1}Y_0(nl;nl;r)$ from one electron in the (*nl*) group to which the equation refers, and secondly, for $l\neq 0$, through inclusion of some terms $r^{-1}Y_k(nl;nl;r)$ with $k\neq 0$, arising partly from the departure of the (*nl*) wave functions from spherical symmetry and partly from exchange within the (*nl*) group.

Equation (1) can be written

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}Y(r)+2\eta(nl;r)-\epsilon_{nl,\,nl}-\frac{l(l+1)}{r^2}\right]\times P(nl;r)=0, \quad (2)$$

where $r^{-1}Y(r)$ is the total potential at radius r and is the same for all (*nl*) functions and

$$2\eta(nl;r)=\frac{2}{r}[Y(nl;r)-Y(r)]-\frac{X(nl;r)}{P(nl;r)}. \quad (3)$$

If $\eta(nl;r)$ were replaced by a function $\eta(r)$ independent of (*nl*), the calculation of atomic structures would be reduced to the solution of a homogeneous differential equation (2) in which the potential term in the operator in square brackets is the same for all wave functions, so that those of the same l value would be orthogonal (as contrasted with those of the self-consistent field without exchange which are not orthogonal). The solution of this set of equations would be much simpler and shorter than the solution of Fock's equation (1), which are essentially integro-differential equations.

The function $\eta(r)$ can be regarded as a way of expressing the effect of exchange approximately by means of a quasipotential which is a function of the local value of r only [as contrasted with an integral over the whole range of r as in Eq. (1)]. Slater[1] has given an argument which suggests that an approximation to such a quasipotential is given by

$$2\eta(r)=\frac{6}{r}\left[\frac{3r}{32\pi^2}\sum_{nl}2(2l+1)P^2(nl;r)\right]^{\frac{1}{3}} \quad (4)$$

[see Pratt[2]; Pratt's $z(r)$ is r times the quantity termed the "averaged exchange potential"; $z(r)/r$ corresponds to the quantity $2\eta(r)$ in Eq. (2)]. This formula (4) was used by Pratt[2] in a calculation for Cu^+, the heaviest ion for which results of calculations of the self-consistent

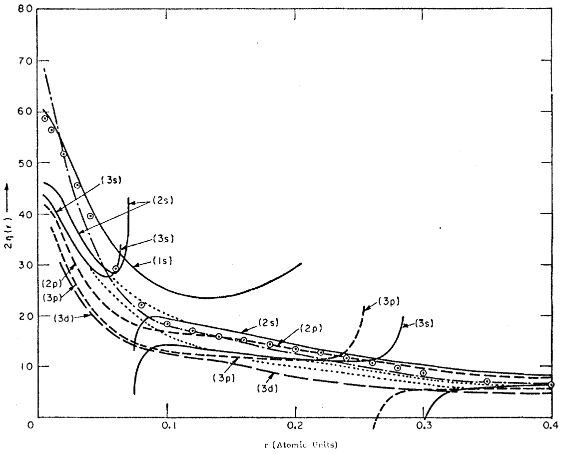

FIG. 1. Exchange quasi-potential $\eta(nl;r)$ for the various (*nl*) wave functions of Cu^+. Ringed points show values of mean η given by formula (7) of text. Dot-dash curve shows "average exchange potential" used by Pratt.

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[1] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[2] G. W. Pratt, Phys. Rev. **88**, 1117 (1952); see formula 7.

field both with exchange[3] and without exchange[4] were available at the time.

The working sheets of W. Hartree's calculations with exchange for Cu$^+$ have been preserved, and it seems of interest to obtain the functions $\eta(nl;r)$ given by formula (3) from these calculations, both to examine the extent of the actual variation of this function with (nl) and to see how an appropriate mean of these functions differs from the function (4) used by Pratt in his calculations.

The results of such an examination are shown in Figs. 1 and 2, Fig. 1 referring to the range $r=0$ to 0.4, and Fig. 2 giving, on different scales of r and of $\eta(nl;r)$, the results from about $r=0.3$ to 2; beyond $r=2$, the wave functions are too small to give significant values of $\eta(nl;r)$. The full curves give the functions $\eta(nl;r)$ for the (ns) wave functions, the broken curves those for the (np) and the $(3d)$ functions. The dot-dash curve in Figs. 1 and 2 gives the "averaged exchange potential" (4) used by Pratt. Pratt gives in his paper[2] a table of $U(r)=\sum_{nl}2(2l+1)P^2(nl;r)$. A convenient form of formula (4) for numerical evaluation is

$$2\eta(r)=[2.0518U(r)/r^2]^{\frac{1}{3}}. \tag{5}$$

It is not to be expected that the total exchange term $\eta(nl;r)$ in Eq. (1) for each (nl) will have nodes exactly at the nodes of $P(nl;r)$, though it is found empirically that each node of $P(nl;r)$ has a node of $X(nl;r)$ near it. The curve of $\eta(nl;r)$ has a vertical asymptote at a node of $P(nl;r)$ [unless a node of $X(nl;r)$ happens to coincide with it]; the branches of the curve of $\eta(nl;r)$ on either side of such a singularity have been joined by a dotted line in Figs. 1 and 2.

It will be seen that for fixed r the variation of $\eta(nl;r)$ with (nl) covers a range of the order of 2:1, so that its replacement by some average over (nl) is only a rather rough way of treating the effects of exchange on atomic structures. In discussion of these results, Slater suggested that if one did want to use such an average, $\bar{\eta}(r)$, the appropriate average would be the mean weighted according to the local electron density of electrons in the different (nl) groups, that is,

$$\bar{\eta}(r)=\frac{\sum_{nl}(2l+1)\eta(nl;r)P^2(nl;r)}{\sum_{nl}(2l+1)P^2(nl;r)}, \tag{6}$$

for a configuration consisting of complete groups only. The values of this function, at various values of r, are indicated in Figs. 1 and 2 by ringed points. The values of this function differ only slightly, except for large r, from the function (4) used by Pratt. A closer comparison between the function $2\bar{\eta}(r)$ [formula (6)] and Pratt's function $2\eta(r)$ [formula (5)] is given in Table I.

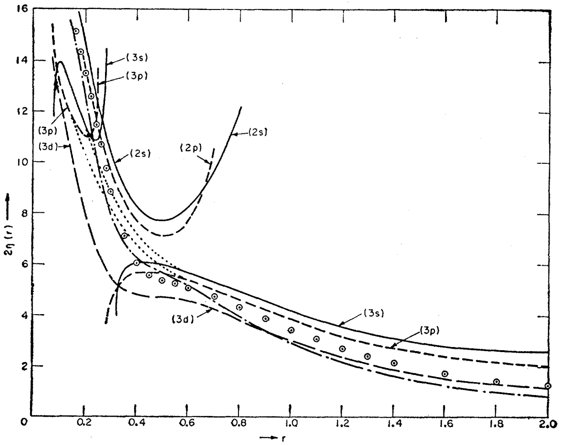

FIG. 2. Exchange quasi-potential $\eta(nl;r)$ for the various (nl) wave functions of Cu$^+$. Ringed points show values of mean η given by formula (7) of text. Dot-dash curve shows "average exchange potential" used by Pratt.

TABLE I. Cu$^+$. Averaged exchange potential.

r (atomic units)	$2\bar{\eta}(r)$ formula (6)	$2\eta(r)$ (Pratt)	r (atomic units)	$2\bar{\eta}(r)$ formula (6)	$2\eta(r)$ (Pratt)
0.005	58.6	68.4	0.7	4.73	4.53
0.01	56.7	62.1	0.8	4.30	3.94
0.02	51.7_5	51.4	0.9	3.85	3.39
0.03	45.5_5	42.5	1.0	3.42	2.92
0.04	39.6	35.5	1.1	3.04	2.52
0.06	29.3	25.8	1.2	2.70	2.17
0.08	22.1_5	20.8	1.3	2.41	1.88
0.10	18.4	18.4	1.4	2.15	1.63
0.12	16.9_5	17.0	1.6	1.74	1.26
0.140	15.9	15.9	1.8	1.45	0.99
0.16	15.1	14.8	2.0	1.24	0.79
0.18	14.3	13.6	2.2	1.07	0.64
0.20	13.5	12.5	2.4	0.95	0.52
0.22	12.5_5	11.4	2.6	0.85	0.43
0.24	11.6	10.4	2.8	0.78	0.35
0.26	10.7	9.5			
0.28	9.7	8.7			
0.30	8.7_8	8.00			
0.35	7.0_7	6.84			
0.40	6.0_0	6.25			
0.45	5.5_5	5.92			
0.50	5.3_6	5.67			
0.55	5.2_3	5.41			
0.60	5.08	5.13			

It seems from this examination that the rather disappointing character of Pratt's results, from the point of view of providing an approximation to the solution of Fock's equations (1) by use of an "averaged exchange potential" (5), must be ascribed to the considerable variation of $\eta(nl;r)$ with (nl), which is discarded in using such an averaged exchange potential.

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[3] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **157**, 490 (1936).

[4] D. R. Hartree, Proc. Roy. Soc. (London) **141**, 282 (1933).