Variable Scale Atomic Wave Functions

J. P. VINTI* AND P. M. MORSE, *Massachusetts Institute of Technology*

(Received January 5, 1933)

In the study of complex atomic spectra by the methods of Slater and Condon, it is desirable that one have a complete set of orthogonal wave functions more nearly correct than the hydrogenic ones. A set of variable-scale wave functions is described in this paper and applied to some simple cases. They are hydrogenic functions of a function of the radius, such that close to the nucleus they behave like the wave functions about a charge Ze and far from the nucleus they behave like the wave function about a charge e. The scale function is chosen so that the integrals arising in calculation can be handled analytically. These functions are not so accurate as the analytic representations of the Hartree functions, but they form a complete orthogonal set, and thus can be used for perturbation problems.

IN The study of complex spectra by the methods of Slater and Condon one needs electronic wave functions which are as nearly correct as possible. The success of the method requires that those nondiagonal terms of the energy matrix corresponding to a change of total quantum number be negligibly small, which in turn requires that the radial parts of the wave function approximate fairly closely to the correct form.

Hydrogenic wave functions are often used, because they form a complete orthogonal set of functions which are possible to handle analytically. However, the correct wave functions differ considerably from the hydrogenic ones, since the effective field on the electron is not a simple coulomb field. A good set of functions to use is the set of analytic representations of the Hartree functions; these can be handled analytically, but they do not form a complete orthogonal set.

The subject of this paper is the investigation of a set of functions which do not correspond to the correct functions as closely as the Hartree ones, but which form a complete orthogonal set which can be handled analytically, and which are much more nearly correct than the hydrogenic type of functions.

The reasoning used in obtaining these functions is somewhat as follows. The effective field on an atomic electron is, to the Hartree approximation, a spherically symmetric coulomb field with an effective nuclear charge which is a function of the distance from the nucleus. The nuclear charge fixes the scale of a hydrogenic wave function. Therefore a hydrogenic wave function whose scale is a function of the distance from the nucleus will be one which corresponds fairly closely to the correct form. A few preliminary tests are made here on this type of wave function to demonstrate its convenience.

THE WAVE FUNCTION

The effective potential V on the electron is spherically symmetric (to the Hartree approximation). The angular factors of the wave function are therefore the usual normalized tesseral harmonics of order m, l, which occur in the hydrogen problem. The behavior of the radial factor S is best expressed by means of the equation for $R \equiv \rho S$ (where ρ is the radial distance in atomic units). This equation is:

$$\frac{d^2R}{d\rho^2}+\left[W-V-\frac{l(l+1)}{\rho^2}\right]R=0,$$

where the energy terms are also in atomic units. The potential V approaches the form $-2Z/\rho$ for small values of ρ and becomes $-2/\rho$ for large values of ρ (Ze is the nuclear charge). If $V=-2Z/\rho$ for all values of ρ, then the characteristic solutions of this equation would be the radial hydrogenic functions, multiplied by ρ:

$$Z^{\frac{1}{2}}N_\rho(2Z\rho/n)^{l+1}e^{-Z\rho/n}L_{n+l}{}^{2l+1}(2Z\rho/n),$$

where $L_{n+l}{}^{2l+1}(x)$ is the $(2l+1)$th derivative with respect to the argument x of the Laguerre poly-

* At present Harrison Research Fellow in Physics, University of Pennsylvania.

nomial of order $n+l$, and N_ρ is a normalizing factor $\{(n-l-1)!/n^2[(n+l)!]^3\}^{\frac{1}{2}}$.

However V is not equal to $-2Z/\rho$ for all values of ρ, and we allow for this by letting the scale factor Z change with ρ. Let x be a function of ρ which has the form $x=Z\rho$ when ρ is small and $x=\rho$ when ρ is large. Let $F(x)$ be the function:

$$(2x/n)^{l+1}e^{-x/n}L_{n+l}{}^{2l+1}(2x/n).$$

Then the function $S(x)=(N_\rho/\rho)(dx/d\rho)^{\frac{1}{2}}F(x)$ is normalized. Also, if x is now a function of ρ containing parameters which are the same for all values of n, $S(n_i)$ will be orthogonal to $S(n_j)$:

$$\int_0^\infty S(n_i)S(n_j)\rho^2 d\rho=\int_0^\infty F(n_i)F(n_j)dx=0,\ n_i\neq n_j.$$

If we can now show that S as defined above is a good approximate solution of the radial equation, the problem of determining the wave function of an atom in any stationary state becomes simply one of determining the parameters in the function $x(\rho)$. For later convenience in calculation it turns out to be advisable to write ρ as an explicit function of x, $\rho=\rho(x)$, rather than to write $x(\rho)$. Now $F(x)$ satisfies the differential equation:

$$\frac{d^2F}{d\rho^2}+\frac{\rho''}{\rho'}\frac{dF}{d\rho}+\left[-\frac{1}{n^2\rho'^2}+\frac{2}{x\rho'^2}-\frac{l(l+1)}{x^2\rho'^2}\right]F=0.$$

Since $R=N_\rho F\rho'^{-\frac{1}{2}}$, R satisfies the equation:

$$\frac{d^2R}{d\rho^2}+\left[\frac{\rho'''}{\rho'^2}+\frac{\rho''}{\rho'}\right]\frac{dR}{d\rho}+\left[\tfrac{1}{2}\frac{\rho'''}{\rho'^3}-\tfrac{1}{4}\frac{\rho''^2}{\rho'^4}\right]R+\left[-\frac{1}{n^2\rho'^2}+\frac{2}{x\rho'^2}-\frac{l(l+1)}{x\rho'^2}\right]R=0.$$

Comparing with the exact equation for R, and taking $-1/(n^2\rho'^2)$ to correspond to W, $-2/(x\rho'^2)$ to V and $l(l+1)/(x\rho'^2)$ to the angular momentum term $l(l+1)/\rho^2$, we see that the approximate equation (of which $\rho'^{-\frac{1}{2}}F(x)$ is an exact solution) contains extra terms: $[(\rho'''/\rho'^2)+(\rho''/\rho')]dR/d\rho$ and $[(1/2)(\rho'''/\rho'^3)-(1/4)(\rho''^2/\rho'^4)]R$. Their presence is not necessarily serious, since the correspondence of the above-mentioned terms to energy, potential, and angular momentum is only approximate, and their presence may actually compensate for this discrepancy, if the parameters in the function are chosen properly.

Thus we have obtained a complete orthogonal set of functions which can be handled analytically if ρ is a simple enough function of x. Presumably a form of ρ can be found which makes R exactly correct, but this form would be so complicated that the functions could not be used. We must sacrifice some accuracy to gain expediency.

According to our discussion of the variation of effective nuclear charge with ρ, we see that ρ must be equal to x/Z for small values of ρ and be equal to x for large values. A function which possesses these properties, and which also makes the various integrals needed amenable to calculation is the following:

$$\rho=x\left[1+\frac{(1/Z)-1}{1+x/c}\right].$$

For this function the various integrals can be expressed in terms of exponentials and integral-logarithms of exponentials.

There remains the parameter c to be fixed so that the set of functions correspond as well as possible to the correct set. This c, once determined, must be the same for all the functions in the set in order that these functions be mutually orthogonal. Its value can be fixed for the problem at hand by various methods, of which two are illustrated in the succeeding section.

Some Applications

One method of fixing the parameter c is by a variational method, giving c the value for which the normal energy is a minimum. For instance, for helium, the energy operator in atomic units is:

$$H=-\nabla_1{}^2-\nabla_2{}^2-\frac{4}{\rho_1}-\frac{4}{\rho_2}+\frac{2}{\rho_{12}}.$$

The wave function to be used is $\Psi=Y_1Y_2S(x_1)\times S(x_2)$, where the S's are those discussed earlier (in this case for the normal state) the Y's are constant angular factors, and the x's are related to the ρ's by the equation given above. We then fix c so that

$$I\equiv\int\bar{\Psi}H\Psi d\tau_1 d\tau_2$$

is a minimum. We find for I the expression $I=I_T+I_V+I_{12}$, where

$$I_T=-2\int_0^\infty S\frac{d}{d\rho}\left(\rho^2\frac{dS}{d\rho}\right)d\rho=-8\int_0^\infty\frac{x^2e^{-2x}}{\rho'^2}\left[1-\frac{2}{x}-\frac{7}{4}\left(\frac{\rho''}{\rho'}\right)^2+\frac{\rho'''}{2\rho'}\right]dx,$$

$$I_V=-8\int_0^\infty S^2\rho d\rho=-8\int_0^\infty\frac{F^2(x)}{\rho}dx,$$

$$I_{12}=2\int\frac{Y_1^2Y_2^2S_1^2S_2^2}{\rho_{12}}d\tau_1d\tau_2=64\int_0^\infty x_1^2e^{-2x_1}\int_{x_1}^\infty\frac{x_2^2e^{-2x_2}}{\rho_2}dx_2.$$

Using the relation between ρ and x, we find:

$$I_V=-8[1+c+c^2Ei(-c)],$$

$$I_{12}=\tfrac{1}{4}(5+2c)+4c^2e^cEi(-c)-2c^2e^{2c}Ei(-2c)(c^2-2c+2)+\tfrac{1}{2}c^2(5-2c).$$

I_T is too cumbersome an expression to set down here; its values are given in Table I.

In carrying out the integration of I_{12}, it was found useful to derive a general formula for

$$I_n(\alpha,c)\equiv\int_c^\infty y^ne^{-\alpha y}Ei(-y)dy.$$

Since this may be useful, we give it here:

$$\alpha^{n+1}I_n(\alpha,c)=Ei(-c)n!e^{-\alpha c}\sum_{j=0}^{n}\frac{(c\alpha)^j}{j!}-n!Ei\{-(\alpha+1)c\}+n!e^{-(\alpha+1)c}\sum_{j=1}^{n}\frac{1}{j}\left(\frac{\alpha}{\alpha+1}\right)^j\sum_{\nu=0}^{j-1}\frac{c^\nu(\alpha+1)^\nu}{\nu!}\quad(n\neq0)$$

$$\alpha I_0(\alpha,c)=E_i(-c)e^{-\alpha c}-Ei\{-(\alpha+1)c\}.$$

A plot of I against c shows that $c=4$ is very close to the minimum; we thus take $c=4$, and obtain -5.69 atomic units as the energy of the normal state of helium (to be compared with the experimental value -5.81 atomic units). The Hartree method gives -5.75[1] *Rh.* However, we are not expecting to obtain as good answers as Hartree obtains, but are expecting to get ones better than hydrogenic functions give. This is true, for the hydrogenic functions give -5.5 atomic units for the energy.

TABLE I.

c	$-(I_v+I_{12})$	I_T	$I\equiv I_T+I_v+I_{12}$
1	9.642	4.245	−5.39
2	10.667	5.076	−5.59
3	11.241	5.578	−5.663
4	11.614	5.922	−5.692
5	11.879	6.204	−5.675

[1] Gaunt, Proc. Camb. Phil. Soc. **24**, 328 (1928).

We now give a few checks of our function. It is a consequence of the virial theorem of quantum mechanics, that, for a discrete state of a system with a coulomb potential, the mean potential energy is equal to twice the mean kinetic energy with reversed sign. In our case this means that the exact wave function would give for the ratio $-\frac{1}{2}(I_v+I_{12})/I_T$ the value unity. For $c=4$, we actually obtain the value 0.98 for this ratio (1.008 for $c=3$ and 0.957 for $c=5$).

The diamagnetic susceptibility[2] of helium, since it is a monatomic gas, is given by a universal constant times $\Sigma_i(\rho_i^2)_{00}$. In order to facilitate comparison with experiment we express the measured susceptibility as $\Sigma_i(\rho_i^2)_{00}$ in atomic units. The latter, according to the measurements of Hector and Wills,[3] has the value 2.34.

[2] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, p. 206, Eq. (2), (Oxford, 1932).

[3] Hector and Wills, Phys. Rev. **24**, 418 (1924).

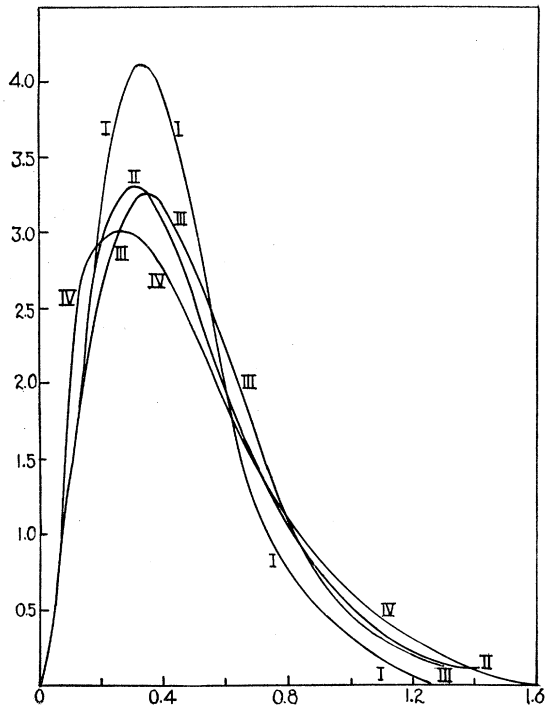

FIG. 1. Electron distribution in normal helium: electrons per Angstrom *vs.* radius in Angstroms. I. Compton-Barrett (from Compton's analysis of Barrett's data on x-ray scattering, II. Hartree, Slater, Hylleraas, III. Pauling, IV. Present method.

Calculation with our wave function gives

$$\sum_i (\rho_i^2)_{00} = (6-3c+5c^2/2-3c^3+7c^4+2c^5) + c^5 e^{2c} Ei(-2c)(16+4c),$$

which for $c=4$, has the value 2.82. The error is thus about 20 percent. It should be noted that, unlike ours, most wave functions for normal helium give too low a value for the susceptibility.

We now compare the electron distribution given by our wave function with that given by the functions of Pauling,[4] Slater[5] Hartree,[6] and Hylleraas,[7] and with that calculated by A. H. Compton,[8] by a Fourier analysis of Barrett's data on the scattering of x-rays by helium. Fig. 1 shows our curve ($U=8\pi\rho^2S^2$) and the other curves. Our curve, like the other curves calculated from wave functions, gives a maximum of about three electrons per Angstrom. The disagreement with the curve calculated from scattering data, which gives a maximum of about four electrons per Angstrom, is not to be looked on as serious, since the latter calculation involves a questionable extrapolation in the Fourier analysis.

However, the chief purpose of these wave functions is the calculation of multiplet separations and line intensities by the method of Slater. A rather severe test of their capabilities would be to compute the positions of the $(1s)(2s)^1S$ and $(1s)(2s)^3S$ levels of helium. This test is severe, because the effective electronic field in helium is probably the farthest from spherical symmetry of any atom, and also because for such a small nuclear charge the advantage of the variable-scale functions are not so apparent. For considerably larger values of Z the effective field departs considerably from a coulomb field, and we should expect a variable-scale function to be considerably better than a hydrogenic one.

It turns out that these functions give for $(1s)(2s)$ a singlet-triplet separation of $0.158Rh$ and the center of gravity of the two terms as $-4.201Rh$. The experimental values are $0.058\ Rh$ and $-4.321Rh$, while the values computed from hydrogenic functions are $0.161Rh$ and $-4.08Rh$. The check is not particularly good, but is better than that for the hydrogenic functions. Perhaps a different method of choosing c would give a better check.

Another method of choosing c is to fit the value of the intensity of radiation of a given line to the experimental value. This was done for the case of the D line in sodium ($3^2P\rightarrow 3^2S$). The value of A, the absolute spontaneous transition probability for this transition has been obtained by Minkowski[9] with a fair degree of accuracy; it is 0.64×10^8 sec.$^{-1}$. To obtain this value with wave functions of the type discussed here for $Z=11$, we must have $c=37$.

It is hoped that further calculations with these functions will demonstrate their utility more fully.

[4] L. Pauling, Proc. Roy. Soc. **A114**, 181 (1927).
[5] J. C. Slater, Phys. Rev. **32**, 349 (1928).
[6] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928).
[7] H. Bethe, Zeits. f. Physik **55**, 431 (1929).
[8] A. H. Compton, Phys. Rev. **35**, 925 (1930).
[9] Minkowski, Zeits. f. Physik **36**, 839 (1926).