The Normal Helium Atom

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A least-squares criterion for the goodness of approximate wave functions is proposed. The root-mean-square energy deviation for the six-term Hylleraas function is calculated to be 3.5 volts. It is shown that no ascending power series in the variables r_1, r_2 and r_{12} can be a formal solution of the Schrödinger equation.

THE problem of determining the Schrödinger eigenfunction and eigenvalue for the lowest state of helium is one of fundamental importance to the theory of atomic structure; if it were solved, we should know whether or not the present formulation of the nonrelativistic many-body problem is correct. The subject has received the attention of several writers, notably Slater,[1] Kellner[2] and Hylleraas.[3, 4, 5] Slater, by numerical methods, arrived at an eigenvalue for the atom and a charge density for an s-electron, but did not represent the wave function analytically; Kellner and Hylleraas used the Ritz variational procedure, in which one guesses at the form of the eigenfunction ψ and allows certain parameters to vary so as to minimize the integral $\int\psi H\psi d\tau$. The latest work on this by Hylleraas[5] resulted in an approximate eigenvalue lower than the experimental term value by an amount which could be attributed to relativistic effects.

The Ritz method results in an upper bound to the true eigenvalue; a lower bound has been sought by Weinstein[6, 7] and MacDonald.[8] Since their methods seem somewhat difficult to justify rigorously, we shall in the present paper try to show how a least-squares method can aid one in judging the relative merits of different approximate wave functions. In addition, we propose to prove that no eigenfunction of the Hylleraas type can be even a *formal* solution of the wave equation.

The method of least squares suggested by Boussinesq[9] consists in adjusting the constants in an approximating function ψ so as to make the integral $I=\int[H-E)\psi]^2d\tau$ as small as possible.[10] Let us set $(H-E)\psi=\epsilon\psi$, where ϵ will in general be a function of x, y and z. For any approximate eigenvalue E, $\epsilon(x, y, z)$ is an indication of how well the wave equation is satisfied at any point. The integral $I=\int\psi^2\epsilon^2d\tau$ may then be looked upon as a mean square energy deviation.[11] We shall calculate its value, using an eigenfunction due to Hylleraas.

For convenience in computation, the final eigenfunction given by Hylleraas in reference 4 will be used. A further refinement was made in reference 5, but the value of E was lowered by only 0.013 volt, so presumably the value of I would not be influenced much by such a change.

The wave function is, then, $\psi=\varphi(ks, kt, ku)$, where

$$\varphi(s, t, u)=e^{-s/2}[c_0+c_1u+c_5u^2+c_3s+c_4s^2+c_2t^2].$$

The variables are $s=r_1+r_2$, $t=-r_1+r_2$ and $u=r_{12}$; the constants are $c_0=1$, $c_1=0.0972$, $c_2=0.0097$, $c_3=-0.0277$, $c_4=0.0025$, $c_5=-0.0024$, and $k=(L/2M)=0.9089645$.

Since it is purely a routine matter to apply H to this wave function and to calculate $\int(H\psi)^2d\tau$, we shall give only the result. The value of this integral is 2.1115. If I be minimized[12] with respect to E, then $E=\int\psi H\psi d\tau$, and $I=\int(H\psi)^2d\tau-E^2$. The constants in ψ may now be varied to

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[2] G. W. Kellner, Zeits. f. Physik **44**, 91 (1927).
[3] E. A. Hylleraas, Zeits. f. Physik **48**, 469 (1928).
[4] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).
[5] E. A. Hylleraas, Zeits. f. Physik **65**, 209 (1930).
[6] D. H. Weinstein, Phys. Rev. **40**, 737 (1932); Phys. Rev. **41**, 839 (1932).
[7] D. H. Weinstein, Proc. Nat. Acad. Sci. **20**, 529 (1934).
[8] J. K. L. MacDonald, Phys. Rev. **43**, 830 (1933); Phys. Rev. **46**, 828 (1934).
[9] J. Boussinesq, *Theorie de la chaleur* (I), p. 316.
[10] We should like to express our appreciation to Mr. R. K. Cook for calling our attention to this method.
[11] One could, alternatively, weight the square of the deviation $\epsilon\psi$ to emphasize regions where the eigenfunction is large.
[12] This fixes the relation between E and the constants $c_0\cdots c_5$. Up to this point E can be assumed as independent of the constants.

make either E or I a minimum. (One would in general expect that E and I do not take on minimum values simultaneously, since the wave function used is only an approximate one.) We shall suppose it is E that is made a minimum. The value given by Hylleraas is $E=-1.45162\ Rh$, so that $I=0.0043$. It follows that $I^{\frac{1}{2}}=0.065\ Rh$, corresponding to about 3.5 electron volts. This root-mean-square deviation would vanish if the wave function were actually a solution of the differential equation.

One cannot, however, necessarily assert that the true eigenvalue lies about 3.5 electron volts below that calculated by Hylleraas. The r.m.s. deviation may be viewed simply as a measure of the goodness of the approximate wave function used. That is, if two different approximate functions should give the same value of E, then one would suppose that function with the smallest r.m.s. deviation to be the better of the two.

Since the actual deviation for some regions of space will in general be larger than the r.m.s. deviation, it seems to us that the above value of 3.5 electron volts is not small. It can be easily verified, in fact, that the deviation becomes *infinite* at any of the singularities, $r_1=0$, $r_2=0$, or $r_{12}=0$. The eigenfunction is thus probably very badly in error in the general neighborhood of any of these points. This prompts an investigation of the relationship of the function to the differential equation. It might seem that matters would be improved by using a power series instead of a polynomial (times an exponential factor). We shall now prove that no series in ascending powers of r_1, r_2 and r_{12} can be a formal solution of the wave equation.

For convenience, put $x=r_1$, $y=r_2$ and $z=r_{12}$. the wave equation is then:

$$\psi_{xx}+(2/x)\psi_x+\psi_{yy}+(2/y)\psi_y+2\psi_{zz}+(4/z)\psi_z$$
$$+[(x^2-y^2+z^2)/xz]\psi_{xz}+[(y^2-x^2+z^2)/yz]\psi_{yz}$$
$$+[(\lambda/4)+(1/x)+(1/y)-(1/2z)]\psi=0.$$

If we expand, $\psi=\sum_0^\infty c_{lmn}x^l y^m z^n$, substitute, and equate coefficients of powers, we find the recursion formula,

$$(l+2)(l+3+n)c_{l+2,\,m,\,n}$$
$$+(m+2)(m+3+n)c_{l,\,m+2,\,n}$$
$$+(n+2)(2n+6+l+m)c_{l,\,m,\,n+2}$$
$$-(l+2)(n+2)c_{l+2,\,m-2,\,n+2}$$
$$-(m+2)(n+2)c_{l-2,\,m+2,\,n+2}+(\lambda/4)c_{lmn}$$
$$+c_{l+1,\,m,\,n}+c_{l,\,m+1,\,n}-\tfrac{1}{2}c_{l,\,m,\,n+1}=0.$$

Substitution of various sets of values of l, m, and n will result in specific relationships enabling us to determine the c_{lmn}'s. We list a few as follows:

$$l=-1,\ m=2,\ n=-1\ ;\ c_{101}=0,$$
$$l=-1,\ m=0,\ n=0\ ;\ 2c_{100}+c_{000}=0,$$
$$l=1,\ m=0,\ n=-1\ ;\ 5c_{101}-\tfrac{1}{2}c_{100}=0.$$

Assuming that $c_{000}=1$, we thus obtain on the one hand $c_{101}=0$ and on the other $c_{101}=-(1/20)$. The fact that at least two inconsistent values of the same coefficient may be obtained means that the power series in question will not satisfy the differential equation, even formally.

In our opinion, the fact that a minimum value of E exists for functions of the Hylleraas type does not shut out the possibility that appreciably lower values of E may result from a use of functions which come closer to satisfying the differential equation. To improve the existing situation one may either construct functions with lower values of E and I, or else look for exact solutions. Attempts along the latter line are now being made. It turns out to be rather easy to find formal solutions, and whatever difficulties there are come in with the imposition of the boundary conditions.