On the Convergence of the Hylleraas Variational Method

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The result of Bartlett, Gibbons and Dunn, that the wave function for He cannot be expressed as a power series in the particle separations r_1, r_2, r_{12}, is discussed in relation to the validity of the Hylleraas variational attack. By a simple analogous example, it is shown that this result does not establish the impossibility of using polynomials in these variables to represent the function as closely as desired. It is further shown that if a formal solution of the wave equation for He exists, then the energy given by the Hylleraas method will converge upon the correct energy and the function will converge in the mean upon the correct function. Even if there exists no formal solution of the wave equation, there is a lower bound to the energy which can be computed with any function, and upon this bound the Hylleraas method will converge. In either case, therefore, the method is justified.

IN a recent article by Bartlett, Gibbons and Dunn,[1] doubt is expressed whether the limit approached by a variational attack upon the helium problem carried out with comparison functions of the Hylleraas type is necessarily identical with the absolute minimum of the energy computed with any function whatever. Expressing the wave function as

$$\psi = \sum_{lmn} a_{lmn} r_1^l r_2^m r_{12}^n,$$

they apply the operator $(H-E)$ to this series term by term. By rearranging terms they then express the wave equation as

$$(H-E)\psi = \sum_{lmn} F_{lmn} r_1^l r_2^m r_{12}^n = 0,$$

the F's being linear combinations of the as yet undetermined a's. If the wave equation is to be satisfied identically at every point, each of the coefficients F must vanish. This condition, however, is found to impose relations among the a's which cannot be satisfied by any set of finite numbers. (It is readily shown that precisely similar results are obtained if one takes ψ in the Hylleraas form,

$$\psi = \sum_{lmn} a_{lmn} r_1^l r_2^m r_{12}^n e^{-\delta(r_1+r_2)}.)$$

Since it is thus shown to be impossible for any Hylleraas series to be a formal solution of the wave equation, Bartlett, Gibbons and Dunn conclude that other forms of trial function in the variational process might give lower results.

The inadequacy of this treatment may be shown by a simple example. Consider the equation

$$y' + (\tfrac{1}{2} - 1/x)y = e^{-x/2}; \quad 0 \leqq x < \infty.$$

If we attempt to find a solution by assuming that

$$y = e^{-x/2} \sum a_n x^n$$

and substituting in the equation, we obtain an impossible condition on the coefficients, namely

$$\sum n a_{n+1} x^n = 1.$$

Yet it is possible to find a series of the form stated which will approximate the desired solution at every point within an arbitrarily small error. For, with the aid of the Laguerre orthogonal functions

$$\varphi_n(x) = (1/n!) e^{-x/2} L_n(x)$$

we can find the uniformly convergent series[2]

$$x \ln x e^{-x/2} = (1-C)\varphi_0 + (C-2)\varphi_1 + \varphi_2/1\cdot 2 + \varphi_3/2\cdot 3 + \cdots,$$

both sides of which satisfy the equation. Now, given any small error ϵ, we know that there is a finite number t of terms of the series which will represent the left side everywhere within ϵ, and these t terms can be rearranged into the form of the exponential times a polynomial in x of degree t. The reason why we may not regard this latter as a true expansion is that, as t is increased to improve the accuracy, the coefficients all increase without limit, instead of staying constant or approaching limits. However, this would not prevent us from determining the best t term approximation S_t by a suitable variation method, as, for example, minimizing $\int_0^\infty (y - S_t)^2 dx$.

In this case the reason why we cannot get a true expansion as a power series times an exponential is clearly because y' becomes infinite at the origin. We could, therefore, not safely use the "improper" expansion obtained above in any process involving differentiation. However, when we examine the helium function from the point of view suggested by this analogy, and identify the derivatives whose be-

[1] J. H. Bartlett, Jr., J. J. Gibbons, Jr., and C. G. Dunn, Phys. Rev. **47**, 697 (1935).

[2] The case satisfies the conditions stated in Madelung, *Die Mathematischen Hilfsmittel der Physiker*, third edition, p. 31.

havior is responsible for the failure of the expansion in a power series, we find that none of the derivatives which occur in the energy integral need be infinite at any point, but that two of them must have finite discontinuities at the origin. There seems to be nothing in this situation which need interfere with the setting up of "improper" expansions which can be used to calculate the integral as closely as desired.

To obtain the result just stated, we assume that an acceptable solution of the wave equation exists, and express it as a function of the variables r_1, r_2, r_{12}. The domain of these variables is bounded in part by three edges, along each of which one of the variables vanishes while the other two are equal to each other. The physical situation at such an edge is similar to that at the origin in the problem of two particles, and the wave function should be analytic in the vanishing coordinate, which corresponds to the radius vector in a local set of spherical coordinates. (The other coordinates should not give any trouble.) We therefore try the assumption that in the neighborhood of any point on an edge, with the possible exception of the origin, we may expand ψ in a multiple Taylor's series. Thus, if the point be $r_1=0$, $r_2=r_{12}=c$, and if the values at this point of ψ, $\partial\psi/\partial r_1$, $\partial\psi/\partial r_{12}$, $\partial^2\psi/\partial r_1^2$, $\partial^2\psi/\partial r_1\partial r_2$ be denoted respectively by ψ^0, $\psi_1{}^0$, $\psi_{12}{}^0$, $\psi^0{}_{1,\,1}$, $\psi^0{}_{1,\,2}$, etc., we have

$$\psi=\psi^0+\psi_1{}^0r_1+\psi_2{}^0(r_2-c)+\psi_{12}{}^0(r_{12}-c)+\tfrac{1}{2}\psi^0{}_{1,\,1}r_1{}^2+\cdots,$$

$$\partial\psi/\partial r_1=\psi_1=\psi_1{}^0+\psi^0{}_{1,\,1}r_1+\psi^0{}_{1,\,2}(r_2-c)+\psi^0{}_{1,\,12}(r_{12}-c)+\tfrac{1}{2}\psi^0{}_{1,\,1,\,1}r_1{}^2+\cdots,\text{ etc.}$$

The wave equation which ψ must satisfy is

$$0=-(H-E)\psi=\psi_{1,\,1}+\psi_{2,\,2}+2\psi_{12,\,12}+E\psi+[\psi+2\psi_1]/r_1+[\psi+2\psi_2]/r_2+[-\psi/2+4\psi_{12}]/r_{12}+[r_1{}^2-r_2{}^2+r_{12}{}^2]\psi_{1,\,12}/r_1r_{12}+[r_2{}^2-r_1{}^2+r_{12}{}^2]\psi_{2,\,12}/r_2r_{12}.$$

It is advantageous to introduce the new variables defined by the equations

$$r_1=u,\qquad r_2=c+v,\qquad r_{12}=c+v+\beta u\qquad(\beta^2\leqq 1),$$

thereby explicitly taking account of the limitation on the magnitude of r_2-r_1. The substitutions are made wherever r_1, r_2, r_{12} occur explicitly, but not in the derivatives. Then upon expanding $1/r_2$ and $1/r_{12}$ in positive powers of v and β and collecting terms, we find

$$\psi=\psi^0+\psi_1{}^0u+(\psi_2{}^0+\psi_{12}{}^0)v+\tfrac{1}{2}\psi^0{}_{1,\,1}u^2+(\psi^0{}_{1,\,12}+\psi^0{}_{1,\,2})uv+\psi_{12}{}^0u\beta+\cdots,$$

$$0=-(H-E)\psi=[\psi+2\psi_1]/u+\psi_{1,\,1}+\psi_{2,\,2}+2\psi_{12,\,12}+2\psi_{2,\,12}+E\psi+[\psi+4\psi_2+8\psi_{12}]/2c+2\psi_{1,\,12}\beta+\psi_{1,\,12}u/c-[\psi+4\psi_2+8\psi_{12}]/2c^2v+\cdots.$$

Upon inserting into the last equation the expansions of ψ and its derivatives, and again collecting terms, we obtain an expression which can vanish identically only if the coefficient of each combination of powers of u, v, β, vanishes separately. Thus, the term in u^{-1} gives $\psi^0+2\psi_1{}^0=0$, while that in β gives $\psi_{12}{}^0+4\psi^0{}_{1,\,12}=0$. There is no difficulty in finding finite values of ψ^0 and its derivatives which satisfy all the relations found in this way. If, now, we investigate the edge $r_{12}=0$, $r_1=r_2$, and remember that the function must be symmetrical with respect to r_1 and r_2, we obtain, among other relations, $\psi^0-8\psi^0{}_{12}=0$ and $\psi_1{}^0-8\psi^0{}_{1,\,12}=0$; and again all relations can be satisfied. When, however, we consider the origin, where the edges intersect, we find it impossible to satisfy both sets of relations at once. Thus, if we assign to ψ a given value ψ^0 at the origin, and assume that its first derivatives are everywhere continuous, then, as we approach the origin along the edge $r_1=0$, it must be that $\partial^2\psi/\partial r_1\partial r_{12}$ approaches the limit $-\frac{1}{32}\psi^0$, whereas if the approach is along the edge $r_{12}=0$ the limiting value is $-\frac{1}{16}\psi^0$. Symmetry requires the same behavior of $\partial^2\psi/\partial r_2\partial r_{12}$. Further examination shows that no other inconsistencies relating to the second derivatives are involved, and since the higher derivatives do not occur in $H\psi$ it is unnecessary to determine their behavior.

While this argument removes the objection raised against the Hylleraas method by Bartlett, Gibbons and Dunn, it does not, of course, establish the validity of that method. We shall now prove that if ψ is any piece-wise continuous single-valued function of r_1, r_2, and r_{12} such that

$$\int\psi^2d\tau=8\pi^2\int_0^\infty dr_1\int_0^\infty dr_2\int_{|r_1-r_2|}^{r_1+r_2}dr_{12}r_1r_2r_{12}\psi^2=1,$$

and if S_t is a sum of t terms in the form

$$S_t=\sum_{lmn}a_{lmn}r_1{}^lr_2{}^mr_{12}{}^ne^{-\delta(r_1+r_2)},$$

then, given any small positive number, ϵ, we can find a finite number t, and a set of finite coefficients a_{lmn}, such that

$$\int(\psi-S_t)^2d\tau<\epsilon.$$

Furthermore, if the Hermitian condition is satisfied ($\int\psi Hfd\tau=\int fH\psi d\tau$ for each term f in the Hylleraas series), then

$$\int(\psi H\psi-S_tHS_t)d\tau<\epsilon.$$

If a formal solution of the wave equation exists, it will (as we shall show) satisfy the Hermitian condition, and the Hylleraas process is therefore justified. We shall finally discuss the significance of the fact that we have no proof of the existence of such a formal solution.

In the simplest form of multiple expansion theory, we have a function $w(x, y, z)$ such that

$$\int_{G_x}dx\int_{G_y}dy\int_{G_z}dzw^2=1,$$

the domains G_x, G_y, G_z, being independent of each other. We can then get a root-mean-square expansion of w in products of the functions of

any three sets which are, respectively, complete normal orthogonal sets in x, y, and z, over the given domains. The problem of expanding ψ in a Hylleraas series is complicated by three circumstances—the terms in the series are neither normal nor orthogonal, the domains of the variables are not independent, and the normalizing condition contains an additional factor $r_1r_2r_{12}$. The first two considerations are easily handled, but the third is more troublesome.

If the form of the problem were not already fixed by the fact that we wish to justify a process which has been actually used, we might seek to avoid this difficulty by absorbing the troublesome factor in the function itself, just as we treat the one-electron problem by considering the radial function to be $r\psi$ instead of ψ. However, if we attempt to expand $\psi(r_1r_2r_{12})^{\frac{1}{2}}$ in a Hylleraas series and then find ψ by dividing out the radical, we obtain an expression which will not permit term-by-term evaluation of the energy integral, because the integrals of the separate terms diverge.

We may surmount the difficulty by using the following theorem: Let φ_n be the general example of a set of functions (of one or more variables) which are complete, normal, and orthogonal with respect to the integration $\int d\tau$. And let ρ be some function, defined within the domain of the φ's, which is nowhere negative and which has an upper bound R. Then, with respect to the integration $\int \rho d\tau$ the set of φ's is complete, though neither normal nor orthogonal. That is to say, given any piece-wise continuous function ψ such that $\int \psi^2 \rho d\tau$ converges, and given any small positive number ϵ, it is possible to set up S, a linear combination of a finite number of φ's, such that $\int (\psi - S)^2 \rho d\tau < \epsilon$.

To prove this, we choose some number η, such that $0 < \eta < R$, and divide the domain into two regions G and H, such that within G, $0 \leqq \rho \leqq \eta$, while within H, $\eta < \rho \leqq R$. Construct the function $\psi(\eta)$, which is equal to ψ in H, and to zero in G. Then

$$\int_{G+H} \psi^2(\eta) d\tau = \int_H \psi^2 d\tau$$

must converge, and $\psi(\eta)$ can be expanded in the φ's. That is, we can always find a finite number $p(\eta)$ such that

$$\int_{G+H} [\psi(\eta) - \sum_{n=0}^{p(\eta)} a_n(\eta)\varphi_n]^2 d\tau < \epsilon/4R,$$

and the a's will be the Fourier coefficients. We abbreviate the sum to $\sum(\eta)$. Then

$$\int_{G+H} [\psi(\eta) - \sum(\eta)]^2 \rho d\tau = \int_G [\sum(\eta)]^2 \rho d\tau + \int_H [\psi - \sum(\eta)]^2 \rho d\tau < \epsilon/4,$$

and this limit holds for each of the two integrals separately. Now, in order to obtain the integral

$$I(\eta) = \int_{G+H} [\psi - \sum(\eta)]^2 \rho d\tau,$$

we have to add the terms

$$\int_G \psi^2 \rho d\tau - 2\int_G \psi \sum(\eta) \rho d\tau.$$

By taking η small enough, but still not zero, we can always secure that the first of these terms will be less than $\epsilon/4$ (since $\int_{G+H} \psi^2 \rho d\tau$ is assumed to converge). By the Schwartz inequality, the absolute value of the second term cannot exceed $\epsilon/2$. Therefore $I(\eta) < \epsilon$, which is the desired proof of completeness of the φ's with respect to $\int \rho d\tau$. Note, however, that they are neither normal nor orthogonal for this integration, and the coefficients $a_n(\eta)$ are not the new Fourier coefficients. As the approximation is improved by taking η smaller and increasing the number of terms, the $a_n(\eta)$ will all change, and may even tend to infinity. This behavior can, of course, be rectified by transforming to the normal orthogonal combinations of the φ_n's, which can always be set up.

Returning to the He problem, we introduce new coordinates

$$x = \delta(r_1 + r_2 - r_{12}),$$
$$y = \delta(r_2 + r_{12} - r_1),$$
$$z = \delta(r_{12} + r_1 - r_2).$$

The normalizing condition satisfied by ψ is then

$$\int \psi^2 d\tau = (\pi^2/4\delta^6) \int_0^\infty \int_0^\infty \int_0^\infty \psi^2 (x+y) \times (y+z)(z+x) dx dy dz$$
$$= (\pi^2/4\delta^6) \int_0^\infty \int_0^\infty \int_0^\infty [\psi e^{\gamma(2x+y+z)}]^2 \times (x+y)(y+z)(z+x) e^{-2\gamma(2x+y+z)} dx dy dz = 1.$$

The conditions for applying our theorem are now satisfied if we take $0<\gamma<\frac{1}{2}$ and identify ρ with $(x+y)(y+z)(z+x)e^{-2\gamma(2x+y+z)}$, and we can obtain a root-mean-square expansion of $\psi e^{\gamma(2x+y+z)}$ in terms of any system of functions which are complete with respect to the integration $\int_0^\infty\int_0^\infty\int_0^\infty dxdydz$. Now, such a set can be constructed in the form $\xi_{pqr}=\varphi_p(2x(1-2\gamma))\varphi_q(y(1-2\gamma))\varphi_r(z(1-2\gamma))$, the φ's being Laguerre orthogonal functions. Hence

$$\int_0^\infty\int_0^\infty\int_0^\infty[\psi e^{\gamma(2x+y+z)}-\sum c_{pqr}\xi_{pqr}]^2 \times(x+y)(y+z)(z+x)e^{-2\gamma(2x+y+z)}dxdydz$$
$$=\int_0^\infty\int_0^\infty\int_0^\infty[\psi-\sum k_{fgh}x^fy^gz^he^{-(2x+y+z)/2}]^2 \times(x+y)(y+z)(z+x)dxdydz<\epsilon,$$

where all the coefficients are finite and the sums are all over a finite number of terms. On going back to the coordinates r_1, r_2, r_{12}, we obtain just the desired completeness relation for the functions of the Hylleraas approximation.

Upon introducing the normal orthogonal combinations of these functions, ζ_n (where n stands for a set of three numbers), we can proceed to a discussion of the energy integral along familiar lines. For any two quadratically integrable functions f and g, with expansion coefficients f_n and g_n, we have the usual form of the completeness relation:

$$\int fgd\tau=\sum_{n=0}^{\infty}f_ng_n,\quad f_n=\int f\zeta_nd\tau,\quad g_n=\int g\zeta_nd\tau.$$

Letting $f=\psi$, $g=H\psi$, $H_{nm}=\int\zeta_nH\zeta_md\tau$, we easily obtain the result

$$\int\psi H\psi d\tau=\sum_{m,\,n=0}^{\infty}\sum\psi_m\psi_nH_{mn},$$

provided that $\int\zeta_nH\psi d\tau=\int\psi H\zeta_nd\tau$.

This condition will certainly be satisfied for the whole operator H, if it is satisfied by each Laplacian separately. Let us consider electron 2 fixed, and designate by $d\tau_1$ integration over all positions of electron 1. Then, by Green's theorem,

$$\int[\zeta_n\nabla_1^2\psi-\psi\nabla_1^2\zeta_n]d\tau_1=\lim_{r_1\to0}\int_{-1}^{+1}d\cos\theta_1\int_0^{2\pi}d\varphi_1 \times r_1^2[\zeta_n\partial\psi/\partial r_1-\psi\partial\zeta_n/\partial r_1]=\lim_{r_1\to0}\int_{-1}^{+1}d\cos\theta_1\int_0^{2\pi}d\varphi_1 \times[r_1\zeta_n\partial(r_1\psi)/\partial r_1-r_1\psi\partial(r_1\zeta_n)/\partial r_1].$$

Now, if ψ be taken as the "unperturbed" function $\psi_0=e^{-2(r_1+r_2)}$, each term in the integrand is found to vanish, for $r_1\psi_0$ and $r_1\zeta_n$ tend to zero with r_1 and their derivatives remain bounded. To get the true function ψ we must alter ψ_0 in such a way as to reduce as much as possible the contribution which the electronic repulsion makes to the energy integral, while producing the minimum disturbance in ψ_0, which already minimizes the remaining contributions. Clearly this will be accomplished by reducing the value of ψ_0 in those parts of configuration space where r_{12} is small, while normalization is preserved by a compensating increase in regions where r_{12} is large. Consequently, for a given small value of r_2, the value of ψ will be less than that of ψ_0 in the region of small r_1, and no matter how peculiar the behavior of ψ may be near the origin, $r_1\psi$ will tend to zero and its derivative remain bounded. For large r_2 it may be that $\psi>\psi_0$, but in this case the essential nature of the singularity cannot be affected. The integrand thus remains zero, and in the final integral $\int[\zeta_nH\psi-\psi H\zeta_n]d\tau$ the contribution from the Laplacian of each electron vanishes upon integration over the coordinates of that electron alone.

The existence of a satisfactory series in the ζ's having been established (always assuming that the function itself exists), we must show that the variation method will actually converge upon this series. It is quite possible that, when a finite number of terms is taken, the variation method will produce a set of coefficients giving a lower energy integral than if the same number of true expansion coefficients had been used. It cannot lead to a higher result, since it must find the lowest result possible. But no such result can be lower than the correct energy E, which is an absolute minimum for all normalized functions. The variation result is therefore constrained to lie between E and a quantity which converges upon E as the approximation is improved, and must itself converge upon E. This conclusion also holds when the Hylleraas functions are used directly, for only operations with finite numbers of terms are considered in the analysis. Now, the ground state function, being nondegenerate, uniquely determines a set of expansion coefficients in the ζ's, and these must be the coefficients upon which the variation process converges, since no others could give a result converging upon E. However, the coefficients of the nonorthogonal Hylleraas terms need

not converge upon any finite limits (as was brought out in discussing the analogy of $x \ln xe^{-x/2}$). There is thus no inconsistency between the present treatment and that of Bartlett, Gibbons and Dunn. Indeed, the behavior of the coefficients obtained in actual computations is in complete harmony with this analysis.

It is important to notice, however, that we may not conclude that the value of the wave function at any point can be computed with arbitrary accuracy by evaluating a finite number of terms of the series. There may be points at which the sum of the series (if it exists) differs from the function by an amount which is not zero, but which contributes nothing to the integrals. In particular, the regions where two particles coincide might be such points. Therefore, we should regard with suspicion such attempts as were made in a previous paper[3] to draw conclusions about the nature of the function at the singularities. Such questions are, however, of no physical significance. Physical properties correspond to integrals over wave functions (or, at least, over finite portions of them), and to the physicist a discussion about a point in configuration-space which contributes nothing to the integrals is as impertinent as the traditional theological discussion about the point of a pin.

Indeed, from this point of view, it is not even pertinent to enquire whether there exists any function which satisfies the wave equation at every point. Suppose we know only that there must exist some number E such that $\int \psi H \psi d\tau$ can never be less than E for any normalized function ψ which satisfies the proper boundary and continuity conditions, but that permissible comparison functions can be constructed such as to make the integral exceed E by as small an amount as desired. (Such a number E must exist unless the integral can decrease without limit.) If, now, we have a trial series of a form which can give an arbitrarily good root-mean-square approximation to every such permissible comparison function, and to its energy integral, it is shown by Courant and Hilbert[4] that the Ritz method, applied to such trial series, must converge upon E. We have shown that the Hylleraas trial series meets these requirements. (The argument about the Hermitian condition can evidently be applied to any suitable comparison function.) That some limit E exists is certain, since the energy integral cannot be as low as the known lowest solution of the problem obtained by omitting the electronic repulsion. Therefore, the Hylleraas method must be capable of giving the correct energy.

Some further discussion of the significance of the coefficients in this case appears to be needed. It should be possible to show, without assuming the existence of an actual minimizing function, that where the state is not degenerate a unique set of coefficients will emerge from the variation process (using, of course, the orthogonalized trial functions), and that for all physical purposes these coefficients are all that is required. The difficulty is in formulating and proving non-degeneracy without referring to the actual wave function. We hope to discuss this matter in a later communication.

We wish to express our gratitude to Professor Edwin C. Kemble for much helpful discussion of this problem.

[3] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933). The H_2 problem is similar to the He problem in this respect.

[4] R. Courant and D. Hilbert, *Methoden der Mathematischen Physik I*, p. 157.