A Lower Limit for the Theoretical Energy of the Normal State of Helium

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The method of using a modification of Weinstein's lower limit for the energy, as given recently by one of the authors, has been applied to the normal state of helium, with the same sequence of functions as was employed by Hylleraas in his upper limit calculations. The ninth approximation leads to the lower limit -1.45508 Hylleraas units, which can very probably be increased to -1.45446, whereas the upper limit found by Hylleraas is -1.45187. The bearing of the results found on the probable location of the true eigenvalue is discussed, as is also the applicability of the method in general.

1. INTRODUCTION

IT is well known that the variational method, as ordinarily used in quantum mechanics, gives an upper limit to the energy. It is evidently desirable to be able to obtain also a lower limit, since in no other way can the accuracy of the result be judged with *certainty*, although the apparent convergence of the sequence of values obtained with the Ritz method may be a strong indication. An expression for a lower limit has been given by Weinstein,[1] although doubts have been expressed concerning its trustworthiness.[2] In a recent note by one of us,[3] however, it was shown that a rigorous proof of a modification of Weinstein's result can be given under assumptions which, though not rigorously proved, are nevertheless of the type made implicitly in many quantum-mechanical calculations, and are almost certainly true. At the same time, a method of applying this result was suggested. In this paper, the method is used to find a lower limit for the normal state of helium. This problem is, perhaps, of especial interest, since the well-known calculations of Hylleraas[4] have furnished an upper limit which is in very close agreement with the experimental value—a fact which is often cited as one of the striking successes of quantum mechanics.

[1] D. H. Weinstein, Proc. Nat. Acad. Sci. **20**, 529 (1934).
[2] See, for instance, J. H. Bartlett, Phys. Rev. **51**, 661 (1937), or W. Romberg, Physik. Zeits. Sowjetunion **8**, 516 (1935).
[3] A. F. Stevenson, Phys. Rev. **53**, 199 (1938).
[4] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929); **65**, 209 (1930). We shall refer to these two papers as H I and H II, respectively.

2. THE LOWER LIMIT FOR EIGENVALUES

We shall first discuss the applicability of the method in general. The result already proved[3] is that if E_0 is the lowest eigenvalue, then $E_0 \geq L$, where the lower limit L is given in terms of a normalized trial function ψ by

$$L=\alpha-(I_2-2\alpha I_1+\alpha^2)^{\frac{1}{2}}, \tag{1}$$

where

$$I_1=\int \psi H\psi d\tau, \quad I_2=\int (H\psi)^2 d\tau,$$

and α is any number $\leq(E_0+E_1)/2$, where E_1 is that eigenvalue nearest to E_0 (and below the continuous spectrum) which has the same symmetry characteristics (with respect to permutation, rotation of axes, etc.) as the eigenfunction corresponding to E_0 (and which are supposed to have been correctly reproduced in the trial function).

A somewhat more general result, proved in an analogous manner, is the following: let the equation be $H\psi=E\rho\psi$ where H is self-adjoint in the complex sense

$$\left(\int f_1 H f_2 d\tau=\int f_2 H^* f_1 d\tau\right),$$

and let $E_0, E_1, \cdots$ be the eigenvalues, arranged in ascending order of magnitude, whose eigenfunctions $\psi_0, \psi_1, \cdots$ have all the same symmetry characteristics. Then if ψ is a trial function, normalized in the sense

$$\int |\psi|^2 \rho d\tau=1,$$

and which is *accurately* orthogonal to $\psi_0, \cdots, \psi_{n-1}$ the expression (1) furnishes a lower limit for the eigenvalue E_n, where now

$$I_1=\int \psi^* H\psi d\tau, \quad I_2=\int |H\psi|^2/\rho \cdot d\tau,$$

$$\alpha \leq (E_n+E_{n+1})/2.$$

We assume that E_{n+1} lies below the continuous spectrum, if there is any.[5]

For the remainder of this section, we shall confine ourselves to the lowest eigenvalue for simplicity. The expression (1), for given ψ, increases steadily[6] with α, so that the best value of α is its greatest allowable one, namely $(E_0+E_1)/2$. In order to apply (1), we therefore first fix α, choosing the greatest value for which the inequality $\alpha \leq (E_0+E_1)/2$ is safely satisfied, and then determine ψ so that L is a maximum, i.e., so that

$$I_2-2\alpha I_1=\text{minimum}. \tag{2}$$

The condition (2) lends itself to the Ritz method in the same way as the more usual upper limit method. Weinstein's original expression corresponds to the value $\alpha=I_1$, which is justified if $I_1 \leq (E_0+E_1)/2$.[7] Romberg[8] has proposed the empirical expression $-I_2^{\frac{1}{2}}$ as a lower limit, which is obtained from (1) with $\alpha=0$. As already pointed out,[3] Romberg's expression depends on the zero of energy; it can, in fact, always be made to fail by proper choice of this zero. Ordinarily, it is true, the zero is chosen to be at some stage of ionization, but examples can be given where it fails even when this "natural" choice is made.[9] Thus although Romberg's expression may well be correct in particular cases, it is clear that no reliance can be placed on it in general. We may here mention that Romberg's[8] example purporting to show that Weinstein's expression (with $\alpha=I_1$) may fail, is not valid, for the restriction $I_1 \leq (E_0+E_1)/2$ has not been taken into account; when this is done, no contradiction is obtained.

The lower limit (1) will usually only be a good approximation to the eigenvalue E_0 if the "mean square deviation"

$$\left(I_2-I_1^2=\int [(H-I_1)\psi]^2 d\tau\right)$$

is small. It is clear that this is a more stringent requirement on ψ than is necessary to make the "mean energy" I_1 a good approximation, so that we may expect that, with any given trial function, the upper limit will give a better result than the lower limit. It is possible that an exception to this statement might occur if E_1 lies far above E_0, so that a large value of α could be taken. Moreover, the lower limit is more laborious to calculate than the upper, so that the present method cannot compete with the more usual one if it is merely desired to find an approximation to the energy, but is only of value when limits to the error are required. It is possible, also, that the function obtained by the lower limit method may be a better approximation to the true eigenfunction for some purposes, since it probably yields a function whose derivatives represent more closely the actual derivatives.[10]

3. Application to the Normal State of Helium

We shall use the notation and units of Hylleraas, namely: unit of length $=a_0/4$, unit of energy $=4$ rydbergs; and for coordinates: $s=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$. The Hamiltonian is $H=T+V$, where the kinetic and potential energy operators are given by[11]

[5] The result $E_n \leq \alpha+(I_2-2\alpha I_1+\alpha^2)^{\frac{1}{2}}$ provided $\alpha<E_n$, may be proved analogously (cf. Weinstein, reference 1). But this upper limit increases steadily with α, so that the best value is reached for $\alpha=-\infty$, which gives $E_n \leq I_1$, which is the usual upper limit expression.

[6] The geometrical picture is useful: L, plotted against α, is a branch of a hyperbola which has the lines $L=I_1$, $L=I_1+2(\alpha-I_1)$ as asymptotes. The smaller the quantity $I_2-I_1^2$, the closer the hyperbola approaches its asymptotes. In the limiting case of $I_2=I_1^2$ (exact solution), the hyperbola degenerates into its asymptotes, and $L=E_0$ for any $\alpha \geq E_0$.

[7] This restriction was mentioned by Weinstein, Phys. Rev. **41**, 839 (1932).

[8] W. Romberg, reference 2.

[9] Thus consider the lowest state of the hydrogen atom, with the trial function $\psi=r^3e^{-kr}$. Then not only does Romberg's expression fail for sufficiently small k (this is *always* so when a scale factor is used), but it even fails for the value of k which is "best" from the point of view of minimizing the upper limit.

[10] Cf. the discussion by James and Coolidge, Phys. Rev. **51**, 860 (1937).

[11] These results follow, e.g., from the variational principle given in H I.

$$-\tfrac{1}{8}T\psi=\frac{\partial^2\psi}{\partial s^2}+\frac{\partial^2\psi}{\partial t^2}+\frac{\partial^2\psi}{\partial u^2}+2\frac{s(u^2-t^2)}{u(s^2-t^2)}\frac{\partial^2\psi}{\partial s\partial u}+2\frac{t(s^2-u^2)}{u(s^2-t^2)}\frac{\partial^2\psi}{\partial t\partial u}+\frac{4s}{s^2-t^2}\frac{\partial\psi}{\partial s}-\frac{4t}{s^2-t^2}\frac{\partial\psi}{\partial t}+\frac{2}{u}\frac{\partial\psi}{\partial u},$$

$$V\psi=\left[-\frac{16s}{s^2-t^2}+\frac{2}{u}\right]\psi.$$

For the trial function, we choose, with Hylleraas,[12]

$$\psi=\phi(ks, kt, ku), \tag{3}$$

where $\phi(s, t, u)=e^{-s/2}\times$(polynomial in s, t^2, u)

$$=\sum_{n=0}^{\infty}c_n\phi_n(s, t, u), \text{ for example.} \tag{4}$$

The following nine functions were used:

$$\phi_0=(1/2)e^{-s/2}, \qquad \phi_1=(1/6)se^{-s/2},$$
$$\phi_2=(1/6)ue^{-s/2}, \qquad \phi_3=(1/24)t^2e^{-s/2},$$
$$\phi_4=(1/24)s^2e^{-s/2}, \qquad \phi_5=(1/24)u^2e^{-s/2},$$
$$\phi_6=(1/24)sue^{-s/2}, \qquad \phi_7=(1/120)t^2ue^{-s/2},$$
$$\phi_8=(1/120)u^3e^{-s/2},$$

the numerical factors being inserted for convenience and to accord with H II.

Substituting (3) and (4) in the variational principle (2), and minimizing with respect to the c's, we obtain, in the usual way, the determinantal equation

$$|k^4A_{ij}+k^3B_{ij}+k^2C_{ij}-2\alpha(k^2M_{ij}+kP_{ij})-\lambda N_{ij}|=0, \tag{5}$$

where $\lambda=I_2-2\alpha I_1$, $A_{ij}=\int T\phi_iT\phi_j d\tau$,

$$B_{ij}=\int(T\phi_iV\phi_j+T\phi_jV\phi_i)d\tau,$$

$$C_{ij}=\int V\phi_iV\phi_j d\tau, \quad M_{ij}=\int\phi_iT\phi_j d\tau, \tag{6}$$

$$P_{ij}=\int\phi_iV\phi_j d\tau, \qquad N_{ij}=\int\phi_i\phi_j d\tau.$$

The symbol $\int d\tau$ in (6) denotes

$$\int d\tau=\tfrac{1}{8}\int_0^{\infty}ds\int_0^{s}du\int_0^{u}dt\cdot u(s^2-t^2),$$

the factor $\frac{1}{8}$ being introduced for convenience and to accord with H II.

The integrals M, P, N are given at once from the tables in H II[13] (though the integrals M, P were calculated independently as a check). The somewhat laborious integrals A, B, C were not previously available, and were calculated and carefully checked. The results are given in Table I.[14]

Equation (5) must be solved for λ and the lowest root minimized with respect to k. The lower limit is then immediately given by $L=\alpha-(\lambda+\alpha^2)^{\frac{1}{2}}$. The constant α must first be fixed. As regards the ground state, the results of the present paper justify *a posteriori* the assumption that $E_0>-1.455$, while for the level E_1—in this case the $1s2s\,^1S$ level—the experimental value is about -1.073, while the theoretical calculation of Hylleraas and Undheim gave -1.07245, which is known to be too high.[15] Thus the value $\alpha=-1.3$ is seen to allow an ample margin for safety, while the value $\alpha=-1.27$ is in all probability also allowable. The detailed calculations were all made with the value $\alpha=-1.3$, but in the final

[12] The Hylleraas function is such that $H\psi$ has singularities which are not, of course, present for the correct eigenfunction, and it might be thought that this would affect the lower limit more adversely than the upper. It could be avoided, for instance, by multiplying the function by the factor $u^2(s^2-t^2)^2$. But this would introduce nodes into the function which should not be there and would also make the calculations more laborious. It was decided, therefore, to use the original Hylleraas functions.

[13] Our M, N are precisely the same as those of H II, while our $P_{ij}=L'_{ij}/2-L_{ij}$ in the notation of that paper.

[14] The integrals are all either rational numbers or else linear functions of the quantities log 2 or π^2 with rational coefficients. As some of the expressions are quite complicated, however, they have all been given in decimal form to 8 places. The last figure is uncertain in some cases.

[15] See, for instance, H. Bethe, *Handbuch der Physik*, second edition, Vol. 24, p. 366.

TABLE I. *Values of integrals A, B and C.*

ij	A_{ij}	B_{ij}	C_{ij}	ij	A_{ij}	B_{ij}	C_{ij}
00	12.00000000	−28.50000000	18.66666667	28	21.33333333	− 57.33333333	48.44444444
01	8.00000000	−28.50000000	24.88888889	33	46.22222222	− 64.58333333	25.75238095
02	9.83333333	−27.67602874	20.53713985	34	15.11111111	− 56.91666667	41.14444444
03	12.66666667	−23.25000000	11.75555556	35	30.66666667	− 60.75000000	33.61111111
04	3.33333333	−26.25000000	31.11111111	36	24.34722222	− 59.68380873	36.91248685
05	8.00000000	−25.41666667	22.00000000	37	59.37222222	− 89.51131767	38.19609000
06	6.20833333	−26.26170260	25.67142482	38	40.31666667	− 84.22564774	49.51987627
07	11.90000000	−22.87404311	12.65570978	44	19.55555556	− 82.50000000	108.88888889
08	6.50000000	−22.90842587	23.20009254	45	17.33333333	− 71.69444444	77.00000000
11	11.55555556	−41.00000000	41.48148148	46	18.19444444	− 77.05922055	89.84998685
12	11.38888889	−38.78713985	34.22856642	47	24.49444444	− 80.57276727	59.05997890
13	15.11111111	−38.75000000	23.51111111	48	24.08333333	− 96.91966036	108.26709849
14	11.55555556	−51.25000000	62.22222222	55	32.88888889	− 78.69444444	60.55555556
15	13.33333333	−46.25000000	44.00000000	56	27.17618296	− 77.08933885	67.66693655
16	12.66666667	−49.01560346	51.34284963	57	43.90641921	− 87.29687209	49.51987627
17	18.63333333	−46.30118296	29.52998949	58	44.97246898	−110.62808623	87.90308623
18	14.16666667	−51.78070978	54.13354925	66	25.38383498	− 78.30555556	77.00000000
22	17.49127392	−39.88888889	29.33333333	67	35.57442380	− 85.08888889	53.77777778
23	21.38888889	−40.25011976	21.09284963	68	36.26666667	−106.40000000	96.88888889
24	10.11111111	−47.95224618	51.34284963	77	90.85444620	−143.73111111	64.24000000
25	20.18539082	−49.73626534	38.66682089	78	68.37333333	−140.58000000	82.80000000
26	17.49127392	−49.86111111	44.00000000	88	76.16000000	−184.06000000	145.09333333
27	25.08120397	−48.62222222	26.88888889				

approximation the value $\alpha=-1.27$ was also considered.

As regards the scale factor k, the upper limit calculation (H I and H II) gives $k=0.844$ in first approximation (i.e., with one function), and $k\leqq 0.9$ for the higher approximations. In our case, the first approximation gave $k=0.907$, and trials with different values of k for the third approximation gave a minimum for λ at $k\leqq 0.935$. The value $k=0.93$ was therefore adopted for the sixth and ninth approximations.

The results obtained, from 1, 3, 6, and 9 functions are given in Table II, where the upper limits found by Hylleraas are also given for comparison. We also give (except for the final approximation) the lower limit obtained by using the Hylleraas "upper limit" function; the value for the sixth approximation is obtained by using the value of I_2 calculated by Bartlett, Gibbons, and Dunn[16] for this particular case. The improvement obtained by maximizing L directly is seen to be significant.

Our results, combined with those of Hylleraas, enable us to say with certainty that the lowest eigenvalue lies between the limits

$$-1.45508<E_0<-1.45187, \qquad (7)$$

the "spread" between these values being 0.174 ev. We can improve our value slightly by using the value $\alpha=-1.27$ (cf. above). The new value of L was estimated approximately from the first order formula

$$\delta L=[1-(\alpha-I_1)/(I_2-2\alpha I_1+\alpha^2)^{\frac{1}{2}}]\delta\alpha$$

and utilization of the Hylleraas value -1.45187 for I_1. (Actually it can be seen that a complete recalculation of L with the new value of α would yield a slightly better value for L). We thus obtain the limits

$$-1.45446<E_0<-1.45187. \qquad (8)$$

The spread is then 0.140 ev.

It has been shown by Coolidge and James[17] that the use of the Ritz method with the Hyl-

TABLE II. *Upper and lower bounds for the energy of the normal state of helium. Unit of energy=4 Rydbergs.*

FUNCTIONS USED	UPPER LIMIT (HYLLERAAS)	LOWER LIMIT	LOWER LIMIT, WITH "UPPER LIMIT" FUNCTION
ϕ_0	−1.42188	−1.77015	−1.7896
ϕ_0, ϕ_2, ϕ_3	−1.45122	−1.47407	−1.4864
$\phi_0-\phi_5$	−1.45162	−1.46073	−1.46519
$\phi_0-\phi_8$	−1.45187	−1.45508	

[16] J. H. Bartlett, J. J. Gibbons, and C. G. Dunn, Phys. Rev. **47**, 679 (1935).

[17] A. S. Coolidge and H. M. James, Phys. Rev. **51**, 855 (1937).

leraas functions yields an upper limit which converges to the true eigenvalue E_0, and their proof can easily be extended to show that the lower limit must also converge to E_0 provided $E_0 < \alpha \leq (E_0+E_1)/2$. The spread between the limits in either (7) or (8) is, however, much greater than the experimental error, so that it cannot be said that complete finality in the helium problem has yet been reached. To carry the approximation farther would be very laborious. Nevertheless, it is probable that E_0 lies close to the Hylleraas value -1.45187, for, as mentioned above, the upper limit is almost certainly a better approximation than the lower limit at any stage of the process, and further, the trend of the values in Table II indicates that the upper limit sequence has converged much more nearly to its limiting value than has the lower limit sequence. However, the fact that the convergence of the latter has also slowed up considerably in going from the sixth to the ninth approximation indicates that possibly E_0 does not lie quite so close to the Hylleraas value as has been generally supposed. On the other hand, the Hylleraas value agrees very closely with the experimental value when the small corrections due to relativity and nuclear motion are included.[18]

[18] H. Bethe, reference 15, 359.

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The Effect of a Direct Electric Field on the Laue Diffraction Photograms

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The effect of a direct electric field (d.e.f.) on the Laue photograms of silica, mica and gypsum crystals has been investigated. It was found that under the action of a d.e.f. (1) the intensity of the Laue reflections is increased, (2) the central spot (which is caused by the rays passing directly through the crystal and the rays reflected backward) is made narrower. If the d.e.f. was applied to the crystals through Al coatings deposited by evaporation on both surfaces of the crystals, the narrowing of the central spot increased only up to a certain intensity of the d.e.f. used. In this case also a time influence was observed. That is to say, if the d.e.f. was applied for a longer time or if sufficiently aged Al coatings were used, the difference in the central spot with and without the d.e.f. disappeared. It was proved that the observed narrowing of the central spot is caused by the alternations provoked in the crystal lattice itself by the d.e.f. and not by the specific properties of the Al coatings. This was done by using instead of the Al coatings obtained by evaporation thin foils of Al pressed on both crystal surfaces for the application of the d.e.f. In this case also the narrowing of the central spot was observed but no time influence was found. The observed phenomena are explained partly by the perfection of the crystal lattice, partly by the shift of the positive and negative ions of the crystal and the positive metallic ions of the deposited Al coatings, which take place in a d.e.f.

MANY authors have studied the influence of electric oscillations, generated in piezoelectric crystals by means of an alternating electric field, on the intensities and the structure of the Laue reflections.[1] It has been found that under the action of electric oscillations the intensity of the Laue spots increases in their intermediate parts, which are due to the reflection of the interior part of the oscillating crystal plate under investigation. Besides this, Fox and Fraser[2] have ascertained that at the same time a widening of the central spot mainly due to the primary x-ray beam takes place. An explanation of these observed phenomena was given[3] by assuming that the perfection of the crystal lattice is disturbed by electric oscillations not only on both surfaces of the crystal plate but also in its interior part which thus contributes to the increase of the intensity of the Laue reflections.

[1] E.g., Fox and Carr, Phys. Rev. **37**, 1622 (1931); Colby and Harris, Phys. Rev. **43**, 562 (1933); Fox and Cork, Phys. Rev. **38**, 1420 (1931); Barrett and Howe, Phys. Rev. **39**, 889 (1932); Nishikawa, Sakisaka, Sumoto, Phys. Rev. **43**, 363 (1933); Jauncey and Deming, Phys. Rev. **48**, 462 (1935).

[2] Fox and Fraser, Phys. Rev. **47**, 15 (1935).

[3] Langer, Phys. Rev. **38**, 573 (1931); **49**, 206 (1936).