

insufficient to produce excitation. These include the distorted wave approximation.

In many collisions the one state phase is positive for the dominant partial waves. By the inequality (34) the one state approximation Q_l' provides a lower bound to the exact Q_l

$$Q_l \geq Q_l', \quad (45)$$

for those energies at which

$$\delta(E) < 2\pi - \delta'(E). \quad (46)$$

Of course $\delta(E)$ is generally not known, but the condition (46) is not very stringent.

In the one state approximation the colliding systems are treated as if they were perfectly rigid, so that no mutual

distortion would occur during the collision. Therefore, such distortion produces an increase in the scattering phase and consequently has the same effect as an attractive potential. This is well-known in the theories of long-range polarization forces and van der Waals' forces. When the adiabatic approximation is applicable to the relative motion of the two colliding systems it is evident from the minimum principle for the energy that mutual distortion is equivalent to an attractive potential.

The one state and many state approximations require the solution of equations for unknown functions. In many cases the box variational method with a linear space \mathcal{U}_2 of finite dimension should be a simpler method of obtaining bounds to scattering phases, as it requires only the eigenvalues of a matrix.

Upper Bounds on Electron-Atomic Hydrogen Scattering Lengths*

LEONARD ROSENBERG, LARRY SPRUCH, AND THOMAS F. O'MALLEY†
Physics Department, New York University, New York, New York

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Recently developed variational techniques for determining upper bounds on scattering lengths are applied to singlet and triplet scattering of zero-energy electrons by atomic hydrogen. The results obtained are not only rigorous but are in fact somewhat lower and therefore somewhat better than those previously obtained by variational methods. We find that the triplet and singlet scattering lengths, A_T and A_S respectively, satisfy the inequalities $A_T \leq 1.91a_0$ and $A_S \leq 6.23a_0$, where a_0 is the Bohr radius. The only assumptions involved in the deduction of these results are that there be no bound triplet state and one and only one bound singlet state. The singlet trial function determined during the course of the calculation generates a singlet effective range, r_{0S} , of about $2.7a_0$. The triplet trial functions which were obtained were not sufficiently accurate to be useful in a determination of the triplet effective range, r_{0T} .

I. INTRODUCTION

THE problem of the scattering of electrons by hydrogen atoms has been attacked since the earliest days of quantum mechanics. For the past ten years, the principal method of attack has been the variational approach, and it seemed for a time from the consistency of the results obtained, even at very low energies, that the variational results obtained were quite reliable. The triplet and singlet scattering lengths, A_T and A_S , were estimated to be $A_T \approx 2.33a_0$ and $A_S \approx 7.02a_0$, respectively,¹ where a_0 is the Bohr radius. However, the recent

work of Ohmura, Hara, and Yamanouchi² makes it likely that the value of A_S is in fact somewhat smaller. These authors use the shape-independent approximation, with the binding energy of H^- taken from theory³ and the singlet effective range r_{0S} computed from the 20-parameter H^- wave function of Hart and Herzberg, and find $A_S \approx 6.1a_0$.⁴ While some questions remain concerning the accuracy of the shape-independent approximation as applied to e^-H singlet scattering, we will indeed show that A_S is considerably lower than the published variational estimates, and may well be close to $6a_0$. The published variational estimates of A_T will also be shown to have been too high.

The method of attack of the present paper is based on the recently developed variational techniques for determining a rigorous upper bound on the scattering

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¹ One of the earliest e^-H variational calculations was performed by H. S. W. Massey and B. Moiseiwitch, *Proc. Roy. Soc. (London)* **A205**, 483 (1951). More recent calculations are discussed by B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, *Proc. Phys. Soc. (London)* **71**, 877 (1958). The estimates of A_T and A_S quoted above are those adopted by these latter authors.

² T. Ohmura, Y. Hara, and T. Yamanouchi, *Progr. Theoret. Phys. (Kyoto)* **22**, 152 (1959); **20**, 82 (1958).

³ J. F. Hart and G. Herzberg, *Phys. Rev.* **106**, 79 (1957).

⁴ More recent, as yet unpublished work by T. Ohmura and H. Ohmura, based on a more accurate H^- function due to Pekeris, leads to a result which differs only slightly from that quoted above.

length.⁵⁻⁸ For this method, it is essential that one know, for a given symmetry, precisely how many composite bound states can be formed of the scattering system and the incident particle (or incident system). It will be assumed in the present paper that there is one and only one singlet bound state, and that there is no triplet bound state. There is strong evidence, both experimentally and theoretically, that this is the case, but the evidence is by no means conclusive. Should it turn out, for either symmetry, that the number of bound states is greater than that which has been assumed, the legitimacy of the bound obtained on the corresponding scattering length in the present paper would be destroyed.

The determination of a bound is slightly simpler for the case of no composite bound state. The triplet case is therefore treated first, in Sec. 2. The singlet case is considered in Sec. 3.

2. TRIPLET SCATTERING

A. Formulation

Consider the scattering of electrons, with zero initial kinetic energy, by hydrogen atoms, for the state of zero total orbital angular momentum. Assume that the total spin angular momentum quantum number is one. The Hamiltonian of the system is

$$H = T + V,$$

where

$$V = e^2 \left(-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}} \right), \quad (2.1)$$

and where $T = (-\hbar^2/2m)(\nabla_1^2 + \nabla_2^2)$ reduces, since we are interested in zero total orbital angular momentum, to

$$T = -\frac{\hbar^2}{2m} \left(\frac{1}{r_1^2} \frac{\partial}{\partial r_1} \frac{\partial}{\partial r_1} + \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \frac{\partial}{\partial r_2} + \frac{2}{r_{12}^2} \frac{\partial}{\partial r_{12}} \frac{\partial}{\partial r_{12}} + \frac{r_1^2 - r_2^2 + r_{12}^2}{r_1 r_{12}} \frac{\partial}{\partial r_1} \frac{\partial}{\partial r_{12}} + \frac{r_2^2 - r_1^2 + r_{12}^2}{r_2 r_{12}} \frac{\partial}{\partial r_2} \frac{\partial}{\partial r_{12}} \right). \quad (2.2)$$

The ground-state energy of the hydrogen atom is of course given by

$$E_H = -\frac{1}{2}e^2/a_0.$$

We now introduce the triplet trial function $\Psi_{Tt}\chi_T$; χ_T is any one of the three triplet spin functions, normalized such that $(\chi_T, \chi_T) = 1$. Ψ_{Tt} is a function of r_1 , r_2 , and r_{12} which is antisymmetric in r_1 and r_2 and which

TABLE I. Upper bounds on electron-atomic hydrogen singlet and triplet scattering lengths. R_K is the consistency ratio.

	Upper bound on A_T/a_0	R_K	Upper bound on A_S/a_0	R_K
No polarization, numerically	A_T static/ $a_0 = 2.35^a$	1.00	A_S static/ $a_0 = 8.1^a$	1.00
Polarization, variationally	2.33 ^b	...	7.03 ^a	1.03
	1.93 ^c	1.34	6.23 ^c	0.996
	1.91 ^d	0.97		

^a M. J. Seaton (see reference 9).

^b H. S. W. Massey and B. Moiseiwitch (see reference 1).

^c Was determined with the trial function given by Eq. (2.6), of the present paper.

^d Was determined with the trial function given by Eq. (2.7), of the present paper.

^e Was determined with the trial function given by Eq. (3.8), of the present paper.

satisfies the boundary conditions

$$\Psi_{Tt} \rightarrow \Psi_{Tt\infty} \equiv (1 - P_{12})[R_H(r_2)(-1 + A_T/r_1)] \quad \text{for } r_1 \text{ or } r_2 \rightarrow \infty. \quad (2.3)$$

R_H is the hydrogen ground-state function, given by

$$R_H(r) = a_0^{-3/2} e^{-r/a_0},$$

while P_{12} is the space exchange operator. We have finally

$$A_T \leq A_{Tt} + (2m/\hbar^2) \int \Psi_{Tt}(T + V - E_H)\Psi_{Tt} d\tau, \quad (2.4)$$

where

$$d\tau = r_1 dr_1 r_2 dr_2 r_{12} dr_{12}. \quad (2.5)$$

B. Published Variational Calculations

The right-hand side of Eq. (2.4) is simply the Kohn-Hulthén variational estimate of A_T . Therefore, though it was not realized at the time of their publication, the various Kohn-Hulthén variational calculations which have been performed¹ represent bounds on as well as variational estimates of A_T . The Kohn results will necessarily be lower and therefore better than the Hulthén estimates; we are here distinguishing between the two standard methods of evaluating the variational parameters that appear in Eq. (2.4).

There have also appeared variational calculations in which "inappropriate" normalization⁷ was used, that is, a normalization different from that of Eq. (2.3) by a factor of $1/A_{Tt}$. The results so obtained do not necessarily represent bounds but can be trivially altered to do so.

Of the variational estimates of A_T which have appeared we mention the calculation of Seaton,⁹ who obtained a numerical solution of the static (or exchange) equation, and the Kohn variational calculation, with the inclusion of polarization, performed by Massey and Moiseiwitch.¹ (See Table I.) Each of these calculations provides a bound on A_T ¹⁰; the small difference between

⁹ M. J. Seaton, Proc. Roy. Soc. (London) **A241**, 522 (1957).

¹⁰ It should be recalled that the static approximation can be thought of as arising from that particular trial function which is equal to a hydrogenic function multiplied by a function of the distance between the incoming electron and the proton, all appropriately symmetrized.

⁵ L. Spruch and L. Rosenberg, Phys. Rev. **116**, 1034 (1959).

⁶ L. Spruch and L. Rosenberg, Phys. Rev. **117**, 1095 (1960).

⁷ L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. **118**, 184 (1960).

⁸ L. Spruch and L. Rosenberg, Nuclear Phys. (to be published).

the two results would seem to indicate that the effects of polarization are unimportant in this problem. Such a conclusion would be incorrect, however, as we shall now see.

C. An Improved Estimate of A_T

The fact that Eq. (2.4) represents a bound on A_T as well as a variational estimate of A_T gives of course much more concrete meaning to any estimates deduced; the fact is further of some considerable practical consequence since it makes it possible for the calculation to proceed in a rather simpler and more systematic fashion than for a variational calculation not based on a minimum principle. In particular, one can choose sets of values of the nonlinear parameters in the trial function and determine the optimum values of the linear parameters for each set according to Kohn's prescription. One need *not* then vary the nonlinear parameters to such an extent as to be able to locate that set for which the result is stationary.¹¹ Rather, one can merely perform a succession of calculations with different sets, each choice guided by the result of the previous calculation, and at whatever stage one decides to stop simply choose that set for which the resultant value is lowest. This is essentially the procedure followed here.

We first considered the spatial trial function

$$\Psi_{Ti} = (1 - P_{12})a_0^{-3/2} [e^{-x_2} A_{Ti} (1 - e^{-bx_1}) / (x_1 a_0) - e^{-x_2} + B e^{-cx_1 - dx_2} + C e^{-fx_1 - gx_2 - hx_{12}}], \quad (2.6)$$

where $x_1 = r_1/a_0$, $x_2 = r_2/a_0$, and $x_{12} = r_{12}/a_0$. The exponential parameters were chosen using the "trial and error" method outlined above,¹² and the lowest bound on A_T obtained using Eq. (2.6) appears in Table I. The corresponding linear variational parameters and exponential parameters are given in Table II. The consistency ratio, R_K , defined by

$$R_K = \left[A_{Ti} + (2m/\hbar^2) \int \Psi_{Ti} (T + V - E_H) \Psi_{Ti} d\tau \right] / A_{Ti},$$

was found to differ considerably from unity. While no attempt was made to determine the optimum set of exponential parameters it did not seem likely that a set would be found which would give a value of R_K close to unity, without raising the bound on A_T . Consequently, we considered a more flexible trial function, which did not, however, add substantially to the com-

plexity of the calculations. We chose

$$\Psi_{Ti} = \Psi_{Ti} [\text{Eq. (2.6)}] + (1 - P_{12}) a_0^{-3/2} D e^{-f'x_1 - g'x_2 - h'x_{12}}. \quad (2.7)$$

The parameters f' , g' , and h' were not varied but simply taken to be one of the sets originally obtained in the analysis based on Eq. (2.6) which gave reasonably good results; the values f , g , and h were taken over intact. The consistency ratio was thereby improved and a slightly lower bound was obtained. (See Table I.)

We note that there exist some questions, in the present problem, concerning the validity of the shape-independent approximation and, indeed, the correctness of the energy dependence which is usually assumed in the effective-range expansion, due to the existence of long-range polarization effects. Nevertheless, we have ignored these points in the present paper and attempted to use the trial function obtained in the variational calculation for an evaluation of the effective range. This attempt was unsuccessful, however; the calculated value of r_{0T} was extremely sensitive to the choice of the exponential parameters. Apparently a more accurate trial function is required, although no such difficulties were encountered in the calculation of the singlet effective range, r_{0S} (see Sec. 3).

While the trial function is not sufficiently accurate to enable one to extract from it information about the effective range, r_{0T} , one can learn something about r_{0T} from the value of A_T . Thus, if there were a triplet bound state with a binding energy relative to that of the hydrogen atom given by $\gamma_T^2 \hbar^2 / 2m$, we would have, in the shape-independent approximation,

$$\gamma_T = 1/A_T + \frac{1}{2} r_{0T} \gamma_T^2,$$

or

$$\gamma_T = [1 \pm (1 - 2r_{0T}/A_T)^{1/2}] / r_{0T}.$$

It follows therefore that if there is *not* to be a triplet bound state, the quantity γ_T can not be a real number, i.e., we must have

$$r_{0T} > \frac{1}{2} A_T.$$

There is no particular reason to believe that this esti-

TABLE II. Table of linear variational parameters and of exponential parameters.

	Singlet, Eq. (3.8)	Triplet, Eq. (2.6)	Triplet, Eq. (2.7)
A_i/a_0	6.26	1.44	1.96
B	-27.92	0.469	0.234
C	27.79	0.184	0.101
D	-0.071
b	0.529	1.50	1.50
c	0.904	0.450	0.450
d	0.814	1.00	1.00
f	0.942	0.990	0.990
g	0.814	-0.145	-0.145
h	-0.030	0.240	0.240
f'	1.00
g'	0.230
h'	-0.150

¹¹ In the absence of a minimum (or maximum) principle such a procedure is not even well defined in principle since there will be in general more than one stationary point for a given form of the trial function.

¹² For the necessary integrals, which are quite straightforward, see L. Spruch and L. Rosenberg, Research Report No. CX-40, Division of Electromagnetic Research, Institute of Mathematical Sciences, New York University (unpublished). A Univac computer was coded to provide the results for each chosen set of exponential parameters. In order that Ψ_{Ti} have the proper asymptotic form the parameters were restricted according to the relations $b > 0$, $c > 0$, $d > 0$, $f + g > 0$, $f + h > 0$, $g + h > 0$.

mate of r_{0T} is an accurate one. We note that in the singlet case, where there is a bound state, similar reasoning leads to the inequality $r_{0S} < \frac{1}{2}A_S$. Of course, a more accurate estimate can be obtained for the singlet case by using the known H^- binding energy (see Sec. 3C).

3. SINGLET SCATTERING

A. Formulation

An expression for an upper bound on the scattering length which is valid when one and only one composite bound state exists has been given previously.⁷ This result, specialized to the case of singlet scattering of electrons by hydrogen atoms, is

$$A_S \leq A_{St} + (2m/\hbar^2) \int \psi_{St}(T+V-E_H)\psi_{St}d\tau - (2m/\hbar^2) \times \left[\int \psi_{Bt}(T+V-E_H)\psi_{St}d\tau \right]^2 / (E_{Bt}-E_H). \quad (3.1)$$

V , T , and $d\tau$ are given by Eqs. (2.1), (2.2), and (2.5), respectively. The trial singlet scattering function is $\Psi_{St}\chi_S$, where χ_S represents the normalized singlet spin function and where the spatial function Ψ_{St} is a function of r_1 , r_2 , and r_{12} which is symmetric in r_1 and r_2 and which satisfies the boundary conditions

$$\Psi_{St} \rightarrow \Psi_{St\infty} \equiv (1+P_{12})[R_H(r_2)(-1+A_{St}/r_1)] \quad \text{for } r_1 \text{ or } r_2 \rightarrow \infty. \quad (3.2)$$

The trial bound-state function is of the form $\Psi_{Bt}\chi_S$, where the spatial part is normalized via

$$\int \Psi_{Bt}^2 d\tau = 1,$$

and must be sufficiently accurate so that

$$E_{Bt} \equiv \int \Psi_{Bt}(T+V)\Psi_{Bt}d\tau < E_H, \quad (3.3)$$

but Ψ_{Bt} is otherwise arbitrary.

It has been shown⁷ that the expression for the bound given above is entirely equivalent to a Kohn-Hulthén variational estimate of the scattering length, with a trial function of the form

$$\Psi_{St} = \Psi_{St'} + b\Psi_{Bt}, \quad (3.4)$$

where Ψ_{Bt} must satisfy Eq. (3.3), where the linear variational parameter b must not appear in $\Psi_{St'}$ or in Ψ_{Bt} , and where $\Psi_{St'}$ must satisfy the boundary conditions imposed on Ψ_{St} in Eq. (3.2).

B. Published Variational Calculations

It was shown previously⁷ that a conversion of the numbers calculated by Borowitz and Greenberg,¹³ in

¹³ S. Borowitz and H. Greenberg, Phys. Rev. **108**, 716 (1957).

such a way as to remedy their "inappropriate" normalization, leads to the upper bound $A_S \leq 7.63a_0$. Their calculation could be readily utilized to obtain a bound because in constructing a trial function, they included an arbitrary multiple of a trial H^- function (developed by Chandrasekhar¹⁴) in the hope that this might prove an accurate representation of the scattering function in the important region for which all interparticle distances are small. Whether or not this hope is in fact realized, it nevertheless follows that their trial function, apart from its normalization, is of precisely the correct form to lead to a bound.

There are a number of other published calculations from which bounds on A_S can be deduced. In particular, it will now be shown that both (a) the static calculation of A_S and (b) the Kohn variational estimate of A_S , as calculated by Seaton,⁹ are actually upper bounds.

The result (a) follows as a particular example of a much more general result that has been obtained previously.⁸ Thus, as a consequence of Eq. (3.1) and the (assumed) fact that there is only one spatially symmetric bound state of H^- , we may conclude that the "exact" static scattering length lies above the true scattering length provided it is possible to find a trial bound state function with a spatial part of the form

$$\Psi_{Bt} = R_H(r_2)f(r_1) + R_H(r_1)f(r_2),$$

and which satisfies Eq. (3.3). Such a function may easily be constructed so that we do obtain a bound from the static calculation.

We now consider the proof of statement (b). The trial function used by Seaton in his Kohn variational calculation can not be written as in Eq. (3.4). However, as is shown in the Appendix, the Kohn estimate lies above A_S if the spatial part of the trial function can be written, in terms of the symmetric functions $\Omega(r_1, r_2, r_{12})$ and $\Phi(r_1, r_2, r_{12})$ which do not contain A_{St} , as

$$\Psi_{St} = A_S\Omega - \Phi, \quad (3.5)$$

where

$$\int \Omega(T+V-E_H)\Omega d\tau < 0, \quad (3.6)$$

and where

$$\left. \begin{aligned} \Omega &\rightarrow R_H(r_2)/r_1 \\ \Phi &\rightarrow R_H(r_2) \end{aligned} \right\} \quad \text{for } r_1 \rightarrow \infty. \quad (3.7)$$

Since the trial function used by Seaton can be written in this form, the calculation provides an upper bound.

The primary significance of the development in the Appendix is not of course that one can utilize previously published calculations, but rather that one has slightly greater freedom in the choice of a trial function which will lead to a bound on the scattering length. This increased freedom will prove useful in the following subsection.

¹⁴ S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

No attempt will be made to consider the other variational calculations which have been performed, for the calculations are sufficiently simple (as opposed, for example, to scattering by a system of more than two particles, or even to neutron-deuteron scattering) so that, forearmed with a minimum principle, it is a trivial matter to obtain results which are lower and therefore better than those previously derived by variational calculations.

C. An Improved Estimate of A_S

We have performed a variational calculation of A_S with the spatial part of the trial function given by

$$\Psi_{St} = (1 + P_{12})a_0^{-3/2} [e^{-x_2}A_{St}(1 - e^{-bx_1})/(x_1a_0) - e^{-x_2} + Be^{-cx_1-dx_2} + Ce^{-fx_1-gx_2-hx_{12}}]. \quad (3.8)$$

According to the previous discussion, an upper bound on A_S will be obtained for those sets of exponential parameters for which the coefficient of B^2 or of C^2 , or of A_{St}^2 , in the integral

$$\int \Psi_{St}(T + V - E_H)\Psi_{St}d\tau,$$

is negative. As it turned out, this condition was satisfied for all sets of exponential parameters considered, so that the subsidiary condition played no role in the actual calculation. (During the latter stages of the calculation the coefficients of B^2 and C^2 were both positive so that it was necessary to invoke the result derived in the Appendix and noted above, that a bound is obtained if the coefficient of A_{St}^2 is negative.) As in the triplet calculation, a fair number of trials were made but it is not entirely clear how close our final set of parameters is to the optimum set for the assumed form of trial function; the lowest bound obtained is given in Table I.

It is somewhat surprising that for the present singlet case, where a bound state exists and where consequently one might expect it to be more difficult to obtain an adequate trial function, it is possible to obtain a very good consistency ratio, R_K , with a trial function with only three linear variational parameters whereas four were required for the presumably simpler triplet case. Of course, a good consistency ratio does not actually guarantee anything whatever regarding the accuracy of the result. Nevertheless, we did not go on in the singlet case to the use of a trial function with four linear variational parameters.

Using the estimate of A_S thus obtained, along with the accurately known binding energy of the H^- ion, the effective range, r_{0S} , was calculated from the shape-independent approximation (we once again put aside any doubts as to the validity of the form of the expansion)

$$\gamma = A_S^{-1} + \frac{1}{2}r_{0S}\gamma^2,$$

where

$$\gamma^2 = (2m/\hbar^2) |E_B - E_H|.$$

We obtain $r_{0S} = 2.70a_0$. The effective range was also calculated from the trial scattering function, using the relation²

$$r_{0S} = (2/A_{St}^2) \int (\Psi_{St\infty}^2 - \Psi_{St}^2) d\tau - 8(1 - 2/A_{St})^2.$$

The last term in this expression arises from the symmetry of the wave function. This equation yields $r_{0S} = 2.78a_0$ which agrees rather well with the previous estimate. These values are to be compared with the value 2.646 ± 0.004 obtained by Ohmura and Ohmura⁴ using the very accurate ground-state H^- function of Pekeris.

If we ignore the seemingly very unlikely possibility that either or both of the scattering lengths are negative, we obtain as a bound on the zero-energy total cross section

$$\sigma_{\text{total}} = \frac{3}{4}4\pi A_T^2 + \frac{1}{4}4\pi A_S^2 \leq 49.8\pi a_0^2.$$

Since we have only obtained one bound, it is difficult to make any estimate of the reliability of the above value. Apart from the general desirability of introducing a trial function with more parameters, it would seem reasonable in any extension of the present calculation to choose a trial function which effectively generates the long-range $1/r^4$ polarization potential.

Note added in proof.—A paper by V. M. Martin, M. J. Seaton and J. B. Wallace [Proc. Phys. Soc. (London) **72**, 701 (1958)] contains a number of approximate calculations of A_S and of A_T . (Note that their definition of A_S and of A_T differs by a sign from ours.) They obtained the value $A_T \approx 1.993a_0$ from a Kohn variational calculation; it follows that this value is a rigorous bound. Though this value is not as accurate as the one obtained in the present paper, it is of considerable interest since the ψ_{Tt} used was deduced on the basis of the adiabatic approximation. While no rigorous conclusions can be arrived at, the fact that our calculation and theirs, one emphasizing short range and the other long range polarization effects, lead to comparable results, would indicate that the bound $1.91a_0$ may be a reasonably accurate estimate of A_T .

Ignoring the physical argument by which their ψ_{Tt} was arrived at, one can write

$$\psi_{Tt} = \psi_t(\text{exchange}) + b\psi_t(\text{adiabatic}),$$

with b a variational parameter. (Their ψ_{Tt} had $b=1$.) The numerical values of the integrals which are then necessary are all given in their article. One finds $b=0.940$ and $A_T \leq 1.992a_0$, so that there is no effective improvement. This result slightly increases the strength of the conclusion of the last paragraph.

On the basis of the theorems that have been deduced so far, it does not seem possible to prove that their Kohn exchange adiabatic estimate of A_S is a bound. It is nevertheless of some interest that the value obtained, $A_S \approx 6.372a_0$, is rather close to our value.

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APPENDIX

It will now be shown that the conditions under which a Kohn variational calculation provides an upper bound on the scattering length can be extended to include the case where the trial function may be written as in Eq. (3.5), subject to the conditions given by Eqs. (3.6) and (3.7).

We are still concerned with the case for which there is one and only one bound state. The result is valid for scattering of one compound system by another, but for clarity of presentation the proof will be given for the problem at hand, the singlet scattering of electrons by hydrogen atoms; use will be made of the notation introduced in the text.

The method of proof is simply to show the identity of the Kohn result, in which the prescribed form of trial function is used, and the rigorous bound. The Kohn variational principle reduces at zero energy to

$$A_S \approx A_{St} + (2m/\hbar^2) \int \Psi_{St}(H - E_H) \Psi_{St} d\tau. \quad (\text{A-1})$$

If we substitute the expression for Ψ_{St} given by Eq. (3.5) into Eq. (A-1), and use the relationship

$$\int \Omega(H - E_H) \Phi d\tau - \int \Phi(H - E_H) \Omega d\tau = -(\hbar^2/2m),$$

we find

$$\begin{aligned} (\hbar^2/2m) A_S \approx & \int \Phi(H - E_H) \Phi d\tau - 2A_{St} \int \Omega(H - E_H) \Phi d\tau \\ & + A_{St}^2 \int \Omega(H - E_H) \Omega d\tau. \end{aligned}$$

Varying the right-hand side with respect to A_{St} leads to

$$A_{St} = \int \Omega(H - E_H) \Phi d\tau / \int \Omega(H - E_H) \Omega d\tau,$$

so that

$$\begin{aligned} (\hbar^2/2m) A_S \approx & \int \Phi(H - E_H) \Phi d\tau \\ & - \left[\int \Omega(H - E_H) \Phi d\tau \right]^2 / \int \Omega(H - E_H) \Omega d\tau. \quad (\text{A-2}) \end{aligned}$$

Now the rigorous upper bound on A_S is given by

$$\begin{aligned} (\hbar^2/2m)(A_S - A_{St}) \leq & \int \Psi_{St'}(H - E_H) \Psi_{St'} d\tau \\ & - \left[\int \Psi_{Bt}(H - E_H) \Psi_{St'} d\tau \right]^2 / \int \Psi_{Bt}(H - E_H) \Psi_{Bt} d\tau. \end{aligned} \quad (\text{A-3})$$

Here Ψ_{Bt} is a function which is normalized and which is sufficiently accurate to give a composite bound state of H^- . Actually, the normalization of Ψ_{Bt} is clearly irrelevant, and it is trivial to show by the use of a limiting process that in fact Ψ_{Bt} need not even be normalizable; a symmetric function which satisfies the boundary condition

$$\Psi_{Bt} \rightarrow \text{const. } R_H(r_2)/r_1 \quad \text{for } r_1 \rightarrow \infty,$$

suffices.¹⁵ We can then set $\Psi_{Bt} = \Omega$. Further, the choice $\Psi_{St'} = \Phi$ is permissible, corresponding to the choice $A_{St'} = 0$. We then find that the upper bound on A_S provided by Eq. (A-3) becomes identical with the Kohn variational estimate, Eq. (A-2), which completes the proof.

The generalization of the above result to the case for which there are precisely N bound states is trivial. It is that the Kohn principle provides an upper bound on the scattering length provided that the trial function contains N linear variational multiples of mutually orthogonal trial bound-state functions, where one of the N linear variational parameters can be the trial scattering length. As discussed previously,⁷ the trial bound-state functions are determined such that they diagonalize the $N \times N$ Hamiltonian matrix; each trial function must be sufficiently accurate to give binding.

In examining the relative merits of the Kohn and Hulthén prescriptions for evaluating the linear variational parameters in the trial function¹⁶ when one bound state exists it is necessary to distinguish between the following two cases:

(a) The variational expression provides an upper bound by virtue of the fact that the trial function can be written as in Eq. (3.4). In this case both methods will lead to a bound but the Kohn method is to be preferred since it will provide a lower and therefore better estimate of the scattering length.

(b) The trial function can be written as in Eq. (3.5)

¹⁵ The limiting process consists of showing that if Ψ_{Bt} is multiplied by $\exp(-\lambda r_1 - \lambda r_2)$ in Eq. (A-3) the integrals are continuous as $\lambda \rightarrow 0$ (see reference 6). Clearly some care is required. Thus, while we have

$$\int \Psi_{Bt}(H - E_H) \Psi_{St'} d\tau = \int \Psi_{St'}(H - E_H) \Psi_{Bt} d\tau,$$

we find that

$$\int \Omega(H - E_H) \Phi d\tau \neq \int \Phi(H - E_H) \Omega d\tau.$$

In writing down Eq. (A-3), we put Ψ_{Bt} on the left in the term which is squared since that is the order for which the limiting process goes through.

¹⁶ See, for example, Eqs. (2.6) and (2.7) of reference 5.

but *not* as in Eq. (3.4). Here the Hulthén method need not provide an upper bound while, as we have just seen, the Kohn method is guaranteed to do so. In this case, it is no longer true that the Kohn estimate must be more accurate. Indeed, an example of the reverse situation is provided by some of Seaton's⁹ results. Nevertheless, one would certainly use the Kohn prin-

ciple, since it possesses the very desirable minimum property.

Similar considerations hold when more than one bound state exists. If no bound states exist case (b) does not arise and, as we have pointed out previously,⁵ the Kohn method should be used to obtain the bound on the scattering length.

Approximate Wave Functions for Atomic Be†

R. E. WATSON*

Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts

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A configuration interaction calculation, involving thirty-seven configurations and including the $(1s)^2(2s)^2$ Hartree-Fock function, has been done for the ground state of atomic Be. Approximately ninety percent of the correlation energy has been incorporated into the final total energy. The results indicate that the correlation energy is associated with two effects, namely that of the "correlation hole" as has been observed for He and that of "orbital degeneracy" (which does not appear in the two-electron He case). The former effect is best handled by the Hylleraas approach and the latter by the configuration interaction method, and the results suggest that an admixture of the two methods would lead to the most rapidly convergent description of the exact four-electron wave function. The errors introduced by handling "high-lying" configurations by second-order perturbation theory rather than by exact configuration interaction are also investigated.

I. INTRODUCTION

THE Hartree-Fock formalism¹ yields approximate solutions of the many-electron Hamiltonian. These solutions are in considerable error if one wishes to use them to predict almost any physically observable quantity. Not only are the solutions in error, but small improvements in the wave functions, as evidenced by a lowering of the expectation values of the total energies, will lead to poorer predictions of some of the observables. The lithium hyperfine interaction² is an example of this. The two standard methods for improving on the Hartree-Fock wave function are (1) that of Hylleraas³ where interelectronic coordinates (r_{ij}) are explicitly included in the wave function and (2) that of configuration interaction where the variational principle is applied to a trial wave function which is a linear combination of Slater determinants. The Hylleraas approach has been very successfully applied to the two-electron (three-particle) ions^{4,5} where total

energies and wave functions of accuracy sufficient to assist in supplying information concerning the nucleus have been obtained.⁴ The configuration interaction approach has yielded much less accurate results for the same problem.^{6,7}

The difference between the He Hartree-Fock function and the exact eigenfunction for the two-electron (nonrelativistic) Hamiltonian occurs because the Hartree-Fock function inadequately describes the behavior of the two electrons when they are close together, i.e., the "correlation hole" is omitted. The comparative success of the Hylleraas method, when applied to He, is due to the fact that it supplies a more rapidly convergent method for describing the "correlation hole."

Both methods increase in difficulty with increasing numbers of particles. This increase is most serious for the Hylleraas approach since the number of interelectronic r_{ij} coordinates increases quadratically with the number of particles while the number of independent one-electron (r_i) coordinates increases only linearly. When going from the Hartree-Fock to more exact eigenfunctions for systems of four or more electrons there often is, as has been suggested by

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* Now at Research and Advanced Development Division, AVCO, Wilmington, Massachusetts.

¹ For example, see D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley and Sons, New York, 1957).

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