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Test of the Polarized Orbital Method: $H^{-\dagger}$

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The polarized-orbital method and many of the common variations and approximations of this approach are tested in a computation of the binding energy of the negative hydrogen ion H^-. It is found that if a trial wave function for H^- is constructed from a distorted atomic wave function in which the first-order perturbed orbital is simply added to the undistorted atomic function, the result is a very poor approximation (binding energy -0.0094 Ry). However, if the trial function is modified, as suggested by Drachman, with the introduction of an additional independent function multiplying the perturbed orbital, the result is quite good, the binding energy being -0.0544 Ry. For comparison, the exact value (due to Pekeris) is -0.0555 Ry.

I. INTRODUCTION

The polarized-orbital method and its variants have furnished reasonably popular procedures in the study of electron-atom scattering. Originally introduced by Bethe,[1] the polarized-orbital (PO) method was revived by Temkin,[2] and, in connection with a solid-state problem, by one of us.[3] In numerous applications in scattering problems, a varying degree of success has been obtained. The simplest approximations work rather well, but refinements may do more harm than good. Recently, the method has been criticized by Mittleman and Peacher as arbitrary and lacking in predictive ability.[4] However, the possibility of using variational methods to remove arbitrary elements has not been adequately explored, and we believe that further investigation into the nature and merits of the PO method is desirable.

To this end, we have calculated the energy of the negative hydrogen ion H^-, using the PO method and many of the common approximations derived from it. The PO method can be formulated in a variational manner: That is, the problem of calculating the energy of H^- is stated as that of minimizing the expectation value of the Hamiltonian with a certain trial function. The calculation is thus free of arbitrariness, although this is not the case for some of the usual simplifications of the full PO method which are not derived from a variational principle. Since an improvement in the trial wave function must give a lower energy, closeness of approach to the known exact value for the energy of H^- serves as a reasonable criterion for the adequacy of the assumed wave function.

Our conclusions are as follows: The conventional definition of the PO wave function yields a very poor value for the binding energy of H^-: -0.0094 Ry, as compared to the presumably exact value of Pekeris[5]: -0.0555 Ry. This is actually inferior to the result obtained in the static-exchange (SE) approximation (or open-shell SE Hartree-Fock): -0.0265 Ry. The wave function of the SE approximation does not attempt to include correlation effects explicitly. We also consider a modification of the PO method recently proposed by Drachman,[6] which will be described in detail below. This yields a binding energy of -0.0544 Ry, which is rather good. It is also shown that the simple adiabatic-exchange (AE) approximation, including only the dipole part of the polarization potential, also yields a reasonably good binding energy, -0.0513 Ry. This approximation is, however, not variational, and therefore it does not necessarily yield an upper bound to the binding energy.

The plan of this paper is as follows: In Sec. II, the definition of the basic method and the various approximations are presented. Section III contains a description of our methods of calculation. Our results are presented in Sec. IV.

II. METHOD

The essential idea of the PO method is that the distortion of an atom or an ion in the field of an external electron or positron must be included in a calculation of scattering, or of the binding energy of the additional particle. The method is not completely defined until a prescription for calculating the distortion is stated; this is, that perturbation theory is to be used to obtain the correction to the atomic wave function due to the external particle, which is regarded as fixed. To be more specific, we specialize to the system of a neutral hydrogen atom plus an additional electron. Let the coordinates of these particles relative to the proton (whose mass is regarded as infinite) be denoted by 1 and 2. The assumed wave function for the system is

$$\Psi_{\mathrm{po}}(1,2)=2^{-1/2}\{[u_0(1)+\chi(1,2)]\,\phi(2)$$

$$\pm[u_0(2)+\chi(2,1)]\phi(1)\}S(1,2). \qquad (2.1)$$

In this equation, u_0 is the wave function for the $1s$ state of the hydrogen atom, $\chi(1,2)$ is the function representing distortion of the atom by an external point charge fixed at coordinate 2, $S(1,2)$ is a normalized two-electron spin function for the singlet or triplet state, and the + or − sign is chosen in accord with the spin state to give an antisymmetric wave function. The H^- ion exists only in the singlet spin state, and our numerical results are restricted to this case. The function $\chi(1,2)$ is obtained by solution of the differential equation of first-order perturbation theory,

$$[H_0(1)-\epsilon_{1s}]\chi(1,2) = [V_c(2)-V(1,2)]u_0(1), \qquad (2.2)$$

where H_0 is the Hamiltonian for an undistorted hydrogen atom (energy ϵ_{1s}) and V_c is the electrostatic potential of the atom [see Eq. (2.9b) below for a definition]. The function $\chi(1,2)$ was obtained by Dalgarno and Lynn.[7] Their expression for χ is rather complicated as it is expressed in confocal elliptic coordinates. It is frequently more convenient to expand χ in partial waves, as follows:

$$\chi(1,2)=\Sigma_l\,\chi_l(r_1,r_2)P_l(\cos\Theta_{12}), \qquad (2.3)$$

in which Θ_{12} is the angle between the coordinates of the two electrons. Expressions for the χ_l were obtained by Reeh.[8]

We have also considered a case in which binding energy of H^- is calculated from a function of this type, (2.1), however, using only the $l=1$, or dipole, component of the perturbed orbital. This will be referred to as the PO-dipole method.

In a calculation of positron-hydrogen scattering, Drachman has proposed a generalization of the PO wave function,[6] which can be stated as follows for the electron-hydrogen system:

$$\psi_D(1,2)=2^{-1/2}\{[u_0(1)\phi(2)+\chi(1,2)F(2)] \pm[u_0(2)\phi(1)+\chi(2,1)F(1)]\}S(1,2). \qquad (2.4)$$

The introduction of an additional independent function F into ψ clearly increases the flexibility of the wave function and should lead to an improvement in the binding energy of H^- and in scattering phase shifts. We will call this modified polarized-orbital method (MPO).

Two approaches exist for the determination of the energy of the system: (i) We may substitute the trial wave function $\psi(1,2)$ into the variational principle, vary ϕ and F, and obtain a pair of coupled integro-differential equations. (ii) Alternately, we may assume some expansion of ϕ and F in a set of known functions, and determine the coefficients variationally. We contend that the use of a variational principle frees the PO method from the charge of arbitrariness in the sense described by Mittleman and Peacher.[4]

The use of standard variational methods, following approach (i), yields the equations

$$\int u_0^*(1)[H-E]\psi_D(1,2)d\tau_1=0, \qquad (2.5a)$$

$$\int \chi^*(1,2)[H-E]\psi_D(1,2)d\tau_1=0. \qquad (2.5b)$$

We write $H=H_0(1)+H_0(2)+V(1,2)$, (2.6a)

where $V(1,2)=e^2/|r_1-r_2|$. (2.6b)

The basic equations (2.5) can be written more explicitly, with the aid of (2.2), as follows:

$$\begin{aligned}&[H_0(2)+V_c(2)-\epsilon]\phi(2)\pm\int u_0^*(1)[\epsilon_{1s}-\epsilon+V(1,2)]\phi(1)d\tau_1\,u_0(2)=-V_p(2)F(2)\\&\quad\mp\int u_0^*(1)[\epsilon_{1s}-\epsilon+V(1,2)]\chi(2,1)F(1)d\tau_1\mp\int u_0^*(1)[V_c(1)-V(1,2)]F(1)\,d\tau_1\,u_0(2),\end{aligned} \qquad (2.7)$$

and

$$\begin{aligned}&\{N(2)[H_0(2)-\epsilon]-V_p(2)+V_3(2)+W(2)+V_N(2)\cdot\nabla\}F(2)\pm\int\chi^*(1,2)[\epsilon+V(1,2)]\\&\quad\times\chi(2,1)F(1)d\tau_1\pm\int u_0^*(1)[V_c(2)-V(1,2)]\chi(2,1)F(1)d\tau_1\pm\int\chi^*(1,2)[V_c(1)-V(1,2)]F(1)d\tau_1u_0(2)\\&\qquad=-V_p(2)\phi(2)\mp\int\chi^*(1,2)[\epsilon_{1s}-\epsilon+V(1,2)]\phi(1)d\tau_1\,u_0(2)\\&\qquad\mp\int u_0^*(1)[V_c(2)-V(1,2)]\phi(1)d\tau_1\,u_0(2)\end{aligned} \qquad (2.8)$$

In Eqs. (2.7) and (2.8) the upper sign in each case refers to the singlet state, the lower to the triplet state. The other quantities are defined as follows:

$$\epsilon = E - \epsilon_{1s} \quad , \tag{2.9a}$$

$$V_c(2) = \int |u_0(1)|^2 V(1,2)\, d\tau_1 \quad , \tag{2.9b}$$

$$V_p(2) = \int \chi^*(1,2) V(1,2) u_0(1)\, d\tau_1 \quad , \tag{2.9c}$$

$$V_3(2) = \int |\chi(1,2)|^2 V(1,2)\, d\tau_1 \quad , \tag{2.9d}$$

$$W(2) = \int \chi^*(1,2)(-\nabla_2^2)\chi(1,2)\, d\tau_1 \, , \tag{2.9e}$$

$$N(2) = \int |\chi(1,2)|^2\, d\tau_1 \quad , \tag{2.9f}$$

$$V_N(2) = -\nabla_2 N(2) \quad . \tag{2.9g}$$

Thus, ϵ is the binding energy of the extra electron in the case of H$^-$. V_C is the ordinary Coulomb potential of the static-charge distribution. V_p is the usual polarization potential containing all multipole components, and V_3 is a third-order polarization potential. The notation for these quantities differs slightly from that of Drachman. The remaining quantities W, N, and V_N coincide with the definitions given by Drachman, who gives a table of their values.[6]

Also, we have the normalization integral (singlet state only)

$$\begin{aligned}\int |\psi_D(1,2)|^2 d\tau_1\, d\tau_2 = \int [\,\phi^2(2) \\ + N(2)F^2(2)]\, d\tau_2 + [\,\int u_0(2)\phi(2)\, d\tau_2]^2 \\ + 2\int u_0(1)\chi(2,1)\phi(2)F(1)\, d\tau_1\, d\tau_2 \\ + \int \chi(1,2)\chi(2,1)F(2)F(1)\, d\tau_2\, d\tau_1 \quad .\end{aligned} \tag{2.10}$$

If the PO wave function (2.1) is used in the variational method, a single equation is obtained,

$$\int [u_0(1) + \chi(1,2)]^* [H - E]\psi(1,2)\, d\tau_1 = 0 \quad . \tag{2.11}$$

This leads to the explicit form

$$\begin{aligned}\{[1 + N(2)][H_0(2) - \epsilon] + V_c(2) + V_p(2) + V_3(2) \\ + W(2) + V_N(2)\cdot\nabla\}\phi(2) = \mp \int u_0^*(1)[\epsilon_{1s} - \epsilon + V_c(1) \\ + V_c(2) - V(1,2)]\phi(1)\, d\tau_1 u_0(2) \mp \int [u_0^*(1) \\ + \chi(1,2)]^*[\epsilon_{1s} - \epsilon + V(1,2)]\chi(2,1)\phi(1)\, d\tau_1 \\ \mp \int \chi^*(1,2)[\epsilon_{1s} - \epsilon + V_c(1)]\phi(1)\, d\tau_1 u_0(2) \\ \mp \int u_0^*(1)[V_c(2) - V(1,2)]\chi(2,1)\phi(1)\, d\tau_1 \quad .\end{aligned} \tag{2.12}$$

Equation (2.12) may be obtained by setting $F = \phi$ in (2.7) and (2.8) and adding the results. The normalization may be obtained from (2.1) in a similar manner.

$$\begin{aligned}\int |\psi_{\mathrm{po}}(1,2)|^2 d\tau_1\, d\tau_2 = \int [1 + N(2)]\phi^2(2) \\ \times d\tau_2 + [\,\int u_0(2)\phi(2)\, d\tau_2]^2 + \int \phi(2)\phi(1) \\ [2u_0(1)\chi(2,1) + \chi(1,2)\chi(2,1)]\, d\tau_1\, d\tau_2 \; .\end{aligned} \tag{2.13}$$

It is obvious that both the coupled pair of Eqs. (2.7) and (2.8), and the single equation (2.11) of the more usual approach, are quite complicated, and as a result, most authors who have used the PO method have made certain approximations in order to simplify their calculations. These approximations include dropping some or all of the exchange terms involving the distorted function χ, and the neglect of some of the direct terms as well. Use of either Eqs. (2.7) and (2.8) or (2.12) will lead to a variational bound on the binding energy of H$^-$ which is destroyed by most common approximations. It is desirable, in order to evaluate the utility of approximations, to compare their results both with the known exact answer and with the consequences of the variational problem which they are intended to approximate. We will now turn to a description of several approximations which have been employed.

The simplest approximation involves neglect of the perturbed function χ in all terms (both direct and exchange). This leads to the relatively simple equation

$$\begin{aligned}[H_0(2) - \epsilon + V_c(2)]\phi(2) = \mp \int u_0^*(1) \\ \times [\epsilon_{1s} - \epsilon + V(1,2)]\phi(1)\, d\tau_1 u_0(2) \quad .\end{aligned} \tag{2.14}$$

This will be called the SE approximation. It does yield a variational bound. The SE approach is a slightly restricted form of the open-shell Hartree-Fock procedure.

Our principal interest is in those methods which attempt to include some of the consequences of the distortion of the atom by the external particle. The simplest of these, the adiabatic-exchange approach, includes only the polarization potential in addition to those terms already in the SE equation (2.14). Even so, there are many possibilities:

One may use the full polarization potential (2.9c), which was given by Dalgarno and Lynn.[7] This will be called the adiabatic-exchange-total (AET) method. Alternately, on substituting the potential (2.6b) into (2.9c), and expanding both $|r_1 - r_2|^{-1}$ and the perturbed orbital χ in Legendre polynomials [see (2.3)], we have

$$V_p(2) = \sum_l V_{p,l}(r_2) , \qquad (2.15a)$$

where
$$V_{p,l} = \frac{4\pi e^2}{(2l+1)} \int u_0(1)$$

$$\times \chi_l(r_1, r_2)(r_<^{\,l}/r_>^{\,l+1}) r_1^2 \, dr_1 , \qquad (2.15b)$$

in which $r_<(r_>)$ is the lesser (greater) of r_1 and r_2. Because the perturbed function χ is orthogonal to u_0,

$$\int u_0(1)\chi(1,2)\,d\tau_1 = 0 \quad , \qquad (2.16)$$

the $l = 0$ (monopole) component of the polarization potential falls off exponentially at large distances. The dipole component ($l = 1$) is the longest-range component (r_2^{-4}) of the polarization potential; and many authors have retained only this term. We call this the adiabatic-exchange-dipole (AED) approximation. The expression for $V_{p,1}$ that we use was first given by Bethe.[1] An additional approximation is sometimes made in which one retains only the "outer" part of the perturbed orbital: That is, one imposes the condition that $r_2 \geq r_1$ in the calculation of χ_1 and $V_{p,1}$.[2,3,9] This latter restriction leads to considerable complications in calculations if handled consistently, and makes relatively little difference to the final results: We will not consider this in detail.

The AED approximation is surprisingly successful in yielding reasonable values of scattering phase shifts; consequently, it has been employed by many authors. For systems with relatively small polarizabilities, it tends to underestimate slightly the attractiveness of the effective potential (compare Temkin and Lamkin[10] with Schwartz [11]); however, when the polarizability is large, too much attraction may be present. An example of the latter case is the triplet metastable state of helium (2^3S).[12] If the complete polarization potential (AET) is employed, the results are much less successful, as the effective potential is now considerably too attractive.[13] The difficulty has been attributed to the monopole ($l = 0$) component of V_p. Although this term decays exponentially at large distances from the atom, it is quite significant at small distances.

The excess attraction produced by the monopole component of the polarization potential is canceled by the distortion potential, whose introduction leads to the extended-polarization method (EP).[14] In this approach, one drops the third-order direct term V_3 and all of the contributions from the perturbed function χ to the exchange terms. All second-order direct terms are retained; however, a transformation can be found which removes N, V_N, and W, and replaces them with the distortion potential V_D, which is, for the case of hydrogen,

$$V_D(2) = \int |\nabla_2 \chi(1,2)|^2 \, d\tau_1 . \qquad (2.17)$$

The EP method thus considers the equation (again for the electron-hydrogen system)

$$[H_0(2) - \epsilon + V_c(2) + V_p(2) + V_D(2)]\phi(2)$$

$$= \mp \int u_0^*(1)[\epsilon_{1s} - \epsilon + V(1,2)]\phi(1)\,d\tau_1 u_0(2) \quad . \qquad (2.18)$$

As a practical matter, this equation differs from that used in the AET approach only by the inclusion of the repulsive distortion potential V_D. This term corrects the excess attraction obtained when the complete polarization potential alone is considered. Unfortunately, evidence from the present calculation and Refs. 12 and 14 indicates that the correction may, in a practical sense, be too large: The effective potential is too repulsive. In view of this, one may ask whether matters would be improved by inclusion of the third-order terms in (2.16). It is known that if the wave function for a system is given to first order in some perturbation, the expectation value of the Hamiltonian with this wave function will be correct through terms of third order in the perturbation. We have, therefore, also investigated an approximation in which all terms on the left-hand side of (2.12) are retained, but only the undistorted exchange is used. Unfortunately, this approximation is not an obvious improvement, as the additional terms are, on the average, repulsive.

A different scheme of approximation was proposed by Temkin and Lamkin. Their method involves the following: (i) Only the dipole component of the perturbation function is retained. (ii) Project on the unperturbed orbital only [i.e., use (2.5a) with $F = \phi$]. (iii) Retain only the portion of the perturbed orbital $\chi_1(r_1, r_2)$ in which $r_2 \geq r_1$. The equation solved may be obtained from (2.7), subject to these modifications. It is to be noted that the second step of this procedure destroys the ability of the method to give a variational bound to the energy of H$^-$ (or to give stationary phase shifts). Nonetheless, the method of Temkin and Lamkin has been found to yield good results for electron-hydrogen scattering,[10] and electron-helium scattering,[15] although it is less successful in positron-hydrogen scattering where it closely resembles the AED approximation.

Sloan modified the equation of Temkin and Lamkin by observing that there was a contribution from derivatives of the step function $\epsilon(r_2 - r_1)$ which is introduced in accord with (iii).[9] In the present case of H^-, the function ϕ is purely s type, so that these terms do not contribute. The equation of Temkin and Lamkin for *spherically symmetric* function $\phi(r)$ is

$$[H_0(2)+V_c(2)+V_{p,1}(2)-\epsilon]\phi(2)\pm\int u_0(1)\times[\epsilon_{1s}-\epsilon+V(1,2)]\phi(1)\,d\tau_1\,u_0(2)\pm\int u_0(1)V(1,2)\phi(1)\chi(2,1)\,d\tau_1=0\,. \qquad (2.19)$$

III. METHODS OF CALCULATION

The direct terms V_p, V_3, and V_D, based on the Dalgarno and Lynn[7] function $\chi(1,2)$, can be written as the sum of the products of infinite integrals and integrals over angles. The infinite integrals were calculated using Gauss-Laguerre quadrature, and integrals over angles were calculated using Gaussian quadrature. The function V_N was obtained by numerical differentiation of N, and finally, W is obtained as follows:

$$W(R)=V_D(R)+(1/R+\tfrac{1}{2}\,d/dr)V_N(R)\quad . \qquad (3.1)$$

The function V_N was also differentiated numerically. Additional details can be found in Appendix A of Ref. 6.

The integro-differential eigenvalue equations considered are of the general type:

$$P''(r)=[F(r)-\epsilon]P(r)+\int S(r,r')P(r')\,dr'\quad . \qquad (3.2)$$

The pair of Eqs. (2.7) and (2.8) was treated by a different method. We need solutions which satisfy the boundary conditions

$$P(0)=0;\quad P(r)\to 0,\ \text{as}\ r\to\infty\quad , \qquad (3.3)$$

$$\text{and}\quad \int_0^\infty [P(r)]^2\,dr=1\quad . \qquad (3.4)$$

Since Eq. (3.2) is essentially homogeneous in P, one may seek solutions satisfying (3.3) and, once such a solution has been obtained, the normalization condition may be easily satisfied. In practice, Eq. (3.2) may be written

$$P''(r)=[F(r)-\epsilon]P(r)+G(r)\quad . \qquad (3.5)$$

To solve (3.5) one initially guesses the eigenvalue and a corresponding wave function proportional to $\exp[-(|\epsilon|)^{1/2}r]$. This guess is used to evaluate the term $G(r)$. Numerov's procedure is then employed to integrate Eq. (3.5) outward from the origin and from a distant point inward. These solutions are carried to a matching point. A solution of Eq. (3.5) with $G(r)=0$ is added to the inward solution, so that the inward solution at the matching point coincides with the outward solution.

The resulting wave function is a solution of Eq. (3.5) except at the matching point. Froese has given a correction formula for the eigenvalue based on the discrepancy at the matching point.[16] A better approximation to the binding energy is obtained using this formula. The process is iterated until the inward and outward solutions at the matching points agree. The iterations are finally stopped when (a) the energy correction is less than 10^{-7} Ry; and (b) the inward homogeneous solution being added is such that the ratio of the homogeneous to inhomogeneous solution at the matching point is less than 10^{-6}. We tested the stability of our solutions by varying the matching points. A step of $0.04a_0$ was used and the starting point for inward integration was taken to be $25a_0$.

In order to avoid the complications of solving directly the pair of coupled integral equations [(2.7) and (2.8)], and to confirm the surprisingly low value of the magnitude of the binding energy tentatively obtained from (2.11), we decided to proceed by conventional variational techniques. The functions ϕ and F were expressed as combinations of Slater orbitals:

$$\phi(1)=\textstyle\sum_i a_i f_i(1)\quad , \qquad (3.6)$$

$$F(1)=\textstyle\sum_i b_i f_i(1)\,, \qquad (3.7)$$

$$\text{where}\quad f_i=[(\zeta_i)^{3/2}/\pi^{1/2}]\,e^{-\zeta_i r}\,. \qquad (3.8)$$

The functions f_i are normalized, but not orthogonal. Standard variational techniques enable us to determine the binding energy ϵ from the lowest eigenvalue of the system ($\epsilon=E-\epsilon_{1s}$):

$$H\vec{u}=ES\vec{u}\quad , \qquad (3.9)$$

where $\vec{u}$ denotes a vector consisting of the coefficients a_i and b_i when the trial wave function is (2.4), and the a_i alone when (2.1) is used. H and S are the Hamiltonian and overlap matrices on the basis of the f_i. Most of our calculations employed five exponential functions and, for convenience, the same functions were employed in the expansion of both ϕ and F.

We decided not to attempt the complicated exchange integrals using the full Dalgarno-Lynn function for χ. Instead, we employed the expansion of χ in spherical coordinates (2.3), and retained the

TABLE I. List of variations and approximate forms of the general PO method.

Approximation	Direct terms retained	Exchange	Variational bound?
SE	V_c	undistorted	yes
AED	V_c, $V_{p,1}$	undistorted	no
AET	V_c, V_p	undistorted	no
EP	V_c, V_p, N, W, V_N	undistorted	no
All direct terms (DT)	All	undistorted	no
PO	All	distorted	yes
Polarized orbital, dipole (POD)	components of above resulting from χ_1	distorted components from χ_1	yes
Temkin-Lamkin (TL)	V_c, $V_{p,1}$(part)	portion of distorted component from χ_1	no
Modified polarized orbital (MPO)	All	distorted	yes

first three terms. This amounts to inclusion of monopole, dipole, and quadrupole terms. For consistency, the quantities of Eq. (2.9) were computed in the same approximation. The differences with respect to the same quantities computed from the full Dalgarno-Lynn functions are generally small. The agreement is excellent at both large and small r since the dominant components in both regions have been retained. The difference is largest at intermediate r (for example, the relative difference of V_p is largest at $r = 3a_0$, where it amounts to 7.6%). The elements of H and S are found by substituting the expansions for ϕ and F into (2.7), (2.8), (2.10), or (2.12) and (2.13). Since the expressions for these elements are quite lengthy, and their calculation is straightforward, we will not give their explicit forms here. Matrix elements involving the perturbed function χ, and those containing the auxiliary functions of Eqs. (2.9c) – (2.9g) were computed by numerical integration. Exchange integrals were carried out to approximately $20a_0$; others to $40a_0$.

We have not attempted to optimize the choice of exponents ζ in an extensive manner, nor have we investigated the effects of inclusion of more than five functions f_i in the expansions of ϕ and F. However, the results obtained when only four functions are considered differ from those involving five functions by only 0.003 Ry. This indicates to us that further improvement resulting from additional functions would probably be small.

IV. RESULTS, CONCLUSIONS, AND DISCUSSIONS

The binding energy of H^-, calculated according to the various approaches listed in Table I and discussed in the text, is presented in Table II. The conclusions we draw from these results are as follows:

(a) The PO wave function (2.1) is a very poor approximation for H^-. It is actually a worse function than is obtained if correlation is neglected and one uses the SE approximation.

This result may seem paradoxical at first because one feels that the addition of the perturbed wave function χ to u_0 should have given the total wave function increased flexibility, and so should yield a lower energy. Such a supposition is not correct, however, since a prescribed function has been added, and only the single function ϕ can be adjusted in either case.

(b) If the PO wave function is modified, as suggested by Drachman, by the insertion of an additional independent function multiplying the perturbed orbital χ [see Eq. (2.4)] a good approximation is obtained. The binding energy in this approximation, – 0.0544 Ry, differs from the exact value by approximately 2%. This function is thus

TABLE II. Binding energies of H^- in various approximations. See Table I for a list of the characteristics of the various approximations. All results (except the "best value") have an uncertainty of about 1 or 2 in the last decimal place given.

Approximation	Binding energy (Ry)
SE	−0.0265
AED	−0.0513
AET	−0.0769
EP	−0.0295
DT	−0.0241
PO	−0.0094
POD	−0.0273
TL	−0.0642
MPO	−0.0544
Best value (Pekeris)	−0.0555

better than a 6-parameter Hylleraas-type wave function (which yields $\epsilon = -0.0529$ Ry) but not so good as an 11-parameter Hylleraas function ($\epsilon = -0.0551$ Ry).[17] The introduction of the additional function F into (2.4) evidently gives the wave function essential additional flexibility.

(c). The best of the approximations of a nonvariational type considered is the AED. The approximation of Temkin and Lamkin also yields a relatively good value of the energy. Qualitatively, these results are consistent with the rather good scattering lengths for singlet e^--H scattering which these approximations produce.[18] However, since these approaches are not variational in character, it is not possible to conclude that the wave function used is correspondingly good.

(d). The other nonvariational approaches studied, AET, EP, and DT (see Table I), are less satisfactory; the errors being in the direction described in Sec. II.

In the case of the EP method, the present results show that the combination of polarization and distortion potentials is too strongly repulsive at small distances. In problems less dependent on the inner region of the effective potential, and more sensitive to the behavior at large distances, such as the calculation of the low-energy p-wave phase shifts for e^--H scattering, the EP method gives decidedly better results than either AED or the Temkin-Lamkin approximation.

(e). The poor results of the PO method appear to be associated with use of the adiabatic perturbed orbital χ in the inner region of the atom. This conclusion is not a new one[4]; and in support of it, we observe that if a variational calculation is made using only the $l = 1$ component of χ (polarized orbital dipole), the resulting binding energy of -0.027 Ry, although not particularly good in itself, is substantially better than that obtained when the monopole component of χ is included. Comparison of the results of the various approximations listed in Table II indicates to us that it is the exchange terms involving the monopole component of χ which are responsible for the most serious difficulties.

TABLE III. Exponents (ζ_i) and coefficients a_i and b_i appearing in the expansions [Eqs. (3.6) and (3.7)] of the functions ϕ and F.

ζ_i	a_i	b_i
0.23	0.237	0.131
0.35	0.173	1.145
0.50	0.706	−0.987
0.75	−0.420	0.246
1.40	0.140	0.007

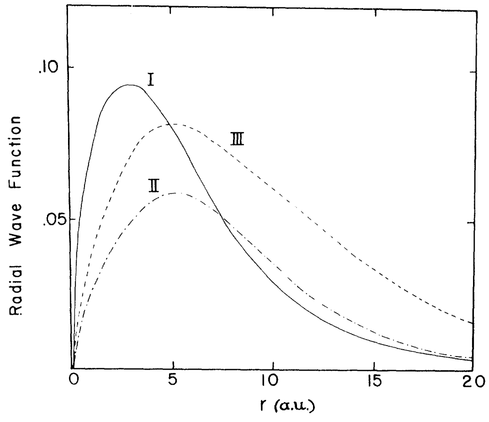

FIG. 1. Radial wave functions ϕ and F (each multiplied by radius r in atomic units) from Eq. (2.4) are shown in curves I and II, respectively. Curve III presents the function ϕ from Eq. (2.1) (also multiplied by r).

The coefficients a_i and b_i [Eqs. (3.6) and (3.7)] in the expansion of the functions ϕ and F appearing in Eq. (2.4) are given in Table III. The functions are so normalized that the total wave function $\psi_D(1, 2)$ is normalized to unity. The functions ϕ and F are shown in Fig. 1 (curves I and II, respectively), where they are compared with the function ϕ from the wave function (2.1) (curve III). The ratio of F to ϕ (II/I) becomes small in the interior of the atom, as the preceding argument suggests. On the other hand, F and ϕ become nearly equal at large distances, indicating that the wave function (2.1) treats atomic distortion correctly at large distances. However, the function ϕ obtained directly, using (2.1), is clearly much too extended.

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[18] The scattering lengths quoted in Ref. 10 are slightly too large owing to the lack of a correction for the long-range potential. If we take this into account, the singlet e^--H scattering lengths given by Temkin and Lamkin become $6.3a_0$ (exchange adiabatic) and $5.6a_0$ (their polarized orbital), respectively. The exact value is $5.965a_0$, due to Schwartz (Ref. 11). However, the polarization potential used by Temkin and Lamkin in their adiabatic-exchange approximation is not the same as the Bethe potential used here in the AED. Our value for the corrected scattering length in the AED is $6.15a_0$, which is closer to the exact value than the corrected result of the Temkin-Lamkin method.

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Localization of Electronic States in One-Dimensional Disordered Systems*

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The localization of electronic states in one-dimensional disordered systems is examined in terms of the reflection and transmission coefficients. The transfer-matrix method is used. The main body of the work deals with a one-dimensional liquid model in which the central part of the potential remains the same in all cells, and only the lengths of the flat arms vary from cell to cell. It is found that the contribution of the initial phase of a wave at the zeroth cell to the phase at the nth cell is reduced by a factor $(1-|r|)/(1+|r|)$ every time in passing through a cell. When the phase memory is completely lost, $\Phi_j \sim \phi_j$, where the reflection coefficient of the jth cell is $r_j = |r| e^{i\phi_j}$. If Φ_j obeys a uniform or nearly uniform probability distribution, the wave function always grows exponentially. It is shown that in most cases, especially when cell size distribution has a wide spread, $P(\Phi)$ is nearly always uniform. All wave functions are localized in a completely disordered system, but in the one-dimensional liquid model nonlocalized states do exist.

I. INTRODUCTION

The existence of localized states in disordered systems is of fundamental importance in the understanding of the electronic properties of systems like random impurities and alloys, amorphous substances, and liquids.[1] As an example, when the wave functions are localized, the electrons can move only by activated hopping. The transport properties are therefore quite different from those of the usual propagating solutions. An exact discussion of the general problem in three dimensions is difficult even in the independent one-electron approximation.

In one-dimensional disordered systems, it has been conjectured by Mott and Twose[2] that all solutions of the Schrödinger equations are localized. A wave function in one-dimensional space is said to be localized if, starting from a point x_0, the envelope of its amplitude decays or grows exponentially with the distance $|x-x_0|$ (see Mott, Ref. 1, p. 52). Proofs have been provided by Borland, Hori, and Minami.[3] These have been reviewed and commented on by Mott[1] and Halperin.[4] Here we