

Ground state and elastic phase shift of the electron-hydrogen system studied in hyperspherical coordinates*

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Using hyperspherical coordinates and adiabatic expansion methods, we obtain the potential curves for the electron-hydrogen system in 1S states. From the lowest potential curve we compute the ground-state energy of H^- to be -1.0547 Ry. We also compute the elastic scattering phase shifts at low energies from the same potential curve. Results are very good at low energies. The variations of important correlation effects as the system expands are also investigated.

I. INTRODUCTION

The electron-hydrogen system has been of great theoretical interest since the early quantum physics. It is the simplest quantum mechanical system that cannot be solved exactly and thus serves as a test for various theoretical models. Even though its ground-state energy has been computed accurately by large-scale variational methods,¹ our understanding of the two-electron dynamics is still quite inadequate.²

This lack of understanding is mainly due to the multidimensional nature of the two-electron wave functions, which are not mapped as conveniently as the radial hydrogenic wave functions. Thus, even though variational calculations give good results, they do not represent clearly the dynamic behavior of the two-electron motion. Another conventional approach starts from the independent-particle model by neglecting the electron-electron correlation effect and describing the motion of each electron in the central potential field that results from the nuclear attraction and an averaged screening by the other electron. In this model, the ground state of H^- is designated as $1s^2\ ^1S$, implying that each electron is described by a $1s$ orbital. Unfortunately, this model does not even predict the existence of a bound state for the H^- system, which is very diffuse and cannot be adequately represented by localized atomic orbitals $1s^2\ ^1S$.

This paper presents results obtained by a method which has been developed for the study of the doubly excited states of helium (isoelectronic to H^-),³ and which can provide both a suitable description of the two-electron dynamics and fairly accurate quantitative results for the bound and scattering problems for the $e-H$ system. Instead of solving the two-electron system variationally, we solve its Schrödinger equation directly by looking for quasiseparability of this equation and of its wave functions in a suitable, hyperspherical co-

ordinate system.

In this coordinate system, the distances r_1 and r_2 of the two electrons from the nucleus are replaced by a hyperradius $R = (r_1^2 + r_2^2)^{1/2}$ and a hyperangle $\alpha = \arctan(r_2/r_1)$. These two coordinates R and α , together with the spherical angles (θ_1, ϕ_1) and (θ_2, ϕ_2) of the two electrons replace the usual independent-particle coordinates (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) of each electron. In this way, the motion of the two electrons is viewed as that of a single particle in a six-dimensional hyperspace under the influence of a multidimensional potential. The coordinate R represents the size of the whole system whereas the five angles $\Omega = \{\alpha, \theta_1, \phi_1, \theta_2, \phi_2\}$ represent the relative positions of the two electrons and their orientation in space. It must be emphasized that the exchange part of the potential does not appear in this picture in its usual nonlocal form but is included in the multidimensional local potential. Furthermore, the constraint due to the identity of the two electrons is equivalent to imposing at each hyperspherical surface a boundary condition on the wave function, as the interchange of two electrons amounts to changing α into $\frac{1}{2}\pi - \alpha$ and interchanging (θ_1, ϕ_1) with (θ_2, ϕ_2) .

In this paper, we present some quantitative results using the methods of I for the $e-H^1S$ system,³ in particular for the ground state of H^- and the elastic scattering phase shift of $e+H$. We will see that this approach provides a clearer physical interpretation of the two-electron dynamics than the independent-particle model does, while its quantitative results are better than those of comparably modest variational calculations. Furthermore, we treat the bound state of H^- and the elastic scattering process by a single set of calculations.

The six-variable Schrödinger equation was reduced to a system of coupled differential equations in I by expanding the wave function in the form $\psi(R, \Omega) = \sum_{\mu} F_{\mu}(R) \Phi_{\mu}(R; \Omega)$. By neglecting the small coupling terms among the equations, one gets a

set of ordinary differential equations for the separate hyperradial wave functions $F_\mu(R)$. Each equation has an effective potential term $U_\mu(R)$ which can be viewed as the field experienced when the system expands. The ground state of H^- is the lowest bound state for the lowest potential curve $U_1(R)$. The elastic-scattering phase shifts are obtained by solving the potential-scattering problem with the same potential $U_1(R)$.

Section II summarizes the method of this calculation which is explained in greater detail in I. Section III presents the lowest potential curve for the $e-H^+S$ system using two different representations of $\Phi_\mu(R; \Omega)$, namely, one in the adiabatic representation which includes the mixing of s^2 , p^2 , and d^2 components, while the other is an intermediate representation that includes only s^2 , thus attributing orbital angular momentum $l=0$ to each electron. The ground state energy of H^- is obtained from the lowest potential curve. In Sec. IV, we compute the elastic scattering phase shifts from this same potential curve. Nonadiabatic coupling with the next higher potential curve is also investigated and comparisons are made with large-scale variational calculations.

II. METHODS OF CALCULATIONS

In atomic units, the Schrödinger equation for the two-electron wave function $\psi(R, \Omega)$ ($\Omega \equiv \{\alpha, \theta_1, \phi_1, \theta_2, \phi_2\}$) in hyperspherical coordinates is

$$\left(\frac{d^2}{dR^2} - \frac{\Lambda^2 + \frac{15}{4}}{R^2} + \frac{C}{R} + 2E \right) (R^{5/2}\psi) = 0, \quad (1a)$$

where

$$\Lambda^2 = -\frac{1}{\sin^2\alpha \cos^2\alpha} \frac{d}{d\alpha} \left(\sin^2\alpha \cos^2\alpha \frac{d}{d\alpha} \right) + \frac{\tilde{I}_1^2}{\cos^2\alpha} + \frac{\tilde{I}_2^2}{\sin^2\alpha} \quad (1b)$$

is the squared grand angular momentum operator and

$$C = \frac{2Z}{\cos\alpha} + \frac{2Z}{\sin\alpha} - \frac{2}{(1 - \sin 2\alpha \cos\theta_{12})^{1/2}} \quad (1c)$$

is an effective nuclear charge. In Eq. (1b), \tilde{I}_1 and \tilde{I}_2 are the usual orbital angular momentum operators for electron 1 and 2. In Eq. (1c), Z is the nuclear charge. The structure of this equation is similar to that of the radial equation of the hydrogen atom, except that Λ^2 and C are now noncommuting operators of the angular variables Ω .

At small R , the behavior of Eq. (1) is dominated by the effective centrifugal potential term $-(\Lambda^2 + \frac{15}{4})/R^2$. The angular part of ψ is then approxi-

mately an eigenfunction of Λ^2 . As R increases, the Coulomb interaction operator C becomes more important and the eigenfunctions of Λ^2 no longer provide a suitable representation. We thus expand $\psi(R, \Omega)$ as

$$R^{5/2}\psi(R, \Omega) = \sum_{\mu} F_{\mu}(R) \Phi_{\mu}(R; \Omega), \quad (2)$$

where R is treated as a parameter in $\Phi_{\mu}(R; \Omega)$ and $\{\Phi_{\mu}(R; \Omega)\}$ forms a complete basis set at each R . With this expansion, the Schrödinger equation (1) is reduced to the matrix form

$$\left[\left(\frac{d^2}{dR^2} + \frac{1/4}{R^2} + 2E \right) \underline{I} - \underline{U}(R) + \underline{W}(R) \right] \vec{F}(R) = 0, \quad (3)$$

where \underline{I} is the identity matrix;

$$U_{\mu,\nu}(R) = \frac{1}{R^2} \left(\Phi_{\mu}(R; \Omega) \left| -\frac{d^2}{d\alpha^2} + \frac{\tilde{I}_1^2}{\cos^2\alpha} + \frac{\tilde{I}_2^2}{\sin^2\alpha} - RC \right| \Phi_{\nu}(R; \Omega) \right) \quad (4)$$

and

$$W_{\mu,\nu}(R) = 2 \left(\Phi_{\mu}(R; \Omega), \frac{d}{dR} \Phi_{\nu}(R; \Omega) \right) \frac{d}{dR} + \left(\Phi_{\mu}(R; \Omega), \frac{d^2}{dR^2} \Phi_{\nu}(R; \Omega) \right). \quad (5)$$

In Eqs. (4) and (5), the parentheses indicate integration over Ω . The evaluation of (5) is discussed in I.

Equation (3) is completely equivalent to the Schrödinger equation (1) without approximation so long as $\{\Phi_{\mu}(R; \Omega)\}$ forms a complete basis set at each R . However, if the coupling term can be neglected in a particular representation, Eq. (3) reduces to the simple ordinary differential equation

$$\left\{ \frac{d^2}{dR^2} - \left[U_{\mu\mu}(R) - \frac{1/4}{R^2} - W_{\mu\mu}(R) \right] + 2E \right\} F_{\mu}(R) = 0, \quad (6)$$

where the terms in the square brackets represents the effective potential field for the motion along R .

In I, we have chosen two representations for $\Phi_{\mu}(R; \Omega)$. Since each $\Phi_{\mu}(R; \Omega)$ reduces at $R \sim 0$ to an eigenfunction $u_{l_1 l_2 m}(\Omega)$ of the Λ^2 operator where l_1, l_2 are the usual orbital angular momentum quantum numbers of the two electrons and m is a quantum number for the excitation in α , $\Phi_{\mu}(R; \Omega)$ was computed by expanding it in terms of $u_{l_1 l_2 m}(\Omega)$ at each R . We obtain the adiabatic representation of Φ_{μ} by diagonalizing the complete matrix of Eq. (4) in the basis $u_{l_1 l_2 m}(\Omega)$. The potential matrix \underline{U} thus obtained is diagonal and the only off-diagonal

matrix elements in Eq. (3) are those of W . In I, however, we also found it convenient to diagonalize separate submatrices of (4) with fixed (l_1, l_2) . The potential curves and basis functions thus obtained, called $v_p^{(l_1 l_2)}(R; \Omega)$ and $\phi_p^{(l_1 l_2)}(R; \Omega)$ respectively, correspond physically to taking into account radial correlations due to the electron-electron interaction while neglecting the angular correlations due to coupling of different pairs of (l_1, l_2) . This representation, to be called intermediate representation, regards (l_1, l_2) as good quantum numbers and has the property that $\phi_p^{(l_1 l_2)}(R; \Omega)$ is separable or almost separable.⁴ This separability is essential for sorting out the behavior of the multivariable wave functions for the complicated doubly-excited states of helium. In this paper, we use both the intermediate representation and the adiabatic representation; as a matter of fact, $v_p^{(l_1 l_2)}(R)$ is obtained as an intermediate step in the calculation of the adiabatic representation to avoid diagonalizing a large matrix directly. That is, we first obtain the potential matrix (4) in the intermediate representation which has nonzero off-diagonal elements only between pairs of $\phi_p^{(l_1 l_2)}$ and $\phi_{p'}^{(l_1' l_2')}$ with $(l_1, l_2) \neq (l_1', l_2')$. The adiabatic potential curves are then obtained by diagonalizing the intermediate potential matrices at each R . Thus, in the adiabatic representation, $\Phi_\mu(R; \Omega)$ is expressed as

$$\Phi_\mu(R; \Omega) = \sum_{(l_1 l_2 \rho)} a_{l_1 l_2 \rho}^{(\mu)}(R) \phi_p^{(l_1 l_2)}(R; \Omega). \quad (7)$$

The values of the mixing coefficients $a_{l_1 l_2 \rho}^{(\mu)}(R)$ at each R tell us how important is the angular coupling among different pairs of (l_1, l_2) .

III. GROUND STATE OF H^-

This section describes calculations for the $e-H^1S$ system.⁵ This system is expected to exhibit the largest correlation effects because both electrons are mainly in the s orbital with antiparallel spins, thus having greater probability of penetrating near the nucleus simultaneously and of interacting strongly with each other. The calculational procedure is detailed in I. Briefly, we obtain the potential matrix $U(R)$ in the intermediate representation first. This is done at each R by diagonalizing the s^2 , p^2 , and d^2 subspaces with 36, 36 and 15 basis functions μ_{00m} , μ_{11m} , and μ_{22m} , respectively, with $m = 0, 2, 4, 6, \dots$. The m values are limited to even integers by symmetry. By obtaining the resulting lowest 12 eigenvalues and their eigenvectors, we construct a 12×12 potential matrix in the intermediate representation. The adiabatic potential curves are then obtained by diagonalizing this potential matrix at each R . With this choice

of basis size, there is no difficulty in achieving good convergence at small and moderate values of R because basis functions with large m are excluded by their associated large centrifugal potential barrier. At larger R , such basis size is inadequate because of the increasing importance of Coulomb potential term. However, as detailed in I, since the wave functions are hydrogenic at large R , we can obtain the potential curves in this region by asymptotic expansion of (4) using $R \rightarrow \infty$ and $\alpha \rightarrow 0$. The potential curves are obtained by joining smoothly at some R_0 where both methods are adequate. For example, R_0 is about 6.5 a.u. for the lowest potential curve of H^- . As a matter of fact, if only the lowest potential curve is required, the basis size can be further reduced, but the same calculation served also to obtain potential curves for doubly-excited states.

Figure 1 shows the lowest two adiabatic potential curves $U_1(R)$ and $U_2(R)$ for the $e-H^1S$ system. Notice that the potential wells of $U_1(R)$ and $U_2(R)$ are located at very different values of R , corresponding roughly to the radius of the ground state and the lowest doubly-excited state of H^- . The curve $U_1(R)$ has a repulsive $0.25/R^2$ behavior at small R and converges to the potential field of the ground state of H at large R . In the intermediate region, we notice a broad and shallow attractive potential well, sufficiently strong to support a bound state, calculated to be -1.0547 Ry as indicated in Fig. 1 by dashed lines. This energy level corresponds to the ground state energy of H^- whose best value is -1.055502 Ry according to Pekeris.¹ Our re-

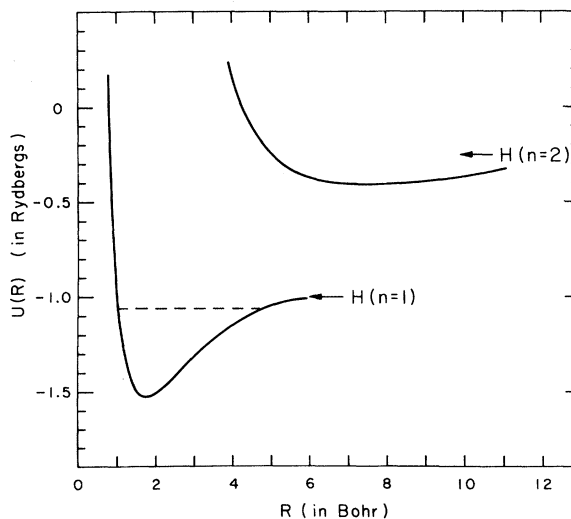


FIG. 1. Lowest two adiabatic potential curves $U_1(R)$ and $U_2(R)$ of $e-H^1S$ system, each converges to the ground state and the first excited state of H , respectively. Dashed lines indicate the position of the H^- ground-state level computed from $U_1(R)$.

sult is comparable to that of an 11-parameter Hylleraas-type calculation.⁶ We would like to mention that our method of calculation gives an upper bound⁷ to the true energy. Better results can be obtained by improving the accuracy of potential curve $U_1(R)$ and by considering the coupling with higher potential curves.

Usually the ground state of H^- is designated as $1s^2^1S$, implying both electrons occupy the $1s$ orbital with opposite spin, but a Hartree-Fock calculation for this configuration fails to give a bound state. Figure 1 shows the ground state of H^- to be very diffuse, being bound by a broad and shallow potential; its radial wave function $F(R)$, shown in Fig. 2, extends over a large region of R which cannot be adequately represented by localized orbitals with the $1s^2^1S$ designation. To examine how good an s^2 representation of the ground state of H^- can be, we computed the eigenvalue from Eq. (6) with the intermediate representation $v_1^{(00)}(R)$ instead of $U_1(R)$. The result was -1.02617 Ry, indicating that even an approximation with both electrons in $l=0$ can yield a bound state for H^- . The inadequacy of a Hartree-Fock $1s^2^1S$ representation is thus mainly due to its lack of radial correlations.

As an index of the importance of angular correlation we plot in Fig. 3 the largest coefficients for p^2 and d^2 components of Eq. (7). These mixing coefficients peak in the intermediate region R where the radial correlations are also important.

IV. ELASTIC-SCATTERING PHASE SHIFT

The phase shifts for 1S elastic electron hydrogen scattering, computed from the potential curve shown in Fig. 1, are given in Table I, column 1-ch, together with the results of the three-state close-coupling calculations by Burke and Schey⁸ and of the variational calculations by Schwartz.⁹ Our phase shifts are better than those of the three-state close-coupling calculation at low energies in spite of our total neglect of coupling between adiabatic

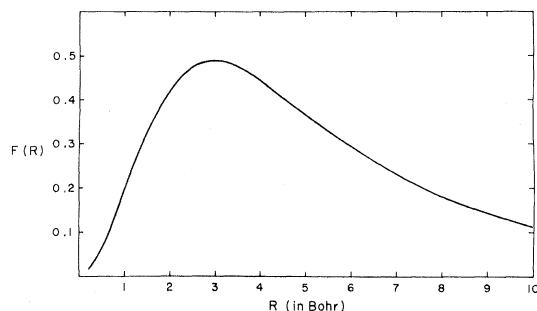


FIG. 2. Radial wave function of the H^- ground state calculated from Eq. (6).

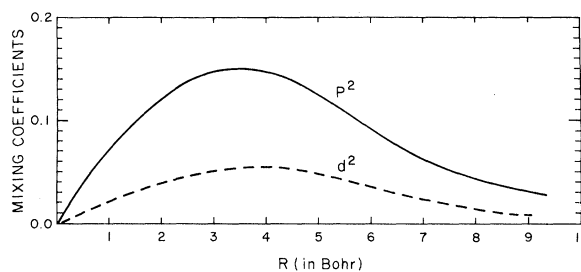


FIG. 3. Angular mixing coefficients $a(p^2)$ and $a(d^2)$ of Eq. (7) for the ground-state channel function at various R .

channels but they become less favorable at higher energies.

In order to illustrate the nonadiabatic effect, we then solved the two-channel coupled differential equations

$$\left[\frac{d^2}{dR^2} - \left(U_1(R) - W_{11}(R) + \frac{1/4}{R^2} \right) + 2E \right] F_1(R) + W_{12}(R)F_2(R) = 0, \quad (8)$$

$$\left[\frac{d^2}{dR^2} - \left(U_2(R) - W_{22}(R) + \frac{1/4}{R^2} \right) + 2E \right] F_2(R) + W_{21}(R)F_1(R) = 0, \quad (9)$$

by an iterative method.¹⁰ Notice that $W_{ij}(R)$ contains a differential operator d/dR which is different from the one included in the close-coupling equations. Because the coupling terms $W_{ij}(R)$ in Eqs. (8) and (9) are small, the phase shift converged to within 0.001 rad in three or four iterations at most. The phase shifts computed in the two-channel approximation are shown in column 2-ch of Table I. Note the improvement of two-channel results especially at higher energies. However, they remain not as good as the three-state close-coupling results for $k > 0.5$. This indicates the need for coupling with still higher channels. We did not develop this approach further because the convergence is not expected to be very fast. A better ap-

TABLE I. Elastic $e-H^1S$ scattering phase shift.

k	3cc ^a	1-ch	2-ch	Schwartz ^b
0.1	2.491	2.513	2.521	2.553
0.2	1.974	1.983	2.023	2.067
0.3	1.596	1.568	1.659	1.696
0.4	1.302	1.242	1.380	1.415
0.5	1.092	0.989	1.142	1.202
0.6	0.93	0.784	0.928	1.041
0.7	0.82	0.618	0.622	0.930

^a Three-state close-coupling calculations, Ref. 8.

^b Reference 9.

proach in this energy region would be to depart from the adiabatic representation of channels but we still do not have any more suitable representation.

V. DISCUSSION

Our results indicate that an adiabatic representation in hyperspherical coordinate affords a useful approximation to low-energy electron-hydrogen scattering. This approach treats the scattering and scattered electron quite symmetrically (in view of the fact that when they are interacting, there is no point in separating one from the other). The lower quality of this approximation at higher energies is understandable since the main coupling term between adiabatic channels is velocity dependent.¹¹

Both the adiabatic-hyperspherical and the close-coupling method rely on eigenfunction expansion but use different choices of eigenfunctions. Our method uses a correlated basis which varies ac-

cording to the radius R of the system while the close-coupling method uses a basis of target eigenfunctions. Intuitively, the close-coupling method works better when the incoming particle does not penetrate deeply into the interaction region while our method works better when the correlation effects are important. From a practical viewpoint, our calculations are much simpler especially when one goes into the higher-energy region where inelastic processes are allowed and many channels are involved. Here the number of coupled differential equations grows quite rapidly in the close-coupling method while in our method it grows only as does the number of physical open channels. We are now extending this approach to electron-impact excitation.

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¹See, for example, C. L. Pekeris, *Phys. Rev.* **126**, 1470, (1962).

²See, for example, the recent review by J. S. Risley, in *Atomic Physics IV. Proceedings of the Fourth International Conference on Atomic Physics, Heidelberg, 1974*, edited by G. zu Putlitz, E. W. Weber, and A. Winnacker (Plenum, New York, 1975).

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⁴The behavior of $\phi_{\beta}^{(1'1'2)}(R; \Omega)$ is studied and plotted in Sec. IV of I.

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¹⁰The author is indebted to Dr. R. F. Stewart for pointing out an effective way of solving an inhomogeneous bound equation by a finite difference method.

¹¹This is studied in I, Sec. IV. See also U. Fano and C. D. Lin, in Ref. 2.