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Effect of a Long-Range Potential on Compound States in the (*e*,H) System*

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A simple five-parameter wave function is constructed and the positions and widths of the lowest two compound states of the (*e*,H) system are calculated for both singlet and triplet spin multiplicities with zero total angular momentum. Very good agreement with previous calculations using more elaborate trial functions is obtained because particular attention is paid to the asymptotic form of the wave function. A method adopted from the double-perturbation theory for the systematic improvement of the calculation of widths and shifts of compound states is presented in an Appendix.

I. INTRODUCTION

A NUMBER of variational calculations have recently been carried out for compound-state level positions in simple electron-atom scattering systems such as the (*e*,H) and (*e*,He$^+$) systems. In these calculations large numbers of variational parameters[1,2] or configuration interactions[3] were used. It is the purpose of this paper to show that with appropriate allowance for the physically required long-range effect for the compound states, a simple variational wave function may be constructed.[4] Such a wave function constructed for the compound states in the (*e*,H) system with only five parameters is capable of yielding values which are comparable to previous variational results for the lowest compound state in each symmetry and lower than previous variational results for higher members of the triplet series.

In the next section the long-range effect in H$^-$ compound states is discussed. A simple orbital wave function which incorporates explicitly the long-range effect is constructed for the projectile electron. A variational calculation is carried out using a simple five-parameter trial wave function obtained in terms of these orbitals. The procedure of our calculation is presented in Sec. III, where the explicit functional form of the trial wave function is given. Utilizing the optimal wave functions, the widths of the states are calculated. Results of the calculation are presented in Sec. IV in which a comparison with other variational and close-coupling calculations is made. Finally, in the Appendix, we show that having obtained such a variational quasistationary wave function, a systematic improvement of the calculation of level width, as well as level shift, can be carried out using a well-known stationary-perturbation method.[5]

II. LONG-RANGE EFFECT

It has been shown by Gailitis and Damburg[6] that in the (*e*,H) scattering system, the interaction between the projectile electron and the degenerate $n=2$ levels of hydrogen at large distances is an attractive r^{-2} long-range potential. This interaction potential can be obtained by asymptotically decoupling the coupled equation for the projectile electron in the $2s$ and $2p$ degenerate field.[6,7] Thus, asymptotically, one has, for the projectile electron, the simple equation

$$\{d^2/dr^2+k_\alpha{}^2-\lambda(\lambda+1)/r^2\}\xi_\alpha(r)=0, \tag{2.1}$$

where k_α is the wave number of the projectile electron, $\lambda(\lambda+1)=1-\sqrt{37}$ is a negative quantity which measures the interaction strength of the r^{-2} potential tail. Such a potential is capable of supporting an infinite number of bound states provided the potential close to the proton is not too singular.[8] The details of the potential in the interior region do not play an important role[9,10] in determining level positions of higher members ($\alpha>0$) in the compound-state series just below the $n=2$ excitation threshold.

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The physical situation becomes more apparent if one examines the extent of delocalization of the solution of Eq. (2.1). The solutions of Eq. (2.1) which satisfy the bound-state exponential-decay boundary condition at infinity are the Hankel function of the first kind,

$$H_{i\lambda_0}{}^{(1)}(i|k_\alpha|r)=\frac{2e^{\pi\lambda_0/2}}{i\pi}\int_0^\infty e^{-|k_\alpha|r\cosh(z)}\times\cos(\lambda_0 z)dz \tag{2.2}$$

$$\xrightarrow[r\to\infty]{} -i\left(\frac{2e^{\pi\lambda_0}}{\pi|k_\alpha|r}\right)^{1/2}e^{-|k_\alpha|r}, \tag{2.3}$$

where $\lambda_0=-i(\lambda+\frac{1}{2})=(\sqrt{37}-5/4)^{1/2}$. Since the wave number $|k_\alpha|$ decreases exponentially with α,[6] we have

$$|k_\alpha|^2\propto e^{-2\pi\alpha/\lambda_0}. \tag{2.4}$$

The range parameters for these solutions [see Eq. (2.3)] are exponentially increasing as a function of α.[9] This is a consequence of the long-range r^{-2} potential tail experienced by the projectile electron in the field created by the degeneracy of the $n=2$ state of hydrogen.

It should be noted that this long-range effect is not confined to the $n=2$ levels. It can be shown quite generally that for each degenerate principal quantum number there may exist one or more such r^{-2} long-range potential tail with different interaction strength $\lambda(\lambda+1)$.[11] As a consequence of this long-range effect, the correlation effect encountered in actual bound states does not impose a serious problem here. This seems to be borne out in a recent variational calculation,[2] where it is found that the lowering in the calculated energy using a 50-term correlated trial wave function from that calculated without correlation terms is less than a small fraction of 1% even for the lowest resonant state.

Since the dominant long-range effect appears to delocalize the orbit of the projectile electron, an appropriate description of the compound state must therefore include this effect. Intuitively one would expect the orbitals for the projectile electron to be of the form[4]

$$\begin{aligned}\phi_\alpha(r)&=d(|k_\alpha|r_0)f_\alpha(r) & r&\leq r_0\\ &=r^{1/2}H_{i\lambda_0}{}^{(1)}(i|k_\alpha|r_0)\,, & r&\geq r_0\end{aligned} \tag{2.5}$$

so that at large r it assumes the solution in a r^{-2} potential tail. The function f_α in Eq. (2.5) is some appropriate polynomial in r and the constant $d(|k_\alpha|r_0)$ is a matching constant for the orbital at r_0.

Now if the long-range potential is indeed the dominant effect in compound-state formation, an adequate quasistationary representation of the compound-state wave function can be constructed in terms of such orbitals. To test this idea, a variational calculation of the compound states in the elastic channel of the (e,H) system is carried out using a simple trial wave function constructed in terms of these orbitals. The joining radius r_0, the exponent decaying amplitude k_α, and the coefficients of the polynomial f_α are treated as parameters. Very encouraging results which substantiate our intuition are obtained. (See Sec. IV.)

III. VARIATIONAL PROCEDURE

The quasistationary representation of the compound-state wave function is given[12] by the bound-state solution of

$$(QHQ-\mathcal{E}_\alpha)Q\Phi_\alpha=0, \tag{3.1}$$

where $\mathcal{E}_\alpha$ is the quasistationary resonance energy, and Q is a projection operator which projects onto the closed-channel portion of the Hilbert space. Hahn *et al.*[13] have pointed out that QHQ satisfies the minimum principle so that the Rayleigh-Ritz variational representation of $Q\Phi_\alpha$ can then be obtained. The choice of n terms in the trial function $Q\Phi^{\text{tr}}$ leads to an $n\times n$ Hamiltonian matrix which when diagonalized gives upper bounds to the n lowest eigenvalues of QHQ.

Since the spacings between the compound states of H⁻ are small and decrease exponentially, it is numerically more flexible to optimize each resonance energy consecutively instead of solving the usual secular equations. For the α_0th compound state, we have the quotient

$$\frac{\langle\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}|QHQ|\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}\rangle}{\langle\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}|\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}\rangle}\geq\mathcal{E}_{\alpha_0}{}^{(\pm)}, \tag{3.2}$$

with

$$\Pi_{\alpha_0}{}^{(\pm)}=1-\sum_{\alpha=0}^{\alpha_0-1}g_\alpha{}^{(\pm)}, \tag{3.3}$$

$$g_\alpha{}^{(\pm)}=|\Pi_\alpha{}^{(\pm)}Q\hat{\Phi}_\alpha{}^{(\pm)}\rangle\langle\Pi_\alpha{}^{(\pm)}Q\hat{\Phi}_\alpha{}^{(\pm)}|\,, \tag{3.4}$$

where the $g_\alpha{}^{(\pm)}$'s are projection operators which project onto the nth optimized wave function. The caret on $Q\Phi_\alpha$ indicates that $Q\hat{\Phi}_\alpha$ is normalized:

$$\langle Q\hat{\Phi}_\alpha{}^{(\pm)}|\Pi_\alpha{}^{(\pm)}|Q\hat{\Phi}_\alpha{}^{(\pm)}\rangle=1. \tag{3.5}$$

The superscripts (+) and (−) in Eqs. (3.2) to (3.5) label the singlet and triplet spin multiplicities. Since the projection operators $g_\alpha{}^{(\pm)}$ are constructed in terms of eigenstates of Q (with unit eigenvalues), it is clear that $g_\alpha{}^{(\pm)}$ commutes with Q so that

$$[\Pi_\alpha{}^{(\pm)},Q]=0. \tag{3.6}$$

This commutation relation, together with the idempotent property of Q, permits us to replace QHQ in Eq. (3.2) by H. We then obtain

$$\frac{\langle\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}|H|\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}\rangle}{\langle\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}|\Pi_{\alpha_0}{}^{(\pm)}Q\Phi_{\alpha_0}{}^{(\pm)}\rangle}\geq\mathcal{E}_{\alpha_0}. \tag{3.7}$$

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[11] (a) P. G. Burke, Advan. Phys. **14**, 521 (1965); (b) M. H. Mittleman, Phys. Rev. **147**, 73 (1966).

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[13] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

For the lowest states $\alpha_0=0$ and $\Pi_{\alpha_0}^{(\pm)}=1$, Eq. (3.7) then reduces to the usual Rayleigh-Ritz quotient for Eq. (3.1).

To account for the long-range effect, we construct our trial variational wave function for the $L=0$ compound states lying just below the $n=2$ excitation threshold in terms of the orbitals given by Eq. (2.5):

$$Q\Phi_\alpha^{(\pm)}=\frac{(4\pi)^{-1}}{r_1r_2}\{[\chi_{20}(r_1)\phi_{\alpha0}^{(\pm)}(r_2)+\gamma_\alpha\chi_{21}(r_1)\phi_{\alpha1}^{(\pm)}(r_2)\times\cos\theta_{12}]\pm[1\leftrightarrow 2]\},\quad \alpha=0,1,\cdots,\qquad(3.8)$$

where the χ_{nl}'s are the radial target-hydrogen wave functions and the subscripts 0 and 1 in the ϕ's denote the s and p characters of the orbitals. The Q-projection operator for the two-electron system[13] is

$$Q=1-p_0(\mathbf{r}_1)-p_0(\mathbf{r}_2)+p_0(\mathbf{r}_1)p_0(\mathbf{r}_2),\qquad(3.9)$$

with

$$p_0(\mathbf{r})=|\chi_{10}(r)Y_{00}(\hat{r})\rangle\langle\chi_{10}(r)Y_{00}(\hat{r})|,\qquad(3.10)$$

where $\chi_{10}(r)Y_{00}(\hat{r})$ is the ground target-hydrogen wave function. Since Q is expressed in terms of p_0 which is orthogonal to χ_{20} and χ_{21}, the requirement that $\Phi_\alpha^{(\pm)}$ be an eigenstate of Q with unit eigenvalue can be easily satisfied by requiring the orbitals $\phi_{\alpha0}^{(\pm)}$ and $\phi_{\alpha1}^{(\pm)}$ given by Eq. (2.5) to be orthogonal to p_0.

The ϕ orbitals can then be expressed as

$$\begin{aligned}\phi_{\alpha0}^{(\pm)}(r)&=d_0(k_\alpha r_0)\sum_{n=1}^{n_0}a_{\alpha n}^{(0)}\left\{r^n-\frac{b_n}{c_2}\chi_{10}(r)\right\},\quad r\leq r_0\\&=r^{1/2}H_{i\lambda0}^{(1)}(i|k_\alpha|r)-\frac{b}{c_3}\chi_{10}(r),\quad r\geq r_0\end{aligned}\qquad(3.11)$$

$$\begin{aligned}\phi_{\alpha1}^{(\pm)}(r)&=d_1(k_\alpha r_0)\sum_{n=1}^{n_0}a_{\alpha n}^{(1)}r^{n+1},\quad r\leq r_0\\&=r^{1/2}H_{i\lambda0}^{(1)}(i|k_\alpha|r),\quad r\geq r_0\end{aligned}\qquad(3.12)$$

with

$$\begin{aligned}b_m&=\int_0^{r_0}r^m\chi_{10}(r)dr=2(m+1)!\left\{1-e^{-r_0}\sum_{t=0}^{m+1}\frac{r_0^t}{t!}\right\},\\b&=\int_{r_0}^{\infty}r^{1/2}H_{i\lambda0}^{(1)}(i|k_\alpha|r)\chi_{10}(r)dr,\\c_2&=\int_0^{r_0}|\chi_{10}(r)|^2dr,\\c_3&=\int_{r_0}^{\infty}|\chi_{10}(r)|^2dr,\\c_2+c_3&=1.\end{aligned}\qquad(3.13)$$

Where, the b's and c's in $\phi_{\alpha0}^{(\pm)}(r)$ arise from the orthogonal constraint between the φ and χ_{10} wave functions and d_0 and d_{i} are the matching constants at $r=r_0$. For the p orbital $\phi_{\alpha1}^{(\pm)}$, the orthogonal constraint is automatically satisfied due to the angular parts of the wave functions. Since any arbitrary constant factor in the series for the interior ($r\leq r_0$) wave function can be absorbed into the matching constants d_0 and d_1, we choose to take $a_{\alpha2}^{(0)}=a_{\alpha2}^{(1)}=1$.

We take the first coefficient in each wave function, $a_{\alpha1}^{(0)}$ and $a_{\alpha1}^{(1)}$, to satisfy the continuity condition of the logarithmic derivatives of the wave function at $r=r_0$.

$$\frac{\partial}{\partial r}\ln\left(\sum_{n=1}^{n_0}a_{\alpha n}^{(0)}\left[r^n-\frac{b_n}{c_2}\chi_{10}(r)\right]\right)\Bigg|_{r=r_0}=\frac{\partial}{\partial r}\ln\left[r^{1/2}H_{i\lambda_0}^{(1)}(i|k\alpha|r)-\frac{b}{c_3}\chi_{10}(r)\right]\Bigg|_{r=r_0}\qquad(3.14)$$

and

$$\frac{\partial}{\partial r}\ln\left[\sum_{n=1}^{n_0}a_{\alpha n}^{(1)}r^{n+1}\right]\Bigg|_{r=r_0}=\frac{\partial}{\partial r}[r^{1/2}H_{i\lambda_0}^{(1)}(i|k_\alpha|r)]|_{r=r_0}.\qquad(3.15)$$

The appropriate expressions for $a_{\alpha1}^{(0)}$ and $a_{\alpha1}^{(1)}$ are then

$$a_{\alpha1}^{(0)}=\frac{\sum_{n=2}^{n_0}a_{\alpha n}^{(0)}\{r_0^n[1-2n+2r_0Y(r_0)]+[1-2r_0-2r_0Y(r_0)](b_n/c_2)\chi_{10}(r_0)\},}{\{r_0-2r_0^2Y(r_0)-[1-2r_0-2r_0Y(r_0)](b_1/c_2)\chi_{10}(r_0)\}},\qquad(3.16)$$

$$a_{\alpha1}^{(1)}=\frac{\sum_{n=2}^{n_0}a_{\alpha n}^{(1)}r_0^{n+1}[1+2n-2r_0Y(r_0)]}{2r_0^3Y(r_0)-3r_0^2},\qquad(3.17)$$

with

$$Y(r_0)=\left[\frac{\partial}{\partial r}\ln H_{i\lambda_0}^{(1)}(i|k_\alpha|r)\right]_{r=r_0}.\qquad(3.18)$$

TABLE I. Level position[a] of the ^1S and ^3S auto-ionization states of H$^-$.

Symmetry	Source	$\mathcal{E}_0^{(\pm)}$	$\mathcal{E}_1^{(\pm)}$	$\mathcal{E}_1^{(\pm)}-\mathcal{E}_0^{(\pm)}$
^1S	Present	9.580	10.177	0.597
	O'Malley-Geltman[b]	9.559	10.178	0.619
	Bhatia-Temkin-Perkins[c]	9.557	10.176	0.616
	Burke-Taylor[d]	9.560	10.1780	0.618
^3S	Present	10.150	10.199	0.049
	O'Malley-Geltman[b]	10.149	10.202	0.053
	Bhatia-Temkin-Perkins[c]	10.146	10.201	0.055
	Burke-Taylor[d]	10.1497	...	...

[a] In eV above the ground state of hydrogen atom.
[b] Reference 1.
[c] Reference 2.
[d] Reference 14.

This then permits the free variation of the rest of the (n_0-2) parameters ($a_{\alpha n}^{(0)}$ and $a_{\alpha n}^{(1)}$, with $2<n\leq n_0$) for the interior wave functions.

Having obtained the optimal wave functions for the quasistationary representation of the compound states, the width of these states can be easily calculated if the outgoing continuum wave functions for the decaying electron are available. The expression for the width is

$$\Gamma_\alpha^{(\pm)}=\frac{k_f}{\pi}\left|\left\langle P\psi\left|\frac{1}{r_{12}}\right|Q\hat{\Phi}_\alpha^{(\pm)}\right\rangle\right|^2, \tag{3.19}$$

where $P=1-Q$ and $P\psi$ is the outgoing channel wave function. The static-exchange approximation for $P\psi$, which yields reasonably good results for the width, is adopted here:

$$P\psi=\frac{1}{(2\pi)^{1/2}}\{\chi_{10}(r_1)F(r_2)+(-)^S\chi_{10}(r_2)F(r_1)\}, \tag{3.20}$$

where $F(r)$ is the scattered wave function obtained from the static-exchange approximation and χ_{10}, as before, is the ground-state wave function of hydrogen. F is normalized to unit outgoing flux.

IV. RESULTS AND DISCUSSION

A variational calculation using the trial wave functions given by Eqs. (3.8), (3.11), and (3.12) has been carried out for the singlet and triplet compound states with zero total angular momentum. In this calculation only five variational parameters γ_α, r_0, k_α, $a_{\alpha 3}^{(0)}$, and $a_{\alpha 3}^{(1)}$ are used. The results are given in Table I. For comparison, other variational results, as well as results obtained from close-coupling calculations, are included in this table. It is seen that our five-parameter variational results, except for the $\alpha=0$ states, are better than the 36-parameter variational results of O'Malley and Geltman.[1] Judging from the agreement, the five-parameter variational wave function is also consistent in accuracy with the 50-term Hylleraas-type correlation variational wave function used by Bhatia *et al.*[2] Since level shifts are included in the $1s$-$2s$-$2p$ close-coupling calculation, a comparison with the close-coupling results without explicit calculation of the level shifts is not meaningful, although our results for the $\alpha=1$ are lower than the $1s$-$2s$-$2p$ close-coupling results of Burke and Taylor[14] with 16 correlation functions. The experimental result[15] for the singlet $\alpha=0$ state is 9.56 ± 0.01.

TABLE II. Optimal parameters.

Symmetry	α	$r_0(a_0)$	$k_\alpha(a_0^{-1})$	γ_α	$a_{\alpha 3}^{(0)}$	$a_{\alpha 3}^{(1)}$
^1S	0	8.5	0.185	1.250	−0.131034	0.004806
	1	8.5	0.043	1.330	0.852049	2.582620
^3S	0	13.0	0.070	1.344	−0.002941	0.813008
	1	13.0	0.0157	1.440	1.227897	1.003915

Examining the energy difference $\mathcal{E}_1-\mathcal{E}_0$ between the levels predicted by the three variational calculations and the close-coupling calculation reveals that the five-parameter variational wave function consistently gives smaller energy differences than all the other calculations.[16] This clearly suggests that the accurate representation of the asymptotic form of the wave function actually provides a lower energy. Further improvement on the simple wave function for $\alpha=0$ states will probably allow even lower $\alpha=1$ energy levels. In the triplet case, even with the present five-parameter wave function for $\alpha=0$, we actually obtain a lower $\alpha=1$ energy than all those previously found. In Table I we have not made a comparison with the nonvariational calculations of Chen[9] and of Temkin and Walker.[10]

It should be noted that in the calculation of $\alpha=1$ states we varied only four of the five parameters: r_0 is kept as a constant equal to the corresponding r_0 values for $\alpha=0$ states. In the course of our search for optimized parameters, we found that the energy levels are not very sensitive to variations of the parameters such as $a_{\alpha 3}^{(0)}$ and $a_{\alpha 3}^{(1)}$ which affect the wave function in the interior region, thus confirming our intuition. In Table II the optimal parameters are tabulated.

The orbitals for the projectile electron are plotted in Figs. 1 and 2 for the parameters given in Table II. As expected, they extend very far in configuration space away from the proton.[9,17] The details of the wave functions at small r are shown in the insets in Figs. 1 and 2 for the singlet and triplet cases, respectively. The node at small r introduced by the orthogonality constraint between the s orbital $\varphi_{00}^{(\pm)}$ and the hydrogen ground state is clear. The reason for the insensitivity of the parameter on the trial wave functions in the interior region is also clear, since the amplitude in this region is very small.

A calculation of the width using these simple five-parameter wave functions has been carried out in the static-exchange approximation. These results are compared with previous results[8,14,18] and with experimental results[15] in Table III. The agreement is reasonably good.

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[14] P. G. Burke and A. J. Taylor, Proc. Phys. Soc. (London) **88**, 549 (1966).

[15] J. W. McGowan, Phys. Rev. **156**, 165 (1967).

[16] We expect the differences between energy shifts of two compound states to be small so that the comparison with the close-coupling results is meaningful.

[17] In the captions of Figs. 4 and 5 of Ref. 9, "Eq. (5.4)" should read "Eq. (5.1)."

[18] P. G. Burke and H. M. Schey, Phys. Rev. **120**, 147 (1962).

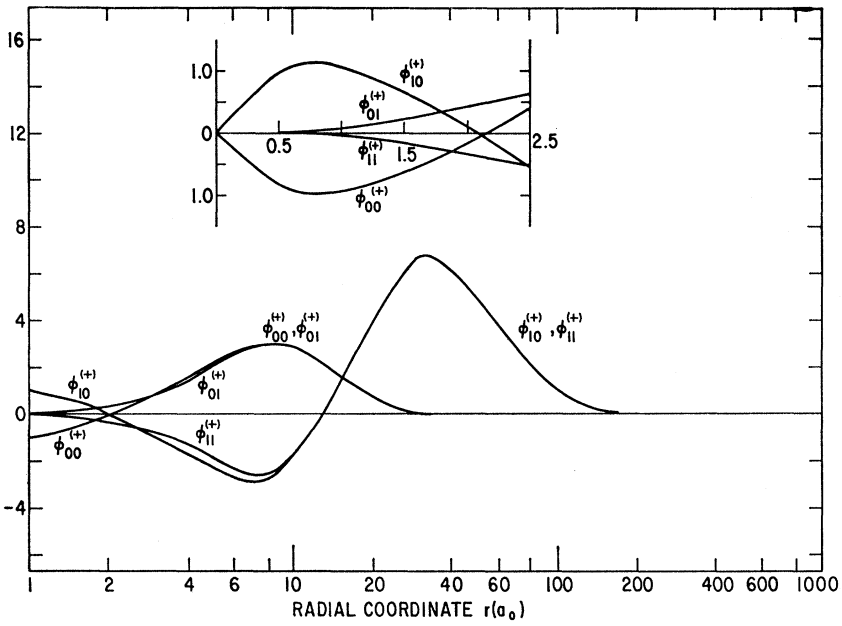

FIG. 1. First two members of the singlet wave functions (unnormalized) for the projectile electron in the field created by the degeneracy of the $n=2$ states of hydrogen. The inset shows the details of the wave functions close to the proton.

We found that the width for the singlet $\alpha=0$ state is more sensitive to variations in the interior parameters than it is for the other states. This is probably due to the fact that a significant portion of the potential which supports the singlet $\alpha=0$ state is of short-range type. The static-exchange wave function used in the present calculation of the width was obtained by solving the static-exchange equation by a noniterative method.

Better results for both the level position and width of the $\alpha=0$ states can be obtained if we take more variational parameters for the interior parts of the orbitals for the projectile electron. This is, however, not the purpose of the present investigation. An improvement which preserves the simplicity of the wave function is possible by permitting the target electron orbitals χ_{20} and χ_{21} to be distorted.

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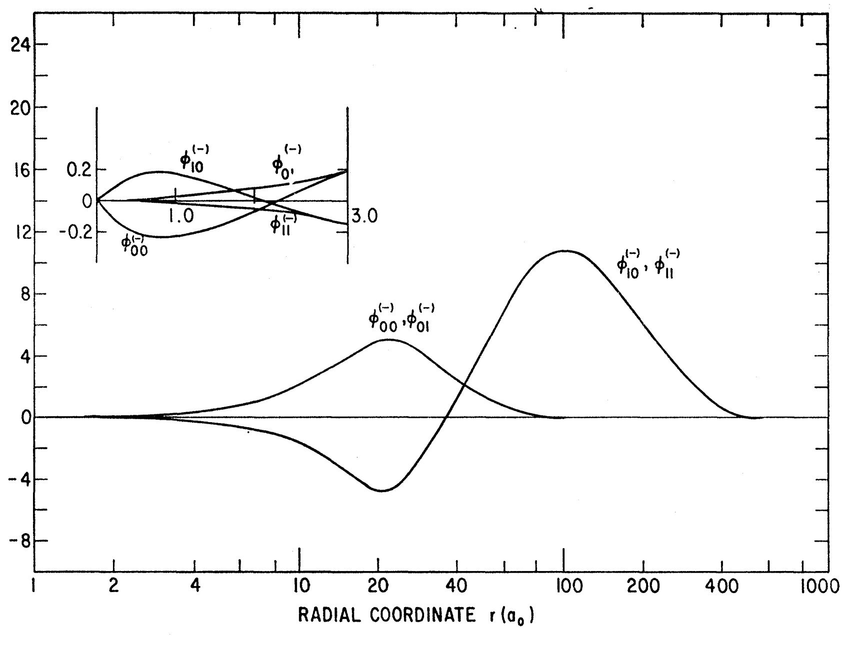

FIG. 2. First two members of the triplet wave functions (unnormalized) for the projectile electron in the field created by the degeneracy of the $n=2$ states of hydrogen. The inset shows the details of the wave functions close to the proton.

TABLE III. Level width of the ^1S and ^3S auto-ionization states of H^-.

Source	$\Gamma_0^{(+)}$ (eV)	$\Gamma_1^{(+)}$ (eV)	$\Gamma_0^{(-)}$ (eV)	$\Gamma_1^{(-)}$ (eV)
Burke-Schey[a,b]	0.0543[c]	0.0024	1.89×10^{-5}	...
Burke-Taylor[b]	0.0475	0.00219	2.06×10^{-5}	...
Chen[d]	0.041	0.00218	2.01×10^{-5}	1.18×10^{-6}
Present	0.0569	0.00306	2.31×10^{-5}	7.03×10^{-7}
McGowan (experiment)[e]	0.043 ± 0.006	...	...	...

[a] Reference 18.
[b] Reference 14.
[c] Revised value [see Ref. 11(a)].
[d] Reference 9.
[e] Reference 15.

APPENDIX: STATIONARY-STATE PERTURBATION METHOD

Feshbach[12] has shown that the quasistationary representation of the compound-state wave function is given by the bound-state solution of

$$(QHQ-\mathcal{E}\alpha)Q\Phi_\alpha=0, \tag{A1}$$

where $\mathcal{E}_\alpha$ is the quasistationary resonance energy. The resonance width Γ_α and the deviation of $\mathcal{E}_\alpha$ from the physical resonance energy E_α are given exactly, for an isolated resonance, by

$$\Delta_\alpha\equiv E_\alpha-\mathcal{E}_\alpha=\langle Q\Phi_\alpha|\mathcal{O}_1|Q\Phi_\alpha\rangle, \tag{A2}$$

$$\Gamma_\alpha=\langle Q\Phi_\alpha|\mathcal{O}_2|Q\Phi_\alpha\rangle, \tag{A3}$$

with

$$\mathcal{O}_1=Q\mathcal{O}_1Q=QHP\mathcal{P}\frac{1}{E-\mathcal{H}}PHQ, \tag{A4}$$

$$\mathcal{O}_2=Q\mathcal{O}_2Q=2\pi QHP\delta(E-\mathcal{H})PHQ, \tag{A5}$$

$$\mathcal{H}=P\left\{H+HQ\left[\frac{1}{E-QHQ}-\frac{|\Phi_\alpha\rangle\langle\Phi_\alpha|}{E-\mathcal{E}_\alpha}\right]QH\right\}P, \tag{A6}$$

where P is a projection operator which projects onto the open-channel portion of the Hilbert space, $Q=1-P$ is its complement,[12] and finally $\mathcal{P}$ in Eq. (A4) signifies the Cauchy principal value. Equations (A2) and (A3) permit us to regard Δ_α and Γ_α as stationary expectation values of the nonlocal but Hermitian operators $\mathcal{O}_1$ and $\mathcal{O}_2$, respectively.

The difficulty in applying these equations arises in solving Eq. (A1), even for such simple systems as (e,H) and (e,He$^+$). Calculation of Δ_α and Γ_α must start with approximate functions $Q\varphi_\alpha$; this results in approximate values for Δ_α and Γ_α which compare unfavorably in accuracy with the approximate values for $\mathcal{E}_\alpha$ so obtained. Thus, we must rely on methods which are capable of improving the accuracy of the calculation with approximate wave functions. Recent work on perturbation theory has shown that systematic corrections to approximate expectation values are quite possible and give quickly converging and reliable results.[5] These same methods can be applied to the evaluation of Δ_α and Γ_α of Eqs. (A2) and (A3).

Suppose the expectation value of $Q\mathcal{O}Q$ is to be found. Then, by writing

$$\mathcal{H}'=QHQ+\mu Q\mathcal{O}Q, \tag{A7}$$

it is easy to show that $\langle Q\Phi_\alpha|\mathcal{O}|Q\Phi_\alpha\rangle$ is the correct first-order (in μ) expression, where $Q\Phi_\alpha$ is an eigenfunction of QHQ. Further discussion of the accuracy is necessary, however, when only approximate eigenfunctions of QHQ, denoted as $Q\varphi_\alpha$, are available.

For this purpose the Hamiltonian is rewritten as

$$\mathcal{H}'=QH_0Q+\lambda QVQ+\mu Q\mathcal{O}Q, \tag{A8}$$

where QH_0Q is an approximate Hamiltonian whose eigenfunctions are $Q\varphi_\alpha$, and QVQ is the correction. This form leads naturally to double-perturbation theory. The correct first-order expression for $\langle Q|\mathcal{O}|Q\rangle$ is then

$$\langle Q\Phi_\alpha|\mathcal{O}|Q\Phi_\alpha\rangle=\langle Q\varphi_\alpha|\mathcal{O}|Q\varphi_\alpha\rangle+2\langle Q\varphi_\alpha|H|Q\chi_\alpha\rangle -2\mathcal{E}_\alpha^{(0)}\langle Q\varphi_\alpha|Q\chi_\alpha\rangle, \tag{A9}$$

where $\mathcal{E}_\alpha^{(0)}=\langle Q\varphi_\alpha|H|Q\varphi_\alpha\rangle$, and $Q\chi_\alpha$ is the solution of the inhomogeneous equation

$$(QH_0Q-\mathcal{E}_\alpha^{(0)})Q\chi_\alpha=(\langle Q\varphi_\alpha|\mathcal{O}|Q\varphi_\alpha\rangle-Q\mathcal{O}Q)Q\varphi_\alpha. \tag{A10}$$

This equation may be solved either numerically or by a stationary principle. For the latter purpose, let $Q\chi_\alpha=QF_\alpha Q\varphi_\alpha$ and estimate QF_α by making stationary the expression[19]

$$J_\alpha=\langle Q\varphi_\alpha QF_\alpha|\sum_j[-\tfrac{1}{2}\nabla_j^2,QF_\alpha] +2(\mathcal{O}-\langle Q\varphi_\alpha|\mathcal{O}|Q\varphi_\alpha\rangle)|Q\varphi_\alpha\rangle. \tag{A11}$$

QF_α may involve only electron coordinates and does not involve a knowledge of H_0. The index j sums over electrons.

In general, double-perturbation theory allows arbitrary accuracy in the evaluation of expectation values, within the adopted approximation to $\mathcal{H}$ [Eq. (A6)].

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[19] See, for example, J. C. Y. Chen and A. Dalgarno, Proc. Phys. Soc. (London) 85, 399 (1965).