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D AUTOIONIZATION STATES OF He AND H^-

A. K. BHATIA

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ABSTRACT

Positions of the lowest $^{1,3}D^e$ autoionization states of He and H^- below the n = 2 level of the He^+ and H have been calculated variationally, using Feshbach's Q-operator formalism. The trial wave function is of the Hylleraas-type with appropriate angular momentum factors. The widths and the shifts of the states have also been calculated. The shifts are found to be positive for all the states calculated here. The results with 112 terms for most states are lower than any previously calculated. The calculated lowest auto-ionization states of the He and H^- (relative to the ground states of He and H respectively) are 59.902 eV and 10.1185 eV, in good agreement with the observed values of 59.9 eV and 10.13 ± 0.015 eV.

D AUTIONIZATION STATES OF THE HE AND H^-

I. Introduction

A number of resonances[1] have been observed in He and H^- below the threshold of He^+ and H. Feshbach's Q-operator formalism has been applied successfully to calculate[2,3] the positions and the widths of the S and P autoionization states. The purpose of this paper is to extend these calculations to the D autoionization states in He and H^- observed below the n = 2 threshold of the respective targets. These states lie in the continuum of electron scattering from single electron target system. They are not the stationary states of the two electron Hamiltonian and they autoionize by electron emission leaving behind bound states of the single electron system. The energy of the state can be written as

$$E = \mathcal{E}_Q + \Delta_Q \tag{1}$$

where $\mathcal{E}_Q$ is calculated variationally and Δ_Q is the shift of $\mathcal{E}_Q$ due to the interaction of the discrete state with the continuum.

The most general D state wave function of even parity of two electrons[5] is

$$\begin{aligned}\Phi(\vec{r}_1, \vec{r}_2) = \{&(f \pm \tilde{f})\,[-\mathcal{D}_2^{0+}(\theta, \phi, \psi) + \sqrt{3}\cos\theta_{12}\,\mathcal{D}_2^{2+}(\theta, \phi, \psi)] \\ &+ (f \mp \tilde{f})\sqrt{3}\sin\theta_{12}\,\mathcal{D}_2^{2-}(\theta, \phi, \psi)\} \qquad (2) \\ &+ \{(g \pm \tilde{g})\,[-\cos\theta_{12}\,\mathcal{D}_2^{0+}(\theta, \phi, \psi) + \sqrt{3}\,\mathcal{D}_2^{2+}(\theta, \phi, \psi)]\}\end{aligned}$$

where the $\mathbb{D}$ are the rotational harmonics, depending on the symmetric Euler angles θ, ϕ, ψ[5]. These functions are eigenfunctions of exchange: indicating that they satisfy the following property

$$\mathcal{E}_{12}\, \mathbb{D}_{\ell}^{\kappa\pm} = \pm(-1)^{\ell+\kappa}\, \mathbb{D}_{\ell}^{\kappa\pm} \tag{3}$$

The trial wave function is of Hylleraas-type when the radial functions $f = f(r_1, r_2, r_{12})$ and $g = g(r_1, r_2, r_{12})$ are given by

$$f(r_1, r_2, r_{12}) = e^{-(\gamma_1 r_1 + \delta_1 r_2)}\, r_2^2 \sum_{\ell\geq 0} \sum_{m\geq 0} \sum_{n\geq 0} C_{\ell m n}^{(1)}\, r_1^{\ell}\, r_2^{m}\, r_{12}^{n} \tag{4a}$$

$$g(r_1, r_2, r_{12}) = e^{-(\gamma_2 r_1 + \delta_2 r_2)}\, r_1 r_2 \sum_{\ell\geq 0} \sum_{m\geq 0} \sum_{n\geq 0} C_{\ell m n}^{(2)}\, r_1^{\ell}\, r_2^{m}\, r_{12}^{n} \tag{4b}$$

It is implied in Eq. (2) that

$$\tilde{f} = f(r_2, r_1, r_{12}) \tag{5a}$$

and

$$\tilde{g} = g(r_2, r_1, r_{12}) \tag{5b}$$

Using the properties (3) and (5) in Eq. (2), we see that the wave function is manifestly space-symmetric (upper sign) or space-antisymmetric (lower sign). The space symmetric and antisymmetric solutions correspond to singlet and triplet states respectively.

To best of our knowledge, this is the first calculation to use Hylleraas-type wave function for the D states. This calculation also shows the practical value of the symmetric Euler angle decomposition for higher angular momentum states.

The eigenvectors in the two radial functions are independent. For simplification in the calculation we have chosen

$$\gamma_1 = \gamma_2 = \gamma$$

$$\delta_1 = \delta_2 = \delta$$

The first term in Eq. (2) is formed by considering one electron in the s state and the other in the d state with total angular momentum equal to 2; the second term is formed by considering both the electrons in the p states with total angular momentum equal to 2. The other combination of the p and f states is included in the above wavefunction. The upper sign corresponds to the singlet states and the lower sign corresponds to the triplet states.

The projection operator is given by

$$Q = 1 - P_1 - P_2 + P_1 P_2 \qquad (6a)$$

$$= 1 - P \qquad (6b)$$

$$P_i = 1 \, |\phi_0 (\vec{r}_i) > < \phi_0 (\vec{r}_i)| \qquad (7)$$

where $\phi_0\ (\vec{r}_i)$ is the ground state of the ith particle in the nuclear field of charge z:

$$\phi_0\ (\vec{r}) = \frac{R_{1s}\ (r)}{r}\ Y_{00}\ (\Omega) \tag{8}$$

$$R_{1s}\ (r) = 2\ z^{3/2}\ e^{-zr} \tag{9}$$

The Q-operator given here is restricted to the autoionization states below the n = 2 threshold. The projection equality, $Q^2 = Q$ is valid here.

II. Calculations and Results

The expectation value of the energy in the restricted $Q\Phi$ space is given by

$$\mathcal{E}_Q = \frac{\langle \Phi\ Q\ H\ Q\ \Phi \rangle}{\langle \Phi\ Q\ \Phi \rangle} \tag{10}$$

The decomposition of Eq. (10) is discussed in the Ref. 2. In Table I we present results for the singlet D states of the He and H^- as a function of the Perkeris numbers for D states i.e., the number of terms

$$N\ (\omega) = 2 \sum_{\omega_i = 0}^{\omega} n\ (\omega_i) \tag{11}$$

where $n\ (\omega_i)$ contains all terms $r_{1\ell}^{\ell}\ r_{2\ell}^{m}\ r_{12}^{n}$ such that $\ell + m + n = 0, 1, 2, \ldots 5$. The factor 2 in Eq. (11) arises due to two types of terms (4a) and (4b) in Eq. (2). The nonlinear parameter γ is kept fixed at 0.70 and 0.50 for He and H^- states respectively. The other non-linear parameter δ is varied to get the optimum $\mathcal{E}_Q$. Only one singlet state of H^- has been calculated. The higher singlet and triplet states do not descend below the $n = 2$ threshold in this calculation due to their enormous size. A general configuration interaction wavefunction instead of Eq. (2) may be better for these states. In Table II we present results for the triplet D states. Some of the results for $N = 8$ and 20 for higher states in Tables I and II lie above threshold of $n = 2$, because they are not optimized for these terms.

An exact formula for the shift Δ_Q of an isolated resonance can be written as follows[6]:

$$\Delta_Q = \frac{1}{2\pi} \mathcal{P} \int \frac{\Gamma(E')\, dE'}{\epsilon - E'} \tag{12}$$

where $\mathcal{P}$ indicates the principal value. The width of the resonance is given by

$$\Gamma(E) = 2k \left| \langle P \Upsilon(E) \right| H \left| Q \Phi \rangle \right|^2 \tag{13}$$

In these formulas rydberg units are used throughout. $Q\Phi$ is the exact eigenfunction of the projected problem and E is the total energy of the resonance. If the Hamiltonian is written in the form

$$H = H_0 + 2/r_{12} \tag{14}$$

with the observation that P and Q commute with H_0 and that $PQ = 0, \Gamma$ (E) reduces to the form

$$\Gamma(E) = 2k \left| \left\langle P\Upsilon(E) \right| \frac{2}{r_{12}} \left| Q\Phi \right\rangle \right|^2 \tag{15}$$

$P\Upsilon(E)$ is the solution of the optical potential problem less the resonant term[4]:

$$(H' - E) P\Upsilon \doteq 0 \tag{16}$$

$$H' = H_{PP} + \mathcal{V}' \tag{17}$$

H_{PP} is the exchange approximation Hamiltonian and $\mathcal{V}'$ is the optical potentials less the resonant term. Various approximations[3] to the potential are possible Since the most important correction to the exchange-approximation phase shifts comes from the polarization[7] of the target, the continuum wave function Υ has been calculated by the method of polarized orbitals[7]:

$$\Upsilon(E) \to \Psi_\ell^{(pol)} = \frac{u(r_1)}{r_1} Y_\ell(\Omega_1) [\phi_0(r_2) + \phi^{(pol)}(r_1, r_2)] \pm (1 \to 2) \tag{18}$$

The explicit inclusion of the z-factor for positive ion targets in the method of polarized orbitals is given in Ref. 8, where

$$\phi^{(po\ell)}_{(r_1, r_2)} = - \frac{\epsilon (r_1, r_2)}{r_1^2} e^{-zr_2} \left(\frac{1}{2} z r_2^2 + r_2\right) \frac{\cos \theta_{12}}{\sqrt{\pi z}} \tag{19}$$

and $\epsilon (r_1, r_2)$ is a step function.

The function $u(r)/r$ is normalized as a plane wave or its Coulomb counterpart:

$$\lim_{r \to \infty} u(r) = \frac{1}{k} \sin\left(k r + \sigma_\ell - \ell \frac{\pi}{2} + \eta_\ell\right) \tag{20}$$

where σ_ℓ is the Coulomb phase factor:

$$\sigma_\ell = \begin{cases} \arg \Gamma \left(\ell + 1 - \frac{i (z-1)}{k}\right) + \frac{z-1}{k} \ell n (2 k r) & z > 1 \\ 0 & z = 1 \end{cases} \tag{21}$$

The quantity η_ℓ is the residual phase shift. The energy of the scattered particle is k^2 and is related to the total energy E by

$$E = E_t + k^2 \tag{22}$$

where E_t is the ground state energy of the target system (He^+ or H).

In Tables III and IV we present our results for the positions, widths and shifts for singlet and triplet states respectively, and compare them with other calculations and experimental results. The positions of the resonance are given relative to the ground state of the target and the results include the reduced mass correction. The reduced rydberg is 13.60350 eV and 13.59794[10] eV for He and H^- respectively. The comparison indicates that the present calculation gives positions of states lower than other calculations except for the 7th state in the singlet and triplet series for He. The shifts for all the states are found to be always positive. The shifts are always small and comparable to the widths. But in few triplet states of He, the shifts are much larger than widths, still small. The calculated lowest singlet autoionization state of He is 59.902 eV in agreement with the observed values of 59.95[11] eV and 59.9[12] eV. The calculated lowest autoionization state of H^- is 10.1185 eV, in good agreement with the experimental value 10.13 ± 0.015 eV of McGowan[13] et al. and is within the experimental error. There are no experimental results available for higher singlet and triplet states. The widths of lowest singlet states of He and H^- agree with the results of Cooper[14] et al. and Burke and Taylor[1] respectively.

In conclusion we will urge measurements of positions and widths of these states for comparison purposes.

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Table I

Auto-Ionization Energies (Ry) as a Function of N for ^1D States of He and H^-

$N(\omega)$	He ($\gamma = 0.7$)								H^- ($\gamma = 0.5$)
	$-\mathcal{E}_1$ $\delta = 1.0$	$-\mathcal{E}_2$ $\delta = 0.5$	$-\mathcal{E}_3$ $\delta = 0.4$	$-\mathcal{E}_4$ $\delta = 0.4$	$-\mathcal{E}_5$ $\delta = 0.3$	$-\mathcal{E}_6$ $\delta = 0.2$	$-\mathcal{E}_7$ $\delta = 0.2$	$-\mathcal{E}_8$ $\delta = 0.2$	$-\mathcal{E}_1$ $\delta = 0.2$
8 (1)	1.403467	1.093372	1.068919	0.943733	0.910025	0.652551	0.502781	0.002152	0.255038
20 (2)	1.405219	1.131226	1.106968	1.033154	1.028373	0.998156	0.967890	0.917407	0.255848
40 (3)	1.405558	1.137801	1.112074	1.062206	1.057408	1.053822	1.024525	1.009070	0.256129
70 (4)	1.405622	1.138604	1.112777	1.071807	1.062111	1.058384	1.038589	1.035262	0.256160
112 (5)	1.405634	1.138752	1.112855	1.073241	1.062920	1.058566	1.043634	1.039609	0.256174

Table II

Auto-Ionization Energies (Ry) as a Function of N for ^3D States of He

$N(\omega)$	He ($\gamma = 0.7$)							
	$-\mathcal{E}_1$ $\delta = 0.4$	$-\mathcal{E}_2$ $\delta = 0.4$	$-\mathcal{E}_3$ $\delta = 0.3$	$-\mathcal{E}_4$ $\delta = 0.3$	$-\mathcal{E}_5$ $\delta = 0.2$	$-\mathcal{E}_6$ $\delta = 0.3$	$-\mathcal{E}_7$ $\delta = 0.2$	$-\mathcal{E}_8$ $\delta = 0.2$
8 (1)	1.155374	1.094690	1.016989	0.984820	0.952665	0.570581	0.494916	0.017835
20 (2)	1.165450	1.117471	1.069293	1.043720	1.033629	0.966562	0.968083	0.917877
40 (3)	1.167327	1.120846	1.081119	1.062914	1.056817	1.026804	1.023591	1.009192
70 (4)	1.167581	1.121296	1.083075	1.066306	1.058428	1.046344	1.038565	1.034619
112 (5)	1.167611	1.121361	1.083336	1.066831	1.058605	1.049449	1.041638	1.037735

Table III

Compilation of Theoretical and Experimental Results. Units: eV

System and State	Resonance Parameters	This Calculation	Cooper et al.[a]	Altick and Moore[b]	Burke et al.[c]	Burke and Taylor[d]	Ormonde et al.[e]	Expt.
He $^1D(1)$	ε	59.8801*		60.115				
	Γ	0.0729	0.0732	0.0748		0.0662		
	Δ	0.0220						
	E	59.902	60.025			59.911		60.0[f,g] 59.95[h] 59.9[i]
$^1D(2)$	ε	63.5106		63.601				
	Γ	0.0187	0.0165	0.0179				
	Δ	0.0044						
	E	63.515	63.575					
$^1D(3)$	ε	63.8629		63.904				
	Γ	5.807×10^{-4}	2.83×10^{-4}	4.04×10^{-4}				
	Δ	1.815×10^{-4}						
	E	63.863	63.897					
$^1D(4)$	ε	64.4018		64.480				
	Γ	7.124×10^{-3}	7.1×10^{-3}	11.6×10^{-3}				
	Δ	1.667×10^{-3}						
	E	64.403	64.429					
$^1D(5)$	ε	64.5422		64.638				
	Γ	4.045×10^{-4}	1.68×10^{-4}	3.11×10^{-4}				
	Δ	1.045×10^{-4}						
	E	64.542	64.557		64.580			
$^1D(6)$	ε	64.6014		64.682				
	Γ	5.104×10^{-7}						
	Δ	1.237×10^{-7}						
	E	64.601	64.611		64.539			
$^1D(7)$	ε	64.8045						
	Γ	1.777×10^{-3}	3.68×10^{-3}					
	Δ	0.691×10^{-3}						
	E	64.805	64.797		64.796			
$^1D(8)$	ε	64.8593						
	Γ	3.891×10^{-4}	0.973×10^{-4}					
	Δ	1.090×10^{-4}						
	E	64.859	64.861		64.880			
H^- $^1D(1)$	ε	10.1145						
	Γ	0.0100				0.0088	0.0088	
	Δ	0.0040						
	E	10.1185				10.125	10.126	10.130 ±.015[j]

[a]Cooper, Ormonde, Humphrey and Burke, Ref. 14.
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Table IV

Compilation of Theoretical Results. Units: eV

System and State	Resonance Parameters	This Calculation	Cooper et al.[a]	Altick and Moore[b]	Burke et al.[c]
He $^3D(1)$	ε	63.1180		63.157	
	Γ	2.715×10^{-6}	1.44×10^{-6}	0.12×10^{-6}	
	Δ	0.260×10^{-3}			
	E	63.118	63.141		
$^3D(2)$	ε	63.7472		63.797	
	Γ	1.919×10^{-4}	2.48×10^{-4}	2.53×10^{-4}	
	Δ	0.917×10^{-4}			
	E	63.747	63.796		
$^3D(3)$	ε	64.2645		64.284	
	Γ	3.305×10^{-6}	0.468×10^{-6}	5.3×10^{-6}	
	Δ	1.203×10^{-4}			
	E	64.265	64.273		
$^3D(4)$	ε	64.4890		64.559	
	Γ	1.362×10^{-4}	0.128×10^{-4}	2.05×10^{-4}	
	Δ	0.502×10^{-4}			
	E	64.489	64.509		64.486
$^3D(5)$	ε	64.6009			
	Γ	1.192×10^{-7}	0.79×10^{-7}		
	Δ	5.101×10^{-7}			
	E	64.601	64.610	64.665	64.562
$^3D(6)$	ε	64.7255			
	Γ	8.899×10^{-8}			
	Δ	6.656×10^{-5}			
	E	64.726			64.710
$^3D(7)$	ε	64.8317			
	Γ	5.967×10^{-5}	7.32×10^{-5}		
	Δ	1.173×10^{-5}			
	E	64.832	64.836		64.823
$^3D(8)$	ε	64.8852			
	Γ	2.596×10^{-7}			
	Δ	1.43×10^{-7}			
	E	64.885			

[a] Cooper, Ormonde, Humphrey and Burke, Ref. 14.
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