

## Hylleraas Variational Calculation of Auto-Ionization States

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Auto-ionization states of two-electron systems ( $H^-$  and He) have been calculated using the Feshbach  $Q$ -projection-operator formalism with a Hylleraas-type variational wave function. Results for most of the  $S$  states in He and the first two in  $H^-$  are lower than any previously calculated. The energy of the lowest  $^1S$  state in He is found to be  $-1.5575487$  Ry using 50 terms, and the convergence indicates that the first 6 figures are significant. Except for the lowest  $^3P$  state in He, calculations of odd-parity  $P$  states do not yield as low results as previous relative partial-wave calculations. Comparison with accurate resonant-energy calculations of Burke and Taylor in  $S$  states allows us to deduce energy shifts which are inherent in the projection-operator technique.

### I. INTRODUCTION

WITH the successful application of the Feshbach  $Q$ -operator formalism<sup>1</sup> to the calculation of atomic auto-ionization states,<sup>2</sup> the possibility of calculating the energy of such states to very high accuracy has been greatly increased. In this paper we consider the calculation of auto-ionization states of He and  $H^-$  using a Hylleraas-type wave function

$$\Psi = e^{-(\mu_1 r_1 + \mu_2 r_2)} \sum_{l,m,n} C_{lmn} r_1^l r_2^m r_{12}^n \pm (1 \leftrightarrow 2). \quad (1.1)$$

The wave function (1.1) is appropriate for  $S$  states of singlet (upper sign) and triplet (lower sign) spin. Previous calculations<sup>2,3</sup> were based on relative partial-wave expansions

$$\Psi_S = \sum_{\lambda=0}^{\infty} \phi_{\lambda}(r_1, r_2) P_{\lambda}(\cos\theta_{12}) \quad (1.2)$$

in which only a finite number of Legendre polynomials  $P_{\lambda}(\cos\theta_{12})$  (relative partial waves) were taken, the associated function  $\phi_{\lambda}(r_1, r_2)$  being of some convenient analytical form. It has been known ever since the pioneer calculations of Hylleraas<sup>4</sup> for low-lying bound states of two-electron systems that expansions of the form (1.1) yield considerably lower energies than (1.2); thus it is immediately tempting to carry through the similar treatment to auto-ionization states. Before proceeding with unbridled enthusiasm, however, one should bear the following reservations well in mind. Auto-ionization states are much larger in size than true bound states; thus the electron-electron singularity, whose accurate treatment is the strong point of (1.1) cannot straight-

away be expected to be of comparable importance for auto-ionization states. If, however, the calculation actually yields lower energies  $\mathcal{E}_Q$ , the meaningfulness of such results must be understood in the context of the fact that the experimental energy  $E$  that is measured is shifted by an amount  $\Delta_Q$  whose magnitude depends on the details of the  $Q$  operator which one uses.<sup>5</sup> (It always being understood that in this calculation we only use the same  $Q$  operator as O'Malley and Geltman.<sup>2</sup>)

$$E = \mathcal{E}_Q + \Delta_Q. \quad (1.3)$$

For strictly experimental purposes, it makes no sense to calculate  $\mathcal{E}_Q$  to greater accuracy than  $\Delta_Q$  warrants unless one knows from some other source what  $\Delta_Q$  is. Furthermore, the experimental value of  $E$  is itself the result of the measurement of some resonance phenomenon associated with a width  $\Gamma$ . This fact is usually expressed by writing the energy as a complex<sup>6</sup> number  $W$ :

$$W = E - \frac{1}{2}i\Gamma. \quad (1.4)$$

In this way the time dependence of the auto-ionization  $e^{-iWt}$  is automatically time-decaying. The prescription of where precisely to put  $E$  within  $\Gamma$  is to some extent arbitrary, and particularly for auto-ionization states (for which  $\Gamma$  is generally very large compared to optical widths), this further renders the concept of an exact  $E$  somewhat arbitrary.

These reservations having been stated, it is still of considerable interest to utilize (1.1) to compute  $\mathcal{E}_Q$ . For in the case of two-electron systems,  $E$  is in principle knowable from direct and very accurate calculations and experiments. Thus one may use accurate calculations of  $\mathcal{E}_Q$  to infer  $\Delta_Q$ , which is of interest since it

\* Part of this work was done while a National Academy of Sciences, National Research Council resident research associate.

<sup>1</sup> H. Feshbach, *Ann. Phys. (N.Y.)* **5**, 537 (1958); **19**, 287 (1962).

<sup>2</sup> T. F. O'Malley and S. Geltman, *Phys. Rev.* **137**, A1344 (1965).

<sup>3</sup> P. L. Altick and E. N. Moore, *Phys. Rev. Letters* **15**, 100 (1965).

<sup>4</sup> E. A. Hylleraas, *Z. Physik* **48**, 469 (1928); **54**, 347 (1929).

<sup>5</sup> It is for this reason that we explicitly use the subscript  $Q$  on the notation used in Ref. 2. In the tables, however, we shall drop the subscript  $Q$  and use the subscript  $n$  to refer to the sequential order in the state in question.

<sup>6</sup> A. Herzenberg and F. Mandl, *Proc. Roy. Soc. (London)* **A274**, 252 (1963).

measures the quality of the  $Q$  operator one has used. One of the chief purposes of this paper is to present such a sufficiently definitive calculation of the lower lying  $\mathcal{E}_Q$ . The formal definition of our  $Q$  operator is given by<sup>7,2</sup>

$$Q = (1 - P_1)(1 - P_2), \quad (1.5)$$

$$P_i = \varphi_0(\mathbf{r}_i) \langle \varphi_0(\mathbf{r}_i), \quad (1.6)$$

where  $\varphi_0(\mathbf{r}_i)$  is the ground state of the  $i$ th particle in the nuclear field of charge  $Z$ :

$$\varphi_0(\mathbf{r}) = [R_{1s}(r)/r] Y_{00}(\Omega), \quad (1.7a)$$

$$R_{1s}(r) = 2Z^{3/2} r e^{-Zr}. \quad (1.7b)$$

$Q$  is thus restricted to the description of auto-ionization states below the  $n=2$  threshold.

Calculations based on (1.1) will also enable an assessment to be made of the importance of the electron-electron repulsion relative to the longer range correlations which are implicit in (1.2). We shall find, for  $S$  states, the expected improvement in using (1.1), the improvement being greater in  $^1S$  than in  $^3S$  states, whereas for  $P$  states, except for the lowest  $^3P$  state in He, the results based on (1.2) are actually superior (because of our restriction of  $\mu_1 = \mu_2$  for  $P$  states) (see Sec. II). We shall also find in those cases where comparison is possible that the associated  $\Delta_Q$  are *positive* and very small for the lowest states, but proportionately more significant for the higher states.

All  $P$  state calculations in this paper refer to odd-parity  $P$  states.

## II. CALCULATION AND RESULTS

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

$$\mathcal{E}_Q = \frac{\langle Q\Psi, H Q\Psi \rangle}{\langle Q\Psi, Q\Psi \rangle} \equiv \frac{\langle \Psi H Q Q \Psi \rangle}{\langle Q\Psi, Q\Psi \rangle}. \quad (2.1)$$

The denominator reduces to  $\langle \Psi Q\Psi \rangle$  under the fundamental projection equality  $Q^2 = Q$ . Utilizing (1.5), we can write the numerator

$$\begin{aligned} \langle \Psi H Q Q \Psi \rangle &= \langle \Psi H \Psi \rangle - \sum_{i=1}^2 [\langle \Psi P_i H \Psi \rangle + \langle \Psi H P_i \Psi \rangle] \\ &+ \sum_{i=1}^2 \sum_{j=1}^2 \langle \Psi P_i H P_j \Psi \rangle + \langle \Psi H P_1 P_2 \Psi \rangle \\ &+ \langle \Psi P_1 P_2 H \Psi \rangle + \langle \Psi P_1 P_2 H P_1 P_2 \Psi \rangle \\ &- \sum_{i=1}^2 [\langle \Psi P_1 P_2 H P_i \Psi \rangle + \langle \Psi P_i H P_1 P_2 \Psi \rangle]. \end{aligned} \quad (2.2a)$$

The (anti) symmetry of  $\Psi$  can be used to show that

certain terms of (2.2a) are equal:

$$\langle \Psi P_1 P_2 H P_2 \Psi \rangle = \langle \Psi P_1 P_2 H P_1 \Psi \rangle, \quad (2.3a)$$

$$\langle \Psi P_1 H P_2 \Psi \rangle = \langle \Psi P_2 H P_1 \Psi \rangle, \quad (2.3b)$$

$$\langle \Psi P_1 H \Psi \rangle = \langle \Psi P_2 H \Psi \rangle, \quad (2.3c)$$

$$\langle \Psi H P_1 \Psi \rangle = \langle \Psi H P_2 \Psi \rangle. \quad (2.3d)$$

Substitution of (2.3) into (2.2a) then yields

$$\begin{aligned} \langle \Psi H Q Q \Psi \rangle &= \langle \Psi H \Psi \rangle - 2[\langle \Psi P_1 H \Psi \rangle + \langle \Psi H P_1 \Psi \rangle] \\ &+ 2\langle \Psi P_1 H P_1 \Psi \rangle + 2\langle \Psi P_1 H P_2 \Psi \rangle \\ &+ [\langle \Psi H P_1 P_2 \Psi \rangle + \langle \Psi P_1 P_2 H \Psi \rangle] \\ &- 2[\langle \Psi P_1 P_2 H P_1 \Psi \rangle + \langle \Psi P_1 H P_1 P_2 \Psi \rangle] \\ &+ \langle \Psi P_1 P_2 H P_1 P_2 \Psi \rangle. \end{aligned} \quad (2.2b)$$

The two quantities in each of the square brackets above are the transpose of each other. Thus if we let  $i$  refer to a triple of indices  $l_i, m_i, n_i$  associated with specific (symmetrized or antisymmetrized) term of (1.1), and  $j$  to another term, then one can readily show, for example, that

$$\langle P_1 H \rangle_{ij} = \langle H P_1 \rangle_{ji}. \quad (2.4)$$

The denominator in (2.1) may correspondingly be so simplified.

The integrations in (2.2b) are then of three basic types. The first is  $\langle \Psi H \Psi \rangle$ . This is just what arises in ordinary energy calculations with Hylleraas-type variational functions, and we shall not discuss it further.

The second is where  $P_1 P_2$  appears but not a single  $P_i$ . An example is  $\langle \Psi H P_1 P_2 \Psi \rangle$ . Such terms can readily be evaluated as indicated below. We shall write symbolically<sup>8</sup>

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = f_i(r_1 r_2 r_{12}) \mathcal{D}_i(\Theta, \Phi, \Psi). \quad (2.5)$$

Then

$$\begin{aligned} \langle \Psi H P_1 P_2 \Psi \rangle &= \int \int d^3 r_1 d^3 r_2 \Psi(\mathbf{r}_1, \mathbf{r}_2) H \varphi_0(\mathbf{r}_1) \varphi_0(\mathbf{r}_2) \\ &\times \int \int d^3 r'_1 d^3 r'_2 \varphi_0(\mathbf{r}'_1) \varphi_0(\mathbf{r}'_2) \Psi(\mathbf{r}'_1, \mathbf{r}'_2). \end{aligned} \quad (2.6a)$$

Use now

$$d^3 r'_1 d^3 r'_2 = r'_1 r'_2 r'_{12} dr'_1 dr'_2 dr'_{12} \sin \Theta' d\Theta' d\Phi' d\Psi',$$

so that

$$\begin{aligned} \langle \Psi H P_1 P_2 \Psi \rangle &= \int \int d^3 r_1 d^3 r_2 \Psi(\mathbf{r}_1, \mathbf{r}_2) H \varphi_0(r_1) \varphi_0(r_2) \\ &\times \int r'_1 r'_2 r'_{12} dr'_1 dr'_2 dr'_{12} \varphi_0(r'_1) \varphi_0(r'_2) f_i(r'_1 r'_2 r'_{12}) \\ &\times \int \mathcal{D}_i(\Theta', \Phi', \Psi') \sin \Theta' d\Theta' d\Phi' d\Psi'. \end{aligned} \quad (2.6b)$$

<sup>7</sup> Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962).

<sup>8</sup> For further details cf. A. K. Bhatia and A. Temkin, Rev. Mod. Phys. **36**, 1050 (1964).

TABLE I. Auto-ionization energies (Ry) as a function of  $N$  for the  $^1S$  states of He and  $H^-$ .

$N$	He									$H^-$	
	$-\varepsilon_1$ ( $\mu_1, \mu_2$ )	$-\varepsilon_2$ ( $\mu_1, \mu_2$ )	$-\varepsilon_3$ ( $\mu_1, \mu_2$ )	$-\varepsilon_4$ ( $\mu_1, \mu_2$ )	$-\varepsilon_5$ ( $\mu_1, \mu_2$ )	$-\varepsilon_6$ ( $\mu_1, \mu_2$ )	$-\varepsilon_7$ ( $\mu_1, \mu_2$ )	$-\varepsilon_8$ ( $\mu_1, \mu_2$ )	$-\varepsilon_9$ ( $\mu_1, \mu_2$ )	$-\varepsilon_1$ ( $\mu_1, \mu_2$ )	$-\varepsilon_2$ ( $\mu_1, \mu_2$ )
7										0.29402394	
13	1.5566129	1.2435445	1.1689668	1.0932644						0.29638831	0.2516244
22	1.5574554	1.2451783	1.1795936	1.0955516	1.0882892					0.29748709	0.2517898
34	1.5575305	1.2454662	1.1800574	1.0962248	1.0895538					0.29753144	0.2519990
40	1.5575447	1.2454711								0.29754265	
45	1.5575482	1.2454763								0.29754735	
48	1.5575485	1.2454810								0.29755217	
50	1.5575487	1.2454819								0.29755787	0.2520166

It is evident from (2.6b) that these terms are nonzero only for  $l=0$  ( $S$  states). The remaining "radial" factor can be handled just as the ordinary Hylleraas terms in  $\langle \Psi H \Psi \rangle$ .

The third type of term contains a single  $P_i$ . An example is  $\langle \Psi H P_1 \Psi \rangle$ . This is the most difficult integral for Hylleraas-type wave functions. In the Appendix we sketch how this is analytically evaluated.

The integers  $l, m, n$  in (1.1) were selected in the Pekeris<sup>9</sup> manner of taking all sets such that  $l+m+n=\omega$ , where  $\omega$  traverses the integers. The total number of terms  $N$  is then a cubic function of  $\omega$  which is 7, 13, 22, 34, 50 for  $\omega=2, 3, 4, 5, 6$  in the singlet case and  $\omega \rightarrow \omega+1$  for a given  $N$  in the triplet case. Our tables contain some values for intermediate  $N$  which therefore correspond to incomplete  $l+m+n=\omega$  sets in the sense defined above.

In Table I we present results for the  $^1S$  states of He and  $H^-$  as a function of the number of terms  $N$  in the expansion (1.1). The nonlinear parameters,  $\mu_1$  and  $\mu_2$  are given at the top of each column. Only in the case of the lowest eigenvalue in  $H^-$  and possibly the lowest two in He do we feel that the first 6 significant figures represent the true  $\mathcal{E}_0$ . As can be seen from Table II, these values are noticeably lower than those calculated by O'Malley and Geltman; however, as one goes to higher eigenvalues the improvement rapidly decreases. Any improvement can be directly attributed to the

presence of two nonlinear parameters in (1.1). States 6-9 have not previously been reported.

For  $P$  states, only in the lowest triplet case for He is any improvement achieved. However, in this case we are restricted to  $\mu_1=\mu_2$  (see below), with 50 linear parameters.

The implication is clear then that the larger and more asymmetric the state the less important the electron-electron repulsive singularity relative to longer range configuration interaction effects. The situation is not really surprising. In  $H^-$  the size of the  $n$ th auto-ionization state is of the order<sup>10</sup>

$$R_n \propto \alpha^2 e^{\pi n / \alpha},$$

where  $\alpha$  is a constant. Thus the size increases exponentially and it is quite enormous even for comparatively low values of  $n$ . As a result, the electrons spend excessively small amounts of time in each other's vicinity, and the exact description of the wave function for close interactions is correspondingly less important.

In particular, our calculated values of the second levels of  $H^-$  may be considerably too high in spite of their being based on 50 terms of the conventional Hylleraas type. Thus the fact that our second  $H^-$  values are above those predicted by Temkin and Walker,<sup>10</sup> the latter may still be correct. Recent preliminary variationally calculated results of J. C. Y. Chen (private communication) using the correct long-range part of

TABLE II. Comparison of  $\mathcal{E}_0$  (Ry) with results of O'Malley and Geltman.

System	$n$	$^1S$		$^3S$		$^1P$		$^3P$	
		Present	O'Malley and Geltman <sup>a</sup>	Present	O'Malley and Geltman <sup>a</sup>	Present	O'Malley and Geltman <sup>a</sup>	Present	O'Malley and Geltman <sup>a</sup>
He	1	-1.557549	-1.55648	-1.205199	-1.20480	-1.38268	-1.38316	-1.522576	-1.52176
	2	-1.245482	-1.23824	-1.119515	-1.12084		-1.19268		-1.16564
	3	-1.180057	-1.17960	-1.097682	-1.10688		-1.12396		-1.10788
	4	-1.096371	-1.10012	-1.065013	-1.06184		-1.09260		-1.07900
	5	-1.089730	-1.08000	-1.056664	-1.05336		-1.08904		-1.06624
$H^-$	1	-0.2975579	-0.29744	-0.254216	-0.25401	-0.24568	-0.25193	-0.284795	-0.28504
	2	-0.2520166	-0.25192	-0.250184	-0.25013		-0.25003		-0.25042

<sup>a</sup> Reference 2.<sup>9</sup> C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).<sup>10</sup> A. Temkin and J. F. Walker, Phys. Rev. **140**, A1520 (1965).

TABLE III. Lowest calculated eigenvalues ( $\mathcal{E}_Q$  in Ry) of  $H_{QQ}$ .

System $n$	$^1S$	$^3S$	$^1P$	$^3P$
He 1	-1.557549	-1.205191	-1.38316 <sup>a</sup>	-1.522576
2	-1.245482	-1.12084 <sup>a</sup>	-1.19268 <sup>b</sup>	-1.16564 <sup>b</sup>
3	-1.180057	-1.10688 <sup>a</sup>	-1.12396 <sup>b</sup>	-1.15492 <sup>a</sup>
4	-1.10012 <sup>a</sup>	-1.065013	-1.09260 <sup>b</sup>	-1.09370 <sup>a</sup>
5	-1.089730	-1.056664	-1.08904 <sup>b</sup>	-1.08167 <sup>a</sup>
6	-1.0553648	-1.0375254	-1.05756 <sup>b</sup>	-1.07546 <sup>a</sup>
H <sup>-</sup> 1	-0.2975579	-0.254216	-0.25193 <sup>a</sup>	-0.28504 <sup>a</sup>
2	-0.252016	-0.250194	-0.25003 <sup>a</sup>	-0.25042 <sup>a</sup>

<sup>a</sup> Reference 2.  
<sup>b</sup> S. Geltman (private communication).  
<sup>c</sup> Reference 3.

the wave function<sup>10</sup> are in agreement with those predictions.

In Table III we have collated the lowest variational results for the lower states of He and H<sup>-</sup>. The calculated results which we include are only those which use the specific form of  $Q$  in Eqs. (1.4) and (1.5). Thus we do not include those of Lipsky and Russek<sup>11</sup> which in effect are based on a different  $Q$  operator.

Our improved accuracy for the lower  $S$  states can also be used together with recent calculations of the corresponding scattering resonant energies  $E$  by Burke and Taylor<sup>12</sup> to yield reliable information about  $\Delta_Q$ . The results are given in Table IV. The major conclusion from it is that  $\Delta_Q$  are small and *positive*. This result is to be contrasted with the results of Burke and McVicar, and Altick and Moore<sup>13</sup> for a subclass of the  $P$  states, labeled<sup>14</sup> by the additional approximate quantum number (+), which yield negative  $\Delta$ . In both papers<sup>13</sup>  $\Delta$  has been deduced by comparing the respective scattering resonance energies with eigenvalues obtained from the full equations by deleting all terms referring to the  $1s$  state. As stated by Burke and McVicar and shown in Ref. 10, for the close-coupling equations, this is *not* formally equivalent to using the

present  $Q$ -operator, Eq. (1.5), unless the continuum functions are orthogonal to the ( $1s$ ) state. However, in the case of Altick and Moore,<sup>13</sup> since their continuum basis is automatically orthogonal to their discrete basis functions their  $Q$ -operator is the same as the present one. Thus we conclude that at least the sign of  $\Delta_Q$  in those  $^1P(+)$  cases is reliably negative, in contrast to the present positive  $S$ -state results.

In practical terms this means that although a variational calculation of  $\mathcal{E}_Q$  will yield an upper bound for  $\mathcal{E}_Q$ , the value will not necessarily be an upper bound on  $E$ . We also note from Table IV that the ratio<sup>5</sup>  $\Delta_n/|\mathcal{E}_{n+1}-\mathcal{E}_n|$  increases rapidly as a function of  $n$ . This means that the relative shift for higher levels is more significant than for the lowest one. A comparison of  $\Delta_n$  with the widths  $\Gamma_n$  for the  $^1S$  states as calculated by Burke and Taylor<sup>12</sup> shows that, whereas  $\Delta_n \ll \Gamma_n$  for  $n=1$ , they are quite comparable thereafter. (The  $n=2$  eigenvalue in He can be classified to a good approximation as the first member of another series<sup>14</sup>)

We have not included any comparison with experiment as the experimental results are adequately summarized in Ref. 2, and nothing qualitatively new is found with our results. The extremely accurate vacuum-ultraviolet results of Madden and Codling<sup>15</sup> merit further comparison; however, in view of our  $\mu_1=\mu_2$  restriction for  $P$  states (the calculation being difficult enough as it is), we shall not attempt such comparison here. We do intend to include two nonlinear parameters and at the same time to examine such perturbations as reduced mass and mass polarization in order to effect a meaningful comparison.

It should be remarked that in comparing with experiment, it is necessary among the other things to convert the rydberg to eV and this conversion factor has varied in the fifth figure from case to case in the eV results presented by O'Malley and Geltman.<sup>2</sup> Thus some of their entries will differ by one unit in the fourth significant figure if the latest value of the rydberg<sup>16</sup> (for

TABLE IV. Values<sup>a</sup> of  $\Delta_n$ .

System and state	$n$	$E_n$ (Ry)	$\mathcal{E}_n$ (Ry)	$\Delta_n$ (Ry)	$\Delta_n$ (eV)	$\Delta_n/ \mathcal{E}_{n+1}-\mathcal{E}_n $
He ( $^1S$ )	1	2.444301	2.4424451	+0.00185	+0.0252	0.0059
	2	2.759783	2.754518	+0.005265	+0.0716	...
	3	2.821582	2.819943	+0.001639	+0.0223	0.0205
He ( $^3S$ )	1	2.7951030	2.794909	+0.00019	+0.0026	...
	1	0.70269	0.70244	+0.00025	+0.0034	0.0055
H <sup>-</sup> ( $^1S$ )	2	0.748091	0.74798	+0.00011	+0.0015	...
	1	0.7460154	0.745784	+0.00023	+0.0031	...

<sup>a</sup> The entries are relative to the ground state of the target systems He<sup>+</sup> and H, respectively. The  $E_n$  are taken from Burke and Taylor (Ref. 12 and private communication); the remaining entries refer to this calculation.

<sup>11</sup> L. Lipsky and A. Russek, Phys. Rev. **142**, 59 (1966). Cf. also references to E. Holg en contained therein. The  $Q$  operator used in these references has the effect of introducing spurious (non-auto-ionization) eigenvalues into the spectrum. For details cf. the article by A. Temkin, in *Autoionization*, edited by A. Temkin (Mono Book Corporation, Baltimore, Maryland, 1966), p. 66 ff.

<sup>12</sup> P. G. Burke and A. J. Taylor, Proc. Phys. Soc. (London) **88**, 549 (1966).

<sup>13</sup> P. G. Burke and D. D. McVicar, Proc. Phys. Soc. (London) **86**, 989 (1965); P. L. Altick and E. N. Moore, Phys. Rev. **147**, 59 (1966).

<sup>14</sup> J. Cooper, U. Fano, and F. Prats, Phys. Rev. Letters **10**, 518 (1963).

<sup>15</sup> R. P. Madden and K. Codling, Phys. Rev. Letters **10**, 516 (1963); Astrophys. J. **141**, 364 (1965).

<sup>16</sup> E. R. Cohen and J. W. M. DuMond, Rev. Mod. Phys. **37**, 537 (1965).

infinite mass)  $R_\infty = 13.60535$  eV be used. Altick and Moore<sup>3</sup> have not given the value of the rydberg that they have used.

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### APPENDIX

We indicate here how one calculates terms of the type  $\langle \Psi H P_1 \Psi \rangle$  as typical of the single  $P_i$  terms occurring in Eq. (2.2b). The state is here explicitly labeled by its angular momentum  $l$ .

$$\begin{aligned} \langle \Psi H P_1 \Psi \rangle &= \int \int d^3 r_1 d^3 r_2 \Psi_l(\mathbf{r}_1, \mathbf{r}_2) H P_1 \Psi_l(\mathbf{r}_1, \mathbf{r}_2) \\ &= \int \int d^3 r_1 d^3 r_2 \Psi_l(\mathbf{r}_1, \mathbf{r}_2) H \varphi_0(\mathbf{r}_1) \int d^3 r_1' \varphi_0(\mathbf{r}_1') \Psi_l(\mathbf{r}_1', \mathbf{r}_2). \end{aligned} \quad (\text{A.1})$$

The second ( $r_1'$ ) integral can be evaluated by introducing the Fourier representation of the delta function:

$$\delta(\mathbf{r}_2 - \mathbf{r}_1) = \frac{1}{(2\pi)^3} \int d^3 q e^{i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)}. \quad (\text{A.2})$$

Then

$$\begin{aligned} &\int d^3 r_1' \varphi_0(\mathbf{r}_1') \Psi_l(\mathbf{r}_1', \mathbf{r}_2) \\ &= \int \int d^3 r_1' d^3 r_2' \delta(\mathbf{r}_2 - \mathbf{r}_2') \varphi_0(\mathbf{r}_1') \Psi_l(\mathbf{r}_1', \mathbf{r}_2') \\ &= \frac{1}{(2\pi)^3} \int d^3 q e^{i\mathbf{q} \cdot \mathbf{r}_2} \int \int d^3 r_1' d^3 r_2' e^{-i\mathbf{q} \cdot \mathbf{r}_2'} \varphi_0(\mathbf{r}_1') \Psi_l(\mathbf{r}_1', \mathbf{r}_2'). \end{aligned} \quad (\text{A.3})$$

Using the spherical angle expansions of  $e^{i\mathbf{q} \cdot \mathbf{r}_2}$  and  $e^{-i\mathbf{q} \cdot \mathbf{r}_2'}$ , we find

$$\begin{aligned} I_l &= 16\pi^2 \sum_{\sigma\mu} Y_{\sigma\mu}(\Omega_2) \int_0^\infty q^2 dq j_\sigma(qr_2) \int \int d^3 r_1' d^3 r_2' j_\sigma(qr_2') \\ &\quad \times Y_{\sigma\mu}^*(\Omega_2') \varphi_0(\mathbf{r}_1') \Psi_l(\mathbf{r}_1', \mathbf{r}_2'), \end{aligned} \quad (\text{A.4})$$

where

$$I_l(\mathbf{r}_2) \equiv \int d^3 r_1' \varphi_0(\mathbf{r}_1') \Psi_l(\mathbf{r}_1', \mathbf{r}_2). \quad (\text{A.5})$$

We shall next sketch the manner in which (A.5) may be integrated. Writing  $\Psi$  symbolically as in (2.5) and expanding  $Y_{\sigma\mu}(\Omega_2')$  symbolically as<sup>8</sup>

$$Y_{\sigma\mu} = \alpha_\sigma(\theta_{12}) \mathfrak{D}_\sigma^{(\mu)}(\Theta, \Phi, \Psi'), \quad (\text{A.6})$$

one may, using the orthonormality of the  $\mathfrak{D}_\sigma^{(\mu)}$ , reduce (A.5) to the form

$$\begin{aligned} I_l &\propto Y_{l0}(\Omega_2) \int q^2 dq j_l(qr_2) \int r_2' dr_2' j_l(qr_2') \\ &\quad \times \int \int r_1' dr_1' r_{12}' dr_{12}' \varphi_0(\mathbf{r}_1') \alpha_l(\theta_{12}') f_l(r_1' r_2' r_{12}'). \end{aligned} \quad (\text{A.7})$$

The last double integral in (A.7) may be performed analytically using the explicit form of  $\alpha_l(\theta_{12}')$  given in Ref. 8. Call this result  $F_l(r_2')$ :

$$F_l(r_2') \equiv \int r_1' dr_1' r_{12}' dr_{12}' \varphi_0(\mathbf{r}_1') \alpha_l(\theta_{12}') f_l(r_1' r_2' r_{12}'). \quad (\text{A.8})$$

And now we observe that in the integration over  $q$ , the functions  $j_l(qr_2) j_l(qr_2')$  act like a delta function; i.e.,<sup>17</sup>

$$\begin{aligned} &\int_0^\infty q^2 dq \int_0^\infty F_l(r_2') j_l(qr_2) j_l(qr_2') r_2' dr_2' \\ &= \frac{1}{2} \pi F_l(r_2) / r_2. \end{aligned} \quad (\text{A.9})$$

This result multiplied by the function  $Y_{l0}(\Omega_2)$  completes the analytical integration of  $I_l(\mathbf{r}_2')$ . The matrix element is then

$$\begin{aligned} \langle \Psi H P_1 \Psi \rangle &\propto \int \int d^3 r_1 d^3 r_2 \Psi_l(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad \times H \varphi_0(\mathbf{r}_1) Y_{l0}(\Omega_2) F_l(r_2) / r_2. \end{aligned} \quad (\text{A.10})$$

With  $F_l(r_2)$  known explicitly, the evaluation of (A.10) is straightforward (but nevertheless extensive, particularly for  $P$  states).

<sup>17</sup> G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, Cambridge, England, 1958), p. 453.