Lamb Shift in the Helium Atom*

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The calculation, first attempted by Kabir and Salpeter, of the mean excitation energy entering in the Lamb shift of the helium ground state is redone by a quite different approach. Our answer, $\ln[k_0/r_y]=4.370 \pm 0.004$, leaves theory and experiment on the ionization energy of helium in agreement within the experimental uncertainty of ± 0.15 cm^{-1}. Incidental results are given for the electrostatic polarizability of He and H$^-$ ground states and there is appended a new discussion of the construction of higher angular momentum eigenfunctions for the three-body problem.

INTRODUCTION

THE nonrelativistic part of the Lamb shift of an atomic energy level was first described by Bethe[1] in terms of the logarithm of the mean excitation energy

$$\ln k_0 = \frac{\sum_n |\langle 0|\mathbf{p}|n\rangle|^2 (E_n-E_0) \ln|E_n-E_0|}{\sum_n |\langle 0|\mathbf{p}|n\rangle|^2 (E_n-E_0)}, \quad (1)$$

defined by a sum over excited states. Direct evaluation of (1) is not difficult for hydrogen, where all the states $|n\rangle$ are known functions. However, the first application to the helium atom by Kabir and Salpeter,[2] yielded the value

$$\ln[k_0/ry]=4.39\pm0.2, \quad (2)$$

where the uncertainty arises from the difficulty of constructing accurate excited state wave functions. The magnitude of the shift of the ionization energy from the helium ground state was thus[3] 1.34 ± 0.2 cm^{-1}.

Combined with the very accurate results of Pekeris[4] on the nonrelativistic eigenvalue plus $\alpha^2 Z^2$ corrections, this yields for the He ionization energy

$$J_{\text{th}}=198\,310.67\pm0.2 \text{ cm}^{-1}, \quad (3a)$$

to be compared with the latest experimental value[5]

$$J_{\text{exp}}=198\,310.82\pm0.15 \text{ cm}^{-1}. \quad (3b)$$

The rough magnitude of the Lamb shift in this two-electron atom is thus verified, but a more accurate check is clearly needed and the difficulty lies entirely in evaluating (1).

METHOD OF CALCULATING $\ln k_0$

Instead of attacking (1) directly we first retreat[6] to an earlier formula in Bethe's[1] paper:

$$\Lambda \equiv \int_0^K k\,dk \sum_n \frac{|\langle 0|\nabla|n\rangle|^2}{E_0-E_n-k}, \quad (4)$$

which most clearly represents the virtual photon (energy k) emission and absorption which gives rise to the Lamb shift. We shall henceforward use atomic units ($a_0=e^2=1$), and ∇ will be the current operator for the general many-electron atom,

$$\nabla = \sum_{i=1}^N \nabla_i \quad \text{(sum over all electrons)}.$$

The relation of (4) to (1) is simply

$$\Lambda = \langle\nabla^2\rangle K + \tfrac{1}{2}Z4\pi\psi_0^2(0)\ln[K/k_0], \quad (K\to\infty)$$

where $\langle\ \rangle$ means expectation value in the state ψ_0 or $|0\rangle$ being studied, and

$$\psi_0^2(0)\equiv\langle \sum_{i=1}^N \delta(\mathbf{r}_i)\rangle.$$

The electron Hamiltonian is

$$H=\sum_{i=1}^N \left(-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right)+\sum_{i<j=1}^N \frac{1}{r_{ij}}. \quad (5)$$

We focus our attention now on the sum over states [call it $-J(k)$] under the k integral in (4). Writing

$$(E_0-H-k)\psi_1=\nabla\psi_0 \quad (6)$$

as a differential equation defining ψ_1, we see that we have for the sum over states simply

$$-J(k)=\langle\psi_1|\nabla|\psi_0\rangle.$$

Thus we write

$$2\pi Z\psi_0^2(0)\ln k_0$$

$$=\lim_{K\to\infty}\left[\langle\nabla^2\rangle K+2\pi Z\psi_0^2(0)\ln K+\int_0^K k\,dk\,J(k)\right]. \quad (7)$$

We attempt to solve the differential Eq. (6) by constructing the stationary expression

$$w(k)=2\langle\psi_0|\nabla|\psi_1\rangle+\langle\psi_1|E_0-H-k|\psi_1\rangle, \quad (8)$$

[1] H. A. Bethe, Phys. Rev. **72**, 399 (1947).

[2] P. K. Kabir and E. E. Salpeter, Phys. Rev. **108**, 1256 (1957).

[3] Included is an additional term contributed by J. Sucher, Phys. Rev. **109**, 1010 (1958).

[4] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958); **115**, 1216 (1959).

[5] G. Herzberg, Proc. Roy. Soc. (London) **A248**, 309 (1958).

[6] The method we shall use here is an outgrowth of earlier work; C. Schwartz and J. J. Tiemann, Ann. Phys. **2**, 178 (1959).

and then varying convenient functions ψ_1 to get a "best" value. The exact value of $w(k)$ is just $J(k)$.[7]

The comparison with the earlier method may be stated as follows. Whereas they carry out variation (or some other approximate) calculations for each excited state and then integrate over states according to (1), we carry out one variational calculation for the complete perturbed function for each value of the photon energy and then integrate over k according to (7). Rather then try to argue which method should be better, we simply stress that they are two independent methods, and proceed to the calculation.

LOW k VALUES

The ground state (approximate) wave function is given in the Hylleraas form (for S states)

$$\psi_0 = \sum_{l,m,n} C_{lmn}^{(0)} e^{-\frac{1}{2}\kappa s} s^{l-m} u^{m-n} t^n, \qquad (9)$$

where $s=r_1+r_2$, $t=-r_1+r_2$, $u=r_{12}$, and n is either even or odd for singlet or triplet states, respectively. The perturbed functions ψ_1 are odd-parity P states which we can represent as[8]

$$\psi_1 = \sum_{l,m,n} C_{lmn}(\mathbf{r}_1 \pm \mathbf{r}_2) e^{-\frac{1}{2}\kappa s} s^{l-m} u^{m-n} t^n, \qquad (10)$$

where the $\pm$ sign is chosen accordingly as n is even or odd, for each spin state.

Variation of the coefficient C_{lmn} in the stationary expression (8) then leads to a system of simultaneous linear equations, which are solved[9] by standard techniques.

There is always raised, against variational calculations, the question of how can one tell how appropriate the form of the trial function was and thus how good the answer is. The best reply we can give is to carry out repeated calculations, taking successively larger numbers of parameters in some systematic way, and then observe experimentally the convergence of the computed answers.[10]

The 18-parameter function given by Kinoshita[11] was used for ψ_0. By comparison of various measures of this approximate ψ_0 with more accurate values given by Pekeris we estimate its useful accuracy to be a few parts in 10^4. In Table I are a few examples showing the accuracy and convergence of $w(k)$. At $k=0$ we should have exactly $w=3$, and the small error $(1.7/10^4)$ is probably attributable to ψ_0. The resultant values are seen to vary smoothly, allowing one to have confidence in an extrapolation, and to guess the residual error. Note that the convergence becomes poorer as k in-

TABLE I. Results of calculation according to Eq. (8) using 18-parameter function for ψ_0.

No. of terms in ψ_1	$w(0)$	$w(4)$	$w(15)$	$w(50)$
4	2.93420	0.85916	0.31150	0.103874
10	2.99749	0.87528	0.32316	0.109542
20	3.00018	0.87622	0.32506	0.111062
35	3.00048	0.87636	0.32557	0.111658
56		0.87638	0.32569	0.111889
84			0.32572	0.111980
Extrapolated to ∞	3.00051	0.87638	0.32573	0.11204

creases. This will be discussed further in the next section.

By a slight modification of the program [replacing the operator $\boldsymbol{\nabla}$ in (8) by $\mathbf{r}$] we were able to calculate accurate values of the static polarizability (at $k=0$). For the ground state of helium we find $\alpha=0.2050 \pm 0.0001$ Å^3, to be compared with the most recent measured value of 0.207 ± 0.001,[12] and for the negative hydrogen ion $\alpha=26.8\pm0.4$ Å^3. Earlier calculations[13] of the latter gave only about one half this value.

HIGH k VALUES

As k goes to infinity the integral $kJ(k)dk$ diverges, and while the divergence is subtracted out in our desired answer (7), we cannot do this numerically. The asymptotic behavior of ψ_1 for large k is easily seen from Eq. (6) and we set

$$\psi_1 = -(1/k)\boldsymbol{\nabla}\psi_0 + U, \qquad (11)$$

for k values larger than some $\tilde{k}$. Substituting into (8) we have

$$J(k) = -\frac{1}{k}\langle \boldsymbol{\nabla}^2 \rangle - \frac{2\pi Z}{k^2}\psi_0^2(0) + \tilde{w}(k), \quad k \geqslant \tilde{k}, \qquad (12)$$

where $\tilde{w}$ is the stationary value of a new variational problem.

$$\tilde{w}(k) = -\frac{2Z}{k}\left\langle \psi_0 \left| \sum_{i=1}^N \frac{\mathbf{r}_i}{r_i^3} \right| U \right\rangle + \langle U | E_0 - H - k | U \rangle. \qquad (13)$$

The integral $\int^\infty kdk\ \tilde{w}(k)$ now converges, but not very rapidly. If we attempt to continue the expansion for $k \to \infty$ of ψ_1 [from (6)] or alternatively of $J(k)$ [from (4)], the next term in (12) is C/k^3, where C is infinite for s electrons. Looking back at the explicit solution for $J(k)$ in the one-electron atom,[6] we see that the next terms in (12) go as $k^{-\frac{5}{2}}$ and $k^{-3} \ln k$.

The reason for this strange behavior is that while we try to expand in inverse powers of k for $k \to \infty$, there is

[7] For the case when ψ_0 is the lowest state $w(k)$ is actually a lower bound for the exact $J(k)$.

[8] See Appendix I.

[9] Actual computations were carried out on high speed electronic digital computers (IBM 704, 709).

[10] This point of view we have taken, implicitly, from Pekeris.

[11] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[12] This value from L. Essen, Proc. Phys. Soc. (London) **B66**, 189 (1953), is just slightly outside agreeing with our value. Recently, however, Johnston, Oudemans, and Cole, J. Chem. Phys. **33**, 1310 (1960), gave a more accurate measurement of $\alpha=0.2068\pm0.0002$ Å^3 which seems to be in definite disagreement with our calculation.

[13] See E. G. Wikner and T. P. Das, Phys. Rev. **107**, 497 (1957).

a singularity in the defining equation (6) at $r=0$. The differential equation for U is

$$(E_0-H-k)U=\frac{Z}{k}\sum_{i=1}^{N}\frac{\mathbf{r}_i}{r_i^3}\psi_0, \qquad (14)$$

and we must now write down an asymptotic solution for large k which is also well behaved at small r. As $r_i\rightarrow 0$ the important terms on the left-hand side of (14) are $\frac{1}{2}\nabla_i^2-k$; and so we add to the obvious particular solution of (14) (for $k\rightarrow\infty$) an approximate solution of the homogeneous equation (for $k\rightarrow\infty$, $r\rightarrow 0$):

$$U\underset{k\rightarrow\infty}{\sim}-\frac{Z}{k^2}\sum_{i=1}^{N}\frac{\mathbf{r}_i}{r_i^3}\psi_0+\text{const}\sum_{i=1}^{N}\frac{\mathbf{r}_i}{r_i^3}e^{-\mu r_i}(1+\mu r_i), \quad (15)$$

where $\mu=(2k)^{\frac{1}{2}}$.

For the constant we take $+(Z/k^2)\psi_0$ so that the r^{-2} singularity in U is cancelled; yet the extra added term goes to zero exponentially fast as $k\rightarrow\infty$ for all $r>0$. Furthermore, (15) has no r^{-1} term (for $r\rightarrow 0$) and it can easily be seen that combining with the term extracted in (11), the entire function ψ_1 goes as r^1 as $r\rightarrow 0$, which is just the way a p-wave should behave. Substituting

$$U=-\frac{Z}{k}\sum_{i=1}^{N}\frac{\mathbf{r}_i}{r_i^3}[1-e^{-\mu r_i}(1+\mu r_i)]\psi_0, \quad \mu=(2k)^{\frac{1}{2}}, \quad (16)$$

into (13) and looking at the leading terms as $k\rightarrow\infty$, we find

$$\tilde{w}(k)\sim\frac{Z^2}{k^3}\left[\sum_{i=1}^{N}\int\frac{dv\,\bar{\rho}_i(r)}{4\pi}\frac{1}{r^2}\int_0^{\mu}p\,dp\,e^{-pr}+\text{const}\right], \quad (17)$$

where $\bar{\rho}_i(r)=\int d\Omega_i\int dv_{\neq i}|\psi_0|^2$ is the radial one-electron density. By performing the obvious partial integrations in (17), we finally find

$$\tilde{w}(k)\underset{k\rightarrow\infty}{\sim}\frac{Z^2}{k^3}\sum_{i=1}^{N}\bar{\rho}_i(0)[(2k)^{\frac{1}{2}}-Z\ln k+C], \quad (18)$$

where the two strange terms appear simply with the same coefficient as the k^{-2} term in (12). By proceeding somewhat farther we have determined the coefficient C of all k^{-3} terms:

$$C=2Z(\tfrac{1}{2}\ln 2-\tfrac{1}{2}-0.5772\cdots)$$

$$+\frac{1}{\sum\bar{\rho}_i(0)}\left[\left\langle\sum_{i\neq j=1}^{N}\frac{\mathbf{r}_i\cdot\mathbf{r}_j}{r_i^3 r_j^3}\right\rangle-\sum_{i=1}^{N}\int_0^{\infty}dr\,\ln r\frac{d^2\bar{\rho}_i(r)}{dr^2}\right]$$

$$=2Z(\tfrac{1}{2}\ln 2+\tfrac{1}{2}-0.5772\cdots)+\frac{1}{\sum\bar{\rho}_i(0)}$$

$$\times\text{finite part of}\left\langle\left|\sum_{i=1}^{N}\frac{\mathbf{r}_i}{r_i^3}\right|^2\right\rangle. \quad (19)$$

TABLE II. Results of calculations according to (13) using 18-parameter function for ψ_0. Numbers in parentheses represent uncertainty in last digit given due to internal inconsistency of the numerical solution.

No. of parameters	$\tilde{w}(50)/4$	$\tilde{w}(300)/4$	$\tilde{w}(3000)/4$
12	4.4893(0)	2.4207(0)	
24	4.8355(0)	2.6010(0)	0.9880(1)
36			0.95 (5)
48	4.8370(0)	2.6045(0)	0.94 (6)

We have checked these results against the expansion of the exact formula for $J(k)$ for the one-electron atom,[6] and we shall use the results as follows for helium.

Variational calculations for $\tilde{w}$ according to (13) are carried out up to some very large value of k, call it $\tilde{K}$, at which (18), (19) become sufficiently accurate. Taking note of the functions involved in the preceding analysis, we use as a basis for the trial function U the following:

$$U=\sum C_{lmn\lambda}r_{12}{}^l r_1 r_1{}^{m-1} r_2{}^n e^{-\frac{1}{2}\kappa'(r_2+\lambda r_1)}\pm(1\leftrightarrow 2), \quad (20)$$

where we use terms both with $\lambda=1$ and $\lambda=2(2k)^{\frac{1}{2}}/\kappa'$. Some results are shown in Table II.

The value $\tilde{w}(50)$ when put in Eq. (13) gives $J(50)=0.11205$ which agrees excellently with the value shown in Table I. The values at $k=300$ are also seen to converge nicely, apparently accurate to better than one part in 10^3. The numbers shown at $k=3000$ are rather typical of the poor results obtained at very high k values. Here the results at 36 and 48 parameters are poorer than those at 24 parameters (remember we are computing a lower bound). Apparently at very large k the matrix involved in the solution of the linear equations

$$\mathbf{Ax}=\mathbf{b},$$

($\mathbf{A}$, matrix; $\mathbf{x}$, $\mathbf{b}$, vectors) is somewhat singular, so that numerical round-off errors accumulate in the solution for $\mathbf{x}$. The internal consistency is measured by the difference between

$$U=\mathbf{x}\cdot\mathbf{b},$$

and

$$V=\mathbf{x}\cdot\mathbf{A}\cdot\mathbf{x},$$

and this discrepancy is shown in Table II along with the quoted values of

$$w=2U-V.$$

In spite of the growing errors (which presumably could be overcome by more elaborate computing techniques), we will still be able to get a very accurate final value, since the contribution to the final integral is getting smaller as k increases and we have the series (18) as a guide.

The value of the constant C computed with the 18 parameter function is 5.18 and the other constants are $\langle\nabla^2\rangle=-6.12573$, $4\pi\psi^2(0)=\sum_i\bar{\rho}_i(0)=45.4971$.

TABLE III. Results of test calculation for hydrogen $1S$ state.

k	w exact	w computed	Fractional error
1.5	0.83058224	0.8305816	$1/10^6$
4.0	0.39507764	0.3950658	$1/40\,000$
7.5	0.23055	0.230499	$1/5000$
17.5	0.10621	0.106091	$1/1000$

k	$k^2\tilde{w}$ exact	$k^2\tilde{w}$ computed	Fractional error
4.0	2.321245	2.321245	$<1/10^6$
31.5	1.253407	1.253407	$<1/10^6$
200	0.61970 ± 0.00005	0.61970	$<1/10^4$
1000	0.31003	0.30942	$1/500$
4999.5	0.14800	0.14729	$1/200$

RESULTS

Table III shows computed results for hydrogen. In our programs the e^2/r_{12} term was deleted and the $1s^2$ state was used for ψ_0. The "exact" values shown in this table are gotten either by explicit evaluation of the integral representation of $J(k)$ given in reference 6 or from the asymptotic expansion of that integral (for $Z=1$):

$$\tilde{w}(k)=\frac{4N}{k^3}\left[(2k)^{\frac{1}{2}}-\ln k+(3\ln2-1)-\frac{(\frac{1}{3}\pi^2+\frac{7}{2})}{(2k)^{\frac{1}{2}}}\right.$$
$$\left.+\frac{2\ln k}{k}+\frac{[9/2-6\ln2-\zeta(3)]}{k}+\cdots\right].$$

For helium, with the results of calculations at 35 points from $k=0$ to $k=50$ we have numerically integrated

$$\int_0^{50} kdk\, J(k)=245.153,$$

and if we add the increment from extrapolating each calculated value (to ∞ number of parameters) we get $J_0^{50}=245.204\pm0.017$, where we have taken the uncertainty as one-third of the extrapolation.

For the high k values we have used calculated values of $\tilde{w}$ from $k=50$ to $k=1000$ shown in Table IV. Here,

TABLE IV. Computed results and extrapolated values for $\tilde{w}/4$ for high k values using 18-parameter ψ_0 for helium $1S$. The numbers 24, 36, 48 are the number of parameters used in the variational calculation.

k	$\tilde{w}/4$ (24)	$\tilde{w}/4$ (36)	$\tilde{w}/4$ (48)	$\tilde{w}/4$ extrapolated
30	5.61499		5.61661	5.6171 ± 0.0005
50	4.83553		4.83704	4.8375 ± 0.0005
65		4.45690		4.4579 ± 0.0010
80		4.16765		4.1687 ± 0.0010
100	3.86751		3.86924	3.8698 ± 0.0006
140		3.44498		3.4465 ± 0.0015
200		3.03055		3.0325 ± 0.0019
300	2.60098		2.60448	2.6056 ± 0.0012
470		2.18711		2.1899 ± 0.0028
700		1.86311		1.8669 ± 0.0038
1000	1.60050		1.60841	1.6110 ± 0.0026
1400		1.3815		1.3875 ± 0.0060

since we do not have many points (at each k), the extrapolation is a crude guess and the uncertainty is taken as the full amount of this extrapolation. We then get

$$\int_{50}^{1000}\frac{kdk\,\tilde{w}(k)}{4\pi\psi^2(0)}=0.7942,$$

with an uncertainty ±0.0005 from the extrapolation at each k value and another uncertainty of ±0.0002 from the numerical integration.

For $k>1000$ we use the asymptotic formula:

$$\frac{\tilde{w}}{4\pi\psi^2(0)}=\frac{4}{k^3}\left[(2k)^{\frac{1}{2}}-2\ln k+5.18+\frac{D}{\sqrt{k}}+\cdots\right];$$

and by comparison with the above expansion for hydrogen with $k\to k/4$, namely,

$$(2k)^{\frac{1}{2}}-2\ln k+4.93-19.2/\sqrt{k}+\cdots,$$

we set $D=-20\pm3$. Then

$$\int_{1000}^{\infty}\frac{kdk\,\tilde{w}(k)}{4\pi\psi^2(0)}=0.3578-0.0553+0.0127$$
$$+(-0.0017\pm0.0003)+\cdots$$
$$=0.3135\pm0.0007,$$

where we have added an uncertainty of ±0.0004 to cover the unknown following terms of this series. Our final calculated value is now

$$(\ln k_0)_{\text{calc}}=\frac{245.204\pm0.017-50\times6.12573}{45.4971}+\ln50$$
$$+0.7942\pm0.0007+0.3135\pm0.0007$$
$$=3.6772\pm0.0018.$$

We need now only assess the accuracy of the 18-parameter function used for the ground state. By comparing various integrals over this wave function with values either known theoretically or given more accurately by Pekeris, we give an additional uncertainty of 5 parts in 10^4. Then adding $\ln2$ to convert back to rydberg units:

$$\ln[k_0/\text{ry}]=4.370\pm0.004.$$

Previous calculations have given

4.39 ± 0.2 (Kabir and Salpeter)

4.37 ± 0.03 (Dalgarno and Stewart)[14]

4.389 ± 0.010 (Zaidi)[15]

Combining with Pekeris' results we have for the ionization energy of He, $J_{\text{th}}=198\,310.685\pm0.005$ cm^{-1} and the experimental value $J_{\text{exp}}=198\,310.82\pm0.15$.

[14] A. Dalgarno and A. L. Stewart, Proc. Phys. Soc. (London) A76, 49 (1960).
[15] M. Zaidi (private communication).

One might add a further theoretical uncertainty of not more than ±0.005 to cover as yet uncalculated terms.

The Lamb shift in helium is verified within about 10%, which is the present experimental uncertainty.

ACKNOWLEDGMENTS

APPENDIX I. REPRESENTATION OF ANGULAR MOMENTUM STATES

Breit[16] has given a general analysis of the angular momentum eigenstates for 2 particles in a central field and has written down the functions for P states. However his method seems rather awkward when applied to states of higher L and we give here an alternative approach.

A state of 2 particles coupled to a total angular momentum L, z component M may be written as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2;L,M)=\sum_{l_1l_2}\psi(l_1,l_2,L,M)f_{l_1l_2}(r_1,r_2), \quad \text{(A.1)}$$

where

$$\psi(l_1,l_2,L,M)=\sum_{m_1m_2}Y_{l_1m_1}(1)Y_{l_2m_2}(2)(l_1m_1l_2m_2|LM) \quad \text{(A.2)}$$

is the vector-coupled state with specified l values for particles 1 and 2. The sum in (A.1) is too extensive and we wish to reduce it by extracting functions of the scalar

$$r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$$

to be combined with the $f(r_1,r_2)$.

We make use of the following formula:

$$\mathbf{r}_1\cdot\mathbf{r}_2\psi(l_1,l_2,LM)=C_{++}\psi(l_1+1, l_2+1, LM)$$
$$+C_{+-}\psi(l_1+1, l_2-1, LM)$$
$$+C_{-+}\psi(l_1-1, l_2+1, LM)$$
$$+C_{--}\psi(l_1-1, l_2-1, LM). \quad \text{(A.3)}$$

It is obvious that these 4 terms give the complete reduction, remembering the selection rules for the vector $\mathbf{r}$, $(\Delta l_1=\pm1)$, and for the scalar

$$\mathbf{r}_1\cdot\mathbf{r}_2(\Delta L=\Delta M=0).$$

Formulas for the coefficients C may easily be written down, but for our construction we need note only the following obvious property: Any coefficient C will vanish unless both the original state, $\psi(l_1,l_2,L)$, and

16 G. Breit, Phys. Rev. **35**, 569 (1930).

the state it multiplies, $\psi(l_1',l_2',L)$ exist; i.e., $C\neq0$ only if

$$|l_1-l_2|\leq L\leq l_1+l_2,$$
$$|l_1'-l_2'|\leq L\leq l_1'+l_2'.$$

We want to use (A.3) to reduce the terms with largest l values to terms with lower l values, introducing $\mathbf{r}_1\cdot\mathbf{r}_2$. Thus, we will be able to rewrite the original expansion (A.1) in the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,L,M)=\sum_{\{l_1,l_2\}}\psi(l_1,l_2,L,M)F_{l_1l_2}(r_1,r_2,r_{12}), \quad \text{(A.4)}$$

involving only a small set of values $\{l_1,l_2\}$ for which the reduction cannot be carried further. From the rules above, we see that the irreducible pairs $\{l_1,l_2\}$ are those values which satisfy

(A): $l_1+l_2=L$, or (B): $l_1+l_2=L+1$,

with the added restriction $|l_1-l_2|\leq L$.

Thus, there are only $(2L+1)$ angular functions needed (for each M); this agrees with Breit's result. Furthermore, we can easily classify the states according to their parity, which is just $(-1)^{l_1}(-1)^{l_2}$; and the two classes (A) and (B) are clearly distinct. A still further simplification occurs when we symmetrize the wave function, since

$$\psi(l_1,l_2,LM)=(-1)^{l_1+l_2-L}\psi(l_2,l_1,LM).$$

These two properties (parity and exchange symmetry) are quite complicated in Breit's description.

Examples: $L=0$.

We have only $l_1=l_2=0$, even parity,

$$\Psi(^{1,3}S^e)=F(r_1,r_2,r_{12})\pm F(r_2,r_1,r_{12})$$

and we will write $F(r_2,r_1,r_{12})=\tilde{F}(r_1,r_2,r_{12})$.

$L=1$,

Odd parity: $(l_1,l_2)=(0,1),(1,0)$;

Even parity: $(l_1,l_2)=(1,1)$.

Using Cartesian vector notation [instead of $r Y_{lm}(\theta,\phi)$], we can write

$$\Psi(^{1,3}P^o)=\mathbf{r}_1F\pm\mathbf{r}_2\tilde{F},$$
$$\Psi(^{1,3}P^e)=\mathbf{r}_1\times\mathbf{r}_2[F\mp\tilde{F}].$$

The above results are given by Breit, but we can proceed easily to higher L.

$L=2$,

Even parity: $(l_1,l_2)=(0,2),(2,0),(1,1)$;

Odd parity: $(l_1,l_2)=(1,2),(2,1)$;

$$\Psi(^{1,3}D^e)=\{\mathbf{r}_1,\mathbf{r}_1\}^2F\pm\{\mathbf{r}_2,\mathbf{r}_2\}^2\tilde{F}+\{\mathbf{r}_1,\mathbf{r}_2\}^2[G\pm\tilde{G}],$$
$$\Psi(^{1,3}D^o)=\{\mathbf{r}_1,\mathbf{r}_1\times\mathbf{r}_2\}^2F\pm\{\mathbf{r}_2,\mathbf{r}_2\times\mathbf{r}_1\}^2\tilde{F},$$

where we have written $\{\mathbf{a},\mathbf{b}\}^2$ for the symmetric

second-rank tensor. For future reference we write down one more:

$$\Psi(^3F^o)=\{r_1,\{r_2,r_2\}^2\}^3F-\{r_2,\{r_1,r_1\}^2\}^3\widetilde{F}$$
$$+\{r_1,r_1,r_1\}^3G-\{r_2,r_2,r_2\}^3\widetilde{G}.$$

The general angular momentum functions here written down (somewhat symbolically) in Cartesian vector form can be constructed for example from the harmonic polynomials of an arbitrary vector, ξ as follows:

$$H_{LM}(\xi)=\xi^L Y_{Lm}(\theta_\xi,\varphi_\xi),$$
$$\psi(l_1,\,l_2,\,L=l_1+l_2,\,M)$$
$$=(r_1\cdot\nabla_\xi)^{l_1}(r_2\cdot\nabla_\xi)^{l_2}H_{LM}(\xi),\quad\quad (A.5)$$
$$\psi(l_1,\,l_2,\,L=l_1+l_2-1,\,M)$$
$$=(r_1\cdot\nabla_\xi)^{l_1-1}(r_2\cdot\nabla_\xi)^{l_2-1}(r_1\times r_2\cdot\nabla_\xi)H_{LM}(\xi).\quad (A.6)$$

APPENDIX II. EVALUATION OF INTEGRALS

Using wave functions of the type (10) we take derivatives in Cartesian form as follows:

$$\nabla_1=\frac{r_1}{r_1}(\partial_s-\partial_t)+\frac{r_1-r_2}{u}\partial_u,$$

$$\nabla_2=\frac{r_2}{r_2}(\partial_s+\partial_t)+\frac{r_2-r_1}{u}\partial_u.$$

Then after taking inner products of vectors and re-expressing scalars as $r_1=(s-t)/2$, $r_2=(s+t)/2$, and $r_1\cdot r_2=\frac{1}{4}(s^2+t^2-2u^2)$, we do the integrals over the Hylleraas volume element:

$$\int_0^\infty ds\int_0^s udu\int_0^u dt(s^2-t^2)=\frac{8}{(4\pi)^2}\int dv_1\int dv_2,$$

yielding rational functions.

With functions of the type (20), we have

$$\nabla_1=\frac{r_1}{r_1}\frac{\partial}{\partial r_1}+\frac{r_1-r_2}{r_{12}}\frac{\partial}{\partial r_{12}};$$

and we average over $\cos\theta_{12}$ as follows:

$$\langle r_{12}{}^l\rangle_{av}=\frac{1}{(l+2)}\sum_{s\text{ odd}}\binom{l+2}{s}r_>{}^{l+1-s}r_<{}^{s-1},\quad (l\geqslant-1).$$

The remaining integrals are of the general form.

$$J_{\mu\nu}(a,b)=\int_0^\infty dr\ e^{-\mu r}r^{a-1}\int_r^\infty ds\ e^{-\nu s}s^{b-a-1},\quad (b\geqslant1)$$

which can be tabulated according to simple recursion formulas proceeding from small values of a, b (for given μ, ν). However, this is not always satisfactory. When, for example, $\mu\ll\nu$, large cancellations may occur in this way and we must instead start from the series,

$$J_{\mu\nu}(a,b)=\sum_{m=0}^\infty \nu^{-b}\frac{(-\mu/\nu)^m}{(m+a)}\frac{(m+b-1)!}{m!},$$

for the largest values of a (at each b) and then iterate downward from (a,b) to $(a-1,\,b-1)$, etc.

If on the other hand, $\mu\gg\nu$, we can start with the single term,

$$J_{\mu\nu}(a,\,b=a)=\frac{(a-1)!}{\mu^a}\left[\ln\left(1+\frac{\mu}{\nu}\right)-\sum_{s=1}^{a-1}\frac{1}{s}\left(\frac{\mu}{\mu+\nu}\right)^s\right],$$

and iterate safely to lower values of a and b ($\leq a$).

For $b\geq a+1$, the upward iteration

$$J_{\mu\nu}(a,b)=\frac{1}{\nu}\left[\frac{(b-2)!}{(\mu+\nu)^{b-1}}+(b-a-1)J_{\mu\nu}(a,\,b-1)\right]$$

is always safe.