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Gordon W. F. Drake  
*University of Windsor*

G. A. Victor

A. Dalgarno

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## Two-Photon Decay of the Singlet and Triplet Metastable States of Helium-like Ions

G. W. F. Drake\*

*Smithsonian Astrophysical Observatory, Cambridge, Massachusetts 02138*

and

G. A. Victor

*Technology Division, GCA Corporation, Bedford, Massachusetts*

and

A. Dalgarno

*Harvard College Observatory and Smithsonian Astrophysical Observatory, Cambridge, Massachusetts 02138*

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The two-photon decay rates and photon energy distributions of the metastable  $2^1S$  and  $2^3S$  states of the helium isoelectronic sequence are calculated by variational procedures for the ions He I through Ne IX.

## I. INTRODUCTION

The helium-like ions C V, O VII, and Ne IX have been identified in the solar corona<sup>1,2</sup> and in high-temperature laboratory plasmas.<sup>3-6</sup> The excited-state populations and the emission spectra of the ions depend upon the radiative lifetimes of the  $1s2s^1S$  and  $1s2s^3S$  metastable states.

The  $2^1S$  state of He<sup>4</sup> cannot decay through any single-photon emission process of either the electric or magnetic type, and Breit and Teller<sup>7</sup> pointed out that the most probable mode of radiative decay is the two-photon emission process terminating in the ground  $1^1S$  state. The presence of nuclear spin causes departures from the normal selection rule forbidding single-photon transitions, and the effects increase with increasing nuclear charge  $Z$ . However, two-photon emission remains the most probable radiative decay mode up to very large values of  $Z$ . The two-photon emission of Ne IX has been observed recently in a laboratory plasma.<sup>5</sup>

The  $2^3S$  metastable state of He<sup>4</sup> can decay through a magnetic-dipole transition because of admixtures in the initial and final wave functions due to spin-orbit and spin-spin interactions,<sup>7</sup> but all higher-order multipole transitions are strictly forbidden. The magnetic-dipole transition probability is negligible for helium, and the two-photon emission terminating in the ground  $1^1S$  state is the most probable mode of radiative decay for the

$2^3S$  state.

For the two-electron ions of higher nuclear charge, the magnetic-dipole transition probability increases initially as  $Z^{16}$  and ultimately as  $Z^6$  with nuclear charge, whereas, as we shall demonstrate, the two-photon decay probability increases initially as  $Z^{10}$  and ultimately as  $Z^6$ . It appears that the single-photon magnetic-dipole decay mode might become competitive with the two-photon decay mode for  $Z$  somewhat greater than 10. For large values of  $Z$ , further modifications occur owing to the nuclear spin and to relativistic and finite nuclear-size effects on the wave functions.

The two-photon decay rate of the  $2^1S$  state of helium was estimated by Dalgarno<sup>8</sup> using oscillator-strength sum rules and was calculated approximately by Dalgarno and Victor<sup>9</sup> using the uncoupled Hartree-Fock method and by Victor<sup>10</sup> using the coupled Hartree-Fock method. For the  $2^3S$  state of helium, only gross estimates are available. Drake and Dalgarno<sup>11</sup> found that the decay probability does not exceed  $10^{-7}$  sec<sup>-1</sup>, and according to Bely,<sup>12</sup> it is near to but does not exceed  $10^{-10}$  sec<sup>-1</sup>. With the exception of the  $2^1S$  state of Li II,<sup>13</sup> no calculations have been carried out for higher nuclear charges. In this paper, we present accurate variational calculations of the two-photon decay rates and emission spectra of the  $2^1S$  and  $2^3S$  metastable states of the helium isoelectronic sequence from He I to Ne IX.

## II. THEORY

Two-photon emission from  $2^1S$  states is qualitatively different from  $2^3S$  two-photon decay because no angular momentum is transported by the photon field in the  $2^1S_0 - 1^1S_0$  transition and because one quantum is transported in the  $2^3S_1 - 1^1S_0$  transition. This difference affects both the angular and the frequency distributions of the two photons.<sup>11</sup> Both decay processes give rise to a broad continuum of photon energies since the only restriction on the photon frequencies,  $\nu_1$  and  $\nu_2$ , is the energy conservation requirement that their sum equal the frequency difference  $\nu_T$  between the initial and final states. Thus the continuum ex-

tends from  $\nu=0$  to  $\nu=\nu_T$  and is symmetric about the central frequency  $\nu_T/2$ .

For  $2^1S$  metastable states, the probability for the simultaneous emission of two photons with frequencies  $\nu_1$  and  $\nu_2$  is given in  $\text{sec}^{-1}$  by<sup>7</sup>

$$A(\nu_1)d\nu_1 = (1024\pi^6 e^4/h^2 c^6) [(\vec{u}_1 \cdot \vec{u}_2)^2]_{\text{av}} \nu_1^3 \nu_2^3 \\ \times \left| \sum_{n'=2}^{\infty} \langle 2^1S | P_z | n'^1P \rangle \langle n'^1P | P_z | 1^1S \rangle \left( \frac{1}{\nu(2^1S - n'^1P) + \nu_2} + \frac{1}{\nu(2^1S - n'^1P) + \nu_1} \right) \right|^2 d\nu_1, \quad (1)$$

where  $\nu(2^1S - n'^1P)$  is the frequency of the  $2^1S - n'^1P$  transition,  $P_z$  is the  $z$  component of the electric dipole-moment operator, and  $\vec{u}_1$  and  $\vec{u}_2$  are unit vectors parallel to the directions of polarization of the two photons. Equation (1) has been averaged over all directions of propagation of the two photons and  $[(\vec{u}_1 \cdot \vec{u}_2)^2]_{\text{av}} = \frac{1}{3}$ . Evidently, the probability of decay is a maximum when  $\nu_1 = \nu_2$  and when the polarization vectors are parallel or antiparallel. The angular factor correlating the directions of propagation of the two photons is  $1 + \cos^2\theta_{12}$ .<sup>14</sup> The total decay rate is given by

$$A = \frac{1}{2} \int_0^{\nu_T} A(\nu_1) d\nu_1, \quad (2)$$

where the factor of  $\frac{1}{2}$  is included because only pairs of photons are counted.

The two-photon decay of the  $2^3S$  states proceeds through the spin-orbit mixing of the intermediate  $^3P_1$  and  $^1P_1$  states. The sum over all intermediate states includes each  $^1P_1$  state mixed with all  $^3P_1$  states and each  $^3P_1$  state mixed with all  $^1P_1$  states. Following Mathis<sup>15</sup> we write the true  $P$  wave functions in the form

$$|n'^3P_1\rangle_{\text{true}} = |n'^3P_1\rangle + \sum_{n''=2}^{\infty} \epsilon_{n'n''} |n''^1P_1\rangle \quad (3)$$

$$\text{and } |n'^1P_1\rangle_{\text{true}} = |n'^1P_1\rangle - \sum_{n''=2}^{\infty} \epsilon_{n'n''} |n''^3P_1\rangle, \quad (4)$$

$$\text{where } \epsilon_{n'n''} = \langle n'^3P_1 | H_1 | n''^1P_1 \rangle / [E(n'^3P) - E(n''^1P)],$$

and  $H_1$  is the spin-orbit interaction operator.<sup>16</sup>  $H_1$  is diagonal in the  $J^2, M_J$  coupling scheme used above (where  $\vec{J} = \vec{L} + \vec{S}$ ), and the matrix elements of  $H_1$  are independent of  $M_J$ .

After averaging over the directions of propagation of the two photons, we obtain for the probability of two-photon emission, in terms of the reduced transition matrix elements of Condon and Shortley,<sup>17</sup>

$$A(\nu_1)d\nu_1 = (1024\pi^6 e^4/3h^2 c^6) (|\vec{u}_1 \times \vec{u}_2|^2)_{\text{av}} \nu_1^3 \nu_2^3 \\ \times \left| \sum_{n',n''}^{\infty} 2^{-1/2} (2^3S || P || n'^3P) \epsilon_{n'n''} (n''^1P || P || 1^1S) \right. \\ \left. \times \left( \frac{1}{\nu(2^3S - n'^3P) + \nu_2} - \frac{1}{\nu(2^3S - n''^1P) + \nu_2} - \frac{1}{\nu(2^3S - n'^3P) + \nu_1} + \frac{1}{\nu(2^3S - n''^1P) + \nu_1} \right) \right|^2 d\nu_1, \quad (5)$$

and  $(|\vec{u}_1 \times \vec{u}_2|^2)_{\text{av}} = \frac{2}{3}$ . Equation (5) has been derived previously.<sup>11,12</sup> The probability of emission is now zero when  $\nu_1 = \nu_2$ , in contrast to the  $2^1S$  decay for which it reaches a maximum when  $\nu_1 = \nu_2$ . The angular factor correlating the directions of propagation of the two photons is  $1 - \cos^2\theta_{12}/3$ <sup>14</sup> and the factor correlating the directions of polarization is  $|\vec{u}_1 \times \vec{u}_2|^2$ .

### III. CALCULATIONS

The infinite summations over intermediate states in (1) and (5) (including the continuum) are conveniently performed by replacing the true intermediate functions by discrete sets of variational functions. Each function of the set has the form

$$\psi^{LSM} L(n) = \frac{1}{\sqrt{2}} (1 \pm P_{12}) \sum_{i,j,k}^N a_{ijk} LS(n) \phi_{ijk} LS(\vec{r}_1, \vec{r}_2) y_{LL_1 L_2}^{ML}(\hat{r}_1, \hat{r}_2), \quad n=1, 2, 3, \dots, N, \quad (6)$$

$$\text{where } \psi_{LL_1L_2}^{M_L}(\hat{r}_1, \hat{r}_2) = \sum_{m_1, m_2} \langle l_1 m_1 l_2 m_2 | LM_L \rangle Y_{l_1 m_1}(\hat{r}_1) Y_{l_2 m_2}(\hat{r}_2), \quad (7)$$

$$\phi_{ijk}^{LS}(\vec{r}_1, \vec{r}_2) = r_1^i r_2^j r_{12}^k \exp(-\alpha^{LS} r_1 - \beta^{LS} r_2), \quad (8)$$

and the quantities  $\langle l_1 m_1 l_2 m_2 | LM_L \rangle$  in (7) are vector coupling coefficients. The positive sign is used in (6) for singlet states and the negative sign for triplet states. For fixed  $\alpha$ ,  $\beta$ , and  $N$ , the secular equation was solved yielding an orthonormal set of  $N$  functions for each  $LS$  symmetry. For the present calculation, the  $^3S$ ,  $^3P$ ,  $^1P$ , and  $^1S$  sets were required. The scale parameters  $\alpha$  and  $\beta$  were chosen so as to minimize the energy of the first root of each symmetry, thereby producing accurate wave functions for the  $2^3S$ ,  $2^3P$ ,  $2^1P$ , and  $1^1S$  states and representative distributions for the remaining excited states. For the  $2^1S$  state,  $\alpha$  and  $\beta$  were chosen to minimize the energy of the second root. The excited-state energies of each symmetry obtained from (6) tend to the observed energies from above as  $N$  is increased, and the oscillator strength sum rules<sup>17</sup> are well satisfied by the finite sets. These wave functions have been applied with success by Victor, Dalgarno, and Taylor<sup>18</sup> to the calculation of the dipole properties of the metastable states of helium.

The evaluation of Eqs. (1) and (5) reduces to the calculation of the dipole moment and spin-orbit operator matrix elements between basis functions of the form (8). The necessary integrals were evaluated analytically in closed form. Some of the details of the calculation of spin-orbit matrix elements between singlet and triplet  $P$  states are given in the Appendix. The results converged to the number of figures quoted in the following section when between 30 and 50 terms were retained in the wave functions.

#### IV. RESULTS

##### $2^1S-1^1S$ Two-Photon Decay

Figure 1 illustrates the shape of the photon distribution for the singlet decay of neutral helium (He I) as a function of frequency, and Fig. 2 illustrates the shape as a function of wavelength. Figures 3 and 4 illustrate the results for Ne IX. On the wavelength scale, the profile no longer appears symmetric and extends to infinite wavelength.

Table I summarizes the integrated singlet decay rates for all the ions from He I through Ne IX. The decay rate increases uniformly along the sequence from  $51.3 \text{ sec}^{-1}$  to  $1.00 \times 10^7 \text{ sec}^{-1}$  and is asymptotically equal to  $16.4(Z-1)^6 \text{ sec}^{-1}$ , which is twice

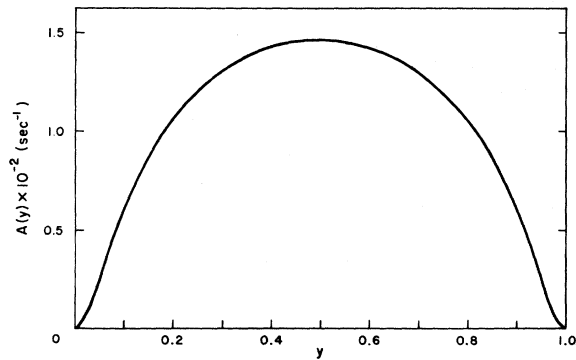


FIG. 1. Photon energy distribution for the  $2^1S-1^1S$  two-photon decay of He I;  $y$  is the fraction of the energy transported by one of the two photons and  $A=51.3 \text{ sec}^{-1}$ .

the two-photon decay rate of the hydrogen  $2^2S$  state with nuclear charge  $(Z-1)$ . The parameter

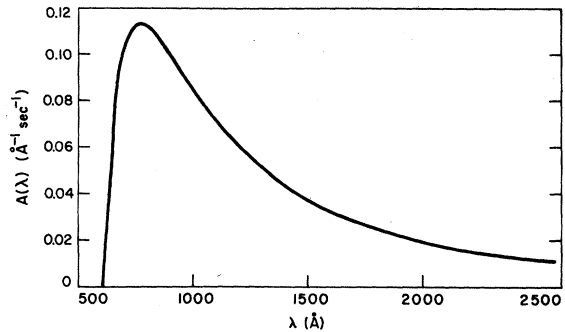


FIG. 2. Photon energy distribution for the  $2^2S-1^1S$  two-photon decay of He I as a function of wavelength.

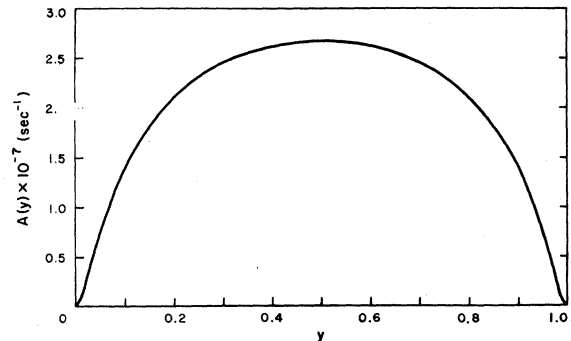


FIG. 3. Photon energy distribution for the  $2^1S-1^1S$  two-photon decay of Ne IX;  $y$  is the fraction of the energy transported by one of the two photons and  $A=1.00 \times 10^7 \text{ sec}^{-1}$ .

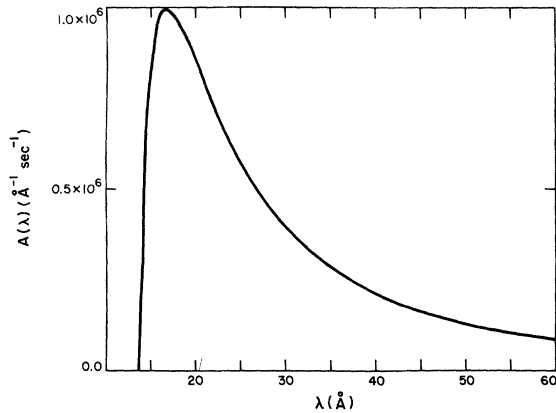


FIG. 4. Photon energy distribution for the  $2^1S-1^1S$  two-photon decay of Ne IX as a function of wavelength.

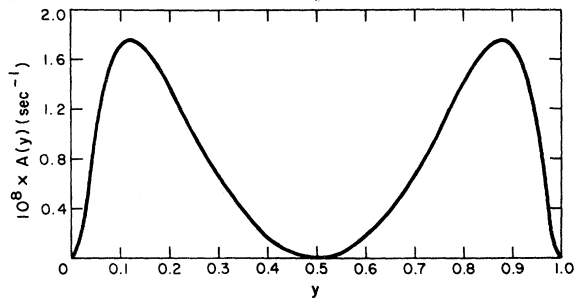


FIG. 5. Photon energy distribution for the  $2^3S-1^1S$  two-photon decay of He I;  $y$  is the fraction of the energy transported by one of the two photons and  $A = 4.02 \times 10^{-9} \text{ sec}^{-1}$ .

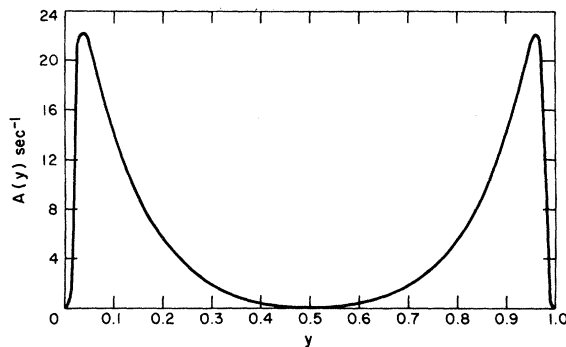


FIG. 6. Photon energy distribution for the  $2^3S-1^1S$  two-photon decay of Ne IX;  $y$  is the fraction of the energy transported by one of the two photons and  $A = 3.20 \text{ sec}^{-1}$ .

$\lambda_{\text{max}}$  in Table I is the position of the profile peak on a wavelength scale. The shape of each profile is given in Table II as a function of  $y$ , the fraction of the  $2^1S-1^1S$  energy difference transported by one of the two photons.

Dalgarno's<sup>8</sup> semiempirical value of  $45 \text{ sec}^{-1}$  and Victor's<sup>10</sup> coupled Hartree-Fock result of  $50 \text{ sec}^{-1}$  for He I compare well with our more accu-

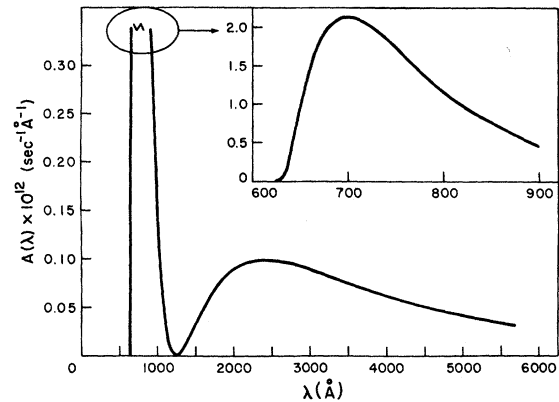


FIG. 7. Photon energy distribution for the  $2^3S-1^1S$  two-photon decay of He I as a function of wavelength.

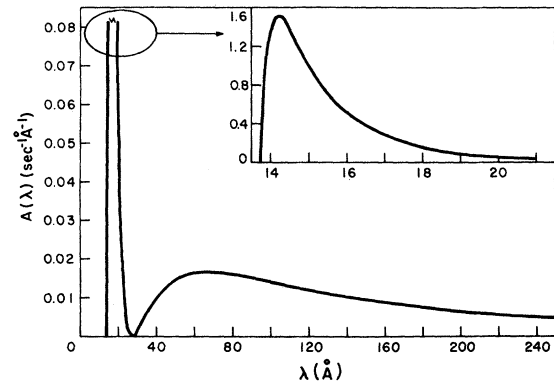


FIG. 8. Photon energy distribution for the  $2^3S-1^1S$  two-photon decay of Ne IX as a function of wavelength.

rate  $51.3 \text{ sec}^{-1}$ . The uncoupled Hartree-Fock procedure<sup>9</sup> overestimates the rate by about 60%.

#### $2^3S-1^1S$ Two-Photon Decay

Figure 5 illustrates the frequency distribution of the photons emitted by neutral helium in the  $2^3S$  state, and Fig. 6 is the corresponding graph for Ne IX. The two peaks become increasingly sharp and move away from the center of the distribution for the higher members of the sequence. Figures 7 and 8 show the same two distributions as a function of wavelength. On the wavelength scale, one peak appears much sharper and more intense than the other, although the areas under the two peaks remain equal.

The triplet decay rates are very much slower than for the singlet states, due partly to the small spin-orbit mixing parameters and partly to cancellation in the frequency factor inside the summations in (5). Since the cancellation is most severe for the diagonal ( $n'=n''$ ) terms, the off-diagonal contributions are of comparable magnitude and it is necessary to compute an extensive array of the  $\epsilon_{n'n''}$  rather than only the diagonal

elements as suggested by Mathis.<sup>15</sup> The leading terms in the  $Z$  expansions of both the diagonal and the off-diagonal contributions to the two-photon decay are  $O(Z^{10})$ .

Table III lists the integrated triplet two-photon decay probabilities. The rates are increasing as  $Z^{10}$ , but for high-nuclear charges ( $\sim 25$ ), where the singlet-triplet mixing becomes complete, the rates will increase as  $Z^6$  as in the  $2^1S$  case. The value for helium is consistent with the limit given by Drake and Dalgarno<sup>11</sup> but not with that given by Bely.<sup>12</sup> The shape of the profile for each ion is given in Table IV as a function of  $y$ .

A brief discussion has been presented elsewhere<sup>19</sup> of the contribution of the two-photon decay of helium-like ions to the emission spectrum of the

solar corona.

TABLE I.  $2^1S$  two-photon decay probabilities.

System	$A$ (sec <sup>-1</sup> )	$\lambda_{\max}$ (Å)
He I	$5.13 \times 10^1$	771
Li II	$1.95 \times 10^3$	258
Be III	$1.81 \times 10^4$	128
B IV	$9.26 \times 10^4$	76.4
C V	$3.31 \times 10^5$	50.9
N VI	$9.43 \times 10^5$	36.1
O VII	$2.31 \times 10^6$	27.1
F VIII	$5.05 \times 10^6$	21.0
Ne IX	$1.00 \times 10^7$	16.7

#### APPENDIX

We describe the calculation of matrix elements of the Pauli approximation to the Breit interaction between  $^1P$  states and  $^3P$  states composed of basis functions  $B_{2S+1}(M_L, M_S)$  of the forms

$$B_1(M_L, 0) = \frac{1}{2} [F_1 Y_0^0(\Omega_1) Y_1^{M_L}(\Omega_2) + F_1^\dagger Y_1^{M_L}(\Omega_1) Y_0^0(\Omega_2)] [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (\text{A. 1})$$

for singlet states, and

$$B_3(M_L, M_S) = 2^{-\frac{1}{2}} [F_3 Y_0^0(\Omega_1) Y_1^{M_L}(\Omega_2) - F_3^\dagger Y_1^{M_L}(\Omega_1) Y_0^0(\Omega_2)] \times \begin{cases} \alpha(1)\alpha(2), & M_S = 1 \\ \beta(1)\beta(2), & M_S = -1 \\ 2^{-1/2} [\alpha(1)\beta(2) + \beta(1)\alpha(2)], & M_S = 0 \end{cases} \quad (\text{A. 2})$$

TABLE II.  $2^1S-1^1S$  two-photon decay energy distribution. In the first column,  $y$  is the fraction of the total energy transported by one of the two photons. The other columns give rates in sec<sup>-1</sup>. The numbers in parentheses are the powers of 10 by which the entries are to be multiplied.

$y$	He I	Li II	Be III	B IV	C V	N VI	O VII	F VIII	Ne IX
0	0	0	0	0	0	0	0	0	0
0.025	7.77(0)	3.79(2)	4.17(3)	2.37(4)	9.27(4)	2.84(5)	7.33(5)	1.67(6)	3.45(6)
0.050	2.52(1)	1.11(3)	1.13(4)	6.11(4)	2.28(5)	6.77(5)	1.70(6)	3.73(6)	7.67(6)
0.075	4.35(1)	1.81(3)	1.74(4)	9.42(4)	3.47(5)	1.01(6)	2.51(6)	5.54(6)	1.11(7)
0.100	5.99(1)	2.42(3)	2.35(4)	1.22(5)	4.44(5)	1.29(6)	3.18(6)	6.97(6)	1.40(7)
0.125	7.42(1)	2.94(3)	2.81(4)	1.45(5)	5.24(5)	1.51(6)	3.72(6)	8.14(6)	1.63(7)
0.150	8.64(1)	3.38(3)	3.20(4)	1.64(5)	5.91(5)	1.70(6)	4.17(6)	9.11(6)	1.82(7)
0.175	9.69(1)	3.74(3)	3.52(4)	1.80(5)	6.46(5)	1.85(6)	4.54(6)	9.91(6)	1.98(7)
0.200	1.06(2)	4.06(3)	3.80(4)	1.93(5)	6.92(5)	1.98(6)	4.85(6)	1.06(7)	2.11(7)
0.225	1.13(2)	4.32(3)	4.03(4)	2.04(5)	7.31(5)	2.09(6)	5.12(6)	1.11(7)	2.22(7)
0.250	1.20(2)	4.54(3)	4.22(4)	2.14(5)	7.64(5)	2.18(6)	5.34(6)	1.16(7)	2.31(7)
0.275	1.25(2)	4.73(3)	4.38(4)	2.22(5)	7.92(5)	2.26(6)	5.52(6)	1.20(7)	2.39(7)
0.300	1.30(2)	4.88(3)	4.52(4)	2.28(5)	8.15(5)	2.33(6)	5.68(6)	1.24(7)	2.46(7)
0.325	1.34(2)	5.02(3)	4.64(4)	2.34(5)	8.35(5)	2.38(6)	5.81(6)	1.26(7)	2.51(7)
0.350	1.37(2)	5.13(3)	4.73(4)	2.38(5)	8.51(5)	2.43(6)	5.92(6)	1.28(7)	2.56(7)
0.375	1.40(2)	5.22(3)	4.81(4)	2.42(5)	8.64(5)	2.46(6)	6.01(6)	1.30(7)	2.59(7)
0.400	1.42(2)	5.29(3)	4.87(4)	2.45(5)	8.74(5)	2.49(6)	6.08(6)	1.32(7)	2.62(7)
0.425	1.43(2)	5.35(3)	4.92(4)	2.47(5)	8.82(5)	2.51(6)	6.13(6)	1.33(7)	2.64(7)
0.450	1.45(2)	5.38(3)	4.95(4)	2.48(5)	8.87(5)	2.53(6)	6.16(6)	1.34(7)	2.66(7)
0.475	1.45(2)	5.41(3)	4.97(4)	2.49(5)	8.91(5)	2.53(6)	6.18(6)	1.34(7)	2.67(7)
0.500	1.45(2)	5.42(3)	4.97(4)	2.50(5)	8.92(5)	2.54(6)	6.19(6)	1.35(7)	2.67(7)



is the spin-orbit interaction, and

$$H_{\text{soo}} = \frac{1}{2}\alpha^2(\vec{s}_1 \cdot \vec{r}_{21} \times \vec{p}_1 - \vec{s}_2 \cdot \vec{r}_{21} \times \vec{p}_2)/r_{12}^3 - \alpha^2[(\vec{s}_1 + \vec{s}_2) \cdot \vec{r}_{21} \times (\vec{p}_2 - \vec{p}_1)]/r_{12}^3 \quad (\text{A. 8})$$

is the spin-other-orbit interaction,  $\alpha$  is the fine-structure constant ( $\sim \frac{1}{137}$ ), and  $\vec{l}_1 = \vec{r}_1 \times \vec{p}_1$ . The second term of  $H_{\text{soo}}$  makes no contribution to matrix elements between singlet and triplet states because it is symmetric in the spin coordinates.

It is convenient to integrate explicitly over the coordinate  $r_{12}$  by replacing the usual two-electron volume element

$$d\vec{r}_1 d\vec{r}_2 = r_1^2 \sin\theta_1 r_2^2 \sin\theta_2 dr_1 d\theta_1 d\phi_1 dr_2 d\theta_2 d\phi_2, \quad (\text{A. 9})$$

$$\text{by } d\vec{r}_1 d\vec{r}_2 = r_1 dr_1 r_2 dr_2 r_{12} dr_{12} \sin\theta_1 d\theta_1 d\phi_1 d\chi, \quad (\text{A. 10})$$

where  $\chi$  is the angle of rotation about  $\vec{r}_1$  (see Ref. 20, p. 382). A matrix element of  $H_{\text{so}}$  between basis functions labeled by  $B_{2S+1}(M_L, M_S)$  then reduces to

$$\begin{aligned} \langle B_3(0,1) | H_{\text{so}} | B_1(1,0) \rangle &= \frac{1}{2}\alpha^2 Z \left\{ -\frac{1}{4}(F_3 | \cos\theta_{12} / r_1^3 | F_1^\dagger) + \frac{1}{4}(F_3^\dagger | 1/r_1^3 | F_1^\dagger) \right. \\ &\quad \left. - \frac{1}{8}c_1 [(F_3 | (1 - \cos^2\theta_{12}) / r_1^3 | F_1^{\dagger'}) + (F_3^\dagger | (-\cos^2\theta_{12}) / r_1^3 | F_1^{\dagger'})] \right\}, \quad (\text{A. 11}) \end{aligned}$$

$$\text{where } \cos\theta_{12} = (r_1^2 + r_2^2 - r_{12}^2) / 2r_1 r_2, \quad (\text{A. 12})$$

$$F_1^{\dagger'} = r_1^{a+1} r_2^{b+1} r_{12}^{c-2} \exp(-\alpha r_1 - \beta r_2), \quad (\text{A. 13})$$

and the heavy round brackets in (A. 11) and in the following equations denote the integral

$$\int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12} dr_{12} \dots \quad (\text{A. 14})$$

It follows from the Hermitian property of  $\vec{l}_1 = \vec{r}_1 \times \vec{p}_1$  that

$$\begin{aligned} &(r_1^{a+1} r_2^{b+1} r_{12}^{c-2} [P_{L+1}(\cos\theta_{12}) - P_{L-1}(\cos\theta_{12})] \exp(-\alpha r_1 - \beta r_2)) \\ &= \begin{cases} +[(2L+1)/c] (r_1^a r_2^b r_{12}^c P_L(\cos\theta_{12}) \exp(-\alpha r_1 - \beta r_2)), & \text{if } c \neq 0, \\ + (2L+1) (r_1^a r_2^b \ln r_{12} P_L(\cos\theta_{12}) \exp(-\alpha r_1 - \beta r_2)), & \text{if } c = 0, \end{cases} \quad (\text{A. 15}) \end{aligned}$$

wherever the integrals exist. By the use of identity (A.15) with  $L=1$ , Eq. (A. 11) assumes the simpler form

$$\begin{aligned} \langle B_3(0,1) | H_{\text{so}} | B_1(1,0) \rangle &= \frac{1}{8}\alpha^2 Z [(F_3^\dagger | 1/r_1^3 | F_1^\dagger) + (c_1/c)(F_3^\dagger | \cos\theta_{12}/r_1^3 | F_1^\dagger) \\ &\quad - (c_3/c)(F_3 | \cos\theta_{12}/r_1^3 | F_1^\dagger)], \quad (\text{A. 16}) \end{aligned}$$

where  $c = c_1 + c_3$ . Similarly, for the spin-other-orbit interaction, we obtain

$$\begin{aligned} \langle B_3(0,1) | H_{\text{soo}} | B_1(1,0) \rangle &= -\frac{\alpha^2}{4} \left\{ \frac{1}{4} \left( F_3 \left| \frac{2\cos\theta_{12} - r_2(\cos^2\theta_{12} + 1)/r_1}{r_{12}^3} \right| F_1^\dagger \right) \right. \\ &\quad \left. - \frac{1}{2} \left( F_3^\dagger \left| \frac{1 - r_2\cos\theta_{12}/r_1}{r_{12}^3} \right| F_1^\dagger \right) - \frac{1}{4} \left( F_3 \left| \frac{1 - \cos^2\theta_{12}}{r_{12}^3} \right| F_1^{\dagger''} \right) - \frac{1}{4} \left( F_3^\dagger \left| \frac{1 - \cos^2\theta_{12}}{r_{12}^3} \right| F_1^{\dagger''} \right) \right\}, \quad (\text{A. 17}) \end{aligned}$$

where

$$F_1^{\dagger''} = \alpha r_1^{a-1} r_2^{b+1} r_{12}^c \exp(-\alpha r_1 - \beta r_2) - \alpha r_1^a r_2^{b+1} r_{12}^c \exp(-\alpha r_1 - \beta r_2). \quad (\text{A. 18})$$



Again using the Hermitian property of  $\vec{r}_{21} \times \vec{p}_1$ , we can show that

$$\begin{aligned} & (r_1^a r_2^b r_{12}^c \exp(-\alpha r_1 - \beta r_2) [2 \cos \theta_{12} - r_2 (\cos^2 \theta_{12} + 1)/r_1]) \\ & = \alpha (r_1^{a-1} r_2^{b+1} r_{12}^c \exp(-\alpha r_1 - \beta r_2) (1 - \cos^2 \theta_{12})) - \alpha (r_1^a r_2^{b+1} r_{12}^c \exp(-\alpha r_1 - \beta r_2) (1 - \cos^2 \theta_{12})) . \end{aligned} \quad (\text{A. 19})$$

By the use of identities (A. 19) and (A. 15), Eq. (A. 17) assumes the simpler form

$$\begin{aligned} \langle B_3(0, 1) | H_{\text{SOO}} | B_1(1, 0) \rangle &= \frac{\alpha^2}{8} \left\{ \left( F_3^\dagger \left| \frac{1 - r_2 \cos \theta_{12} / r_1}{r_{12}^3} \right| F_1^\dagger \right) \right. \\ & \left. + \frac{1}{c-1} \left[ \left( F_3 \left| \frac{\cos \theta_{12}}{r_1 r_{12}} \left( \frac{a_3}{r_1} - \alpha_3 \right) \right| F_1^\dagger \right) \left( F_3^\dagger \left| \frac{\cos \theta_{12}}{r_1 r_{12}} \left( \frac{a_1}{r_1} - \alpha_1 \right) \right| F_1 \right) \right] \right\} , \end{aligned} \quad (\text{A. 20})$$

where  $c = c_1 + c_3$  and

$$\begin{aligned} & (c-1)^{-1} (r_1^a r_2^b r_{12}^{c-1} \cos \theta_{12} \exp(-\alpha r_1 - \beta r_2)) \\ & = (r_1^a r_2^b \ln r_{12} \cos \theta_{12} \exp(-\alpha r_1 - \beta r_2)) , \quad \text{for } c = 1 . \end{aligned} \quad (\text{A. 21})$$

In calculating the radial integrals involving  $\cos \theta_{12}$ , it is useful to note that

$$(r_1^a r_2^b r_{12}^c P_l(\cos \theta_{12}) \exp(-\alpha r_1 - \beta r_2)) \equiv 0 , \quad \text{for } c = 0, 2, 4, \dots, 2(l-1) . \quad (\text{A. 22})$$

All the necessary integrals were calculated analytically in closed form. No further approximations or truncations were made.

Since the operator  $H_3 = H_{\text{SO}} + H_{\text{SOO}}$  is diagonal in the  $J^2, M_J$  coupling scheme and the matrix elements are independent of  $M_J$  it is convenient to make the transformation

$$\langle B_3(1, M_J) | H_3 | B_1(1, M_J) \rangle = - (2/\sqrt{2}) \langle B_3(0, 1) | H_3 | B_1(1, 0) \rangle , \quad M_J = 1, 0, -1 , \quad (\text{A. 23})$$

where the matrix element on the right is to be calculated from (A. 16) and (A. 20).

\*National Academy of Science Postdoctoral Fellow.

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