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Singlet-Triplet Mixing in the Helium Sequence*

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Accurate variational calculations are presented for the off-diagonal matrix elements of the Breit interaction between the 2^1P and 2^3P states of several members of the helium isoelectronic sequence. A comparison is made with recent Z-expansion calculations, which are accurate through terms of order α^2Z^3. The comparison shows that the Z-expansion method for off-diagonal mixing is potentially useful in the theory of many-electron atoms. The effect of singlet-triplet mixing on the 2^3P excitation cross sections is briefly discussed.

I. INTRODUCTION

Recent variational calculations by Schwartz[11] and by Schiff *et al.*[2] have established the usefulness of the Pauli approximation to the Breit interaction[3] for the calculation of relativistic corrections to the eigenvalues of the ^1P and ^3P states of He and Li^+, and for the relativistic ^3P splittings. Off-diagonal matrix elements of the Breit interaction, which were not included in the above calculations, play an important role in the radiative decay of $^3P_1$ states. For example, the intercombination 2^3P_1-1^1S transition becomes more probable than the allowed 2^3P_1-2^3S transition for all the helium-like ions beyond C v.[4] The N vi and O vii 2^3P_1-1^1S oscillator strengths have recently been measured[5] and are compared with accurate calculations in Ref. 4. We present here off-diagonal matrix elements of the Breit interaction between 2^1P_1 and 2^3P_1 states for several members of the helium sequence.

2. THEORY AND CALCULATIONS

The terms in the Pauli approximation to the Breit interaction which contribute to singlet-triplet transitions may be written (in atomic units)

$$B=\tfrac{1}{2}\alpha^2Z(\vec{l}_1\cdot\vec{s}_1/r_1^3+\vec{l}_2\cdot\vec{s}_2/r_2^3)$$
$$+\tfrac{1}{2}\alpha^2[\vec{s}_1\cdot(\vec{r}_2-\vec{r}_1)\times\vec{p}_1-\vec{s}_2\cdot(\vec{r}_2-\vec{r}_1)\times\vec{p}_2]/r_{12}^3\ , \quad (1)$$

where α is the fine structure constant, Z is the nuclear charge, and $\vec{l}=\vec{r}\times\vec{p}$. The first term is the spin-orbit interaction and the second the spin-other-orbit interaction (excluding terms symmetric in s_1 and s_2). Equation (1) is correct through terms of order α^2Z and α^2, and can be used consistently only within the framework of first-order perturbation theory.

Matrix elements of B were evaluated between the 2^3P_1 and 2^1P_1 states of the helium-like ions He I to Ne IX represented by correlated variational wave functions in Hylleraas co-ordinates as described by Drake, Victor, and Dalgarno.[6]

3. RESULTS AND DISCUSSION

The variationally calculated first-order perturbation coefficients

$$\langle 2^3P_1|B|2^1P_1\rangle/[E_0(2^3P)-E_0(2^1P)]\ ,$$

where the E_0 are the exact nonrelativistic eigenvalues, are presented in the first column of Table I. 50-term wave functions were used for He and Li^+ and 30-term wave functions for the remaining ions. The figures quoted have converged up to a possible small underestimate in the final figure.

Matrix elements of B have also been calculated within the relativistic Z-expansion theory of Layzer and Bahcall[7] by Thomis Doyle.[8] Her matrix elements are

$$\langle 2^3P_1|H_0+B|2^3P_1\rangle=E_0(2^3P)-\frac{59}{3\times2^7}\alpha^2Z^4$$
$$-\frac{235}{3\times2^{10}}\alpha^4Z^6+0.145\,266\alpha^2Z^3\ , \quad (2)$$

TABLE I. Comparison of 2^1P_1-2^3P_1 mixing parameter ratios b/a.

Z	Variational	Z expansion
2	2.785×10^{-4}	2.70×10^{-4}
3	7.689×10^{-4}	8.64×10^{-4}
4	1.702×10^{-3}	1.88×10^{-3}
5	3.212×10^{-3}	3.49×10^{-3}
6	5.435×10^{-3}	5.83×10^{-3}
7	8.508×10^{-3}	9.03×10^{-3}
8	1.257×10^{-2}	1.32×10^{-2}
9	1.776×10^{-2}	1.86×10^{-2}
10	2.421×10^{-2}	2.51×10^{-2}
15		8.01×10^{-2}
20		1.74×10^{-1}
25		2.91×10^{-1}
30		4.03×10^{-1}
∞		$1/\sqrt{2}$

$$\langle 2^1P_1|H_0+B|2^1P_1\rangle = E_0(2^1P) - \frac{55}{3\times 2^7}\alpha^2Z^4 - \frac{215}{3\times 2^{10}}\alpha^4Z^6 + 0.040\,566\alpha^2Z^3 \quad (3)$$

$$\langle 2^3P_1|H_0+B|2^1P_1\rangle = \frac{\sqrt{2}}{3\times 2^5}\alpha^2Z^4 + \frac{5\sqrt{2}}{3\times 2^8}\alpha^4Z^6 - 0.023\,605\alpha^2Z^3 \quad , \quad (4)$$

where the terms in α^2Z^4 and α^4Z^6 arise from the expansion of the Sommerfeld formula for relativistic one-electron energies, and the term in α^2Z^3 is the leading two-electron relativistic contribution arising in part from the Breit interaction and in part from the relativistic expansion of matrix elements of $1/r_{12}$.

Writing the eigenfunctions which diagonalize H_0+B in the $n=2$ subspace in the form

$$|1\rangle = a|2^3P_1\rangle - b|2^1P_1\rangle \quad , \quad (5)$$

$$|2\rangle = b|2^3P_1\rangle + a|2^1P_1\rangle \quad , \quad (6)$$

and using the matrix elements (2), (3), and (4), we obtain the ratios b/a listed in the second column of Table I. The agreement between the results of columns 1 and 2 is satisfactory and improves with increasing Z.[9] The Z-expansion wave functions have the advantage of tending correctly to j-j coupled one-electron Dirac spinors in the limit of large Z.[7] Z-expansion mixing parameters for $Z=15$ to 30 are included to indicate the degree of saturation in the singlet-triplet mixing and the departure from the low-Z behavior. The good agreement with the variational calculations for $Z \leq 10$ indicates the potential utility of applying the relativistic Z-expansion theory to transitions in many-electron atoms.

It may be possible to investigate the singlet-triplet mixing ratios directly by comparing the cross sections for electron-impact excitation of the 2^1P_1 and 2^3P_1 states. Since the exchange cross section decreases much more rapidly with electron-impact energy than the direct cross section,[10] virtual transitions through the 2^1P_1 state should dominate the 2^3P_1 excitation cross section at sufficiently high energies. The effect of spin-orbit mixing is unimportant for neutral helium at impact energies below about 20 keV, but should affect the triplet cross sections of helium-like ions at much lower energies.

Excitation of the 2^3P_1 state by *proton* impact can proceed only through singlet-triplet mixing since there is no exchange process. Scaling by a factor of $(b/a)^2$ the Born calculations of Bell, Kennedy, and Kingston[11] for the proton excitation of the helium 2^1P_1 state, we obtain a maximum cross section for 2^3P_1 excitation of 1.8×10^{-24} cm^2 at a proton-impact energy of 45 keV.

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[9]However the numbers will ultimately disagree with increasing Z since the diagonalization in column 1 is only through first order. The error thus introduced is less than 0.5% for $Z \leq 10$. For larger Z, the Pauli approximation itself begins to break down.

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