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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 $\alpha^2 Z^3$. 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.

1. INTRODUCTION

Recent variational calculations by Schwartz¹¹ and by Schiff *et al.*² have established the usefulness of the Pauli approximation to the Breit interaction³ 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 measured⁵ 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)

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

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 $\alpha^2 Z$ 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 Bahcall⁷ by Thomis Doyle.⁸ Her matrix elements are

$$\langle 2^3P_1 | H_0 + B | 2^3P_1 \rangle = E_0(2^3P) - \frac{59}{3 \times 2^7} \alpha^2 Z^4 - \frac{235}{3 \times 2^{10}} \alpha^4 Z^6 + 0.145266 \alpha^2 Z^3, \quad (2)$$

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}
∞		$1/\sqrt{2}$

$$\langle 2^1P_1 | H_0 + B | 2^1P_1 \rangle = E_0(2^1P) - \frac{55}{3 \times 2^7} \alpha^2 Z^4 - \frac{215}{3 \times 2^{10}} \alpha^4 Z^6 + 0.040566 \alpha^2 Z^3, \quad (3)$$

$$\langle 2^3P_1 | H_0 + B | 2^1P_1 \rangle = \frac{\sqrt{2}}{3 \times 2^5} \alpha^2 Z^4 + \frac{5\sqrt{2}}{3 \times 2^8} \alpha^4 Z^6 - 0.023605 \alpha^2 Z^3, \quad (4)$$

where the terms in $\alpha^2 Z^4$ and $\alpha^4 Z^6$ arise from the expansion of the Sommerfeld formula for relativistic one-electron energies, and the term in $\alpha^2 Z^3$ 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

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

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

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 Kingston¹¹ 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} cm² at a proton-impact energy of 45 keV.

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