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Gordon W. F. Drake
University of Windsor

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Singlet-Triplet Mixing in the Helium Sequence*

G. W. F. Drake†

Smithsonian Institution Astrophysical Observatory, Cambridge, Massachusetts 02138

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Accurate variational calculations are presented for the off-diagonal matrix elements of the Breit interaction between the \( 2^3P \) and \( 2^3P \) states of several members of the helium iso-electronic sequence. A comparison is made with recent \( Z \)-expansion calculations, which are accurate through terms of order \( \alpha^2Z^7 \). 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 and by Schiff et al. have established the usefulness of the Pauli approximation to the Breit interaction for the calculation of relativistic corrections to the eigenvalues of the \( 1^P \) and \( 3^P \) states of \( \text{He} \) and \( \text{Li}^+ \), and for the relativistic \( 3^P \) 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 \( 3^P \) states. For example, the intercombination \( 2^3P_-1^1S \) transition becomes more probable than the allowed \( 2^3P_-2^3S \) transition for all the helium-like ions beyond \( \text{C} \) (see Table I). The \( \text{N} \) \( \text{v} \) and \( \text{O} \) \( \text{vii} \) \( 2^3P_-1^1S \) oscillator strengths have recently been measured and are compared with accurate calculations in Ref. 4. We present here off-diagonal matrix elements of the Breit interaction between \( 2^1P \) and \( 2^3P \) 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)

\[
B = \frac{1}{2} \alpha^2 Z (\mathbf{l}_1 \cdot \mathbf{s}_1/r_1^3 + \mathbf{l}_2 \cdot \mathbf{s}_2/r_2^3) + \frac{1}{2} \alpha^2 (\mathbf{F}_1 \cdot (\mathbf{F}_2 - \mathbf{F}_1) \times \mathbf{S}_1 - \mathbf{F}_2 \cdot (\mathbf{F}_2 - \mathbf{F}_1) \times \mathbf{S}_2)/r_{12}^3 ,
\]

(1)

where \( \alpha \) is the fine structure constant, \( Z \) is the nuclear charge, and \( \mathbf{F} = \mathbf{r} \times \mathbf{S} \). 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 \( \alpha^2Z \) and \( \alpha^4 \), and can be used consistently only within the framework of first-order perturbation theory.

Matrix elements of \( B \) were evaluated between the \( 2^3P \) and \( 2^1P \) states of the helium-like ions \( \text{He} \) to \( \text{Ne} \) represented by correlated variational wave functions in Hylleraas co-ordinates as described by Drake, Victor, and Dalgarno.

3. RESULTS AND DISCUSSION

The variationally calculated first-order perturbation coefficients

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

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 \( \text{He} \) and \( \text{Li}^+ \) 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 by Thomis Doyle. Her matrix elements are

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

(2)

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\( Z \) & \text{Variational} & \text{Expansion} \\
\hline
2 & \( 2.785 \times 10^{-4} \) & \( 2.70 \times 10^{-4} \) \\
3 & \( 7.689 \times 10^{-4} \) & \( 8.64 \times 10^{-4} \) \\
4 & \( 1.702 \times 10^{-4} \) & \( 1.88 \times 10^{-4} \) \\
5 & \( 3.212 \times 10^{-4} \) & \( 3.49 \times 10^{-4} \) \\
6 & \( 5.435 \times 10^{-4} \) & \( 5.83 \times 10^{-4} \) \\
7 & \( 8.508 \times 10^{-4} \) & \( 9.00 \times 10^{-4} \) \\
8 & \( 1.257 \times 10^{-3} \) & \( 1.32 \times 10^{-3} \) \\
9 & \( 1.776 \times 10^{-3} \) & \( 1.86 \times 10^{-3} \) \\
10 & \( 2.421 \times 10^{-4} \) & \( 2.51 \times 10^{-3} \) \\
15 & \( 8.01 \times 10^{-2} \) & \\
20 & \( 1.74 \times 10^{-1} \) & \\
25 & \( 2.91 \times 10^{-1} \) & \\
30 & \( 4.05 \times 10^{-1} \) & \\
\hline
\end{tabular}
\caption{Comparison of \( 2^3P_1-2^3P_1 \) mixing parameter ratios \( h/a \).}
\end{table}
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\begin{align*}
\langle 2P_{1/2} | H_0 + B | 2P_{3/2} \rangle &= E_0(2P) - \frac{55}{3 \times 2^7} \alpha^2 Z^5 - \frac{215}{3 \times 2^5} \alpha^4 Z^6 + 0.040566 \alpha^2 Z^3, \\
\langle 2P_{1/2} | H_0 + B | 2P_{1/2} \rangle &= \frac{\sqrt{2}}{3 \times 2^7} \alpha^2 Z^4 + \frac{5 \sqrt{2}}{3 \times 2^7} \alpha^4 Z^6 \\
&- 0.023605 \alpha^2 Z^3,
\end{align*}

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

\begin{align*}
|1\rangle &= a|2P_{3/2}\rangle - b|2P_{1/2}\rangle, \\
|2\rangle &= b|2P_{3/2}\rangle + a|2P_{1/2}\rangle,
\end{align*}

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 \( Z \).

The \( Z \)-expansion wave functions have the advantage of tending correctly to \( j-j \) coupled one-electron Dirac spinors in the limit of large \( Z \). \( Z \)-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 \( 2P_1 \) and \( 2P_3 \) states. Since the exchange cross section decreases much more rapidly with electron-impact energy than the direct cross section, \( \gamma \) virtual transitions through the \( 2P_1 \) state should dominate the \( 2P_3 \) 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 \( 2P_1 \) state by \( \text{proton} \) impact can proceed only through singlet-triplet mixing since there is no exchange process. Scaling by a factor of \( (b/a) \), the Born calculations of Bell, Kennedy, and Kingston\(^{11}\) for the proton excitation of the helium \( 2P_1 \) state, we obtain a maximum cross section for \( 2P_3 \) excitation of \( 1.8 \times 10^{-24} \) cm\(^2\) at a proton-impact energy of 45 keV.

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\(^1\)National Academy of Science Visiting Research Associate.


\(^{11}\)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.
