1972

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Eigenvalues of the $2p^3p^3P$ and $2p^3d^13D$
Bound States of the Helium Isoelectronic Sequence

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(Received 9 August 1971)

The $1/Z$ expansion method is used to calculate the eigenvalues of the $2p^3p^3P$ and $2p^3d^13D$ states of the helium isoelectronic sequence. The results are compared to variational calculations for neutral helium. Wavelengths are predicted for a number of transitions originating in doubly excited states of the heliumlike ions up to Fe XXV. The results for neutral helium are compared to recent beam-foil experiments and alternative line identifications are made. The predicted wavelength for the $2p^3d^2D-2p^2^3P$ transition is 3014 Å, in close agreement with the line observed by Berry et al. at 3012 ± 2 Å.

I. INTRODUCTION

The existence of doubly excited states in neutral helium has been known for many years through studies of the helium arc spectrum\textsuperscript{1,2} and the energy-loss spectrum in electron-helium scattering.\textsuperscript{3} States such as the $2p^3p^1L$ sequence give rise to sharp spectral lines since they are prevented from autoionizing by parity and angular-momentum selection rules. Recent studies of these states by the trapped-electron method\textsuperscript{4} and beam-foil spectroscopy\textsuperscript{5,6} emphasize the need for accurate calculations of their positions and radiative lifetimes. In addition, lines involving doubly excited states of the heliumlike ions have been observed in solar flares\textsuperscript{7} and the solar corona.\textsuperscript{8}

The $2p^3^2P$ state has been studied by several authors.\textsuperscript{9-12} The most extensive calculations by Aashamar,\textsuperscript{10} including mass polarization and relativistic effects, predict a $2p^3^2P-1s2p^3^2P$ transition frequency of 312,217 cm$^{-1}$, in slight disagreement with the old experimental value, 312,118 cm$^{-1}$.\textsuperscript{8} The $2p^3p^3P$ states of the helium sequence have been studied by Drake and Dalgarno.\textsuperscript{11}

In this paper, the $1/Z$ expansion perturbation method is applied to the bound $2p^3d^13D$ and $2p^3p^3P$ states of the helium sequence. Wavelengths are predicted for transitions originating from the doubly excited states for the heliumlike ions with $Z < 26$ (Fe XXV). Variational calculations for neutral helium are presented as a check on the accuracy of the perturbation expansion. The results suggest that the line observed by Berry et al. at 306 ± 1 Å is the $2p^3d^1D-1s^3d^1D$ transition ($\lambda = 305.4$ Å).

II. $1/Z$ EXPANSION METHOD

An accurate and efficient method of generating wave functions for the entire helium isoelectronic sequence is provided by the Hylleraas-Scherr-Knight variation-perturbation procedure.\textsuperscript{14} The Schrödinger equation to be solved is

\begin{equation}
(H - E)\psi = 0 ,
\end{equation}

where

\begin{equation}
H = H_0 + Z^{-1}V_{12} ,
\end{equation}

\begin{equation}
H_0 = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - 1/r_1 - 1/r_2 ,
\end{equation}

\begin{equation}
V_{12} = 1/r_{12} .
\end{equation}

The unit of energy is $Z^2$ a.u., and the unit of length is $Z^{-1} a_0$. Introducing the perturbation expansions
TABLE I. Energy expansion coefficients (a.u.).

<table>
<thead>
<tr>
<th>Order</th>
<th>$2p3p , ^3P$ (a.u.)</th>
<th>$2p3d , ^1D$ (a.u.)</th>
<th>$2p3d , ^3D$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.180 555 6</td>
<td>-0.180 555 6</td>
<td>-0.180 555 6</td>
</tr>
<tr>
<td>1</td>
<td>+0.064 412 1</td>
<td>+0.093 299 9</td>
<td>+0.104 511 3</td>
</tr>
<tr>
<td>2</td>
<td>-0.036 770 2</td>
<td>-0.024 570 9</td>
<td>-0.044 901 4</td>
</tr>
<tr>
<td>3</td>
<td>-0.002 399 5</td>
<td>-0.004 018 1</td>
<td>-0.001 352 9</td>
</tr>
<tr>
<td>4</td>
<td>+0.002 943 1</td>
<td>+0.003 799 9</td>
<td>+0.001 377 6</td>
</tr>
<tr>
<td>5</td>
<td>+0.001 057 9</td>
<td>+0.003 149 3</td>
<td>+0.000 411 7</td>
</tr>
<tr>
<td>6</td>
<td>+0.002 323 2</td>
<td>+0.002 516 0</td>
<td>+0.000 593 0</td>
</tr>
<tr>
<td>7</td>
<td>+0.000 461 5</td>
<td>+0.001 963 5</td>
<td>-0.000 697 2</td>
</tr>
<tr>
<td>8</td>
<td>+0.000 379 7</td>
<td>+0.001 398 5</td>
<td>-0.000 486 9</td>
</tr>
<tr>
<td>9</td>
<td>+0.002 078 2</td>
<td>+0.000 866 1</td>
<td>-0.001 290 9</td>
</tr>
</tbody>
</table>

\[ \Psi = \psi_0 + \sum_{n=1}^{\infty} \psi_n Z^{-n}, \]  
\[ E = E_0 + \sum_{n=1}^{\infty} E_n Z^{-n}, \]

and the zero-order term satisfies the hydrogenic equation

\[ (H_0 - E_0) \psi_0 = 0, \]

where \( \psi_n, n > 0, \) satisfy a series of perturbation equations which are often solved by finding the stationary values of the functional

\[ J_n = \langle n | H_0 - E_0 | n \rangle + 2 \langle n | V_{12} - E_1 | n - 1 \rangle - \sum_{k=1}^{n} \sum_{l=0}^{n-k} E_k \langle n - k - l | 2n - l \rangle = 0. \]

The \( \psi_n \) with \( m < n \) are known exactly.

In the formulation of Dalgalzo and Drake, a set of \( M \) orthonormal functions \( \phi_i \) is introduced, each of which is constructed from a linear combination of \( M \) functions of the form

\[ \chi_j = \sum_{l=1}^{M} \sum_{m} \langle l | m | \lambda_{m} \rangle L_{13} \sum_{l} Y_{m}^{(1)} (r_1, \theta_1), \]

where

\[ Y_{m}^{(1)} (r_1, \theta_1) = \sum_{m} \langle l | m | \lambda_{m} \rangle L_{13} \sum_{l} Y_{m}^{(1)} (r_1), \]

and satisfies

\[ \langle \phi_i | H_0 | \psi_n \rangle = \epsilon_i \delta_{ij}. \]

TABLE II. Variational eigenvalues for helium (a.u.).

<table>
<thead>
<tr>
<th></th>
<th>$2p3p , ^3P$</th>
<th>$2p3p , ^3P$</th>
<th>$2p3d , ^1D$</th>
<th>$2p3d , ^3D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta_{\text{opt}} )</td>
<td>0.54</td>
<td>0.54</td>
<td>0.54</td>
<td>0.49</td>
</tr>
<tr>
<td>( E_{\text{var}} )</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
</tr>
</tbody>
</table>

TABLE III. \( 1/Z \) expansion eigenvalues for the helium sequence (a.u.).

<table>
<thead>
<tr>
<th>( Z )</th>
<th>$2p3p , ^3P$</th>
<th>$2p3p , ^3P$</th>
<th>$2p3d , ^1D$</th>
<th>$2p3d , ^3D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
</tr>
<tr>
<td>3</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
</tr>
<tr>
<td>4</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
</tr>
<tr>
<td>5</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
<td>-0.563 785 56</td>
</tr>
</tbody>
</table>

The table indicates the interchange of labels 1 and 2 in (9), with the (+) sign referring to singlet states and the (−) sign to triplet states. The scale factors \( \alpha \) and \( \beta \) are set equal to their hydrogenic values, for example, \( \alpha = 1/2 \) and \( \beta = 1/3 \) for the \( 2p3d \, ^1D \) states. Then one of the \( \phi_i \)'s, say \( \phi_0 \), is the exact hydrogenic \( \psi_{0} \) with \( \epsilon_0 = E_0 \) and the remaining basis functions \( \phi_i (i = 1, 2, \ldots, M) \) form a synthetic representation of the spectrum of \( H_0 \). If we expand \( \psi_n \) in the finite basis set

\[ \psi_n = \sum_{i=1}^{M} \phi_i (\psi_n), \]

and evaluate \( J_n \), demanding that its value be stationary with respect to variations of the \( a_{ix} \)'s, then \( \psi_n \) and \( E_n \) are determined by the recurrence relations

\[ \langle \phi_i | H_0 | \psi_n \rangle = \epsilon_i \delta_{ij}. \]
and

\[ E_n = \langle \Psi_{n+1} | V_{12} | \Psi_0 \rangle - \sum_{p=1}^{n-1} E_p \langle \Psi_{n-p} | \Psi_0 \rangle. \]  

(14)

With a finite basis set, the above equations provide approximations to \( E_n \) and \( E_p \) (but not bounds) up to some finite order. Since the accuracy almost certainly increases with increasing \( Z \), a variational bound calculation for \( Z = 2 \) was performed to establish the accuracy of the nonrelativistic eigenvalues for the entire isoelectronic sequence. The results of the variational and \( 1/Z \) expansion calculations are given in Sec. III.

III. EIGENVALUES AND PREDICTED WAVELENGTHS

Wave functions for the helium isoelectronic sequence were constructed from (13) and (14), using 50-term basis sets. The \( 1/Z \) expansion coefficients for the \( 2p3p1P \), \( 2p3d1D \), and \( 2p3d3P \) eigenvalues are given through 9th order in Table I. The series was arbitrarily truncated at 9th order because the higher-order coefficients are unreliable with this size basis sets. The coefficients for the \( 2p3p1P \) state were listed previously by Drake and Dalgarno. 11

The expansions summed through 9th order for neutral helium are compared with variational calculations in Table II. The variational basis sets contain 20, 30, 40, and 50 terms. In each case, we set \( \alpha = 1 \) and minimized the energy with respect to \( \beta \) for the 50-term basis set. The optimized values of \( \beta \) are also given in Table II. The comparison indicates the number of figures after the decimal that are reliable in the \( 1/Z \) expansion eigenvalues for the remainder of the isoelectronic sequence. The latter eigenvalues, summed through 9th order, are listed in Table III. For large \( Z \), relativistic corrections should also be included.

We give in Table IV the predicted nonrelativistic wavelengths for several transitions, using the variational eigenvalues for neutral helium where available.

IV. DISCUSSION

Berry et al. 4 have tentatively identified their 306 \pm 1 \AA line as the helium \( 2p3p1P-1s3p3P \) transition with a theoretical wavelength of 305.8 \AA. However they did not observe the companion \( 2p3p1P-1s2p3P \) transition at 291.1 \AA, thus casting doubt on the identification. Both transitions involve one-electron jumps and should be of comparable intensity. Our results show that the observed line could equally well be the \( 2p3d1D-1s3d3D \) transition expected to lie at 305.4 \AA. In addition, the \( 2p3d3P-2p3P \) transition wavelength is predicted to be 3014 \AA. In unpublished work, 18 a line has been observed at 3012 \pm 2 \AA in agreement with the predicted wavelength. If our identification is correct, then theirs is the first observation of the \( 2p3d3D \) state. A weak line was also observed

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( 1s2p1P-2p3p1P )</th>
<th>( 1s2p1P-2p3p3P )</th>
<th>( 1s2p1P-2p3P1P )</th>
<th>( 1s2p1P-2p3p3P )</th>
<th>( 1s2p1P-2p3P3P )</th>
<th>( 1s2p1P-2p3p1P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>230.27</td>
<td>251.87</td>
<td>238.11</td>
<td>250.74</td>
<td>258.95</td>
<td>250.74</td>
</tr>
<tr>
<td>3</td>
<td>141.62</td>
<td>164.89</td>
<td>155.3</td>
<td>165.8</td>
<td>173.7</td>
<td>165.8</td>
</tr>
<tr>
<td>4</td>
<td>78.66</td>
<td>96.08</td>
<td>88.79</td>
<td>96.77</td>
<td>104.77</td>
<td>96.77</td>
</tr>
<tr>
<td>5</td>
<td>50.05</td>
<td>58.38</td>
<td>57.38</td>
<td>58.78</td>
<td>66.28</td>
<td>58.78</td>
</tr>
<tr>
<td>6</td>
<td>36.20</td>
<td>45.86</td>
<td>40.10</td>
<td>45.86</td>
<td>53.86</td>
<td>45.86</td>
</tr>
<tr>
<td>7</td>
<td>25.34</td>
<td>32.79</td>
<td>29.60</td>
<td>32.86</td>
<td>40.86</td>
<td>32.86</td>
</tr>
<tr>
<td>8</td>
<td>19.35</td>
<td>26.00</td>
<td>22.74</td>
<td>26.00</td>
<td>34.00</td>
<td>26.00</td>
</tr>
<tr>
<td>9</td>
<td>15.26</td>
<td>21.76</td>
<td>19.63</td>
<td>21.76</td>
<td>29.76</td>
<td>21.76</td>
</tr>
<tr>
<td>11</td>
<td>10.19</td>
<td>15.70</td>
<td>13.12</td>
<td>15.70</td>
<td>23.12</td>
<td>15.70</td>
</tr>
</tbody>
</table>

These wavelengths were calculated using a value of 109737.3 cm\(^{-1}\) for Rydberg's constant.

1s2p and 1s3p states for helium were obtained from Schiff, Lifson, Pekeris, and Rabinowits, Phys. Rev. 140, A1104 (1965); the 2p\(^3\)P state from Ref. 10; the 2p\(^3\)D state from Ref. 11; the 1s3d states from Ref. 15; and the 2s2p states from G. W. F. Drake and A. Dalgarno, Proc. Roy. Soc. (London) A220, 549 (1971).

Wavelength calculated from 1/Z expansion energy for 1s3d states for helium.
at 2365 ± 5 Å, corresponding well to the 2s2p 3P−1s3d 4D transition predicted to be 2364 Å.

Calculations of the oscillator strengths for these transitions are in progress.

ACKNOWLEDGMENTS

We are grateful to Dr. H. G. Berry, Dr. I. Martinson, and their associates for communicating the results of their experiments in advance of publication. We thank Dr. A. Dalgarno for his helpful comments on the manuscript. Research support by the National Research Council of Canada and by the National Science Foundation is gratefully acknowledged.

16H. G. Berry (private communication).

PHYSICAL REVIEW A
VOLUME 5, NUMBER 1
JANUARY 1972

Permutation Symmetry and the N-Electron Problem

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The techniques of tensor algebra customarily applied to exploit spatial symmetry are applied to exploit permutational symmetry of the N-electron problem. In the approximation of no spin-orbit coupling, the results are nontrivial and give a further reduction of what is normally regarded as the reduced matrix element with respect to spatial symmetry alone. The required 3-j coefficients of the permutation group are evaluated in an appendix so that intermediate-group-theoretical indices that have no direct physical significance are eliminated from the formulation. The spin integral for any operator can always be reduced to known integrals of the fundamental Pauli operators. Thus all matrix elements can be reduced to a corresponding spin-free form with known weighting coefficients. An explicit expression is given for the matrix element of an operator suitable for evaluating spin-own-orbit coupling or spin density at the nucleus. A recursion relation for the Clebsch-Gordan coefficients of bipartition representations of S el in terms of its subgroups and the 9-j symbols of SU(2) is developed in the appendix. For one of the representations being the totally symmetric representation, the Clebsch-Gordan coefficient is known and the recursion relation (the group-orthogonality relation in this case) can be considered as giving nontrivial sum rules on the 9-j symbols of SU(2).

I. INTRODUCTION

In most atomic, molecular, and solid-state electron problems one is interested, at least as a zero-order approximation, in the solutions of a Hamiltonian for N interacting indistinguishable Fermions having no direct spin-orbit interaction. Not only do the permutations of the particle spin and orbit coordinates commute with the Hamiltonian, but the direct-product permutations of the spin and orbit coordinates considered separately also commute with the Hamiltonian. It follows from the theory of group representations that the eigensolutions of the model Hamiltonian are characterized by the irreducible representations of the symmetric group on N particles in spin and orbit space separately. If the spin basis is restricted to Nth-rank products of the one-particle two-dimensional basis, then the admissible spin irreducible representations are limited to those connected with the bipartitions of N determined by the total spin value S, viz., \( S, \frac{1}{2} N + S, \frac{1}{2} N - S \). The admissible orbital irreducible