

**Pekeris C L.** Ground state of two-electron atoms. *Phys. Rev.* **112**:1649-58, 1958.  
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In this paper, a new method is developed for solving the Schrödinger wave equation for two-electron atoms and is applied to atoms with nuclear charges  $Z$  ranging from 1 to 10. In addition to the nonrelativistic energy eigenvalues, the mass-polarization and relativistic corrections are also evaluated. From this and the experimental ionization potential, the Lamb shift is deduced. [The  $SC^2$  indicates that this paper has been cited in over 440 publications since 1958.]

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By the use of *perimetric coordinates* (a name I coined), it was possible to represent the solution of the Schrödinger wave equation for two-electron atoms by a series in orthogonal functions of three variables, each ranging independently from 0 to  $\infty$ . The coefficients in this series were found (directly from the wave equation) to obey a 33-term recursion relation. The vanishing of the determinant of these equations yielded the energy eigenvalue and the coefficients. E.B. Wilson wrote, "No integrals were evaluated, all the elements of his secular equation were integers (and most were zeros) and he achieved eight place accuracy. (Incidentally, he also calculated error limits.)"<sup>1</sup> The new method was applied in subsequent papers to evaluate the Lamb shift, term-values of excited S and P states, lower bounds to the energy, fine- and hyperfine-structure, and oscillator strengths (f-values) in He.

Chandrasekhar commented on the paper as follows: "Until 1953<sup>2</sup> all physicists firmly believed that with 8 parameters Hylleraas<sup>3</sup> had achieved an accuracy better than what you now have with 214 parameters."<sup>4</sup> "...There is no basis for supposing that this oft quoted result of Hylleraas is valid."<sup>2</sup>

The paper and those that followed it brought forth enthusiastic letters: "monumental" (Herz-

berg), "will become a 'classic'" (Coulson), "final and definitive" (Chandrasekhar), "ingenious" (Salpeter), "beautiful piece of work" (Goudsmit), "my appreciation and admiration for your number D(0) is at least of order 715" (V. Hughes).

D(0), the electron charge density at the nucleus, enters in the theory of the hyperfine splitting of He<sup>2</sup>, which was measured by V. Hughes and co-workers<sup>5</sup> to an accuracy of two parts in 10<sup>7</sup>, and we determined D(0) by solving a determinant of order 715, to be followed by one of order 1078, which yielded an accuracy for D(0) of five parts in 10<sup>8</sup>.

In the case of the ground state of He, Herzberg achieved an experimental accuracy of 0.15 cm<sup>-1</sup> for the ionization potential,<sup>6</sup> while our accuracy ranged from 0.01 cm<sup>-1</sup> to 0.0001 cm<sup>-1</sup>. Similar agreement was achieved for the 2<sup>1</sup>S, 2<sup>3</sup>S states of He as well as for the 1<sup>1</sup>S and 2<sup>3</sup>S states of Li<sup>+</sup>.

It therefore came as a shock to find, on July 31, 1961, that our theoretical value for the ionization potential of the 2<sup>1</sup>S state of Li<sup>+</sup> came out 118,699.430 cm<sup>-1</sup>, as against Herzberg and Moore's<sup>7</sup> experimental value of 120,008.30 cm<sup>-1</sup>. Herzberg and Moore refined a previous measurement by Series and Willis<sup>8</sup> of the 8517 Å line, achieving an accuracy of 0.10 cm<sup>-1</sup>. The discrepancy of 1300 cm<sup>-1</sup> meant that the 2<sup>1</sup>S-2<sup>1</sup>P transition in Li<sup>+</sup> is not the 8517 Å line, but one at 9584 Å. As I was about to write to Herzberg asking him to send his "source" to Rank at Pennsylvania State University, who agreed to search for the 9584 Å line, a letter arrived from Aage Bohr (August 15, 1961) stating, "In order to assist in your detective work, we are sending you the library copy of Werner's thesis from 1927." In his thesis Werner retracted his identification of the 8517 Å line, which he had published in *Nature* in 1926,<sup>9</sup> and on which Series and Willis based their identification. On June 8, 1962, a preprint of a paper by Edlén and Toresson arrived, reporting an accurate measurement of the 9584 Å line, which they found to be "in perfect agreement with the value calculated by Pekeris."<sup>10</sup>

I am indebted to my former assistant Yigal Accad, to whom every word stored in our homemade computer, WEIZAC, was at any moment as distinct as the fingers on his hand.

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