

### Rydberg states of helium: A new recoil term

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The mass-polarization shift in the energy levels of  $1sNL$  states of helium contains a term of second order in the ratio of the electron mass to that of the nucleus that is independent of  $L$ . Although inherent in an earlier work [Phys. Rev. A **33**, 2780 (1986)], it was not pointed out there since only  $L$ -dependent splittings were of interest. The derivation is very simple and yields a correction of significance for the calculation of absolute ionization energies.

By choosing Jacobi coordinates to describe the excited  $1sNL$  Rydberg states of helium, it is possible to account for nuclear recoil almost by inspection.<sup>1</sup> These coordinates are

$$\begin{aligned} \mathbf{R} &= m' \left[ m \mathbf{r}_M + \frac{K}{2} (\mathbf{r}_1 + \mathbf{r}_2) \right], \\ \mathbf{r} &= m (\mathbf{r}_1 - \mathbf{r}_M), \\ \mathbf{x} &= m' \left[ \mathbf{r}_2 - m \mathbf{r}_M - \frac{K}{2} \mathbf{r}_1 \right], \end{aligned} \tag{1}$$

where  $K = 2/(1+M) = 2.7415 \times 10^{-4}$  for  $\text{He}^4$ ,  $m = 1 - K/2$ ,  $m' = 1/(1+K/2)$ ,  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the coordinates of the two electrons of mass  $m_e = 1$ , and  $\mathbf{r}_M$  is the coordinate of the nucleus of mass  $M$ . The Jacobi coordinates represent the laboratory coordinate of the center of mass, the position of the inner electron relative to the nucleus, and the position of the outer electron relative to the center of mass of the core, respectively. In these coordinates the Hamiltonian in reduced Rydberg units  $R = m \text{ Ry}$  is

$$H = - \left[ \nabla_r^2 + \frac{4}{r} \right] - \mu \left[ \nabla_x^2 + \frac{2}{x} \right] + V(\mathbf{x}, \mathbf{r}), \tag{2}$$

where

$$V(\mathbf{x}, \mathbf{r}) = \mu \left[ \frac{2}{x} + \frac{2}{|\mathbf{x} - m' \mathbf{r}|} - \frac{4}{\left| \mathbf{x} + \frac{K\mu}{2} \mathbf{r} \right|} \right]$$

and

$$\mu = \frac{m'}{m} = \frac{1}{1 - K^2/4}.$$

As usual, the kinetic energy of the center of mass is ignorable and has been omitted. [These expressions are slightly different in appearance from those in Ref. 1 but are equivalent; the main difference comes from rescaling the coordinate ( $x$ ) of the outer electron by a factor of  $1 - K^2/4$ .] In the earlier work<sup>1</sup> I emphasized the fact that in these coordinates no explicit "mass-polarization"

operator appears in the kinetic energy, while the effect of the finite nuclear mass is now in the potential-energy term. From Eq. (2) it is clear that even before any perturbation calculations involving  $V$  are performed the energy can be written in the following form:

$$E_0(1sNL) = - \left[ 4 + \frac{\mu}{N^2} \right] R. \tag{3}$$

This differs from the usual expression without the quantity  $\mu$  by

$$\Delta = (1 - \mu) \frac{R}{N^2} = - \left[ \frac{K^2}{4 - K^2} \right] \frac{R}{N^2}, \tag{4}$$

which evidently sums a power series in  $K^2$ . The correction appears trivial, but this is due to the felicitous choice of coordinates. If the usual coordinates (measuring the positions of both electrons from the nucleus) had been used, it would have been necessary to carry out a perturbation calculation involving the mass-polarization operator to second order just to obtain the  $K^2$  correction.

Physically, this term is transparent. The inner electron is properly understood as moving in a hydrogenic orbit about a nucleus of charge 2 and mass  $M$  and described by a one-body equation with the usual reduced mass  $m$ . For sufficiently high values of  $N$  and  $L$ , however, the outer electron moves in a hydrogenic orbit about a "nucleus" of charge  $+1$  and mass  $M + 1$ ; this requires a slightly larger reduced mass  $m'$  and yields slightly more binding. In this approximation the energies are exactly hydrogenic and independent of  $L$ . For the analysis of fine-structure splittings (as in Ref. 1) this energy shift is irrelevant. It should be remembered, however, that the Jacobi coordinates are inherently unsymmetric under interchange of the two electrons; if exchange effects are large, as they are for low- $L$  states, the use of these coordinates is not advantageous.

Suppose now that one were to perform a variational calculation of the energy of a Rydberg state of helium, using the usual coordinates. If the mass-polarization operator were used as a perturbation (as is often done for the ground state<sup>2</sup>) only the correction linear in  $K$

could be obtained. In order to include higher powers of  $K$  it would be necessary to retain the mass-polarization operator as part of the Hamiltonian during the variational procedure.<sup>3</sup>

Recently, just such a variational calculation using the conventional coordinates and including the mass-polarization operator has determined the binding energies of several excited states of helium with unprecedented accuracy.<sup>4</sup> The wave function used was properly symmetrized and gave a  $K$ -dependent energy contribution for both singlet and triplet  $3D$  states. For comparison with the unsymmetric technique described here one should examine the mean of the energies of the two spin states. The mean value of the  $K$ -dependent shift is

$$\bar{\Delta}(3D) = -1.1203 \times 10^{-4}K - 0.1120K^2/4 \text{ Ry} . \quad (5)$$

The large size of the coefficient of the quadratic term seemed surprising,<sup>4</sup> but the predicted second-order shift from Eq. (4) alone is

$$\bar{\Delta}_2(3D) = -\frac{1}{9} \frac{K^2}{4} \text{ Ry} = -0.1111 \frac{K^2}{4} \text{ Ry} . \quad (6)$$

This result differs from the variational one by less than 1% and explains the magnitude. Note that this correction equals  $61.8/N^2$  MHz, and for the  $N=3$  states amounts to 6.9 MHz, a quite significant shift.

By taking into account the perturbation due to  $V$  [Eq. (2)] we can improve the above result. For  $x > r$  the following expansion results:

$$V(\mathbf{x}, \mathbf{r}) = \sum_{l=1}^{\infty} C_l \frac{2r^l}{x^{l+1}} P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}) , \quad (7)$$

where

$$C_l = \mu \left[ (m')^l - 2 \left[ -\frac{K\mu}{2} \right]^l \right] .$$

This differs from the usual multipole expansion to the extent that  $C_l$  differs from unity. For the leading dipole ( $l=1$ ) term

$$C_1 = \frac{1 + \frac{K}{2}}{\left[ 1 - \frac{K^2}{4} \right]^2} \approx 1 + \frac{K}{2} + \frac{K^2}{2} . \quad (8)$$

There is thus an additional term in the energy due to the dipole polarizability of the core ( $\alpha_1 = \frac{9}{32}$ ); since this is of second order in  $V$  (and  $C_1$ ) it has the form<sup>5</sup>

$$\begin{aligned} \Delta_{\text{pol}} &= -\alpha_1 (K + \frac{5}{4}K^2) \left\langle \frac{1}{x^4} \right\rangle \\ &= -\frac{\alpha_1 [3N^2 - L(L+1)] (K + \frac{5}{4}K^2)}{2N^5 (L - \frac{1}{2}) L (L + \frac{1}{2}) (L+1) (L + \frac{3}{2})} . \end{aligned} \quad (9)$$

For the  $3D$  states investigated by Drake,<sup>4</sup> the mass-dependent correction, including all the above effects, becomes

$$\begin{aligned} \bar{\Delta}(3D) &= -\frac{K}{6480} - \frac{145}{1296} \left[ \frac{K^2}{4} \right] \\ &= -1.5432 \times 10^{-4}K - 0.11188 \frac{K^2}{4} \text{ Ry} . \end{aligned} \quad (10)$$

The quadratic term now agrees to 0.1% with the variational result of Eq. (5). The linear term is of the right order of magnitude but significantly too large, due probably to the failure of the dipole polarization potential at short distances.<sup>6</sup> I expect the results to improve very rapidly with increasing  $L$ , and for high enough  $L$  the simple,  $L$ -independent quadratic term will dominate. It will be interesting to watch the progress of Drake's program of precision calculations towards high  $L$ .

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<sup>1</sup>R. J. Drachman, Phys. Rev. A **33**, 2780 (1986). A similar method was used for Auger transitions in mesic atoms by Z. Fried and A. D. Martin [Nuovo Cimento **29**, 574 (1963)].

<sup>2</sup>C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

<sup>3</sup>A. K. Bhatia and R. J. Drachman, Phys. Rev. A **35**, 4051 (1987).

<sup>4</sup>G. W. F. Drake, Phys. Rev. Lett. **59**, 1549 (1987).

<sup>5</sup>K. Bockasten, Phys. Rev. A **9**, 1087 (1974).

<sup>6</sup>G. W. F. Drake (private communication) has also calculated the second-order shift in the  $1s2P$  states of helium, obtaining  $\bar{\Delta}_2(2P) = -0.3731K^2/4 \text{ Ry}$ . Using the present method I find  $\bar{\Delta}_2(2P) = -0.3086K^2/4$ , a fairly good result for such a small value of  $L$ .