RELATIVISTIC CORRECTIONS IN A SERIES OF HELIUM EXCITED STATES

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Relativistic corrections to order $(v/c)^2$ are applied to the helium excited states $2\ ^{1,3}P$, $3\ ^{1,3}D$,..., $8\ ^{1,3}K$. Simple correlated open-shell wavefunctions are employed and the Breit operators H_1 through H_5 treated as perturbations. Account is also taken of mass polarization and lowest-order one electron Lamb shift. The energies thus calculated agree with experiment to within $2.2\ \mathrm{cm}^{-1}$ or better.

1. Introduction

The importance of relativistic and radiative corrections in atomic and molecular systems has been emphasized by several authors [1,2]. The usual point of departure has been the Breit equation [3], a generalization of the Dirac equation representing two relativistic particles in an external field. This theory is believed to be correct to terms of order $(v/c)^2$.

In this paper we propose to calculate relativistic corrections for a series of excited states in helium. This work is motivated in part by the high precision to which these energy levels are now known — approaching one part in ten million. The sequence of excited states 1s2p2 $^{1,3}P$, 1s3d3 $^{1,3}D$, 1s4f4 $^{1,3}F$,... is attractive from a theoretical point of view in that these represent the lowest states of their respective symmetry types. Thus the simplest form of the variational principle is applicable. Moreover, the non-relativistic electron correlation problem is expected to be minimal, particularly for the higher states in the sequence.

2. Method and results

2.1. Determination of wavefunction

The use of Breit's equation, together with the Pauli approximation (low Z) means that the relativistic corrections to be calculated can be accurate only to with-

in a few percent. As sufficiently accurate non-relativistic wavefunctions for this purpose, we shall employ correlated open-shell functions of the type

$$u(r_1, r_2) = [1s(1)nl(2) \pm 1s(2)nl(1)](1 + \gamma r_{12}), \quad (1)$$

$$1s \equiv e^{-\alpha r}, \quad nl \equiv r^l e^{-\beta r} Y_{l,m}(\theta, \varphi),$$

in which α, β, and γ are optimized variational parameters. Table 1 lists the optimum non-relativistic energies obtained with (1) with and without the correlation parameter γ. Comparison with the more accurate non-relativistic energies for the 2P and 3D states listed in table 2 indicates that the wavefunction (1) gives energies accurate to within a few tenths of a percent for the 2P states, and better for higher

Table 1
Non-relativistic energies for open-shell wavefunction [eq. (1)] with and without correlation parameter (in hartree)

	$-E(\gamma = 0)$	$-E$(optimum γ)
2 ^{1}P	2.122390092	2.122449327
2 ^{3}P	2.130691334	2.130821427
3 ^{1}D	2.055546095	2.055549141
3 ^{3}D	2.055571814	2.055574820
4 ^{1}F	2.031249981	2.031250256
4 ^{3}F	2 031250030	2.031250308
5 ^{1,3}G	2.020000000	2.020000039
6 ^{1,3}H	2.013888890	2.013888900
7 ^{1,3}I	2.010204081	2.010204083
8 ^{1,3}K	2.007812500	2.007812500

Table 2
Expectation values for helium (in hartree)

	$-H_0$	$-(H_1 + H_4)$	H_2	ϵ_2
2 ¹P	2.1238429 a)	0.000104931	−0.00000964	0.000004953
2 ³P	2.1331641 a)	0.000097505	0.000001943	−0.000007937
3 ¹D	2.055614 b)	0.000104021	0.000000037	−0.000000025
3 ³D	2.055630 b)	0.000104008	0.000000048	−0.000000025
4 ¹,³F	2.031250$_{03}$	0.000104987	0.000000013	−0.000000004
5 ¹,³G	2.020000$_4$	0.000105497	0.000000005	−0.000000001
6 ¹,³H	2.0138889[	0.000105791	0.000000002	0.000000000
7 ¹,³I	2.01020498	0.000105974	0.000000001	0.000000000
8 ¹,³K	2.00781250	0.000106149	0.000000000	0.000000000
	H_3	H_5		H_3	H_5
2 ¹P	0	0.000000773	3 ³D$_2$	0.000000034	−0.000000066
2 ³P$_2$	−0.000001276	0.000000229	3 ³D$_1$	0.000000135	0.000000066
2 ³P$_1$	0.000000638	−0.000001145	4 ³F$_4$	−0.000000020	0.000000003
2 ³P$_0$	0.000001914	0.000002290	4 ³F$_3$	0.000000005	−0.000000010
3 ¹D	0	0.000000002	4 ³F$_2$	0.000000025	0.000000008
3 ³D$_3$	−0.000000101	0.000000019			

a) Non-relativistic 2P energies, ref. [4].   b) Non-relativistic 3D energies, ref. [5].

states. One must be careful not to conclude that (1) will determine relativistic corrections to the same accuracy as the non-relativistic energy, because the relativistic operators may be, and generally are more sensitive to correlation effects than the non-relativistic hamiltonian. In effect, then, results obtained using (1) will have variable precision with respect to better wavefunctions, but should maintain the requisite accuracy of a few percent.

A detailed comparison of our 2P and 3D non-relativistic energies with the more elaborate calculations [4,5] listed in table 2 indicates that the correlation parameter γ picks up only about 5% of the correlation energy. This being the case, the 4F energy in table 1 can be trusted to no more than 6 digits, the 5G energy to 7 digits, etc.

2.2. Relativistic calculations

Table 2 lists the results obtained with (1). The operators involved, in the Pauli approximation, are [3], in atomic units, and with $p = -i\nabla$: non-relativistic hamiltonian:

$$H_0 = \tfrac{1}{2}p_1^2 + \tfrac{1}{2}p_2^2 - Z/r_1 - Z/r_2 + 1/r_{12};$$ (2)

"variation of mass with velocity":

$$H_1 = -(1/8c^2)(p_1^4 + p_2^4);$$ (3)

Breit retardation term:

$$H_2 = -(r_{12}^{-1}/2c^2)[p_1 \cdot p_2 + r_{12}^{-2}(r_{12}r_{12} : p_1 p_2)];$$ (4)

spin—orbit coupling:

$$H_3 = (1/2c^2)\{[E_1 \times p_1 + 2r_{12}^{-3}(r_{12} \times p_2)] \cdot s_1$$

$$+ [E_2 \times p_2 + 2r_{12}^{-3}(r_{21} \times p_1)] \cdot s_2\},$$ (5)

where $E_i = Zr_i/r_i^3 - r_{12}/r_{12}^3$;

Darwin term (Zitterbewegung):

$$H_4 = (i/4c^2)(p_1 \cdot E_1 + p_2 \cdot E_2);$$ (6)

spin—spin interaction:

$$H_5 = (1/c^2)\{-\tfrac{8}{3}\pi s_1 \cdot s_2 \delta^3(r_{12})$$

$$+ r_{12}^{-3} s_1 \cdot s_2 - 3r_{12}^{-2}(s_1 \cdot r_{12})(s_2 \cdot r_{12})]\ r_{12} > 0\}.$$ (7)

In addition, table 3 includes the lowest order Lamb shift for the s electron, given by [3]:

$$(4Z^4/3\pi c^3)[2 \log(c/Z) - \log(2K_0/Z^2) + \tfrac{19}{30}]$$

$$= 0.00001610 \text{ hartree},$$ (8)

with K_0 taken as $19.77\, Z^2/2$ hartree. Table 2 also includes the mass polarization and electron exchange correction, given by [3]:

$$\epsilon_2 = -(m/M)\mathbf{V}_1 \cdot \mathbf{V}_2 , \tag{9}$$

which is a correction for nuclear motion in addition to the correction incorporated in the ^{4}He Rydberg constant, taken here as [6] 219444.551 cm^{-1} hartree^{-1}. The speed of light was taken as [6] 137.035973 au. Table 2 reports the expectation value of $H_1 + H_4$ because the sum is more easily calculated than the individual values.

For states in this sequence with $l \geqslant 6$ the energy is adequately approximated by $H_0 + H_1 + H_4 +$ Lamb shift. With $n = l + 1$ the principal quantum number of the excited electron, the asymptotic forms for these expectation values are:

$$H_0 = -Z^2/2 - (Z-1)^2/2n^2 ,$$

$$H_1 + H_4 = -(1/8c^2)\{Z^4 + [(Z-1)^4/n^2]$$

$$\times [1/n^2 - 4 + 4/n(n - \tfrac{1}{2})]\} , \tag{10}$$

with the Lamb shift given by (8).

3. Discussion

Computed energies are compared with experiment in table 3. In all cases, agreement to within 2.2 cm^{-1}, approximately 5 parts per million, is attained. A clear trend toward decreasing error with increasing l is indicated. How much of this trend is due to inaccuracy in the wavefunction, and how much is due to higher order corrections to the Breit operators, further radiative corrections, etc., remains unanswered here. Perkeris [8] calculated the energy of the ground state of helium using a much more elaborate wavefunction, and obtained agreement with experiment to within 0.2 cm^{-1}. He ignored H_2, which is small, and employed a two-particle Lamb shift contribution [9], as opposed to our equation (8), which gives the one-particle s-electron contribution. For the ground state, the difference between these two estimates is 1.2 cm^{-1}, so that generally speak-

Table 3
Total energies for helium excited states (in cm^{-1})

	$E_{\text{calc.}}$	$E_{\text{exp.}}$[a]	Error
$2\,^1$P	466084.20	466084 65	0.45
$2\,^3$P$_2$	468130.65	468132.79	2.14
$2\,^3$P$_1$	468130.53	468132.71	2.18
$2\,^3$P$_0$	468129.49	468131.72	2.22
$3\,^1$D	451112.5$_8$	451114.58	2.0
$3\,^3$D$_3$	451116.1$_1$	451118.01	1.9
$3\,^3$D$_2$	451116.0$_9$	451118.01	1.9
$3\,^3$D$_1$	451116.0$_4$	451117.96	1.9
$4\,^1$F	445766.$_{31}$	445767.67	1.3
$4\,^3$F$_4$[b]	445766.$_{32}$	445767.66	1.3
$5\,^{1,3}$G	443297.7$_0$	443297.92	0.2$_2$
$6\,^{1,3}$H	441956.63	441956.76	0.13
$7\,^{1,3}$I	441148.06	441148.13	0.07
$8\,^{1,3}$K	440623.26		

a) Ref. [7]; experimental error ± 0.05 cm^{-1}.
b) j not specified for experimental value.

ing it would be necessary to improve our estimate of the Lamb shift before calculations with a more accurate wavefunction could be considered relevant.

The reported errors for the 4F and 5G states are somewhat difficult to interpret, because as much as half of these values can be ascribed to the errors in the non-relativistic energy. Nevertheless, taking this into account does not appreciably alter the trend toward decreasing error. We may conclude that the $(v/c)^2$ approximation works very well when the average interelectron distance is large. This is easy to rationalize, because field strengths, and therefore velocities, are largest when the particles are close together; thus higher order relativistic corrections for two widely separated electrons should be small.

References

[1] A. Froman, Rev. Mod. Phys. 32 (1960) 317.
[2] R.E. Moss, Advanced molecular quantum mechanics (Chapman and Hall, London, 1973).
[3] H. Bethe and E.E. Salpeter, Quantum mechanics of one- and two-electron atoms (Springer, Berlin, 1957).
[4] C.L. Pekeris et al., Phys. Rev. 126 (1962) 1057.
[5] R.T. Brown, J. Chem. Phys. 48 (1968) 4698.
[6] Codata Bulletin 11; Recommended Consistent Values of the Fundamental Physical Constants (1973).
[7] W.C. Martin, J. Phys. Chem. Ref. Data 2 (1973) 262.
[8] C.L. Pekeris, Phys. Rev. 115 (1959) 1216.
[9] P.K. Kabir and E.E. Salpeter, Phys. Rev. 108 (1957) 1256.