

Numerical calculation of the level shift of the autoionizing states of atoms

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A modification in the procedure for calculating level shifts of atoms described by Sharma and Bowtell [Can. J. Phys. 51, 1637 (1973)] is proposed which, while retaining the extreme simplicity of the procedure, improves its accuracy substantially. Attention is drawn to certain curious and puzzling features associated with the procedure which require further investigation.

Sharma and Bowtell,^{1,2} whose notation we use throughout, have described a novel method of evaluating the quantum-mechanical sum

$$\Delta\epsilon = \mathcal{P} \sum_{m \geq 2} \frac{|\langle \Psi_0(1smp \ ^{1,3}P) | 1/r_{12} | \Psi_0(2s2p \ ^{1,3}P) \rangle|^2}{E_0(2s2p) - E_0(1smp)}, \tag{1}$$

which with a suitable choice of the Feshbach projection operator³⁻⁵ is the level shift for the autoionizing 2s2p^{1,3}P state of heliumlike ions. In this method the sum turns out to be an integral involving the solution of a differential equation and the Cauchy principal value is taken by "orthogonalizing" the solution to the solution of the corresponding homogeneous equation. For brevity we can write the basic differential equations [(22) and (23) of Ref. 1] as

$$(L_1 - \frac{1}{4})\psi_i = F_i(r), \quad i = 1, 2. \tag{2}$$

The notation ψ (without subscript) is used for the solution of the corresponding homogeneous equation and ϕ_i ($i = 1, 2$) for the solutions that are orthogonalized to ψ .

Define

$$A = \langle \phi_1 | F_1 \rangle, \tag{3}$$

$$B = \langle \phi_1 | F_2 \rangle = \langle \phi_2 | F_1 \rangle, \tag{4}$$

$$C = \langle \phi_2 | F_2 \rangle. \tag{5}$$

Then $\Delta\epsilon$ is simply given by

$$\Delta\epsilon = A + C \pm B \tag{6}$$

in natural atomic units, the positive sign being taken for the triplet and the negative sign for the singlet.

In 1976, Horak and Lewis⁶ evaluated the sum (1) directly by two different methods: one purely numerical and the other partly analytic and partly numerical. Since the summand in (1) is itself an integral and the generalized sum \sum is an infinite sum over discrete values and an integration over the continuum, a direct evaluation of (1) is a formidable task which is both lengthy and tedious, requiring an enormous amount of work (a thousand times or

more) compared to that required in the method of Sharma and Bowtell.¹ Horak and Lewis⁶ found that the values of A , B , and C calculated by their two different methods agreed to at least four significant figures. If their calculations were correct then there were errors of (2-5)% in the values calculated by Sharma and Bowtell.¹ Though errors of this magnitude are negligible because of the uncertainty in the position of the actual autoionizing level in the energy spectrum (see Refs. 7 and 8 for further discussion), it would be nice to know the source of error particularly because the procedure developed by Sharma and Bowtell⁹ for evaluation of similar sums occurring in bound-state energies is known to yield extremely accurate values (though bound-state sums do not contain singularities and there is no requirement of orthogonality to a non-square-integrable function).

In this work we have studied the possible sources of error in the procedures of Sharma and Bowtell and are able to propose a modification which, while retaining the simplicity of the original method, makes its accuracy comparable to that of Horak and Lewis. We found that the source of error in the calculations of Sharma and Bowtell originates chiefly from their failure to go to large enough values of r in evaluating ψ_i/ψ ($i = 1, 2$). We investigated the behavior of ψ_i/ψ at the maxima of ψ . Define

$$\alpha_m = \psi_i/\psi \tag{7}$$

at the m th maxima of ψ . We found that the convergence of α_m to a constant value was extremely slow and α_m as a function of r could be approximated by

$$\alpha_{1n}(r) = 0.9861385 + 0.0637104/r - 0.1740261/r^2, \tag{8}$$

$$\alpha_{2n}(r) = 0.9611513 + 0.0374655/r - 0.1023376/r^2. \tag{9}$$

Taking the r -independent terms in (8) and (9) as $\lim(\psi_i/\psi)$, we calculated A , B , and C . The values are set out in Table I together with those of Sharma and Bowtell¹ and Lewis and Horak.⁶

TABLE I. Comparison of numerical values.

	Sharma and Bowtell ^a	Horak and Lewis ^b (part analytic)	Horak and Lewis ^b (purely numerical)	This work
$10^4 A$	4.6898	4.489 115	4.489 117	4.489 15
$-10^4 B$	5.1441	5.262 417	5.262 267	5.262 25
$10^4 C$	2.0276	1.958 683	1.958 105	1.958 07

^aReference 1.^bReference 6.

The satisfying agreement with both sets of values of Horak and Lewis⁶ makes the modified procedure in which $\lim(\psi_i/\psi)$ is calculated by fitting α_{in} to a formula of the form $a + b/r + c/r^2$, accurate without adding much to the labor involved in the execution of the computing program.

During our investigation we observed that the factors of $1/r$ in (8) and (9) were in the ratio of 1.700 51:1, which is a very good approximation of the ratio $\langle\psi|F_1\rangle:\langle\psi|F_2\rangle$ [the value obtained by Sharma and Bowtell¹ (unpublished) was 1.700 463:1]. This explains why Sharma and Bowtell¹ had such good agreement for their values of $\langle\phi_1|F_2\rangle$ and $\langle\phi_2|F_1\rangle$ even though they had not achieved orthogonalization of ϕ_i to ψ to a sufficient degree of accuracy. Sharma and Bowtell¹ had stated that "chances that the procedure described above [by them] will accidentally lead to such a ratio are practically nil": Our observation shows that if $\lim(\psi_i/\psi)$ are evaluated by the procedure of Sharma and Bowtell,¹ then the ratio of unwanted ψ remaining in their ϕ_i 's is to a fairly high degree of accuracy what they thought had zero proba-

bility. F_1 and F_2 are not independent; they come from the Coulomb and exchange parts of the contributions of the same family of virtual transitions:

$$2s2p^{1,3}P \rightarrow ls\gamma p^{1,3}P,$$

with γ being an index that takes both discrete and continuum values. At this stage we do not think that it is a mere coincidence that the ratio of the $(1/r)$ -independent terms in (8) and (9) is the same as $\langle\psi|F_1\rangle:\langle\psi|F_2\rangle$, though we are unable to offer an explanation. The true explanation of this curious and puzzling fact might lie in a theoretical justification of the expansions (8) and (9). This also suggests that expansions (8) and (9) are more than convenient formulae to fit a number of data approaching a constant value at large r . The explanation of all these mysterious facts remains an open question.

It is interesting to observe that the method described here can be used to calculate the level shift of any autoionizing state of any atom or atomic ion.

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