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LETTER TO THE EDITOR

The high-n form of the radiation-damped S-matrix

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Abstract. There now exist two different formalisms for the high-n form of the radiation-damped S-matrix. These two formalisms give nearly identical results for all physical systems and either may be used in calculations. However, there is some uncertainty as to which is the more exact form. It is shown that Bell and Seaton made four approximations that prevented them from deriving the correct form due to Hickman. A corrected derivation is given in this letter. It is shown that the poles of a two-channel S-matrix have an unphysical high-n form when using the formalism of Bell and Seaton, but behave nicely using the formalism of Hickman. Also, two statements about Robicheaux *et al* (1995) in a recent paper by Pradhan and Zhang are corrected.

For over a decade, there have been questions raised about the correct form for the close-coupling equations when one electron is in a Rydberg state outside of a core that can decay radiatively. The first formalism was introduced by Hickman (1984) using very plausible heuristic arguments; this formalism consists of replacing the real core energy, E_c, in the close-coupling equations with a complex energy, $E_c - \mathrm{i}R/2$, where R is the radiative decay rate of the core. The second formalism was introduced by Bell and Seaton (1985) based on the general radiation damping formalism of Davies and Seaton (1969); this formalism consists of replacing the real principal quantum number, ν, in the multichannel quantum defect theory (MQDT) with a complex principal quantum number, $\nu + \mathrm{i}R\nu^3/2z^2$, where z is the residual charge of the ion. Seaton (1984) gave an intuitive derivation of the Bell and Seaton result because in Bell and Seaton this simple result was obtained after a *tour de force* derivation involving ~ 200 equations. Although Hickman's formalism was much more physically plausible, the Bell and Seaton formalism was preferred in calculations because it had been derived from first principles (only LaGattuta and Hahn (1985) attempted model calculations using Hickman's formalism); it appeared that Hickman's formalism was a good approximation of that by Bell and Seaton. A recent paper by Pradhan and Zhang (1997) is an example illustrating the controversy in that the work of Hickman is not even mentioned.

This issue was reopened by Robicheaux *et al* (1995). Using a very powerful and flexible formalism for describing general radiation damping, we were able to derive the form for the close-coupling equations using five equations (section VIB). Strikingly, the final form consisted of replacing the real core energy, E_c, in the close-coupling equations with a complex energy $E_c - \mathrm{i}R/2$ (i.e. identical to the formalism of Hickman). As both formalisms have now been derived from first principles, a natural question is which is the more exact formalism and which is the approximation? Is Bell and Seaton's formalism a good approximation to Hickman's more exact formalism (or vice versa)?

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There are four arguments for supposing that Hickman's formalism is more exact and that Bell and Seaton's formalism is approximate: (i) Hickman's formalism is more physically appealing and can be trivially generalized to cases where the asymptotic potential is not $1/r$; (ii) the derivation of Hickman's formalism is much simpler and therefore there is less opportunity for inadvertent approximations; (iii) the poles of the S-matrix have a more intuitively correct form using Hickman's formalism. (Arguments (i) and (iii) depend on personal taste and argument, (ii) rests on the assumption that Robicheaux *et al* are less likely to make mistakes than Bell and Seaton; thus these arguments are not very compelling by themselves.) (iv) It is possible to identify four approximations in Bell and Seaton's derivation; removing these four approximations, but otherwise following Bell and Seaton's derivation, results in a final formula that is identical to that of Hickman. Together, these four arguments make it overwhelmingly likely that Bell and Seaton's formalism is a good *approximation* of Hickman's more exact formalism.

In the derivation that follows, I will use the notation of Bell and Seaton unless stated otherwise. Equations taken from this paper will be denoted with a BS. Bell and Seaton used the general radiation damping formalism of Davies and Seaton which was shown to be formally equivalent to that used by Robicheaux *et al* (see section VC). Thus the differences between Hickman and Bell and Seaton must arise in an approximate implementation. The final form of Bell and Seaton rests on a derivation given in their section 6 for a two-channel case; this derivation will be examined in detail.

Assume that channel α is open and channel γ is closed and that the core state for channel γ decays to that for channel α with a rate R. Let

$$\chi = \begin{pmatrix} \chi_{\alpha\alpha} & \chi_{\alpha\gamma} \\ \chi_{\gamma\alpha} & \chi_{\gamma\gamma} \end{pmatrix} \qquad \text{(6.5 BS)}$$

be the unphysical S-matrix obtained by allowing both channels to be open. The complex quantum defect is defined in equation (6.12 BS) to be $\chi_{\gamma\gamma} = \exp[2\pi \mathrm{i}\mu_\gamma]$; μ_γ has real and imaginary parts $\mu_\gamma = p + \mathrm{i}q$ (equation (6.13 BS)) where p and q are real and $q > 0$. Without radiation damping, the physical S-matrix has poles at $\nu_n = n - \mu_\gamma$ (equation (6.14 BS)) or energies $E_n = -z^2/2\nu_n^2$ (equation (6.15 BS)) relative to the γ threshold. The important parameter for describing radiation damping in this two-channel case is

$$T = \sum_n (P_\gamma(\nu)|P_\gamma(\nu_n))\left(E - E_n + \tfrac{1}{2}\mathrm{i}R\right)^{-1} t(\nu_n)/t(\nu) \qquad \text{(6.50 BS)}$$

where $P_\gamma(\nu)$ is the radial wavefunction in channel γ (equation (A.2.3 BS)), $(P_\gamma(\nu)|P_\gamma(\nu_n)$ is a radial overlap integral (equation (A.2.1 BS)) and $t(\nu)$ is a complex normalization factor (equation (6.9 BS)). There are no approximations in these equations.

Bell and Seaton use four approximations to evaluate the expression for T. These approximations are not necessary for obtaining a final result.

Approximation (i). Bell and Seaton use an approximate expression for the radial overlap:

$$(P_\gamma(\nu)|P_\gamma(\nu_n)) \simeq \frac{\sin \pi(\nu - \nu_n)}{\nu - \nu_n} \qquad \text{(A.2.12 BS)}$$

instead of the exact expression

$$(P_\gamma(\nu)|P_\gamma(\nu_n)) = \frac{z^2}{E_\nu - E_n}(\nu\nu_n)^{-3/2}\frac{\sin \pi(\nu - \nu_n)}{\pi} \qquad (1)$$

obtained from equations (A.2.8 BS)–(A.2.11 BS) and where $E_\nu = -z^2/2\nu^2$ (equation (A.2.5 BS)). $(P_\gamma(\nu)$ is replaced by its complex conjugate if ν is complex (equation (A.2.12

BS)).) The approximate expression (A.2.12 BS) arises by using the large-n approximation $E_\nu - E_{\nu'} \simeq -z^2(\nu' - \nu)/\nu^3$.

Approximation (ii). Bell and Seaton use the approximation for the ratio of t's:

$$t(\nu_n)/t(\nu) \simeq \exp[\mathrm{i}\pi(\nu - \nu_n)] \tag{6.53 BS}$$

instead of the exact expression

$$t(\nu_n)/t(\nu) = (\nu/\nu_n)^{3/2} \exp[\mathrm{i}\pi(\nu - \nu_n)]. \tag{6.51 BS}$$

The approximate expression (6.53 BS) arises by using the large-n approximation $\nu/\nu_n \simeq 1$.

Approximation (iii). Bell and Seaton use an approximate expression for energy differences for real ν:

$$E_\nu - E_n \simeq (z^2/\nu^3)(\nu - \nu_n) \tag{6.54 BS}$$

instead of the exact expression

$$E_\nu - E_n = z^2/2\nu_n^2 - z^2/2\nu^2. \tag{2}$$

The approximate expression (6.54 BS) arises from the large-n approximation $\delta E/\delta\nu \simeq z^2/\nu^3$.

Approximation (iv). Bell and Seaton use an approximate expression for complex energy differences:

$$E_\nu - E_n + \tfrac{1}{2}\mathrm{i}R \simeq (z^2/\nu^3)[\nu - \nu_n + \mathrm{i}\Delta(\nu)] \tag{6.55 BS}$$

instead of the exact expression

$$E_\nu - E_n + \tfrac{1}{2}\mathrm{i}R = z^2/2\nu_n^2 - z^2/2(\nu + \mathrm{i}\Delta)^2. \tag{3}$$

The approximate expression (6.55 BS) again arises from the large-n approximation $\delta E/\delta\nu \simeq z^2/\nu^3$. In what follows, I will use a parameter not defined by Bell and Seaton:

$$\bar{\nu} = \nu + \mathrm{i}\Delta \tag{4}$$

or equivalently

$$E_\nu - E_n + \tfrac{1}{2}\mathrm{i}R = z^2/2\nu_n^2 - z^2/2\bar{\nu}^2 \equiv E_{\bar{\nu}} - E_n. \tag{5}$$

Exact derivation. The derivation of Bell and Seaton section 6.5.2 (evaluation of T) can proceed but now using the exact expressions. First substitute in equation (6.50 BS) for the ratio of the t's using the *exact* expression (6.51 BS),

$$T = \sum_n (P_\gamma(\nu)|P_\gamma(\nu_n))(E_{\bar{\nu}} - E_n)^{-1}(\nu/\nu_n)^{3/2} \exp[\mathrm{i}\pi(\nu - \nu_n)] \tag{6}$$

where $E_{\bar{\nu}} = E_\nu + \mathrm{i}R/2$ has been used. Use the *exact* overlap expression (1) to eliminate $(E_{\bar{\nu}} - E_n)^{-1}$:

$$T = -\pi \sum_n (P_\gamma(\nu)|P_\gamma(\nu_n))(P_\gamma^*(\nu_n)|P_\gamma(\bar{\nu}))\sqrt{\bar{\nu}^3\nu^3/z^4}\,\frac{\exp[\mathrm{i}\pi(\nu - \nu_n)]}{\sin\pi(\nu_n - \bar{\nu})}. \tag{7}$$

Because the ratio

$$\frac{\exp[\mathrm{i}\pi(\nu - \nu_n)]}{\sin\pi(\nu_n - \bar{\nu})} = -\frac{\exp[\mathrm{i}\pi(\nu + \mu_\gamma)]}{\sin\pi(\bar{\nu} + \mu_\gamma)} \tag{8}$$

is independent of n, the only terms that depend on n are in the overlaps. Using closure gives

$$T = \pi(P_\gamma(\nu)|P_\gamma(\bar{\nu}))\sqrt{\bar{\nu}^3\nu^3/z^4}\,\frac{\exp[\mathrm{i}\pi(\nu+\mu_\gamma)]}{\sin\pi(\bar{\nu}+\mu_\gamma)}. \tag{9}$$

(Note that closure is not exact because only the bound states are summed over but the continuum is not integrated over; the error is of the same size as in the Bell and Seaton closure derivation. The size of this error is roughly $\delta\mu^2/n$, where $\delta\mu$ is the difference between the quantum defect of the autoionizing state and the final state; $\delta\mu$ will typically be much less than 0.01 for ions thus making this a very good approximation.) Now again use the *exact* expression for the overlap, equation (1), to obtain

$$T = (E_\nu - E_{\bar{\nu}})^{-1}\frac{\sin\pi(\nu-\bar{\nu})}{\sin\pi(\bar{\nu}+\mu_\gamma)}\exp[\mathrm{i}\pi(\nu+\mu_\gamma)]. \tag{10}$$

Using $E_\nu - E_{\bar{\nu}} = -\mathrm{i}R/2$ and multiplying the numerator and denominator by $\exp[\mathrm{i}\pi(\mu_\gamma-\bar{\nu})]$ gives

$$T = \frac{2\mathrm{i}}{R}(\mathrm{e}^{2\mathrm{i}\pi(\nu-\bar{\nu})}-1)\mathrm{e}^{2\mathrm{i}\pi\mu_\gamma}/(\mathrm{e}^{2\mathrm{i}\pi\mu_\gamma}-\mathrm{e}^{-2\mathrm{i}\pi\bar{\nu}}). \tag{11}$$

Now use the definition of $\chi_{\gamma\gamma} = \exp[2\pi\mathrm{i}\mu_\gamma]$, equation (6.12 BS), and define the parameter

$$g(\nu) = \exp[2\mathrm{i}\pi(\nu-\bar{\nu})] \tag{12}$$

to obtain

$$T = \frac{2\mathrm{i}}{R}[g(\nu)-1]\chi_{\gamma\gamma}/[\chi_{\gamma\gamma}-g(\nu)\,\mathrm{e}^{-2\mathrm{i}\pi\nu}]. \tag{6.65 BS}$$

This expression for T is the same as in Bell and Seaton except they used the *approximate* expression

$$g(\nu) \simeq \exp(\pi\nu^3R/z^2). \tag{6.66 BS}$$

This approximate form for g is obtained from the exact expression, equation (12), by expanding $\nu-\bar{\nu}$ to lowest order in R. Equations (6.67)–(6.71) of Bell and Seaton are exact as long as the exact value of $g(\nu)$ is used instead of the approximate expression (6.66 BS). In particular, the physical S-matrix is given by

$$S_{\alpha\alpha} = \chi_{\alpha\alpha} - \chi_{\alpha\gamma}[\chi_{\gamma\gamma}-g(\nu)\,\mathrm{e}^{-2\mathrm{i}\pi\nu}]^{-1}\chi_{\gamma\alpha} \tag{6.71 BS}$$

which is equivalent to

$$S_{\alpha\alpha} = \chi_{\alpha\alpha} - \chi_{\alpha\gamma}[\chi_{\gamma\gamma}-\mathrm{e}^{-2\mathrm{i}\pi\bar{\nu}}]^{-1}\chi_{\gamma\alpha} \tag{13}$$

when using the *exact* form for $g(\nu)$, equation (12). This is equivalent to substituting $E_\mathrm{c}-\mathrm{i}R/2$ for the core energy in the close-coupling expansion. (Note that this form of the S-matrix does give an unphysical discontinuity at threshold proportional to $\exp(-\pi Z\sqrt{2/R})$; for the example below the size of the discontinuity is $\mathrm{e}^{-7025} \sim 10^{-3051}$ which is negligibly small for most applications.)

This derivation shows that if the four high-n approximations are eliminated from the derivation in Bell and Seaton, then *the formalism of Davies and Seaton is equivalent to that of Hickman* for a Rydberg electron attached to a radiating core. The main reason Bell and Seaton's original derivation did not reproduce Hickman's formalism is that at high n the spacing of successive resonances becomes much smaller than the radiative decay rate of the core, R. Thus the small change in energy $E_\nu \to E_\nu + \mathrm{i}R/2$ becomes a substantial change in principal quantum number $\nu \to \bar{\nu}$. Removing approximation (iv) is the key to showing that the formalism of Davies and Seaton is equivalent to that of Hickman. The reason for the difference also shows why the two formalisms give nearly identical results for all physical systems. Most autoionizing resonances have widths much smaller than the Rydberg spacing z^2/ν^3. As n increases Bell and Seaton's formalism differs increasingly from Hickman's. But before this approximation breaks down, the radiative rate becomes much larger than the autoionization rate; for this case, the branching ratio for autoionization is very small so order of magnitude errors are irrelevant in practice (for example, the difference between branching ratios of 10^{-3} and 10^{-5} is physically irrelevant).

Recently, Pradhan and Zhang (1997) made several comments regarding the accuracy of Bell and Seaton's results and several purported assertions in Robicheaux *et al* (1995). Pradhan and Zhang assert that we stated reservations about the precision and utility of Bell and Seaton's formalism. This is incorrect. There are no statements in Robicheaux *et al* that are in any way related to judgements about the utility of Bell and Seaton's formalism. Bell and Seaton's formalism is *a very good approximation* to the more exact formalism by Hickman (in all known cases); however, because it is such a good approximation, agreement with experiment does not indicate that the formalism is exact because no experiments to date can distinguish between Bell and Seaton's approximate formalism and Hickman's more exact treatment.

Pradhan and Zhang also state 'This contradicts the assertions of Robicheaux *et al* (1995), made without reporting any calculations, that the BS theory leads to 'strange poles in the S-matrix'.' This is also incorrect. The direct quote 'strange poles in the S-matrix' which they attribute to Robicheaux *et al* is not in this paper; in fact, the issue of poles in the S-matrix is not addressed at all. Therefore, it is not surprising that we have not reported any calculations supporting these non-existent assertions. While Robicheaux *et al* did not make this assertion, it is nevertheless true that the approximate form of the S-matrix due to Bell and Seaton has a strange sequence of poles when $\nu^3 R/z^2 \gg 1$. The more exact form by Hickman has a physically reasonable sequence of poles.

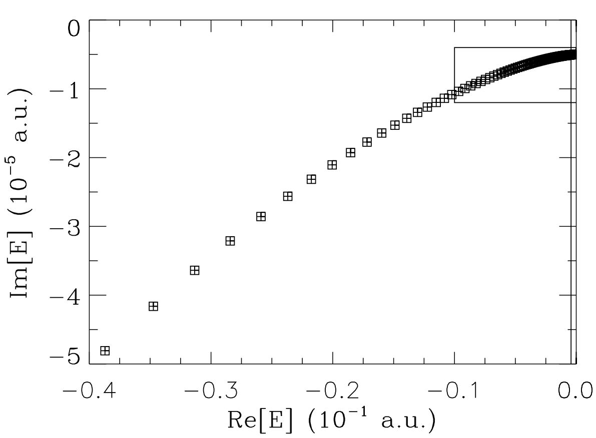

Figure 1. The poles of the S-matrix using the exact form due to Hickman (squares) and the approximate form due to Bell and Seaton (pluses). The energy where the Rydberg spacing equals $R/2$ is marked with a vertical line. The boxed region is expanded in figure 2.

To demonstrate this, examine the position of the poles for the two-channel case above. Using Hickman's formalism, the poles are at $\bar{\nu} = n - \mu_\gamma = n - p - \mathrm{i}q$; this gives poles at

$$E_n^{\mathrm{H}} = -\frac{z^2}{2(n-p-\mathrm{i}q)^2} - \frac{\mathrm{i}R}{2} \simeq -\frac{z^2}{2(n-p)^2} - \frac{\mathrm{i}z^2 q}{(n-p)^3} - \frac{\mathrm{i}R}{2}. \tag{14}$$

This equation makes physical sense since the imaginary part is simply minus the sum of the autoionization and radiative decay rates; these different decay paths are distinguishable. In contrast, using Bell and Seaton's formalism, the poles are at

$$\exp(-2\mathrm{i}\pi\nu + \pi\nu^3 R/z^2) = \exp(2\mathrm{i}\pi\mu_\gamma) \tag{15}$$

where $\nu = z/\sqrt{-2E_n^{\mathrm{BS}}}$. This transcendental equation has no simple solution except for $\nu^3 R/z^2 \ll 1$, where the $E_n^{\mathrm{BS}} \simeq E_n^{\mathrm{H}}$.

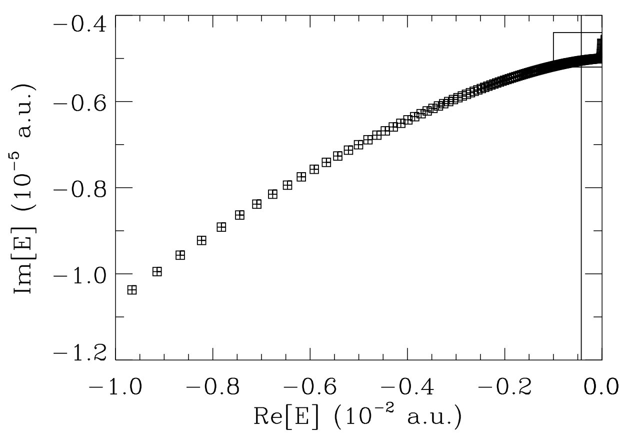

Figure 2. Same as figure 1. The boxed region is expanded in figure 3. Note the change in scale for the real part of the energy.

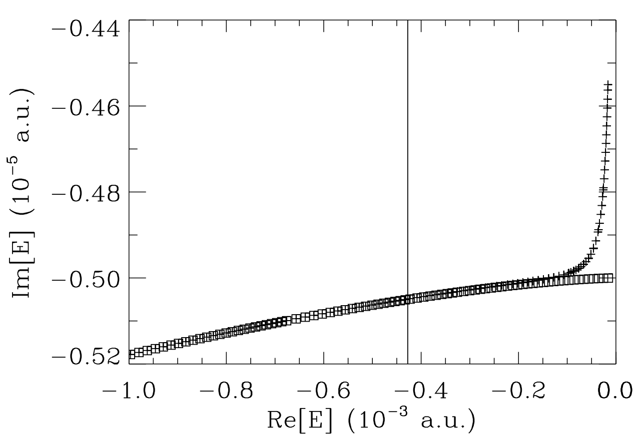

Figure 3. Same as figure 1. Note that the decay rates of the very high-n states using Bell and Seaton's formalism are less than the radiative decay rate of the core. Only a fraction of the states has been plotted for clarity. Note the change in scale for the real part of the energy.

The results of a model calculation are plotted in figures 1–3 for $p = 0.03$, $q = 0.01$, $R = 10^{-5}$ au and $z = 5$. The poles of the S-matrix are plotted in the complex energy plane with squares for the poles from the more exact equation (14) and with pluses using the approximate form from equation (15). The vertical line marks the energy where the Rydberg spacing equals $R/2$. It is clear that over a huge range of n, the results are nearly identical. Note that the branching ratio for autoionization has dropped to $\sim 10^{-3}$ before the two results begin to disagree. But clearly the poles of the S-matrix using Bell and Seaton's approximate form have a strange behaviour at high n. The widths of the resonances are going to 0 and therefore becoming smaller than the radiative decay rate of the core state. This is certainly unphysical behaviour.

In conclusion, we have shown that a more accurate derivation using Davies and Seaton's formalism corrects the final result of Bell and Seaton so that it agrees exactly with Hickman's formalism for a Rydberg electron outside of a core that can decay radiatively. The original derivation of Bell and Seaton *must be considered an approximation to the more exact formalism by Hickman*. However, it must be stressed that Bell and Seaton's formalism accurately reproduces Hickman's formalism until the Rydberg spacing becomes much smaller than the radiative decay rate of the core. Thus, the *approximate* results of Bell and Seaton will probably be accurate enough for all practical calculations because the physically important range for dielectronic recombination is when the Rydberg spacing is larger than the radiative decay rate of the core.

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References

Bell R H and Seaton M J 1985 *J. Phys. B: At. Mol. Phys.* **18** 1589
Davies P C W and Seaton M J 1969 *J. Phys. B: At. Mol. Phys.* **2** 757
Hickman A P 1984 *J. Phys. B: At. Mol. Phys.* **17** L101
LaGattuta K and Hahn Y 1985 *Phys. Rev.* A **31** 1415
Pradhan A K and Zhang H L 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** L571
Robicheaux F, Gorczyca T W, Pindzola M S and Badnell N R 1995 *Phys. Rev.* A **52** 1319
Seaton M J 1984 *J. Phys. B: At. Mol. Phys.* **17** L531