The screened hydrogenic model: Analytic formulae for matrix elements of radiative and collisional rates in complex ions

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A B S T R A C T

There is an ongoing need for numerically efficient algorithms that are capable of calculating the radiative and collisional rates of arbitrarily complex ions that are present in hot plasmas to a level of accuracy that surpasses that available in many existing approximations. Hydrogen-like solutions for determining these rates in more general ions by use of an effective (and generally non-integer) atomic number frequently give poor results and are of limited validity. This paper illustrates that results accurate to of order 20% can be obtained for matrix elements of both rates for arbitrarily complex ions by use of hydrogenic wavefunctions that use different effective atomic numbers for the initial and final sub-shells. Not only does this allow for the realistic modelling of inner shell transitions, it naturally allows for the physical effect of orbital relaxation. It is shown that the integral of the generalised oscillator strength used by the Plane-wave Born approximation has an analytic solution that can be reduced to a form suitable for efficient numerical integration over an arbitrary electron distribution. Extensive use of the computer algebra package Mathematica® has generated a unique formula for each transition and the results have been transformed to efficient fortran 90 code for all transitions between non-relativistic sub-shells with principal quantum numbers $n \leq 10$. In the case of the collisional matrix elements these are typically two to three orders of magnitude faster to calculate than by direct numerical evaluation. The fortran code is available upon request from the author.

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1. Introduction

The need for simple formulae in atomic physics is well established and the literature abounds with many approximations for a wide range of atomic properties. Particularly well known is the principle of using a fictitious effective atomic number (hereafter referred to by its usual notation of Z^*) in order to determine the binding energies of the electrons in complex ions [1–4]. With the binding energies known, related properties such as transition energies and ion probabilities can easily be determined, and providing that appropriate sets of screening constants are used to calculate Z^*, these results can often be accurate to within a few percent even for the more exotic ionic configurations that readily occur in hot plasmas.

Knowing the electron binding energies is however often only a small part of a problem. The greater part may relate to the rates at which radiation is emitted or absorbed between bound electrons, and how strongly free electrons excite transitions between them. For such processes the situation is much less satisfactory, particularly with respect to the collisional excitation rates. There are few generic approximations available that claim to give results much

better than a factor 2 or that are justified beyond a very restricted sub-set of problems that is frequently seen as small by the requirements of the modern atomic physicist. Notable collisional excitation approximations that are in widespread use can be broken in two categories: those that attempt to mimic the energy transfer of the impacting free electron through Gaunt factors [5–7], and those based upon parameterised fits to iso-electronic sequences [8]. The choice of appropriate Gaunt factors for use in the first category is crucial in obtaining reasonable results [9] and much work exists in parameterising Gaunt factors based upon more detailed calculations [10]. Parameterised fits to iso-electronic sequences generally provide more accurate results but these, as well as the Gaunt factor based methods, rapidly become inaccurate as one moves away from the ions upon which the fits are based. This point is becoming ever more important as modelling, particularly of non-LTE plasma kinetics [11], often requires the use of rates for ions involving inner shell transitions with multiple hole states. Additionally it is worth noting that many of these approximations are based upon the assumption of a Maxwellian free electron distribution, which is a further deficiency for non-LTE modelling.

An obvious attempt to improve the situation is to build upon the successful approach of using the hydrogenic approximation with an

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effective atomic number. Such an approach is adequate for ionisation rates [12] but attempts to use this for processes between different bound sub-shells of an ion generally fail because a single Z^* cannot adequately match both the initial and final sub-shell wavefunctions. This is certainly the case if one considers transitions involving an electron from within the core of bound electrons. Here the screening effect of the inner electrons upon the outer electrons implies that the Z^*s of the initial and final sub-shells must be very different. Moreover, the very act of the electron moving between the upper and lower sub-shells results in a re-arrangement of the remaining bound electrons that results in further differences in the Z^*s between the two sub-shells. This is the effect of orbital relaxation which is known to be important if one aims to determine the position of spectral lines to within ∼ 1% [13–15].

Evaluation of the relevant rate involves an integration of the product of the two wavefunctions and thus small changes in one or the other wavefunction can lead to very large changes in the numerical value of the integral − what is needed are approximations that use different effective Z^*s for the initial and final sub-shells. Whilst there is a very large body of work on the hydrogen atom and its integrals (for example see the references given in [16]), there is apparently little work on the more general case involving transitions between states of different Z^*s. A handful of notable works [16–20] give matrix elements for radiative transitions involving different Z^*s but these appear to be largely unknown and one of the aims of this paper is to briefly illustrate the utility of these formulae. The most probable reason for the lack of wider recognition of these works is that the formulae are different for each possible transition between allowed sub-shells and that these formulae rapidly become cumbersome to determine by hand for even small values of the principal quantum numbers. For the case of the collisional rates, there does not appear to be any recognition in the literature that the relevant matrix elements may be similarly determined within the framework of the plane-wave Born (PWB) approximation.

That the necessary formulae are different for each possible transition should no longer be viewed as an impediment to their wider use given the power of current computer systems and the ease with which such results can be obtained with computational algebra programs. This work has made extensive use of the Mathematica® package to ultimately generate Fortran 90 code that contains an efficient representation of the radiative and the PWB collisional rates for all possible transitions between sub-shells with principal quantum numbers $n \leq 10$. (It is interesting to observe that [16] used the computer algebra package MACSYMA in a similar manner 20 years ago for a much smaller set of radiative rates.) The main value of this work is in the production of the collisional rates, however these are more naturally presented after a brief reminder of the underlying principles and a re-iteration of the radiative rates along with an example of their use.

2. General theory

The correctly normalised radial wavefunction for a single electron with principal and angular quantum numbers n and l respectively, bound to a point nucleus of charge Z^*, is given by:

$$P\left(n, l, Z^*, r\right) = \sqrt{\frac{2^{2+2l}Z^*(n-l-1)!}{n^2(n+l)!}}\left(\frac{rZ^*}{n}\right)^{l+1}$$
$$\times \exp\left(-\frac{rZ^*}{n}\right)L_{n-l-1}^{2l+1}\left(\frac{2rZ^*}{n}\right) \tag{1}$$

where $L_s^t(x)$ is the generalised Laguerre polynomial. The precise form of the normalisation constant in (1) depends upon the exact form of these polynomials, and to be explicit we use the form:

$$L_s^t(x) = \sum_{j=0}^{s}\binom{t+s}{s-j}\frac{(-x)^j}{j!} \tag{2}$$

where the first factor in the sum is the binomial coefficient.

Equation (1) is of course the solution to the Schrödinger equation and is non-relativistic in nature. It is therefore limited to cases where Z^* is small enough that the degeneracy in l with respect to the total angular momentum j is not lifted. Hence it is limited to the lower half of the periodic table. As we are using only hydrogenic approximations, we need not consider the angular dependence of the wavefunction since the different m components of each wavefunction are degenerate and spherically symmetric.

This work proceeds by using a different form of equation (1) for each of the initial and final sub-shells involved in the transition with effective Z^*s of Z_a and Z_b respectively. This physically implies that the two sub-shells are solutions of the Schrödinger equation in different potentials and thus the two wavefunctions will not necessarily be orthogonal, which could give cause for concern. A short discussion on this matter is therefore warranted.

First, it should be acknowledged that in reality there is no physical reason why the wavefunctions in the initial and final sub-shells should be orthogonal. Physically, the potentials in multi-electron atoms must be different between the two states. Orthogonality is a mathematical property of the solutions of the Schrödinger equation for bound electrons in hydrogen, and the mathematical machinery of angular momentum coupling theory as applied to multi-electron atoms through "standard" Racah algebra [21] is built upon the assumption that wavefunctions of equal l remain mutually orthogonal. This allows the atomic Hamilitonian to be given in terms of one-electron matrix elements. Alternative formalisms do exist that permit the rigorous use of non-orthogonal wavefunctions [22], but the required mathematics is more complex than for Racah based algebra, and related atomic structure codes [23] are not as widely used as those based on more traditional methods [21,24]. It is also worth noting that the imposition of orthogonality within mathematical formalisms that do not explicitly require it, can in fact lead to incorrect results [25].

On a more practical consideration, the one-electron matrix elements used for the radiative and collisional rates in the next sections, do not explicitly require orthogonality. Of course we imply it through the use of hydrogenic wavefunctions, but we are in fact using these to represent electrons in multi-electron atoms (via Z^*), and as already argued, these need not be orthogonal. In any case in the one-electron atom, neglecting Stark, Zeeman and hyperfine splitting, all of which are beyond the scope of this work, there are no radiative transitions possible between sub-shells of equal l quantum numbers. This is explicitly clear through the 3j symbol that arises in the matrix element (see equation (5) in the next section). For the collisional rates, the generalised oscillator strengths and selection rules (equations (8) and (9)) do permit non-zero contributions from wavefunctions of equal l. However, there is again no *a-priori* requirement for orthogonality involved here and thus use of non-orthogonal wavefunctions is not incorrect. (Moreover, of the 1485 possible transitions between sub-shells of $n \leq 10$, only 165 involve $\Delta l = 0$.)

However, use of the work here would be formally incorrect if it was used to calculate the one-electron matrix elements of the Hamiltonians for detailed atomic structure calculations based on standard Racah techniques [21]. Here the eigen-components resulting from different sub-shells may require matrix elements from wavefunctions that should be orthogonalised and thus use of these results may then be incorrect. (One example that would be sensitive to orthogonality would be configuration interaction (CI) calculations giving rise to an admixture of states that in reality