LETTER TO THE EDITOR

Use of hydrogenic transition probabilities for non-penetrating Rydberg states with core polarisation

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Abstract. A procedure for including the effects of core polarisation in transition probability estimates for non-penetrating states in multi-electron atoms is described. By combining the non-penetrating transition moment parametrisation of Hameed with the familiar spectroscopic term value polarisation formula, an analogous formula for correcting hydrogenic transition probabilities is obtained. The procedure is used to estimate lifetimes for non-penetrating states in S V and Cl VI and the corrections are compared with experimental accuracies.

High angular momentum Rydberg states in multi-electron atoms are often strongly populated in the beam–foil light source, permitting studies of their transition wavelengths and lifetimes. These wavelengths can be accurately predicted using the spectroscopic term value polarisation formula (Bockasten 1956, Edlén 1964), in which these states are modelled as a hydrogen-like electron orbiting a deformable core of charge. Measured lifetimes for these states are also often compared with hydrogenic calculations, scaled for the core charge, but the details of the procedure vary. Some authors scale the hydrogen lifetimes directly, while others use the physical wavelengths to convert either the hydrogenic oscillator strengths or the hydrogenic line strengths to transition probabilities, which are then summed over decay channels to obtain the reciprocal lifetimes. The differences are usually small, but in some cases the lifetimes computed by these alternative procedures can differ systematically by 10%, and none of these approaches treats core polarisation effects in a consistent manner. A core polarisation parametrisation of the transition moment between two non-penetrating states has been developed by Hameed (1969), which can be combined with the term value polarisation formula to obtain a consistent description of transition probabilities within the context of this model. The purpose of this letter is to call attention to the applicability of this formulation to highly excited and highly ionised systems, to express the resulting formula in a convenient and practical form, and to apply it to some specific cases where the core polarisation model could be tested by precision lifetime measurements.

Term values of non-core-penetrating states in multi-electron atoms are often described using the spectroscopic term value polarisation formula, which combines the hydrogen-like term value with additional energy contributions associated with core polarisation, computed using hydrogen-like expectation values for the powers of the radius, yielding (Bockasten 1956, Edlén 1964)

$$T_{nl} = R\left(\frac{\zeta}{n}\right)^2\left[1+\left(\frac{\alpha\zeta}{n}\right)^2\left(\frac{n}{l+\frac{1}{2}}-\frac{3}{4}\right)\right] + Ra_0\alpha_d\langle nl|r^{-4}|nl\rangle + Ra_0\alpha_q\langle nl|r^{-6}|nl\rangle. \tag{1}$$

Here T_{nl} is the predicted term value (in cm^{-1}) for a Rydberg level of principal and angular momentum quantum numbers n and l and net charge (nuclear charge minus core electrons) ζ. R is the reduced-mass-corrected Rydberg constant (also in cm^{-1}), α is the fine-structure constant, a_0 is the Bohr radius, and α_d and α_q are the electric dipole and quadrupole polarisabilities of the ionic core. Properly, the value of a_0 should also be corrected for reduced mass, but this is usually neglected and left to reside in the empirical α_d and α_q values. Here CGS units will be retained so that these atomic quantities will explicitly appear. The expectation values for powers of r are computed from hydrogenic wavefunctions $|nl\rangle$ for a one-electron atom of central charge ζe. Empirical values for α_d and α_q for a given ion can be deduced by applying equation (1) to known term values, and can then be used to predict term values for all other non-penetrating states of that ion. The effective values for α_d obtained in this manner usually agree quite well with theoretical estimates and non-spectroscopic measurements of the dipole polarisability, but α_q often contains contributions in addition to pure quadrupole polarisability, since penetration (Vogel 1973) and non-adiabatic effects (Öpik 1967) have an n dependence similar to that of the quadrupole polarisation. Equation (1) has been applied to many situations where n and l are substantially greater than the corresponding values for any of the core electrons, but the concept of 'non-penetrating' is here somewhat heuristic, and includes those terms in a given ion which are well described by equation (1). Clearly both the magnitudes of α_d and α_q and the terms which can be considered non-penetrating are very sensitive to the presence of open-shell electrons in the core. Wavelengths for transitions between non-penetrating levels can be obtained from equation (1) using

$$\lambda_{nl,n'l'} = 1/(T_{n'l'} - T_{nl}) \tag{2}$$

where $n > n'$.

It has been pointed out (Bersuker 1957, Hameed *et al* 1968) that a consistent treatment of core polarisation in the calculation of atomic dipole transition probabilities in the independent-particle picture requires not only the inclusion of the polarisation interaction in the model potential, but also a modification of the one-electron transition operator to include both the dipole moment of the valence electron and the induced dipole moment of the core. Thus the total transition moment d between states ψ_i and ψ_f is written

$$\langle\psi_i|d|\psi_f\rangle = -e\langle\psi_i|r - \alpha_d f(r)r/r^3|\psi_f\rangle \tag{3}$$

where $f(r)$ is the ratio of the true induced dipole moment operator to its asymptotic form at large r (usually modelled by a small r cut-off function). Properly α_d should be the dynamic polarisability at the transition frequency, but if this is small compared with the core excitation frequencies the static approximation is valid. Equation (3) has been used by a number of workers to compute corrections to oscillator strengths, mainly for low n and l states in neutral and singly ionised alkali systems. These corrections have usually been quite small, although cases have been found (Shevelko 1974) where they are substantial. These corrections can become large when there are severe cancellation effects in the transition moment of the valence electron (Curtis and Ellis 1978), but such cases must be excluded from the simple description discussed here. In general the treatment of core polarisation requires the inclusion of the polarisation interaction in the model potential, the use of equation (3) in the computation of the transition moment, and an appropriate penetration cut-off function $f(r)$. A much simpler treatment is possible for non-penetrating transitions, such that both states can be

represented by hydrogen-like wavefunctions, at least one of which vanishes where $f(r)$ deviates from unity. For non-penetrating states connected by Laporte's rule, the radial portion of equation (3) can be written

$$\langle nl|d|n'l'\rangle = -ea_o \mathscr{R}_{nl}^{n'l'}(1 - \alpha_d K)/\zeta \tag{4}$$

where

$$\mathscr{R}_{nl}^{n'l'} \equiv \langle nl|r|n'l'\rangle_{\zeta=1}/a_0 \tag{5}$$

is the radial transition integral for hydrogen, and

$$K \equiv \langle nl|r^{-2}|n'l'\rangle/\langle nl|r|n'l'\rangle. \tag{6}$$

Hameed (1969) has pointed out that K is a very simple function, proportional to the square of the transition energy. It is the well known ratio of the acceleration and length forms (Chandrasekhar 1945) of the dipole transition element, which can be deduced from first principles for exact wavefunctions, e.g. by consideration of the general commutation relation (Bethe and Salpeter 1957)

$$[\mathscr{H}, [\mathscr{H}, r]] = 2Ra_0^2 \nabla V \tag{7}$$

where $\mathscr{H}$ is the Hamiltonian for a general atomic potential V. For a one-electron system with potential $V = -2\zeta Ra_0/r$, equation (7) implies, for Laporte's rule connected states,

$$(T_{n'l'} - T_{nl})^2 \langle nl|r|n'l'\rangle = 4\zeta R^2 a_0^3 \langle nl|r^{-2}|n'l'\rangle. \tag{8}$$

Thus, provided no small r cut-off is necessary, the ratio of these integrals is always positive. Since this development assumes that core polarisation effects are small, it is clear that $0 \leqslant \alpha_d K \ll 1$, so the core polarisation corrections will always act to reduce the transition moment in this non-penetrating approximation.

In a purely hydrogen-like formulation the transition energy would be given by the Balmer formula, but here the term value and transition moment parametrisations can be combined, using equations (1) and (2) to express equations (6) and (8) as

$$K = [4\zeta a_0^3 (R\lambda_{nl,n'l'})^2]^{-1}. \tag{9}$$

Since only the dipole polarisability contributes to the transition moment, measured physical wavelengths might provide a valid description in equation (9) even in circumstances where term values exhibit penetration effects which distort the quadrupole portion of equation (1) (Vogel 1973).

In this formulation both the wavelength and the transition moment have been corrected for core polarisation, so the transition probability, the oscillator strength and the line strength all have their standard definitions (cf Wiese *et al* 1966) and no one is favoured. However, since highly excited non-penetrating state transitions are usually observed in emission, only the equation for transition probabilities will be presented here. The line transition probability $A_{nl,n'l'}$ (averaged over initial-state and summed over final-state magnetic quantum numbers) between Laporte's rule connected levels in a quasi-hydrogen-like multi-electron atom is given by

$$A_{nl,n'l'} = \frac{\max(l,l')}{\zeta^2(2l+1)} \frac{32\pi^3 \alpha c a_0^2/3}{(\lambda_{nl,n'l'})^3} \left(1 - \frac{\alpha_d/a_0^3}{4\zeta(R\lambda_{nl,n'l'})^2}\right)^2 |\mathscr{R}_{nl}^{n'l'}|^2. \tag{10}$$

For ease in computation, $32\pi^3 \alpha c a_0^2/3 = (1265 \cdot 38)^3$ Å^3 ns^{-1}. The squared transition element for the hydrogen atom $|\mathscr{R}_{nl}^{n'l'}|^2$ is available in tabulated form for n and $n' \leqslant 20$ (Green *et al* 1957). Alternatively, published tabulations of the transition probabilities

for hydrogen (e.g. Lindgård and Nielsen 1977, Wiese *et al* 1966) can be corrected directly by multiplication by $\zeta^4(1-\alpha_d K)^2$ and by the cube of the wavelength ratio (scaled-hydrogen-like/core-polarisation-corrected).

Members of the Mg isoelectronic sequence provide a useful application of this formulation, since they have particularly large polarisabilities due to the $1s^2 2s^2 2p^6 3s$ core, and transitions with the same n and n' but differing l and l' can easily be resolved in beam–foil spectra. For S v Dynefors and Martinson (1978) have obtained the values $\alpha_d = 2 \cdot 45 \, a_0^3$ and $\alpha_q = 8 \cdot 8 \, a_0^5$, while for Cl vi Bashkin *et al* (1973) have obtained $\alpha_d = 1 \cdot 62 \, a_0^3$ and $\alpha_q = 9 \cdot 0 \, a_0^5$. Classical spectroscopic studies in Al ii (Kaufman and Hagan 1979), Si iii (Toresson 1961) and P iv (Zetterberg and Magnusson 1977) indicate that equation (1) adequately describes both the singlet and triplet term values for the 3s*nl* Rydberg series for all n provided $l \geqslant 4$. On these grounds, transitions from states in these ions with $l \geqslant 5$ can reasonably be expected to follow equation (10). The $3sng \, ^{1,3}G$ states are a borderline case, since they are well described by equation (1), but their decay is coupled through transitions to the $3snf \, ^{1,3}F$ terms, which have non-negligible singlet–triplet splittings, exhibit series perturbations, and are not well described by equation (1). Since the F terms of this sequence tend to have small quantum defects, it would be interesting to compare measured G lifetimes with predictions from equation (10) made using measured F–G transition wavelengths. Lifetimes in S v and Cl vi for $n = 6$–8 and $l = 5$–7, computed using equations (1), (2) and (10) and the hydrogenic tabulations of Green *et al* (1957), are presented and compared with available measurements in table 1. To indicate the size of the core polarisation corrections, table 1 also lists hydrogen-like lifetime estimates obtained by neglecting core polarisation entirely, and by including it incompletely through conversions of the hydrogenic oscillator strengths and hydrogenic line strengths using physical

Table 1.

Ion	State	Lifetime (ns)				
		$\tau(A)^a$	$\tau(f)^b$	$\tau(S)^c$	$\tau(\text{Pol})^d$	$\tau(\text{Exp})$
S v	3s 6h	0·97	0·91	0·89	0·908	$1 \cdot 0 \pm 0 \cdot 1^e$
	7h	1·54	1·45	1·41	1·459	
	7i	2·16	2·13	2·11	2·128	
	8h	2·28	2·16	2·11	2·195	
	8i	3·21	3·17	3·14	3·181	
	8k	4·29	4·27	4·26	4·272	
Cl vi	3s 6h	0·47	0·43	0·41	0·425	
	7h	0·74	0·68	0·66	0·683	$0 \cdot 58 \pm 0 \cdot 06^f$
	7i	1·04	1·02	1·01	1·024	
	8h	1·10	1·02	0·98	1·030	$1 \cdot 7^g$
	8i	1·55	1·52	1·51	1·531	
	8k	2·07	2·06	2·05	2·061	

[a] Computed from hydrogenic lifetimes.
[b] Computed from hydrogenic oscillator strengths and physical wavelengths.
[c] Computed from hydrogenic line strengths and physical wavelengths.
[d] Computed from equation (10).
[e] Dynefors and Martinson (1978).
[f] Bhardwaj *et al* (1974).
[g] Order of magnitude estimate, Bhardwaj *et al* (1974).

wavelengths. In a number of the examples the lifetimes computed using equation (10) are quite close to those obtained using hydrogenic oscillator strengths and physical wavelengths. However no such tendency occurs in the individual decay transition probabilities, and none of these other procedures accurately reproduces the branching ratios predicted by equation (10).

Clearly the present measurement accuracies are not adequate to test these polarisation corrections, but table 1 indicates that these corrections can be non-negligible. Lifetime determinations for high n and l states involve some experimental difficulties, but measurements with refined but realisable precision could provide valuable tests of this simple core polarisation model.

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