

LETTER TO THE EDITOR

Computation of M1 decay rates in intermediate coupling using empirical spectroscopic data

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Abstract. A procedure is developed by which M1 decay rates for a system with intermediate coupling can be computed from the corresponding rates in pure *LS* coupling and simple factors obtained from measured energy separations. Applications are made to the *nsnp* configurations in the Be, Mg and Zn isoelectronic sequences which are compared with *ab initio* MCDF calculations.

A knowledge of magnetic dipole (M1) transitions is important in the study of highly ionised atomic systems because both the energy separations and the transition rates between the connected levels scale as higher powers of the nuclear charge Z than do the gross structure energies and the electric dipole transition rates. Since M1 transitions in highly ionised systems often occur in a convenient wavelength region in which reflective optics can be used, they provide a useful diagnostic tool in the study of high-temperature plasmas. In addition, these transitions can play a significant role in the cascade repopulation of resonance and intercombination lines when studied by time-resolved techniques such as fast ion beam excitation by a thin foil.

In pure *LS* coupling, M1 transitions connect only $\Delta J = \pm 1$ fine-structure levels within the same spectroscopic term. Furthermore, these M1 rates involve only monopole radial integrals and can be computed from transition wavelengths and simple angular-momentum factors. In intermediate coupling, levels of common J acquire a mixture of L and S basis states, so the possibilities for M1 transitions are increased and the computation of decay rates requires a knowledge of the degree of intermediate coupling.

Ab initio calculation of M1 transition probabilities by multiconfiguration Dirac-Fock (MCDF) methods takes intermediate coupling into account directly through the composition of the wavefunctions. However, this mixing is also manifested experimentally in the observed splitting of the levels within the configuration. A method is described herein, which exploits a semiempirical parametrisation of the intermediate coupling to predict M1 transition rates, that requires only observed energy splittings and known *LS* coupling rates. Comparisons are presented between these predictions and *ab initio* MCDF calculations for *nsnp* configurations in the Be, Mg and Zn isoelectronic sequences.

To formulate the problem, the M1 transition rate A is given by

$$(2J + 1)A(\gamma J, \gamma' J') = [2999/\lambda(\gamma J, \gamma' J')]^3 S_{M1}(\gamma J, \gamma' J') \quad (1)$$

where A is in s^{-1} , the wavelength λ is in nm, the constant $2\pi\alpha(a_0c/3)^{1/3}$ is 2999 in these units, J is the total angular momentum and γ denotes all other quantum numbers. The transition matrix S_{M1} is given by

$$S_{M1}(\gamma J, \gamma' J') = \sum_{MM'} |\langle \gamma JM | M | \gamma' J' M' \rangle|^2 \quad (2)$$

where $M = -(L+2S)e/2mc$ is the magnetic dipole operator. For pure LS coupling S_{M1} vanishes unless $\gamma = \gamma'$, so $S = S'$ and $L = L'$, and is given by (Pasternack 1940, Shortley 1940)

$$S_{M1}(LSJ, LSJ \pm 1) = [+]^2 [(L+S+1)^2 - J^2] [J^2 - (L-S)^2] / 4J_{\pm} \quad (3)$$

$$S_{M1}(LSJ, LSJ) = [+]^2 (2J+1) [S(S+1) - L(L+1) + 3J(J+1)]^2 / 4J(J+1) \quad (4)$$

where $[+]^2$ denotes the sign of the unsquared quantity in equation (2). These relationships could also be utilised for intermediate coupling if it were possible to specify the LS basis state makeup of the wavefunctions of the physical states. This information is also contained in the energy level data, and can be specified semiempirically.

As an example, consider the $nsn'l$ configuration, for which there are four levels (labelled 0-3 here). Neglecting possible configuration interaction mixings, these levels can be represented without loss of generality by wavefunctions of the form

$$|0\rangle = |^3L_{L-1}\rangle \quad (5)$$

$$|1\rangle = -[Lx^2/(2L+1)]^{1/2} |^1L_L\rangle + [1 - Lx^2/(2L+1)]^{1/2} |^3L_L\rangle \quad (6)$$

$$|2\rangle = |^3L_{L+1}\rangle \quad (7)$$

$$|3\rangle = [1 - Lx^2/(2L+1)]^{1/2} |^1L_L\rangle + [Lx^2/(2L+1)]^{1/2} |^3L_L\rangle. \quad (8)$$

For pure LS coupling $x = 0$, for pure jj coupling $x = 1$ (cf Condon and Shortley 1935) and for intermediate coupling $0 \leq x \leq 1$. Although x could be defined through formal Racah algebra, the goal here is to specify x through a semiempirical parametrisation.

In pure LS coupling there would be only two M1 transitions within this configuration, connecting the levels $1 \rightarrow 0$ and $2 \rightarrow 1$. In the case of intermediate coupling the two $J = L$ levels both contain non-zero amounts of the two $J = L$ LS basis states. Thus for the four intermediate coupled states, the M1 matrix elements can be written as

$$S_{M1}(1, 0) = [1 - Lx^2/(2L+1)] S_{M1}(^3L_L, ^3L_{L-1}) \quad (9)$$

$$S_{M1}(2, 1) = [1 - Lx^2/(2L+1)] S_{M1}(^3L_{L+1}, ^3L_L) \quad (10)$$

$$S_{M1}(3, 0) = Lx^2/(2L+1) S_{M1}(^3L_L, ^3L_{L-1}) \quad (11)$$

$$S_{M1}(3, 1) = [1 - Lx^2/(2L+1)] [Lx^2/(2L+1)] \times \{ [S_{M1}(^3L_L, ^3L_L)]^{1/2} - [S_{M1}(^1L_L, ^1L_L)]^{1/2} \}^2 \quad (12)$$

$$S_{M1}(3, 2) = [Lx^2/(2L+1)] S_{M1}(^3L_L, ^3L_{L+1}). \quad (13)$$

If a suitable semiempirical definition of x could be obtained, the M1 rates could be determined directly from energy level data. In spectroscopic studies, the degree of intermediate coupling in an $nsn'l$ configuration is often characterised in terms of the spin-orbit energy ζ_l and the Slater energy G_1 as (cf Edlén 1964, pp 113-4)

$$\frac{(2L+1)\zeta_l}{4G_1 + (2L+1)\zeta_l} = \frac{E(2) - E(0)}{E(3) + E(1) - 2E(0)}. \quad (14)$$

This quantity shares with x the limiting values 0 and 1 for pure LS and jj coupling. (A similar but more complicated characterisation of the spin mixing can be obtained from the eigenvector transformation to intermediate coupling.)

To make this example more specific, consider the $L = l = 1$ sp case. Here the M1 rates can be obtained from equations (1-14) and (neglecting configuration interaction and deviations from unit monopole moments in the radial integrals) are given by the simple formulae

$$A(1, 0) = \frac{2}{3}(1 - x^2/3)[2999/\lambda(1, 0)]^3 \quad (15)$$

$$A(2, 1) = \frac{1}{2}(1 - x^2/3)[2999/\lambda(2, 1)]^3 \quad (16)$$

$$A(3, 0) = \frac{2}{3}(x^2/3)[2999/\lambda(3, 0)]^3 \quad (17)$$

$$A(3, 1) = \frac{1}{2}(1 - x^2/3)(x^2/3)[2999/\lambda(3, 1)]^3 \quad (18)$$

$$A(3, 2) = \frac{5}{6}(x^2/3)[2999/\lambda(3, 2)]^3 \quad (19)$$

where

$$x = [E(2) - E(0)]/[E(3) + E(1) - 2E(0)] \quad (20)$$

and for energies E measured in cm^{-1}

$$\lambda(i, f) = 10^7/[E(i) - E(f)]. \quad (21)$$

We have utilised equations (15-21) to specify M1 decay rates for selected ions in the $2s2p$ Be, $3s3p$ Mg and $4s4p$ Zn isoelectronic sequences. The sources for experimental energy levels were as follows: for the Be sequence Edlén (1979, 1980), for the Mg sequence Litzén and Redfors (1987) and for the Zn sequence Churilov *et al* (1988). For the Be sequence the measured data were supplemented by the calculated energy levels of Cheng *et al* (1979) for $Z \geq 36$. For the Mg sequence the $Z = 54$ energy levels were obtained by semiempirical extrapolation, as described by Curtis and Ramanujam (1981) (this method has also been applied to the Zn sequence (Curtis 1983)).

To test the validity of these semiempirical computations, *ab initio* calculations were performed using the program MCDF developed by Grant and co-workers (Grant *et al* 1980). In the case of the Be sequence, $2s2p$ is the only $n = 2$ configuration with odd parity, so this was a single-configuration calculation. For the Mg sequence the $3s3p$ and $3p3d$ configurations were included, whereas for the Zn sequence the $4s4p$, $4p4d$ and $4d4f$ configurations were included. For single-configuration calculations MCDF values for x can be uniquely obtained from the LS amplitudes of the computed wavefunctions. For multiconfiguration calculations this specification is ambiguous due to the larger number of contributing amplitudes, but the range of values obtained from various amplitudes here was reasonably narrow.

Table 1 presents these results and shows that the agreement between semiempirical and *ab initio* calculations is quite close for both the parameter x and for the decay rates and that the discrepancies introduced by configuration interaction are small. As a further test, single-configuration Dirac-Fock (SCDF) calculations were also made for a number of cases. In some cases these single-configuration semiempirical estimates were in closer agreement with MCDF than with SCDF calculations, indicating that the use of measured wavelengths can be more significant than configuration interaction effects in the matrix element.

These results indicate that equations (15-21) provide a simple means for reliably predicting M1 transition rates from measured data alone. Similar sets of equations

Table 1. M1 transition probabilities within the *nsnp* configurations in the Be, Mg and Zn isoelectronic sequences. The semiempirical (*SE*) values were obtained from computed energy level data using equations (15–21). The multiconfiguration Dirac–Fock values are *ab initio* calculations made using the program MCDF (Grant 1980).

<i>Z</i>	Ion	<i>x</i>			<i>A</i> (1, 0)			<i>A</i> (2, 1)			<i>A</i> (3, 0)			<i>A</i> (3, 1)			<i>A</i> (3, 2)		
		<i>SE</i>	MCDF		<i>SE</i>	MCDF		<i>SE</i>	MCDF		<i>SE</i>	MCDF		<i>SE</i>	MCDF		<i>SE</i>	MCDF	
2s2p Be isoelectronic sequence																			
12	Mg ⁰⁸⁺	0.027	0.023		2.55 (–2)†	2.52 (–2)	2.02 (–1)	1.98 (–1)	9.95 (0)	7.91 (0)	7.27 (0)	6.08 (0)	1.14 (1)	9.39 (0)					
16	S ¹²⁺	0.072	0.062		1.43 (0)	1.42 (0)	1.23 (1)	1.22 (1)	2.14 (2)	1.73 (2)	1.50 (2)	1.26 (2)	2.13 (2)	1.78 (2)					
20	Ca ¹⁶⁺	0.142	0.128		2.52 (1)	2.54 (1)	2.77 (2)	2.72 (2)	2.14 (3)	1.83 (3)	1.40 (3)	1.24 (3)	1.65 (3)	1.47 (3)					
24	Cr ²⁰⁺	0.234	0.221		2.15 (2)	2.20 (2)	3.46 (3)	3.39 (3)	1.39 (4)	1.29 (4)	8.36 (3)	8.00 (3)	7.37 (3)	7.20 (3)					
28	Ni ²⁴⁺	0.336	0.334		1.16 (3)	1.13 (3)	2.92 (4)	2.86 (4)	7.02 (4)	7.05 (4)	3.86 (4)	3.99 (4)	2.25 (4)	2.40 (4)					
36	Kr ³²⁺	0.526	0.564		9.97 (3)	9.87 (3)	9.25 (5)	9.07 (5)	1.13 (6)	1.25 (6)	5.67 (5)	6.31 (5)	1.07 (5)	1.21 (5)					
42	Mo ³⁸⁺	0.647	0.697		2.72 (4)	2.67 (4)	7.58 (6)	7.32 (6)	6.98 (6)	7.87 (6)	3.44 (6)	3.84 (6)	2.29 (5)	2.63 (5)					
48	Cd ⁴⁴⁺	0.739	0.789		5.47 (4)	5.35 (4)	4.58 (7)	4.37 (7)	3.62 (7)	4.02 (7)	1.79 (7)	1.95 (7)	4.16 (5)	4.70 (5)					
54	Xe ⁵⁰⁺	0.806	0.851		9.14 (4)	8.96 (4)	2.21 (8)	2.10 (8)	1.62 (8)	1.75 (8)	8.03 (7)	8.50 (7)	6.84 (5)	7.56 (5)					
64	Gd ⁶⁰⁺	0.879	0.912		1.70 (5)	1.68 (5)	2.14 (9)	2.01 (9)	1.48 (9)	1.52 (9)	7.40 (8)	7.51 (8)	1.37 (6)	1.46 (6)					
74	W ⁷⁰⁺	0.922	0.945		2.63 (5)	2.64 (5)	1.53 (10)	1.42 (10)	1.03 (10)	1.02 (10)	5.20 (9)	5.10 (9)	2.51 (6)	2.57 (6)					
92	U ⁸⁸⁺	0.962	0.974		4.18 (5)	4.30 (5)	3.33 (11)	2.95 (11)	2.22 (11)	2.04 (11)	1.12 (11)	1.02 (11)	6.58 (6)	6.38 (6)					
3s3p Mg isoelectronic sequence																			
25	Mn ¹³⁺	0.143	0.12		2.02 (0)	2.05 (0)	2.02 (1)	1.97 (1)	1.60 (2)	1.32 (2)	1.04 (2)	8.74 (1)	1.23 (2)	1.05 (2)					
30	Zn ¹⁸⁺	0.245	0.21		2.42 (1)	2.48 (1)	3.69 (2)	3.62 (2)	1.42 (3)	1.31 (3)	8.40 (2)	7.89 (2)	7.14 (2)	6.91 (2)					
54	Xe ⁴²⁺	0.709	0.75		5.40 (3)	5.49 (3)	2.54 (6)	2.44 (6)	2.11 (6)	2.39 (6)	1.03 (6)	1.14 (6)	3.37 (4)	4.25 (4)					
4s4p Zn isoelectronic sequence																			
42	Mo ¹²⁺	0.301	0.28		7.87 (0)	8.53 (0)	1.52 (2)	1.42 (2)	4.38 (2)	4.16 (2)	2.46 (2)	2.41 (2)	1.67 (2)	1.82 (2)					
50	Sn ²⁰⁺	0.479	0.48		9.31 (1)	1.04 (2)	5.12 (3)	4.84 (3)	7.32 (3)	7.92 (3)	3.67 (3)	4.02 (3)	9.65 (2)	1.24 (3)					

† The number in parentheses denotes the power of ten by which the number should be multiplied.

can easily be formulated for other configurations. Although powerful *ab initio* methods are now widely available which can be applied to M1 transition rates, this simple semiempirical approach provides unique predictions that are independent of methodological details. These can serve as a basis against which experimental and theoretical results can be compared.

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