

Branching fractions for the Mg-like $3s3p$ – $3s3d$ and $3s3p$ – $3p^2$ transition arrays

James Steiner and Lorenzo J Curtis

Department of Physics and Astronomy, University of Toledo, Toledo OH 43606, USA

E-mail: ljc@physics.utoledo.edu

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Abstract

Semiempirical methods are used to characterize and parametrize the effects of intermediate coupling and configuration interaction on the energy levels of the $3s3p$, $3p^2$ and $3s3d$ configurations for ions in the Mg isoelectronic sequence. These parametrizations are then used to predict the branching fractions for the $3s3p$ – $3p^2$ and $3s3p$ – $3s3d$ transition arrays. The predictions are compared with the MCHF calculations for S V and Fe XV, and good agreement is obtained. The application of this method to deduce transition probabilities and oscillator strengths from lifetime measurements is discussed.

A large base of measured lifetime data now exists for excited levels in atomic ions [1]. Many applications of atomic structure data require the use of transition probabilities and oscillator strengths, which can be obtained from lifetimes for branched decays by combining lifetime data with branching fraction values. Unlike lifetime measurements, branching fraction measurements require an intensity versus wavelength calibration of the detection system. For multiply ionized atomic spectra this presents severe challenges, associated both with the characteristics of the spectroscopic light sources, and with the lack of calibration standards in the ultraviolet region where these spectra occur. Correspondingly, branching fraction measurements in multiply charged ions are at present virtually nonexistent [2].

The existing base of atomic lifetime data has provided extensive tests of theoretical calculations, and has demonstrated the importance of the inclusion of intermediate coupling, configuration interaction, electron correlation, and many other theoretical considerations. However, lacking a similar base of branching fraction data, similar tests of theory have not been made for these relative quantities. Thus, the possibility exists that theoretical calculations for the ratios of transition probabilities could be less sensitive to the various perturbations, and a reliable base of transition probability and oscillator strength data might then be developed using precision lifetime measurements and theoretically computed branching fractions.

It has been demonstrated that branching fractions can be specified for the transition arrays ns^2np^2 – ns^2npn' s in the Si [3], Ge [4], Sn [5] and Pb [6] isoelectronic sequences. This

was achieved through the use of energy level data to semiempirically specify the intermediate coupling amplitudes. In these systems it was shown that the effects of configuration interaction are negligible, and that the branching fractions can be accurately specified by singlet–triplet mixing amplitudes and LS -coupling coefficients. Here we report an extension and testing of these methods for transitions in the Mg isoelectronic sequence. These transitions possess strong configuration mixing in addition to intermediate coupling, and it is shown that reliable branching ratios can be obtained here also by a suitably extended semiempirical formulation.

To further develop these semiempirical methods, we consider the magnesium isoelectronic sequence, which is simple enough to be theoretically and semiempirically tractable, yet strongly affected by intermediate coupling, configuration interaction and relativistic corrections. For this study we have chosen the $3s3p$ – $3s3d$ and $3s3p$ – $3p^2$ transitions because they display both intermediate coupling and configuration interaction in a strong but analysable way. In addition, since these transition arrays are the only E1 transitions available for decay of the $3s3d$ and $3p^2$ configurations, the transition probabilities can be obtained from their lifetimes and these transition array branching fractions alone. This method also tests the non-relativistic Schrödinger approximation, wherein only the radial function depends on the central potential. In this approximation, all members of the transition array involve the same E1 transition moment, so ratios depend only on angular factors.

The $3s3p$ configuration contains the $^3P_0^o$, $^3P_1^o$, $^3P_2^o$, $^1P_1^o$ levels, and intermediate coupling mixes the $^3P_1^o$ and $^1P_1^o$ levels. The $3s3d$ configuration contains the 3D_1 , 3D_2 , 3D_3 , 1D_2 levels, and intermediate coupling mixes the 3D_2 and 1D_2 levels. The $3p^2$ configuration contains the 3P_0 , 3P_1 , 3P_2 , 1D_2 , 1S_0 levels, and configuration interaction separately mixes the 3P_0 and 1S_0 levels and the 3P_2 and 1D_2 levels. Since both the $3s3d$ and $3p^2$ configurations contain 1D_2 levels, there is strong configuration mixing between these two levels. Thus, although there are significant intermediate coupling and configuration interaction effects among these systems, all of the couplings are only pairwise, and the normalized amplitudes of each of the mixings can be characterized by a single quantity.

For pure configurations for which no more than two levels possess the same total angular momentum J , intermediate coupling mixing amplitudes can be expressed as a mixing angle θ_J . Thus the eigenvectors of the levels of an $s\ell$ configuration can be written as

$$\begin{aligned} |^3L'_{\ell-1}\rangle &= |^3L_{\ell-1}\rangle \\ |^3L'_\ell\rangle &= \cos\theta_\ell|^3L_\ell\rangle - \sin\theta_\ell|^1L_\ell\rangle \\ |^3L'_{\ell+1}\rangle &= |^3L_{\ell+1}\rangle \\ |^1L'_\ell\rangle &= \sin\theta_\ell|^3L_\ell\rangle + \cos\theta_\ell|^1L_\ell\rangle, \end{aligned} \tag{1}$$

where the primes denote that the LS designation is only nominal. Similarly, eigenvectors of levels of a p^2 configuration can be written as

$$\begin{aligned} |^3P'_0\rangle &= \cos\theta_0|^3P_0\rangle - \sin\theta_0|^1S_0\rangle \\ |^3P'_1\rangle &= |^3P_0\rangle \\ |^3P'_2\rangle &= \cos\theta_2|^3P_2\rangle - \sin\theta_2|^1D_2\rangle \\ |^1D'_2\rangle &= \sin\theta_2|^3P_2\rangle + \cos\theta_2|^1D_2\rangle \\ |^1S'_0\rangle &= \sin\theta_0|^3P_0\rangle + \cos\theta_0|^1S_0\rangle. \end{aligned} \tag{2}$$

The mixing angles can be formulated in terms of direct and exchange Slater and spin–orbit parameters [7].

For the sp ($\ell = 1$) and sd ($\ell = 2$) configurations the energy level can be written [7] in terms of the Coulomb energy E_ℓ , the exchange Slater energy G_ℓ and the diagonal and off-diagonal spin–orbit energies ζ_ℓ and ζ'_ℓ , as

$$\begin{aligned} {}^3\text{L}_{\ell-1} &= E_\ell - G_\ell - (\ell + 1)\zeta_\ell/2 \\ {}^3\text{L}_\ell &= E_\ell - \zeta_\ell/4 - \Delta_\ell \\ {}^3\text{L}_{\ell+1} &= E_\ell - G_\ell + \ell\zeta_\ell/2 \\ {}^1\text{L}_\ell &= E_\ell - \zeta_\ell/4 + \Delta_\ell, \end{aligned} \quad (3)$$

where

$$\Delta_\ell \equiv \sqrt{(G_\ell + \zeta_\ell/4)^2 + \ell(\ell + 1)\zeta'_\ell{}^2/4}. \quad (4)$$

The singlet–triplet mixing angle is given by

$$\cot(2\theta) = \frac{2G_\ell + \zeta_\ell/2}{\sqrt{\ell(\ell + 1)\zeta'_\ell}}. \quad (5)$$

Although they are equal for a pure configuration, the separate definition of diagonal and off-diagonal spin–orbit parameters has a number of advantages. It was suggested by Wolfe [8] as a possible means to include the effects of spin–other-orbit interaction, and by King and VanVleck [9] to allow for differences between the singlet and triplet radial wavefunctions. Here the primary reason is to introduce the same number of parameters as energy levels, so as to obtain a simple remapping of the data and not an overdetermined fit. This permits the energy levels to be reconstructed from the mapping parameters to their full accuracy. In addition, the agreement between diagonal and off-diagonal spin–orbit parameters provides a test of the single configuration representation.

For the p² configuration the level energies can be written in terms of the Coulomb energy E_{pp} , the direct tensor Slater energy F_2 , the diagonal spin–orbit energy ζ_{pp} , and the $J = 2$ and 0 off-diagonal spin–orbit energies ζ'_{pp} and ζ''_{pp} respectively, as

$$\begin{aligned} {}^3\text{P}_0 &= E_{pp} + 5F_2/2 - \zeta_{pp}/2 - \Delta_0 \\ {}^3\text{P}_1 &= E_{pp} - 5F_2 - \zeta_{pp}/2 \\ {}^3\text{P}_2 &= E_{pp} - 2F_2 + \zeta_{pp}/4 - \Delta_2 \\ {}^1\text{D}_2 &= E_{pp} - 2F_2 + \zeta_{pp}/4 + \Delta_2 \\ {}^1\text{S}_0 &= E_{pp} + 5F_2/2 - \zeta_{pp}/2 + \Delta_0, \end{aligned} \quad (6)$$

where

$$\begin{aligned} \Delta_0 &= \sqrt{(15F_2/2 + \zeta_{pp}/2)^2 + 2\zeta''_{pp}{}^2} \\ \Delta_2 &= \sqrt{(3F_2 - \zeta_{pp}/4)^2 + \zeta'_{pp}{}^2/2}. \end{aligned} \quad (7)$$

The singlet–triplet mixing angles are given by

$$\cot(2\theta_2) = \frac{12F_2 - \zeta_{pp}}{2\sqrt{2}\zeta'_{pp}} \quad (8)$$

and

$$\cot(2\theta_0) = \frac{15F_2 + \zeta_{pp}}{2\sqrt{2}\zeta''_{pp}}. \quad (9)$$

Both the 3s3d and the 3p² configurations contain a ¹D₂ level. The measured data confirm the theoretical prediction that configuration interaction causes an effective repulsion between

Table 1. Input data (energies in cm^{-1}).

Ion	Level	Energy	Level	Energy	Level	Energy
S V	$^3P_0^o$	83 024.0	3D_1	234 941.5	3P_0	199 967.2
	$^3P_1^o$	83 393.5	3D_2	234 947.1	3P_1	200 370.6
	$^3P_2^o$	84 155.2	3D_3	234 956.0	3P_2	201 146.0
	$^1P_1^o$	127 150.7	1D_2	270 700.4	1D_2	193 739.1
				1S_0	235 350.0	
Fe XV	$^3P_0^o$	233 910	3D_1	678 830	3P_0	554 500
	$^3P_1^o$	239 660	3D_2	679 785	3P_1	564 570
	$^3P_2^o$	253 820	3D_3	681 410	3P_2	581 690
	$^1P_1^o$	351 914	1D_2	762 103	1D_2	559 590
				1S_0	659 627	

Data are from the NIST critical compilation of [11].

Table 2. Fitted parameters (energies in cm^{-1} , angles in degrees).

Ion	3s3p		3s3d		3p ²	
	Parameter	Value	Parameter	Value	Parameter	Value
S V	G_1	21 683	G_2	125.8	F_2	2305
	ζ_1	754	ζ_2	5.8	ζ_{pp}	783
	ζ'_1	814	ζ'_2	5.8	ζ'_{pp}	450
			$^1D_2(\text{fit})$	235 200	ζ''_{pp}	459
					$^1D_2(\text{fit})$	214 600
		θ_1	0.753°	θ_2	1.612°	θ_2
				θ_0	-1.05°	
Fe XV	G_1	51 922	G_2	10 073	F_2	5666
	ζ_1	13 273	ζ_2	1032	ζ_{pp}	19 037
	ζ'_1	14 053	ζ'_2	1032	ζ'_{pp}	10 059
			$^1D_2(\text{fit})$	700 600	ζ''_{pp}	5370
					$^1D_2(\text{fit})$	610 000
		θ_1	5.10°	θ_2	3.49°	θ_2
				θ_0	-4.15°	

the levels, displacing them significantly from the positions they would occupy in the absence of this mixing. In order to characterize this effect, we have obtained effective values for the two 1D_2 levels by varying each so as to minimize the differences between the spin-orbit energies as defined on the diagonal the off-diagonal matrix elements. If it is assumed that the configuration mixing primarily affects the 1D_2 levels, then this fitting of the 1D_2 levels should produce a set of energy levels consistent with a pure single configuration, and indicative of the intermediate coupling that affects it.

Studies were carried out over a wide range of ions in the Mg isoelectronic sequence using the NIST Atomic Spectra Database [11]. For Mg I, Al II and Si III the fine structure of the 3s3d level is inverted, and for P IV the fine structure has not been resolved experimentally. Above Fe XV the data base is somewhat fragmentary. We therefore carried out our isoelectronic comparisons from S V to Fe XV. The results varied smoothly between these two ions, so we report herein the results for S V and Fe XV.

The input data for the energy levels of the S V and Fe XV ions are listed in table 1, and are drawn from the NIST on-line Database [11]. The reduction of these energies to Slater and

Table 3. Branching fractions.

Transition	S V			Fe VX			<i>LS</i>
	$\lambda(\text{\AA})$	BF		$\lambda(\text{\AA})$	BF		
		SE	MCHF		SE	MCHF	
3s3p–3p ²							
³ P ₁ ^o – ³ P ₀	857.83	100	100	317.62	99.9	99.6	100
¹ P ₁ ^o –	1373.32	0.003	0.01	493.62	0.1	0.4	0
³ P ₀ ^o – ³ P ₁	852.18	33.8	33.9	302.43	36.4	36.7	33.3
³ P ₁ ^o –	854.87	25.1	25.2	307.78	25.9	25.8	25.0
³ P ₂ ^o –	860.47	41.3	41.0	321.8	37.7	37.5	41.6
¹ P ₁ ^o –	1365.75	0.0003	0.0007	470.24	0.0004	0.05	0
³ P ₁ ^o – ³ P ₂	849.24	25.4	25.4	292.37	27.0	25.0	25.0
³ P ₂ ^o –	854.77	74.6	74.6	305.00	70.7	72.0	75.0
¹ P ₁ ^o –	1351.44	0.01	0.03	435.21	2.3	3.0	0
³ P ₁ ^o – ¹ D ₂	906.24	(0.01)	5.4	270.02	(4)	29.2	0
³ P ₂ ^o –	912.54	(0.2)	2.7	280.76	(12)	39.8	0
¹ P ₁ ^o –	1501.76	(99.8)	92.0	387.47	(88)	31.0	100
³ P ₁ ^o – ¹ S ₀	658.08	0.04	0.06	238.11	1.1	1.7	0
¹ P ₁ ^o –	924.22	100	99.9	324.98	98.9	98.3	100
3s3p–3s3d							
³ P ₀ ^o – ³ D ₁	658.25	55.8	55.7	224.76	56.5	56.9	55.6
³ P ₁ ^o –	659.86	41.5	41.5	227.70	40.5	40.5	41.7
³ P ₂ ^o –	663.19	2.7	2.7	235.29	2.5	2.5	2.8
¹ P ₁ ^o –	927.72	0.01	0.01	305.89	0.5	0.1	0
³ P ₁ ^o – ³ D ₂	659.83	75.3	75.2	227.51	76.9	76.6	75.0
³ P ₂ ^o –	663.17	24.7	24.8	234.76	23.1	23.3	25.0
¹ P ₁ ^o –	927.67	0.01	0.04	305.00	0.01	0.1	0
³ P ₂ ^o – ³ D ₃	663.13	100	100	233.87	100	100	100
³ P ₁ ^o – ¹ D ₂	533.88	(0.3)	0.02	191.41	(4)	1.0	0
³ P ₂ ^o –	536.06	(0.01)	0.001	196.74	(0.04)	0.04	0
¹ P ₁ ^o –	696.62	(99.7)	100	243.79	(95.9)	99.0	100

BR denotes branching fractions, expressed in per cent. SE denotes semiempirical estimates from this work, MCHF denotes multiconfiguration Hartree-Fock calculations [12], and *LS* denotes *LS*-coupling coefficients. The SE values for ¹D₂ are enclosed in parentheses to indicate that they are heavily affected by configuration mixing, and not well suited to description by these methods.

spin-orbit parameters, the fits to the ¹D₂ effective energies and the resultant mixing angles, are all given in table 2. It can be seen that the fitting of the two configuration-mixed energy levels had the effect of elevating the lower ¹D₂ level, and of depressing the upper ¹D₂ level, both by approximately 10%. This fitting thus provides a semiempirical characterization of the familiar ‘repulsion’ that occurs between configuration-mixed levels.

Expressions for the E1 transition matrices based on *LS*-coupling coefficients and the corresponding mixing angles have been presented elsewhere: for the sp–sd transitions in [10, 7]; for the sp–p² transitions in [3, 7]. These expressions were used together with the wavelength-cubed factors to obtain the semiempirically predicted branching fractions (BF).

Semiempirical (SE) calculations made using the methods described above are listed in table 3. These values are compared in table 3 with multiconfiguration Hartree-Fock (MCHF)

values deduced (by culling the appropriate transition probabilities and normalizing them to a sum over lower levels for each upper level) from the compilation of Tachiev and Froese Fischer [12]. A comparison is also made with the simple *LS*-coupling coefficients.

Despite significant mixing due to both intermediate coupling and configuration interaction, the results are in striking agreement for all levels except the 1D_2 , which are strongly mixed with each other. The accuracy of the parametrization is in part due to the fact that deviations from the *LS* model are small enough to be accounted for by semiempirical means. However it is useful to note that for the $3s3p-3p^2$ transitions of the 1D_2 level, the configuration interaction effects are so strong that the normally forbidden singlet–triplet intercombination transitions dominate over the nominally allowed singlet–singlet transitions. (Note that in these calculations the fitted 1D_2 energy levels were used to compute the effective transition elements, but the measured energies were used in the wavelength-cubed factors.)

It is significant to note that, despite these strong perturbative effects, the branching fractions for all levels except the 1D_2 are described to good accuracy by these simple semiempirical methods. These results provide some confirmation in the assumption that sums over transition probabilities (lifetimes) require detailed specification of many perturbing interactions, whereas ratios of transition probabilities (branching fractions) can be significantly less sensitive to these perturbations. We therefore suggest that prudent application of these semiempirical methods could increase the available base of branched transition probability data in multiply charged ions.

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