Semi-empirical branching fractions of the $3s^23p^2$–$3s3p^3$ $J = 2$ transition array in P II[1]

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Abstract: A semi-empirical method is used to characterize the $3s^23p^2$–$3s3p^3$ $J = 2$ transition array in P II. In this method Slater, spin–orbit, and radial parameters are fitted to experimental energy levels to obtain a description of the array in terms of LS-coupling basis vectors. The intermediate coupling (IC) and configuration interaction (CI) amplitudes so obtained are then used to predict the branching fractions of transitions within the array. These two configurations are particularly interesting because the $3s^23p^2$ has been shown to be virtually free of CI, but affected by IC, whereas the $3s3p^3$ is virtually free of IC, but affected by CI.

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Résumé : Nous utilisons une méthode semi-empirique pour caractériser la série de transitions $3s^23p^2$–$3s3p^3$ $J = 2$ dans P II. Dans cette méthode, les paramètres de Slater, de spin–orbite et radial, sont ajustés aux données expérimentales en termes d'une base de vecteurs de couplage LS. Nous obtenons les amplitudes de couplage intermédiaire (IC) et d'interaction de configuration (IC) et nous les utilisons pour prédire les rapports de branchement des transitions dans la série. Ces deux configurations sont particulièrement intéressantes parce qu'on a découvert que le $3s^23p^2$ est pratiquement libre de CI, mais est affecté par IC, alors que c'est l'inverse pour le $3s3p^3$.

[Traduit par la Rédaction]

1. Introduction

Great strides have been made in the measurement of atomic lifetimes, and a large database now exists [1]. The specification of atomic transition rates has many applications, such as in the interpretation of astrophysical data, atmospheric physics, combustion, the modeling and diagnosis of thermonuclear plasmas, nonlinear optics, isotope separation, and the development of new types of lasers [2]. Most applications, however, require a knowledge of transition probabilities and oscillator strengths that (except for unbranched decays) can be deduced from lifetime data only through the knowledge of branching fractions. The measurement of branching fractions involves many challenges [3], such as the lack of intensity calibration standards in the ultraviolet range. Theoretical methods can often provide accurate estimates for strong LS-allowed transitions, where the theoretical calculation represents only a small correction to the LS value. For LS-forbidden transitions, where the theoretical correction comprises the entire amplitude, the accuracy can be greatly diminished. These weak transitions are important, since they provide unsaturated absorption line shapes. Thus, semi-empirical methods that incorporate experimental energy-level data into the specification of branching fractions offer an attractive alternative. The purpose of this paper is to attempt to extend those methods, using as an example a transition array in P II, which was studied for an application in astrophysics [4].

In light atoms, with a small central charge, relativistic effects are generally small, and it is convenient to describe such systems using the LS-coupling model. In any multielectron atomic system, however, LS-coupling fails as a precise model due to direct and exchange Coulomb interactions and spin–orbit effects. These interactions can be taken into account using the intermediate coupling (IC) model. In this approximation, each electron is described by a distinct wavefunction that is a linear combination of LS basis states with different L or S, but the same J. The IC model preserves the convenience of utilizing LS selection rules when identifying transitions, and it can be generalized to include configuration interaction (CI), in which the orthonormal basis set is extended to include LS states from different configurations.

In earlier studies [5] of the Si isoelectronic sequence, it was determined that both the $3s^23p^2$ ground configuration and the $3s^23p4s$ excited configuration are virtually free of CI, but both are affected by a significant amount of IC. Thus the IC amplitudes can be computed from the measured energies of, for the ground configuration the $^3P_{0,1,2}$, $^1D_2$, and $^1S_0$ levels and, for the excited configuration the $^3P^o_{0,1,2}$, $^1P^o_0$ levels.

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Table 1. Branching fractions (%).

Transition	Hibbert [13]	Tayal [14]	Fischer [15]	LS [20]	SE[a]	Exptl[b]
$^3P_1$–$^3D^o_2$	80.8	79.0	79.6	75.3	69.1	—
$^3P_2$–$^3D^o_2$	19.2	21.0	20.3	24.7	30.9	—
$^3P_1$–$^3P^o_2$	24.2	24.1	24.4	25.2	31.8	23±2
$^3P_2$–$^3P^o_2$	75.8	75.9	75.6	74.8	68.2	77±6

[a]This work, semi-empirical characterization of IC and CI.
[b]This work, experimental beam-foil excitation.

The $3s3p^3$ configuration provides a quite different case, since the half-filled p subshell has no linear dependence on the spin–orbit parameter, and Hund's rule favors high spin states. Thus the $3s^23p^2$–$3s3p^3$ transition array provides an instructive example in which the lower levels have substantial IC, but little CI, and the upper levels have substantial CI, but little IC.

To use the IC–CI model successfully to characterize an atomic system, it is necessary to obtain the mixing amplitudes that give the electronic eigenstates of the atom in terms of an LS basis set. These amplitudes may be determined ab initio, using iterative energy-minimization algorithms such as multi-configuration Hartree–Fock (MCHF) [6], or they can be arrived at semi-empirically. In this paper we use the latter approach, which incorporates the typically high spectroscopic precision of measured energy-level data [7, 8] into the calculation. Another possible method involves deducing IC amplitudes from Zeeman effect measurements of magnetic *g*-factors [9], but energy-level measurements are usually of much higher precision.

In the semi-empirical technique we use to model the system, the energies contained within the various interactions described above are treated as parameters and fitted to measured energy-level data. These parameters include the Slater direct and exchange energies, F^k and G^k; the spin–orbit energies, ζ_k; and the radial configuration interaction energy, R_k [10]. Linear combinations of the parameters are placed in a symmetric nondiagonal interaction matrix expressed in the finite LS basis of interest, where each matrix element corresponds to the Hamiltonian between two LS states. IC and CI mixing amplitudes are obtained by diagonalizing the matrix and finding its eigenvectors (cf. [11].), which correspond to single-electron wavefunctions in terms of LS basis states.

Thus, the energy parameters may be adjusted so that the roots of the characteristic equation of the interaction matrix fit these experimental coefficients [12]. This is accomplished using a numerical least-squares algorithm that searches parameter space for the global minimum of a χ^2 surface. When such a minimum is encountered, its parameter coordinates are printed and the interaction matrix may be expressed numerically. The eigenvalues and eigenvectors of the interaction matrix can then be found, giving the IC and CI mixing amplitudes that facilitate semi-empirical computation of branching fractions.

2. Application of the semi-empirical method to $3s3p^3$ $J = 2$ transitions in P II

In an earlier study [4] we performed fast ion beam measurements of lifetimes and relative intensities to determine the branching fractions and oscillator strengths of the $3s^23p^2$–$3s^23p4s$ transition array in P II. This was done to verify the phosphorus abundances in the interstellar medium of our galaxy. Both the upper and lower configurations of this array are virtually free of CI, but both exhibit significant IC. This study indicated that a semi-empirical calculation that utilizes measured energy level values to specify intermediate coupling amplitudes [5] produced results that were in excellent agreement with our experimental values and with recent theoretical calculations [13–15].

In addition to this astrophysical application, there is also theoretical interest [16, 17] in the branched decay of the metastable $3s3p^3\ ^5S^o_2$ level in P II. In an ion trap measurement [18], the lifetime of this level has been determined to be 1.67 μs. This level has the branched intercombination decays $3s^23p^2\ ^3P_{1,2}$–$3s3p^3\ ^5S^o_2$, and both the lifetime [18] and the branching ratio [19] of the two intercombination channels have been measured, and provide important tests of theoretical methods. The use of these intercombination lines as a diagnostic of astrophysical and laboratory plasmas has also been suggested [16].

The $J = 0$ and $J = 3$ levels each contain only a single LS eigenvector ($^3P^o_0$ and $^3D^o_3$) and are not affected by IC. The $J = 1$ and $J = 2$ levels each contain four LS eigenvectors ($^3S^o_1$, $^1P^o_1$, $^3P^o_1$, $^3D^o_1$, and $^5S^o_2$, $^3P^o_2$, $^1D^o_2$, $^3D^o_2$). Because of the half-filled p shell, however, there is no linear dependence on the spin–orbit interaction to produce IC. There is quadratic dependence, and since the spin–orbit interaction varies as Z^4, IC could increase with increasing Z along the isoelectronic sequence.

To gain insight into these two applications, we sought to extend this semi-empirical method to characterize the effects of CI and IC in a more intuitive manner than is afforded by ab initio numerical calculations. Thus we undertook this study of the dipole-allowed transitions in P II of the $J = 2$ levels of the $3s3p^3$ configuration to the various levels of the $3s^23p^2$ configuration.

3. Calculations

Due to significant configuration interaction between the $3s3p^3$ and $3s^23p3d$ upper states, it was necessary to devise an 8×8 interaction matrix for $J = 2$ that would take the levels of both of these upper configurations into account. This matrix included the average configuration energies of the upper and lower levels E_A and E_B in addition to the other parameters mentioned earlier, making ten parameters total. The coefficients of the various parameters were determined from tables in Condon and Shortley [20]. The model was underdetermined, so, to make the system overdetermined and "steer"

the χ^2 fit into a physical result with some empirical and ab initio information, E_A and E_B were set to the measured average configuration energies, while R_1, ζ_p, and ζ_d were fixed to MCHF [6] values.

An attempt was made to predict branching fractions for the desired $3s^23p^2$–$3s3p^3$ transitions in the P II spectrum using the semi-empirical intermediate-coupling method of Curtis [11]. This method has been used successfully for branching fractions in two-electron spectra [5], and can in principle be extended to more complex configurations [12]. In the present case we considered the CI between the $3s3p^3$ and $3s^23p3d$ configurations as well as the IC caused by the spin–orbit interactions within those configurations and also within the $3s^23p^2$ configuration.

For this upper $J = 2$ case, we set up the 8×8 energy matrix for the basis states,

$|3s3p^3\ ^5S^o_2\rangle$, $|3s^23p3d\ ^3F^o_2\rangle$
$|3s3p^3\ ^3D^o_2\rangle$, $|3s^23p3d\ ^3D^o_2\rangle$
$|3s3p^3\ ^3P^o_2\rangle$, $|3s^23p3d\ ^3P^o_2\rangle$
$|3s3p^3\ ^1D^o_2\rangle$, $|3s^23p3d\ ^1D^o_2\rangle$

We then performed a nonlinear, weighted least-squares fit of the eigenvalues of the 8×8 matrix to the observed energy levels.

The resulting eigenvectors showed mixing amplitudes ranging up to about 0.26, with the strongest resulting from the CI between each term of $3s3p^3$ and the corresponding term of $3s^23p3d$. (This should not be surprising since the p^2–sd interaction is often strong.) Using these eigenvectors and a semi-empirical determination of the IC eigenvectors for the ground state configuration, we computed transition probabilities and hence branching fractions. Comparisons of the semi-empirical values (denoted SE) with theory [13–15] and the LS-coupling limit [20] (denoted LS) are given in Table 1, together with our preliminary experimental results (denoted Exptl).

The experimental measurements reported here were obtained from relative intensity measurements using the Toledo Heavy Ion Accelerator for beam-foil excitation.

Clearly a comparison of the semi-empirical results with the theoretical and experimental values indicates an overestimate of the deviation from pure LS-coupling. This is probably due to the very small amount of IC in the case of the $3s3p^3$ configuration that was being parametrized. The fact that the method did yield convergence, however, encourages its extension to systems for which IC effects are more substantial.

As one example, studies of these same transitions might be extended to isoelectronic ions of higher Z, where the quadratic nature of the spin–orbit interaction might increase the IC coupling to a point where it is commensurate with the CI, allowing the matrix to be diagonalized with more accuracy. Another application might be to high-Z ions such as the Pb sequence, where the complexity is challenging to theoretical methods.

4. Conclusions

A semi-empirical method that utilizes measured energy level data to deduce branching fractions in transition arrays between two pure, but intermediate-coupled configurations has been extended to include the effects of configuration interaction. The method has been applied to an unusual situation that occurs in P II, in which the lower configuration has IC, but no CI, and an upper configuration that has CI, but little IC.

Although the results obtained in this analysis are inferior to those obtained by ab initio theoretical methods, the fact that the approach uses measured energy levels to specify the branching fractions suggests that it could be useful if applied to very heavy many-electron systems, which could test theoretical methods in this regime.

In view of the lack of comprehensive data for branching fractions, this method provides a possible alternative. Plans are underway to upgrade the ion source of the Toledo Heavy Ion Accelerator to produce multiply-charged higher-energy beams that can facilitate such measurements.

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References

1. L.J. Curtis. Phys. Scr. **T120**, 9 (2005). doi:10.1088/0031-8949/2005/T120/001.
2. L.J. Curtis. *In* Handbook of atomic, molecular, and optical physics. Chap. 17. *Edited by* G.W.F. Drake. Springer–Verlag, Berlin, Germany. 2005. pp. 259–266.
3. L.J. Curtis, S.R. Federman, S. Torok, M. Brown, S. Cheng, R.E. Irving, and R.M. Schectman. Comments At. Mol. Opt. Phys. Phys. Scr. **75**, C1 (2007).
4. S.R. Federman, M. Brown, S. Torok, S. Cheng, R.E. Irving, R.M. Schectman, and L.J. Curtis. Astrophys. J. **660**, 919 (2007). doi:10.1086/513463.
5. L.J. Curtis. J. Phys. B, **33**, L259 (2000). doi:10.1088/0953-4075/33/7/103.
6. C.F. Fischer, T. Brage, and P. Jönsson. Computational atomic structure. Institute of Physics, Bristol, UK. 1997.
7. W.C. Martin, R. Zalubas, and A. Musgrove. J. Phys. Chem. Ref. Data, **14**, 751 (1985). doi:10.1063/1.555736.
8. N. Svendenius, C.E. Magnusson, and P.O. Zetterberg. Phys. Scr. **27**, 339 (1983). doi:10.1088/0031-8949/27/5/005.
9. H. Li. J. Opt. Soc. Am. **62**, 1483 (1972). doi:10.1364/JOSA.62.001483.
10. L.J. Curtis. Atomic structure and lifetimes: a conceptual approach. Cambridge University Press, Cambridge, UK. 2003.
11. L.J. Curtis. Phys. Rev. A, **40**, 6958 (1989). doi:10.1103/PhysRevA.40.6958. PMID:9902107.
12. L.J. Curtis, Z.B. Rudzikas, and D.G. Ellis. Phys. Rev. A, **44**, 776 (1991). doi:10.1103/PhysRevA.44.776. PMID:9905732.
13. A. Hibbert. Phys. Scr. **38**, 37 (1988). doi:10.1088/0031-8949/38/1/006.
14. S.S. Tayal. Astrophys. J. **146**, Suppl., 459 (2003). doi:10.1086/367856.
15. C. Froese Fischer, G. Tachiev, and A. Irimia. At. Data Nucl. Data Tables, **92**, 607 (2006). doi:10.1016/j.adt.2006.03.001.
16. D.G. Ellis and I. Martinson. Phys. Scr. **30**, 255 (1984). doi:10.1088/0031-8949/30/4/007.
17. M. Andersson and T. Brage. J. Phys. B, **40**, 709 (2007). doi:10.1088/0953-4075/40/4/006.

18. A.G. Calamai, X. Han, and W.H. Parkinson. Phys. Rev. A, **45**, 2716 (1992). doi:10.1103/PhysRevA.45.2716. PMID: 9907299.
19. J.J. Curry and J.E. Lawler. Astron. Astrophys. **328**, 752 (1997).
20. E.U. Condon and G.H. Shortley. The theory of atomic spectra. University Press, Oxford, UK. 1935.