Cancellation effects in alkalilike doublet lifetimes

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A recent lifetime measurement of the $7p$ levels in Pb IV yielded an anomalous ratio $\tau(^2P_{1/2})/\tau(^2P_{3/2}) \cong 6$. This result is shown to be a consequence of a nearly complete cancellation in the $6s$–$7p$ radial transition moment of the $^2P_{1/2}$ level, coupled with the influence of wavelength-cubed factors on the $7s$–$7p$, $6d$–$7p$, and $6s^2$–$7p$ transition probabilities. Cancellation effects that suppress the intensity of one branch of the decay of a level are a common feature of $\Delta n > 0$ transitions in alkali sequences, but this measurement demonstrates that these effects can also produce strong lifetime anomalies. The cancellation effects that produce this specific lifetime anomaly are examined isoelectronically, and the use of lifetime measurements near such cancellations as a probe of secondary interactions is discussed.

Une mesure récente du temps de vie des niveaux $7p$ de Pb IV a fourni la valeur anormale de 6 pour le rapport $\tau(^2P_{1/2})/\tau(^2P_{3/2})$. On montre que ce résultat est la conséquence d'une annulation presque complète dans le moment radical de transition $6s$–$7p$ du niveau $^2P_{1/2}$, couplée avec l'influence de facteurs proportionnels au cube de la longueur d'onde sur les probabilités de transition $7s$–$7p$, $6d$–$7p$ et $6s^2$–$7p$. Les effets d'annulation qui suppriment l'intensité d'une branche de la décroissance d'un niveau sont une caractéristique commune des transition $\Delta n > 0$ dans les séquences alcalines, mais cette mesure démontre que les effets en question peuvent aussi donner lieu à de fortes anomalites des temps de vie. Les effets qui produisent ce cas spécifique d'anomalie sont examinés du point de vue isoélectronique, et l'utilisation des mesures de temps de vie au voisinage de telles annulations comme moyen de sonder les interactions secondaires est discutée.

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1. Introduction

Atomic transition moments sometimes exhibit cancellation effects that can cause a normally strong transition to be weak or totally absent in certain observed spectra. These cancellation effects can have important consequences and applications and for example, can cause low-lying resonance transitions (that would otherwise be saturated in absorption spectra) to possess an experimentally analyzable unsaturated line shape. This suppression of the primary decay interaction also can cause *ab initio* calculations to become extremely sensitive to effects such as electron correlation, configuration interaction, relativistic corrections, higher order moments, etc. The existence of a cancellation can permit these secondary interactions to be probed through systematic measurements in the vicinity of the cancellation, e.g., along an isoelectronic sequence, across a fine structure multiplet, or along a Rydberg series.

In systems with multiple out-of-shell electrons, cancellations can occur as a result of the mixing of amplitudes due to configuration interaction, which must be studied on an individual basis. Another type of cancellation can occur within a single-electron radial integral, as a result of phase shifts in the wave function due to core polarization and penetration. These radial integral cancellations, which are the subject of this note, can be systematized through quantum defect parametrizations, and the conditions for their occurrence can be predicted by simple methods.

It has long been known that intensity anomalies occur for $\Delta n > 0$ alkalilike doublet transitions. Rasetti (1) found in 1924 that the relative intensities of the $6s$–$7p$ fine structure doublet lines in Cs I deviated significantly from the 2:1 rule that had been established for the lowest member of the principal series in the various alkali spectra. Similar results (2) were obtained for doublet intensity ratios in other ns–$n'p$ ($n' > n$) transitions in neutral atoms, and in 1930 Fermi (3) presented a theoretical explanation for these anomalies. In ionized atoms the effect was even more striking, and it was noted in early vacuum ultraviolet (VUV) studies that both of the fine structure lines of the $3s$–$4p$ multiplet in Mg II were very weak in comparison to the corresponding transitions in Na I (B. Edlén, personal communication).

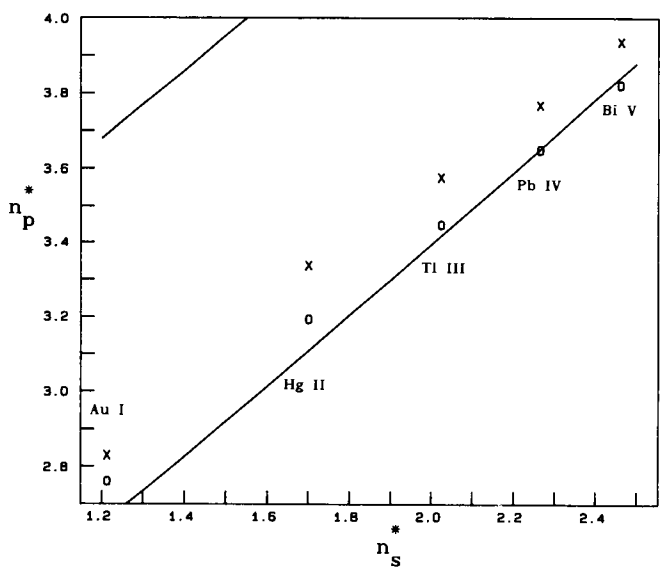

FIG. 1. Plot of n_p^* vs. n_s^* for the $7s$–$7p$ transitions in the isoelectronic ions Au I, Hg II, Tl III, and Pb IV. The J-dependent fine structures are denoted by (0) for $^2S_{1/2}$–$^2P_{1/2}$ and by (×) for $^2S_{1/2}$–$^2P_{3/2}$. The solid lines trace the loci where cancellations occur in the radial matrix element as calculated by quantum defect methods.

The existence of large cancellation effects in a specific transition probability does not necessarily lead to a correspondingly large anomaly in the lifetime of the upper level. Since these cancellations occur only in $\Delta n \neq 0$ transitions, other decay branches usually exist, and f sum rules tend to redistribute the missing oscillator strength among the other allowed exit channels. A recent lifetime measurement of the $7p$ levels in Pb IV provides an example in which both intensity and lifetime anom-

TABLE 1. Coulomb approximation calculations for the transition probabilities and lifetimes for the $6s$–$7p$, $7s$–$7p$, and $6d$–$7p$ levels in Pb IV, with comparisons to the measured lifetimes

Transition	J–J'	λ(Å)	$A(\text{ns}^{-1})^a$	J–J'	λ(Å)	$A(\text{ns}^{-1})^a$
$6s\ ^2S_J - 7p\ ^2P_{J'}$	1/2–1/2	477	0.0072	1/2–3/2	459	0.3758
$7s\ ^2S_J - 7p\ ^2P_{J'}$	1/2–1/2	4051	0.1849	1/2–3/2	3054	0.3983
$6d\ ^2D_J - 7p\ ^2P_{J'}$	3/2–1/2	3964	0.1717	3/2–3/2	3004	0.0302
				5/2–3/2	3222	0.2436
$6s^2\ ^2D_J - 7p\ ^2P_{J'}$	3/2–1/2	1147	—	3/2–3/2	1049	—
				5/2–3/2	858	—
Total $A(\text{ns}^{-1})$			0.3638			1.0479
Calculated lifetime[a] (ns)			2.75			0.95
Experimental lifetime[b] (ns)			2.90 ± 0.15			0.48 ± 0.05

[a]Coulomb approximation calculation using the program of ref. 15.
[b]Beam foil measurement, ref. 4.

alies occur. In this beam foil study (4), which utilized the correlated analysis of decay curves (ANDC) method (5) to account for cascade repopulation, it was observed that the $7p\ ^2P_{1/2}$ level had a lifetime six times longer than that of the $7p\ ^2P_{3/2}$ level. The purpose of this note is to explore the cancellation effects that produced this anomaly, and to examine the theoretical implications of this result.

2. Semi-empirical formulation

In alkalilike systems, cancellation effects can be formulated in terms of differential phase shifts of the upper and lower state radial wave functions due to polarization and penetration contributions to the quantum defect. As the central charge increases along an isoelectronic sequence, the phase of the radial wave function (in terms of the charge-scaled radial coordinate) is drawn in for a core-polarizing orbital and pushed out for a core-penetrating orbital. Differential phase shifts of this type in the initial and final state radial wave functions lead to regular isoelectronic cancellations in the transition moment, which sometimes correspond to physical ions, as a continuous function of Z.

We earlier developed a simple graphical technique (6–8), based on the quantum defect method, that uses empirical data to locate regions of likely cancellation. It can be shown both by the use of the Wentzel–Kramers–Brillouin (WKB) approximation (9) and by numerical computations (10) that the transition matrix in the single electron model can be written as a periodic function of the effective quantum numbers n_l^* and $n_{l'}^*$ of the lower and upper levels. The zeros of this periodic function are prescribed by the condition (6)

$$[1] \quad n_{l'}^* = n_l^* + k + \frac{1}{2} + a_{ll'} + \frac{b_{ll'}}{n_l^*} + \frac{c_{ll'}}{n_l^{*2}} - \frac{\alpha_{ll'}}{(n_{l'}^{*2}/n_l^* - 1)} - \frac{\beta_{ll'}}{(n_{l'}^{*2}/n_l^{*2} - 1)}$$

where numerical values for $a_{ll'}$, $b_{ll'}$, $c_{ll'}$, $\alpha_{ll'}$, and $\beta_{ll'}$, are given in ref. 10, and k is an arbitrary integer that defines each member of a family of curves. Thus the loci of the cancellation nodes in the quantum defect approximation can be displayed on a single generic plot of $n_{l'}^*$ vs. n_l^* for all transitions for each pair of l' and l values and their upper–lower transposed values $l \Leftrightarrow l'$. The positions of the experimentally determined effective quantum numbers for a specific transition in a given isoelectronic sequence can be added to this plot, and cancellation effects can be expected wherever the experimental loci cross the computed nodes. An example is shown in Fig. 1.

The precise values of $n_{l'}^*$ and n_l^* for which a cancellation will actually occur are expected to differ slightly from those predicted by the plot, since small perturbations neglected in the quantum defect calculation could shift the position of the cancellation nodes. Examples of shifts in the positions of the cancellation nodes caused by core polarization corrections are presented in ref. 8. this is the basis for the technique of "disappearance spectroscopy," in which a given transition is experimentally traced along an isoelectronic sequence in search of weak or anomalously absent intensities. In this manner the position of the cancellation can be determined by interpolation even if it does not correspond to the Z of a physical ion. Similarly, experimental measurements of intensities and lifetimes among fine structure components can be used to locate the exact position of the cancellation. These studies can provide a useful probe of secondary interactions that would otherwise be masked by the interaction that is absent at cancellation.

3. Results

Figure 1 presents a plot of the quantum defects for the $6s$–$7p$ transitions obtained from experimental energy level data for the ions Au I (11, 12), Hg II (11), Tl III (13), Pb IV (13), and Bi V (11, 14), together with the cancellation nodes predicted by [1]. The fine structure lines of these doublets are denoted by (0) for $J = 1/2$–$1/2$, and by (×) for $J = 1/2$–$3/2$, and the cancellation nodes are traced by solid lines. Notice that the 1/2–1/2 point coincides with the cancellation node for Pb IV. A similar study of the $7s$–$7p$ and $6d$–$7p$ transitions showed that they lie in a region of their plots that is well separated from all cancellation nodes.

Table 1 presents calculations of the transition probabilities made using the Coulomb approximation (15), which yield lifetimes that agree with the results of similar calculations reported in ref. 4. Cancellation effects cause the resonance transition probability of the $^2P_{1/2}$ level to be reduced by a factor of 50. Furthermore, the wavelength-cubed dependence reduces the transition probabilities of the $^2P_{1/2}$ level relative to those of the $^2P_{3/2}$ level by a factor of two for the $7s$–$7p$ and $6d$–$7p$ decay channels. The branches to the $5d^9\ 6s^2\ ^2D_J$ levels require a configuration interaction calculation and were neglected here. However, the wavelength-cubed dependence would also reduce the transition probability of the $^2P_{1/2}$ level relative to those of the $^2P_{3/2}$ level by over a factor two for the $6s^2$–$7p$ channel. Since these transitions at 858 and 1147 Å were observed in the meas-

urements of ref. 4 (with the 1147 Å line considerably weaker, as expected from λ^3), these channels should be included in a proper *ab initio* calculation.

Table 1 also presents a comparison between computed and measured (4) lifetimes. Although the computed results presented here qualitatively reproduce the experimental observation that the lifetime of the $^2P_{1/2}$ level is much longer than that of the $^2P_{3/2}$ level, the $6s\ ^2S_{1/2} - 7p\ ^2P_{1/2}$ calculation cannot be expected to be reliable in the presence of such strong cancellation effects. However, for a transition that is so close to cancellation, it can be argued that the use of the correct experimental energies in a semiempirical Coulomb approximation calculation may make it superior to a more sophisticated *ab initio* calculation that does not precisely reproduce the experimental energy values.

The position of the cancellation nodes in Fig. 1 represents an estimate of this phenomenon in the simplest semiempirical approximation, and the study of the J dependence of the $7p$ lifetime ratio along the Au sequence could permit the true physical position of these nodes to be determined. Lifetime measurements already exist for Pb IV (4) and Bi V (16), and a measurement of the $7p$ lifetimes in Tl III could be used to interpolate values through the cancellation node. This example illustrates that isoelectronic studies of the J dependence of lifetimes near cancellations in alkalilike isoelectronic sequences can sensitively test *ab initio* calculational approaches.

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1. F. Rasetti. Nuovo Cimento Ser. 8, **1**, 115 (1924).
2. H. E. White. Introduction to atomic spectra. McGraw–Hill, New York. 1934. pp. 118–121.
3. E. Fermi. Z. Phys. **59**, 680 (1930).
4. E. H. Pinnington, W. Ansbacher, A. Tauheed, and J. A. Kernahan. Can. J. Phys. **69**, 594 (1991).
5. L. J. Curtis, H. G. Berry, and J. Bromander. Phys. Lett. **34A**, 169 (1971).
6. L. J. Curtis and D. G. Ellis. J. Phys. B: At. Mol. Phys. **11**, L543 (1978).
7. L. J. Curtis and D. G. Ellis. J. Phys. B: At. Mol. Phys. **13**, L431 (1980).
8. L. J. Curtis. J. Opt. Soc. Am. **71**, 566 (1981).
9. C. Fabre and S. Haroche. *In* Rydberg states of atoms and molecules. *Edited by* R. F. Stebbings and F. B. Dunning. Cambridge Univ. Press, Cambridge. 1983. pp. 117–164.
10. A. Burgess and M. J. Seaton. Mon. Not. R. Astron. Soc. **120**, 121 (1960); Rev. Mod. Phys. **30**, 992 (1958).
11. C. E. Moore. Atomic energy levels. Vol. III. United States National Bureau of Standards Reference Data Series 35, U.S. Government Office, Washington DC. 1957 (reissued 1971).
12. J. C. Ehrhardt and S. P. Davis. J. Opt. Soc. Am. **61**, 1342 (1971).
13. F. Gutmann and A. M. Crooker. Can. J. Phys. **51**, 1823 (1973).
14. A. J. J. Raassen, A. A. van der Valk, and Y. N. Joshi. J. Phys. B: At. Mol. Phys. **22**, 13 (1989).
15. C. E. Theodosiou. Coulomb approximation program CAMATREL. University of Toledo. 1982.
16. W. Ansbacher, E. H. Pinnington, A. Tauheed, and J. A. Kernahan. Phys. Scr. **40**, 454 (1989).