Cancellations in atomic dipole transition moments in the Cu isoelectronic sequence

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A number of cancellation anomalies in lifetimes and emitted intensities in the Cu isoelectronic sequence are predicted, and their use as an experimental probe of small perturbations is discussed.

The spectra of alkalilike ions often exhibit anomalously weak or even vanishing intensities for an isolated member of an isoelectronic sequence, a Rydberg series, or a fine structure multiplet because of cancellation effects in the dipole transition moment. A knowledge of the precise location of these cancellation occurrences is useful in the interpretation of spectroscopic measurements, and their study can provide a probe of small perturbations (core polarization, configuration interaction, higher moments, relativistic corrections, etc.) that are normally concealed by the dominant interaction. A simple graphical technique has been developed[1,2] by which these cancellation conditions can be located from experimental energy-level data. The Cu isoelectronic sequence has recently been the object of a number of spectroscopic investigations,[3-12] and the purpose of this paper is to apply this graphical technique to identify specific transitions in this sequence that should be severely affected by cancellations and to consider the influences of various small perturbations on the cancellations.

By using the formalism of the quantum defect theory (QDT),[13] cancellation conditions can be expressed as a continuous function of the effective quantum numbers n_l^* and $n_{l'}^*$ of the two Rydberg series connected by the transition. Through a plot of n_l^* versus $n_{l'}^*$ cancellation conditions are displayed as a calculable[1,13,14] family of nodal curves, and a physical transition in a given ion is represented by a point with its coordinates deduced from measured term values. A portion of such a plot for the nd–$n'f$ transitions in the Cu sequence is shown in Fig. 1 (the individual fine structure components do not show up on a plot of this scale). The division markers on the transition loci represent (from left to right) the ions Cu I through Mo XIV, with enlarged markers at As V and Sr X. In cases for which no measured values are available, an interlocking set of isoelectronic interpolations and Ritz parameter extrapolations was used to estimate the effective quantum numbers.[15]

From Fig. 1 it can be seen that the QDT predicts strong cancellation effects in the following transitions and charge regions: in $4d$–$5f$ between Kr VIII and Rb IX, in $4d$–$6f$ for Br VII, in $4d$–$7f$ between Se VI and Br VII, in $5d$–$6f$ for Y XI, in $5d$–$7f$ for Rb IX, and in $6d$–$7f$ between Mo XIV and Tc XV. A similar plot for the np–$n'd$ transitions in this sequence was presented in Ref. 1, which predicted a cancellation in $4p$–$5d$ for Kr VIII; an extension of this plot suggests additional cancellations in $4p$–$6d$ for Br VII and in $5p$–$6d$ for Sr X.

In the QDT it is assumed that fine structure splittings and other relativistic effects can be accounted for entirely by the external portion of the wave function through the use of the experimental effective quantum numbers. A test of this assumption for the Cu sequence is possible, since Dirac–Hartree–Fock (DHF) calculations are available[16] for a number of the transitions discussed above. A comparison with Ref. 16 shows that the charge state regions of maximum cancellation predicted by the QDT and DHF calculations are in good agreement for the $4d$–$5f$, $4d$–$6f$, $4p$–$5d$, $4p$–$6d$, and $5p$–$6d$ transitions, but that DHF calculations predict the cancellation in $5d$–$6f$ to be about one ionization stage lower (in Sr X rather than Y XI) than does the QDT. There are also differences between the DHF and QDT predictions for the relative oscillator strengths for the individual fine structure components near cancellations. The DHF predictions for the excitation energies have been found to be slightly lower (about 1% for Kr VIII[5] and decreasing with increasing stage of ionization) than

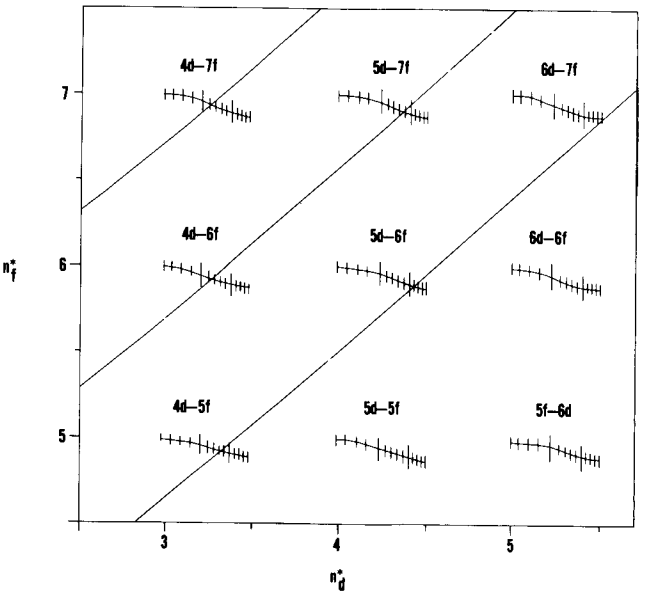

Fig. 1. Plot of n_d^* versus n_f^*. The empirical values are indicated for each Rydberg transition by an isoelectronically connected locus, marked with a vertical line at each ion from Cu I to Mo XIV (enlarged for As V and Sr X to guide the eye). The curves represent the computed cancellation nodes.

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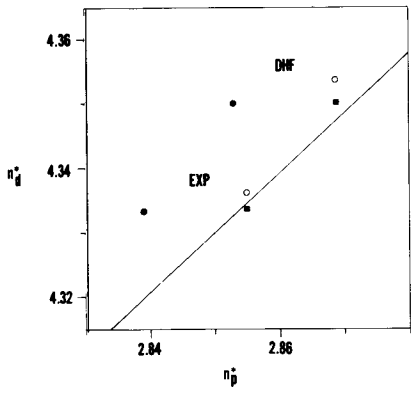

Fig. 2. Plot of n_p^* versus n_d^* in the vicinity of the cancellation in Kr VIII. Solid circles, $^2P_{1/2}$–$^2D_{3/2}$; solid squares, $^2P_{3/2}$–$^2D_{3/2}$; open circles, $^2P_{3/2}$–$^2D_{5/2}$. Both the experimental values (Ref. 5) and the DHF values (Refs. 16 and 17) are given. The curve is the computed cancellation node.

the measured values, which could introduce shifts in the sensitive region near a cancellation. Figure 2 shows a plot of n_p^* versus n_d^* near the $4p$–$5d$ cancellation in Kr VIII, enlarged to show the individual fine structure components. Both the experimental values[5] (using the ionization potential suggested in the note added in proof of Ref. 5) and the DHF values[16] (using an ionization potential computed by Cheng[17]) of the effective quantum numbers are plotted here. This clearly indicates how sensitive the proximity of the individual fine structure components to the cancellation node is to the values of the effective quantum numbers and the calculation of the node. To gain insight into the relationship between DHF and QDT computations, DHF values for the excitation energies[16] and ionization potentials[17] were used to deduce theoretical n^* values, which were then used as inputs to a QDT calculation of the oscillator strength.[13] However, these oscillator strengths were generally found to be in poorer agreement with the full DHF calculations than were QDT calculations using experimental n^* values.

There is already some experimental verification for the predictions of Figs. 1 and 2. Acquista and Reader[6] have studied the $4d$–$5f$ transition intensity isoelectronically and have found that, although it is fairly strong for Y XI–Mo XIV (Refs. 8–11), in Sr X (Ref. 6) the $4d\ ^2D_{5/2}$–$5f\ ^2F_{7/2}$ is weak and the $4d\ ^2P_{3/2}$–$5f\ ^2F_{5/2}$ is totally absent. Figure 1 predicts that the $4d$–$5f$ cancellation centers between Kr VIII and Rb IX. In a beam–foil experiment, Livingston *et al.*[5] observed two weak lines that were assigned to the Kr VIII $4d$–$5f$ transition. These lines were also searched for but not found in low-inductance spark spectra taken by Reader.[18] The $4p$–$5d$ transition was absent for Kr VIII in both the beam–foil spectra of Livingston *et al.*[5] and the spark spectra of Reader,[18] although it is seen in both Se VI (Ref. 3) and Sr X (Ref. 6).

In the vicinity of a cancellation, small perturbations can shift the position of the cancellation in effective quantum-number space and cause substantial changes in the predicted oscillator strengths for the physical ions. As a qualitative example of this type of shift, estimates were made of the contribution of core polarization to a number of these transitions, using a semiempirical approach. Nonrelativistic Hartree–Fock calculations[19] were carried out using a simple model that includes core polarization effects in the transition operator[20,21] but not in the model potential. The dipole polarizability α_d of the nickel-like core was estimated using a classical deformable core model[22] to describe the nonpenetrating $l \geq 4$ term values in Kr VIII, Y XI, Zr XII, and Mo XIV (the Nb XIII data inferred negative polarizabilities and were excluded). These results are only order-of-magnitude estimates but could be roughly represented by $\alpha_d \simeq [9/(\zeta + 7)]^4 a_0^3$, where ζ is the net charge of the core. Since the d and f wave functions are only weakly core penetrating, the sensitivity of the r^{-2} induced-dipole-moment integral[20,21] to the small r cutoff (which is important when s–p transitions are corrected for core polarization) was slight. The results are shown in Fig. 3. The solid lines denote the basic Hartree–Fock calculations for the oscillator strength (with $\alpha_d = 0$), and the dashed curves include core polarization, as described above. Although these calculations contain many uncertainties, they clearly illustrate how isoelectronic measurements of the intensities of these transitions near a cancellation could provide information about effects such as core polarization. These intensity measurements could be made, for example, relative to the $4d$–$6p$ transitions, which are of similar wavelength but have no cancellations for multiply ionized states.

Transitions between s and p Rydberg series in alkalilike systems provide another interesting example, since the isoelectronic n_s^*–n_p^* loci are nearly parallel to the nodal lines. This leads to a situation in which near cancellations occur not only for a single transition in a single ion but for several neighboring ions in the sequence and for many different members of the Rydberg series. An example of this is shown in Fig. 4. Notice that the ns–$n'p$ transitions fall close to cancellation nodes for Zn II, Ga III, and Ge IV for all $n' > n$ (this behavior is typical for n_s^*–n_p^* plots for all alkalilike systems). Thus the resonance branches of all but the lowest lying np levels are strongly canceling for the first few ions of this sequence, leading to a lengthening of the level lifetimes. Unfortunately, the use of this single configuration model is

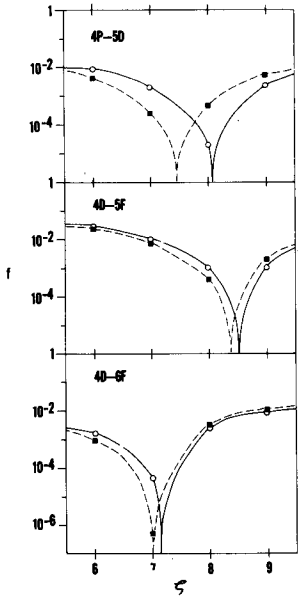

Fig. 3. Semilogarithmic plot of oscillator strength versus core charge. Solid lines trace standard Hartree–Fock calculations; dashed lines trace calculations corrected for core polarization effects.

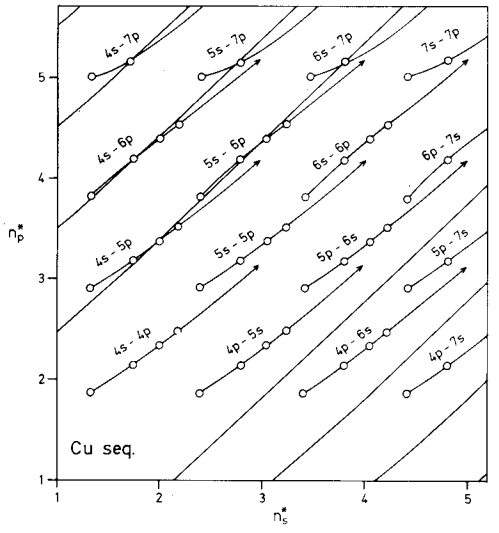

Fig. 4. Plot of n_s^* versus n_p^*. The circles represent the experimental values for the ions Cu I–Ge IV, and the curves represent the computed cancellation nodes.

Table 1. Lifetimes (in nsec) of the $n > 4$ ^2P Levels of Zn II (from Ref. 15)

n	$\tau(^2P_{1/2})$	$\tau(^2P_{3/2})$
5	17.1	15.5
6	70.2	64.9
7	231.3	177.1
8	15.4	209.4

probably unreliable for these low stages of ionization, since configuration interaction with excited core states (which move into the single-electron continuum for higher stages of ionization) can lead to substantial perturbations. The principal series in Zn II provides an interesting example, since the $3d^{10}$ np and $3d^9$ $4s4p$ configurations interact strongly, leading to pronounced fine structure perturbations.[23] This perturbation is extremely strong for the $8p$ $^2P_{1/2}$ level, affecting its energy so greatly that it moves *off* the cancellation node. The numerical Coulomb approximation calculations of Ref. 15 are reproduced in Table 1 to illustrate an unusual effect. The anomalously short lifetime of the $8p$ $^2P_{1/2}$ level (15.4 nsec) arises from the fact that it is the only level in this table that *does not* have severe cancellation effects in this QDT treatment. Measurements of the relative lifetimes of this fine structure multiplet could provide a useful test of the effect of configuration interaction on these cancellation effects and determine whether the QDT has any applicability in the presence of such perturbations.

Thus experimental studies both of emitted intensities and of lifetimes in the vicinity of cancellations can provide a sensitive probe of small perturbations to the transition process.

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