J. Phys. B: Atom. Molec. Phys. **13** (1980) L431–L435. Printed in Great Britain

LETTER TO THE EDITOR

Cancellations in transition probabilities of the K I isoelectronic sequence

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Received 15 May 1980

Abstract. The use of anomalies in emitted intensities due to cancellations of the transition integral is suggested as a probe of small model-dependent effects. Calculations of predicted anomalies in both the total intensity and in the relative intensities of fine-structure components are presented for specific transitions in certain ions of the K I isoelectronic sequence, which indicate the experimental feasibility of this approach.

The Hartree–Fock method and its variations have been found to predict dipole transition probabilities in alkali-like systems accurately in those cases for which precise experimental measurements are available. However, such calculations are untested and probably unreliable where cancellations cause the transition integral to approach zero, since they become extremely sensitive to small effects such as electron correlations, configuration interaction, relativistic corrections, higher multipole moments, etc, whose inclusion in the Hartree–Fock picture is highly model dependent. Thus experimental studies of lifetimes and emitted intensities near a cancellation could serve as sensitive probes of small contributions to the transition process. Exactly at a cancellation, radiation would of course be unobservable. However, the cancellation could be located by a study of the approach to extinction in neighbouring systems either (*a*) along an isoelectronic sequence, (*b*) along a Rydberg series or (*c*) within a fine-structure multiplet. A shift in the position of the cancellation from that predicted by the unperturbed theory would indicate the presence and magnitude of corrections to this model. A simple graphical technique based on the semiempirical quantum defect method was developed earlier (Curtis and Ellis 1978) which is useful in identifying transitions for which cancellation effects are severe, and thus for which small corrections should become important. In a recent letter, Theodosiou (1980) presented a theoretical study of cancellation effects in potassium and caesium which included core polarisation and fine-structure effects. The purpose of the present letter is to apply the simple graphical methods to the potassium isoelectronic sequence to illustrate how a systematic study of the experimental intensity anomalies near cancellation conditions could provide a very sensitive probe of small perturbations to the transition interaction.

Our approach here is to study transitions near a change of sign in the dipole transition moment of the valence electron of an alkali-like system, such that

$$\langle \psi_i | \boldsymbol{d} | \psi_k \rangle \simeq 0 \tag{1}$$

where ψ_i and ψ_k are computed within some well defined single configuration picture.

0022-3700/80/140431+05$01.50

The Hartree–Fock (HF) and the quantum defect methods (QDM) offer two such alternatives. Although the *ab initio* HF (Froese Fischer 1969, 1972) method is usually preferable to the semiempirical QDM (Bates and Damgaard 1949, Seaton 1958, Burgess and Seaton 1960) in situations far from cancellations, the HF method often exhibits small systematic shifts in predicted energy levels relative to measured values, to which the cancellation could be very sensitive. Thus it is arguable that the QDM, which utilises experimental energy levels, could yield a better estimate of the transition moment near a cancellation.

In order to locate conditions which approach equation (1) in Rydberg transitions along an isoelectronic sequence, a simple graphical method based on the QDM was developed earlier (Curtis and Ellis 1978). Here cancellation conditions are formulated as a continuous function of the effective quantum numbers, n_l^* and $n_{l'}^*$, of the two Rydberg series connected by the transitions. Through a plot of n_l^* against $n_{l'}^*$, cancellation conditions are displayed as a calculable 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. Isoelectronic trajectories for the various Rydberg transitions can be plotted and their crossing with a nodal curve indicates a possible physical cancellation. A portion of such a plot for the np–n'd transition in the potassium isoelectronic sequence is shown in figure 1. Each connected string of circles represents a particular transition np–n'd; the circles represent, from left to right along a given string, K I, Ca II, Sc III, Ti IV, V V, Cr VI and Mn VII. The quantum defects are either taken from or extrapolated from the values listed by Lindgård and Nielsen (1977). This plot clearly exposes eight possibilities for physical cancellations, summarised in table 1.

Oscillator strengths for these transitions for the ions Ca II–Zn XII have been computed by Biémont (1976) using HF methods, which also exhibit the cancellation

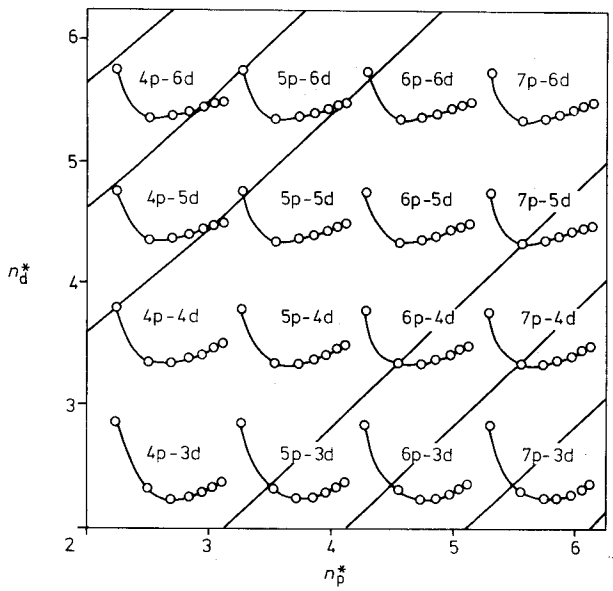

Figure 1. Plot of n_d^* against n_p^* along the K I isoelectronic sequence for transitions between the four lowest levels of the ^{2}D and ^{2}P Rydberg series. The circles represent, from left to right, the ions K I–Mn VII. The full lines denote the loci of vanishing oscillator strength. Strong cancellation effects are to be expected where a circle falls on a line.

Table 1.

Rydberg transition	Ions near cancellation
4p–4d	K I
4p–5d	Cr VI
4p–6d	V V
5p–6d	K I, Mn VII
6p–4d	Ca II
7p–4d	Ca II
7p–5d	Ca II

effects indicated in figure 1 and table 1. The calculations of Theodosiou (1980) indicated a cancellation in the np–6d system near 5p, which is clearly seen from figure 1. The 5p–6d system is particularly interesting in that it intersects two cancellation loci, at K I and at Mn VII, a fact not revealed by Theodosiou's formulation. This possibility of a double crossing arises because of the unfilled $n = 3$ shell which leads to a drop in n_d^* between K I and Ca II as the 3d level sinks below the 4p level.

The nearness of a transition to cancellation conditions should also manifest itself in intensity anomalies among the individual fine-structure components of a given transition multiplet. In principle, anomalous relative line intensities within a multiplet could be calculated by use of the Dirac–Hartree–Fock approach (Cheng and Kim 1978), but energy levels predicted by such methods also exhibit small systematic shifts relative to measured values (Reader and Acquista 1979), to which the relative intensities would be very sensitive. Johnson and Cheng (1979) have suggested a Dirac–Coulomb extension of the QDM. The non-relativistic QDM is also a valid approach to the study of fine-structure anomalies in the strengths of one-electron transitions near cancellations. The relative precision of any calculated oscillator strength is of course poor when a cancellation causes the result to be very small. Nevertheless, the way in which f depends on the effective quantum numbers of the initial and final levels should be correctly predicted by the non-relativistic QDM for any transition involving a single active electron whose wavefunction is largely external to the atom's other electrons. Independent of the mechanism which causes the fine-structure levels to have different energies, the QDM and the Coulomb approximation allow the transition matrix element to be related directly to the measured energies. Even in a system with unusually large or inverted fine structure, the active electron's motion in the outer portions of its orbit is usually non-relativistic, therefore, the ordinary Schrödinger QDM gives the correct connection between the binding energy and the outer wavefunction (and thus between energy and the oscillator strength) even when the Dirac equation is necessary for a treatment of the inner portions of the wavefunction where the speed and effective charge are much greater. For example, in the one-electron spectra under discussion, the oscillator strength predicted by the Dirac QDM (Johnson and Cheng 1979) differs from that given by the non-relativistic QDM only to order $(\alpha\zeta/n)^2$ where ζ is the core charge, not the nuclear charge Z.

As an example of a predicted near cancellation, consider the fine structure of the 6p–8d line in K I. Table 2 shows the wavelengths and normal relative intensities of the transitions involved, along with the oscillator strengths predicted by the QDM and the corresponding predicted relative intensities. The $^2P_{1/2}$–$^2D_{3/2}$ transition is suppressed by a factor of ten because it is closer to the cancellation than the other fine-structure

Table 2.

6p–8d transition	λ(Å)	*f*(QDM)	Relative emission intensities	
			Standard	QDM
$^2P_{3/2}$–$^2D_{5/2}$	23 978·1	$10{\cdot}1\times10^{-6}$	9	15
$^2P_{3/2}$–$^2D_{3/2}$	23 977·5	$9{\cdot}2\times10^{-6}$	1	1·5
$^2P_{1/2}$–$^2D_{3/2}$	23 929	$1{\cdot}2\times10^{-6}$	5	1·0

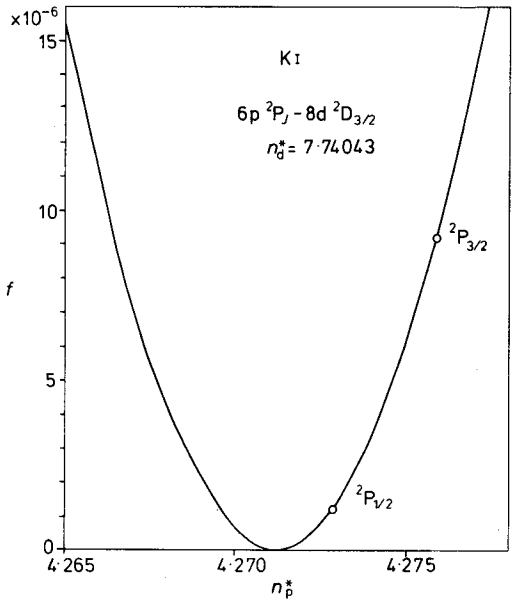

Figure 2. Plot of *f* (6p–8d) against n_p^* for fixed n_d^*, using the quantum defect theory. The circles represent the effective quantum numbers corresponding to the $6p^2P_{1/2}$–$8d^2D_{3/2}$ and $6p^2P_{3/2}$–$8d^2D_{3/2}$ transitions, and illustrate the intensity anomalies which can occur among fine-structure transitions near a cancellation.

components. Figure 2 shows the oscillator strength predicted by the QDM, as a function of n_p^* with fixed $n_d^* = 7{\cdot}7404$ corresponding to the $^2D_{3/2}$ level. The circles mark the *f* values predicted for the components $P_{1/2}$–$D_{3/2}$ ($n_p^* = 4{\cdot}2729$) and $P_{3/2}$–$D_{3/2}$ ($n_p^* = 4{\cdot}2759$). (These experimental effective quantum numbers are taken from Risberg (1956).) Near the cancellation the form of the curve is simply

$$f = 0{\cdot}044 \sin^2(n_p^* - 0{\cdot}2712)\pi. \tag{2}$$

These results suggest two types of measurements. First, isoelectronic measurements of a given transition to determine whether or not the physical cancellation occurs at the same values of effective quantum numbers as does the theoretical cancellation, for example, a measurement of the 4p–5d transitions in V V, Cr VI and Mn VII which could be interpolated in effective quantum number space to locate the physical cancellation. Second, a study of relative intensities of fine-structure components (such as those shown in figure 2) could similarly be interpolated to locate the physical

cancellation. Such measurements would allow the determination of the various model parameters (see, for example, Theodosiou 1980) which are built into model potential calculations in a situation in which these perturbations are dominant.

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