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Labeling conventions in isoelectronic sequences

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The isoelectronic exposition of atomic structure properties involves labeling ambiguities when more than one level of the same total angular momentum and parity is present, and an energy ordered labeling of these levels can lead to apparent isoelectronic discontinuities. For example, in the recent oscillator strength calculations for S-like ions by Saloman and Kim [Phys. Rev. A **38**, 577 (1988)], abrupt changes in the rates were sometimes observed between one isoelectronic element and the next. We suggest an alternative labeling scheme that removes these discontinuities and produces a smooth isoelectronic variation. This alternative labeling offers advantages for data exposition and for semiempirical interpolation and extrapolation.

Spectroscopic studies often exploit isoelectronic regularities, in which a property of one or more specific levels in a sequence of ions with the same number of electrons varies slowly and smoothly as a function of the nuclear charge Z.[1] Unfortunately, ambiguities exist[2,3] in the definition of the isoelectronic trajectory, and standard spectroscopic labels do not provide a general operational specification of the levels. In a general case where configuration interaction and intermediate coupling are present, a manifold of mutually interacting energy levels E exists for each set of eigenvalues for the total angular momentum J and the parity Π. Depending upon the purpose, various labeling schemes within this manifold can be selected as a basis for a connected isoelectronic trajectory (e.g., labeled according to energy ordering, dominant orbital configuration, dominant angular momentum coupling scheme, etc.). Ambiguities in labeling are particularly troublesome if the energies of two levels from the same J-Π manifold coincide at some value of Z, since this introduces a choice as to whether the isoelectronic trajectory is to be treated as a "crossing" or an "avoided crossing." It has been shown[2,3] that either choice of labeling can create apparent discontinuities which conceal empirically useful isoelectronic regularities. However, it is often possible to select a labeling that optimizes isoelectronic regularities.

As an example, we consider the multiconfiguration Dirac-Fock (MCDF) calculations recently reported by Saloman and Kim[4,5] for the energies and the $M1$ and $E2$ line strengths, oscillator strengths, and transition probabilities for the five lowest-lying levels in the sulfur isoelectronic sequence. They found sudden changes in the transition rates from one element to the next, which cause irregular isoelectronic patterns. By an alternative labeling scheme, we show that these discontinuities can be removed, and replaced by slowly varying and highly regular isoelectronic trajectories. This labeling scheme has clear advantages for the joint exposition of calculations and experimental data and for predictive semiempirical interpolations and extrapolations.[6]

Extensive discussions of the labeling of isoelectronic trends for energy levels and oscillator strengths (f values) in the presence of level crossings have been presented by Froese Fischer[2] and Cowan.[3] These make clear that, from a theoretical point of view, the energy eigenvalue curves for two states with the same J and Π do not actually cross, but retain their energy ordering. However, their eigenvector compositions exchange roles at the avoided crossing, and behave as though they did cross. As stated by Cowan,[3] "Thus, though the eigenvalue curves do not cross, the eigenvectors at the extremes are essentially the same as though the curves *did* cross. This point is very important for the proper quantum-state labeling of experimental energy levels, but is not always fully appreciated." Froese Fischer[2] demonstrates through calculational examples using fractional values for Z that strict isoelectronic continuity of an f value is maintained only if levels are labeled by their energy ordering (i.e. when f values are isoelectronically traced for transitions from the jth level having a certain J-Π value to the kth level having another J-Π value). However, in the vicinity of an avoided crossing this rigorous continuity is at the expense of overall regularity, since the corresponding f values undergo a rapid isoelectronic interchange of their long term trends. If the avoided crossing occurs between two integer Z values, a smooth and isoelectronically regular curve can be obtained by joining the two discontinuous trends as if there had been a crossing. Froese Fischer recommends that for a "long-range interaction" (in which the mutual interaction persists over many values of Z) the trajectories should be plotted as an *avoided crossing,* so as to retain the continuity of the function. For a

"short-range interaction" (occurring between integer Z values, or affecting only a few Z values) the trajectory should be plotted as a *crossing*, to retain the slow and smooth overall regularity.

Thus, although the labeling of states by an energy ordering of each J-II value provides the theoretical advantage of yielding f values that are a continuous (albeit irregular) function of Z, this labeling is poorly suited to semiempirical exposition and to predictive interpolation and extrapolation. The spectroscopic custom of labeling a level by its dominant configuration and its dominant angular momentum coupling scheme is also unsatisfactory, because these dominances can change over the sequence. Since the isoelectronic exposition of spectroscopic data is primarily a utilitarian procedure, intended to display regularities, optimization of isoelectronic regularity itself provides a valid criterion for labeling the elements of a J-II manifold that should be isoelectronically connected. The decision of whether the levels are treated as a "crossing" or "avoided crossing" can be made by selecting the choice that isoelectronically connects a desired quantity with better regularity. The recent calculations of Refs. 4 and 5 provide an excellent illustration of the practical application of this criterion.

In their calculations for the sulfur sequence, Saloman and Kim[4,5] have noted dramatic discontinuities in both the energy levels and the oscillator strengths, and have concluded that the multiconfiguration approach is essential to the observation of these discontinuities. In their calculation they include the relativistic combinations of four of the ten possible even parity nonrelativistic basis configurations with an open $n=3$ shell, and trace the isoelectronic trajectories of the five lowest lying (avoided crossing) levels, which include the first and second lowest lying $J=2$ levels (nominally denoted $^3P_2$ and $^1D_2$, respectively), the lowest lying $J=1$ level (nominally denoted $^3P_1$), and the first and second lowest lying $J=0$ levels (nominally denoted $^3P_0$ and $^1S_0$, respectively).

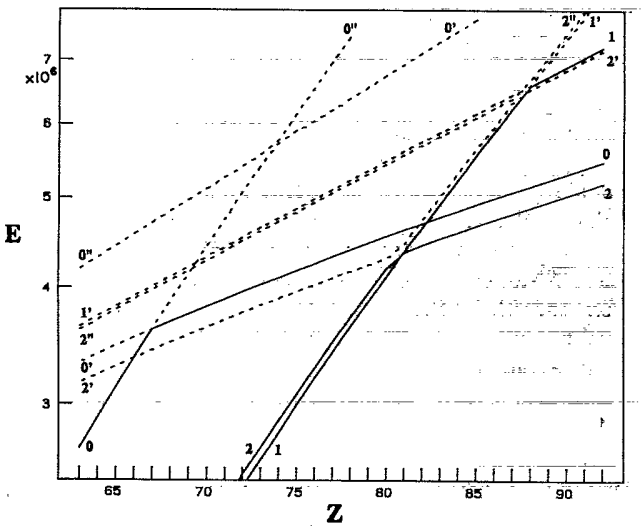

FIG. 1. Isoelectronic plot of the energy levels ordered 3–10 in the sulfur sequence, labeled by J, J', and J'' to indicate the energy ordering of each J manifold. Solid lines trace levels 3–5, and dashed lines trace levels 6–10. The eigenvector composition is characterized by the slope of the lines, with the steeper slope being dominantly $3p^4$, and the shallower slope being dominantly $3p^23d^2$.

In order to test the application of the relabeling criterion, we have repeated these calculations using the MCDF code developed by Grant and co-workers.[7] The lowest two of these five levels have $J=2$ and $J=0$ (nominally $^3P_2$ and $^3P_0$) and have no avoided crossings with other members of their manifolds. (A crossing between the $^3P_1$ and $^3P_0$ levels occurs[8] between $Z=28$ and 29, but since these differ in J there is no mixing of the levels.) Our calculations of the isoelectronic trajectories of energy levels 3–10 for $63 \le Z \le 92$ are shown in Fig. 1. The solid lines denote three isoelectronic trajectories considered by Saloman and Kim, and the dashed lines indicate the trajectories of the other levels with which they have avoided crossings. The levels are labeled by J, with unprimes, primes, and double primes to indicate the energy ordering of each manifold. The nearly linear loci obtained by connecting solid and dashed lines through the avoided crossings characterize the dominant configurations, with the steeper slopes corresponding to $3p^4$ and the shallower slopes corresponding to $3p^23d^2$ (relative to a filled $3s^2$ core).

In this region of Z, the levels are well described by relativisitic orbital configurations and jj coupling notation, and the avoided crossing regions are characterized by

J	Z	Configuration	Label
2	80,81	$3p_{1/2}3p^3_{3/2}(1/2,3/2)_2$ $3p^2_{1/2}3d^2_{3/2}(3/2,3/2)_2$	$^1D_2$
1	89,90	$3p_{1/2}3p^3_{3/2}(1/2,3/2)_1$ $3p^2_{1/2}3d_{3/2}3d_{5/2}(3/2,5/2)_1$	$^3P_1$
0	68,69	$3p^4_{3/2}(1/2,1/2)_0$ $3p^2_{1/2}3d^2_{3/2}(3/2,3/2)_0$	$^1S_0$

For p^4 configurations in the jj coupling limit ($\zeta_p \gg F_2$ in terms of Slater parameters), the spin-orbit interaction is attractive for $(3/2,3/2)_{2,0}$ levels and repulsive for the $(1/2,3/2)_{1,2}$ and $(1/2,1/2)_0$ levels.[1] Because of this, interlopers from other configurations plunge through the $(1/2,3/2)_{1,2}$ and $(1/2,1/2)_0$ levels at high Z, leading to (dependent upon the values of J) crossings or avoided crossings.

Since the amplitude mixtures of the two levels interchange roles at an avoided crossing, labeling them as avoided crossings will certainly lead to large discontinuities in atomic structure properties such as oscillator strengths. However, if the levels were labeled as if these were crossings (that is, by joining the solid and dashed lines in Fig. 1 at the avoided crossing), f value isoelectronic trajectories that are slowly varying and highly regular are obtained.

This is illustrated in Fig. 2, which presents a plot of the oscillator strengths for $M1$ transitions between the $J=2$ ground level and the first excited (solid curve) and second

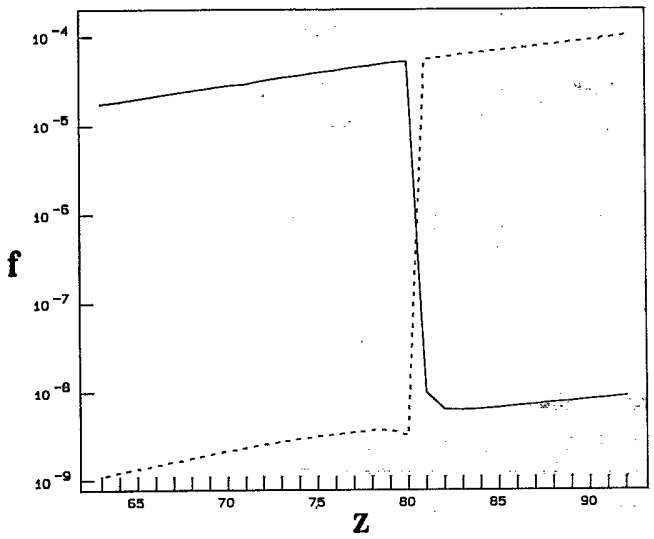

FIG. 2. Isoelectronic plot of oscillator strengths for transitions between the $J=2$ ground level and the first (solid curve) and second (dashed curve) excited $J=2$ levels. The upper portions of both curves are dominated by the $3p_{1/2}3p_{3/2}^3$ configuration; the lower portions of both curves are dominated by the $3p_{1/2}^2 3d_{3/2}^2$ configuration.

excited (dashed curve) $J=2$ levels. The solid curve thus corresponds to the $^3P_2$-$^1D_2$ transition shown in Fig. 4 of Ref. 4. If the upper portions of the solid and dashed curves are joined and traced, a smooth variation with the dominant configuration $3p_{1/2}3p_{3/2}^3$ is obtained. If the lower portions of the solid and dashed curves are similarly joined and traced, a smooth variation with the dominant configuration $3p_{1/2}^2 3d_{3/2}^2$ is obtained. Similar results are obtained for $E2$ transitions, and for transitions involving the $J=0$ level avoided crossing between $Z=68$ and 69 and the $J=1$ avoided crossing between $Z=89$ and 90. A similar plot can also be made for a discontinuity that occurs in the calculations for the Si isoelectronic sequence of Huang,[9] where the level labeled as $^1D_2$ undergoes an avoided crossing with another level between $Z=76$ and 77.

Our calculations indicate that there is little configuration interaction between these levels at physical Z values, as is evidenced by the fact that the amplitudes of the designated orbital configuration and jj basis states are over 99% pure on both sides of the avoided crossing. Thus, while it was necessary to consider more than one relativistic configuration to obtain the manifolds that produce the avoided crossings, it was not necessary to make a multiconfiguration calculation to obtain quantitative agreement. For values of Z that do not coincide exactly with the avoided crossing point, individual single configuration calculations were made and combined to obtain the transition rates and energy level crossings that agree to within a few percent with our multiconfiguration calculations and with the results of Ref. 5.

It should be emphasized that the use of relativistic orbital configurations and jj coupling states is useful here only because the crossings occur near the high-Z end of the sequence and there is little configuration interaction in this system. At the low-Z end of the sequence, where LS coupling better describes the system, dominance of a single jj amplitude in the level wave functions ceases. However, the criterion of smooth isoelectronic behavior still permits the trajectory to be traced. In cases where configuration interaction is stronger, the dominant configuration can change along the isoelectronically smooth trajectory, and labels should be used that are configuration and term value neutral.

The labeling of levels as described here is clearly arbitrary, and the advantages of various schemes can differ among specific theoretical and experimental applications. However, the exploitation of isoelectronic regularities is an essential tool of atomic spectroscopy, which should not be inhibited by artificial limitations imposed by notation. We therefore recommend that isoelectronic expositions of both theoretical computations and experimental measurements be presented in terms of the labeling scheme that best displays the inherent isoelectronic regularities.

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