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Oscillator-strength trends in the presence of level crossings

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A configuration-interaction model is used to study line strengths and gf values for transitions in which level crossing occurs in either the initial or final state. It is shown that the line strength varies continuously for the lowest eigenstate, for example, but not for the eigenstate with a given dominant component. The latter exhibits marked irregularities in the vicinity of a crossover. Some plots for line strengths are presented showing the possible types of irregularities using a model interaction matrix. Computed gf-value trends for $3p$ or $4p\ ^2P$-$(3s\ ^2 4s, 3s\,3p\ ^2)\ ^2S$ transitions, as a function of Z, illustrate some of these irregularities.

INTRODUCTION

Systematic trends in the oscillator strengths (or f values) have been found for many transitions[1] in atomic systems. The trends most frequently considered are those for transitions along an isoelectronic sequence where only the nuclear charge Z of the many-electron system varies. Z-dependent perturbation theory is usually used to study the highly ionized species of such sequences with Z^{-1} as a perturbation parameter.[2] For this reason, it is customary to consider the f value also as a function of Z^{-1} or occasionally $(Z-\sigma)^{-1}$, where σ is a screening parameter.

There are several advantages to studying f values for an isoelectronic sequence rather than isolated atoms or ions. When the f value varies systematically, known values may be interpolated (or extrapolated) to neighboring atoms or ions. In the case of experimental data, new values may be compared with existing data for other atoms or ions, not in the usual sense of values agreeing but rather in the sense that values exhibit a smooth trend.[3] In their critically evaluated tables of f values, Smith and Wiese[4] relied extensively on the smooth behavior of f values in predicting the most reliable estimates. Neither of these procedures is valid when irregularities are present.

Most of the trends considered to date have been for resonance transitions where smooth trends could be drawn. However, irregularities have been found.[5] One of the earliest examples was the f-value trend for the $2s^2 2p\ ^2P - 2s^2 3s\ ^2S$ transition where the energy levels of the interacting configurations, $2s^2 3s\ ^2S$ and $2s\,2p^2\ ^2S$, cross as one proceeds along the isoelectronic sequence. Irregularities were also found in the $4s\ ^2S - 4p\ ^2P$ f-value trend of the Al I isoelectronic sequence.[6] In this sequence each irregularity was associated with the crossing of the energy level of a configuration interacting with either $4s\ ^2S$ or $4p\ ^2P$, but *not all crossovers produced irregularities*.

It must be remembered that physical f values are defined only for integral values of Z. Theoretical calculations are not restricted in this way, but it is customary to perform calculations for integral values only and then join these values by a smooth curve. Clearly the structure of the f-value trend in the vicinity of a crossover may not be depicted adequately by such a procedure, particularly if the crossover is rapid and does not occur near an integral Z value.

As Weiss[5] pointed out, level crossings are common in atomic spectroscopy and pose a problem whenever systematic trends are used for prediction. For example, energy-level data for ions in an isoelectronic sequence often become unavailable for multiply ionized atoms in the vicinity of a crossover that causes an irregularity in the level structure.

Level crossing occurs in an isoelectronic sequence whenever "plunging" configurations are present. These are configurations whose energies lie above the ionization limit in neutral atoms, but, as the nuclear charge increases, their energy levels come down into the bound spectrum, crossing many states with which they interact. In the second-row isoelectronic sequences (Mg and higher), these are configurations involving one or more $3d$ electrons. For larger atoms, configurations with $4f$ electrons play a similar role. Because of the prevalence of such crossovers in the more complex atoms, a detailed study of f-value trends in the presence of crossovers may be helpful in the analysis of such trends.

In this paper, we investigate the behavior of an f-value trend when the energy levels of two interacting configurations cross. A configuration-interaction model will be used to predict the f-value behavior analytically, under certain assumptions. Some examples will be given to show that

theoretical f values exhibit similar irregularities when not restricted to integral values of Z. Finally, guidelines will be presented for the study of f-value trends in the presence of crossovers.

A LEVEL-CROSSING MODEL

Let us consider a gf value for a transition from an initial state i to a final state k. Let the wave functions for the states by ψ_i and ψ_k, respectively. Suppose further that the initial state is a superposition of two interacting configurations, i.e.,

$$\psi_i = c_1\Phi_1 + c_2\Phi_2 , \tag{1}$$

where Φ_1, Φ_2 are configuration-state functions. In a configuration-interaction model, the mixing coefficients are eigenvectors of the interaction matrix

$$\mathrm{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}, \quad H_{jj'} = \langle \Phi_j | H | \Phi_{j'} \rangle .$$

Suppose that now, as Z varies, the diagonal energies, H_{11} and H_{22}, cross and the values of $H_{12} = H_{21}$ remain essentially constant. If we choose an energy scale such that this interaction is unity with the average energy corresponding to the zero of the energy scale, then the 2×2 interaction matrix is of the form

$$H = \begin{bmatrix} a & 1 \\ 1 & -a \end{bmatrix}.$$

In this model, the crossing of the levels occurs as the variable a changes sign. The eigenvalues of the matrix are

$$E_{l,u}(a) = \pm(1 + a^2)^{1/2} , \tag{2}$$

where $E_l(a)$ is the lower and $E_u(a)$ the upper eigenvalue. As is well known, the two energy curves—one for the upper and one for the lower state—are continuous and do not actually cross. The corresponding eigenvectors $\vec{c}(a) = (c_1(a), c_2(a))^t$ are given by the equations

$$c_1(a) = (a + E)c_2(a) , \tag{3a}$$

$$c_2(a) = [2(1 + a^2 + aE)]^{-1/2} . \tag{3b}$$

For the upper (+) solution, the phases of the two components are the same whereas for the lower (−) solution, the phases are opposite in this model. In a more general model, the relative phase of the upper solution has the same sign as the interaction, the lower solution having the opposite sign. The important observation for our purposes is the fact that the relative phases of both eigenvectors remain unchanged during a crossover and that they are positive for one eigenvector, negative for the other.

Many symmetries exist between the four components of the eigenvectors. It is easy to show that

$$c_{2u}(a) = c_{1u}(-a), \quad c_{2l}(a) = c_{1u}(a) ,$$

$$c_{1l}(a) = -c_{2u}(a) = -c_{1u}(-a) .$$

The line strength S for a transition is proportional to the square of the transition-matrix element $\langle \psi_k | \vec{\mathbf{r}} | \psi_i \rangle$. By Eq. (1), this element may be expressed as

$$\langle \psi_k | \vec{\mathbf{r}} | \psi_i \rangle = c_1(a)\langle \psi_k | \vec{\mathbf{r}} | \Phi_1 \rangle + c_2(a)\langle \psi_k | \vec{\mathbf{r}} | \Phi_2 \rangle$$
$$= c_1(a)b_1 + c_2(a)b_2 ,$$

where $b_i = \langle \psi_k | \vec{\mathbf{r}} | \Phi_i \rangle$ and $i = 1$ or 2. We shall treat these parameters as constants in the vicinity of a crossover. Let us assume $|b_1| \geq |b_2|$. Then the matrix element is proportioned to

$$M^{(1)}(a, b) = c_1(a) + c_2(a)b , \tag{4a}$$

where

$$b = b_2/b_1$$

and consequently, $-1 \leq b \leq 1$. Similarly, when $|b_2| \geq |b_1|$ we can define

$$M^{(2)}(a, b) = c_1(a)b + c_2(a) . \tag{4b}$$

Finally, we define

$$S^{(i)}(a, b) = [M^{(i)}(a, b)]^2 , \quad i = 1 \text{ or } 2 . \tag{5}$$

Again symmetries are present. In particular,

$$S_u^{(2)}(a, b) = S_u^{(1)}(-a, b) ,$$

$$S_l^{(2)}(a, b) = S_l^{(1)}(-a, b) ,$$

and so the function $S^{(2)}$ need not be considered further. Also,

$$S_l(a, -b) = S_u(-a, b) ,$$

so that the range of b may be restricted as well.

In Fig. 1, plots of $S_u^{(1)}(a, b)$ (dark) and $S_l^{(1)}(a, b)$ (light) are presented for a series of b values. Several important points can be observed. The line strength for both the upper and the lower state varies continuously with a. In atomic physics, however, it is customary to identify states by their dominant component and plot f values for transitions between states with specified dominant components. As a goes through zero, the dominant component of the state changes and it then becomes necessary in Fig. 1, to switch from a dark curve to a light curve or vice versa. Only when $b = 0$ does this result in a continuous line strength, that is, when a transition is allowed to only one of the interacting configura-

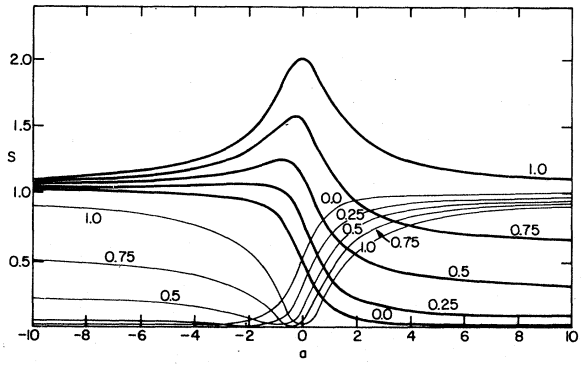

FIG. 1. The line strengths $S_u^{(1)}(a,b)$ (dark) and $S_l^{(1)}(a,b)$ (light), as a function of a for several values $-b = 0(0.25)1.0$.

tions. In this case, the resulting curve exhibits a cusp at $a=0$. Also, $S_u(a,0)+S_l(a,0)=1$. As the interaction increases the mixing, the line strength is transferred from one state to the other. Thus, one decreases whereas the other increases until at $a=0$ the two are identical in magnitude. Once the crossover has occurred, the interactions again decrease and the reverse process takes place. When b is not equal to zero, a *jump discontinuity* in the line strength is present for transitions with a specified dominant component.

This discontinuity results from the fact that, as one changes from an upper state to a lower state (or vice versa), the relative phase of the two components changes. From Eq. (4) it is clear that, for a specified value of b, in one case the relative phase leads to an enhancement in the magnitude of the matrix element, the two terms having the same sign, whereas for the other there will be cancellation, the two terms having opposite sign. In following the line strength for a transiton through a crossover, a transfer occurs from an enhancement situation to a cancellation situation (or vice versa) resulting in the discontinuity. On the other hand, when the interaction is small "before" and "after" the level crossing, then the line strengths in the two regions will be similar that is, $S_u(-a,b)\simeq S_l(a,b)$, as a becomes large.

SOME *gf* CALCULATIONS

The above analysis introduced several assumptions for simplicity. In this section, we present some *gf* values calculated using a configuration-interaction model and show that similar trends are obtained.

In the earlier study of $4s\,^2S-4p\,^2P$ transitions in the Al*I* sequence, it was found that the energy levels of the configurations $3s^24s\,^2S$ and $3s3p^2\,^2S$ crossed between Si*II* ($Z=14$) and P*III* ($Z=15$), but no irregularity was observed. In order to check the trend more carefully at nonintegral values of Z, a model calculation was performed. Transitions from both $3p\,^2P$ and $4p\,^2P$ were considered.

For each Z, a basis set of radial functions was determined for which the energy

$$E=\tfrac{1}{3}[E(3p)+E(4s)+E(4p)]$$

was stationary. These functions were then used to compute the interaction matrix for the configurations $3s^24s$ and $3s3p^2\,^2S$ that define the two ^2S mixed states. The crossover of the two energy levels *in this model* occurs very close to $Z=14.45$. For lower values of Z, the lowest ^2S state (^2S_l) has $3s^24s\,^2S$ as a dominant component, but as Z increases, the $3s3p^2$ configuration comes plunging down into the discrete spectrum from the continuum in Al*I*. For $Z>14.45$ it is the lowest ^2S state in the Al*I* isoelectronic sequence.

In Fig. 2, the *gf*-value trends for transitions from $3p\,^2P$ to each of these states are plotted, namely, $3p\,^2P-{}^2S_l$ (lower) and $3p\,^2P-{}^2S_u$ (upper). In this case, both transition-matrix elements, $\langle 3s^23p|\vec{r}|3s^24s\rangle$ and $\langle 3s^23p|\vec{r}|3s3p^2\rangle$, are nonzero and the ratio corresponds closely to $b=-0.9$. In fact, the curves are similar to the line-strength curves in Fig. 1 for $b=-1.0$, though the interaction builds up and dies down more rapidly. The darker curve for the $3p\,^2P-4s\,^2S$ transition has a marked discontinuity, going from an enhancement peak in the *gf* value to a zero. The lighter curve for $3p\,^2P-3s3p^2\,^2S$ does just the reverse. On the other hand, since the crossover is dis-

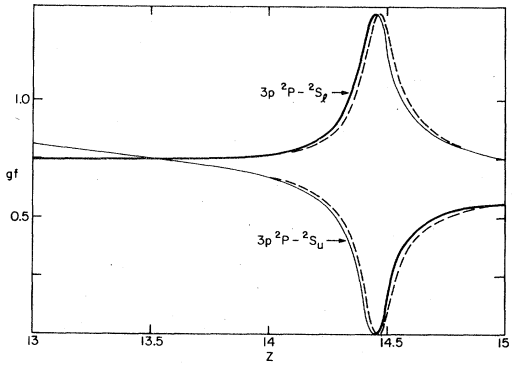

FIG. 2. Theoretical *gf* values for $3p\,^2P-{}^2S_l$ (lower) and $3p\,^2P-{}^2S_u$ (upper) transitions as a function of Z. The dashed curve depicts the shift due to relativistic effects, the dark curve the *gf* values for the $3p\,^2P-4s\,^2S$ transition, and the light curve the $3p\,^2P-3s3p^2\,^2S$ transition. A single-configuration approximation was used for the ^2P state and two configurations for the ^2S states.

tinctly in the middle of an interval and the interaction has a short "range", the three values corresponding to $Z = 13$, 14, and 15 can readily be joined with a smooth curve.

Relativistic effects are usually small for light atoms, but the effects such as the mass correction, Darwin term, and spin-spin contact which shift the energy of a configuration as a whole without being J dependent, may affect configurations differently. Consequently, the crossover point may be shifted. In Fig. 2 the dashed curve shows a small shift due to these relativistic effects. Because of the rapid change of the gf value in the vicinity of a crossover, the shift may produce an appreciable change in the gf value for a particular Z value. Clearly, relativistic effects become important in the level-crossing region, even for light atoms.

In Fig. 3, $|gf|$ values are plotted for $^2S - 4p\,^2P$ transitions (since these may now be either in absorption or emission, only the absolute value is considered). This is a case where $b = 0$ with only the $\langle 3s^2 4s | \vec{r} | 3s^2 4p \rangle$ transition matrix contributing to the oscillator strength. The dark curve represents the $4s\,^2S - 4p\,^2P$ transition and the light curve the $4s\,^2S - 3p\,^2P$ transition.

A gf value is proportional to the product of the transition energy and the line strength. Because of the interaction, the two transition energies are not precisely the same at a crossover. However, if the interaction is small compared with the transition energy, as in the present case, then this difference may be ignored and the curves are essentially continuous with exactly half the gf value distributed to each trend at the cross-

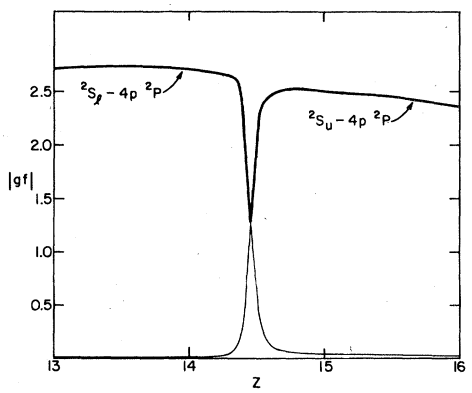

FIG. 3. Theoretical $|gf|$ values for the ^2S_l (lower)-$4p\,^2P$ and ^2S_u(upper)-$4p\,^2P$ transitions as a function of Z. The dark curve depicts the gf values for the $4s\,^2S$-$4p\,^2P$ transition and the light curve the $|gf|$ values for the $3s3p^2\,^2S$-$4p\,^2P$ transition. A two-configuration approximation was used for the ^2S states and a single configuration for the ^2P state.

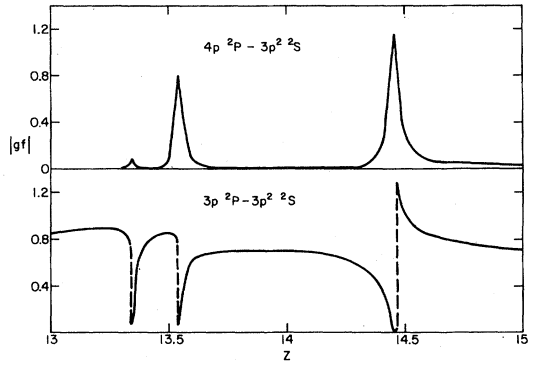

FIG. 4. Theoretical $|gf|$ values for $3p^2P - 3s3p^2\,^2S$ and $4p^2P - 3s3p^2\,^2S$ as a function of Z using the four configuration-interaction model $(3s3p^2,\ 3s^24s,\ 3s^25s,\ 3s^26s)^2S$.

over point. Clearly the values for integral Z may again be joined by a smooth curve in this case without any structure.

Finally, it should be remembered, that the f-value trend for the plunging $3s3p^2\,^2S$ configuration (light curve in Figs. 2 and 3) was computed from a two-configuration-interaction model. In fact, this configuration interacts with the whole $3s^2ns\,^2S$ Rydberg series. To see the effect of this interaction, a second calculation was undertaken in which radial functions were determined such that $E = \frac{1}{5}[E(4s) + E(5s) + E(6s) + E(3p) + E(3p)]$ was stationary. A configuration-interaction calculation including the four configurations $(3s3p^2,\ 3s^24s,\ 3s^25s,\ 3s^26s)^2S$ determined the wave function for the mixed state having $3s3p^2\,^2S$ as a dominant component.

The effect on the $|gf|$ value is depicted in Fig. 4. As Z increases, the $3s3p^2\,^2S$ configuration first crosses $3s^26s$, then $3s^25s$, and finally, $3s^24s$. The $|gf|$ value from $3p\,^2P$ (lower portion of Fig. 4) is quite different from that from $4p\,^2P$ (upper portion). In the former, a transition to $3p\,^2P$ is allowed from all the interacting ^2S configurations (corresponding to $b \neq 0$ in our model), whereas in the latter the transition between the dominant components $3s3p^2\,^2S - 4p\,^2P$ is not allowed (corresponding to $b = 0$). The latter shows clearly that the interaction of $3s3p^2$ with $3s^2ns$ is largely a "local" interaction being appreciable only in the vicinity of a crossover. The peaks vary in magnitude mainly because of the variation in the transition-matrix element $\langle 4p | \vec{r} | ns \rangle$ and, to a lesser extent on the variation in ΔE, which becomes zero at about $Z = 13.8$ where $4p\,^2P$ and $3s3p^2\,^2S$ cross. The lower portion of Fig. 4 exhibits the type of discontinuities associated with different b values. The discontinuity at $Z \simeq 14.45$ is similar to that of the light curve in Fig. 2.

CONCLUSION

The above study has shown that the *gf* value, when treated mathematically as a function of Z^{-1}, may exhibit a jump discontinuity at a crossover point, where the energy levels of two interacting configurations cross. On the other hand, continuous *gf* trends are obtained for transitions from the *j*th eigenstate of a given initial-state symmetry to the *k*th eigenstate of the final-state symmetry. This suggests that *gf* values should be plotted for transitions between levels rather than configurations. Indeed, in a study of $3s^23d\,^2D$ and $3s3p^2\,^2D$ mixing in Al*I* it was shown that mixing coefficients for the lowest ^2D varied smoothly with $1/(Z-12)$ even though level crossing occured at $Z \simeq 13.6$.[7] For this reason the *f*-value trends for transitions from the $3s^23p\,^2P$ ground state in Al*I* are often plotted for transitions to the lowest ^2D or the second lowest ^2D,[3,7,8] rather than for a given dominant component in the final state.

The $3s^23d\,^2D$ and $3s^3p^2\,^2D$ interaction is an example of a "long-range" interaction. Because the two configurations are in the same complex, the interaction remains strong for all Z values. In such cases it seems reasonable to plot *gf* trends in a fashion which assures continuity mathematically.

In other instances the interaction is of such a "short-range" nature that, in proceeding from one atom (or ion) to the next in an isoelectronic sequence the effect of the crossover may not be noticeable unless it occurs near an integral Z value. In such cases it seems more reasonable to plot *gf* trends for a specific transition, keeping in mind that an irregularity has occurred. Since solid lines often imply continuity, it may be more appropriate, then, simply to link points for integral values of Z in some fashion.

With these comments the $4s\,^2S - 4p\,^2P$ *f*-value trends published earlier may be interpreted more accurately. Plunging configurations with three outer electrons in the $n=3$ shell cross either $3s^24s$ or $3s^24p$ in different intervals. The Hartree-Fock energies of $3s3p^2\,^2S$ and $3s3d^2\,^2S$ cross the $4s\,^2S$ energy in the intervals (14, 15) and (23, 24), respectively, and $3s3p(^3P)3d\,^2P$ and $3s3p(^1P)3d\,^1P$ cross $4p\,^2P$ in (16, 17) and (17, 18), respectively. All are short-range interactions with the effect of reducing the *f* value (the transition-matrix element of $4s\,^2S$ or $4p\,^2P$ with the interacting configuration of the other state is zero, that is, $b=0$ in our model analysis). Interactions with other configurations in the $n=3$ shell such as the interaction of $3p^2(^1D)3d\,^2S$ with $3s3d^2(^1S)^2S$ merely modify the crossover point somewhat. In any event, only two crossovers occurred near an integral value of Z, producing noticeable irregularities in the *f* value. In retrospect, the theoretical *f*-value trend as a function of Z^{-1} should have had four sharply pronounced reductions to about half the *f* value in the vicinity of each crossover.

The structure of a *gf*-value trend for a plunging configuration, as depicted in Fig. 4, is reminiscent of line shapes for transitions to autoionizing states or plots of photoionization cross sections.[9] There is an important difference, however. We saw earlier that, even though $3s3p^2\,^2S$ interacts with the whole $3s^2ns$-Rydberg series, in the vicinity of a crossover the dominant effect is from the two-configuration interaction. A bound configuration lying above the ionization threshold, interacts with a continuum of unbound states, lying partly above and partly below the bound configuration. Thus there is a continuum of interactions and as the energy of the final states passes through a resonance, the transition probability changes rapidly but *continuously* from an enhancement to an interference phenomenon.

In this paper, we have focused on one type of irregularity in a *gf*-value trend, namely, the irregularity that results when energy levels of interacting configurations cross either in the initial or final state. Other types of irregularities may also occur. For example, the transition-matrix element between the dominant components of the initial and final state may have a zero. The latter was found by Curtis and Ellis[10] to be the cause of a pronounced minimum in the *f*-value curve for the $4p\,^2P_{3/2} - 5d\,^2D_{5/2}$ transition in the Cu*I* sequence. Such irregularities, however, lead to a continuous *f*-value curve and are solely due to the fact that the transition-matrix element is squared. The latter may well exhibit a regular trend.

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