

Determination of lifetimes and nonadiabatic correlations from measured dipole polarizabilities

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Abstract

In atomic systems for which the total oscillator strength of excitations from the ground state is dominated by the transition to the lowest resonance level, the f -sum rule provides a bracketing inequality connecting the lifetime τ of that level to the dipole polarizability α_d . This relationship has been used previously to deduce α_d from τ . It is shown here that improved spectroscopic accuracies now permit this procedure to be inverted, with τ deduced from a value for α_d obtained spectroscopically using the core polarization model. A similar quantitative relationship exists connecting the nonadiabatic correlation factor β to τ , and thus also to α_d . The method is applied to a recent measurement of α_d for Kr^{6+} to obtain the values $\tau(4s4p\ ^1P_1) = 0.096 \pm 0.003$ ns and $\beta(\text{Kr}^{6+}) = 1.71 \pm 0.03a_0^5$. It is shown that the use of this method to make precision lifetime determinations for a small number of ions in an isoelectronic sequence permits the exploitation of observed semiempirical regularities to specify the lifetimes of all ions in that sequence.

1. Introduction

Dipole polarizabilities α_d have long been determined from spectroscopic studies of high Rydberg states, interpreted in the context of the core polarization model [1]. Through the study of the energy levels of high n and ℓ states, the effective polarizabilities of the core (one stage of ionization higher than the Rydberg ion) can be extracted.

In systems for which the oscillator strength of excitations from the ground state is dominated by the lowest-lying resonance transition, an alternative method can be used to determine α_d . Using a relationship that connects oscillator strengths and excitation energies with α_d and invoking the f -sum rule, an inequality can be established. If the dominant resonance transition is unbranched, the value of α_d can be tightly bracketed using a precision measurement of the lifetime τ of that transition (e.g. [2–4]). Similar relationships connect the nonadiabatic correlation factor β (a measure of the inability of the core to follow the motion of the outer electron), which allow this quantity to be specified in the same manner.

This paper demonstrates that improved spectroscopic accuracies now permit the spectroscopic and time-resolved methods to be coupled, and the bracketing procedure inverted. Thus a precision spectroscopic determination of α_d using the core polarization model is used to deduce τ , and that result is then used to evaluate β .

2. Formulation

As an illustrative example of this approach, consider the resonance transitions for ions in the Zn isoelectronic sequence. This system has a $4s^2\ ^1S_0$ ground state outside a filled $3d^{10}$ Ni-like core. The oscillator strength for the ground-state excitation series $4s^2\ ^1S_0 - 4snp\ ^1P_1^o$ is dominated by the strong, low-lying ($\Delta n = 0$) $n = 4$ transition. The dipole polarizability of these ions will influence the energy levels of high Rydberg states in atoms and ions of the adjacent Ga isoelectronic sequence, from which α_d can be deduced using the long-range core polarization model [1].

2.1. Bracketing inequalities

The value for α_d for the ground state of a Zn-like ion can be related to the oscillator strengths $f_{4s,np}$ and transition energies $E_{4s,np}$ for the $4s^2\ ^1S_0 - 4snp\ ^1P_1^o$ Rydberg series through the relationship [5]

$$\alpha_d = \sum'_n \frac{f_{4s,np}}{E_{4s,np}^2}, \quad (1)$$

expressed here in atomic units (energies in Hartrees, lengths in Bohr radii a_0). The prime on the summation indicates that this also includes an integral over continuum states. The f -sum rule [6, 7] provides the additional relationship

$$N_e = \sum'_n f_{4s,np} \quad (2)$$

where N_e is the number of active electrons.

For ions with ns and ns^2 ground states, the oscillator strength of the lowest resonance transition often dominates the sum [3] in equation (2). A possible explanation for this fact involves strong cancellation effects that can occur in the line strength factor for $\Delta n \neq 0$ transitions, but not for the $\Delta n = 0$ transition [8]. Since the lowest resonance transition is unbranched, its oscillator strength can be specified from lifetime measurements alone, with no need for branching fraction data. The f -sum rule provides a value for the remaining summed oscillator strength, and the second resonance level $4s5p\ ^1P_1^o$ provides a lower bound to subsequent excitation energies. This yields a bracketing inequality [9]

$$\frac{f_{4s,4p}}{E_{4s,4p}^2} \leq \alpha_d \leq \frac{f_{4s,4p}}{E_{4s,4p}^2} + \frac{N_e - f_{4s,4p}}{E_{4s,5p}^2}. \quad (3)$$

This expression has been used to specify values and uncertainty limits for α_d from measured lifetime values [2–4]. However, the relationship can also be inverted to yield a bracketing inequality for the oscillator strength

$$\frac{\alpha_d E_{4s,5p}^2 - N_e}{E_{4s,5p}^2 / E_{4s,4p}^2 - 1} \leq f_{4s,4p} \leq \alpha_d E_{4s,4p}^2. \quad (4)$$

In addition to adiabatic correlations such as α_d , there are also relationships connecting oscillator strengths to other quantities such as the lowest order nonadiabatic correlation β [10].

In long-range interactions of a Rydberg ion, this quantity is a measure of the inability of the core to instantaneously follow the motion of the outer electron. It is defined (in au) as

$$\beta = \frac{1}{2} \sum'_n \frac{f_{4s,np}}{E_{4s,np}^3}. \quad (5)$$

By the same arguments that were presented above for α_d , the quantity β has the bracketing inequality

$$\frac{f_{4s,4p}}{E_{4s,4p}^3} \leq 2\beta \leq \frac{f_{4s,4p}}{E_{4s,4p}^3} + \frac{N_e - f_{4s,4p}}{E_{4s,5p}^3}. \quad (6)$$

After the measured value for α_d has been used to deduce f_{4s4p} , the process can be reversed to prescribe the value for β .

3. Quantitative application

As a numerical application of this approach, consider the recent measurement by Lundeen and Fehrenbach [11] of a precise (1.5%) value of α_d for Zn-like Kr^{6+} . This was done using high-resolution spectroscopy of high Rydberg levels of Kr^{5+} , interpreted in the context of the long-range core polarization model [1].

The lifetime of the $4s4p \ ^1P_1^o$ level is particularly interesting because its measurement by decay curve analysis is complicated by heavy cascade repopulation. Early measurements using multiexponential curve fitting yielded a value 0.19 ± 0.02 ns [12, 13]. A later measurement that used the ANDC method [14] to make a correlated analysis of the primary and cascade decay curves yielded a value 0.101 ± 0.010 ns [15]. However, a subsequent study [16] suggested that one of the lines attributed to a relevant cascade channel may have been misidentified. While the inherent stimulus-response correlation between the cascade and primary decay curves makes misidentification in a successful ANDC analysis extremely unlikely, an independent determination of this lifetime could also confirm the identification. Theoretical calculations have yielded values 0.0991 ns [17] and 0.0953 ns [18].

The expressions developed in the previous section can be applied to this new measurement of α_d for Kr^{6+} . Values for the $n = 4$ and 5 energies are available ($E_{4s,4p} = 0.778\,382$ au [19] and $E_{4s,5p} = 2.267\,961$ au [16]), and Lundeen and Fehrenbach [11] provide the value $\alpha_d = 2.69 \pm 0.04a_0^3$.

3.1. Evaluation of the f -sum rule

The only remaining unknown is N_e , which can be expected to be close to two, the number of out-of-shell $4s^2$ electrons in the ground state. There could also be small additional contributions from the closed-shell $3d^{10}$ Ni-like Kr^{8+} inner core. However, the Kr^{8+} ion is relatively rigid, with a calculated polarizability $\alpha_d = 0.2021a_0^3$ [20]. To account for the possibility of an inner core contribution to the oscillator strength of Kr^{6+} , denote

$$N_e = 2 + \Delta N_e \quad (7)$$

where ΔN_e is a small fraction. For example, in studies of the f -value sums for Mg^+ and Ca^+ [3], values $\Delta N_e \approx 0.1$ were obtained.

Another consideration that could affect the validity of the f -sum rule is the degree to which intermediate coupling produces singlet–triplet mixing between the $4s4p \ ^1P_1^o$ and $^3P_1^o$ levels. This can be investigated by extracting the mixing amplitudes from the measured energy spacings [21] among the $4s4p \ ^3P_2^o$, $^3P_1^o$, $^1P_0^o$ levels (0.534 853 au, 0.547 192 au, 0.576 662 au)

and the $4s4p\ ^1P_1^o$ level (see above). Since there are three intervals and only two amplitudes, the system is overdetermined. The two normalized amplitudes can be expressed as a single mixing angle θ . A solution involving only two of the splittings (taking the average energy of the $J = 1$ levels) is given by

$$\cot(2\theta) = \pm \frac{1}{\sqrt{2}} \left[\frac{3(^3P_1^o + ^1P_1^o - 2^3P_0^o)}{(^3P_2^o - ^3P_0^o)} - 1 \right] \quad (8)$$

(here the energy levels are designated by their spectroscopic symbols). This yields a value $\tan\theta = 0.0857$ which, combined with the ratio of the $^3P_1^o$ and $^1P_1^o$ excitation energies, indicates that singlet–triplet mixing decreases the oscillator strength of the resonance line by only 0.52%. Checking the overdetermination, the mixing amplitudes obtained from equation (8) reproduced the $^1P_1^o$ – $^3P_1^o$ splitting to within 0.082%, consistent with the assumption of a pure single configuration.

3.2. Determination of the oscillator strength and lifetime

Inserting equation (7) and the values for $E_{4s,4p}$, $E_{4s,5p}$ and α_d into equation (4),

$$1.5804 - 0.1335\Delta N_e \leq f_{4s,4p} \leq 1.6298. \quad (9)$$

As can be seen from equations (3) and (6), N_e affects only the upper bound on the bracketing of α_d and β . Since equation (4) is an inversion of equation (3), only the lower bound of $f_{4s,4p}$ is affected by N_e . Thus there is a slight downward shift with increasing ΔN_e for the lower bound of $f_{4s,4p}$. For $\Delta N_e = 0.1$, the lower bound shifts from 1.5804 to 1.5670, a 0.85% reduction. If we accept this as a reasonable value for ΔN_e , the inequality becomes

$$1.5670 \leq f_{4s,4p} \leq 1.6298, \quad (10)$$

which has a centroid $f_{4s,4p} = 1.598$ and a spread of ± 0.031 , or 2%. Since this determination involves inequalities rather than equalities, this value for $f_{4s,4p}$ was inserted into equation (3) to test reciprocity. This recovered a value for α_d of $2.687 a_0^3$, consistent within the tight bracketing of the inequalities. Tests using $\Delta N_e = 0$ and 0.2 were also made, which shifted the value of $f_{4s,4p}$ by only ± 0.007 .

If the bracketing half-width is combined in quadrature with the 1.5% uncertainty in the measurement of α_d , the value deduced is

$$f_{4s,4p} = 1.60 \pm 0.04. \quad (11)$$

The fact that 1.6 units of the oscillator strength reside in $f_{4s,4p}$ means that there are only ≈ 0.5 units of oscillator strength spread over all of the other bound and continuum states. A lifetime measurement [16] for the $4s5p\ ^1P_1^o$ level yields an upper limit (assuming 100% branching to ground) $f_{4s,5p} \leq 0.063$, illustrating the dominance of $f_{4s,4p}$ in the sum. Moreover, the low-lying intrashell nature of the $n = 4$ transition leads to a large ratio $E_{4s,5p}^2/E_{4s,4p}^2 \approx 8.5$, further decreasing the contribution of higher-lying levels to the inequality. For these reasons, the bracketing inequality is very tight, and relatively insensitive to ΔN_e .

For an unbranched transition, the relationship [22] between the lifetime and the oscillator strength is (energy in au)

$$\frac{g_{4p}}{\tau_{4p}} = \frac{2c\alpha^4}{a_0} E_{4s,4p}^2 g_{4s} f_{4s,4p} \quad (12)$$

where g_k denotes the degeneracies of the levels and α is the fine structure constant. Making this conversion, the result in equation (11) corresponds to a lifetime

$$\tau_{4p} = 0.096 \pm 0.003 \text{ ns}. \quad (13)$$

This confirms the ANDC measurement 0.101 ± 0.010 ns [15] with a significant improvement in accuracy, and also corroborates the correctness of the identification of the cascade in that ANDC analysis. The value is also in good agreement with theoretical estimates [17, 18].

3.3. Determination of the nonadiabatic correlation

Having established the value of $f_{4s,4p}$, this can be used in equation (6) to bracket the value of β . This yields values

$$1.6947 \leq \beta \leq 1.7119 + 0.0428\Delta N_e. \quad (14)$$

Because equation (6) involves the cube of the excitation energies and $E_{4s,5p}^3/E_{4s,4p}^3 \approx 25$, the effect of ΔN_e on the bracketing is even less in the case of β . Again using the estimate $\Delta N_e = 0.1$

$$1.6947 \leq \beta \leq 1.7162. \quad (15)$$

Taking the central value and combining the bracketing width in quadrature with the uncertainty in the measurement of α_d , the value obtained is

$$\beta = 1.71 \pm 0.03\alpha_0^5. \quad (16)$$

Theoretical values for this quantity are not available, but such calculations could provide a useful test of the method.

4. Application to isoelectronic sequences

The quantum-mechanical aspects of both the emission lifetime τ_{4p} and the absorption oscillator strength $f_{4s,4p}$ are derived from the dipole transition element as expressed in the line strength factor $S_{4s,4p}$ [22]:

$$S_{4s,4p} = S_{4p,4s} = |\langle \Psi_{4s} | \mathbf{r} | \Psi_{4p} \rangle|^2. \quad (17)$$

While this quantity is theoretically defined, it can alternatively be treated as an empirically-determined experimental parameter. It can be deduced from the oscillator strength using [22]

$$g_{4s} f_{4s,4p} = \frac{2}{3} E_{4s,4p} S_{4s,4p} \quad (18)$$

(energy in au), where $f_{4s,4p}$ is determined either from the measured value of τ_{4p} using equation (12), or from the measured value of α_d using equation (4).

There is much empirical evidence [23–27] indicating that ions with one or two out-of-shell electrons exhibit a nearly linear isoelectronic variation when the line strength factor is scaled quadratically with the nuclear charge Z and plotted against a suitably chosen reciprocal screened charge. Thus

$$Z^2 S = S_H + B/(Z - C) \quad (19)$$

where the trend approaches the hydrogenic limit S_H for large Z [23]. An example is shown in figure 1. The solid diamond represents the hydrogenic value $S_H = 1080$.

In the case of two-valence-electron systems, it is also possible to take into account the effects of intermediate coupling [24] using the singlet–triplet mixing angle obtained from equation (8). First, line strength factors $S(\text{Res})$ and $S(\text{Int})$ are deduced from measured lifetimes for the resonance and intercombination transitions. These are then corrected for the effects of intermediate coupling to obtain effective line strengths $S_r(\text{Res})$ and $S_r(\text{Int})$ using the relationships

$$S_r(\text{Res}) \equiv S(\text{Res})/\cos^2 \theta \quad S_r(\text{Int}) \equiv S(\text{Int})/\sin^2 \theta. \quad (20)$$

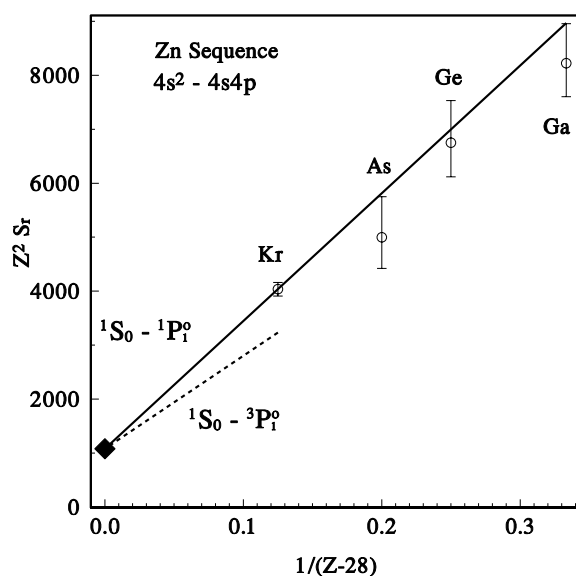


Figure 1. Isoelectric interpolation of the reduced line strengths for the $4s^2-4s4p$ transitions in the Zn sequence.

This approach was applied to the Zn sequence earlier [25]. Based on lifetime measurements (generally of $\approx 10\%$ precision) of the resonance transitions in Ga II, Ge III, As IV and Kr VII, and of the intercombination transitions in Kr VII, Nb XII, Mo XIII and Ag XVIII, empirical lifetimes were predicted for all charged ions from gallium to uranium. The precise determination of the Kr VII lifetime reported here provides a means to substantially improve the determination of the singlet lifetimes in this sequence, as is evident from figure 1.

In the past this approach has been hindered by the lack of high precision measurements for multiply-charged ions. Measurements at the 1% level are largely limited to neutral and singly ionized atoms [28], where methods such as laser selective excitation of a static sample can be employed. However, the regularity exhibited by isoelectronic data expositions occurs for multiply-ionized systems, where the interactions are predominantly central. Most measurements in multiply-charged ions are made through non-selective excitation of a fast ion beam. The uncertainties in this type of measurement are typically 5–10%, often increasing with degree of ionicity. Thus the use of the method described here to obtain a 3% measurement in a six-times ionized atom represents a significant advance in the predictive accuracy of this method.

It is clear from figure 1 that the Kr VII point, together with the hydrogenic asymptote at high Z , establishes the fit to unprecedented accuracy. If measurements of modest accuracy are sufficient to establish a screening constant C that produces linearity in this plotting exposition, then a single measurement of high accuracy can be connected with the hydrogenic asymptote to specify all members of the sequence. If a second ion in this sequence could be measured to this precision, it would provide a means of confirming the linearity and further sharpening the predictions.

Similar predictive semiempirical parametrizations of measured data have been carried out for the Mg [24], Cd [26] and Hg [27] sequences. These studies could be greatly improved by the addition of lifetime values deduced from precision spectroscopic determinations of α_d using the methods described here. When a comprehensive isoelectronic parametrization has

been made for τ , the results can be utilized to provide a similar isoelectronic data base for α_d and β .

5. Accuracy of the method

As has been described above, the accuracy of this method involves the uncertainties in the measured quantities, the magnitude of and the uncertainties in the width of the bracketing inequality, and the validity of the single configuration approximation. Uncertainties in the energy levels are usually well below the 1% level and do not contribute to the uncertainty. The single configuration approximation can be tested using the overdetermination of the level separations.

The width of the bracketing inequality (and hence the influence of its uncertainty) will be small if: $f_{4s,4p}$ is large; $E_{4s,4p}$ is small; and $E_{4s,5p}$ is close to the ionization limit. For ions of the Mg, Zn, Cd and Hg sequences these criteria are generally satisfied, and the propagation of uncertainties within the method should be comparable to or smaller than the experimental uncertainties in a 1–2% spectroscopic determination of α_d .

Additional tests of the method could be made if precision time-resolved measurements of τ and precision spectroscopic measurements of α_d could both be performed for the same ion, allowing a cross-check of consistency and reciprocity. The accuracy of the method could also be probed by theoretical investigations of the magnitude of inner-shell contributions to ground-state oscillator strengths.

6. Conclusion

For ionic systems for which the ground-state oscillator strength is concentrated in the lowest-lying resonance transition, this method provides a means to interconnect α_d , β and τ . If, as in this case, a precision measurement of α_d is available, τ and β can be deduced. Alternatively, if a precision measurement of τ is available, α_d and β can be specified. Moreover, screening parametrizations of reduced-line-strength data have been shown to permit accurate isoelectronic interpolation and smoothing for entire isoelectronic sequences, based on a small number of precisely measured lifetimes. This method could permit similar isoelectronic specification α_d and β . These quantities could also be efficiently deduced from *ab initio* theoretical calculations of the intrashell oscillator strength.

It is hoped that the opportunity to exploit these interconnections will stimulate additional precision spectroscopic studies of this type in similar systems.

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