SEMI-EMPIRICAL REGULARITIES IN THE SPECTRA AND TRANSITION PROBABILITIES OF HEAVY AND HIGHLY IONISED ATOMS

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Semi-empirical methods are being used to systematise available data for one and two valence electron isoelectronic sequences to provide accurate estimates of energy levels, fine structure separations, transition probabilities, ionisation potentials, etc. in very heavy and very highly ionised atoms. Through core polarisation and core penetration models, quantum defect formulations and charge screening parameterisations, quantifiable regularities have been discovered which can be tested for higher ionisation stages by fast ion beam methods. The techniques are described and several applications are presented.

1. Introduction

Fast ion beam methods provide a convenient means for the study of very heavy and very highly ionised atoms, for which little spectroscopic data presently exist. High wavelength resolution of a fast moving source can be achieved through optical refocussing techniques, but there is a need for very accurate wavelength predictions and precisely known calibration lines. The accuracies required for spectroscopic classification often exceed the present capabilities of ab initio theoretical calculations for highly relativistic many-electron systems and semi-empirical data parameterisations can often provide more accurate predictions. As one moves up in ionisation stage along an isoelectronic sequence, the inner core electron orbits shrink more rapidly than the outer active electron orbit, and parameterised single electron models can provide very accurate extrapolations. In association with a program of experimental fast ion beam studies, we are making extensive use of semi-empirical methods to systematise available data and to predict wavelengths and lifetimes in very heavy and very highly ionised systems. Several applications will be described below.

2. Polarisation and penetration models

For states of sufficiently high principal and orbital angular momentum quantum numbers n and l, the active electron and the passive core are essentially coupled only by central electrostatic interactions, and the term values T (freed of magnetic fine structure and exchange effects by an appropriate configuration average) are well represented by [1,2]

$$T = R\left[\langle \zeta r^{-1}\rangle + \alpha^2\left(\langle \zeta^2 r^{-2}\rangle - \tfrac{3}{4}\langle \zeta r^{-1}\rangle^2\right)\right.$$

$$\left. + \langle \alpha_d r^{-4}\rangle + \langle (\alpha_q - 6\beta) r^{-6}\rangle + \dots\right], \qquad (1)$$

where R is the reduced-mass-corrected Rydberg energy, α is the fine structure constant, ζ is the central charge (in units of e), r is the distance from the active electron to the nucleus (in units of a_0, the reduced-mass-corrected Bohr radius), α_d and α_q are the dipole and quadrupole polarisabilities of the core (in units of a_0^3 and a_0^5, respectively) and β is a measure of the inability of the core to follow the motion of the outer electron (in units a_0^5). Higher order moments and retardation effects [3] could also be included, but are here neglected.

A standard approach [1] has been to consider "non-penetrating states" and replace the averages over reciprocal powers of the radius in eq. (1) by their hydrogenlike values. Term values can then be parameterised by adjusting effective values for the quantities α_d and $\alpha_q - 6\beta$. This method is very useful for determining ionisation potentials by extrapolation along a Rydberg series. However, the values for the core parameters inferred from different Rydberg series in the same ion often differ substantially (particularly in the case of $\alpha_q - 6\beta$). This is usually ascribed to penetration effects, and although it has little effect on the determination of the ionisation potential, it severely limits the reliability of the polarisation approach for prediction of term values in higher Rydberg series. This is illustrated for Si III in fig. 1. According to the polarisation model, data plotted in this manner should fall along a straight line with a slope $\alpha_q - 6\beta$ and an intercept α_d. This is reasonably so in fig. 1 for the h series, but there is also an apparent trend for the intercept to increase and the slope to decrease with increasing l. These remarks are clearly speculative, since the results plotted are sliding spark data [4] so the i series is subject to shifts and broadening due to the Stark effect, and since the g series probably contains configuration interaction effects.
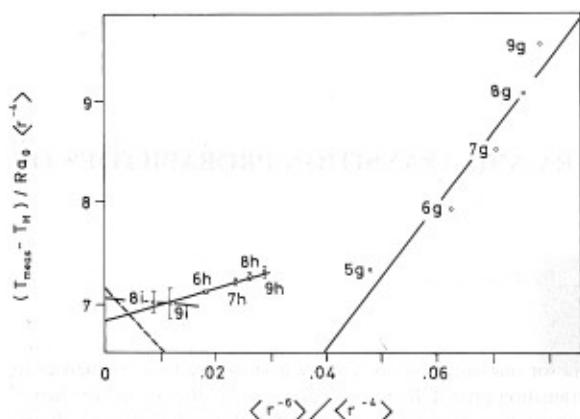
Fig. 1. Core polarisation analysis for Si III. For non-penetrating orbits the quantities labelling the axes are linearly related with an intercept α_d and a slope $\alpha_q - 6\beta$. The solid lines denote fits to the individual l Rydberg series and the dashed line indicates the theoretical prediction. Data are from ref. 4.

However, similar tendencies are observed in many other systems [5] and the validity of this approach is worthy of examination before extrapolations are made to the very high n and l states that can be produced in field-free fast ion beams.

Isoelectronic sequences with two valence electrons provide a good probe of this method, since in these systems core polarisation effects arise mainly from the single out-of-shell core electron, so that α_d, α_q and β can be easily and reliably calculated theoretically [6,7]. Moreover, the relatively large polarisabilities of these cores strongly break the hydrogenic l degeneracy, giving rise to well separated and easily identified families of lines that would be useful for calibration purposes if their wavelengths could be accurately predicted. Calcu-

lations have been made [6,7] up to high stages of ionisation and differ systematically from values inferred from measurements. The theoretical α_d is always slightly larger than the measured intercept and the theoretical $\alpha_q - 6\beta$ differs not only in magnitude, but also in sign from the measured slope, both determined on a plot similar to fig. 1. For the Si III example, the theoretical values are $\alpha_d = 7.22$ and $\alpha_q - 6\beta = -55.6$, and the intercept and slope corresponding to these values are indicated by the dashed line in fig. 1.

We have attempted to incorporate penetration effects into this analysis by a simple classical extension of the polarisation model [2]. The penetrated portion of the core charge is modelled as a hollow spherical shell of radius ρ that has a quantity of charge $-\Delta\zeta$ uniformly distributed over its surface. (The model might be picturesquely described as a quantised Kepler orbit that pierces a Ptolemaic sphere of charge.) It is further assumed that α_d and $\alpha_q - 6\beta$ vanish for $r < \rho$. For $r > \rho$ theoretical values can be used for α_d, α_q and β, whereas ρ and $\Delta\zeta$ are adjusted to fit the data. Clearly a volume distribution of charge would be a more realistic model than this hollow shell, but this would also destroy the Keplerian ellipticity of the internal orbit, and sacrifice the major advantage of the model, which is its simplicity. A better representation of the data can be achieved by a compromise in which the hollow shell is retained, but the surface charge is allowed to increase weakly with the depth of penetration. An empirical Ansatz that has been found to achieve this quite well is

$$\Delta\zeta = \Delta\zeta_0 \exp(B/P), \tag{2}$$

where $\Delta\zeta_0$ and B are adjustable parameters and P is the classical perihelion distance as computed from the external orbit segment. The results of a weighted non-linear least-squares adjustment of ρ, $\Delta\zeta_0$ and B to the data

Table 1
Results of weighted non-linear least-squares adjustment of ρ, $\Delta\zeta_0$ and B, to the data of fig. 1.

Config.	T(obs)	T(obs) $- T$(fit) [a]	$\Delta\zeta$	ρ	$\Delta\zeta_0$	B
3s5g	39 837.39	0.00	0.021			
6g	27 665.16	−0.21	0.041			
7g	20 321.31	+0.69	0.056	11.84	2.47×10^{-4}	20.44
8g	15 554.55	−0.45	0.068			
9g	12 285.7	−0.50	0.076			
3s6h	27 449.91	0.00	0.011			
7h	20 202.00	0.00	0.015	7.95	1.09×10^{-3}	16.17
8h	15 464.9	0.0	0.018			
9h	12 217.3	0.0	0.020			
3s8i	15 444.3	0.0	0.007	8.92	6.54×10^{-3}	−
9i	12 202.3	0.0	0.007			

[a] $\alpha_d = 7.22$, $\alpha_q = 10.4$, $\beta = 11.0$.

shown in fig. 1 are given in table 1. Magnetic fine structure and exchange effects have been eliminated by a weighted configuration average described in ref. 2. Although the method requires separate values for ρ, $\Delta\zeta_0$, and B for each series it seems likely that, as more data become available, a pattern for their variation with l and with ζ might emerge that could reduce the number of free parameters further.

The method has already been successfully applied to a number of other systems. For example, in Cs I [8] this method correctly reproduces term value measurements [9] for $l \geqslant 3$ and agrees with quantum defect measurements [10] for $n \leqslant 109$. For He I [11] the method has been very accurately tested using rf measurements [12,13] of $\Delta n = 0$ transitions, where the gross energy contribution is absent and the precision with which polarisation and penetration energies can be determined is substantially improved. In this case the method has been found to reproduce $n > 6$ D–F, F–G and G–H $\Delta n = 0$ separations to within about 1 MHz.

The polarisation approach can also provide predictions for transition probabilities, since the one-electron transition moment should properly include both the dipole moment of the valence electron and the dipole moment induced in the core. The former is proportional to r, the latter to α_d/r^2. For non-penetrating states the transition moments of r and r^{-2} can be related by a simple identity (the relationship between the length and acceleration forms of the operator). Using this relationship the transition probability can be written as [14]

$$\zeta^2 \lambda_{ik}^3 A_{ik} = \left[1 - \alpha_d/4\zeta R^2 \lambda_{ik}^2\right]\left[\lambda_{ik}^3(\text{H}) A_{ik}(\text{H})\right] \qquad (3)$$

where A_{ik} and λ_{ik} are the transition probability and wavelength of the ion in question and $A_{ik}(\text{H})$ and $\lambda_{ik}(\text{H})$ are the corresponding quantities in neutral hydrogen. Although the polarisation corrections in eq. (3) are usually small, they can approach 10% in two-valence-electron systems.

3. Quantum defect formulations

Although the classical picture does not provide a very satisfactory basis for transition probability calculations [15], the quantum defect method is a useful bridge between the semi-classical model and the ab initio quantum mechanical formulation. This method can be formulated [16] in terms of simple approximate functional relationships that can lead to insights concerning large classes of states and ions which are less apparent in a full ab initio treatment. The historical origin of this method, the Rydberg–Ritz parameterisation of the Balmer formula, is equivalent to the polarisation–penetration model described in section 2, since it can easily be shown [2] that both the polarisation and penetration corrections to the gross energy are proportional to n^{-3}.

This is the phenomenological basis for the quantum defect δ, since

$$T \equiv R\zeta^2/(n-\delta)^2 = R(\zeta/n)^2[1 + 2\delta/n + \cdots]. \qquad (4)$$

The quantum mechanical basis is provided by the realisation that the ionic core modifies the wave function in the external region simply by shifting the phase of the nodes of a corresponding hydrogenic wave function by $\delta\pi$ [17]. For highly penetrating orbits δ can be quite large, causing the external wave function to exhibit fewer nodes than would the hydrogenic equivalent (i.e., owing to the phase shift, some of the nodes are drawn inside the core, causing the external wave function to resemble a hydrogenic state of lower n).

Insights concerning the various contributions to δ can be gained by comparing eqs. (1) and (4). As one moves up in charge state along an isoelectronic sequence the core shrinks relative to the active electron. This causes the penetration portion of δ to sharply diminish, whereas the polarisation portion of δ first increases with increasing ζ, then passes through a maximum and ultimately decreases toward zero as ζ^{-2}. The latter occurs because at low ζ differential screening causes the core polarisabilities to stiffen much faster with ζ than the valence electron draws in. For large ζ the differential screening becomes negligible relative to the gross energy scaling factor ζ^2. The relativistic portion of δ increases as ζ^2 but its relative magnitude is small. This decrease in δ with increasing ζ causes nodes to move out of the core and into the external region. For overlap integrals which favour the external region, such as the dipole transition element, the difference in outward march of the nodes of the upper and lower states can cause regular oscillations, and hence regular cancellations, in the integral. A knowledge of the precise
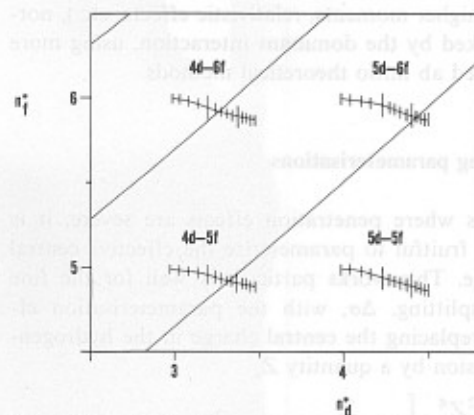

Fig. 2. Plot of effective quantum numbers for d–f transitions in the Cu sequence. Ions from Cu I to Mo XIV are designated (from left to right) by division markers on the loci. The solid lines denote cancellations in the dipole transition integral as predicted by quantum defect theory.

location of such cancellations is useful both in the classification of spectra and in the study of small perturbations which become measurable when the dominant interaction is absent. We have developed [18,19] a simple graphical technique which we have used to locate likely cancellations in Rydberg transition of ions of the Li, Na, K, Cu, Rb and Cs isoelectronic sequences.

An application of this approach to the d–f transitions of the Cu isoelectronic sequence is shown in fig. 2. A locus is drawn in the space of the effective quantum numbers ($n^* = n - \delta$) of the upper and lower state for each transition, with the ions (from left to right) Cu I through Mo XIV indicated by division markers. The downward slope of the locus signifies that the d-state quantum defects arise mainly from penetration effects (since they are large and decrease with ζ) whereas the f-state quantum defects arise mainly from polarisation effects (which have not yet reached their maximum value with increasing ζ). The solid lines designate the nodes of sign change in the dipole transition integral, which correspond to cancellations in the transition probability. Notice that for the ions at the neutral end of the sequence these integrals have the opposite sign from the hydrogenic (high ζ) case, indicating that at low ζ nodes are concealed within the core. Intersections on this plot indicate that intensity anomalies should be exhibited for 4d–5f transitions near Kr VIII, for 4d–6f transitions near Br VII and for 5d–6f transitions near Y XI. Some of these indications have been verified by recent observations [20], motivating pursuit of a program of "disappearance spectroscopy" in which *missing* lines are studied. By a comparative study of relative intensities along either an isoelectronic sequence or a Rydberg series or within a fine structure multiplet, the position of exact cancellation could be experimentally pinpointed. This knowledge could be used to sensitively probe small effects (core polarisation, configuration interaction, higher moments, relativistic effects, etc.), normally masked by the dominant interaction, using more sophisticated ab initio theoretical methods.

4. Screening parameterisations

In cases where penetration effects are severe, it is sometimes fruitful to parameterise the effective central core charge. This works particularly well for the fine structure splitting, $\Delta\sigma$, with the parameterisation effected by replacing the central charge in the hydrogen-like expression by a quantity Z_s

$$\Delta\sigma = \frac{R\alpha^2 Z_s^4}{n^3 l(l+1)}\left[1 + \sum_{i=1}^{\infty} C_{nli}(\alpha Z_s)^{2i} + \text{QED corrections}\right], \quad (5)$$

where C_{nli} denotes a set of rational fractions given in ref. 21. Eq. (5) is used to transform measured values for $\Delta\sigma$ into values for Z_s. It has been found [1,22] that there is often a high degree of empirical linearity between the screening and the reciprocal of the screened charge, expressed as

$$(Z - Z_s) \cong S_0 + b/Z_s. \quad (6)$$

In many cases the fidelity of this purely empirical relationship is astonishing. An example is shown in fig. 3 for the $^2P^0$ and ^2D fine structure separations in the Cu isoelectronic sequence. Eq. (6) reproduces the data to within experimental accuracies for all but the first few stages of ionisation, where effects such as exchange core polarisation [23,24] become significant. No data are presently available to test the persistence of this linearity for $Z > 68$, but there $Z - Z_s$ is small and slowly varying relative to Z, so the fine structure predictions become less sensitive to the rigour of eq. (6). Fig. 3 includes many recent measurements [20,25–28] which were correctly predicted earlier by this procedure [29]. This method is very sensitive to inconsistencies, and a recent revision [30] in the 6p $^2P_{1/2}$ level in Mo XIV removed a anomaly earlier noted by this procedure [31].
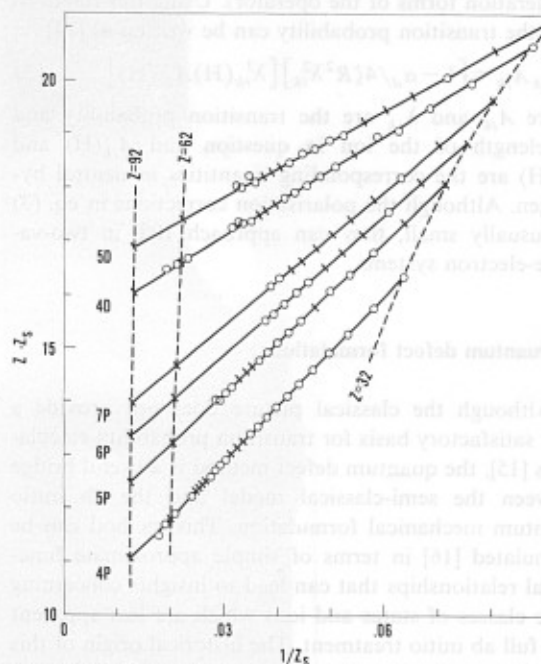
Additional regularities can be recognised by ex-

Fig. 3. Effective screening versus reciprocal screened charge for the $^2P^0$ and ^2D fine structure splittings in the Cu sequence. Circles represent measured data (with division markers where data are missing), solid lines denote linear fits and dashed lines trace specific ions through the various Rydberg terms.

amination of the dependence of the linear fits in fig. 3 as functions of n and l. One empirical regularity is seen if eq. (6) is rewritten in the form

$$Z_s = \left[(Z - S_0) + \sqrt{(Z - S_0)^2 - (Z_0 - S_0)^2} \right] / 2, \quad (7)$$

where $Z_0 = S_0 + 2\sqrt{b}$ is the lowest ionisation stage of the sequence to which the formula is applicable. It is interesting to note that Z_0 seems to coincide with the onset of significant curvatures in the $Z - Z_s$ versus $1/Z_s$ plot. These curvatures (which are not adequately described by a higher order polynomial in $1/Z_s$) probably arise from effects such as exchange core polarisation which are more important at the neutral end of the sequence. It has been observed that Z_0 often turns out to be approximately the same number for many different multiplets in the same isoelectronic sequence. For example, in the Cu sequence [22], $Z_0 \simeq 30.9$ for all $^2P^0$ and D multiplets, which rules out only the first three members of the sequence. For the Mg sequence [32] $Z_0 = 11.5$, so no members are ruled out. Another empirical regularity has also been noticed (with the help of a computer graphics terminal and many trials), namely

$$S_0 \simeq q(n - n_0)^\gamma, \quad (7)$$

where n_0 is the principal quantum number of the highest closed shell of the core and q and γ are constants for a given Rydberg series. Eq. (7) has only been tested for the Cu sequence, but there five fitted parameters (one set of values of q and γ each for the $^2P^0$ and ^2D series and Z_0) have been used to predict [21] the fine structure splittings for the $n = 4-8$ $^2P^0$ and $n = 4-6$ ^2D term values for all ions from As V to U LXIV. For the two-valence-electron Mg I sequence, the 3s3p and 3s4p configurations are reasonably unperturbed and can also be treated using this formalism [32]. Here, not only the fine structure separations, but also the direct and exchange Slater integrals could be accurately described by screening parameterisations.

5. Conclusion

The semi-empirical methods described here are simple and utilitarian. Their value does not require a firm physical basis but resides solely in the success with which they reproduce measured data. The parameters developed do, however, summarise large and unwieldy bodies of data in exceedingly concise form. The regularities in these parameterisations which have emerged are often quite striking, and it is possible that a confrontation between ab initio theory and experiment in terms of these quantities (describing whole series and sequences at once) could be an efficient and instructive approach.

Fast ion beam spectroscopy is the only present means

of production of heavy and highly ionised atoms in an environment in which high n and l states are not strongly field quenched and it therefore provides the means of confirmation or refutation of these semi-empirical methods.

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Discussion

Hibbert: Could you use these schemes for predicting fine structure splittings? I'm thinking of the work that Eric Pinnington and ourselves have been doing, and also Dr. Veje, on xenon ions – could you predict the fine structure splittings of the high levels of Xe VII?

Curtis: Yes, if there were some data on lower or higher charge states to connect to, or, if it were possible to make some homologous estimate of what the screening parameters might be. It's nice in that, no matter which way you move, there seem to be regularities. It seems to be smooth whether you go homologously, isoelectronically, or up a Rydberg series, provided you have a system which doesn't have something dramatic happening. And if there's something dramatic happening, that's also interesting. So again, yes, if there's data to base it on or if

there is a way to make estimates of the screening parametrisation and to scale them somehow.

Hibbert: Certainly I think there might be data for the homologous atoms.

Mowat: Those are very nice straight lines. Do the data points deviate from the lines by 1% or 1/10% or some order of magnitude like that?

Curtis: The screening parameters may deviate by 1/10% or 1% or so, but the fine structures don't. As you go to high Z the screening is falling off – giving less and less screening as the orbit and core shrink. Suppose we look at uranium. It has a high Z and also low screening, so even if the screening is off by a percent or so, the accuracy in the fine structure separation itself is very good. In almost every case it's within the accuracy of the experimental data point. There are only a few cases in which the points fell off the line to within more than the experimental uncertainties and in those cases we have gone back to the authors. Usually they have remeasured it and found that the point was wrong. It's a very good way to recognise things that are wrong. If you see a point which is off then there either must be a misclassification or else there is something very interesting going on, for example, a plunging level going through.