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Dipole Polarisabilities for Single Valence Electron Ions

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Abstract

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Estimates of ground state static electric dipole polarisabilities, utilising the numerical Coulomb approximation, are presented for ions of the Li, Na and Cu isoelectronic sequences to as high as 23 stages of ionisation. Comparisons are made with experimental results from spectroscopic studies of core polarised non-penetrating states in the Be, Mg and Zn isoelectronic sequences, which indicate that these estimates can provide a useful guide in spectroscopic analysis.

Non-penetrating states in highly ionised multi-electron atoms are often strongly populated in low density light sources such as beam-foil and theta pinch excitation. Transitions between these states have been identified using the spectroscopic polarisation formula [1], in which non-penetrating terms are described by two empirical parameters, phenomenologically associated with the dipolar and quadrupolar polarisabilities of the ionic core. The Be, Mg and Zn isoelectronic sequences show particularly large polarisation effects, and the transition wavelengths for a given pair of principal quantum numbers often differ so greatly from each other and from the hydrogen-like value that trial estimates of the effective polarisabilities are useful and sometimes necessary for their identification. To facilitate such spectroscopic studies, calculations of the dipole polarisabilities for the ionic cores appropriate to these isoelectronic sequences, computed utilising the numerical Coulomb approximation [2, 3], are herein presented and compared with spectroscopic data.

States of high principal and orbital angular momentum quantum numbers n and l in multi-electron atoms are useful, e.g., in spectroscopic studies of excitations, in the determination of ionisation potentials, and in the estimation of core polarisabilities. These states tend to be free of series perturbations and non-adiabatic core couplings and can be described by a simple quasi hydrogen-like parametrisation. Thus the term value $T(n, l)$ is written [1] as

$$T(n, l) = T_{\mathrm{H}}(n, l) + A(Z)P(n, l)[1 + k(Z)q(n, l)] \qquad (1)$$

where $T_{\mathrm{H}}(n, l)$ is the hydrogen-like Sommerfeld–Dirac term value, to which a core polarisation correction is added. Here $P(n, l)$ and $q(n, l)$ are quantities involving the hydrogen-like expectation values which are tabulated in [1] and [4], while $A(Z)$ and $k(Z)$ are empirical parameters which together specify all non-penetrating term values for a given ion. Experience indicates that $A(Z)$ is very closely related to the dipole polarisability α_{d} and is often well represented by theoretical estimates using

$$A(Z) \cong \alpha_{\mathrm{d}} \zeta^4 \qquad (2)$$

where ζ is the net core charge (nuclear charge minus core electrons). In this context α_{d} is usually expressed in units a_0^3 (where a_0 is the Bohr radius). Although the quantity $A(Z)k(Z)$ is conceptually associated with the quadrupole polarisability, other effects (core penetration, non-adiabatic processes, etc.) often reside in its empirical value [5, 6] and it is less reliably predicted by theoretical calculations.

The polarisation corrections have been found to be very large in the cases of the Be, Mg and Zn two valence electron isoelectronic sequences, owing to the high polarisabilities of their single valence electron cores. The dipole polarisabilities can easily be computed for such alkali-like cores, if contributions from the closed shells are neglected, using the well known formula [7]

$$\alpha_{\mathrm{d}} = 4R^2 \sum_{n=n_0}^{\infty} f_{n_0 n} \lambda_{n_0 n}^2 \qquad (3)$$

Here R is the Rydberg constant (in cm^{-1}) while $f_{n_0 n}$ and $\lambda_{n_0 n}$ are the absorption oscillator strength and wavelength (in cm) for the $n_0 s$–np transitions, with $n_0 = 2$, 3 and 4 for the Li, Na and Cu isoelectronic sequences.

The calculation of oscillator strengths for these single valence electron isoelectronic sequences has been the object of many investigations by a number of theoretical approaches. The computations of Lindgård and Nielsen [2] and of Lindgård et al. [3] using the semi-empirical numerical Coulomb approximation are very comprehensive and generally agree with ab initio calculations, where available, to within better than 10%. This accuracy should be adequate to serve as a comparison to spectroscopic results, and to study the validity of eq. (2). As a point of information, it was noticed that for Ga^{21+} through Se^{24+}, [2] inadvertently interchanges the fine structure component upon which the multiplet value is based, and appropriate corrections were made to achieve consistency.

Table I summarizes the estimates of α_{d} obtained from eq. (3) using the tabulations of [2] and [3]. It was necessary to truncate the sum at some finite value of n (although levels up to $n = 12$ are included in these tabulations for many ions). The errors introduced through this finite truncation can be estimated [8] individually using f sum rules and the diminishing nature of the series wavelength. These errors are very small, and it can be observed that for these alkali-like sequences the $n = n_0$ element contains over 95% of the sum. Thus the high core polarisability of the alkaline earth isoelectronic sequences is directly attributable to the large oscillator strengths and low excitation energies of the $\Delta n = 0$ alkali metal sequence resonance transitions [9]. It has been suggested by Flannery and Stewart [10] that the dominance of the $\Delta n = 0$ transitions could cause the isoelectronic behaviour of α_{d} to vary as the cube rather than the fourth power of the reciprocal screened charge as is usually assumed. The theoretical results in Table I were therefore fitted by a three parameter (proportionality constant, screening constant and power constant) adjustment of

Table I

ζ	Ion	$\alpha_d(a_0^3)$	$A(Z)/\zeta^4$	Ion	$\alpha_d(a_0^3)$	$A(Z)/\zeta^4$	Ion	$\alpha_d(a_0^3)$	$A(Z)/\zeta^4$
1	Be	23.9	[24.4][a]	Mg	33.9		Zn	18.1	
2	B	7.67	[7.83][a]	Al	13.8	12.18[c]	Ga	9.95	
3	C	3.39	[3.45][a]	Si	7.22	6.858[d]	Ge	6.25	
4	N	1.78	1.606[b]	P	4.30	3.699[e]	As	4.27	
5	O	1.05	[1.06][a]	S	2.79	2.45[f]	Se	3.05	
6	F	0.668		Cl	1.92	1.62[g]	Br	2.27	
7	Ne	0.450		Ar	1.38		Kr	1.74	
8	Na	0.317		K	1.02		Rb	1.37	
9	Mg	0.231		Ca	0.782		Sr	1.10	
10	Al	0.173		Sc	0.605		Y	0.900	
11	Si	0.132		Ti	0.478		Zr	0.745	
12	P	0.103		V	0.384		Nb	0.626	
13	S	0.0813		Cr	0.312		Mo	0.531	
14	Cl	0.0655		Mn	0.257		Tc	0.451	
15	Ar			Fe	0.215		Ru	0.388	
16	K	0.043[h]		Co	0.181		Rh	0.336	
17	Ca	0.0358		Ni	0.153		Pd	0.293	
18	Sc	0.0300		Cu	0.130		Ag	0.256	
19	Ti	0.0249		Zn	0.112		Cd	0.224	
20.	V	0.0210		Ga	0.095[i]		In	0.198	
21	Cr	0.0178		Ge	0.082[i]				
22	Mn	0.015[h]		As	0.072[i]				
23	Fe	0.0133		Se	0.062[i]				

a Ölme [12], recommended average of theoretical values.
b Hallin [11].
c Data of Kaufman and Hagan [14], reduced herein.
d Toresson [15].
e Zetterberg and Magnusson, [16].
f Dynefors and Martinson [17].
g Bashkin et al. [18].
h Only $\Delta n = 0$ f value included.
i Error in [2] corrected, see text.

a power law function, yielding

$$\alpha_d(\text{Li Seq}) \cong 1160/(\zeta + 2.21)^{3.52} \quad (4)$$

$$\alpha_d(\text{Na Seq}) \cong 1310/(\zeta + 2.44)^{3.05} \quad (5)$$

$$\alpha_d(\text{Cu Seq}) \cong 1220/(\zeta + 3.77)^{2.75} \quad (6)$$

which reproduce the calculations in Table I to within a few percent for all multiply charged ions. Thus the linear extrapolations of $\alpha_d^{-1/4}$ vs. ζ [1] which work well for inert gas like cores are not applicable here.

Comparisons with experimental values for $A(Z)/\zeta^4$ are also given in Table I. In the Be (Li core) sequence only the N IV study of Hallin [11] made an independent determination of $A(Z)$. Studies of B II [12], C III [12] and O V [13] all used theoretical estimates of α_d as inputs. Recommended averages of (and primary references to) various theoretical calculations are given in [12] and are listed in brackets in Table I. For the Mg (Na core) sequence, published values for $A(Z)$ exist for Si III–Cl VI [15–18], and a value for Al II can be deduced from published data [14]. No values of $A(Z)$ have yet been published for the Zn (Cu core) sequence.

There is a clear tendency for the experimental values to be smaller than the theoretical estimates by, on the average, a little more than 10%. Further evidence for this trend can be seen if the published O V data of Bockasten and Johansson [13] are re-analysed with $A(Z)$ left as a free parameter. The exact value obtained depends upon the weighting and terms included, but these data clearly infer a value $A(Z)/\zeta^4 < 1$ for O^{5+}.

Of the measurements cited, the value of $A(Z)$ for P V has probably the most precise determination, and its uncertainties could not account for the 15% deviation from these theoretical estimates. A number of other sources with ab initio calculations of f values for low values of n are available for this ion, but they infer similar results. For example the f values of Crossley and Dalgarno [19] yield $\alpha_d = 4.1$, those of Biemont [20] yield $\alpha_d = 4.6$ and the calculations of Froese Fischer [21] are consistent with [2] and likewise yield $\alpha_d = 4.3$.

On the basis of presently available data it appears that the effective core polarisabilities for spectroscopic studies of two valence electron ions can be approximately predicted by a slight downward correction of the theoretical values tabulated herein. Thus this very simple calculation could provide a useful guide in identifying non-penetrating transitions in highly ionised members of these isolectronic sequences.

References

1. Edlén, B., in Handb. der Physik 27, Springer-Verlag, Berlin, 1964, pp. 80–220.
2. Lindgård, A. and Nielsen, S. E., Atomic Data and Nuclear Data Tables 19, 533 (1977).
3. Lindgård, A., Curtis, L. J., Martinson, I. and Nielsen, S. E., Physica Scripta (in press)
4. Edlén, B., Physica Scripta 17, 565 (1978).
5. Öpik, U., Proc. Phys. Soc. 92, 566 (1967).
6. Vogel, P., Nucl. Intsr. Meth. 110, 241 (1973).
7. Dalgarno, A. and Kingston, A. E., Proc. Phys. Soc. 73, 455 (1959).
8. Miller, T. M. and Bederson, B., in Advances in Atomic and Molecular Physics 13, (eds D. R. Bates and B. Bederson), p 11, Academic Press, New York, 1977.
9. Van Vleck, J. H. and Whitelaw, N. G., Phys. Rev. 44, 551 (1933).
10. Flannery, M. R. and Stewart, A. L., Proc. Phys. Soc. 82, 188

(1963).
11. Hallin, R., Arkiv Fysik **32**, 201 (1966).
12. Ölme, A., Physica Scripta **1**, 256 (1970).
13. Bockasten, K. and Johansson, K. B., Arkiv Fysik **38**, 563 (1968).
14. Kaufman V. and Hagan, L., J. Opt. Soc. Am. **69**, 232 (1979).
15. Toresson, Y. G., Arkiv Fysik **18**, 389 (1960).
16. Zetterberg, P. O. and Magnusson, C. E., Physica Scripta **15**, 189 (1977).
17. Dynefors. B. I. and Martinson, I., Physica Scripta **17**, 123 (1978).
18. Bashkin, S., Bromander, J. Leavitt, J. A. and Martinson, I., Physica Scripta **8**, 285 (1973).
19. Crossley, R. J. S. and Dalgarno, A., Proc. Roy. Soc. London **A286**, 510 (1965) [Charge expansion results as cited by W. L. Wiese, M. W. Smith and B. M. Miles in Atomic Transition Probabilities Volume II, NSRDS-NBS 22, p. 120, U.S. Govt. Printing Office, Washington D.C., 1969].
20. Biemont, E., J. Quant. Spectrosc. Radiat. Transfer **15**, 531 (1975).
21. Froese Fischer. C.. Can. J. Phys. **54**. 1465 (1976).