Comments

Theoretical estimates of quadrupole polarization and dynamical correlation effects in single-valence-electron ions

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Theoretical estimates for the quadrupole polarizability α_q and the dynamical correlation factor β are presented for 66 ions in the Li, Na, and Cu isoelectronic sequences. Unlike the dipole polarizability, the theoretical values for these quantities do not agree with analogous empirical parameters deduced from spectroscopic data for the Be, Mg, and Zn isoelectronic sequences using an unpenetrated deformable core model. However, modifications to this model have been suggested which utilize these theoretical values in the prediction of transition wavelengths.

Accurate estimates of transition wavelengths between high n and l states in two valence electron ions are valuable, e.g., in providing wavelength calibration standards for fast ion beam spectroscopic sources.[1] In these alkaline earthlike systems the quasi-hydrogenlike outer electron has the hydrogenic degeneracy broken by the strong polarizability of the alkalilike core, providing easily distinguished and well separated families of lines. Existing spectroscopic data for such systems have been successfully parametrized using a deformable core model, and Dalgarno and Shorer[2] have recently proposed a semiempirical method which utilizes theoretical polarizabilities and non adiabatic corrections to predict unknown transition wavelengths. The purpose of this note is to provide a tabulation of theoretical quadrupole polarizabilities and dynamical correlation factors for one valence electron cores (two valence electron spectra) and to examine some of the difficulties which arise in their interpretation when compared with empirical results.

Term values for states in which one electron has n and l (principal and orbital angular momentum) quantum numbers much higher than those of any of the other electrons can often be accurately represented by the formula[3]

$$T = T_H + B_4 \langle r^{-4} \rangle + B_6 \langle r^{-6} \rangle , \tag{1}$$

where T is the physical term value, T_H, $\langle r^{-4} \rangle$, and $\langle r^{-6} \rangle$ are hydrogenlike calculations for the term value and radial expectation values for a single electron orbiting a deformable core of charge ζe, and B_4 and B_6 are empirically deduced constants. For ions in the alkalilike Li (Ref. 4) and Na (Ref. 5) isoelectronic sequences, Eq. (1)

has been found to describe reasonably well all states for which the orbital angular momentum of the valence electron exceeds that of any of the electrons in the inert gaslike core. For the alkaline earthlike Be (Refs. 6 and 7) and Mg (Refs. 8–11) isoelectronic sequences, term values have also been found to be described by Eq. (1), provided the analysis is restricted to much higher angular momenta $l \geq 5$. It has been suggested[2,12] that this formalism might also be applicable to $l = 3$ and 4 terms in alkaline earths if appropriate penetration corrections were made to the radial expectation values.

If Eq. (1) is compared with the theoretical expression for a long range nonpenetrating electron-ion interaction[13,14] the B_4 and B_6 values can be associated with theoretically calculable quantities. In this model

$$B_4 = \alpha_d , \tag{2}$$

$$B_6 = \alpha_q - 6\beta , \tag{3}$$

where α_d and α_q are the dipolar and quadrupolar polarizabilities of the core, and β is a measure of the inability of the core to follow the motion of the outer electron. Here quantities are expressed with T and T_H in units of the Rydberg energy R, r in units of the Bohr radius a_0, α_d in units of a_0^3, and α_q and β units of a_0^5. (Since the radial expectation values are here defined in terms of core charge scaled hydrogenlike wave functions, they contain implicitly the appropriate powers of ζ.) Empirical fits of spectroscopic data to Eq. (1) indicate that B_4 is well represented by Eq. (2), but as will be seen below, B_6 is not accurately represented by Eq. (3) unless there is some reinterpretation of the quantities T_H, $\langle r^{-4} \rangle$,

and $\langle r^{-6} \rangle$.

The quantities α_d and β are proportional to weighted sums of squares of the ground-state transition moment $\langle n_0 s \,|\, r \,|\, np \rangle$, and can thus be expressed as sums of the corresponding oscillator strengths $f_{n_0 s, \, np}$, weighted by reciprocal powers of the appropriate differences between the energy levels E_{nl}, and are given by[14]

$$\alpha_d = 4R^2 \sum_{n \geqslant n_0} \frac{f_{n_0 s, \, np}}{(E_{np} - E_{n_0 s})^2} , \tag{4}$$

$$\beta = 4R^3 \sum_{n \geqslant n_0} \frac{f_{n_0 s, \, np}}{(E_{np} - E_{n_0 s})^3} . \tag{5}$$

Thus α_d and β can easily be obtained from any comprehensive compilation of oscillator strengths. For these two valence electron spectra the cores

are alkalilike, and these sums are dominated by the strong $\Delta n = 0$ resonance transition. Uncertainties due to truncations in these sums can also be estimated[14] by using f sum rules and limiting series wavelengths, but these are generally very small for alkalilike systems. The quantity α_q is proportional to the square of the ground-state quadrupole matrix element $\langle n_0 s \,|\, r^2 \,|\, nd \rangle$. This can be calculated directly, but it can also be obtained from sums of dipole matrix elements, by virtue of

$$\langle n_0 s \,|\, r^2 \,|\, nd \rangle = \sum_{n'} \langle n_0 s \,|\, r \,|\, n'p \rangle \langle n'p \,|\, r \,|\, nd \rangle \tag{6}$$

and, therefore, α_q can also be deduced from a complilation of oscillator strengths. Using the definitions of α_q (Ref. 14) and $f_{nl, \, n'l'}$, (Ref. 15) it can be shown that

$$\alpha_q = \frac{54 R^3}{5} \sum_{n \geqslant n_0} \frac{1}{(E_{nd} - E_{n_0 s})} \left[\sum_{n' \geqslant n_0} (-)^\Phi \left(\frac{f_{n_0 s, \, n'p} f_{n'p, \, nd}}{(E_{n'p} - E_{n_0 s})(E_{nd} - E_{n'p})} \right)^{1/2} \right]^2 . \tag{7}$$

Here $(-)^\Phi$ is the relative sign of $\langle n_0 s \,|\, r \,|\, n'p \rangle$ and $\langle n'p \,|\, r \,|\, nd \rangle$, which can be determined by a simple graphical method[16] using effective quantum numbers and quantum defect theory. (Notice that for $n' > n$ the tabulated absorption oscillator strength $f_{nd, \, n'p}$ must be multiplied by $-\frac{5}{3}$ to account for the reversal of the degeneracies and sign of the energy difference.)

We have earlier[17] used Eq. (4) and the oscillator strength compilations of Ref. 15 to estimate α_d for the Li, Na, and Cu core sequences, which were found to predict values of B_4 which were systematically about 10% higher than available empirical values for the Be and Mg spectral sequences. Similar calculations for α_q and β are presented in Table I, obtained using Eqs. (7) and (5) and the oscillator strength compilations of Refs. 15 and 18. (For α_q the n sum was truncated in cases where the tabulations of Ref. 15 went to very high n, since these contributions can be strongly affected by neglected contributions of very high n'.) These compilations are based on the numerical Coulomb approximation, and were selected for use here because they provide a comprehensive set of values up to high stages of ionization for all three of these isoelectronic sequences. Compilations of nonrelativistic Hartree-Fock calculations up to fairly high stages of ionization are also available for the Li (Ref. 19) and Na (Ref. 20) isoelectronic sequences, and relativistic Hartree-Fock calculations[21] are available for many ions in the Cu sequence. A comparison indicates that the numerical Coulomb and Hartree-Fock compilations yield essentially equivalent results for α_q and β for the Li sequence and for the higher ionization stages of the Na and Cu se-

quences, while for few times ionized members of the Na and Cu sequences the numerical Coulomb method yields slightly lower values than the other methods. For the ions Be^{1+}-Al^{10+} and Mg^{1+}-S^{5+} direct Hartree-Fock calculations for α_q (Refs. 22 and 23) are available, and these results can be duplicated and extended by inserting the Hartree-Fock oscillator strengths[19,20] into Eq. (7). Quadrupole polarizabilities for the Li and Na isoelectronic sequences have been estimated recently by Kastner and Wolf[24] using an extrapolation method. Their values for Li are in reasonable agreement with the values in Table I and Refs. 22 and 23, but their values for the Na sequence differ substantially from other available results.

Table I also lists values for $\alpha_q - 6\beta$, juxtiposed with all published values for B_6. It is clear that $\alpha_q - 6\beta$ is dominated by β, and is negative for all ions in all three sequences, in marked contrast to the empirical values for B_6. Penetration effects have been cited[12] as a possible cause for this disagreement, although there are many other interactions which could lead to an incomplete separation of the active electrons from the core. Dalgarno and Shorer[2] have suggested an alternative empirical approach to Eq. (1) in which penetration corrections to T_H are made using a Dirac-Hartree-Fock representation of the core orbitals, and the termination of the polarization interaction within the core is represented by an empirically determined small-r cutoff radius in each of the expectation values $\langle r^{-4} \rangle$ and $\langle r^{-6} \rangle$. This model utilizes theoretical values for α_d, α_q, and β, as given in Ref. 17 and Table I, with the parametrization residing entirely in the empirical

TABLE I. Units are a_0^5. The sign and integer following significant figures represent powers of 10. Parentheses denote source reference.

Core Charge ζ	Be Spectral (Li Core) Sequence					Mg Spectral (Na Core) Sequence					Zn Spectral (Cu Core) Sequence			
	Ion	α_q	β	$\alpha_q - 6\beta$	B_6	Ion	α_q	β	$\alpha_q - 6\beta$	B_6	Ion	α_q	β	$\alpha_q - 6\beta$
1	Be	0.524 + 2	0.807 + 2	−0.432 + 3		Mg	0.137 + 3	0.104 + 3	−0.486 + 3		Zn	0.729 + 2	0.404 + 2	−0.169 + 3
2	B	0.704 + 1	0.169 + 2	−0.946 + 2		Al	0.308 + 2	0.281 + 2	−0.138 + 3		Ga	0.240 + 2	0.165 + 2	−0.748 + 2
3	C	0.160 + 1	0.558 + 1	−0.319 + 2		Si	0.104 + 2	0.110 + 2	−0.556 + 2		Ge	0.113 + 2	0.825 + 1	−0.382 + 2
4	N	0.492 + 0	0.235 + 1	−0.136 + 2	0.544 + 1 (6)	P	0.436 + 1	0.524 + 1	−0.271 + 2	0.162 + 2 (8)	As	0.610 + 1	0.469 + 1	−0.220 + 2
5	O	0.184 + 0	0.115 + 1	−0.673 + 1	0.225 + 1 (7)	S	0.212 + 1	0.284 + 1	−0.149 + 2	0.183 + 2 (9)	Se	0.353 + 1	0.287 + 1	−0.137 + 2
6	F	0.824 − 1	0.628 + 0	−0.369 + 1		Cl	0.114 + 1	0.167 + 1	−0.887 + 1	0.881 + 1 (10)	Br	0.224 + 1	0.186 + 1	−0.894 + 1
7	Ne	0.381 − 1	0.370 + 0	−0.218 + 1		Ar	0.648 + 0	0.105 + 1	−0.564 + 1	0.900 + 1 (11)	Kr	0.143 + 1	0.127 + 1	−0.619 + 1
8	Na	0.196 − 1	0.231 + 0	−0.136 + 1		K	0.393 + 0	0.689 + 0	−0.374 + 1		Rb	0.975 + 0	0.897 + 0	−0.441 + 1
9	Mg	0.108 − 1	0.150 + 0	−0.892 + 0		Ca	0.252 + 0	0.472 + 0	−0.259 + 1		Sr	0.686 + 0	0.652 + 0	−0.323 + 1
10	Al	0.633 − 2	0.102 + 0	−0.603 + 0		Sc	0.164 + 0	0.332 + 0	−0.183 + 1		Y	0.492 + 0	0.488 + 0	−0.244 + 1
11	Si	0.386 − 2	0.707 − 1	−0.420 + 0		Ti	0.110 + 0	0.239 + 0	−0.132 + 1		Zr	0.364 + 0	0.371 + 0	−0.186 + 1
12	P	0.276 − 2	0.504 − 1	−0.300 + 0		V	0.778 − 1	0.176 + 0	−0.979 + 0		Nb	0.273 + 0	0.288 + 0	−0.146 + 1
13	S	0.169 − 2	0.366 − 1	−0.218 + 0		Cr	0.553 − 1	0.132 + 0	−0.738 + 0		Mo	0.212 + 0	0.227 + 0	−0.115 + 1
14	Cl	0.125 − 2	0.270 − 1	−0.161 + 0		Mn	0.393 − 1	0.101 + 0	−0.567 + 0		Tc	0.163 + 0	0.180 + 0	−0.915 + 0
15	Ar	0.800 − 3ᵃ	0.200 − 1ᵃ	−0.120 + 0		Fe	0.296 − 1	0.781 − 1	−0.439 + 0		Ru	0.128 + 0	0.145 + 0	−0.740 + 0
16	K	0.560 − 3ᵃ	0.152 − 1	−0.900 − 1		Co	0.221 − 1	0.612 − 1	−0.345 + 0		Rh	0.102 + 0	0.118 + 0	−0.604 + 0
17	Ca	0.426 − 3	0.116 − 1	−0.693 − 1		Ni	0.169 − 1	0.483 − 1	−0.273 + 0		Pd	0.821 − 1	0.963 − 1	−0.496 + 0
18	Sc	0.278 − 3	0.900 − 2	−0.537 − 1		Cu	0.133 − 1	0.386 − 1	−0.218 + 0		Ag	0.666 − 1	0.794 − 1	−0.410 + 0
19	Ti	0.202 − 3	0.690 − 2	−0.412 − 1		Zn	0.101 − 1	0.314 − 1	−0.178 + 0		Cd	0.544 − 1	0.658 − 1	−0.340 + 0
20	V	0.152 − 3	0.542 − 2	−0.323 − 1		Ga	0.788 − 2	0.248 − 1	−0.141 + 0		In	0.450 − 1	0.549 − 1	−0.285 + 0
21	Cr	0.121 − 3	0.425 − 2	−0.254 − 1		Ge	0.626 − 2	0.202 − 1	−0.115 + 0					
22	Mn	0.910 − 4ᵃ	0.337 − 2	−0.200 − 1		As	0.501 − 2	0.167 − 1	−0.952 − 1					
23	Fe	0.697 − 4	0.276 − 2	−0.165 − 1		Se	0.399 − 2	0.136 − 1	−0.776 − 1					

ᵃ Interpolated.

cut-off radii.

Although term value measurements for high n and l states are presently sparse, such states are copiously produced in low-density light sources such as beam-foil excitation. The results in Table I can thus be used to test polarization models such as the one proposed by Dalgarno and Shorer[2] when measurements for higher ionization stages in these sequences become available.

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