Semiclassical parametrization of the $6snh$-$6sni$-$6snk$ intervals in Ba I

L. J. Curtis, P. S. Ramanujam, and C. E. Theodosiou
Department of Physics and Astronomy, University of Toledo, Toledo, Ohio 43606
(Received 13 January 1983)

A semiclassical core-polarization-penetration model is used to parametrize the $6snh$-$6sni$ and $6sni$-$6snk$ intervals in Ba I which were recently measured by Gallagher, Kachru, and Tran. The parametrization represents the existing data to within experimental uncertainties, and extrapolative predictions along these Rydberg series are presented.

The parametrization of high-n and -l states in multielectron atoms through their modeling as a single electron in the electric field of a deformable core of charge has a long and successful history.[1] It is particularly interesting when applied to singly excited states of two-valence-electron systems, where the static polarizabilities and nonadiabatic correlations of the core are due primarily to the single out-of-shell core electron and can often be reliably calculated theoretically. Through comparisons between corresponding theoretical and empirical values, insights concerning the applicability of this model can be obtained.[2,3] Radio-frequency resonance techniques have provided a major breakthrough in the testing of these methods, since they make possible the direct measurement of electrostatic intervals with the same n but different l, revealing the polarization, penetration, and relativistic energies directly and in exclusion of the much larger gross energy. This has permitted the model to be stringently tested on the simplest and most reliably calculable case of He I,[4] demonstrating that this system can be very accurately described by an extension of the core-polarization model that includes core-penetration effects in a simple semiclassical manner.[3-6] Recently, Gallagher, Kachru, and Tran[7] have measured a number of $6snh$-$6sni$-$6snk$ intervals in Ba I, providing another precision test of these semiclassical methods in a system of much greater complexity than He I. We have therefore applied the methods described in Refs. 3–6 to the data of Ref. 7, and have also performed Hartree-Slater calculations for the adiabatic and nonadiabatic polarizabilities of the Ba^+ core.

In the standard core-polarization model, the term value T (with magnetic fine-structure and exchange effects removed by a suitable configuration average) is represented by[1-7]

$$T = R\left[\langle \zeta r^{-1}\rangle + \alpha^2\left(\langle \zeta^2 r^{-2}\rangle - \tfrac{3}{4}\langle \zeta r^{-1}\rangle^2\right) + \langle \alpha_d r^{-4}\rangle + \langle (\alpha_q - 6\beta) r^{-6}\rangle\right] , \quad (1)$$

where R is the reduced-mass–corrected Rydberg energy, α is the fine-structure constant, ζ is the net central core 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), and α_d and α_q are the dipole and quadrupole polarizabilities of the core (in units a_0^3 and a_0^5). β is the nonadiabatic correlation factor (in units a_0^5), a measure of the inability of the core to instantaneously adjust to the motion of the electron.[8-12] Higher-order moments, higher-order nonadiabatic effects, and retardation effects have also been variously suggested [cf. reference citations in Ref. 4], but the results of the study in He I (Ref. 4) indicated that the inclusion of these effects actually worsened the fit, suggesting that these contributions are negligible or nullified. In the traditional nonpenetrating analysis[1] the quantities ζ, α_d, and $\alpha_q - 6\beta$ are considered as independent of r and factored outside the expectation values $\langle r^{-k}\rangle$, which are represented by their hydrogenic values. Intrashell intervals $\Delta E = T(n,l) - T(n,l')$ are then independent of gross energy by virtue of the hydrogenic l degeneracy of $\langle r^{-1}\rangle$.

In our modification of the approach, the lack of separability of the core and active electron is taken into account by subdividing the expectation value into an internal and an external portion, such that for $r < \rho$, $\zeta \rightarrow \zeta + \Delta\zeta$ and $\alpha_d = \alpha_q = \beta = 0$. This is done very simply and semiclassically, with the use of elementary integrations over quantized Kepler orbits. Thus, for each Rydberg series, the core is modeled as a hollow sphere of radius $\rho(l)$ and surface charge $\Delta\zeta(l)$. In the external region the electron is assumed to move on an orbit segment of semimajor axis $a = n^2$ (in units of a_0) and eccentricity $\epsilon = [1 - l(l+1)/n^2]^{1/2}$. In the internal region the orbit segment has a semimajor axis a' and an eccentricity ϵ' determined from conservation of energy and angular momentum across the boundary. The "penetrating" expectation values in Eq. (1) are computed by integrating along the orbit path from the internal perihelion to the external aphelion and renormalizing to the effective period. Thus

$$\langle \gamma r^{-s}\rangle = \frac{\gamma' \int_{r<\rho} [dt\, r^{-s}]_{a'\epsilon'} + \gamma \int_{r>\rho} [dt\, r^{-s}]_{a\epsilon}}{\int_{r<\rho} [dt]_{a'\epsilon'} + \int_{r>\rho} [dt]_{a\epsilon}} , \quad (2)$$

where γ' and γ are the internal and external values of the corresponding quantities ζ, α_d, or $\alpha_q - 6\beta$ as given in Eq. (1). The values of $\rho(l)$ and $\Delta\zeta(l)$ are adjusted by weighted nonlinear least-squares methods to parametrize the data. The approach considers the core and active electron to be separable in the external region, and, when possible, utilizes the theoretical calculations of α_d and $\alpha_q - 6\beta$ for the core. Penetration effects are included not only in the polarization energy, but also in the gross and fine-structure energies. By its empirical nature, all effects not explicitly described in the model reside in the effective penetration parameters. Since these parameters are formulated so as to depend only upon l and not upon n, they permit extrapolations along the Rydberg series. The success or failure of the approach is judged on the basis of the accuracy with which it represents the data.

Gallagher, Kachru, and Tran[7] have also performed a core-polarization analysis of their Ba I data, but by an approach somewhat different from ours. They formulate the nonadiabatic effects with use of the method of Van Vleck and Whitelaw,[13] in which a separate *ab initio* calculation of the dynamical polarizability of the combined core and active

electron system is made for each excited state of the electron. Thus this analysis includes the effects of core penetration in the computation of core-polarization energies, but the l dependence of penetration effects on the gross energy is neglected. In their polarization analysis, Gallagher *et al.*[7] interpret the coefficients of $\langle r^{-4}\rangle$ and $\langle r^{-6}\rangle$ to directly represent the adiabatic dipole and quadrupole polarizabilities, and all nonadiabatic effects are left to reside in the state-by-state *ab initio* calculation. This interpretation leads to "an impossible negative quadrupole polarizability"[7] when a standard nonpenetrating polarization analysis[1] is made, but this is removed by abandoning the assumption of factorizability of the core and active electron contributions. In our approach, as described above by Eq. (1), the negative coefficient of the $\langle r^{-6}\rangle$ term arises automatically from the coefficient $\alpha_q - 6\beta$, which has been shown[2] to be negative for the alkalilike cores for all members of the Be, Mg, and Zn isoelectronic sequences.

If both the $6snh$-$6sni$ and the $6sni$-$6snk$ intervals of Ref. 7 are fitted to Eq. (1) with use of the unpenetrated hydrogenic values for $\langle r^{-4}\rangle$ and $\langle r^{-6}\rangle$, values for α_d and $\alpha_q - 6\beta$ of 147.5 and -6785 are inferred, although the n dependence of either set of Rydberg intervals would suggest a much lower (and inconsistent) value for α_d and a positive value for $\alpha_q - 6\beta$. This clearly implies that penetration effects in expectation values of high reciprocal powers of r are substantial, and should be included in the analysis.

To reduce the number of fitting parameters, we have made theoretical calculations for the adiabatic dipole and quadrupole polarizabilities and the nonadiabatic correlation correction for the Ba^+ core using the Coulomb approximation[14–16] and the Hartree-Slater method.[17] The desired quantities are given by

$$\alpha_d = \left(\frac{4R}{3}\right) \sum_n \frac{|\langle 6s|r|np\rangle|^2}{E_{np} - E_{6s}} , \tag{3}$$

$$\beta = \left(\frac{4R^2}{3}\right) \sum_n \frac{|\langle 6s|r|np\rangle|^2}{(E_{np} - E_{6s})^2} , \tag{4}$$

$$\alpha_q = \left(\frac{4R}{5}\right) \sum_n \frac{|\langle 6s|r^2|nd\rangle|^2}{E_{nd} - E_{6s}} . \tag{5}$$

The results are summarized in Table I, and indicate a substantial difference in the value of α_d obtained by the two methods, the Hartree-Slater being over 20% larger than the Coulomb result. The values for $\alpha_q - 6\beta$ are in much closer agreement for the two methods. Since the fit is very sensitive to the value of α_d, we found it necessary to allow α_d to vary as a free parameter in our analysis, but $\alpha_q - 6\beta$ was fixed at the Hartree-Slater value. Our fitted value for α_d was 111.8, which is smaller than either calculation. Possible explanations for this discrepancy will be discussed below.

TABLE I. Adiabatic and nonadiabatic polarizabilities for Ba^+. Column A reduced from the oscillator strength tabulations of Lindgård and Nielson (Ref. 14) by the methods of Refs. 2. Column B obtained from the analytic expansion code of Ref. 15. Column C obtained by the method of Ref. 16 as applied by Ref. 7. Column D obtained from the code described in Ref. 17.

Quantity	Coulomb approximation A	B	C	Hartree-Slater D
α_d (a_0^3)	117.1	118.7	122.6	144.1
α_q (a_0^5)	2245.1	2370.0	2589	3102.7
β (a_0^5)	584.2	590.7	· · ·	719.1
$\alpha_q - 6\beta$	−1260.4	−1174.2	· · ·	−1211.9

The results of our fit to the $6snh$-$6sni$ and the $6sni$-$6snk$ intervals are given in Table II. The experimental values quoted are from Ref. 7, simply averaged over the two fine-structure intervals (this is the appropriate "spinless average"[4] for a situation in which the electrostatic singlet-triplet splitting dominates over the magnetic fine structure). The uncertainties are the quadrature sum of the quoted uncertainties in the fine-structure components, the $6sng$-$6snh$ and $6sng$-$6sni$ frequencies, and the $6sng$-$6sni$ and $6sng$-$6snk$ frequencies, which were subtracted to obtain each of the studied intervals. It was assumed that the $6snk$ series is nonpenetrating, and separate values of the penetration parameters $\rho(h)$, $\Delta\zeta(h)$ and $\rho(i)$, $\Delta\zeta(i)$ were fitted for the $6sni$ and $6snh$ series. The theoretical value was used for $\alpha_q - 6\beta$, but as described above, α_d was adjusted as a fitting parameter. Fits were also attempted incorporating the retardation corrections due to the finiteness of the speed of light suggested by Kelsey and Spruch,[18] but these corrections were found to be negligible. The fit is reliable to within a few MHz, and predictions are presented for $n = 16$, 17, 24, and 25 for h-i and for $n = 16$, 17, 22, and 23 for i-k.

Gallagher *et al.*[7] also report measurements for the $6sng$-$6snh$ intervals, but show that the $6sng$ series is strongly perturbed by the interloping $5d7d$ configuration. With both our penetration analysis and the *ab initio* calculation of Ref. 7, the centroid of the $6sng$-$6snh$ series could be brought into consistency with the core-polarization model, but the perturbation was clearly reflected in the individual n components, and the $6sng$-$6snh$ intervals were not used in the analysis.

In order to accurately represent the data, the least-squares fit to our model demanded a significant contribution from the variation with l of the penetration corrections to the gross energy. This is clearly indicated by the breakdown into monopole, dipole, and quadrupole contributions to Eq. (1) which is also given in Table II. Although our model is purely phenomenological, and other effects not explicitly included in the model (exchange, configuration interaction, penetration of the k series, etc.) reside implicitly in the fitted parameters, the semiempirical result motivated us to make theoretical estimates of the magnitude of these contributions. We therefore performed a Hartree-Fock[19] calculation of the potential $Z(r)/r$ due to Ba^+ and computed the difference between the expectation values of $Z(r)/r$ and ζ/r for the h and i orbitals, using hydrogenic wave functions. These indicated that the $6s$ charge distribution extends to $17a_0$, well beyond the $6a_0$ cutoff built into most Hartree-Slater programs through the Latter[20] procedure. We obtained corrections of 10–20 MHz for the h states and 0.1–0.2 MHz for the i states, which, although small, are not negligible if MHz accuracies are desired.

This model parametrization provides a concise way of summarizing experimental measurements, and a means of making very precise extrapolative predictions along Rydberg series. It also indicates the need for theoretical methods for describing l-dependent intrashell polarization and penetration effects in high-Z systems on a MHz level of precision. The results indicate that the data can be fitted with use of the theoretical values for the quadrupole polarizability and nonadiabatic correlation factor of the core. It was necessary to use a value for the core dipole polarizability slightly

TABLE II. Observed and fitted intervals. Fitted estimates were obtained from Eq. (1) with the values $\rho(h)=15.666$, $\Delta\zeta(h)=0.019\,107$; $\rho(i)=22.375$, $\Delta\zeta(i)=0.007\,184$; $\rho(k)>28$; $\alpha_d=111.8$, $\alpha_q-6\beta=-1211.9$. The fits are broken down into dipole ($\langle r^{-4}\rangle$), quadrupole ($\langle r^{-6}\rangle$), and monopole (all other) contributions to Eq. (1).

Interval	ΔE (MHz) Obs. (uncert.)	Fit	Obs. − Fit	Monopole	Dipole	Quadrupole
$6s\,16h$-$6s\,16i$		15 284		3004	12 933	−653
$6s\,17h$-$6s\,17i$		12 841		2825	10 543	−527
$6s\,18h$-$6s\,18i$	10 876(3)	10 880	−4	2580	8734	−434
$6s\,19h$-$6s\,19i$	9300(2)	9292	+8	2326	7328	−362
$6s\,20h$-$6s\,20i$	7988(2)	7994	−6	2085	6215	−306
$6s\,21h$-$6s\,21i$	6925(2)	6925	0	1865	5321	−261
$6s\,22h$-$6s\,22i$	6039(2)	6038	+1	1669	4594	−225
$6s\,23h$-$6s\,23i$	5295(2)	5294	+1	1494	3995	−195
$6s\,24h$-$6s\,24i$		4667		1341	3496	−170
$6s\,25h$-$6s\,25i$		4135		1206	3079	−150
$6s\,16i$-$6s\,16k$		6770		3604	3258	−92
$6s\,17i$-$6s\,17k$		5727		3344	2454	−71
$6s\,18i$-$6s\,18k$	4869(4)	4869	0	3024	1901	−56
$6s\,19i$-$6s\,19k$	4168(4)	4166	+2	2705	1506	−45
$6s\,20i$-$6s\,20k$	3587(3)	3588	−1	2409	1216	−37
$6s\,21i$-$6s\,21k$	3109(4)	3109	0	2144	996	−31
$6s\,22i$-$6s\,22k$		2711		1910	827	−26
$6s\,23i$-$6s\,23k$		2377		1704	695	−22

smaller than the theoretical predictions, but this may not be significant since other processes may be included in these empirical effective parameters. Clearly, the virtue of this model lies not in any physical significance attributable to its parametrizations, but rather in the very high precision with which it is able to describe and extrapolate measured data.

We are grateful to Dr. T. F. Gallagher for providing us with experimental data prior to publication. This work was supported by the Fundamental Interactions Branch, Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AS-05-80ER10676.

[1]References to the early development of the semiempirical core-polarization approach have been summarized by K. Bockasten, Phys. Rev. 102, 729 (1956). Many examples of its application have been given by B. Edlén, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1964), Vol. 27, pp. 80–220.
[2]L. J. Curtis, Phys. Scr. 21, 162 (1980); Phys. Rev. A 23, 362 (1981).
[3]L. J. Curtis, Nucl. Instrum. Methods 202, 333 (1982).
[4]L. J. Curtis and P. S. Ramanujam, Phys. Rev. A 25, 3090 (1982).
[5]L. J. Curtis, J. Phys. B 14, 1373 (1981).
[6]L. J. Curtis and P. S. Ramanujam, J. Opt. Soc. Am. 71, 1315 (1981).
[7]T. F. Gallagher, R. Kachru, and N. H. Tran, Phys. Rev. A 26, 2611 (1982).
[8]M. H. Mittleman and K. M. Watson, Phys. Rev. 113, 198 (1959).
[9]H. Eissa and U. Öpik, Proc. Phys. Soc. London 92, 556 (1967).
[10]C. J. Kleinman, Y. Hahn, and L. Spruch, Phys. Rev. 165, 53 (1968).
[11]J. Callaway, R. W. LaBahn, R. T. Pu, and W. M. Duxler, Phys. Rev. 168, 12 (1968).
[12]A. G. Vaidyanathan and P. Shorer, Phys. Rev. A 25, 3108 (1982).
[13]J. H. Van Vleck and N. G. Whitelaw, Phys. Rev. 44, 551 (1933).
[14]A. Lindgård and S. E. Nielsen, At. Data Nucl. Data Tables 19, 533 (1977).
[15]D. R. Bates and A. Damgaard, Philos. Trans. R. Soc. London, Ser. A 242, 101 (1949).
[16]M. L. Zimmerman, M. G. Littman, M. M. Kash, and D. Kleppner, Phys. Rev. A 20, 2251 (1979).
[17]J. P. Desclaux, Comput. Phys. Commun. 1, 216 (1969).
[18]E. J. Kelsey and L. Spruch, Phys. Rev. A 18, 15 (1978).
[19]C. Froese Fischer, Comput. Phys. Commun. 14, 145 (1978).
[20]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963)