Near-degeneracy effect on energy shifts in some highly charged few-electron Rydberg ions

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(Received 1 December 1995; revised manuscript received 5 December 1996)

In view of recent high-precision measurements of transition energies between levels of berylliumlike Rydberg ions of S^{12+} and O^{4+} in (high-angular-momentum) Rydberg states, we introduce a modified polarization model that allows one to estimate level energies even in the case of near degeneracy, that is, when an excitation energy of the Rydberg electron is nearly equal but opposite to that of the ionic core. Estimates as well as rigorous upper and lower bounds for the dominant second-order perturbation-theory dipole contributions to the line shifts (with continuum states included) are given. Agreement with the measured line shifts is very much improved over that of the usual polarization model, but the range of estimates remains, in many cases, rather larger than the experimental uncertainty; our primary purpose is to assist experimentalists planning studies of other Rydberg ions by providing estimates which are improved *and* which remain trivial to apply. [S1050-2947(97)04005-5]

PACS number(s): 32.10.Dk, 31.10.+z, 32.80.Rm

I. POLARIZATION MODEL

Rydberg transition energies of few-electron atoms and ions between states of high angular momentum are often well described in terms of the polarization properties of the ionic core. While the standard polarization model (the many papers on the subject include [1–4]) yields rather accurate results for the helium atom [5] and heliumlike ions, it can fail for more complex ions. In particular, recent experiments on the energy differences between some high-angular-momentum Rydberg states of the berylliumlike ions S^{12+} [6] and O^{4+} [7] — using beam-foil and laser-stimulated recombination spectroscopy, respectively, the latter leading to a considerable improvement in experimental accuracy — revealed substantial disagreement between the measured values and those predicted by the polarization model. The failure of the standard polarization model can be traced to the occurrence of near degeneracies between Rydberg levels of the overlapping series related to the $1s\,^2 2s$ ground state and the low-lying $1s\,^2 2p$ excited state of the lithiumlike core. Other approaches such as multichannel quantum defect theory (MQDT) [8] should one day give better results than polarization model approaches, but might, at present, not be useful, as sufficiently complete energy level data are not yet available. For the studies of the ionic high-angular-momentum Rydberg states in question, the modified polarization model to be presented appears particularly well suited; little input data is required, the degree of numerical complexity is exceedingly low, and account is taken of near degeneracies within interacting Rydberg series.

Transition energies of Rydberg electrons are usually explainable using second-order perturbation theory. We write $H=H_c+H_{\rm Ryd}+W$, where H_c is the full Hamiltonian of the core with nuclear charge Z, while $H_{\rm Ryd}$ is the screened Hamiltonian containing the interaction of the Rydberg electron and a nucleus, for berylliumlike ions, of effective charge $(Z-3)$. The residual Coulomb interaction W of the Rydberg electron and the core is expanded into multipole operators,

$$W(\vec{r}_0,\{\vec{r}_i\})=e^2\sum_{l=1}^{\infty}\frac{w_l}{r_0^{l+1}},$$

where $\vec{r}_0$ and $\{\vec{r}_i\}$ $(r=|\vec{r}|)$ are the coordinates of the Rydberg electron and the core electrons, respectively, and $w_l=\Sigma_i r_i^l P_l(\cos\theta_{i0})$. Here P_l denotes the Legendre polynomial of order l, and θ_{i0} denotes the angle between the ith core electron and the Rydberg electron. Since the excitation energy of the $1s\,^2 2s$ state to the $1s\,^2 2p$ state for O^{4+} is only 12 eV (compared to 83 eV for the $3p$ state and a comparable energy for the $3d$ state), we neglect all quadrupole and higher multipole contributions and all dipole contributions but that of the $2p$ state and make the one-term dipole approximation $W\approx W_1=e^2 w_1/r_0^2$ with $w_1=\Sigma_i z_i$. We introduce the core energies $E(1s\,^2 2s)$ and $E(1s\,^2 2p)$, their difference $\Delta E_c=E(1s\,^2 2p)-E(1s\,^2 2s)$, the ($j$ averaged) Dirac hydrogenlike Rydberg energies E_{nl}, their nonrelativistic counterparts E_n, and the differences $\Delta E_{n'n}=E_{n'}-E_n$. The energy E^*_{nl} of the ion with a $1s\,^2 2s$ core and a Rydberg electron in the state $|nl\rangle$ is then $E^*_{nl}=E(1s\,^2 2s)+E_{nl}+\delta E^*_{nl}$, where the energy change δE^*_{nl} due to the interaction potential W_1 is approximated in one-term second-order perturbation theory as

$$\delta E_{nl}=-\sum\!\!\!\!\!\!\int \frac{|\langle 2s;\vec{n}|W_1|2p\mu;\vec{n}'\rangle|^2}{\Delta E_c+\Delta E_{n'n}} \equiv -\sum\!\!\!\!\!\!\int \frac{M_{\vec{n}'\vec{n}}}{\Delta E_c+\Delta E_{n'n}}, \quad (1)$$

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where $\vec{n}=(n,l,m)$, $\vec{n}'=(n',l',m')$, m, m', and μ are angular-momentum projections, $1s^2$ is understood, and $\sum\!\!\!\!\!\!\int$ represents an average over m, a sum over μ, and a sum over bound states and an integration of continuum states (n',l',m'), with $l'=l\pm1$. In the study of δE_{nl} it is sufficient to use nonrelativistic energies.

To estimate δE_{nl} one can [2] start from Eq. (1), *assume* that $|\Delta E_{n'n}/\Delta E_c|\ll 1$ for the most significant excitations, and expand out the denominators in powers of $\Delta E_{n'n}/\Delta E_c$. Retaining the first two terms, one obtains the well-known polarization model estimates for level shifts δE_{nl} in the dipole approximation [1,2,9]

$$\delta E_{nl}^{(\mathrm{pol})} \approx -\sum\!\!\!\!\!\!\int \frac{M_{\vec{n}'\vec{n}}}{\Delta E_c}\left(1-\frac{\Delta E_{n'n}}{\Delta E_c}\right)$$
$$= -\frac{\alpha_d}{2}\left\langle \frac{e^2}{r_0^4}\right\rangle_{nl} + 3\,\beta_d a_0 \left\langle \frac{e^2}{r_0^6}\right\rangle_{nl}$$
$$\equiv \delta E_{nl,\alpha} + \delta E_{nl,\beta} \qquad (2)$$

by use of closure. $\langle A\rangle_{nl}$ denotes the expectation value of A for the Rydberg state (n,l), α_d is the static electric-dipole polarizability of the core,

$$\alpha_d = 2\frac{e^2}{\Delta E_c}\left|\langle s|\sum_i z_i|p\rangle\right|^2,$$

β_d is the coefficient of the lowest-order nonadiabatic contribution,

$$\beta_d = \left(\frac{e^2}{\Delta E_c}\right)^2\left|\langle s|\sum_i z_i|p\rangle\right|^2,$$

and a_0 the Bohr radius. The first term in Eq. (2) describes the usual adiabatic dipole polarization picture, where the Rydberg electron deforms the core, and the induced dipole gives rise to an attractive potential $\propto 1/r_0^4$ on the Rydberg electron, assuming that the motion of the Rydberg electron is sufficiently slow for the dipole of the core to instantaneously adjust its direction to the position of the Rydberg electron. Some nonadiabatic corrections, with the misalignment of Rydberg electron and dipole axis leading to a weakening of the attractive potential, are accounted for by the second term. (These are not relativistic retardation corrections, which would be significant only for much larger values of n. They are nonrelativistic corrections whose origin is the simple fact that the core electrons have inertia.) Further contributions to Eq. (2) that involve core transitions to different principal core quantum numbers are of negligible size, as stated above. Equally, effects due to penetration of the core by the Rydberg electron are very small for the high-l Rydberg states discussed here. In the third column of Table I, we reproduce the measured fine-structure splittings [7] for the Rydberg states of O^{4+} for transitions $n_1=16$ to $n_2=9$, 10 for various values of l_1 and $l_2=l_1-1$. They are evidently in serious disagreement with the results of Eq. (2) listed in the fourth column.

TABLE I. Experimental line shifts $\delta E=(\delta E_{n_1l_1}-\delta E_{n_2l_2})-(\delta E_{n_1n_2}-\delta E_{n_2n_2-1})$ among the fine-structure components of the inter-Rydberg transitions from $n_1=16$ to $n_2=9$,10 in O^{4+} and some theoretical estimates, in units of 10^{-3} eV. The line shift for the transition to the state of maximum angular momentum for the given n_2 has been taken as a reference line. $\underline{\delta E}$ and $\overline{\delta E}$ are lower and upper bounds, respectively, on δE.

n_1-n_2	l_1-l_2	$\delta E^{(\mathrm{expt})}$ [a]	$\delta E^{(\mathrm{pol})}$ [b]	$\delta E^{(B)}$ [c]	$\underline{\delta E}\,\vert\,\overline{\delta E}$ [d]	$\delta E^{(\mathrm{av})}$ [e]
16−9	9−8	0.0	0.0	0.0	0.0|0.0	0.0
	8−7	0.30(2)	0.25	0.24	0.27|0.31	0.29
	7−6	1.09(2)	0.71	0.85	0.96|1.14	1.05
	6−5	5.04(3)	1.18	4.37	4.26|5.45	4.85
16−10	10−9	0.0	0.0	0.0	0.0|0.0	0.0
	9−8	0.12(2)	0.09	0.09	0.09|0.10	0.10
	8−7	0.32(2)	0.27	0.25	0.30|0.33	0.31
	7−6	0.93(2)	0.59	0.71	0.80|0.99	0.89
	6−5	4.68(3)	0.86	4.12	3.92|5.03	4.48

[a] Experimental line shifts, from Ref. [7].
[b] Polarization model, $\alpha_d=1.05a_0^3$, $\beta_d=1.15a_0^4$ [16].
[c] Differences of bound state contributions, $\Delta E_c=12.092$ eV [17].
[d] Lower and upper bounds on $\delta E_{n_1l_1}-\delta E_{n_2l_2}$.
[e] *ad hoc* estimates $(\overline{\delta E}+\underline{\delta E})/2$.

II. MODIFIED POLARIZATION MODEL

The primary reason for the failure of the polarization model for O^{4+} lies in the occurrence of near degeneracies; the expansion which enabled us to approximate Eq. (1) by Eq. (2) is not then valid. We are therefore led to introduce a modified polarization model, one which provides a considerable improvement and which can be readily used by experimentalists preparing to study similar ions. Before doing so, we remark that the existence of near degeneracies and their significance has been noted previously on a number of occasions and, in particular, in Ref. [7], which is our primary focus. The appearance of such degeneracies, accepted in that paper on the basis of experimental data, can be placed on a more general footing by a slight extension of a study [3] of the Z dependence of the various contributions to energy levels of interest. The contributions studied in Ref. [3] included not only the α_d and β_d terms of Eq. (2), but terms which, as noted above, could be largely ignored for the Rydberg states of O^{4+}. These latter contributions are an α_q/r_0^6 term, where α_q is the static quadrupole polarizability of the core, and a penetration contribution W_p. We wish to contrast ionic cores which demand *intershell* transitions — when the transition of an electron in a given shell to a virtual excited state in the same shell is not allowed — with ionic cores which allow *intrashell* transitions. To simplify the discussion we consider heliumlike cores (for lithiumlike Rydberg ions, with $1s$ to $2p$ dipole transitions) and lithiumlike cores (for berylliumlike Rydberg ions, with $2s$ to $2p$ dipole transitions). Since a length scales as $1/Z$, we are led to the results in the second column of Table II, valid for either type of core. [We note that α_q is proportional to the square of an (off-diagonal) matrix element of r_i^2, and W_q is proportional to the (diagonal) element of $1/r_0$, for $r_0<r_i$.] We now turn to the Z dependence of ΔE_c. For heliumlike cores ΔE_c scales as Z^2. For lithiumlike cores, however, we have

TABLE II. Z dependence of various contributions to the energy level for ionic cores which do not allow virtual transitions to electronic states within a partially occupied shell — heliumlike cores, for example — and ionic cores that do allow such transitions — lithiumlike or beryllium cores, for example.

Contribution	General expression	He-like core	Li-like core
α_d/r_0^4	$Z^2/\Delta E_c$	Z^0	Z
β_d/r_0^6	$Z^4/\Delta E_c$	Z^0	Z^2
α_q/r_0^6	$Z^2/\Delta E_c$	Z^0	Z^0
W_p	Z	Z	Z

$$\Delta E_c = -\frac{(Z-\sigma_{2p})^2}{8}+\frac{(Z-\sigma_{2s})^2}{8} = \frac{Z(\sigma_{2p}-\sigma_{2s})}{4}+\frac{\sigma_{2s}^2-\sigma_{2p}^2}{8},$$

where the σ's are screening factors; ΔE_c is then linear in Z, and therefore, for large Z, proportional to Z. For α_q, the transition is intershell for both cores, and we arrive at the results in columns three and four of Table II. (For some ionic cores, such as those in a $1s\,^2 2s\,^2 2p\,^6 3s^2$ configuration which allow a $3s$ to $3d$ transition, ΔE_c would be proportional to Z, rather than Z^2.) The above results were all stated previously [3], and the point was made that Rydberg ions of large Z with lithiumlike cores should prove to be good testing grounds for the existence of the β_d/r_0^6 term, for which there was little experimental evidence at the time. The slight extension of the above study relates to the validity of the $\Delta E_{n'n}/\Delta E_c$ expansion. $\Delta E_{n'n}$ is proportional to

$$\Delta E_{n'n} \propto (Z-Z_c)^2\left(\frac{1}{n^2}-\frac{1}{n'^2}\right),$$

where Z_c is the number of electrons in the core, for both types of cores. For heliumlike cores, with $\Delta E_c \propto Z^2$, $\Delta E_{n'n}/\Delta E_c$ is small compared to unity over a wide range of Z, whereas for lithiumlike cores, with $\Delta E_c \propto Z$, the stronger Z dependence of $\Delta E_{n'n}/\Delta E_c$ can compensate for the $(1/n^2-1/n'^2)$ factor. One then finds (rather large) values of n' for which $-\Delta E_{n'n}$ can be of comparable size to ΔE_c. In O^{4+}, for example, $\Delta E_c \approx 12$ eV while $\Delta E_{n'n} \approx -10$ eV for $n=10$ and $n'=5$, which leads to an energy denominator of ≈ 2 eV. Partial account of the effect of near resonances on δE_{nl} can be taken by the analysis of bound-state contributions in a detailed treatment of the configuration interactions in the interlacing Rydberg series $1s\,^2 2snl$ and $1s\,^2 2pn'l'$. However, continuum contributions must also be accounted for, and we will now show how to at least estimate the effect of continuum contributions, in a form which is trivial to apply, given a few pieces of data, to other berylliumlike Rydberg ions.

We begin by splitting the second-order sum of Eq. (1) into a sum $\Sigma^{(B)}$ over bound states and an integration denoted by $\int^{(K)}$ over continuum states, and, hence, decompose the shift into $\delta E_{nl} = \delta E_{nl}^{(B)} + \delta E_{nl}^{(K)}$, where

$$\delta E_{nl}^{(B)} = -\sum^{(B)} \frac{M_{\vec{n}'\vec{n}}}{\Delta E_c + \Delta E_{n'n}}, \tag{3a}$$

$$\delta E_{nl}^{(K)} = -\int^{(K)} \frac{M_{\vec{n}'\vec{n}}}{\Delta E_c + \Delta E_{n'n}}. \tag{3b}$$

The bound-state contribution $\delta E_{nl}^{(B)}$ can be evaluated directly, since $M_{\vec{n}'\vec{n}}$ and $\Delta E_{n'n}$ can be expressed analytically for bound states. We summed the terms up to $n'=50$; the higher terms fall off roughly as $(n')^{-3}$ and can be neglected to the numerical precision listed. It should be emphasized that the near-degeneracy terms can strongly dominate the bound-state contributions. For $(n,l)=(10,5)$ in O^{4+} the $(n',l')=(5,4)$ term represents $\approx 74\%$ of the bound-state contribution. The bound-state contribution differences, listed in the fifth column of Table I, give results that are substantially better than the polarization result of Eq. (2), but the significance of that fact is not clear since the continuum contribution has not yet been estimated. Note also that the bound-state contributions $\delta E_{nl}^{(B)}$ yield upper bounds on single level shifts δE_{nl}, but the inequalities $\delta E_{n_1 l_1} < \delta E_{n_1 l_1}^{(B)}$ and $\delta E_{n_2 l_2} < \delta E_{n_2 l_2}^{(B)}$ provide neither an upper nor lower bound on the line shift $\delta E_{n_1 l_1} - \delta E_{n_2 l_2}$.

The continuum contribution $\delta E_{nl}^{(K)}$ cannot be evaluated directly, but can be bounded above and below by using bounds on $-1/(\Delta E_c + E_{n'} - E_n)$, modifying a procedure described, for example, in [10]. The idea is to use the inequalities $-1 < -1/(1+x) < -1+x$ for $x>0$ to derive bounds on the energy denominator in the integral component $\int^{(K)}$ of Eq. (3b), and, hence, on the integral. However, instead of using $\Delta E_{n'n}/\Delta E_c$ as the expansion parameter x [as is done to obtain the usual polarization model prediction Eq. (2) of the level shift], it is more advantageous to let $x = E_{n'}/(\Delta E_c - E_n)$ (in particular, for continuum energies $E_{n'} \gtrsim 0$). Thus, since the continuum energies $E_{n'}$ are positive (and the E_n are negative), we let $\Delta E_{c+n} \equiv \Delta E_c + |E_n|$ and write

$$\frac{-M_{\vec{n}'\vec{n}}}{\Delta E_{c+n}} \leqslant \frac{-M_{\vec{n}'\vec{n}}}{\Delta E_{c+n}+E_{n'}} \leqslant \frac{-M_{\vec{n}'\vec{n}}}{\Delta E_{c+n}}\left(1-\frac{E_{n'}}{\Delta E_{c+n}}\right) \tag{4}$$

in the terms under the integral component $\int^{(K)}$ of Eqs. (3), and thereby obtain lower and upper bounds for the continuum integral [11]. In each of the formal bounds thereby obtained, we rewrite $\int^{(K)}$ as $\sum\!\!\!\!\!\!\int - \Sigma^{(B)}$. We use closure for $\sum\!\!\!\!\!\!\int$ as in the polarization model discussed above — the sums to be evaluated by closure are the same as those which arose there — while the bound-state sum $\Sigma^{(B)}$ is evaluated directly. This yields lower and upper bounds for the continuum contribution $\underline{\delta E}_{nl}^{(K)} \leqslant \delta E_{nl}^{(K)} \leqslant \overline{\delta E}_{nl}^{(K)}$ that are given by

$$\underline{\delta E}_{nl}^{(K)} = (1-\eta)\,\delta E_{nl,\alpha} + \frac{1}{\Delta E_{c+n}}\sum^{(B)} M_{\vec{n}'\vec{n}}, \tag{5}$$

$$\overline{\delta E}_{nl}^{(K)} = (1-\eta^2)\,\delta E_{nl,\alpha} + (1-\eta)^2\,\delta E_{nl,\beta} + \frac{1}{\Delta E_{c+n}}\sum^{(B)} M_{\vec{n}'\vec{n}}\left(1-\frac{E_{n'}}{\Delta E_{c+n}}\right), \tag{6}$$

TABLE III. Specific contributions to the estimates of the single transition line $(n_1,l_1)=(16,6)$ to $(n_2,l_2)=(9,5)$, in units of 10^{-3} eV. $\delta E_{nl,\alpha}$ and $\delta E_{nl,\beta}$ give the adiabatic and nonadiabatic contributions, respectively, $\delta E_{nl}^{(\mathrm{pol})}$ is their sum, see Eq. (2), and $\delta E_{nl}^{(\mathrm{rel})}=E_{nl}-E_n$ is the relativistic correction. $\delta E_{nl}^{(B)}$ is the bound-state contribution. $\underline{\delta E}_{nl}^{(K)}$, $\overline{\delta E}_{nl}^{(K)}$ and $\underline{\delta E}_{nl}$, $\overline{\delta E}_{nl}$ give lower, upper bounds on the continuum contribution $\delta E_{nl}^{(K)}$ and on the level shift δE_{nl}, respectively; see Eqs. (6), (5).

(n,l)	$\delta E_{nl,\alpha}$	$\delta E_{nl,\beta}$	$\delta E_{nl}^{(\mathrm{pol})}$	$\delta E_{nl}^{(\mathrm{rel})}$	$\delta E_{nl}^{(B)}$	$\underline{\delta E}_{nl}^{(K)}$	$\overline{\delta E}_{nl}^{(K)}$	$\underline{\delta E}_{nl}$	$\overline{\delta E}_{nl}$
(16,6)	-0.28	0.08	-0.20	-0.01	-0.24	-0.13	-0.04	-0.37	-0.28
(9,5)	-3.34	1.74	-1.60	-0.06	-4.83	-1.12	-0.02	-5.95	-4.86

where we have written $\eta=|E_n|/(\Delta E_c+|E_n|)$. The lower and upper bounds on δE_{nl} are then $\underline{\delta E}_{nl}=\delta E_{nl}^{(B)}+\underline{\delta E}_{nl}^{(K)}$ and $\overline{\delta E}_{nl}=\delta E_{nl}^{(B)}+\overline{\delta E}_{nl}^{(K)}$ (see Table III). Before discussing the numerical values obtained from the above expressions, we make two comments. First, our procedure comprises three improvements over the usual polarization model procedure discussed above. (i) We have determined the (dominant) bound-state contribution to δE_{nl} exactly. (ii) We have obtained rigorous upper and lower bounds on the single level shifts δE_{nl}; these immediately provide rigorous upper and lower bounds on the resulting line shifts. (iii) The expansion parameter $E_{n'}/(\Delta E_c+|E_n|)$ is smaller, often much smaller, than the usual expansion parameter $(E_{n'}+|E_n|)/\Delta E_c$. Second, when the expansion in powers of $|\Delta E_{n'n}|/\Delta E_c$ is possible, we find that the first two terms of the expansion can be expressed as an expectation value $\delta E_{n,l}\approx\delta E_{nl}^{(\mathrm{pol})}=\langle V\rangle_{nl}$ of a local potential

$$V(\vec{r}_0)=\frac{\alpha_d}{2}\frac{e^2}{r_0^4}+3\beta_d a_0\frac{e^2}{r_0^6},$$

with $V(\vec{r}_0)$ independent of n and l. The simple form of $V(\vec{r}_0)$ arose by the use of closure. However, the bounds $\underline{\delta E}_{nl}$ and $\overline{\delta E}_{nl}$ cannot be expressed in terms of a local potential since neither $\delta E_{nl}^{(B)}$ nor $\delta E_{nl}^{(K)}$, separately, is a sum over a complete set.

III. APPLICATION TO O^{4+} AND S^{12+}

The resulting bounds on the line shifts are listed in the sixth column of Table I. All experimental electric fine-structure splittings lie well within the calculated bounds, and the width of the bounding interval is reasonably small. It must be emphasized that the bounds are *not* on δE_{nl}^* but on the δE_{nl} of Eq. (1). To obtain better estimates of δE_{nl}^*, one could consider effects such as retardation, the reduced mass effect, relativistic kinematic effects, and higher-order perturbations. These can, in principle, lead to significant shifts of individual levels, but the resulting corrections to the energy *differences* considered here should be negligible. However, the inclusion of an additional term in the expansion of the dominator in Eq. (1) should lead to a better lower bound.

In an experimental search for transition lines, it can be helpful to know the range of possible values of the lines shift — provided here by the upper and lower bounds — and to have some convenient starting point. A possible starting point is given by the average $\delta E_{nl}^{(\mathrm{av})}=(\underline{\delta E}_{nl}+\overline{\delta E}_{nl})/2$ of the two bounds. This *ad hoc* prescription works unreasonably well for the O^{4+} line shifts considered (to better than 5% for eight of the nine cases listed); see the last column of Table I.

With respect to S^{12+} $(1s\,^2 2s8k-1s\,^2 2s7i)$, the bound-state sum $\delta E_{nl}^{(B)}$ yields 1126.24 Å, which is to be compared to a measured transition energy corresponding to 1126.41(15) Å [6]. This estimate lies within a standard deviation of the experimental value, and it may well account for the measurement. In particular, we again get a considerable improvement over the value of 1126.90 Å predicted by the polarization model. The bounds on the energy shift obtained by using Eqs. (5) and (6) yield 1125.69 Å and 1126.72 Å, and the estimate found by averaging corresponds to 1126.25 Å.

While the transition energy for S^{12+} can be reproduced to within the experimental error [6] by multiconfiguration Dirac-Fock (MCDF) calculations using the GRASP atomic structure package [12], this approach fails for the more precise O^{4+} transition energies in Table I [7]. The MCDF calculations, in general, appear to be hampered by the large spatial extension of the high-angular-momentum Rydberg wave functions as compared to the small size of the ionic core. As concerns MQDT, which was applied to low and intermediate-angular-momentum Rydberg levels of neutral Be [13], the extension of this method to the high-angular-momentum ionic Rydberg states may warrant additional studies. However, no routine method seems to be at hand for calculating the energy shifts considered here to the precision obtained in the experiments.

We note that if there are a few values of (n',l'), namely, (n_i',l_i') with $i=1$ to N, for which $|\Delta E_{n'n}/\Delta E_c|$ is not small, one can obtain the simple estimate (not a bound)

$$\delta E_{nl}=\delta E_{nl}^{(\mathrm{pol})}-\sum_i\left(\frac{\Delta E_{n_i'n}}{\Delta E_c}\right)^2\frac{M_{n_i'n}}{\Delta E_c+\Delta E_{n_i'n}},$$

which can be given an interpretation in terms of nonadiabatic wave functions [14]. Work in progress aims at a similar interpretation of the main formulas of this paper.

The substantial improvement in the agreement between theory and experiment for the two ions considered strongly suggests that the modified polarization model can be used to determine energy differences for many other highly charged

Rydberg ions; for many ions α_d, β_d, and ΔE_c are known or can be estimated, and the matrix elements in Eqs. (5), (6) are trivial to calculate [15].

These theoretical estimates — which are also readily applied to cores in which more than one excitation is significant, if the additional levels have known energies and known transition rates — can make the experimental search for Rydberg transitions in few-electron ions much simpler.

ACKNOWLEDGMENTS

We thank H. A. Weidenmüller and D. Schwalm for fruitful discussions and support. This work was funded in part by the German Federal Minister for Education, Science, Research and Technology (BMBF) under Contract No. 06 HD 562 I (3). L.S. was partially supported by the National Science Foundation under Grant No. PHY-9019745 and by the Humboldt Foundation.

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