

## Dynamical contributions to the quantum defects of calcium

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Nonadiabatic effects on the structure of Rydberg states of alkaline-earth atoms are examined and found to be large in many cases. Calculations for the quantum defects of the singlet  $F$  and  $G$  series in calcium, including dynamical contributions, are shown to be in good agreement with recent experimental data. This is in contrast to predictions based on the adiabatic core-polarization model, which significantly overestimates the quantum defects. Values for quantum defects of Ca for  $l \geq 4$  are presented.

### I. INTRODUCTION

The progression of energy levels for hydrogen-like atoms can be conveniently described by the expression

$$E_n = -\frac{1}{2} \frac{Z^2}{(n - \delta_l)^2}, \quad (1)$$

where  $\delta_l$ , the quantum defect, represents the effects of interactions between the valence electron and the atomic core or any short-range spherical perturbation in a many-electron system.<sup>1</sup> (Atomic units are used unless otherwise indicated.) For alkali-metal atoms,  $\delta_l$  is nearly constant over a series of levels having a given angular momentum  $l$ . The quantum-defect formula allows the energy-level scheme of these atoms to be characterized succinctly with the use of a few general parameters. In two-electron systems such as the alkaline-earth atoms, there are many states which can be treated using the one-electron approximation. For these states, the quantum defect of Eq. (1) remains a convenient parameter for the prediction of the energy levels.

For states having angular momentum less than the maximum angular momentum of a core electron, the quantum defects are usually large and are determined primarily by the penetration of the core by the Rydberg electron. For "nonpenetrating" states, in which  $l$  is greater than the maximum core angular momentum, core penetration is small and the quantum defects are usually less than 0.1. The dominant electron-core interaction in these states arises from the polarization of the core by

the Rydberg electron. The associated quantum defect is usually calculated in an adiabatic fashion with the Rydberg electron treated as stationary: The expression

$$E_{\text{pol}} = \sum_l -\frac{1}{2} \alpha_l \langle r^{-2(l+1)} \rangle, \quad (2)$$

where  $\alpha_l$  is the  $2^l$ -pole polarizability, is used to determine the polarization energy. This model has worked well for the alkali atoms where the cores are closed shells and thus insensitive to the dynamics of the outermost electron.<sup>2</sup>

Eissa and Öpik<sup>3</sup> have considered nonadiabatic corrections<sup>4</sup> to the polarization interaction of alkali and alkalilike systems and have found them to be small, generally less than a few percent of the total polarization energy. In two-electron systems, however, nonadiabatic effects can be large due to correlations between the Rydberg electron and the valence electron in the open-shell core. Dynamical effects on atoms such as the alkaline earths can therefore be anticipated to be much more substantial than for the alkalis. Thus these systems are well suited to testing the theory of Eissa and Öpik and demonstrating the important role dynamical effects can have on the polarization energy.

In this paper we confirm the validity of the Eissa and Öpik theory by examining critically some singlet  $F$  and  $G$  states of calcium for which the nonadiabatic corrections are large, typically as much as 50% of the static term. We then discuss how the results can be used to predict the general structure of calcium Rydberg states and Rydberg states of other alkaline-earth atoms.

## II. THEORY

In this section we recapitulate the method of Eissa and Öpik, applicable to atoms with a spherically symmetric core.

The Hamiltonian for the atom, neglecting the interaction between the Rydberg electron and the core, is taken as

$$H^0 = H_C + H_R . \quad (3)$$

$H_C$  is the Hamiltonian for the ionic core consisting of  $N$  electrons and  $H_R$  is the Hamiltonian for the Rydberg electron in the field of the screened nucleus. The Rydberg electron-core interaction is

$$W = \sum_{i=1}^N \left[ \frac{1}{|\vec{R} - \vec{r}_i|} - \frac{1}{R} \right] \quad (4)$$

with  $\vec{R}$  the position vector of the Rydberg electron and  $\vec{r}_i$  the position vector of the  $i$ th core electron.

The unperturbed eigenfunctions of the core and

Rydberg electrons satisfy

$$\begin{aligned} H_C \Phi^0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) &= \epsilon^0 \Phi^0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) , \\ H_R \psi^0(R) &= \eta^0 \psi^0(\vec{R}) , \end{aligned} \quad (5)$$

with  $\epsilon^0$  and  $\eta^0$  the respective eigenenergies. In lowest order the total atomic wave function is written as

$$\Psi^0(\vec{R}, \vec{r}_i) = \Phi^0(\vec{r}_i) \psi^0(\vec{R}) . \quad (6)$$

Note that by writing the wave function in this nonsymmetrized form, exchange effects between the core and Rydberg electron have been neglected. Through first order the wave function is

$$\Psi^1(\vec{R}, \vec{r}_i) = (\Phi^0 + \Phi^1)(\psi^0 + \psi^1) . \quad (7)$$

The first-order correction to the hydrogenic energy vanishes due to the spherical symmetry of the core. The second-order correction can be obtained by minimizing the functional<sup>5</sup>

$$E^{(2)} = 2 \langle \Phi^1 \psi^0 + \Phi^0 \psi^1 | W | \Phi^0 \psi^0 \rangle + \langle \Phi^1 \psi^0 + \Phi^0 \psi^1 | H^0 - (\epsilon^0 + \eta^0) | \Phi^1 \psi^0 + \Phi^0 \psi^1 \rangle . \quad (8)$$

The first-order correction to the Rydberg electron wave function  $\psi^1$  vanishes. Upon expanding  $W$  in terms of Legendre polynomials, assuming that  $R > r_i$ , the correction to the  $l$ th term in the expansion for the core wave function can be written as<sup>3</sup>

$$\Phi_i^{(1)}(\vec{R}, \vec{r}_i) = \beta_l(R) R^{-l-1} \chi_l(\hat{R}, \vec{r}_i) . \quad (9)$$

$\chi_l$  is the adiabatic core distortion, that is, the first-order correction to the core wave function in the adiabatic model, and the term  $\beta_l(R)$  allows for a change in its magnitude due to dynamical effects. Equation (8) thus takes the form

$$E^{(2)} = \sum_l \int_0^\infty R^{-2l-2} P(R)^2 \left\{ \alpha_l \left[ \frac{1}{2} \beta(R)^2 - \beta(R) \right] + \frac{1}{2} \langle \chi_l | \chi_l \rangle \left[ l(l+1) R^{-2} \beta(R)^2 + \left[ \frac{l+1}{R} \beta(R) - \frac{d\beta}{dR} \right]^2 \right] \right\} dR \quad (10)$$

with  $P(R)$  the radial portion of the Rydberg electron wave function and

$$\alpha_l = \frac{2}{2l+1} \sum_{n \neq 0} \frac{|\langle 0 | r^l | n \rangle|^2}{\epsilon_n - \epsilon_0} \quad (11)$$

the  $2^l$ -pole polarizability.

Parametrizing  $\beta_l(R)$  as  $y_0^{(l)} + y_2^{(l)}/R^2$ , the  $y_i^{(l)}$ 's are determined from the simultaneous differential equations resulting from the minimization of the energy functional.  $y_2^{(1)}$  in the Eissa-Öpik model is analogous to the quantity " $6\beta$ " in alternative approaches to the dynamical contribution.<sup>4</sup> Because of the neglect of exchange, the Legendre expansion, and the particular parametrization of  $\beta$ , the radial integrals diverge at small  $R$ . A cutoff radius  $R_0$ , which is of the order of the core radius, is therefore used as the lower limit of integration in the resulting matrix elements. As discussed in the subsequent sections, the results are insensitive to the choice of cutoff radius.

Minimization of the energy functional through the dipole and quadrupole terms leads to the following correction to the hydrogenic energy:

$$E^{(2)} = -\frac{1}{2} \alpha_1 (y_0^{(1)}) \langle r^{-4} \rangle + y_2^{(1)} \langle r^{-6} \rangle - \frac{1}{2} \alpha_2 (y_0^{(2)}) \langle r^{-6} \rangle + y_2^{(2)} \langle r^{-8} \rangle . \quad (12)$$

This reduces to the customary adiabatic result for  $y_0^{(l)} \rightarrow 1$  and  $y_2^{(l)} \rightarrow 0$ .

### III. APPLICATIONS TO CALCIUM

#### A. Core parameters

The dipole and quadrupole polarizabilities were determined by evaluating the first several terms in the summations of Eq. (11) employing matrix elements calculated with relativistic Hartree-Fock wave functions.<sup>6</sup> Experimental excitation energies from Risberg<sup>7</sup> were used to evaluate the energy denominators.

The alkaline-earth cores are isoelectronic to the alkali atoms and share the property that most of the oscillator strength lies in the resonance transition. A single term in the summation for the dipole polarizability constitutes over 99% of the contribution to the summation. For the quadrupole polarizability, three terms were retained in the summation. By using the sum rule

$$\begin{aligned} \sum_{n=n_i+1}^{\infty} \frac{|\langle 0 | r^l | n \rangle|^2}{\epsilon_n - \epsilon_0} &\leq \frac{1}{(\epsilon_{n_i+1} - \epsilon_0)} \sum_{n=n_i+1}^{\infty} |\langle 0 | r^l | n \rangle|^2 \\ &= \frac{1}{(\epsilon_{n_i+1} - \epsilon_0)} \left[ \langle 0 | r^{2l} | 0 \rangle - \sum_{n=0}^{n_i} |\langle 0 | r^l | n \rangle|^2 \right] \end{aligned} \quad (13)$$

we found that the remaining terms could change the Hartree-Fock polarizability by no more than 5%. Since the norms of the adiabatic core distortions used in Eq. (10),

$$\langle \chi_l | \chi_l \rangle = \frac{1}{(2l+1)} \sum_n \frac{|\langle 0 | r^l | n \rangle|^2}{(\epsilon_n - \epsilon_0)^2}, \quad (14)$$

have a higher-power energy denominator than the polarizabilities, they are even less sensitive to the truncation of the sum. The polarizabilities and norms used to calculate the polarization energy are listed in Table I.

#### B. Contributions to the quantum defects

The expression for the energy of the Rydberg level, Eq. (1), can be expanded in the form

$$E_{n,l} = -Z^2 \left\{ \frac{1}{2n^2} + \frac{\delta_l}{n^3} \left[ 1 + O \left( \frac{\delta_l}{n} \right) \right] \right\} \quad (15)$$

for states with  $\delta_l \ll n$ . This expansion enables a quantum defect to be associated with any perturbation energy which has the form  $-C/n^3$ , where  $C$

is approximately constant as a function of principal quantum number. In particular, since the interactions which occur between the Rydberg electron and the core for nonpenetrating Rydberg states give rise to energy shifts which scale as  $n^{-3}$ , these shifts can be described simply in the quantum-defect model. The various interactions and their contributions to the quantum defects are now discussed.

*Polarization contributions.* Polarization contributions were calculated using both the dynamical model discussed in Sec. II and the usual adiabatic model, including dipolar and quadrupolar terms. The polarization energy using the dynamical model was found to be fairly insensitive to the inner cut-off radius  $R_0$ . For the  $^1F$  state the polarization quantum defect changed by 3% as  $R_0$  was varied between 2.5 and 4.0 a.u. For the higher  $l$  states, the change was even less. While the expression used for calculating polarization effects is not valid for distances less than the core radius, where exchange effects must be included, for the high  $l$  states this is not a serious problem as core penetration is insignificant. Table II compares the results of the two models where it is noted that the adiabatic theory predicts a significantly larger contribution to the quantum defect for both the  $^1F$  and  $^1G$  states.

*Nonpolarization contribution.* Nonpolarization contributions include those arising from core penetration, relativistic and retardation effects, and residual configuration interaction. Table III contains the calculated quantum defects for these nonpolarization interactions for the  $15^1F$  and  $13^1G$  states.

TABLE I. Calculated core parameters, in a.u., used in the evaluation of the polarization energy.

	Dipolar	Quadrupolar
$\alpha$	89	987
$\langle \chi   \chi \rangle$	386	5657

TABLE II. Polarization quantum defects for the  $4s\ 15f\ ^1F$  and  $4s\ 13g\ ^1G$  states of calcium in the adiabatic and dynamical models  $A(B)=A \times 10^B$ .

	$4s\ 15f$	$\delta_{\text{pol}}^{\text{dipole}}$	$4s\ 13g$	$\delta_{\text{pol}}^{\text{quadrupole}}$	$4s\ 13g$
Adiabatic	1.38(-1)		3.70(-2)	4.23(-2)	3.81(-3)
Dynamical	8.84(-2)		3.07(-2)	1.11(-2)	1.79(-3)

### 1. Penetration contributions

The zero-order energy was calculated by solving for the energy of the Rydberg electron in the field of a Hartree-Slater core.<sup>8</sup> The difference between this energy and the hydrogenic energy represents a contribution to the quantum defect from the penetration of the electron into the non-Coulombic region at small  $r$ . The energies were calculated using the Cooley method<sup>9</sup> for solving the nonrelativistic Schrödinger equation in the Hartree-Slater potential. As expected, penetration effects had a negligible influence on the levels with  $l \geq 4$ .

### 2. Relativistic corrections

Relativistic effects are not large for the Rydberg states of interest in this work. Allowance was made for the energy change resulting from the relativistic variation of mass with velocity. The hydrogenic expression

$$E_{\text{rel}} = \frac{\alpha^2}{2n^4} \left[ \frac{n}{l+1/2} - \frac{3}{4} \right] \quad (16)$$

was used. For singlet states  $\vec{L} \cdot \vec{S}$  vanishes, leading to the absence of any fine-structure splitting.

### 3. Retardation corrections

Nonadiabatic effects arising from retardation were estimated using the model of Kelsey and Spruch,<sup>10</sup> who introduced a correction to the polar-

ization potential

$$V_{\text{retard}} = \frac{11}{4\pi} \frac{\alpha}{R^5} \alpha_1. \quad (17)$$

Retardation effects are also noted to be negligible for the Rydberg states considered in this work.

### 4. Configuration-interaction corrections

For the  $^1F$  state, a further correction was made to estimate contributions to the energy shifts from configuration interactions. The  $4s\ nf\ ^1F$  series in calcium is strongly perturbed at low  $n$  by the  $3d\ 4p$  interloper. The effect of this interloper on the Rydberg states was determined by fitting available experimental energy levels for this series to a modified Ritz expansion for the quantum defect<sup>11</sup>:

$$\delta = a + bt + ct^2 + \frac{d}{t - t_{\text{interloper}}}, \quad (18)$$

where

$$t = \frac{1}{(n^*)^2} = \frac{E_{\text{ion}} - E_{\text{measured}}}{R} \quad (19)$$

with  $E_{\text{ion}} = 49\ 305.92 \pm 0.10\ \text{cm}^{-1}$  and  $R = 109\ 735.81\ \text{cm}^{-1}$  for calcium.<sup>12</sup>

The last term in Eq. (18) is a measure of the residual configuration interaction in the perturbative limit, which is a valid approximation for the Rydberg  $^1F$  states since the configuration interaction for this series is strongly localized at low  $n$ . Table IV depicts the fit and compares the results

TABLE III. Nonpolarization contributions to the quantum defects of the  $4s\ 15f\ ^1F$  and  $4s\ 13g\ ^1G$  states of calcium.  $A(B)=A \times 10^B$ .

	$\delta_{\text{pen}}$	$\delta_{\text{rel}}$	$\delta_{\text{retard}}$	$\delta_{\text{config}}$	$\delta_{\text{tot,nonpln}}$
$4s\ 15f$	2.27(-3)	7.61(-6)	-9.81(-6)	-1.12(-2)	-8.93(-3)
$4s\ 13g$	1.73(-5)	5.92(-6)	-5.31(-7)		2.27(-5)

TABLE IV. Fitted coefficients in the Ritz expansion for the quantum defect of the  $^1F$  series in calcium with the inclusion of one interloper.  $A(B)=A \times 10^B$ .

	$a$	$b$	$c$	$d$
Present work	1.085(-1)	-8.928(-1)	7.325	8.46(-4)
Risberg (Ref. 6)	1.052(-1)	-7.708(-1)	4.677	7.44(-4)

with a previous determination by Risberg<sup>7</sup> which was based on a smaller number of data points.

### C. Results and discussion

Table V compares experimental quantum defects for the  $^1F$  and  $^1G$  states with those predicted by the adiabatic and dynamical models. Nonadiabatic effects are clearly seen to play an important role in determining the structure of these states. The agreement between the Eissa-Öpik model and experiment may seem rather unexpected for systems where the dynamical corrections are large. However, Öpik<sup>14</sup> has obtained similar results in studying the polarization interaction between two neutral atoms, where dynamical effects are even larger than those studied in this work. The incorporation of nonadiabatic influences by including the  $\beta(R)$  term in the first-order correction to the wave function thus seems to be a good approximation over a wide range of interaction strengths.

For states with  $l \geq 4$ , the quantum defects are dominated by the polarization interaction and thus can be predicted reliably using the Eissa-Öpik model. It was found that by including only dipolar contributions with hydrogenic expressions for  $\langle r^{-4} \rangle$  and  $\langle r^{-6} \rangle$ , the quantum defects obtained were within 10% of the results of the more elaborate calculation of Sec. II. The major source of the discrepancy when this simplification is made arises from the neglect of the quadrupolar interaction, which was found to be significant only for the  $G$  state.

In Table VI, the  $y_i^{(1)}$  for the  $G, H, I$  states are

presented, with the  $y_i^{(2)}$  included for the  $G$  state, as calculated for  $n = 20$ . These parameters are nearly constant as a function of the principal quantum number  $n$ . For states with  $l > 6$ , the polarization interaction is predominantly due to the adiabatic dipole interaction, the higher-order correlations between the valence electron and the Rydberg electron being significantly reduced as a result of the stronger centrifugal barrier. For these states the  $n, l$  dependence of  $E_{\text{pol}}$  is dominated by the factor

$$\langle r^{-4} \rangle = \frac{[3n^2 - l(l+1)]}{2n^5(l + \frac{3}{2})(l+1)(l + \frac{1}{2})l(l - \frac{1}{2})}$$

in the hydrogenic approximation. Using this expression, quantum defects for states not tabulated can be obtained.

Although we have studied a particular element, the case of calcium is expected to be typical of other alkaline-earth atoms. For the heavier elements such as strontium and barium, nonadiabatic effects may be even more pronounced due to the larger core polarizabilities and distortion functions. The calculational techniques used in this work to estimate the core parameters for calcium could in principle be used to estimate the analogous quantities in other alkaline-earth atoms. The case of calcium was simplified by the need for summing over only three states to obtain a good estimate of the quadrupole polarizability. In the event that a direct summation over states becomes unwieldy for Sr and Ba, other techniques are available<sup>15</sup> to estimate the core parameters, which can then be used in conjunction with the Eissa-Öpik model to predict the structure of the high  $l$  states.

TABLE V. Comparison of quantum defects calculated in the adiabatic and dynamical models with experiment.  $A(B)=A \times 10^B$ .

	Adiabatic	Dynamical	Expt. (Refs. 12 and 13)
4s 15f	1.71(-1)	9.06(-2)	9.32 ± 0.10(-2)
4s 13g	4.08(-2)	3.25(-2)	3.25(-2) <sup>a</sup>

<sup>a</sup> Average of two measurements.

TABLE VI.  $y_i^{(j)}$ , where  $\delta_{\text{pol}} = \frac{1}{2}\alpha_1 n^3(y_0^{(1)}\langle r^{-4} \rangle + y_2^{(1)}\langle r^{-6} \rangle) + \frac{1}{2}\alpha_2 n^3(y_0^{(2)}\langle r^{-6} \rangle + y_2^{(2)}\langle r^{-8} \rangle)$ .

$l$	$y_0^{(1)}$	$y_2^{(1)}$	$y_0^{(2)}$	$y_2^{(2)}$
4	0.80	-0.56	0.33	-0.01
5	0.98	-16.6		
6	1.02	-33.7		

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