

## Core polarization and quantum defects in high-angular-momentum states of alkali atoms\*

Richard R. Freeman<sup>†</sup> and Daniel Kleppner

Research Laboratory of Electronics and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 7 July 1976)

We discuss the systematics of energy levels of high-angular-momentum Rydberg states of alkali-metal atoms, and show that they are well described by a quantum-defect model. Polarization of the core electrons by the valence electron is shown to be the dominant contribution to the quantum defect. As an example, recently observed splittings between the  $l = 3, 4,$  and  $5$  levels in various Rydberg states of sodium are analyzed to yield values for the core polarizabilities. Effective values of the dipole and quadrupole polarizability of  $1.0015(15)$  and  $0.48(15)$  a.u., respectively, are obtained. Implications for the precise determination of the structure of highly excited Rydberg states in alkali atoms are discussed.

### I. INTRODUCTION

The optical spectrum of the alkali metals is described by the celebrated Rydberg formula  $W_A = -1/2(n - \delta_l)^2$ , where the quantum defect  $\delta_l$  is approximately constant for fixed angular momentum  $l$ . The quantum-defect picture follows quite directly from the model of a valence electron interacting with a nucleus of charge  $Z$  and a fixed core of  $Z - 1$  inner-shell electrons. The quantum defect drops rapidly for  $l > l_{\text{core}}$ , where  $l_{\text{core}}$  is the maximum angular momentum of a core electron.

The nature of the quantum-defect picture has taken new importance with recent advances in Rydberg states of atoms. In particular, it is now possible to measure accurately term separations of high-angular-momentum states. For hydrogen these separations vanish except for fine-structure effects, and so for nonhydrogenic systems even a small quantum defect plays a major role in the level structure. The questions arise as to whether a quantum-defect model is appropriate for high-angular-momentum states of alkali metals, and whether the quantum defects can be related to simple properties of the core distribution. We shall demonstrate that the answer to both questions is *yes*. The quantum-defect model is useful for high- as well as low-angular-momentum states; for large  $l$ , the quantum defect is simply related to the electrostatic polarizability of the core electrons (i.e., of the alkali ion).

In this paper we develop a simple quantum-defect theory for high-angular-momentum Rydberg levels of the alkali metals, emphasizing the central nature of core polarization and its relation to the level structure. We observe that measurements of the splittings between angular-momentum components within a term can provide precise values for the core polarizabilities. As an application, we present values for the dipole and quadrupole polarizabilities of Na obtained from microwave

measurements of the splittings of  $l = 3, 4,$  and  $5$  Rydberg states reported by Gallagher, Hill, and Edelstein.<sup>1,2</sup>

We should point out that the usefulness of the polarization model in analyzing the hydrogenic ( $l > 2$ ) Rydberg states of He has been described by Deutsch,<sup>3</sup> and that high-resolution data on such states have been acquired in an elegant series of experiments employing radio-frequency spectroscopy to derive the term structure of He by Wing and his colleagues.<sup>4</sup>

### II. QUANTUM-DEFECT DESCRIPTION

One aim of a quantum-defect description is to express the energy as

$$E = -\frac{1}{2}[(n - \delta_l)^2]^{-1}, \quad (1)$$

where  $\delta_l$  is a constant or a very slowly varying function of  $n$ . (Atomic units are used unless otherwise indicated.) For Rydberg states with  $\delta_l \ll 1$ ,  $n \gg 1$ , we can write

$$E = -1/2n^2 - (\delta_l/n^3)[1 + O(\delta/n)]. \quad (2)$$

Thus, if a perturbation energy has the form  $-A/n^3$ , where  $A$  is a constant or a slowly varying function of  $n$ , we can immediately identify  $A$  with the quantum defect. More generally, if the perturbation consists of several terms, each of the form  $-A_i/n^3$ , then the total energy shift is  $-\sum A_i/n^3$ , and this gives rise to a quantum defect  $\delta = \sum \delta_i$ , where  $\delta_i = A_i$ .

For an alkali in a state with  $l > l_{\text{core}}$ , a "non-penetrating" state, we can write

$$E(n, l) = E_0 + E_{\text{pol}} + E_{\text{pen}} + E_{\text{rel}}, \quad (3)$$

where  $E_0 = -1/2n^2$  (we neglect reduced-mass effects for the present),  $E_{\text{pol}}$  is the polarization energy,  $E_{\text{pen}}$  is the energy shift due to core penetration, and  $E_{\text{rel}}$  represents the spin-orbit energy and the relativistic energy shift. The last three terms

in Eq. (3) are assumed to be sufficiently small to be treated by a perturbation expansion.

As discussed in Sec. III, the  $n$  dependence of  $E_{\text{po1}}$  is dominated by the factor  $\langle r^{-4} \rangle \approx n^{-3} l^{-5}$ . The core-penetration energy also varies as  $n^{-3}$ , for in high-angular-momentum states the energy is nearly proportional to the density of the valence electron at the core which varies as  $n^{-3}$ . For non-penetrating states  $E_{\text{rel}}$  acquires the hydrogenic value  $n^{-3}[\alpha^2/(j \pm \frac{1}{2})]$ , where  $\alpha$  is the fine-structure constant, and  $j$  is the angular momentum. Thus, all three perturbation terms in Eq. (3) scale as  $n^{-3}$  and we can write

$$\begin{aligned} E(n, l) - E_0(n, l) &= -n^{-3} \delta_l \\ &= -n^{-3} (\delta_{\text{po1}}^l + \delta_{\text{pen}}^l + \delta_{\text{rel}}^l). \end{aligned} \quad (4)$$

In high-angular-momentum states,  $E_{\text{pen}} \ll E_{\text{po1}}$  or  $E_{\text{rel}}$ , and it can be considered as a small correction to the total quantum defect. For large  $l$ ,  $E_{\text{rel}}$  is hydrogenic and may be easily computed.

$\delta_{\text{po1}}^l$  can be evaluated from the potential<sup>5</sup>

$$V_{\text{po1}} = -\frac{1}{2} \alpha'_d (1/r^4) - \frac{1}{2} \alpha'_Q (1/r^6) + V'_{\text{po1}}, \quad (5)$$

where  $\alpha'_d$ ,  $\alpha'_Q$  are the effective dipolar and quadrupolar polarizabilities, respectively, and  $V'_{\text{po1}}$  represents higher-order terms which can be neglected. The effective polarizabilities differ slightly from the polarizabilities for the alkali ion due to nonadiabatic effects associated with the valence electron's motion. We shall consider these corrections in Sec. III, and retain the form of Eq. (5), even though the constants must be regarded as to some extent phenomenological.

If we write  $E_{\text{po1}} = E_{\text{po1}}^d + E_{\text{po1}}^Q$ , we have, using the hydrogenic value for  $\langle r^{-4} \rangle$ ,  $\langle r^{-6} \rangle$ ,<sup>3</sup>

$$E_{\text{po1}}^d = -\frac{1}{2} \alpha'_d \frac{1}{n^3} \frac{3/2}{l^5} \left[ 1 + f_d \left( \frac{l^2}{n^2} \right) \right], \quad (6)$$

$$E_{\text{po1}}^Q = -\frac{1}{2} \alpha'_Q \frac{1}{n^3} \frac{35/8}{l^9} \left[ 1 + f_Q \left( \frac{l^2}{n^2} \right) \right], \quad (7)$$

where  $f_d$  and  $f_Q$  represent small, higher order corrections, of order  $l^2/n^2$ . The full expansions of  $\langle r^{-4} \rangle$  and  $\langle r^{-6} \rangle$ , given in the Appendix, are used for actual calculations of the energies. The form of Eqs. (6) and (7) is convenient for discussing systematics. The polarization contribution to the quantum defect can be written

$$\begin{aligned} \delta_{\text{po1}} &= \delta_{\text{po1}}^d + \delta_{\text{po1}}^Q \\ &= \frac{3}{4} \alpha'_d l^{-5} \left[ 1 + f_d \left( \frac{l^2}{n^2} \right) \right] \\ &\quad + \frac{35}{16} \alpha'_Q l^{-9} \left[ 1 + f_Q \left( \frac{l^2}{n^2} \right) \right]. \end{aligned} \quad (8)$$

We see that the  $l$  dependence of  $\delta_{\text{po1}}$  is dominantly  $l^{-5}$  and that the  $n$  dependence arises from the

terms  $f(l^2/n^2)$ . By combining Eqs. (4) and (8) we obtain

$$\begin{aligned} \delta_l &= \frac{3}{4} \alpha'_d l^{-5} \left[ 1 + f_d \left( \frac{l^2}{n^2} \right) \right] + \frac{35}{16} \alpha'_Q l^{-9} \left[ 1 + f_Q \left( \frac{l^2}{n^2} \right) \right] \\ &\quad + \delta_{\text{pen}}^l + \delta_{\text{rel}}^l. \end{aligned} \quad (9)$$

If the polarizabilities are known and the penetration and relativistic contributions have been calculated or measured, this expression can be used to predict the energy levels. Alternatively, one can employ Eq. (9) to extract the polarizabilities from the measured energy splittings, which is the procedure followed in Sec. III.

### III. APPLICATION TO SODIUM

Gallagher, Edelstein, and Hill<sup>1,2</sup> have measured  $f$ - $g$  and  $g$ - $h$  level separations within terms of sodium for  $n = 13$ – $17$ . Their experimental method involved two-step laser excitation to the  $nd$  level, followed by microwave excitation of the  $nf$ ,  $ng$ , and  $nh$  levels. They have analyzed their data to yield values for the fine structure for the  $f$ ,  $g$ , and  $h$  levels, and have shown that, to within their experimental uncertainty, the fine-structure intervals are given by the hydrogenic formula. In this section we shall use their data to extract values for the dipole and quadrupole polarizability of the core electrons of Na.

In Table I we list the  $nf$ - $ng$  and  $ng$ - $nh$  splittings calculated from the observed  $nd$ - $nf$  transition frequencies,<sup>1</sup> and from the  $nd$ - $ng$  and  $nd$ - $nh$  transition frequencies.<sup>2</sup> In each case we have corrected the observed splittings for the relativistic effects, a straightforward task given that the fine structure is hydrogenic. We take these derived splittings to be the raw data.

To extract the polarizabilities from the data in Table I, each splitting must be further corrected for the penetration energy of the states. We have calculated the penetration energy for each state by perturbation theory

$$E_{\text{pen}}(n, l) = \int_0^\infty |\psi(n, l)|^2 V' r^2 dr, \quad (10)$$

TABLE I. Derived  $nf$ - $ng$  and  $ng$ - $nh$  splittings in Na corrected for fine structure.<sup>a</sup>

$n$	$f$ - $g$ (MHz)	$g$ - $h$ (MHz)
13	3500.9(1.8)	812.1(5.2)
14	2803.7(1.5)	654.3(5.2)
15	2291(2.4)	533.4(4.2)
16	1890.1(1.3)	
17	1574.9(1.2)	

<sup>a</sup> From Refs. 1 and 2.

where  $V'$  is the perturbation potential due to the core electrons, and  $\psi(n, l)$  is the hydrogenic wave function for the  $(n, l)$  state of the valence electron. This procedure is valid provided that the energy determined in Eq. (10) remains much smaller than the term separation at  $n$ . That is, we require

$$|E_{\text{pen}}(n, l)| \ll n^{-3} \quad (11)$$

or

$$n^3 |E_{\text{pen}}(n, l)| \equiv \delta_{\text{pen}} \ll 1. \quad (12)$$

This condition is easily satisfied in sodium for states with  $l \geq 3$ .

$E_{\text{pen}}(n, l)$  is sensitive to the long-range behavior of the core electron's charge distribution, a quantity difficult to calculate reliably. We obtained values for  $V'$  using the tabulated normalized wave functions for  $\text{Na}^+$  as calculated by Hartree,<sup>6</sup> and from the charge density for  $\text{Na}^+$  computed with the Herman-Skillman self-consistent-field program based upon the Hartree-Fock-Slater method.<sup>7</sup> The two methods give values of  $E_{\text{pen}}(n, l)$  which agree within 25%. As the results of Table II suggest, this disagreement is tolerable because the penetration energy is relatively small, about 1% of the  $f$ - $g$  separation and negligible for the  $g$ - $h$  separation. Nevertheless, it is the major source of uncertainty in the final value for the quadrupole polarizability.

To extract the core polarizabilities we rewrite Eq. (3) to give

$$\Delta E_{\text{expt}}(l, l') = \alpha'_d A_d(l, l') + \alpha'_Q A_Q(l, l') + E_{\text{pen}}(l) - E_{\text{pen}}(l'), \quad (13)$$

where

$$A_d(l, l') = \frac{1}{2} \langle r^{-4} \rangle_{l, l'}, \quad (14a)$$

$$A_Q(l, l') = \frac{1}{2} \langle r^{-6} \rangle_{l, l'}. \quad (14b)$$

A single pair of observations for two different sets of  $l$  and  $l'$  are sufficient to determine  $\alpha'_d$  and  $\alpha'_Q$  from Eq. (13); a series of observations for different values of  $n$  overdetermines the polarizabilities. Values of  $A_d$  and  $A_Q$  are given in Table III.

TABLE II. Magnitude of  $E_{\text{pen}}(n, l)$ .

$n$	$nf$ - $ng$ splitting (MHz)	$E_{\text{pen}}(l=3)^a$ (MHz)	$\delta_{\text{pen}}(l=3)$
13	3500.9(1.8)	30.3	$1.01 \times 10^{-5}$
14	2803.7(1.5)	24.1	$1.00 \times 10^{-5}$
15	2291.5(2.4)	19.4	$0.99 \times 10^{-5}$
16	1890.1(1.3)	15.8	$0.98 \times 10^{-5}$
17	1574.9(1.2)	13.1	$0.98 \times 10^{-5}$

<sup>a</sup> Calculated from Eq. (10) using  $V'$  determined from charge density of  $\text{Na}^+$  as given by Hartree (Ref. 6).

TABLE III. Magnitudes of coefficients for Eq. (13).

$n$	$\Delta E_{\text{expt}}(l, l')$ (MHz)	$A_d(l, l')$ (MHz)	$A_Q(l, l')$ (MHz)	$E_{\text{pen}}$ (MHz)
<i>nf-ng transitions</i>				
13	3500.9(1.8)	3396.06	146.91	30.3(10.0)
14	2803.7(1.5)	2725.72	118.54	24.1(8.0)
15	2291.5(2.4)	2220.57	96.96	19.4(6.5)
16	1890.1(1.3)	1832.78	80.30	15.8(5.2)
17	1574.9(1.2)	1529.84	67.22	13.1(4.4)
<i>ng-nh transitions</i>				
13	812.1(5.2)	807.44	10.11	< 1.0
14	654.3(5.2)	649.10	8.20	< 1.0
15	533.4(4.2)	529.43	6.73	< 1.0

The eight sets of equations for  $\alpha'_d$  and  $\alpha'_Q$  were solved simultaneously; the results are consistent with the uncertainty of each set, and yield the following values:

$$\alpha'_d = 1.0015(15) \text{ a.u.}, \quad \alpha'_Q = 0.48(15) \text{ a.u.} \quad (15)$$

The uncertainty in  $\alpha'_d$  is due to the experimental uncertainties; the uncertainty in  $\alpha'_Q$  is due chiefly to the uncertainty in the penetration correction. For convenience, the results are given in terms of quantum defects in Table IV.

#### IV. DISCUSSION

##### A. Nonadiabatic effects

The polarization potential defined by Eq. (1) is based on a static model: in reality, the motion of the valence electron introduces dynamical effects which modify the polarization constants and, to some extent, the form of the potential. Eissa and Opik<sup>8</sup> have investigated nonadiabatic effects in Na and have shown that the polarization potential can be written

$$V_{\text{pol}} = -\frac{1}{2} \alpha_d y_0^d \frac{1}{r^4} - \frac{1}{2} (\alpha_Q y_0^Q + \alpha_d y_1^d) \frac{1}{r^6} + \dots, \quad (16)$$

where the  $y$ 's are slowly varying functions of  $n$  and  $l$ . Comparing this result with Eq. (5) yields

$$\alpha_d = \alpha'_d / y_0^d, \quad \alpha_Q = [\alpha'_Q - \alpha'_d (y_1^d / y_0^d)] / y_0^Q. \quad (17)$$

For the  $4f$  state of Na, Eissa and Opik obtained

$$y_0^d = 1.004, \quad y_0^Q = 0.964, \quad y_1^d = -1.41.$$

Unfortunately, there is no simple way to extrapolate these results to higher values of  $n$ . [Eissa and Opik considered several other alkali systems, however, and these reveal that  $y_0^d$  changes only slowly with  $n$ . For example, in potassium,  $y_0^d(4F) = 1.012$ ; while  $y_0^d(9F) = 1.022$ .] For lack of an ac-

TABLE IV. Derived quantum defects.

$n$	$l=3$			$l=4$			$l=5$		
	$\delta_{\text{pol}}^d$ ( $\times 10^{-3}$ )	$\delta_{\text{pol}}^Q$ ( $\times 10^{-3}$ )	$\delta_{\text{pen}}$ ( $\times 10^{-5}$ )	$\delta_{\text{pol}}^d$ ( $\times 10^{-4}$ )	$\delta_{\text{pol}}^Q$ ( $\times 10^{-6}$ )	$\delta_{\text{pen}}$	$\delta_{\text{pol}}^d$ ( $\times 10^{-4}$ )	$\delta_{\text{pol}}^Q$ ( $\times 10^{-7}$ )	$\delta_{\text{pen}}$
13	1.55	2.54	1.01	4.16	1.87	$< 10^{-6}$	1.46	2.53	$< 10^{-7}$
14	1.55	2.56	1.00	4.17	1.90	$< 10^{-6}$	1.47	2.59	$< 10^{-7}$
15	1.55	2.58	0.99	4.20	1.92	$< 10^{-6}$	1.49	2.63	$< 10^{-7}$
16	1.56	2.60	0.98	4.22	1.94	$< 10^{-6}$	1.50	2.67	$< 10^{-7}$
17	1.56	2.61	0.98	4.23	1.96	$< 10^{-6}$	1.50	2.71	$< 10^{-7}$

curate value of  $y_0^d$  for the states of interest,  $n = 13-17$ , we shall use the value  $y_0^d = 1.004$ , yielding

$$\alpha_d = 0.998 . \quad (18)$$

The uncertainty, due entirely to the nonadiabatic correction, is estimated to be a few percent. Our result is in reasonable agreement with the value calculated by Lahiri and Mukherji,<sup>9</sup>  $\alpha_d = 0.9459$ , and the value derived by Opik<sup>10</sup> from spectroscopic data,  $\alpha_d = 0.978$ .

The situation with respect to the quadrupole polarizability is less satisfactory, for here nonadiabatic effects are large, and the calculated correction less reliable. From Eq. (17), using our experimental value  $\alpha'_Q = 0.48$ , we obtain  $\alpha_Q = 1.91$ . This is in reasonable agreement with the value  $\alpha_Q = 1.53$  calculated by Lahiri and Mukherji,<sup>9</sup> but the nonadiabatic correction must be investigated in greater detail before much confidence can be assigned to the results.

An alternative approach to the nonadiabatic effects is to make sufficiently precise measurements on enough levels to reveal the functional form represented by Eq. (16). We have analyzed the data of Gallagher *et al.*<sup>1,2</sup> on a term-by-term basis to determine whether there are any systematic variation of the effective polarizabilities with  $n$ . The results for  $\alpha'_d$  show that the difference between  $n = 13$  and  $n = 15$  is no greater than  $2 \times 10^{-3}$ . Much higher experimental precision should be obtainable for the levels of the alkalis; such data would be invaluable in investigating the nonadiabatic effects. In any case, a more-complete theoretical study of nonadiabatic effects of the polarization and the penetration interactions is badly needed.

### B. Applications

Although uncertainties in the nonadiabatic corrections are an important theoretical problem, the measured effective polarizabilities can be used to predict level structure with some confidence. As the data in Table IV reveal, the entire quadrupole interaction decreases so rapid-

ly with  $l$  that even a large uncertainty in  $\alpha'_Q$  has little effect on level structure. Also, as  $l$  increases, possible nonadiabatic corrections to  $\alpha'_d$  become less significant.

The polarization potential plays an important role in the systematics of level structure at low electric fields. At zero field,  $V_{\text{pol}}$  breaks the  $l$  degeneracy of the nonrelativistic hydrogenic system; Stark splitting becomes second order and  $l$  is a good quantum number. These effects are illustrated by the level diagram for the  $n = 10$ ,  $m = 0$  manifold shown in Fig. 1.

At a field of 5 kV/cm [ Fig. 1(a) ], the Stark levels are separated by an interval of  $7 \text{ cm}^{-1}$ , and can be readily resolved with a tunable laser.<sup>11</sup> If the field is then decreased, each level adiabatically connects to a state of well-defined  $l$  [ Figs. 1(b) and 1(c) ]. Thus, any value of  $l$  can be populated. (This method does not provide access to high- $m$  states, for  $m$  remains a good quantum number at all field values.)

The maximum electric field which can be applied without mixing values of  $l$  can be estimated by comparing the polarization energy and electric matrix element for two adjacent terms:

$$\Delta V_{\text{pol}}(l, l+1) \simeq \frac{15}{4} \alpha'_d (1/n^3) (1/l^6) , \quad (19)$$

$$\langle n, l+1 | zE | n, l \rangle \simeq \frac{3}{2} n^2 (1 - l^2/n^2)^{1/2} E . \quad (20)$$

For the polarization energy to dominate the Stark interaction, we require

$$E \lesssim \frac{5}{2} \alpha'_d (1/n^3) (1/l^6) (1 - l^2/n^2)^{-1/2} . \quad (21)$$

For the  $n = 10$ ,  $l = 4$  ( $g$  state) of Na, for instance, this yields  $E \lesssim 33 \text{ V/cm}$ .

In order to vary the applied field adiabatically, the rate of change of the field must be small compared to the separation of adjacent levels. The closest levels at zero field in Fig. 1(c) are the  $l = 9$  and  $l = 8$  states: their separation is  $0.002 \text{ cm}^{-1}$ , or  $4 \times 10^8 \text{ rad/sec}$ . If the field is reduced from 5 kV/cm to close to zero in greater than 25 nsec, these states will follow adiabatically. Lower-lying states can be "switched" much more rapidly.

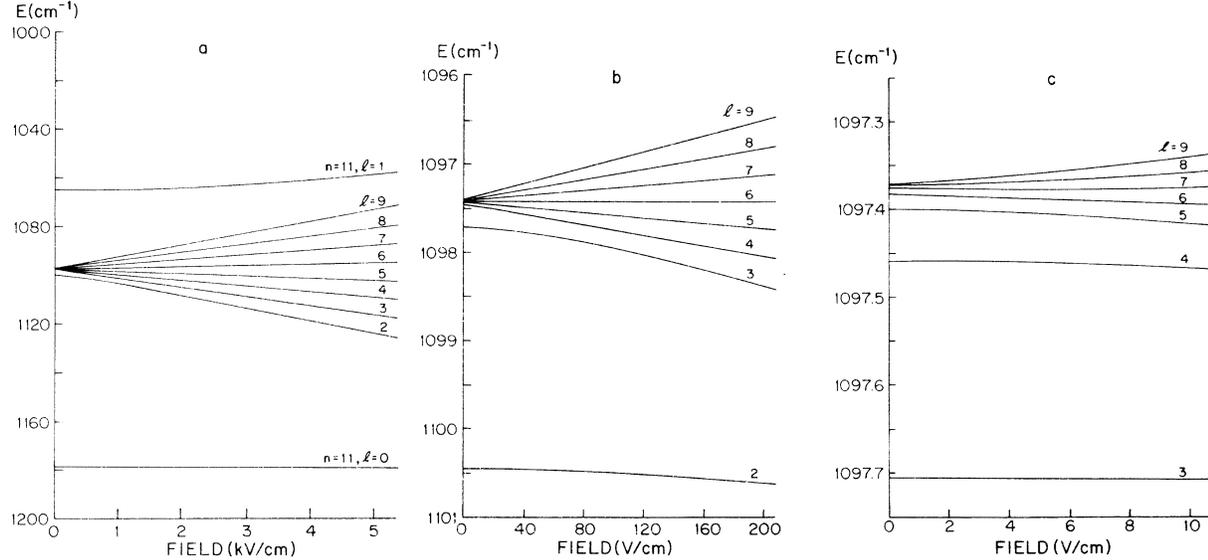


FIG. 1. (a)  $m=0$  energy levels for Na near the  $n=10$  term as a function of electric field. The fine structure has been ignored. The levels are labeled by the corresponding value of angular momentum each level possesses at zero electric field. On this scale the  $l=0$  ( $s$  state) and  $l=1$  ( $p$  state) of the next-higher-lying term ( $n=11$ ) are present due to their large quantum defects. The quantum defect of the  $l=2$  ( $d$  state) level is large enough to produce an initially quadratic Stark effect. (b)  $m=0$ ,  $n=10$  energy levels as in (a) with a 40-fold increase in the energy scale. The quantum defects of the states are calculated from the model given in the text. On this scale the initial Stark effect for the  $l=2$ , 3, and 4 levels is clearly seen to be quadratic. (c)  $m=0$ ,  $n=10$  energy levels as in (b) with a tenfold increase in the energy scale. All of the individual Stark states connect to states with a definite value of  $l$  at zero electric field. The fine structure, left out in this calculation, would split each level but not appreciably change the overall pattern.

Fine structure, which is neglected in Fig. 1, will play an important role in low electric fields at large  $l$ . If  $E_{\text{rel}} > E_{\text{pol}}$ ,  $j$ , not  $l$ , is a good quantum number. For nonpenetrating states,  $E_{\text{rel}} = \frac{1}{2}(\alpha^2/n^3)[1/(j+\frac{1}{2})] \sim (\alpha^2/n^3)(1/l)$ . Since  $E_{\text{pol}} \sim (1/n^3)(1/l^5)$ , the relativistic energy dominates at large  $l$ . The characteristic value for the coupling to change is given by  $l=15.4$  ( $\alpha_d$ )<sup>1/4</sup>. Thus, fine structure will appreciably split the energy levels of Fig. 1(c), though it would not change the overall pattern.

It is interesting to note that the quantum defect of the  $d$  state, the lowest "nonpenetrating" state of sodium, 0.0145, is due predominantly to the polarization interaction—only about 10% is actually due to penetration. For the  $p$  state the quantum defect, due essentially entirely to penetration, is 0.85. Thus, the categorization of states as "penetrating" for  $l < l_{\text{core}}$  and nonpenetrating for  $l > l_{\text{core}}$

is quite realistic. The quadrupole contribution to the  $d$  state, polarization energy is, however, 30% of the dipole contribution, which suggests that the perturbation approximation which underlies the polarization model is starting to break down. Nevertheless, even for this state the model can be of some use in predicting the  $n$  dependence of the quantum defect.

#### ACKNOWLEDGMENTS

The authors would like to thank Tom Gallagher for making available the values of the  $\Delta l$  splittings before their publication. We also wish to thank Myron Zimmerman for help in computing the energy diagrams. One of the authors (D.K.) would like to thank C. Bottcher for a helpful conversation, and for support from a NATO Senior Fellowship in Science.

#### APPENDIX

The energy separation between two  $l$  levels of the same term for which  $\delta_{\text{pen}}$  and  $\delta_{\text{rel}}$  cannot be neglected is

$$E(l, l') = (1/n^3) \left[ \frac{1}{2} \alpha'_d n^3 (\langle r^{-4} \rangle_l - \langle r^{-4} \rangle_{l'}) + \frac{1}{2} \alpha'_Q n^3 (\langle r^{-6} \rangle_l - \langle r^{-6} \rangle_{l'}) + (\delta_{\text{pen}}^l - \delta_{\text{pen}}^{l'}) + (\delta_{\text{rel}}^l - \delta_{\text{rel}}^{l'}) \right], \quad (\text{A1})$$

where

$$\langle r^{-4} \rangle_l^n = \frac{3n^2 - l(l+1)}{2n^5(l - \frac{1}{2})(l + \frac{1}{2})(l+1)(l + \frac{3}{2})} \quad (\text{A2})$$

and

$$\langle r^{-6} \rangle_l^n = \frac{35n^4 - 5n^2(6l(l+1) - 5) + 3(l-1)l(l+1)(l+2)}{8n^7(l - \frac{3}{2})(l-1)(l - \frac{1}{2})(l + \frac{1}{2})(l+1)(l + \frac{3}{2})(l+2)(l + \frac{5}{2})} \quad (\text{A3})$$

\*Work supported by the NSF.

†Present address: Bell Laboratories, Holmdel, N.J. 07733.

<sup>1</sup>T. F. Gallagher, R. M. Hill, and S. A. Edelstein, *Phys. Rev. A* **13**, 1448 (1976).

<sup>2</sup>T. F. Gallagher, R. M. Hill, and S. A. Edelstein, *Phys. Rev. A* **14**, 744 (1976).

<sup>3</sup>C. Deutsch, *Phys. Rev. A* **2**, 43 (1970); **3**, 1516(E) (1971); **13**, 2311 (1976).

<sup>4</sup>K. B. McAdam and W. H. Wing, *Phys. Rev. A* **12**, 1464 (1975); W. H. Wing and W. E. Lamb, Jr., *Phys. Rev. Lett.* **28**, 265 (1972); W. H. Wing, K. R. Lea, and W. E. Lamb, Jr., in *Atomic Physics*, edited by S. J. Smith and G. K. Walters (Plenum, New York, 1973), Vol. 3, p. 119.

<sup>5</sup>J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605

(1933). This work represented the first attempt to associate the core polarizability of an alkali ion with the spectroscopy of the neutral atom. Also, B. Edlén, *Encyclopedia of Physics* (Springer, Berlin, 1964), Vol. XXVII, p. 125.

<sup>6</sup>D. R. Hartree and W. Hartree, *Proc. R. Soc. A* **193**, 299 (1948).

<sup>7</sup>F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).

<sup>8</sup>H. Eissa and U. Öpik, *Proc. Phys. Soc. Lond.* **92**, 556 (1967).

<sup>9</sup>J. Lahiri and A. Mukherji, *Phys. Rev.* **153**, 386 (1967).

<sup>10</sup>U. Öpik, *Proc. Phys. Soc. Lond.* **92**, 566 (1967).

<sup>11</sup>M. Littman, M. Zimmerman, T. Ducas, R. Freeman, and D. Kleppner, *Phys. Rev. Lett.* **36**, 788 (1976).