

# PHYSICAL REVIEW A

## GENERAL PHYSICS

THIRD SERIES, VOLUME 32, NUMBER 5

NOVEMBER 1985

### Determination of core polarizabilities in sodium by numerical integration of Schrödinger's equation

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(Received 31 May 1984; revised manuscript received 3 July 1985)

In this investigation term values for high-angular-momentum states in sodium are calculated by numerical integration of Schrödinger's wave equation. It is assumed that a single valence electron (Rydberg electron) interacts with the atom's nucleus and a core of electrons. Polarization and penetration are taken into account and effective polarizabilities determined by fitting calculations to observed splittings between  $l=3, 4,$  and  $5$  states of sodium. The effective dipole and quadrupole polarizabilities are found to be  $0.9965(100)$  and  $0.376(150)$  a.u., respectively, and an improvement over a previous comparison of *ab initio* theory and experiment is made for the quadrupole polarizability.

#### I. INTRODUCTION

Highly excited (Rydberg) atoms of sodium can be described by a simple model in which a single valence electron interacts with a nucleus containing 11 protons and a core of 10 electrons. Experiments<sup>1</sup> show the energy-level schemes of such atoms to be almost hydrogenic in character. The small differences between the sodium and hydrogen energy-level schemes are due for the most part to the penetration and polarization of the electron core by the valence electron. These effects also split levels corresponding to the same principal quantum number  $n$  and different angular-momentum quantum number  $l$ . The  $d-f$ ,  $d-g$ , and  $d-h$  splittings have been measured in the region  $11 \leq n \leq 17$  by Gallagher, Hill, and Edelstein.<sup>2,3</sup> Freeman and Kleppner<sup>4</sup> have used these splittings to theoretically determine effective dipole and quadrupole polarizabilities, two parameters that describe the core polarization by the valence electron. Their calculations utilized a polarization potential which follows from a model that assumes the electron core to be static. Actually the valence electron dynamically affects the core of electrons. These nonadiabatic effects have been investigated by Eissa and Öpik.<sup>5</sup>

Freeman and Kleppner used first-order perturbation theory to determine the effects of penetration and polarization. The present investigation is similar to theirs except calculations were also carried out by a method involving the numerical integration of Schrödinger's wave equation. The purposes of this investigation were (1) to determine the effective dipole and quadrupole polarizabilities in sodium by a numerical method which, in principle, is superior to the perturbation theory used by Freeman

and Kleppner, and (2) to compare the results found by numerical integration of Schrödinger's wave equation with the results found by first-order perturbation theory.

#### II. DISCUSSION AND RESULTS

##### A. The Hamiltonian

The Hamiltonian for this situation contains a potential-energy function which can be expressed as a sum of Coulombic, penetration, and polarization terms. In the present work, as in the Freeman and Kleppner<sup>4</sup> investigation, the effect of penetration was calculated by using Hartree<sup>6</sup> wave functions for the core of electrons. The potential-energy function used to describe the effect of polarization is

$$V_{\text{pol}} = -\frac{1}{2}\alpha'_d(1/r^4)[1 - e^{-(r/W_0)^4}] - \frac{1}{2}\alpha'_Q(1/r^6)[1 - e^{-(r/W_0)^6}], \quad (1)$$

where  $\alpha'_d$  and  $\alpha'_Q$  are the effective dipole and quadrupole polarizabilities in atomic units. The terms in the square brackets of Eq. (1) are cutoff factors which keep the potential finite at  $r=0$ . These factors were not included in the polarization potential used by Freeman and Kleppner since their perturbation calculations did not require the potential to be finite at  $r=0$ . As long as the value of  $W_0$  in Eq. (1) is less than about 1 a.u., calculated results are found to be independent of  $W_0$  for nonpenetrating orbits. Therefore  $W_0$  was arbitrarily set at 0.6 a.u. The resulting polarization potential is similar to one used by Dalgarno *et al.*<sup>7</sup>

TABLE I. Calculated and observed energy-level splittings.

Levels	Expt. <sup>a</sup>	NI	Splittings (MHz)		
			PT1	PT(FK) <sup>b</sup>	PT2
13 <i>f</i> -13 <i>g</i>	3501.0(1.1)	3499.6	3499.5	3501.9	3500.2
14 <i>f</i> -14 <i>g</i>	2803.7(1.2)	2809.5	2809.5	2810.7	2809.9
15 <i>f</i> -15 <i>g</i>	2291.8(0.9)	2289.2	2289.2	2289.8	2289.4
16 <i>f</i> -16 <i>g</i>	1890.6(0.7)	1889.5	1889.6	1889.8	1889.8
17 <i>f</i> -17 <i>g</i>	1576.4(0.6)	1577.5	1577.6	1577.5	1577.8
13 <i>g</i> -13 <i>h</i>	802.7(2.9)	809.7	809.7	813.6	813.6
14 <i>g</i> -14 <i>h</i>	655.4(3.0)	650.9	650.9	654.1	654.1
15 <i>g</i> -15 <i>h</i>	534.7(2.3)	530.9	530.9	533.5	533.5
$\alpha'_d$		0.9965	0.9947	1.0015	1.0015
$\alpha'_Q$		0.376	0.633	0.48	0.48

<sup>a</sup>Derived from results in Refs. 2 and 3 by the method described in Ref. 4.

<sup>b</sup>Perturbation-theory results from Ref. 4. NI, PT1, and PT2 values were calculated in the present investigation. The values of  $\alpha'_d$  and  $\alpha'_Q$  used in each of the calculations are also given.

### B. Numerical integration calculations

In the work of Freeman and Kleppner, the fine-structure and relativity effects were subtracted from the experimental *f-g* and *g-h* splittings.<sup>2,3</sup> The effective dipole and quadrupole polarizabilities were then adjusted to fit calculated splittings to these derived experimental splittings. In the present investigation the derived experimental splittings were recalculated and found to be in disagreement with the derived experimental splittings that Freeman and Kleppner used. The discrepancy was most evident for the 13*g*-13*h* splitting. Therefore term values were determined by numerical integration (NI) of Schrödinger's equation and splittings were adjusted to fit the newly derived splittings given in Table I. The numerical integration procedure will be discussed in Sec. III.

Table I presents a comparison of experimental theoretical splittings. The theoretical splittings of Freeman and Kleppner [PT(FK)] are not explicitly given in their paper but can be calculated from other quantities which they report. To obtain these splittings, they adjusted  $\alpha'_d$  and  $\alpha'_Q$  to be 1.0015(15) and 0.48(15) a.u., respectively.<sup>4</sup> The NI values were determined by the numerical integration technique. These splittings were obtained by adjusting  $\alpha'_d$  and  $\alpha'_Q$  to be 0.9965(100) and 0.376(150) a.u., respectively.

### C. Perturbation-theory calculations

First-order perturbation theory (PT) was used for three sets of calculations in this investigation. In the first set (PT1) the effective polarizabilities were adjusted so that calculated splittings fitted the derived experimental splittings given in Table I.  $\alpha'_d$  and  $\alpha'_Q$  were found to be 0.9947 and 0.633 a.u., respectively, for this fit. These calculations were made so that perturbation-theory and NI polarizabilities could be compared. The PT(FK) polarizabilities are not as suitable for this comparison as are the PT1 polarizabilities since Freeman and Kleppner did not fit their calculations to the same derived splittings as were used for the NI calculations. The value of  $\alpha'_Q$  found from the PT1 calculations (0.633 a.u.) is significantly different from the value of  $\alpha'_Q$  found from the NI calculations

(0.376 a.u.).

In the second set of perturbation calculations, the Freeman and Kleppner effective polarizabilities (1.0015 and 0.48 a.u.) were used in the polarization potential given by Eq. (1). This produced the PT2 splittings given in Table I. It can be seen that there is close agreement between the PT2 and PT(FK) values. This agreement shows that the calculated results are independent of the magnitude of  $W_0$  used in Eq. (1). (In the PT2 calculations  $W_0=0.6$  a.u. and in the Freeman-Kleppner calculations  $W_0=0$ .)

In the third set of perturbation-theory calculations (PT3), the effective polarizabilities 0.9965 and 0.376 a.u. were used. In Table II, term values found in this way are compared to term values found by numerical integration of Schrödinger's equation. Since the same polarizabilities were used for the NI and PT3 calculations, the differences in the term values indicate the error which is introduced into the calculation by using first-order perturbation theory. For  $n=13-17$  and  $l=3$  this error ranges from 32.8 to 14.9 MHz, which is appreciably larger than the uncertainty in the experimental splittings.<sup>2,3</sup> In this table  $V_{\text{sum}}$  is the sum of the contributions of polarization ( $V_{\text{pol}}$ ) and penetration ( $V_{\text{pen}}$ ).

The PT1, PT2, and PT3 calculations yield the same values for  $V_{\text{pen}}$  since the penetration potential is the same for each. These  $V_{\text{pen}}$  values are listed in Table II and are in agreement with the perturbation calculations of Freeman and Kleppner<sup>4</sup> and Theodosiou.<sup>8</sup> However, Table II shows the NI values for  $V_{\text{pen}}$  to be larger than the perturbation-theory calculations by an amount ranging from about 6 to 3 MHz for  $n=13-17$  and  $l=3$ .

### D. The correction of polarizabilities for nonadiabatic effects

Freeman and Kleppner have used the theory of Eissa and Öpik<sup>5</sup> to correct their effect polarizabilities for nonadiabatic effects. The effective parameters determined from the NI and PT1 calculations were corrected in the same way. Table III gives the corrected results ( $\alpha_d$  and

TABLE II. Comparison of term values found by the numerical integration and perturbation methods.

Method <sup>a</sup>	<i>n</i>	<i>l</i>	<i>E</i>	<i>V</i> <sub>pol</sub>	<i>V</i> <sub>pen</sub>	<i>V</i> <sub>sum</sub>
NI	13	3	19 470 804.0	4745.7	35.6	4781.3
PT3	13	3	19 470 771.2	4684.0	29.4	4713.4
Diff.			32.8	61.7	6.2	67.9
NI	14	3	16 788 322.3	3812.7	28.9	3841.6
PT3	14	3	16 788 295.8	3763.1	23.8	3786.9
Diff.			26.5	49.6	5.1	54.7
NI	15	3	14 624 281.3	3108.4	23.7	3132.1
PT3	15	3	14 624 259.7	3067.9	19.6	3087.5
Diff.			21.6	40.5	4.1	44.6
NI	16	3	12 853 207.3	2567.0	19.7	2586.7
PT3	16	3	12 853 189.4	2533.5	16.2	2549.7
Diff.			17.9	33.5	3.5	37.0
NI	17	3	11 385 410.2	2144.1	16.5	2160.6
PT3	17	3	11 385 395.3	2116.1	13.6	2129.7
Diff.			14.9	28.0	2.9	30.9
NI	13	4	19 467 304.4	1247.9	0.115	1248.0
PT3	13	4	19 467 303.1	1245.3	0.109	1245.4
Diff.			1.3	2.6	0.006	2.6
NI	14	4	16 785 512.8	1004.8	0.094	1004.9
PT3	14	4	16 785 511.8	1002.8	0.089	1002.9
Diff.			1.0	2.0	0.005	2.0
NI	15	4	14 621 992.1	820.7	0.078	820.8
PT3	15	4	14 621 991.3	819.0	0.074	819.1
Diff.			0.8	1.7	0.004	1.7
NI	16	4	12 851 317.8	678.7	0.066	678.8
PT3	16	4	12 851 317.1	677.3	0.062	677.4
Diff.			0.7	1.4	0.004	1.4
NI	17	4	11 383 832.7	567.6	0.055	567.7
PT3	17	4	11 383 832.1	566.4	0.053	566.5
Diff.			0.6	1.2	0.002	1.2

<sup>a</sup> $\alpha'_d = 0.9965$  and  $\alpha'_Q = 0.376$  a.u. for both sets of calculations. The values of  $V_{pol}$  and  $V_{pen}$  are the contributions of polarization and penetration.  $V_{sum}$  is the sum of these contributions. The "Diff." values are the differences in the calculations. All energies are in MHz.

$\alpha_Q$ ) and compares them to polarizabilities determined from spectroscopic data<sup>9</sup> and *ab initio* theory.<sup>10,11</sup> There is fairly good agreement among the different values of  $\alpha_d$ . Freeman and Kleppner have pointed out the less satisfactory agreement between their value of  $\alpha_Q$  and the value of  $\alpha_Q$  found in Ref. 10. They attributed the discrepancy to the low reliability of the parameters in the theory they used to correct their effective polarizabilities for nonadiabatic effects. There is even less agreement between the value of  $\alpha_Q$  found from the PT1 fit and the values calcu-

lated in Refs. 10 and 11. However, the value of  $\alpha_Q$  found from the NI calculations agrees more closely with the results from Refs. 10 and 11 than do the results of perturbation calculations. This indicates that part of the discrepancy between the results of the perturbation calculations and the results of Refs. 10 and 11 should be attributed to the fact that first-order perturbation theory does not predict term values for states with  $l = 3$  to a degree of accuracy comparable to the accuracy of the experimental data.

TABLE III. Comparison of polarizabilities in sodium. The NI and PT1 results are from the present investigation and the PT(FK) results are from Ref.4. The value from Ref. 9 was derived from spectroscopic data and those from Refs. 10 and 11 are calculations made *ab initio*.

	NI	PT1	PT(FK)	Ref. 9	Ref. 10	Ref. 11
$\alpha_d$	0.993	0.991	0.998	0.978	0.9459	0.9457
$\alpha_Q$	1.84	2.11	1.91		1.53	1.521

### III. COMMENTS ON THE NUMERICAL INTEGRATIONS

All calculations for this investigation were carried out in double precision on an IBM 4341 computer. Two methods of numerical integration were used and they produced term values that agreed to one-tenth of a MHz. The first was the Runge-Kutta method.<sup>12</sup> For these integrations the radial wave equation for the eigenfunction  $R(r)$  was first transformed with the equation

$$R(r) = r^{l-1}w(r). \quad (2)$$

This transformation produced the following differential equation:

$$w'' = 2l \left[ \frac{w}{r^2} - \frac{w'}{r} \right] + 2[E + V(r)]w, \quad (3)$$

where  $w = w(r)$  is the function which was determined by numerical integration. The function  $V(r)$  includes the Coulombic, penetration, and polarization potentials. From the work of Fano and Theodosiou<sup>13</sup> it follows that the starting values (at  $r=0$ ) for the numerical integration are  $w=0$ ,  $w'=1$ , and  $w'' = -2Z/(l+1)$ . The second set of numerical integrations was carried out by the Numerov method.<sup>14-16</sup>

Even though the results were essentially the same for both the Runge-Kutta and Numerov methods, the Runge-Kutta calculations proved to be more efficient. For both procedures the dependence of calculated term values on the radial step size was investigated. For the Runge-Kutta method, step sizes less than 0.1 a.u. all produced the same term values. For the Numerov method it was found that radial step sizes of 0.04, 0.02, and 0.01 a.u. all produced different term values. Fortunately in this case a linear relationship was found to exist between the

step size and the calculated term value. It was therefore possible to make extrapolations to find term values that would occur at zero step size. The extrapolated Numerov values were always equal to the values determined by the Runge-Kutta method. It may be that the Runge-Kutta calculations were made more efficient through the use of the transformation given in Eq. (2). This transformation cannot be used in conjunction with the Numerov method since it leaves a first derivative term in Schrödinger's equation. For the Numerov method to be used, such a term must be eliminated by a different transformation.

A test of the Runge-Kutta method was made by using it to calculate energy levels in hydrogen with  $n=13-17$  and  $l=3, 4$ , and 5. Energies calculated in this way were found to agree to within one-tenth of a MHz with the known energy levels in hydrogen.

### IV. SUMMARY

It has been shown that the NI calculations yield a value for  $\alpha_0$  which is in better agreement with the *ab initio* results given in Refs. 10 and 11 than is the value determined by perturbation theory. This investigation also indicates that first-order perturbation theory cannot describe  $l=3$  states in sodium with a degree of accuracy comparable to the accuracy of experimental data.

### ACKNOWLEDGMENTS

I would like to thank Dr. Deborah K. Watson, Department of Physics and Astronomy, The University of Oklahoma, for reading and making helpful comments on the manuscript of this paper. I would also like to thank Dr. Grady D. Carney, Department of Chemistry, New York Institute of Technology, for his assistance with the manuscript and the Numerov calculations.

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