Brief Reports

Determination of core polarizabilities, quantum defects, and fine structure in sodium

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In this investigation, term values in sodium are found by numerical integration of Schrödinger's wave equation. Effective core polarizabilities are determined by fitting calculations to experimental data. The fit includes quantum defects in low-angular-momentum states which were not previously used. When penetration and exchange are taken into account and the effective dipole and quadrupole polarizabilities are corrected for nonadiabatic effects, the dipole and quadrupole polarizabilities are found to be 0.998(100) and 1.36(40) a.u., respectively. Quantum defects and fine structure are also calculated for states not included in the initial fit and are found to be in good agreement with experimental results.

I. INTRODUCTION

Polarization and penetration of the core electrons in the sodium atom by the valence electron cause the splitting of Rydberg states that have the same principal quantum number n but different angular momentum quantum number l. The d-f, d-g, and d-h splittings have been experimentally determined in the region $11 \leq n \leq 17$ by Gallagher, Hill, and Edelstein[1,2] and used to theoretically determine the effective dipole and quadrupole polarizabilities in singly ionized sodium.[3,4] In those calculations the two polarizabilities were adjusted to fit splittings between states with $l > 2$. Recently, a two-parameter polarization formula was used to fit term values in the neutral nitrogen atom.[5] Here too the formula was fitted to data corresponding to states with $l > 2$.

In the present investigation, it was found that the two effective polarizabilities and the theory of Ref. 4 produced quantum defects in $l = 0$, 1, and 2 states which did not match the experimental sodium quantum defects.[6,7] One purpose of the present investigation was to achieve a fit to both high- and low-angular-momentum states in sodium, by modifying the polarization potential to include four parameters. These parameters were adjusted so that calculated term values produced not only the experimental splittings of Gallagher *et al.*[1,2] but also the measured quantum defects[2,7] in the two regions $l = 2$, $n = 13$–17, and $l = 1$, $n = 31$–33. Another purpose was to calculate fine structure and quantum defects in both high- and low-angular-momentum states in sodium and to compare these results with experimental values.[6,8] The present investigation is an extension of the work reported in Ref. 4

and that paper details the method used for determining term values by numerical integration of Schrödinger's wave equation.

II. DISCUSSION AND RESULTS

A. The Hamiltonian

The Hamiltonian for the present investigation is the same as that used in Ref. 4, except for the polarization potential V_{pol}. Actually, three different polarization potentials were used and the results of all three potential functions will be compared in Sec. III.

The first polarization potential function included an octupole term. This function has the form

$$V_{pol} = -\tfrac{1}{2}\alpha'_d (1/r^4)[1 - e^{-(r/W_0)^s}]$$
$$-\tfrac{1}{2}\alpha'_Q (1/r^6)[1 - e^{-(r/W_0)^t}]$$
$$-\tfrac{1}{2}\alpha'_o (1/r^8)[1 - e^{-(r/W_0)^u}], \qquad (1)$$

where α'_d, α'_Q, and α'_o are the effective dipole, quadrupole, and octupole polarizabilities of the sodium ion. The terms in the square brackets are cutoff factors which are similar to those used by Dalgarno *et al.*[9] and Bottcher.[10] As in Ref. 4, the effect of penetration was calculated by using Hartree wave functions[11] for the core electrons. Two sets of calculations were made. In one set of calculations (I), the powers of r/W_0 in the cutoff factors (s, t, and u) were taken to be 6, 8, and 10 and in another set (II) they were taken to be 4, 6, and 8, respectively. In

both cases the slope of V_{pol} is zero at $r = 0$. In the first case, V_{pol} is zero at $r = 0$, which is desirable if V_{pol} is to be used to simulate just the effect of polarization. In the second case, V_{pol} is not zero near $r = 0$, and it can be used to simulate exchange inside the electron core, and polarization for larger values of r. For II, the strength of the exchange effect is determined by the value of W_0. The smaller the value of W_0, the larger the value of V_{pol} inside the core.

The second polarization potential used in this investigation was the same as Eq. (1), except that the octupole term was replaced by the following term:

$$-\tfrac{1}{2}\alpha_7'(1/r^7)[1-e^{-(r/W_0)^\mu}] \, , \tag{2}$$

where α_7' is an adjustable parameter.

The third polarization potential only included the dipole and quadrupole terms. In this case the parameter W_0 was replaced by two parameters, one in each of the two cutoff factors, and these parameters were varied independently. In this way four parameters were varied just as in the other two potential functions.

B. Relativity corrections

Quantum defects were determined from calculated term values which were first corrected for relativity using the Pauli approximation.[12] In this approximation, the wave functions which were generated numerically were used to calculate two integrals, W_a and W_b, by first-order perturbation theory. W_a is the standard correction for relativity. W_b can be considered in two parts: the fine-structure correction due to the spin-orbit interaction and a special spin correction which is zero in hydrogen except when $l = 0$. For sodium this correction is not zero even for states with $l > 0$ because of the effect of the core electrons. However, it was found to be negligible for states with $l > 1$.

C. Determination of parameters using Eq. (1)

The parameters α_d', α_Q', α_o', and W_0 in Eq. (1) were adjusted to obtain good fits to the experimental splittings[1,2] and quantum defects.[2,7] The fits I and II to the splittings were about the same as those found in Ref. 4, and models I and II both produced good fits to the experimental quantum defects. However, as will be discussed in Sec. II D, model II was used to make accurate calculations of fine structure in sodium, whereas the model I was unsuccessful in this regard. Therefore model II was found to be the better of the two models. Table I compares fit II and the experimental quantum defects. Table II gives the best-fit parameters for both fits. The uncertainties in the II parameters were found by varying the parameters and finding the ranges over which reasonably good fits to the data were still obtained.

D. Comparison of experimental and theoretical quantum defects and fine structure

Risberg[6] has measured quantum defects and fine structure in sodium for relatively low values of n. Quantum

TABLE I. Observed and calculated quantum defects. Numbers in parentheses denote uncertainties in the last figure of each value.

Levels	Quantum defects	
	Expt.	Calc. (II)
$31p$	0.855 00(4)[a]	0.855 014
$32p$	0.855 00(4)[a]	0.855 006
$33p$	0.854 98(4)[a]	0.855 000
$13d$	0.014 653(5)[b]	0.014 654
$14d$	0.014 688(5)[b]	0.014 690
$15d$	0.014 719(6)[b]	0.014 719
$16d$	0.014 751(6)[b]	0.014 743
$17d$	0.014 759(7)[b]	0.014 762

[a]Experimental quantum defects from Ref. 7.
[b]Experimental quantum defects from Ref. 2.

defects and fine structure were calculated using the polarization potential expressed in Eq. (1). Calculations were made without exchange (I) and with exchange (II) and compared to the Risberg data. The previously determined best-fit parameters were used, and relativistic and fine-structure corrections were found using the Pauli approximation[12] as described above.

The comparison between the calculated results for model II and the Risberg data is given in Table III for $l = 1$ and 2. This table also includes calculations of fine-structure and quantum defects in states for which there are no data reported by Risberg. Even though the parameters were found by fitting data corresponding to states with $n > 12$, there is still a very good match between the experimental and theoretical quantum defects for states with lower values of n. (The quality of fits I and II to the quantum defects was the same.) The experimental quantum defects show an appreciable variation with n for low-energy states. Even this variation is closely reproduced in the theory. Good agreement between the experimental and theoretical quantum defects was also found for $l = 3$ states. For $l = 0$ states, the theoretical results were 1% higher than the experimental results.

The model II spin-orbit splittings for $l = 1$ states are in better agreement with the Risberg data than are the results of other theoretical investigations.[13,14] On the other hand, the model-I spin-orbit splittings for these states were found to be about 33% too small. This discrepancy is attributed to the fact that the effect of exchange was not accounted for in the model-I calculations.

The experimental results reveal an anomalous doublet inversion for the $l = 2$ states. Previous investigations have shown that the inversion can be reproduced by using many-body theory[13] or configuration mixing.[15,16] No at-

TABLE II. Parameters found in this investigation. Values are in atomic units.

	I	II
α_d'	0.9992	1.0022 $\pm$ 0.007
α_Q'	0.1927	-0.0928 ± 0.2
α_o'	0.9923	3.2318 $\pm$ 0.5
W_0	0.8339	1.0648 $\pm$ 0.008

TABLE III.   Observed and calculated fine-structure and quantum defects.

| Level | ΔT (cm^{-1}) | | Quantum defects | |
	Expt.[a]	Calc. (II)	Expt.[a]	Calc. (II)[b]
3p	17.196	16.735	0.8829	0.8819
4p	5.59	5.448	0.8669	0.8664
5p	2.47	2.409	0.8616	0.8613
6p	1.29	1.268	0.8592	0.8590
7p	0.75	0.747	0.8579	0.8578
8p	0.48	0.476	0.8571	0.8570
9p		0.322		0.8565
10p		0.228		0.8562
11p		0.167		0.8559
12p		0.126		0.8558
13p		0.097		0.8556
14p		0.077		0.8555
15p		0.062		0.8554
3d	−0.050	0.051	0.0103	0.0102
4d	−0.035	0.024	0.0123	0.0122
5d	−0.020	0.013	0.0132	0.0132
6d	−0.013	0.0076	0.0137	0.0137
7d		0.0049	0.0141	0.0140
8d		0.0033	0.0143	0.0142
9d		0.0023	0.0145	0.0144
10d		0.0017	0.0148	0.1045
11d		0.0013	0.150	0.0146

[a]The experimental values are from Ref. 6. The quantum defects are the weighted averages of the quantum defects of states which are split by the spin-orbit effect or the quantum defects of the unresolved states.
[b]The calculated quantum defects correspond to the center of gravity of the two separate term values that result from spin-orbit splitting

tempt has been made in this investigation to account for the inversion and Table III reveals the poor agreement between the $l=2$ experimental and theoretical results. However, these theoretical results are in good agreement with the first-order Hartree-Fock calculations in Ref. 13.

Calculations with exchange (II) were also made of quantum defects and fine structure in $l=1$ states in the region $23 \leq n \leq 36$ and the results were compared to the experimental results of Fabre et al.[8] It is not surprising that the experimental and theoretical quantum defects are in good agreement, since the polarization parameters were

TABLE IV.   Observed and calculated fine structure in p states of sodium. Values are given in MHz.

n	Expt.[a]	Calc. (II)
23	495	483
24	433	423
25	380	373
32	176	174
33	162	158
34	147	144
35	135	132
36	124	121

[a]Reference 8.

TABLE V.   Comparison of calculated polarizabilities for models I and II with ab initio results. Values are in atomic units. Numbers in parentheses denote uncertainties in the last figures of each value.

	I	II	Ref. 18	Ref. 19
α_d	0.995	0.998(100)	0.9459	0.9457
α_Q	1.66	1.36(40)	1.53	1.521

previously adjusted so that the theory would fit experimental quantum defects in this region. However, there is also excellent agreement between the experimental and theoretical fine structure as can be seen in Table IV. This agreement further indicates the ability of the present method of analysis to successfully calculate fine structure in sodium

E. Correction of polarizabilities for nonadiabatic effects

The theory of Eissa and Öpik[17] was used to correct the effective polarizabilities α_d' and α_Q' for nonadiabatic effects. Table V compares the corrected polarizabilities (α_d and α_Q) to polarizabilities determined in ab initio calculations.[18,19] The calculations made without exchange (I) and with exchange (II) both yield quadrupole polarizabilities which are within uncertainties of the ab initio results. The uncertainties in the model-II polarizabilities were determined from estimated uncertainties in the parameters of the Eissa and Öpik theory and the uncertainties in the parameters listed in Table II.

III. COMPARISON OF FITS OBTAINED WITH VARIOUS POLARIZATION POTENTIALS

Fits were also made with a polarization potential that had the octupole term of Eq. (1) replaced by the term given in expression (2). These fits were just as good as the fits made when the octupole term was used. However, with this modification the quadrupole polarizability after correction for nonadiabatic effects was found to be 0.73 a.u. This value does not agree as well with the ab initio results[18,19] as does the result found when the octupole term is used.

In another attempt to fit the data, a polarization potential was used which only included the dipole and quadrupole terms and which had W_0 replaced by two parameters, one in each of the cutoff factors. The four parameters were varied over wide ranges and no set of parameters was found to fit all the data very well. In this case, many sets of parameters resulted in good fits to the splittings and the $l=1$ quantum defects. But best-fit parameters always produced $l=2$ quantum defects which were less than the experimental quantum defects by approximately 10%. This agreement is not good as the agreement found with the other two potentials.

IV. SUMMARY

In previous investigations,[3,4] V_{pol} included two adjustable parameters. In the present investigation, the polarization potential was modified in three different ways to

include two additional parameters so that $l = 1$ and 2 quantum defects could also be fitted. The potential which included an octupole term proved to be more satisfactory than the other two potentials. It produced a quadrupole polarizability which agreed better with the *ab initio* results than did the polarization potential which included the α_7' term. It also fitted experimental data better than the polarization potential which included the dipole and quadru-

pole terms and a different W_0 parameter for each of the polarization potential terms. There may be other models which could do as well as the ones reported in this investigation but no others were tried.

After the parameters were determined, the model was used to calculate fine structure and quantum defects in states not initially included in the fit. These results show good agreement with experimental results.

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