

On the dipole polarizabilities of alkali atoms

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The wave functions calculated for alkali atoms based on a pseudopotential model have been used to calculate polarizabilities of the alkali atoms in their ground states. Our calculated polarizabilities are higher than those obtained in earlier experiments. However, recent improved measurements are in fairly good agreement with our calculations. The recent measurements are also supported by experimental results on oscillator strengths. The versatility of the pseudopotential model is thus illustrated.

1. INTRODUCTION

A pseudopotential model (Rapp & Ward 1971, McMillan 1971, Rapp & Chang 1972, 1973) of alkali atoms has been used to determine approximate one-electron wave functions for various electronic states of alkali atoms for use in scattering calculations (McMillan 1971, Chang & Rapp 1973, Rapp & Chang 1973). The one adjustable parameter in this method is the scale factor for the exponential inner core, and this is selected for each atom to obtain the correct energy for the ground state. The energies calculated for the various excited states are then in good agreement with experiment. Since the energies of electronic states are not necessarily a good test of the accuracy of a wave function, we decided to apply our wave functions to calculate polarizabilities of the alkali atoms. Polarizabilities are known to be more sensitive to the forms of the wave functions used (Sternheimer 1954, 1962). Experimental values of the polarizabilities are available for comparison (Chamberlain & Zorn 1963, Salop *et al* 1961, Molof *et al* 1973). Other calculations are also available based on different approaches (Sternheimer 1954, Dalgarno & Kingston 1959, Parkinson 1960, Sundbom 1958). The other theories can be divided between those that make a model for the wave functions and proceed to calculate appropriate quantum mechanical integrals (Sternheimer 1954, Parkinson 1960, Sundbom 1958), and semi-empirical treatments which make use of experimental data on oscillator strengths (Dalgarno & Kingston 1959). In the present work, we calculate essentially exact polarizabilities within the framework of the one-electron pseudopotential model.

2. PSEUDOPOTENTIAL MODEL AND ALKALI WAVE FUNCTIONS

The pseudopotential we use has been described previously (McMillan 1971, Rapp & Chang 1972).

A single outer electron is assumed to move in the potential

$$\hat{V}(r) = -\frac{1}{r} \left\{ 1 + (Z-1)\exp(-r/A) \left(1 + \frac{r}{2A} \right) \right\}, \quad \dots \quad (1)$$

where Z is the nuclear charge, and the parameter A is adjusted to give the correct energy of the ground state of each atom. The values of A for Li, Na, K, Rb and Cs are given in table 1.

The energies calculated for excited states are also summarized in table 1. The experimental energies of states involving fine structure splitting are the lowest of each multiplet. It can be seen that the energies agree best for the lighter alkalis, and in general the states of higher angular momentum are best represented by the pseudopotential model because there is relatively little penetration of the core by the valence electron. In fact, for the $3d$ state, the wave functions for Li and Na lie so completely outside the inner core that they are very nearly hydrogenic. Tabulated wave functions were obtained by numerical integration of the Schrodinger equation for the potential $V(r)$. Starting functions were obtained near $r \cong 0$ for this integration by noting that near the origin the wave function becomes hydrogenic with nuclear charge Z . A predictor-corrector method was used to integrate the Schrodinger equation for the potential $V(r)$. Analytical functions were fitted to the tabulated numerical functions to facilitate evaluation of integrals involving these functions. These functions were of the form

$$\psi_{nlm}(r, \theta, \phi) = \frac{u_{nl}}{r}(r) Y_l^m(\theta, \phi), \quad \dots \quad (2)$$

where the Y_l^m are spherical harmonics, and the radial functions $u_{nl}(r)$ were put in the form

$$u_{nl}(r) = N r^{a+1} (r-r_1)^b (r-r_2)^c (r-r_3)^d (r-r_4)^e (r-r_5)^f \sum_{j=1}^4 G_j \exp(-p_j r), \quad \dots \quad (3)$$

with $G_1 = 1$. The values of the constants for the various states are given in table 2.

3. CALCULATION OF POLARIZABILITIES

The calculation of polarizabilities has been clearly described by Sternheimer (1954, 1962). The wave equation for a one electron atom in an external electric field ξ is

$$(-\frac{1}{2}\nabla^2 + V(r) - E)\psi = \xi r \cos \theta \psi. \quad \dots \quad (4)$$

By writing $\psi = \psi_0 + \phi$ and $E = W + \epsilon$, where ψ_0 satisfies the unperturbed equation

$$(-\frac{1}{2}\nabla^2 + V(r) - W)\psi_0 = 0, \quad \dots \quad (5)$$

Table 2. Constants in the wave functions given in eq. (3)

Table 2. Constants in the wave function ψ

State	a	b	c	d	e	f	r_1	r_2	r_3	r_4	r_5	N	P_1	G_2	P_2	G_3	P_3	G_4	μ_4	
Lithium																				
2S	0	1	0	0	0	0	0.87					0.67193	0.713	1.603	2.051					
2P	1	0	0	0	0	0						0.21922	0.518	0.834	1.750					
2S	0	1	1	0	0	0	4.65	0.92				0.056376	0.433	2.898	1.368					
3P	1	1	0	0	0	0	5.71					0.022354	0.345	0.760	1.343					
3D	2	0	0	0	0	0						0.009016	0.333							
4S	0	1	1	1	0	0	0.83	4.35	11.7			0.002325	0.301	2.441	0.799					
Sodium																				
3S	0	1	0	0	0	0	0.96					0.70224	0.710	*	3.60					
3P	1	0	0	0	0	0						0.14874	0.440	-25.4	3.80					
3D	2	0	0	0	0	0						0.009079	0.334							
Potassium																				
4S	0	1	1	1	0	0	0.10	0.40	1.34			0.046020	0.817	26.27	1.672	1.08E03	4.90			
4P	1	1	1	0	0	0	0.34	1.43				0.018767	0.659	17.50	1.398	1.18E03	4.85			
Rubidium																				
5S	0	1	1	1	1	0	0.05	0.19	0.48	1.40		0.0056367	0.837	14.40	1.304	2.42E02	2.16	7.01E04	6.71	
5P	1	1	1	1	0	0	0.16	0.45	1.58			0.0024362	0.677	48.41	1.345	7.34E04	6.44			
Cesium																				
6S	0	1	1	1	1	1	0.03	0.12	0.28	0.60	1.60	0.00082772	0.856	64.24	1.443	3.18E03	2.71	1.76E06	7.52	
6P	1	1	1	1	1	0	0.10	0.26	0.58	1.80		0.00039073	0.723	62.98	1.312	2.73E03	2.56	2.44E06	7.71	

* insert: -14.0 (0.340-r).

with W the unperturbed energy, we obtain (after neglecting second order terms) the equation

$$(-\frac{1}{2}\nabla^2 + V(r) - W)\phi \cong \xi r \cos \theta \psi_0 \quad \dots (6)$$

This equation can be solved for ϕ by substituting

$$\phi = \xi \frac{f(r)}{r} \cos \theta, \quad \dots (7)$$

eq. (6) then becomes

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{1}{r^2} + V(r) - W \right] f(r) = r^2 \psi_0. \quad \dots (8)$$

Eq. (7) can be solved by numerical integration noting that ψ_0 and W correspond to the ground s -state of the alkali, and that $f(r)$ is proportional to r times a p -radial function of that atom near the origin (Sterhneiner 1954, 1962). The polarizability may then be calculated from the integral

$$\alpha = \frac{D}{\xi} = \frac{8\pi}{3} \int_0^\infty \psi_0 f(r) r^2 dr. \quad \dots (9)$$

As Dalgarno & Lewis (1955) have shown, this procedure is equivalent to the second-order perturbation theory result:

$$\alpha = 2 \sum_n \frac{\langle s | r \cos \theta | np \rangle^2}{W_s - W_{np}} \quad \dots (10)$$

provided the sum is taken over all p states including the continuum, and $\langle s |$ represents the ground s -state. Use of Eq. (10) with only the first p -state included in the sum

$$\alpha \cong \frac{\langle s | r \cos \theta | p \rangle^2}{W_s - W_p}$$

will always be an underestimate. One further problem is the polarization of the core produced by the dipole between the nucleus and the valence electron. Sternheimer (1954, 1962) has shown that the correction of the polarizability of the atom due to the core is

$$\alpha_{core} = (1 - \xi_{val}) \alpha_{ion}, \quad \dots (12)$$

where α_{ion} is the polarizability of the ion core, and ξ_{val} is a measure of the electric field at the core produced by the dipole valence electron, and is given by

$$\xi_{val} = \frac{8\pi}{3} \int_0^\infty \psi_0 f(r) \frac{dr}{r} \quad \dots (13)$$

Sternheimer (1954, 1962) has calculated ξ_{val} , and estimated α_{core} by using the experimental values of α_{ion} . He multiplied his ξ_{val} by a core penetration factor less than unity. Since we do not understand his reasoning on this point, we have simply omitted this factor. Thus, our corrections for the polarization of the core are given by eq. (12).

4. RESULTS

After numerical integration of eq. (8) for each substance, the resulting numerical functions $f(r)$ were fitted by analytical functions as tabulated in table 3. For hydrogen, $f(r)$ agreed with the known exact solution of eq. (8). Upon analytic integration of eq. (9), the polarizabilities were calculated. The results are given in the first row of table 4. The core corrections due to Sternheimer are given in table 5. After correction for the core, the calculated exact polarizabilities for our one-electron model are as given in the second row of table 4. We believe that these are the accurate polarizabilities predicted by our one-electron model. The results are quite close to those of Sternheimer (1954, 1962) who used valence wave functions which are similar in many respects to those we employed. Our results slightly exceed the experimental values (Molof *et al* 1973), the errors being generally in the range 5 to 7%. As Sternheimer (1954, 1962) has discussed, exchange interactions with the core probability produce an effective outer valence electron which is drawn in slightly. Only a small change in the size of the ground state wave function will produce a relatively large change in the calculated polarizability.

Dalgarno & Kingston (1959) performed a calculation of polarizabilities based on eq. (11) as an approximation. Noting that the integral in eq. (11) is the same as that which appears in oscillator strengths, they used the spectroscopically determined oscillator strengths in eq. (11) to estimate the polarizabilities. Using the definition of oscillator strength

$$f_{sp} = 2(W_s - W_p) \langle s | r \cos \theta | p \rangle^2, \quad \dots (14)$$

it follows that

$$\alpha = f_{sp} / (W_s - W_p)^2, \quad \dots (15)$$

in the approximation of eq. (11). There is a question as to what values of W_p to use in eq. (15) since the p -state is split by the spin-orbit interaction. We used energy values $2/3 W_{3/2} + 1/3 W_{1/2}$ where the subscript on W denotes the total angular momentum, and $2/3$ and $1/3$ are the respective relative multiplicities. Then using the experimental values of f_{sp} given in table 6, we calculate the polarizabilities given in row 8 of table 4. These values are slightly different from those given by Dalgarno & Kingston due to our choice of p -state energies. It can be seen that there is good agreement of these values with the older experiments.

However, when compared with Molof *et al* (1973), these predictions are too low. An approximate theory based on the leading term in a perturbation series will of course tend to be low. An illustration of this is provided by the use of our one-electron functions to calculate f_{sp} and α by perturbation theory. We find the f_{sp} values given in table 6. Converting to polarizability via eq. (15), we obtain rows 3 and 4. in table 4. It can be seen that our calculated values of oscillator strength and polarizability are in good agreement with those of Dalgarno &

Table 3. The functions $f(R)$ obtained by numerical integration

Atom	$f(R)$	$\alpha(\text{\AA}^3)$
H	$(R^3 + R^2)e^{-R}$.6669
Li	$9.30086(0.3919R + R^2 + 0.1922R^3)(e^{-0.585R})$	24.63
Na	$1.854R(R-.985)(R+7.363)(e^{-0.576R} + 1.954e^{-1.07R})$	24.91
K	$9.6313.R.(R-.343)(R-1.442)(e^{-0.600R} + 18.746e^{-1.93R})$	49.56
Rb	$1.62863R(R-.158)(R-.452)(R-1.602)(e^{-0.635R} + 10.42e^{-1.19R} + 1018e^{-3.85R})$	54.01
Cs	$.66902.R.(R-.101)(R-.263)(R-.581)(R-1.83)(e^{-0.739R} + 33.54e^{-1.49R} + 19228e^{-3.31R})$	70.63

Table 4. Polarizabilities of alkali atoms (\AA^3)

Row	Method	Li	Na	K	Rb	Cs
1	This calc. (exact) (uncorrected)	24.6	24.9	49.6	54.0	70.7
2	Exact-corrected for core	24.6	24.5	47.3	50.2	62.6
3	1 term pert. (uncorrected)	24.5	22.6	44.3	48.4	61.7
4	1 term pert. corrected for core	24.5	22.3	42.0	44.6	53.7
5	Salp <i>et al</i> (1961)	20 ± 3	20.0 ± 2.5	36.5 ± 4.5	40 ± 5	52.5 ± 6.5
6	Chamberlain & Zorn (1963)	22 ± 2	21.5 ± 2	38 ± 4	38 ± 4	48 ± 6
7	Sternheimer (1954, 1962)	24.9	22.9	44.4	49.1	67.7
8	Dalgarno & Kingston (1959)	24.1	24.3	41.7	44.0	52.5
9	Molof (1973)	—	23.6 ± 0.8	43.7 ± 1.3	47.5 ± 1.5	59.6 ± 1.2

Table 5. Corrections to polarizability using core polarization by outer electron—Steinheimer (1954, 1962) (\AA^3)

	Li	Na	K	Rb	Cs
ξ	2.57	2.66	3.27	3.39	3.85
α_{ion}	0.03	0.22	1.0	1.6	2.8
correction = $(1-\xi)\alpha_{ion}$	-0.047	-0.365	-2.27	-3.82	-7.98

Table 6. Oscillator strengths for the resonance transition in alkalis (atomic units)

Substance	(f_{sp}) expt.	f_{cale}	f_{cale} with core correction
Li	0.75	0.762	0.76
Na	0.98	0.913	0.90
K	0.99	1.051	1.003
Rb	1.00	1.101	1.023
Cs	0.98	1.153	1.004

Kingston (1959) provided that we make the core correction*. However, a comparison of rows 2 and 4 of table 4 shows that the secondary terms in eq. (10) are not negligible and the approximation of eq. (11) becomes progressively worse for higher alkalis. Had Dalgarno & Kingston (1959) included higher terms in eq. (10), they would have been led to higher polarizabilities also.

It is worthwhile noting that there is a conflict between the experimental values of the oscillator strengths and the older experimental polarizabilities. Using eq. (10) expressed in terms of oscillator strength

$$\alpha = 2 \sum_n (W_s - W_{np})^{-2} f_{s,np} \quad \dots (16)$$

$$f_{s,np} = 2(W_s - W_{np}) < s | r \cos \theta | np >^2, \quad \dots (17)$$

we find that the experimental values of the resonance transition oscillator strengths (first term in series of eq. (16)) is large enough to produce an α in good agreement with the experimental data of Chamberlain (1963) and Salop *et al* (1961). If higher terms in eq. (16) are non-negligible (as we calculate them to be), then there is a fundamental conflict between experimental oscillator strength and the old polarizability data, the polarizabilities being too low. The new data of Molof *et al* (1973) on polarizabilities are in reasonable conformity with the experimental oscillator strengths.

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* The core correction was made to f_{sp} by assuming that the ratio of the corrected f_{sp} to the uncorrected f_{sp} is the same as the ratio of corrected to uncorrected polarizability.

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