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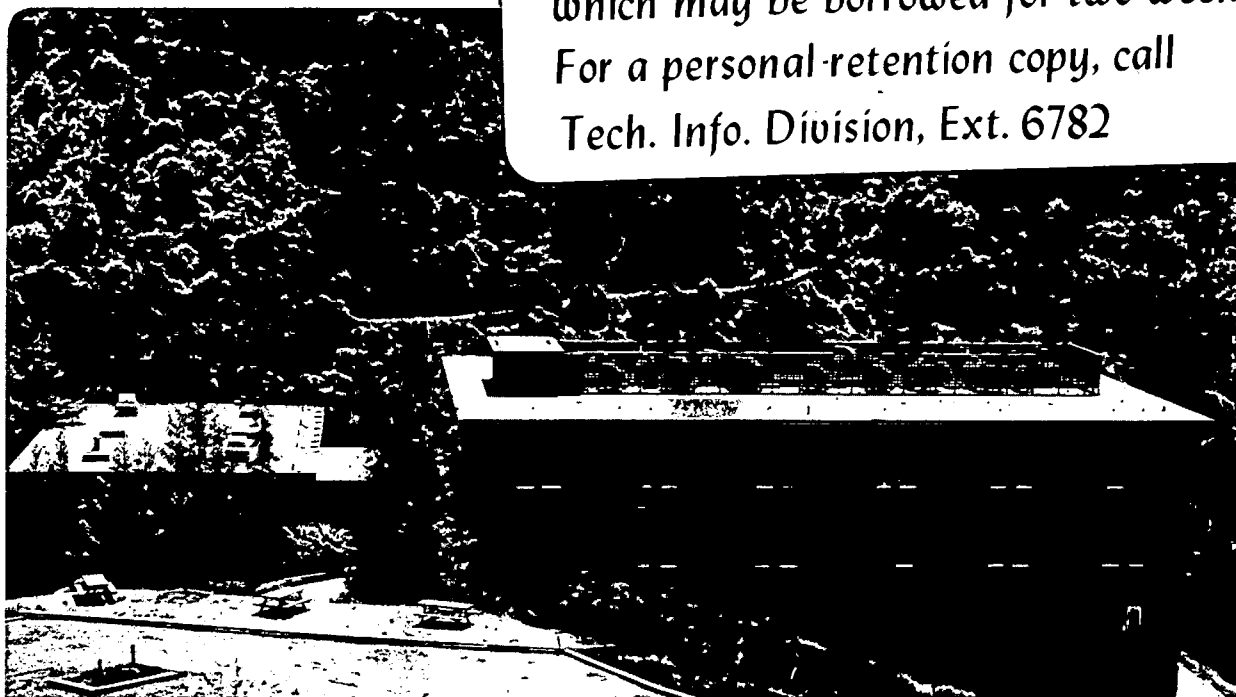## UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RELIABLE STATIC ELECTRIC DIPOLE POLARIZABILITIES
FOR HEAVY ELEMENTS

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Reliable Static Electric Dipole Polarizabilities

For Heavy Elements

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Abstract

The static electric dipole polariz-
abilities for Rb and Cs were obtained from
finite-field SCF and CI calculations using
relativistic effective potentials developed
by Christiansen and co-workers. Our re-
sults agree with the experimental values
of Molof and co-workers to within about 5%.
By contrast, calculations using Phillips-
Kleinman type potentials for Cs were
seriously in error.

Introduction

Reasonably accurate static electric dipole polarizabilities are available for the lighter elements. But with the exception of the alkali metals and the rare gases, this is not generally the case for the heavier atoms. Experimentally this is due in large measure to difficulties in obtaining well·behaved atomic gas samples. Computationally, for the heavier elements there are simply too many electrons to make rigorous all-electron calculations possible. Miller and Bederson [1] have recently published an extensive review of the problems, both experimental and theoretical.

In view of the utility of polarizabilities in explaining and predicting a large variety of atomic and molecular collision phenomena, a straight forward method for obtaining reliable values could prove quite useful. Meyer and co-workers [2,3] have demonstrated the effectiveness of _ab initio_ electronic structure calculations in predicting polarizabilities for the lighter atoms. In the following sections we will show that the recent development of reliable effective core potentials may make such techniques applicable to the heavier elements. Konowalow and co-workers [4,5] have already used Phillips-Kleinman type effective potentials to compute the polarizabilities of Zn, Cd, and Hg. Unfortunately it is difficult to gauge the reliability of these calculations due to the absence of accurate experimental values. Furthermore, effective potentials of the Phillips-Kleinman type, when used in molecular calculations, frequently give anomalously short bond lengths and large dissociation energies which have been attributed to the behavior of the

potentials in the tail region[6]. As pointed out in the
past [7] these problems have their origin in the choice of
pseudoorbitals used to define the potentials. The Phillips-
Kleinman pseudoorbitals underestimate the Hartree-Fock elec-
tron density in the tail region by as much as 10 to 30 percent.
Due to the terribly diffuse nature of the distortion of the
electron charge distribution in a weak field [8], one may be
skeptical of the use of Phillips-Kleinman type effective
potentials for polarizability calculations.

In the present work the recently developed "shape-consistent"
relativistic effective potentials of Christiansen and co-workers
[7] have been used to compute the polarizabilities of Rb and Cs
at both the SCF and CI levels using a finite field formalism.
These values are compared with the accurate experimental values
of Molof et al.[9]. In addition, for comparison we have computed
the SCF polarizability for Cs using a Phillips-Kleinman type
relativistic effective potential.

Calculations and Results

Eight-electron relativistic effective potentials were gen-
erated from Rb^+ and Cs^+ atomic Dirac-Fock wavefunctions [10].
The important details are given in references 7 and 11 and will
not be repeated here. The s and $p_{1/2}$ and $p_{3/2}$ potentials were
obtained from the ground state ions. The $d_{3/2}$, $d_{5/2}$, $f_{5/2}$ and
$f_{7/2}$ potentials were obtained from atomic wavefunctions in which
a single $p_{3/2}$ electron was promoted into the appropriate d or f
type spinors. These relativistic effective potentials (REP)
were then used in nine-electron neutral Rb and Cs calculations.

Basis sets were obtained by first optimizing (using LS coupling) double-zeta (4s, 2p) STO sets of functions for the ground state atoms. These basis sets were then augmented by adding single diffuse s functions whose exponents were related to the next higher values by factors of roughly $3^{-1/2}$. Then three diffuse p type functions were added with exponents corresponding roughly to the three lowest s exponents. Finally two diffuse d functions were added. The complete basis sets for both Rb and Cs are given in Table I.

The external electric field used in these calculations was obtained by placing an additional point charge on the z axis at a considerable distance from the nucleus. A typical field was 0.002 in atomic units. The change in electronic energy due to the field was then assumed to follow the relation

$$\Delta E = \frac{1}{2} \alpha F^2 \qquad (1)$$

where α is the polarizability and F is the external field. The magnitude and position of the external charge was then varied over wide ranges to ensure that the higher corrections due to the field and field derivatives were negligible.

The polarizabilities were computed from equation (1) by carrying out fully relativistic (including spin-orbit coupling) SCF calculations using the above basis sets and effective potentials, with and without the external fields. The resulting coupled-SCF polarizabilities are listed in Table II along with the coupled-Hartree-Fock values obtained by Meyer and co-workers [2,3]

for Li, Na, and K. The experimental values from Molof et al.[9] are included for comparison. Although the errors (relative to experiment) in the present SCF polarizabilities are quite large (54% and 68% for Rb and Cs) this appears to continue the trend established by Meyer and co-workers for the lighter alkali metals. If the present calculations are reliable, correlation corrections for the heavier alkali's cannot be ignored. Meyer and co-workers have suggested that for the lighter alkali's this error is due principally to the correlation of the outer s electron with the p electrons of the next inner shell. In a conventional CI calculation this sort of correlation is obtained by simultaneously promoting the outer s electron along with a p electron into the next higher p and d shells. In the present case these types of promotions would be included in a standard "singles and doubles" CI calculation. However, the presence of the spin-orbit operator complicates things considerably. Fortunately it was found in subsequent SCF calculations from which the spin-orbit integrals had been removed, that to the number of figures listed in Table II, the polarizability was unaffected by spin-orbit coupling. Thus we were able to carry out conventional CI calculations. The results are shown in the last column of Table II. The present correlated values are in excellent agreement with experiment. In fact, the relative errors in our calculations appear to be of the same magnitude as found in the previous light atom calculations suggesting that for these purposes the effective potential approximations introduce negligible error.

To determine whether our previous criticisms of Phillips-Kleinman type effective potentials are valid, we performed similar finite-field SCF calculations for Cs using a Phillips-Kleinman potential generated from the relativistic Cowan and Griffin [12] wavefunctions for Cs^+. Basis sets and field strengths were chosen as before. For neutral Cs we obtained a polarizability of 77.6 $\overset{\circ}{A}^3$. Assuming that our previous coupled SCF values are correct, the Phillips-Kleinman calculation underestimates the polarizability by more than 20%.

Conclusion

We have shown that, when combined with the appropriate basis sets and finite-field and correlation formalisms, the relativistic "shape consistent" effective potentials developed by Christiansen and co-workers are capable of reproducing the accurate experimental polarizabilities of Molof, et al., to a high degree of reliability. Considering the magnitudes of the Rb and Cs polarizabilities and correlation corrections, the above calculations should provide a severe test of our technique. Although we cannot always count on the spin-orbit effects being negligible, methods for avoiding the difficulties usually associated with spin-orbit operators in highly correlated wavefunctions have been developed in principle [13] and their implementation will be reported in future publications.

Acknowledgments

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Table I.   Rb and Cs (5s, 5p, 2d) STO Basis Sets Used in the
Present Calculations

	Rb				Cs		
n	ζs	ζp	ζd	n	ζs	ζp	ζd
4	3.0583	2.8023	1.55	5	3.1853	2.9283	1.77
4	1.3811	1.5512	0.91	5	1.8061	1.7700	1.0
5	0.9792	0.98		6	1.2133	1.21	
5	0.6760	0.68		6	0.7934	0.79	
5	0.47	0.47		6	0.46	0.46	

Table II. Experimental and Computed Alkali Metal
Polarizabilities ($\overset{\circ}{A}{}^{3}$)

	Exp($\pm$2%)[a]	Coupled SCF (% error)	Correlated (% error)
Li	24.3	25.2 (+4)[b]	24.4 (0)[b]
Na	23.6	28.6 (+21)[b]	24.5 (+4)[b]
K	43.4	61.9 (+43)[b]	42.6 (-2)[b]
Rb	47.3	72.9 (+54)	49.8 (+5)
Cs	59.6	100. (+68)	61.3 (+3)

[a] from Reference 9.

[b] from References 2 and 3.