Upper and lower bounds to atomic and molecular properties. IV. Electric polarizabilities of three-electron atoms by a lower-bound procedure

James S. Sims, Stanley A. Hagstrom, and John R. Rumble, Jr.*
Department of Chemistry, Indiana University, Bloomington, Indiana 47401
(Received 15 December 1975)

Wave functions, which include interelectron coordinates r_{ij} explicitly, are employed for the $1s^2ns\,^2S$ and $1s^22p\,^2P_1$ states of Li I in obtaining lower bounds and Hylleraas variation-perturbation estimates of dipole polarizabilities for the four lowest ^2S states of Li I. The results of this study are polarizabilities for the four lowest ^2S states of Li I with probable accuracy 2–5%. In addition, the latest experimental result for the $2\,^2S$ state of Li I is found to be in excellent agreement with our result.

I. INTRODUCTION

The work reported herein represents another step toward the ultimate goal of quantum-chemical calculations, namely, the accurate prediction of experimentally measurable properties. The static dipole polarizability[1] for the four lowest states of Li I has been calculated by the Hylleraas variation-perturbation technique,[2] using some of the best variational wave functions available (on an energy criterion). These results have been rigorously bounded from below using a procedure by Weinhold[3] (previously applied to Be I[4]). The results obtained for the ground state are in excellent agreement with the new experimental results of Molof *et al.*[5]

The actual computational procedure is a three-step process and has been discussed in detail previously.[4] First, a very accurate Hylleraas–configuration-interaction (CI) variational calculation is performed, for both the ^2S and ^2P states of Li I.[6] Second, the resulting wave functions are used in the Hylleraas procedure[7] to calculate the static dipole polarizability. Finally, the wave functions are used to compute the lower bound by Weinhold's formula.[8]

II. RESULTS

Lower bounds to the static dipole polarizabilities were calculated for the lowest four ^2S states of Li I. The results of our calculations are tabulated in Table I, and compared with previous calculations and experiments in Table II. In Table I, we include the conventional Hylleraas variation-perturbation (VP) result obtained from a 150-term ^2S and 120-term ^2P wave functions. This value is not a rigorous bound, but since the result is the most extensive available, we feel it supercedes previous similar estimates and give it in Table II as our recommended calculated value. The recent experimental work of Molof *et al.*[5] agrees extremely well with the VP calculation, and lies above the *rigorous* lower bound, unlike previous experiments. Because of this excellent agreement, as well as the closeness of the lower bound (3.3%), we believe that the static dipole polarizability for Li I for the ground state ^2S is now well defined.

The very large static dipole polarizabilities found for the $3\,^2S$, $4\,^2S$, and $5\,^2S$ states of Li I are not at all unexpected. In recent experimental work, Fabre and Haroche[9] have found such trends even more pronounced in the Rydberg states of Na.

In Table II we present a comprehensive comparison of the present results with various previous theoretical values. The underlined values are ruled out by our rigorous bounds. The rest of the values fall above our rigorous bounds and cannot be ruled out. Our results agree well with the recent calculations of Adelman and Szabo.[20] They obtain an analytic expression for the 2^j-pole elec-

TABLE I. Computed values for Li I.[a]

State	$10^2\epsilon$	E	S_{a-}	$\alpha-$	α_{VP}
$2\,^2S$	1.1237	−7.478 023	0.999 873	(23.47)	(24.27)
$3\,^2S$	2.7935	−7.354 10	0.999 220	(605.8)	(558.7)
$4\,^2S$	5.4031	−7.318 40	0.997 081	(5097.)	(4328.)
$5\,^2S$	9.9230	−7.303 40	0.990 153	(24910.)	(17990.)

[a] Wave functions and definitions of quantities are given in Paper III (Ref. 6). Values are in a.u. except for values in parentheses, which are in units of Å^3.

TABLE II. Comparison of our polarizability results for three-electron atoms with other calculations. Values reported here are in cubic angstroms ($Å^3$). Our results in a_0^3 were converted to $Å^3$ by use of $1\,a_0 = 0.529\,167$ Å.

Method	Ref.	$2\,^2S$	$3\,^2S$	$4\,^2S$	$5\,^2S$
Stark	10	27			
Coulomb	11	25.6			
Coupled Hartree-Fock (CHF)	12	25.37			
Variation-perturbation (VP)	13	25.23			
CHF	14	25.2			
Perturbation theory (PT)	15	24.96			
Sternheimer	16	24.9			
Many-body PT	17	24.84			
Sternheimer	18	24.74			
Pseudopotential	19	24.6			
Coulomb	20	24.3			
Experimental	5	24.3			
Present results		24.27	605.8	5097	24910
Rigorous lower bounds (present calculation)		23.47	558.7	4328	17990
Oscillator strength moments	21	24.17			
PT	22	23.4			
Experimental (Beam)	23	22±2			
Approximate unrestricted HF	24	21.0			
Experimental	25	20±3			

tric polarizability of an atom in a Coulomb-like approximation. Their claim of having obtained an accurate expression for dipole polarizabilities of monovalent s-state atoms appears to be supported by our calculations.

III. CONCLUSIONS

On the basis of the results presented here, it seems reasonable to conclude that the introduction of r_{ij} coordinates for an atomic wave function with $N \geq 3$ can lead to reliable polarizability values (2–5% accuracy). Recommended values for the polarizabilities of the four lowest ^2S states have been presented for Li I. Our calculations for the $2\,^2S$ state of Li I rule out earlier experimental work and confirm the latest experimental results.

ACKNOWLEDGMENT

One of us (J.S.S.) would like to thank Peg Blanton for helpful conversations during the course of this work.

*Present address: Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colo. 80309.

[1]For a tabulation of static dipole polarizabilities of all neutral atoms in their ground electronic states, see R. R. Teachout and R. T. Pack, At. Data 3, 195 (1971).

[2]For an extensive review of quantal procedures, see A. Dalgarno, Adv. Phys. 11, 281 (1962).

[3]F. Weinhold, Adv. Quantum Chem. 6, 226 (1972).

[4]J. S. Sims and J. R. Rumble, Jr., Phys. Rev. A 8, 2231 (1973).

[5]R. W. Molof, H. L. Schwartz, T. M. Miller, and B. Bederson, Phys. Rev. A 10, 1131 (1974).

[6]J. S. Sims, S. A. Hagstrom, and J. R. Rumble, Jr., Phys. Rev. A 13, 242 (1976).

[7]Reference 4, Eq. (14).

[8]Reference 4, Eqs. (12) and (13).

[9]C. Fabre and S. Haroche, Opt. Commun. 15, 254 (1975).

[10]E. Fues, Z. Phys. 82, 536 (1933).

[11]D. R. Bates and A. Damgaard, Philos. Trans. Soc. Lond. 242A, 101 (1950).

[12]W. J. Stevens and F. P. Billingsley, II, Phys. Rev. A 8, 2236 (1973).

[13]P. K. Mukherjee, R. K. Moitra, and A. Mukherji, Int. J. Quantum Chem. 5, 637 (1971).

[14]P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).

[15]M. M. Heaton and A. L. Stewart, J. Phys. B 3, 431 (1970).

[16]R. M. Sternheimer, Phys. Rev. 96, 951 (1954); 127, 1220 (1962).

[17]E. S. Chang, R. T. Pu, and T. P. Das, Phys. Rev. 174, 16 (1968).

[18]R. M. Sternheimer, Phys. Rev. 183, 112 (1969).

[19]D. M. Rapp (unpublished).
[20]S. A. Adelman and A. Szabo, J. Chem. Phys. 58, 687 (1973).
[21]G. M. Stacey and A. Dalgarno, J. Chem. Phys. 48, 2515 (1968).
[22]G. W. F. Drake and M. Cohen, J. Chem. Phys. 48, 1168 (1968).
[23]G. E. Chamberlain and J. C. Zorn, Phys. Rev. 129, 677 (1963).
[24]P. W. Langhoff and R. P. Hurst, Phys. Rev. 139, 1415 (1965).
[25]A. Salop, E. Polkack, and B. Bederson, Phys. Rev. 124, 1431 (1961).