

Finite perturbation calculation for the static dipole polarizabilities of the atoms Na through Ca

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Static dipole polarizabilities are calculated from pseudonatural orbital configuration expansion wave functions for the ground states of the atoms Na through Ca with an accuracy estimated to about 2%. The resulting values are (in the order Na–Ca) 165.02, 71.32, 56.27, 36.32, 24.52, 19.60, 14.71, 11.096, 287.6, and 153.9 a.u. The influence of the electron correlation on the polarizabilities is shown to reflect its influence on the radial distribution of the electrons.

Werner and one of us¹ have recently shown that the finite perturbation technique, when applied to sufficiently correlated wave functions, is capable of producing molecular dipole polarizabilities with uncertainties of less than 2%. This method has also been applied to the first-row atoms,² for which an even better accuracy might be expected. Indeed, the two precise experimental values available, 164.0 ± 3.4 for Li³ and 2.669 for Ne⁴ (for units see Table I), are in excellent agreement with the calculated values of 164.5 and 2.676, respectively. Comparison with results from other sophisticated methods which take electron correlation into account, such as perturbation variation with configuration interaction (CI), many-body perturbation theory or finite perturbation with multiconfiguration–self-consistent-field (SCF) wave functions, indicated that for the first time an even accuracy had been achieved over the whole row. Since reliable experimental as well as theoretical data are missing for the polarizabilities of the second-row atoms, with the exception of Na and Ar, we felt it desirable to extend the above work to the atoms of the second row.

As before, our calculations use the coupled-electron-pair approximation based on a pseudonatural orbital configuration expansion⁵ (PNO-CEPA) the applicability of which for polarizability calculations has been investigated in detail in Ref. 1. The basis sets adopted for the second-row atoms consist of 14s, 11p, 4d Gaussian-type functions, and special consideration has been given to their “soft parts” because they are essential for polarization effects.¹ Thus, of the 12s, 9p energy-optimized sets of Huzinaga⁶ the two most diffuse s functions have been replaced by four functions with exponents $\alpha_{10+i} = \alpha_{10}/q^i$, $i = 1, 2, 3, 4$ with $q = (\alpha_{10}/\alpha_{12})^{0.36}$, and the three most diffuse p functions are replaced by five functions with exponents $\alpha_{6+i} = \alpha_6/2.4^i$,

$i = 1, 2, 3, 4, 5$. In addition, four d sets have been included with exponents obtained from α_{11} of the p set by multiplying with 3, 9, 32, and 128 (Na–Al), or 1, 3, 9, and 32 (Al–Ar), respectively.⁷

Since the effect of f functions had been found negligible, they have been discarded in this work. The field strengths used vary from 0.001 for Na to 0.01 for Ar and imply only nonlinearities of less than 0.2%. The PNO configuration expansion includes all M-shell single substitutions, those “diagonal”⁵ double substitutions which contribute more than 10^{-4} hartree to the correlation energy, and in order to be on the safe side some off-diagonal double substitutions when low-lying double substitutions appear. The correlation between the valence and the next inner shell has been taken into account for the atoms Na through P as well as for K and Ca up to correlation contributions of more than 10^{-5} hartree.

Our results are collected in Table I, which gives also experimental values, as far as known to us, and results of other calculations. Again, agreement with the accurately known polarizabilities of Na and Ar is very good. Also the values for K and Ca lie within the experimental-error bounds. A large discrepancy appears for Mg, where our value lies considerably outside of the bounds estimated from semiempirical oscillator strength sums. The coupled Hartree-Fock results of Kaneko *et al.*⁸ for Mg and Ar agree well with our SCF results which strengthens our belief that the basis sets are saturated. The simplifications introduced by Thorhallsson, Fisk, and Fraga⁹ into the SCF perturbation formalism are seen to lead to rather serious errors, and their deviations show no systematic trend when first-row and second-row atoms are compared. The only previous *ab initio* calculation taking electron correlation into account is apparently Doran’s many-body perturbation

TABLE I. Calculated and experimental values for the polarizabilities. ^a

	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca
This work, SCF	192.76	81.87	63.07	38.83	25.41	19.17	14.20	10.693	418.0	186.2
This work, valence shell correlation only	192.76	75.81	57.47	36.70	24.68	19.60	14.71	11.096	418.0	176.6
This work, inclusive intershell correlation	165.02	71.32	56.27	36.32	24.52				287.6	153.9
Experimental values	159.2 ± 3.4 ^b 164.6 ± 11.5 ^f							11.074 ^{c,d} 11.080 ^c	292.8 ± 6.1 ^b 305.0 ± 21.6 ^f	168.7 ± 16.9 ^e
Oscillator strength summation	164.0 ± 0.7 ^g 167.4 ⁱ	47 ≤ $\bar{\alpha}$ ≤ 63 ^g 35 ≤ $\bar{\alpha}$ ≤ 62 ^h							279.8 ± 1.0 ^g 288.0 ⁱ	
Coupled Hartree Fock, Ref. 8	125.5	81.24						10.59		
Approximate uncoupled Hartree Fock, Ref. 9		91.1	74.2	45.95	29.8	23.3	17.6	13.43	251.7	228.1
Other methods	162.6 ± 8.1 ^k 168.7 ^m 160.6 ^m 234 ⁿ	89.3 ⁿ						10.98 ^l		
Anisotropy ^o			-24.43	+9.60		-4.88	+2.16			

^a Mean static dipole polarizabilities $\bar{\alpha} = \frac{2}{3}\alpha(M=\pm 1) + \frac{1}{3}\alpha(M=0)$ (anisotropy, see last line). All values in a.u. = $1.482 \cdot 10^{-25} \text{ cm}^3 = 1.049 \cdot 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$.

^b Reference 3.

^c R. R. Teachout and R. T. Pack, At. Data 3, 195 (1971).

^d ±0.013.

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^l Reference 10, many-body perturbation theory.

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ⁿ S. Hameed, Phys. Rev. A 4, 543 (1971), double perturbation based on numerical Hartree-Fock functions.

^o $\alpha(M=\pm 1) - \alpha(M=0)$.

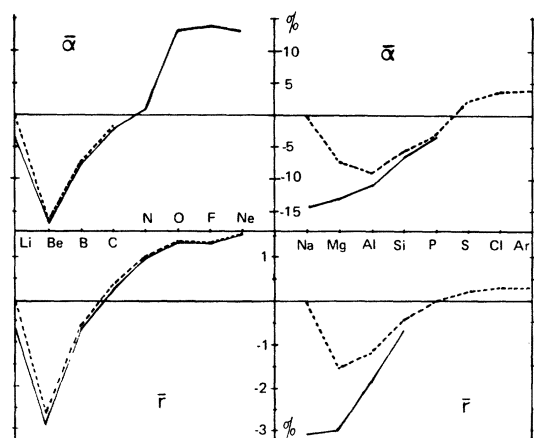


FIG. 1. Relative correlation contribution to the polarizabilities (upper part) and to the size of the valence shell $\bar{r} = \langle r^2 \rangle_{\text{val}}^{1/2}$ (lower part). Dashed lines: valence shell correlation only; solid lines: inclusive intershell correlation.

treatment of Ar.¹⁰

By comparing our SCF and CEPA results, electron correlation is seen to contribute to the polarizabilities between -31% for K and $+4\%$ for Ar. The relative correlation contributions to the polarizabilities are compared in the upper part of Fig. 1 for the corresponding atoms of the first and second row. As long as only valence shell correlation is considered, both rows show the same typical behavior. Intershell correlation, which is almost negligible for all first-row atoms, adds a considerable negative effect at the left side of the second row. It decreases from atom to atom by nearly a factor of 2 and is reduced to 0.5% for P so that neglecting it for the remaining atoms seems justified.

In Ref. 2 the correlation effect on the polarizabilities has been related qualitatively to its effect on the radial electron distribution.¹¹ In order to substantiate this we have computed the mean value of r^2 which is, as is well known, connected with the atomic diamagnetic susceptibility through the relation $\chi = (2e^2/3mc^2)\langle r^2 \rangle$. The corresponding values, calculated with and without inclusion of correlation, are listed in Table II. The valence shell quantity $\bar{r} = \langle r^2 \rangle_{\text{val}}^{1/2}$ may be regarded as a measure for the size of the valence shell.¹² The relative changes of \bar{r} upon inclusion of correlation which is drawn in the lower part of Fig. 1 shows a striking resemblance to the behavior of the polarizabilities. Thus it seems justified to relate the latter qualitatively to the contraction or expansion of the electron distribution when going from an independent particle wave function to a correlated one.

Two effects can be observed:

(a) Unoccupied low-lying p orbitals make a very effective angular correlation possible; i.e., if one wants to describe a state where two s electrons tend to keep apart from each other by preferring a geometrical configuration on different sides of the nucleus, one has to admix configurations to the ground state with the two s electrons excited into two p orbitals. In case there exist low-lying unoccupied p orbitals in the atom, this means that this type of correlation is favored, in contrast to the case where such orbitals are energetically more expensive. This preference of opposite configurations will, however, ultimately lead to a reduction of the shielding of the nuclear potential and thus to a contraction of the valence shell.

(b) In an analogous way, electrons tend to avoid each other by one keeping nearer to the nucleus and the other farther away (in/out correlation).

TABLE II. Calculated diamagnetic susceptibilities per mole.^a

	He ^c	Li	Be	B	C	N	O	F	Ne ^d	
SCF ^b	1.879	14.77	13.73	12.57	10.94	9.582	8.884	8.126	7.433	
CEPA	1.890	14.59	12.98	12.40	10.99	9.766	9.123	8.341	7.646	
	Na	Mg	Al	Si	P	S	Cl	Ar ^e	K	Ca
SCF ^b	21.66	23.54	26.55	25.58	24.01	23.16	21.92	20.64	40.74	44.92
CEPA	20.66	22.35	25.66	25.24	23.99	23.24	22.03	20.76	37.95	42.35

^a Unit -10^{-6} cm^3 .

^b These values are practically identical with those reported by S. Fraga and J. Karwowski, Technical Report: Tables of Hartree-Fock atomic data, University of Alberta, Edmonton, Alberta, Canada, 1974 (unpublished).

^c Experimental value: 1.88 [*Handbook of Chemistry and Physics*, 52nd ed., edited by R. C. Weast (Chemical Rubber, Cleveland, Ohio, 1972), p. E 109].

^d Experimental values 6.74 (Ref. c), 7.77 [G. G. Havens, Phys. Rev. **43**, 992 (1933)], 6.62 [K. E. Mann, Z. Phys. **98**, 548 (1936)].

^e Experimental values 19.6, 19.5, 19.15 (same references as in d).

This is achieved by configurations using orbitals with additional radial nodes and is more effective for a more diffuse distribution since in this case the excitation energies are lower.

In terms of the virial theorem we may say that the changes in the means values of the kinetic and potential energies due to the doubly excited configurations are such that $2 \Delta T < |\Delta V|$ in case (a), but $2 \Delta T > |\Delta V|$ in case (b). This then necessitates a radial contraction or expansion, respectively, of the wave function which is achieved by the admixture of single substitutions.

Effect (a) dominates at the left side of each row because there are empty p orbitals available. Since their number becomes smaller when going to the right side of the row this effect diminishes and thus effect (b) becomes dominant. Both effects are more pronounced in the first row than in the second row. On the one hand, we ascribe this to the presence of a large core in the second row which hinders a drastic contraction, and on the other hand, excitation energies are lower in the more diffuse valence shell so that $-2 \Delta T / \Delta V$ is

closer to one.

The dominant effect of the intershell correlation on the valence shell distribution is of type (a) and is known as core polarization. Therefore this part of the correlation effect leads also to a contraction of the electron distribution and a reduction of the polarizability. That this effect is much larger for the second row will be mainly due to the larger core and its larger polarizability. The strong decrease going from left to right is again caused by filling up the valence shell p orbitals which are required for angular correlation between valence shell electrons and core. In other words, core polarization becomes more and more difficult as the effects of the valence electrons neutralize each other.

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⁵W. Meyer, *J. Chem. Phys.* **58**, 1017 (1973); "CEPA" stands for coupled-electron-pair approximation.

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⁷For the third-row atoms K and Ca, a $16s$, $13p$, $4d$ orbital basis has been used with exponents of the s functions covering the range from 132185 to 0.0059 (for K) and 146348 to 0.0096 (for Ca), of p functions covering the range from 762.5 (K) and 868.6 (Ca) to

0.012 and of d functions from 0.60 to 0.012 in both cases.

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¹¹It is intuitively clear that the polarizability will increase with increasing size of the atom. However, an approximate quantitative relation has been established long before by J. G. Kirkwood [*Phys. Z.* **33**, 57 (1932)] and by J. P. Vinti [*Phys. Rev.* **41**, 813 (1932)]; cf. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 946.

¹²The "valence shell" density matrix has been obtained by subtracting the SCF core from the total density matrix.