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Finite perturbation calculations for the static dipole polarizabilities of the first-row atoms

Hans-Joachim Werner and Wilfried Meyer
Institut für Physikalische Chemie, Johannes Gutenberg Universität, Mainz, Germany

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Static dipole polarizabilities are calculated from self-consistent–field and highly correlated wave functions for the ground states of the atoms Li through Ne. The correlation contributions to the polarizabilities are found to vary between − 16% for Be and + 14% for F. The polarizabilities as obtained from the coupled-electron-pair approximation are expected to be accurate to about 2%.

We have recently calculated static dipole polarizabilities for several small molecules[1] by applying the finite perturbation method to highly correlated wave functions as obtained from the pseudonatural-orbital configuration interaction (PNO-CI) and the coupled-electron-pair approximation[2] (CEPA). The results, which are summarized in Table I, show for the latter approach agreement with experiment to better than 2%. In the case of the first-row atoms, with the exception of neon, experimental values are either missing or rather uncertain and theoretical calculations have produced results which vary considerably. Therefore we felt it worthwhile to apply our approach to the ground states of these systems.

For experimental and theoretical work on the static dipole polarizabilities of neutral atoms up to 1970, we refer to the excellent compilation by Teachout and Pack.[3] Numerous calculations have been performed by the uncoupled and coupled Hartree-Fock methods[4,5] (UCHF and CHF, respectively). The more recent CHF results[6-13] show good agreement with each other and are certainly close to the limit of this method, which may therefore serve for valuable checks on the basis sets and as a reference for the further improvements in the calculations. In terms of double perturbation theory, the UCHF method corresponds to neglecting electron correlation completely whereas the CHF method includes all first-order correlation effects and some of second order.[14]

TABLE I. Mean static dipole polarizabilities calculated from SCF and correlated wave functions (taken from Ref. 1).[a]

Method[b]	HF	H_2O	NH_3	CH_4	CO
HF	4.98	8.68	13.61	16.69	12.40
PNO-CI	5.50	9.52	14.55	17.08	12.87
PNO-CEPA	5.67	9.86	14.96	17.22	13.13
Expt.	5.60	9.82	14.82	17.28	13.08

[a] In atomic units (1 a.u. = 14.8176 Å^3).

[b] Since we use a finite perturbation, the method is fully defined by the type of wave function employed.

The correlation contributions up to second order have been investigated by calculations following many-body perturbation theory[15-20] (MBPT). The convergence of the perturbation series seems to depend considerably on the particular system. For example, first- and second-order effects are reported by Matsubara *et al.*[18] to be remarkably small for Ne (−2 and 0.002%, respectively, of the total polarizability), whereas Miller and Kelly[19] find contributions of −60 and +13%, respectively, for $\alpha(M_L = 0)$ of C. Consequently, the latter authors attribute to their final result an uncertainty of 10%. A similar situation was found for Be where indeed a 20% discrepancy remains between the MBPT result of Kelly[15] and the values obtained by Kolker and Michels[21] and Robb[22] using the variation-perturbation approach[23] together with quite extended configuration expansions for the unperturbed and perturbed wave functions. This approach is certainly most powerful for systems with only a few valence electrons, but with an increasing number of electrons it becomes difficult to guarantee a balanced treatment of the unperturbed and the perturbed wave functions for the simple reason that the latter has a multiconfigurational structure already at the lowest approximation. Variation-perturbation calculations with CI have indeed produced rather low values for the polarizabilities of C,[22] N,[24] and Ne,[25] indicating a certain preference for the unperturbed states.

A relatively simple alternative to the perturbative approaches is offered by the method of finite perturbation as introduced by Cohen and Roothaan[5] for Hartree-Fock wave functions. It involves only the state under consideration, and electron correlation may be accounted for by standard configuration-expansion techniques without further difficulties. The wave functions are calculated in the presence of an external field with finite but small field strength F. The polarizabilities may then be evaluated from the dipole-moment expectation values as $\mu(F)/F$. This method has recently been applied to multiconfiguration-self-consistent-field (MC-

SCF) wave functions by Stevens, Billingsley, and Kraus.[26,27] They ascribe to their results an uncertainty of ±5%. The only accurate experimental value available, that for neon,[28] deviates by +10% from their predictions, however.

As for the molecules mentioned above, we use the finite perturbation method together with CI-type wave functions which account for a large fraction of the electron correlation. A description of the PNO-CI and PNO-CEPA methods used is given in Ref. 2. Their applicability to calculating dipole polarizabilities has been investigated in detail in Ref. 1. We only note here that the CEPA wave function, which is not variational but accounts approximately for the unlinked cluster effects, has been manifested to yield systematically better results than the variational CI for such properties like ionization energies,[2] spectroscopic constants,[2,29] dipole moments,[29] as well as polarizabilities (see Table I). Based on the experience regarding dipole moments, version 1 of CEPA [Eq. (14′) of Ref. 2] is used throughout.

Two sets of Gaussian-type basis functions have been employed for each atom: an 11*s*, 6*p*, 3*d* basis as derived in Ref. 1, and an even larger basis of size 12*s*, 8*p*, 4*d*. The latter one was derived from the Huzinaga[30] 11*s*, 7*p* basis by adding one further function for each type with exponents obtained from the smallest ones by dividing by 2.5. The *d* exponents were obtained from the exponent of the added *p* function by multiplying with 1, 3, 9, and 32, respectively. The *p* exponents for Li and Be were derived from those of B by simply scaling with 0.275 and 0.55, respectively. Owing to the size of the basis sets, the polarizability results are quite insensitive to the actual values of the exponents as long as the relevant regions are covered. The SCF as well as the CEPA results from the two basis sets differ by less than 0.5% in all cases. They are expected to be very close to the respective limits since including functions with larger l values does not change the calculated polarizabilities markedly.

The PNO-CI/CEPA wave functions contain all configurations which are doubly substituted with respect to the restricted Hartree-Fock (RHF) determinant and which contribute to the correlation energy more than 10^{-4} hartree (0.5×10^{-4} for Li and Be). Actually, the calculated polarizabilities appear to be stable for threshold values below 10^{-3} hartree.[1] Of course, a full set of singly substituted configurations, which are known to be essential for the accurate determination of properties, is always taken into account. These wave functions cover about (75–80)% of the total correlation energies of the atoms. The relatively large defect in the correlation energy is due to dismissing basis functions with $l > 2$.

The field strengths F have been chosen so as to minimize numerical errors and those due to the neglect of hyperpolarizability terms. For the atoms B through Ne field strengths of 0.01 a.u. were

TABLE II. Mean static dipole polarizabilities $\bar{\alpha} = \frac{2}{3}\alpha(M_L = \pm 1) + \frac{1}{3}\alpha(M_L = 0)$ for the ground states of the first-row atoms.[a]

Method	Li	Be	B	C	N	O	F	Ne
RHF	170.3	45.63	22.16	12.07	7.365	4.772	3.291	2.368
PNO-CI	166.8	39.44	20.73	11.83	7.398	5.244	3.641	2.618
PNO-CEPA	164.5	37.84	20.47	11.84	7.430	5.412	3.759	2.676
Expt.[b]	148 ± 13, 182				7.63 ± 0.4	5.2 ± 0.4		2.669
CHF[c]	168–170.3	42.2–45.6	21.2	11.46	7.356	4.630	3.266	2.35–2.38
MCSCF (base)[d]	170.5	45.55	22.1	11.8	6.88	4.70	3.28	2.369
MCSCF (corr.)[d]		36.51	19.2	11.2	6.82	4.65	3.17	2.389
MBPT[e]	167.6	46.77		10.40		5.282		2.672 2.603
Pert. var. (CI)[f]	161.8	37.05 38.14		8.81	5.844			2.479
Approx. UCHF[g]	108	52.44	23.15	11.81	7.019	4.94	3.61	2.665

[a] For units see footnote of Table I.

[b] References 32 and 33 for Li, 31 for N and O, 28 for Ne.

[c] References 6–9 for Li, 3 and 9–12 for Be, 13 for B through F, 3 for Ne.

[d] Reference 27.

[e] References 17 for Li, 15 for Be, 19 for C, 16 for O, 18 and 20 for Ne.

[f] References 36 for Li, 21 and 22 for Be, 22 for C, 24 for N, 25 for Ne.

[g] J. Thorhallson, C. Fisu, and S. Fraga, Theor. Chim. Acta 10, 388 (1968); for further UCHF values see Ref. 3.

TABLE III. Polarizability anisotropies (in atomic units) $\alpha(M_L=\pm 1)-\alpha(M_L=0)$ for the ground states of the first-row atoms.

Method	B	C	O	F
RHF	−7.55	2.95	−0.556	0.299
PNO-CI	−6.95	2.55	−0.834	0.405
PNO-CEPA	−7.04	2.54	−0.948	0.439
MCSCF (base) [a]	−7.69	2.63	−0.54	0.27
MCSCF (corr.) [a]	−5.94	2.43	−0.54	0.27
MBPT [b]		1.06	+0.202	
			+0.505	

[a] Reference 27.

[b] References 19 for C, 16 for O.

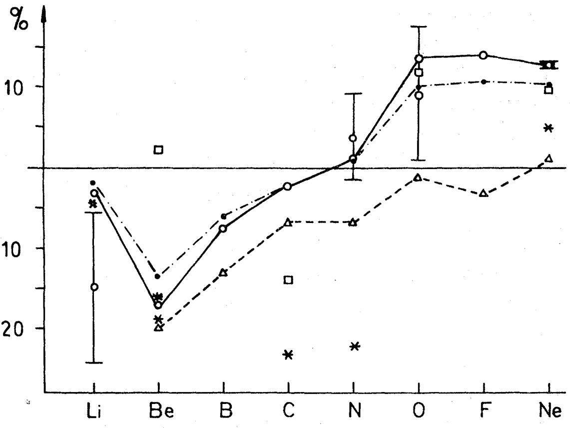

FIG. 1. Relative correlation contributions to the mean dipole polarizabilities of the first row atoms. All values are referred to the RHF results from this work. Solid line with open circles, CEPA; dash-dot line with solid circles, PNO-CI; dashed line with triangles, MCSCF; squares, MBPT; asterisks, perturbation variation calculations with CI; error bars with open circles, experimental values and error bounds. For references see Table II.

found to be satisfactory. For Li and Be, which are more easily polarized, field strengths of 0.002 and 0.005 a.u., respectively, suffice. For these field strengths the above errors are found to be less than 1%.

Table II presents our results for the mean dipole polarizabilities, which are weighted averages over the different M_L projections arising from the atomic ground states. The corresponding anisotropies are given in Table III. The CEPA polarizability for Ne is in excellent agreement with accurate experimental values.[28] Our results for O and N lie also within the experimental error bounds given by Alpher *et al.*[31] For Li we consider the value of Chamberlain and Zorn[32] obtained from atomic beam deflection measurements as probably somewhat too small whereas the value of Fues[33] derived from Stark splitting on bulk lithium is certainly too large. No experimental values seem to be available for the atoms Be, B, and C. Based on the systematic investigations performed in Ref. 1, and considering the agreement with experiment for Ne and the molecules listed in Table I, we ascribe to our CEPA results an uncertainty of about 2%.

Figure 1 displays the relative correlation contributions to the mean polarizabilities obtained by various methods. All values are referred to our RHF results which are in good agreement with previous CHF values. This definition for correlation contributions seems appropriate for the finite perturbation method but differs from that customary in perturbation calculations.[14] We find two competing correlation effects.

(a) Correlated electrons have a somewhat larger mean kinetic energy which results in a slightly more diffuse charge distribution and a larger polarizability. This effect dominates for all molecules and the atoms O through Ne. The results of an independent electron-pair calculation as introduced by Sinanoglu[34] and Nesbet[35] show for Ne that all pairs add to this effect, with a particularly large effect from the $2p\sigma$-$2p\sigma$ pair (Table IV). (This pair is responsible for the noticeable correlation effect on the anisotropies of O and F.)

(b) Spin orbitals that are unoccupied in the SCF wave function of the unperturbed system, and therefore fully available for polarizing the charge distribution, become fractionally occupied in the correlated wave function, thereby reducing the polarizability. This effect is seen to be dominant for the atoms Be through C due to the low-lying unoccupied p orbitals. This is illustrated by the observation that just removing the singly substituted configuration $2s\rightarrow 2p\sigma$ from the wave function increases the calculated polarizabilities of the

TABLE IV. Polarizability contributions from independently correlated electron pairs for neon (in atomic units).

Pair	$\alpha_{\mathrm{CI}}-\alpha_{\mathrm{SCF}}$
$2s$ $2s$	0.0065
$2s$ $2p\pi$	0.0241
$2s$ $2p\sigma$	0.0507
$2p\pi_x$ $2p\pi_x$	0.0168
$2p\sigma$ $2p\sigma$	0.0787
$2p\pi_x$ $2p\pi_y$	0.0402
$2p\pi$ $2p\sigma$	0.1039
sum	0.4657
CEPA	0.3113

[a] The same set of configurations is used in the independent pair calculations and the CEPA calculation.

states B($^2\Sigma^+$), C($^3\Pi$), and N($^4\Sigma^+$) by about 14, 8, and 4%, respectively.

For comparison, results of previous calculations are included in the Tables II and III and—as far as they go beyond SCF—also in Fig. 1. In the MC-SCF treatment of Stevens and Billingsley[27] effect (b) is apparently accounted for, but effect (a) which is distributed over many configurations, seems to be missing so that the differences to our CEPA results increase monotonically towards the left end of the row. Similarly, we find good agreement with the variation-perturbation results for[36] Li and[21] Be but Robb's values for[22] C and[24] N are obviously too small. The MBPT results agree well with our CEPA values for Ne but for Be and C there appear deviations of +20 and −14%, respectively, and the anisotropies for O differ even in their sign. Note that, according to Table IV, the polarizability from independently correlated electron pairs overshoots the CEPA polarizability by 5% in the case of Ne. This underlines the difficulties encountered in perturbational treatments since the coupling elements between the substituted configurations of different pairs—their neglect causes the increase of the correlation effect on the polarizability—correspond to three-body and four-body interactions which appear only beyond second order of perturbation theory.

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