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Finite-perturbation calculation of static quadrupole and mixed dipole-octupole polarizabilities for the ground states of the first-row atoms

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Static quadrupole and mixed dipole-octupole polarizabilities are calculated from correlated wave functions for the ground states of the first-row atoms with estimated uncertainties of less than 3%. The following mean quadrupole polarizabilities are obtained for the atoms Li through Ne (in atomic units): 1428; 301.8; 145.7; 64.20; 30.72; 21.20; 12.69; 7.726. Correlation contributions are found to range from −12% (Be) to +20% (O).

It has recently been demonstrated that the finite-perturbation method, when applied to sufficiently correlated wave functions, is capable of producing static dipole polarizabilities of atoms[1,2] and small molecules[3] with high accuracy: in all cases, where precise experimental values are available, the calculated values were found to deviate by less than 2%. Here we apply this method to calculating atomic quadrupole and mixed dipole octupole polarizabilities. These properties are practically inaccessible to measurement but there is nevertheless considerable interest in these data. In particular, the long-range potential for scattering processes between atoms and ions or molecules with large permanent moments may be strongly affected or even be dominated by the induction interaction which depends directly on the atomic polarizabilities. Furthermore, accurate static quadrupole polarizabilities may be very useful for estimating the long-range dispersion attraction and provide a valuable check for the more difficult calculation of dynamic polarizabilities by means of many-body perturbation techniques.

In the finite-perturbation method, the polarizabilities are obtained from moments calculated under the presence of finite external fields by numerical differentiation with respect to the field strength. In the case of atoms one needs only consider external potentials of the form

$$V=\sum_{l} r^{l} P_{l}(\cos\vartheta)\cdot f_{l}\,,$$

and obtains the polarizability constants

$$\alpha_{ll'}(ALM)=\frac{\partial}{\partial f_{l}}\,\langle\psi(V)|\sum_{i} r_{i}^{l'} P_{l'}(\cos\vartheta_{i})\,|\psi(V)\rangle\,,$$

where $\psi(V)$ coincides with the state $|ALM\rangle$ for $V=0$. Nonzero constants result only for $l+l'$ even and $|l-l'|\leq 2L$. The response of an atomic system to a general external field can be obtained—to second order in the perturbation—from the above defined polarizabilities by means of the Wigner-Eckart theorem. Since we have not found a compact treatment of the general case in the literature, the pertinent formulas are given in the Appendix for the readers convenience. The induced interaction with a distant moment of order k depends on the distance R like $R^{-(k+l+l')}$. Although the mixed-pole polarizabilities ($l\neq l'$) do not contribute to the orientation averaged interaction since the mean polarizabilities, $\overline{\alpha}_{l'}=\sum_{M}\alpha_{l'}(ALM)/(2L+1)$, are nonzero only for $l=l'$, they are significant for the orientation dependence of the interaction. Indeed, as our calculations show, the dipole-octupole anisotropy is about twice as large as the anisotropy of the quadrupole polarizability.

The advantage of the finite-perturbation method for polarizability calculations lies in the fact that well-established standard techniques for unperturbed systems are directly applicable. As in our previous investigations on dipole polarizabilities, our wave function is obtained from the coupled electron-pair approximation based on a configuration expansion in terms of pseudonatural orbitals (PNO-CEPA).[4] Since the essential features of this method regarding its application to polarizability calculations have previously been discussed in detail[3] we need only mention here some special points of the present work.

Within the region of field strength which were required for sufficient numerical significance of the calculated moments, the nonlinearity of the induced moments appeared to be considerably larger for the quadrupole perturbation than was observed in the dipole case. This is not surprising since, on the one hand, due to the r^2 dependence of the perturbing potential the polarization effect is strongly

TABLE I. Exponents η of Gaussian type basis functions.

Type of orbital	Exponents
s	$\eta_1 - \eta_{10}$ from Huzinaga[a] $\eta_{11} = 0.369\eta_{10}$
p	$\eta_1 - \eta_5$ from Huzinaga[a] $\eta_6 = \eta_5/2.5$; $\eta_7 = \eta_6/2.5$
	For Li and Be values of B scaled by 0.277 and 0.581, respectively.
d	$\eta_1 = 4.67\eta_{10}(s)$; $\eta_2 = \frac{1}{4}\eta_1$; $\eta_3 = \frac{1}{3}\eta_2$
f	$\eta_1 = 2\eta_5(p)$; $\eta_2 = \frac{1}{3}\eta_1$; $\eta_3 = \eta_2/2.88$

[a] From Ref. 5.

concentrated in the outer fringes of the charge distribution, which are relatively difficult to describe in a numerically stable way and thus require a not too small *f*. On the other hand, a basis set designed to describe well the wave function in the outer regions may then extend into the saddle-point region of the effective one-electron potential, the distance of which behaves in the quadrupole case like $f^{-1/3}$.

Experimenting with various polynomial fits we found that the numerical errors in the polarizability could be kept below 0.5% by choosing five equidistant fields with the largest producing a relative deformation of about 1%–2%, and by fitting the moments with a polynomial of degree 3. (For states with $M=L$ this implies only two independent calculations, of course.) Within the above defined region the nonlinearity is not larger than 10%.

The second derivatives of the moments are not considered to provide useful information about the hyperpolarizabilities since the basis sets have not been adapted to give this quantity.

Several basis sets of Gaussian-type functions have been constructed with the *d* and *f* exponents roughly optimized to give maximal polarizability. The basis sets finally adopted are of size 11*s*, 7*p*, 3*d*, 3*f*, and are obtained from Huzinaga's optimized atomic 10*s*, 5*p* sets[5] as described in Table I. The convergence of the calculated quadrupole polarizabilities with increasing size of the basis sets follows closely the pattern observed for the dipole polarizability and it is estimated that the remaining basis set errors are smaller than 1%. This applies as well to the convergence with respect to the threshold values for selecting singly and doubly substituted configurations and to the inclusion of off-diagonal *PNO* configurations. The total error is thus estimated to be smaller than 3%.

The results of our calculations are given in Tables II–IV. Comparison of our self-consistent field (SCF) mean-quadrupole polarizabilities with recent coupled Hartree-Fock results[6] shows deviations of less than 1% with the exception of O(^3P) where our value is larger by 4%. This substantiates the above given error estimates. The correlation contribution behaves qualitatively in the same manner as that for the dipole polarizability so that the discussions given in Ref. 2 applies for the quadrupole polarizability as well. That is, for the left half of the row angular correlation is dominant and leads to a shrinking of the charge distribution which results in a reduced polarizability whereas for the right half of the row there is strong in-out correlation leading to an expansion of the charge distribution and an increased polarizability.

As far as known to us, the only other calculation including electron correlation is a many-body perturbation treatment of the rare-gas atoms by Dor-

TABLE II. Mean static quadrupole polarizabilities $\bar{\alpha}_q = \Sigma_M \alpha_{22}(XLM)/(2L+1)$ (a.u. = 0.041 505 Å^5).

Method	Li	Be	B	C	N	O	F	Ne
SCF	1481.0	339.1	133.9	54.76	25.66	16.90	10.40	6.464
CEPA, valence Shell correlation		304.3	145.7	64.20	30.72	21.20	12.69	7.726
CEPA, included *K/L* shell correlation	1428.0	301.8						
Correlation contribution	−3.7%	−11.6%	8.1%	14.7%	16.5%	20.3%	18.0%	15.9%
Coupled HF		342.4[a] 342.1[b]	134.0[c]	55.2[c]	25.6[c]	16.3[c]	10.3[c]	6.457[d] 6.46[c]
MBPT								6.416[e]
Coulomb approximation	1397.0[f]	167.9[f]						

[a] Reference 10.
[b] Reference 11.
[c] Reference 6.
[d] Reference 12.
[e] Reference 7.
[f] Reference 13.

TABLE III. Anisotropies ($\alpha_{M=1}-\alpha_{M=0}$) of the quadrupole and mixed dipole-octupole polarizabilities (a.u.).

l	l'	Method	B	C	O	F
2	2	SCF	−65.1	19.55	−5.56	2.53
		CEPA	−62.32	20.21	−7.28	3.23
3	1	SCF	−110.5	32.08	−10.85	4.41
		CEPA	−130.7	33.36	−14.39	5.43

an.[7] His value for Ne is about 15% lower than ours and is even smaller than our SCF value and other coupled Hartree-Fock (HF) values (including his own). On the basis of the systematic behavior of the correlation contributions, as obtained in our investigations, we consider Dorans correlation effect as highly unlikely. It may be noted that a 15% correction of the static quadrupole polarizability asks for a similar correction of the dynamic polarizability and thus for Dorans C_8 value for Ne. This point is further discussed in a study on the Ne-Ne Van der Waals potential.[8]

Following a suggestion by Gislason and Rajan[9] who expect a linear relationship between $\log\alpha_q$ and $\log\alpha_d$ we have plotted $\ln\tilde{\alpha}_q$ vs $\ln\tilde{\alpha}_d$ in Fig. 1, $\tilde{\alpha}$ denoting $\alpha/n_{\text{val elec}}$; a least-square fit yields $\ln\tilde{\alpha}_q = 1.264\ln\tilde{\alpha}_d + 1.372$. This can be understood as follows: according to Kirkwood and Vinti[15] $\tilde{\alpha}_d \simeq \langle\widetilde{r^2}\rangle^2$ and a similar treatment of $\tilde{\alpha}_q$ leads to $\tilde{\alpha}_q \simeq \langle\widetilde{r^4}\rangle^2/\langle\widetilde{r^2}\rangle$. From our previous calculation[2] we find $\tilde{\alpha}_d \simeq \langle\widetilde{r^2}\rangle^{2.107}$ and from a calculation for Be and Ne $\langle\widetilde{r^4}\rangle \simeq \langle\widetilde{r^2}\rangle^{1.828}$. Thus one obtains $\tilde{\alpha}_q \simeq \langle\widetilde{r^2}\rangle^{2.656} \simeq \tilde{\alpha}_d^{2.656/2.107} \simeq \tilde{\alpha}_d^{1.261}$.

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APPENDIX

An atomic system subjected to an external potential may have the multipole moments $\mu_l^m = \langle\psi|Q_l^m|\psi\rangle$, where

$$Q_l^m = \left(\frac{4\pi}{2l+1}\right)^{1/2} \sum_i r_i^l Y_l^m(\vartheta_i, \varphi_i)\,.$$

TABLE IV. Static quadrupole moments $q = \langle XL0|\sum_i r_i^2 P_2(\cos\vartheta_i)|XL0\rangle$ (a.u.).

Method	B	C	O	F
SCF	2.550	−1.544	0.921	−0.669
CEPA	2.413	−1.447	0.990	−0.701

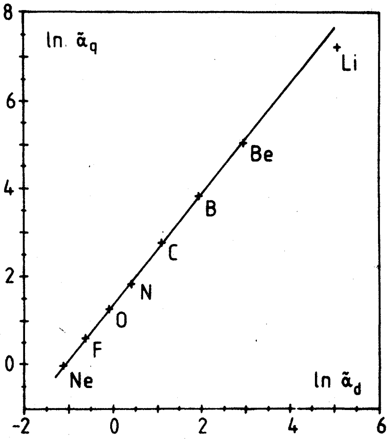

FIG. 1. $\ln(\alpha_q/n_{\text{val elec}})$ vs $\ln(\alpha_d/n_{\text{val elec}})$ in a.u.

Expanding the potential as $V=\sum_{l',m'} Q_{l'}^{m'} f_{l'}^{m'}$, the polarizability tensor may be defined as $\alpha_{ll'}^{mm'} = (\partial\mu_l^m/\partial f_{l'}^{m'})_{f=0}$. According to second-order perturbation theory, the tensor components $\alpha_{ll'}^{mm'}$ are associated with the operators

$$T_{ll'}^{mm'} = Q_l^m R_{AL} Q_{l'}^{m'} + Q_{l'}^{m'} R_{AL} Q_l^m\,,$$

where

$$R_{AL} = \left(1 - \sum_M |ALM\rangle\langle ALM|\right) / (\langle ALM|\hat{H}|ALM\rangle - \hat{H})\,.$$

The quantization axis for the atomic states $|ALM\rangle$ can be chosen in such a way that the first-order interaction matrix is diagonal only in the case $L=1$ or for special forms of the external potential. In general, the nondegenerate eigenfunctions will have the form $\sum_M c_M|ALM\rangle$ and the calculation of the second-order (induction) energy requires all matrix elements $\langle ALM|T_{ll'}^{mm'}|ALM'\rangle$.

Then, as usual,[14] we may introduce the standard components of the tensor operator $T_{ll'}^{mm'}$ by

$$T_{ll',l''}^{m''} = \sum_m \langle ll'm(m''-m)|l''m''\rangle T_{ll'}^{m,m-m''}\,,$$

and all matrix elements $\langle ALM|T_{l''}^{m''}|ALM'\rangle$ can be calculated by the Wigner-Eckart theorem from reduced matrix elements

$$\langle ALM|T_{l''}^{m''}|ALM'\rangle = (2L+1)^{-1/2}\langle Ll''M'm''|LM\rangle\langle AL||T_{ll',l''}||AL\rangle\,.$$

If we now define the standard polarizabilities by

$$\alpha_{ll',l''} = (-)^{(l+l'-l'')/2}\langle AL||T_{ll',l''}||AL\rangle\,,$$

arbitrary matrix elements of T are given by

$$\langle ALM | T_{ll'}^{mm'} | ALM' \rangle = \sum_{l''} (-)^{L-M'+(l+l'-l'')/2} (2l''+1)^{-1/2} \times \delta_{M-M', m+m'} \langle LLM(-M)' | l''M-M' \rangle \times \langle ll'mm' | l''m+m' \rangle \alpha_{ll', l''} .$$

Nonzero contributions require l'' even and

$$|l-l'| \leq l'' \lesssim \min(l+l', 2L).$$

The standard polarizabilities $\alpha_{ll', l''}$ are directly connected with the mean polarizabilities ($l'' = 0$) and polarization anisotropies ($l'' \neq 0$). Thus, for the former, one finds

$$\overline{\alpha}_{ll'}(AL) = (-)^m (2L+1)^{-1} \sum_{M} \langle ALM | T_{ll'}^{m-m} | ALM \rangle = \delta_{l,l'} \alpha_{ll,0} (2L+1)^{-1/2} (2L+1)^{-1/2}.$$

The anisotropy for $L = 1$ states is usually defined as

$$\Delta\alpha_{ll'}(A1) = \langle A11 | T_{ll'}^{00} | A11 \rangle - \langle A10 | T_{ll'}^{00} | A10 \rangle = (-)^{(l+l')/2+1} \left(\tfrac{3}{10}\right)^{1/2} \langle ll'00 | 20 \rangle \alpha_{ll', 2} .$$

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