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Local Polarizabilities in Molecules, Based on *ab initio* Hartree–Fock Calculations

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A method to separate the total molecular polarizability, calculated in the uncoupled Hartree–Fock approximations, into local contributions is proposed. The method is tested for H_2, H_2O, H_2CO and C_6H_6 and the results are discussed. It is found that the ratio of the polarizability contributions for two atoms in a molecule almost only depends on the type of atoms and is almost independant of molecule.

Key words: Local polarizabilities – Uncoupled Hartree–Fock – Induction energy.

1. Introduction

The study of intermolecular interactions by means of theoretical chemical methods has increased drastically during the past ten years and several reviews have been published on different aspects of the subject. Recently a series of volumes that will cover both theoretical and experimental work on intermolecular interactions [1] has started being published and the reader is referred to the references given therein for a review of the subject.

From the theoretical point of view, two basically different approaches are possible, one is the straightforward *ab initio* or semi-empirical supermolecule approach and the other is an approach based on perturbation theory. In both schemes it is possible to partition the interaction energy into contributions that have physical meaning [2–5]. Different partioning schemes give different terms but most schemes have the first four terms in Eq. (1) in common:

$$\Delta E = \Delta E_{\mathrm{COU}} + \Delta E_{\mathrm{EXREP}} + \Delta E_{\mathrm{IND}} + \Delta E_{\mathrm{DISP}} + \Delta E_{\mathrm{MIX}}. \tag{1}$$

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Here COU stands for coulomb or electrostatic, EXREP for exchange repulsion, IND for induction and DISP for dispersion. The last term contains all interactions that are not included in the other terms. This term is usually small. The first two terms in Eq. (1) are basically of first order in a perturbation approach and often give the major contributions to the interaction energy.

However for some systems the second order terms may be equally important. Especially, this is so for the interaction between non-polar molecules, where the dispersion interaction is the dominating binding force [6], but also for the interaction between polar and non-polar molecules where both dispersion and induction forces may be important. Even for polar molecules the induction and dispersion interactions may give important contributions to the total binding energy since the two first order terms have different signs.

The two second order terms mentioned above are dependent on the polarizabilities of the interacting molecules, and may be estimated if the static and dynamic polarizabilities and charge distributions of the interacting molecules are known. However, for a large molecule a description based on considering the interacting molecules as point polarizabilities seems less adequate. In this work two schemes for separating the total polarizabilities into local contributions, based on *ab initio* molecular orbital calculations will be discussed. The problem of dividing the total polarizability into local contributions has been considered by LeFevre and LeFevre [7], who used the concept of bond polarizabilities which later has been used for semiempirical estimates of the dispersion interaction by Kołos [8].

2. Theory

Below the theoretical background for the calculation of the local contributions of the polarizability tensor will be presented. Throughout this section it is assumed that the uncoupled Hartree-Fock (UCHF) approximation is used, leading to the following expression for one component of the polarizability tensor:

$$P_{xx'} = 4 \sum_{i,j} \frac{\langle \psi_i | x | \psi_j \rangle \langle \psi_i | x' | \psi_j \rangle}{\varepsilon_j - \varepsilon_i}. \tag{2}$$

Here ψ_i is an occupied orbital in the unperturbed system and ψ_j a virtual orbital. These orbitals are expanded as linear combinations of a set of basis functions. It is then possible to define a center (usually an atom) to which each basis function belongs. If we number the centers by K and the basis functions of this center by k_K we may write

$$\psi_i = \sum_K \sum_{k_K} C_{ik_K} \chi_{k_K}. \tag{3}$$

If Eq. (3) is introduced into Eq. (2) one obtains

$$P_{xx'} = 4 \sum_{i,j} \frac{1}{\varepsilon_j - \varepsilon_i} \sum_K \sum_{k_K} \sum_L \sum_{l_L} \sum_M \sum_{m_M} \sum_N \sum_{n_N} C_{ik_K} C_{jl_L} C_{im_M} C_{jn_N}$$

$$\langle \chi_{k_K} | x | \chi_{l_L} \rangle \langle_{m_M} | x' | \chi_{n_N} \rangle. \tag{4a}$$

From Eq. (4a) it is easily seen that the total polarizability can be separated into contributions with four indices referring to different centers according to Eq. (4b)

$$P_{xx'}^{ABCD} = 4\sum_{i,j}\frac{1}{\varepsilon_j-\varepsilon_i}\sum_{k_A}\sum_{l_B}\sum_{m_C}\sum_{n_D} C_{ik_A}C_{jl_B}C_{im_C}C_{jn_D} \langle\chi_{k_A}|x|\chi_{l_B}\rangle\langle\chi_{m_C}|x'|\chi_{n_D}\rangle. \tag{4b}$$

Using Eq. (4b) one may define one and two center local polarizabilities by summation over nuclear indices. It should however be observed that the four indices k_A, l_B, m_C and n_D are not equivalent, since k_A and l_B refer to occupied orbitals and n_C and m_D to virtual orbitals. Considering that the virtual orbitals giving the largest contributions to the polarizabilities are quite diffuse, the partitioning of these orbitals into local contributions seems less meaningful, and one is tempted to perform the summation over the virtual orbitals first.

One then obtains

$$P_{xx'}^{AC} = \sum_{B}\sum_{D} P_{xx'}^{ABCD} \tag{5a}$$

$$P_{xx'}^{A} = \sum_{B}\sum_{C}\sum_{D} P_{xx'}^{ABCD}. \tag{5b}$$

Another way to proceed would be to sum over C and D leading to Eq. (6):

$$P_{xx'}^{AB} = \sum_{C}\sum_{D} P_{xx'}^{ABCD} = 4\sum_{i,j}\frac{1}{\varepsilon_j-\varepsilon_i}\sum_{k_A}\sum_{l_B} C_{i,k_A}C_{j,l_B} \langle\chi_{k_A}|x|\chi_{l_B}\rangle\langle\psi_i|x'|\psi_j\rangle. \tag{6a}$$

It could easily be shown that Eq. (6a) is equivalent to

$$P_{xx'}^{AB} = 2\sum_{k_A l_B} \Delta D_{k_A l_B}^{x'} \langle\chi_{k_A}|x|\chi_{l_B}\rangle \tag{6b}$$

where $\Delta D_{k_A l_B}^{x'}$ is the change in density matrix element $k_A l_B$ due to an electric field in the x' direction. The advantage of Eq. (6b) is that it in contrast to Eq. (5) is generalizable to variational calculations. The proposed schemes are however not unique and it should be noted that the calculated local polarizabilities are dependent on the choice of origin. This is easily understood from the fact that the integral $\langle\chi_i|x|\chi_j\rangle$ is invariant to changes in origin due to the orthogonality of χ_i and χ_j, but this is not true for the contribution to the integral from basis functions located on a pair of centers since

$$\sum_{k_A}\sum_{l_B} C_{i,k_A}C_{j,l_B}\langle\chi_{k_A}|\chi_{l_B}\rangle \neq 0. \tag{7}$$

In Table 1 the calculated values for the local polarizabilities obtained with Eqs. (5) and (6a), if the transition dipoles $\langle\chi_i|x|\chi_j\rangle$ are expanded around the center of symmetry, are given together with the values obtained with Eq. (5) if one of the hydrogen atoms is taken as origin for the calculation. It is seen that the local polarizabilities depend rather strongly on the choice of origin. This ambiguity

Table 1. Local polarizabilities obtained according to Eqs. (5) and (6a) for the H_2 molecule (in a.u.)[a]

	Eq. (5)				Eq. (6)	
	Origin at the center of mass		Origin in H_2		Origin at the center of mass	
Centers	$P_\parallel$	$P_\perp$	$P_\parallel$	$P_\perp$	$P_\parallel$	$P_\perp$
H_1H_1	1.291	0.233	1.957	0.233	2.936	0.268
H_1H_2	1.175	0.195	1.097	0.195	−0.470	0.160
H_2H_2	1.291	0.233	0.779	0.233	2.936	0.268
H_1	2.466	0.438	3.055	0.438		
H_2	2.466	0.438	1.877	0.438		
Tot.	4.932	0.876	4.932	0.876	4.932	0.876

[a] See Ref. [12] for basis set information.

is however removed by expanding the transition dipoles around their center of charge χ_{ij} defined by [9]

$$X_{ij}=\tfrac{1}{2}(X_i+X_j) \tag{8}$$

where X_i is the center of charge for orbital i.

A consequence of the need of defining different origins for different transition dipoles is that the possibility of transforming Eq. (6a) into Eq. (6b) is lost and thus it seems most reasonable to use Eq. (5) together with Eq. (8) as a definition of the local polarizabilities.

3. Results and Discussions

We have in the previous sections discussed the importance of molecular polarizabilities for the understanding of intermolecular interactions, and the possibility of dividing the total polarizability into local contributions. In this paragraph the local polarizabilities, for a few molecules, calculated in the UCHF approximation will be presented and discussed.

In Tables 2–5 we present the results obtained according to Eq. (5) and Eq. (8) for H_2, H_2O, H_2CO and C_6H_6. In general it could be stated that the quality of the basis sets is such, that the UCHF-limit polarizabilities should be reproduced within 10%. Consequently the local polarizabilities obtained for different molecules should be comparable and a few remarks may be made.

1. The polarizability of an atom in the direction of a bond is usually larger than that perpendicular to the bond. (The oxygen atom in water is an exception, probably due to its lone-pair electrons.)
2. The ratio of the traces of the polarizability tensors between two kinds of atoms in the same molecule is almost constant for the studied molecules.
3. The negative polarizabilities that are obtained for bond electrons in systems with double bonds have a complex origin, but can to some extent be understood

Table 2. Local polarizabilities for the H_2 molecule calculated according to Eqs. (5) and (8). Only symmetry unique contributions are given. Atomic units are used[a]

Centers	$P_{\parallel}$	$P_{\perp}$	$P_{\parallel}+2P_{\perp}$
H_1H_1	1.33	0.75	2.83
H_1H_2	1.11	0.65	2.41
H_1	2.44	1.39	5.23
Tot.	4.88	2.79	10.46

[a] See Ref. [13] for basis set information.

Table 3. Local polarizabilities for the H_2O molecule calculated according to Eqs. (5) and (8). Only symmetry unique contributions are given. Atomic units are used[a]

Centers	P^b_{xx}	P^b_{yy}	P^b_{zz}	Tr	
OO	3.03	4.42	3.88	0.00	11.33
OH_1	0.43	0.20	0.41	0.39	1.04
H_1H_1	1.22	0.35	0.51	0.25	2.08
H_1H_2	0.08	0.02	0.05	0.00	0.15
O	3.89	4.82	4.70	0.00	13.41
H	1.73	0.56	0.97	0.64	3.26
Tot.	7.35	5.94	6.64	0.00	19.93

[a] See Ref. [14] for basis set information.

[b] The molecule is placed in the *xz* plane with the C_2-symmetry axis along the *z* axis.

Table 4. Local polarizabilities for the H_2CO molecule calculated according to Eqs. (5) and (8). Only symmetry unique contributions are given. Atomic units are used[a]

Centers	P^b_{xx}	P^b_{yy}	P^b_{zz}	P^b_{xz}	Tr
OO	7.73	6.66	7.73	0.00	21.12
OC	−2.98	−0.73	1.18	0.00	−2.53
OH_1	−0.17	−0.10	0.38	−0.13	0.11
CC	5.12	4.02	3.60	0.00	12.74
CH_1	1.04	0.48	0.44	−0.16	1.96
H_1H_1	1.22	0.34	0.83	−0.65	2.39
H_1H_2	0.26	−0.04	0.00	0.00	0.22
O	4.41	5.73	9.67	0.00	19.81
C	4.21	4.24	5.67	0.00	14.12
H_1	2.35	0.68	1.66	−0.94	4.69
Tot.	13.32	11.35	18.66	0.00	43.33

[a] See Ref. [15] for basis set information.

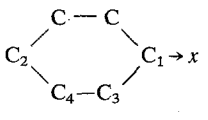
[b] The molecule is placed in the *xz* plane and the C_2-symmetry axis is along the *z* axis.

Table 5. Local polarizabilities for benzene calculated according to Eqs. (5) and (8). Only symmetry unique contributions are given. Atomic units are used[a]

Centers	P^{b}_{xx}	P^{b}_{yy}	P^{b}_{zz}	P^{b}_{xy}	Tr
C_1C_1	11.38	1.98	4.75	0.00	18.11
C_1C_2	2.48	0.33	−0.59	0.00	2.22
C_1C_3	−0.68	0.80	1.17	−1.29	1.29
C_1C_4	0.30	0.26	−0.20	−0.02	0.36
C_1H_1	−1.23	0.47	0.38	0.00	−0.38
C_1H_2	0.01	0.00	−0.01	0.00	0.00
C_1H_3	−0.15	0.05	−0.05	−0.10	−0.15
C_1H_4	0.11	0.04	−0.04	−0.05	0.11
H_1H_1	7.38	0.67	0.52	0.00	8.57
H_1H_2	−0.01	0.00	0.01	0.00	0.00
H_1H_3	−0.11	−0.01	0.02	0.09	−0.10
H_1H_4	0.05	0.01	0.01	−0.03	0.07
C_1	11.74	5.04	6.26	0.00	23.04
H_1	6.01	1.18	0.76	0.00	7.95
Tot.	71.91	71.91	42.12	0.00	196.04

[a] See Ref. [16] for basis set information.

[b] The molecule is placed in the xy plane. The carbon atoms are numbered according to



and the hydrogen atoms in a similar way.

from the nodal structure and the polarity of the orbitals, but also the non-orthogonality of the basisfunctions is of importance.

We may finally conclude that the proposed partitioning scheme is also reasonable from the point of view that the local polarizabilities are large for atoms with many electrons and smaller for atoms with fewer. A more rigorous test would be to see if it is possible to obtain good intermolecular potentials with their aid. One may not expect drastic effects for systems consisting of small molecules and since accurate intermolecular potentials only exists for such systems it is not possible at present to judge the efficiency of the proposed schemes.

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12. A basis set consisting of (5s, 1p, 1d) contracted to [3s, 1p, 1d] is used [10], with a p exponent of 0.8 and a d exponent of 1.0
13. The basis set referenced in Table 1 has been augmented with one diffuse s, p, d function
14. A basis set of (9s, 5p) basis functions contracted to (5s, 3p) [11] which has been augmented with 2 diffuse s functions, 2 diffuse p functions, and 1 valence and 1 diffuse d function has been used used for oxygen and a basis set of (5s) basis functions contracted to 3s [10] which has been augmented with 1 diffuse s function and 1 valence and 1 diffuse p function, has been used for hydrogen
15. The basis set for hydrogen is the same as was in water. The basis set used for C and O is similar to that used for O in the water calculation except that one diffuse s and p function less has been added to the original basis set
16. A basis set consisting of (9s, 5p) contracted to (4s, 2p) [11] and augmented with 1 diffuse s and p function and 1 valence d function has been used for C, and a 5s basis set contracted to 2s and augmented with a valence p orbital has been used for hydrogen

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