Topologically partitioned dynamic polarizabilities using the theory of atoms in molecules

Christof Hättig, Georg Jansen, Bernd A. Heß, and János G. Ángyán

Abstract: Frequency-dependent distributed polarizabilities have been determined from time-dependent Hartree–Fock calculations, using the partitioning of the molecular space suggested by Bader's topological theory of atoms in molecules. The basis set dependence of the distributed dynamic polarizabilities is analyzed in terms of the first few Cauchy moments, for the carbon monoxide, water, cyanogen, urea and benzene molecules. Two alternative relocalization schemes have been considered in order to reduce the number of distributed dynamic polarizability parameters. The first one, closely related to the atomic polarizability model of Bader, leads to atomic charge–dipole and dipole–dipole polarizabilities, describing the response of the molecular charge distribution to a uniform external field, in terms of atomic charges and dipoles. The second scheme, similar to that suggested by Stone, retains the fully distributed description of the dynamic charge-flow polarizabilities, while all two-center dipole–dipole and charge–dipole contributions are condensed in one-center dynamic dipole–dipole polarizabilities.

Key words: Bader-partitioning, distributed dynamic polarizabilities, Cauchy-moments, benzene, polarizability of; urea, polarizability of.

Résumé : Faisant appel à des calculs de Hartree–Fock dépendant du temps et utilisant la partition de l'espace moléculaire suggérée par la théorie topologique des atomes dans les molécules de Bader, nous avons déterminé des polarisabilités dynamiques distribuées. L'influence de la base a éte analysé en termes des premiers moments de Cauchy pour les molécules suivantes : monoxyde de carbone, eau, cyanogène, urée et benzène. Afin de réduire le nombre des paramètres de polarisabilité dynamique distribuée, deux méthodes alternatives de relocalisation ont été considérées. La première, qui est fortement apparentée au modèle de polarisabilité atomique de Bader, conduit aux polarisabilités atomiques charge–dipôle et dipôle–dipôle décrivant la réponse de la distribution de charge moléculaire à un champ externe uniforme en termes de charges et de dipôles atomiques. Le deuxième méthode, semblable à celle suggérée par Stone, maintient la description totalement distribuée des polarisabilités dynamique de flux de charges, alors que toutes les contributions dipôle–dipôle et charge–dipôle à deux centres sont réduites à des polarisabilités dynamiques dipôle–dipôle à un centre.

Mots clés : méthode de partition de Bader, polarisabilités dynamiques distribuées, moments de Cauchy, polarisabilité du benzène, polarisabilité de l'urée.

[Traduit par la rédaction]

I. Introduction

Frequency-dependent (dynamic) multipole polarizabilities, which describe the response of a molecular system under the influence of a time-dependent external multipolar field, play an important role in the interpretation of many physical phenomena. They contain information concerning, for example, the refractive index, Rayleigh scattering cross sections, and Raman intensities (1, 2), etc. Dynamic polarizabilities, taken at imaginary frequencies, can be used to calculate long-range dispersion coefficients (3), which are of outstanding importance in the theory of intermolecular interactions. Since dynamic polarizability tensors are difficult to measure experimentally, there is an increasing demand for the reliable theoretical calculation of their components.

The dynamic charge density susceptibility function, $\alpha(\boldsymbol{r},\boldsymbol{r}';\omega)$, describes the linear response of a molecular charge distribution to an arbitrary time-dependent external field (4). The multipole components of a molecular dynamic polarizability tensor, $\alpha_{lm,l'm'}(\omega)$, are related to the dynamic charge density susceptibility function via the following relationship:

$$[1] \qquad \alpha_{lm,l'm'}(\omega) = \int\int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' R^0_{lm}(\boldsymbol{r})\alpha(\boldsymbol{r},\boldsymbol{r}';\omega)R^0_{l'm'}(\boldsymbol{r}')$$

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C. Hättig and B.A. Heß. Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, D-53115 Bonn, Germany.
G. Jansen and J.G. Ángyán.[1] Laboratoire de chimie théorique, Université Henri Poincaré, Unité de recherche associée au Centre national de la recherche scientifique, nº 510, B.P. 239, F-54506 Vandœuvre-lès-Nancy Cedex, France.

[1] Author to whom correspondence may be addressed. Fax: +33.83.91.25.30. E-mail: angyan@lctn.u-nancy.fr

where $R^0_{lm}(\boldsymbol{r}) = R_{lm}(\boldsymbol{r} - \boldsymbol{R}_0)$ is a regular solid harmonics, taken with respect to the molecular origin $\boldsymbol{R}_0$. Obviously, by taking the above integral over the molecular volume, a certain amount of information about the details of the spatial distribution of response properties is lost. This can be a nuisance, especially in the case of relatively large, extended molecular systems. The difficulty can partially be circumvented by the concept of *distributed* polarizabilities (5), by attributing specific response parameters to atoms and to pairs of atoms (or functional groups) in the molecule. The formal definition of distributed dynamic polarizabilities involves double integration over the volumes Ω_A and Ω_B, corresponding to atoms or functional groups of the molecule:

$$[2] \qquad \alpha^{AB}_{lm,l'm'}(\omega) = \int_{\Omega_A}\int_{\Omega_B} d\boldsymbol{r}d\boldsymbol{r}' R^A_{lm}(\boldsymbol{r})\alpha(\boldsymbol{r},\boldsymbol{r}';\omega)R^B_{l'm'}(\boldsymbol{r}')$$

Once the atomic volumes, Ω_A, are defined, we have, by virtue of eq. [2], an exact partitioning of the total dynamic polarizabilities, eq. [1]. Thus the response of the molecular charge density to an external non-uniform field is described by atomic charges, dipoles (multipoles, ${}^{ind}Q^A_{lm}$, in general), induced by a set of multipolar field components, $F^B_{l'm'}$, acting at atom B. Accordingly, we can speak of charge–charge (charge-flow) polarizabilities, corresponding to atomic charges induced by the differences in the external potential at different atoms, charge–dipole polarizabilities, describing the atomic charge induced by the external field at different atoms, etc. Charge–multipole polarizabilities satisfy the following sum rule (5):

$$[3] \qquad \sum_A \alpha^{AB}_{00,lm} = 0$$

reflecting the fact that the effect of an external perturbation cannot change the total charge of the system.

The theory of atoms in molecules (AIM) of Bader (6, 7) constitutes an excellent general framework to partition properties of molecular systems into atomic contributions. Atomic regions, Ω_A, surrounded by the atomic surface, $S_A(\boldsymbol{r})$, are defined in an unambiguous manner on the basis of the topological features of the electron density, by the zero-flux condition $\nabla\rho(\boldsymbol{r}) \cdot \boldsymbol{n}(\boldsymbol{r}) = 0$ for $\forall \boldsymbol{r} \in S_A(\boldsymbol{r})$. Application of the principle of stationary action to these atomic regions, in fact open quantum subsystems, leads to a complete quantum mechanical description of their properties. Furthermore, it has been shown (6) that the topological definition of atoms and functional groups (as an assembly of atoms) allows one to maximize the transferability of their properties between various systems.

Application of the topological definition of atoms to partition static (zero-frequency) polarizabilities leads to a consistent set of distributed static polarizability parameters, free of any physically unjustified basis set dependence (8). In fact, distributed polarizability parameters, as obtained by various basis set partitioning schemes, were not stable enough with respect to extension of the basis set: for example, in extended basis sets the charge-flow polarizabilities became extremely large (9). Topologically partitioned polarizabilities do not vary more strongly with the basis set than do the total polarizability components. Furthermore, a recent study on a series of hydrocarbons confirms the transferability of these topologically distributed static polarizabilities (10). Calculation of intermolecular induction energies has shown that the fully distributed description leads to reasonable interaction energies even in those cases where the molecule-centered expansion of electrostatic and induction energies fails completely (11) (e.g., for the cyanogen dimer).

One-center atomic polarizabilities have been investigated recently by Bader and co-workers (12–14) by finite perturbation techniques. In contrast to the fully distributed polarizabilities, which, due to their nonlocal character, are able to describe the charge density response to a non-uniform external field, Bader's atomic polarizabilities

$$[4] \qquad \alpha^{A,mol}_{lm,l'm'}(\omega) = \int_{\Omega_A}\int d\boldsymbol{r}d\boldsymbol{r}' R^A_{lm}(\boldsymbol{r})\alpha(\boldsymbol{r},\boldsymbol{r}';\omega)R^0_{l'm'}(\boldsymbol{r}')$$

give the atomic multipole, ${}^{ind}Q^A_{lm}$ induced by an external field component $F_{l'm'}$ applied globally to the molecule at its origin. Therefore it is justified to call these quantities "atom–molecule" polarizabilities. For example, the application of a uniform external field F_β gives rise to induced atomic charges and dipoles, which are described by the $\alpha^{A,mol}_{q\beta}$ and $\alpha^{A,mol}_{\alpha\beta}$ charge–dipole and dipole–dipole atom–molecule polarizabilities. To cope with empirical additivity schemes, based on atomic dipole–dipole polarizabilities, the charge–dipole contributions have to be converted to atomic dipole–dipole polarizabilities (13). Unfortunately, there is no unique way to do that; therefore each case should be carefully examined in order to obtain chemically meaningful atomic polarizabilities, as has been done for hydrocarbons (14). Although Bader's atomic polarizabilities are conceptually very helpful in developing additivity and transferability schemes for atomic and group contributions, they are probably less appropriate for the calculation of intermolecular interactions, where molecules are subject to non-uniform external fields.

The present paper extends our earlier study of distributed static polarizabilities (8) to their dynamic counterparts. After a brief overview of the most important working equations, we are going to examine the basis-set sensitivity of topologically partitioned dynamic polarizability components, represented by their Cauchy moments. Since the main goal of our study is to explore the behaviour of the topological partitioning scheme, it has been judged sufficient to calculate Cauchy moments at the simple TDHF (time-dependent Hartree–Fock) level. A simple algorithm, inspired by the scheme proposed by Le Sueuer and Stone (15), is given for partial relocalization of the fully distributed nonlocal Cauchy moments, allowing us to reduce considerably the number of parameters characterizing the dynamic response properties of a molecular system.

II. Method

In full analogy with its molecular counterpart, a distributed dynamic polarizability component for real wave functions, taken at the real frequency, ω, is defined as

$$[5] \qquad \alpha^{AB}_{lm,l'm'}(\omega) = \sum_{n\neq 0} \frac{2(E_n - E_0)\langle 0|\hat{Q}^A_{lm}|n\rangle\langle n|\hat{Q}^B_{l'm'}|0\rangle}{(E_n - E_0)^2 - \omega^2}$$

$$= \sum_{n\neq 0} \frac{f^{AB}_{lm,l'm'}(n)}{(E_n - E_0)^2 - \omega^2}$$

and it can be expanded in a Cauchy power series:

$$[6] \qquad \alpha^{AB}_{lm,l'm'}(\omega) = \sum_{k=0}^{\infty} \omega^{2k} S^{AB}_{lm,l'm'}(-2k-2)$$

where the distributed Cauchy moments (16), $S^{AB}_{lm,l'm'}(k)$, are given by the sum-over-states formula:

$$[7] \qquad S^{AB}_{lm,l'm'}(k) = \sum_{n\neq 0} (E_n - E_0)^k f^{AB}_{lm,l'm'}(n)$$

and $f^{AB}_{lm,l'm'}(n)$ denotes the generalized oscillator strengths of the transition between the ground and the nth electronic state $|n\rangle$, with energy E_n. Static polarizabilities correspond to Cauchy moments of order -2:

$$\alpha^{AB}_{lm,l'm'}(0) = S^{AB}_{lm,l'm'}(-2)$$

In the time-dependent Hartree–Fock approximation the dynamic polarizability components can be obtained by solving the following generalized eigenvalue problem (17):

$$[8] \qquad (\boldsymbol{A}+\boldsymbol{B})C_n = \omega^2_{on}(\boldsymbol{A}-\boldsymbol{B})^{-1}C_n$$

for the TDHF excitation energies, ω_{on} and amplitudes, C_n, which are normalized according to $C_n^T(\boldsymbol{A}-\boldsymbol{B})C_n = 1$. The matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ are defined in terms of occupied i,j and virtual a,b orbitals, as usual:

$$[9] \qquad A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ab}\delta_{ij} + 2(ai|jb) - (ab|ij)$$

$$B_{ia,jb} = 2(ai|bj) - (bi|ja)$$

The generalized oscillator strengths are given in this approach by

$$[10] \qquad f^{AB}_{lm,l'm'}(n) = 2\sum_{ia}(i|\hat{Q}^A_{lm}|a)C_{ia,n}\sum_{jb}(j|\hat{Q}^B_{l'm'}|b)C_{jb,n}$$

and they can be used directly to calculate dynamic polarizabilities at a given frequency ω, with the help of expressions [5] and [7], respectively.

The atomic multipole moment operators, $\hat{Q}^A_{lm}$, are defined by their matrix elements:

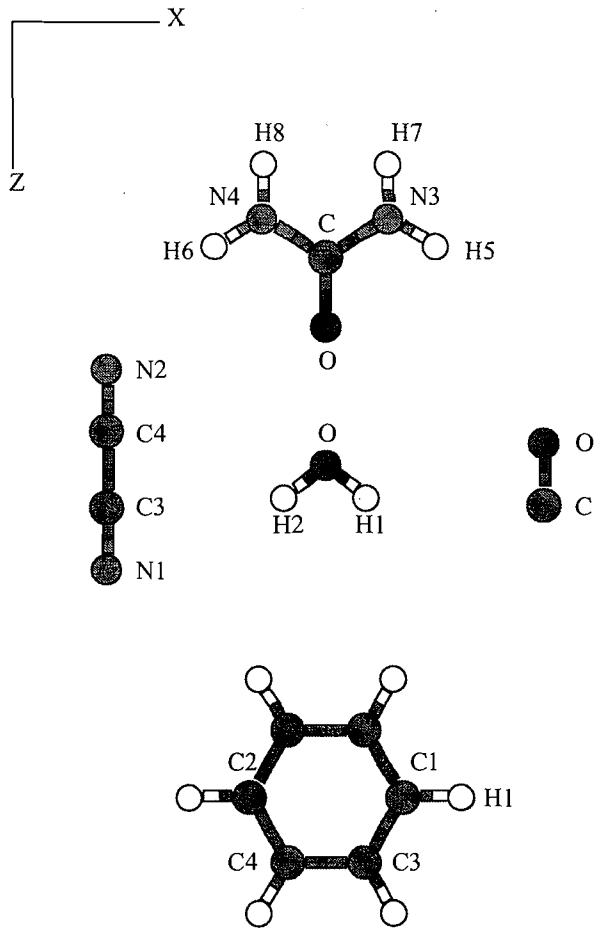
$$[11] \qquad (i|\hat{Q}^A_{lm}|a) = \int_{\Omega_A} d\boldsymbol{r}\phi^*_i(\boldsymbol{r})R^A_{lm}(\boldsymbol{r})\phi_a(\boldsymbol{r})$$

where the volume of integration extends over the atomic basin, limited by a zero-flux surface of the unperturbed molecule.

Total molecular Cauchy moments can be calculated either by replacing the atomic transition integrals in expression [11] by molecular ones, or by reconstituting them from distributed Cauchy moments via translation of the atomic components to the common molecular origin (5).

A series of molecules, carbon monoxide, water, cyanogen, urea, and benzene, has been selected to study the basis-set sensitivity of the frequency-dependent distributed polarizabilities, by examining the behavior of Cauchy moments in five different contracted Gaussian type orbital (CGTO) basis sets.

Fig. 1. Orientation of the molecules in the coordinate frame.



Calculations on CO, H_2O, cyanogen (NCCN), and benzene were done at their experimental gas-phase geometries (18–20). In the case of urea, a planar geometry was used, determined by low-temperature neutron-diffraction measurements (21) of the crystal. The orientation of the molecules is defined in Fig. 1.

Self-consistent field (SCF) calculations were performed with the MOLCAS program (22). We have used the 6-31G** valence double-zeta polarization, the 6-311G(2d,2p) valence triple-zeta double polarization, and the 6-311++G(2d,2p) valence triple-zeta double polarization plus diffuse functions basis sets. The polarization basis set of Sadlej (23), optimized for molecular polarizabilities and electrostatic properties, consists of (6s4p)/[3s2p] and (10s6p4d)/[5s3p2d] contracted sets for H and other atoms, respectively. The largest basis set in our study was derived from that of Widmark et al. (24) by keeping the same exponents. Only the innermost three s- and two p-functions were contracted for the hydrogen atom, resulting in a (8s4p)/[6s3p] CGTO set, and for the other atoms we contracted only the innermost five s-, four p-, and two d-functions, thus yielding (14s9p4d)/[10s6p3d] sets. This basis set contains also the diffuse functions essential for a reliable prediction of polarization properties. Except for the case of 6-31G** basis set, five-component d-functions were always employed.

Table 1. Cauchy moments (in au) calculated with various basis sets, compared to CDOSD, experimental, or theoretical values.

Component	6-31G**	6-311G(2d,2p)	6-311++G(2d,2p)	[5s3p2d]	[10s6p3d]	Literature
CO						
$S_{xx}(-2)$	7.766	9.335	10.069	11.089	11.255	11.89[a]
$S_{xx}(-4)$	28.686	31.833	38.432	41.459	41.806	46.61[a]
$S_{xx}(-6)$	207.822	219.815	270.726	275.343	277.421	301.4[a]
$S_{zz}(-2)$	12.237	12.759	14.313	14.435	14.447	15.46[a]
$S_{zz}(-4)$	26.557	28.821	40.581	41.178	41.224	51.56[a]
$S_{zz}(-6)$	68.251	77.617	143.372	145.178	145.770	275.7[a]
$\bar{S}(-2)$	9.256	10.476	11.484	12.204	12.299	13.08[a]
$\bar{S}(-4)$	27.976	30.829	39.148	41.365	41.612	48.26[a]
$\bar{S}(-6)$	161.298	172.415	228.275	231.955	233.537	292.9[a]
H_2O						
$S_{xx}(-2)$	7.024	7.945	8.269	9.167	9.153	9.68[b]
$S_{xx}(-4)$	16.145	16.215	17.613	20.894	20.716	
$S_{xx}(-6)$	49.603	47.597	52.015	60.631	60.145	
$S_{yy}(-2)$	2.928	4.873	6.681	7.821	7.855	9.19[b]
$S_{yy}(-4)$	4.623	11.244	21.747	25.679	25.884	
$S_{yy}(-6)$	30.644	80.289	152.013	164.178	170.006	
$S_{zz}(-2)$	5.108	6.519	7.180	8.488	8.438	9.47[b]
$S_{zz}(-4)$	11.514	14.030	17.814	22.637	22.276	
$S_{zz}(-6)$	45.422	58.102	81.464	93.415	92.753	
$\bar{S}(-2)$	5.020	6.446	7.377	8.492	8.482	9.642[c]
$\bar{S}(-4)$	10.761	13.830	19.058	23.070	22.959	35.42[c]
$\bar{S}(-6)$	41.890	61.996	95.164	106.075	107.635	240.1[c]
NCCN						
$S_{xx}(-2)$	13.467	17.345	18.618	21.128	21.635	
$S_{xx}(-4)$	34.741	39.111	51.580	63.180	62.464	
$S_{xx}(-6)$	174.000	170.119	260.312	287.172	279.676	
$S_{zz}(-2)$	48.388	48.818	52.487	52.694	52.682	
$S_{zz}(-4)$	239.897	247.833	293.798	295.554	295.975	
$S_{zz}(-6)$	1407.708	1493.164	1916.611	1933.662	1940.971	
$(NH_2)_2CO$						
$S_{xx}(-2)$	27.592	31.048	33.070	35.910	35.947	38.152[d]
$S_{xx}(-4)$	77.715	91.748	113.048	127.305	127.379	
$S_{xx}(-6)$	338.232	431.891	645.837	722.183	729.192	
$S_{yy}(-2)$	12.211	17.556	22.654	24.451	24.465	26.007[d]
$S_{yy}(-4)$	13.128	30.385	67.873	73.931	73.737	
$S_{yy}(-6)$	35.348	129.243	401.943	425.506	426.063	
$S_{zz}(-2)$	30.018	32.239	35.491	37.269	37.252	39.661[d]
$S_{zz}(-4)$	89.383	94.754	127.309	138.619	138.591	
$S_{zz}(-6)$	452.368	487.789	801.181	871.198	879.491	
Benzene						
$S_{xx}(-2)$	70.536	74.869	78.528	80.216		
$S_{xx}(-4)$	417.986	463.618	543.681	560.331		
$S_{xx}(-6)$	4128.978	4834.773	6286.459	6408.163		
$S_{yy}(-2)$	21.382	31.929	44.817	45.784		
$S_{yy}(-4)$	21.857	59.189	205.160	210.467		
$S_{yy}(-6)$	43.236	253.599	1696.201	1750.928		
$\bar{S}(-2)$	54.151	60.556	67.291	68.739		67.79[e]
$\bar{S}(-4)$	285.943	328.808	430.841	443.710		430.4 [e]
$\bar{S}(-6)$	2767.064	3307.715	4756.373	4855.751		4932[e]

[a]CDOSD data (27).
[b]From rotational Raman spectra (30).
[c]CDOSD data (28).
[d]RAS-SCF linear response calculations (31).
[e]CDOSD data (29).

Cauchy moments and dynamic polarizabilities at fixed values of the frequency were calculated with a self-written TDHF program that uses the necessary transformed two-electron integral blocks produced by either a nonstandard link after a closed-shell SCF run of Gaussian 92 (25), or by the MOLCAS-2 suite of programs (22). Our code makes use of eq. [8] and thus inversion of the $(\boldsymbol{A} - \boldsymbol{B})$ matrix is required. This becomes prohibitive for cases with many single excitations. Due to the implementation of Abelian point group symmetries in our code (available when working with MOLCAS), we were able to treat all molecules even with the large [10s6p3d] basis set, except for benzene, where this basis set had to be left out. The occupied/virtual one-electron integral blocks of the distributed moments were generated by a modified version of the Proaim program (26).

III. Results and discussion

The first three molecular Cauchy moments, $S(-2), S(-4)$, and $S(-6)$, which enter in the power series expansion for the dynamic polarizability as calculated by the five basis sets, are listed in Table 1. In the case of CO, H_2O, and C_6H_6 they are compared with the available data obtained by the CDOSD (constrained dipole oscillator strength distribution) method of Meath and co-workers (27–29). Anisotropic static polarizabilities were taken from the experimental data of Murphy (30) for water, and from the theoretical calculations of Sanchez de Merás et al. (31) for urea. In the TDHF calculations on CO and H_2O even the largest-basis results remain significantly smaller than the CDOSD values and the error is enhanced with increasing order of the Cauchy moments. In the case of CO the Sadlej polarization and the [10s6p3d] basis calculations have about −13 and −21% error with respect to the CDOSD results for the mean $S(-4)$ and $S(-6)$ Cauchy moments. The errors are much larger in the case of the water molecule: they are 35 and 55%, respectively. This is in agreement with the observation of Spackman, who underlined the relatively poor quality of the higher Cauchy moments (32), calculated by the TDHF method. Electron correlation, taken into account, for example, by the recently developed time-dependent MP2 (TDMP2) approach, can bring these Cauchy moments into closer agreement with experiment (33, 34). The TDHF results for benzene are in remarkably good agreement with recent CDOSD data. The errors in the mean Cauchy moments of order −2, −4, and −6 are +0.7%, +0.1%, and −3.6% with the 6-311++G(2d,2p) basis set, while they are +1.4%, +3.1%, and +1.5% when using the [5s3p2d] basis set of Sadlej. The good quality of the higher Cauchy moments is probably partly due to the success of the TDHF method in reproducing the first dipole-allowed excitation energy in reasonable agreement with the experiment (6.56 eV calculated vs. 6.9 eV) and partly to the overwhelming importance of the charge-flow contribution to the static *and* dynamic polarizabilities (see below).

The basis set dependence of the higher $S(-4)$ and $S(-6)$ Cauchy moments is similar to that of the static polarizability, $S(-2)$, but the effects are more pronounced. Out-of-plane polarizability components are influenced much more by the quality of the basis set than are the in-plane components. In CO the parallel Cauchy moment components are in reasonable agreement with CDOSD values (below 10%), while the perpendicular ones are in error by 20 and 47%! In the water molecule $S_{yy}(-2)$ varies by a factor of 2.7 between the smallest and the largest basis set, while the higher-order Cauchy moment, $S_{yy}(-6)$, is enhanced by a factor of 5.7. In urea and benzene the approximately twofold enhancement of the out-of-plane static polarizability increases to a 12- and 40-fold enhancement, respectively. The in-plane polarizability components are relatively insensitive to the choice of basis set.

Coming now to the distributed models, selected distributed dipole–dipole Cauchy moment components have been plotted against the basis set quality in Figs. 2 and 3 for the two smallest systems, CO and H_2O. In addition to the static polarizability, $S(-2)$, and the $S(-6)$ Cauchy moment, the $S(0)$ Cauchy moments are also represented in these figures. Zeroth-order Cauchy moments correspond to the high-frequency limit of the multipolar dynamic polarizability components. The $S_{1,1}(0)$ dipolar components, according to the Thomas–Reiche–Kuhn (TRK) sum rule (35), are equal to the total number of electrons in the molecule. For SCF wave functions the TRK sum rule is satisfied in the basis set limit, therefore $S_{\alpha\alpha}(0)$ can be considered as a measure of the basis set completeness in the subspace of dipole excitations.

The general trends observed in the two molecules represented in Figs. 2 and 3 are identical, and they remain the same for the other three molecules, not represented here. Although the TRK sum rule is relatively poorly satisfied for the [5s3p2d] polarization basis set, this basis describes the static polarizability as well as the higher Cauchy moments in very good agreement with the larger [10s6p3d] basis. In fact, this basis set has been optimized by Sadlej to faithfully reproduce molecular polarizabilities, while the description of compact p- and d-orbitals, important for good fulfillment of the TRK sum rule, is less complete. This observation is in agreement with the experience of Mulder and Meath (36), who found that the importance of the core basis set in reproducing various sum rules increases with increasing Cauchy order.

Distributed atom–atom dipole polarizabilities, represented in Fig. 4, vary with the basis set quality in a similar way as the total polarizability components. One could expect that basis set effects would be reflected mostly by distributed dipole–dipole polarizabilities, while charge-flow terms would be reasonably described even by a relatively poor basis set. Distributed static polarizabilities confirm this rule (cf. Fig. 4), but the same is not necessarily true for higher Cauchy moments, i.e., for the frequency dependence of the polarizabilities. The increase in magnitude of the $S(-6)$ charge–charge and charge–dipole Cauchy moments for CO between the 6-311G(2d,2p) and 6-311++G(2d,2p) basis sets in Fig. 4 indicates that diffuse functions are indispensable for their good description.

Analysis of the different kinds of fully distributed terms becomes more and more complicated in larger molecules, due to the increasing number of parameters. Therefore one should envisage some "relocalization" scheme, which simplifies the model but preserves the advantages of the distributed description. As a first step in this direction, we analyzed the various kinds of distributed contributions to the molecular dipole–dipole Cauchy moments.

The molecular dynamic dipole–dipole polarizability, as

Fig. 2. Distributed dipole–dipole Cauchy moments for CO.

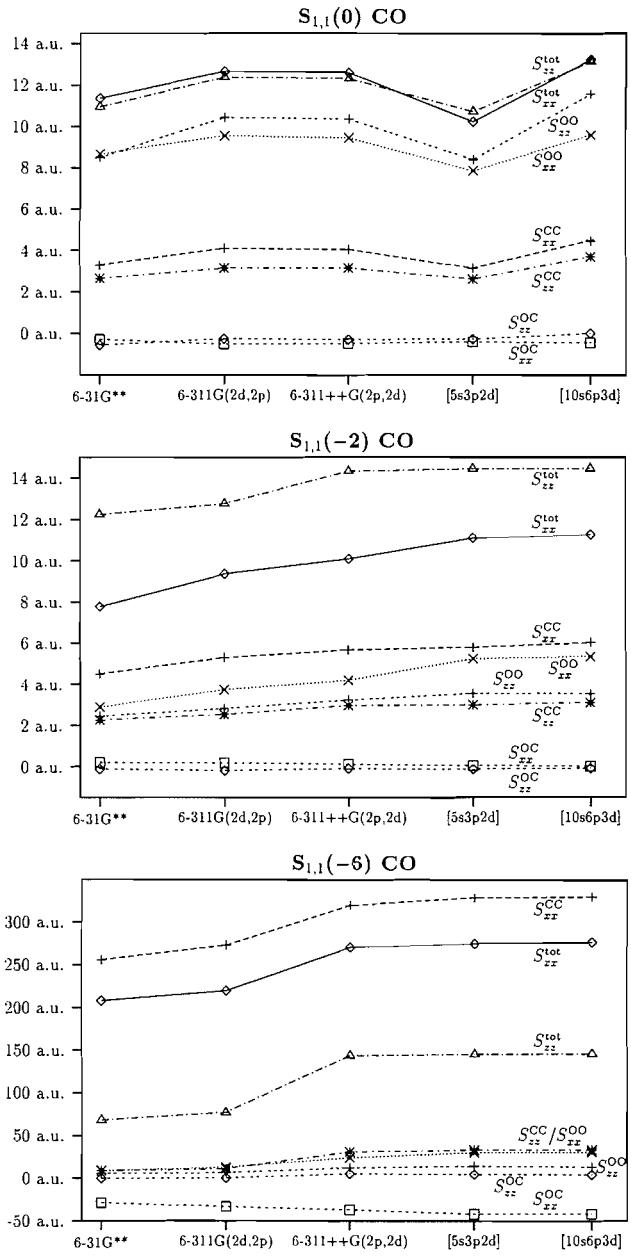
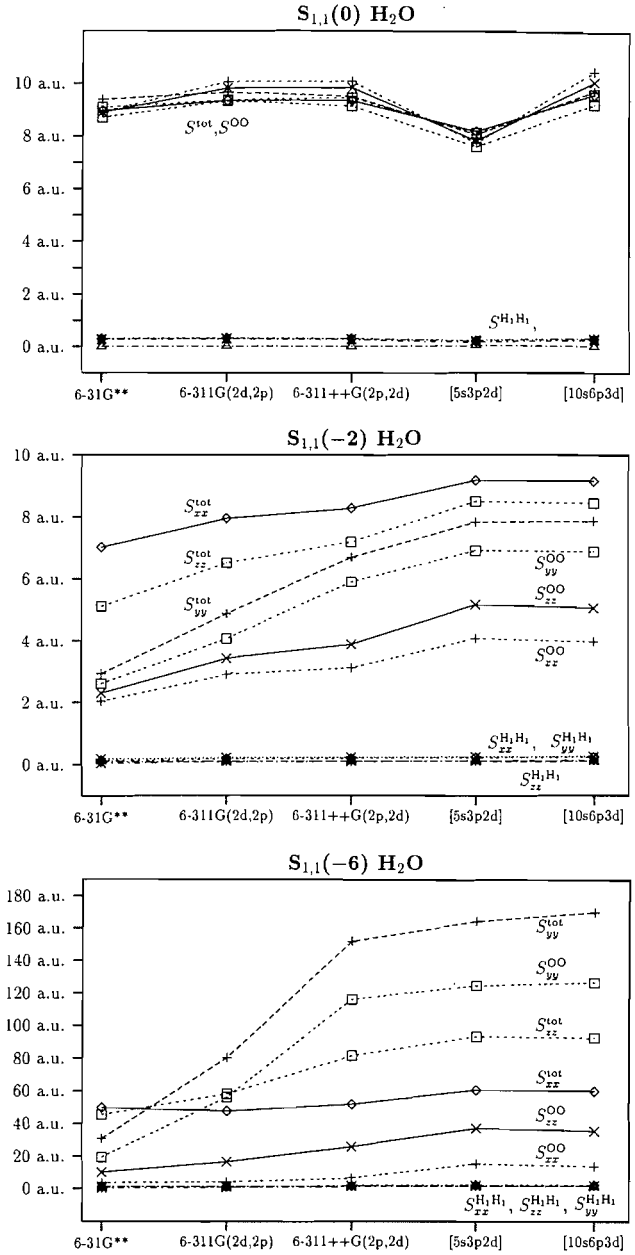


Fig. 3. Distributed dipole–dipole Cauchy moments for H_2O.



well as the corresponding Cauchy moments, can be broken down into various kinds of distributed components:[2]

$$[12]\qquad \alpha_{\alpha\beta}(\omega) = \alpha_{\alpha\beta}^{[\mu\mu,1-c]}(\omega) + \alpha_{\alpha\beta}^{[\mu\mu,2-c]}(\omega) + \alpha_{\alpha\beta}^{[q\mu]}(\omega) + \alpha_{\alpha\beta}^{[qq]}(\omega)$$

where Greek subscripts $\alpha\beta$ stand for the Cartesian components x, y, z, and the one- and two-center dipole–dipole, the charge–dipole and charge–charge contributions are defined as:

$$[13]\qquad \alpha_{\alpha\beta}^{[\mu\mu,1-c]}(\omega) = \sum_{A} \alpha_{\alpha\beta}^{AA}(\omega)$$

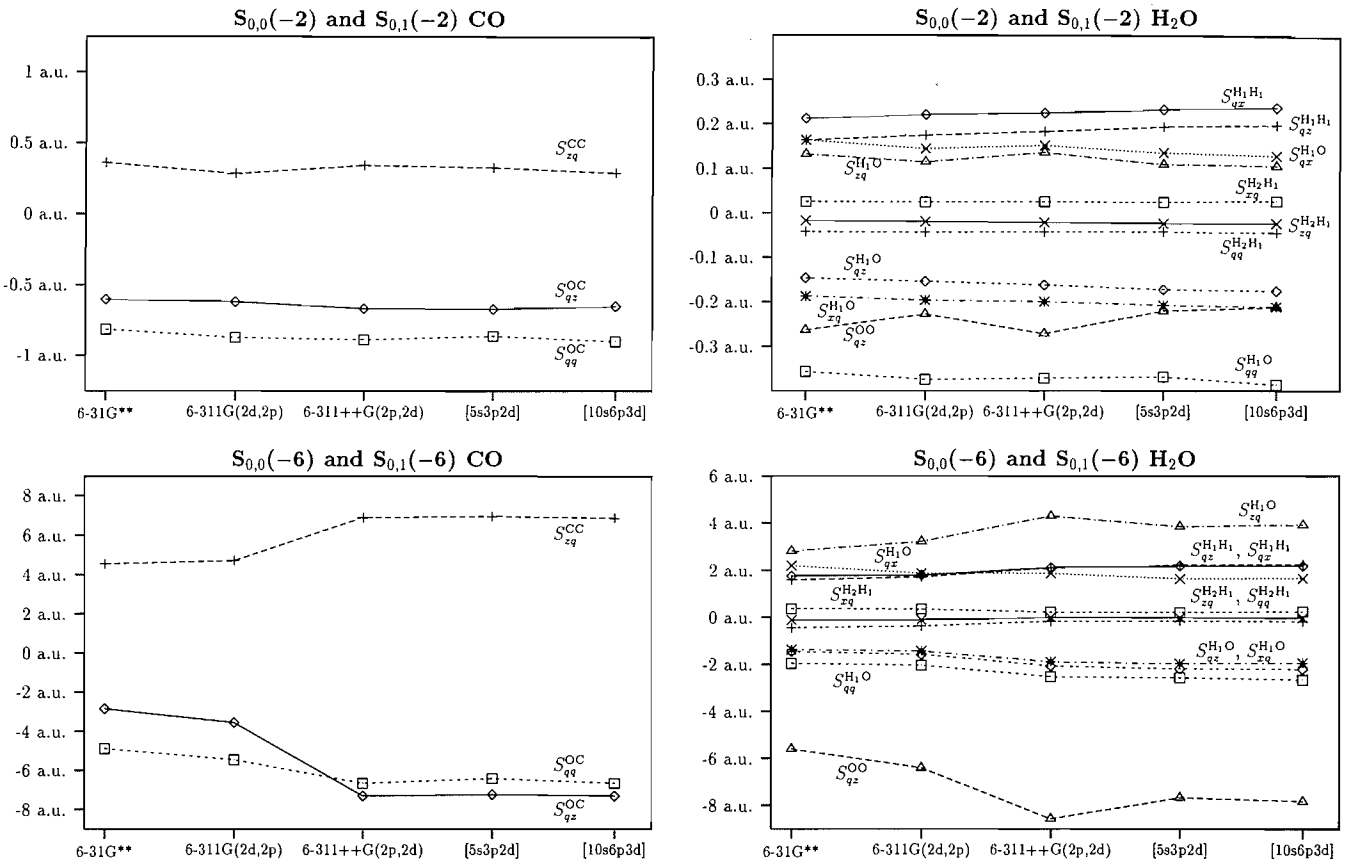
$$[14]\qquad \alpha_{\alpha\beta}^{[\mu\mu,2-c]}(\omega) = \sum_{A} \sum_{B\neq A} \alpha_{\alpha\beta}^{AB}(\omega)$$

$$[15]\qquad \alpha_{\alpha\beta}^{[q\mu]}(\omega) = \sum_{A} \sum_{B} R_{\alpha}^{A} \alpha_{q\beta}^{AB}(\omega) + \alpha_{\alpha q}^{AB}(\omega) R_{\beta}^{B}$$

$$[16]\qquad \alpha_{\alpha\beta}^{[qq]}(\omega) = \sum_{A} \sum_{B} R_{\alpha}^{A} \alpha_{qq}^{AB}(\omega) R_{\beta}^{B}$$

[2] For the sake of simplicity, the formulae in the text are written for the polarizabilities, $\alpha_{\alpha\beta}$, but they are valid *mutatis mutandis* for the corresponding Cauchy moments.

Fig. 4. Distributed charge-flow Cauchy moments for CO and H_2O.



and R_α^A is the α component of the vector from the molecular origin to the Ath atom. Contribution of the different terms depends on the chemical system and on the geometry, as is exemplified by the data for water and benzene molecules in Table 2, calculated with the polarization basis set of Sadlej.

Out-of plane molecular polarizabilities have only one- and two-center dipole–dipole components, since no atomic charge transfer is possible in this direction. The one-center contribution is always considerably larger than the two-center one, although the latter becomes increasingly important for higher order Cauchy moments in all cases. The charge-flow contribution to in-plane polarizabilities is always significant, and it even becomes the most important term for conjugated systems like benzene (and also for cyanogen), where it accounts for 80% of the total in-plane dipole polarizability. The distributed charge–dipole Cauchy moments contribute by 10–30% to the total molecular quantities, and their importance increases for higher orders.

The basis set dependence of distributed components in the larger systems, cyanogen and urea, is illustrated in Figs. 5 and 6, by regrouping all dipole–dipole and charge–dipole contributions in a single term, $S^{[\mu]}(k)$, and denoting the sum of charge–charge contributions by $S^{[q]}(k)$. In the case of the static polarizability, $S(-2)$, the sum of charge–charge terms is quite insensitive to the basis set and, in agreement with the experience obtained by detailed analysis of the smaller systems, the basis set variation of the total Cauchy moments is reflected by the sum of distributed dipole–dipole and charge–dipole Cauchy moments. The situation changes considerably for the contributions to the $S(-6)$ Cauchy moments. Here, the basis set dependence of the charge–charge terms is of comparable importance to that of the dipolar contributions, and diffuse functions are imperatively needed for a good reproduction of charge-flow contributions to higher Cauchy moments as well.

The data discussed above can serve as a starting point in appreciating the advantages or disadvantages of different partial relocalization schemes of distributed polarizabilities and Cauchy moments. Let us consider first the "atom–molecule" polarizabilities. The total molecular dynamic polarizabilities can be reconstituted from dipole–dipole and charge–dipole atom–molecule polarizabilities in the following manner (the argument ω will be omitted for the sake of notational simplicity):

$$[17] \qquad \alpha_{\alpha\beta} = \sum_A (\alpha_{\alpha\beta}^{A,mol} + R_\alpha^A \alpha_{q\beta}^{A,mol})$$

where

$$[18] \qquad \alpha_{\alpha\beta}^{A,mol} = \sum_B \alpha_{\alpha\beta}^{AB} + \alpha_{\alpha q}^{AB} R_\beta^B$$

$$[19] \qquad \alpha_{q\beta}^{A,mol} = \sum_B \alpha_{q\beta}^{AB} + \alpha_{qq}^{AB} R_\beta^B$$

Table 2. Decomposition of total Cauchy moments for water and benzene molecules calculated with the Sadlej [5s3p2d] polarization basis set. Numbers in parentheses indicate the percentage contribution to the total reconstituted Cauchy moment from distributed one- and two-centered dipole–dipole, dipole–charge, and charge–charge contributions.

αβ	k	$S_{\alpha\beta}^{[dd,1\text{-}c]}(k)$	$S_{\alpha\beta}^{[dd,2\text{-}c]}(k)$	$S_{\alpha\beta}^{[qd]}(k)$	$S_{\alpha\beta}^{[qq]}(k)$	$S_{\alpha\beta}^{total}(k)^a$	$S_{\alpha\beta}^{full}(k)$
H_2O							
xx	−2	4.5603	0.4973	2.2581	1.8506	9.1663	9.1669
		(49.75)	(5.43)	(24.63)	(20.19)	(−0.01)	
yy	−2	7.1535	0.6663	0.0000	0.0000	7.8198	7.8211
		(91.48)	(8.52)	(0.00)	(0.00)	(−0.02)	
zz	−2	5.6120	0.7248	1.2452	0.9054	8.4874	8.4879
		(66.12)	(8.54)	(14.67)	(10.67)	(−0.01)	
xx	−6	19.2028	6.4873	23.0117	11.8993	60.6010	60.6306
		(31.69)	(10.70)	(37.97)	(19.64)	(−0.05)	
yy	−6	128.0793	35.9794	0.0000	0.0000	164.0587	164.1782
		(78.07)	(21.93)	(0.00)	(0.00)	(−0.07)	
zz	−6	41.6719	18.6769	26.7305	6.3165	93.3958	93.4152
		(44.62)	(20.00)	(28.62)	(6.76)	(−0.02)	
C_6H_6							
xx	−2	15.5331	0.8625	4.1356	59.6587	80.1899	80.2164
	−2	(19.37)	(1.08)	(5.16)	(74.40)	(−0.03)	
yy	−2	42.0741	3.6293	0.0000	0.0000	45.7035	45.7836
	−2	(92.06)	(7.94)	(0.00)	(0.00)	(−0.17)	
xx	−6	431.6299	−107.4498	1661.8356	4414.3488	6400.3644	6408.1626
	−6	(6.74)	(−1.68)	(25.96)	(68.97)	(−0.12)	
yy	−6	1452.5266	285.9955	0.0000	0.0000	1738.5221	1750.9281
	−6	(83.55)	(16.45)	(0.00)	(0.00)	(−0.71)	

[a]The number in parentheses below the $S_{\alpha\beta}^{total}$ indicates the percentage error with respect to $S_{\alpha\beta}^{full}$, the Cauchy moment calculated with analytic molecular multipole transition integrals (last column).

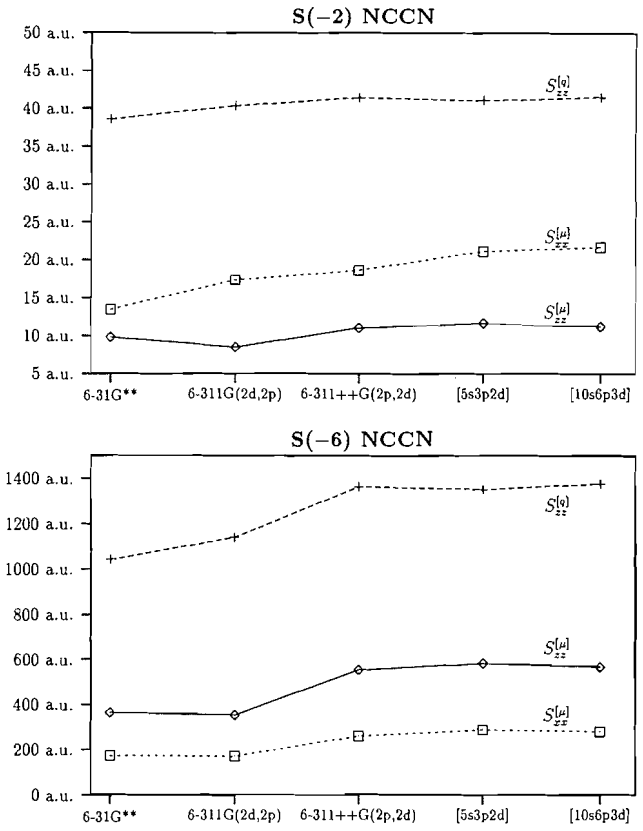
A selected set of significant components of the Cauchy moments $S_{\alpha\beta}^{A,mol}(k)$ as well as of $S_{q\beta}^{A,mol}(k)$ are listed in Table 3. The atom–molecule charge–dipole polarizabilities are relatively large for atoms at the extremities of the molecule, such as the nitrogen in cyanogen, the oxygen in urea, and the hydrogens in benzene. An interesting feature, already remarked by Bader and co-workers in the case of hydrocarbons, is the counter-polarization of "buried" atoms, such as the carbon in cyanogen and in urea: the induced dipole is in the opposite direction with respect to the applied field on the molecule.

A more conventional model, including exclusively atomic dipole–dipole polarizabilities, could be obtained by transforming the charge–dipole terms to atomic dipole–dipole contributions. Taking the molecular center of mass as the molecular origin, a set of atomic polarizabilities can be obtained (cf. the term in parentheses in eq. [17] that can be compared to other models available in the literature. For example, Åstrand et al. proposed a polarizable intermolecular potential for the urea molecule, in which an isotropic polarizability was assigned to each atom (37). A similar model can be constructed from our atom–molecule polarizabilities, using eq. [17]. The mean polarizability of urea, corresponding to the model of Åstrand et al. ($\alpha(C) = 0.0$, $\alpha(O) = 9.62$, $\alpha(N) = 2.63$, $\alpha(H_{cis}) = \alpha(H_{trans}) = 2.14$), is 23.44 au, i.e., practically identical to our 6-31G** result. Taking this basis set, we obtain a model, that is quite similar to theirs: ($\alpha(C) = 0.20$, $\alpha(O) = 6.40$, $\alpha(N) = 3.71$, $\alpha(H_{cis}) = \alpha(H_{trans}) = 2.32$). With the Sadlej polarization basis set, the qualitative features of the model remain unchanged: the polarizability of the carbon is practically zero, and the hydrogen polarizability (coming mainly from induced charge contributions) is about 2.5 au. However, the mean polarizabilities of the O and N atoms are considerably enhanced: they are 9.45 and and 6.21 au, respectively, reflecting the better quality of this basis set.

Atom–molecule polarizabilities have two main drawbacks. First, the external field is supposed to be uniform, which is a considerable restriction for the study of the intermolecular interaction of larger molecules, where a really nonlocal picture would be more appropriate. Second, the charge–dipole parameter cannot be combined in a simple, origin-independent way (the atomic contributions obtained from eq. [17] depend on the choice of the molecular origin) with the atomic dipole–dipole polarizability, except in some special cases.

A closer look at the expression for atom–molecule charge–dipole polarizability shows that only the charge-flow terms are responsible for the impossibility of assigning it to atomic dipole polarizabilities in an origin-independent way. A straightforward solution to this problem, already suggested by Le Sueur and Stone (15), is to keep charge-flow polarizabilities fully distributed, and relocalize only the dipole–dipole and charge–dipole terms, which can be done in a strictly origin-independent way. After a little algebra, using the sum rule, eq. [3], one gets the following expression for the relocalized atomic dipole polarizability:

Fig. 5. Breakdown of the molecular dipole–dipole Cauchy moments to distributed charge–charge ($S^{[q]}_{\alpha\beta}$) and dipole–dipole plus charge–dipole ($S^{[\mu]}_{\alpha\beta}$) contributions ($S^{[q]}_{\alpha\beta} + S^{[\mu]}_{\alpha\beta} = S^{tot}_{\alpha\beta}$) for cyanogen.

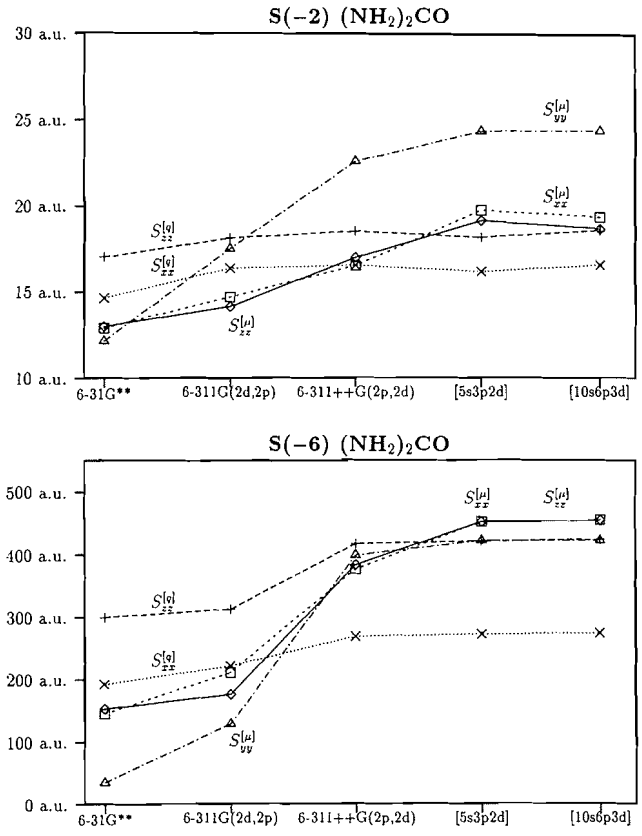


$$[20]\qquad \tilde{\alpha}^{A}_{\alpha\beta} = \frac{1}{2}\sum_{B}(\alpha^{AB}_{\alpha\beta} + \alpha^{BA}_{\alpha\beta}) + r^{AB}_{\alpha}(\alpha^{AB}_{q\beta} - \alpha^{BA}_{q\beta}) + r^{AB}_{\beta}(\alpha^{BA}_{\alpha q} - \alpha^{AB}_{\alpha q})$$

with $\boldsymbol{r}^{AB} = \boldsymbol{R}^{A} - \boldsymbol{R}^{B}$, the vector of interatomic distance. In this scheme all two-center charge–dipole and dipole–dipole terms are distributed in an equal manner between the centers in question. The resulting atomic dipole polarizability tensors are symmetric, unlike the atom–molecule polarizabilities, for which $\alpha^{A,mol}_{\alpha\beta} \neq \alpha^{A,mol}_{\beta\alpha}$. The charge-flow and the relocalized atomic Cauchy moments according to expression [20] are listed in Tables 4 and 5, respectively.

The charge–charge Cauchy moments (Table 4) are expected to be significant mainly between covalently bonded atoms: chemical bonds are natural paths for transferring electrons in a molecule. (A consistent formulation of the covalent bond order using the topological definition of atoms in molecules has been discussed in ref. 38.) The relative magnitude of charge-flow Cauchy moments for pairs of formally nonbonded atoms seems to increase with the order (e.g., N1–C3 compared to N2–C3 in urea, or the *meta* (C1–C4) charge flow in benzene). Several of the examples discussed here (cyanogen, urea, benzene) are conjugated systems, where surprisingly high charge flow may take place between quite distant atoms. For example, the end-to-end N1–N2 charge flow in cyanogen is larger than the charge flow between the first neighbor C3 and C4 atoms. This is already true for $S^{AB}_{qq}(-2)$, and the difference becomes even more important for the moments $S^{AB}_{qq}(-4)$ and $S^{AB}_{qq}(-6)$. Similar trends can be observed for benzene and urea.

Fig. 6. Breakdown of the molecular dipole–dipole Cauchy moments for urea.



Atomic dipole–dipole polarizabilities according to eq. [20] are larger than the corresponding atom–molecule dipole–dipole polarizabilities, since they include the totality of the charge–dipole contributions. Nevertheless, the main qualitative features are similar: negative in-plane polarizabilities for "buried" atoms and relatively small positive out-of-plane components. Hydrogen atoms have consistently small dipole–dipole atomic Cauchy moments ($S(-2)$ usually smaller than 1 au), when connected to the electronegative O and N atoms, but in benzene the component along the C—H bond becomes larger than 2 au. According to these observations a "united atom" description for the XH_n functional groups might be a reasonable model. In the same spirit, the water molecule could be regarded as a single dipole – polarizable oxygen site, bearing about 75% of the total molecular polarizability, and an additional charge transfer contribution between the oxygen and the hydrogen atoms.

IV. Summary and conclusions

We have shown that the atoms-in-molecules theory of Bader constitutes an appropriate framework for partitioning dy-

Table 3. Atomic Cauchy moments relocalized according to eq. [17] as calculated with the [5s3p2d] polarization basis of Sadlej.

Atom	αβ	$k = -2$	$k = -4$	$k = -6$	Atom	αβ	$k = -2$	$k = -4$	$k = -6$
CO					**$(NH_2)_2CO$**				
C	*qz*	2.840	8.157	27.890	O	*qz*	4.040	20.536	157.946
C	*xx*	5.816	34.816	286.874	O	*xx*	5.720	16.794	103.316
C	*zz*	4.281	13.838	52.718	O	*yy*	6.300	15.136	46.390
					O	*zz*	5.823	23.333	153.960
O	*qz*	−2.841	−8.161	−27.906					
O	*xx*	5.251	6.528	−12.216	C	*qz*	−0.299	−2.995	−29.198
O	*zz*	4.097	9.941	32.967	C	*xx*	−0.246	−1.072	−6.497
					C	*yy*	1.167	2.035	4.219
NCCN					C	*zz*	−0.353	−1.511	−10.652
N1	*qz*	7.022	41.509	275.900					
N1	*xx*	7.423	22.710	107.027	N3	*qx*	1.300	7.114	52.473
N1	*zz*	4.982	21.733	129.246	N3	*qz*	−0.731	−5.069	−47.188
					N3	*xx*	4.174	15.123	89.123
C3	*qz*	−2.388	−17.403	−121.326	N3	*xz*	−0.746	−7.251	−68.018
C3	*xx*	3.133	8.831	36.272	N3	*yy*	7.580	24.726	152.727
C3	*zz*	0.019	4.156	34.704	N3	*zx*	−0.601	−5.258	−42.308
					N3	*zz*	3.236	9.087	52.246
H_2O									
O	*qz*	−1.380	−3.965	−17.777	H5	*qx*	1.540	4.181	15.247
O	*xx*	4.687	9.022	22.934	H5	*qz*	0.507	0.338	−4.694
O	*yy*	7.240	23.153	142.193	H5	*xx*	1.162	3.995	17.230
O	*zz*	5.777	14.218	54.700	H5	*xz*	0.167	0.228	−2.622
					H5	*yy*	0.390	1.453	13.102
H1	*qx*	1.042	2.627	8.181	H5	*zx*	0.365	1.843	10.407
H1	*qz*	0.690	1.982	8.888	H5	*zz*	0.452	0.723	0.812
H1	*xx*	0.750	2.176	7.131					
H1	*yy*	0.290	1.257	10.933	H7	*qx*	0.328	2.087	15.299
H1	*zz*	0.591	2.013	9.507	H7	*qz*	−1.646	−4.043	−12.518
H1	*xz*	0.329	1.363	6.725	H7	*xx*	0.468	0.846	2.176
H1	*zx*	0.459	1.711	6.222	H7	*xz*	−0.088	−0.406	−1.368
					H7	*yy*	0.451	1.920	19.847
					H7	*zx*	−0.294	−2.128	−16.780
					H7	*zz*	1.320	4.516	18.070
C_6H_6					**C_6H_6**				
C1	*qx*	2.444	30.750	439.660	H1	*qx*	2.997	14.410	123.512
C1	*xx*	1.707	14.894	193.089	H1	*xx*	2.492	15.159	132.166
C1	*yy*	6.340	29.408	230.630	H1	*yy*	1.280	5.526	59.166
C1	*zz*	0.958	8.358	109.510	H1	*zz*	0.998	−1.210	−49.735

namic polarizabilities and leads to a physically consistent set of atom–atom parameters describing the nonlocal response of the molecular charge density to a time-dependent external field. The basis set dependence of distributed dynamic polarizabilities has been studied through their first three distributed Cauchy moments, which vary in parallel with the total Cauchy moments when improving the basis set quality.

In the case of static polarizabilities ($S(-2)$ Cauchy moments) the basis set dependence is manifested almost exclusively in the distributed dipole–dipole contributions, and charge-flow terms are quite well described by relatively poor basis sets. Nevertheless, diffuse functions seem to be important for the description of higher order charge–charge Cauchy moments. Static charge–charge polarizabilities between distant pairs of atoms may be quite large in conjugated systems and in all cases the importance of charge-flow Cauchy moments between nonbonded and (or) distant atoms increases with increasing order.

Two alternative schemes have been considered to "relocalize" the fully distributed, nonlocal dynamic polarizabilities. The atom–molecule polarizabilities, closely related to the atomic polarizabilities recently studied by Bader and coworkers, describe induced atomic charges and dipoles of a molecule in a uniform external field. Description of the response in non-uniform fields is possible only by considering higher rank (e.g., charge–quadrupole, dipole–quadrupole, charge–octupole., etc.) atom–molecule polarizabilities, with all the pitfalls of the single-centered Taylor expansion of the external field for spatially extended systems. The other model, which retains all charge-flow terms fully distributed and relocalizes only the charge–dipole contributions, is better suited to the description of molecules in non-uniform fields.

Table 4. Selected atomic charge–charge Cauchy moments calculated with the Sadlej basis.

A	B	−2	−4	−6	A	B	−2	−4	−6
CO					**H_2O**				
O	C	−0.864	−2.029	−6.424	O	O	0.739	1.419	5.153
NCCN					H1	H1	0.411	0.829	2.742
N1	N1	1.796	7.859	46.904	H1	O	−0.369	−0.709	−2.576
C3	C3	1.735	3.809	16.131	**$(NH_2)_2CO$**				
C3	N1	−1.256	−4.501	−24.785	C	C	0.912	1.156	3.942
C4	C3	−0.437	−0.259	−2.133	O	C	−0.385	−1.075	−7.581
N2	N1	−0.499	−4.309	−32.909	O	O	1.034	4.387	33.777
C3	N2	−0.042	0.952	10.788	N3	O	−0.211	−1.122	−10.099
C_6H_6					N3	C	−0.242	−0.055	1.467
C1	C1	2.389	13.142	211.131	N3	N3	1.405	2.550	12.162
C2	C1	−0.316	−8.224	−185.061	N4	N3	−0.124	−0.394	−2.248
C3	C1	−0.800	−7.159	−150.812	H5	N3	−0.375	−0.345	0.157
C4	C1	0.103	5.264	139.301	H5	N4	−0.022	−0.067	−0.135
H1	H1	0.868	2.291	12.929	H7	N3	−0.402	−0.417	−0.263
C1	H1	−0.421	1.054	32.952	H5	H5	0.545	0.961	2.536
C1	H2	−0.055	−1.401	−31.303	H7	H7	0.583	1.110	3.524
C1	H3	−0.102	−1.116	−23.644					

Table 5. Relocalized atomic Cauchy moments according to eq. [20] as calculated with the [5s3p2d] polarization basis of Sadlej.

Atom	αβ	−2	−4	−6	Atom		−2	−4	−6
CO					**$(NH_2)_2CO$**				
C	*xx*	5.816	34.816	286.874	C	*xx*	−0.174	−1.289	−17.168
C	*zz*	4.975	17.709	67.547	C	*yy*	1.167	2.035	4.219
O	*xx*	5.251	6.528	−12.216	C	*zz*	0.062	0.631	1.573
O	*zz*	5.532	14.237	48.385	O	*xx*	6.613	25.564	180.699
H_2O					O	*yy*	6.300	15.136	46.390
O	*xx*	5.280	10.491	28.593	O	*zz*	6.502	30.927	217.008
O	*yy*	7.240	23.153	142.193	N3	*xx*	4.679	17.992	103.108
O	*zz*	6.156	15.303	59.565	N3	*xz*	−0.463	−6.177	−57.070
H1	*xx*	1.018	3.259	10.055	N3	*yy*	7.580	24.726	152.727
H1	*yy*	0.290	1.257	10.933	N3	*zz*	4.157	13.532	84.676
H1	*zz*	0.713	2.796	13.757	H5	*xx*	1.239	5.434	24.629
H1	*xz*	0.515	2.254	10.090	H5	*xz*	0.236	0.952	1.554
NCCN					H5	*yy*	0.390	1.453	13.102
N1	*xx*	7.423	22.710	107.027	H5	*zz*	0.696	2.115	7.816
N1	*zz*	6.140	36.533	255.015	H7	*xx*	0.726	2.799	16.462
C3	*xx*	3.133	8.831	36.272	H7	*xz*	−0.201	−1.910	−16.255
C3	*zz*	−0.312	6.251	35.749	H7	*yy*	0.451	1.920	19.847
					H7	*zz*	1.429	6.002	24.104
C_6H_6					**C_6H_6**				
C1	*xx*	2.334	25.515	351.294	H1	*xx*	2.179	19.741	199.755
C1	*zz*	0.970	12.261	137.368	H1	*zz*	1.370	2.065	−26.243
C1	*yy*	6.340	29.408	230.630	H1	*yy*	1.280	5.526	59.166

Considering the increasing importance of distant charge-flow contributions with increasing Cauchy order, this second model seems to be more appropriate for the relocalization of distributed dynamic polarizabilities.

The main use of distributed dynamic polarizabilities, which have been characterized in the present study by their various Cauchy moments, is in the field of intermolecular interactions. We have recently developed an efficient computational scheme for obtaining multicentered multipolar dispersion energies. In the case of relatively small molecules, where the dipolar approximation is valid, one can obtain reliable dispersion energies by the CDOSD method (39). Theoretically calculated distributed dynamic polarizabilities allow us to extend the practical utility of the multipolar approximation to larger systems as well. To attain this goal the accuracy of the polarizability calculations has to be improved by

including electron correlation (for example by the TDMP2 method (33)) and the number of independent polarizability components has to be kept at a reasonably low level by the application of appropriate relocalization schemes. Work in these directions is in progress.

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