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Distributed polarizabilities using the topological theory of atoms in molecules

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Abstract

Distributed atom–atom multipolar polarizabilities have been calculated at the coupled perturbed Hartree–Fock (CPHF) level, using Bader's topological theory to partition the molecular charge density into atomic domains. The proposed scheme applies without difficulty to molecules of arbitrary shape and symmetry and maintains a remarkable stability of the individual atomic polarizability components with respect to basis set extension, exemplified by the molecules CO, H_2O, NH_3 and BF_3.

1. Introduction

The use of distributed polarizabilities to calculate induction forces between molecules offers a conceptually attractive framework to diminish convergence problems raised by single-centered molecular polarizability descriptions of the induced charge densities [1].

The induction energy of a molecule under the influence of an external potential, $V(\boldsymbol{r})$ (e.g. created by the permanent charge distribution of an interacting partner), is

$$U_{\mathrm{ind}} = -\tfrac{1}{2}\int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{r}'\, V(\boldsymbol{r})\alpha(\boldsymbol{r},\boldsymbol{r}')V(\boldsymbol{r}')\,. \tag{1}$$

Here $\alpha(\boldsymbol{r}, \boldsymbol{r}')$ is the charge density susceptibility function [2,3] which describes the nonlocal response of the molecule. This means that the perturbation $V(\boldsymbol{r}')$ at point $\boldsymbol{r}'$ propagates in the system and gives rise to a change of its charge density,

$$\Delta\varrho(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}'\,\alpha(\boldsymbol{r},\boldsymbol{r}')V(\boldsymbol{r}')\,, \tag{2}$$

at point $\boldsymbol{r}$.

There are several empirical and semi-empirical models, which take into account the nonlocal character of the polarizability response, either by charge-flow terms [4], or by considering explicitly the interaction of induced atomic dipoles [5–7].

A detailed discussion of a rigorous theory of distributed multipole polarizabilities, as a natural extension of the distributed multipole moment analysis [8–11], is due to Stone [12]. Accordingly, the induction energy can be written as

$$U_{\mathrm{ind}} = -\tfrac{1}{2}\sum_{\mathrm{A}}\sum_{lm}\sum_{\mathrm{B}}\sum_{l'm'} V^{\mathrm{A}}_{lm}\alpha^{\mathrm{AB}}_{lm,l'm'}V^{\mathrm{B}}_{l'm'}\,, \tag{3}$$

where V^{A}_{lm} denotes the coefficients of a multicenter expansion of the external potential about center $\boldsymbol{r}^{\mathrm{A}}$ in terms of regular spherical harmonics.

The distributed multipole polarizabilities $\alpha^{\mathrm{AB}}_{lm,l'm'}$ can be calculated in the coupled perturbed Hartree–Fock (CPHF) approximation [13] as

$$\alpha^{\mathrm{AB}}_{lm,l'm'} = 4\sum_{ia}\sum_{jb}\langle i|\hat{Q}_{lm}|a\rangle^{\dagger}_{\mathrm{A}}(\mathbf{G}^{-1})_{ia,jb} \times\langle j|\hat{Q}_{l'm'}|b\rangle_{\mathrm{B}}\,, \tag{4}$$

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where the matrix **G**,

$$G_{ia,jb}=4(ai|jb)-(aj|ib)-(ab|ij)$$
$$+\delta_{ia,jb}(\epsilon_a-\epsilon_i)\,, \qquad (5)$$

is defined in terms of electron repulsion integrals in the basis of occupied (i,j) and virtual (a,b) orbitals obtained from closed shell Hartree–Fock theory, having orbital energies ϵ_i, ϵ_a. The integrals $\langle i|\hat{Q}_{lm}|a\rangle_A$ represent an arbitrary atomic (or other) partition of the transition multipole moment matrix elements, using $\boldsymbol{r}^A$ as origin.

In a recent paper Le Sueur and Stone have discussed how different choices of partitioning the transition matrix elements influence the distributed polarizability components and the convergence of the induction energy [14]. The main conclusion was that Hilbert-space partitioning schemes, either in an atomic orbital basis (e.g. Mulliken partition), or in the basis of primitive orbitals (e.g. DMA partition) lead to unphysically large distributed polarizability components and are therefore inappropriate for the calculation of induction energies.

The smoothed Gauss–Hermite partitioning scheme, proposed in the same paper [14], represents a considerable improvement concerning the stability of the polarizability components. Nevertheless, because of the use of a sharpness parameter which may vary with the basis set, this algorithm is still close in spirit to basis set partitioning schemes and consequently might not lead to reasonably basis-set-independent distributed polarizabilities.

A possible way to obtain stable results is to apply space partitioning techniques. Their practical use raises no problem when the definition of the limiting surface is straightforward, as it is for linear molecules [12]. For molecules of arbitrary shape one would need a well-defined unique scheme, leading to disjoint volume elements around the atoms or functional groups. A natural partitioning scheme in three-dimensional real space, which satisfies these conditions, has been elaborated by Bader, in the framework of his topological theory of atoms in molecules [15,16].

The purpose of the present Letter is to demonstrate that distributed polarizabilities, calculated in the atomic basins as defined by Bader, offer a particularly stable and physically consistent picture to describe and understand polarizability distributions in molecules.

2. Theory

Bader's topological theory of atoms in molecules consists of partitioning the three-dimensional physical space into disjoint regions, Ω_A. These regions are separated by surfaces, $S_A(\boldsymbol{r})$, where the electronic charge density, $\varrho(\boldsymbol{r})$, satisfies the so-called zero-flux condition, $\nabla\varrho(\boldsymbol{r})\cdot\boldsymbol{n}(\boldsymbol{r})=0$ for $\forall\boldsymbol{r}\in S_A(\boldsymbol{r})$ [15,16]. These regions, the atomic basins, are almost always centered on the atoms in the molecule and they can be treated as quantum mechanically separate systems. Atomic properties are obtained by integration over atomic basins.

In the following we shall consider a partition of the twofold integral in the expression of the induction energy (1) in terms of the atomic basins Ω_A^0 of the unperturbed molecule,

$$U_{\mathrm{ind}}=-\tfrac{1}{2}\sum_A\sum_B\int_{\Omega_A^0}\mathrm{d}\boldsymbol{r}\int_{\Omega_B^0}\mathrm{d}\boldsymbol{r}'\,V(\boldsymbol{r})$$
$$\times\alpha(\boldsymbol{r},\boldsymbol{r}')V(\boldsymbol{r}')\,. \qquad (6)$$

The perturbing electric potential, $V(\boldsymbol{r})$, can be developed in Taylor series in terms of regular spherical harmonics about the centers $\boldsymbol{r}^A$ of the atomic basins,

$$V(\boldsymbol{r})=\sum_{lm}V_{lm}^A R_{lm}^A(\boldsymbol{r}),\quad \boldsymbol{r}\in\Omega_A\,, \qquad (7)$$

where a shorthand notation has been introduced for the regular spherical harmonics, $R_{lm}^A(\boldsymbol{r})=R_{lm}(\boldsymbol{r}-\boldsymbol{R}^A)$.

Substituting this expansion in Eq. (6) and performing the integrations we obtain the induction energy in the form of Eq. (3), where the distributed atom–atom multipole polarizabilities are defined by

$$\alpha_{lm,l'm'}^{AB}=\int_{\Omega_A^0}\mathrm{d}\boldsymbol{r}\int_{\Omega_B^0}\mathrm{d}\boldsymbol{r}'\,R_{lm}^A(\boldsymbol{r})$$
$$\times\alpha(\boldsymbol{r},\boldsymbol{r}')R_{l'm'}^B(\boldsymbol{r}')\,. \qquad (8)$$

The distributed polarizability components can be calculated by the expression (4), using transition multipole moment integrals evaluated within the atomic basins Ω_A^0,

$$\langle i|\hat{Q}_{lm}|a\rangle_A = \int_{\Omega_A^0} \mathrm{d}r\,\phi_i^*(r) R_{lm}^A(r)\phi_a(r)\,. \tag{9}$$

Let us remark that the induced distributed multipole moments, ΔQ_{lm}^A, calculated according to

$$\Delta Q_{lm}^A = \sum_B \sum_{l'm'} \alpha_{lm,l'm'}^{AB} V_{l'm'}^B \tag{10}$$

are not strictly equal to those calculated by a finite field method using Bader's partitioning,

$$\Delta Q_{lm}^A \neq \int_{\Omega_A} \mathrm{d}r\, R_{lm}^A(r)\varrho(r) - \int_{\Omega_A^0} \mathrm{d}r\, R_{lm}^A(r)\varrho^0(r)\,, \tag{11}$$

where $\varrho(r)$ and $\varrho^0(r)$ are the charge densities in the presence and the absence of an external potential, respectively. This discrepancy is due to the variation of the zero-flux boundary surfaces of the atoms in the presence of the external perturbation [17]. Nevertheless, both approaches provide a consistent picture of charge density response and conserve the total polarizabilities.

General formulae to recalculate total molecular polarizability components from distributed ones have been given by Stone [12]. Here we cite the expression necessary to reconstitute the total dipole polarizability from the distributed charge-flow, α_{qq}^{AB}, charge–dipole, $\alpha_{q\beta}^{AB}$, dipole–charge, $\alpha_{\alpha q}^{AB}$, and dipole–dipole, $\alpha_{\alpha\beta}^{AB}$, components, centered at r_α^A and r_β^B,

$$\alpha_{\alpha\beta} = \sum_A \sum_B \left(r_\alpha^A \alpha_{qq}^{AB} r_\beta^B + r_\alpha^A \alpha_{q\beta}^{AB} + \alpha_{\alpha q}^{AB} r_\beta^B + \alpha_{\alpha\beta}^{AB}\right). \tag{12}$$

An important property of the distributed charge-flow and charge–multipole polarizabilities is a sum rule, which follows from the conservation of the total molecular charge,

$$\sum_A \alpha_{qt}^{AB} = 0\,, \tag{13}$$

where $t = q, x, y, z, \ldots$. As is immediately evident from the definition (8), the following symmetry property holds:

$$\alpha_{ts}^{AB} = \alpha_{st}^{BA}\,. \tag{14}$$

Atomic dipole polarizabilities, as defined by Bader [17,18], can be calculated by summing over one of the distribution center indices:

$$\alpha_{\alpha\beta}^A(\text{Bader}) = \int_{\Omega_A^0} \mathrm{d}r \int \mathrm{d}r'\,(r_\alpha - r_\alpha^A)\alpha(r,r')r'_\beta = \sum_B \left(r_\alpha^A \alpha_{qq}^{AB} r_\beta^B + r_\alpha^A \alpha_{q\beta}^{AB} + \alpha_{\alpha q}^{AB} r_\beta^B + \alpha_{\alpha\beta}^{AB}\right). \tag{15}$$

This definition allows to have a unique partition of the molecular dipole polarizability to atomic contributions, but its utilization is related to a one-center expansion of the perturbing potential. Therefore its use is limited to the case where the perturbing external field is uniform, which is most often not the case for intermolecular interactions.

3. Calculations

A series of simple molecules, CO, H_2O, NH_3 and BF_3 has been used to illustrate the performance of distributed polarizabilities in Bader's partition. Since most of the difficulties of previous attempts were related to the basis-set dependence of the results, we paid particular attention to this question.

A total of six different contracted Gaussian-type orbitals (CGTOs) basis sets was used in the calculations. Four standard basis sets, denoted as 6-31G**, 6-311G(d, p), 6-311G(2d, 2p), and 6-311++G(2d, 2p), were taken from the GAUSSIAN basis set library [19]. For the molecules without hydrogen atoms they are designated as 6-31G*, 6-311G(d), 6-311G(2d), and 6-311+G(2d), respectively.

A basis set, designed for the study of polarization properties, has been taken from Sadlej's work [20]. For the hydrogen atom it consists of a (6s4p)/[3s2p] contracted set and for the other atoms of (10s6p4d)/[5s3p2d] contracted sets. Since no basis set of this type was available for the boron atom, it has been generated according to the same prescriptions [20] by starting from the (9s5p) primitive GTO basis set of van Duijneveldt [21], adding diffuse s and p functions and a set of four d functions with the same exponents as the outermost p functions. It was contracted using the expansion coefficients of a symmetrized SCF calculation for the $B(^2P)$ state. The contracted basis set yields an average polarizability of 21.18 au for the boron atom, while the uncontracted one yields 21.26 au.

The largest basis set in our study has been derived from that of Widmark et al. [22] by keeping the same exponents. Only the innermost three s and two p functions have been contracted for the hydrogen atom, resulting in a (8s4p)/[6s3p] CGTO set, and for the other atoms 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 6-31G* basis set always five-component d functions were employed.

The calculated total polarizabilities for the two largest basis sets are in excellent agreement with high-quality literature values (see ref. [23] and references therein).

In order to define the orientation of the coordinate systems for all molecules included in the present study the Cartesian coordinates of the atoms are given in Table 1 based on experimental geometries.

The polarizabilities were calculated with a self-written CPHF program which employs the necessary transformed two-electron integral blocks produced by a non-standard link after a closed-shell SCF run of GAUSSIAN 92 [19]. The occupied/virtual one-electron integral blocks of the distributed moments were generated by a modified version of the PROAIM program [24].

Table 1
Cartesian coordinates (in bohr) given with respect to the center of mass of the sample molecules

Atom	x	y	z
CO			
C	0.00000	0.00000	1.21812
O	0.00000	0.00000	−0.91388
H_2O			
O	0.00000	0.00000	−0.12391
$H_{1,2}$	±1.43047	0.00000	0.98328
NH_3			
N	0.00000	0.00000	0.12783
H_1	0.00000	1.77130	−0.59205
$H_{2,3}$	±1.53399	−0.88565	−0.59205
BF_3			
B	0.00000	0.00000	0.00000
F_1	0.00000	0.00000	2.47932
$F_{2,3}$	±2.14715	0.00000	−1.23966

4. Results and discussion

Selected distributed polarizability components have been collected in Tables 2–5. With the exception of CO, where all the independent components were listed, only the most significant elements have been tabulated.

For all the studied molecules the individual distributed polarizability components are remarkably stable with respect to extension of the basis set and to addition of diffuse functions. The charge–charge, dipole–charge and charge–dipole polarizabilities vary only moderately on basis set extension, the former by about 10%. Their value is in the order of 0.1–1.0, which corresponds to the chemical intuition that intramolecular charge transfers, due to weak external perturbations, should be limited to a fraction of the electronic charge.

The one-center dipole–dipole polarizability components may change considerably with the basis, but their variation runs completely in parallel with the improvement of the total molecular dipole–dipole polarizability. All of the distributed dipole–dipole polarizabilities are smaller than the total ones, which speaks for their physical relevance.

In the case of CO (Table 2) the charge-flow polarizability is relatively high (0.9) and the atomic dipole polarizabilities of the carbon and oxygen atoms are quite close to each other. It is interesting to note that we had some difficulties to make the numerical integration procedure converge for CO. This is the origin of the slight discrepancies (less than 0.5%) of the total CPHF polarizabilities as calculated from molecular transition moment integrals and determined from the distributed polarizabilities according to formula (12) (c.f. the total polarizabilities given in parentheses in Table 2). Similar effects were observed in the case of BF_3, but the overall agreement (deviations below 10^{-3} au) is satisfactory for all basis sets in the case of water and ammonia.

As is demonstrated by the case of water (c.f. Table 3) the atomic dipole–dipole polarizabilities are almost exclusively responsible for the basis set dependence of the total polarizabilities. The contribution of the charge-flow, charge–dipole and dipole–charge terms is practically constant: it varies between 2.09 and 2.17 au for the zz component and between 4.13

Table 2
Selected components of the distributed polarizabilities (in au) of the CO molecule, using different basis sets. The total polarizabilities recalculated from the distributed components according to Eq. (12) are given in parentheses

Component	6-31G*	6-311G(d)	6-311G(2d)	6-311++G(2d)	[5s3p2d]	[10s6p3d]
α_{qq}^{OC}	−0.816	−0.868	−0.874	−0.889	−0.864	−0.902
α_{qz}^{OC}	−0.603	−0.630	−0.621	−0.668	−0.674	−0.653
α_{zq}^{OC}	0.361	0.373	0.285	0.343	0.326	0.290
α_{xx}^{OC}	0.186	0.270	0.176	0.121	0.347	−0.024
α_{zz}^{OC}	−0.127	−0.114	−0.194	−0.102	−0.141	−0.118
α_{xx}^{CC}	4.521	5.008	5.289	5.695	5.795	5.990
α_{zz}^{CC}	2.245	2.447	2.515	2.950	2.986	3.067
α_{xx}^{OO}	2.886	2.686	3.717	4.173	5.219	5.312
α_{zz}^{OO}	2.431	2.400	2.802	3.219	3.543	3.498
α_{xx}^{tot}	7.766	8.243	9.335	10.069	11.089	11.255
	(7.779)	(8.235)	(9.357)	(10.110)	(11.084)	(11.255)
α_{zz}^{tot}	12.237	12.848	12.759	14.313	14.435	14.447
	(12.239)	(12.846)	(12.762)	(14.316)	(14.435)	(14.447)

Table 3
Selected components of the distributed polarizabilities (in au) of the H_2O molecule, using different basis sets. The total polarizabilities recalculated from the distributed components according to Eq. (12) are identical with those obtained from direct calculation

Component	6-31G**	6-311G(d, p)	6-311G(2d, 2p)	6-311++G(2d, 2p)	[5s3p2d]	[10s6p3d]
$\alpha_{qq}^{OH_1}$	−0.358	−0.383	−0.375	−0.372	−0.369	−0.387
$\alpha_{qq}^{H_1H_2}$	−0.043	−0.046	−0.044	−0.042	−0.042	−0.044
α_{qz}^{OO}	−0.264	−0.302	−0.228	−0.272	−0.220	−0.212
$\alpha_{qz}^{H_1H_1}$	0.164	0.176	0.174	0.183	0.194	0.198
$\alpha_{qz}^{OH_1}$	−0.146	−0.157	−0.154	−0.162	−0.171	−0.175
$\alpha_{zq}^{OH_1}$	0.132	0.151	0.114	0.136	0.110	0.106
$\alpha_{xx}^{H_1H_1}$	0.182	0.199	0.213	0.228	0.247	0.259
$\alpha_{yy}^{H_1H_1}$	0.042	0.068	0.101	0.106	0.124	0.140
$\alpha_{zz}^{H_1H_1}$	0.125	0.148	0.171	0.196	0.228	0.239
α_{xx}^{OO}	2.039	2.075	2.897	3.111	4.067	3.968
α_{yy}^{OO}	2.608	3.263	4.069	5.888	6.906	6.884
α_{zz}^{OO}	2.298	2.267	3.430	3.869	5.156	5.055
α_{xx}^{tot}	7.024	7.363	7.945	8.269	9.167	9.153
α_{yy}^{tot}	2.928	3.763	4.873	6.681	7.821	7.855
α_{zz}^{tot}	5.108	5.483	6.519	7.180	8.488	8.438

and 4.23 for the xx term, when the basis changes from 6-31G** to [10s6p3d]. The atomic dipole–dipole polarizabilities vary much more: α_{zz}^{OO} changes from 5.11 to 8.49, α_{xx}^{OO} from 7.02 to 9.16.

This observation suggests that the molecular polarizability of large systems could be estimated from a relatively low basis set level, which describes charge-flow terms correctly, and afterwards the basis set dependent monoatomic contribution could be corrected by model calculations on related small systems.

The distributed polarizability model of Millot and Stone [25] can be compared to our 6-311++G(2d, 2p) results for water, since they yield comparable total polarizabilities. Although the overall features are similar (taking into account the difference in the molecular orientation) one can remark that in their model the charge-flow terms are higher, the one-center dipole–dipole polarizabilities are smaller for oxygen and larger for hydrogen atoms than in our approach.

For NH_3 Table 4 shows that the dipole–dipole polarizability of the nitrogen atom contributes by about

Table 4
Selected components of the distributed polarizabilities (in au) of the NH_3 molecule, using different basis sets. The total polarizabilities recalculated from the distributed components according to Eq. (12) are identical with those obtained from direct calculation

Component	6-31G**	6-311G(d, p)	6-311G(2d, 2p)	6-311++G(2d, 2p)	[5s3p2d]	[10s6p3d]
$\alpha_{qq}^{NH_1}$	−0.493	−0.512	−0.524	−0.525	−0.509	−0.532
$\alpha_{qq}^{H_1H_2}$	−0.074	−0.077	−0.080	−0.079	−0.077	−0.078
α_{qz}^{NN}	0.271	0.270	0.255	0.380	0.377	0.336
$\alpha_{qy}^{H_1H_1}$	0.379	0.382	0.391	0.395	0.409	0.407
$\alpha_{qz}^{H_1H_1}$	−0.164	−0.169	−0.177	−0.195	−0.211	−0.210
$\alpha_{qy}^{NH_1}$	−0.280	−0.280	−0.287	−0.288	−0.299	−0.297
$\alpha_{qz}^{NH_1}$	0.134	0.139	0.141	0.154	0.158	0.158
$\alpha_{zq}^{NH_1}$	−0.090	−0.090	−0.085	−0.127	−0.126	−0.112
$\alpha_{zz}^{NH_1}$	0.118	0.181	0.229	0.304	0.363	0.346
$\alpha_{xx}^{H_1H_1}$	0.119	0.191	0.326	0.338	0.372	0.411
$\alpha_{yy}^{H_1H_1}$	0.400	0.438	0.467	0.481	0.510	0.530
$\alpha_{zz}^{H_1H_1}$	0.180	0.244	0.358	0.426	0.475	0.502
α_{xx}^{NN}	2.112	2.397	3.100	3.482	4.327	4.302
α_{zz}^{NN}	2.713	3.896	4.662	6.770	7.722	7.747
α_{xx}^{tot}	9.457	9.897	10.903	11.519	12.748	12.732
α_{zz}^{tot}	5.677	7.475	8.862	11.871	13.272	13.246

Table 5
Selected components of the distributed polarizabilities (in au) of the BF_3 molecule, using different basis sets. The total polarizabilities recalculated from the distributed components according to Eq. (12) are given in parentheses

Component	6-31G**	6-311G(dp)	6-311G(2d, 2p)	6-311++G(2d, 2p)	[5s3p2d]
$\alpha_{qq}^{BF_1}$	−0.066	−0.081	−0.071	−0.071	−0.068
$\alpha_{qq}^{F_1F_2}$	−0.111	−0.112	−0.113	−0.114	−0.115
$\alpha_{qz}^{F_1F_1}$	0.194	0.240	0.209	0.233	0.221
$\alpha_{qz}^{BF_1}$	−0.117	−0.134	−0.112	−0.110	−0.110
$\alpha_{zq}^{BF_1}$	−0.017	−0.022	−0.019	−0.019	−0.018
$\alpha_{xx}^{F_1F_1}$	1.986	1.631	2.292	2.561	3.221
$\alpha_{yy}^{F_1F_1}$	2.381	2.047	2.835	3.150	3.847
$\alpha_{zz}^{F_1F_1}$	1.906	1.915	2.121	2.549	2.772
α_{yy}^{BB}	0.080	0.126	0.098	0.097	0.093
α_{zz}^{BB}	0.031	0.040	0.036	0.036	0.032
α_{yy}^{tot}	7.845	7.313	9.236	10.085	11.850
	(7.814)	(7.277)	(9.202)	(10.048)	(11.833)
α_{zz}^{tot}	10.942	11.182	12.222	13.588	14.658
	(10.942)	(11.181)	(12.221)	(13.587)	(14.656)

50% to the total α_{zz}. In the case of the perpendicular $\alpha_{yy}=\alpha_{xx}$ components this contribution is reduced to about one third. The contribution of the charge-flow, charge–dipole and dipole–charge terms to the total α_{zz} is similar to the case of water: it varies between 1.74 and 2.03 au for the different basis set showing the relative basis-set independence of these terms.

As can be seen from Table 5, the charge-flow polarizability in BF_3 is almost negligibly small. Interestingly it is stronger for the nonbonded F–F contacts than for the B–F bonds. The atomic dipole polarizability of the boron is negligible and most of the contribution stems from the atomic polarizabilities of the fluorine atoms. This observation is in perfect agreement with the electronic structure of this molecule, which is dominated by an extremely ionic bond be-

tween boron and fluorine (the net charge of boron is found to be 2.5 e in the Bader partitioning).

In conclusion, Bader's atomic partition scheme offers a convenient, physically well-founded, basis set independent framework for discussing the polarizability distributions in terms of atomic multipole polarizabilities. Values close to the Hartree–Fock limit have been obtained with distributed components which always remained stable. The physical insight gained by this analysis might be useful to develop more sophisticated and accurate representations of induction forces for small molecules and opens the way to design novel and efficient approximations to treat the polarizability in larger molecules and in biopolymers.

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