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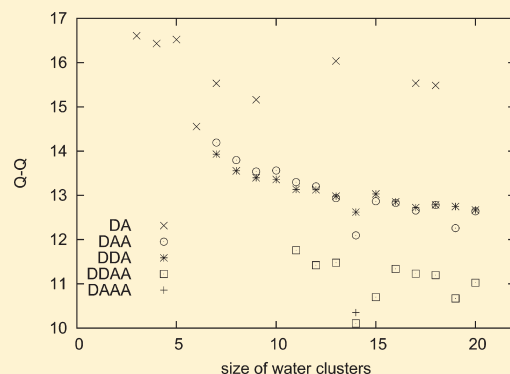
# Partitioning of Higher Multipole Polarizabilities: Numerical Evaluation of Transferability

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**ABSTRACT:** In this work, the partitioning of higher multipole polarizabilities, such as dipole–quadrupole, quadrupole–dipole, and quadrupole–quadrupole polarizabilities, into atomic contributions is studied. Partitioning of higher multipole polarizabilities is necessary in the study of accurate interaction energies where dispersion interactions are of importance. The fractional occupation Hirshfeld-I (FOHI) method is used to calculate the atomic polarizabilities and is briefly explained together with the methodology for partitioning of the polarizabilities. The atomic multipole polarizabilities are calculated for different sets of molecules, linear alkanes, water clusters, and small organic molecules with different functional groups. It is found that the atomic and group contributions of the dipole and quadrupole polarizabilities are transferable as a function of the functional groups.



## 1. INTRODUCTION

Additivity and transferability of properties of functional groups in molecules is one of the fundamental concepts in chemistry, as stressed in Bader's monumental contribution to this field.<sup>1</sup> This is also the case for group polarizabilities, which have been well studied experimentally.<sup>2,3</sup> Theoretically, different approaches have been suggested to partition the multipole polarizabilities.

When considering the partitioning of polarizability, one can distinguish two main approaches. On the one hand, one can attempt to describe the response of an atom-in-molecule to the local field, influenced by the neighboring atoms. Applequist<sup>4</sup> was the first to propose an empirical approach in this context by partitioning the polarizability into atomic contributions based on a dipole–induced dipole model. Subsequently, Stone<sup>5,6</sup> developed a more elaborate model based on the matrix elements of the multipole moment operator, which are partitioned between different regions of the molecule. Stone's model was implemented using different partitioning methods,<sup>7</sup> the best results obtained with Bader's topological theory.<sup>8,9</sup> In more recent attempts, Yang et al.<sup>10</sup> developed a model where the atomic dipole moments, obtained using the Hirshfeld method,<sup>11</sup> corrected by the charge distribution of the neighboring atoms, are used to estimate the local polarizabilities.

Alternatively, one can calculate the response of an atom-in-molecule to the applied field. Such an approach has the advantage of being closely related to the unpartitioned molecular property and does not require empirical or point-dipole models for the estimation of the induced field. Bader et al.<sup>12,13</sup> applied the quantum theory of atoms in molecules (QTAIM) theory to partition the molecular polarizability into atomic and group contributions. Later on, a fuzzy-atom method, based on the

Hirshfeld partitioning method,<sup>11,14</sup> for partitioning of the molecular dipole polarizability was introduced by some of the authors.<sup>15–17</sup> In this work, we will apply an extension of the Hirshfeld-I method, namely, the fractional occupation iterative Hirshfeld (FOHI) method,<sup>18</sup> to partition higher multipole polarizabilities.

Applications of these methods for the study of polarizabilities of atoms and groups of atoms for properties such as additivity and transferability,<sup>15,16,19,20</sup> dependence on the structure,<sup>21,22</sup> and Raman spectral intensities<sup>23–25</sup> are numerous. Studies involving the partitioning of higher multipole polarizabilities, for instance, the dipole–quadrupole polarizability and quadrupole polarizability,<sup>13,26</sup> are less common because the multipole polarizabilities involving the quadrupole moment are origin-dependent. By making use of a translation formula, which centers the quadrupole moment on the atom calculated, this dependence of the origin can be avoided. In this way, intrinsic atomic polarizabilities involving the quadrupole moment can easily be compared between different molecules.

The higher multipole polarizabilities are necessary in the study of accurate interaction energies where dispersion interactions are of importance.<sup>27–29</sup> These van der Waals interactions, which are of nonlocal and long-range character, can be related to the multipole polarizabilities of the systems.<sup>30</sup> Within the family of methods that are designed to estimate the contribution of

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dispersion to the interaction energy, mostly with the goal to correct the results of local density functional theory (DFT) methods, multipole polarizabilities play a central role. Yet, the characteristics of the higher multipole polarizabilities used in these methods are not very well-known. Furthermore, within the pairwise additivity approach, these methods require the knowledge of atomic polarizabilities of atoms-in-molecules, which cannot be obtained experimentally. In order to retain the anisotropic character of the dispersion interaction, one needs atomic polarizability tensors, which requires the use of a non-empirical partitioning method. Atomic multipole polarizabilities are, for example, also needed in polarizable force fields and Raman optical activity spectroscopy.<sup>31</sup>

The goal of this article is two-fold. First of all, partitioning of multipole polarizabilities by means of the Fractional Occupational Hirshfeld-I method (FOHI)<sup>18</sup> will be presented. A brief explanation of the FOHI method will be given in section 2.1, followed by the methodology for partitioning of dipole, dipole–quadrupole, and quadrupole polarizabilities in section 2.2. After a brief description of the computational details in section 3, the multipole atomic polarizabilities for different sets of molecules will be evaluated in order to establish their characteristics such as transferability. This will be achieved in two parts, where first a comparison will be made between the two possible definitions of atomic dipole–quadrupole polarizability for a set diatomic molecules in section 4.1, followed by a discussion of the quadrupole polarizability for a collection of systems including linear alkanes, water clusters, and a set of small organic molecules in section 4.2. Conclusions will be drawn in section 5.

## 2. METHOD

**2.1. The FOHI Method.** A partitioning method has to be applied in order to calculate atomic polarizabilities. In this case, we will use the FOHI method.<sup>18</sup> The Hirshfeld method<sup>11</sup> is a partitioning method that uses a weight function in order to divide the molecular density  $\rho(\vec{r})$  into atomic densities  $\rho_a(\vec{r})$

$$\rho_a(\vec{r}) = w_a(\vec{r})\rho(\vec{r}) \quad (1)$$

The Hirshfeld method uses diffuse boundaries where the weight function of an atom  $a$  can be, in principle, not equal to 0 at any point  $\vec{r}$  of the space. The “share” of each atom at point  $\vec{r}$  is relative to the share of the free atom in the promolecular density

$$w_a^H(\vec{r}) = \frac{\rho_a^{[0]}(\vec{r})}{\sum_b \rho_b^{[0]}(\vec{r})} \quad (2)$$

The promolecular density is defined as the sum of the densities of the isolated atoms  $\rho_b^{[0]}$ , positioned at the same coordinates as the atomic nuclei in the real molecule. Integration of the atomic density leads to the population of every atom

$$N_a = \int \rho_a(\vec{r}) d\vec{r} = \int w_a(\vec{r})\rho(\vec{r}) d\vec{r} \quad (3)$$

In the original Hirshfeld method, the isolated atoms are usually chosen as neutral atoms. The arbitrary character of the choice of the isolated atomic densities to build up the promolecular density is one of the major criticisms of this method.<sup>14</sup> This problem has been solved by making use of an iterative procedure, the Hirshfeld-I (HI) method.<sup>14</sup> In this method, the promolecule in each iteration is constructed from atomic densities obtained in

the previous iteration, thus allowing the atomic populations of the atoms-in-molecules to change.

The FOHI method is based on the HI method but uses another approach to build up the promolecule.<sup>32</sup> In every iteration, an atomic SCF calculation based on fractional occupation is performed for every atom of the promolecule. The orbitals for a spherically symmetric atom with a given charge are calculated in the restricted approach using fractional occupations for degenerate valence orbitals, while all other orbitals lower in energy are fully occupied. For the atomic SCF calculations, the same level of theory (DFT functional and basis set) is used as that for the molecular system. For example, in a given iteration, for a carbon atom with a charge of  $-0.4$ , the occupation of the 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> orbitals would be 2, 2, 0.8, 0.8, and 0.8.

The new method can be summarized as follows:

- On the basis of the atomic charge, atomic SCF calculations are performed based on fractional occupations to compute the corresponding densities for every atom in the system. In the first step, the charge of every atom is set equal to 0.
- The promolecular density is constructed based on the atomic densities and is used to calculate the weight function.
- A Hirshfeld partitioning of the molecular density is performed using the weight function that was constructed in the previous step.
- The atomic charge of every atom is compared with the corresponding value in the previous iteration. If convergence is not reached, the previous steps are repeated.

The main advantage of the FOHI method lies in the fact that not only the charge of the promolecular atoms is constructed self-consistently but also the spin. In the case of closed-shell molecules examined in this work, this means that the choice of promolecular atomic densities is restricted to singlets. This is not the case in the HI method, which interpolates between the atomic densities of atoms with a different charge and spin state. The atoms used in the HI method were calculated at the Hartree–Fock level and are therefore not necessarily singlets. This means that for closed-shell molecules, the atoms in the promolecule do not have zero spin, as one assumes that they should.

**2.2. Partitioning of Polarizabilities.** On the basis of the coupled perturbed Kohn–Sham (CPKS) method, the elements of the polarizability tensor are given by<sup>33</sup>

$$\alpha_{ij} = -\text{tr}[\mathbf{H}^{(i)}\mathbf{D}^{(j)}] = -\int i\rho^{(j)}(\vec{r}) d\vec{r} \quad (4)$$

$\mathbf{H}^{(i)}$  and  $\mathbf{D}^{(j)}$  are the dipole moment and the first-order density matrices along Cartesian directions  $i$  and  $j$ , respectively.  $\rho^{(j)}$  represents the perturbed molecular electron density in the presence of an electric field, applied along Cartesian direction  $j$ .

The  $ij$  element of the intrinsic atomic polarizability tensor for atom  $a$  is defined as<sup>15</sup>

$$\alpha_{ij}^a = -\int (i - a_i)w_a(\vec{r})\rho^{(j)}(\vec{r}) d\vec{r} \quad (5)$$

where  $a_i$  is the coordinate of atom  $a$  in the Cartesian direction  $i$ . The dipole Hamiltonian is centered on atom  $a$ , and the electron density perturbed by an electric dipole field is independent of the origin. The  $w_a$  is the FOHI weight

function, which partitions the perturbed molecular density into atomic densities. Note that this definition of atomic polarizability describes the response of the atom to an applied field, contrary to the possibility of defining the response to the local field.<sup>10</sup>

The elements of the total molecular polarizability tensor can be reconstructed exactly by summing over all of the intrinsic polarizabilities of the atoms in the molecule and their respective charge delocalization contributions<sup>15</sup>

$$\alpha_{ij} = \sum_a \alpha_{ij}^a + a_i q_a^{(j)} \quad (6)$$

where  $q_a^{(j)} = -\int w_a(\vec{r}) \rho^{(j)}(\vec{r}) d\vec{r}$  is the first-order perturbed atomic charge. In this work, we will only focus on the intrinsic polarizabilities. The charge delocalization terms depend on the coordinates of the atoms and reflect the nonadditivity of the polarizability.

The intrinsic dipole–quadrupole polarizability can be defined in two ways. One can define it as the change in the quadrupole moment with an applied dipole moment field (Q–D).

$$A_{ij,k}^a = - \int \Theta_{ij}^a w_a(\vec{r}) \rho_a^{(k)}(\vec{r}) d\vec{r} \quad (7)$$

Here,  $\Theta_{ij}^a = (1/2)(3(i - a_i)(j - a_j) - r^2 \delta_{ij})$  is the traceless electric quadrupole moment, centered on atom  $a$ , with  $r^2 = (x - a_x)^2 + (y - a_y)^2 + (z - a_z)^2$ .

One can also define the atomic dipole–quadrupole polarizability as the change in the dipole moment with an applied quadrupole field (D–Q).

$$A_{i,jk}^a = - \int (i - a_i) w_a(\vec{r}) \rho_a^{(jk)}(\vec{r}) d\vec{r} \quad (8)$$

The electron density perturbed by an electric quadrupole field is origin-dependent. To solve this problem,  $\rho_a^{(jk)}$  is defined as the electron density perturbed by an electric quadrupole field centered on the atom  $a$ . The quadrupole field is shifted so that its origin is at the center of the atom calculated. Centering the applied quadrupole field on atom  $a$  is achieved by the following translation formula

$$\begin{aligned} \rho_a^{(ij)} &= \rho^{(ij)} - \frac{3}{2}(a_i \rho^{(j)} + a_j \rho^{(i)}) \\ &+ \delta_{ij}(a_x \rho^{(x)} + a_y \rho^{(y)} + a_z \rho^{(z)}) \end{aligned} \quad (9)$$

where  $\rho^{(ij)}$ ,  $\rho^{(i)}$ , and  $\rho^{(j)}$  are perturbed densities calculated with fields centered at the origin of the molecule. The two definitions of the dipole–quadrupole polarizability will be compared in section 4.1. The intrinsic atomic quadrupole (Q–Q) polarizability tensor can be defined in a similar way

$$C_{ij,kl}^a = - \int \Theta_{ij}^a w_a(\vec{r}) \rho_a^{(kl)}(\vec{r}) d\vec{r} \quad (10)$$

All of the polarizabilities involving higher multipoles are origin-dependent. However, due to the centering of the quadrupole moments in eqs 7, 8, and 10 on the center of the atoms, the resulting atomic intrinsic polarizability tensor elements are invariant on translation.

However, because the tensor elements are not invariant upon rotation, we will confine the discussion, where possible, to the

**Table 1. Atomic Dipole–Quadrupole (D–Q) and Atomic Quadrupole–Dipole (Q–D) Polarizabilities of Diatomic Molecules<sup>a</sup>**

			$A_{\parallel}$	$A_{\perp}$
CO	C	D–Q	−7.108	−7.079
		Q–D	−5.132	−5.780
	O	D–Q	0.923	0.984
		Q–D	−0.381	−0.313
CS	C	D–Q	−5.172	−9.103
		Q–D	−2.807	−2.719
	S	D–Q	3.633	8.054
		Q–D	0.993	1.684
HCl	Cl	D–Q	0.314	−0.819
		Q–D	1.069	0.474
	H	D–Q	1.263	1.472
		Q–D	0.801	0.175
HF	F	D–Q	−1.198	−0.727
		Q–D	−0.642	−0.345
	H	D–Q	0.606	0.366
		Q–D	0.120	−0.016

<sup>a</sup>  $A_{\parallel}$  is the component in the direction of the molecular axis, and  $A_{\perp}$  is the component orthogonal to the molecular axis. All values are in au.

isotropic values defined as<sup>30</sup>

$$\alpha^{\text{iso}} = \frac{1}{3} \text{tr}(\alpha) \quad (11)$$

$$C^{\text{iso}} = \frac{1}{5} \text{tr}(C) \quad (12)$$

The quadrupole–quadrupole polarizability tensor as defined in eq 10 is a  $9 \times 9$  tensor; therefore, the trace in eq 12 is given by the sum of the diagonal elements.

### 3. COMPUTATIONAL DETAILS

The geometries were optimized using the B3LYP functional<sup>34</sup> and the aug-cc-pVTZ basis set<sup>35</sup> with the Gaussian09 program.<sup>36</sup> The molecular polarizabilities were determined with the finite field approach using electric dipole moment and quadrupole moment fields of  $\pm 0.0001$  au. The atomic polarizabilities were calculated based on FOHI method.<sup>18</sup> The atomic densities were calculated every iteration using the BRABO package,<sup>37</sup> with the same functional and basis set as those for the molecules. The STOCK program<sup>38</sup> was used to evaluate the atomic polarizabilities.

### 4. DISCUSSION

**4.1. Dipole–Quadrupole Polarizability and Quadrupole–Dipole Polarizability.** The Q–D (eq 7) and D–Q (eq 8) atomic polarizabilities will be compared for a small set of molecules. Because the isotropic value of the dipole–quadrupole polarizability is always 0, only a discussion of separate tensor elements is possible. Because, in the general case, the dipole–quadrupole polarizability has 15 independent tensor elements, we will restrict the discussion to diatomic systems aligned along the  $z$ -axis, where only two independent tensor elements can be distinguished due to the axial symmetry ( $C_{\infty v}$ ).<sup>30</sup> As a result, the D–Q and Q–D can be expressed in terms of components

**Table 2. Atomic Dipole (D–D) and Atomic Quadrupole (Q–Q) Polarizabilities of Carbon Atoms in Linear Alkanes<sup>a</sup>**

		D–D	Q–Q			D–D	Q–Q
CH <sub>4</sub>	C <sub>1</sub>	6.494	26.182	C <sub>8</sub> H <sub>18</sub>	C <sub>1</sub>	4.598	23.832
C <sub>2</sub> H <sub>6</sub>	C <sub>1</sub>	4.569	21.811		C <sub>2</sub>	2.544	14.967
C <sub>3</sub> H <sub>8</sub>	C <sub>1</sub>	4.513	23.542		C <sub>3</sub>	2.401	15.943
	C <sub>2</sub>	2.750	14.890		C <sub>4</sub>	2.375	16.288
C <sub>4</sub> H <sub>10</sub>	C <sub>1</sub>	4.509	23.650	C <sub>9</sub> H <sub>20</sub>	C <sub>1</sub>	4.509	23.524
	C <sub>2</sub>	2.621	15.308		C <sub>2</sub>	2.562	15.627
C <sub>5</sub> H <sub>12</sub>	C <sub>1</sub>	4.499	23.432		C <sub>3</sub>	2.411	16.089
	C <sub>2</sub>	2.602	15.376		C <sub>4</sub>	2.385	16.153
	C <sub>3</sub>	2.482	15.879		C <sub>5</sub>	2.330	16.136
C <sub>6</sub> H <sub>14</sub>	C <sub>1</sub>	4.502	23.298	C <sub>10</sub> H <sub>22</sub>	C <sub>1</sub>	4.516	23.506
	C <sub>2</sub>	2.581	15.295		C <sub>2</sub>	2.561	15.644
	C <sub>3</sub>	2.445	15.973		C <sub>3</sub>	2.411	16.087
C <sub>7</sub> H <sub>16</sub>	C <sub>1</sub>	4.506	23.198		C <sub>4</sub>	2.382	16.182
	C <sub>2</sub>	2.578	15.243		C <sub>5</sub>	2.325	16.103
	C <sub>3</sub>	2.432	15.912	C <sub>11</sub> H <sub>24</sub>	C <sub>1</sub>	4.515	23.432
	C <sub>4</sub>	2.430	16.090		C <sub>2</sub>	2.562	15.631
					C <sub>3</sub>	2.408	16.110
					C <sub>4</sub>	2.380	16.155
					C <sub>5</sub>	2.320	16.127
					C <sub>6</sub>	2.360	16.027

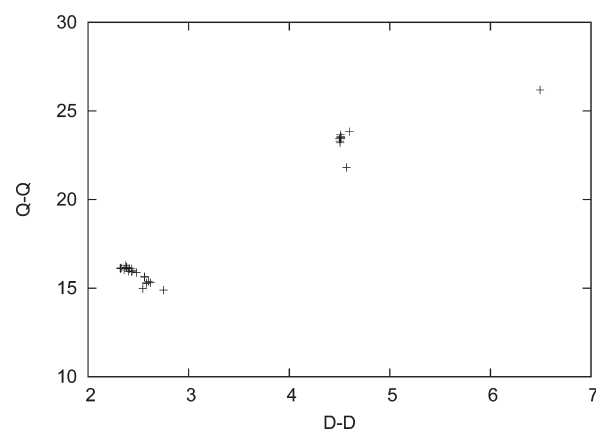
<sup>a</sup> All values are in au. Only values of the unique carbon atoms are shown. The carbon atoms are numbered starting from the outside of the molecule towards the center of the molecule.

orthogonal ( $A_{\perp}$ ) or parallel ( $A_{\parallel}$ ) to the molecular axis.

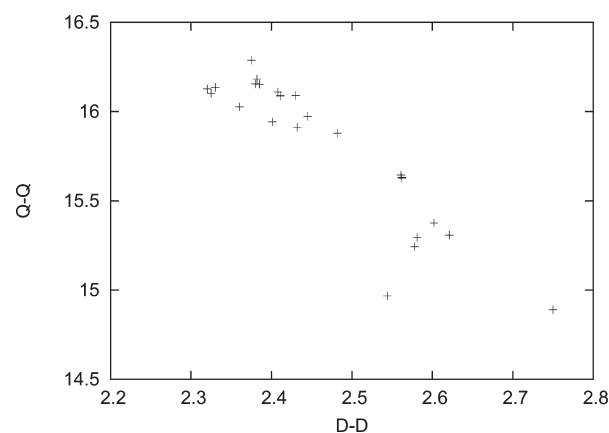
$$\begin{aligned} A_{\parallel} &= A_{z,zz} = -2A_{z,xx} = -2A_{z,yy} \\ A_{\perp} &= A_{x,xz} = A_{x,zx} = A_{y,yz} = A_{y,zy} \end{aligned} \quad (13)$$

The tensor elements of the molecules CO and CS have been compared previously using a QTAIM partitioning of the dipole–quadrupole polarizability.<sup>13</sup> (Note that this was one of the very first papers on the numerical evaluation of molecular A tensor elements, which appeared in the Can. J. Chem. issue in honor of Richard Bader's 65th birthday.)

The results of the D–Q and Q–D polarizability of CO, CS, HF, and HCl can be found in Table 1. First, the D–Q polarizabilities of the CO and CS molecule will be compared. For CO, the D–Q polarizabilities for carbon and oxygen are –7.1 and 0.9, respectively, in both directions. However, for the CS molecule, the values of the D–Q polarizabilities for both atoms are dependent on the direction. For carbon, the D–Q polarizability is –5.1 along the axis and –9.1 orthogonal to the axis and 3.6 and 8.0 for sulfur, respectively. The D–Q polarizability is much larger for sulfur than that for oxygen. For the Q–D polarizability, the same conclusions can be drawn for the oxygen and the sulfur atoms. For the carbon atom, the Q–D polarizability in CO is –5.1 in the direction along the axis and –5.7 orthogonal to the axis. For carbon in the CS molecule, the Q–D polarizability is –2.8 in both directions. The atomic D–Q and Q–D polarizabilities of CO and CS were studied before,<sup>13</sup> but a direct comparison is hampered by a different approach of the definition of the atomic values. Moreover, in ref 13, the quadrupole moment is not centered on the atom but on the mass center of the molecule.



**Figure 1.** Atomic quadrupole polarizability as a function of the atomic dipole polarizability for carbon atoms in linear alkanes. All values are in au.

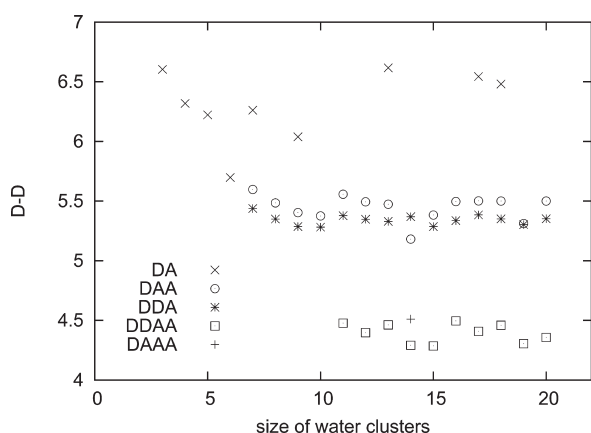


**Figure 2.** Atomic quadrupole polarizability as a function of the atomic dipole polarizability for methylene carbon atoms in linear alkanes. All values are in au.

In HF, the D–Q and Q–D polarizabilities for fluor are all negative. For chlorine in HCl, this is only the case for the orthogonal Q–D component. The D–Q and Q–D polarizabilities of the hydrogen atom are larger in HCl as compared to those in HF. As can be concluded from the four diatomic molecules that we discussed, it is not evident to attach a direct chemical meaning to the atomic D–Q and Q–D polarizabilities.

**4.2. Quadrupole Atomic Polarizability.** The first set of molecules that we would like to discuss are the linear alkanes. Some properties of this set of molecules have been studied thoroughly. For example, the additivity of the energy,<sup>39–41</sup> molecular volumes,<sup>42</sup> and polarizabilities<sup>20,43</sup> of hydrocarbons has been treated previously. By using the partitioning scheme above, we calculated the intrinsic atomic dipole polarizabilities (D–D) and the intrinsic atomic quadrupole polarizabilities (Q–Q) of linear alkanes ranging from methane to undecane, the results of which can be found in Table 2. Only the unique carbon atoms in every molecule are presented. The carbon atoms are numbered starting from the outside of the molecule toward the center of the molecule. Methane has exceptionally high values, a D–D of 6.494 and a Q–Q of 26.182. In contrast to the other linear alkanes, the carbon atom in methane is only shielded by hydrogen atoms. For all other molecules, the



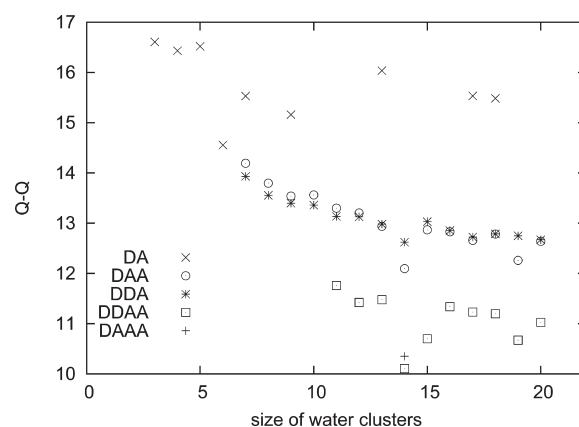


**Figure 3.** Molecular dipole polarizability of water (in au) as a function of the cluster size. Different types of water molecules can be identified in the water clusters.

polarizabilities of the methyl carbon atoms are higher compared to those for the methylene carbon atoms. The D–D and Q–Q values for the methyl carbon atoms are approximately 4.5 and 23.5, while the D–D and Q–Q values for the methylene atoms are in the ranges of 2.3–2.8 and 14.8–16.2, respectively.

The values of Table 2 are plotted in Figure 1. The graph illustrates that the atomic polarizabilities can be divided into three groups, methane, methyl carbon atoms, and methylene carbon atoms. The methylene carbon atoms are more shielded from the electric field and therefore have lower polarizabilities. The polarizabilities of the methyl carbon atoms and methylene carbon atoms are transferable between different molecules. In Figure 2, only the values of the methylene groups are plotted, where three groups can be identified.<sup>20</sup> The values of the D–D and Q–Q of the first group are in the ranges of 2.3–2.5 and 15.7–16.4, respectively. This group was identified as the methylene carbon atoms attached to two methylene groups. The following group has values of the D–D and Q–Q, which are in the ranges of 2.5–2.7 and 14.8–15.7, respectively. This group contains the methylene carbon atoms that are connected to one methyl group and one methylene group. There is one methylene carbon atom with D–D and Q–Q values of 2.750 and 14.890, which is attached to two methyl groups. A methylene carbon atom attached to two methyl groups is a unique case that only occurs in propane. It can be concluded that the values of the D–D and Q–Q are transferable over the linear alkanes. For the complete set of carbon atoms, there seems to be a linear correlation with a positive slope. For the methylene carbon atoms, a linear correlation with a negative slope can be identified.

The following set of molecules that we would like to discuss are water clusters. Partitioning of water clusters into molecular polarizabilities has been studied previously.<sup>15</sup> For water clusters up to 20 water molecules, the molecular dipole polarizability and molecular quadrupole polarizability will be compared. Figure 3 shows the intrinsic molecular polarizability as a function of the size of the water clusters. The intrinsic molecular polarizabilities depend on the number of hydrogen bonds that the molecule forms with its neighbor. A water molecule that donates a hydrogen atom to form a hydrogen bond is a D-type water molecule. If the water molecule accepts a hydrogen bond through oxygen, it is an A-type water molecule. In this way, four common types of water molecules can be identified, DA, DAA, DDA, and



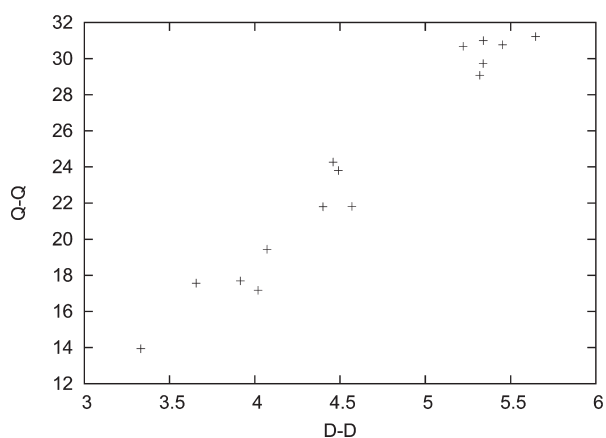
**Figure 4.** Molecular quadrupole polarizability of water (in au) as a function of the cluster size. Different types of water molecules can be identified in the water clusters.

**Table 3. Dipole (D–D) and Quadrupole (Q–Q) Polarizabilities for Methyl Carbon Atoms, Carbonyl Functional Groups, and Oxygen ( $sp^3$ ) Atoms<sup>a</sup>**

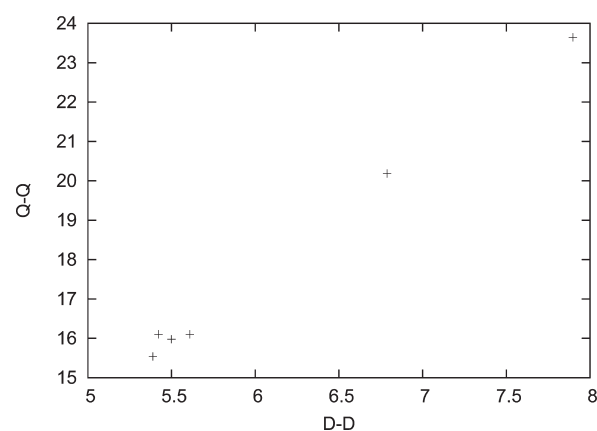
Name	Molecule	C (methyl)		Carbonyl		O ( $sp^3$ )	
		D-D	Q-Q	D-D	Q-Q	D-D	Q-Q
methyl fluoride	<chem>FC(F)(F)F</chem>	4.019	17.173				
ethane	<chem>CC</chem>	4.569	21.811				
methanol	<chem>CO</chem>	3.915	17.693			4.592	11.672
acetone	<chem>CC(=O)C</chem>	5.319	29.079	5.500	15.977		
acetaldehyde	<chem>CC=O</chem>	5.647	31.219	6.787	20.187		
acetic acid	<chem>CC(=O)O</chem>	5.453	30.768	5.609	16.100	4.756	13.215
acetamide	<chem>CC(=O)N</chem>	5.339	29.721	5.422	16.103		
methylamine	<chem>CN</chem>	4.072	19.441				
methyl chloride	<chem>CCl</chem>	5.222	30.684				
ethanol	<chem>CCO</chem>	4.400	21.800			3.973	9.564
1-propanol	<chem>CCCO</chem>	3.331	13.937			3.981	9.612
isopropanol	<chem>CC(C)O</chem>	4.490	23.801			3.883	10.134
ethylene glycol	<chem>OCCO</chem>					3.708	9.097
formaldehyde	<chem>C=O</chem>			7.898	23.645		
dimethyl ether	<chem>COC</chem>	4.459	24.266			2.603	5.790
methyl acetate	<chem>CC(=O)OC</chem>	5.340	30.999	5.388	15.538	2.939	7.378
		3.656	17.562				

<sup>a</sup> All values are in au.

DDAA. The more hydrogen bonds that the water molecule accepts or donates, the lower its intrinsic molecular polarizability.



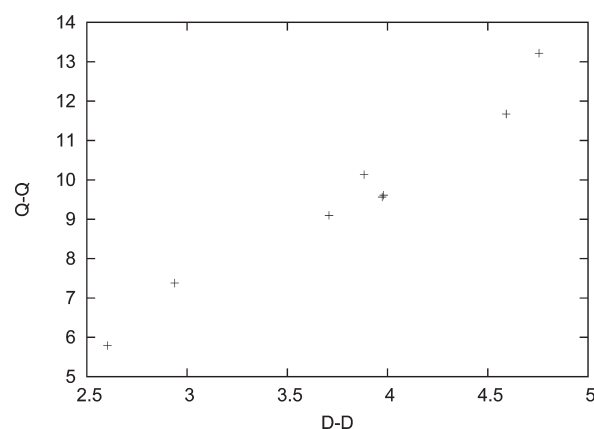
**Figure 5.** Atomic quadrupole polarizability as a function of the atomic dipole polarizability for methyl carbon atoms. All values are in au.



**Figure 6.** Quadrupole polarizability as a function of the dipole polarizability for the carbonyl functional groups. All values are in au.

Until the cluster size of five water molecules, the intrinsic molecular polarizability decreases strongly, which is related to the length of the hydrogen bonds.<sup>15</sup> Starting from seven water molecules, different types of water molecules can be identified. With increasing cluster size, the average intrinsic molecular polarizability of every type of water molecule is approximately equal. The DA water molecules have the largest intrinsic molecular polarizability because this type of molecule forms only two hydrogen bonds. The polarizabilities of the DAA and DDA molecules are in the range of 5.1 and 5.6, with DDA molecules having a slightly lower polarizability, except for the cluster with 14 molecules. This cluster is exceptional because a DAAA molecule could be identified. The DAAA and DDAA form four hydrogen bonds and therefore have much lower polarizabilities, which are around 4.4. Figure 4 shows the intrinsic quadrupole polarizability as a function of the size of the water clusters, and the same conclusions as with the previous graph can be made here.

The polarizabilities will finally be compared for a set of molecules with a range of functional groups, of which the results can be found in Table 3. First, we compare the polarizabilities of the methyl carbon atoms over molecules with different functional groups. The polarizabilities of the methyl carbon atom were found to be transferable over the linear alkanes. This is not the



**Figure 7.** Quadrupole polarizability as a function of the dipole polarizability for the O ( $sp^3$ ) atoms. All values are in au.

case anymore when different functional groups are introduced. The effect on the properties of the methyl groups caused by functional groups was studied before.<sup>44,45</sup> It was found that the polarizabilities of the methyl groups decrease as the electronegativities of the first-bonded neighbor increase. As can be seen in Figure 5, there is indeed a linear dependence between the dipole and quadrupole polarizabilities with a correlation of 0.976. There is one group, with D–D and Q–Q of 5.5 and 30, respectively, that separates itself from the rest. This group contains all of the molecules where the first-bonded neighbor is a carbonyl functional group or a chlorine atom.

The polarizabilities of the carbonyl functional groups are plotted in Figure 6. The polarizabilities of the carbonyl functional group are more localized with a D–D and Q–Q of 5.5 and 16, respectively. However, there are two exceptions, one with a D–D and Q–Q of 6.787 and 20.187, respectively, and one with a D–D and Q–Q of 7.898 and 23.645, respectively. The two exceptions were identified when the carbonyl is part of an aldehyde functional group. This difference is caused by the neighbors on the atoms.<sup>45</sup> In a ketone, the carbonyl functional group is enclosed by two carbon atoms, where in an aldehyde, there is at least one hydrogen atom bonded to the carbonyl. Therefore, the volume that the carbonyl functional group encloses is smaller in a ketone than that in an aldehyde and less polarizable. The correlation between the dipole and quadrupole polarizabilities is 0.998.

The values of the oxygen atoms with  $sp^3$  hybridization are plotted in Figure 7, which have a correlation of 0.980. Methanol being an exception, with a D–D and Q–Q of 4.592 and 11.672, respectively, the polarizabilities of the other alcohols are grouped together with a D–D and Q–Q of around 3.8 and 9.5, respectively. The highest polarizability with a D–D and Q–Q of 4.756 and 13.215, respectively, is from the oxygen atom in the carboxylic acid functional group. The atomic polarizabilities with a D–D and Q–Q lower than 3.0 and 8.0, respectively, are oxygen atoms connected to two carbon atoms.

## 5. CONCLUSION

The molecular dipole, dipole–quadrupole, and quadrupole polarizabilities were partitioned into atomic contributions by making use of the fractional occupation Hirshfeld-I (FOHI) method.

There are two possibilities to define the dipole–quadrupole polarizability. However, both definitions are difficult to interpret because the isotropic values are 0 in both cases. One possibility is to compare elements of the tensor with each other.<sup>13</sup> On the basis of group-theoretical methods, there are two independent elements of the tensor for diatomic molecules. However, even for diatomic molecules, the results are not transferable, and there is no clear connection between the two definitions.

The results of the quadrupole polarizability show a lot of similarities compared to the dipole polarizability. For linear alkanes, the atomic dipole and quadrupole polarizabilities for carbon atoms are transferable over the molecules. For the dipole polarizability, the carbon atoms were distributed in methyl and methylene groups. This last group was split up further based on which bond the group formed.<sup>20</sup> This distribution was also found for quadrupole polarizabilities.

The dipole and quadrupole polarizabilities of water clusters containing up to 20 water molecules have also been examined. In these clusters, different types of water molecules can be distinguished based on the number and type of hydrogen bonds that it forms. The molecular dipole and quadrupole polarizabilities were found to be dependent on the type of water molecule, and the properties were found to be transferable between water clusters of different size.<sup>15</sup>

The last set examined consists of small organic molecules with different functional groups. The study of the atomic and group contributions of dipole polarizabilities as a function of the functional groups has been treated previously.<sup>44–46</sup> The dipole and quadrupole polarizabilities are partitioned into group contributions based on different functional groups. The polarizabilities of the functional groups are transferable, but the bonds that the functional group forms can have a great influence on the polarizabilities.

In conclusion, we have found that no chemical information can be trivially extracted from the atomic dipole–quadrupole polarizabilities, reflecting the anisotropic character of the property. On the other hand, atomic dipole and quadrupole polarizabilities were found to exhibit very similar trends, such as dependence on the type of the atoms, chemical surrounding, and general transferability. In future studies, the computational methodology developed in this paper will be exploited in the evaluation of higher-order ( $1/(R_n)$ ;  $n > 6$ ) terms in the perturbation expansion of dispersion energies.

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