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First-Principles Calculation of Local Atomic Polarizabilities

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Common methods of determining atomic polarizabilities suffer from the inclusion of nonlocal effects such as charge polarization. A new method is described for determining fully *ab initio* atomic polarizabilities based on calculating the response of atomic multipoles to the local electrostatic potential. The localized atomic polarizabilities are then used to calculate induction energies that are compared to *ab initio* induction energies to test their usefulness in practical applications. These polarizabilities are shown to be an improvement over the corresponding molecular polarizabilities, in terms of both absolute accuracy and the convergence of the multipolar induction series. The transferability of localized polarizabilities for the alkane series is also discussed.

1. Introduction

With the increase of computational power, it has become routine to perform molecular simulations involving thousands of atoms, especially in biological systems of interest.[1] These simulations are a valuable tool for the understanding of molecular properties in the condensed phase, including aqueous and nonaqueous solutions, as well as investigating phase transitions and liquid structure.[2]

Molecular simulations involve the exploration of the potential energy surface for the relevant system, and thus rely on the accurate determination of the forces between molecules. To simulate large systems, molecular simulation methods usually rely on atom−atom potentials, where an "atom" may also refer to a region in the molecule such as a functional group, which can be described using the united-atom approximation, or a lone pair or π-bond. Atom−atom potentials typically involve intramolecular terms describing pairs of atoms, which include bonds, bond angles, and dihedral terms, and intermolecular terms that involve nonbonded atoms, which include both repulsion and long-range terms.

As well as increasing the size of the system that can be studied, the power of modern computers also enables the development and use of more accurate potential models. One area where potentials may be improved is in the treatment of long range induction and dispersion forces, which are important for the simulation of weakly interacting systems, such as those involving van der Waals forces or hydrogen bonding. To accomplish this within the atom−atom ansatz, it is necessary to determine localized polarizabilities for the atoms, where "localized" means that the polarizabilities involve only the response of a single atom or region to the potential at the center of that region.

There are several methods for determining atomic polarizabilities, which can be divided into fitting and partitioning approaches. Of the fitting approaches, Thole's method[3] may be used to obtain isotropic atomic polarizabilities by fitting to the overall molecular polarizability; however, the method is limited to dipole−dipole polarizabilities. An alternative is to fit point-to-point induction energies computed on a grid surrounding the molecule[4,5] to a set of atomic polarizabilities. This method can yield dipole, quadrupole, and higher multipole polarizabilities, but it becomes impractical for large molecules due to unphysical negative polarizabilities.[4] The partitioning approaches may be divided into real-space and basis-space partitioning. In real-space partitioning, the molecule is divided into atomic regions using either integration grids[6] or by using Bader's theory of atoms in molecules,[7] and these regions used to determine the atomic polarizabilities. Basis-space partitioning, such as the method proposed by Le Sueur and Stone,[8] uses partitioning based on basis functions centered on the atoms to determine atomic polarizabilities. Both of these methods result in nonlocal polarizabilities between atomic sites, with large charge flow terms that are difficult to localize.

In this paper, a method is described for generating localized atomic polarizabilities, based on calculating the polarization of the molecule in a finite field and localizing the resulting atomic multipoles. The methodology is presented in section 2, and preliminary results and conclusions are given in section 3. All results in the paper are in atomic units; the atomic unit of length is the bohr, $a_0 = 5.291772 \times 10^{-11}$ m, and the atomic unit of energy is the Hartree, $E_h = 4.35975 \times 10^{-18}$ J.

2. Theory

Atomic polarizabilities describe the response of the multipoles, Q^{A}, of a region A to an electrostatic potential, V^{A}, applied at the origin, $\vec{r}_{\mathrm{A}}$, of the region. Using a standard notation, this response can be written in terms of atomic polarizabilities $\alpha^{\mathrm{A}}_{l\kappa,l'\kappa'}$ as

$$\Delta Q^{\mathrm{A}}_{l\kappa} = -\sum_{l'\kappa'} \alpha^{\mathrm{A}}_{l\kappa,l'\kappa'} V^{\mathrm{A}}_{l'\kappa'} \hat{R}_{l'\kappa'}(\vec{r} - \vec{r}_{\mathrm{A}}) \qquad (1)$$

where $l\kappa$ refer to the real components of the spherical harmonics,[9] $V^{\mathrm{A}}_{l'\kappa'}$ is the magnitude of the $l'\kappa'$ component of the applied potential expanded about the origin of region A, and $\hat{R}$ is the corresponding real spherical harmonic operator.

If the atomic polarizabilities obey eq 1, they can be calculated by placing the molecule in a series of external potentials, and solving for the polarizabilities based on the change in the multipoles of region A induced by the different potentials $V^{\mathrm{A}}_{l'\kappa'}$. It is also necessary to calculate the atomic multipoles $Q^{\mathrm{A}}_{l\kappa}$, and

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TABLE 1: Localization Procedure for the CO Molecule[a]

	Polarization $-\delta(Q^A_{l0})/\delta V^A_{l''0}$			
	$l'' = 1$			
	$l = 0$	$l = 1$	$l = 2$	$l = 3$
	Before Localizing			
C	−3.733	3.157	−6.631	3.636
O	3.733	3.397	−1.355	−3.659
	After Localizing			
C	0	7.137	1.853	21.724
O	0	7.377	−9.839	14.430
	$l'' = 2$			
	$l = 0$	$l = 1$	$l = 2$	$l = 3$
	Before Localizing			
C	6.939	−9.826	53.488	−41.241
O	−6.939	17.145	4.129	−2.360
	After Localizing			
C	0	−13.363	45.948	−48.543
O	0	5.888	28.130	−62.306
	$l'' = 3$			
	$l = 0$	$l = 1$	$l = 2$	$l = 3$
	Before Localizing			
C	−58.840	−5.540	−196.436	270.622
O	58.840	−71.668	144.108	−64.337
	After Localizing			
C	0	40.127	−155.486	259.027
O	0	8.111	30.434	156.643

[a] See text for details. All quantities are in atomic units.

Stone's distributed multipole analysis (DMA) algorithm[10] is used for this purpose. However, this formulation of atomic polarizabilities produces nonlocal polarization, because a potential applied to one region of the molecule causes a response in another region. For example, applying a potential difference between two regions causes charge flow between the regions that can only be described by using nonlocal charge-flow polarizabilities. This effect is not restricted to the DMA algorithm but occurs for all commonly used methods of calculating atomic multipoles.

If polarizabilities are to be local and are to obey eq 1, then it must be concluded that nonlocal effects arise from the method of calculation of the atomic multipoles and their response to the potential. The procedure described here for localizing polarizabilities can therefore be seen as making small modifications to the DMA algorithm, such that nonlocal response effects disappear.

TABLE 2: Atomic and Molecular Polarizabilities for the CO Molecule[a]

	$\alpha_{l''\kappa',l\kappa}$		
	$l\kappa = 10$	$l\kappa = 20$	$l\kappa = 30$
	Atomic		
$\alpha^{C}_{10,l\kappa}$	7.137	1.853	21.724
$\alpha^{C}_{20,l\kappa}$	1.853	49.899	−2.228
$\alpha^{C}_{30,l\kappa}$	21.724	−2.228	177.844
$\alpha^{O}_{10,l\kappa}$	7.377	−9.839	14.430
$\alpha^{O}_{20,l\kappa}$	−9.839	49.108	−93.070
$\alpha^{O}_{30,l\kappa}$	14.430	−93.070	405.089
	Molecular		
$\alpha^{C}_{10,l\kappa}$	14.513	−7.475	48.238
$\alpha^{C}_{20,l\kappa}$	−7.475	115.119	−193.311
$\alpha^{C}_{30,l\kappa}$	48.238	−193.311	1174.687

[a] See text for details. All quantities are in atomic units.

TABLE 3: Molecular Isotropic and Anisotropic Polarizabilities from This Work and Experimental Values from the Literature[a]

	$\bar{\alpha}_1$	$\Delta\alpha_1$	$\bar{\alpha}_2$
CO	12.15 13.18 [ref 18]	3.54	86.17
CO_2	15.02 17.81 [ref 20], 16.92 [ref 18]	11.90 14.82 [ref 21]	118.06
H_2O	7.97 9.64 [ref 22], 10.13 [ref 18]	1.34 0.67 [refs 23 and 24]	27.43
C_2H_2	22.53 23.53 [ref 18]	12.57	170.57
C_2H_4	27.48 27.70 [ref 19], 28.26 [ref 18]	13.31 11.4 [ref 25]	269.93

[a] All quantities are in atomic units.

The method chosen to localize the polarizabilities involves removing nonlocal polarizabilities of the lowest rank first, and progressively increasing the multipole rank to obtain dipole polarizabilites, quadrupole polarizabilities, and so forth. At each stage in the procedure an external potential, $V_{l''\kappa''}\mathrm{R}(\vec{r})$, is applied to the molecule where initially $l'' = 1$. This potential is then expanded about the origin of each region to give the local potential $V^A_{l'\kappa'}$ of eq 1 (where $V^A_{l''\kappa'} = V_{l''\kappa''}\delta_{\kappa',\kappa''}$, and contributions to the local potential with $l' < l''$ also occur due to the change of origin). The DMA multipoles, $Q^A_{l\kappa}$, are differentiated analytically with respect to the local potential to obtain the polarization, $\Delta Q^A_{l\kappa}$, per unit applied potential, for each region.

The charge polarization, ΔQ^A_{00}, induced by the applied potential is the lowest-rank nonlocal polarization effect. To localize the charge, it is assumed, for each pair of regions A and B, that a certain amount of charge on A, $Q^{A\rightarrow B}_{00}$, is "incorrectly" assigned to region A by the DMA when the external potential is applied, and that this charge should have been assigned to region B. The method for determining the size of $Q^{A\rightarrow B}_{00}$ is described below. The "unwanted" charge, $Q^{A\rightarrow B}_{00}$, on A is then removed from region A and reexpanded as a multipole series about the center of region B, producing a new charge, dipole, quadrupole, ... at B. By transferring "unwanted" charges between each pair of regions, the total charge polarization is made zero in each region, as required.

After the "unwanted" charges have been eliminated in this way, the new "localized" polarization components $\Delta Q^A_{l\kappa}$, which include the contributions obtained from moving the charges, are used to obtain the atomic polarizabilities $\alpha^A_{l\kappa,l'\kappa'}$, for each region A, with $l' = l''$ and all l values up to a maximum desired multipole rank. Because local polarizabilities should be symmetric, this also produces atomic polarizabilities $\alpha^A_{l\kappa,l'\kappa'}$ with $l = l''$ and $l' \geq l''$. However, when $l = l' = l''$ and $\kappa \neq \kappa'$ the value of $\alpha^A_{l''\kappa,l''\kappa'}$ obtained from eq 1 using an $l''\kappa$ potential is not always equal to the value of $\alpha^A_{l''\kappa,l''\kappa'}$ obtained from an l'',κ' potential. This is interpreted as an "incorrect" assignment of the atomic multipole in the external potential, and it is corrected in an analogous way to "unwanted" charge polarization effects.

Once the local polarizabilities have been obtained for $l'' = 1$, an $l'' = 2$ external potential is applied and the calculation proceeds in a similar fashion. First the amount of "unwanted" charge is determined for each region and then removed as described above. The change in atomic dipoles should then agree with eq 1, using the dipole−dipole and dipole−quadrupole polarizabilities, $\alpha^A_{l\kappa,l'\kappa'}$, obtained with the $l'' = 1$ potential in the previous step. If the atomic dipoles produced by the $l'' = 2$

TABLE 4: Molecular Isotropic and Anisotropic Polarizabilities from This Work and from the Literature[a]

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
$\bar{\alpha}_1$	16.00	27.33	38.75	50.26	61.90	73.62
	16.52 [ref 18]	28.52 [ref 18]	39.96 [ref 18]	51.88 [ref 18]	64.64 [ref 18]	77.25 [ref 18]
		29.61 [ref 15]	42.09 [ref 15]	54.07 [ref 15]	66.07 [ref 15]	78.04 [ref 15]
$\Delta\alpha$	0.00	3.30	5.61	10.73	15.65	21.77
		4.3 [ref 16]	7.0 [ref 16]	11.5 [ref 16]	15.9 [ref 16]	21.1 [ref 16]
$\bar{\alpha}_2$	110.82	360.29	740.40	1360.58	2264.64	3537.34

[a] All quantities are in atomic units.

TABLE 5: Atomic Isotropic and Anisotropic Polarizabilities

	$\bar{\alpha}_1$	$\Delta\alpha_1$	$\bar{\alpha}_2$
		CO	
C	7.37	0.34	37.75
O	4.79	3.88	19.00
		CO_2	
C	3.97	3.48	13.11
O	5.53	4.21	15.66
		H_2O	
O	5.69	0.96	17.67
H	1.14	1.79	1.78
		C_2H_2	
C	9.46	4.07	47.80
H	1.80	2.22	12.08
CH	11.26	6.28	64.31
		C_2H_4	
C	7.54	6.10	42.68
H	3.10	4.09	16.78
CH_2	13.74	6.66	98.72

[a] All quantities are in atomic units.

TABLE 6: Alkane Atomic Isotropic and Anisotropic Polarizabilities[a]

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
$\bar{\alpha}_1$ C($CH_{3(4)}$)	3.00	4.21	4.44	5.22	6.07	5.20
$\Delta\alpha_1$ C($CH_{3(4)}$)	0.00	3.11	7.27	7.11	7.96	6.72
$\bar{\alpha}_2$ C($CH_{3(4)}$)	1.69	11.36	11.01	19.60	20.33	8.60
$\bar{\alpha}_1$ C(CH_2) A			3.72	3.65	5.56	5.23
$\Delta\alpha_1$ C(CH_2) A			4.43	5.60	6.97	4.70
$\bar{\alpha}_2$ C(CH_2) A			−3.62	0.65	17.63	−4.76
$\bar{\alpha}_1$ C(CH_2) B					2.58	3.75
$\Delta\alpha_1$ C(CH_2) B					6.92	11.01
$\bar{\alpha}_2$ C(CH_2) B					−6.25	9.55
$\bar{\alpha}_1$ H($CH_{3(4)}$) A	3.25	3.15	3.19	3.15	3.23	3.34
$\Delta\alpha_1$ H($CH_{3(4)}$) A	2.96	3.37	4.02	4.43	4.72	5.19
$\bar{\alpha}_2$ H($CH_{3(4)}$) A	15.88	13.67	15.04	11.07	11.80	11.00
$\bar{\alpha}_1$ H(CH_3) B			3.23	3.11	3.08	3.05
$\Delta\alpha_1$ H(CH_3) B			3.40	3.54	3.49	3.54
$\bar{\alpha}_2$ H(CH_3) B			18.65	17.51	16.96	16.08
$\bar{\alpha}_1$ H(CH_2) A			3.43	3.44	3.40	3.30
$\Delta\alpha_1$ H(CH_2) A			3.43	3.61	3.90	3.74
$\bar{\alpha}_2$ H(CH_2) A			15.88	20.31	24.74	18.27
$\bar{\alpha}_1$ H(CH_2) B					3.37	3.30
$\Delta\alpha_1$ H(CH_2) B					3.66	4.00
$\bar{\alpha}_2$ H(CH_2) B					19.48	23.37

[a] The A methylene groups for carbons are located adjacent to a methyl group, and the A methyl hydrogens are the hydrogens above and below the molecular plane. The B methylene groups for carbons are located between two methylene groups. All quantities are in atomic units.

TABLE 7: United Atom Isotropic and Anisotropic Polarizabilities[a]

	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
$\bar{\alpha}_1$ C(CH_3)	13.67	14.08	14.63	15.41	14.48
$\Delta\alpha_1$ C(CH_3)	1.65	5.68	4.81	6.35	5.27
$\bar{\alpha}_2$ C(CH_3)	97.16	107.70	111.48	112.04	100.44
$\bar{\alpha}_1$ C(CH_2) A		10.58	10.50	12.38	12.04
$\Delta\alpha_1$ C(CH_2) A		6.59	3.31	3.92	1.99
$\bar{\alpha}_2$ C(CH_2) A		63.83	79.22	106.75	83.01
$\bar{\alpha}_1$ C(CH_2) B				9.35	10.29
$\Delta\alpha_1$ C(CH_2) B				5.06	8.52
$\bar{\alpha}_2$ C(CH_2) B				71.35	85.14

[a] The A methylene groups for carbons are located adjacent to a methyl group. All quantities are in atomic units.

potential do not agree, the "unwanted" dipoles, $Q_{1\kappa}^{A\rightarrow B}$, are removed from each region A by reexpanding them as multipole series about the center of region B, which produces new dipoles, quadrupoles, octupoles, ... in region B. Then, from eq 1, the resulting "localized" polarization components $\Delta Q_{l\kappa}^{A}$ are used to give the quadrupole polarizabilities, $\alpha_{l\kappa,l'\kappa'}^{A}$, with ($l = 2$, $l' \geq 2$) and ($l \geq 2$, $l' = 2$). Finally, the quadrupole−quadrupole polarizabilities, $\alpha_{2\kappa,2\kappa'}^{A}(\kappa \neq \kappa')$, are corrected so that $\alpha_{2\kappa,2\kappa'}^{A} = \alpha_{2\kappa',2\kappa}^{A}$ by interpreting any difference between the two as an "unwanted" quadrupole and localizing it in the same way as the charges and dipoles. This procedure is repeated for higher l'', if required, up to the maximum desired multipole rank.

Now the question of how much "unwanted" charge, $Q_{00}^{A\rightarrow B}$, and higher multipoles, $Q_{l\kappa}^{A\rightarrow B}$ to redistribute from region A to B is addressed. The same method is used independent of multipole component, $l\kappa$, and external potential component $l'\kappa'$. For every region A in the molecule, the following equations must be satisfied, to ensure that the amount of "unwanted" multipole in each region becomes zero after the redistribution has occurred:

$$\sum_{B} (Q_{l\kappa}^{A\rightarrow B} - Q_{l\kappa}^{B\rightarrow A}) = \delta Q_{l\kappa}^{A} \tag{2}$$

where $\delta Q_{l\kappa}^{A}$ is an "unwanted" multipole of A, according to the previous discussion. This set of N conditions gives $N - 1$ linearly independent equations (because the sum of all N equations is zero), for the $^1/_2N(N - 1)$ different pairs of regions (A,B). There are therefore multiple solutions for $N > 2$ regions, and additional constraints are introduced to obtain a unique solution. These are chosen so that "unwanted" multipoles are in general reexpanded about the centers B that are as close to A as possible, similar to the procedure of Le Sueur and Stone,[8] because this optimizes the convergence of the multipole expansion. Specifically, a system of coupled "time-dependent" first-order differential equations is introduced for the "unwanted" multipoles in the different regions A:

$$\frac{dQ_{l\kappa}^{A}(t)}{dt} = \sum_{B\neq A} k_{AB}(Q_{l\kappa}^{B}(t) - Q_{l\kappa}^{A}(t)) \tag{3}$$

where the initial conditions ($t = 0$) are the "unwanted" multipoles in each region, $Q_{l\kappa}^{A}(0) = \delta Q_{l\kappa}^{A}$, and the rate constant, k_{AB}, is simply chosen to be one if the regions A and B are neighbors and zero otherwise. Regions are centered at the atomic nuclei, and two regions are chosen to be neighbors if a chemical bond exists between nuclei of the two regions.

TABLE 8: Comparison between Induction Energies Calculated (ab Initio) and Using Polarizabilities[a]

	atomic			united atom			molecular		
	$l = 1$	$l = 2$	$l = 3$	$l = 1$	$l = 2$	$l = 3$	$l = 1$	$l = 2$	$l = 3$
H_2O									
rms %	0.21	0.07	0.02				0.46	0.07	0.03
max. %	−5.84	−2.36	1.23				−13.94	−2.78	1.22
CO_2									
rms %	0.23	0.14	0.02				0.76	0.45	0.07
max. %	−5.36	−2.30	0.82				−14.09	−7.59	−1.77
CH_4									
rms %	0.23	0.15	0.04				0.59	0.14	0.08
max. %	6.50	4.15	4.04				−20.25	−6.68	−2.63
C_2H_2									
rms %	0.29	0.12	0.02	0.32	0.11	0.02	0.50	0.20	0.05
max. %	−7.13	3.40	2.42	−10.55	−5.47	−1.53	−16.14	−8.49	−3.42
C_2H_4									
rms %	0.39	0.12	0.07	0.51	0.14	0.09	0.68	0.27	0.07
max. %	11.13	3.06	−2.25	−17.98	−6.41	−3.82	−21.14	−8.91	−3.69
C_2H_6									
rms %	0.17	0.12	0.04	0.58	0.16	0.09	0.89	0.41	0.10
max. %	7.14	3.47	4.41	−22.78	−8.06	−4.67	−25.22	−11.73	−4.77
C_3H_8									
rms %	0.18	0.09	0.05	0.46	0.12	0.07	0.91	0.45	0.17
max. %	5.95	2.91	5.49	−16.81	−6.01	−3.27	−25.11	−12.86	9.10
C_4H_{10}									
rms %	0.16	0.10	0.05	0.44	0.12	0.07	1.24	0.72	0.31
max. %	7.32	2.33	3.28	−16.47	−5.97	−3.50	−29.82	−18.36	−10.32
C_5H_{12}									
rms %	0.25	0.12	0.07	0.49	0.14	0.08	1.77	1.18	0.71
max. %	10.09	−3.35	4.90	−18.13	−6.26	−4.13	−37.36	37.11	37.37
C_6H_{14}									
rms %	0.23	0.12	0.07	0.46	0.14	0.08	2.15	1.70	1.33
max. %	6.06	−2.69	5.80	−17.47	−7.38	4.31	−50.75	−62.33	−100.36

[a] See text for details. All values are in atomic units.

The amount of multipole $Q_{l\kappa}$ on A that is reexpanded about B is then given by

$$Q_{l\kappa}^{A\to B} = \frac{1}{2}\int_0^\infty k_{AB}(Q_{l\kappa}^{A}(t) - Q_{l\kappa}^{B}(t))\,dt \tag{4}$$

where $Q_{l\kappa}^{A}(t)$ are the solutions of eq 3, which are simple linear combinations of exponentially decaying functions of t. Since the sum of the "unwanted" multipoles is always zero, $Q_{l\kappa}^{A}(\infty) = 0$ for all A.

As an example of the localization procedure, results for the CO molecule with bond length $R = 2.132a_0$, the origin of coordinates at the bond center, and the oxygen atom on the positive z-axis, are presented in Tables 1 and 2. The coupled Hartree−Fock (CHF) method is used with an aug-cc-pVDZ basis set.[11] Results for $\kappa'' = 0$ are shown. The procedure is similar, but simpler, for $\kappa'' \neq 0$, because an applied potential with $\kappa'' \neq 0$ produces no charge flow.

The molecule is first placed in an external V_{10} potential, and the resulting polarizations for carbon and oxygen are given in Table 1 in the first C and O rows. The amount of "unwanted" charge is $\delta Q_{00}^{O} = +3.733$ and $\delta Q_{00}^{C} = -3.733$. Solving eqs 3 and 4 gives $\Delta Q_{00}^{O\to C} = {}^{1}/_{2}\delta Q_{00}^{O}$; this charge is removed from the oxygen atom and reexpanded as a multipole series on carbon and vice versa. The resulting atomic polarizations are presented in Table 1 in the second C and O rows. From these results, the local atomic polarizabilities, $\alpha_{10,l\kappa}$ ($l\kappa = 10, 20, 30$), for each atom are obtained, as shown in Table 2. The molecule is then placed in an external V_{20} potential and the resulting polarizations are given in Table 1, in the third C and O rows. The "unwanted" charge polarization of 6.939 is removed first. This gives a zero charge on each atom and a new total dipole polarization of −17.223 on carbon and +9.748 on oxygen. From eq 1, the correct values of the atomic dipole polarization in a V_{20} potential, using the dipole−dipole and dipole−quadrupole polarizabilities determined in the first stage, are −13.363 for carbon and 5.888 for oxygen. The "unwanted" dipole on each atom is therefore $\delta Q_{10}^{O} = +3.860$ and $\delta Q_{10}^{C} = -3.860$. These dipoles are removed from the oxygen atom and reexpanded as a multipole series on carbon, and vice versa. Each atom now has a zero charge and the correct dipole polarization. The resulting atomic polarizations are presented in Table 1 in the fourth C and O rows. The localized ΔQ_{20} and ΔQ_{30} polarizations still contain contributions from the local V_{10} potential, and these contributions are removed using eq 1 to obtain the quadrupole−quadrupole and quadrupole-octupole polarizabilities presented in Table 2. Finally, the molecule is placed in an external V_{30} potential, and the resulting polarizations are presented in Table 1 in the fifth C and O rows. The atomic $\alpha_{30,30}$ polarizabilities are obtained by first correcting the charge polarization, followed by the dipole and quadrupole polarizations. The resulting atomic polarizations are presented in Table 1 in the last C and O rows, and when corrected for the contributions from the local V_{10} and V_{20} potentials they give the octupole−octupole polarizabilities shown in Table 2.

3. Results and Conclusions

To obtain results to test this atomic polarizability method with reasonable computational effort, coupled Hartree−Fock (CHF) theory is used with an aug-cc-pVDZ basis set. The systems chosen for study are carbon dioxide, water, ethylene, acetylene, and the all-trans conformers of the alkane series (C_nH_{2n+2}, $n = 1 - 6$), to compare the polarizabilities of similar functional groups. For all the molecules studied, the geometry is optimized at the Hartree−Fock level using the same basis set and the highest available molecular symmetry. A more precise determination of the molecular geometry is not considered necessary, as the aim of this preliminary work is not to produce quantitative results. Frequency calculations using HF/aug-cc-pVDZ show that all the molecular geometries are minima, with the exception of C_6H_{14}, which has a small imaginary frequency of $i\omega = 7.46$ cm^{-1}. All geometry optimizations and frequency calculations are performed using the 2006 version of Molpro.[12] The CHF polarization is calculated at each site for multipoles $Q^{A}_{l\kappa}$ up to $l = 3$, in external potentials $V_{l'',\kappa''}$ up to $l'' = 3$, after which the localization algorithm of section 2 is applied to determine the atomic polarizabilities. Two separate sets of atomic polarizabilities are calculated for the hydrocarbons: all-atom polarizabilities, where each atom constitutes a separate region, and united-atom polarizabilities, where each region is composed of a CH_n group and is centered at the carbon nucleus.

The molecular polarizabilities are presented in Tables 3 and 4. The isotropic ($\bar{\alpha}_1$) and anisotropic ($\Delta\alpha_1$) components of the dipole−dipole polarizabilities and the isotropic ($\bar{\alpha}_2$) component of the quadrupole−quadrupole polarizability are defined as

$$\bar{\alpha}_1 = \frac{1}{3}\sum_{\kappa} \alpha_{1\kappa,1\kappa} \tag{5}$$

$$\Delta\alpha_1 = \left[\frac{1}{2}\left((\alpha_{10,10} - \alpha_{11c,11c})^2 + (\alpha_{10,10} - \alpha_{11s,11s})^2 + (\alpha_{11c,11c} - \alpha_{11s,11s})^2\right) + 3({\alpha_{10,11c}}^2 + {\alpha_{10,11s}}^2 + {\alpha_{11c,11s}}^2)\right]^{1/2} \tag{6}$$

$$\bar{\alpha}_2 = \frac{1}{5}\sum_{\kappa} \alpha_{2\kappa,2\kappa} \tag{7}$$

As expected, it is found that the CHF polarizabilities underestimate the experimental values, but the agreement is qualitatively reasonable.

For each molecule studied, the calculation of the atomic polarizabilities proceeds in the same manner as for the CO molecule presented in section 2. For the terminal atoms A, which are either hydrogen atoms or the oxygen atoms in CO_2, the "unwanted" multipole $\delta Q^{A}_{l\kappa}$ is removed by reexpanding $^{1}/_{2}\delta Q^{A}_{l\kappa}$ about the only atom B bonded to A, and $-^{1}/_{2}Q^{A}_{l\kappa}$ from B is reexpanded about A. Analogous, although somewhat more complicated expressions, obtained by solving eqs 3 and 4, are used to redistribute the remaining "unwanted" polarizations. In the case of nonlinear molecules, it is also necessary to remove "unwanted" off-diagonal polarizations, which occur when $\alpha^{A}_{l\kappa,l\kappa'} \neq \alpha^{A}_{l\kappa',l\kappa}$. This is done by expanding the "unwanted" multipole such that the resulting polarizabilities are equal to the mean value $(\alpha^{A}_{l\kappa,l\kappa'} + \alpha^{A}_{l\kappa',l\kappa})/2$.

The results for the isotropic and anisotropic atomic polarizabilities of CO, CO_2, H_2O, C_2H_2, and C_2H_4 are presented in Table 5. The diagonal localized polarizabilities are all positive, and the carbon atom typically has the largest polarizability in the molecule, except in the case of carbon dioxide where the more electronegative oxygen atoms are larger. The size of the $\bar{\alpha}_2$ polarizabilities for the atoms are also much less than half of the corresponding molecular $\bar{\alpha}_2$ values, which suggests improved convergence properties for the atomic multipole series. The united-atom polarizabilities for acetylene and ethylene show similar trends, and comparison between the atomic and united-atom polarizabilities suggests that combining a carbon atom and its bonded hydrogens into a single region does not introduce any spurious results.

The results for the alkane atomic polarizabilities are presented in Table 6. The results are similar to those for the smaller molecules, although the isotropic quadrupole polarizability is negative for the A methylene carbons in C_3H_8 and C_6H_{14}, and the B methylene carbon in C_5H_{12}. The values of the isotropic dipole polarizabilities for carbon and hydrogen compare well with the average values of Ferraro et al.[13] The hydrogen polarizabilities are remarkably constant, with the isotropic dipole polarizability varying by less than 6% independent of which carbon it is bonded to. The "united-atom" results for the alkanes are presented in Table 7. For the methyl regions, excluding ethane, the isotropic and anisotropic polarizabilities vary by less than 6% and 15%, respectively. The quadrupole polarizabilities vary by less than 7%. The trends for the methylene groups display similar behavior. This suggests that combining carbons and their bonded hydrogens into united atoms leads to the possibility of transferability of polarizabilities between different molecules.

To test the usefulness of the atomic polarizabilities in practical applications, point-to-point induction energies[4] are calculated using the atomic polarizabilities, and using *ab initio* methods, and the two are compared. The point-to-point induction energy is defined as the second-order change in energy when two nonpolarizable point charges are located near the molecule. The *ab initio* energies are calculated using CHF theory. The atomic polarizabilities give point-to-point energies between points P and Q according to

$$E_{\mathrm{ind}} = -\frac{1}{2}\sum_{l\kappa,l'\kappa',\mathrm{A}} T^{\mathrm{PA}}_{0,l\kappa}\alpha^{\mathrm{A}}_{l\kappa,l'\kappa'}T^{\mathrm{AQ}}_{l'\kappa',0} \tag{8}$$

where the sum is over atomic sites A and components of the polarizability $l\kappa,l'\kappa'$, and $T^{\mathrm{AQ}}_{l\kappa,0}$ is an interaction function describing the $l\kappa$ component of the potential at atom A produced by a point charge at Q.[9] The point-to-point induction energies for each molecule are computed using points from the van der Waals envelope, which is defined as the region that is at least 2 van der Waals radii from every atom, and no further than 4 van der Waals radii from at least one atom. Using 25 batches of $N = 500$ points, the $N(N + 1)/2$ unique energies for each batch are used to determine the deviations between the multipole induction energies, determined using eq 8, and the *ab initio* CHF induction energies. The results are presented in Table 8. The "atomic" results use polarizabilities on every nucleus, "united atom" results do not have polarizabilities on H atoms, and the "molecular" results treat the molecule as a single region. The root-mean-square (rms) error and the maximum error ($E_{\mathrm{CHF}} - E_{\mathrm{model}}$) are expressed as a percentage of the total range of energies, and the sum in eq 8 is truncated at $l = l' = 1$, 2, and 3, for each model. The rms and maximum error results shown in Table 8 for the alkanes are consistent with values reported by Williams and Stone,[4,14] which are determined by minimizing the rms based on local atomic polarizability models to the induction energy surface.

The comparison of the induction energies calculated using atomic polarizabilities with *ab initio* CHF results indicate that the atomic and united-atom polarizabilities perform well, especially as the size of the molecule increases. The atomic polarizabilities generally perform better than the united-atom polarizabilities, although they appear to be converging to the same result as the maximum angular momentum l is increased. When including up to $l = 2$ polarizabilities in each of the models, the rms results generally differ by only a few hundredths of a percent. The improved convergence of the atomic polarizability models, relative to using polarizabilities at the center of the molecule, is evident, especially for the larger alkanes, where the molecular convergence is very slow, or nonexistent, as l is increased.

4. Discussion

From the results of section 3, it is concluded that using atomic polarizabilities up to a maximum rank of $l = 2$ is sufficient to reproduce the *ab initio* second-order induction energies closely, which agrees with the conclusions of Williams and Stone.[4] Although using the atomic polarizabilities is more accurate than the united-atom models, the added simplicity of the united-atom model is appealing, and the possibilities for transferability with the united-atom polarizabilities is promising.

The theory presented in section 2 can also be applied to frequency dependent polarizabilities, which can then be used to determine atomic dispersion energy coefficients. These can then be used to determine second-order dispersion energies between atomic sites in a similar fashion to induction energies. Work along these lines is currently in progress.

The DMA algorithm that is currently used does not allow for the efficient incorporation of diffuse basis functions, leading to unphysical polarizations when the DMA is applied for large diffuse basis sets, as well as erratic convergence of atomic multipoles as a function of basis set. Current efforts are under way to resolve this using recent results of Stone.[17]

The choice of k_{AB} in section 2 is another area under investigation. The current approach requires an *a priori* knowledge of the bonding in a molecule to decide which regions are “neighbors”. In cases where there may not be an obvious choice of “neighbor”, such as reaction transition states or van der Waals bonds, a more sophisticated method is needed. By extending the “rate constant” argument of section 2 to let multipole “flow” between regions depends on properties such as the charge density shared between A and B, the value of k_{AB} could be allowed to vary based on calculated properties of the molecule.

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References and Notes

(1) Karplus, M.; McCammon, J. A. *Nat. Struct. Biol.* **2002**, *9*, 646.

(2) Allen, M. P.; Tildesley, D. J. *Computer Simulations of Liquids*; Clarendon: Oxford, U.K., 1989.

(3) van Duijnen, P. Th.; Swart, M. *J. Phys. Chem. A* **1998**, *102*, 2399.

(4) Williams, G. J.; Stone, A. J. *J. Chem. Phys.* **2003**, *119*, 4620.

(5) Dehez, F.; Chipot, C.; Millot, C.; Ángyán, J. *Chem. Phys. Lett.* **2001**, *338*, 180.

(6) Le Sueur, C. R.; Stone, A. J. *Mol. Phys.* **1993**, *78*, 1267.

(7) Ángyán, J.; Jansen, G.; Loos, M.; Hättig, C.; Hess, B. A. *Chem. Phys. Lett.* **1994**, *219*, 267.

(8) Le Sueur, C.; Stone, A. J. *Mol. Phys.* **1994**, *83*, 293.

(9) Stone A. J. *The Theory of Intermolecular Forces*; Clarendon: Oxford, U.K., 1996.

(10) Stone, A. J. *Chem. Phys. Lett.* **1981**, *83*, 233.

(11) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/02/06, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, U.S.A., and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06−76RLO 1830. Contact Karen Schuchardt for further information.

(12) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; et al. MOLPRO, version 2006.1, a package of ab initio programs, see www.molpro.net, Cardiff, U.K., 2006.

(13) Ferraro, M. B.; Caputo, M. C.; Lazzeretti, P. *J. Chem. Phys.* **1998**, *109*, 2987.

(14) Williams, G. J.; Stone, A. J. *Mol. Phys.* **2004**, *102*, 985.

(15) Jhanwar, B. L.; Meath, W. J.; MacDonald, J. C. F. *Can. J. Phys.* **1981**, *59*, 185.

(16) Haverkort, J. E. M.; Bass, F.; Beenakker, J. J. M. *Chem. Phys.* **1983**, *79*, 105.

(17) Stone, A. J. *J. Chem. Theory Comput.* **2005**, *1*, 1128.

(18) Olney, T. N.; Cann, N. M.; Cooper, G.; Brion, C. E. *Chem. Phys.* **1997**, *223*, 54.

(19) Hohm, U.; Trümper, U. *J. Raman. Spectrosc.* **1995**, *26*, 1095.

(20) Jhanwar, B. L.; Meath, W. J. *Chem. Phys.* **1982**, *67*, 185.

(21) Alms, G. R.; Burnham, A. K.; Flygare, W. H. *J. Chem. Phys.* **1975**, *63*, 3221.

(22) Zeiss, G. D.; Meath, W. J. *Mol. Phys.* **1977**, *33*, 1155.

(23) Dougherty, J.; Spackman, M. A. *Mol. Phys.* **1994**, *82*, 193.

(24) Dynamic value at 514.5 nm.

(25) Spackman, M. A. *J. Phys. Chem.* **1989**, *93*, 7594.