# MOLECULAR POLARIZABILITIES CALCULATED WITH A MODIFIED DIPOLE INTERACTION

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The point dipole interaction model for molecular polarizability recently proposed by Applequist, Carl, and Fung is modified by replacing the point dipole interaction by an interaction between smeared out dipoles. Rules are developed to indicate plausible forms for this modified interaction. The polarizabilities of a wide range of chemically different molecules can be calculated, using for each atom one polarizability independent of its chemical environment. The errors are comparable to experimental uncertainty. Special care is taken to produce a model that tends to avoid infinite polarizabilities without use of cutoffs at short distances.

## 1. Introduction

The accurate calculation of the effects of polarizability on electrostatic interaction is an interesting problem in various fields. Traditionally the polarizability of molecules was calculated to predict optical rotation [1] and London dispersion forces [2]. More recently, inclusion of polarizability in molecular dynamics calculations has been studied [3]. Finally in many cases the stabilization of e.g. a charged or a dipolar molecule surrounded by a polarizable solvent is important. It has been shown that this effect can be included into quantum mechanical calculations on such a molecule, where the solvent is approximated by a set of interacting polarizabilities [4]. In all these cases one tries to avoid simulating the polarizability by introduction of a dielectric, because this macroscopic concept cannot be used but with the greatest care on the molecular level.

The interactive dipole model of Applequist et al. [5], based on the early work of Silberstein [6] seems to be a good starting point to treat the polarizability of arbitrary configurations of polarizable atoms. This model is surprisingly successful in predicting mean polarizabilities and

is easily extended to the other fields mentioned, either by a matrix inversion method or by iterative solution of the equations for the interaction of the induced dipoles. Applequist et al. [5] used isotropic atom polarizabilities. They observed that their model predicts mean polarizabilities very well but that the predicted anisotropy is too large. Birge [7] showed that the large anisotropy can be removed by inclusion of the effect of electron repulsion, which essentially decreases the polarizability component in the direction of the bond and gives errors in the anisotropy comparable to the experimental uncertainty. Birge needs 14 parameters to describe the atomic polarizabilities in different chemical environments and their tendencies to resist excessive polarizability along the bonds.

The transferability of these parameters to other classes of molecules is rather bad [5]. This property is shared by all previous parameterizations. It is therefore interesting to discover trends in these parameters. This will give more insight into the physical process of polarization and may give new parameters that are more readily transferable. This paper shows that a suitably chosen modification of the interaction

decreases the errors in predicted polarizabilities, while the number of parameters is strongly reduced.

In the next section the theory of the point dipole interaction is repeated, and extended for our purposes. The third section then gives a procedure for modifying the interaction.

## 2. The point dipole model

The modified dipole interaction model developed in this paper is based on the early work of Silberstein [6] and the more recent application of Silberstein's model by Applequist et al. [5]. The nomenclature of the latter authors will be used and the reader is referred to refs. [5, 8] for a detailed discussion of the point dipole interaction model. The difference between the procedures presented here and those outlined by Applequist et al. is the modification of the dipole field tensor. The atomic polarizability tensor remains isotropic. This is in contrast with Birge's model [7], which modifies the atomic polarizability tensor and keeps the field tensor unchanged.

The molecule is considered as an arrangement of $N$ atoms each of which has a polarizability. The induced dipole moment at atom $p$ i.e. $\mu_p$, can be calculated as a function of the applied electric field $E_p$ at atom $p$:

$$\mu_p = \alpha_p \left[ E_p - \sum_{q \neq p}^{N} T_{pq} \mu_q \right], \tag{1}$$

where $\alpha_p$ is the atomic polarizability tensor of atom $p$ and $T_{pq}$ is the dipole field tensor

$$T_{pq} = (r_{pq}^{-3})I - 3(r_{pq}^{-5}) \begin{bmatrix} x^2 & xy & xz \\ yx & y^2 & yz \\ zx & zy & z^2 \end{bmatrix}, \tag{2}$$

where $I$ is the unit tensor, $r_{pq}$ is the distance between atoms $p$ and $q$, and $x$, $y$ and $z$ are the cartesian components of the vector connecting atoms $p$ and $q$. Eq. (1) can be rearranged into the single matrix equation

$$\tilde{A} \tilde{\mu} = \hat{E}, \tag{3}$$

where $\tilde{A}$ is a $3N \times 3N$ matrix containing the inverse of the atom polarizability tensors along the $3 \times 3$ "diagonals" which are coupled by the dipole field tensors. Inversion of $\tilde{A}$ yields $\tilde{B}$, a symmetric matrix called relay matrix, which plays the role of a super polarizability;

$$\tilde{\mu} = \tilde{B} \tilde{E} \tag{4}$$

$$\tilde{B} = \tilde{A}^{-1} = (\tilde{\alpha}^{-1} + \tilde{T})^{-1}. \tag{5}$$

The molecular polarizability is the response to a uniform applied field $E$ and is thus obtained by contraction of $\tilde{B}$ to a $3 \times 3$ tensor $\alpha_{mol}$:

$$\mu_{mol} = \left[ \sum_{p}^{N} \sum_{q}^{N} B_{pq} \right] E = \alpha_{mol} E. \tag{6}$$

Diagonalization of $\alpha_{mol}$ yields the three components of the polarizability. In more general cases the whole matrix $\tilde{B}$ is needed [4], and in molecular dynamics eq. (3) may not be solved by matrix inversion but by an iterative procedure.

A well known property of the method presented so far, is that it may lead to infinite molecular polarizabilities. For a diatomic molecule the values of the polarizabilities parallel and perpendicular to the bond axis can be derived from the above:

$$\alpha_{\parallel} = (\alpha_A + \alpha_B + 4\alpha_A \alpha_B / r^3)/(1 - 4\alpha_A \alpha_B / r^6), \tag{7}$$

$$\alpha_{\perp} = (\alpha_A + \alpha_B - 2\alpha_A \alpha_B / r^3)/(1 - \alpha_A \alpha_B / r^6). \tag{8}$$

When $r$ approaches $(4\alpha_A \alpha_B)^{1/6}$, $\alpha_{\parallel}$ goes to infinity. This is caused by the cooperative interaction (head to tail) between two induced dipoles in the direction of the bond. The general criterion for a physically meaningful solution is that the matrix $\tilde{A}$, and therefore also its inverse $\tilde{B}$, be positive definite. A matrix $A$ is positive definite if all its eigenvalues are positive or, equivalently, if $\mu^{\dagger} A \mu > 0$ for all vectors $\mu$. That $\tilde{A}$ and $\tilde{B}$ must be positive definite can be seen in two ways. First, when $\tilde{B}$ has a negative eigenvalue $-b$ then, when we take $\tilde{E}$ equal to the corresponding eigenvector we obtain

$$\tilde{\mu} = \tilde{B} \tilde{E} = -b \tilde{E}, \tag{9}$$

which means that $\tilde{\mu}$ and $\tilde{E}$ are in opposite directions. Here we will only consider frequen-

cies of the electric field that are so low that $\tilde{\mu}$ can follow the variations in $\tilde{E}$. This means that $\tilde{\mu}$ and $\tilde{E}$ may not be in opposite directions. That such a system is metastable is seen from the reaction of the total energy to a small perturbation $\delta\tilde{\mu}$ in the dipoles. The total energy $U$ is the energy of interaction between the dipoles, plus the energy needed to polarize the atoms. The latter energy is equal to $\frac{1}{2}\sum_p \mu_p^\dagger \alpha_p^{-1} \mu_p$ and therefore:

$$U = -\tilde{\mu}^\dagger \cdot \tilde{E} + \tfrac{1}{2}\tilde{\mu}^\dagger \tilde{T}\tilde{\mu} + \tfrac{1}{2}\tilde{\mu}^\dagger \tilde{\alpha}^{-1}\tilde{\mu}$$
$$= -\tilde{\mu}^\dagger \cdot \tilde{E} + \tfrac{1}{2}\tilde{\mu}^\dagger \tilde{A}\tilde{\mu}. \tag{10}$$

After a perturbation $\delta\tilde{\mu}$ we have

$$\delta U = -\delta\tilde{\mu}^\dagger \cdot \tilde{E} + \delta\tilde{\mu}^\dagger \tilde{A}\tilde{\mu} + \tfrac{1}{2}\delta\tilde{\mu}^\dagger \tilde{A}\delta\tilde{\mu}^\dagger. \tag{11}$$

In the equilibrium state, where (3) is satisfied, the first order contribution to $\delta U$ vanishes. For the equilibrium to be stable, the second order change in $U$ must be positive for all $\delta\tilde{\mu}$, so

$$\delta^2 U = \delta\tilde{\mu}^\dagger \tilde{A}\delta\tilde{\mu} > 0 \quad \text{for all } \delta\tilde{\mu}, \tag{12}$$

which means that $\tilde{A}$ must be positive definite. When $\tilde{A}$ is not positive definite then $\delta^2 U < 0$ for some $\delta\tilde{\mu}$ and the system is metastable. A small perturbation will make all dipoles grow to infinity. Further insight is gained by the introduction of the very useful tensor $t$, defined by:

$$(T_{pq})_{ij} = \delta_{ij}r^{-3} - 3x_i x_j r^{-5}$$
$$= (\alpha_p\alpha_q)^{-1/2}(\delta_{ij}u^{-3} - 3u_i u_j u^{-5})$$
$$= (\alpha_p\alpha_q)^{-1/2}t_{ij}(u), \tag{13}$$

where $u = x/(\alpha_p\alpha_q)^{1/6}$ and $\delta_{ij}$ is the Kronecker delta.

$$\mathbf{T}_{pq}(x) = (\alpha_p\alpha_q)^{-1/2}\mathbf{t}\{x/(\alpha_p\alpha_q)^{1/6}\}, \tag{14}$$

$t$ is a *shape function* which does not depend on $p$ and $q$. In this paper only isotropic polarizabilities will be used. Then $\tilde{\alpha}$ is diagonal and we have

$$\tilde{T} = \tilde{\alpha}^{-1/2}\tilde{t}\tilde{\alpha}^{-1/2}, \tag{15}$$

$$\tilde{A} = \tilde{\alpha}^{-1} + \tilde{T} = \tilde{\alpha}^{-1/2}(\tilde{I}+\tilde{t})\tilde{\alpha}^{-1/2}. \tag{16}$$

Now

$$\tilde{\mu}^\dagger \tilde{A}\tilde{\mu} = (\tilde{\alpha}^{-1/2}\tilde{\mu})^\dagger(\tilde{I}+\tilde{t})(\tilde{\alpha}^{-1/2}\tilde{\mu}). \tag{17}$$

When $\tilde{I}+\tilde{t}$ is positive definite then the rhs of eq. (17) *is positive for all* $\tilde{\mu}$ and therefore $\tilde{A}$ is positive definite. Thus, $\tilde{A}$ is positive definite when all eigenvalues of $\tilde{t}$ are larger than $-1$.

## 3. The modified dipole interaction

When in the point dipole interaction atoms are coming closer than a certain limit, the polarizability becomes infinite. In reality this is never observed. There must be some process which damps the interaction. This process is probably already at work between bonded atoms because Applequist needs rather small atomic polarizabilities to describe molecules and he observes that his predicted anisotropies are too large. The idea developed in this section is that the damping effect may be simulated by changing the interaction tensor **T** such that it does not behave as $r^{-3}$ for small $r$. A set of more or less tentative principles will be given which were used as guidelines to investigate which changes to **T** might be applied for obtaining a good fit to experimental data, while avoiding unphysical forms. The principles were chosen so as to supply possible starting points for future theoretical analysis. The following list is given in the order of roughly increasing tentativeness:

(a) **T** must remain a tensor to ensure that rotation of the coordinate system does not change the result of the calculation.

(b) The most essential idea of the model is that the interaction between any two polarizabilities is of the same form. In a classical macroscopic system, consisting of any set of conducting bodies or bodies of some dielectric constant, when all the dimensions of the system, i.e. the dimensions of the bodies and the distances between them are expanded by some factor, then all the polarizabilities increase by the third power of that factor. In classical electrostatics this transformation is equivalent to a change of the unit of length. Simple extrapolation of the scaling property to the atomic world is strictly speaking not allowed because atoms have internal structure and are not

homogeneous as macroscopic bodies are. Nevertheless, we may hope that the macroscopic scaling principle is still approximately valid.

When we write $\mathbf{T}$ in the form (14) with arbitrary $\mathbf{t}$ and if in eqs. (5) and (14) we multiply all $x$ by a factor of $k$ and all polarizabilities by $k^3$ then $\tilde{\alpha}$ changes to $k^3\tilde{\alpha}$ and $\tilde{\mathbf{T}}$ to $k^{-3}\tilde{\mathbf{T}}$ and so $\tilde{\mathbf{B}}$, which denotes the total polarizability, changes to

$$\tilde{\mathbf{B}}' = \{(k^3\tilde{\alpha})^{-1} - (k^{-3}\tilde{\mathbf{T}})\}^{-1} = k^3\tilde{\mathbf{B}}. \tag{18}$$

This shows that in the point dipole case the scaling property exists and that it is preserved when (14) is satisfied. We may consider $\mathbf{t}$ as the interaction between two atoms with unit polarizability. In this model it will be assumed that $\mathbf{t}(u)$ remains independent of the atoms involved so that we need only study the interaction between unit polarizabilities to know all the interactions. Note that $(\alpha_p\alpha_q)^{1/6}$ has the dimension of length and that it may be associated with the average radius of atoms $p$ and $q$, so that we may say that $\mathbf{t}$ is only a function of an effective distance of interaction $u$. The quantum mechanical detail of atoms $p$ and $q$ apart from their "radius", is thus neglected.

The use of $(\alpha_p\alpha_q)^{1/6}$ as the scaling distance is arbitrary. Forms like $(\alpha_p^{1/3} + \alpha_q^{1/3})/2$ and $\{(\alpha_p + \alpha_q)/2\}^{1/3}$ are also possible, but they do not allow the elegant forms of eqs. (15) through (17).

(c) $t_{ij}(u)$ is constrained to the tensor form

$$t_{ij}(u) = -\partial^2\varphi(u)/\partial u_i \partial u_j, \tag{19}$$

where $\varphi$ is some spherically symmetric potential. This assumption is made to retain the interpretation of $\mathbf{t}$ as a dipole-dipole interaction where a dipole is thought to be built up from two infinitesimally shifted monopoles, which in our case will not be point charges. Then $\varphi$ is the corresponding monopole–monopole interaction. Noting that $\partial/\partial u_i f(u) = u_i f'(u)/u$ and $\partial u_i/\partial u_i = \delta_{ij}$ it is easily seen that

$$\varepsilon_i \equiv -\partial\varphi(u)/\partial u_i = -(u_i/u)\varphi', \tag{20}$$

where $\varepsilon_i$ is the electric field and

$$t_{ij} = -\partial^2\varphi/\partial u_i \partial u_j$$
$$= (\varphi'/u - \varphi'')u_i u_j/u^2 - \varphi'/u\delta_{ij}. \tag{21}$$

(d) In the point dipole case $\varphi = u^{-1}$ so $\varphi' = -u^{-2}$, $\varphi'' = 2u^{-3}$ and

$$t_{ij} = \delta_{ij}u^{-3} - 3u_i u_j u^{-5}. \tag{22}$$

These relations describe the limiting behaviour for large $u$, when the atoms do not touch.

(e) For a homonuclear diatomic molecule, solution of (1)–(6) for two atoms of unit polarizability shows

$$\alpha_{\parallel} = \frac{2}{1-\varphi''} \quad \text{and} \quad \alpha_{\perp} = \frac{2}{1-\varphi'/u}. \tag{23}$$

We assume that $\alpha_{\parallel} = \alpha_{\perp}$ when $u = 0$, making the compound atom isotropic. Then $\varphi'' = \varphi'/u$ for small $u$. Solution of this differential equation shows that in this region we have to first order $\varphi' = cu$, with $c$ an arbitrary constant. This behaviour can also be obtained from the assumption that $\varphi$ is the potential of some "well behaved" charge distribution $\rho$. We start with the well known relation

$$\varepsilon_i(u) = \frac{u_i}{u^3} \int_0^u 4\pi\rho u^2 \, du, \tag{24}$$

saying that the field at $u$ for a spherically symmetric charge density is equal to that of the charge contained in the sphere with radius $u$, concentrated at the centre. Because of (20)

$$\varphi' = -\frac{1}{u^2} \int_0^u 4\pi\rho u^2 \, du. \tag{25}$$

When $\rho$ is finite when $u$ approaches zero we have to first order in this region:

$$\varphi' = -\frac{1}{u^2} \int_0^u 4\pi\rho(0)u^2 \, du = -\tfrac{4}{3}\pi\rho(0)u \tag{26}$$

and

$$\varphi'' = -\tfrac{4}{3}\pi\rho(0) \tag{27}$$

and we see that $c = -\tfrac{4}{3}\pi\rho(0)$, a negative quantity when $\rho$ is everywhere positive. Furthermore for large $u$, when $\rho$ decreases fast enough

$$\int_0^u 4\pi\rho u^2 \, du \approx \int_0^\infty 4\pi\rho u^2 \, du = Q, \tag{28}$$

the total charge. So in this region $\varphi' \approx -Q/u^2$ which shows that $Q = 1$.

It would be more elegant to consider $\varphi$ as the interaction between two charge distributions, instead of that between a point charge and a charge distribution;

$$\varphi(u) = \int \int \mathrm{d}u_1^3 \, \mathrm{d}u_2^3 \, \rho(u_1) \, \rho(u_2 + u)/u_{12}. \qquad (29)$$

This may be necessary for further theoretical investigation. For the present, however, we are satisfied with a procedure which gives us smooth curves which roughly follow physical intuition. We conclude that $t$ is derivable from some density $\rho$, which must be finite at the origin, fall off rapidly for large $r$, and must contain a total charge of unity. Thus the unit point charge giving the point dipole equations can be considered to be "smeared out".

(f) In the previous section it was shown that it is the descaled tensor $\tilde{t}$ which governs the stability of a polarizable system. The requirement that all its eigenvalues be greater than $-1$ is rather complicated. However, from eq. (23) we see that the polarizability of a diatomic molecule remains finite when $\varphi''$ and $\varphi'/u$ are less than unity, independent of the values of the $\alpha$'s and $u$'s. In polyatomic molecules favourable interactions between pairs of atoms may push the polarisability to infinity even though each pair is separately stable. Therefore unity is an upper limit. However the interaction decreases rapidly with distance and geometrical restrictions do not allow favourable interaction between every possible number of atoms. Therefore the limit of the instability region will probably not be impractically low. Numerical experience indicates that, with the forms studied in this paper, infinite polarizabilities become improbable when $\varphi''$ and $\varphi'/u$ remain below 0.6. Concluding we assume that infinite polarizabilities will become highly improbable if not impossible when $\varphi''$ and $\varphi'/u$ are below 0.5 for every value of $u$, independent of the values of the atomic polarizabilities.

## 4. Calculations

Some forty more or less different functions to fit the polarizabilities of the sixteen molecules

considered by Birge [7] were examined. In each case the atomic polarizabilities and the parameters in the interaction tensor were varied simultaneously to minimize the root mean square $\sigma$ of the relative errors in the 48 components. Directly in the beginning, it became clear that per atom only one isotropic polarizability independent of its valence state is needed. Introduction of different $\alpha$'s for one atom did not significantly improve the fits. Thus it seems that the apparent additive polarizability of an atom is strongly correlated to the geometry. For example a carbonyl O is certainly different from a hydroxyl O, but this difference is sufficiently displayed in the geometry of its surroundings. The scaling principle describes this effect very well.

Further it appeared that one must be careful not to use a too flexible fit function because this flexibility often leads only to wildly fluctuating functions giving artificially good results which are physically meaningless. This is why the optimum form of $T$ could not be obtained by simply using a general function with many parameters. Only smooth shapes of $\varphi'/u$ and $\varphi''$ could be accepted. After the restriction to a tensor $t$ derivable from some well behaved density $\rho$, functions of the types presented in table 1 were tried. This table gives an impression of the variation in the results when $\rho$ is varied. Of the one parameter forms $\rho_1 \ldots \rho_4$, $\rho_4$ is the simplest and, surprisingly, the best. This function is a simple conical charge density with 1.662 Å as the radius of its base (for an atom of unit polarizability). $\rho_5$ and $\rho_6$ have been tested to see whether there was a preference for a more curved shape of $\rho$. This preference is rather small as is seen from the small decrease of $\sigma$ going from $\rho_4$ to $\rho_6$, and from the small coefficient with which $\rho_5$ is mixed in. Case 7 was tried in order to study the behaviour when principle (c) was relaxed i.e. when $t$ was not constrained to be the second derivative of a potential. For this purpose the factors $\varphi'/u - \varphi''$ and $\varphi'/u$ in (21) were chosen to be of the form $\rho_4$ but they were allowed to have different radii $a$ and $b$. Not much use was made of this freedom to decrease $\sigma$ or to make $a$ and $b$ different. Therefore, it may be concluded that the factors

Table 1

Charge densities and the corresponding values of the fitting error and the parameters

| | $\sigma$ [a] (%) | $\sigma_1$ [b] (%) | $\alpha_H$ (Å$^3$) | $\alpha_C$ (Å$^3$) | $\alpha_N$ (Å$^3$) | $\alpha_O$ (Å$^3$) | |
|---|---|---|---|---|---|---|---|
| $\rho_1 = a^3/8\pi \exp(-au)$ | 7.06 | 3.37 | 0.427 | 1.285 | 0.967 | 0.786 | $a = 2.089$ |
| $\varphi'_1/u = -\frac{1}{2}u^{-3}\{2-(a^2u^2+2au+2)\exp(-au)\}$ | | | | | | | |
| $\rho_2 = 3a/4\pi \exp(-au^3)$ | 6.47 | 3.84 | 0.496 | 1.334 | 1.073 | 0.837 | $a = 0.572$ |
| $\varphi'_2/u = -u^{-3}\{1-\exp(-au^3)\}$ | | | | | | | |
| $\rho_3 = 3a/4\pi\{1-(1+1/au^3)\exp(-1/au^3)\}$ | 6.78 | 4.22 | 0.471 | 1.288 | 1.024 | 0.801 | $a = 0.425$ |
| $\varphi'_3/u = -a\{1-\exp(-1/au^3)\}$ | | | | | | | |
| $\rho_4 = 3/\pi(a-u)/a^4 \quad u < a$ | 6.13 | 3.32 | 0.514 | 1.405 | 1.105 | 0.862 | $a = 1.662$ |
| $\quad = 0 \qquad\qquad u \geqslant a$ | | | | | | | |
| $\varphi'_4/u = -(4a-3u)/a^4 \quad u < a$ | | | | | | | |
| $\quad = -u^{-3} \qquad\quad u \geqslant a$ | | | | | | | |
| $\rho_5 = 15/2\pi(a-u)^2/a^5 \quad u < a$ | 6.79 | 3.35 | 0.449 | 1.232 | 1.079 | 0.835 | $a = 2.143$ |
| $\quad = 0 \qquad\qquad\quad u \geqslant a$ | | | | | | | |
| $\varphi'_5/u = -(10a^2+15au-6u^2)/a^5 \quad u < a$ | | | | | | | |
| $\quad = -u^{-3} \qquad\qquad\qquad\quad u \geqslant a$ | | | | | | | |
| $\rho_6 = b\rho_4+(1-b)\rho_5$ | 6.11 | 3.13 | 0.506 | 1.387 | 1.095 | 0.857 | $a = 1.702$ |
| | | | | | | | $b = 0.913$ |
| $\varphi''_7-\varphi'_7/u = 3a^{-4}u \quad u < a$ | 6.07 | 3.13 | 0.547 | 1.492 | 1.157 | 0.887 | $a = 1.604$ |
| $\quad = 3u^{-3} \qquad u \geqslant a$ | | | | | | | $b = 1.566$ |
| $\varphi'_7/u = -(4b-3u)/b^4 \quad u < b$ | | | | | | | |
| $\quad = -u^{-3} \qquad\quad u \geqslant b$ | | | | | | | |
| Applequist et al. [5] | 15.4 [c] | 3.39 | | | | | |
| Birge [7] | 8.6 | 3.39 | | | | | |

[a] $\sigma$ = the r.m.s. value of the relative errors in the 48 components. This is the quantity that was minimized.

[b] $\sigma_1$ = the r.m.s. value of the relative errors in the 16 mean polarizabilities.

[c] This number does not include the four linear molecules. Including these raises $\sigma$ to 31.6%. The densities $\rho$ determine the interaction. $\varphi'/u$ is given for convenience. $\varphi''$ can be calculated by taking the derivative. The values for Applequist and Birge have been computed from their tables.

in front of $u_iu_j$ and $\delta_{ij}$ in eq. (21) tend to obey principle (c).

There is little preference for the hydrogen atom like density $\rho_1$, and also $\rho_2$ and $\rho_3$ do not do as well as $\rho_4$. Therefore $\rho_4$ is a rather ideal form to be used in this kind of calculation. Table 2 shows the actual values of the polarizabilities of the 16 molecules together with 6 added ones to check the model. The worst fits seem to be obtained for molecules containing oxygen. Of the added molecules the mean polarizabilities are predicted with an r.m.s. error of 3.5%. This shows that the parameter values may be transferred to chemically quite different classes of compounds.

The functions $\varphi'/u$, $\varphi''$ and $\rho$ are plotted in fig. 1. The scaled interaction distances for bonded atoms lie in the region $u = 0.9$ to 1.4.

Table 2
Molecular polarizabilities of various molecules at 5893 Å[a]

| Compound | | Molecular polarizabilities | | | |
|---|---|---|---|---|---|
| | | $\bar{\alpha}(\text{Å}^3)$ | $\alpha_1(\text{Å}^3)$ | $\alpha_2(\text{Å}^3)$ | $\alpha_3(\text{Å}^3)$ |
| $H_2$ | E | 0.79 | 0.93 | 0.72 | 0.72 |
| | A | 0.80 | 1.92 | 0.24 | 0.24 |
| | B | 0.80 | 0.94 | 0.73 | 0.73 |
| | T | 0.76 | 0.90 | 0.69 | 0.69 |
| $N_2$ | E | 1.76 | 2.38 | 1.45 | 1.45 |
| | A | 1.76 | 3.84 | 0.72 | 0.72 |
| | B | 1.76 | 2.38 | 1.45 | 1.45 |
| | T | 1.72 | 2.13 | 1.52 | 1.52 |
| $O_2$ | E | 1.60 | 2.35 | 1.21 | 1.21 |
| | A | 1.60 | 3.11 | 0.85 | 0.85 |
| | B | 1.60 | 2.36 | 1.23 | 1.23 |
| | T | 1.49 | 1.96 | 1.26 | 1.26 |
| CO | E | 1.95 | 2.60 | 1.63 | 1.63 |
| | A | 1.95 | 4.23 | 0.81 | 0.81 |
| | B | 1.95 | 2.60 | 1.62 | 1.62 |
| | T | 1.82 | 2.23 | 1.61 | 1.61 |
| ethane | E | 4.48 | 5.49 | 3.98 | 3.98 |
| | E | 4.48 | 4.99 | 4.22 | 4.22 |
| | A | 4.46 | 6.24 | 3.57 | 3.57 |
| | B | 4.46 | 5.89 | 3.74 | 3.74 |
| | T | 4.46 | 4.93 | 4.24 | 4.24 |
| propane | E | 6.38 | 7.66 | 5.74 | 5.74 |
| | A | 6.58 | 8.94 | 5.71 | 5.08 |
| | B | 6.58 | 7.21 | 6.39 | 6.13 |
| | T | 6.29 | 7.18 | 5.98 | 5.69 |
| cyclopentane | E | 9.15 | 9.88 | 9.17 | 8.40 |
| | A | 9.05 | 10.01 | 9.97 | 7.15 |
| | B | 9.05 | 9.89 | 9.72 | 7.51 |
| | T | 9.12 | 9.56 | 9.60 | 8.20 |
| cyclohexane | E | 11.00 | 11.81 | 11.81 | 9.38 |
| | A | 10.95 | 12.25 | 12.25 | 8.35 |
| | B | 10.95 | 12.04 | 12.04 | 8.76 |
| | T | 10.95 | 11.69 | 11.69 | 9.47 |
| dimethyl ether | E | 5.24 | 6.38 | 4.94 | 4.39 |
| | A | 5.20 | 7.04 | 4.18 | 4.37 |
| | B | 5.20 | 6.00 | 4.18 | 5.41 |
| | T | 5.24 | 6.55 | 4.58 | 4.57 |
| p-dioxane | E | 8.60 | 9.40 | 9.40 | 7.00 |
| | A | 8.68 | 10.07 | 9.63 | 6.35 |
| | B | 8.68 | 10.14 | 9.43 | 6.47 |
| | T | 8.84 | 10.53 | 8.59 | 7.40 |
| methanol | E | 3.32 | 4.09 | 3.23 | 2.65 |
| | A | 3.04 | 3.71 | 2.75 | 2.65 |
| | B | 3.04 | 3.81 | 2.81 | 2.50 |
| | T | 3.34 | 3.97 | 3.11 | 2.96 |

Table 2 (continued)

| | | | | | |
|---|---|---|---|---|---|
| ethanol | E | 5.08 | 5.76 | 4.98 | 4.50 |
| | A | 5.11 | 7.10 | 4.30 | 3.93 |
| | B | 5.11 | 6.03 | 4.93 | 4.39 |
| | T | 5.26 | 6.39 | 4.82 | 4.55 |
| formaldehyde | E | 2.45 | 2.76 | 2.76 | 1.83 |
| | A | 2.31 | 3.81 | 2.19 | 0.94 |
| | B | 2.31 | 3.09 | 2.56 | 1.29 |
| | T | 2.54 | 3.07 | 2.70 | 1.86 |
| acetone | E | 6.39 | 7.37 | 7.37 | 4.42 |
| | E | 6.39 | 7.16 | 7.14 | 4.88 |
| | A | 6.46 | 7.16 | 7.12 | 5.09 |
| | B | 6.46 | 7.19 | 7.07 | 5.11 |
| | T | 6.32 | 7.30 | 6.50 | 5.15 |
| acetonitrile | E | 4.48 | 5.74 | 3.85 | 3.85 |
| | A | 4.14 | 6.66 | 2.88 | 2.88 |
| | B | 4.14 | 5.89 | 3.27 | 3.27 |
| | T | 4.24 | 5.62 | 3.57 | 3.57 |
| 22-DMPN $(CH_3)_3CCN$ | E | 9.59 | 10.71 | 9.03 | 9.03 |
| | A | 9.84 | 10.61 | 9.48 | 9.42 |
| | B | 9.84 | 10.71 | 9.40 | 9.40 |
| | T | 9.83 | 10.68 | 9.41 | 9.41 |
| water | E | 1.49 | | | |
| | A | 1.12 | 0.53 | 1.83 | 1.00 |
| | T | 1.44 | 1.32 | 1.87 | 1.12 |
| ethylene oxide | E | 4.43 | | | |
| | A | 6.52 | 3.20 | 12.23 | 4.13 |
| | T | 4.39 | 3.88 | 5.09 | 4.18 |
| $HCONH_2$ | E | 4.08 | 5.24 | $\alpha_2+\alpha_3 = 7.01$ | |
| | A | 4.07 | 6.87 | 4.04 | 1.32 |
| | T | 3.79 | 4.86 | 4.04 | 2.50 |
| $CH_3CONH_2$ | E | 5.67 | 6.70 | $\alpha_2+\alpha_3 = 10.30$ | |
| | A | 5.72 | 7.50 | 5.79 | 3.87 |
| | T | 5.71 | 6.30 | 6.70 | 4.13 |
| propanol | E | 6.97 | | | |
| | A | 7.02 | 8.85 | 6.68 | 5.54 |
| | T | 7.17 | 9.07 | 6.42 | 6.05 |
| methane | E | 2.62 | 2.62 | 2.62 | 2.62 |
| | A | 2.58 | 2.58 | 2.58 | 2.58 |
| | T | 2.55 | 2.55 | 2.55 | 2.55 |

[a] E: Experimental data are taken from tables V and VI of ref. [5].
A: Point dipole interaction model [5].
B: Anisotropic atom point dipole interaction model [7].
T: Model with modified dipole interaction (this work).
The 16 molecules above the separating line were used to fit the model to. The additional molecules were used as a check of the model. Note that Applequist et al. fitted to all the molecules except water and ethylene oxide which they used as a check.
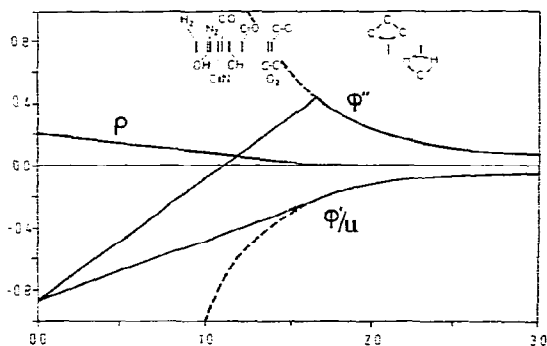
Fig. 1. The functions $\varphi''$ and $\varphi'/u$ governing the polarizabilities parallel and perpendicular to the bond axis. $u$ is the scaled distance $r/(\alpha_1\alpha_2)^{1/6}$. Below $u = 1.662$ the polarizabilities are damped with respect to the point dipole case (———). At the top the positions of some bonds are shown. $\rho$ is the density from which $\varphi'/u$ and $\varphi''$ were derived in case 4 of table 1.

Atoms separated by two bonds appear at $u = 2.1$. Thus the functions are not really fitted in the regions $u < 0.9$ and $1.4 < u < 2.1$. In these regions they must be assumed to be smooth. The cusp in $\varphi''$ at $u = 1.662$ looks bad but will probably not be serious. The maximum value of $\varphi''$ is 0.44 which is probably small enough to give no infinite polarizabilities in practice.

When two atoms approach each other from infinity the interaction between their dipoles induced by an external field results in a separation of $\varphi''$ and $\varphi'/u$. These two functions govern the polarizability along the bond and perpendicular to it, respectively, according to eq. (23). Thus $\alpha_\parallel$ is amplified and $\alpha_\perp$ is damped. Because for $u > 1.662$ $\varphi''$ is twice as large as $\varphi'/u$, the mean polarizability is approximately conserved. When the atoms penetrate, the interaction is effectively damped with respect to the point dipole case. The anisotropy is also damped because $\varphi''$ and $\varphi'/u$ approach each other. The interpretation may be that when two atoms touch, a new body is formed with an elongated shape giving an anisotropic polarizability, as in classical electrostatics. When the atoms penetrate further the shape becomes less elongated until at $u = 0$ a composite spherical atom is formed. Of course the model does not

pretend to predict the polarizabilities of atoms as built up from smaller atoms. For $u \ll 1$ the individuality of the constituent atoms disappears and probably only quantum mechanics can describe the gradual transition to the polarizability of the compound atom. This region is unimportant for most applications but it is gratifying that the polarizability is damped in this region, and therefore no problems are to be expected when, accidentally, atoms come into close contact in e.g. MD calculations.

## 5. Discussion

The present model, using only five parameters gives an improved fit with respect to Birge using 14, and Applequist using eight parameters. Part of the improvement is due to the complete optimization used, where Applequist and Birge used partial optimizations. The error in the components is 6% and in the mean polarizabilities 3.5% which are about the experimental errors. The parameter values of the model are transferable to different classes of molecules in contrast to those of Applequist and Birge. This fact, together with the small number of parameters indicates that the physical process behind the interaction of polarizabilities is reasonably described. The ideal situation in this kind of semiclassical model would be to predict experimental molecular polarizabilities from experimental atomic polarizabilities. The point dipole interaction is strongly amplifying and therefore atomic polarizabilities are needed which are much smaller than the additive values, especially for H with its short bonding distances. Conversely the smeared-out dipole interaction is on the average mildly damping and therefore it is accompanied with atomic polarizabilities which are about 20% higher than the additive ones. Hartree–Fock polarizabilities are considered to be 20 to 60% higher than experimental values. But especially the hydrogen value, which is exact, shows that the smeared-out dipole model approaches the ideal more closely than the point dipole model (table 3).

Table 3
Polarizabilities of atoms in polyatomic molecules at 5893 Å

| Atom | Polarizability (Å$^3$) | | | |
|---|---|---|---|---|
| | additive model[a] | Applequist et al.[a] | Hartree–Fock[b] | this work |
| H(alkane) | 0.407 | 0.135 | 0.667[c] | 0.514 |
| H(alcohol) | 0.405 | 0.135 | | |
| H(aldehyde) | | 0.167 | | |
| H(amide) | | 0.161 | | |
| C(alkane) | 1.027 | 0.878 | 1.74 | 1.405 |
| C(carbonyl) | 1.027 | 0.616 | | |
| C(nitrile) | 0.928 | 0.36 | | |
| N(amide) | | 0.530 | 1.00 | 1.105 |
| N(nitrile) | 1.236 | 0.520 | | |
| O(alcohol) | 0.604 | 0.465 | 0.73 | 0.862 |
| O(ether) | 0.651 | 0.465 | | |
| O(carbonyl) | 0.841 | 0.434 | | |

[a] Ref. [5].
[b] Ref. [14] from variation-perturbation theory.
[c] Exact.

It is interesting to note that Applequist's atomic values for C, N and O decrease in chemical environments with shorter bond distances. In the present model this trend is produced automatically by damping the interaction more strongly with shorter distances.

The present model is connected to some notions recently suggested by other authors. Oxtoby and Gelbart [9] proposed to describe the interaction of the induced dipoles of penetrating atoms as the interaction between penetrating dipole densities. This is equivalent to the principle that the dipole field tensor must be the second derivative of the interaction between smeared out charge distributions. This notion has been criticized [10, 11] but its success suggests that it has some value. Maybe any approximation which uses the point dipole interaction for large distances until the atoms "touch" and then damps the interaction in a smooth way, making it zero for $r = 0$, will do reasonably. The freedom to choose the density function and the generally decent behaviour of the polarizability are further responsible for the good results. Thus the value of this kind of approximation may be largely empirical.

Bounds and Hinchcliffe [12] and Winicur [13] noted that the anisotropies of diatomic molecules are very similar as functions of the internuclear distance and that they seem to be determined by the "shape" of the molecule, defined by a suitably chosen measure of its length-to-width ratio. This is strongly connected to the scaling principle of the present model which uses $r_{pq}(\alpha_p\alpha_q)^{-1/6}$ as a shape parameter.

Inclusion of the effects of smearing out and the scaling principle into the interaction tensor is thus a generalization of existing notions of the apparent "classical" behaviour of the molecular polarizability. The small number of parameters, their transferability to different systems, and the consistent physical picture give confidence to the calculations in difficult cases such as formation of hydrogen bonds, strong deformation of bonds and close contacts between different molecules or different parts of large molecules. Because each atom has only one polarizability, ambiguity in the assignment of the valence state to the atom has no consequences. The model is simple enough to be applied to large systems. No exclusion of bonded interactions or arbitrary cutoffs at short contacts occurring otherwise are needed. Hence the present method is very well suited to be incorporated into empirical energy expressions, as they are used, e.g. in molecular dynamics calculations, energy optimization of crystal and protein structures, etc. These computational schemes might be improved considerably in this way.

## Acknowledgement

## Appendix: Details of the computation

Probably any computer program using Applequist's point dipole interaction model in spectroscopy, molecular dynamics, Monte Carlo

or energy minimization, can be easily adapted to the smeared-out dipole interaction. When $r$ is the distance vector between two atoms with polarizability $\alpha_1$ and $\alpha_2$ and $s = 1.662(\alpha_1\alpha_2)^{1/6}$ then when $r > s$ we have, exactly as in Applequist's model

$$T_{ij} = \delta_{ij}/r^3 - 3r_ir_j/r^5. \tag{A.1}$$

When $r < s$ the interaction has to be changed into

$$T_{ij} = (4v^3 - 3v^4)\delta_{ij}/r^3 - 3v^4(r_ir_j/r^5), \tag{A.2}$$

where $v = r/s$.

A FORTRAN program, running on a CDC Cyber 170/670 computer, under NOS, and which calculates and fits molecular polarizabilities, can be obtained from the author.

In MD and MC calculations, polarizability is, for practical reasons, often treated by changing the magnitude or the position of the point charges in the molecule as a function of the electric field. Artificial devices are then usually needed to prevent excessive polarization. It may be possible to mimic the smeared-out dipole model also in these calculations. An obvious guess would be to use a modified electric field, viz. the field of a smeared-out charge distribution:

$$E_i = r_i/r^3 \quad [r > s], \tag{A.3}$$

$$E_i = (4v^3 - 3v^4)r_i/r^3 \quad [r < s]. \tag{A.4}$$

For the calculation of the total energy the corresponding potential is given by

$$\varphi = 1/r, \quad [r > s]. \tag{A.5}$$

$$\varphi = (v^4 - 2v^3 + 2v)/r \quad [r < s]. \tag{A.6}$$

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