

Polarization catastrophe

C9926: Problems and Issues of Molecular Modeling

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History

Goal: To accurately calculate the effects of polarizability on electrostatic interaction (stabilization of a charged or a dipolar molecule surrounded by a polarizable solvent)

Applequist et al. used **isotropic atom polarizabilities**, which is defined as the ratio of the induced dipole moment of an atom to the electric field, that produces this dipole moment

This model predicts mean polarizabilities very well but that the predicted anisotropy is too large

Birge 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

Birge used **14 parameters** to describe the atomic polarizabilities in different chemical environments and their tendencies to resist excessive polarizability along the bonds

However, the transferability of these parameters to other classes of molecules is bad

Thole's approach

Point dipole -> smeared-out dipoles

Molecule is considered as an arrangement of N atoms each of which has a polarizability.

Induced dipole moment μ_p at atom p can be calculated as a function of the applied electric field, \mathbf{E} , at atom p

$$\mu_p = \alpha_p \left[\mathbf{E}_p - \sum_{q \neq p}^N \mathbf{T}_{pq} \mu_q \right]$$

α is the atomic polarizability tensor of atom p

\mathbf{T}_p is the dipole field tensor

r_{pq} the distance between atoms p and q, and x, y and z are the cartesian components of the vector connecting atoms p and q

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

The atomic polarizability tensor remains isotropic

This is in contrast with Birge's model, which modifies atomic polarizability tensor keeping the field tensor unchanged

Problem

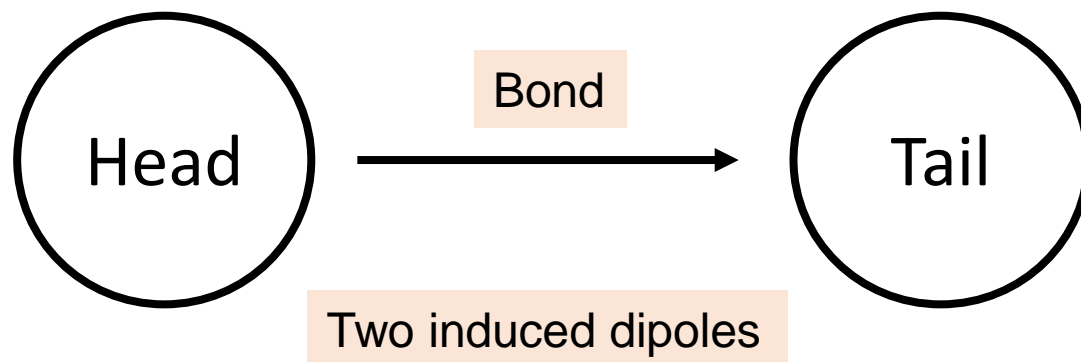
Infinite molecular polarizabilities

For a diatomic molecule AB, the values of the polarizabilities parallel and perpendicular to the bond axis can be derived as follows:

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

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

When r approaches $(4\alpha_A\alpha_B)^{1/6}$, all goes to infinity



When the point dipole interaction atoms come closer than a certain limit, the polarizability becomes infinite, which is unreal **—————→ Polarization catastrophe**

Solution -> the modification of the dipole field tensor, \mathbf{T} , so that it does not behave as the third power of the distance, r , at small r

a dipole is thought to be built up from two infinitesimally shifted monopoles, which in this case will not be point charges, but **two charge distributions**

The corresponding monopole-monopole interaction of some “well-behaved” charge distribution of density ρ is

the field at \mathbf{u} for a spherically symmetric charge density is equal to that of the charge contained in the sphere with radius \mathbf{u} , concentrated at the center

And ρ is finite when \mathbf{u} approaches zero

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

and

$$\varphi'' = -\frac{4}{3}\pi\rho(0)$$

Thus, the unit point charge giving the point dipole equations can be considered “**smearred out**”

Verified !!!

The polarizabilities of a wide range of chemically different molecules were calculated using for each atom a polarizability independent of its chemical environment -

Model1: point dipole interaction,

Model2: anisotropic atom point dipole interaction model,

Model3: modified dipole interaction.

When two atoms approach each other from infinity the interaction between their dipoles induced by an external field results in two functions:

$$\varphi' \quad \varphi''$$

which govern the polarizability along the bond and perpendicular to it.

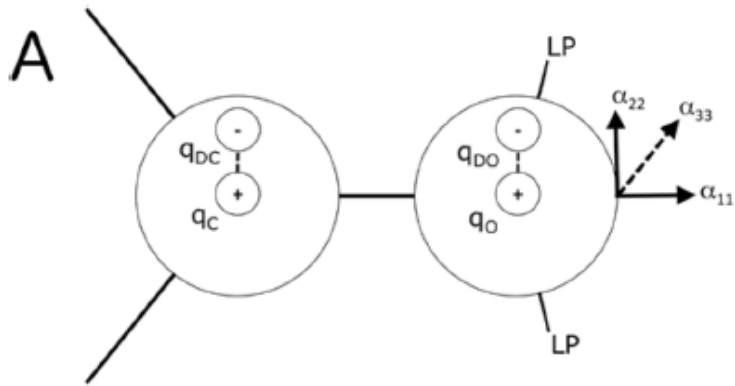
Along the bond is amplified and perpendicular is damped, keeping the mean polarizability approximately conserved.

When the atoms penetrate, the interaction is effectively damped with respect to the point dipole case.

When two atoms touch, a new body is formed with an elongated shape giving 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.

Drude Oscillator Model



Drude oscillators to carbon and oxygen atoms (q_{DC} and q_{DO}) via harmonic springs

The charges assigned to the Drude oscillator (q_D) and to the core atom (q_A) are such that total charge $q = q_A + q_D$

LP: Lone pairs on the oxygen atom

α_{11} , α_{22} , and α_{33} are the tensor components of the anisotropic atomic polarizability

The isotropic polarizability, α , of a given atom is described by the distribution of the total charge on the atom, q , between the core atom and its Drude oscillator, which is attached to the core atom via a harmonic spring

$$\alpha = \frac{q_D^2}{k_D} \quad k_D \text{ is the force constant of the Drude-atom harmonic bond}$$

displacement, d , between the Drude oscillator and the core atom in response to an electric field, E ,

$$\mathbf{d} = \frac{q_D \mathbf{E}}{k_D}$$

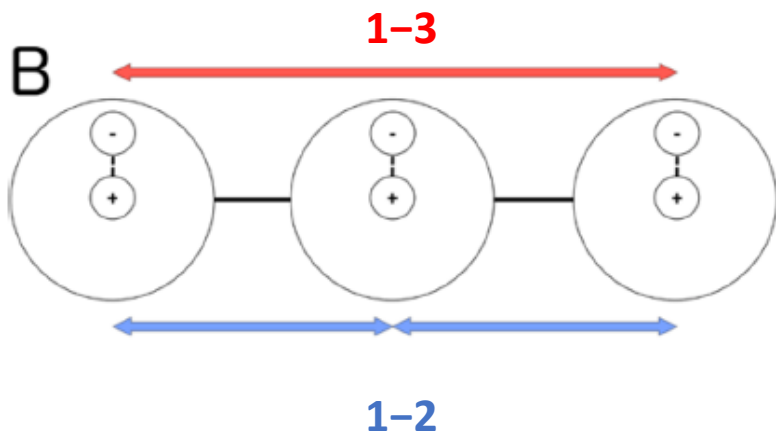
the induced atomic dipole $\mu = \frac{q_D^2 \mathbf{E}}{k_D}$

harmonic self-polarization term $U_{\text{self}}(\mathbf{d}) = \frac{1}{2} k_D \mathbf{d}^2$

anisotropic form is achieved by

$$U_{\text{self}} = \frac{1}{2} ([\mathbf{K}_{11}^{(D)}] d_1^2 + [\mathbf{K}_{22}^{(D)}] d_2^2 + [\mathbf{K}_{33}^{(D)}] d_3^2)$$

Explicit inclusion of dipole–dipole interactions for atoms within three bonds



These interactions are treated explicitly via **Thole screening** in the Drude-2013 force field, contributing to anisotropic molecular polarizability.

$$S_{ij}(r_{ij}) = 1 - \left[\left(1 + \frac{ar_{ij}}{2(\alpha_i\alpha_j)^{1/6}} \right) \right] \exp \left[\frac{-ar_{ij}}{(\alpha_i\alpha_j)^{1/6}} \right]$$

a is a damping constant

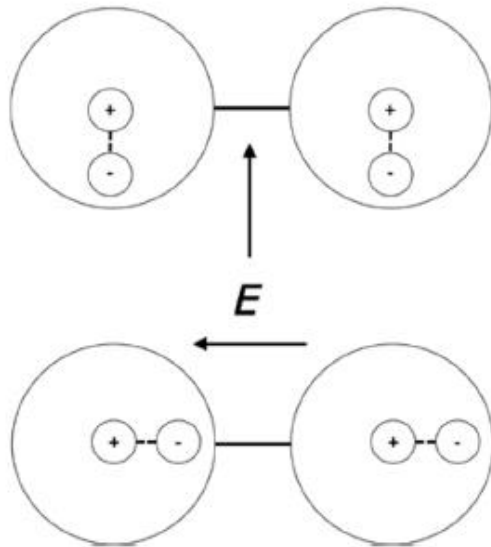
Thole smeared charge distribution $\rho = \frac{a^3}{8\pi} \exp \left[-a \frac{r_{ij}}{(\alpha_i\alpha_j)^{1/6}} \right]$

Subsequently, atom-specific values were implemented, as they may be assigned to fine-tune the molecular polarizability tensor

$$a = a_i + a_j$$

Directional response of the Drude oscillators to external electric fields (E)

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due to the 1–2 dipole–dipole interactions when the electric field is perpendicular to the bond, the 1–2 dipoles damp each other, leading to a smaller polarization response compared to the electric field being parallel to the bond leading to the 1–2 dipoles enhancing each other.

Molecular Dynamics Algorithm

In the **induced point dipole representation**, each atomic site is assigned a dipole that is calculated using an iterative self consistent field (SCF) procedure.

the positions of the Drude oscillators are solved via energy minimization at each integration step

Solution: Lagrangian approach where each Drude oscillator is ascribed a small mass (m_D) that is subtracted from the parent atom such that the total mass of the Drude-atom pair remained equal to the atomic mass.

Velocity-Verlet algorithm is used to numerically integrate the equations of motion calculating the forces on the Drude-atom centers of mass (R_i) and Drude-atom displacements (d_i)

$$\frac{\partial U}{\partial \mathbf{d}_i} = 0$$

computationally demanding

$$\mathbf{F}_{R,i} = -\frac{\partial U}{\partial \mathbf{r}_i} - \frac{\partial U}{\partial \mathbf{r}_{D,i}}$$

$$\mathbf{F}_{d,i} = -\left(1 - \frac{m_D}{m_i}\right) \frac{\partial U}{\partial \mathbf{r}_{D,i}} + \left(\frac{m_D}{m_i}\right) \frac{\partial U}{\partial \mathbf{r}_i}$$

1

Polarization catastrophe can occur when the forces acting on the Drude oscillator cause large displacement from its core atom

prevented by using “hard-wall constraint”

The constraint reflects the Drude oscillator back toward its core atom, along the Drude–atom bond, if it reaches a predefined limit

2

Divalent ions are prone to “polarization catastrophe” due to a Coulombic singularity that can arise when the Drude particle on the ion interacts with the core charge on the water oxygen.

circumvented by using a through-space **Thole screening** same as used for bonded dipoles