JACOBS
UNIVERSITY

Intermolecular forces

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I. OUTLINE

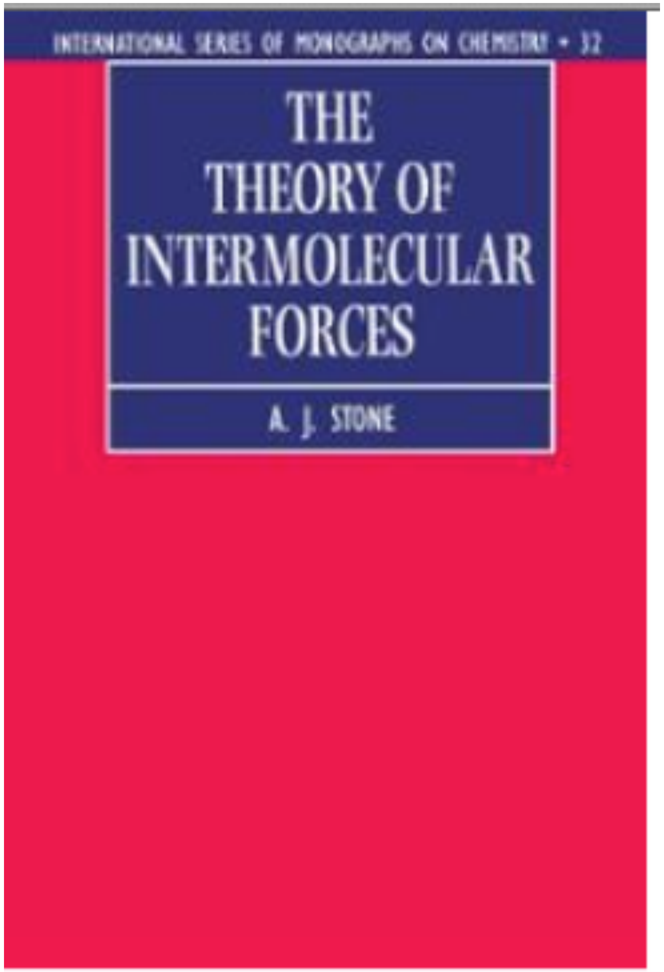
- **THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD**
  - *A. NON-DEGENERATE PERTURBATION THEORY*
  - *B. TAYLOR SERIES FOR EXTERNAL POTENTIAL*
  - *C. EXPRESSION FOR THE ENERGY*

- **ELECTROSTATIC INTERACTIONS BETWEEN MOLECULES**
  - *A. PERTUBATION THEORY OF INTERMOLECULAR FORCES AT LONG RANGE*
  - *B. MULTIPOLE EXPANSION*
  - *C. ELECTROSTATIC ENERGY*
  - *D. INDUCTION ENERGY*

- **CONVERGENCE OF THE MULTIPOLE EXPANSION**

- **DISTRIBUTED MULTIPOLES**
  - *A. POINT-CHARGE MODELS*
  - *B. OTHER MODELS*

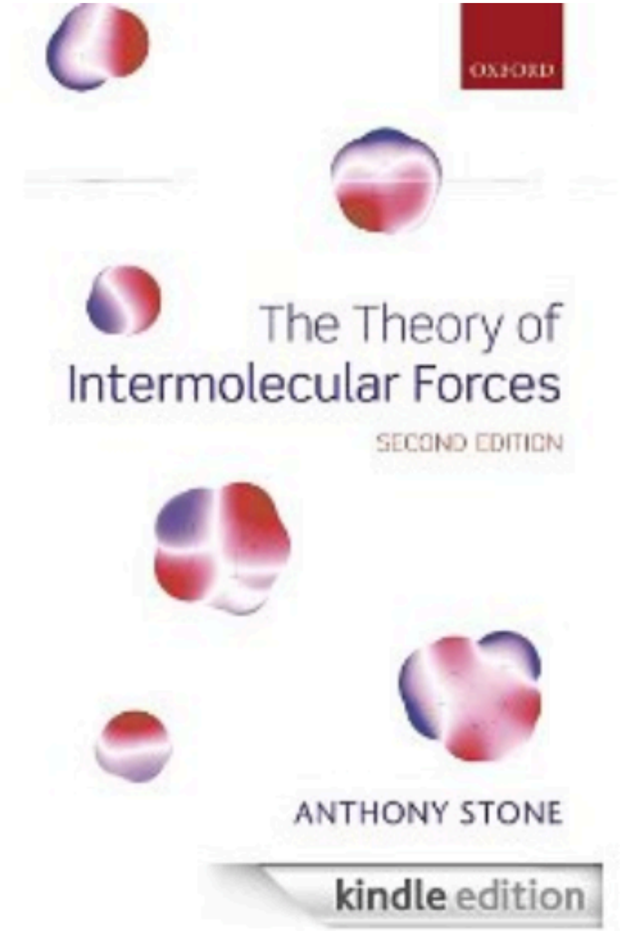
- **DISTRIBUTED POLARIZABILITIES**
  - *A. THE APPLEQUIST MODEL*
  - *B. THE THOLE MODEL*



INTERNATIONAL SERIES OF MONOGRAPHS ON CHEMISTRY • 32

THE
THEORY OF
INTERMOLECULAR
FORCES

A. J. STONE



OXFORD

The Theory of
Intermolecular Forces
SECOND EDITION

ANTHONY STONE

kindle edition

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

A. NON-DEGENERATE PERTURBATION THEORY

$$\hat{H} = \hat{H}^0 + \hat{H}' \longrightarrow \text{PERTURBATION}$$

TOTAL HAMILTONIAN

UNPERTURBED HAMILTONIAN

THE EIGENFUNCTIONS OF THE UNPERTURBED PROBLEM ARE $|n\rangle$, WITH EIGENVALUES W_n:

$$\hat{H}^0|n\rangle = W_n|n\rangle \qquad |0\rangle \longrightarrow \text{NON-DEGENERATE GROUND STATE}$$

THE ENERGY OF THE SYSTEM IS GIVEN BY:

$$W = W_0 + W_0' + W_0'' + \ldots$$

$$\boxed{W_0' = \langle 0|\hat{H}'|0\rangle}$$

FIRST-ORDER ENERGY (expectation value of perturbation for ground state)

$$\boxed{W_0'' = -\sum_{n\neq 0} \frac{\langle 0|\hat{H}'|n\rangle\langle n|\hat{H}'|0\rangle}{W_n - W_0}}$$

SECOND-ORDER ENERGY
(Rayleigh-Schrödinger perturbation theory)

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

B. TAYLOR SERIES FOR EXTERNAL POTENTIAL

$$\hat{H}' = \boxed{\sum_a}\,\boxed{e_a}\,\boxed{\hat{V}(\mathbf{a})} \longrightarrow$$

ELECTRIC POTENTIAL AT POSITION OF *a* PARTICLE $\mathbf{a} = \mathbf{i}a_x + \mathbf{j}a_y + \mathbf{k}a_z$

CHARGE FOR *a* PARTICLE

SUM OVER ALL NUCLEI AND ELECTRONS IN THE MOLECULE

TAYLOR SERIES FOR ELECTRIC POTENTIAL AROUND ORIGIN **0** :

$$\hat{H}' = V(\mathbf{0})\boxed{\sum_a e_a} + \sum_\alpha \frac{\partial V(\mathbf{0})}{\partial a_\alpha}\boxed{\sum_a e_a a_\alpha} + \frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\boxed{\sum_a e_a a_\alpha a_\beta} + \ldots$$

$$\hat{H}' = V(\mathbf{0})\boxed{\hat{M}} + \sum_\alpha \frac{\partial V(\mathbf{0})}{\partial a_\alpha}\boxed{\hat{M}_\alpha} + \frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\boxed{\hat{M}_{\alpha\beta}} + \ldots$$

ZEROTH MOMENT: $\hat{M} = \sum_a e_a = q \longrightarrow$ **TOTAL CHARGE**

FIRST MOMENT: $\hat{M}_\alpha = \sum_a e_a a_\alpha = \hat{\mu}_\alpha \longrightarrow$ **DIPOLE MOMENT**

SECOND MOMENT: $\hat{M}_{\alpha\beta} = \sum_a e_a a_\alpha a_\beta$

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

B. TAYLOR SERIES FOR EXTERNAL POTENTIAL

SECOND MOMENT: $\hat{M}_{\alpha\beta} = \sum_a e_a a_\alpha a_\beta$

$$\hat{M}'_{\alpha\beta} = \hat{M}_{\alpha\beta} - \boxed{k}\boxed{\delta_{\alpha\beta}} \longrightarrow \text{KRONECKER DELTA}$$

CONSTANT

$$\begin{aligned}
\frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\hat{M}'_{\alpha\beta} &= \frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\hat{M}_{\alpha\beta} - \frac{1}{2}k\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\delta_{\alpha\beta} \\
&= \frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\hat{M}_{\alpha\beta} - \frac{1}{2}k\sum_{\alpha}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha^2} \\
&= \frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\hat{M}_{\alpha\beta}
\end{aligned}$$

$\nabla^2 V(\mathbf{0}) = \sum_\alpha \frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha^2} = 0$ LAPLACE'S EQUATION

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

B. TAYLOR SERIES FOR EXTERNAL POTENTIAL

SECOND MOMENT: $\hat{M}_{\alpha\beta} = \sum_a e_a a_\alpha a_\beta$

WE CHOOSE *k* SO THAT $\hat{M}'_{\alpha\beta}$ BECOMES TRACELESS:

$$\sum_\alpha \hat{M}'_{\alpha\alpha} = \hat{M}'_{xx} + \hat{M}'_{yy} + \hat{M}'_{zz} = 0$$

$$\sum_\alpha \hat{M}'_{\alpha\alpha} = \sum_\alpha \hat{M}_{\alpha\alpha} - k \sum_\alpha \delta_{\alpha\alpha}$$

$$\sum_\alpha \hat{M}_{\alpha\alpha} - 3k = 0 \qquad k = \tfrac{1}{3} \sum_a e_a a^2$$

THEN WE HAVE:

$$\begin{aligned} \hat{M}'_{\alpha\beta} &= \hat{M}_{\alpha\beta} - k\delta_{\alpha\beta} \\ &= \sum_a e_a a_\alpha a_\beta - \delta_{\alpha\beta}\frac{1}{3}\sum_a e_a a^2 \\ &= \sum_a e_a \left(a_\alpha a_\beta - \frac{1}{3} a^2 \delta_{\alpha\beta} \right) \\ &= \frac{2}{3}\hat{\Theta}_{\alpha\beta} \longrightarrow \end{aligned}$$

QUADRUPOLE MOMENT

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

B. TAYLOR SERIES FOR EXTERNAL POTENTIAL

$$\hat{H}' = V(\mathbf{0})\boxed{\hat{M}} + \sum_\alpha \frac{\partial V(\mathbf{0})}{\partial a_\alpha}\boxed{\hat{M}_\alpha} + \frac{1}{2}\sum_{\alpha,\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\boxed{\hat{M}_{\alpha\beta}} + \ldots$$

ZEROTH MOMENT: $\hat{M} = \sum_a e_a = q \longrightarrow$ **TOTAL CHARGE**

FIRST MOMENT: $\hat{M}_\alpha = \sum_a e_a a_\alpha = \hat{\mu}_\alpha \longrightarrow$ **DIPOLE MOMENT**

SECOND MOMENT: $\hat{M}'_{\alpha\beta} = \frac{2}{3}\hat{\Theta}_{\alpha\beta} \longrightarrow$ **QUADRUPOLE MOMENT**

$$\begin{aligned}\hat{H}' &= V(\mathbf{0})\boxed{q} + \sum_\alpha \frac{\partial V(\mathbf{0})}{\partial a_\alpha}\boxed{\hat{\mu}_\alpha} + \frac{1}{3}\sum_{\alpha\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\boxed{\hat{\Theta}_{\alpha\beta}} + \ldots \\ &+ \frac{1}{(2n-1)!!}\sum_{\alpha,\beta,\ldots,\nu}\frac{\partial^n V(\mathbf{0})}{\partial a_\alpha \partial a_\beta \ldots \partial a_\nu}\hat{\xi}^{(n)}_{\alpha\beta\ldots\nu} + \ldots\end{aligned}$$

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

B. TAYLOR SERIES FOR EXTERNAL POTENTIAL

$$\begin{aligned}\hat{H}' &= V(\mathbf{0})q + \sum_{\alpha} \frac{\partial V(\mathbf{0})}{\partial a_\alpha}\hat{\mu}_\alpha + \frac{1}{3}\sum_{\alpha\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\hat{\Theta}_{\alpha\beta} + \ldots \\ &+ \frac{1}{(2n-1)!!}\sum_{\alpha,\beta,\ldots,\nu}\frac{\partial^n V(\mathbf{0})}{\partial a_\alpha \partial a_\beta \ldots \partial a_\nu}\hat{\xi}^{(n)}_{\alpha\beta\ldots\nu} + \ldots\end{aligned}$$

$$(2n-1)!! = (2n-1)(3n-3)\ldots 5\times 3\times 1$$

MULTIPOLE MOMENT OPERATOR OF RANK *n*:

$$\hat{\xi}^{(n)}_{\alpha\beta\ldots\nu} = \frac{(-1)^n}{n!}\sum_a e_a a^{2n+1}\frac{\partial}{\partial a_\nu}\cdots\frac{\partial}{\partial a_\beta}\frac{\partial}{\partial a_\alpha}\left(\frac{1}{a}\right)$$

- The total number of independent components is *2n+1*
- Traceless with respect to any pair of suffixes $\hat{\xi}^{(n)}_{\alpha\alpha\ldots\nu} = 0$

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

C. EXPRESSION FOR THE ENERGY

FIRST-ORDER ENERGY (expectation value of perturbation for ground state)

$$W_0' = V(\mathbf{0})q + \sum_\alpha \frac{\partial V(\mathbf{0})}{\partial a_\alpha}\mu_\alpha + \frac{1}{3}\sum_{\alpha,\beta} \frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\Theta_{\alpha\beta} + \dots$$

$$\mu_\alpha = \langle 0|\hat{\mu}_\alpha|0\rangle \qquad \Theta_{\alpha\beta} = \langle 0|\hat{\Theta}_{\alpha\beta}|0\rangle$$

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

C. EXPRESSION FOR THE ENERGY

SECOND-ORDER ENERGY (Rayleigh-Schrödinger perturbation theory)

$$W_0'' = -\frac{1}{2}\sum_{\alpha,\beta}\alpha_{\alpha\beta}\frac{\partial V(\mathbf{0})}{\partial a_\alpha}\frac{\partial V(\mathbf{0})}{\partial a_\beta} - \frac{1}{3}\sum_{\alpha,\beta,\gamma}A_{\alpha,\beta\gamma}\frac{\partial V(\mathbf{0})}{\partial a_\alpha}\frac{\partial^2 V(\mathbf{0})}{\partial a_\beta \partial a_\gamma} - \frac{1}{6}\sum_{\alpha,\beta,\gamma,\delta}C_{\alpha\beta,\gamma\delta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta}\frac{\partial^2 V(\mathbf{0})}{\partial a_\gamma \partial a_\delta} - \dots$$

SET OF POLARIZABILITIES:

$$\alpha_{\alpha\beta} = \sum_{n\neq 0}\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\mu}_\beta|0\rangle + \langle 0|\hat{\mu}_\beta|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{W_n - W_0}$$

$$A_{\alpha,\beta\gamma} = \sum_{n\neq 0}\frac{\langle 0|\hat{\mu}_\alpha|n\rangle\langle n|\hat{\Theta}_{\beta\gamma}|0\rangle + \langle 0|\hat{\Theta}_{\beta\gamma}|n\rangle\langle n|\hat{\mu}_\alpha|0\rangle}{W_n - W_0}$$

$$C_{\alpha\beta,\gamma\delta} = \frac{1}{3}\sum_{n\neq 0}\frac{\langle 0|\hat{\Theta}_{\alpha\beta}|n\rangle\langle n|\hat{\Theta}_{\gamma\delta}|0\rangle + \langle 0|\hat{\Theta}_{\gamma\delta}|n\rangle\langle n|\hat{\Theta}_{\alpha\beta}|0\rangle}{W_n - W_0}$$

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

C. EXPRESSION FOR THE ENERGY

TOTAL ENERGY

$$\begin{aligned} W &= W_0 \\ &+ qV(\mathbf{0}) - \sum_{\alpha} \mu_\alpha E_\alpha(\mathbf{0}) - \frac{1}{3}\sum_{\alpha,\beta} \Theta_{\alpha\beta} E_{\alpha\beta}(\mathbf{0}) - \dots \\ &- \frac{1}{2}\sum_{\alpha,\beta} \alpha_{\alpha\beta} E_\alpha(\mathbf{0}) E_\beta(\mathbf{0}) - \frac{1}{3}\sum_{\alpha,\beta,\gamma} A_{\alpha,\beta\gamma} E_\alpha(\mathbf{0}) E_{\beta\gamma}(\mathbf{0}) - \frac{1}{6}\sum_{\alpha,\beta,\gamma\delta} C_{\alpha\beta,\gamma\delta} E_{\alpha\beta}(\mathbf{0}) E_{\gamma\delta}(\mathbf{0}) - \dots \end{aligned}$$

$$E_\alpha(\mathbf{0}) = -\frac{\partial V(\mathbf{0})}{\partial a_\alpha} \longrightarrow$$ **ELECTRIC FIELD**

$$E_{\alpha\beta}(\mathbf{0}) = -\frac{\partial^2 V(\mathbf{0})}{\partial a_\alpha \partial a_\beta} \longrightarrow$$ **FIELD GRADIENT**

II. THE ENERGY OF A MOLECULE IN AN ELECTRIC FIELD

C. EXPRESSION FOR THE ENERGY

TOTAL ENERGY

$$\begin{aligned} W &= W_0 \\ &+ qV(\mathbf{0}) - \sum_{\alpha} \mu_\alpha E_\alpha(\mathbf{0}) - \frac{1}{3}\sum_{\alpha,\beta} \Theta_{\alpha\beta} E_{\alpha\beta}(\mathbf{0}) - \ldots \\ &- \frac{1}{2}\sum_{\alpha,\beta} \alpha_{\alpha\beta} E_\alpha(\mathbf{0}) E_\beta(\mathbf{0}) - \frac{1}{3}\sum_{\alpha,\beta,\gamma} A_{\alpha,\beta\gamma} E_\alpha(\mathbf{0}) E_{\beta\gamma}(\mathbf{0}) - \frac{1}{6}\sum_{\alpha,\beta,\gamma\delta} C_{\alpha\beta,\gamma\delta} E_{\alpha\beta}(\mathbf{0}) E_{\gamma\delta}(\mathbf{0}) - \ldots \end{aligned}$$

$$-\frac{\partial W}{\partial E_\xi(\mathbf{0})} = \underset{\downarrow}{\boxed{\mu_\alpha}}\delta_{\alpha\xi} + \underset{\downarrow}{\boxed{\sum_\beta \alpha_{\xi\beta} E_\beta(\mathbf{0})}} + \frac{1}{3}\underset{\downarrow}{\boxed{\sum_{\beta,\gamma} A_{\xi,\beta\gamma} E_{\beta\gamma}(\mathbf{0})}} + \ldots$$

STATIC DIPOLE MOMENT

DIPOLE INDUCED BY AN APPLIED ELECTRIC FIELD

DIPOLE INDUCED BY AN APPLIED FIELD GRADIENT

$$-3\frac{\partial W}{\partial E_{\xi\eta}(\mathbf{0})} = \underset{\downarrow}{\boxed{\Theta_{\xi\eta}}} + \underset{\downarrow}{\boxed{\sum_\alpha A_{\alpha,\xi\eta} E_\alpha(\mathbf{0})}} + \underset{\downarrow}{\boxed{\sum_{\alpha,\beta} C_{\alpha\beta,\xi\eta} E_{\alpha\beta}(\mathbf{0})}} + \ldots$$

STATIC QUADRUPOLE MOMENT

QUADRUPOLE INDUCED BY AN APPLIED ELECTRIC FIELD

QUADRUPOLE INDUCED BY AN APPLIED FIELD GRADIENT

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

A. PERTURBATION THEORY OF INTERMOLECULAR FORCES AT LONG RANGE

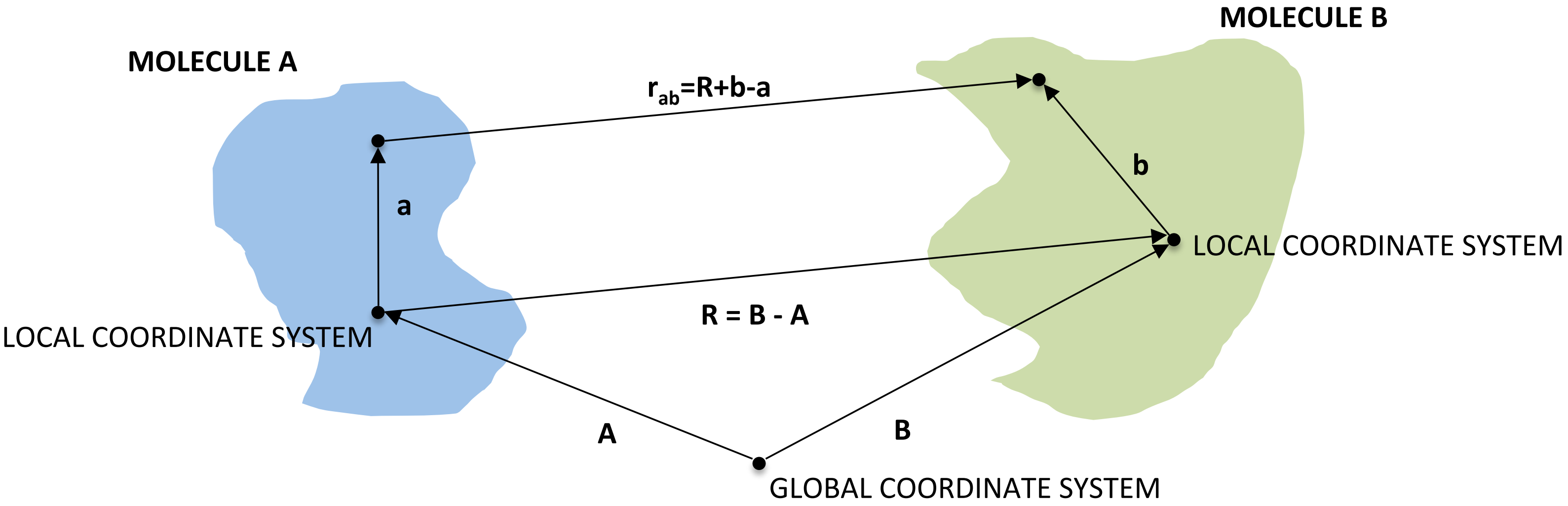
- IF THE MOLECULES ARE FAR ENOUGH APART THE OVERLAP BETWEEN THEIR WAVEFUNCTIONS CAN BE IGNORED

- THE HAMILTONIAN FOR EACH MOLECULE IS DEFINED IN TERMS OF ITS PRIVATE SET OF ELECTRONS AND NUCLEI

$$\hat{H}^0 = \hat{H}^A + \hat{H}^B \longrightarrow$$ **UNPERTURBED HAMILTONIAN FOR THE SYSTEM COMPOSED BY MOLECULES A AND B**

$$\hat{H}' = \sum_{a \in A} \sum_{b \in B} \frac{e_a e_b}{4\pi\varepsilon_0 r_{ab}} \longrightarrow$$ **ELECTROSTATIC INTERACTION BETWEEN PARTICLES (I.E., ELECTRONS AND NUCLEI) OF MOLECULE A AND THOSE OF B**

permittivity of free space



III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

A. PERTURBATION THEORY OF INTERMOLECULAR FORCES AT LONG RANGE

$$\hat{H}' = \sum_{a\in A}\sum_{b\in B}\frac{e_a e_b}{4\pi\varepsilon_0 r_{ab}}$$

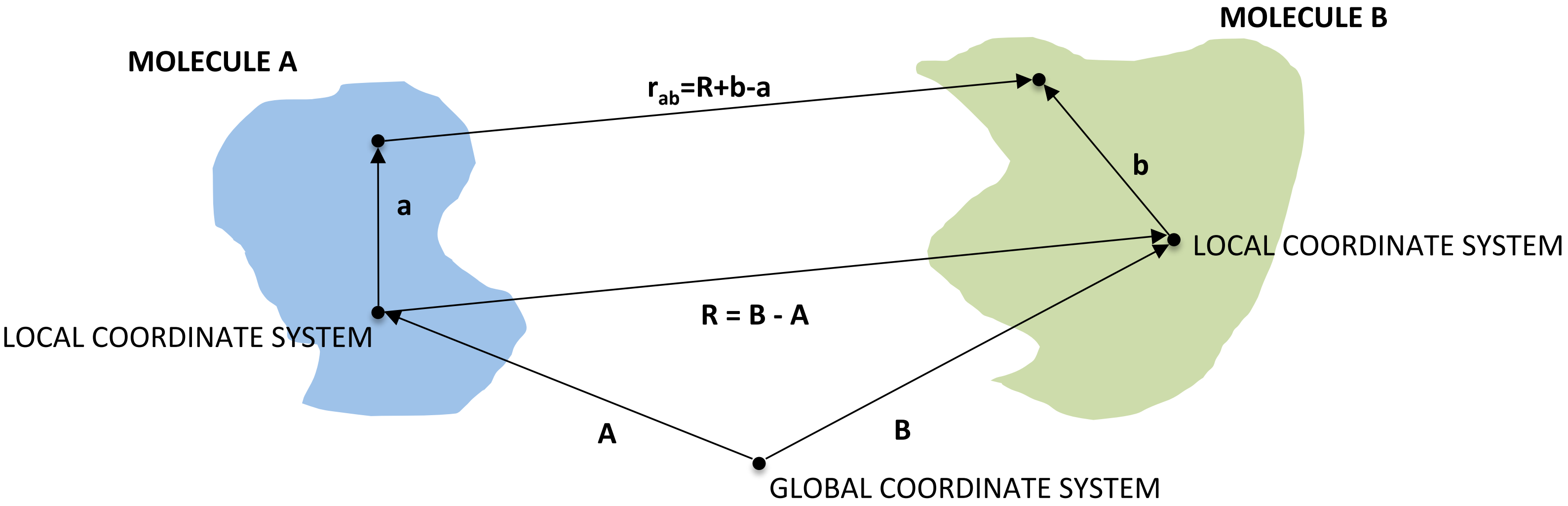
$$\hat{V}^A(\mathbf{B}+\mathbf{b}) = \sum_{a\in A}\frac{e_a}{4\pi\varepsilon_0 r_{ab}} \quad \Rightarrow \quad \hat{H}' = \sum_{b\in B} e_b \hat{V}^A(\mathbf{B}+\mathbf{b})$$

POTENTIAL GENERATED BY MOLECULE A
AT POINT B + b

$$\hat{\rho}^A(\mathbf{r}) = \sum_{a\in A} e_a \delta(\mathbf{r}-\mathbf{a}) \quad \Rightarrow \quad \hat{H}' = \int \frac{\hat{\rho}^A(\mathbf{r})\hat{\rho}^B(\mathbf{r}')}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}'$$

Dirac delta

CHARGE DENSITY OPERATOR
FOR MOLECULE A



III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

A. PERTURBATION THEORY OF INTERMOLECULAR FORCES AT LONG RANGE

- THE UNPERTURBATED STATES ARE SIMPLE PRODUCT FUNCTIONS $\Psi_m^A \Psi_n^B$, WHICH WE ABBREVIATE TO $|mn\rangle$, AND THEY ARE EIGFUNCTIONS OF $\hat{H}^0$:

$$\hat{H}^0|mn\rangle = (\hat{H}^A + \hat{H}^B)|mn\rangle = (W_m^A + W_n^B)|mn\rangle = W_{mn}|mn\rangle$$

- FOR CLOSED-SHELL MOLECULES, NON-DEGENERATE RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY GIVES THE ENERGY TO SECOND ORDER OF THE GROUND STATE, LABELLED BY *m=n=0*:

$$W = W_{00} + W'_{00} + W''_{00}$$

$$W_{00} = W_0^A + W_0^B$$

$$W'_{00} = \langle 00|\hat{H}'|00\rangle$$

$$W''_{00} = -\sum_{mn\neq 00} \frac{\langle 00|\hat{H}'|mn\rangle\langle mn|\hat{H}|00\rangle}{W_{mn} - W_{00}}$$

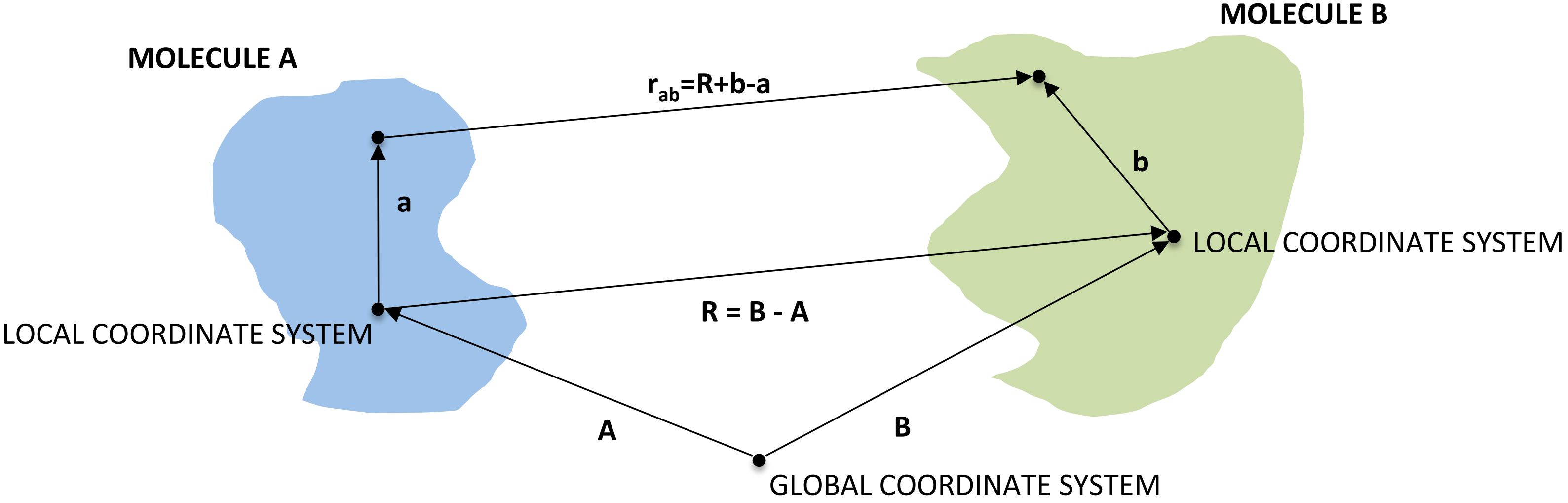
III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

B. MULTIPOLE EXPANSION

$$\hat{H}' = \sum_{b \in B} e_b \hat{V}^A(\mathbf{B} + \mathbf{b})$$

TAYLOR SERIES FOR ELECTRIC POTENTIAL
AROUND **b = 0** + CONCLUSIONS PREVIOUS SECTION

$$\begin{aligned} \hat{H}' &= q^B V^A(\mathbf{B}) + \sum_{\alpha} \hat{\mu}^B_\alpha \frac{\partial V^A(\mathbf{B})}{\partial b_\alpha} + \frac{1}{3} \sum_{\alpha,\beta} \hat{\Theta}^B_{\alpha\beta} \frac{\partial^2 V^A(\mathbf{B})}{\partial b_\alpha \partial b_\beta} + \dots \\ &= q^B V^A(\mathbf{B}) + \sum_{\alpha} \hat{\mu}^B_\alpha \frac{\partial V^A(\mathbf{B})}{\partial R_\alpha} + \frac{1}{3} \sum_{\alpha,\beta} \hat{\Theta}^B_{\alpha\beta} \frac{\partial^2 V^A(\mathbf{B})}{\partial R_\alpha \partial R_\beta} + \dots \end{aligned}$$



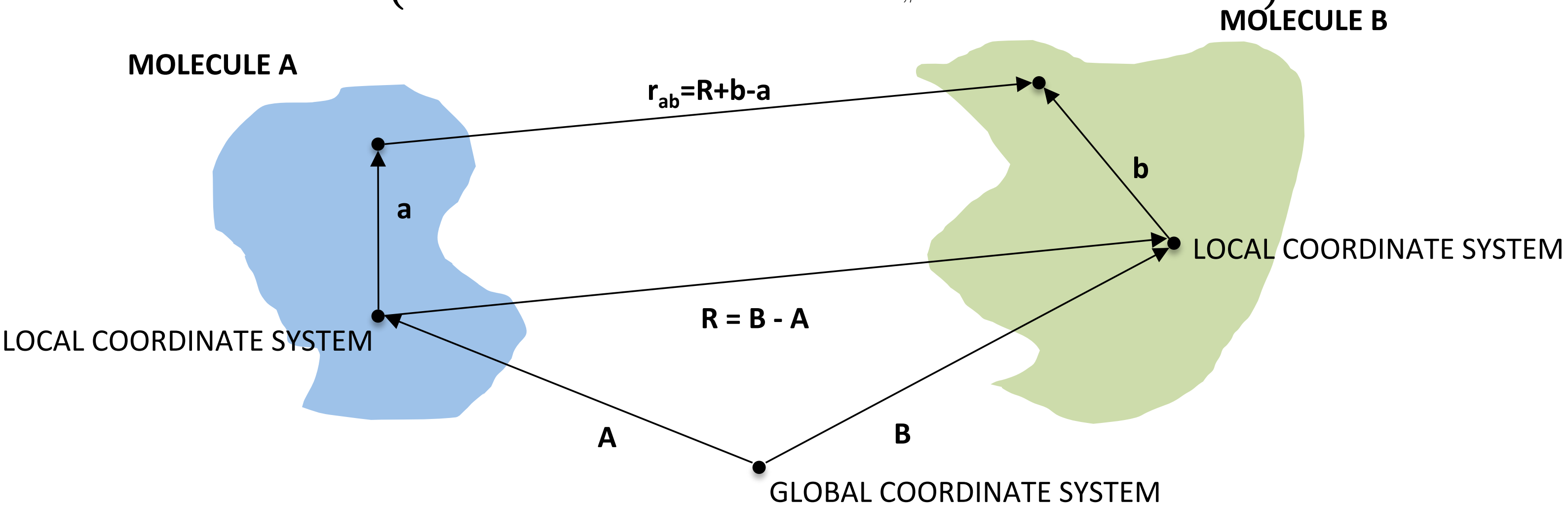
III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

B. MULTIPOLE EXPANSION

$$V^A(\mathbf{B}) = \sum_a \frac{e_a}{4\pi\varepsilon_0|\mathbf{R}-\mathbf{a}|}$$

TAYLOR SERIES FOR ELECTRIC POTENTIAL AROUND **a = 0**

$$\begin{aligned}
V^A(\mathbf{B}) &= \sum_a \frac{e_a}{4\pi\varepsilon_0}\left\{\frac{1}{R} + \sum_\alpha a_\alpha \left(\frac{\partial}{\partial a_\alpha}\frac{1}{|\mathbf{R}-\mathbf{a}|}\right)_{\mathbf{a=0}} + \frac{1}{2}\sum_{\alpha,\beta} a_\alpha a_\beta \left(\frac{\partial^2}{\partial a_\alpha \partial a_\beta}\frac{1}{|\mathbf{R}-\mathbf{a}|}\right)_{\mathbf{a=0}} + \dots\right\} \\
&= \sum_a \frac{e_a}{4\pi\varepsilon_0}\left\{\frac{1}{R} - \sum_\alpha a_\alpha \left(\frac{\partial}{\partial R_\alpha}\frac{1}{|\mathbf{R}-\mathbf{a}|}\right)_{\mathbf{a=0}} + \frac{1}{2}\sum_{\alpha,\beta} a_\alpha a_\beta \left(\frac{\partial^2}{\partial R_\alpha \partial R_\beta}\frac{1}{|\mathbf{R}-\mathbf{a}|}\right)_{\mathbf{a=0}} - \dots\right\} \\
&= \frac{1}{4\pi\varepsilon_0}\left\{\hat{M}\left(\frac{1}{R}\right) - \sum_\alpha \hat{M}_\alpha \nabla_\alpha \left(\frac{1}{R}\right) + \frac{1}{2}\sum_{\alpha,\beta} \hat{M}_{\alpha\beta}\nabla_\alpha\nabla_\beta\left(\frac{1}{R}\right) - \dots\right\}
\end{aligned}$$



III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

B. MULTIPOLE EXPANSION

$$V^A(\mathbf{B}) = \frac{1}{4\pi\varepsilon_0}\left\{\boxed{\hat{M}}\left(\frac{1}{R}\right) - \sum_\alpha \boxed{\hat{M}_\alpha}\nabla_\alpha\left(\frac{1}{R}\right) + \frac{1}{2}\sum_{\alpha,\beta}\boxed{\hat{M}_{\alpha\beta}}\nabla_\alpha\nabla_\beta\left(\frac{1}{R}\right) - \ldots\right\}$$

ZEROTH MOMENT: $\hat{M} = \sum_a e_a = q^A \longrightarrow$ **TOTAL CHARGE**

FIRST MOMENT: $\hat{M}_\alpha = \sum_a e_a a_\alpha = \hat{\mu}^A \longrightarrow$ **DIPOLE MOMENT**

SECOND MOMENT: $\hat{M}_{\alpha\beta} = \sum_a e_a a_\alpha a_\beta$

$$\hat{M}'_{\alpha\beta} = \hat{M}_{\alpha\beta} - k\delta_{\alpha\beta}$$

$\nabla^2\left(\frac{1}{R}\right) = 0$ (LAPLACE'S EQUATION)

$$\frac{1}{2}\sum_{\alpha,\beta}\hat{M}'_{\alpha\beta}\nabla_\alpha\nabla_\beta\left(\frac{1}{R}\right) = \frac{1}{2}\sum_{\alpha,\beta}\hat{M}_{\alpha\beta}\nabla_\alpha\nabla_\beta\left(\frac{1}{R}\right) - \frac{1}{2}k\sum_\alpha\nabla_\alpha^2\left(\frac{1}{R}\right) \overset{\downarrow}{=} \frac{1}{2}\sum_{\alpha,\beta}\hat{M}_{\alpha\beta}\nabla_\alpha\nabla_\beta\left(\frac{1}{R}\right)$$

$$\sum_\alpha \hat{M}'_{\alpha\alpha} = \hat{M}'_{xx} + \hat{M}'_{yy} + \hat{M}'_{zz} = 0$$

$$\sum_\alpha \hat{M}'_{\alpha\alpha} = \sum_\alpha \hat{M}_{\alpha\alpha} - k\sum_\alpha\delta_{\alpha\alpha} \qquad k = \frac{1}{3}\sum_a e_a a^2$$

$\hat{M}'_{\alpha\beta} = \frac{2}{3}\hat{\Theta}^A_{\alpha\beta} \longrightarrow$ **QUADRUPOLE MOMENT**

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

B. MULTIPOLE EXPANSION

$$\begin{aligned}
V^A(\mathbf{B}) &= T\boxed{q^A} - \sum_{\alpha} T_\alpha \boxed{\hat{\mu}^A_\alpha} + \frac{1}{3}\sum_{\alpha,\beta} T_{\alpha\beta}\boxed{\hat{\Theta}^A_{\alpha\beta}} - \ldots \\
&+ \frac{(-1)^n}{(2n-1)!!}\sum_{\alpha,\beta,\ldots,\nu} T^{(n)}_{\alpha\beta\ldots\nu}\hat{\xi}^{(n)A}_{\alpha\beta\ldots\nu} + \ldots \\
T &= \frac{1}{4\pi\varepsilon_0 R} \\
T_\alpha &= \frac{1}{4\pi\varepsilon_0}\nabla_\alpha\left(\frac{1}{R}\right) = -\frac{R_\alpha}{4\pi\varepsilon_0 R^3} \\
T_{\alpha\beta} &= \frac{1}{4\pi\varepsilon_0}\nabla_\alpha\nabla_\beta\left(\frac{1}{R}\right) = \frac{3R_\alpha R_\beta - R^2\delta_{\alpha\beta}}{4\pi\varepsilon_0 R^5} \\
T^{(n)}_{\alpha\beta\ldots\nu} &= \frac{1}{4\pi\varepsilon_0}\nabla_\alpha\nabla_\beta\ldots\nabla_\nu\left(\frac{1}{R}\right)
\end{aligned}$$

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

B. MULTIPOLE EXPANSION

$$\begin{aligned}
V^A(\mathbf{B}) &= T\boxed{q^A} - \sum_{\alpha} T_\alpha \boxed{\hat{\mu}^A_\alpha} + \frac{1}{3}\sum_{\alpha,\beta} T_{\alpha\beta}\boxed{\hat{\Theta}^A_{\alpha\beta}} - \dots \\
&+ \frac{(-1)^n}{(2n-1)!!}\sum_{\alpha,\beta,\dots,\nu} T^{(n)}_{\alpha\beta\dots\nu}\hat{\xi}^{(n)A}_{\alpha\beta\dots\nu} + \dots
\end{aligned}$$

$$\begin{aligned}
\hat{H}' &= q^B\left(Tq^A - \sum_{\alpha} T_\alpha \hat{\mu}^A_\alpha + \frac{1}{3}\sum_{\alpha,\beta} T_{\alpha\beta}\hat{\Theta}^A_{\alpha\beta} - \dots\right) \\
&+ \sum_{\alpha}\hat{\mu}^B_\alpha\left(T_\alpha q^A - \sum_{\beta} T_{\alpha\beta}\hat{\mu}^A_\beta + \frac{1}{3}\sum_{\beta,\gamma} T_{\alpha\beta\gamma}\hat{\Theta}^A_{\beta\gamma} - \dots\right) \\
&+ \frac{1}{3}\sum_{\alpha,\beta}\hat{\Theta}^B_{\alpha\beta}\left(T_{\alpha\beta} q^A - \sum_{\gamma} T_{\alpha\beta\gamma}\hat{\mu}^A_\gamma + \frac{1}{3}\sum_{\gamma,\delta} T_{\alpha\beta\gamma\delta}\hat{\Theta}^A_{\gamma\delta} - \dots\right)
\end{aligned}$$

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

C. ELECTROSTATIC ENERGY

$$U_{el}^{AB} \equiv W'_{00} = \langle 00|\hat{H}'|00\rangle$$

$$\boxed{\hat{H}' = \int \frac{\hat{\rho}^A(\mathbf{r})\hat{\rho}^B(\mathbf{r}')}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}'}$$

MULTIPOLE EXPANSION

$$U_{el}^{AB} = \int \frac{\rho^A(\mathbf{r})\rho^B(\mathbf{r}')}{4\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}d^3\mathbf{r}'$$

EXACT ELECTROSTATIC ENERGY

$$\rho^A(\mathbf{r}) = \langle 0|\hat{\rho}^A(\mathbf{r})|0\rangle$$

CHARGE DISTRIBUTION FOR MOLECULE A

$$\begin{aligned} U_{el}^{AB} &= q^A T q^B + \sum_{\alpha} T_\alpha \left(q^A \mu_\alpha^B - \mu_\alpha^A q^B\right) + \frac{1}{3}\sum_{\alpha,\beta} T_{\alpha\beta}\left(q^A \Theta_{\alpha\beta}^B - \Theta_{\alpha\beta}^A q^B\right) + \dots \\ &- \sum_{\alpha,\beta} \mu_\alpha^A T_{\alpha\beta} \mu_\beta^B - \frac{1}{3}\sum_{\alpha,\beta,\gamma}\left(\mu_\alpha^A \Theta_{\beta\gamma}^B - \Theta_{\beta\gamma}^A \mu_\alpha^B\right) + \dots \\ &+ \frac{1}{9}\sum_{\alpha,\beta,\gamma,\delta} \Theta_{\alpha\beta}^A T_{\alpha\beta\gamma\delta} \Theta_{\gamma\delta}^B + \dots \end{aligned}$$

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

D. INDUCTION ENERGY

$$W''_{00} = \boxed{U^{A}_{ind}} + \boxed{U^{B}_{ind}} + \boxed{U_{disp}}$$

DISPERSION ENERGY

INDUCTION ENERGY
MOLECULE A

INDUCTION ENERGY
MOLECULE B

$$\boxed{U^{A}_{ind} = -\sum_{m\neq 0} \frac{\langle 00|\hat{H}'|m0\rangle\langle m0\hat{H}'|00\rangle}{W^{A}_{m} - W^{A}_{0}}}$$

MOLECULE A IS EXCITED
BUT B IS IN ITS GROUND STATE

$$\boxed{U^{B}_{ind} = -\sum_{n\neq 0} \frac{\langle 00|\hat{H}'|0n\rangle\langle 0n|\hat{H}'|00\rangle}{W^{B}_{n} - W^{B}_{0}}}$$

MOLECULE B IS EXCITED
BUT A IS IN ITS GROUND STATE

$$\boxed{U_{disp} = -\sum_{n\neq 0, m\neq 0} \frac{\langle 00|\hat{H}'|mn\rangle\langle mn|\hat{H}'|00\rangle}{W^{A}_{m} + W^{B}_{n} - W^{A}_{0} - W^{B}_{0}}}$$

BOTH MOLECULES ARE EXCITED

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

D. INDUCTION ENERGY

MULTIPOLE EXPANSION

$$\begin{aligned} U^B_{ind} &= -\sum_{n\neq0}\langle 00|q^A T q^B + \sum_{\alpha} T_\alpha (q^A \hat{\mu}^B_\alpha - \hat{\mu}^A_\alpha q^B) - \sum_{\alpha,\beta} \hat{\mu}^A_\alpha T_{\alpha\beta} \hat{\mu}^B_\beta + \ldots |0n\rangle \\ &\times \langle 0n|q^A T q^B + \sum_{\alpha'} T_{\alpha'} (q^A \hat{\mu}^B_{\alpha'} - \hat{\mu}^A_{\alpha'} q^B) - \sum_{\alpha',\beta'} \hat{\mu}^A_{\alpha'} T_{\alpha'\beta'} \hat{\mu}^B_{\beta'} + \ldots |00\rangle \\ &\times (W^B_n - W^B_0)^{-1} \end{aligned}$$

INTEGRATION OVER THE COORDIANTES OF MOLECULE A

$$\begin{aligned} U^B_{ind} &= -\sum_{n\neq0}\langle 0|\sum_{\alpha} q^A T_\alpha \hat{\mu}^B_\alpha - \sum_{\alpha,\beta} \mu^A_\alpha T_{\alpha\beta} \hat{\mu}^B_\beta + \ldots |n\rangle \\ &\times \langle n|\sum_{\alpha'} q^A T_{\alpha'} \hat{\mu}^B_{\alpha'} - \sum_{\alpha',\beta'} \mu^A_{\alpha'} T_{\alpha'\beta'} \hat{\mu}^B_{\beta'} + \ldots |0\rangle \\ &\times (W^B_n - W^B_0)^{-1} \end{aligned}$$

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

D. INDUCTION ENERGY

MULTIPOLE EXPANSION

$$\begin{aligned}
U^B_{ind} &= -\sum_{n\neq 0}\langle 0|\sum_{\alpha} q^A T_\alpha \hat{\mu}^B_\alpha - \sum_{\alpha,\beta}\mu^A_\alpha T_{\alpha\beta}\hat{\mu}^B_\beta + \ldots |n\rangle \\
&\times \langle n|\sum_{\alpha'} q^A T_{\alpha'}\hat{\mu}^B_{\alpha'} - \sum_{\alpha',\beta'}\mu^A_{\alpha'} T_{\alpha'\beta'}\hat{\mu}^B_{\beta'} + \ldots |0\rangle \\
&\times (W^B_n - W^B_0)^{-1}
\end{aligned}$$

$$\Downarrow$$

$$\begin{aligned}
U^B_{ind} &= -\sum_{\alpha,\alpha'}\left(q^A T_\alpha - \sum_\beta \mu^A_\beta T_{\alpha\beta} + \ldots\right) \\
&\times \sum_{n\neq 0}\langle 0|\hat{\mu}^B_\alpha|n\rangle\langle n|\hat{\mu}^B_{\alpha'}|0\rangle(W^B_n - W^B_0)^{-1} \\
&\times \left(q^A T_{\alpha'} - \sum_{\beta'}\mu^A_{\beta'} T_{\alpha'\beta'} + \ldots\right)
\end{aligned}$$

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

D. INDUCTION ENERGY

MULTIPOLE EXPANSION

$$
\begin{aligned}
U^B_{ind} &= -\sum_{\alpha,\alpha'} \left(q^A T_\alpha - \sum_\beta \mu^A_\beta T_{\alpha\beta} + \ldots \right) \\
&\times \sum_{n\neq 0} \langle 0|\hat{\mu}^B_\alpha|n\rangle\langle n|\hat{\mu}^B_{\alpha'}|0\rangle (W^B_n - W^B_0)^{-1} \\
&\times \left(q^A T_{\alpha'} - \sum_{\beta'} \mu^A_{\beta'} T_{\alpha'\beta'} + \ldots \right)
\end{aligned}
$$

USING POLARIZABILITY DEFINITION

$$
U^B_{ind} = -\tfrac{1}{2}\textstyle\sum_{\alpha,\alpha'} \left(q^A T_\alpha - \sum_\beta \mu^A_\beta T_{\alpha\beta} + \ldots \right) \alpha^B_{\alpha\alpha'} \left(q^A T_{\alpha'} - \sum_{\beta'} \mu^A_{\beta'} T_{\alpha'\beta'} + \ldots \right)
$$

III. ELECTROSTATIC INTERACTION BETWEEN MOLECULES

D. INDUCTION ENERGY

MULTIPOLE EXPANSION

$$U^B_{ind} = -\frac{1}{2}\sum_{\alpha,\alpha'}\left(q^A T_\alpha - \sum_\beta \mu^A_\beta T_{\alpha\beta} + \ldots\right)\alpha^B_{\alpha\alpha'}\left(q^A T_{\alpha'} - \sum_{\beta'} \mu^A_{\beta'} T_{\alpha'\beta'} + \ldots\right)$$

$$E^A_\alpha(\mathbf{B}) = -\frac{\partial V^A(\mathbf{B})}{\partial B_\alpha} = -\frac{\partial V^A(\mathbf{B})}{\partial R_\alpha} = -T_\alpha q^A - \sum_\beta T_{\alpha\beta}\hat{\mu}^A_\beta - \ldots$$

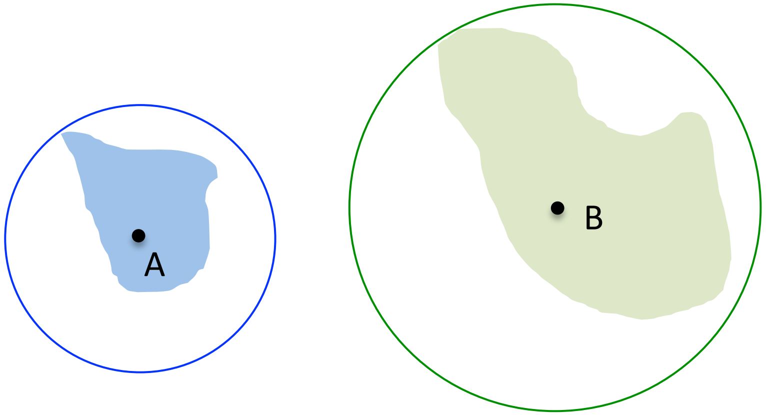
ELECTRIC FIELD AT **B** DUE TO MOLECULE A

$$U^B_{ind} = -\frac{1}{2}\sum_{\alpha,\boxed{\alpha'}} E^A_\alpha(\mathbf{B})\boxed{\alpha^B_{\alpha\alpha'}E^A_{\alpha'}(\mathbf{B})} - \ldots$$

DIPOLE IN MOLECULE B INDUCED
BY ELECTRIC FIELD DUE TO MOLECULE A

IV. CONVERGENCE OF THE MULTIPOLE EXPANSION

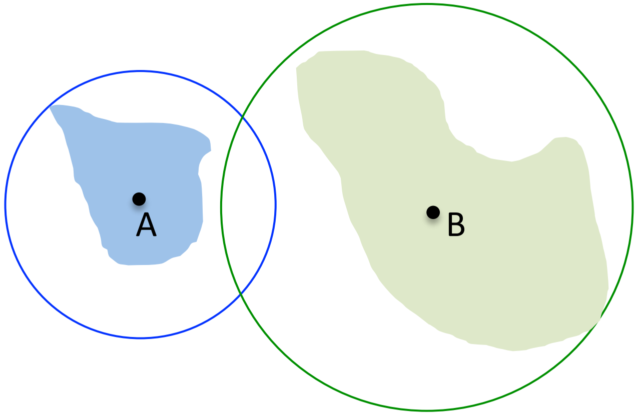
CONVERGENT MULTIPOLE EXPANSION



DIVERGENT SPHERE FOR MOLECULE A

DIVERGENT SPHERE FOR MOLECULE B

DIVERGENT MULTIPOLE EXPANSION



- DIVERGENCE SPHERE ENCLOSE ALL CHARGES BELONGING TO A MOLECULE
- FOR MOLECULES, THE MULTIPOLE EXPANSION SHOULD ALWAYS DIVERGE BECAUSE THE CHARGE DISTRIBUTION EXTENDS FORMALLY TO INFINITIY, EVEN THOUGH IT DIES AWAY EXPONENTIALLY WITH DISTANCE
- WHEN WAVEFUNCTIONS ARE REPRESENTED BY EXPANSION IN TERMS OF GAUSSIAN FUNCTIONS CENTERED AT THE NUCLEI, IT CAN BE SHOWN THAT THE DIVERGENCE SPHERE IS THE SPHERE ENCLOSING JUST THE NUCLEI[1,2]
- EVEN WHEN THE DIVERGENCE SPHERE DON'T OVERLAP, THE MULTIPOLE EXPANSION WILL CONVERGE SLOWLY IF THE MOLECULES ARE NOT WIDELY SEPARATED

[1] A. J. Stone and, M. Alderton, *Molec. Phys.* **56**, 1047 (1985) [2] F. Vigné-Maeder and P. Claveire, *J. Chem. Phys.* **88**, 4934 (1988)

IV. CONVERGENCE OF THE MULTIPOLE EXPANSION

- SOLUTION: USE A **DISTRIBUTED MULTIPOLE EXPANSION** IN WHICH THE MOLECULE IS DIVIDED INTO REGIONS, EACH DESCRIBED BY ITS OWN MULTIPOLE MOMENTS

- A REGION WILL USUALLY BE AN **ATOM** OR **SMALL GROUP OF ATOMS**

- EACH REGION HAS ITS OWN ORIGIN, USUALLY CENTERED AT THE NUCLEUS FOR AN ATOMIC REGION. WE USE THE TERM **SITE** FOR THE ORIGIN OF A REGION

$$\hat{H}' = \underbrace{\sum\nolimits_{a\in A}}_{\downarrow} \underbrace{\sum\nolimits_{b\in B}}_{\searrow} \left[q^a T^{ab} q^b + \sum\nolimits_\alpha T^{ab}_\alpha \left(q^a \hat{\mu}^b_\alpha - \hat{\mu}^a_\alpha q^b\right) - \sum\nolimits_{\alpha,\beta} \hat{\mu}^a_\alpha T^{ab}_{\alpha\beta} \hat{\mu}^b_\beta + \ldots \right]$$

SUM OVER SITES
OF MOLECULE A

SUM OVER SITES
OF MOLECULE B

V. DISTRIBUTED MULTIPOLES

A. POINT-CHARGE MODELS

- THE SIMPLEST ROUTE TO A POINT-CHARGE MODEL:
  - ✓ DEFINE SITES ON ALL ATOMS
  - ✓ THROW AWAY THE DIPOLE AND HIGHER MOMENTS

SUM OVER ATOMS OF MOLECULE A

SUM OVER ATOMS OF MOLECULE B

$$U_{el} = \sum_{a\in A}\sum_{b\in B}\left[q^a T^{ab} q^b + \sum_{\alpha} T^{ab}_{\alpha}\left(q^a \mu^b_{\alpha} - \mu^a_{\alpha} q^b\right) - \sum_{\alpha,\beta} \mu^a_{\alpha} T^{ab}_{\alpha\beta} \mu^b_{\beta} + \ldots\right]$$

$$\simeq \sum_{a\in A}\sum_{b\in B} q^a T^{ab} q^b = \sum_{a\in A}\sum_{b\in B} \frac{q^a q^b}{4\pi\varepsilon_0 r_{ab}}$$

r_{ab} → DISTANCE BETWEEN ATOMS A AND B

- ✓ DISADVANTAGE: THE TRUNCATION OF THE MULTIPOLE EXPANSION WILL BE SATISFACTORY ONLY IF THE DISCARDED MOMENTS ARE SMALL, BUT ATOMIC DIPOLES AND QUADRUPOLES WILL BE PARTICULARLY IMPORTANT IN THE POLAR GROUPS THAT ARE COMMON IN PROTEINS, NUCLEIC ACIDS AND BIOLOGICAL SYSTEMS

V. DISTRIBUTED MULTIPOLES

A. POINT-CHARGE MODELS

- NEXT STEP: MODIFY THE ATOMIC CHARGES TO TAKE INTO ACCOUNT AS FAR AS POSSIBLE THE EFFECTS OF THESE OMITTED MOMENTS

  ✓ FIT ATOMIC CHARGES TO REPRODUCE THE CORRECT MOLECULAR POTENTIAL[1,2,3,4]

  ✓ DISADVANTAGE:

  "THE CHARGE DISTRIBUTION IN A MOLECULE IS MUCH TOO ANISOTROPIC TO BE SUCCESFULLY DESCRIBED BY ANY SINGLE SET OF ATOM-CENTERED CHARGES UNLESS ONLY LONG-DISTANCE INTERACTIONS ARE OF INTEREST. OTHERWISE IT IS NECESSARY TO INCLUDE AT LEAST ATOMIC DIPOLE MOMENTS, AND POSSIBLY HIGHER TERMS AS WELL."[5]

- NEXT STEP: ONE WAY TO OVERCOME THIS PROBLEM IS TO INTRODUCE ADDITIONAL SITES (**OFF-ATOM CHARGES**), BUT THIS INCREASES THE NUMBER OF SITES TO BE HANDLED, AND THE CHOICE OF ADDITIONAL SITES IS OFTEN SOMEWHAT ARBITRARY

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[1] F. A. Momany, *J. Chem. Phys.* **82**, 592 (1978) [2] S. R. Cox and D. E. Williams, *J. Comput. Chem.* **2**, 304 (1981)
[3] U. C. Singh and P. A. Kollman, *J. Comput. Chem.* **5**, 129 (1984) [4] G. G. Ferenczy, *J. Comput. Chem.* **12**, 913 (1991)
[5] K. B. Wiberg and P. R. Rablen, *J. Comput. Chem.* **14**, 1504 (1993)

V. DISTRIBUTED MULTIPOLES

B. OTHER MODELS

- DISTRIBUTED MULTIPOLE ANALYSIS (DMA)[1,2]
- QUANTUM THEORY OF ATOMS IN MOLECULES (QTAIM)[3]
- DISADVANTAGE OF THESE MODELS: IN ENERGY OPTIMIZATION OR DYNAMICAL SIMULATION IT BECOMES NECESSARY TO KEEP TRACK OF THE ORIENTATIONS AS WELL AS THE POSITION OF EACH ATOM

[1] A. J. Stone , *Phys. Lett.* **83**, 233 (1981) [2] A. J. Stone and M. Alderton, *Mol. Phys.* **56**, 1047 (1985)
[3] R. F. W. Bader, *Atoms in Molecules.* Oxford University Press, Oxford, 1990

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL[1,2]

- AN ISOTROPIC POLARIZABILITY α^a IS ASSIGNED TO EACH *a* ATOM

- IN AN EXTERNAL FIELD, EACH *a* ATOM BECOMES POLARIZED, AND DEVELOPS AN INDUCED DIPOLE MOMENT $\Delta\boldsymbol{\mu}^a$, IN ADDITION TO ANY STATIC DIPOLE THAT MAY EXIST IN THE ABSENCE OF A FIELD

- THE INDUCED DIPOLE MOMENTS ARE CAUSED NOT ONLY BY THE **EXTERNAL FIELD** BUT BY THE **FIELDS ARISING FROM INDUCED DIPOLE MOMENTS** ON OTHER ATOMS SO THAT THE INDUCED MOMENTA ON ATOM *a* IS

$$\Delta\mu_\alpha^a = \alpha^a \left(\boxed{E_\alpha^a} + \boxed{\sum_{b\neq a} \sum_\beta T_{\alpha\beta}^{ab} \Delta\mu_\beta^b} \right)$$

$$T_{\alpha\beta}^{ab} = \frac{3r_{ab,\alpha} r_{ab,\beta} - r_{ab}^2 \delta_{\alpha\beta}}{4\pi\varepsilon_0 r_{ab}^5}$$

$$r_{ab,\alpha} = r_{b,\alpha} - r_{a,\alpha}$$

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[1] L. Silberstein , *Phil. Mag.* **33**, 92, 215, 521 (1917)

[2] J. Applequist, J. R. Carl and K.-K. Fung, *J. Am. Soc.* **94**, 2952 (1972)

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL

$$\Delta\mu_\alpha^a = \alpha^a \left(E_\alpha^a + \sum_{b\neq a} \sum_\beta T_{\alpha\beta}^{ab} \Delta\mu_\beta^b \right)$$

$$\Downarrow$$

$$(\alpha^a)^{-1} \Delta\mu_\alpha^a - \sum_{b\neq a} \sum_\beta T_{\alpha\beta}^{ab} \Delta\mu_\beta^b = E_\alpha^a$$

$$\Downarrow$$

$$\sum_{b,\beta} B_{\alpha\beta}^{ab} \Delta\mu_\beta^b = E_\alpha^a \qquad B_{\alpha\beta}^{ab} = \begin{cases} (\alpha^a)^{-1} & a = b \\ -T_{\alpha\beta}^{ab} & a \neq b \end{cases}$$

$$\Downarrow$$

$$\Delta\mu_\alpha^a = \sum_{b,\beta} A_{\alpha\beta}^{ab} E_\beta^b \qquad \mathbf{A} = \mathbf{B}^{-1}$$

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL

$$\Delta\mu^a_\alpha = \sum_{b,\beta} A^{ab}_{\alpha\beta} E^b_\beta \qquad \mathbf{A} = \mathbf{B}^{-1}$$

$$\boxed{\Delta u^{tot}_\alpha} = \sum_a \Delta\mu^a_\alpha = \sum_{a,b,\beta} A^{ab}_{\alpha\beta} E^b_\beta$$

TOTAL (MOLECULE) INDUCED MOMENT

UNIFORM EXTERNAL FIELD $E^b_\beta = E_\beta$

$$\boxed{\alpha^{tot}_{\alpha\beta}} = \sum_{a,b} A^{ab}_{\alpha\beta}$$

TOTAL (MOLECULE) POLARIZABILITY

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL

- EXAMPLE: DIATOMIC MOLECULE WITH BOND LENGTH *R*
  - ✓ MOLECULAR AXIS ALONG *z* AXIS
  - ✓ ATOMS LABELLED AS *a* AND *b*
  - ✓ $p = \frac{1}{4\pi\varepsilon_0 R^3}$ $X = p^2\alpha^a\alpha^b$

$$\mathbf{B} = \begin{array}{cc} & \begin{array}{cccccc} a & & & b & & \\ x & y & z & x & y & z \end{array} \\ \begin{array}{c} a\,x \\ y \\ z \\ b\,x \\ y \\ z \end{array} & \left(\begin{array}{cccccc} (\alpha^a)^{-1} & 0 & 0 & p & 0 & 0 \\ 0 & (\alpha^a)^{-1} & 0 & 0 & p & 0 \\ 0 & 0 & (\alpha^a)^{-1} & 0 & 0 & -2p \\ p & 0 & 0 & (\alpha^b)^{-1} & 0 & 0 \\ 0 & p & 0 & 0 & (\alpha^b)^{-1} & 0 \\ 0 & 0 & -2p & 0 & 0 & (\alpha^b)^{-1} \end{array}\right) \end{array}.$$

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL

- EXAMPLE: DIATOMIC MOLECULE WITH BOND LENGTH *R*
  - ✓ MOLECULAR AXIS ALONG *z* AXIS
  - ✓ ATOMS LABELLED AS *a* AND *b*
  - ✓ $p = \frac{1}{4\pi\varepsilon_0 R^3}$ $X = p^2\alpha^a\alpha^b$

$$\mathbf{A} = \begin{pmatrix} \frac{\alpha^a}{1-X} & 0 & 0 & -\frac{p\alpha^a\alpha^b}{1-X} & 0 & 0 \\ 0 & \frac{\alpha^a}{1-X} & 0 & 0 & -\frac{p\alpha^a\alpha^b}{1-X} & 0 \\ 0 & 0 & \frac{\alpha^a}{1-4Z} & 0 & 0 & \frac{2p\alpha^a\alpha^b}{1-4Z} \\ -\frac{p\alpha^a\alpha^b}{1-X} & 0 & 0 & \frac{\alpha^b}{1-X} & 0 & 0 \\ 0 & -\frac{p\alpha^a\alpha^b}{1-X} & 0 & 0 & \frac{\alpha^b}{1-X} & 0 \\ 0 & 0 & \frac{2p\alpha^a\alpha^b}{1-4Z} & 0 & 0 & \frac{\alpha^b}{1-4Z} \end{pmatrix}$$

$Z = X$

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL

- EXAMPLE: DIATOMIC MOLECULE WITH BOND LENGTH *R*
  - ✓ MOLECULAR AXIS ALONG *z* AXIS
  - ✓ ATOMS LABELLED AS *a* AND *b*
  - ✓ $p = \frac{1}{4\pi\varepsilon_0 R^3}$ $X = p^2\alpha^a\alpha^b$

$$\Delta\mu_z^{tot} = \Delta\mu_z^a + \Delta\mu_z^b = \frac{\alpha^a+\alpha^b+4p\alpha^a\alpha^b}{1-4X}E_z$$

MOLECULE INDUCED MOMENT FOR AN UNIFORM FIELD IN THE *z* DIRECTION

$$\Delta\mu_x^{tot} = \Delta\mu_x^a + \Delta\mu_x^b = \frac{\alpha^a+\alpha^b-2p\alpha^a\alpha^b}{1-X}E_x$$

MOLECULE INDUCED MOMENT FOR AN UNIFORM FIELD IN THE *x* DIRECTION

$$\alpha_{||}^{tot} = \frac{\alpha^a+\alpha^b+4p\alpha^a\alpha^b}{1-4p^2\alpha^a\alpha^b}$$

PARALLEL POLARIZABILITY

$$\alpha_{\perp}^{tot} = \frac{\alpha^a+\alpha^b-2p\alpha^a\alpha^b}{1-p^2\alpha^a\alpha^b}$$

PERPENDICULAR POLARIZABILITY

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL

- GIVEN THE EXPERIMENTAL POLARIZABILITIES FOR THE MOLECULE, WE CAN WORK BACK TO THE ATOM POLARIZABILITIES. FROM EXPERIEMNTAL DATA FOR MANY MOLECULES, TOGETHER WITH ASSUMPTIONS ABOUT TRANSFERIBILITY OF THE ATOM POLARIZABILITIES, IT IS POSSIBLE TO ASSIGN POLARIZABILITIES FOR A VARIETY OF ATOMS

- LIMIT CASES:

  - ✓ ATOMS ARE FAR REMOVED FROM EACH OTHER (AN ASSEMBLY OF ISOLATED ATOMS)

$$\lim_{R\to\infty} p = \lim_{R\to\infty} \frac{1}{4\pi\varepsilon_0 R^3} = 0$$

$$\alpha^{tot} = \alpha^a + \alpha^b$$

  - ✓ ATOMS VERY CLOSE: ELEMENTS OF **A** MATRIX DIVERGE

$$4p^2\alpha^a\alpha^b = 1 \Longrightarrow R^6 = \frac{4\alpha^a\alpha^b}{(4\pi\varepsilon_0)^2}$$

$$p^2\alpha^a\alpha^b = 1 \Longrightarrow R^6 = \frac{\alpha^a\alpha^b}{(4\pi\varepsilon_0)^2}$$

V. DISTRIBUTED POLARIZABILITIES

A. THE APPLEQUIST MODEL

- DISADVANTAGE: ***POLARIZATION CATASTROPHE***
  WHEN ATOMS ARE CLOSE TOGETHER IT IS NO LONGER VALID USE THE MULTIPOLE EXPANSION BECAUSE THE DIVERGENCE SPHERES OVERLAP

V. DISTRIBUTED POLARIZABILITIES

A. THE THOLE MODEL[1]

- INTRODUCE A DAMPING SCHEME TO SUPRESS THE SINGULARITY IN WHICH THE DIPOLE FIELD TENSORS CAN BE DERIVED FROM THE FIRST-ORDER ELEMENTS

$$T_{\alpha}^{ab,D} = -\frac{\lambda_3 r_{ab,\alpha}}{4\pi\varepsilon_0 r_{ab}^3}$$

$$T_{\alpha\beta}^{ab,D} = \frac{3\lambda_5 r_{ab,\alpha} r_{ab,\beta} - \lambda_3 r_{ab}^2 \delta_{\alpha\beta}}{4\pi\varepsilon_0 r_{ab}^5}$$

THOLE SCREENING PARAMETER

EFFECTIVE DISTANCE

$$\lambda_3 = 1 - e^{-a_T u^3} \qquad \lambda_5 = \lambda_3 - \underset{\uparrow}{a_T} u^3 e^{-a_T u^3} \qquad u = \frac{r_{ab}}{(\alpha^a \alpha^b)^{1/6}}$$

$$\lim_{r_{ab}\to 0} T_{\alpha}^{ab,D} = \lim_{r_{ab}\to 0} T_{\alpha\beta}^{ab,D} = 0$$

$$\Delta\mu_{\alpha}^{a} = \alpha^a \left(E_{\alpha}^{a} + \sum_{b\neq a} T_{\alpha\beta}^{ab,D} \Delta\mu_{\beta}^{b} \right)$$

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[1] B. T. Thole , *Chem. Phys.* **59**, 341 (1981)

V. DISTRIBUTED POLARIZABILITIES

A. THE THOLE MODEL

- DISADVANTAGE:
  - ✓ THE THOLE (AND APPLEQUIST) MODEL TREATS THE ATOMS OF A MOLECULE AS DISTINTICT ISOLATED ENTITIES, INTERACTING ONLY THROUGH MULTIPOLE INTERACTIONS
  - ✓ IN REALITY, IT IS POSSIBLE FOR ELECTRONS TO MOVE FROM ONE ATOM TO ANOTHER IN RESPONSE TO THE EXTERNAL FIELD AND, THUS, THE MULTIPOLE DESCRIPTION OF THEIR INTERACTIONS IS INADEQUATE

THANKS FOR YOUR ATTENTION!!!!