Intermolecular interactions

János Ángyán

Équipe Modélisaton Quantique et Cristallographique, LCM3B

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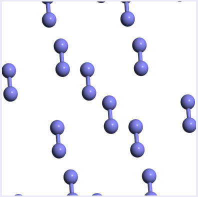
Part I

Introduction

What are intermolecular forces?

N_2 crystal



- why are the N_2 molecules arranged this way?
- what are the optimal intermolecular distances?
- what is the physical origin of the interactions that govern the structure?

Intermolecular interactions

- fragments (subsystems) are well-defined and preserve their identity
- usually between closed shell molecules, ions or atoms
- much weaker than chemical bonding
- long range

Why are intermolecular forces interesting?

Intermolecular forces play an important rôle in numerous fields

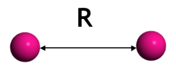
- Deviations of gases from ideal behaviour (pressure, viscosity, diffusion, thermal conductivity).
- Existence of condensed phases matter
- Properties of solids and liquids e.g. melting and boiling points.
- Organization of matter solids, crystal structures
- Polymorphism requires a very accurate knowledge of intermolecular forces.
- Liquid structure (pair distribution function, etc.)
- Reaction mechanisms (steric effects,
- Organization of soft matter, biopolymers.
- Heterogeneous catalysis
- Formation of surface monolayers, micelles and membranes,
- Transport of ions and molecules across biological membranes
- Atmospheric chemistry, etc...

Gecko feet adhesion by van der Waals forces

Autumn et al. *Proc. Natl. Acad. Sci.* 99 (2002) 122.

Intermolecular potential

Ar$_2$ dimer



At infinitely large distance, there is no interaction: the energy is the sum of the energy of isolated atoms

$$E_{\text{tot}}(\infty) = E_A + E_B$$

At an arbitrary, finite R distance, the total energy

$$E_{\text{tot}}(R) = E_A + E_B + U(R)$$

Interaction-dependent contribution, $U(R)$,the interaction energy or *intermolecular pair-potential*

$$\begin{aligned} U(R) &= E_{\text{tot}}(R) - E_{\text{tot}}(\infty) \\ &= E_{\text{tot}}(R) - E_A - E_B \end{aligned}$$

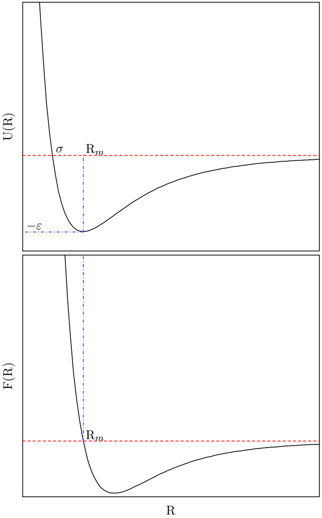
The intermolecular pair-potential is the work to bring together the two systems from infinity to the distance R, against *the intermolecular force*, $F(R)$

$$U(R) = \int_R^\infty F(r) dr$$

where

$$F(R) = -\frac{dE_{\text{tot}}}{dR} = -\frac{dU}{dR}$$

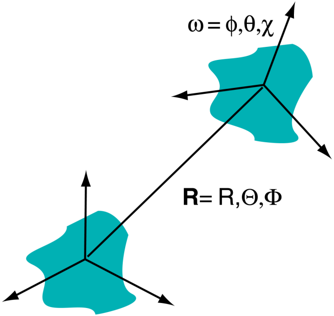
Potential and force



- σ is the hard core radius
- ε is the well depth
- repulsive for $R < R_m$
- attractive for $R > R_m$
- for $\sigma < R < R_m$ negative, but repulsive

Intermolecular energy can negative, but the interaction is repulsive (F>0).

General intermolecular potential



- For polyatomic subsystems the intermolecular interaction energy

$$U(\boldsymbol{R}, \boldsymbol{\omega}; \boldsymbol{q}_A, \boldsymbol{q}_B)$$

depends on the relative position and orientation $\{\boldsymbol{R}, \boldsymbol{\omega}\}$ and on the internal coordinates $\{\boldsymbol{q}_A, \boldsymbol{q}_B\}$

- $\boldsymbol{R}$: intermolecular vector (in polar coordinates)
- $\boldsymbol{\omega}$: relative Euler-angles

Even if we neglect the intramolecular degrees of freedom, $\{\boldsymbol{q}_A, \boldsymbol{q}_B\}$, the intermolecular PES (potential energy surface) is six-dimensional.

Cluster expansion of the interaction energy

The interaction energy can be decomposed to the sum of one-, two-, three-, etc. body contributions

$$U_N = \sum_i U_i + \frac{1}{2}\sum_{ij} U_{ij} + \frac{1}{3!}\sum_{ijk} U_{ijk} + \frac{1}{4!}\sum_{ijkl} U_{ijkl} + \dots$$

- one-body: geometrical deformation of the monomers
- two-body: dominating term (additivity)
- three-body, four-body, etc. (non-additivity)

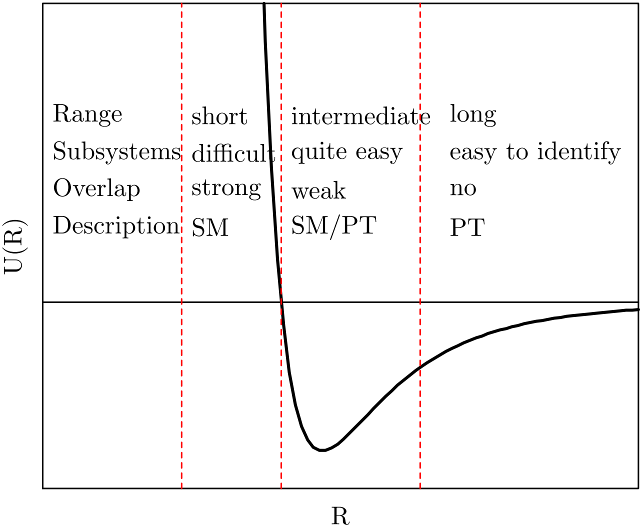
Effective (system-dependent) pair-potential

$$U_N = \sum_i U_i + \frac{1}{2}\sum_{ij} U_{ij}^{\text{eff}}(N)$$

may be quite different from the pure pair-potential.

Attention: an effective pair-potential, usually obtained by fitting condensed-phase experimental data, is usually not valid for simple binary complexes.

Interaction ranges



Range	short	intermediate	long
Subsystems	difficult	quite easy	easy to identify
Overlap	strong	weak	no
Description	SM	SM/PT	PT

Calculation of intermolecular interaction energy

$$\hat{H}_{AB} = \hat{H}_A + \hat{H}_A + \lambda \hat{V}_{AB}$$

Supermolecule approach

$$U = \Delta E = E(AB) - E(A) - E(B)$$

difference of the total energies (large numbers)

- technically very simple
- does not depend on the intensity of the interaction
- difficult to interpret in terms of the monomer properties
- energy components may have large errors with respect to the interaction energy
- systematic errors (BSSE)

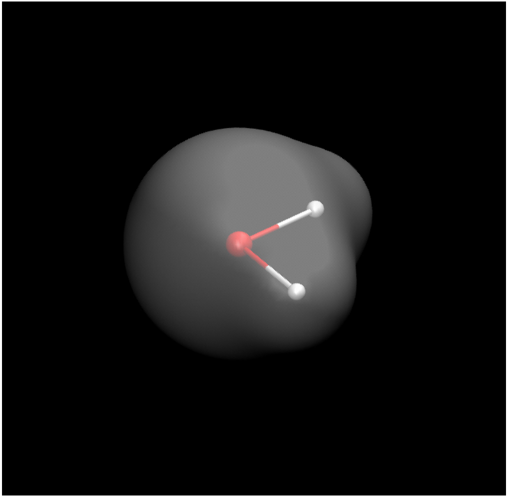
Perturbation theory

$$U = \Delta E = \sum_{n=1}^{\infty} \lambda^n \Delta E^{(n)}$$

directly, from the power series expansion in the strength of interaction

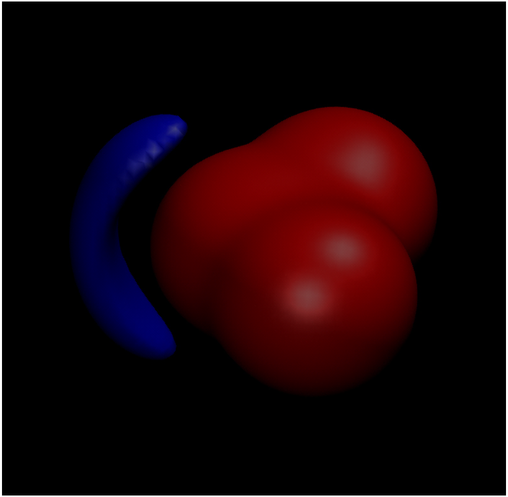
- leads directly to the interaction energy
- based on the monomer wavefunction/properties
- easy to interpret (physical insight, decomposition)
- provides basis of approximate analytical energy expressions
- is the expansion convergent?

Water molecule density



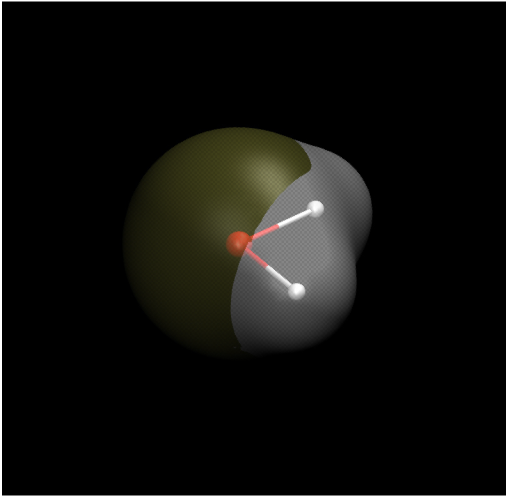
Electron density isosurface at 0.05 e/Å^3

Water molecule electrostatic potential



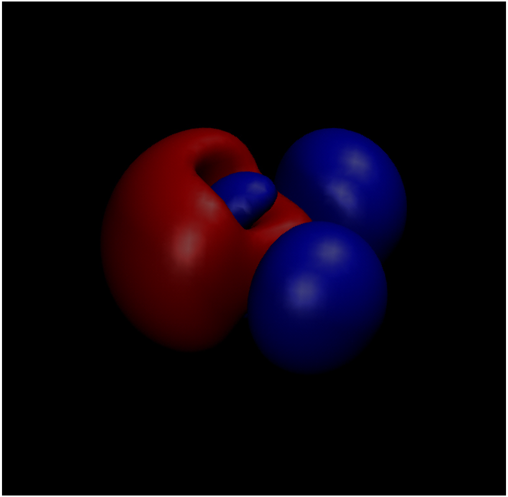
Electrostatic potential isosurfaces at ±0.1 e/Å^3

Change of electron density under field



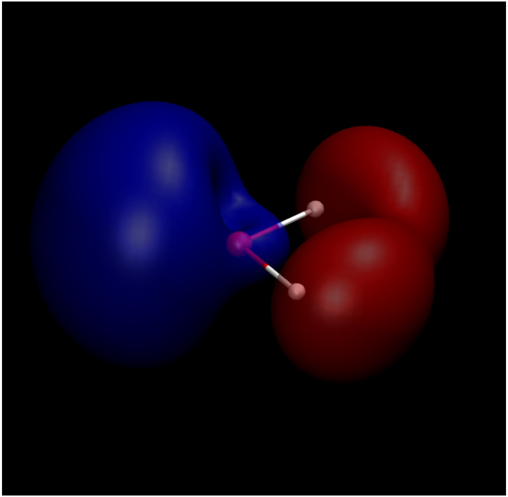
F_z=0.028 a.u.; electron density isosurface at ±0.05 e/Å^3

Change of electron density under field



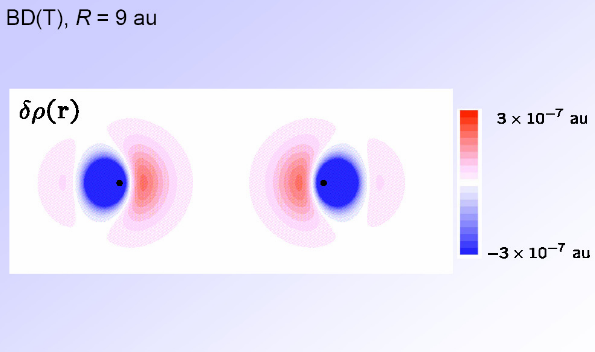
$F_z = 0.028$ a.u.; deformation density isosurfaces at ±0.001 e/Å^3

Change of electrostatic potential under field



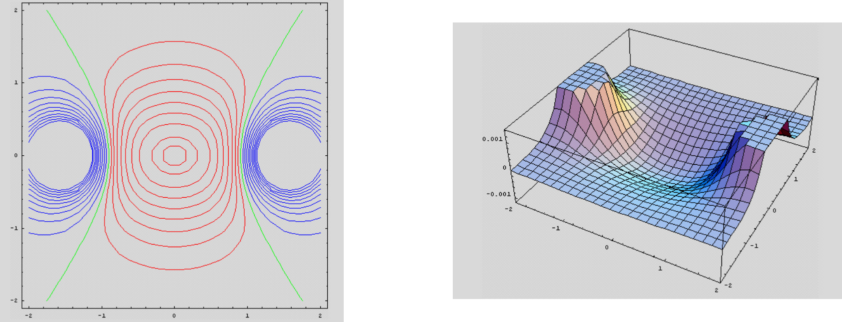
$F_z = 0.028$ a.u.; potential difference isosurface at ± 0.01 e/Å^3

Long-range correlation effect on the density



He dimer: attractive London dispersion forces are due to tiny charge density rearrangements, predicted by Feynmann in 1939.

Short range antisymmetry effect on the density



He dimer deformation density $\delta\varrho(\boldsymbol{r}) = \varrho_{\mathrm{He}_2}(\boldsymbol{r}) - \varrho_{\mathrm{He}_a}(\boldsymbol{r}) - \varrho_{\mathrm{He}_b}(\boldsymbol{r})$

At short distances electrons density is depleted between the two closed shell atom consequence of the Pauli principle.

Main contributions to the interaction energy

Contribution	Pairwise Additive?	Sign	Comment
Long-range ($U \sim R^{-n}$)			
Electrostatic	Yes	$\pm$	Strong orientation dependence
Induction	No	$-$	Strongly non-additive
Dispersion	approx.	$-$	Always present
Short-range ($U \sim \mathrm{e}^{-\alpha R}$)			
Penetration	Yes	$-$	Can be repulsive at very short range
Overlap repulsion	No	$+$	Dominates at very short range
Damping	approx.	$+$	Antisym. effect on induction and disp.
Charge transfer	No	$-$	Donor-acceptor interaction

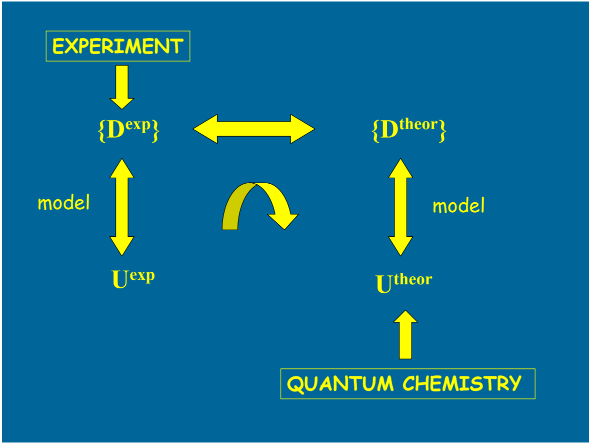
Part II

Experimental sources

Experimental sources of intermolecular forces

- crystal structure analysis
- thermodynamical properties: heat of vaporization (Trouton's rule)
- crystal structures
    - ionic crystals
    - rare gas solids
- physico-chemical properties: bulk modulus, phonon spectrum, etc.
- virial coefficients of real gases
- viscosity, thermal conductivity (collision integrals)
- spectroscopy: VRT (vibration-rotation tunneling)

Theory vs. experiments



EXPERIMENT

$\{D^{exp}\}$

$\{D^{theor}\}$

model

model

U^{exp}

U^{theor}

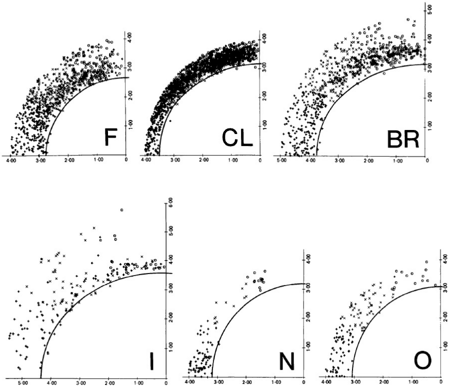
QUANTUM CHEMISTRY

Crystal structure analysis

- van de Waals radii (Pauling, Bondi)
- anisotropy of the interactions
- properties of the hydrogen bond

Interacting atoms are often aspheric

Pauling and Bondi compiled nonbonded interatomic distances from crystal structures: tables of spherical van der Waals radii.

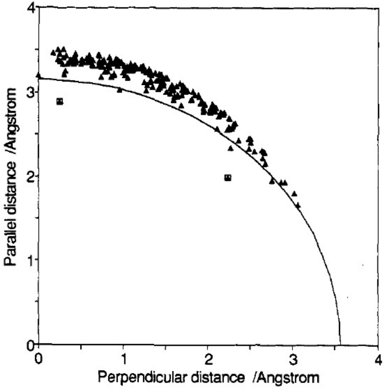


Atom	Bondi	r_{max}	r_{min}
F	1.47	1.38	1.30
Cl	1.76	1.78	1.58
Br	1.85	1.84	1.54
I	1.98	2.13	1.76
N	1.70	1.60	1.60
O	1.50	1.54	1.54
S	1.74	2.03	1.60
Se	2.00	2.15	1.70

Bondi's vdW radii and major and minor anisotropic radii proposed by Nyburg and Faerman.

Nyburg and Faerman, Acta Cryst. B. **41** (1985) 274

Anisotropic Cl$\cdots$Cl contacts



S.L. Price et al. , J.A.C.S. **116** (1994) 4910

Trouton's rule

- Empirical relationship between enthalpy of vaporization, ΔH_{vap} and boiling point, T_{b} at atmospheric pressure

$$\Delta H_{\text{vap}} \approx 10RT_{\text{b}} = 85\text{J K}^{-1}\text{mol}^{-1}$$

- Can be explained by the fact that the change in Gibbs free energy is zero at the boiling point, T_{b},

$$\Delta G_{\text{vap}} = 0$$

$$\Delta H_{\text{vap}} = T_{\text{b}} \Delta S_{\text{vap}}$$

- Rough estimate of the entropy change by the liquid/gas volume variation:

$$\Delta S_{\text{vap}} = R \ln \left(V_g / V_l \right) \approx R \ln 1000 \approx 7R \approx 57\text{J K}^{-1}\text{mol}^{-1}$$

- The remaining contribution of $3R$ can be attributed to liquid *structure*.

Well depths from Trouton's rule

The latent heat of evaporation can be approximated by the energy required to separate the liquid to its constituents is ε (zp energy neglected). The total energy for N molecules, each having n neighbours is

$$\Delta H_{\mathsf{vap}} \approx 10RT_{\mathsf{b}} \approx \frac{1}{2}N_A n\,\varepsilon$$

An estimation of of the well-depth, ε is given in terms of T_{b}

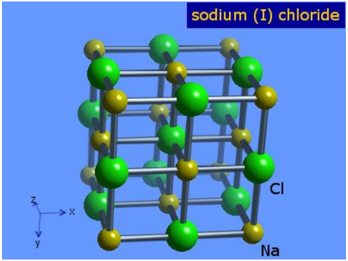
$$\varepsilon/k_B \approx 20T_{\mathsf{b}}/n$$

Table: Pair potential well-depths from Trouton's rule

	T_{b}/K	n	$(20T_{\mathsf{b}}/n)$/K	(ε/k_B)/K	ε/kJ mol^{-1}
He	4.2	12	7	11	0.09
Ar	87.0	12	145	142	1.18
Xe	166.0	12	277	281	2.34
CH_4	111.5	12	186	180-300	1.5-2.50
H_2O	373.2	4	1866	≈2400	≈20

Ionic crystals

- NaCl crystallizes in fcc lattice
- lattice parameter $a = 5.64$Å
- ions are in (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
- lattice energy $U_{\text{latt}} = -764.4$ kJ/mol



Cohesion energy is the sum of the Coulomb (Madelung) and repulsion energy:

$$U_{\text{coh}} = U_C + U_R$$

where U_C is a lattice sum of 1/r interactions, U_R is approximated by the Born-Mayer potential.

Ionic crystals – Born-Mayer potential

Born-Mayer potential:

$$U_C = Q^2 \sum_j (\pm)_j r_j^{-1} \qquad\qquad U_R = \sum_i B\mathrm{e}^{-r_i/\rho}$$

The lattice sum (Madelung energy) is conditionally convergent, so special techniques (e.g. Ewald summation) are needed to evaluate them. For a NaCl lattice, the energy can be expressed using the *Madelung constant*, $\alpha = 1.7476$,

$$U_C = -Q^2 \frac{2\alpha}{a} = -1389.9 \times \frac{2 \cdot 1.7476}{5.64} \mathrm{kJ/mol} = -861.3 \mathrm{kJ/mol}$$

The repulsion energy is short-range, therefore it is sufficient to sum over the 6 first-neighbours:

$$U_R = \sum_i B\mathrm{e}^{-r_i/\rho} = 6B\mathrm{e}^{-a/2\rho}$$

Ionic crystals – parameters of the BM potential

The Born-Mayer potential has two unknown parameters, B and ρ.

- Repulsion energy

$$U_R = U_{\mathrm{coh}}^{\mathrm{exp}} - U_C = -764.4 + 861.3 = 96.9\mathrm{kJ/mol}$$

- Condition of equilibrium in the minimum of the lattice energy

$$\frac{\partial U_{\mathrm{coh}}}{\partial a} = -Q^2 \frac{2\alpha}{a^2} - \frac{6B}{2\rho} \mathrm{e}^{-a/2\rho} = -\frac{U_c}{a} - \frac{U_R}{2\rho} = 0$$

  Effective "ion radius" is obtained from the repulsion and Madelung energies

$$\rho = -\frac{1}{2} \frac{U_R}{U_C} \cdot a = 0.3164$$

- The B parameter of the Born-Mayer potential is

$$B = \frac{U_R}{6\mathrm{e}^{-a/2\rho}} = 1.168 \cdot 10^5 \mathrm{kJ/mol}$$

Ionic crystals – check the potential

The quality of this potential can be checked by calculating the *bulk modulus*

$$K = V\frac{\partial^2 U_{\text{coh}}}{\partial V^2}$$

where the volume of 1 mole NaCl is $V = N_A a^3/4$. The volume derivative can be calculated as lattice-parameter derivative:

$$\frac{\partial}{\partial V} = \left(\frac{\partial V}{\partial a}\right)^{-1}\frac{\partial}{\partial a}$$

Bulk modulus for the NaCl structure

$$\begin{aligned} K &= \frac{N_A a^3}{4}\left(\frac{4}{3N_A a^2}\right)^2\frac{\partial^2 U_{\text{coh}}}{\partial a^2} \\ &= \frac{4}{9N_A a}\frac{\partial^2 U_{\text{coh}}}{\partial a^2} \end{aligned}$$

Second derivative of the cohesion energy

$$\begin{aligned} \frac{\partial^2 U_{\text{coh}}}{\partial a^2} &= -\frac{\partial}{\partial a}\left(\frac{Q^2 2\alpha}{a^2}\right) - \frac{1}{2\rho}\frac{\partial U_R}{\partial a} \\ &= \frac{2}{a^2}U_C + \frac{1}{4\rho^2}U_R \end{aligned}$$

Theoretical bulk modulus

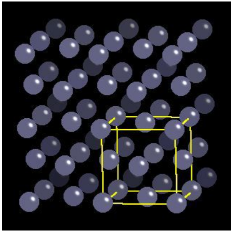
$$\begin{aligned} K &= \frac{4}{9N_A a}\left(\frac{2U_C}{a^2} + \frac{U_R}{4\rho^2}\right) \\ &= 14.8016 \text{ kJ/mol/Å}^3 \end{aligned}$$

Conversion to gigapascal
1 kJ/mol/Å^3 = 1.667 GPa, i.e.

$$\begin{aligned} K^{\text{theor}} &= 24.57 \text{ GPa} \\ K^{\text{exp}} &= 24 \text{ GPa} \end{aligned}$$

Rare gas crystal

- Ar crystallizes in fcc lattice
- lattice parameter $a = 5.3109$Å
- ions are in (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
- lattice energy $U_{\text{latt}} = -8.4732$ kJ/mol (after zpe correction)



Cohesion energy is the sum of pair potentials

$$U_{\text{coh}} = \frac{N}{2} \sum_{ij} U_{LJ}(r_{ij})$$

where $N = 4$, number of atoms in the unit cell, and U_{LJ} is the Lennard-Jones potential:

$$U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

Rare gas crystals - lattice sums

Lattice sums can be calculated from the number of neighbours at the multiples of the nearest-neighbour distance $d = a/\sqrt{2}$:

shell	1	2	3	4	5	i
r	d	$\sqrt{2}d$	$\sqrt{3}d$	$2d$	$\sqrt{5}d$	$f_i \cdot d$
m_i	12	6	24	12	24	m_i

General form of the lattice sums

$$\sum_i^{\text{shells}} m_i \left(\frac{\sigma}{f_i d}\right)^n = \sum_i^{\text{shells}} m_i f_i^{-n} \left(\frac{\sigma}{d}\right)^n = p_n \left(\frac{\sigma}{d}\right)^n$$

Lattice sum for the 6- and 12-potentials

i	1	5	fcc(∞)	hcp (∞)
$p_{12} = \sum_i m_i f_i^{-12}$	12	12.13114	12.13188	12.13229
$p_6 = \sum_i m_i f_i^{-6}$	12	14.01839	14.45392	14.45489

Cohesion energy of the rare-gas lattice in terms of lattice sums

$$U_{\text{coh}} = \frac{N\varepsilon}{2}\left[p_{12}\left(\frac{\sigma}{d}\right)^{12} - p_6\left(\frac{\sigma}{d}\right)^6\right]$$

Rare gas crystals - fit parameters

Stability condition

$$\frac{\partial U_{\mathrm{coh}}}{\partial d} = -12 p_{12} \left(\frac{\sigma}{d}\right)^{12} \frac{1}{d} + 6 p_6 \left(\frac{\sigma}{d}\right)^{6} \frac{1}{d} = 0$$

yields the σ parameter as a function of d, the nearest-neighbour distance

$$d = \sqrt[6]{\frac{2p_{12}}{p_6}} \cdot \sigma = 1.09026\sigma$$

Lattice constant $a = 1.54186\sigma$.
Cohesion energy can be expressed in the function of ε.

$$U_{\mathrm{coh}} = \frac{N\varepsilon}{2} \left[p_{12} \left(\frac{p_6}{2p_{12}}\right)^2 - p_6 \left(\frac{p_6}{2p_{12}}\right) \right]$$

or:

$$U_{\mathrm{coh}} = -\frac{N}{8} \frac{p_6^2}{p_{12}} \, \varepsilon = -2.1525 \, N \, \varepsilon$$

Rare gas crystals - structure

$$a = 1.54186\,\sigma$$

$$U_{\text{coh}} = -2.1525\,N\,\varepsilon$$

Lattice parameters (in Å) and cohesion energies (in μH) from "monomer" Lennard-Jones potentials:

	r_e	D_e	σ	a_{calc}	U_{calc}	a_{exp}	U_{exp}
Ne	3.091	133.8	2.75	4.25	1152	4.35	1002
Ar	3.757	453.5	3.35	5.16	3904	5.23	3268
Kr	4.008	637.1	3.57	5.51	5485	5.61	4502
Xe	4.363	893.9	3.89	5.99	7696	6.10	6239

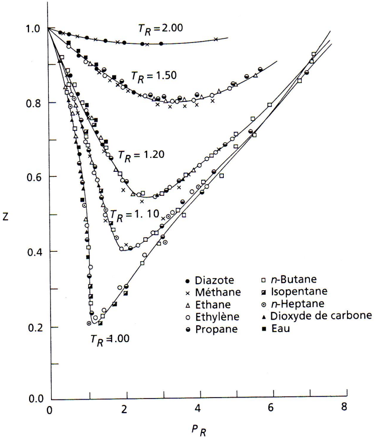
The cohesion energy error is increasing: large cooperative effects.

Deviations from the ideal gas

Equation of state for an ideal gas (noninteracting point masses)

$$P\overline{V} = RT$$

where P is the pressure, $\overline{V}$ is molar volume, and $R = 8.31 J\,K^{-1}\,\text{mol}^{-1}$ is the gas constant.



The standard molar volume $\overline{V}_s$ (1 atm, T=273.15 K^o) of real gases are different from the ideal value (22414 cm^3).

He: 22377 cm^3

CH_4: 22396 cm^3

NH_3: 22094 cm^3

Considerable deviations can be observed in the behaviour of the compression factor, $z = \frac{P\overline{V}}{RT}$.

van der Waals equation of state

The van der Waals equation of state accounts for these deviations by introducing two empirical constants, a and b

$$\left(P + \frac{a}{\overline{V}^2}\right)(\overline{V} - b) = RT$$

- excluded volume in a binary collision $\frac{4}{3}\pi\sigma^3$

$$b = \frac{2}{3}\pi N_A \sigma^3$$

- reduction of pressure due to intermolecular attraction: the number of binary interactions is proportional to the square of the density, $(a/\overline{V}^2)$

van der Waals equation of state

Rearrange as

$$\frac{P\overline{V}}{RT} = \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}}$$

expanded in the reciprocal volume

$$\frac{P\overline{V}}{RT} = 1 + \frac{b - a/RT}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \frac{b^3}{\overline{V}^3}$$

- repulsive interactions raise the pressure
- attractive forces reduce the pressure
- at low T attraction (a), at high T or high pressure repulsion (b) dominates

the constants a and b can be obtained from critical parameters P_c, V_c and T_c, where $(\partial P/\partial V)_T$ and $\partial^2 P/\partial V^2)_T$ are both zero:

$$a = \frac{9}{8} RT_c V_c = 3P_c V_c^2 \qquad b = \frac{1}{3} V_c$$

Virial equation of state

Virial equation of state – power series of $(1/V)$

$$z = \frac{PV}{RT} = 1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \frac{B_4}{V^3} + \dots$$

where the second virial coefficient depends on the pair interactions

$$B_2(T) = -2\pi N \int_0^\infty \left(\mathrm{e}^{-u(R)/kT} - 1\right) R^2 dR$$

The pair potential $u(R)$ can be obtained by "inversion": mapping measured $B_2(T)$ points to $u(R)$ – without *a priori* assumptions.

Equations of state - generalities

The total energy is a function of x_α external parameters

$$E = E(x_1, x_2, \dots x_n)$$

Define generalized forces corresponding to external parameters

$$\overline{X}_\alpha = -\frac{\overline{\partial E}}{\partial x_\alpha}$$

In statistical mechanics the equations of state describe the relationship of the external parameters, the generalized forces and the temperature:

$$\overline{X}_\alpha = kT \frac{\partial \ln Z}{\partial x_\alpha}$$

where Z is the partition function. For the special case of volume $(x_\alpha = V)$ and pressure $(\overline{X}_\alpha = P)$

$$\overline{P} = kT \frac{\partial \ln Z}{\partial V}$$

The semi-classical partition function

$$Z = \frac{1}{N! h^{3N}} \iint \ldots \int \mathrm{e}^{-(K+U)/kT}\, d^3\vec{p}_1 d^3\vec{p}_2 \ldots d^3\vec{p}_N d^3\vec{r}_1 d^3\vec{r}_2 \ldots d^3\vec{r}_N$$

is a product of two terms, depending on the kinetic and the potential energy, respectively:

$$K = \frac{1}{2m} \sum p_j^2 \qquad\qquad U = \frac{1}{2} \sum_{jk} u_{jk}$$

$$Z = \frac{1}{N! h^{3N}} \underbrace{\iint \ldots \int \mathrm{e}^{-K/kT}\, d^3\vec{p}_1 d^3\vec{p}_2 \ldots d^3\vec{p}_N}_{(2\pi m k T)^{3N/2}} \underbrace{\iint \ldots \int \mathrm{e}^{-U/kT}\, d^3\vec{r}_1 d^3\vec{r}_2 \ldots d^3\vec{r}_N}_{Z_U}$$

Partition function

$$Z = \frac{1}{N!} \left(\frac{2\pi m k T}{h^2} \right)^{3N/2} \cdot Z_U$$

Equations of state - ideal gas

For an ideal gas $u_{ij} \to 0$ (or if T is high $kT \to \infty$)

$$\mathrm{e}^{-U/kT} \to 1 \qquad\qquad Z_U = V^N$$

and the corresponding partition function

$$\ln Z_{id} = \ln \frac{1}{N!} + N \left[\ln V + \frac{3}{2} \ln kT + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) \right]$$

Equation of state for an ideal gas

$$P = kT \frac{\partial \ln Z_{id}}{\partial V} = \frac{NkT}{V}$$

or

$$PV = NkT$$

Equations of state - real gas

For a real gas with low number density ($n = N/V$ small) an approximate expression can be obtained for the configurational partition function.
Take the *average* potential energy with $\beta = 1/kT$, which satisfies the following relationship

$$\overline{U} = \frac{\iiint U \mathrm{e}^{-\beta U}\, d^3\vec{r}_1 d^3\vec{r}_2 \ldots d^3\vec{r}_N}{\iiint \mathrm{e}^{-\beta U}\, d^3\vec{r}_1 d^3\vec{r}_2 \ldots d^3\vec{r}_N} = -\frac{\partial}{\partial \beta} \ln Z_U$$

The logarithm of the partition function is

$$\ln Z_U(\beta) = N \ln V - \int_0^\beta \overline{U}(\beta')d\beta'$$

In a low-density system the $\overline{U}$, the average potential energy of $1/2N(N-1)$ molecule pairs is equal $N^2/2$-fold of the average potential energy of an arbitrary pair of molecules:

$$\overline{U} = \frac{1}{2}N(N-1)\,\overline{u} \approx \frac{1}{2}N^2\overline{u}$$

The average potential energy of a *pair of molecules*

$$\overline{u} = \frac{\int u(R)\mathrm{e}^{-\beta u(R)}\, d^3\vec{R}}{\int \mathrm{e}^{-\beta u(R)}\, d^3\vec{R}} = -\frac{\partial}{\partial\beta} \ln \int \mathrm{e}^{-\beta u(R)} d^3\vec{R}$$

Since $u(R) = 0$ almost everywhere, excepted the small distances, it is worthwhile to transform the integral as

$$\int \mathrm{e}^{-\beta u(R)}\, d^3\vec{R} = \int \left[1 + \left(\mathrm{e}^{-\beta u(R)} - 1\right)\right]\, d^3\vec{R} = V + I(\beta)$$

The quantity in parentheses is the Mayer-function $f(R) = \mathrm{e}^{-\beta u(R)} - 1$, and its integral over the intermolecular separation, R is

$$I(\beta) = 4\pi \int_0^\infty \left(\mathrm{e}^{-\beta u(R)} - 1\right) R^2 dR$$

Calculate the average potential energy for a pair of molecules

$$\overline{u} = \frac{\partial}{\partial\beta} \ln\left[V + I(\beta)\right] = \frac{\partial}{\partial\beta}\left[\ln V + \ln\left(1 + \frac{I(\beta)}{V}\right)\right] \approx -\frac{1}{V}\cdot\frac{\partial I(\beta)}{\partial\beta}$$

which is substituted in the expression of the configurational partition function

$$\ln Z_U(\beta) = N\ln V + \frac{1}{2}\frac{N^2}{V}\left[I(0) - I(\beta)\right]$$

The equation of state is

$$\frac{P}{kT} = \frac{\partial \ln Z}{\partial V} = \frac{\partial \ln Z}{\partial V_U} = \frac{N}{V} - \frac{1}{2}\frac{N^2}{V^2}I(\beta)$$

or

$$\frac{PV}{RT} = \frac{PV}{NkT} = 1 - \frac{4\pi}{2}\frac{N}{V}\int_0^\infty \left(e^{-\beta u(R)} - 1\right)R^2 dR$$

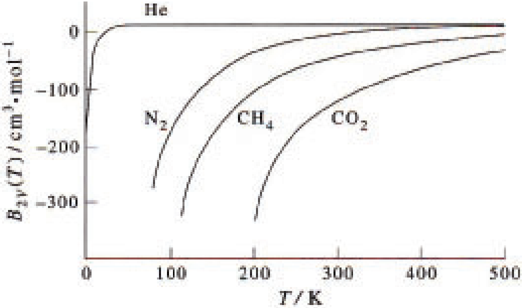
This is the first term of the virial equation of state:

$$z = \frac{PV}{RT} = 1 + \sum_{n=1}^{\infty} \frac{B_{n+1}}{V^n}$$

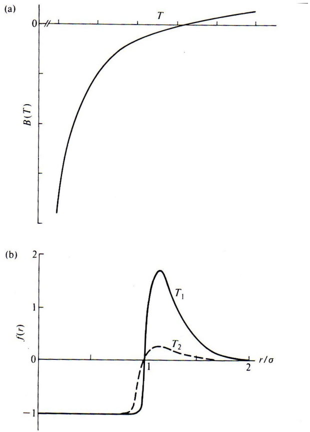
and the virial coefficient is

$$B_2(T) = -2\pi N \int_0^{\infty} \left(\mathrm{e}^{-u(R)/kT} - 1 \right) R^2 dR$$

Temperature dependence of the virial coefficient



Temperature dependence of the virial coefficient



$T\backslash R$	small $(u > 0)$	large $(u < 0)$	
low $kT < u_0$	$+$	− −	$B_2 < 0$
high $kT > u_0$	$+$	−	$B_2 > 0$

$$f(R) = \mathrm{e}^{-u(R)/kT} - 1$$

Third virial coefficients

$$B_3(T) = B_3^{\mathsf{add}} + \Delta B_3$$

For a strictly additive potential

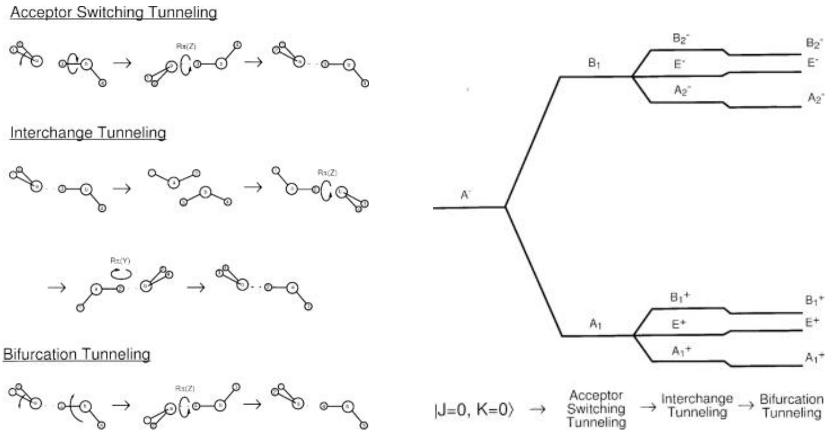
$$B_3^{\mathsf{add}} = -\frac{N}{3} 8\pi^3 \iiint f_{12}\, f_{13}\, f_{23}\, r_{12}\, r_{13}\, r_{23}\, dr_{12}\, dr_{13}\, dr_{23}$$

The non-additivity correction depends on the 3-body potential ΔU_3

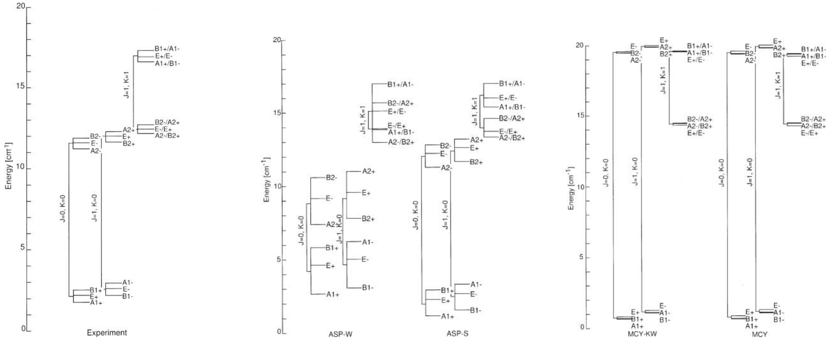
$$\Delta B_3 = \frac{N}{3} 8\pi^3 \iiint \left(\mathrm{e}^{-\Delta U_3/kT} - 1\right) \mathrm{e}^{-U_2/kT} r_{12}\, r_{13}\, r_{23}\, dr_{12}\, dr_{13}\, dr_{23}$$

For rare gases ΔB_3 is up to 50% of the third virial coefficient!

VRT spectroscopy



Calculated splitting due to tunneling is very sensitive to the height and shape of the barrier – stringent test of the PES.



Experimental vs. calculated VRT splittings with different water-water potentials. None of the 14 potentials was found to be fully satisfactory.

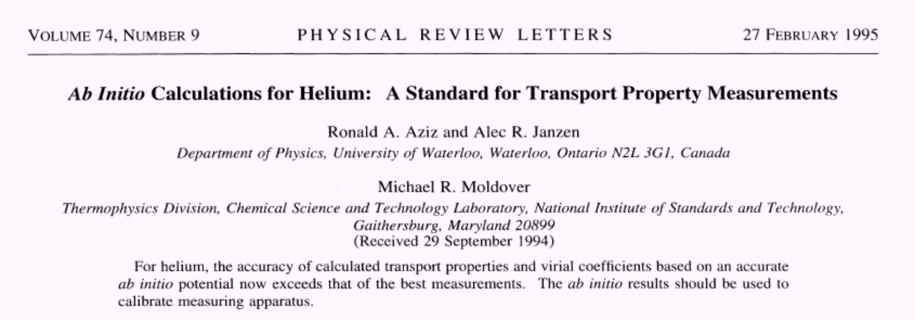
Fellers, Braly, Saykally, Leforestier, *J. Chem. Phys.* **110** (1999) 6306

Further experimental techniques

- transport properties of gases: thermal conductivity, diffusion coefficient, viscosity
- lattice vibrations (phonon dispersion)
- liquid structure: atom-atom pair distribution functions from X-ray and N scattering, diffusion coefficient (velocity autocorrelation function)
- rotational fine structure of vibrational spectra
- molecular beam experiments: scattering cross sections
- etc....

Further reading: Rigby, Smith, Wakeham, Maitland: The forces between molecules, Clarendon Press, Oxford (1986).

Match theory vs. experiment: advantage theory...



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Ab Initio Calculations for Helium: A Standard for Transport Property Measurements

Ronald A. Aziz and Alec R. Janzen
Department of Physics, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Michael R. Moldover
Thermophysics Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899
(Received 29 September 1994)

For helium, the accuracy of calculated transport properties and virial coefficients based on an accurate *ab initio* potential now exceeds that of the best measurements. The *ab initio* results should be used to calibrate measuring apparatus.

Part III

Long range electrostatic interaction

Poisson's equation

Force between two point charges

$$\boldsymbol{F} = \frac{q\,q'}{|\boldsymbol{r}-\boldsymbol{r}'|^3}(\boldsymbol{r}-\boldsymbol{r}')$$

and the electric field is the force acting on a unit charge in interaction with q' placed at the origin:

$$\boldsymbol{E}(\boldsymbol{r}) = \frac{q'}{|\boldsymbol{r}|^3}\boldsymbol{r}$$

Using the superposition law, the electric field of a continuous charge distribution

$$\boldsymbol{E}(\boldsymbol{r}) = \int d\boldsymbol{r}'\,\frac{\rho(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|^3}\,(\boldsymbol{r}-\boldsymbol{r}')$$

Take the divergence of both sides and use

$$\boldsymbol{\nabla}\cdot\frac{(\boldsymbol{r}-\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|^3} = 4\pi\,\delta(\boldsymbol{r}-\boldsymbol{r}')$$

therefore

$$\begin{aligned}\boldsymbol{\nabla}\cdot\boldsymbol{E}(\boldsymbol{r}) &= 4\pi\int d\boldsymbol{r}'\delta(\boldsymbol{r}-\boldsymbol{r}')\rho(\boldsymbol{r}')\\ &= 4\pi\,\rho(\boldsymbol{r})\end{aligned}$$

Since the field is the negative gradient of the potential:

$$\boldsymbol{E}(\boldsymbol{r}) = -\boldsymbol{\nabla}\cdot V(\boldsymbol{r})$$

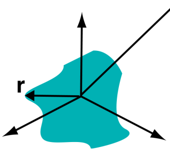
one gets Poisson's equation

$$\boldsymbol{\nabla}^2 V(\boldsymbol{r}) = -4\pi\,\rho(\boldsymbol{r})$$

The electrostatic potential is

$$V(\boldsymbol{r}) = \int d\boldsymbol{r}'\,\frac{\rho(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

Taylor expansion of the electrostatic potential



Potential $V(\boldsymbol{R})$ of the charge distribution $\varrho(\boldsymbol{r})$

$$V(\boldsymbol{R}) = \int d\boldsymbol{r}\, \frac{\varrho(\boldsymbol{r})}{|\boldsymbol{R}-\boldsymbol{r}|} = \int d\boldsymbol{r}\, T(\boldsymbol{R}-\boldsymbol{r})\, \varrho(\boldsymbol{r})$$

can be expanded in Taylor series around $\boldsymbol{r} = 0$ ($|\boldsymbol{r}| < |\boldsymbol{R}|$).

Taylor expansion in Cartesian coordinates of the Coulomb interaction function

$$T(\boldsymbol{R}-\boldsymbol{r}) = \frac{1}{R} - \frac{1}{1!}\sum_{\alpha} r_\alpha \nabla_\alpha\left(\frac{1}{R}\right) + \frac{1}{2!}\sum_{\alpha}\sum_{\beta} r_\alpha r_\beta \nabla_\alpha \nabla_\beta\left(\frac{1}{R}\right) - \frac{1}{3!}\sum_{\alpha}\sum_{\beta}\sum_{\gamma} r_\alpha r_\beta r_\gamma \nabla_\alpha \nabla_\beta \nabla_\gamma\left(\frac{1}{R}\right) + \dots$$

Attention to alternating signs!

Expanded electrostatic potential

Taylor expansion in the electrostatic potential expression

$$V(\boldsymbol{R}) = T(\boldsymbol{R}) \int d\boldsymbol{r} \varrho(\boldsymbol{r}) - T_\alpha(\boldsymbol{R}) \int d\boldsymbol{r} r_\alpha \varrho(\boldsymbol{r}) + \frac{1}{2!} \sum_\alpha \sum_\beta T_{\alpha\beta}(\boldsymbol{R}) \int d\boldsymbol{r} r_\alpha r_\beta \varrho(\boldsymbol{r})$$

$$- \frac{1}{3!} \sum_\alpha \sum_\beta \sum_\gamma T_{\alpha\beta\gamma}(\boldsymbol{R}) \int d\boldsymbol{r} r_\alpha r_\beta r_\gamma \varrho(\boldsymbol{r}) + \dots$$

Multipole moments

$$q = \int d\boldsymbol{r} \varrho(\boldsymbol{r})$$

$$m_\alpha = \int d\boldsymbol{r} r_\alpha \varrho(\boldsymbol{r})$$

$$Q_{\alpha\beta} = \int d\boldsymbol{r} r_\alpha r_\beta \varrho(\boldsymbol{r})$$

$$O_{\alpha\beta\gamma} = \int d\boldsymbol{r} r_\alpha r_\beta r_\gamma \varrho(\boldsymbol{r})$$

$$\xi_{\alpha\beta\dots\nu} = \int d\boldsymbol{r} r^{(n)}_{\alpha\beta\dots\nu} \varrho(\boldsymbol{r})$$

Cartesian interaction tensors

$$T(\boldsymbol{R}) = \frac{1}{R}$$

$$T_\alpha(\boldsymbol{R}) = \nabla_\alpha \left(\frac{1}{R}\right)$$

$$T_{\alpha\beta}(\boldsymbol{R}) = \nabla_\alpha \nabla_\beta \left(\frac{1}{R}\right)$$

$$T_{\alpha\beta\gamma}(\boldsymbol{R}) = \nabla_\alpha \nabla_\beta \nabla_\gamma \left(\frac{1}{R}\right)$$

$$T_{\alpha\beta\dots\nu}(\boldsymbol{R}) = \nabla_\alpha \nabla_\beta \dots \nabla_\nu \left(\frac{1}{R}\right)$$

Tensor notation

- generalization of the notion of scalar, vector and matrix
- its *rank* is the number of indices
  - rank 0: scalar e.g. charge q
  - rank 1: vector e.g. dipole $\mu_\alpha = \{\mu_x, \mu_y, \mu_z\}$
  - rank 2: matrix e.g. quadrupole $\Theta_{\alpha\beta}$
  - rank 3: e.g octupole $\Omega_{\alpha\beta\gamma}$
- its *dimension* is the range of the indices (e.g. 3-dimensional)
- Kronecker delta is defined as

$$\delta_{\alpha\beta} = \begin{cases} 1, & \text{if } \alpha = \beta; \\ 0, & \text{if } \alpha \neq \beta. \end{cases}$$

- Einstein summation convention over repeated indices:

$$\begin{aligned} A_{\alpha\alpha} &= A_{xx} + A_{yy} + A_{zz} = \mathrm{Tr}\boldsymbol{A} && \text{trace} \\ \mu_\alpha V_\alpha &= \mu_x V_x + \mu_y V_y + \mu_z V_z && \text{contraction} \\ \delta_{\alpha\alpha} &= \delta_{xx} + \delta_{yy} + \delta_{zz} = 3 && \text{(not equal to 1!)} \end{aligned}$$

Electrostatic potential, field, field gradient...

Using the tensor notation the potential is simply

$$V(\boldsymbol{R}) = qT(\boldsymbol{R}) - m_\alpha T_\alpha(\boldsymbol{R}) + \frac{1}{2!}Q_{\alpha\beta}T_{\alpha\beta}(\boldsymbol{R}) - \ldots + \frac{(-)^n}{n!}\xi_{\alpha\beta\ldots\nu}T_{\alpha\beta\ldots\nu}(\boldsymbol{R})$$

The electric field is the negative gradient of the potential:

$$F_\alpha(\boldsymbol{R}) = -\nabla_\alpha V(\boldsymbol{R})$$

Since $\nabla_\alpha T_{\beta\gamma\ldots\nu}(\boldsymbol{R}) = T_{\alpha\beta\gamma\ldots\nu}(\boldsymbol{R})$ – the rank of interaction tensor is increased,

$$F_\gamma(\boldsymbol{R}) = -qT_\gamma(\boldsymbol{R}) + m_\alpha T_{\alpha\gamma}(\boldsymbol{R}) - \frac{1}{2!}Q_{\alpha\beta}T_{\alpha\beta\gamma}(\boldsymbol{R}) + \ldots$$

It is "easy" to obtain higher derivatives: just add another suffix to the interaction tensors. Field gradient:

$$F_{\gamma\epsilon}(\boldsymbol{R}) = -qT_{\gamma\epsilon}(\boldsymbol{R}) + m_\alpha T_{\alpha\gamma\epsilon}(\boldsymbol{R}) - \frac{1}{2!}Q_{\alpha\beta}T_{\alpha\beta\gamma\epsilon}(\boldsymbol{R}) + \ldots$$

Let us look at in more details the expansion of the electrostatic potential

$$V(\boldsymbol{R}) = \sum_i \frac{q_i}{|\boldsymbol{R} - \boldsymbol{r}_i|}$$

Expand in Taylor series as

$$V(\boldsymbol{R}) = \sum_i q_i$$
$$\times \left\{ \frac{1}{R} + r_{i\alpha} \left(\frac{\partial}{\partial r_{i\alpha}} \frac{1}{|\boldsymbol{R} - \boldsymbol{r}_i|} \right)_{\boldsymbol{r}_{i\alpha}=0} + \frac{1}{2} r_{i\alpha} r_{i\beta} \left(\frac{\partial^2}{\partial r_{i\alpha} \partial r_{i\beta}} \frac{1}{|\boldsymbol{R} - \boldsymbol{r}_i|} \right)_{\boldsymbol{r}_{i\alpha}=0} + \ldots \right\}$$

Change derivative w.r.t. $r_{i\alpha}$ to R_α (change of sign!):

$$V(\boldsymbol{R}) = \sum_i q_i$$
$$\times \left\{ \frac{1}{R} + r_{i\alpha} \left(-\frac{\partial}{\partial R_\alpha} \frac{1}{|\boldsymbol{R} - \boldsymbol{r}_i|} \right)_{\boldsymbol{r}_{i\alpha}=0} + \frac{1}{2} r_{i\alpha} r_{i\beta} \left(\frac{\partial^2}{\partial R_\alpha \partial R_\beta} \frac{1}{|\boldsymbol{R} - \boldsymbol{r}_i|} \right)_{\boldsymbol{r}_{i\alpha}=0} + \ldots \right\}$$

Set $\boldsymbol{r}_{i\alpha} = 0$

$$V(\boldsymbol{R}) = \sum_i q_i \left\{ \frac{1}{R} - r_{i\alpha} \nabla_\alpha \frac{1}{R} + \frac{1}{2} r_{i\alpha} r_{i\beta} \nabla_\alpha \nabla_\beta \frac{1}{R} - \frac{1}{3!} r_{i\alpha} r_{i\beta} r_{i\gamma} \nabla_\alpha \nabla_\beta \nabla_\gamma \frac{1}{R} + \ldots \right\}$$
$$= qT - m_\alpha T_\alpha + \frac{1}{2} Q_{\alpha\beta} T_{\alpha\beta} - \frac{1}{3!} O_{\alpha\beta\gamma} T_{\alpha\beta\gamma}$$

Calculation of cartesian interaction tensors

They are defined as

$$T = \frac{1}{R} = R^{-1} = \frac{1}{\sqrt{R_x^2 + R_y^2 + R_z^2}}$$

Use the following derivation rules:

$$\nabla_\alpha R_\beta = \delta_{\alpha\beta} \qquad \nabla_\alpha R^n = n R_\alpha R^{(n-2)} \qquad \nabla_\alpha R^{-n} = -n R_\alpha R^{-(n+2)}$$

- First order

$$T_\alpha(\boldsymbol{R}) = \nabla_\alpha T(\boldsymbol{R}) = -R_\alpha R^{-3}$$

- Second order

$$\begin{aligned} T_{\alpha\beta}(\boldsymbol{R}) &= \nabla_\alpha \nabla_\beta T(\boldsymbol{R}) = -\nabla_\alpha R_\beta R^{-3} = -\delta_{\alpha\beta} R^{-3} + 3 R_\alpha R_\beta R^{-5} \\ &= (3 R_\alpha R_\beta - R^2 \delta_{\alpha\beta}) R^{-5} \end{aligned}$$

- Third order

$$\begin{aligned} T_{\alpha\beta\gamma}(\boldsymbol{R}) &= \nabla_\alpha \nabla_\beta \nabla_\gamma T(\boldsymbol{R}) = \delta_\alpha (3 R_\beta R_\gamma - R^2 \delta_{\beta\gamma}) R^{-5} \\ &= 3\delta_{\alpha\beta} R_\gamma R^{-5} + 3\delta_{\alpha\gamma} R_\beta R^{-5} + 3\delta_{\beta\gamma} R_\alpha R^{-5} + 3 \cdot 5 \cdot R_\alpha R_\beta R_\gamma R^{-7} \\ &= 3 \left(5 R_\alpha R_\beta R_\gamma - R^2 \left(R_\alpha \delta_{\beta\gamma} + R_\beta \delta_{\gamma\alpha} + R_\gamma \delta_{\alpha\beta} \right) \right) R^{-7} \end{aligned}$$

Properties of cartesian interaction tensors

- Symmetric w.r.t. permutation of indices – order of differentiation does not matter

$$T_{\alpha\beta\gamma} = T_{\beta\alpha\gamma} = T_{\beta\gamma\alpha} = \ldots$$

- Contraction of any pairs of indices gives zero:

$$T_{\alpha\beta\ldots\beta\ldots\nu} = 0$$

- For instance, at second order:

$$T_{\alpha\alpha} = (3R_\alpha R_\alpha - R^2\delta_{\alpha\alpha})R^{-5} = (3R^2 - R^2\,3)R^{-5} = 0$$

- $(1/R)$ satisfies the Laplace equation:

$$\nabla^2 \frac{1}{R} = \nabla_\alpha \nabla_\alpha \frac{1}{R} = 0$$

Traced Cartesian multipole moments

There are several conventions in the literature to define multipole moments.
The previously defined traced cartesian multipole moments

$$\xi^{(n)}_{\alpha\beta\ldots\nu} = \int d\boldsymbol{r}\, r^{(n)}_{\alpha\beta\ldots\nu}\varrho(\boldsymbol{r})$$

are symmetric tensors $\xi_{\alpha\beta} = \xi_{\beta\alpha}$ and their trace is nonzero

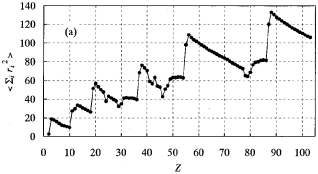
$$\xi_{\alpha\alpha} \doteq \sum_{\alpha} \xi_{\alpha\alpha} \neq 0$$

They are called *unnormalized traced Cartesian multipoles*.
The *unabridged multipoles* of Applequist differ from them by a normalization factor:

$$\mu^{(n)}_{\alpha\beta\ldots\nu} = \frac{1}{n!}\xi^{(n)}_{\alpha\beta\ldots\nu}$$

Meaning of the trace

- Spatial extent



The trace of the *second moment* of a charge distribution is used to characterize its spatial extent, $\langle \sum_i r_i^2 \rangle$ (a kind of scalar moment of inertia for the electrons).

- The full charge density can be reconstructed from traced multipoles. Consider the Fourier transform of $\varrho(\boldsymbol{r})$

$$\varrho(\boldsymbol{k}) = \int d\boldsymbol{r} \mathrm{e}^{i\boldsymbol{kr}} \varrho(\boldsymbol{r})$$

and expand the exponential

$$\varrho(\boldsymbol{k}) = \underbrace{\int d\boldsymbol{r}\, \varrho(\boldsymbol{r})}_{q} + ik_\alpha \underbrace{\int d\boldsymbol{r}\, r_\alpha\, \varrho(\boldsymbol{r})}_{m_\alpha} - \frac{1}{2!} k_\alpha k_\beta \underbrace{\int d\boldsymbol{r}\, r_\alpha r_\beta\, \varrho(\boldsymbol{r})}_{Q_{\alpha\beta}} + \ldots$$

Traceless Cartesian multipoles (Buckingham)

Potential of the second moment

$$V^{(2)}(\boldsymbol{R}) = \frac{1}{2} Q_{\alpha\beta} T_{\alpha\beta}(\boldsymbol{R})$$

Since the $T(\boldsymbol{R}) = \frac{1}{R}$ function satisfies the Laplace equation

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

$$\sum_{\alpha} \nabla_{\alpha} \nabla_{\alpha} \left(\frac{1}{R} \right) = \sum_{\alpha} T_{\alpha\alpha}(\boldsymbol{R}) = 0$$

we can add to the quadrupole potential an arbitrary quantity

$$\lambda \delta_{\alpha\beta} T_{\alpha\beta}(\boldsymbol{R})$$

without changing its value

$$V^{(2)}(\boldsymbol{R}) = \frac{1}{2} \left(Q_{\alpha\beta} + \lambda \delta_{\alpha\beta} \right) T_{\alpha\beta}(\boldsymbol{R})$$

Let us choose λ such as the trace of $Q_{\alpha\beta}$

$$\lambda = -\frac{1}{3} Q_{\alpha\alpha} = -\frac{1}{3} \sum_{\alpha} Q_{\alpha\alpha} = r^2$$

The new expression of the quadrupole potential

$$\begin{aligned} V^{(2)}(\boldsymbol{R}) &= \frac{1}{2} \cdot \frac{1}{3} \int d\boldsymbol{r} \left(3 r_\alpha r_\beta - r^2 \delta_{\alpha\beta} \right) \varrho(\boldsymbol{r}) T_{\alpha\beta}(\boldsymbol{R}) \\ &= \frac{1}{3} \Theta_{\alpha\beta} T_{\alpha\beta}(\boldsymbol{R}) \end{aligned}$$

in terms of the traceless cartesian quadrupole moment

$$\Theta_{\alpha\beta} = \frac{1}{2} \int d\boldsymbol{r} \left(3 r_\alpha r_\beta - r^2 \delta_{\alpha\beta} \right) \varrho(\boldsymbol{r})$$

Traceless (Buckingham) multipole moments

General definition

$$M^{(n)}_{\alpha\beta\ldots\nu} = \frac{(-)^n}{n!} \int d\boldsymbol{r}\, \varrho(\boldsymbol{r}) r^{2n+1} \frac{\partial^n}{\partial r_\alpha \partial \ldots r_\nu} \left(\frac{1}{r}\right)$$

Electrostatic potential

$$V(\boldsymbol{R}) = \sum_n \frac{(-)^n}{(2n-1)!!} M^{(n)}_{\alpha\beta\ldots\nu} T^{(n)}_{\alpha\beta\ldots\nu}(\boldsymbol{R})$$

where the notation $(2n-1)!!$ means

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

The traceless multipoles do not contain the full information about the $\varrho(\boldsymbol{r})$ charge distribution, since they are undetermined up to an arbitrary spherically symmetric component.
Example of quadrupole:

$$M^{(2)}_{\alpha\beta} = \frac{1}{2} \int d\boldsymbol{r}\, \varrho(\boldsymbol{r})\, r^5 \,(3 r_\alpha r_\beta - \delta_{\alpha\beta} r^2) r^{-5} = \Theta_{\alpha\beta}$$

Dipole moments

Typical values of dipole moments

	D	a.u.	10^{30} Cm
H2O	1.85	0.728	6.17
H2S	0.98	0.386	3.27
HF	1.91	0.751	6.37
HCl	1.08	0.425	3.60
HBr	0.80	0.315	2.67
HI	0.42	0.165	1.40
CO	0.12	0.047	0.40
NH3	1.47	0.578	4.90
PH3	0.58	0.228	1.93
AsH3	0.20	0.079	0.67
NaCl	9.00	3.541	30.02
H2CO	2.33	0.917	7.77
CH3CN	3.91	1.538	13.04

- Traditional unit is Debye:
  1 D=10^{-18} e.s.u.
- SI units are impractical
  1 D $= 3.33564 \times 10^{-30}$ C m
  1 C m $= 0.29979 \times 10^{30}$ D
  1 C m $= 0.11795 \times 10^{-30}$ a.u.
- Atomic units are convenient:
  1 a.u. $= 2.54177$ D
  1 a.u. $= 8.47836 \times 10^{-30}$ C m

Quantum chemical calculation of dipole moments

- Good basis set with polarization function needed
- Hartree-Fock overestimates dipole moments
- Correlated methods are recommended
- DFT methods are usually not too bad

Mol	HF/POL	MP2/POL	BLYP/POL	B3LYP/cc-pVTZ	B3LYP/POL	exp.
CO	-0.25	0.31	0.19	0.13	0.10	0.12
H_2O	1.98	1.85	1.80	1.92	1.86	1.85
H_2S	1.11	1.03	0.97	1.19	1.01	0.98
HF	1.92	1.80	1.75	1.83	1.80	1.83
HCl	1.21	1.14	1.08	1.21	1.12	1.11
NH_3	1.62	1.52	1.48	1.59	1.52	1.47
PH_3	0.71	0.62	0.59	0.53	0.62	0.58
SO_2	1.99	1.54	1.57	2.01	1.67	1.63

Quadrupole moments

- Quadrupole moment is a second-order tensor: matrix

$$\boldsymbol{\Theta} = \frac{1}{2}\sum_i q_i \begin{pmatrix} 3x_ix_i - r_i^2 & 3x_iy_i & 3x_iz_i \\ 3x_iy_i & 3y_iy_i - r_i^2 & 3y_iz_i \\ 3x_iz_i & 3y_iz_i & 3z_iz_i - r_i^2 \end{pmatrix}$$

- tensor notations:

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_i q_i\left(3r_{i\alpha}r_{i\beta} - r_i^2\delta_{\alpha\beta}\right)$$

- Symmetrical
- Traceless
- Has the dimensions of [charge]×[length]^2, so the atomic units are $ea_0^2 = 4.49 \times 10^{-40}$ C m
  Other units: Buckinghams (B) 1 B = 1 DÅ= 10^{-26} e.s.u.
  1 a.u. =1.3450×10^{-26} e.s.u. = 4.487×10^{-40} C m^2

Estimation of quadrupole moments

The traceless quadrupole moment tensor has five independent components:

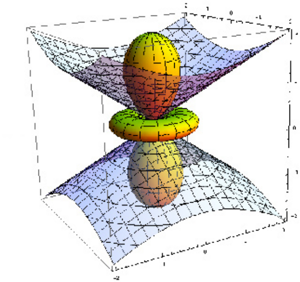
- $\Theta_{\alpha\beta} = \Theta_{\beta\alpha}$
- Trace is zero: $\Theta_{\alpha\alpha} = 0$
- Independent components: $\Theta_{zz}, \Theta_{xx} - \Theta_{yy}, \Theta_{xy}, \Theta_{yz}, \Theta_{xz}$

For systems with axial symmetry, $\Theta_{xx} - \Theta_{yy} = 0$ and we have

$$\Theta_{zz} = \frac{1}{2} \sum_i q_i(3z_i^2 - r_i^2)$$

$$= \frac{1}{2} \sum_i q_i\, r_i^2(3\frac{z_i^2}{r_i^2} - 1)$$

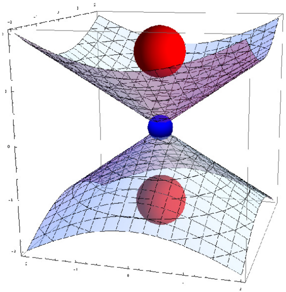
$$= \frac{1}{2} \sum_i q_i r_i^2\, (3 \cos \theta^2 - 1)$$



Angular function $1/2(3 \cos \theta^2 - 1) > 0$ near the z-axis ($\theta < 54.736^\circ$ or $\theta > 125.264^\circ$) so positive charge in these regions contribute positively, while positive charge near the xy plane ($54.736^\circ < \theta < 125.264^\circ$) contribute negatively.

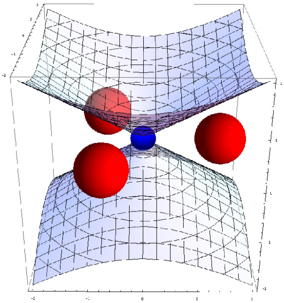
Quadrupole moments

CO_2



Negatively charged O atoms on the z axis lead to negative quadrupole moment of -3.3 a.u.

BX_3



Negatively charged X(=F,Cl) atoms in the xy plane lead to a positive quadrupole moment: BF_3 $\sim$ 2.5 a.u.; BCl_3 $\sim$ 1.5 a.u. (Theory: 3.0 a.u. and 0.8 a.u.)

Some experimental quadrupole moments

Molecule	D Å	a.u.	10^{-40}Cm^2
H_2	+0.6	+0.45	+2.1
N_2	-1.4	-1.04	-4.9
HCl	+3.8	+2.83	+12.3
CO	-2.5	-1.86	-8.2
benzene	-8.5	-6.32	-29.7
C_6F_6	+9.5	+7.06	+31.7
ethane	-0.8	-0.59	-2.7
C_3H_3	+1.6	+1.19	+5.3
NH_3	-2.3	-1.71	-7.7

Water (xz plane $-z$ axis to O)

$$\mathbf{\Theta} = \begin{pmatrix} +2.63 & 0 & 0 \\ 0 & -2.50 & 0 \\ 0 & 0 & -0.13 \end{pmatrix}$$

$H_2C{=}CH_2$ (yz plane z axis along C=C)

$$\mathbf{\Theta} = \begin{pmatrix} -3.25 & 0 & 0 \\ 0 & +1.62 & 0 \\ 0 & 0 & +1.62 \end{pmatrix}$$

Change of origin: dipole moments

- Dipole moment of a point charge distribution

$$\mu_\alpha = \sum_i q_i r_{i\alpha}$$

In a new frame obtained after a translation by a vector $\boldsymbol{R}$

$$\mu'_\alpha = \sum_i q_i (r_{i\alpha} - R_\alpha) = \sum_i q_i r_{i\alpha} - R_\alpha \sum_i q_i = \mu_\alpha - R_\alpha q_{\text{tot}}$$

- Dipole of a neutral system ($q_{\text{tot}} = 0$) is invariant to translation of origin.
- Dipole moment of a charged system can always be set zero if the origin is at the center of charge (barycenter).

Change of origin: quadrupole moment

- Change of origin; $\boldsymbol{r}' = \boldsymbol{r} - \boldsymbol{R}$

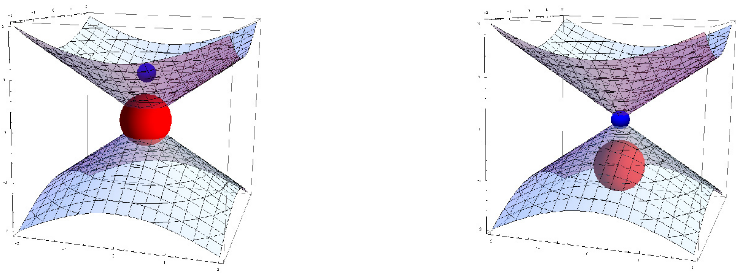
$$\begin{aligned}\Theta'_{\alpha\beta} &= \frac{1}{2}\left(3(r-R)_\alpha (r-R)_\beta - |\boldsymbol{r}-\boldsymbol{R}|^2 \delta_{\alpha\beta}\right) \\ &= \Theta_{\alpha\beta} - \frac{3}{2} R_\alpha \mu_\beta - \frac{3}{2} R_\beta \mu_\alpha + \boldsymbol{\mu}\cdot\boldsymbol{R}\delta_{\alpha\beta} + \frac{1}{2} q(3R_\alpha R_\beta - R^2 \delta_{\alpha\beta})\end{aligned}$$

- In general, it is not possible to find a *center of dipole* (5 quadrupole components to be annihilated, only 3 translational degrees of freedom)
- For molecules with 3-fold (or higher) axis of symmetry $\Theta_{zz} = -2\Theta_{xx} = -2\Theta_{yy}$ and only 1 nonzero dipole (μ_z):

$$\Theta'_{zz} = \Theta_{zz} - 2R_z\mu_z$$

thus $R_z = \frac{1}{2}\Theta_{zz}\mu_z^{-1}$ is the center of dipole

Change of origin: quadrupole moment



Quadrupole relative to the center of mass

$\Theta_{zz} > 0$

Quadrupole relative to the H atom

$\Theta_{zz} < 0$

Hydrogen fluoride molecule

Electrostatic energy

- Work to assemble a set of point charges q_i at $\boldsymbol{r}_i$ is

$$U = \frac{1}{2} \sum_i q_i \, V(\boldsymbol{r}_i)$$

- Generalized for continuous charge distributions

$$U = \frac{1}{2} \int d\boldsymbol{r} \, \varrho(\boldsymbol{r}) \, V(\boldsymbol{r})$$

- Using the expression of the potential we obtain the *total electrostatic energy*

$$U = \frac{1}{2} \iint d\boldsymbol{r} d\boldsymbol{r}' \, \frac{\varrho(\boldsymbol{r})\varrho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

- Shorthand notation

$$U = \frac{1}{2} \, \varrho_{\boldsymbol{r}} \, \varrho_{\boldsymbol{r}'} \, T_{\boldsymbol{r}\boldsymbol{r}'}$$

- The charge distribution is partitioned to two (or more) pieces:

$$\varrho_{\boldsymbol{r}} = \varrho_{\boldsymbol{r}}^A + \varrho_{\boldsymbol{r}}^B$$

- Total electrostatic energy splits on several contributions:

$$U = \frac{1}{2} \, (\varrho_{\boldsymbol{r}}^A + \varrho_{\boldsymbol{r}}^B)(\varrho_{\boldsymbol{r}'}^A + \varrho_{\boldsymbol{r}'}^B) \, T_{\boldsymbol{r}\boldsymbol{r}'}$$

- splits to a self-energy contribution

$$U_{self} = \frac{1}{2} \, \varrho_{\boldsymbol{r}}^A \, \varrho_{\boldsymbol{r}'}^A \, T_{\boldsymbol{r}\boldsymbol{r}'} + \frac{1}{2} \, \varrho_{\boldsymbol{r}}^B \, \varrho_{\boldsymbol{r}'}^B \, T_{\boldsymbol{r}\boldsymbol{r}'}$$

- and an interaction energy

$$U_{int} = \varrho_{\boldsymbol{r}}^A \, \varrho_{\boldsymbol{r}'}^B \, T_{\boldsymbol{r}\boldsymbol{r}'}$$

- We are interested in the *electrostatic interaction energy*

Electrostatic interaction energy

Electrostatic interaction energy of two charge distributions is the interaction of one charge distribution with the potential of the other.

$$\begin{aligned} U &= \iint d\boldsymbol{r} d\boldsymbol{r}' \, \frac{\varrho^A(\boldsymbol{r})\varrho^B(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \\ &= \int d\boldsymbol{r} \, \varrho^A(\boldsymbol{r}) V^B(\boldsymbol{r}) \\ &= \int d\boldsymbol{r}' \, \varrho^B(\boldsymbol{r}') V^A(\boldsymbol{r}') \end{aligned}$$

We know how to calculate the potential created by a charge distribution;
what is the energy of $\varrho(\boldsymbol{r})$ in an external potential?

Charge distribution in an external potential

Choose the origin inside the charge distribution, $\varrho(\boldsymbol{r})$ and expand the external potential in Taylor series around the origin

$$V(\boldsymbol{r}) = V(0) + r_\alpha V_\alpha(0) + \frac{1}{2!} r_\alpha r_\beta V_{\alpha\beta}(0) + \frac{1}{3!} r_\alpha r_\beta r_\gamma V_{\alpha\beta\gamma}(0) + \dots$$

From the expression of the interaction energy

$$\begin{aligned} U = \int d\boldsymbol{r}\, \varrho(\boldsymbol{r}) V(\boldsymbol{r}) &= \int d\boldsymbol{r}\, \varrho(\boldsymbol{r}) V(0) + \int d\boldsymbol{r}\, \varrho(\boldsymbol{r}) r_\alpha V_\alpha(0) \\ &+ \frac{1}{2!} \int d\boldsymbol{r}\, \varrho(\boldsymbol{r}) r_\alpha r_\beta V_{\alpha\beta}(0) + \frac{1}{3!} \int d\boldsymbol{r}\, \varrho(\boldsymbol{r}) r_\alpha r_\beta r_\gamma V_{\alpha\beta\gamma}(0) + \dots \end{aligned}$$

where one recognizes the unnormalized traced multipoles,

$$U = \xi V + \xi_\alpha V_\alpha + \frac{1}{2!} \xi_{\alpha\beta} V_{\alpha\beta} + \frac{1}{3!} \xi_{\alpha\beta\gamma} V_{\alpha\beta\gamma} + \dots$$

Interaction with external potential

By the virtue of the Laplace equation, $V_{\alpha\alpha} = 0$, the trace of $\xi_{\alpha\beta} = Q_{\alpha\beta}$, i.e. $\frac{1}{3}Q_{\alpha\alpha}$ can be subtracted from the quadrupolar energy

$$\frac{1}{2}Q_{\alpha\beta}V_{\alpha\beta} = \frac{1}{2}V_{\alpha\beta}(Q_{\alpha\beta} - \delta_{\alpha\beta}\frac{1}{3}Q_{\alpha\alpha}) = \frac{1}{3}V_{\alpha\beta}\Theta_{\alpha\beta}$$

By similar manipulations at higher orders one obtains the interaction energy in terms of traceless Buckingham multipole moments

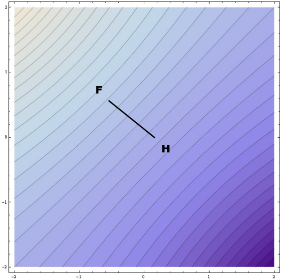
$$\begin{aligned} U = qV + \mu_\alpha V_\alpha + \frac{1}{3}\Theta_{\alpha\beta}V_{\alpha\beta} + \frac{1}{3\cdot 5}\Omega_{\alpha\beta\gamma}V_{\alpha\beta\gamma} \\ + \frac{1}{3\cdot 5\cdot 7}\Phi_{\alpha\beta\gamma\delta}V_{\alpha\beta\gamma\delta} + \frac{1}{(2n-1)!!}M^{(n)}_{\alpha\ldots\nu}V_{\alpha\ldots\nu} \end{aligned}$$

The energy is the scalar product of the field with dipole, field gradient with quadrupole and higher field gradients with the corresponding multipole tensors.

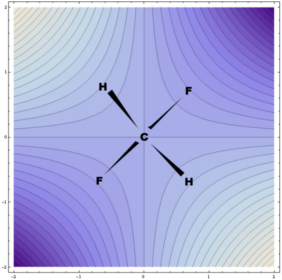
Attention: the result may depend on the choice of origin!

Multipoles in field, field gradient

Dipole/field interaction



Quadrupole/field-gradient interaction



$$U = F_x\mu_x + F_y\mu_y < 0$$

$$U = \frac{1}{3}F_{xy}\Theta_{xy} > 0$$

Multipole-multipole interaction energy

Take two sets of multipoles. Double Taylor series of the Coulomb interaction

$$\begin{aligned}\frac{1}{|\boldsymbol{\tau}-\boldsymbol{\tau}'|} &= \frac{1}{|\boldsymbol{B}+\boldsymbol{s}-\boldsymbol{A}-\boldsymbol{r}|} = \frac{1}{|\boldsymbol{R}-(\boldsymbol{r}-\boldsymbol{s})|} = \\ &= \frac{1}{R} + (r_\alpha - s_\alpha)\nabla_\alpha\left(\frac{1}{R}\right) + \frac{1}{2!}(r_\alpha - s_\alpha)(r_\beta - s_\beta)\nabla_\alpha\nabla_\beta\left(\frac{1}{R}\right) + \ldots\end{aligned}$$

which leads directly to an expression of the interaction energy of two multipole charge distributions in terms of their traced Cartesian moments

$$\begin{aligned}U(\boldsymbol{R}) = {} & q^A q^B\, T(\boldsymbol{R}) + (m^A_\alpha q^B - q^A m_\alpha)\, T_\alpha(\boldsymbol{R}) \\ & + \frac{1}{2!}(Q^A_{\alpha\beta} q^B + q^A Q^B_{\alpha\beta} - m^A_\alpha m^B_\beta - m^A_\beta m^B_\alpha)\, T_{\alpha\beta}(\boldsymbol{R}) + \ldots\end{aligned}$$

Using the traceless (Buckingham) moments

$$U(\boldsymbol{R}) = \sum_{\ell_1 \ell_2} \frac{(-)^{\ell_1}}{(2\ell_1 - 1)!!(2\ell_2 - 1)!!} M^{(\ell_1)[\mathrm{A}]}_{\alpha_1\ldots\nu_1} T^{(\ell_1+\ell_2)}_{\alpha_1\ldots\nu_1\alpha_2\ldots\nu_2}(\boldsymbol{R}) M^{(\ell_2)[\mathrm{B}]}_{\alpha_2\ldots\nu_2}$$

Multipole interactions - general remarks

Multipole-multipole interactions with traceless moments:

$$\begin{aligned}U &= q^A\,T\,q^B + \mu^A_\alpha\,T_\alpha\,q^B - q^A\,T_\alpha\,\mu_\alpha \\ &- \mu^A_\alpha\,T_{\alpha\beta}\,\mu^B_\beta + \frac{1}{3}\Theta^A_{\alpha\beta}\,T_{\alpha\beta}\,q^B + \frac{1}{3}q^A\,T_{\alpha\beta}\,\Theta^B_{\alpha\beta} \\ &+ \frac{1}{15}q^A\,T_{\alpha\beta\gamma}\,\Omega^B_{\alpha\beta\gamma} - \frac{1}{15}\Omega^A_{\alpha\beta\gamma}\,T_{\alpha\beta\gamma}\,q^B - \frac{1}{3}\mu^A_\alpha\,T_{\alpha\beta\gamma}\,\Theta^B_{\beta\gamma} + \frac{1}{3}\Theta^A_{\beta\gamma}\,T_{\alpha\beta\gamma}\,\mu^B_\alpha \\ &+ \frac{1}{9}\Theta^A_{\alpha\beta}\,T_{\alpha\beta\gamma\delta}\,\Theta^B_{\gamma\delta} + \ldots\end{aligned}$$

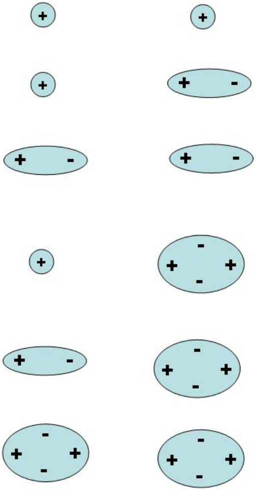
The interaction between multipoles of rank $[n_A]$ and rank $[n_B]$ is:

$$U = M^{[n_A]}M^{[n_B]} \times R^{-n_A-n_B-1} \times \text{angular factor}$$

Strongly orientation dependent

Electrostatic energy can be truncated either by the highest rank of multipole (e.g. up to Θ-Θ) or by the highest rank of the interaction tensor (e.g. up to R^{-5}, including q-Φ interactions).

Summary of multipole-multipole interactions



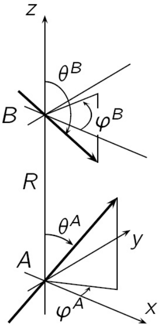
Charge - Charge	R^{-1}
Charge - Dipole	R^{-2}
Dipole - Dipole	R^{-3}
Charge - Quadrupole	R^{-3}
Dipole - Quadrupole	R^{-4}
Quadrupole - Quadrupole	R^{-5}

Dipole-dipole interaction

Dipole-dipole interaction energy

$$\begin{aligned} U_{\mu\mu} &= -\mu_\alpha^A \, T_{\alpha\beta} \, \mu_\beta^B \\ &= -\mu_\alpha^A \frac{3R_\alpha R_\beta - R^2\delta_{\alpha\beta}}{R^5} \mu_\beta^B \\ &= \frac{\boldsymbol{\mu}^A \cdot \boldsymbol{\mu}^B - 3\,(\boldsymbol{\mu}^A \cdot \hat{\boldsymbol{R}})\,(\boldsymbol{\mu}^B \cdot \hat{\boldsymbol{R}})}{R^3} \end{aligned}$$

A convenient setting of the coordinates is the z axis along the intermolecular vector from $\boldsymbol{A}$ to $\boldsymbol{B}$. The dipoles are specified by their polar angles.



$$\boldsymbol{R} = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix}, \qquad \boldsymbol{\mu}^A = \mu^A \begin{pmatrix} \sin\theta_A \cos\phi_A \\ \sin\theta_A \sin\phi_A \\ \cos\theta_A \end{pmatrix} \qquad \boldsymbol{\mu}^B = \mu^B \begin{pmatrix} \sin\theta_B \cos\phi_B \\ \sin\theta_B \sin\phi_B \\ \cos\theta_B \end{pmatrix}$$

Dipole-dipole interaction

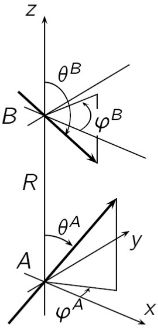
The dipole-dipole interaction energy becomes

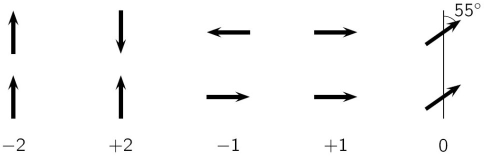
$$U_{\mu\mu} = -\frac{\mu^A \mu^B}{R^3}\left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi\right)$$

with $\phi = \phi_B - \phi_A$

The most favorable orientation at a given distance R is $\theta_A = \theta_B = 0$, where the interaction energy is $-2\mu^A\mu^B/R^3$.

Another favorable orientation is $\theta_A = \theta_B = \pi/2, \phi = \pi$, with the interaction energy $-\mu^A\mu^B/R^3$



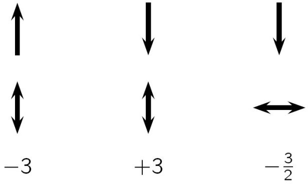


Dipole-quadrupole interaction

Dipole-quadrupole interaction energy of two linear molecules:

$$U_{\mu\Theta} = -\frac{3\mu^A\Theta^B}{2R^4}\left(2\sin\theta_A \sin\theta_B \cos\theta_B \cos\phi - \cos\theta_A(3\cos^2\theta_B - 1)\right)$$

Some of the special configurations:

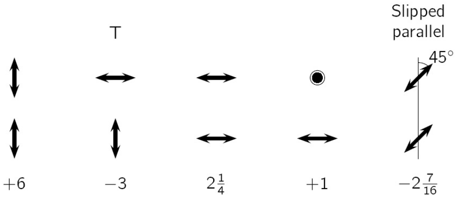


Quadrupole-quadrupole interaction

Quadrupole-quadrupole interaction energy between two symmetric top molecules. non-zero quadrupole moment components are $\Theta_{zz} = \Theta$ and $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\Theta$

$$U_{\Theta\Theta} = \frac{3\Theta^A\Theta^B}{4R^5}\big[1 - 5\cos^2\theta_A - 5\cos^2\theta_B - 15\cos^2\theta_A\cos^2\theta_B + 2(4\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi)^2\big]$$

The most favorable structures are the T-shaped and slipped parallel. Both of these occur sometimes in the same crystal structures of quadrupolar molecules (e.g. N_2, CO, benzene).



Interaction of two HX molecules

Competition of three multipolar interactions. Angular dependence for linear molecules (symmetric tops) is the following:

- dipole-dipole

$$U_{\mu\mu} = -\frac{\mu^A \mu^B}{R^3}(2\cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\varphi)$$

- dipole-quadrupole

$$U_{\mu\Theta} = \frac{3\mu^A \Theta^B}{4R^4}[\cos\theta_A(3\cos^2\theta_B - 1) - \sin\theta_A \sin 2\theta_B \cos\varphi]$$

- quadrupole-quadrupole

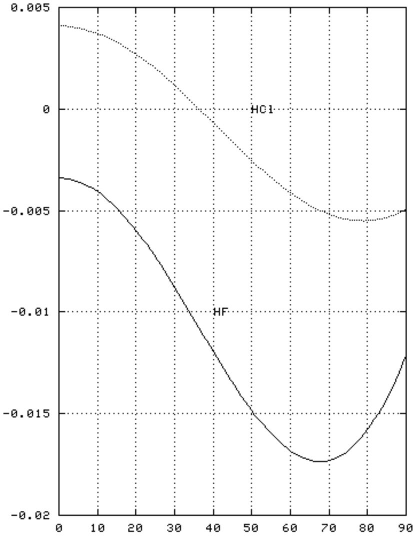
$$U_{\Theta\Theta} = \frac{\Theta^A \Theta^B}{R^5}\frac{3}{4}[1 - 5\cos^2\theta_A - 5\cos^2\theta_B - 15\cos^2\theta_A \cos^2\theta_B + 2(4\cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\varphi)^2]$$

The structure is characterized by $\theta_A \approx 0$ and $\varphi = 0$, $\mu^A = \mu^B = \mu$ and $\Theta^A = \Theta^B = \Theta$. The sum of the 4 interaction terms (two for $U_{\mu\Theta}$)

$$\begin{aligned} U = &- \frac{\mu^2}{R^3} \cdot 2\cos\theta \\ &+ \frac{\mu\Theta}{R^4} \cdot \frac{3}{2}[(3\cos^2\theta - 1) - 2\cos\theta] \\ &+ \frac{\Theta^2}{R^5} \cdot 3(3\cos^2\theta - 1) \end{aligned}$$

Introduce the parameter $\lambda = \frac{\Theta}{\mu R}$

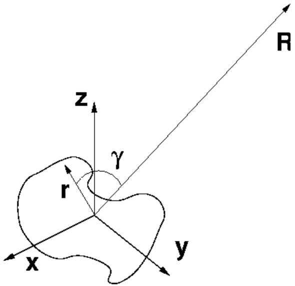
$$\begin{aligned} U &= \frac{\mu^2}{R^3}\left\{-2\cos\theta + \lambda\frac{3}{2}[(3\cos^2\theta - 1) - 2\cos\theta] + \lambda^2 3(3\cos^2\theta - 1)\right\} \\ &= \frac{\mu^2}{2R^3}\left\{3\lambda(1+2\lambda)(3\cos^2\theta - 1) - 2(2+3\lambda)\cos\theta\right\} \end{aligned}$$



Electrostatic interaction energy is plotted for the

- HF dimer
  $\mu = 0.72 e a_0$,
  $\Theta = 1.875 e a_0^2$
  $R = 5.1 a_0$;
  minimum at 68 degrees
  (exp. 60)
- HCl dimer
  $\mu = 0.433 e a_0$,
  $\Theta = 2.8 e a_0^2$
  $R = 6.8 a_0$;
  minimum at 79 degrees

Legendre expansion of the potential



The distance $|\boldsymbol{R}-\boldsymbol{r}|$ can be expressed with the help of the cosine rule

$$(\boldsymbol{R}-\boldsymbol{r})\cdot(\boldsymbol{R}-\boldsymbol{r}) = R^2 + r^2 - 2Rr\cos\gamma$$

The Coulomb interaction $T(\boldsymbol{R}-\boldsymbol{r})=1/|\boldsymbol{R}-\boldsymbol{r}|$ can be written in two alternative forms

$$T(\boldsymbol{R}-\boldsymbol{r}) = \begin{cases} \frac{1}{R}\left[1+\left(\frac{r}{R}\right)^2 - 2\left(\frac{r}{R}\right)\cos\gamma\right]^{-1/2} & \text{if} \quad r < R, \\ \\ \frac{1}{r}\left[1+\left(\frac{R}{r}\right)^2 - 2\left(\frac{R}{r}\right)\cos\gamma\right]^{-1/2} & \text{if} \quad r > R. \end{cases}$$

The expression in brackets is just the generator function of the Legendre polynomials

$$(1+t^2-2t\cos\gamma)^{-1/2}=\sum_{l}^{\infty}P_l(\cos\gamma)\,t^l \qquad |t|<1$$

The first few Legendre polynomials

$$\begin{aligned}
P_0(x)&=1\\
P_1(x)&=x\\
P_2(x)&=\frac{1}{2}(3x^2-1)\\
P_3(x)&=\frac{1}{2}(5x^3-3x)\\
P_4(x)&=\frac{1}{8}(35x^4-30x^2+3)
\end{aligned}$$

and at an arbitrary order they can be obtained from the recurrence relation

$$(2l+1)xP_l=(l+1)P_{l+1}+lP_{l-1}$$

Depending on the space domains, either the first ($r < R$), or the second ($R < r$) form of the generator function can be applied:

$$T(\boldsymbol{R}-\boldsymbol{r}) = \begin{cases} \sum_l^{\infty} \frac{r^l}{R^{l+1}} P_l(\cos\gamma) & \text{if} \quad r < R \\ \\ \sum_l^{\infty} \frac{R^l}{r^{l+1}} P_l(\cos\gamma) & \text{if} \quad r > R \end{cases}$$

The formulae for the two domains of space ($r < R, r > R$) are usually expressed in the following condensed form

$$T(\boldsymbol{R}-\boldsymbol{r}) = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\gamma)$$

The lowest-order terms explicitly for $r = |\boldsymbol{r}| \ll |\boldsymbol{R}|$

$$\frac{1}{|\boldsymbol{R}-\boldsymbol{r}|} = \frac{1}{R} + \frac{\boldsymbol{r}\cdot\boldsymbol{R}}{R^3} + \frac{3(\boldsymbol{r}\cdot\boldsymbol{R})^2 - r^2 R^2}{2R^5} + \frac{5(\boldsymbol{r}\cdot\boldsymbol{R})^3 - 3\,(\boldsymbol{r}\cdot\boldsymbol{R})\,r^2 R^2}{2R^7} + \ldots$$

where we used that $r\,R\cos\gamma = \boldsymbol{r}\cdot\boldsymbol{R}$

Exercises

- Find the 4th order term of the Legendre expansion of $1/|\boldsymbol{R} - \boldsymbol{r}|$ in the above form (i.e. using scalar products of the vectors $\boldsymbol{r}$ and $\boldsymbol{R}$).

- Derive the Legendre expansion in the above form up to 4th order making use of the series expansion

$$\frac{1}{\sqrt{1+x}} = 1 - \frac{x}{2} + \frac{3x^2}{8} - \frac{5x^3}{16} + \frac{35x^4}{128} - \ldots$$

Spherical harmonic expansion

Addition theorem of spherical harmonics

$$P_l(\cos\gamma) = \left(\frac{4\pi}{2l+1}\right)\sum_{m=-l}^{l} Y_{lm}(\omega)Y^*_{lm}(\Omega)$$

where $\omega = (\theta, \phi)$ and $\Omega = (\Theta, \Phi)$ are the angular components of the polar coordinates of $\boldsymbol{r}$ and $\boldsymbol{R}$, respectively.
The (complex) spherical harmonics for $m \geq 0$

$$Y_{lm}(\omega) = (-)^m \left(\frac{2l+1}{4\pi}\right)\left(\frac{(l-m)!}{(l+m)!}\right)^{1/2} P_{\ell m}(\cos\theta)\exp(im\phi)$$

and for $m \leq 0$

$$Y_{l\underline{m}}(\omega) = (-)^m Y^*_{lm}(\omega)$$

Here we used the associated Legendre polynomials, that are defined for $m > 0$ through the derivatives of $P_l(x)$ as

$$P_{\ell m}(x) = (1-x^2)^{m/2}\left(\frac{d}{dx}\right)^m P_\ell(x)$$

$$\begin{aligned}
P_{00}(\cos\theta) &= 1\\
P_{10}(\cos\theta) &= \cos\theta\\
P_{11}(\cos\theta) &= \sin\theta\\
P_{20}(\cos\theta) &= \frac{1}{2}(3\cos^2\theta - 1)\\
P_{21}(\cos\theta) &= 3\sin\theta\cos\theta\\
P_{22}(\cos\theta) &= 3\sin^2\theta
\end{aligned}$$

Finally, we obtain the spherical harmonics form of the interaction kernel

$$T(\boldsymbol{R}-\boldsymbol{r}) = \left(\frac{4\pi}{2l+1}\right)\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{r_<^l}{r_>^{l+1}}Y_{lm}(\omega)Y_{lm}^*(\Omega)$$

Potential outside of the charge distribution

If the charge distribution $\varrho(\boldsymbol{r})$ vanishes in the points R where we want to calculate the potential, the condition $r < R$ is always satisfied

$$V(\boldsymbol{R}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left(\frac{4\pi}{2l+1} \right) Y^{*}_{\ell m}(\Omega) R^{-\ell-1} \int d\boldsymbol{r} Y_{\ell m}(\omega) r^{\ell} \varrho(\boldsymbol{r})$$

Define the modified spherical harmonics

$$C_{\ell m}(\omega) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{\ell m}(\omega)$$

as well as the regular, $R_{\ell m}(\boldsymbol{r})$, and irregular, $I_{\ell m}(\boldsymbol{r})$, spherical harmonics

$$R_{\ell m}(\boldsymbol{r}) = r^{\ell} C_{\ell m}(\omega) \qquad I_{\ell m}(\boldsymbol{r}) = r^{-\ell-1} C_{\ell m}(\omega)$$

Using these functions, in terms of complex spherical harmonics multipole moments, $Q_{\ell m}$

$$Q_{\ell m} = \int d\boldsymbol{r}\, R_{\ell m}(\boldsymbol{r})\varrho(\boldsymbol{r})$$

the potential becomes

$$V(\boldsymbol{R}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (-)^m I_{\ell m}(\boldsymbol{R}) \int d\boldsymbol{r}\, R_{\ell \underline{m}}(\boldsymbol{r})\varrho(\boldsymbol{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (-)^m I_{\ell m}(\boldsymbol{R}) Q_{\ell \underline{m}}$$

It is more practical to use real spherical harmonics instead the complex ones

$$Q_{\ell mc} = \sqrt{\frac{1}{2}}\left[(-)^m Q_{\ell m} + Q_{\ell \underline{m}}\right]$$
$$Q_{\ell ms} = \sqrt{\frac{1}{2}}\left[(-)^m Q_{\ell m} - Q_{\ell \underline{m}}\right]$$

The absolute value of the multipole moment

$$\overline{Q}_{\ell}^{2} = \sum_{m=-\ell}^{\ell} Q_{\ell m} Q_{\ell m}^{*} = \sum_{\kappa} Q_{\ell \kappa}^{2}$$

This quantity is invariant with respect to the orientation of the frame.

Transformation of spherical and cartesian moments

Relationship of the real spherical harmonics and Cartesian multipole moments

$Q_{\ell mc/s}$	$\xi^{(n)}_{\alpha\ldots\nu}$	$M^{(n)}_{\alpha\ldots\nu}$
Q_{00}	q	q
Q_{10}	m_z	μ_z
Q_{11c}	m_x	μ_x
Q_{11s}	m_y	μ_y
Q_{20}	$\frac{1}{2}(2Q_{zz} - Q_{xx} - Q_{yy})$	Θ_{zz}
Q_{21c}	$\sqrt{3}Q_{xz}$	$\sqrt{\frac{4}{3}}\Theta_{xz}$
Q_{21s}	$\sqrt{3}Q_{yz}$	$\sqrt{\frac{4}{3}}\Theta_{yz}$
Q_{22c}	$\frac{\sqrt{3}}{2}(Q_{xx} - Q_{yy})$	$\frac{1}{\sqrt{3}}(\Theta_{xx} - \Theta_{yy})$
Q_{22s}	$\sqrt{3}Q_{xy}$	$\sqrt{\frac{4}{3}}\Theta_{xy}$

Spherical harmonics expansion of the interaction

One can obtain the bipolar expansion by applying the previously derived result for $|\boldsymbol{r}_B - \boldsymbol{r}_A| < |\boldsymbol{R}|$

$$\frac{1}{|\boldsymbol{R} + \boldsymbol{r}_B - \boldsymbol{r}_A|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} (-)^m R_{l\underline{m}}(\boldsymbol{r}_B - \boldsymbol{r}_A) I_{lm}(\boldsymbol{R})$$

According to the addition theorem of regular spherical harmonics

$$R_{l\underline{m}}(\boldsymbol{r}_B + \boldsymbol{r}_A) = \sum_{l_A l_B} \sum_{m_A m_B} \delta_{l_A+l_B,l} (-)^{l-m} \left(\frac{(2l+1)!}{(2l_A)!(2l_B)!} \right)^{1/2} \times$$
$$\times \begin{pmatrix} l_A & l_B & l \\ m_A & m_B & m \end{pmatrix} R_{l_A m_A}(\boldsymbol{r}_A) R_{l_B m_B}(\boldsymbol{r}_B)$$

where $\begin{pmatrix} l_A & l_B & l \\ m_A & m_B & m \end{pmatrix}$ a Wigner $3j$ coefficient.

Use that $R_{lm}(-\boldsymbol{r}) = (-)^l R_{lm}(\boldsymbol{r})$, and the multipole expansion of the interaction energy becomes

$$U(\boldsymbol{R}) = \sum_{l_A l_B} \sum_{m_A m_B m} (-)^{l_B} \left(\frac{(2l_A + 2l_B + 1)!}{(2l_A)!(2l_B)!} \right)^{1/2} \times \\ \times \begin{pmatrix} l_A & l_B & l_A + l_B \\ m_A & m_B & m \end{pmatrix} Q^A_{l_A m_A} Q^B_{l_B m_B} I_{l_A+l_B,m}(\boldsymbol{R})$$

The multipole moments are expressed in a global coordinate system.
Transform the multipoles to a local coordinate system

$$\tilde{Q}_{lk} = \sum_m Q_{lm} D^l_{mk}(\Omega)$$

where $\Omega = (\alpha, \beta, \gamma)$ is the rotation that takes the global axes to the local ones, and $D^l_{mk}(\Omega)$ are the elements of the (hermitian) Wigner rotation matrices.Inversely, the global multipole components can be written in terms of the local ones

$$Q_{lm} = \sum_k \tilde{Q}_{lk} D^l_{km}(\Omega^{-1}) = \sum_k \tilde{Q}_{lk} [D^l_{km}(\Omega)]^*$$

Insert the local-frame multipole moments and define a new orientation-dependent function

$$\bar{S}^{k_A k_B}_{l_A l_B j} = i^{l_A - l_B - j} \left[\begin{pmatrix} l_A & l_B & j \\ 0 & 0 & 0 \end{pmatrix} \right]^{-1} \times$$
$$\times \sum_{m_A m_B m} [D^{l_A}_{k_A m_A}(\Omega_A)]^* [D^{l_B}_{k_B m_B}(\Omega_B)]^* C_{jm}(\theta, \phi) \begin{pmatrix} l_A & l_B & l_A + l_B \\ m_A & m_B & m \end{pmatrix}$$

where θ, ϕ are the polar angles of the intermolecular vector. In terms of these functions and expanding the Wigner $3j$ symbols one obtains

$$U(\boldsymbol{R}) = \sum_{l_A l_B} \sum_{m_A m_B m} \binom{l_A + l_B}{l_A} \tilde{Q}^A_{l_A m_A} \tilde{Q}^B_{l_B m_B} \bar{S}^{m_A m_B}_{l_A l_B l_A + l_B} R^{-l_A - l_B - 1}$$

or after transformation to real components

$$U(\boldsymbol{R}) = \sum_{l_A l_B} \sum_{\kappa_A \kappa_B m} \binom{l_A + l_B}{l_A} \tilde{Q}^A_{l_A \kappa_A} \tilde{Q}^B_{l_B \kappa_B} \bar{S}^{\kappa_A \kappa_B}_{l_A l_B l_A + l_B} R^{-l_A - l_B - 1}$$

One can define the spherical analogue of the interaction tensors

$$T_{l_1\kappa_1,l_2\kappa_2} = \binom{l_A + l_B}{l_A} \bar{S}^{\kappa_1\kappa_2}_{l_1 l_2 l_1+l_2} R^{-l_1-l_2-1}$$

and the electrostatic interaction energy (operator) takes the simple form

$$U = \sum_{l_A l_B} \sum_{\kappa_A \kappa_B m} \tilde{Q}^A_{l_A\kappa_A} T_{l_A\kappa_A,l_B\kappa_B} \tilde{Q}_{l_B\kappa_B} = \sum_{tu} \tilde{Q}^A_t T^{AB}_{tu} \tilde{Q}^B_u$$

with $t, u = \{l\kappa\}$.
The T tensors can be expressed in terms of the unit vectors of the respective local coordinate systems, and the vector $\boldsymbol{R}$.

Interaction tensors between local frames

Following the derivation of Hättig and Heß (Mol.Phys. 81 (1994) 813), the interaction energy in space-fixed frame

$$U = \iint d\boldsymbol{r} d\boldsymbol{s} \, \frac{\varrho^A_{\mathsf{SF}}(\boldsymbol{r})\varrho^B_{\mathsf{SF}}(\boldsymbol{s})}{|\boldsymbol{s}-\boldsymbol{r}|}$$

Let us write the rotation matrices from the space-fixed (global) to the molecule-fixed (local) frame as $\hat{R}(\Omega_A)$ and $\hat{R}(\Omega_B)$, where $\Omega = (\alpha, \beta, \gamma)$ are the Euler angles, and the coordinates

$$\boldsymbol{r} = \boldsymbol{A} + \hat{R}(\Omega_A)\boldsymbol{r}_A \qquad \text{and} \qquad \boldsymbol{s} = \boldsymbol{B} + \hat{R}(\Omega_B)\boldsymbol{r}_B$$

Use the notation $\boldsymbol{R} = \boldsymbol{B} - \boldsymbol{A}$ and that the length of a vector does not change by rotation

$$|\boldsymbol{s}-\boldsymbol{r}| = |\boldsymbol{R} + \hat{R}(\Omega_B)\boldsymbol{r}_B - \hat{R}(\Omega_A)\boldsymbol{r}_A| = |\hat{R}^{-1}(\Omega_A)\boldsymbol{R} + \hat{R}^{-1}(\Omega_A)\hat{R}(\Omega_B)\boldsymbol{r}_B - \boldsymbol{r}_A|$$

Electrostatic energy in molecule-fixed charge distributions

$$U = \iint d\boldsymbol{r}_A d\boldsymbol{r}_B \frac{\varrho^A_{\mathsf{MF}}(\boldsymbol{r}_A)\varrho^B_{\mathsf{MF}}(\boldsymbol{r}_B)}{|\hat{R}^{-1}(\Omega_A)\boldsymbol{R} + \hat{R}^{-1}(\Omega_A)\hat{R}(\Omega_B)\boldsymbol{r}_B - \boldsymbol{r}_A|} =$$

$$= \sum_{l_1}^{\infty}\sum_{\kappa_1} Q^A_{l_1\kappa_1} \cdot \int d\boldsymbol{r}_B I_{l_1\kappa_1}(\hat{R}^{-1}(\Omega_A)\boldsymbol{R} + \hat{R}^{-1}(\Omega_A)\hat{R}(\Omega_B)\boldsymbol{r}_B) \cdot \varrho^B_{\mathsf{MF}}(\boldsymbol{r}_B)$$

The irregular spherical harmonics can be expanded in Taylor series

$$I_{l_1\kappa_1}(\hat{R}_A^{-1}\boldsymbol{R} + \hat{R}_A^{-1}\hat{R}_B\boldsymbol{r}_B) =$$

$$= \sum_{l_2=0}^{\infty} \frac{1}{l_2!}(\hat{R}_A^{-1}\hat{R}_B\boldsymbol{r}_B \cdot \boldsymbol{\nabla}_{\hat{R}_A^{-1}\boldsymbol{R}})^{l_2} \cdot I_{l_1\kappa_1}(\hat{R}_A^{-1}\boldsymbol{R}) =$$

$$= \sum_{l_2=0}^{\infty} \frac{1}{l_2!}(\boldsymbol{r}_B \cdot \boldsymbol{\nabla}_{\hat{R}_B^{-1}\boldsymbol{R}})^{l_2} \cdot I_{l_1\kappa_1}(\hat{R}_A^{-1}\boldsymbol{R})$$

and in terms of spherical tensors as

$$I_{l_1\kappa_1}(\hat{R}_A^{-1}\boldsymbol{R}+\hat{R}_A^{-1}\hat{R}_B\boldsymbol{r}_B)=$$

$$=\sum_{l_2=0}^{\infty}\sum_{\kappa_2}\frac{1}{(2l_2-1)!!}R_{l_2\kappa_2}(\boldsymbol{r}_B)\cdot R_{l_2\kappa_2}(\boldsymbol{\nabla}_{\hat{R}_B^{-1}\boldsymbol{R}})\cdot I_{l_1\kappa_1}(\hat{R}_A^{-1}\boldsymbol{R})$$

Using the identity $I_{l\kappa}(\boldsymbol{R})=(-)^l R_{l\kappa}(\boldsymbol{\nabla})(1/R)$, the interaction energy becomes

$$U=\sum_{l_1}^{\infty}\sum_{\kappa_1}\sum_{l_2}^{\infty}\sum_{\kappa_2}Q^A_{l_1\kappa_1}\cdot Q^B_{l_2\kappa_2}\cdot T^{AB}_{l_1\kappa_1l_2\kappa_2}$$

with $T^{AB}_{l_1\kappa_1l_2\kappa_2}$ interaction tensor

$$T^{AB}_{l_1\kappa_1l_2\kappa_2}(R,\Omega_A,\Omega_B)=\frac{(-)^{l_1}}{(2l_1-1)!!}\cdot\frac{1}{(2l_2-1)!!}R_{l_2\kappa_2}(\hat{R}_B^{-1}\boldsymbol{\nabla}_{\boldsymbol{R}})R_{l_1\kappa_1}(\hat{R}_A^{-1}\boldsymbol{\nabla}_{\boldsymbol{R}})\frac{1}{R}$$

The rotated internuclear vector and the rotated differential operators can be expressed in terms of direction cosines and the internuclear distance R. The rotation matrices can be written in terms of the unit vectors of the molecule fixed frame in the space-fixed system

$$\hat{R}_A = (\boldsymbol{e}_x^{(A)}, \boldsymbol{e}_y^{(A)}, \boldsymbol{e}_z^{(A)}) \qquad \text{and} \qquad \hat{R}_B = (\boldsymbol{e}_x^{(B)}, \boldsymbol{e}_y^{(B)}, \boldsymbol{e}_x^{(B)})$$

the intermolecular unit vector, $\boldsymbol{e}_{AB} = \boldsymbol{R}/R$ and the direction cosines, $r_\alpha^A = \boldsymbol{e}_\alpha^{(A)} \cdot \boldsymbol{e}_{AB}$ and

$$c_{\alpha\beta} = \boldsymbol{e}_\beta^{(B)} \cdot \boldsymbol{e}_\alpha^{(A)}.$$

For instance

$$T_{20,00} = \frac{1}{2}(3{r_\alpha^A}^2 - 1)R^{-3}$$
$$T_{1\alpha,1\beta} = (3r_\alpha^A r_\beta^B + c_{\alpha\beta})R^{-3}$$

Computation of the general expressions in both cartesian and spherical tensors are quite costly and scale as L^6, where L is the order of $1/R$ expansion. Using an intermediate coordinate transformation, Hättig derived general recurrence relations, which scale as L^4 (CPL, 260(1996)341).

Part IV

Induction energy

Electrostatic interaction Hamiltonian

Place a molecule in an external electrostatic field. The interaction Hamiltonian is

$$\hat{V} = \sum_k q_k V(\boldsymbol{r}_k) \qquad \text{with} \qquad q_k = e, Z$$

Let us define the operator of the total charge density

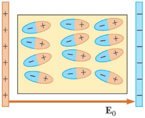
$$\hat{\varrho}(\boldsymbol{r}) = \sum_\alpha Z_\alpha \delta(\boldsymbol{r} - \boldsymbol{R}_\alpha) - \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

permitting to express the interaction Hamiltonian in the compact form as

$$\hat{V} = \int d\boldsymbol{r}\, \hat{\varrho}(\boldsymbol{r})\, V(\boldsymbol{r})$$

Molecule in a uniform electric field

Place molecules between two plates of a capacitor:



The electrostatic potential can be written in terms of the 3 components of the uniform electric field

$$V(\boldsymbol{r}) = V_0 + \sum_\alpha F_\alpha r_\alpha = V_0 + F_\alpha r_\alpha$$

(Einstein summation convention on repeated indices)

The interaction operator with the field of the capacitor simplifies as

$$\hat{V} = \int d\boldsymbol{r}\, \hat{\varrho}(\boldsymbol{r}) \left(V_0 + F_\alpha r_\alpha\right) = V_0 \hat{q} + F_\alpha \hat{\mu}_\alpha$$

where the operators of the total charge and total dipole moment of the molecule are

$$\hat{q} = \int d\boldsymbol{r}\, \hat{\varrho}(\boldsymbol{r}) \qquad \hat{\mu}_\alpha = \int d\boldsymbol{r}\, \hat{\varrho}(\boldsymbol{r}) r_\alpha$$

Schrödinger equation with perturbation

We are looking for the ground state solution of the problem

$$\hat{H}\psi = (\hat{H}_0 + \hat{V})\psi = E\psi$$

and we already know the (exact) solution of the zero-order problem

$$\hat{H}_0\varphi_0 = E_0\varphi_0$$

Let us write $\Delta E = E - E_0$, the energy correction

$$(\hat{H}_0 - E_0)\psi = (\Delta E - \hat{V})\psi$$

and in order to fix the phase of ψ, impose the intermediate normalization

$$\langle\varphi_0|\psi\rangle = 1$$

Introduce the reduced resolvent operator as

$$\hat{R}_0 = (1 - |\varphi_0\rangle\langle\varphi_0|)(\hat{H}_0 - E_0)^{-1}$$

which can be regarded as the inverse of the operator $\hat{H}_0 - E_0$ in the space of functions orthogonal to φ_0

$$\hat{R}_0(\hat{H}_0 - E_0) = 1 - |\varphi_0\rangle\langle\varphi_0|$$

Multiplying the Schrödinger equation by $\hat{R}_0$

$$\hat{R}_0(\hat{H}_0 - E_0)\psi = \hat{R}_0(\Delta E - \hat{V})\psi$$

using the definition of the resolvent and the intermediate normalization an equation is obtained for the wave function

$$\psi = \varphi_0 + \hat{R}_0(\Delta E - \hat{V})\psi$$

After multiplication of the Schrödinger equation by $\langle\varphi_0|$

$$\langle\varphi_0|(\hat{H}_0 - E_0)|\psi\rangle = \langle\varphi_0|(\Delta E - \hat{V})|\psi\rangle$$

we get the energy correction

$$\Delta E = \langle\varphi_0|\hat{V}|\psi\rangle$$

Iterative solution

These equations can be solved iteratively

$$\begin{aligned} \Delta E_n &= \langle \varphi_0 | \hat{V} | \psi_{n-1} \rangle \\ \psi_n &= \varphi_0 + \hat{R}_0 (\Delta E_n - \hat{V}) \psi_{n-1} \end{aligned}$$

To the lowest orders of iteration we find by using $\psi_0 = \varphi_0$ and $\hat{R}_0 \varphi_0 = 0$

$$\begin{aligned} \Delta E_1 &= \langle \varphi_0 | \hat{V} | \psi_0 \rangle \\ \psi_1 &= \varphi_0 - \hat{R}_0 \hat{V} \psi_0 \\ \Delta E_2 &= \langle \varphi_0 | \hat{V} | \psi_1 \rangle = \langle \varphi_0 | \hat{V} | \psi_0 \rangle - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \psi_0 \rangle = \Delta E_1 - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \psi_0 \rangle \\ \psi_2 &= \varphi_0 - \hat{R}_0 (\Delta E_2 - \hat{V}) \psi_1 \\ &= \varphi_0 - \hat{R}_0 (\langle \varphi_0 | \hat{V} | \psi_0 \rangle - \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \psi_0 \rangle - \hat{V})(\varphi_0 - \hat{R}_0 \hat{V} \psi_0) \\ &= \varphi^{(1)} - \hat{R}_0 (\hat{V} - \Delta E_2) \hat{R}_0 \hat{V} \varphi_0 \end{aligned}$$

H-atom in electric field

Hamiltonian of the H-atom in an electric field, F_z

$$\hat{H} = \hat{H}_0 + \hat{z} F_z \qquad \text{where} \qquad \hat{H}_0 = -\frac{1}{2}\Delta - \frac{1}{r}$$

The Hamiltonian of the isolated H-atom has
the lowest eigenvalue $E_0 = -\frac{1}{2}$ and eigenfunction $\varphi_0 = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-r}$.
First iteration in the energy yields zero

$$\Delta E_1 = F_z \langle \varphi_0 | \hat{z} | \psi_0 \rangle = \mu_z \cdot F_z = 0$$

First iteration in the wave function leads to the equation

$$\psi_1 = \varphi_0 - \hat{R}_0 \hat{V} \varphi_0$$

$$(\hat{H}_0 - E_0)\psi_1 = -\left(\hat{V} - \Delta E_1\right) \varphi_0$$

$$\left(-\frac{1}{2}\Delta - \frac{1}{r} + \frac{1}{2}\right) \psi_1 = -\frac{1}{\sqrt{\pi}} \, F_z \, z \, \mathrm{e}^{-r}$$

which has the solution

$$\psi_1 = -\frac{F_z}{\sqrt{\pi}} \, z \, \left(\frac{r}{2} - 1\right) \mathrm{e}^{-r}$$

Second energy iteration

$$\Delta E_2 = F_z \langle \varphi_0 | \hat{z} | \psi_1 \rangle = -\frac{9}{4} \cdot F_z^2$$

This leads to a development of the energy in the powers of F_z

$$E = E_0 + \Delta E_2 = E_0 - \frac{9}{4} \cdot F_z^2$$

the dipole polarizability is

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_z^2} \right)_{F_z = 0} = \frac{9}{2} \ \text{a.u.}$$

Perturbation approach

Assuming that the iteration process converges, the exact wave function and energy can be expanded in power series of a perturbation parameter λ

$$(\hat{H}_0 + \lambda \hat{V})\psi = \Delta E \psi$$

as

$$\Delta E = \sum_{n=1}^{\infty} \lambda^n \Delta E^{(n)} \qquad \text{and} \qquad \psi = \sum_{n=0}^{\infty} \lambda^n \psi^{(n)}$$

Substitute the series expansions in

$$\Delta E = \langle \varphi_0 | \hat{V} | \psi \rangle \qquad \text{and} \qquad \psi = \varphi_0 + \hat{R}_0 (\Delta E - \hat{V}) \psi$$

leading to

$$\sum_{n=1} \lambda^n \Delta E^{(n)} = \sum_{m=0} \lambda^{m+1} \langle \varphi_0 | \hat{V} | \psi^{(m)} \rangle$$

$$\sum_{n=1} \lambda^n \psi^{(n)} = \varphi_0 + \hat{R}_0 \left(\sum_{m=1} \lambda^m \Delta E^{(m)} - \lambda \hat{V} \right) \sum_{k=1} \lambda^k \psi^{(k)}$$

Collect terms of the same power in λ to obtain the general recursion formulae

$$\Delta E^{(n)} = \langle \varphi_0 | \hat{V} | \psi^{(n-1)} \rangle$$

$$\psi^{(n)} = -\hat{R}_0 \hat{V} \psi^{(n-1)} - \sum_{k=1}^{n-1} \Delta E^{(k)} \hat{R}_0 \psi^{(n-k)}$$

The reduced resolvent has the spectral resolution

$$\hat{R}_0 = \sum_{k \neq 0} \frac{|\varphi_0\rangle\langle\varphi_0|}{E_k - E_0}$$

First order

$$\Delta E^{(1)} = \langle \varphi_0 | \hat{V} | \varphi_0 \rangle$$

$$\psi^{(1)} = -\hat{R}_0 \hat{V} \varphi_0 = -\sum_{k \neq 0} \frac{\langle \varphi_k | \hat{V} | \varphi_0 \rangle}{E_k - E_0} \varphi_k$$

The wave function corrections are often expressed in terms of the expansion coefficients $c_k^{(n)} = \langle \varphi_k | \psi^{(n)} \rangle$ on the basis of the eigenfunctions of the zero order Hamiltonian

$$c_k^{(1)} = -\sum_{k \neq 0} \frac{\langle \varphi_k | \hat{V} | \varphi_0 \rangle}{E_k - E_0}$$

Second order

Energy

$$E^{(2)} = \langle \varphi_0 | \hat{V} | \psi^{(1)} \rangle = -\langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle$$
$$= -\sum_{k \neq 0} \frac{\langle \varphi_0 | \hat{V} | \varphi_k \rangle \langle \varphi_k | \hat{V} | \varphi_0 \rangle}{E_k - E_0}$$

Wave function

$$\varphi^{(2)} = \hat{R}_0 \hat{V} \hat{R}_0 \hat{V} \psi^{(1)} + \hat{R}_0 E^{(1)} \hat{R}_0 \hat{V} \psi^{(0)} =$$
$$= \hat{R}_0 \hat{V} \hat{R}_0 \hat{V} \varphi_0 - \hat{R}_0 \langle \hat{V} \rangle \hat{R}_0 \hat{V} \varphi_0 = \hat{R}_0 \overline{V} \hat{R}_0 \hat{V} \varphi_0$$

where we used the definitions

$$\langle \hat{V} \rangle = \langle \varphi_0 | \hat{V} | \varphi_0 \rangle \qquad \text{and} \qquad \overline{V} = \hat{V} - \langle \hat{V} \rangle$$

Third order

$$
\begin{aligned}
\Delta E^{(3)} &= \langle \varphi_0 | \hat{V} | \psi^{(2)} \rangle = -\langle \varphi_0 | \hat{V} \hat{R}_0 \overline{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle \\
&= \sum_{k \neq 0} \sum_{l \neq 0} \frac{\langle \varphi_0 | \hat{V} | \varphi_k \rangle \langle \varphi_k | \overline{V} | \varphi_l \rangle \langle \varphi_l | \hat{V} | \varphi_0 \rangle}{(E_k - E_0)(E_l - E_0)}
\end{aligned}
$$

Summary of energy corrections

$$\Delta E^{(1)} = \langle \hat{V} \rangle$$

$$\Delta E^{(2)} = \langle \hat{V} \hat{R}_0 \hat{V} \rangle$$

$$\Delta E^{(3)} = \langle \hat{V} \hat{R}_0 \overline{V} \hat{R}_0 \hat{V} \rangle$$

$$\Delta E^{(4)} = \langle \hat{V} \hat{R}_0 \left(\overline{V} \hat{R}_0 \overline{V} - \langle \overline{V} \hat{R}_0 \overline{V} \rangle \right) \hat{R}_0 \hat{V} \rangle$$

$$\begin{aligned}\Delta E^{(5)} = \langle \hat{V} \hat{R}_0 (& \overline{V} \hat{R}_0 \overline{V} \hat{R}_0 \overline{V} - \langle \overline{V} \hat{R}_0 \overline{V} \hat{R}_0 \overline{V} \rangle \\ & - \overline{V} \hat{R}_0 \langle \overline{V} \hat{R}_0 \overline{V} \rangle - \langle \overline{V} \hat{R}_0 \overline{V} \rangle \hat{R}_0 \overline{V}) \hat{R}_0 \hat{V} \rangle\end{aligned}$$

Energy with the first-order wave function

The energy (Rayleigh quotient)

$$E = \frac{\langle \psi | \hat{H} + \lambda \hat{V} | \psi \rangle}{\langle \psi | \psi \rangle}$$

with the first order wave function, $\psi = \varphi_0 - \lambda \hat{R}_0 \hat{V} \varphi_0$

$$E = \frac{\langle \varphi_0 - \lambda \varphi_0 \hat{V} \hat{R}_0 | \hat{H} + \lambda \hat{V} | \varphi_0 - \lambda \hat{R}_0 \hat{V} \varphi_0 \rangle}{1 + \lambda^2 \langle \varphi_0 \hat{V} \hat{R}_0 | \hat{R}_0 \hat{V} \varphi_0 \rangle}$$

After expanding the denominator and using that $\hat{R}_0 \hat{H}_0 \varphi_0 = 0$

$$\begin{aligned} E = \big(E_0 + \lambda E^{(1)} - 2\lambda^2 \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{V} | \varphi_0 \rangle + \\ + \lambda^2 \langle \varphi_0 | \hat{V} \hat{R}_0 (\hat{H} + \lambda \hat{V}) \hat{R}_0 \hat{V} | \varphi_0 \rangle \big) \times \\ \times \big(1 - \lambda^2 \langle \varphi_0 \hat{V} \hat{R}_0 | \hat{R}_0 \hat{V} \varphi_0 \rangle \big) \end{aligned}$$

and collecting terms of the same order

$$\begin{aligned} E = E_0 + \lambda E^{(1)} - & \\ & - \lambda^2 2\langle\varphi_0|\hat{V}\hat{R}_0\hat{V}|\varphi_0\rangle - \\ & - \lambda^2 \langle\varphi_0|\hat{V}\hat{R}_0(\hat{H} - E_0)\hat{R}_0\hat{V}|\varphi_0\rangle \\ & + \lambda^3 \langle\varphi_0|\hat{V}\hat{R}_0(\hat{V} - E^{(1)})\hat{R}_0\hat{V}|\varphi_0\rangle \end{aligned}$$

Use that $E^{(1)} = \langle\hat{V}\rangle$ and $\hat{R}_0(\hat{H} - E_0) = 1 - |\varphi_0\rangle\langle\varphi_0|$ and obtain the previously derived 3rd order energy expression

$$E = E_0 + \langle\varphi_0|\hat{V}|\varphi_0\rangle - \langle\varphi_0|\hat{V}\hat{R}_0\hat{V}|\varphi_0\rangle + \langle\varphi_0|\hat{V}\hat{R}_0(\hat{V} - \langle\hat{V}\rangle)\hat{R}_0\hat{V}|\varphi_0\rangle$$

This result can be generalized: the nth order wave function determines the (2n+1)th order energy expression, provided the normalization is taken into account. This is Wigner's $(2n+1)$ theorem.

Deformation energy and perturbation energy

Up to second order the Rayleigh quotient can be written as a sum of two terms, the expectation value of the zero order Hamiltonian

$$\frac{\langle\varphi - \lambda\varphi\hat{V}\hat{R}_0|\hat{H}|\varphi - \lambda\hat{R}_0\hat{V}\varphi\rangle}{1+\lambda^2\langle\varphi\hat{V}\hat{R}_0|\hat{R}_0\hat{V}\varphi\rangle} = E_0 + \lambda^2\langle\varphi|\hat{V}\hat{R}_0\hat{V}|\varphi\rangle = E_0 + \Delta E^{(2)}_{\mathrm{def}}$$

and the expectation value of the perturbation operator

$$\frac{\langle\varphi - \lambda\varphi\hat{V}\hat{R}_0|\lambda\hat{V}|\varphi - \lambda\hat{R}_0\hat{V}\varphi\rangle}{1+\lambda^2\langle\varphi\hat{V}\hat{R}_0|\hat{R}_0\hat{V}\varphi\rangle} = \lambda\langle\varphi|\hat{V}|\varphi\rangle - \lambda^2 2\langle\varphi|\hat{V}\hat{R}_0\hat{V}|\varphi\rangle = E^{(1)} + \Delta E^{(2)}_{\mathrm{stab}}$$

The second order correction to the expectation value of the perturbation is twice the second order energy correction and it is twice the *energy raise* of the wave function due to the deformation of the wave function.

$$\Delta E^{(2)}_{\mathrm{stab}} = -2\Delta E^{(2)}_{\mathrm{def}}$$

$$\Delta E^{(2)} = \Delta E^{(2)}_{\mathrm{stab}} - \Delta E^{(2)}_{\mathrm{def}} = \frac{1}{2}\Delta E^{(2)}_{\mathrm{stab}}$$

Molecule in external potential

In first order of the perturbation theory

$$\Delta E^{(1)} = \langle\psi_0|\hat{q}|\psi_0\rangle \cdot V_0 + \langle\psi_0|\hat{\mu}_\alpha|\psi_0\rangle \cdot F_\alpha = qV_0 + F_\alpha\mu_\alpha$$

one retrieves the classical charge-potential and dipole-field interactions.
In second-order of the perturbation theory

$$\Delta E^{(2)} = -\langle\psi_0|\hat{V}\hat{R}_0\hat{V}|\psi_0\rangle = -\sum_{k\neq 0} \frac{\langle\psi_0|\hat{V}|\psi_k\rangle\langle\psi_k|\hat{V}|\psi_0\rangle}{E_k - E_0}$$

The matrix elements $\langle\psi_0|\hat{q}|\psi_k\rangle = 0$, since the eigenstates are orthogonal. Only the dipolar term survives

$$\Delta E^{(2)} = -\sum_{\alpha\beta} F_\alpha \langle\psi_0|\hat{\mu}_\alpha\hat{R}_0\hat{\mu}_\beta|\psi_0\rangle F_\beta$$

Using the definition of the dipolar linear response function (polarizability)

$$\Delta E^{(2)} = -\frac{1}{2}\sum_{\alpha\beta} F_\alpha \alpha_{\alpha\beta} F_\beta$$

In third order of the perturbation theory

$$\Delta E^{(3)} = -\langle \psi_0 | \hat{V} \hat{R}_0 \overline{V} \hat{R}_0 \hat{V} | \psi_0 \rangle$$

Insert the interaction operator, and remember that $\overline{V} = \hat{V} - \langle \hat{V} \rangle$,

$$\begin{aligned}\Delta E^{(3)} = &- \sum_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma \times \\ &\left\{ \sum_{k\neq 0} \sum_{l \neq 0} \frac{\langle \psi_0 | \hat{\mu}_\alpha | \psi_k \rangle \langle \psi_k | \hat{\mu}_\beta | \psi_l \rangle \langle \psi_l | \hat{\mu}_\gamma | \psi_0 \rangle}{(E_k - E_0)(E_l - E_0)} - \right. \\ &\left. \langle \psi_0 | \hat{\mu}_\beta | \psi_0 \rangle \sum_{k \neq 0} \frac{\langle \psi_0 | \hat{\mu}_\alpha | \psi_k \rangle \langle \psi_k | \hat{\mu}_\gamma | \psi_0 \rangle}{(E_k - E_0)^2} \right\} = \\ = &- \frac{1}{6} \sum_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma \, \beta_{\alpha\beta\gamma}\end{aligned}$$

where $\beta_{\alpha\beta\gamma}$ is the first dipolar hyperpolarizability (non-linear response function).

Multipole polarizabilities

Dipole polarizability is a symmetric tensor

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ & \alpha_{yy} & \alpha_{yz} \\ & & \alpha_{zz} \end{pmatrix}$$

The SI units of polarizability are Farad m^2, or equivalently, $\mathrm{C}^2\ \mathrm{m}^2\ \mathrm{J}^{-1}$ or $\mathrm{C\ m}^2\ \mathrm{V}^{-1}$. Other units are volume (Å^3 or bohr^3). 1 a.u. $=$ $\mathrm{bohr}^3 = 0.148185\ \text{Å}^3 = 0.16488 \times 10^{-40}$ Farad m^2. $1\ \mathrm{C}^2\ \mathrm{m}^2\ \mathrm{J}^{-1} = 0.8988 \times 10^{16} \mathrm{cm}^3 = 6.065 \times 10^{40}$ a.u.

Proportional to the volume, as it can be seen by introducing an average excitation energy and using the resolution of identity for the polarizability of a one-electron system

$$\alpha = \frac{1}{3} \sum_{n \neq 0} \frac{2\langle 0|\hat{r}_\alpha|n\rangle\langle n|\hat{r}_\alpha|0\rangle}{\Delta E_{0n}} \approx \frac{2}{3\,\overline{U}} \left(\langle 0|\hat{r}^2|0\rangle - \langle 0|\hat{r}_\alpha|0\rangle\langle 0|\hat{r}_\alpha|0\rangle\right)$$

and inversely proportional to the excitation energy.

As any second-rank tensor, it can be decomposed into irreducible parts, according to

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}^{(0)} + \boldsymbol{\alpha}^{(1)} + \boldsymbol{\alpha}^{(2)}$$

where

$$\begin{aligned}
\alpha^{(0)}_{\alpha\beta} &= \frac{1}{3}\mathrm{Tr}(\boldsymbol{\alpha})\delta_{\alpha\beta} \\
\alpha^{(1)}_{\alpha\beta} &= \frac{1}{2}(\alpha_{\alpha\beta} - \alpha_{\beta\alpha}) = 0 \\
\alpha^{(2)}_{\alpha\beta} &= \frac{1}{2}(\alpha_{\alpha\beta} + \alpha_{\beta\alpha}) - \frac{1}{3}\mathrm{Tr}(\boldsymbol{\alpha})\delta_{\alpha\beta}
\end{aligned}$$

$\boldsymbol{\alpha}^{(1)}$ vanishes, since $\boldsymbol{\alpha}$ is symmetric. In a principal-axis system we have the decomposition

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{pmatrix} + \begin{pmatrix} \alpha_{xx} - \alpha & 0 & 0 \\ 0 & \alpha_{yy} - \alpha & 0 \\ 0 & 0 & \alpha_{zz} - \alpha \end{pmatrix}$$

The first trace-invariant quantity that can be formed is the mean polarizability

$$\alpha = \frac{1}{3}\mathrm{Tr}\boldsymbol{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

and the second trace-invariant is the polarizability anisotropy, γ, defined as the positive root of

$$\gamma^2 = \frac{1}{2}[3\mathrm{Tr}(\boldsymbol{\alpha}^2) - \mathrm{Tr}(\boldsymbol{\alpha})^2]$$

or in components

$$\gamma^2 = \frac{1}{2}[3\alpha_{\alpha\beta}\alpha_{\beta\alpha} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}]$$

which can be written in a principal axis system

$$\gamma^2 = \frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]$$

and makes clear that this quantity vanishes for spherically symmetric systems.
For linear molecules $\alpha_{zz} = \alpha_{\parallel}$ and $\alpha_{xx} = \alpha_{yy} = \alpha_{\perp}$ and the polarizability anisotropy, γ

$$\gamma = \alpha_{\parallel} - \alpha_{\perp}$$

Translation of polarizabilities

The dipole-dipole polarizability is always origin-independent.

Higher-rank multipole polarizabilities are (always) origin-dependent.
For instance, the $A_{z,zz}$ component involves the $\hat{\Theta}_{zz}$ operator. After a shift of the origin by $\boldsymbol{c} = (0, 0, c)$

$$\hat{\Theta}^{C}_{zz} = \hat{\Theta}^{O}_{zz} - 2c\hat{\mu}^{O}_{z}$$

and the dipole-quadrupole polarizability at the new origin is

$$A^{C}_{z,zz} = \sum_{n\neq 0} \frac{\langle 0|\hat{\mu}^{O}_{z}|n\rangle\langle n|\hat{\Theta}^{O}_{zz} - 2c\hat{\mu}^{O}_{z}|0\rangle}{\Delta E_{0n}} = A^{O}_{z,zz} - 2c\alpha_{zz}$$

This means that the origin (and the dipole polarizability) should always be specified when $A_{\alpha,\beta\gamma}$ is given.

Spherical harmonic polarizabilities

The general multipole polarizabilities, defined in terms of the (irreducible) multipole moment operators, $\hat{Q}_{\ell m}$

$$\alpha_{\ell_1 m_1, \ell_2 m_2} = \sum_{n \neq 0} \frac{\langle 0|\hat{Q}_{\ell_1 m_1}|n\rangle\langle n|\hat{Q}_{\ell_2 m_2}|0\rangle + \langle 0|\hat{Q}_{\ell_2 m_2}|n\rangle\langle n|\hat{Q}_{\ell_1 m_1}|0\rangle}{\Delta E_{0n}}$$

is a reducible spherical tensor quantity, which can be decomposed into irreducible parts as

$$\alpha_{\ell_1 \ell_2 : kq} = \sum_{m_1 m_2} C(\ell_1 \ell_2 k; m_1 m_2 q) \alpha_{\ell_1 m_1, \ell_2 m_2}$$

where $C(\ell_1 \ell_2 k; m_1 m_2 q)$ are the Clebsch-Gordan coefficients.
Since $C = 0$, unless $k = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \ldots, |\ell_1 - \ell_2|$, the nonzero irreducible parts of the dipole-dipole polarizability can be only with $k = 0, 2$, for the dipole-quadrupole polarizability, $k = 1, 3$, etc. For instance,

$$\alpha_{11:00} = \sqrt{\frac{1}{3}}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\alpha_{11:20} = \sqrt{\frac{2}{3}}\gamma$$

Induction energy

Consider a potential and its derivatives created by a molecule A at the center of molecule B.
The corresponding perturbation energy will be induction energy. At the second order:
Taking into account that $\langle\psi_0^B|\hat{q}^B|\psi_b^B\rangle = 0$, one has the leading terms of the induction energy:

$$
\begin{aligned}
&E^{(2)}(\text{ind,B}) = \\
&-(T_\alpha q^A - T_{\alpha\beta}\mu_\alpha^A + \ldots)\sum_{b\neq 0}\frac{\langle 0|\hat{\mu}_\alpha^B|b\rangle\langle b|\hat{\mu}_{\alpha'}^B|0\rangle}{\Delta E_{0b}^B}(T_{\alpha'} q^A - T_{\alpha'\beta'}\mu_{\alpha'}^A + \ldots) - \\
&-(T_{\alpha\beta} q^A + T_{\alpha\beta\gamma}\mu_\gamma^A + \ldots)\sum_{b\neq 0}\frac{\langle 0|\hat{\Theta}_{\alpha\beta}^B|b\rangle\langle b|\hat{\mu}_{\alpha'}^B|0\rangle}{\Delta E_{0b}^B}(T_{\alpha'} q^A - T_{\alpha'\beta'}\mu_{\beta'}^A + \ldots) - \\
&-(T_\alpha q^A - T_{\alpha\beta}\mu_\alpha^A + \ldots)\sum_{b\neq 0}\frac{\langle 0|\hat{\mu}_\alpha^B|b\rangle\langle b|\hat{\Theta}_{\alpha'\beta'}^B|0\rangle}{\Delta E_{0b}^B}(T_{\alpha'\beta'} q^A + T_{\alpha'\beta'\gamma'}\mu_\gamma^A + \ldots) - \\
&-(T_{\alpha\beta} q^A + T_{\alpha\beta\gamma}\mu_{\gamma'}^A + \ldots)\sum_{b\neq 0}\frac{\langle 0|\hat{\Theta}_{\alpha\beta}^B|b\rangle\langle b|\hat{\Theta}_{\alpha'\beta'}^B|0\rangle}{\Delta E_{0b}^B}(T_{\alpha'\beta'} q^A - T_{\alpha'\beta'\gamma'}\mu_{\gamma'}^A + \ldots)\ldots
\end{aligned}
$$

Introduce the multipole polarizabilities

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

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

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

and identify the parentheses as the electric field, field gradient, etc.

$$F_\alpha^A = -(T_\alpha q^A - T_{\alpha\beta}\mu_\alpha^A + \ldots)$$
$$F_{\alpha\beta}^A = -(T_{\alpha\beta} q^A + T_{\alpha\beta\gamma}\mu_\gamma^A + \ldots)$$

The induction energy in terms of the field (and its gradients) and the multipolar polarizabilities

$$E^{(2)}(\text{ind,B}) = -\frac{1}{2}F_\alpha^A \alpha_{\alpha,\alpha'}^B F_{\alpha'}^A - \frac{1}{3}F_\alpha^A A_{\alpha,\alpha'\beta'}^B F_{\alpha'\beta'}^A - \frac{1}{6}F_{\alpha\beta}^A C_{\alpha\beta,\alpha'\beta'}^B F_{\alpha'\beta'}^A + \ldots$$

Induction energy - spherical tensor components

In the spherical tensor formalism, the general polarizability component

$$\alpha_{\ell\kappa,\ell'\kappa'} = \sum_{n\neq 0} \frac{\langle 0|\hat{Q}_{\ell\kappa}|n\rangle\langle n|\hat{Q}_{\ell'\kappa'}|0\rangle + \langle 0|\hat{Q}_{\ell'\kappa'}|n\rangle\langle n|\hat{Q}_{\ell\kappa}|0\rangle}{\Delta E_{0n}}$$

and the induction energy takes the form

$$E^{(2)}(\text{ind,B}) = -\frac{1}{2}\sum_{\ell\kappa}\sum_{\ell'\kappa'} \alpha^{B}_{\ell\kappa\ell'\kappa'} V^{A}_{\ell\kappa} V^{A}_{\ell'\kappa'} = -\frac{1}{2}\sum_{\ell\kappa} \Delta Q^{B}_{\ell\kappa\ell} V^{A}_{\ell\kappa}$$

where $\Delta Q^{B}_{\ell\kappa\ell}$ are the induced moments of B

$$\Delta Q^{B}_{\ell\kappa} = \sum_{\ell'\kappa'} \alpha^{B}_{\ell\kappa\ell'\kappa'} V^{A}_{\ell'\kappa'}$$

Truncation of the multipolar induction energy

The multipolar induction energy can be truncated

- according to the powers of $(1/R)^N$
  does not ensure that the induction energy is negative
- according to the maximum rank of the multipole operators (L)
  always negative

Distance dependence of the induction energy

Interaction of a spherically symmetric polarizability $\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}$ with multipoles:

- charge

$$E(\mathrm{ind}, q) = -\frac{1}{2} q T_\alpha \alpha_{\alpha\beta} T_\beta q = -\frac{1}{2} q^2 T_\alpha T_\alpha \alpha = -\frac{1}{2} q^2 \sum_\alpha \frac{\alpha R_\alpha^2}{R^3 R^3} = -\frac{1}{2} \frac{q^2 \alpha}{R^4}$$

- dipole

$$E(\mathrm{ind}, \mu) = -\frac{1}{2} \mu_\alpha T_{\alpha\beta} \alpha_{\beta\beta'} T_{\beta'\alpha'} \mu_{\alpha'} = -\frac{1}{2} \frac{\mu^2 \alpha (3\cos^2\theta + 1)}{R^6}$$

- quadrupole

$$E(\mathrm{ind}, \Theta) \sim R^{-8}$$

Convergence of the induction energy

The multipole-expanded interaction Hamiltonian of a H-atom + proton system is

$$V_{\mathrm{mult}} = \frac{1}{R}\left[1 - \sum_{n=0}^{\infty}\left(\frac{r}{R}\right)^{n} P_n(\cos\theta)\right]$$

The exact second order multipole energy (Dalgarno & Lynn, 1957)

$$E^{(2)} = -\sum_{n=1}^{\infty}\frac{(2n+2)!(n+2)}{n(n+1)R^{(2n+2)}}$$

The ratio of successive terms

$$\lim_{n\to\infty}\frac{2n(n+3)(2n+3)}{(n+2)R^2} = \infty$$

indicates that for any value of R the series is divergent.

Non-additivity of the induction energy

- charge-polarizability interaction

$$U_{q\alpha} = -\frac{1}{2}\alpha F^2 = -\frac{1}{2}\alpha\frac{q^2}{R^4}$$

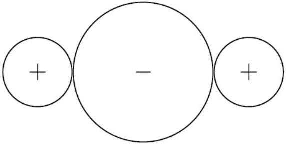
- two charges of opposite signs: F is doubled

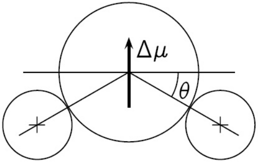
$$U_{\{q_1+q_2\}\alpha} = 4U_{q\alpha} \neq U_{q_1\alpha} + U_{q_2\alpha}$$

- two charges of the same sign: F is zero

$$U_{\{q_1+q_2\}\alpha} = 0 \neq U_{q_1\alpha} + U_{q_2\alpha}$$

- this effect explains the arrangement of Mg^{2+} cations (and other alkaline earth cations) around the polarizable Cl$-$ anions in crystal and molten phases: induction effects arising with an angle Mg-Cl-Mg <180 effectively reduce the cation-cation repulsion. If the anion is not large enough (F$-$) this phenomenon does not take place.





Cooperativity of induction

- Interaction of polarizable particles enhance the overall polarization effect.
- The induced dipoles $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ are obtained from the *total local fields*

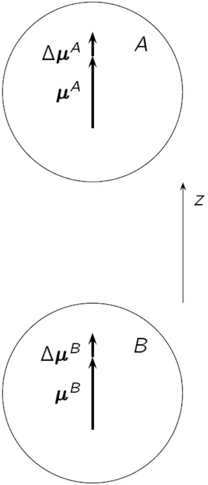
$$\boldsymbol{p}_1 = \boldsymbol{\alpha}_1 \boldsymbol{F}_1 = \boldsymbol{\alpha}_1 \left(\boldsymbol{E} + \boldsymbol{T}_{12} \cdot \boldsymbol{p}_2 \right)$$
$$\boldsymbol{p}_2 = \boldsymbol{\alpha}_2 \boldsymbol{F}_2 = \boldsymbol{\alpha}_2 \left(\boldsymbol{E} + \boldsymbol{T}_{21} \cdot \boldsymbol{p}_1 \right)$$

- The solution of this coupled system of equations:

$$\begin{pmatrix} \boldsymbol{p}_1 \\ \boldsymbol{p}_2 \end{pmatrix} = \begin{pmatrix} \boldsymbol{\alpha}_1^{-1} & -\boldsymbol{T} \\ -\boldsymbol{T} & \boldsymbol{\alpha}_2^{-1} \end{pmatrix}^{-1} \begin{pmatrix} \boldsymbol{E} \\ \boldsymbol{E} \end{pmatrix}$$

- The effective polarizability is:

$$\frac{1}{1 - \boldsymbol{T}^2 \boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2} \begin{pmatrix} \boldsymbol{\alpha}_1 & \boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 \boldsymbol{T} \\ \boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2 \boldsymbol{T} & \boldsymbol{\alpha}_2 \end{pmatrix}$$



Part V

Charge fluctuation interactions

Thermally averaged interactions

- Thermal average of orientation-dependent interactions $U(\Omega)$, where $\Omega = (\theta, \phi)$

$$\langle U_{q\mu} \rangle = \frac{\int d\Omega U(\Omega) \mathrm{e}^{-U(\Omega)/kT}}{\int d\Omega \mathrm{e}^{-U(\Omega)/kT}}$$

- Expand the exponential ($U(\Omega)/kT \ll 1$):

$$\begin{aligned} \langle U_{q\mu}|\rangle &\approx \frac{\int d\Omega (U(\Omega) - U^2(\Omega)/kT + \ldots)}{\int d\Omega (1 - U(\Omega)/kT + \ldots)} \\ &= \left(\overline{U} - \overline{U^2}/kT\right)\left(1 + \overline{U}^2/kT\right) \\ &= \overline{U} - (\overline{U^2}/kT - \overline{U}^2/kT) + \ldots \end{aligned}$$

where

$$\overline{U^n} = \int d\Omega U^n(\Omega) = \iint U^n(\theta, \phi) \sin\theta d\theta d\phi$$

$$\overline{\cos^n \theta} = \begin{cases} 0, & n = 2k+1; \\ \frac{1}{2k+1}, & n = 2k. \end{cases}$$

$$\overline{\cos^n \phi} =$$

$$\overline{\sin^n \phi} = \begin{cases} 0, & n = 2k+1; \\ \frac{(2k-1)!!}{2^k k!}, & n = 2k. \end{cases}$$

k	$\overline{\cos^{2k} \theta}$	$\overline{\sin^{2k} \theta}$	$\overline{\cos^{2k} \phi}$
1	1/3	2/3	1/2
2	1/5	8/15	3/8
3	1/7	16/35	5/16
4	1/9	128/315	35/128

Charge-dipole interaction

- Charge-dipole interaction

$$U_{q\mu} = \frac{q_A \mu_B}{R^2} \cos\theta$$

- Thermal averages

$$\overline{U}_{q\mu} = \frac{q\mu}{R^2} \overline{\cos\theta} = 0$$

$$\overline{U^2}_{q\mu} = \frac{q^2 \mu^2}{R^4} \overline{\cos^2\theta} = \frac{1}{3} \frac{q^2 \mu^2}{R^4}$$

- Analogous to the charge-polarizability interaction:

$$\langle U_{q\mu} \rangle = -\frac{1}{3kT} \frac{q^2 \mu^2}{R^4}$$

Dipole-dipole (Keesom) interaction

- Dipole-dipole interaction

$$U_{\mu\mu} = -\frac{\mu_A \mu_B}{R^2} \left(2 \cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\varphi \right)$$

- Thermal average

$$\langle U_{\mu\mu} \rangle = -\overline{U^2}_{\mu\mu} / kT$$

$$\begin{aligned}\overline{U^2}_{\mu\mu} &= -\frac{1}{kT} \frac{\mu_A^2 \mu_B^2}{R^6} \left(4 \, \overline{\cos^2\theta_A} \, \overline{\cos^2\theta_B} - \overline{\sin^2\theta_A} \, \overline{\sin^2\theta_B} \, \overline{\cos^2\varphi} + \text{cross terms} \right) \\ &= -\frac{1}{kT} \frac{\mu_A^2 \mu_B^2}{R^6} \left(4 \times \frac{1}{3} \times \frac{1}{3} - \frac{2}{3} \times \frac{2}{3} \times \frac{1}{2} \right) = -\frac{2}{3kT} \frac{\mu_A^2 \mu_B^2}{R^6}\end{aligned}$$

- Keesom forces:

$$\langle U_{\mu\mu} \rangle = -\frac{2}{3kT} \frac{\mu_A^2 \mu_B^2}{R^6}$$

Correlation of thermal fluctuations give rise to universally attractive interactions.

London dispersion forces

$$E_{\text{disp}} = -\frac{1}{2\pi}\int d\omega\, \alpha_1(r_1, r_1'|i\omega)\, T(r_1, r_2)\, \alpha_2(r_2, r_2'|i\omega)\, T(r_2', r_1')$$

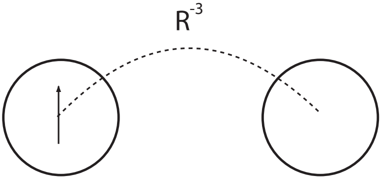
- universally attractive
- always attractive and decays as R^{-6}
- long-range dynamical correlation

London dispersion forces

$$E_{\mathsf{disp}} = -\frac{1}{2\pi} \int d\omega \, \alpha_1(r_1, r_1'|i\omega) \, T(r_1, r_2) \, \alpha_2(r_2, r_2'|i\omega) \, T(r_2', r_1')$$

- universally attractive
- always attractive and decays as R^{-6}
- long-range dynamical correlation

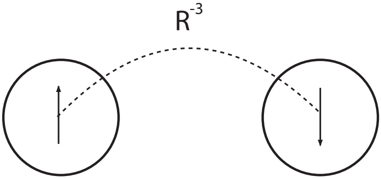
London dispersion forces



$$E_{\mathsf{disp}} = -\frac{1}{2\pi}\int d\omega\, \alpha_1(r_1, r_1'|i\omega)\, T(r_1, r_2)\, \alpha_2(r_2, r_2'|i\omega)\, T(r_2', r_1')$$

- universally attractive
- always attractive and decays as R^{-6}
- long-range dynamical correlation

London dispersion forces



$$E_{\text{disp}} = -\frac{1}{2\pi}\int d\omega\, \alpha_1(r_1, r_1'|i\omega)\, T(r_1, r_2)\, \alpha_2(r_2, r_2'|i\omega)\, T(r_2', r_1')$$

- universally attractive
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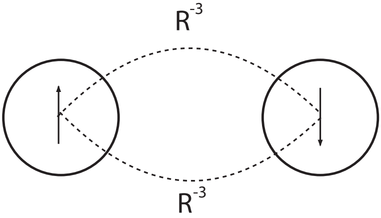
London dispersion forces



$$E_{\text{disp}} = -\frac{1}{2\pi}\int d\omega\, \alpha_1(r_1, r_1'|i\omega)\, T(r_1, r_2)\, \alpha_2(r_2, r_2'|i\omega)\, T(r_2', r_1')$$

- universally attractive
- always attractive and decays as R^{-6}
- long-range dynamical correlation

Long-range intermolecular RSPT

The solution of the Schrödinger equation for the non-interacting complex

$$\left(\hat{H}^A + \hat{H}^B\right) \varphi_k = E_0 \varphi_k$$

can be obtained from the solutions of the isolated subsystem Schrödinger equations

$$\hat{H}^A \psi_a^A = E_a^A \psi_a^A \qquad \hat{H}^B \psi_b^B = E_b^B \psi_b^B$$

$$\hat{H}^X = \sum_{i \in X} \left(\hat{T}_i - \sum_{\alpha \in X} \frac{Z_\alpha}{r_{i\alpha}} \right) + \sum_{\substack{i,j \in X \\ i<j}} \frac{1}{r_{ij}} + \sum_{\substack{a,b \in X \\ \alpha < \alpha'}} \frac{Z_\alpha Z_{\alpha'}}{R_{\alpha\alpha'}}$$

as simple products (not antisymmetric for intermolecular electron exchange) of the monomer wave functions

$$\varphi_k = \psi_a^A \psi_b^B$$

and the eigenvalues are the sum of monomer eigenvalues

$$E_k = E_a^A + E_b^B$$

Partition of the Hamiltonian

Since the subsystems are distinguishable (preserve their identities), each of the $N = N_A + N_B$ electrons and $M = M_A + M_B$ nuclei can be assigned to one of the subsystems. Subtracting from the total Hamiltonian

$$\hat{H} = \sum_{i=1}^{N_A+N_B} \left(\hat{T}_i - \sum_{\alpha=1}^{M_A+M_B} \frac{Z_\alpha}{r_{i\alpha}} \right) + \frac{1}{2} \sum_{i,j=1}^{N_A+N_B} \frac{1}{r_{ij}} + \sum_{\alpha,\beta=1}^{M_A+M_B} \frac{Z_\alpha Z_{\alpha'}}{R_{\alpha\alpha'}}$$

the sum of monomer Hamiltonians one obtains the operator of the intermolecular interaction

$$\hat{V} = \sum_{\alpha\in A} \sum_{\beta\in B} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \sum_{i\in A} \sum_{\beta\in B} \frac{Z_\beta}{r_{i\beta}} - \sum_{\alpha\in A} \sum_{j\in B} \frac{Z_a}{r_{\alpha j}} + \sum_{i\in A} \sum_{j\in B} \frac{1}{r_{ij}}$$

In the absence of any "natural" perturbation parameter, we shall consider an adiabatic switching of the interaction between the subsystems:

$$\hat{H}(\lambda) = \hat{H}^A + \hat{H}^B + \lambda \hat{V}$$

Longuet-Higgins form of the interaction operator

The interaction operator can be written in a more compact and separable form, based on the charge density operator, defined as

$$\hat{\varrho}^X(\boldsymbol{r}) = \sum_{\alpha \in X} Z_\alpha \delta(\boldsymbol{r} - \boldsymbol{R}_\alpha) - \sum_{i \in X} \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

with the matrix elements

$$\langle \psi_a | \hat{\varrho}^A(\boldsymbol{r}) | \psi_{a'} \rangle = \delta_{aa'} \sum_{\alpha \in X} Z_\alpha \delta(\boldsymbol{r} - \boldsymbol{R}_\alpha) - P(aa' | \boldsymbol{r}, \boldsymbol{r}')$$

where $P(aa'|\boldsymbol{r}, \boldsymbol{r}')$ is an element one the one particle density matrix.

The state charge density

$$\varrho_{aa}(\boldsymbol{r}) = \sum_{\alpha \in X} Z_\alpha \delta(\boldsymbol{r} - \boldsymbol{R}_\alpha) - P(aa|\boldsymbol{r}, \boldsymbol{r})$$

contains the contribution of both electrons and nuclei.

Transition charge density

$$\varrho_{aa'}(\boldsymbol{r}) = -P(aa'|\boldsymbol{r}, \boldsymbol{r})$$

Using $\hat{\varrho}(\boldsymbol{r})$ and the Coulomb-kernel function, $T(\boldsymbol{r}, \boldsymbol{r}') = |\boldsymbol{r} - \boldsymbol{r}'|$, the interaction operator is

$$\hat{V} = \int d\boldsymbol{r} \int d\boldsymbol{r}' \, \hat{\varrho}^A(\boldsymbol{r}) T(\boldsymbol{r}, \boldsymbol{r}') \hat{\varrho}^B(\boldsymbol{r}')$$

By a straightforward generalization of the Einstein summation convention

$$\hat{V} = \hat{\varrho}^A_{\boldsymbol{r}} T_{\boldsymbol{r},\boldsymbol{r}'} \hat{\varrho}^B_{\boldsymbol{r}'}$$

The polarization approximation

Direct application of the RSPT to the the above problem with the eigenfunction of $\hat{H}_0 = \hat{H}_A + \hat{H}_B$ as zeroth order wave function:

$$E^{(n)}_{\text{pol}} = \langle \varphi_0 | \hat{V} | \varphi^{(n-1)}_{\text{pol}} \rangle$$

$$\varphi^{(n)}_{\text{pol}} = -\hat{R}_0 \hat{V} \varphi^{(n-1)}_{\text{pol}} - \sum_{k=1}^{n-1} \Delta E^{(k)} \hat{R}_0 \varphi^{(n-k)}_{\text{pol}}$$

This is called the polarization approximation (antisymmetry requirement neglected).

First order: electrostatic energy

The first-order interaction energy in this approximation is

$$E^{(1)}_{\mathsf{pol}} = \langle \psi^A_0 \psi^B_0 | \hat{V} | \psi^A_0 \psi^B_0 \rangle$$

Using the Longuet-Higgins operator

$$E^{(1)}_{\mathsf{pol}} = \int d\boldsymbol{r} \int d\boldsymbol{r}' \langle \psi^A | \hat{\varrho}^A(\boldsymbol{r}) | \psi^A \rangle T(\boldsymbol{r}, \boldsymbol{r}') \langle \psi^B | \hat{\varrho}^B(\boldsymbol{r}') | \psi^B \rangle$$

it is easy to see that it is the Coulomb interaction of the charge densities of the two subsystems.

$$E^{(1)}_{\mathsf{pol}} = \int d\boldsymbol{r} \int d\boldsymbol{r}' \, \varrho^A_{00}(\boldsymbol{r}) T(\boldsymbol{r}, \boldsymbol{r}') \varrho^B_{00}(\boldsymbol{r}')$$

Electrostatic potential of the subsystems

$$V^A(\boldsymbol{r}) = \int d\boldsymbol{r}' T(\boldsymbol{r}, \boldsymbol{r}') \varrho^A_{00}(\boldsymbol{r}') \qquad V^B(\boldsymbol{r}) = \int d\boldsymbol{r}' T(\boldsymbol{r}, \boldsymbol{r}') \varrho^B_{00}(\boldsymbol{r}')$$

Alternative form of the first order interaction energy

$$E^{(1)}_{\mathsf{pol}} = \int d\boldsymbol{r} \, \varrho^A_{00}(\boldsymbol{r}) V^B(\boldsymbol{r}) = \int d\boldsymbol{r} \, \varrho^B_{00}(\boldsymbol{r}) V^A(\boldsymbol{r})$$

Second order energy in the polarization approximation

The second-order interaction energy

$$E^{(2)}_{\text{pol}} = -\sum_{ab \neq 00} \frac{|\langle \psi_0^A \psi_0^B | \hat{V} | \psi_a^A \psi_b^B \rangle|^2}{\Delta E^A_{0a} + \Delta E^B_{0b}}$$

can be written as a sum of three terms, each having a different physical meaning.

$$\begin{aligned} E^{(2)}_{\text{pol}} = & -\sum_{b \neq 0} \frac{|\langle \psi_0^A \psi_0^B | \hat{V} | \psi_0^A \psi_b^B \rangle|^2}{\Delta E^B_{0b}} && \text{induction} \quad A \rightarrow B \\ & -\sum_{a \neq 0} \frac{|\langle \psi_0^A \psi_0^B | \hat{V} | \psi_a^A \psi_0^B \rangle|^2}{\Delta E^A_{0a}} && \text{induction} \quad A \leftarrow B \\ & -\sum_{\substack{a \neq 0 \\ b \neq 0}} \frac{|\langle \psi_0^A \psi_0^B | \hat{V} | \psi_a^A \psi_b^B \rangle|^2}{\Delta E^A_{0a} + \Delta E^B_{0b}} && \text{dispersion} \end{aligned}$$

These terms correspond to the following decomposition of the reduced resolvent

$$\hat{R}_0 = \sum_{\substack{a,b \\ (ab) \neq (00)}} \frac{|\psi_a^A \psi_b^B \rangle \langle \psi_a^A \psi_b^B|}{E_a^A - E_0^A + E_a^B - E_0^B} = R_0^A O^A + R_0^B O^B + R_0^{AB} = R_0(\text{ind}) + R_0(\text{disp})$$

Induction energy

$$\begin{aligned}\Delta E^{(2)}(\mathsf{ind}, A \leftarrow B) &= -\langle \psi_0^A \psi_0^B | \hat{V} \hat{R}_0^A \hat{O}^B \hat{V} | \psi_0^A \psi_0^B \rangle \\ &= -V_{\boldsymbol{r}}^B \langle \varrho_{\boldsymbol{r}}^A \hat{R}_0 \varrho_{\boldsymbol{r}'}^A \rangle V_{\boldsymbol{r}}^B = -\frac{1}{2} V_{\boldsymbol{r}}^B K(\varrho_{\boldsymbol{r}}^A, \varrho_{\boldsymbol{r}'}^A) V_{\boldsymbol{r}}^B\end{aligned}$$

The $K(\varrho_{\boldsymbol{r}}^A, \varrho_{\boldsymbol{r}'}^A) = \alpha(\boldsymbol{r}, \boldsymbol{r}'; \omega = 0)$ charge density linear response function (susceptibility) is a kind of generalized polarizability function, which gives the induced charge density in a static external potential

$$\Delta \varrho^A(\boldsymbol{r}) = \int d\boldsymbol{r}' \alpha(\boldsymbol{r}, \boldsymbol{r}'; \omega = 0) V^B(\boldsymbol{r}')$$

The sum-over-states definition of the charge density susceptibility at the ω frequency is

$$\alpha(\boldsymbol{r}, \boldsymbol{r}'; \omega) = \frac{1}{\hbar} \sum_{a \neq 0} \frac{\left[\langle 0 | \hat{\varrho}(\boldsymbol{r}) | a \rangle \langle 0 | \hat{\varrho}(\boldsymbol{r}') | a \rangle + \langle 0 | \hat{\varrho}(\boldsymbol{r}') | a \rangle \langle 0 | \hat{\varrho}(\boldsymbol{r}) | a \rangle\right] \omega_{0a}}{\omega_{0a}^2 - \omega^2}$$

The induction energy can be regarded as the stabilization energy due to interaction of the induced charge density with the electrostatic potential of the partner

$$\Delta E^{(2)}_{\text{stab}} = -\int d\boldsymbol{r} \Delta\varrho^{A}(\boldsymbol{r}) V^{B}(\boldsymbol{r})$$

partially compensated by the (positive) deformation energy, spent to polarize the charge distribution

$$\Delta E^{(2)}_{\text{def}} = -\frac{1}{2}\Delta E^{(2)}_{\text{stab}}$$

Which means that the induction energy

$$\Delta E^{(2)}(\text{ind}, A \leftarrow B) = \Delta E^{(2)}_{\text{stab}} + \Delta E^{(2)}_{\text{def}} = \frac{1}{2}\Delta E^{(2)}_{\text{stab}}$$

is the half of the stabilization energy (in the linear response approximation).
Note: do not mix up the terminology "polarization" and "induction"...

Dispersion energy

$$\begin{aligned}\Delta E^{(2)}(\mathsf{disp}) &= -\langle \psi_0^A \psi_0^B | \hat{V} \hat{R}_0^{AB} \hat{V} | \psi_0^A \psi_0^B \rangle \\ &= \iiiint T(\boldsymbol{r}, \boldsymbol{s}) T(\boldsymbol{r}', \boldsymbol{s}') \frac{1}{\hbar} \sum_{a \neq 0} \sum_{b \neq 0} \frac{\varrho_{0a}^A(\boldsymbol{r}) \varrho_{0a}^A(\boldsymbol{r}') \varrho_{0b}^B(\boldsymbol{s}) \varrho_{0b}^B(\boldsymbol{s}')}{\omega_{0a}^A + \omega_{0b}^B}\end{aligned}$$

We can transform the double sum according to subsystems using the following identity

$$\frac{1}{x+y} = \frac{2}{\pi} \int_0^\infty \frac{x}{x^2+\omega^2} \frac{y}{y^2+\omega^2} d\omega$$

which leads to a separable form at the expense of an additional integral in the frequency domain

$$\begin{aligned}\Delta E^{(2)}(\mathsf{disp}) = \iiiint T(\boldsymbol{r}, \boldsymbol{s}) T(\boldsymbol{r}', \boldsymbol{s}') \times \\ \frac{2}{\pi} \int d\omega \frac{1}{\hbar} \sum_{a \neq 0} \frac{\omega_{0a}^A \varrho_{0a}^A(\boldsymbol{r}) \varrho_{0a}^A(\boldsymbol{r}')}{{\omega_{0a}^A}^2 + \omega^2} \sum_{b \neq 0} \frac{\omega_{0b}^B \varrho_{0b}^B(\boldsymbol{s}) \varrho_{0b}^B(\boldsymbol{s}')}{{\omega_{0b}^B}^2 + \omega^2}\end{aligned}$$

Dispersion energy

We can recognize in the two separate sums the dynamic charge density susceptibilities at imaginary frequencies of both subsystems, i.e.

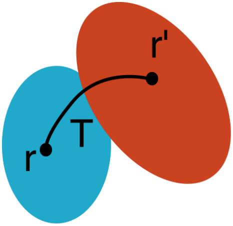
$$\alpha(\boldsymbol{r},\boldsymbol{r}';i\omega)=\frac{1}{\hbar}\sum_{a\neq 0}\frac{\left[\langle 0|\hat{\varrho}(\boldsymbol{r})|a\rangle\langle 0|\hat{\varrho}(\boldsymbol{r}')|a\rangle+\langle 0|\hat{\varrho}(\boldsymbol{r}')|a\rangle\langle 0|\hat{\varrho}(\boldsymbol{r})|a\rangle\right]\omega_{0a}}{\omega_{0a}^2+\omega^2}$$

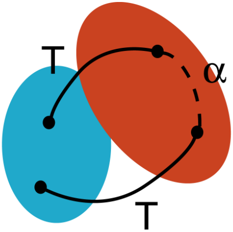
Final expression of the dispersion energy (Casimir-Polder)

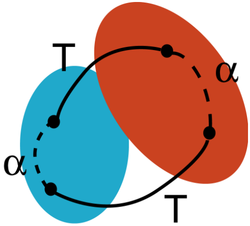
$$\Delta E^{(2)}(\mathrm{disp})=\frac{\hbar}{2\pi}\int_0^\infty d\omega\iiiint d\boldsymbol{r}\,d\boldsymbol{r}'\,d\boldsymbol{s}\,d\boldsymbol{s}'\times$$
$$\times\,\alpha^A(\boldsymbol{r},\boldsymbol{r}';i\omega)T(\boldsymbol{r}',\boldsymbol{s}')\alpha^B(\boldsymbol{s},\boldsymbol{s}';i\omega)T(\boldsymbol{r},\boldsymbol{s})$$

Corresponds to the Coulomb correlation of fluctuating charge densities of the two systems. (Cf. fluctuation-dissipation theorem).

Summary of second order terms







$\varrho^A_r T_{rs} \varrho^B_s$ $\varrho^A_r T_{rs} \alpha^B_{ss'} T_{s'r'} \varrho^A_{r'}$ $T_{rs} \alpha^B_{ss'} T_{s'r'} \alpha^A_{r'r}$

electrostatic induction dispersion

Third order induction energy

Third order energy

$$\Delta E^{(3)} = \varphi_0|\hat{V}\hat{R}_0(\hat{V} - \langle\hat{V}\rangle)\hat{R}_0\hat{V}|\varphi_0\rangle$$

Decomposition of the reduced resolvent

$$R_0(\mathrm{ind}) = R_0^A O^B + O^A R_0^B \qquad R_0(\mathrm{disp}) = R_0^{AB}$$

Pure induction part of the third order energy can be expanded

$$\begin{aligned}\Delta E^{(3)}(\mathrm{ind}) &= \langle\varphi_0|\hat{V}\hat{R}_0(\mathrm{ind})\left[\hat{V} - \langle\hat{V}\rangle\right]\hat{R}_0(\mathrm{ind})\hat{V}|\varphi_0\rangle \\ &= T_{rs}T_{r's'}T_{r''s''}\times \\ &\langle\varphi_0^A\varphi_0^B|\hat{\varrho}_r^A\hat{\varrho}_s^B\hat{R}_0(\mathrm{ind})\left[\hat{\varrho}_r^A\hat{\varrho}_s^B - \langle\hat{\varrho}_{r'}^A\hat{\varrho}_{s'}^B\rangle\right]\hat{R}_0(\mathrm{ind})\ \hat{\varrho}_{r''}^A\hat{\varrho}_{s''}^B|\varphi_0^A\varphi_0^B\rangle\end{aligned}$$

Two kinds of terms are obtained

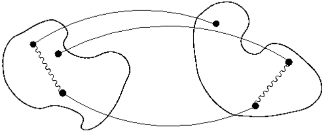
- hyperpolarizability term (nonlinear response), e.g.

$$T_{rs}T_{r's'}T_{r''s''}\langle\hat{\varrho}_r^A\rangle\langle\hat{\varrho}_{r'}^A\rangle\langle\hat{\varrho}_{r''}^A\rangle\underbrace{\langle\hat{\varrho}_s^B\,\hat{R}_0^B\,(\hat{\varrho}_{s'}^B-\langle\hat{\varrho}_{s'}^B\rangle)\hat{R}_0^B\,\hat{\varrho}_{s''}^B\rangle}_{\frac{1}{6}\beta^B(s,s',s'')}$$

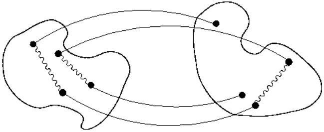
- iterated linear response terms, e.g.

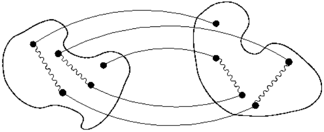
$$T_{rs}T_{r's'}T_{r''s''}\langle\hat{\varrho}_r^A\rangle\underbrace{\langle\hat{\varrho}_s^B\,\hat{R}_0^B\,\hat{\varrho}_{s'}^B\rangle}_{\frac{1}{2}\alpha^B(s,s')}\underbrace{\langle\hat{\varrho}_{r'}^A\,\hat{R}_0^A\,\hat{\varrho}_{r''}^A\rangle}_{\frac{1}{2}\alpha^A(r',r'')}\langle\hat{\varrho}_{s''}^B\rangle$$

Graphical representation of the iterated linear response terms



Analogous terms appear in higher order terms, that can be iterated up to self-consistency





The Hamiltonian operator of a ternary complex

$$\hat{H}_A + \hat{H}_B + \hat{H}_C + \hat{V}_{AB} + \hat{V}_{AC} + \hat{V}_{BC}$$

is "additive".

- First order energy is strictly additive

$$\begin{aligned}
\Delta E^{(1)}_{ABC} &= \langle \psi^A \psi^B \psi^C | \hat{V}_{AB} + \hat{V}_{AC} + \hat{V}_{BC} | \psi^A \psi^B \psi^C \rangle \\
&= \langle \psi^A \psi^B | \hat{V}_{AB} | \psi^A \psi^B \rangle \langle \psi^C | \psi^C \rangle + \\
&+ \langle \psi^A \psi^C | \hat{V}_{AC} | \psi^A \psi^C \rangle \langle \psi^B | \psi^B \rangle + \\
&+ \langle \psi^B \psi^C | \hat{V}_{BC} | \psi^B \psi^C \rangle \langle \psi^A | \psi^A \rangle \\
&= \Delta E^{(2)}_{AB} + \Delta E^{(2)}_{AC} + \Delta E^{(2)}_{BC}
\end{aligned}$$

- Second order energy

$$\Delta E^{(2)}_{ABC} = \langle \psi^A \psi^B \psi^C | (\hat{V}_{AB} + \hat{V}_{AC} + \hat{V}_{BC}) \hat{R}_0 (\hat{V}_{AB} + \hat{V}_{AC} + \hat{V}_{BC}) | \psi^A \psi^B \psi^C \rangle$$

The resolvent can be decomposed as

$$\begin{aligned}
\hat{R}_0 &= \hat{R}_0^{ABC} \\
&+ \hat{R}_0^{AB} \hat{O}^C + \hat{R}_0^{BC} \hat{O}^A + \hat{R}_0^{CA} \hat{O}^B && \text{2-body dispersion} \\
&+ \hat{R}_0^{A} \hat{O}^B \hat{O}^C + \hat{R}_0^{B} \hat{O}^C \hat{O}^A + \hat{R}_0^{C} \hat{O}^A \hat{O}^B && \text{induction}
\end{aligned}$$

Three types of contributions according to the interaction operators

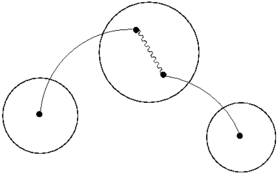
- "Diagonal" term

$$\begin{aligned}&\langle\psi^A\psi^B\psi^C|\hat{V}_{AB}\hat{R}_0\hat{V}_{AB}|\psi^A\psi^B\psi^C\rangle =\\ &\langle\psi^A\psi^B|\hat{V}_{AB}\langle\psi^C|\hat{R}_0|\psi^C\rangle\hat{V}_{AB}|\psi^A\psi^B\rangle =\\ &\langle\psi^A\psi^B|\hat{V}_{AB}(\hat{R}_0^{AB}+\hat{R}_0^{A}\hat{O}^B+\hat{R}_0^{B}\hat{O}^A)\hat{V}_{AB}|\psi^A\psi^B\rangle = \Delta E_{AB}^{(2)}\end{aligned}$$

- "Off-diagonal" term

$$\begin{aligned}&\langle\psi^A\psi^B\psi^C|\hat{V}_{AB}\hat{R}_0\hat{V}_{AC}|\psi^A\psi^B\psi^C\rangle =\\ &\langle\psi^A\psi^B|\hat{V}_{AB}\langle\psi^C|\hat{R}_0|\psi^B\rangle\hat{V}_{AC}|\psi^A\psi^C\rangle =\\ &\langle\psi^A\psi^B|\hat{V}_{AB}|\psi^B\rangle\hat{R}_0^A\langle\psi^C|\hat{V}_{AC}|\psi^A\psi^C\rangle =\\ &T_{rs}T_{r's'}\varrho_s^B\langle\hat{\varrho}_r^A\hat{R}_0^A\hat{\varrho}_{r'}^A\rangle\varrho_{s'}^C\end{aligned}$$

non-additive 3-body induction interaction.



London dispersion energy

Dispersion interaction energy in spherical tensor formalism

$$E^{(2)}(\mathsf{disp}) = -\sum_{a\neq 0}\sum_{b\neq 0}\sum_{\ell_A m_A}\sum_{\ell_B m_B}$$

$$\times\ \frac{\langle 00|\hat{Q}^A_{\ell_A m_A} T_{\ell_A m_A,\ell_B m_B} \hat{Q}^B_{\ell_B m_B}|ab\rangle\langle ab|\hat{Q}^A_{\ell'_A m'_A} T_{\ell'_A m'_A,\ell'_B m'_B} \hat{Q}^B_{\ell'_B m'_B}|00\rangle}{\Delta E^A_{0a} + \Delta E^B_{0b}}$$

Applying the Casimir-Polder method

$$E^{(2)}(\mathsf{disp}) = -\frac{2}{\hbar\pi} T_{\ell_A m_A,\ell_B m_B} T_{\ell'_A m'_A,\ell'_B m'_B} \times$$

$$\times \int d\omega \sum_{a\neq 0}^{\infty} \frac{\langle 0|\hat{Q}^A_{\ell_A m_A}|a\rangle\langle a|\hat{Q}^A_{\ell'_A m'_A}|0\rangle\omega_{0a}}{\omega^2_{0a}+\omega^2} \sum_{b\neq 0}^{\infty} \frac{\langle 0|\hat{Q}^B_{\ell_B m_B}|b\rangle\langle b|\hat{Q}^B_{\ell'_B m'_B}|0\rangle\omega_{0b}}{\omega^2_{0b}+\omega^2}$$

Dynamic (frequency-dependent) multipole polarizabilities in molecule-fixed frame

$$\alpha_{\ell m,\ell' m'}(\omega) = \sum_{n\neq 0} \frac{2\omega_{0n}\langle 0|\hat{Q}_{\ell m}|a\rangle\langle a|\hat{Q}_{\ell' m'}|0\rangle}{\omega_{0a}^2 - \omega^2}$$

related to the charge density susceptibility

$$\alpha_{\ell m,\ell' m'}(\omega) = \iint d\boldsymbol{r}\, d\boldsymbol{r}' R_{\ell m}(\boldsymbol{r})\alpha(\boldsymbol{r},\boldsymbol{r}'|\omega)R_{\ell' m'}(\boldsymbol{r}')$$

Dispersion energy

$$E^{(2)}(\mathrm{disp}) = -\sum T_{\ell_A m_A,\ell_B m_B} T_{\ell'_A m'_A,\ell'_B m'_B} X^{AB}_{\ell_A m_A \ell_B m_B \ell'_A m'_A,\ell'_B m'_B}$$

The Casimir-Polder or dispersion integrals are defined as

$$X^{AB}_{\ell_A m_A \ell_B m_B \ell'_A m'_A, \ell'_B} = \frac{\hbar}{2\pi} \int d\omega \alpha^{A}_{\ell_A m_A, \ell'_A m'_A}(i\omega) \alpha^{B}_{\ell_B m_B, \ell'_B m'_B}(i\omega)$$

The dispersion integrals can be calculated by numerical quadrature as

$$X^{AB} = \frac{\hbar}{2\pi} \sum_{j=1}^{M} w(\omega_j) \alpha^{A}(i\omega_j) \alpha^{B}(i\omega_j)$$

With a Gauss-Chebyshev quadrature scheme the grid points are chosen as

$$\omega_j = \cot\left(\pi \frac{2j-1}{4M}\right)$$

and the weights

$$w(\omega_j) = \frac{2\pi}{4M \sin^2(\pi(2j-1)/4M)}$$

Typically, with 5 and 7 grid points one has an accuracy of 0.1 %.

Numerically more efficient procedure (for high-rank calculations) is to contract first the polarizabilities with the interaction tensors (in local frame) and perform the numerical integration afterwards (Hättig, 1996).
In this form the interaction tensors and X^{AB} are both reducible: they transform according to the double and quadruple product group of $SO(3)$. In terms of irreducible tensors, the dispersion coefficients are of the form (Wormer)

$$C^{L_A L_B L}_{\ell_A \ell'_A \ell_B \ell'_B} = \sum_{m_A m'_A} \sum_{m_B m'_B} X^{AB}_{\ell_A m_A \ell_B m_B \ell'_A m'_A, \ell'_B m'_B} \cdot \text{factor}$$

The algebraic factor depends on the Wigner $3j$ and $9j$ coefficients. These coefficients are coupled to the following form

$$C^{L_A L_B L}_n \qquad (n = \ell_A + \ell_B + \ell'_A + \ell'_B + 2)$$

For atoms in S-state, for example,

$$E^{(2)}_{\text{disp}} = -\sum_{n=3}^{\infty} C_{2n} R^{-2n}$$

$$C_{2n} = \sum_{\ell=1}^{n-2} C(\ell; n-k-1)$$

$$C(\ell;\ell') = \frac{(2\ell+2\ell')!}{(2\ell)!(2\ell')!} \frac{1}{2\pi} \int d\omega \alpha^A_\ell(i\omega) \alpha^B_{\ell'}(i\omega)$$

The dispersion integral depends on the properties of the individual molecules and independent of the intermolecular geometry. The complete expression can be expressed in terms of irreducible spherical tensor components.

- dipole-dipole leading term $R^{-3}R^{-3} \sim R^{-6}$
- dipole-quadrupole would be $R^{-3}R^{-4} \sim R^{-7}$,
  after averaging over all orientations, it gives zero
- quadrupole-quadrupole term $R^{-4}R^{-4} \sim R^{-8}$
- dipole-octopole and quadrupole-qudrupole R^{-10}

Dipolar dispersion energy

The leading multipolar term in the dispersion interaction energy

$$E^{(2)}(\text{disp}) = -\sum_{a\neq 0}\sum_{b\neq 0} \frac{\langle 00|\hat{\mu}^A_\alpha T_{\alpha\beta}\hat{\mu}^B_\beta|ab\rangle\langle ab|\hat{\mu}^A_\gamma T_{\gamma\delta}\hat{\mu}^B_\delta|00\rangle}{\Delta E^A_{0a} + \Delta E^B_{0b}}$$

- Casimir-Polder formula

$$E^{(2)}(\text{disp}) = -T_{\alpha\beta}T_{\gamma\delta}\frac{2}{\hbar\pi}\int d\omega \sum_{a\neq 0}^{\infty}\frac{\langle 0|\hat{\mu}^A_\alpha|a\rangle\langle a|\hat{\mu}^A_\gamma|0\rangle\omega_{0a}}{\omega_{0a}^2+\omega^2}\sum_{b\neq 0}^{\infty}\frac{\langle 0|\hat{\mu}^B_\beta|b\rangle\langle b|\hat{\mu}^B_\delta|0\rangle\omega_{0b}}{\omega_{0b}^2+\omega^2}$$

- Unsöld approximation

$$E^{(2)}(\text{disp}) = -T_{\alpha\beta}T_{\gamma\delta}\sum_{a\neq 0}^{\infty}\sum_{b\neq 0}^{\infty}\frac{\Delta E^A_{0a}\Delta E^B_{0b}}{\Delta E^A_{0a}+\Delta E^B_{0b}}\frac{\langle 0|\hat{\mu}^A_\alpha|a\rangle\langle a|\hat{\mu}^A_\gamma|0\rangle}{\omega^A_{0a}}\frac{\langle 0|\hat{\mu}^B_\beta|b\rangle\langle b|\hat{\mu}^B_\delta|0\rangle}{\omega^B_{0b}}$$

In order to factor this latter expression, we use the identity

$$\frac{\Delta E_{0a}^{A} \Delta E_{0b}^{B}}{\Delta E_{0a}^{A} + \Delta E_{0b}^{B}} = \frac{U_A U_B}{U_A + U_B}(1 + \Delta_{ab})$$

with

$$\Delta_{ab} = \frac{1/U_A - 1/E_{0a}^{A} + 1/U_B - 1/E_{0b}^{B}}{1/E_{0a}^{A} + 1/E_{0b}^{B}}$$

that can be made negligibly small by choosing appropriate average excitation energies U_A and U_B

$$E^{(2)}(\text{disp}) \approx -\frac{U_A U_B}{4(U_A + U_B)} T_{\alpha\beta} T_{\gamma\delta} \alpha_{\alpha\gamma}^{A} \alpha_{\beta\delta}^{B}$$

In both expressions we can separate the orientation-independent spherically averaged and various orientation-dependent components, by using the decomposition of the polarizabilities to irreducible parts. The spherically averaged component becomes in both cases

$$T_{\alpha\beta}T_{\gamma\delta}\alpha^A\delta_{\alpha\gamma}\alpha^B\delta_{\beta\delta} = \alpha^A\alpha^B T_{\alpha\beta}T_{\alpha\beta} = \alpha^A\alpha^B\frac{6}{R^6}$$

leading to the general expression

$$E^{(2)}(\text{disp}) \approx -\frac{C_6}{R^6}$$

with the C_6 coefficient

$$C_6 = 3\hbar\int d\omega\alpha^A(i\omega)\alpha^B(i\omega) \qquad \text{(Casimir-Polder)}$$

$$C_6 \approx \frac{3U_AU_B}{2(U_A+U_B)}\alpha^A\alpha^B \qquad \text{(London)}$$

Experimental oscillator strength distributions can be used to determine "experimental" C_6 coefficients.
Roughly proportional to the square of the polarizability/volume.
Some typical values

system	C_6	C_8	C_{10}
H· · · H	6.5	124.4	1135
He· · · He	1.46	13.9	182
Ne· · · Ne	6.6	57	700
Ar· · · Ar	64.3	1130	25000
Kr· · · Kr	133	2500	60000
Xe· · · Xe	286		

Combining rules can be deduced from the London-formula

$$C_6^{AB} \approx \sqrt{C_6^{AA}\, C_6^{BB}}$$

Approximate dispersion energy

The average excitation energy of the London formula is an empirical parameter, either the first ionization potential (quite bad) or the first excitation energy (somewhat better) is used.
Similar expressions can be derived from the Casimir-Polder expression, by considering some general properties of the average dynamic dipole-dipole polarizabilities

$$\alpha(i\omega) = \frac{1}{\hbar} \sum_{k \neq 0} \frac{2\omega_{0k} |\langle 0|\hat{x}|k\rangle|^2}{\omega_{0k}^2 + \omega^2}$$

We are looking for the simplest, one-term approximation in the form

$$\alpha(i\omega) \approx \frac{\overline{\omega}^2}{\overline{\omega}^2 + \omega^2} \cdot a$$

Parameters a and $\overline{\omega}$ will be found from the asymptotic behaviour of $\alpha(i\omega)$.

For $\omega = 0$ one gets the static polarizability, $a = \alpha(0)$.
For $\omega \to \infty$ one gets the Thomas-Reiche-Kuhn sum rule, the number of electrons

$$\alpha(i\omega) \to \frac{1}{\hbar^2\omega^2} \sum_{n\neq 0} 2\Delta E_{0n} x_{0n}^2 = \frac{n}{\hbar^2\omega^2}$$

In this limit we have

$$\begin{aligned} \frac{a}{\omega^2/\overline{\omega}^2} &= \frac{n}{\hbar^2\omega^2} \\ \overline{\omega}^2 &= \frac{n}{\hbar^2\alpha(0)} \\ \overline{\omega} &= \frac{1}{\hbar}\sqrt{\frac{n}{\alpha(0)}} \end{aligned}$$

which leads to the Mavroyannis-Stephen (Slater-Kirkwood) approximation

$$C_6 \approx \frac{3\alpha^A\alpha^B}{(\alpha^A/n^A)^{1/2} + (\alpha^B/n^B)^{1/2}}$$

Take another, equivalent form of the dynamic polarizability

$$\alpha(\omega) = \alpha^+(\omega) + \alpha^+(-\omega) = \frac{1}{3\hbar}\sum_{n\neq 0}\frac{|\boldsymbol{r}_{on}|^2}{\omega_{0n}+\omega} + \frac{1}{3\hbar}\sum_{n\neq 0}\frac{|\boldsymbol{r}_{on}|^2}{\omega_{0n}-\omega}$$

For $\omega = 0$

$$\alpha^+(\omega) = \frac{1}{2}\alpha(0)$$

For $\omega \to \infty$

$$\hbar\omega\alpha^+(\omega) \to \frac{1}{3}\sum_{n\neq 0}|\boldsymbol{r}_{0n}|^2 = \frac{1}{3}\left[\langle 0|\boldsymbol{r}^2|0\rangle - \langle 0|\boldsymbol{r}|0\rangle^2 = \frac{1}{3}(\Delta\boldsymbol{r})^2\right.$$

Considering a one-term approximation

$$\alpha^+(\omega) = \frac{a'}{\hbar(\overline{\omega}' + \omega)}$$

Taking the limiting cases one obtains

$$a' = \frac{1}{2}\alpha(0) \qquad\qquad \overline{\omega} = \frac{2}{3\hbar}\,\frac{(\Delta \boldsymbol{r})^2}{\alpha}$$

and we get the Salem-Tang-Karplus approximation

$$C_6 = \frac{\alpha^A \alpha^B}{\alpha^A/(\Delta \boldsymbol{r}_A)^2 + \alpha^B(\Delta \boldsymbol{r}_B)^2}$$

For dimers it is identical to the Alexander upper bound

$$C_6 \leq \frac{3}{4}S(-2)S(-1) = \frac{1}{2}\alpha(\Delta \boldsymbol{r}_B)^2$$

Solutions of the H + H dispersion problem

The multipolar interaction Hamiltonian for two H atoms lying on the z axis, separated by a distance R_0 is

$$\begin{aligned}\hat{V} = & -2[R_0^{-3}\xi_1\xi_2 \cos\theta_1 \cos\theta_2 \\ & + \beta\xi_1\xi_2^2 \cos\theta_1(3\cos^2\theta_2 - 1) \\ & + \gamma\xi_1^2\xi_2^2(3\cos^2\theta_1 - 1)(3\cos^2\theta_2 - 1) + \ldots\end{aligned}$$

with polar coordinates $\xi_{1,2} = r_{1,2}$, $\alpha = (\sqrt{6}/2)R_0^{-3}$, $\beta = (\sqrt{(}30)/4)R_0^{-4}$ and $\gamma = (\sqrt{70}/8)R^{-5}$.
By direct summation over the excited states, Eisenchitz and London obtained for the dipolar dispersion energy

$$E^{(2)} = -\frac{12}{R_0^6}\sum_{n,m}\frac{\Delta E_{0n} z_{0n}^2 \Delta E_{0m} z_{0m}^2}{\left(1 - \frac{1}{n^2}\right)\left(1 - \frac{1}{m^2}\right)\left(2 - \frac{1}{n^2} - \frac{1}{m^2}\right)}$$

It is difficult to make converge this expression, because of the discrete-continuum matrix elements. The best value is $C_6 = 6.47$.

The difficulties of the sum-over-states solution can be avoided by solving directly for the first-order wave function using the Ansatz proposed by Slater and Kirkwood,

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_0(r_1, r_2)[1 + \phi(\boldsymbol{r}_1, \boldsymbol{r}_2)]$$

with the ground state unperturbed wave function of the dimer, $\psi_0(r_1, r_2)$. The two-particle correlation function, ϕ, satisfies the differential equation

$$\frac{1}{2}\boldsymbol{\nabla}^2\phi + (\boldsymbol{\nabla} \ln \psi_0) \cdot \boldsymbol{\nabla}\phi) - v = 0$$

where v can be one of the multipolar terms of the interaction Hamiltonian. Taking the correlation function in the form

$$\phi = \frac{vR(\xi, \xi')}{E_0}$$

leads to a differential equation for $R(\xi, \xi')$.
Slater and Kirkwood (1931) obtained an approximate solution, leading to $C_6 = 6.23$. Pauling and Beach (1935) used special orbitals to construct the Hamiltonian matrix and obtained $C_6 = 6.49903$, $C_8 = 124.399$ and $C_{10} = 1135.21$. Recent exact solutions obtained by Choy (P.R.A. 62 (2000) 012506) using orthogonal polynomials, confirm these values.

Part VI

Short-range forces and their origin

Short-range forces and their origin

- Penetration effects
- Overlap repulsion – failure of the polarization approximation of PT
- Damping effects

Penetration effects: potential in the overlap region

Take a charge distribution

$$\varrho(\boldsymbol{r}) = f(\omega)\sigma(r)$$

with a radial part, which vanishes only at $r \to \infty$. The general expression of the potential is

$$V(\boldsymbol{R}) = \sum_{l=0}^{\infty} \left(\frac{4\pi}{2l+1} \right) \int_0^{\infty} dr r^2 \frac{r_<^l}{r_>^{l+1}} \sigma(r) \sum_{m=-l}^{l} \int d\omega Y_{lm}(\omega) Y_{lm}^*(\Omega)$$

The radial integral should be divided in two parts

$$I(R) = \int_0^R dr r^2 \frac{r^l}{R^{l+1}} \sigma(r) + \int_R^{\infty} dr r^2 \frac{R^l}{r^{l+1}} \sigma(r)$$

Potential in the overlap region

For instance, take an exponential function (STO)

$$\sigma(r) = r^n \mathrm{e}^{-ar}$$

Use the integration rules

$$\int_0^\infty dr r^n \mathrm{e}^{-ar} = \frac{n!}{a^{n+1}} \qquad \int_R^\infty dr r^n \mathrm{e}^{-ar} = \frac{n!}{a^{n+1}} \sum_{k=0}^{n} \frac{(aR)^k}{k!} \mathrm{e}^{-ar}$$

The radial integral

$$I(R) = \frac{n!}{a^{n+1}} \cdot \frac{1}{R^{l+1}} \left[1 - \sum_{k=0}^{n+2+l} \frac{(aR)^k}{k!} \mathrm{e}^{-ar} + R^{2l+1} \sum_{k=0}^{n+1-l} \frac{(aR)^k}{k!} \mathrm{e}^{-ar} \right]$$

The potential of a 1s function $(l = 0, n = 0)$

$$\sigma(r) = \frac{\alpha^3}{\pi^3} \mathrm{e}^{-2\alpha r} \qquad V_{(1s)^2}(\boldsymbol{R}) = \frac{1}{R} \left[1 - (1 + \alpha R) \mathrm{e}^{-2\alpha R} \right]$$

In general, the potential of a charge distribution can be separated to a multipolar and penetration component.

Exact multipolar part of the potential

In quantum chemistry, molecular charge densities are usually developed on Gaussian basis functions

$$\varrho(\boldsymbol{r}) = \sum Z_\alpha \delta(\boldsymbol{r} - \boldsymbol{R}) - \sum_{\mu\nu} P_{\mu\nu} \chi_\mu^*(\boldsymbol{r}) \chi_\nu(\boldsymbol{r})$$

For this case, the multipolar potential can be exactly evaluated.
Let us consider the $\chi_\nu(\boldsymbol{r})$ functions as primitive Gaussian functions of the general form

$$\chi(\boldsymbol{r}) = \mathcal{R}(r) Y_{lm}(\theta, \phi)$$

The electronic contribution to the charge density is the sum of two types of terms:

- One-center densities, both basis functions are on the same atomic center

  $$\varrho_{\mu\nu}(\boldsymbol{r}) = \mathcal{R}_\mu(r)\mathcal{R}_\nu(r)Y_{l_\mu m_\mu}(\omega)Y_{l_\nu m_\nu}(\omega)$$

  Apply the sum rule (Clebsch-Gordan series)

  $$Y_{l_\mu m_\mu}(\omega)Y_{l_\nu m_\nu}(\omega) = \sum_{lm} K_{l_\mu l_\nu l}^{\bar{m}_\mu m_\nu m} Y_{lm}(\omega)$$

  with

  $$|l_\mu - l_\nu| < l < l_\mu + l_\nu \qquad \text{and} \qquad -m_\mu + m_\nu + m = 0$$

  The one-center densities can be written as a finite series of multipolar potentials (maximal order is $l_\mu + l_\nu$) around the natural expansion centre.

- Two-center densities can be handled in an analogous way, by using the Gaussian addition theorem, which leads to the natural expansion centre, the "barycenter"

  $$R_{\mu\nu} = \frac{\alpha_\mu \boldsymbol{R}_\mu + \alpha_\nu \boldsymbol{R}_\nu}{\alpha_\mu + \alpha_\nu}$$

  The multipole expansion wrt to the barycenter is finite, with the highest rank of multipole of $l_\mu + l_\nu$.

Beyond the polarization approximation

The RSPT applied to intermolecular interaction is often called *polarization approximation*, since it neglects effects that are related to the antisymmetry of the total wave function. In the following we shall discuss the failure of the polarisation approximation and one of the possible methods to remedy this situation.

H atom + proton system

Zeroth order Hamiltonian and wave function and the perturbation potential are

$$H_0 = -\frac{1}{2}\Delta - \frac{1}{r_A} \qquad \varphi_0 = 1s_A \qquad \hat{V} = -\frac{1}{r_B} + \frac{1}{R}$$

At $R \leq 0.05$ a.u. (limit of united atoms) RSPT yields

$$E_{el}(R) = -2 + \frac{8}{3}R^2 + \frac{16}{3}R^3 + \mathcal{O}(R^4)$$

For very large intermolecular distances, $R > 12$ a.u., the total energy can be approximated as

$$E(R) = E_{el} + \frac{1}{R} = -\frac{2.25}{R^4} - \frac{7.5}{R^6} + \mathcal{O}(R^{-7})$$

Convergence of the polarization approximation for H_2^+

$$\Delta(n) = 100\left(1 - \frac{\sum_{k=1}^{n} \Delta E^{(k)}}{\Delta E_{\text{exact}}}\right)$$

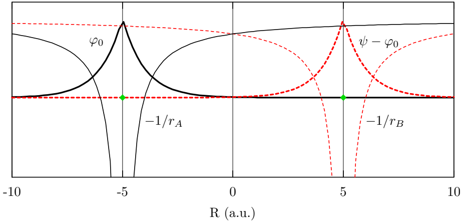
	R = 3.0		R = 12.5	
n	ΔE^n	$\Delta(n)$	ΔE^n	$\Delta(n)$
1	3.3050(-03)	10.26	1.5000(-11)	100.000
2	-2.5686(-02)	71.14	-9.4250(-05)	27.809
3	-1.1074(-02)	56.87	-1.2599(-06)	26.844
4	-9.8501(-03)	44.17	-1.5711(-07)	26.723
5	-8.0099(-03)	33.84	-1.5409(-08)	26.711
6	-6.7955(-03)	25.08	-3.8934(-09)	26.708
8	-4.5279(-03)	12.03	-1.5287(-09)	26.706
12	-1.3808(-03)	-0.41	-1.3304(-09)	26.702
16	+2.3496(-05)	-2.40	-1.3244(-09)	26.698
20	+3.0523(-05)	-1.07	-1.3241(-09)	26.694
30	-3.6059(-05)	0.30	-1.3241(-09)	26.683
38	-1.3906(-05)	-0.07	-1.3241(-09)	26.675

Chalasinski et al. IJQC **11** (1977) 247

At large R the exact wave function (with intermediate normalization) is

$$\psi = \varphi_A + \varphi_B \approx 1s_A + 1s_B$$

i.e. the modification brought by the perturbation $\hat{V}$ is not small at all.



- near A
  - $\hat{V}$ is small, therefore $\varphi_0 = 1s_A$ is good approximation
- near B
  - $\hat{V}$ is big, therefore $\varphi_0 = 1s_A$ is very bad approximation.
    Expand the $\psi_B = 1s_B$ function by the eigenfunctions of A-centered basis

$$\psi_B = \sum_k \langle \psi_B | a_k \rangle a_k$$

At larger R bad convergence, since $\{a_k\}$ vanish exponentially at B.

$$\Delta E = \underbrace{\langle \varphi_0 | \hat{V} \varphi_A \rangle}_{\text{rapid convergence}} + \underbrace{\langle \varphi_0 | \hat{V} \varphi_A \rangle}_{\text{obtained only at inf. order}}$$

Example of two H atoms

Interaction of two H atoms

$$\hat{V} = -\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}}$$

Unperturbed wave function

$$\varphi_0 = a_0(1)b_0(2)$$

The RSPT charge density is a simple superposition of the 1s densities,

$$\varrho(\boldsymbol{r}) = \varrho_{1s}(\boldsymbol{r} - \boldsymbol{x}) + \varrho_{1s}(\boldsymbol{r} + \boldsymbol{x})$$

In case of overlapping electron densities the antisymmetrized (triplet) wave function is

$$\psi_0 = \frac{1}{\sqrt{2(1 - S^2)}} \left[a_0(1)b_0(2) - a_0(2)b_0(1)\right]$$

and the symmetry-adapted charge density is

$$\varrho(\boldsymbol{r}) = \frac{1}{1 - S^2} \left[\varrho_{1s}(\boldsymbol{r} - \boldsymbol{x}) + \varrho_{1s}(\boldsymbol{r} + \boldsymbol{x}) - 2S1s(\boldsymbol{r} - \boldsymbol{x})1s(\boldsymbol{r} + \boldsymbol{x})\right]$$

Density

- depleted between nuclei

$$\varrho(\boldsymbol{r}=0)=\frac{1}{1-S^2}\left[2\varrho_{1s}(\boldsymbol{x})-2S\varrho_{1s}(\boldsymbol{x})\right]=\frac{2}{1+S}\varrho_{1s}(\boldsymbol{x})<2\varrho_{1s}(\boldsymbol{x})$$

- enhanced outside the nuclei, e.g. at $\boldsymbol{r}=2\boldsymbol{x}$

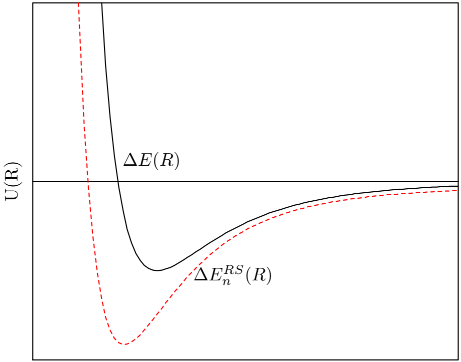
$$\varrho(2\boldsymbol{x})\approx\frac{1}{1-S^2}\left[\varrho_{1s}(\boldsymbol{x})+\varrho_{1s}(3\boldsymbol{x})\right]\approx\frac{1}{1-S^2}\varrho_{1s}(\boldsymbol{x})>\varrho_{1s}(\boldsymbol{x})$$

The Hellmann-Feynmann forces will be repulsive.

- electron tunnels in both directions ⇒ exchange tunneling
- due to $\frac{1}{r_{12}}$ the electronic motions become correlated ⇒ dispersion

In many-electron systems the RSPT ground state violates Pauli-principle ⇒ antisymmetrized product would be a better ψ_0, but it is not eigenfunction of $\hat{H}_0$.

Behaviour of the RSPT interaction energy



- At short distances RSPT (polarization approximation) misses the repulsion: no acceptable minimum
- At large distance $\Delta E(R) - \Delta E_n^{(RS)}(R)$ vanishes exponentially, therefore the polarization approximation is acceptable.

Symmetry failure

Why is the polarization approximation wrong at short and intermediate distances?

- Antisymmetrizer commutes with total Hamiltonian

  $$\left[\hat{A}, (\hat{H} + \lambda\hat{V})\right] = 0$$

  but neither with $\hat{H}_0$, nor with $\hat{V}$

  $$[\hat{A}, \hat{H}_0] \neq 0 \qquad\qquad [\hat{A}, \hat{V}] \neq 0$$

  It follows from the commutation rules that

  $$[\hat{A}, \hat{H}_0] = -\lambda[\hat{A}, \hat{V}]$$

  i.e. non-zero zeroth-order and non-zero first order quantities are equal to each other: no unambiguous definition of the perturbation order.

Symmetry failure

- Antisymmetrized product states of the subsystems

  $$\hat{A}\varphi_a^A \varphi_b^B$$

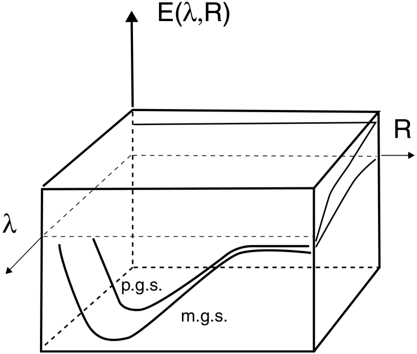
  form a non-orthogonal set. A hermitian operator has always a orthogonal eigenfunctions. There can be no Hermitian Hamiltonian associated with these zeroth-order wave functions.
- Symmetry dilemma: Zeroth order Hamiltonian $\hat{H}(\lambda = 0) = \hat{H}_A + \hat{H}_B$ has lower symmetry than $\hat{H}(\lambda = 1)$!

  $$\begin{array}{cc} \hat{H}_A + \hat{H}_B & \mathcal{S}_{N_A} \bigotimes \mathcal{S}_{N_B} \\ \hat{H} & \mathcal{S}_{N_A+N_B} \end{array}$$

  The direct product the symmetric groups of rank N_A and N_B is a subgroup of $\mathcal{S}_{N_A+N_B}$.

Consequence: the polarization approximation is only asymptotically convergent, i.e. at a given intermolecular distance and orientation one cannot obtain the exact energy as a power series of the λ perturbational parameter. In the practice, PA is divergent at higher than 2nd order.

Claverie's analysis



The lowest eigenfunction of $\hat{H}(\lambda = 0)$ is a "bosonic" state, which is connected with the physically forbidden *mathematical ground state* of $\hat{H}(\lambda=1)$, while the *physical ground state* of $\hat{H}(\lambda=1)$ is connected with an excited state of $\hat{H}(\lambda=0)$.
Difference of p.g.s. and m.g.s. decreases exponentially with R.
Since the m.g.s. becomes repulsive only at chemical bond distances, polarization approximation misses the repulsive effects.

Two possible strategies:

- abandon the usual partition and find a $\hat{H}_0$ for which $\hat{A}\varphi_0$ is eigenfunction
- maintain the partition, but reject RSPT

Symmetrized RS perturbation theory

Let the $(N_A + N_B)$-electron antisymmetrizer

$$\hat{A} = \frac{1}{\sqrt{(N_A + N_B)!}} \sum_{P \in \mathcal{S}_{N_A+N_B}} (-1)^P P$$

and set the following zeroth order approximation to the wave function, satisfying the intermediate normalization

$$\psi_0 = N_0 \hat{A} \varphi_0 \qquad\qquad N_0 = \langle \varphi_0 | \hat{A} \varphi_0 \rangle^{-1}$$

First iteration in the energy

$$\Delta E_1 = N_0 \langle \varphi_0 | \hat{V} \hat{A} \varphi_0 \rangle$$

First iteration in the wave function

$$\psi_1^{SRS} = \varphi_0 + N_0 \hat{R}_0 (\Delta E_1 - \hat{V}) \hat{A} \varphi_0$$

which is to be compared with the RSPT (polarization approximation, PA) result

$$\psi_1^{PA} = \varphi_0 - \hat{R}_0 \hat{V} \varphi_0$$

where the second term vanishes as $R \to \infty$.

Separation of the $\hat{V}$-dependent component of the first wave function iteration

$$
\begin{gathered}
[\hat{H}_0 + \hat{V}, \hat{A}] = 0 \\
-\hat{V}\hat{A} = \hat{H}_0\hat{A} - \hat{A}(\hat{H}_0 + \hat{V}) \\
(\Delta E_1 - \hat{V})\hat{A} = \hat{A}\Delta E_1 + \hat{H}_0\hat{A} - \hat{A}\hat{H}_0 - \hat{A}\hat{V} \\
(\Delta E_1 - \hat{V})\hat{A} = \hat{A}(\Delta E_1 - \hat{V}) + [\hat{H}_0 - E_0, \hat{A}] \\
\hat{R}_0[\hat{H}_0 - E_0, \hat{A}]\varphi_0 = \hat{A}\varphi_0 - \langle\varphi_0|\hat{A}\varphi_0\rangle\varphi_0 \\
N_0\hat{R}_0(\Delta E_1 - \hat{V})\hat{A}\varphi_0 = N_0\hat{A}\varphi_0 - N_0\langle\varphi_0|\hat{A}\varphi_0\rangle\varphi_0 + N_0\hat{R}_0\hat{A}(\Delta E_1 - \hat{V})\varphi_0 \\
= N_0\hat{A}\varphi_0 - \varphi_0 + \psi^{(1)}
\end{gathered}
$$

The first iteration of the wave function can be decomposed as

$$\psi_1 = \varphi_0 + \psi_0^{(\mathrm{exch})} + \psi^{(1)}$$

i.e. a large exchange correction

$$\psi_0^{(\mathrm{exch})} = N_0 \hat{A} \varphi_0 - \varphi_0$$

and a small $\hat{V}$-dependent correction,

$$\psi^{(1)} = N_0 \hat{R}_0 \hat{A} (\Delta E_1 - \hat{V}) \varphi_0$$

The second energy iteration gives

$$\Delta E_2 = \langle \varphi_0 | \hat{V} \psi_1 \rangle = E^{(1)} + E^{(2)}$$

with

$$E^{(2)} = N_0 \langle \varphi_0 | \hat{V} \hat{R}_0 \hat{A} (\Delta E_1 - \hat{V}) \varphi_0 \rangle$$

and due to the hermiticity of $\hat{V}$ and $\hat{A}$

$$E^{(2)} = N_0 \langle \varphi_{\mathrm{pol}}^{(1)} | \hat{A} (\hat{V} - \Delta E_1) \varphi_0 \rangle$$

Separation of exchange contributions

At any order of the SRS perturbation theory, the energy correction can be rigorously decomposed as a sum of exponentially decaying exchange component and the polarization component

$$E^{(n)} = E^{(n)}_{\text{pol}} + E^{(n)}_{\text{exch}}$$

This can be done using the decomposition of the total antisymmetrizer as

$$\hat{A} = \frac{N_A!N_B!}{(N_A+N_B)!}\hat{A}_A\hat{A}_B(1+\mathcal{P})$$

where $\mathcal{P}$ is the sum of inter-system permutations.
First order exchange energy

$$E^{(1)}_{\text{exch}} = \frac{\langle\varphi_0|\hat{V}\mathcal{P}\varphi_0\rangle - \langle\varphi_0|\hat{V}\varphi_0\rangle\langle\varphi_0|\mathcal{P}\varphi_0\rangle}{1+\langle\varphi_0|\mathcal{P}\varphi_0\rangle}$$

Second order exchange energy

$$E^{(2)}_{\text{exch}} = \frac{\langle\varphi^{(1)}_{\text{pol}}|\hat{V}\mathcal{P}\varphi_0\rangle - \langle\varphi^{(1)}_{\text{pol}}|\hat{V}\varphi_0\rangle\langle\varphi_0|\mathcal{P}\varphi_0\rangle}{1+\langle\varphi_0|\mathcal{P}\varphi_0\rangle}$$

Symmetry adapted perturbation theory (SAPT)

(Jeziorski, Moszynski, Szalewicz and Williams)

Zeroth-order wave Hamiltonian is the sum of isolated molecule Fock operators and the solutions are expanded in a triple perturbation series

$$\hat{H} = \hat{F}^A + \hat{F}^B + \zeta \hat{V} + \lambda_A \hat{W}_A + \lambda_B \hat{W}_B$$

Consecutive application of the RSPT (polarization approximation) and symmetry adapted perturbation theory (exchange corrections) leads to the following expression of the interaction energy:

$$\Delta E = \sum_{n=0}^{\infty} \Delta E_{\text{pol}}^{(n)} + \sum_{n=0}^{\infty} \Delta E_{\text{exch}}^{(n)}$$

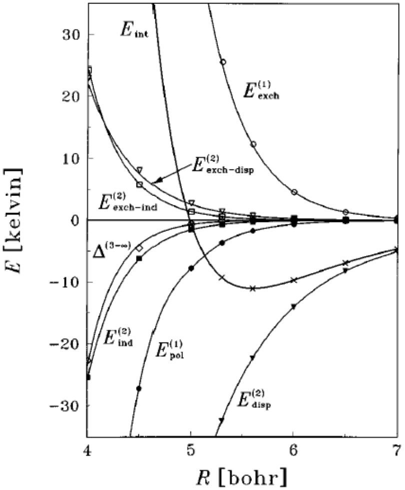
and both components are developed in the orders of the intramolecular correlation operator

$$\Delta E_{\text{pol}}^{(n)} = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \Delta E_{\text{pol}}^{(nij)} \qquad \Delta E_{\text{exch}}^{(n)} = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \Delta E_{\text{exch}}^{(nij)}$$

SAPT

Symbol	Name	Description
$E_{\text{pol}}^{(10)}$	Electrostatic	Classical electrostatic interaction of unperturbed Hartree-Fock charge distributions
$E_{\text{pol}}^{(1n)}$	Electrostatic: correlation corrections	Correlation correction to the electrostatic energy from the nth order intramolecular correlation effects on the charge distributions
$E_{\text{exch}}^{(10)}$	Exchange (overlap) repulsion	Repulsion of the closed shells: modification of the interaction energy of Hartree-Fock monomers due to the intermolecular antisymmetrization
$E_{\text{exch}}^{(1n)}$	Exchange (overlap) repulsion: correlation corrections	Intramolecular correlation correction to closed-shell repulsion

Symbol	Name	Description
$E_{\text{ind}}^{(20)}$	Induction energy	Energy arising from the distortion of each molecule in the field of the unperturbed Hartree-Fock charge distribution of the other
$E_{\text{ind-exch}}^{(20)}$	Exchange induction	Modification to the induction energy due to antisymmetry effects
$E_{\text{disp}}^{(20)}$	Dispersion energy	Energy arising from the correlated fluctuations of the of the unperturbed Hartree-Fock charge distribution of each molecule
$E_{\text{disp-exch}}^{(20)}$	Exchange dispersion	Modification to the dispersion energy due to antisymmetry effects
$E_{\text{ind}}^{(2n)}$	Induction energy: correlation corrections	Corrections to the induction energy due to intramolecular correlation effects
$E_{\text{disp}}^{(2n)}$	Dispersion energy: correlation corrections	Corrections to the dispersion energy due to intramolecular correlation effects



SAPT decomposition of the He_2 interaction energy
(After: Korona et al. J. Chem. Phys. **106** (1997), 5109)