Natural Sciences Tripos: Part III Chemistry — course M4

Intermolecular Forces

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Contents

1. Introduction

Recommended books

- I. G. Kaplan, *Intermolecular Interactions* (Wiley 2006).

  Mainly oriented to theorists. A valuable resource.

- M. Rigby, E. B. Smith, W. A. Wakeham & G. C. Maitland, *The Forces between Molecules* (O.U.P. 1986).

  Mainly concerned with experimental techniques for investigating intermolecular forces.

- A. J. Stone, *The Theory of Intermolecular Forces* (O.U.P. 1996).
  See also the corrections, if your library has an early copy:
  The main reference.
  Hardback:
  http://www-stone.ch.cam.ac.uk/timf/corrections1996.pdf.
  Paperback:
  http://www-stone.ch.cam.ac.uk/timf/corrections1997.pdf.
  The 2000 reprint includes all these corrections.

Why study intermolecular forces?

Intermolecular forces play an important rôle in all the following:

- Deviations of gases from ideality (pressure, viscosity, diffusion, thermal conductivity).
- Properties of solids and liquids – e.g. melting and boiling points. The very existence of condensed phases depends on intermolecular forces.
- Crystal structures. Understanding polymorphism requires a very accurate knowledge of intermolecular forces.
- Liquid structures; e.g. liquid crystals.
- Steric effects in reactions.
- Tertiary structure of proteins.
- Modern drug design methods.
- The formation of surface monolayers, micelles and membranes, and the transport of ions and molecules across biological membranes.
- Interactions between molecules and surfaces: in heterogeneous catalysis, in industrial processes, in atmospheric chemistry and elsewhere.

- Conventional sources of experimental information were averages over the whole potential surface.

  E.g. gas non-ideality: second virial coefficient, viscosity, diffusion constants, etc.

- Recent spectroscopic techniques at very low temperatures provide detailed information about energy levels in the region of the potential energy minimum, which in turn provide information, via tunnelling splittings, about barriers between equivalent minima and hence about rearrangement pathways.

  E.g. Studies of water dimer and trimer lead to a better understanding of liquid water.

- With modern theoretical methods we can study intermolecular forces accurately and in great detail.

  Ab initio intermolecular perturbation theory gives the individual terms in the interaction.

2. Basic ideas

Energy *vs.* distance

Gases condense, so there must be an attractive force between the molecules at long range.

Liquids have finite volume and low compressibility, so there must be a steep repulsive region at shorter distances.

The depth of the well is conventionally called ε or D_e, the position of the minimum is R_e, and the position where the repulsive branch crosses the axis is σ, often called the *collision diameter*.
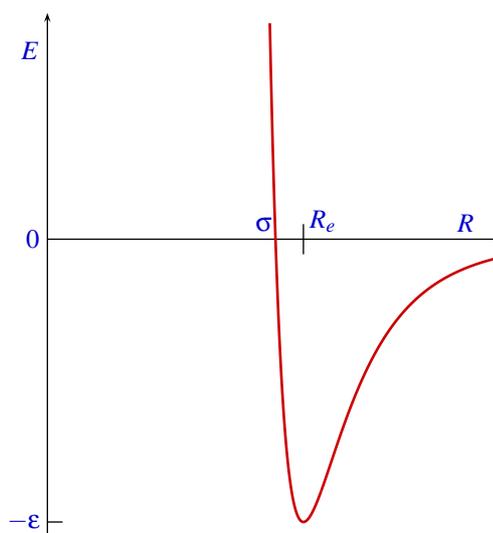
The value of R_e can be obtained easily and fairly accurately. Methods include

- rotational spectroscopy on the complex formed by a pair of molecules;

- x-ray diffraction of crystal structures.

Pauling showed in the 1930s that atoms in molecules can be assigned 'Van der Waals radii' so that they pack in crystals with the separation between adjacent atoms determined reasonably accurately by the sum of their radii.

Examples of Van der Waals radii (Ångstrom):

N	O	F	Ne	
1.50	1.40	1.35	1.54	Pauling (1960)
1.55	1.52	1.47	1.54	Bondi (1964)
P	S	Cl	Ar	
1.90	1.85	1.80	1.88	Pauling
1.80	1.80	1.75	1.88	Bondi

The well-depth ε is not so easy to determine. A rough value can be found from Trouton's rule.

For liquid and vapour in equilibrium, i.e., at the boiling-point,

$$\Delta G_{\mathrm{vap}} = \Delta H_{\mathrm{vap}} - T_b \Delta S_{\mathrm{vap}} = 0. \tag{2.1}$$

$\Delta S > 0$ for vapourization; a rough (under)estimate is

$$\Delta S_{\mathrm{vap}} \approx R \ln(V_g/V_l) \approx R \ln 1000 \approx 7R = 57\,\mathrm{J\,K^{-1}\,mol^{-1}}. \tag{2.2}$$

It is an underestimate because the liquid is more ordered than a dense gas.

Trouton's empirical rule asserts that $\Delta S_{\mathrm{vap}} \approx 85\,\mathrm{J\,K^{-1}\,mol^{-1}} \approx 10R$, or more for associated liquids. So

$$\Delta H_{\mathrm{vap}} = T_b \Delta S_{\mathrm{vap}} \approx 10RT_b. \tag{2.3}$$

From Trouton's rule:

$$\Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}} \approx 10 R T_b. \tag{2.3}$$

If we identify ΔH_{vap} with the energy needed to separate every atom from its n neighbours, we have

$$\Delta H_{\text{vap}} \approx \tfrac{1}{2} N_A n \varepsilon.$$

(We need the $\frac{1}{2}$ to avoid counting each interaction twice.)

That is

$$\tfrac{1}{2} N_A n \varepsilon \approx 10 R T_b$$

i.e.

$$\varepsilon \approx 20 k_B T_b / n. \tag{2.4}$$

The inert gases are approximately close-packed in the liquid, as in the solid, so $n \approx 12$. Methane is similar.

Water has a much more open structure, with $n \approx 4$, because of hydrogen bonding.

	T_b/K	n	$(20T_b/n)/\text{K}$	$(\varepsilon_{\text{exp}}/k_B)/\text{K}$	$\varepsilon_{\text{exp}}/\text{kJ mol}^{-1}$
He	4.2	12	7	11	0.1
Ar	87	12	145	142	1.2
Xe	166	12	277	281	2.3
CH_4	111.5	12	186	$180-300$	$1.5-2.5$
H_2O	373.2	4	1866	2400 approx.	20

Note that there is a big difference between D_0 and D_e because the binding is quite weak. Intermolecular potentials are also often very anharmonic.

The important interactions between molecules are all fundamentally electrostatic, arising from Coulomb interactions between the particles in the molecules.

There are magnetic interactions too, but they are very weak and need not concern us.

'Long-range' interactions persist even at distances where the molecular wavefunctions no longer overlap. They have a distance dependence which is some inverse power of R.

'Short-range' interactions are present only when the wavefunctions do overlap. They have a distance dependence approximately of the form $\exp(-\alpha R)$, where α is typically around $2\,\mathrm{bohr}^{-1}$.

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
Resonance	No	$\pm$	Degenerate states only
Magnetic	Yes	$\pm$	Very small
Short–range ($U \sim e^{-\alpha R}$)			
Exchange-Repulsion	No	$+$	Dominates at very short range
Charge Transfer	No	$-$	Donor–acceptor interaction
Penetration	Yes	$\pm$	Can be repulsive at very short range
Damping	approx.	$+$	Modification of dispersion and induction

If we have just two molecules we can write the energy as

$$W(A,B) = W_A + W_B + U_{AB},\qquad(3.1)$$

where W_A is the energy of the isolated molecule A and U_{AB}, the *pair potential*, describes the interaction between A and B.

For three molecules, the equivalent expression is

$$W(A,B,C) = W_A + W_B + W_C + U_{AB} + U_{AC} + U_{BC},\qquad(3.2)$$

This is usually only an approximation, because the presence of each molecule modifies the interaction between the other two. We should write

$$W(A,B,C) = W_A + W_B + W_C + U_{AB} + U_{AC} + U_{BC} + U_{ABC},\qquad(3.3)$$

where U_{ABC} is the *three-body correction*.

For a system of many molecules we have

$$W = \sum_A W_A + \sum_{A>B} U_{AB} + \sum_{A>B>C} U_{ABC} + \sum_{A>B>C>D} U_{ABCD} + \cdots,\qquad(3.4)$$

with four-body, five-body, ... terms.

All these terms depend on the relative geometry of the molecules involved — orientations as well as distances, in general.

The interaction energy is said to be *pairwise additive* if the three-body, four-body and higher terms are zero.

In practice the four-body and higher terms are usually quite small, but the three-body terms are often large.

We begin with the two-body interaction. The Hamiltonian for a pair of interacting molecules (labeled A and B) is

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \lambda \mathcal{V} \tag{4.1}$$

where $\mathcal{H}_A$ and $\mathcal{H}_B$ are the Hamiltonians for A and B and $\mathcal{V}$ is the interaction operator which describes the interaction of the electrons and nuclei of A with those of B:

$$\mathcal{V} = \frac{1}{4\pi\varepsilon_0} \sum_{a \in A} \sum_{b \in B} \frac{e_a e_b}{r_{ab}}, \tag{4.2}$$

where e_a and e_b are the charges of particles a and b and r_{ab} is the distance between these particles.

Let's assume we know the eigenfunctions and eigenvalues of the unperturbed Hamiltonians:

$$\mathcal{H}_A |m_A\rangle = W_m^A |m_A\rangle,$$
$$\mathcal{H}_B |n_B\rangle = W_n^B |n_B\rangle. \tag{4.3}$$

If $\lambda = 0$, then the dimer wavefunction is $\psi^{(0)} = |0_A 0_B\rangle$ and energy $W^{(0)} = W_0^A + W_0^B$. For non-zero λ we develop a perturbation expansion for the wavefunction and energy as follows:

$$\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \cdots,$$
$$W = W^{(0)} + \lambda W^{(1)} + \lambda^2 W^{(2)} + \cdots \tag{4.4}$$

The interaction energy is given by

$$W_{\text{int}} = W^{(1)} + W^{(2)} + \cdots. \tag{4.5}$$

At first-order,

$$W^{(1)} = \langle 0_A 0_B | \mathcal{V} | 0_A 0_B \rangle \tag{4.6}$$
$$= \iint \rho_A(\mathbf{r}_1) \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2) \rho_B(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \tag{4.7}$$

where $\rho_A = N \int \cdots \int |\varphi_A(1, 2, ..., N)|^2 d\mathbf{r}_2...\mathbf{r}_N$ is the electron density. This is the usual formula for the electrostatic interaction energy of two charge distributions and will be called U_{es}.

$$W^{(2)} = -\sum_{mn \neq 00} \frac{|\langle 0_A 0_B | \mathcal{V} | m_A n_B \rangle|^2}{W_m^A + W_n^B - W_0^A - W_0^B}. \tag{4.8}$$

The only term excluded in the summation is the one for which *both* molecules are in the ground state, so we take separately the terms for which one molecule is in the ground state and the other is not. This gives three terms:

$$U_{\text{ind}}^A = -\sum_{m \neq 0} \frac{|\langle 0_A 0_B | \mathcal{V} | m_A 0_B \rangle|^2}{W_m^A - W_0^A}, \tag{4.9}$$

$$U_{\text{ind}}^B = -\sum_{n \neq 0} \frac{|\langle 0_A 0_B | \mathcal{V} | 0_A n_B \rangle|^2}{W_n^B - W_0^B}, \tag{4.10}$$

$$U_{\text{disp}} = -\sum_{m \neq 0} \sum_{n \neq 0} \frac{|\langle 0_A 0_B | \mathcal{V} | m_A n_B \rangle|^2}{W_m^A + W_n^B - W_0^A - W_0^B}. \tag{4.11}$$

We shall see that U_{ind}^A describes the change in energy of molecule *A* in response to the electric field of molecule *B*. It is the *induction energy* of molecule *A*. Similarly U_{ind}^B is the induction energy of molecule *B*. The final term, U_{disp}, is the *dispersion energy*.

Consider the induction energy U_{ind}^A:

$$U_{\text{ind}}^A = -\sum_{m \neq 0} \frac{|\langle 0_A 0_B | \mathcal{V} | m_A 0_B \rangle|^2}{W_m^A - W_0^A}, \tag{4.12}$$

$$= -\sum_{m \neq 0} \frac{|\langle 0_A | \mathcal{V}[\rho_B] | m_A \rangle|^2}{W_m^A - W_0^A}, \tag{4.13}$$

where $V[\rho_B] = \sum_{\mathbf{r}_i} \int \rho_B(\mathbf{r}) \mathcal{V}(\mathbf{r}_i, \mathbf{r}) d\mathbf{r}$ is the electrostatic potential due to the unperturbed charge density of B. Now consider the Hamiltonian $\mathcal{H} = \mathcal{H}_A + \xi \mathcal{V}[\rho_B]$ and develop the usual perturbation expansion for the ground state energy

$$E = E^{(0)} + \xi E^{(1)} + \xi^2 E^{(2)} + \cdots. \tag{4.14}$$

The second-order energy correction is clearly just U_{ind}^A:

$$E^{(2)} = -\sum_{m \neq 0} \frac{|\langle 0_A | \mathcal{V}[\rho_B] | m_A \rangle|^2}{W_m^A - W_0^A} = U_{\text{ind}}^A. \tag{4.15}$$

Differentiating E twice w.r.t. ξ and setting $\xi \to 0$, we get

$$\frac{1}{2}\frac{\partial^2 E}{\partial \xi^2}\big|_{\xi \to 0} = U_{\text{ind}}^A. \tag{4.16}$$

Thus the induction energy can be interpreted as the second-order energy response of a molecule to the electrostatic field of the partner. It clearly doesn't matter where the field comes from. In general, $V[\rho_B]$ will be replaced by the electrostatic potential of the *environment*.

We will come back to this interpretation when we construct the asymptotic forms of the interaction energy components.

Eq.(4.16) gives us a way of calculating the induction energy using the method of finite-differences:

$$U_{\text{ind}}^A \approx \tfrac{1}{2}\frac{E(-\varepsilon) - 2E(0) + E(\varepsilon)}{2\varepsilon^2}. \tag{4.17}$$

Dispersion: Drude model

The dispersion energy cannot be described in terms of classical interactions as the electrostatic and induction terms can. A semi-classical picture is required.
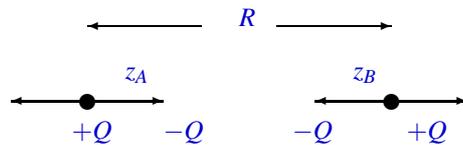
Model each molecule with a fixed charge $+Q$ at the centre and an oscillating charge $-Q$. In the usual scaled units (i.e. energy in units of $h\nu = \hbar\omega$, length in units of $(\hbar^2/km)^{1/4}$) the Hamiltonian is (assuming infinite separation):

$$\mathcal{H} = -\tfrac{1}{2}\frac{\partial^2}{\partial z_A{}^2} + \tfrac{1}{2}z_A{}^2 - \tfrac{1}{2}\frac{\partial^2}{\partial z_B{}^2} + \tfrac{1}{2}z_B{}^2. \tag{4.18}$$

The energy is the sum of the individual energies, i.e., $E_{v_A v_B} = v_A + v_B + 1$. The ground state energy ($v_A = v_B = 0$) is 1 unit, i.e. $h\nu$.

If the instantaneous displacements are $z_A(t)$ and $z_B(t)$, the dipole moments on A and B are $\mu_A = -Qz_A(t)$ and $\mu_B = -Qz_B(t)$, respectively.

At a finite separation R, these dipoles interact. The general form of the dipole–dipole interaction energy is (derived later)

$$U_{\mu\mu} = -\frac{\mu_A\mu_B}{R^3}\left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\varphi\right),$$

Here, $\theta_A = \theta_B = \pi$ and $\varphi = 0$ so the Hamiltonian at finite separations has the additional term cz_Az_B where $c = -\frac{2Q^2}{R^3}$.

Using the new variables $Z_1 = \sqrt{\frac{1}{2}}(z_A + z_B)$ and $Z_2 = \sqrt{\frac{1}{2}}(z_A - z_B)$, the potential term in the Hamiltonian becomes

$$V = \tfrac{1}{2}z_A{}^2 + cz_Az_B + \tfrac{1}{2}z_B{}^2 = \tfrac{1}{2}(1+c)Z_1{}^2 + \tfrac{1}{2}(1-c)Z_2{}^2, \qquad (4.19)$$

while the kinetic energy is unchanged in form:

$$T = -\tfrac{1}{2}\frac{\partial^2}{\partial z_A{}^2} - \tfrac{1}{2}\frac{\partial^2}{\partial z_B{}^2} = -\tfrac{1}{2}\frac{\partial^2}{\partial Z_1{}^2} - \tfrac{1}{2}\frac{\partial^2}{\partial Z_2{}^2}. \qquad (4.20)$$

The dispersion energy: a correlation effect

So we now have an oscillator Z_1 with frequency $\sqrt{1+c}$, and another, Z_2, with frequency $\sqrt{1-c}$. The allowed energies (in the original scaled units) are now $(v_1 + \tfrac{1}{2})\sqrt{1+c} + (v_2 + \tfrac{1}{2})\sqrt{1-c}$.

In a classical system the coupling doesn't change the minimum energy, which occurs when both oscillators are at rest. That is, $z_A = z_B = 0$, so $Z_1 = Z_2 = 0$ also, and the total energy is zero.

A quantum system, however, has zero-point energy: 1 unit in the original uncoupled system.

When $v_1 = v_2 = 0$ the energy of the interacting system is

$$E = \tfrac{1}{2}(\sqrt{1+c} + \sqrt{1-c}) = \tfrac{1}{2}[(1 + \tfrac{1}{2}c - \tfrac{1}{8}c^2 + \cdots) + (1 - \tfrac{1}{2}c - \tfrac{1}{8}c^2 - \cdots)]$$
$$= 1 - \tfrac{1}{8}c^2 - \cdots. \qquad (4.21)$$

That is, the zero-point energy is smaller for the correlated oscillators than for the uncoupled ones, whether c is positive or negative. The stabilization energy is the Drude approximation to the disperion.

The Drude expression for the dispersion energy is $-\frac{1}{8}c^2 = -\frac{Q^4}{2R^6}$ which varies as $\frac{1}{R^6}$. The coefficient of this term is usually labeled C_6 and, inserting the energy factors scaled out, is defined as

$$C_6 = \frac{\hbar\omega Q^4}{2(4\pi\varepsilon_0)^2 k^2}. \tag{4.22}$$

We now need to relate Q and k to measurable quantities. This is done using classical ideas.

If the charge $-Q$ extends by z in an electric field E then balancing forces we must have $kz = -QE$, or $z = -\frac{QE}{k}$. Now, by definition, $\mu = -zQ = \frac{Q^2}{k}E$. But, by definition of the polarizability, $\mu = \alpha E$, therefore

$$\alpha = \frac{Q^2}{k}. \tag{4.23}$$

This allows us to re-write the C_6 as

$$C_6 = \frac{\hbar\omega\alpha^2}{2(4\pi\varepsilon_0)^2}. \tag{4.24}$$

In 3-dimensions this expression becomes

$$C_6 = \frac{3\hbar\omega\alpha^2}{4(4\pi\varepsilon_0)^2}, \tag{4.25}$$

and taking, as London did, $\hbar\omega = E_I$, the ionization energy, we get

$$C_6 = \frac{3E_I\alpha^2}{4(4\pi\varepsilon_0)^2}. \tag{4.26}$$

This is an approximation, but it contains all the correct physics. The dispersion energy is always attractive (at second-order) and can be interpreted as arising from a correlation in the electronic fluctuations on the molecules.

This is a purely quantum phenomenon and has no classical analogue.

We shall re-derive this approximation for C_6 later using more sophisticated means.

The expressions for the interaction energy components obtained from perturbation theory are valid for all intermolecular separations.

At short intermolecular separations, when the molecular wavefunctions overlap, the dimer wavefunction must be antisymmetrized with respect to electron exchange between the monomers. This leads to additional terms in the interaction energy: The exchange energies.

At large intermolecular separations, the interaction operator $\mathcal{V}$ can be expanded in the *multipole series* and the interaction energy components can be written in terms of properties of the unperturbed monomers.

We will look at this multipole expansion now and come back to exchange effects later.

5.1 A Molecule in an External Potential

We start with the electrostatic interaction, because it is the fundamental interaction from which the other terms in the potential are derived.

We consider the energy of a molecule in an external electric field. Eventually we will take this to be the field due to some other molecule.

The dipole moment

Consider the interaction of a molecule with a uniform electric field F in the z direction.

The electrostatic potential of this field is $V = -Fz$, and the energy of the molecule in the field is

$$U_{es} = -F \sum_a e_a z_a, \qquad (5.1)$$

where e_a is the charge on particle a and $z_a = r_{az}$ is the z component of its position vector $\mathbf{r}_a$.

We are led to define the *electric dipole moment*:

$$\mu = \sum_a e_a \mathbf{r}_a, \qquad (5.2)$$

Then (5.1) becomes simply $U_{es} = -F\mu_z$, or, more generally,

$$U_{es} = -\mathbf{F} \cdot \mu. \qquad (5.3)$$

The dipole moment: units and numerical values

The traditional unit of measurement for dipole moments is the Debye:
$1\,\mathrm{D} = 10^{-18}\,\mathrm{esu}$.

In SI units, molecular dipole moments have very small values, of the order of $10^{-29}\,\mathrm{Cm}$.

It is often more convenient to use atomic units: the atomic unit of dipole moment is
$ea_0 = 2.54\,\mathrm{D} = 8.5 \times 10^{-30}\,\mathrm{Cm}$.

Typical values for small polar molecules are of the order of 1 atomic unit or a few Debye.

	μ/D	$\mu/10^{-30}\,\mathrm{Cm}$	μ/ea_0
NH_3	1.47	4.9	0.58
H_2O	1.85	6.2	0.73
HF	1.83	6.1	0.72
HCl	1.11	3.7	0.44
H_2CO	2.33	7.8	0.92
CH_3CN	3.91	13.1	1.54

There is a useful tabulation of dipole moments and other molecular properties in Gray and Gubbins (1984), Appendix D.

μ can also be described as the *first moment* of the charge distribution. The *zeroth moment* is just the total charge:

$$q = \sum_a e_a. \tag{5.4}$$

It is an integer multiple of the elementary charge e, and is constant for an isolated molecule.

If we have a molecule in a *non-uniform* electric field, we need to go further. The interaction energy of an assembly of charged particles, such as a molecule, with an external potential is

$$U_{\text{es}} = \sum_a e_a V(\mathbf{A} + \mathbf{r}_a), \tag{5.5}$$

where $\mathbf{r}_a$ is the position of particle a relative to some molecular origin $\mathbf{A}$.

It is convenient to write $V(\mathbf{A}) = V$, $(\nabla_\alpha V)_{\mathbf{A}} = V_\alpha$, etc.

Remember that the electric field is $F_\alpha = -\nabla_\alpha V = -V_\alpha$.

We also use the Einstein repeated-suffix summation convention:

- Greek suffixes α, β, etc., take the values x, y or z.

- Where a suffix is repeated in one term, a sum over these three values is implied; so for instance,

$$M_{\gamma\gamma} \equiv M_{xx} + M_{yy} + M_{zz},$$
$$\mu_\alpha V_\alpha \equiv \mu_x V_x + \mu_y V_y + \mu_z V_z.$$

- The quantity $\delta_{\alpha\beta}$ is the Kronecker delta:

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

Notice that $\delta_{\gamma\gamma} \equiv \delta_{xx} + \delta_{yy} + \delta_{zz} = 3$ (not 1).

The second moment

Recall from eq. (5.5) that $U_{es} = \sum_a e_a V(\mathbf{A} + \mathbf{r}_a)$.

We expand the potential in a Taylor series:

$$V(\mathbf{A} + \mathbf{r}_a) = V(\mathbf{A}) + \sum_\alpha r_{a\alpha}(\nabla_\alpha V)_\mathbf{A} + \tfrac{1}{2}\sum_{\alpha\beta} r_{a\alpha}r_{a\beta}(\nabla_\alpha\nabla_\beta V)_\mathbf{A} + \cdots.$$

$$= V + r_{a\alpha}V_\alpha + \tfrac{1}{2}r_{a\alpha}r_{a\beta}V_{\alpha\beta} + \cdots.$$

The energy becomes

$$U_{es} = \sum_a e_a V(\mathbf{A} + \mathbf{r}_a) = V\sum_a e_a + V_\alpha \sum_a e_a r_{a\alpha} + \tfrac{1}{2}V_{\alpha\beta}\sum_a e_a r_{a\alpha}r_{a\beta} + \cdots.$$

We can recognize the charge and dipole moment in the first two terms to express this in the form

$$U_{es} = qV + \mu_\alpha V_\alpha + \tfrac{1}{2}M_{\alpha\beta}V_{\alpha\beta} + \cdots,$$

where we have also introduced $M_{\alpha\beta} = \sum_a e_a r_{a\alpha}r_{a\beta}$, the *second moment* of the charge distribution.

The second moment for a spherical atom

The energy is

$$U_{es} = qV + \mu_\alpha V_\alpha + \tfrac{1}{2}M_{\alpha\beta}V_{\alpha\beta} + \cdots, \tag{5.6}$$

The second moment $M_{\alpha\beta}$ is not a very convenient quantity to use. To see why, consider an argon atom in the external field.

Because of the atom's spherical symmetry, its second moment has components $M_{xx} = M_{yy} = M_{zz} = M$, say, while $M_{xy} = M_{xz} = \cdots = 0$. That is, $M_{\alpha\beta} = M\delta_{\alpha\beta}$, where $\delta_{\alpha\beta}$ is the Kronecker delta.

Now the term in the energy involving the second moment becomes

$$\tfrac{1}{2}M_{\alpha\beta}V_{\alpha\beta} = \tfrac{1}{2}M\delta_{\alpha\beta}V_{\alpha\beta} = \tfrac{1}{2}MV_{\alpha\alpha} = \tfrac{1}{2}M\nabla^2 V = 0, \tag{5.7}$$

where the last step arises because the external field satisfies Laplace's equation.

So the second moment of a spherical atom contributes nothing to the energy of interaction with an external field.

Thus a spherical atom has a non-zero second moment, but there is no interaction with the external field.

In matrix form, this second moment is $\mathbf{M} = \begin{pmatrix} M & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & M \end{pmatrix}$.

For a molecule, we can write

$$\mathbf{M} = \begin{pmatrix} M_{xx} & ? & ? \\ ? & M_{yy} & ? \\ ? & ? & M_{zz} \end{pmatrix} = \begin{pmatrix} M_{xx} - M & ? & ? \\ ? & M_{yy} - M & ? \\ ? & ? & M_{zz} - M \end{pmatrix} + \begin{pmatrix} M & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & M \end{pmatrix}.$$

(The off-diagonal elements are irrelevant for the moment.) The second term contributes nothing to the energy, whatever the value of M.

We choose M so that the first term is traceless, i.e. so that $M_{xx} + M_{yy} + M_{zz} - 3M = 0$ or $M = \frac{1}{3}M_{\gamma\gamma}$.

The *quadrupole moment* is defined as this traceless modified second moment, though for historical reasons we also multiply by $\frac{3}{2}$:

$$\begin{aligned} \Theta_{\alpha\beta} &= \tfrac{3}{2}\left(M_{\alpha\beta} - \left(\tfrac{1}{3}M_{\gamma\gamma}\right)\delta_{\alpha\beta} \right) \\ &= \sum_a e_a \left(\tfrac{3}{2} r_{a\alpha} r_{a\beta} - \tfrac{1}{2} r_a^2 \delta_{\alpha\beta} \right). \end{aligned} \tag{5.8}$$

The quadrupole moment is zero by definition for a spherical atom, and describes only the non-spherical part of the second moment.

In terms of the quadrupole moment, the energy becomes

$$U_{es} = qV + \mu_\alpha V_\alpha + \tfrac{1}{3}\Theta_{\alpha\beta}V_{\alpha\beta} + \cdots. \tag{5.9}$$

The quadrupole moment has dimensions of $[\text{charge}] \times [\text{length}]^2$, so the atomic unit is $ea_0^2 = 4.49 \times 10^{-40}\,\text{C}\,\text{m}^2$. A typical value for a small molecule is a few atomic units.

In a uniform electric field F_ξ, the field is the same everywhere and its derivatives with respect to position are all zero.

The field at any molecule due to neighbouring molecules is often highly non-uniform. That is, the electric field F_ξ varies from place to place, and the *field gradient* $F_{\xi\eta} = \partial F_\xi/\partial x_\eta$ may be nonzero.
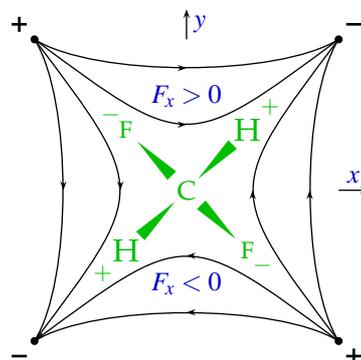
In the example illustrated, $F_x < 0$ when $y < 0$ and $F_x > 0$ when $y > 0$, so that $F_{xy} = \partial F_x/\partial y > 0$ (and $V_{xy} < 0$).

A CH_2F_2 molecule in the position shown has a positive quadrupole moment Θ_{xy}, and its interaction energy $\frac{1}{3}\Theta_{\alpha\beta}V_{\alpha\beta}$ with the field gradient is negative.

There are five independent components of $\Theta_{\alpha\beta}$, because $\Theta_{\alpha\beta} = \Theta_{\beta\alpha}$ and $\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$. Thus the independent components are Θ_{zz}, $\Theta_{xx} - \Theta_{yy}$, Θ_{xy}, Θ_{xz} and Θ_{yz}.

Of these, only Θ_{zz} may be non-zero for a linear molecule or symmetric top. It can be written alternatively as

$$\Theta_{zz} = \sum_a e_a\left(\tfrac{3}{2}z_a^2 - \tfrac{1}{2}r_a^2\right) \qquad (5.10)$$

$$= \sum_a \tfrac{1}{2}e_a r_a^2(3\cos^2\theta_a - 1), \qquad (5.11)$$

$$\tfrac{1}{2}(3\cos^2\theta - 1)$$

where $(r_a, \theta_a, \varphi_a)$ are the polar coordinates describing the position of particle a.
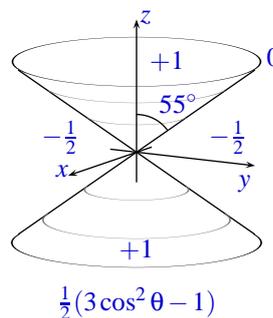
From this we can see that positive charge near the z axis ($\cos^2\theta > \frac{1}{3}$, i.e. $\theta < 55°$ or $\theta > 125°$) contributes positively to Θ_{zz} and negative charge contributes negatively, while charges in the region near the xy plane ($55° < \theta < 125°$) contribute with the opposite sign.

Quadrupole moments

z

$+1$ 0

$55°$

$-\frac{1}{2}$ $-\frac{1}{2}$

x y

$+1$

O

C $\Theta_{zz} = -3.3ea_0^2$

O
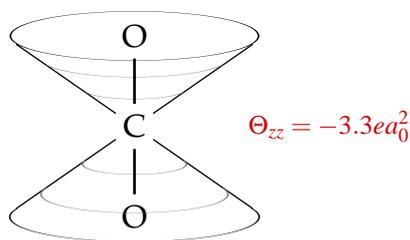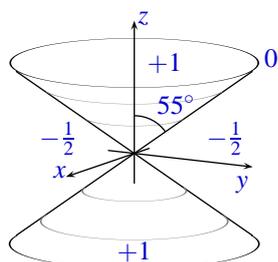
CO_2 has negatively charged O atoms on the z axis and has a negative quadrupole moment of $-3.3ea_0^2$.

F — B — F

F $\Theta_{zz} > 0$
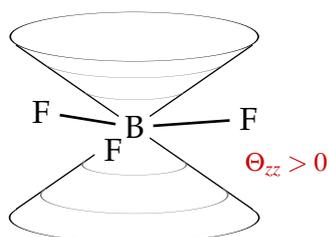
BF_3 has negatively-charged atoms in the xy plane, leading to a positive quadrupole moment.

Atomic quadrupole moments

The charge distribution of an individual atom may be non-spherical, leading to a non-zero quadrupole moment. An electron in a p_z orbital has most of its electron density in the region where $\frac{1}{2}(3\cos^2\theta - 1)$ is positive, and so contributes negatively to Θ_{zz}.

A complete p shell is spherical, but a Cl atom with a hole in the $3p_z$ orbital has a positive Θ_{zz}.

Similarly, HCl has a positive quadrupole moment, in part because the p_σ orbital is involved in bonding, while the p_π orbitals are non-bonding and more diffuse. (Remember that there's also an r^2 factor in the quadrupole moment.)

$\Theta_{zz} < 0$
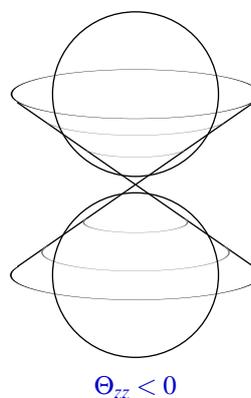
Molecules with lower symmetry have other non-zero components. To find out which, we just have to look up the functions x^2, y^2, z^2, xy, xz and yz in the character table and see which are symmetric. The general rule that $\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$ always applies.

The water molecule has C_{2v} symmetry, and the character table shows that it can have non-zero Θ_{xx}, Θ_{yy} and Θ_{zz}.
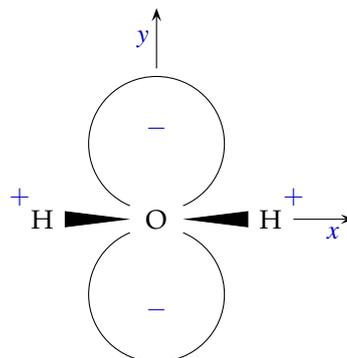
With axes as shown, $\Theta_{xx} - \Theta_{yy} = \left\langle \sum_a \frac{3}{2}(x_a^2 - y_a^2) \right\rangle > 0$. In fact

$$\Theta_{xx} = 1.96 ea_o^2,$$
$$\Theta_{yy} = -1.86 ea_0^2,$$
$$\Theta_{zz} = -0.10 ea_0^2.$$

Change of origin   38

If the origin is changed to a new position at **d** relative to the old origin, the multipole moments may change. Using primed quantities to refer to the new origin, the dipole moment becomes

$$\mu_\alpha' = \sum_a e_a r_{a\alpha}'$$
$$= \sum_a e_a (r_{a\alpha} - d_\alpha)$$
$$= \mu_\alpha - q d_\alpha. \qquad (5.12)$$

If the charge q is non-zero, the dipole moment depends on the choice of origin.
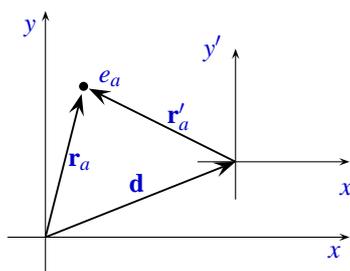
For the quadrupole moment:

$$\Theta'_{\alpha\beta} = \sum_a e_a\left(\tfrac{3}{2}r'_{a\alpha}r'_{a\beta} - \tfrac{1}{2}(r'_a)^2\delta_{\alpha\beta}\right)$$

$$= \Theta_{\alpha\beta} - \tfrac{3}{2}d_\alpha\mu_\beta - \tfrac{3}{2}d_\beta\mu_\alpha + (\mathbf{d}\cdot\mu)\delta_{\alpha\beta} + \tfrac{1}{2}q(3d_\alpha d_\beta - d^2\delta_{\alpha\beta}). \qquad (5.13)$$

HF has a positive quadrupole moment Θ_{zz} if we take the origin at the F atom or the centre of mass, but if we were to take the origin at the H atom Θ_{zz} would be negative.

$$\Theta_{zz} > 0 \qquad\qquad\qquad \Theta_{zz} < 0$$
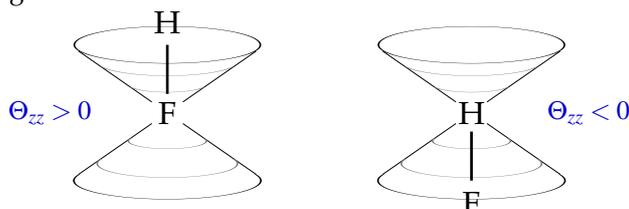
The quadrupole moment is independent of origin if q and μ are both zero, but otherwise it is essential to specify the origin of coordinates when giving values for quadrupole moments.

Higher multipoles

So far we have met the charge, dipole moment and quadrupole moment:

$$q^A = \sum e_a, \qquad\qquad (5.4)$$

$$\mu^A_\alpha = \sum e_a r_{a\alpha}, \qquad\qquad (5.2)$$

$$\Theta^A_{\alpha\beta} = \sum e_a\left(\tfrac{3}{2}r_{a\alpha}r_{a\beta} - \tfrac{1}{2}r_a^2\delta_{\alpha\beta}\right). \qquad\qquad (5.8)$$

We can define higher moments in a similar way. The multipole moment of rank n (the '2^n-pole moment') is

$$\xi^{(n)A}_{\alpha\beta\ldots\nu} \equiv (-)^n\frac{1}{n!}\sum_a e_a r_a^{2n+1}\frac{\partial}{\partial r_{a\alpha}}\frac{\partial}{\partial r_{a\beta}}\cdots\frac{\partial}{\partial r_{a\nu}}\left(\frac{1}{r_a}\right). \qquad (5.14)$$

From the definition it follows that the multipole moment $\xi^{(n)A}_{\alpha\beta\ldots\nu}$ is unchanged by any permutation of its suffixes, and is traceless with respect to any pair of suffixes. (That is, if we set any two suffixes equal to x, y and z in turn, and add up the results, we get zero.) These properties imply that although $\xi^{(n)A}_{\alpha\beta\ldots\nu}$ has 3^n components, only $2n+1$ of them are independent.

An equivalent definition of the multipole moments can be given in terms of spherical harmonics:

$$Q_{nm} = \sum_a e_a r_a^n C_{nm}(\theta_a, \varphi_a), \tag{5.15}$$

where

$$C_{nm} = \sqrt{\frac{4\pi}{2n+1}} Y_{nm} \tag{5.16}$$

is a modified spherical harmonic, and $(r_a, \theta_a, \varphi_a)$ are the spherical polar coordinates of the position $\mathbf{r}_a$ of particle a.

This definition explicitly leads to $2n+1$ independent components, which can be expressed in terms of the Cartesian components. It is a more convenient definition for advanced work, but the Cartesian definition is easier to handle in simple applications.

The electrostatic energy becomes

$$U_{\text{es}} = V q^A + V_\alpha \mu_\alpha^A + \frac{1}{3} V_{\alpha\beta} \Theta_{\alpha\beta}^A + \cdots$$
$$+ \frac{1}{(2n-1)!!} V_{\alpha\beta\ldots\nu} \xi_{\alpha\beta\ldots\nu}^{(n)A} + \cdots, \tag{5.17}$$

where $(2n-1)!! \equiv (2n-1)(2n-3)\ldots5.3.1$.

Recall that V can be any external potential acting on A. This equation describes the interaction of molecule A with such a potential, in terms of its multipole moments and the potential and its derivatives at the centre of the molecule (i.e., at $\mathbf{A}$).

The same expression can be written in terms of the *electric field* $F_\alpha = -V_\alpha$, the *field gradient* $F_{\alpha\beta} = -V_{\alpha\beta}$, and so on.

6. The Asymptotic form of the interaction operator

The electrostatic interaction between two molecules, in its simplest form, is just the sum of the coulombic interactions between the particles comprising them:

$$\mathcal{V} = \frac{1}{4\pi\varepsilon_0} \sum_{a \in A} \sum_{b \in B} \frac{e_a e_b}{r_{ab}}$$
$$= \frac{1}{4\pi\varepsilon_0} \sum_a \sum_b \frac{e_a e_b}{|\mathbf{R} - \mathbf{r}_a + \mathbf{r}_b|}, \qquad (6.1)$$

where e_a is the charge of particle a, which is at position $\mathbf{r}_a$ relative to the 'centre' of molecule A at $\mathbf{A}$. The choice of 'centre' is arbitrary, though one choice may be more sensible than others. $\mathbf{R}$ is the vector $\mathbf{B} - \mathbf{A}$ from the centre of A to the centre of B.
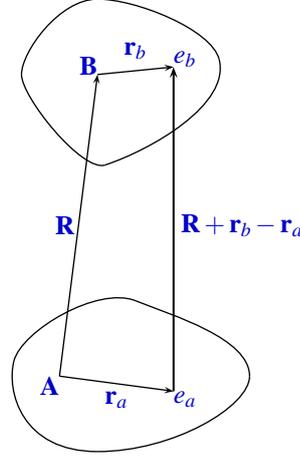
The multipole expansion

The electrostatic energy is

$$\mathcal{V} = \frac{1}{4\pi\varepsilon_0} \sum_{a \in A} \sum_{b \in B} \frac{e_a e_b}{r_{ab}} = \frac{1}{4\pi\varepsilon_0} \sum_a \sum_b \frac{e_a e_b}{|\mathbf{R} - \mathbf{r}_a + \mathbf{r}_b|}. \qquad (6.2)$$

We can write this as the energy of the multipoles of molecule A in the field at $\mathbf{A}$ due to molecule B (eq. (5.17)):

$$\mathcal{V} = q^A V^A + \hat{\mu}_\alpha^A V_\alpha^A + \tfrac{1}{3} \hat{\Theta}_{\alpha\beta}^A V_{\alpha\beta}^A + \cdots \qquad (6.3)$$

or as the energy of the multipoles of molecule B in the field at $\mathbf{B}$ due to molecule A:

$$\mathcal{V} = q^B V^B + \hat{\mu}_\alpha^B V_\alpha^B + \tfrac{1}{3} \hat{\Theta}_{\alpha\beta}^B V_{\alpha\beta}^B + \cdots, \qquad (6.4)$$

We shall use the second form. Note that we are now treating the interaction as an operator.

Interaction functions

To use eq. (6.4) we need the potential at **B** due to A.

We consider first just the charge q^A of molecule A.

The electrostatic potential at **B** due to this charge is $V^B = q^A/4\pi\varepsilon_0 R$.

We define a new quantity T by

$$T = \frac{1}{4\pi\varepsilon_0 R}, \tag{6.5}$$

so that $V^B = q^A T$.

To derive the interaction in multipole expansion form we need the fields, i.e. the derivatives of T.

Differentiating functions of R

If the vector **R** has components (X, Y, Z), then $R = \sqrt{X^2 + Y^2 + Z^2}$, so that

$$\frac{\partial R}{\partial X} = \frac{\partial}{\partial X}(X^2 + Y^2 + Z^2)^{1/2} = \tfrac{1}{2}(X^2 + Y^2 + Z^2)^{-1/2} \times 2X = \frac{X}{R}.$$

More generally, $\partial R/\partial R_\alpha = R_\alpha/R$.

Then, using the chain rule, the first derivative of T is given by

$$4\pi\varepsilon_0 T_\alpha = \frac{\partial}{\partial R_\alpha}\frac{1}{R} = -\frac{1}{R^2} \times \frac{R_\alpha}{R} = -\frac{R_\alpha}{R^3}. \tag{6.6}$$

For the second derivative, note that $\partial R_\beta/\partial R_\alpha$ is 1 if $\alpha = \beta$ and 0 otherwise; i.e., $\partial R_\beta/\partial R_\alpha = \delta_{\alpha\beta}$.

Then

$$
\begin{aligned}
4\pi\varepsilon_0 T_{\alpha\beta} &= \frac{\partial^2}{\partial R_\alpha R_\beta} \frac{1}{R} \\
&= -\frac{\partial}{\partial R_\alpha} \frac{R_\beta}{R^3} \\
&= -\frac{1}{R^3}\delta_{\alpha\beta} + R_\beta \cdot \frac{3}{R^4} \cdot \frac{R_\alpha}{R} \\
&= \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{R^5} \\
&= \frac{3\hat{R}_\alpha \hat{R}_\beta - \delta_{\alpha\beta}}{R^3}
\end{aligned}
\tag{6.7}
$$

where the last line is expressed in terms of components $\hat{R}_\alpha = R_\alpha/R$ of the unit vector $\hat{\mathbf{R}} = \mathbf{R}/R$.

In general we define the nth-rank *interaction tensor* by

$$
T_{\alpha\beta\ldots\nu} \equiv \frac{1}{4\pi\varepsilon_0} \nabla_\alpha \nabla_\beta \ldots \nabla_\nu \frac{1}{R}.
\tag{6.8}
$$

$T_{\alpha\beta\ldots\nu}$ (n suffixes) is R^{-n-1} times a polynomial of degree n in the components of the unit vector $\hat{\mathbf{R}}$.

Now the energy is

$$
\mathcal{V} = V^B q^B + V^B_\alpha \hat{\mu}^B_\alpha + \tfrac{1}{3}V^B_{\alpha\beta}\hat{\Theta}^B_{\alpha\beta} + \cdots,
\tag{6.9}
$$

and $V_B = q^A T$, so in terms of the interaction tensors T, T_α, etc., the energy of molecule B in the field of a point charge q^A at $\mathbf{A}$ becomes

$$
\mathcal{V} = q^A T q^B + q^A T_\alpha \hat{\mu}^B_\alpha + \tfrac{1}{3}q^A T_{\alpha\beta}\hat{\Theta}^B_{\alpha\beta} + \cdots.
\tag{6.10}
$$

More generally, the potential at **B** due to A is

$$V^B = \sum_a \frac{e_a}{4\pi\varepsilon_0 |\mathbf{R} - \mathbf{r}_a|}. \tag{6.11}$$

We expand this as a Taylor series:

$$V^B = \sum_a \frac{e_a}{4\pi\varepsilon_0}$$
$$\times \left\{ \frac{1}{R} + r_{a\alpha} \left(\frac{\partial}{\partial r_{a\alpha}} \frac{1}{|\mathbf{R} - \mathbf{r}_a|} \right)_{\mathbf{r}_a=0} + \tfrac{1}{2} r_{a\alpha} r_{a\beta} \left(\frac{\partial^2}{\partial r_{a\alpha} r_{a\beta}} \frac{1}{|\mathbf{R} - \mathbf{r}_a|} \right)_{\mathbf{r}_a=0} + \cdots \right\}. \tag{6.12}$$

Now we can change the derivative w.r.t. $r_{a\alpha}$ to a derivative w.r.t. $R_{a\alpha}$, provided we change the sign:

$$V^B = \sum_a \frac{e_a}{4\pi\varepsilon_0}$$
$$\times \left\{ \frac{1}{R} + r_{a\alpha} \left(-\frac{\partial}{\partial R_\alpha} \frac{1}{|\mathbf{R} - \mathbf{r}_a|} \right)_{\mathbf{r}_a=0} + \tfrac{1}{2} r_{a\alpha} r_{a\beta} \left(\frac{\partial^2}{\partial R_\alpha R_\beta} \frac{1}{|\mathbf{R} - \mathbf{r}_a|} \right)_{\mathbf{r}_a=0} + \cdots \right\}. \tag{6.13}$$

When we set $\mathbf{r}_a = 0$ in the derivatives the expression simplifies:

$$V^B = \sum_a \frac{e_a}{4\pi\varepsilon_0} \left\{ \frac{1}{R} - r_{a\alpha} \nabla_\alpha \frac{1}{R} + \tfrac{1}{2} r_{a\alpha} r_{a\beta} \nabla_\alpha \nabla_\beta \frac{1}{R} - \cdots \right\}$$
$$= \sum_a e_a \left(T - r_{a\alpha} T_\alpha + \tfrac{1}{2} r_{a\alpha} r_{a\beta} T_{\alpha\beta} - \cdots \right)$$
$$= q^A T - \hat{\mu}_\alpha^A T_\alpha + \tfrac{1}{3} \hat{\Theta}_{\alpha\beta}^A T_{\alpha\beta} - \cdots. \tag{6.14}$$

Differentiating the potential to get the fields is now (formally) trivial: we just add another suffix to each $T_{...}$ for each derivative. So, for example,

$$V_\gamma^B = q^A T_\gamma - \hat{\mu}_\alpha^A T_{\alpha\gamma} + \tfrac{1}{3} \hat{\Theta}_{\alpha\beta}^A T_{\alpha\beta\gamma} - \cdots. \tag{6.15}$$

We can now construct the electrostatic interaction in terms of the multipole moments. We need to be careful with the suffixes.

$$
\begin{aligned}
\mathcal{V} &= V^B q^B + V^B_\alpha \hat{\mu}^B_\alpha + V^B_{\alpha\beta} \hat{\Theta}^B_{\alpha\beta} + \cdots \\
&= (q^A T - \hat{\mu}^A_\xi T_\xi + \tfrac{1}{3} \hat{\Theta}^A_{\xi\eta} T_{\xi\eta} + \cdots) q^B \\
&\quad + (q^A T_\alpha - \hat{\mu}^A_\xi T_{\xi\alpha} + \tfrac{1}{3} \hat{\Theta}^A_{\xi\eta} T_{\xi\eta\alpha} + \cdots) \hat{\mu}^B_\alpha \\
&\quad + (q^A T_{\alpha\beta} - \hat{\mu}^A_\xi T_{\xi\alpha\beta} + \tfrac{1}{3} \hat{\Theta}^A_{\xi\eta} T_{\xi\eta\alpha\beta} + \cdots) \tfrac{1}{3} \hat{\Theta}^B_{\alpha\beta} + \cdots \\
&= q^A T q^B + q^A T_\alpha \hat{\mu}^B_\alpha - \hat{\mu}^A_\xi T_\xi q^B + q^A T_{\alpha\beta} \tfrac{1}{3} \hat{\Theta}^B_{\alpha\beta} - \hat{\mu}^A_\xi T_{\xi\beta} \hat{\mu}^B_\beta + \tfrac{1}{3} \hat{\Theta}^A_{\xi\eta} T_{\xi\eta} q^B \\
&\quad - \hat{\mu}^A_\xi T_{\xi\alpha\beta} \tfrac{1}{3} \hat{\Theta}^B_{\alpha\beta} + \tfrac{1}{3} \hat{\Theta}^A_{\xi\eta} T_{\xi\eta\alpha} \hat{\mu}^B_\alpha + \tfrac{1}{3} \hat{\Theta}^A_{\xi\eta} T_{\xi\eta\alpha\beta} \tfrac{1}{3} \hat{\Theta}^B_{\alpha\beta} + \cdots \quad (6.16)
\end{aligned}
$$

For neutral species, the charges are zero, and the leading term is the dipole-dipole interaction:

$$
\mathcal{V} = -\hat{\mu}^A_\alpha T_{\alpha\beta} \hat{\mu}^B_\beta - \tfrac{1}{3} \hat{\mu}^A_\alpha T_{\alpha\beta\gamma} \hat{\Theta}^B_{\beta\gamma} + \tfrac{1}{3} \hat{\Theta}^A_{\alpha\beta} T_{\alpha\beta\gamma} \hat{\mu}^B_\gamma + \tfrac{1}{9} \hat{\Theta}^A_{\alpha\beta} T_{\alpha\beta\gamma\delta} \hat{\Theta}^B_{\gamma\delta} + \cdots \quad (6.17)
$$

The multipole expansion of the electrostatic interaction between two neutral molecules has the form

$$
\begin{aligned}
\mathcal{V} &= -\hat{\mu}^A_\alpha T_{\alpha\beta} \hat{\mu}^B_\beta - \tfrac{1}{3} \hat{\mu}^A_\alpha T_{\alpha\beta\gamma} \hat{\Theta}^B_{\beta\gamma} + \tfrac{1}{3} \hat{\Theta}^A_{\alpha\beta} T_{\alpha\beta\gamma} \hat{\mu}^B_\gamma \\
&\quad - \tfrac{1}{15} \hat{\mu}^A_\alpha T_{\alpha\beta\gamma\delta} \hat{\Omega}^B_{\beta\gamma\delta} + \tfrac{1}{9} \hat{\Theta}^A_{\alpha\beta} T_{\alpha\beta\gamma\delta} \hat{\Theta}^B_{\gamma\delta} - \tfrac{1}{15} \hat{\Omega}^A_{\alpha\beta\gamma} T_{\alpha\beta\gamma\delta} \hat{\mu}^B_\delta + \cdots \quad (6.18)
\end{aligned}
$$

We can now use this expanded form of the interaction operator in the perturbation theory expressions for the electrostatic, induction and dispersion energies we have already derived.

7.1 The Electrostatic energy

The first-order energy is just the expectation value of $\mathcal{V}$ over the ground-state wavefunction for the non-interacting two-molecule system, i.e. the product $0_A 0_B$:

$$U_{\text{es}} = \langle 0_A 0_B | \mathcal{V} | 0_A 0_B \rangle. \tag{7.1}$$

This leads to an energy expression in which the multipole moment operators are simply replaced by their expectation values:

$$
\begin{aligned}
U_{\text{es}} = &-\mu_\alpha^A T_{\alpha\beta} \mu_\beta^B - \tfrac{1}{3}\mu_\alpha^A T_{\alpha\beta\gamma}\Theta_{\beta\gamma}^B + \tfrac{1}{3}\Theta_{\alpha\beta}^A T_{\alpha\beta\gamma}\mu_\gamma^B \\
&-\tfrac{1}{15}\mu_\alpha^A T_{\alpha\beta\gamma\delta}\Omega_{\beta\gamma\delta}^B + \tfrac{1}{9}\Theta_{\alpha\beta}^A T_{\alpha\beta\gamma\delta}\Theta_{\gamma\delta}^B - \tfrac{1}{15}\Omega_{\alpha\beta\gamma}^A T_{\alpha\beta\gamma\delta}\mu_\delta^B + \cdots
\end{aligned} \tag{7.2}
$$

The *rank* of a multipole moment is 0 for the charge (zeroth moment), 1 for the dipole (first moment), 2 for the quadrupole (derived from the second moment) and so on.

The interaction between multipole moments Q_k^A and $Q_{k'}^B$, with ranks k and k', involves a $T_{\alpha\beta\ldots}$ with $k + k'$ suffixes, and has the form

$$\frac{Q_k^A Q_{k'}^B}{4\pi\varepsilon_0} \times R^{-k-k'-1} \times \text{angular factor.}$$

The angular factor depends on the direction of $\mathbf{R}$ and the orientations of A and B. It averages to zero

- over all orientations of molecule A (unless $k = 0$) *or*

- over all orientations of molecule B (unless $k' = 0$) *or*

- over all directions of $\mathbf{R}$ (unless $k = k' = 0$).

Consequently the electrostatic interaction is strongly orientation-dependent, and it has a strong influence on structure.

The dipole–dipole interaction energy is

$$U_{\mu\mu} = -\mu_\alpha^A T_{\alpha\beta} \mu_\beta^B$$

$$= -\mu_\alpha^A \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{4\pi\varepsilon_0 R^5} \mu_\beta^B$$

$$= \frac{R^2 \mu^A \cdot \mu^B - 3(\mu^A \cdot \mathbf{R})(\mu^B \cdot \mathbf{R})}{4\pi\varepsilon_0 R^5}. \qquad (7.3)$$

It is often convenient to choose coordinates with the z axis along $\mathbf{R}$, with the origin at $\mathbf{A}$. The direction of μ^A is specified by polar angles θ_A and φ_A and the direction of μ^B by θ_B and φ_B. Then

$$\mathbf{R} = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix}, \qquad \mu^A = \mu^A \begin{pmatrix} \sin\theta^A \cos\varphi^A \\ \sin\theta^A \sin\varphi^A \\ \cos\theta^A \end{pmatrix}, \qquad \mu^B = \mu^B \begin{pmatrix} \sin\theta^B \cos\varphi^B \\ \sin\theta^B \sin\varphi^B \\ \cos\theta^B \end{pmatrix}.$$
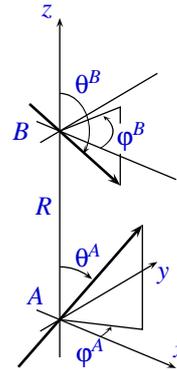
The dipole–dipole interaction becomes

$$U_{\mu\mu} = -\frac{\mu^A \mu^B}{4\pi\varepsilon_0 R^3} \left(2\cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\varphi \right),$$

where $\varphi = \varphi_B - \varphi_A$.

The most favourable orientation, at a given distance R, is $\theta_A = \theta_B = 0$, when the interaction energy is $-2\mu^A \mu^B / 4\pi\varepsilon_0 R^3$.

The geometry with $\theta_A = \theta_B = \pi/2$, $\varphi = \pi$ has energy $-\mu^A \mu^B / 4\pi\varepsilon_0 R^3$ and is also favourable.

$$\frac{\mu^A \mu^B}{4\pi\varepsilon_0 R^3} \times$$

| -2 | $+2$ | -1 | $+1$ | 0 |

Another important interaction is the one between two non-polar ($\mu = 0$) quadrupoles. For a linear molecule or symmetric top, the only non-zero components of the quadrupole moment are $\Theta_{zz} = \Theta$ and $\Theta_{xx} = \Theta_{yy} = -\frac{1}{2}\Theta$.

Note that the distance dependence is R^{-5} in this case.

$$\frac{\Theta^A \Theta^B}{4\pi\varepsilon_0 R^5} \quad \times \quad +6 \qquad -3 \qquad 2\tfrac{1}{4} \qquad +1 \qquad -2\tfrac{7}{16}$$
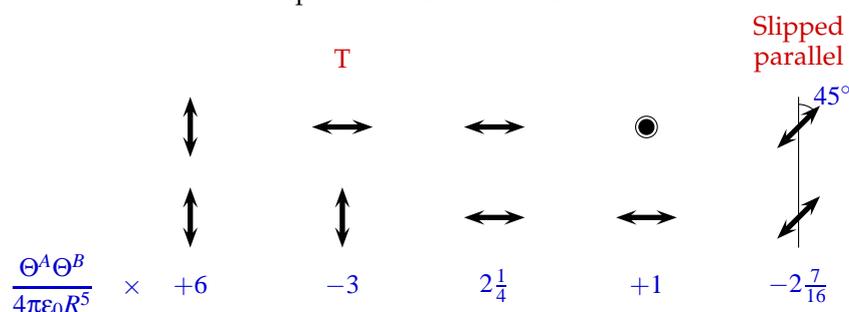
In this case the favourable structures are the 'T' and the 'slipped-parallel' geometries. The better angular factor for the T structure is often counteracted by a smaller separation in the slipped-parallel geometry, and both structures are commonly observed, often in the same crystal.

Many molecules have both a dipole and a quadrupole moment, and the interaction between such molecules involves not only the dipole–dipole and quadrupole–quadrupole terms but also the quadrupole–dipole and dipole–quadrupole.

$$\frac{\Theta^A \mu^B}{4\pi\varepsilon_0 R^4} \quad \times \quad -3 \qquad +3 \qquad -\tfrac{3}{2}$$
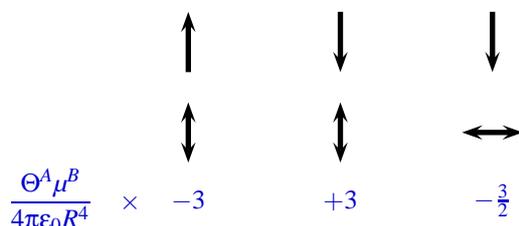
In such cases, the preferred geometry is a compromise between all the effects.

For HF dimer, for instance, the observed geometry is neither T-shaped (as the quadrupole–quadrupole interaction would favour) nor linear (as the dipole–dipole interaction would suggest), but is a non-linear structure with the F–H···F angle close to linear and the FH···F–H angle in the region of 120°.

Let's look at the leading (dipole–dipole) term in the perturbation $\mathcal{V}$, i.e. $-\hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B$. U_{ind}^B (see Eq. (4.11)) becomes

$$U_{ind}^B = -\sum_{n\neq 0} \frac{\langle 0_A 0_B | \hat{\mu}_\alpha^A T_{\alpha\beta} \hat{\mu}_\beta^B | 0_A n_B \rangle \langle 0_A n_B | \hat{\mu}_\delta^A T_{\gamma\delta} \hat{\mu}_\gamma^B | 0_A 0_B \rangle}{W_n^B - W_0^B}$$

$$= -\mu_\alpha^A T_{\alpha\beta} \sum_{n\neq 0} \frac{\langle 0_B | \hat{\mu}_\beta^B | n_B \rangle \langle n_B | \hat{\mu}_\gamma^B | 0 \rangle}{W_n^B - W_0^B} T_{\gamma\delta} \mu_\delta^A$$

$$= -\tfrac{1}{2} \mu_\alpha^A T_{\alpha\beta} \alpha_{\beta\gamma}^B T_{\gamma\delta} \mu_\delta^A. \tag{7.4}$$

Now $-\mu_\beta^A T_{\alpha\beta}$ is the electric field F_α^B at B due to the dipole moment of A, and similarly $-T_{\gamma\delta} \mu_\delta^A = F_\gamma^B$. Thus U_{ind}^B can be written in the form

$$U_{ind}^B = -\tfrac{1}{2} \alpha_{\alpha\gamma}^B F_\alpha^B F_\gamma^B. \tag{7.5}$$

In this example the electric field arises purely from the dipole moment of A, but the source of the field is immaterial. Consequently this result applies equally to the general case of a molecule in the field of all its neighbours.

Induction: Physical interpretation   60

If a molecule is placed in an external electric field $\mathbf{F}$, the electrons experience forces in one direction and the nuclei in another, and the charge distribution distorts. The result is that there is an induced dipole moment $\Delta\mu$. The induced dipole need not be parallel to the applied field, and it is given by the expression

$$\Delta\mu_\xi = \alpha_{\xi\eta} F_\eta, \tag{7.6}$$

where $\alpha_{\xi\eta}$ is the *polarizability tensor*.

E.g. in benzene, the electrons can move more freely in the molecular plane than perpendicular to it, so α_{xx} and α_{yy} (which are equal by symmetry) are larger than α_{zz}.
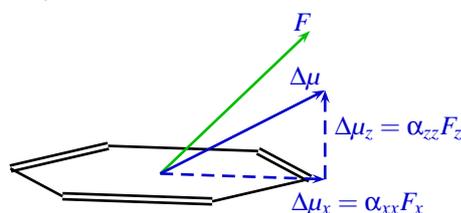
When the electrons distort in response to the field, there is an associated change in the energy. By the variational principle it must be negative, and it takes the form

$$U_{ind} = -\tfrac{1}{2} \alpha_{\xi\eta} F_\xi F_\eta. \tag{7.7}$$

The induction energy: General form

More generally, the energy of interaction between the molecule and a uniform external electric field can be written as a power series in the field:

$$U = -\mu^0_\xi F_\xi - \tfrac{1}{2}\alpha_{\xi\eta}F_\xi F_\eta - \tfrac{1}{6}\beta_{\xi\eta\zeta}F_\xi F_\eta F_\zeta - \cdots, \tag{7.8}$$

where $\beta_{\xi\eta\zeta}$ is the *hyperpolarizability tensor*.

The derivative of this expression with respect to external field is the dipole moment as a function of applied field:

$$\mu_\xi = -\frac{\partial U}{\partial F_\xi} = \mu^0_\xi + \alpha_{\xi\eta}F_\eta + \tfrac{1}{2}\beta_{\xi\eta\zeta}F_\eta F_\zeta + \cdots. \tag{7.9}$$

For simplicity we shall ignore the non-linear hyperpolarizability terms.

Mean polarizability and polarizability anisotropy

For an atom or ion, the induced dipole is always parallel to the electric field, so the polarizability tensor takes the form $\alpha_{\xi\eta} = \overline{\alpha}\delta_{\xi\eta}$, and

$$\Delta\mu_\xi = \overline{\alpha}\delta_{\xi\eta}F_\eta = \overline{\alpha}F_\xi. \tag{7.10}$$

The induction energy becomes

$$U_{\text{ind}} = -\tfrac{1}{2}\overline{\alpha}\delta_{\xi\eta}F_\xi F_\eta = -\tfrac{1}{2}\overline{\alpha}F_\xi F_\xi = -\tfrac{1}{2}\overline{\alpha}F^2. \tag{7.11}$$

In general, we can write

$$\alpha_{\xi\eta} = \overline{\alpha}\delta_{\xi\eta} + \Delta\alpha_{\xi\eta}, \tag{7.12}$$

where

- $\overline{\alpha} = \tfrac{1}{3}\alpha_{\xi\xi}$ is the *mean polarizability*,

- $\Delta\alpha_{\xi\eta}$ is the *polarizability anisotropy*.

The polarizability anisotropy is zero for atoms and ions. The same is true for spherical-top molecules, and it is a good approximation for some less symmetrical molecules.

7.3 Non-additivity of the induction energy

The field at an atom due to a neighbouring dipole μ is $F = 2\mu/R^3$, so the induction energy is $-\frac{1}{2}\alpha F^2 = -2\alpha\mu^2/R^6$.

1

If there are two neighbouring dipoles their fields can add, so that the induction energy is $-\frac{1}{2}\alpha(2F)^2 = -8\alpha\mu^2/R^6 \ldots$

4

... or they can cancel, so that the field and the induction energy are both zero.

0

In both cases the total energy differs greatly from the sum of two pair interactions: the induction energy is strongly non-additive. This makes the induction energy very awkward to handle computationally.
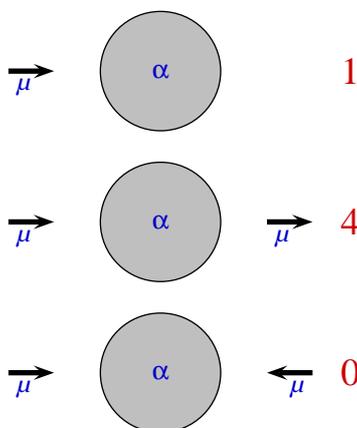
Example: alkaline-earth halides

A striking example of the non-additivity of the induction energy is provided by the alkaline-earth halides such as $MgCl_2$. One might expect the Mg^{2+} ions to be arranged symmetrically around each Cl^- ion. However the electric field at the Cl^- ion is zero in this arrangement, so that the induction energy is also zero.

A less symmetrical arrangement, right, leads to a non-zero field at the Cl^- ion and hence a non-zero induction energy, at the cost of a slightly increased repulsion between the Mg^{2+} ions. If the polarizability of the halide ion is large enough, the distorted structure is favoured, and it is this structure that is observed, except in the fluorides.
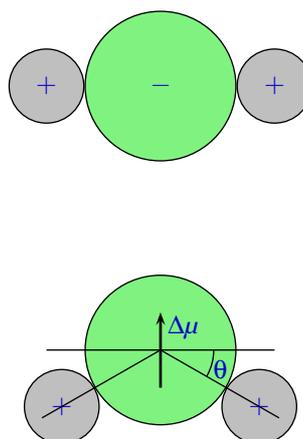
See Wilson and Madden (1994).

Cooperative induction

Another aspect of the non-additivity of the induction energy is its cooperative nature.

In the example shown, each atom is polarized by the *total* dipole of the other, including the induced dipole:

$$\Delta\mu_z^A = \alpha_{zz}^A F_z^A = -\alpha_{zz}^A T_{zz}(\mu_z^B + \Delta\mu_z^B),$$
$$\Delta\mu_z^B = \alpha_{zz}^B F_z^B = -\alpha_{zz}^B T_{zz}(\mu_z^A + \Delta\mu_z^A). \quad (7.13)$$

The induced dipole and the induction energy are enhanced as a result.

The effect is particularly important in hydrogen-bonded liquids such as water.
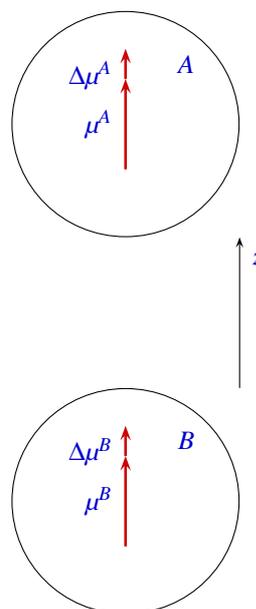
Quadrupole polarizabilities

If a tetrahedral molecule such as CH_4 is placed in a field gradient F_{xy} as shown, the two H atoms in the regions where $xy > 0$ will become positively charged, and those where $xy < 0$ will become negatively charged. The result is a dipole in the z direction and a Θ_{xy} quadrupole moment.
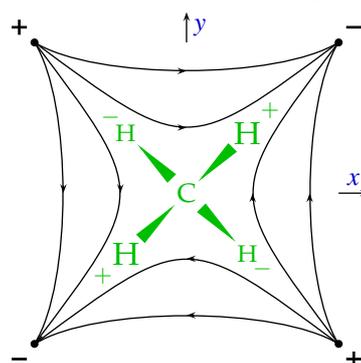
The polarizabilities that describe these effects are the *dipole–quadrupole polarizability* $A_{\xi,\eta\zeta}$ and the *quadrupole–quadrupole polarizability* $C_{\xi\eta,\lambda\zeta}$. In this case,

$$\mu_z = \tfrac{1}{3}A_{z,xy}F_{xy},$$
$$\Theta_{xy} = C_{xy,xy}F_{xy}, \quad (7.14)$$

so both $A_{z,xy}$ and $C_{xy,xy}$ are non-zero for methane and other tetrahedral molecules.

Quadrupole polarizabilities and the induction energy

In a tetrahedral molecule, a uniform field in the z direction induces a quadrupole moment Θ_{xy}. The dipole–quadrupole polarizability describes this effect too:

$$\Theta_{xy} = A_{z,xy} F_z. \tag{7.15}$$

Standard group-theoretical techniques can be used to find the non-zero components of these polarizabilities in any symmetry. For example, the dipole–quadrupole polarizability must change sign under inversion (because F_z changes sign and Θ_{xy} doesn't). If inversion is a symmetry operation, it will leave $A_{\xi,\eta\zeta}$ unchanged, so all components of A must be zero in this case.

In a non-uniform electric field, the induction energy is

$$
\begin{aligned}
U_{\text{ind}} = &-\tfrac{1}{2}\alpha_{\xi\eta}F_\xi F_\eta \\
&-\tfrac{1}{3}A_{\xi,\eta\zeta}F_\xi F_{\eta\zeta} \\
&-\tfrac{1}{6}C_{\xi\eta,\lambda\zeta}F_{\xi\eta}F_{\lambda\zeta} - \cdots
\end{aligned}
\tag{7.16}
$$

7.4 The dispersion energy

We again consider only the dipole-dipole term in $\mathcal{V}$:

$$
\begin{aligned}
U_{\text{disp}}^{(6)} &= -\sum_{m_A \neq 0}\sum_{n_B \neq 0} \frac{\langle 0_A 0_B | \hat{\mu}_\alpha^A T_{\alpha\beta}\hat{\mu}_\beta^B | m_A n_B\rangle\langle m_A n_B | \hat{\mu}_\gamma^A T_{\gamma\delta}\hat{\mu}_\delta^B | 0_A 0_B\rangle}{W_m^A - W_0^A + W_n^B - W_0^B} \\
&= -T_{\alpha\beta}T_{\gamma\delta}\sum_{m_A \neq 0}\sum_{n_B \neq 0} \frac{\langle 0_A | \hat{\mu}_\alpha^A | m_A\rangle\langle m_A | \hat{\mu}_\gamma^A | 0_A\rangle\langle 0_B | \hat{\mu}_\beta^B | n_B\rangle\langle n_B | \hat{\mu}_\delta^B | 0_B\rangle}{W_m^A - W_0^A + W_n^B - W_0^B}.
\end{aligned}
\tag{7.17}
$$

This is an inconvenient expression to deal with, because although the matrix elements can be factorised into a part referring to A and a part referring to B, the denominator cannot.

One way to handle it was first introduced by London, and uses the *Unsöld* or *average-energy* approximation: we assume that the significant terms in the sum over m_A (i.e. those with large numerators) all have excitation energies $W_m^A - W_0^A$ close to some average excitation energy U_A, and that the significant terms for B all have excitation energies close to some average energy U_B.

Using the average-energy approximation:

$$U_{\text{disp}}^{(6)} \approx -T_{\alpha\beta}T_{\gamma\delta} \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A|\hat{\mu}_\alpha^A|m_A\rangle\langle m_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_B|\hat{\mu}_\beta^B|n_B\rangle\langle n_B|\hat{\mu}_\delta^B|0_B\rangle}{U_A + U_B}$$

$$= -\frac{U_A U_B}{U_A + U_B}T_{\alpha\beta}T_{\gamma\delta} \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A|\hat{\mu}_\alpha^A|m_A\rangle\langle m_A|\hat{\mu}_\gamma^A|0_A\rangle\langle 0_B|\hat{\mu}_\beta^B|n_B\rangle\langle n_B|\hat{\mu}_\delta^B|0_B\rangle}{U_A U_B}$$

$$\approx -\frac{U_A U_B}{4(U_A + U_B)}T_{\alpha\beta}T_{\gamma\delta}\alpha_{\alpha\gamma}^A\alpha_{\beta\delta}^B \tag{7.18}$$

(using the average-energy approximation in the polarizability formula).

For atoms, $\alpha_{\alpha\gamma}$ reduces to $\alpha\delta_{\alpha\gamma}$, and this becomes

$$U_{\text{disp}}^{(6)} = -\frac{U_A U_B}{4(U_A + U_B)}\alpha^A\alpha^B T_{\alpha\beta}T_{\alpha\beta} = -\frac{3U_A U_B}{2(U_A + U_B)}\frac{\alpha^A\alpha^B}{(4\pi\varepsilon_0)^2 R^6}, \tag{7.19}$$

because $T_{\alpha\beta}T_{\alpha\beta} = 6/(4\pi\varepsilon_0)^2 R^6$.

$$U_{\text{disp}}^{(6)} = -\frac{3U_A U_B}{2(U_A + U_B)}\frac{\alpha^A\alpha^B}{(4\pi\varepsilon_0)^2 R^6}, \tag{7.20}$$

This is the London formula for the dispersion energy between two atoms, often written as $-C_6 R^{-6}$. Compare this with the Drude approximation eq. (4.26).

- Notice the R^{-6} distance dependence.

- The dispersion coefficient C_6 is proportional to the polarizabilities of both atoms.

- All molecules are polarizable, so dispersion is universal.

- The same formula can be used for molecules, when it gives the dispersion interaction averaged over relative orientations of the two molecules.

- This doesn't give a practical formula for determining C_6, both because it's an approximation and because we don't know U_A or U_B.

A better method

An alternative approach yields an exact formula. It depends on the identity:

$$\frac{1}{A+B} = \frac{2}{\pi} \int_0^\infty \frac{AB}{(A^2+u^2)(B^2+u^2)} \, du, \tag{7.21}$$

which is valid for positive A and B. Applying this formula to the energy denominator in the dispersion energy formula, eq. (7.17), with $\hbar A = W_m^A - W_0^A = \hbar\omega_m^A$, we get

$$U_{\text{disp}}^{(6)} = -\frac{2\hbar}{\pi} T_{\alpha\beta} T_{\gamma\delta} \int_0^\infty {\sum_m}' \frac{\langle 0_A|\hat{\mu}_\alpha^A|m_A\rangle\langle m_A|\hat{\mu}_\gamma^A|0_A\rangle \omega_m^A}{\hbar\big((\omega_m^A)^2+u^2\big)}$$

$$\times {\sum_n}' \frac{\omega_n^B\langle 0_B|\hat{\mu}_\beta^B|n_B\rangle\langle n_B|\hat{\mu}_\delta^B|0_B\rangle}{\hbar\big((\omega_n^B)^2+u^2\big)} \, du. \tag{7.22}$$

We can recognize in the two sums over states the expressions for the polarizabilities of A and B at the imaginary frequency iu, so the result is

$$U_{\text{disp}}^{(6)} = -\frac{\hbar}{2\pi} T_{\alpha\beta} T_{\gamma\delta} \int_0^\infty \alpha_{\alpha\gamma}^A(iu)\alpha_{\beta\delta}^B(iu) \, du. \tag{7.23}$$

The exact formula

$$U_{\text{disp}}^{(6)} = -\frac{\hbar}{2\pi} T_{\alpha\beta} T_{\gamma\delta} \int_0^\infty \alpha_{\alpha\gamma}^A(iu)\alpha_{\beta\delta}^B(iu) \, du. \tag{7.24}$$

For spherical atoms, this reduces in the same way as before to give

$$C_6 = \frac{3\hbar}{(4\pi\varepsilon_0)^2\pi} \int_0^\infty \alpha^A(iu)\alpha^B(iu) \, du. \tag{7.25}$$

- These formulae are formally exact in the limit of large R.

- The polarizabilities can be computed accurately *ab initio* ...

- ... and determined experimentally from data on spectral intensities and frequencies — see, e.g., Kumar and Meath (1985), Meath and Kumar (1990).

Dispersion coefficients

Dispersion coefficients (C_6 coefficients) have dimensions of $[\text{energy}] \times [\text{length}]^6$. In atomic units this becomes $E_h a_0^6$, but many other units are used.

	$C_6/E_h a_0^6$	$\alpha/4\pi\varepsilon_0 a_0^3$		$C_6/E_h a_0^6$	$\alpha/4\pi\varepsilon_0 a_0^3$
$\text{He} \cdots \text{He}$	1·46	1·39	$\text{CO} \cdots \text{CO}$	81·4	13·36
$\text{Ne} \cdots \text{Ne}$	6·6	2·00	$\text{SO}_2 \cdots \text{SO}_2$	294	26·3
$\text{Ar} \cdots \text{Ar}$	64·3	11·08	$\text{CS}_2 \cdots \text{CS}_2$	871	58·7
$\text{Xe} \cdots \text{Xe}$	286	27·67	$\text{HCCH} \cdots \text{HCCH}$	204·1	23·6
$\text{Ar} \cdots \text{Xe}$	134·5		$\text{C}_6\text{H}_6 \cdots \text{C}_6\text{H}_6$	1723	70·2
$\text{He} \cdots \text{CO}$	10·7		$\text{HCCH} \cdots \text{C}_6\text{H}_6$	593·0	

- The values increase rapidly with the number of electrons, corresponding to increasing polarizability.

- As both the London formula and the exact formula suggest, mixed C_6 coefficients may be obtained reasonably accurately from the geometric mean formula, $C_6^{AB} \approx \sqrt{C_6^{AA} C_6^{BB}}$.

Higher terms

The dipole–dipole perturbation that we have used gives only the leading terms in a power series in $1/R$. In general,

$$U_{\text{disp}} = -\frac{C_6}{R^6} - \frac{C_7}{R^7} - \frac{C_8}{R^8} - \dots \tag{7.26}$$

The additional terms arise when dipole–quadrupole, quadrupole–quadrupole, ... terms in the electrostatic perturbation are included.
A general contribution to the dispersion energy looks like

$$-\frac{\hbar}{2\pi} T^{(m+p)} T^{(n+q)} \int \alpha_{(m,n)}^A(\mathrm{i}u) \alpha_{(p,q)}^B(\mathrm{i}u)\, \mathrm{d}u \tag{7.27}$$

where $\alpha_{(m,n)}$ is a polarizability describing the rank m response to a rank n field or *vice versa*, and $T^{(m+p)}$ is an interaction function with $m + p$ suffixes. For example $A_{\alpha,\beta\gamma}$ is an $\alpha_{(1,2)}$. The distance dependence of such a term is $R^{-(m+n+p+q+2)}$.

To get an R^{-7} term we need an $\alpha_{1,1}$ on one molecule and $\alpha_{1,2}$ on the other, and this will give zero for centrosymmetric molecules, where the A tensor vanishes. For similar reasons, all the odd terms vanish for such molecules.

We have used perturbation theory to derive the electrostatic, induction and dispersion components of the interaction energy. This was done without full antisymmetrization of the dimer wavefunction. For small intermolecular separations, the effects of antisymmetrization become very important and lead to additional terms in the interaction energy. These are the *exchange* energies.

At short-range, the expanded forms of the electrostatic, induction and dispersion energies is no longer valid. This occurs for two reasons: (1) Overlap effects become important and must be included. This leads to the *penetration* energy. And (2), the multipole expansion diverges and must be *damped* to remove the singularities.

There is an additional short-range term: the *Charge Transfer*. which is quite non-trivial in origin and can be regarded as a part of the induction energy. It is basis-set-dependent.

We will first derive some properties of the molecular wavefunction that will be useful in understanding these effects.

Suppose that we have a hydrogen-like atom, nuclear charge Z, interacting with a proton.

The only non-zero multipole moment in each case is the charge, and at long range, the interaction energy is $T q_A q_B = (Z-1)e^2/4\pi\varepsilon_0 R$, since the total charge on the hydrogen-like atom is $Z-1$.

If the proton is close enough to penetrate inside the electron cloud of the atom, however, we have to solve Poisson's equation:

$$\nabla^2 V = -\rho/\varepsilon_0. \tag{8.1}$$

For the hydrogen-like atom, the charge density is

$$\rho = Ze\delta(\mathbf{R}) - \frac{eZ^3}{\pi a_0^3}\exp(-2ZR/a_0). \tag{8.2}$$

The first term here is the nuclear charge and the second describes the electron density.

We have to solve

$$\nabla^2 V = -\rho/\varepsilon_0 \quad \text{with} \quad \rho = Ze\delta(\mathbf{R}) - \frac{eZ^3}{\pi a_0^3}\exp(-2ZR/a_0). \qquad (8.3)$$

It is not too difficult to show that the potential satisfying this equation is

$$V = \frac{e}{4\pi\varepsilon_0}\left\{\frac{Z-1}{R} + \exp(-2ZR/a_0)\left(\frac{Z}{a_0} + \frac{1}{R}\right)\right\}. \qquad (8.4)$$

So the energy eV of a proton in this potential has two terms:

- The long-range term $(Z-1)e^2/4\pi\varepsilon_0 R$;

- A *penetration* term $\dfrac{e^2}{4\pi\varepsilon_0}\exp(-2ZR/a_0)\left(\dfrac{Z}{a_0} + \dfrac{1}{R}\right)$.

Here the penetration term is positive (repulsive). Normally it is negative, because it is the electron cloud of each molecule that penetrates into the other, rather than the nuclei.

In common with other short-range terms, the penetration term decays exponentially with increasing separation.

8.2 Damping

The long-range theory gives the dispersion energy between two atoms in the form

$$U_{\text{disp}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots, \qquad (8.5)$$

This clearly cannot be correct in the limit $R \to 0$ — the electronic energy remains finite in that limit, and the nucleus–nucleus repulsion behaves like $1/R$.

Consequently the dispersion energy must take a different form at short range.

As in the case of the short-range repulsion, it is necessary to take exchange of electrons between the molecules into account, and the theory becomes extremely complicated.

For atoms the dispersion energy can be described by a modified expression:

$$U_{\text{disp}} = -f_6(R)\frac{C_6}{R^6} - f_8(R)\frac{C_8}{R^8} - f_{10}(R)\frac{C_{10}}{R^{10}} - \cdots, \tag{8.6}$$

where the $f_n(R)$ are *damping functions*.

The damping functions must satisfy the following conditions:

- $f_n(R) \to 1$ as $R \to \infty$, to recover the long-range formula.

- $f_n(R) \to R^n$ as $R \to 0$, to suppress the singularity.

The form of the damping functions is very hard to calculate. It is usual to use simple model functions that have the right behaviour. The most widely used damping functions are probably those proposed by Tang and Toennies (1984). They are incomplete gamma functions:

$$f_n(R) = 1 - \exp(-bR) \sum_{k=0}^{n} \frac{(bR)^k}{k!} \tag{8.7}$$
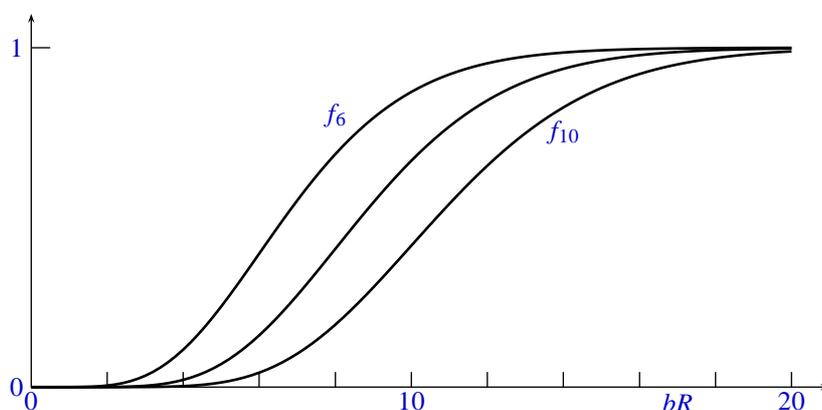
We must take account of the fact that the electrons are indistinguishable and that the wavefunction should be antisymmetric. The wavefunction then becomes

$$\psi = \varphi_A(1)\varphi_B(2) - \varphi_A(2)\varphi_B(1). \tag{8.8}$$

(Remember that the electrons have parallel spin; that is, the spin function is one of the symmetric triplet spin functions.)

This wavefunction is not yet normalized; the normalization integral is

$$\langle\psi|\psi\rangle = \int \Big[\varphi_A(1)^2\varphi_B(2)^2 - 2\varphi_A(1)\varphi_B(2)\varphi_A(2)\varphi_B(1)$$
$$+ \varphi_A(2)^2\varphi_B(1)^2\Big]\, d\tau_1\, d\tau_2$$
$$= 2 - 2S^2, \tag{8.9}$$

where

$$S = \int \varphi_A(1)\varphi_B(1)\, d\tau_1. \tag{8.10}$$

The density for electron 1 is obtained by integrating over electron 2:

$$\rho_1 = \frac{\int |\psi|^2\, d\tau_2}{\langle\psi|\psi\rangle},$$

but the electrons are indistinguishable, so we just multiply by 2 to get the total density:

$$\rho = \frac{2}{2 - 2S^2} \int |\psi|^2\, d\tau_2$$
$$= \frac{1}{1 - S^2} \int \left(\varphi_A(1)^2\varphi_B(2)^2 - 2\varphi_A(1)\varphi_B(2)\varphi_A(2)\varphi_B(1) + \varphi_A(2)^2\varphi_B(1)^2\right) d\tau_2$$
$$= \frac{1}{1 - S^2}(\varphi_A^2 + \varphi_B^2 - 2S\varphi_A\varphi_B). \tag{8.11}$$

At long range, $S \to 0$, so the antisymmetrization makes no difference, but at short range the antisymmetrization and the consequent renormalization affects the charge distribution.

$$\rho = \frac{1}{1 - S^2}(\varphi_A^2 + \varphi_B^2 - 2S\varphi_A\varphi_B)$$
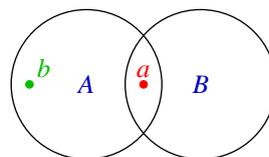
We can see what happens by considering two regions:

(*a*) Midway between the nuclei, $\varphi_A = \varphi_B$ and the electron density is

$$\rho = \frac{2\varphi_A^2(1 - S)}{1 - S^2} = \frac{2\varphi_A^2}{1 + S}, \tag{8.12}$$

which is *less* than the value of $2\varphi_A^2$ obtained by adding together the charge densities of the individual atoms.

(*b*) At a point on the internuclear axis at the far side of atom *A* from atom *B*, where $\varphi_B \approx 0$, the electron density is

$$\rho = \frac{\varphi_A^2}{1 - S^2}, \tag{8.13}$$

which is *greater* than the density for the unperturbed *A* atom.
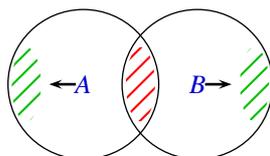
The electron density is no longer the sum of densities for two spherical atoms, but is decreased between the nuclei and increased in the region beyond the nuclei.

Now the Hellmann–Feynman theorem tells us that we can calculate the forces on the nuclei by treating the charge density of the rest of the system classically.

For two spherical neutral atoms the force on each nucleus would be zero, but when electron density is moved from between the nuclei to the ends of the molecule, each nucleus feels a force in the direction away from the other.

That is, there is a repulsive interaction.

8.3 Charge transfer

A charge-transfer interaction can
occur when we have

- an electron donor D (low
  ionization energy I_D)

- an electron acceptor A (high
  electron affinity A_A)

The system then has a low-lying
excited state $|D^+A^-\rangle$ at energy
$I_D - A_A + U_{es}$, where U_{es} describes the
electrostatic attraction between D^+
and A^-, and is negative.

As the molecules approach, we have the usual intermolecular potential
energy curve for $|DA\rangle$. For $|D^+A^-\rangle$, this is modified by the attractive U_{es} term.

Normally $|D^+A^-\rangle$ stays above $|DA\rangle$, because electron affinities are generally
much smaller than ionization energies. We are not concerned here with cases
like the alkali halides, where the ionic state becomes the ground state at short
range.
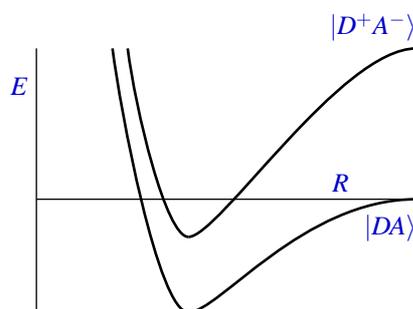
Charge transfer transitions

The charge-transfer state $|D^+A^-\rangle$ can
mix with the ground state $|DA\rangle$ as a
result of the intermolecular
interaction:

$$|\widetilde{DA}\rangle = |DA\rangle + \lambda|D^+A^-\rangle,$$
$$|\widetilde{D^+A^-}\rangle = |D^+A^-\rangle - \lambda|DA\rangle,$$

where λ is some mixing coefficient.
There is an allowed electronic
transition between these two states,
with transition amplitude

$$\langle \widetilde{DA}|\hat{\mu}|\widetilde{D^+A^-}\rangle = \langle DA|\hat{\mu}|D^+A^-\rangle \boxed{+ \lambda\langle D^+A^-|\hat{\mu}|D^+A^-\rangle}$$
$$- \lambda\langle DA|\hat{\mu}|DA\rangle - \lambda^2\langle D^+A^-|\hat{\mu}|DA\rangle. \qquad (8.14)$$

The important term here is the second one, which is λ times the dipole
moment of the charge-transfer state $|D^+A^-\rangle$, which is large. Consequently,
unless λ is very small, the electronic transition between the two states is very
intense.
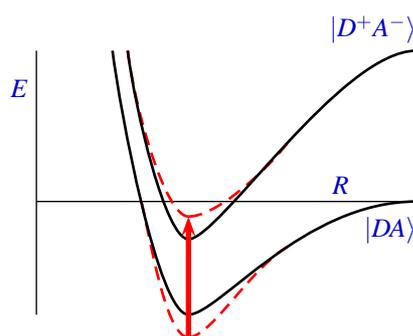
These transitions are called *charge transfer transitions*. Their characteristic features are

- They are very intense.

- They occur only in the complex, and not in either component on its own.

This explanation for their occurrence was first given by Mulliken (1952).

Associated with the mixing between the states $|DA\rangle$ and $|D^+A^-\rangle$ is a change in the energy of both states: they push each other apart, so that the ground state is stabilized.

This stabilization was for a long time assumed to be the main source of the binding between the components of a charge-transfer complex.

With the development of modern *ab initio* methods of calculating intermolecular interactions it has become apparent that other contributions, in particular the electrostatic and dispersion interactions, are responsible for most of the binding, and the charge-transfer term is relatively unimportant.

However it cannot be neglected in donor–acceptor complexes.

9. Distributed Multipoles 88

9.1 Convergence of the multipole series

The multipole expansion converges only if the charge distributions are far enough apart. We construct spheres centred at the local origin of each charge distribution and just enclosing the charges in it.

If the spheres overlap (*top*) the multipole series diverges.

If they do not (*bottom*), it converges.
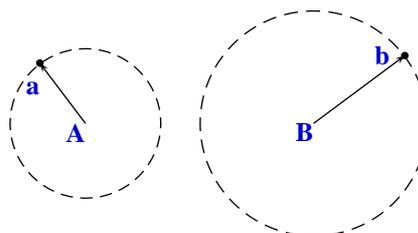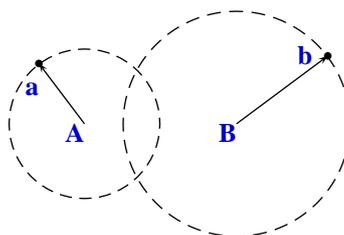
Since molecular charge distributions formally extend to infinity, we might conclude that the multipole series never converges. Fortunately it turns out that this result applies only to the point charges, i.e., the nuclei, and not to the electronic charge distribution. Consequently the convergence spheres should be drawn to enclose the nuclei only.

Even so, it is possible for quite small molecules to approach so closely that their convergence spheres overlap. Even when they do not overlap, convergence of the multipole series may be slow.

The solution is to divide the molecule up into *regions*, each enclosing a single atom or a functional group, and to use a separate multipole expansion for each region.

This leads to a *distributed multipole* description, and the method for determining the multipoles from an *ab initio* wavefunction is called *distributed multipole analysis*.

If the molecular orbitals ψ_k are written as linear combinations of atomic basis functions φ_i:

$$\psi_k = \sum_i c_{ik}\varphi_i, \tag{9.1}$$

the electron density takes the form of a sum of products of the basis functions:

$$\rho(\mathbf{r}) = \sum P_{ij}\varphi_i(\mathbf{r})\varphi_j(\mathbf{r}), \tag{9.2}$$

where P_{ij} is an element of the *density matrix*. This does not depend on any approximations; in principle it is exact if the basis is complete.

Consequently we need to examine the products $\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})$ of pairs of basis functions.

Boys' formula

Boys (1950) showed that the product of two spherical gaussian functions, centred at $\mathbf{a}$ and $\mathbf{b}$, can be expressed as a single gaussian at an intermediate point $\mathbf{p}$, the *overlap centre*:

$$\exp\left[-\zeta_a(\mathbf{r}-\mathbf{a})^2\right]\exp\left[-\zeta_b(\mathbf{r}-\mathbf{b})^2\right]$$
$$= \exp\left[-\frac{\zeta_a\zeta_b}{\zeta_a+\zeta_b}(\mathbf{a}-\mathbf{b})^2\right]\exp\left[(\zeta_a+\zeta_b)(\mathbf{r}-\mathbf{p})^2\right], \qquad (9.3)$$

where $\mathbf{p} = (\zeta_a\mathbf{a}+\zeta_b\mathbf{b})/(\zeta_a+\zeta_b)$.

If the factors $\varphi_i(\mathbf{r})$ and $\varphi_j(\mathbf{r})$ in the product $\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})$ are both spherical gaussian functions, the product is a spherical gaussian and its multipole expansion about $\mathbf{p}$ contains only a charge term.

A p function at a is a gaussian $\exp\left[-\zeta_a(\mathbf{r}-\mathbf{a})^2\right]$ multiplied by a component of $\mathbf{r}-\mathbf{a}$. A basis function with angular momentum l involves a polynomial of degree l in the components of $\mathbf{r}-\mathbf{a}$, and the product of functions of angular momenta l and l' can be expressed in terms of a polynomial of degree $l+l'$ in the components of $\mathbf{r}-\mathbf{p}$.

9.2 Distributed multipole analysis
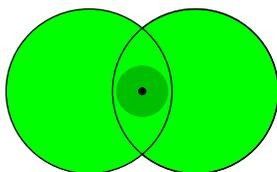
If a basis of gaussian functions is used, the product of two *s* functions is spherically symmetric and can be represented completely just by a point charge at the 'overlap centre' of the two gaussian functions.
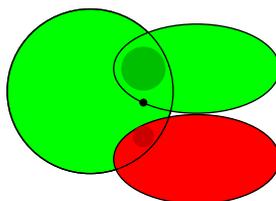
The product of an *s* orbital and a *p* orbital has only charge and dipole components, . . .
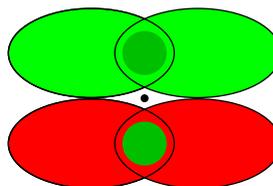
. . . and the product of two *p* functions has charge, dipole and quadrupole components.

If the overlap centre is not at an atom, we can move the origin of the multipole expansion to the nearest distributed multipole site, using the formulae for change of origin. The multipole expansion will no longer terminate, but the higher terms will be small.

We may take the sites wherever we like, but they will usually be at the atoms. For small molecules we may wish to use additional sites at the centres of bonds; for larger molecules we may wish to use a single site to describe a group of atoms such as a methyl group.

This procedure is exact and very fast, but for modern large basis sets with diffuse basis functions it has to be modified somewhat. When a product $\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})$ in eq. (9.2) has exponents ζ_a or ζ_b that are small, the product function extends over several atoms, and it is better to calculate the distributed multipoles by numerical quadrature over a grid of points. The grid can be defined so that each point is associated with a particular site, and the multipoles for each site are obtained by quadrature over the points belonging to that site.

This description then includes, at each site,

- Charges, describing electronegativity effects in a familiar way;

- Dipoles, arising from overlap of s and p orbitals and describing lone pairs and other atomic distortions;

- Quadrupoles, arising from the overlap of p orbitals, and associated with π bonds, for example.

- Octopoles and hexadecapoles can be included if very high accuracy is required.

Examples
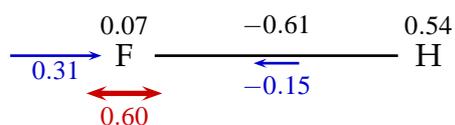
0.07	−0.61	0.54	Charges
F ——————————————— H			Dipoles
0.31	−0.15		Quadrupoles
0.60			

0.5	−1.0	0.5	Charges
N ——————————————— N			Dipoles
0.8		−0.8	Quadrupoles
1.3			

0.3	−0.4	0.1	Charges
C ——————————————— O			Dipoles
0.66		−0.40	Quadrupoles
−0.55	0.68	0.21	

−1.1

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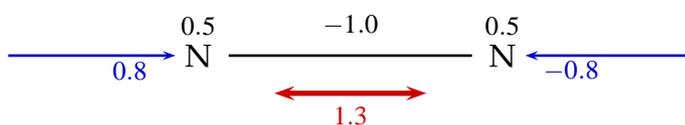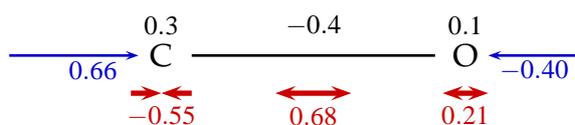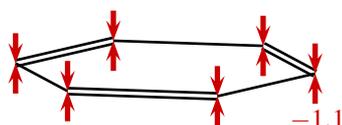
10. The hydrogen bond

The hydrogen bond is a case where all of the main terms in the intermolecular interaction have some part to play, but the most important contributions are electrostatic and repulsion.

- In the hydrogen bond –A–H···B–, A and B are both electronegative, so the charge distribution is –A$^-$–H$^+$···B$^-$–, and there is a strong electrostatic attraction between H and B. There is also an electrostatic repulsion between A and B which tends to keep the hydrogen bond linear.

- Since A is electronegative, the electron density on the H atom is relatively small, and the repulsion between B and H is not very strong.

  Consequently the A···B distance can be quite short — in the strongest hydrogen bonds it may be less than the sum of their Van der Waals radii. This leads to Pauli repulsion between the atoms A and B, which also tends to keep the bond linear.

Features of the hydrogen bond

- The A–H bond lengthens for strong hydrogen bonds. For O–H⋯O bonds, the O–H bond lengthens from 0.96 Å in a free O–H to as much as 1.07 Å in KH_2PO_4, where the O⋯O distance is 2.5 Å.

- The A–H vibration *frequency* decreases and in liquids the spectrum becomes very broad. (H-bond red shift.) This is because the $B^-\cdots H^+$ interaction shifts the minimum and reduces the curvature at the bottom of the well — i.e. the force constant. In liquids the effect depends strongly on the local geometry.

A ← H → B

A–H

$H^+\cdots B^-$

Total
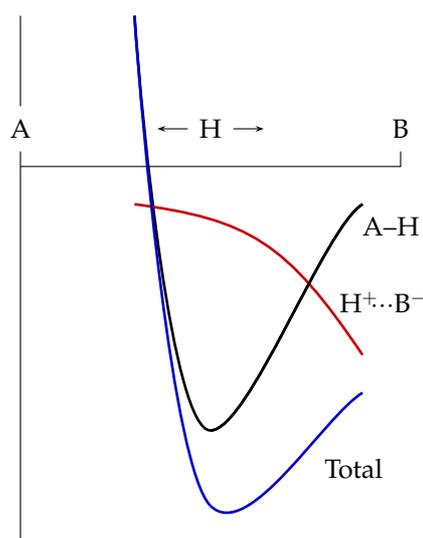
Features of the hydrogen bond

- The A–H vibration *intensity* increases by an order of magnitude or more. The H^+ induces a dipole in B which varies strongly with the H⋯B distance, and the vibrational intensity depends on the dipole derivative.

A ← H → B

A–H

$H^+\cdots B^-$

Total
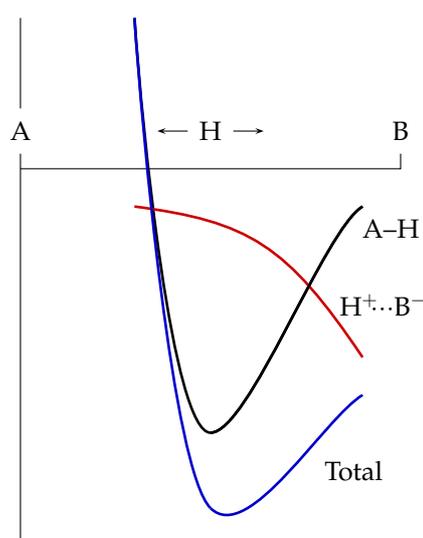
Predicting hydrogen-bonded structures

Because the main contributions to the hydrogen-bond interaction are the electrostatic and repulsion terms, and the electrostatic term accounts for most of the orientation dependence, they can be used alone to predict structures of hydrogen-bonded complexes.

The *Buckingham–Fowler model* (Buckingham and Fowler, 1985) provides a quantitative treatment:

- The electrostatic interaction is described by an accurate distributed multipole analysis,

- and the repulsion by a simple hard-sphere model, using standard Van der Waals radii for the heavy atoms and ignoring any repulsion involving the H atom.

This simple picture gives angular geometries correct to within a few degrees in most hydrogen-bonded complexes.

Limitations of the Buckingham–Fowler model

The simplicity of the repulsion model means that where there is more than one possible geometry their relative energies are sometimes predicted incorrectly.

For example, this model suggests incorrectly that the hydrogen-bonded structure Cl–F···H–F has a lower energy than the 'anti-hydrogen-bonded' structure H–F···Cl–F.

However the *structure* of H–F···Cl–F is given correctly. The relative *energies* are incorrect because the standard van der Waals radius for Cl is too large.
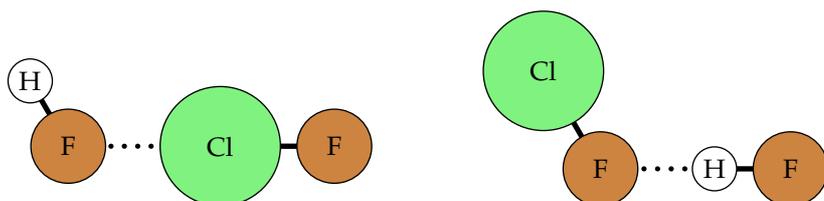
Other terms make important contributions to the energy, but are less
important in determining structure because they are less sensitive to
orientation.

- *Dispersion* provides a significant attractive component.

- *Induction* is important in clusters and condensed phases because of its
  cooperative characteristics.

- *Charge transfer* makes a significant contribution, though not a dominant
  one.

For the water dimer in its equilibrium geometry, the contributions given by
two alternative methods of calculation are, in $kJ\,mol^{-1}$:

	IMPT	SAPT
Electrostatic	−25.8	−31.6
Repulsion	21.3	35.4
Dispersion	−9.2	−11.1
Induction	−4.5 }	−11.4
Charge Transfer	−3.7	
Higher-order corrections		−3.2
Total	−21.9	−20.9

IMPT (InterMolecular Perturbation Theory) (Hayes and Stone, 1984) was the
first successful method for calculating intermolecular interactions *ab initio*.

SAPT (Symmetry Adapted Perturbation Theory) (Jeziorski *et al.*, 1994) is a
later, more accurate, method that includes electron correlation effects.

Intermolecular interactions at long range are relatively easy to calculate in terms of properties of the individual molecules. At short range, however, this approach fails.

Two main methods are available for the calculation of intermolecular interactions *ab initio* at short range: the *Supermolecule method* and *Intermolecular perturbation theory*.

11.1 The supermolecule method

The supermolecule method is very simple in concept:

$$U_{A\cdots B} = E_{A\cdots B} - E_A - E_B.$$

It is also easy to use with any basis set and at any level of theory.

However there are significant disadvantages.

Disadvantages of the supermolecule method 104

- The result is a difference of energies, so there is no variational principle.

- The interaction energy is given as a single number — no physical separation or interpretation.

- Basis set superposition error:
  In the dimer calculation, the basis functions of each molecule become available to improve the description of the other. This leads to a spurious lowering of the energy. The standard treatment for this problem is the *counterpoise method* of Boys and Bernardi (1970): the calculations on the monomers are carried out at each dimer configuration using the *dimer* basis, i.e. with additional 'ghost orbitals' where the basis functions of the other monomer would be.

- Size consistency:
  Some correlation methods (in particular SDCI) give different results for $A\cdots B$ at infinity and for $E_A + E_B$ when each monomer energy is calculated separately. MP2 and coupled-cluster methods avoid this problem.

Supermolecule method with DFT

- Much faster than conventional methods.

- Avoids size consistency problem.

- BSSE remains an issue.

- Still just a single number.

- No dispersion energy.

kJ mol^{-1}	P	sP	T
CCSD(T)	-5.06	-8.41	-9.79
B3LYP	13.26	11.00	2.55
PW91	5.90	3.31	-2.72

Tsuzuki and Lüthi, J. Chem. Phys. **114**, 3949 (2001)

11.2 Short-range perturbation theory

The problem with perturbation theory at short range is the following. Suppose that we separate the Hamiltonian in the obvious way:

$$\mathcal{H} = \mathcal{H}^0 + \lambda\mathcal{H}' = \mathcal{H}(A) + \mathcal{H}(B) + \lambda\mathcal{H}', \tag{11.1}$$

where $\mathcal{H}(A)$ is the Hamiltonian for molecule A alone and $\mathcal{H}(B)$ similarly. Then we have to assign some of the electrons (and nuclei) to A and the rest to B, while $\mathcal{H}'$ describes interactions between these two sets of particles. It follows that $\mathcal{H}^0$ is not invariant to permutations that exchange electrons between the molecules, and neither is $\mathcal{H}'$, but the complete Hamiltonian must be invariant because it must treat all electrons equally. That is,

$$[P, \mathcal{H}] = 0 \quad \text{but} \quad [P, \mathcal{H}^0] = -[P, \lambda\mathcal{H}'] \neq 0, \tag{11.2}$$

and we have an equality between a zeroth-order quantity and a first-order quantity. This destroys the usual separation of the perturbation equations into first-order, second-order and so on.

Many procedures were proposed to overcome the difficulties with short-range perturbation theory, but the first practical method was the InterMolecular Perturbation Theory of Hayes and Stone (1984). This used a matrix solution of the problem in a basis of non-orthogonal Slater determinants constructed from the molecular orbitals of the two molecules.

- Relatively simple and inexpensive.

- SCF unperturbed wavefunctions, so no zeroth-order correlation effects.

- Uncoupled P.T. for second-order terms.

Symmetry-Adapted Perturbation Theory (SAPT) 08

Jeziorski *et al.* (1994)

This method uses a perturbation expansion in the correlation as well as the intermolecular interaction. It is formally an iterative procedure in which projection techniques are used to ensure that the energy is calculated from a correctly-antisymmetrized wavefunction. The Hamiltonian is

$$\mathcal{H} = \mathcal{F}_A + \mathcal{F}_B + \xi W_A + \eta W_B + \lambda V,$$

where

$$\mathcal{F}_A, \mathcal{F}_B \quad \text{are the Fock operators,}$$
$$W_A, W_B \quad \text{are the Møller–Plesset operators,}$$
$$V \quad \text{is the intermolecular perturbation.}$$

Because this method includes correlation corrections it is potentially much more accurate than IMPT, but it is very demanding in computational resources.

Symmetry-Adapted Perturbation Theory (SAPT-DFT)

Misquitta *et al.* (2005)   Hesselmann *et al.* (2005)

The latest development in symmetry-adapted perturbation theory involves the use of Density Functional Theory. The first-order components (U_{es} and U_{exch}) are calculated using the Hamiltonian

$$\mathcal{H} = \mathcal{K}_A + \mathcal{K}_B + \lambda V,$$

where

$$\mathcal{K}_A, \mathcal{K}_B \quad \text{are the Kohn–Sham operators,}$$
$$V \quad \text{is the intermolecular perturbation.}$$

The second-order components (U_{ind} and U_{disp} etc.) are calculated using Kohn–Sham linear response theory — recall that the second-order energies are *response* energies.

This procedure is much simpler and faster than the original SAPT. However it is necessary to use asymptotically-corrected functionals to get good results.

12. Building a model potential   110

Calculating intermolecular interactions *ab initio* is very time-consuming, and it is impractical for detailed studies even of small molecular clusters. For reactions of small molecules in solution, Car–Parrinello simulations, in which the electronic problem is solved using Density Functional Theory in parallel with the evolution of the nuclear coordinates, are becoming feasible but are still very demanding computationally. For studies of proteins in aqueous solution, such methods are out of the question.

It is therefore usual in such applications to use models, in which the interactions are represented more or less accurately by analytical mathematical functions. They are usually constructed by assembling simple functions that describe the different contributions to the interaction, often by fitting to the results of *ab initio* calculations or to experimental data or both.

Repulsion and dispersion are universal. They are commonly described in atom–atom form.

The Lennard-Jones potential

The Lennard-Jones potential has been used for many years:

$$U_{\text{LJ}} = \sum_{ab} 4\varepsilon_{ab} \left[\left(\frac{\sigma_{ab}}{R_{ab}} \right)^{12} - \left(\frac{\sigma_{ab}}{R_{ab}} \right)^6 \right], \tag{12.1}$$

where ε_{ab} and σ_{ab} are well-depth and size parameters describing the interaction between atoms a (in molecule A) and b (in molecule B).

The R^{-12} repulsion is too steep, and to get the well-depth right the coefficient of the R^{-6} term has to be much larger than the true dispersion coefficient, so the long-range description is also wrong.

The L-J potential is computationally convenient, so it was widely used when computers were limited in performance. Although this is no longer a significant consideration it is still used.

The exp-6 potential

A much better form is the 'exp-6' potential:

$$U_{\text{exp-6}} = \sum_{ab} \left\{ K \exp\left[\alpha_{ab}(\rho_{ab} - R_{ab}) \right] - \frac{C_6^{ab}}{R_{ab}^6} \right\}. \tag{12.2}$$

Here there is an explicit dispersion term, while the repulsive part of the interaction is in exponential or 'Born–Mayer' form. K is an arbitrary energy unit (e.g. 1 milliHartree). The parameter ρ_{ab} is the separation at which the repulsion reaches a value of K, so it is a size parameter. α describes the hardness of the repulsion, and is typically around $2\,\text{bohr}^{-1}$.

A disadvantage of the exp-6 form is that the dispersion term tends to $-\infty$ as $R \to 0$, while the repulsion remains finite. Consequently this form of atom–atom potential reaches a maximum on the repulsive wall at some value of R and then dives to $-\infty$. This normally happens for values of R well inside the repulsive reggion, but it leads to difficulties in some simulations. It can be overcome by damping the dispersion, but that makes the potential more complicated.

Models of the electrostatic interaction

The electrostatic interaction is very commonly described using atomic point charges:

$$U_{es} = \sum_{ab} \frac{q_a q_b}{4\pi\varepsilon_0 R_{ab}}. \tag{12.3}$$

The point charges are usually obtained nowadays by fitting them so as to reproduce the electrostatic potential of the molecule as accurately as possible.

A distributed-multipole model, with atomic multipoles up to quadrupole, gives a much better description but is computationally more demanding.

In either case, the necessary parameters can be obtained from calculations on the isolated molecules. The repulsion, on the other hand, can only be obtained from calculations on the complex at many different relative configurations, so its determination is much more difficult.

Anisotropy

In their simplest form, all of these expressions treat the atoms as spherical. Inclusion of higher moments in a distributed-multipole model describes the anisotropy of atoms in the molecular environment.

Better accuracy can be achieved by allowing the parameters in the repulsion model (ρ and α in the exp-6 model) to depend on the relative orientation of the atoms a and b, but this increases the computational cost. In the same way, the dispersion can be described more accurately by allowing the C_6^{ab} coefficients to depend on orientation.

Because of the steepness of the repulsion, the intermolecular potential is very sensitive to anisotropy in the repulsion.

Atoms in molecules are not spherical

This effect has been illustrated graphically by the work of Nyburg and Faerman (1985), who explored the distances of closest approach of atoms in crystals. Their plots show very clearly the non-spherical shape of atoms in molecules, especially for halogens.
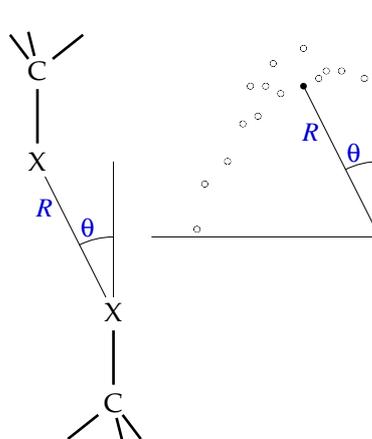
Crystals with a pair of atoms in the geometry shown were entered as points on a scatter plot according to the (R, θ) values. The points on the plot map out an effective van der Waals surface for the atom concerned.

Example: Most diatomics crystallize in a cubic structure. The halogen diatomics Cl_2, Br_2 and I_2 have a different structure. It arises because these halogen atoms in molecules are not spherical but are flattened at the ends.
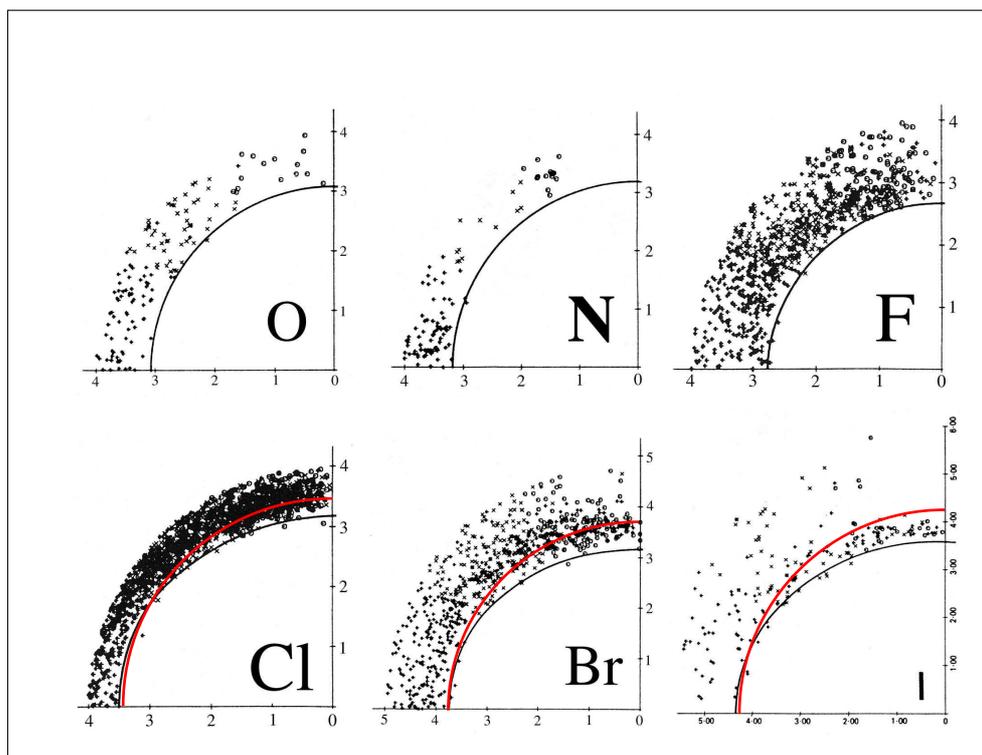
Models of induction

The induction term is frequently omitted altogether, because its inclusion adds greatly to the computational cost. The induced moments of any one molecule in a cluster or liquid depends on the field at that molecule, which in turn depends on the moments of all the other molecules, including their induced moments. The simultaneous equations describing this situation have to be solved at each step of the simulation. This is not difficult — it can be done iteratively in just a few steps — but it adds to the computation time.

Often the effect of induction is included in part by modifying the electrostatic term. In models of liquid water, for instance, it is common to use values of the point charges that yield an enhanced molecular dipole moment of around 2.3 D, rather than the value of 1.8 D that is appropriate for the isolated molecule.

Clearly such an approach cannot reproduce any of the non-additive character of induction.

Molecular mechanics

For studies of proteins and other large flexible molecules, a complete 'force field' includes 'intermolecular' terms between different molecules and between atoms in the same molecule that are not directly bonded, and intramolecular terms describing bond bends, stretches and torsions. In protein studies it is essential to include the water solvent in some way, either by including explicit water molecules in the simulation or by approximating the effect of solvent, for example by treating it as a continuous dielectric medium. The resulting potential model is very elaborate — there are many dozens of parameters, even if the simplest form is used for each potential term.

For more details, see Leach (2001), Ch. 3.

Part III Chemistry 2007–2008 — Course M4

Intermolecular Forces

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