

THEORY OF INTERMOLECULAR INTERACTIONS

There are two principal methods of calculating the intermolecular interactions: the supermolecular method and the perturbational method. Both assume the Born–Oppenheimer approximation.

INTERACTION ENERGY CONCEPT

$$E_{\text{int}}(\mathbf{R}) = E_{ABC\dots}(\mathbf{R}) - [E_A(\mathbf{R}) + E_B(\mathbf{R}) + E_C(\mathbf{R}) + \dots],$$

where $E_{ABC\dots}(\mathbf{R})$ is the electronic energy of the total system, and $E_A(\mathbf{R})$, $E_B(\mathbf{R})$, $E_C(\mathbf{R})$, . . . are the electronic energies of the interacting subsystems, calculated *at the same positions of the nuclei as those in the total system*.

BINDING ENERGY

$$E_{\text{bind}} = E_{ABC\dots}(\mathbf{R}_{\text{opt}(\text{tot})}) - \sum_{j=A,B,C,\dots} E_j(\mathbf{R}_{\text{opt}(j)}). \quad (?)\mathbf{R}_{\text{opt}(j)}$$

DISSOCIATION ENERGY

$$E_{\text{diss}} = E_{\text{bind}} - \left[\Delta E_{0,\text{tot}} - \sum_{j=A,B,C,\dots} \Delta E_{0,j} \right],$$

Where $\Delta E_{0,\text{tot}}$ stands for what is known as the zero vibration energy

$$\Delta E_{0,\text{tot}} = \frac{1}{2} \sum_i h\nu_{i,\text{tot}}, \quad \Delta E_{0,A} = \frac{1}{2} \sum_i h\nu_{i,A}$$

SUPERMOLECULAR APPROACH

Interaction of two subsystems: A and B.

ACCURACY SHOULD BE THE SAME

This problem is already encountered at the stage of basis set choice. For example, suppose we have decided to carry out the calculations within the Hartree-Fock method in the LCAO-MO approximation. The same method has to be used for AB, A and B. However what does this really mean? Should we use the following protocol:

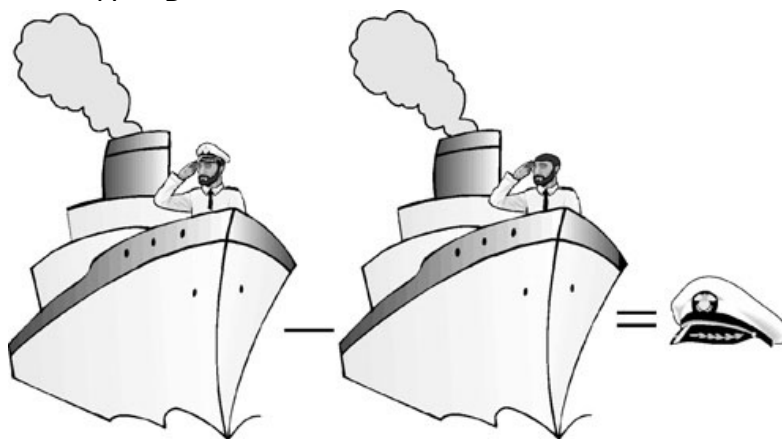
BASIS SET SUPERPOSITION ERROR (BSSE)

When the calculations are performed for E_{AB} within the basis set Ω we calculate implicitly not only the interaction energy, but also we allow the individual subsystems to lower their energy. Conclusion: by subtracting from E_{AB} the energies: E_A calculated with Ω_A and E_B with Ω_B , we are left not only with the interaction energy (as should be), but also with an unwanted and nonphysical extra term (an error) connected with the artificial lowering of the subsystems' energies, when calculating E_{AB} . This error is called the BSSE (Basis Set Superposition Error).

GOOD AND BAD NEWS ABOUT THE SUPERMOLECULAR METHOD

The resulting E_{int} has two disadvantages:

- 1) it does not tell us anything about why the particular value is obtained.
- 2) Formally everything is perfect, but there is a cancellation of significant digits in E_{AB} and $(E_{\text{A}}+E_{\text{B}})$, that may lead to a very poor interaction energy.



Important advantage

A big advantage of the supermolecular method is its applicability at any intermolecular distance, i.e. independently of how strong the interaction is.

PERTURBATIONAL APPROACH TO INTERMOLECULAR INTERACTION

POLARIZATION APPROXIMATION

According to the Rayleigh–Schrödinger perturbation theory the unperturbed Hamiltonian $\hat{H}^{(0)}$ is a sum of the isolated molecules' Hamiltonians:

$$\hat{H}^{(0)} = \hat{H}_A + \hat{H}_B.$$

Then the perturbation operator is: $H^{(1)} \equiv V$.

In the **polarization approximation**, the zeroth-order wave function will be taken as a product

$$\psi_0^{(0)} = \psi_{A,0} \psi_{B,0},$$

where $\psi_{A,0}$ and $\psi_{B,0}$ are the exact ground state wave functions for the isolated molecules A and B respectively, i.e.

$$\hat{H}_A \psi_{A,0} = E_{A,0} \psi_{A,0},$$

$$\hat{H}_B \psi_{B,0} = E_{B,0} \psi_{B,0}.$$

The chosen $\psi^{(0)}_0$ has a wonderful feature, namely it represents an eigenfunction of the $H^{(0)}$ operator, as is required by the Rayleigh–Schrödinger perturbation theory. But the function $\psi^{(0)}_0$ **is not antisymmetric** with respect to the electron exchanges between molecules, while the exact function has to be antisymmetric with respect to any exchange of electron labels.

We will assume that, because of the large separation of the two molecules, the electrons of molecule A are **distinguishable** from the electrons of molecule B. We have to stress the classical flavour of this approximation.

Secondly, we assume that the exact wave functions of both isolated molecules: ψ_{A0} and ψ_{B0} are at our disposal. Of course, function $\psi^{(0)}_0$ is only an approximation to the exact wave function of the total system. Intuition tells us that this approximation is probably very good, because we assume the perturbation is small and the **product function** $\psi_0^{(0)} = \psi_{A,0}\psi_{B,0}$, is an exact wave function for the non-interacting system.

First order effect: electrostatic energy

$$E_0^{(1)} \equiv E_{\text{elst}} \equiv E_{\text{pol}}^{(1)} = \langle \psi_0^{(0)} | V | \psi_0^{(0)} \rangle,$$

The electrostatic energy represents the Coulombic interaction of two “frozen” charge distributions corresponding to the isolated molecules A and B, because it is the mean value of the Coulombic interaction energy operator V calculated with the wave function $\psi_0^{(0)}$ being the product of the wave functions of the isolated molecules $\psi_0^{(0)} = \psi_{A0} \psi_{B0}$.

Second-order energy: induction and dispersion energies

The second-order energy in the polarization approximation approach can be expressed in a slightly different way. The n -th state of the total system at long intermolecular distances corresponds to some states n_A and n_B of the individual molecules, i.e.

$$\psi_n^{(0)} = \psi_{A,n_A} \psi_{B,n_B}$$

and

$$E_n^{(0)} = E_{A,n_A} + E_{B,n_B}.$$

Using this assumption, the second-order correction to the ground-state energy (we assume $n = 0$ and $\psi^{(0)}_0 = \psi_{A0} \psi_{B0}$) can be expressed as

$$E_0^{(2)} = \sum_{n_A} \sum'_{n_B} \frac{|\langle \psi_{A,n_A} \psi_{B,n_B} | V | \psi_{A,0} \psi_{B,0} \rangle|^2}{(E_{A,0} - E_{A,n_A}) + (E_{B,0} - E_{B,n_B})},$$

where “prime” in the summation means excluding $n = 0$, or $(n_A, n_B) = (0, 0)$. The quantity $E_0^{(2)}$ can be divided in the following way

$$E_0^{(2)} = \sum_{n_A} \sum'_{n_B} \dots = \sum_{(n_A=0, n_B \neq 0)} \dots + \sum_{(n_A \neq 0, n_B=0)} \dots + \sum_{(n_A \neq 0, n_B \neq 0)} \dots$$

Let us construct a matrix A (of infinite dimension) composed of the element $A_{00} = 0$ and the other elements calculated from the formula

$$A_{n_A, n_B} = \frac{|\langle \psi_{A, n_A} \psi_{B, n_B} | V | \psi_{A, 0} \psi_{B, 0} \rangle|^2}{(E_{A, 0} - E_{A, n_A}) + (E_{B, 0} - E_{B, n_B})}$$

and divide it into the following parts: I ($n_B \neq 0$), II ($n_A \neq 0$), III ($(n_A \neq 0, n_B \neq 0)$)

The quantity $E^{(2)}_0$ is a sum of all the elements of A. This summation will be carried out in three steps.

First, part I, ($n_A = 0$) represents the **induction energy** associated with forcing a change in the charge distribution of the molecule B by the charge distribution of the isolated (“frozen”) molecule A.

Second, part II ($n_B = 0$) has a similar meaning, but the roles of the molecules are interchanged.

Finally, part III, (n_A and n_B not equal to zero) represents the *dispersion energy*.

Therefore

$$E_0^{(2)} = E_{\text{ind}}(A \rightarrow B) + E_{\text{ind}}(B \rightarrow A) + E_{\text{disp}},$$

$$E_{\text{ind}}(A \rightarrow B) = \sum'_{n_B} \frac{|\langle \psi_{A,0} \psi_{B,n_B} | V | \psi_{A,0} \psi_{B,0} \rangle|^2}{(E_{B,0} - E_{B,n_B})},$$

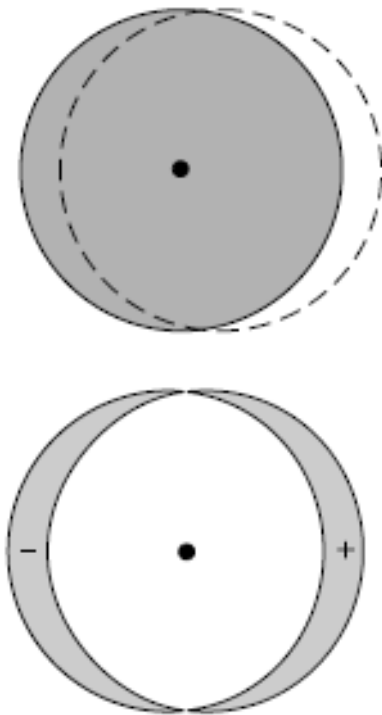
$$E_{\text{ind}}(B \rightarrow A) = \sum'_{n_A} \frac{|\langle \psi_{A,n_A} \psi_{B,0} | V | \psi_{A,0} \psi_{B,0} \rangle|^2}{(E_{A,0} - E_{A,n_A})},$$

$$E_{\text{disp}} = \sum'_{n_A} \sum'_{n_B} \frac{|\langle \psi_{A,n_A} \psi_{B,n_B} | V | \psi_{A,0} \psi_{B,0} \rangle|^2}{(E_{A,0} - E_{A,n_A}) + (E_{B,0} - E_{B,n_B})}.$$

In these formulas we sometimes see arguments for the interacting molecules undergoing excitations.

We have to recall however that all the time we are interested in the ground state of the total system, and calculating its energy and wave function. The excited state wave functions appearing in the formulas are the consequence of the fact that the first-order correction to the wave function is expanded in a complete basis set chosen deliberately as $\{\psi_n^{(0)}\}$. If we took another basis set, e.g., the wave functions of another isoelectronic molecule, we would obtain the same numerical results (although the formulas will not hold), but the argument would be removed.

From the mathematical point of view, ***the very essence of the perturbation theory means a small deformation of the starting $\psi_0^{(0)}$ function.*** This tiny deformation is the target of the expansion in the basis set $\{\psi_n^{(0)}\}$.



A perturbation of the wave function is a *small correction*.

Fig. (a) shows in a schematic way, how a wave function, spherically symmetric with respect to the nucleus, can be transformed into a function that is shifted off the nucleus.

The function representing the correction is shown schematically in Fig. (b). Please note the function has symmetry of a p orbital.

INTERMOLECULAR INTERACTIONS: PHYSICAL INTERPRETATION

The very essence of the multipole expansion is a *replacement* of the Coulombic interaction of two particles (one from molecule A, the other from the molecule B) by an infinite sum of interactions of what are called multipoles, where each interaction term has in the denominator an integer power of the distance (called the *intermolecular distance R*) between the origins of the two coordinate systems localized in the individual molecules.

The multipole expansion describes the intermolecular interaction of two non-spherically symmetric, distant objects by the “interaction” of deviations (multipoles) from spherical symmetry.

Let us introduce two Cartesian coordinate systems with x and y axes in one system parallel to the corresponding axes in the other system, and with the z axes collinear. One of the systems is connected to molecule A, the other one to molecule B, and the distance between the origins is R (“intermolecular distance”).

The **operator V of the interaction energy** of two molecules may be written as

$$V = - \sum_j \sum_a \frac{Z_a}{r_{aj}} - \sum_i \sum_b \frac{Z_b}{r_{bi}} + \sum_{ij} \frac{1}{r_{ij}} + \sum_a \sum_b \frac{Z_a Z_b}{R_{ab}},$$

where the summations over i and a correspond to all electrons and nuclei of molecule A, and over j and b of molecule B.

In \mathbf{V} terms with inverse interparticle distance are present. For any such term we may write the corresponding multipole expansion where s is smaller of numbers k and l):

$$-\frac{Z_a}{r_{aj}} = \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(a)^* \hat{M}_B^{(l,m)}(j),$$

$$-\frac{Z_b}{r_{bi}} = \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(i)^* \hat{M}_B^{(l,m)}(b),$$

$$\frac{1}{r_{ij}} = \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(i)^* \hat{M}_B^{(l,m)}(j),$$

$$\frac{Z_a Z_b}{R_{ab}} = \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(a)^* \hat{M}_B^{(l,m)}(b),$$

with
$$A_{kl|m|} = (-1)^{l+m} \frac{(k+l)!}{(k+|m|)!(l+|m|)!}$$

and the multipole moment $M_C^{(km)}(n)$ pertains to particle n and is calculated in “its” coordinate system $C = A, B$. For example,

$$\hat{M}_A^{(k,m)}(a) = Z_a R_a^k P_k^{|m|}(\cos \theta_a) \exp(im\phi_a)$$

When all such expansions are inserted into the formula for \mathbf{V} , we may perform the following chain of transformations:

$$\begin{aligned}
 V &= -\sum_j \sum_a \frac{Z_a}{r_{aj}} - \sum_i \sum_b \frac{Z_b}{r_{bi}} + \sum_{ij} \frac{1}{r_{ij}} + \sum_a \sum_b \frac{Z_a Z_b}{R_{ab}} \\
 &\cong \sum_j \sum_a \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(a) * \hat{M}_B^{(l,m)}(j) \\
 &\quad + \sum_i \sum_b \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(i) * \hat{M}_B^{(l,m)}(b) \\
 &\quad + \sum_{ij} \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(i) * \hat{M}_B^{(l,m)}(j) \\
 &\quad + \sum_a \sum_b \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)}(a) * \hat{M}_B^{(l,m)}(b)
 \end{aligned}$$

$$\begin{aligned}
&= \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \left\{ \left[\sum_a \hat{M}_A^{(k,m)}(a) \right]^* \left[\sum_j \hat{M}_B^{(l,m)}(j) \right] \right. \\
&\quad + \left[\sum_i \hat{M}_A^{(k,m)}(i) \right]^* \left[\sum_b \hat{M}_B^{(l,m)}(b) \right] + \left[\sum_i \hat{M}_A^{(k,m)}(i) \right]^* \left[\sum_j \hat{M}_B^{(l,m)}(j) \right] \\
&\quad \left. + \left[\sum_a \hat{M}_A^{(k,m)}(a) \right]^* \left[\sum_b \hat{M}_B^{(l,m)}(b) \right] \right\} \\
&= \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \left[\sum_a \hat{M}_A^{(k,m)}(a) + \sum_i \hat{M}_A^{(k,m)}(i) \right]^* \\
&\quad \times \left[\sum_b \hat{M}_B^{(l,m)}(b) + \sum_j \hat{M}_B^{(l,m)}(j) \right] \\
&= \sum_{k=0} \sum_{l=0} \sum_{m=-s}^{m=s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_A^{(k,m)*} \hat{M}_B^{(l,m)}.
\end{aligned}$$

In the square brackets we can recognize the multipole moment operators for the total molecules calculated in “their” coordinate systems

$$\begin{aligned}
\hat{M}_A^{(k,m)} &= \sum_a \hat{M}_A^{(k,m)}(a) + \sum_i \hat{M}_A^{(k,m)}(i), \\
\hat{M}_B^{(l,m)} &= \sum_b \hat{M}_B^{(l,m)}(b) + \sum_j \hat{M}_B^{(l,m)}(j).
\end{aligned}$$

The lowest moment is the net charge (monopole) of the molecules

$$\hat{M}_A^{(0,0)} = q_A = (Z_A - n_A),$$

$$\hat{M}_B^{(0,0)} = q_B = (Z_B - n_B),$$

where Z_A is the sum of all the nuclear charges of molecule A, and n_A is its number of electrons (similarly for B).

The next moment is $M_A^{(1,0)}$, which is a component of the dipole operator equal to

$$\hat{M}_A^{(1,0)} = -\sum_i z_i + \sum_a Z_a z_a,$$

In this way we can rewrite the initial potential V into the final multipole form:

$$V = \frac{q_A q_B}{R} - R^{-2}(q_A \hat{\mu}_{Bz} - q_B \hat{\mu}_{Az}) + R^{-3}(\hat{\mu}_{Ax} \hat{\mu}_{Bx} + \hat{\mu}_{Ay} \hat{\mu}_{By} - 2\hat{\mu}_{Az} \hat{\mu}_{Bz})$$

$$+ R^{-3}(q_A \hat{Q}_{B,z^2} + q_B \hat{Q}_{A,z^2}) + \dots,$$

$$\hat{M}^{(0,0)} = qr^0 P_0^0(\cos \theta) \exp(i0\phi) = q.$$

MONOPOLE

The monopole for a particle simply means its charge.

Let us go to $k = 1$, i.e. to the dipole moment. Since $m = -1, 0, +1$, the dipole moment has three components. First, let us consider $\hat{M}^{(1,0)}$

$$\hat{M}^{(1,0)} = qr^1 P_1^0(\cos \theta) \exp(i0\phi) = qr \cos \theta = qz.$$

DIPOLE MOMENT OPERATOR

Thus the z -component of the dipole moment operator of a single particle is equal to qz . The other components are:

$$\begin{aligned} M^{(1,1)} &= qr^1 P_1^1(\cos \theta) \exp(i\phi) = qr \sin \theta (\cos \phi + i \sin \phi) \\ &= q(x + iy), \end{aligned}$$

$$\begin{aligned} M^{(1,-1)} &= qr^1 P_1^1(\cos \theta) \exp(-i\phi) = qr \sin \theta (\cos \phi - i \sin \phi) \\ &= q(x - iy). \end{aligned}$$

After a careful (but a little boring) derivation, we arrive at Table X.1 (up to the octupole). Just to make the table simpler, every multipole moment of the particle has been divided by q . Thus the operator of the 2^k -pole moment of a charged particle simply represents a k -th degree polynomial of x y z .

Table X.1. Multipole moments $\hat{M}^{(k,m)}$ divided by q

$k \backslash m$	0	± 1	± 2	± 3
0 charge	1	-	-	-
1 dipole	z	$x + iy$ $x - iy$	-	-
2 quadrupole	$\frac{1}{2}(3z^2 - r^2)$	$3z(x + iy)$ $3z(x - iy)$	$3(x + iy)^2$ $3(x - iy)^2$	-
3 octupole	$\frac{1}{2}(5z^3 - 3zr^2)$	$\frac{3}{2}(x + iy)(5z^2 - r^2)$ $\frac{3}{2}(x - iy)(5z^2 - r^2)$	$15z(x + iy)^2$ $15z(x - iy)^2$	$15(x + iy)^3$ $15(x - iy)^3$

The multipoles depend on the coordinate system chosen

Any multipole moment value (except the monopole) depends on our imagination because we are free to choose any coordinate system, e.g., the z coordinate of the particle in such a system will also depend on us!

It turns out that if we calculate the multipole moments, then the lowest non-vanishing multipole moment does not depend on the coordinate system translation, the other moments in general do depend on it.

This is not peculiar for the multipole moments but represents a property of every term of the form $x^n y^l z^m$. Indeed, $k = n + l + m$ tells us that we have to do with a 2^k -pole. Let us shift the origin of the coordinate system by the vector L . Then the $x^n y^l z^m$ moment calculated in the new coordinate system, i.e. $x'^n y'^l z'^m$ is equal to

$$\begin{aligned}(x')^n (y')^l (z')^m &= (x + L_x)^n (y + L_y)^l (z + L_z)^m \\ &= x^n y^l z^m + \text{a linear combination of lower multipole moments.}\end{aligned}$$

If, for some reason, all the lower moments are equal to zero, this would mean the invariance of the moment of choice of the coordinate system.

Let us take, e.g., the system ZnCl^+ .

In the first approximation, the system may be approximated by *two point-like charges Zn^{2+} and Cl^-* . Let us locate these charges on the z axis in such a way that Zn^{2+} has the coordinate $z = 0$, and Cl^- : $z = 5$. Now we would like to calculate the z component of the dipole moment:

$$M^{(10)} = \mu_z = q_1 z_1 + q_2 z_2 = (+2)0 + (-1)5 = -5. \quad \text{a co } \text{ZnCl}_2 \dots?$$

What if we had chosen another coordinate system? Let us check what would happen if the origin of the coordinate system were shifted towards the positive z by 10 units. In such a case the ions have the coordinates $z_1 = -10$, and $z_2 = -5$, and, as the z component of the dipole moment we obtain

$$M^{(10)'} = \mu_z' = q_1 z_1' + q_2 z_2' = (+2)(-10) + (-1)(-5) = -15.$$

Thus, the dipole moment depends on the choice of the coordinate system. However, the monopole of the system is equal to $(+2) + (-1) = +1$ and this number will not change with any shift of the coordinate system. Therefore,

the dipole moment of a molecular ion depends on us, through arbitrary choice of the coordinate system.

Interaction energy of non-point like multipoles

In our chemical understanding of intermolecular interactions, multipole–multipole (mainly dipole–dipole, as for interactions in, e.g., water) interactions play an important role. The dipolar molecules have non-zero dimensions and therefore they represent something other than point-like dipoles. Let us clarify this by taking the simple example of two dipolar systems located on the z axis (Fig. X.3): the system A consists of the two charges +1 at z = 0 and -1 at z = 1, while system B also has two charges +1 with z = 10 and -1 with z = 11.

The first idea is that ***we have to do with the interaction of two dipoles*** and that's all there is to it. Let us ***check whether everything is OK***. The checking is very easy, because what really interacts are the charges, no dipoles whatsoever. Thus the exact interaction of systems A and B is $(+1)(+1)/10 + (+1)(-1)/11 + (-1)(+1)/9 + (-1)(-1)/10 = 2/10 - 1/11 - 1/9 = -0.0020202$. What would give such a dipole–dipole interaction? Such a task immediately poses the question of how such an interaction is to be calculated.

The first advantage of the multipole expansion is that it produces the formulae for the multipole–multipole interactions.

We have the dipole–dipole term in the form $R^{-3}(\mu_{ax}\mu_{bx} + \mu_{ay}\mu_{by} - 2\mu_{az}\mu_{bz}) = R^{-3}(-2\mu_{az}\mu_{bz})$, because the x and y components of our dipole moments are equal zero. Since A and B are neutral, it is absolutely irrelevant which coordinate system is to be chosen to calculate the dipole moment components. Therefore let us use the global coordinate system, in which the positions of the charges have been specified. Thus, $\mu_{az} = (+1) \cdot 0 + (-1) \cdot 1 = -1$ and $\mu_{bz} = (+1) \cdot 10 + (-1) \cdot 11 = -1$.

přesněji $+1 \cdot (-.5) + (-1) \cdot .5 = -1$
 quadr. $+1 \cdot (-.5)^2 + (-1) \cdot (.5)^2 = 0$

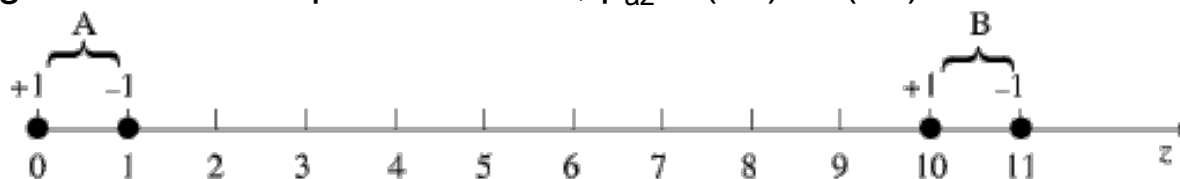


Fig. X.3. The interaction of *non-pointlike* dipoles also contains interactions of higher multipoles.

What is R (intermolecular)?

We are forced to choose the two local coordinate systems in A and B. We *arbitrarily decide here to locate these origins in the* middle of each dipolar system, and therefore $R = 10$. It looks like a reasonable choice, and as will be shown later on, it really is. We are all set to calculate the dipole–dipole interaction:

$$-2 \cdot 10^{-3}(-1)(-1) = -0.0020000. \text{ **Close!**}$$

The **exact calculated** interaction energy is -0.0020202 .

Where is the rest?

Is there any error in our dipole–dipole interaction formula? We simply forgot that our dipolar systems represent not only the dipole moments, but also have non-zero octupole moments (the quadrupoles are equal zero) and non-zero higher odd-order multipoles.

How come, however, that such a simple dipolar system also has a non-zero octupole moment?

The answer is simple: it is because the dipole is not point-like.

The conclusion from this story is that the reader has to pay attention to whether we have to deal with point-like or non-point-like multipole moments.

Properties of the multipole expansion

When performing multipole expansions, at least three simple questions arise:

- a) How do we truncate the expansion, i.e. how do we choose the values of n_k and n_l in the multipole expansion?
- b) Since the multipole moments depend, in general, on the coordinate system chosen, what sort of miracle makes the multipole expansion *of the energy, independent* of the coordinate system?
- c) When does the multipole expansion make sense, i.e. when does it converge?

Truncating the multipole expansion and its coordinate system dependence

It turns out that questions *a and b are closely related* to each other. When n_k and n_l are finite and non-zero then the result of the multipole expansion is ***in general coordinate-dependent***. If, n_k and n_l satisfy

$$n_k + n_l = \text{const},$$

we may shift both coordinate systems (the same translation for both) however we like, and the interaction energy calculated remains invariant.

Such a recipe for n_k and n_l corresponds to taking all the terms with a given power of R^{-1} .

If we take all the terms with a given R^{-m} dependence, the result does not depend on the same translations of both coordinate systems.

This means that to maintain the invariance of the energy with respect to equal translations of both coordinate systems, we have to calculate all terms satisfying $n_k + n_l = n_{\max}$ in the multipole expansion.

If, e.g., $n_{\max} = 2$, we have to calculate the term proportional to R^{-1} or the charge–charge interaction (it will be invariant), proportional to R^{-2} or charge–dipole and dipole–charge terms (their sum is also invariant), proportional to R^{-3} or charge–quadrupole, quadrupole–charge and dipole–dipole (their sum is invariant as well).

Let us take such a complete set of terms with $k + l = 2$.

Let us begin with the charge–dipole term. The term in the multipole expansion corresponds to $k = 0$ and $l = 2$:

$$(-1)^2 \frac{2!}{2!R^3} \hat{M}^{(00)}(1) * \hat{M}^{(20)}(2) = q_1 q_2 R^{-3} \frac{1}{2} (3z_2^2 - r_2^2).$$

The next term ($k = 1, l = 1$) has three contributions coming from the summation over m :

$$\begin{aligned} & (-1) \frac{2!}{1!1!R^3} \hat{M}^{(10)}(1) * \hat{M}^{(10)}(2) + (-1)^2 \frac{2!}{2!2!R^3} \hat{M}^{(11)}(1) * \hat{M}^{(11)}(2) \\ & + (-1)^0 \frac{2!}{2!2!R^3} \hat{M}^{(1-1)}(1) * \hat{M}^{(1-1)}(2) = q_1 q_2 R^{-3} [(x_1 x_2 + y_1 y_2) - 2z_1 z_2]. \end{aligned}$$

The third term ($k = 2, l = 0$):

$$(-1)^2 \frac{2!}{2!R^3} \hat{M}^{(20)}(1) * \hat{M}^{(00)}(2) = q_1 q_2 R^{-3} \frac{1}{2} (3z_1^2 - r_1^2).$$

taking $z + T$ instead of z ...

$$q_1 q_2 R^{-3} \left[\frac{1}{2} (3(z_2 + T)^2 - x_2^2 - y_2^2 - (z_2 + T)^2) \right]$$
$$= q_1 q_2 R^{-3} \left[\frac{1}{2} (3z_2^2 - r_2^2) + \frac{1}{2} (6Tz_2 + 3T^2 - 2Tz_2 - T^2) \right],$$

The complete set does not depend on T !

c) Convergence of the multipole expansion

the multipole expansion convergence depends on how the molecules are located in space with respect to one another. The convergence criterion reads

$$|\mathbf{r}_{b2} - \mathbf{r}_{a1}| < R,$$

where \mathbf{r}_{a1} denotes the vector pointing the particle 1 from its coordinate system origin, similarly for vector \mathbf{r}_{b2} .

When the two particles are in their non-overlapping spheres, the multipole expansion converges.

ELECTROSTATIC ENERGY IN THE MULTIPOLE REPRESENTATION AND THE PENETRATION ENERGY

Electrostatic energy represents the first-order correction in polarization perturbational theory and is the mean value of V with the product wave function $\psi^{(0)}_0 = \psi_{A0}\psi_{B0}$. Because we have the multipole representation of V , we may insert it into formula

$$E_0^{(1)} \equiv E_{\text{elst}} \equiv E_{\text{pol}}^{(1)} = \langle \psi_0^{(0)} | V | \psi_0^{(0)} \rangle,$$

In the polarization approximation we know perfectly well which electrons belong to molecule A and which belong to B, therefore we perform the integration separately over the electrons of molecule A and those of molecule B.

Formally the expression for $E_0^{(1)} = E_{\text{elst}}$ *has to be of exactly the same form* as the multipole representation of V , the only difference being that in V we have the molecular multipole *operators*, whereas in E_{elst} we have the molecular multipoles themselves as the *mean values of the corresponding* molecular multipole operators in the ground state .

However, they are equivalent **only when:**

- a) the multipole form converges
- b) objects are non-overlapping

If the electronic charge distributions penetrate, it causes a small difference (*penetration energy* E_{penetr}) between the E_{elst} calculated with and without the multipole expansion

$$E_{elst} = E_{multipol} + E_{penetr},$$

Jak rychle roste E_{pen} ?

Where

$$E_{multipol} = \frac{q_A q_B}{R} - R^{-2}(q_A \mu_{Bz} - q_B \mu_{Az}) + R^{-3}(\mu_{Ax} \mu_{Bx} + \mu_{Ay} \mu_{By} - 2\mu_{Az} \mu_{Bz}) + R^{-3}(q_A Q_{B,z^2} + q_B Q_{A,z^2}) + \dots$$

The molecular multipoles are:

$$q_A = \langle \psi_{A,0} | - \sum_i 1 + \sum_a Z_a | \psi_{A,0} \rangle = \left(- \sum_i 1 + \sum_a Z_a \right) \langle \psi_{A,0} | \psi_{A,0} \rangle$$

$$\mu_{Ax} = \langle \psi_{A,0} | \hat{\mu}_{Ax} | \psi_{A,0} \rangle = \langle \psi_{A,0} | - \sum_i x_i + \sum_a Z_a x_a | \psi_{A,0} \rangle$$

$$= \langle \psi_{A,0} | - \sum_i x_i | \psi_{A,0} \rangle + \sum_a Z_a x_a$$

INDUCTION ENERGY IN THE MULTIPOLE REPRESENTATION

The induction energy contribution consists of two parts: $E_{\text{ind}}(A \rightarrow B)$ and $E_{\text{ind}}(B \rightarrow A)$ or, respectively, the polarization energy of molecule B in the electric field of the unperturbed molecule A and *vice versa*.

If we insert the multipole representation of V into the induction energy $E_{\text{ind}}(A \rightarrow B)$ then

$$\begin{aligned}
 E_{\text{ind}}(A \rightarrow B) &= \sum'_{n_B} \frac{|\langle \psi_{A,0} \psi_{B,n_B} | V | \psi_{A,0} \psi_{B,0} \rangle|^2}{E_{B,0} - E_{B,n_B}} && \text{the zeros come from the orthogonality} \\
 &= \sum'_{n_B} \frac{1}{E_{B,0} - E_{B,n_B}} \left\{ \left| R^{-1} q_A \cdot 0 - R^{-2} q_A \langle \psi_{B,n_B} | \hat{\mu}_{Bz} \psi_{B,0} \rangle + R^{-2} \cdot 0 \right. \right. \\
 &\quad \left. \left. + R^{-3} [\mu_{Ax} \langle \psi_{B,n_B} | \hat{\mu}_{Bx} \psi_{B,0} \rangle + \mu_{Ay} \langle \psi_{B,n_B} | \hat{\mu}_{By} \psi_{B,0} \rangle \right. \right. \\
 &\quad \left. \left. - 2\mu_{Az} \langle \psi_{B,n_B} | \hat{\mu}_{Bz} \psi_{B,0} \rangle] + \dots \right|^2 \right. \\
 &= \sum'_{n_B} \frac{1}{E_{B,0} - E_{B,n_B}} \left\{ \left| -R^{-2} q_A \langle \psi_{B,n_B} | \hat{\mu}_{Bz} \psi_{B,0} \rangle \right. \right. \\
 &\quad \left. \left. + R^{-3} [\mu_{Ax} \langle \psi_{B,n_B} | \hat{\mu}_{Bx} \psi_{B,0} \rangle + \mu_{Ay} \langle \psi_{B,n_B} | \hat{\mu}_{By} \psi_{B,0} \rangle \right. \right. \\
 &\quad \left. \left. - 2\mu_{Az} \langle \psi_{B,n_B} | \hat{\mu}_{Bz} \psi_{B,0} \rangle] + \dots \right|^2 \right. \\
 &= -\frac{1}{2} \frac{1}{R^4} q_A^2 \alpha_{B,zz} + \dots,
 \end{aligned}$$

A molecule in the electric field of another molecule

Note that $\frac{1}{R^2} q_A^2$ represents the square of the electric field intensity $\mathcal{E}_2(A \rightarrow B) = \frac{q_A}{R^2}$ measured on molecule B and created by the net charge of molecule A. Therefore, we have

$$E_{\text{ind}}(A \rightarrow B) = -\frac{1}{2} \alpha_{B,22} \mathcal{E}_2^2(A \rightarrow B) + \dots$$

DISPERSION ENERGY IN THE MULTIPOLE REPRESENTATION

After inserting V in the multipole representation into the expression for the dispersion energy we obtain

$$\begin{aligned}
 E_{\text{disp}} &= \sum'_{n_A} \sum'_{n_B} \frac{1}{(E_{A,0} - E_{A,n_A}) + (E_{B,0} - E_{B,n_B})} \\
 &\quad \times \left| R^{-1} q_A q_B \cdot 0 \cdot 0 - R^{-2} q_A \cdot 0 \cdot (\mu_{Bz})_{n_B,0} \right. \\
 &\quad \left. - R^{-2} q_B \cdot 0 \cdot (\mu_{Az})_{n_A,0} + R^{-3} [(\mu_{Ax})_{n_A,0} (\mu_{Bx})_{n_B,0} + (\mu_{Ay})_{n_A,0} (\mu_{By})_{n_B,0} \right. \\
 &\quad \left. - 2(\mu_{Az})_{n_A,0} (\mu_{Bz})_{n_B,0}] + \dots \right|^2 \\
 &= \sum'_{n_A} \sum'_{n_B} \left| R^{-3} [(\mu_{Ax})_{n_A,0} (\mu_{Bx})_{n_B,0} + (\mu_{Ay})_{n_A,0} (\mu_{By})_{n_B,0} \right. \\
 &\quad \left. - 2(\mu_{Az})_{n_A,0} (\mu_{Bz})_{n_B,0}] + \dots \right|^2 [(E_{A,0} - E_{A,n_A}) + (E_{B,0} - E_{B,n_B})]^{-1}
 \end{aligned}$$

Hence, if we squared the total expression, the most important term would be the dipole–dipole contribution with the asymptotic R^{-6} distance dependence.

The dispersion interaction is a pure correlation effect and therefore the methods used in a supermolecular approach, that do not take into account the electronic correlation (as for example the Hartree–Fock method) are unable to produce any non-zero dispersion contribution.

A few simple and useful rules:

1. The dispersion energy always decays as R^{-6} .
2. The electrostatic energy vanishes as $R^{-(k+l+1)}$ where the 2^k -pole and 2^l -pole represent the lowest non-vanishing multipoles of the interacting subsystems.
3. The induction energy vanishes as $R^{-2(k+2)}$ where the 2^k -pole is the lower of the two lowest non-zero permanent multipoles of the molecules A and B. The formula is easy to understand if we take into account that the lowest *induced* multipole is always a dipole ($l = 1$), and that the induction effect is of the second order PT (hence 2 in the exponent).

SYMMETRY ADAPTED PERTURBATION THEORIES

- the polarization approximation, i.e. ignoring the Pauli principle becomes *a very poor approximation*,
- the multipole expansion becomes invalid.

POLARIZATION APPROXIMATION IS ILLEGAL!!