

X. MULTIPOLE EXPANSION

What is the multipole expansion for?

In the perturbational theory of intermolecular interactions (Chapter 13) the perturbation operator (V) plays an important role. The operator contains all the Coulombic charge–charge interactions, where one of the point charges belongs to subsystem A , the second to B . Therefore, according to the assumption behind the perturbational approach (large intermolecular distance) there is a *guarantee* that both charges are distant in space. For example, for two interacting hydrogen atoms (electron 1 at the nucleus a , electron 2 at nucleus b , a.u. are used)

$$V = -\frac{1}{r_{a2}} + \frac{1}{r_{12}} - \frac{1}{r_{b1}} + \frac{1}{R}, \quad (\text{X.1})$$

where R stands for the internuclear distance. A short inspection convinces us that the mean value of the operator $-\frac{1}{r_{a2}} + \frac{1}{r_{12}}$, with the wave function¹ $\psi_{A,n_1}(1)\psi_{B,n_2}(2)$, would give something close to zero, because both distances in the denominators are almost equal to each other, Fig. X.1.a. The same can be said of the two other terms of V . This is why, the situation is similar (see Chapter 13) to weighing the captain's hat, which we criticized so harshly in the supermolecular approach to supermolecular forces, see Fig. 13.4.

What could we do to prevent a loss of accuracy? This is precisely the goal of the multipole expansion for each of the operators $\frac{1}{r_{ij}}$.

Coordinate system

What is the multipole expansion really? We will explain this in a moment. Let us begin quietly with introducing two Cartesian coordinate systems: one on molecule A , the second on molecule B (Fig. X.1.b).

This can be done in several ways. Let us begin by choosing the origins of the coordinate systems. How do we choose them? Is it irrelevant? It turns out that the choice is important. Let us stop the problem here and come back to it later on. Just as a signal, let me communicate the conclusion: the origins should be chosen in the neighbourhood of the centres of mass (charges) of the interacting molecules. Let

¹ $\psi_{A,n_1}(1)$ means an excited state (n_1 is the corresponding quantum number) of atom A , $\psi_{B,n_2}(2)$ similarly for atom B . Note that electron 1 is always close to nucleus a , electron 2 close to nucleus b , while A and B are far distant.

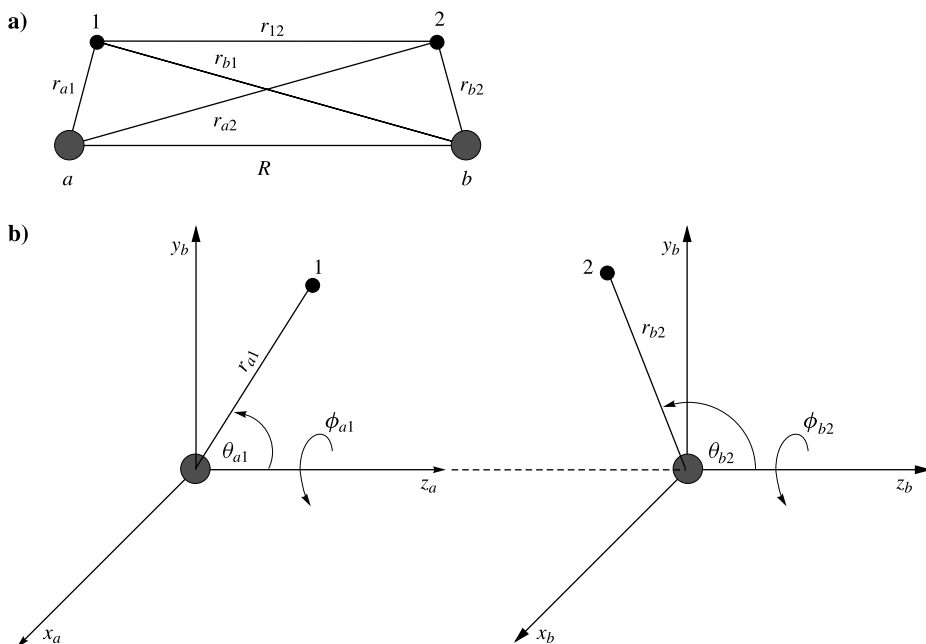


Fig. X.1. The coordinate system used in the multipole expansion. (a) Interparticle distances. The large black dots denote the origins of the two Cartesian coordinate systems, labelled a and b , respectively. We assume particle 1 always resides close to a , particle 2 always close to b . The figure gives a notation related to the distances considered. (b) Two Cartesian coordinate systems (and their polar counterparts): one associated with the centre a , the second one with centre b (the x and y axes are parallel in both systems, the z axes are collinear). Note that the two coordinate systems are not on the same footing: the z axis of a points towards b , while the coordinate system b does not point to a . Sometimes in the literature we introduce an alternative coordinate system with “equal footing” by changing $z_b \rightarrow -z_b$ (then the two coordinate systems point to each other), but this leads to different “handedness” (“right-” or “left-handed”) of the systems and subsequently to complications for chiral molecules. Let us stick to the “non-equivalent choice”.

us introduce the axes by taking the z axes (z_a and z_b) collinear pointing in the same direction, axes x_a and x_b as well as y_a and y_b , pairwise parallel.

The multipole series and the multipole operators of a particle

With such a coordinate system the Coulomb interaction of particles 1 and 2 (with charges q_1 and q_2) can be expanded using the following approximation²

$$\frac{q_1 q_2}{r_{12}} \cong \sum_{k=0}^{n_k} \sum_{l=0}^{n_l} \sum_{m=-s}^{m=+s} A_{kl|m|} R^{-(k+l+1)} \hat{M}_a^{(k,m)}(1)^* \hat{M}_b^{(l,m)}(2), \quad (\text{X.2})$$

²It represents an approximation because it is not valid for $R < |\mathbf{r}_{a1} - \mathbf{r}_{b2}|$, and this may happen in real systems (the electron clouds extend to infinity), also because n_k, n_l are finite instead of equal to ∞ .

where the coefficient

$$A_{kl|m|} = (-1)^{l+m} \frac{(k+l)!}{(k+|m|)!(l+|m|)!} \quad (\text{X.3})$$

whereas

MULTIPOLE MOMENT OPERATORS

$\hat{M}_a^{(k,m)}(1)$ and $\hat{M}_b^{(l,m)}(2)$ represent, respectively, the m -th components of the 2^k -pole and 2^l -pole of particle 1 in the coordinate system on a and of particle 2 in the coordinate system on b :

$$\hat{M}_a^{(k,m)}(1) = q_1 r_{a1}^k P_k^{|m|}(\cos \theta_{a1}) \exp(im\phi_{a1}), \quad (\text{X.4})$$

$$\hat{M}_b^{(l,m)}(2) = q_2 r_{b2}^l P_l^{|m|}(\cos \theta_{b2}) \exp(im\phi_{b2}), \quad (\text{X.5})$$

with r, θ, ϕ standing for the spherical coordinates of a particle (in coordinate system a or b , Fig. X.1.b), the associated Legendre polynomials $P_k^{|m|}$ with $|m| \leq k$ are defined as (cf. p. 176)

$$P_k^{|m|}(x) = \frac{1}{2^k k!} (1-x^2)^{|m|/2} \frac{d^{k+|m|}}{dx^{k+|m|}} (x^2-1)^k, \quad (\text{X.6})$$

n_k and n_l in principle have to be equal to ∞ , but in practice take finite integer values, s is the lower of the summation indices k, l .

Maybe an additional remark would be useful concerning the nomenclature: any multipole may be called a 2^k -pole (however strange this name looks), because this “multi” means the number 2^k . If we know how to make powers of two, and in addition have some contact with the world of the ancient Greeks and Romans, we will know how to compose the names of the successive multipoles: $2^0 = 1$, hence *monopole*; $2^1 = 2$, hence *dipole*, $2^2 = 4$, hence, *quadrupole*, etc. The names, however, are of no importance. The formulae for the multipoles are important.

Multipole moment operators for many particles

A while ago a definition of the multipole moments of a single point-like charged particle was introduced. However, the multipole moments will be calculated in future, practically always for a molecule. Then,

THE TOTAL MULTIPOLE MOMENT OPERATOR

The total multipole moment operator represents the sum of the same operators for the individual particles (of course, all them have to be calculated in the same coordinate system): $\hat{M}_a^{(k,m)}(A) = \sum_{i \in A} \hat{M}_a^{(k,m)}(i)$.

The first thing we have to stress about multipole moments is that, in principle, they depend on the choice of the coordinate system (Fig. X.2).

This will soon be seen when inspecting the formulae for multipole moments.

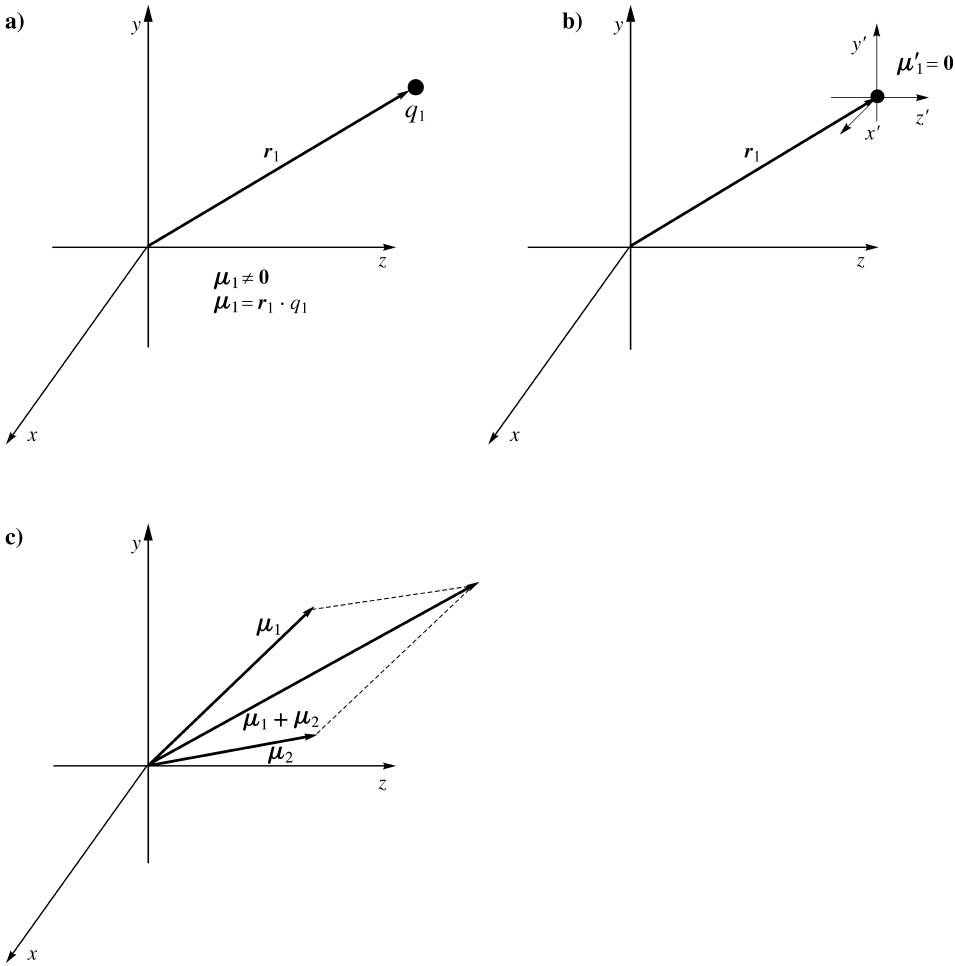


Fig. X.2. The multipole moments (or, simply multipoles) in general depend on the choice of coordinate system. (a) The dipole moment of a point-like particle with charge q_1 is equal to μ_1 . (b) The dipole moment of the same particle in a coordinate system with the origin on the particle. Here we obtain $\mu'_1 = 0$. (c) The dipole moment of two particles represents the sum of the dipole moments of the individual particles (in a common coordinate system).

Examples

Let us take a few examples for particle 1 in the coordinate system a (for the sake of simplicity we skip the indices). The case with $k = 0$ is obviously the simplest one, and we should always begin with the simplest things. If $k = 0$, then (because of $P_k^{(m)}$) $m = 0$, and the monopole therefore has a single component $M^{(00)}$

$$\hat{M}^{(0,0)} = qr^0 P_0^0(\cos \theta) \exp(i0\phi) = q. \quad (\text{X.7})$$

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	$\frac{1}{2}(5z^3 - 3zr^2)$	$\frac{3}{2}(x + iy)(5z^2 - r^2)$ $\frac{3}{2}(x - iy)(5z^2 - r^2)$	$15z(x + iy)^2$ $15z(x - iy)^2$	$15(x + iy)^3$ $15(x - iy)^3$

Hence,

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 $\hat{M}^{(1,0)}$

$$\hat{M}^{(1,0)} = qr^1 P_1^0(\cos \theta) \exp(i0\phi) = qr \cos \theta = qz. \tag{X.8}$$

DIPOLE MOMENT OPERATOR

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

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

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 .

The multipoles depend on the coordinate system chosen

Evidently any multipole moment value (except the monopole) depends on my imagination because I am free to choose any coordinate system I want and, e.g.,

the z coordinate of the particle in such a system will also depend on me! 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 moments defined by eqs. (X.4) or (X.5), 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

$$(x')^n (y')^l (z')^m = (x + L_x)^n (y + L_y)^l (z + L_z)^m \\ = x^n y^l z^m + \text{a linear combination of lower multipole moments.} \quad (\text{X.9})$$

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^{++} and Cl^- . Let us locate these charges on the z axis in such a way that Zn^{++} has the coordinate $z = 0$, and Cl^- $z = 5$. Now we would like to calculate the z component of the dipole moment:³ $M^{(1,0)} = \mu_z = q_1 z_1 + q_2 z_2 = (+2)0 + (-1)5 = -5$. 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

$$M^{(1,0)'} = \mu'_z = q_1 z'_1 + q_2 z'_2 = (+2)(-10) + (-1)(-5) = -15. \quad (\text{X.10})$$

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

³Since we have to do with point charges, the calculation of the multipole moments reduces simply to inserting the values of the coordinates of the corresponding charges into the multipole operator.

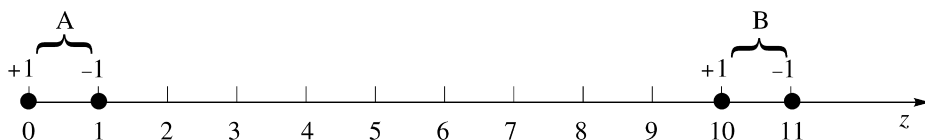


Fig. X.3. The interaction of *non-pointlike* dipoles also contains interactions of higher multipoles.

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 $R^{-3}(\mu_{ax}\mu_{bx} + \mu_{ay}\mu_{by} - 2\mu_{az}\mu_{bz}) = -2R^{-3}\mu_{az}\mu_{bz}$, 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 $\mu_{bz} = (+1) \cdot 10 + (-1) \cdot 11 = -1$.

What is R ?

Now, we are encountering a serious problem (which we *always* encounter in the multipole expansion), what is R ? 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: $-2 \cdot 10^{-3}(-1)(-1) = -0.0020000$. 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, and we did not take them into account. If somebody calculated all the interactions of such multipoles, we would recover the correct interaction energy with any desired accuracy. 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

Table X.2. Are the multipole moments zero or non-zero?

	Li ⁺	HCl	H ₂	CH ₄	HCl ⁺
monopole $k = 0$	q	0	0	0	q
dipole $k = 1$	0	μ	0	0	μ
quadrupole $k = 2$	0	Q	Q	0	Q
octupole $k = 3$	0	Oct	0	Oct	Oct

point-like.⁴ 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.

Just as a little exercise, Table X.2 shows which multipole moments are zero and which are non-zero for a few simple chemical systems. All this follows from the symmetry of their nuclear framework in the electronic ground state.

Properties of the multipole expansion

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

- How do we truncate the expansion, i.e. how do we choose the values of n_k and n_l in eq. (X.2)?
- 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?
- 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,⁵ then, however horrifying it might be, the result of the multipole expansion is in general coordinate-dependent. If, however, 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.⁶ Such a recipe for n_k and n_l corresponds to taking all the terms with a given power of R^{-1} .

In other words, 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.

⁴Just think about a multipole component of the form qz^m calculated with respect to the centre of each subsystem.

⁵Zero would introduce large errors in most applications.

⁶L.Z. Stolarczyk, L. Piela, *Int. J. Quantum Chem.* 15 (1979) 701.

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 imagine scientists calculating the interaction energy of two molecules. As will be shown later, in their multipole expansion they will have the charges of both interacting *molecules*, their dipole moments, their quadrupole moments, etc. Our scientists are systematic fellows, and therefore I bet they will begin by calculating the multipole moments for each molecule, up to a certain maximum multipole moment (say, the quadrupole; the calculations become more and more involved, which makes their decision easier). Then they will be ready to calculate all the individual multipole–multipole interaction contributions. They will make a table of such interactions (rows: the multipole moments of *A*; columns: the multipole moments of *B*) and calculate all the entries in their table. Then many of their colleagues would sum *all* the entries of the table in order not to waste their time. This will be a mistake. The scientists might not suspect that, due to this procedure, their result depends on the choice of coordinate system, which is always embarrassing. However, our scientists will do something else. They will sum the entries corresponding to: charge–charge, charge–dipole, dipole–charge, charge–quadrupole, quadrupole–charge, dipole–dipole and they will throw the other entries into the waste paper basket. Having made this decision, the scientists will gain a lot: their interaction energy will not depend on how they translated the *a* and *b* coordinate systems.

Now, we will illustrate this by a simple formulae and see how it works in practice. We have said before that it is decisive to take the complete set of terms with the given dependence on R^{-1} . Otherwise horrible things happen. Let us take such a complete set of terms with $k + l = 2$. We will see how nicely they behave upon the translation of the coordinate system, and how nasty the behaviour of individual terms is. 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 ($k = 2, l = 0$):

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

Note that each of the calculated terms depends separately on the translation along the z axis of the origins of the interacting objects. Indeed, by taking $z + T$ instead of z we obtain: for the first term

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

for the second term

$$\begin{aligned} q_1 q_2 R^{-3} & [(x_1 x_2 + y_1 y_2) - 2(z_1 + T)(z_2 + T)] \\ & = q_1 q_2 R^{-3} [(x_1 x_2 + y_1 y_2) - 2z_1 z_2] + R^{-3} [-2Tz_1 - 2Tz_2 - 2T^2], \end{aligned}$$

for the third term

$$\begin{aligned} q_1 q_2 R^{-3} & \frac{1}{2} (3(z_1 + T)^2 - x_1^2 - y_1^2 - (z_1 + T)^2) \\ & = q_1 q_2 R^{-3} \left[\frac{1}{2} (3z_1^2 - r_1^2) + \frac{1}{2} (6Tz_1 + 3T^2 - 2Tz_1 - T^2) \right]. \end{aligned}$$

If someone still has the illusion that the coordinate system dependence is negligible, this is about the right time to change their opinion. Evidently, each term depends on what we chose as T , and T can be *anything*! If I were really malicious, I would obtain a monstrous dependence on T .

Now, let us add all the individual terms together to form the complete set for $k + l = 2$:

$$\begin{aligned} q_1 q_2 & \left\{ R^{-3} \left[\frac{1}{2} (3z_2 - r_2^2) + (2Tz_2 + T^2) \right] + R^{-3} [(x_1 x_2 + y_1 y_2) - 2z_1 z_2] \right. \\ & \quad \left. + R^{-3} [-2Tz_1 - 2Tz_2 - 2T^2] + R^{-3} \left[\frac{1}{2} (3z_1 - r_1^2) + (2Tz_1 + T^2) \right] \right\} \\ & = q_1 q_2 R^{-3} \left\{ \frac{1}{2} (3z_2 - r_2^2) + [(x_1 x_2 + y_1 y_2) - 2z_1 z_2] + \frac{1}{2} (3z_1 - r_1^2) \right\}. \end{aligned}$$

The dependence on T has disappeared as if touched by a magic wand.⁷ *The complete set does not depend on T !* This is what I wanted to show.

⁷We may also prove that equal but arbitrary rotations of both coordinate systems about the z axis also lead to a similar invariance of interaction energy.

Convergence of the multipole expansion

I owe the reader an explanation about the convergence of the multipole expansion (point c, Fig. X.4). Well,

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

$$|\mathbf{r}_{b2} - \mathbf{r}_{a1}| < R, \quad (\text{X.11})$$

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

The readers will easily be convinced if they draw two spheres that are tangent to each other (this is the most dangerous situation) and then consider possible \mathbf{r}_{a1} and \mathbf{r}_{b2} vectors. Whatever the \mathbf{r}_{a1} and \mathbf{r}_{b2} vectors are, our criterion will be fulfilled. The criterion is, however, even more general than to allow two non-overlapping

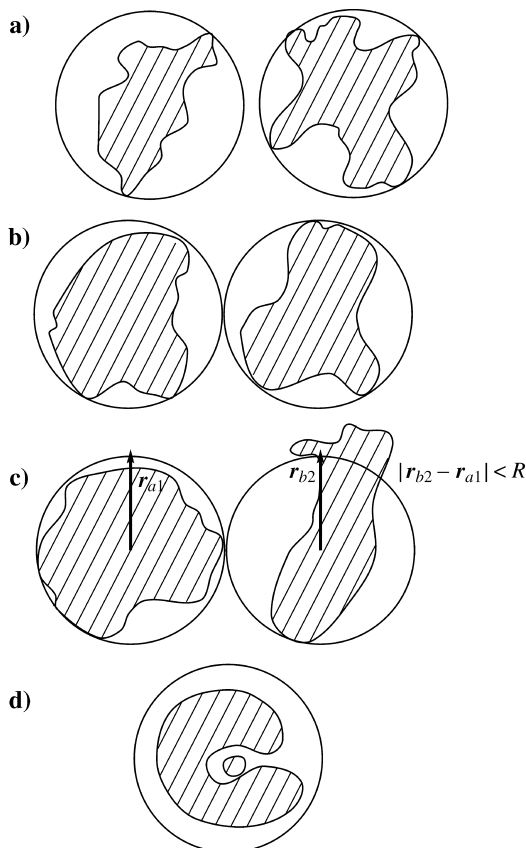


Fig. X.4. Convergence of the multipole expansion. The expansion converges in situations (a–c), diverges in (d).

spheres. It is easy to find locations of the two particles that are outside the spheres, and yet the convergence criterion is fulfilled. For example, let us take two tangent spheres with radii ρ_1 and ρ_2 (their centres are on the x axis) as well as vectors $\mathbf{r}_{a1} = (0, \rho_1, 0)$ and $\mathbf{r}_{b2} = (0, u, 0)$, where $u = \rho_1 + R/10$ and $u > \rho_2$. Then, $|\mathbf{r}_{b2} - \mathbf{r}_{a1}| = R/10 < R$, i.e. the convergence criterion is satisfied, despite the fact that particle 2 is outside its sphere.

For our purposes it is sufficient to remember that

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

Can we make such an assumption? Our goal is the application of the multipole expansion in the case of intermolecular interactions. Are we able to enclose both molecules in two non-overlapping spheres? Sometimes certainly not, e.g., if a small molecule A is to be docked in the cavity of a large molecule B . This is a very interesting case (Fig. X.4.d), but what we have most often in quantum chemistry are two *distant* molecules. Is everything all right then? Apparently the molecules can be enclosed in the spheres, but if we recall that the electronic density extends to infinity (although it decays very fast), we feel a little scared. *Almost* the whole density distribution could be enclosed in such spheres, but outside the spheres there is also something. It turns out that this very fact causes

the multipole expansion for the interaction energy of such diffused charge distributions to diverge, i.e. if we go to very high terms we will get infinity.

However strange it might look, in mathematics we are also able to extract very useful information from divergent series, if they converge *asymptotically*, see p. 210. This is precisely the situation when multipole expansion is applied to the diffuse charge distributions that such molecules have. This is why the multipole expansion is useful.⁸ It also has the important advantage of being physically appealing, because thanks to it we may interpret interaction energy in terms of the properties of the individual interacting molecules (their charges, dipole, quadrupole, etc. moments).

⁸If the calculations were feasible to a high degree of accuracy, the multipole expansion might be of small importance.