

Multipole Expansion

What Is the Multipole Expansion For?

In the perturbational theory of intermolecular interactions (see 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 the 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 (the electron 1 at the nucleus a , the electron 2 at the nucleus b , atomic units 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 (see Fig. X.1a). The same can be said about the two other terms of V . This is why the situation is similar (see Chapter 13) to weighing the captain's hat, criticized so harshly by us in the supermolecular approach to the supermolecular forces (see Fig. 13.4).

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

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

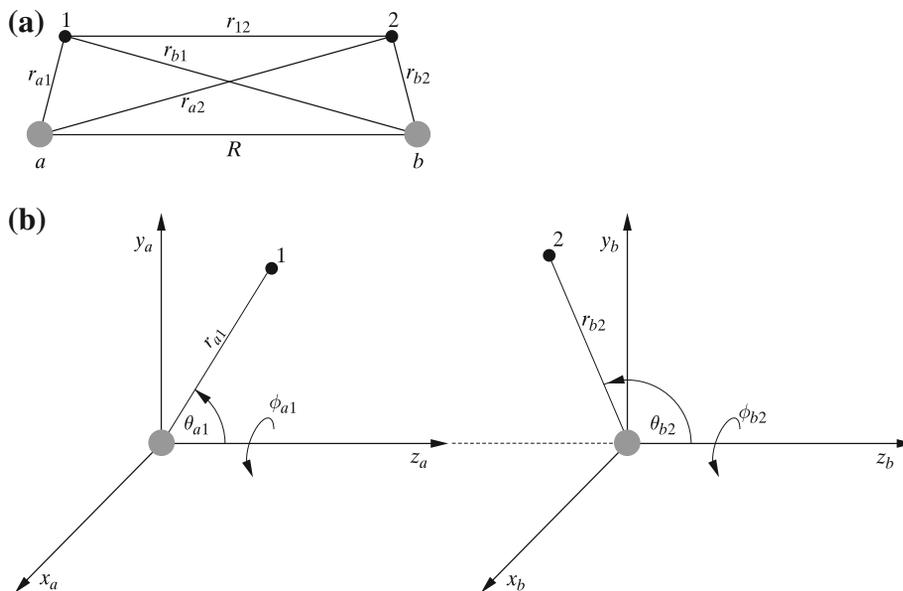


Fig. X.1. The coordinate system used in the multipole expansion. (a) The interparticle distances. The large gray dots denote the origins of the two Cartesian coordinate systems, labeled by a and b , respectively. One assumes particle 1 always resides close to a , and particle 2 is always close to b . The figure gives the notation related to the distances considered. (b) Two Cartesian coordinate systems (and their polar counterparts): one associated with the center a , the second one with the center b (the x - and y -axes are parallel in both systems, the z -axes are colinear). Note that the two coordinate systems are not on the same footing: the z -axis of a points to b , while the coordinate system b does not point to a . Sometimes in the literature one introduces an alternative coordinate system with the “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.

Coordinate System

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

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 here and come back to this problem later on. Just for signaling, let me communicate the conclusion: the origins should be chosen in the neighborhood of the centers of mass (charges) of the interacting molecules. Let us introduce the axes by taking the z -axes (z_a and z_b) colinear pointing in the same direction, and axes x_a and x_b as well as y_a and y_b pairwise parallel.

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:

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

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 the coordinate system a or b ; see Fig. X.1), the associated Legendre polynomials $P_k^{|m|}$ with $|m| \leq k$ are defined as (cf. p. 200)

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

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

Maybe an additional remark concerning the nomenclature is called for here any multipole may be called a 2^k -pole (however strange this name looks), because “*multi*” means the number 2^k . If we know how to make powers of 2, and in addition, we got some contact with the world of ancient Greeks and Romans, then 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 formulas for the multipoles are what is important.

Multipole Moment Operators for Many Particles

Above, a definition of the multipole moments of a single point-like charged particle has been introduced. However, the multipole moments will almost always be calculated in the future for a molecule. Then,

² It represents an approximation because it is not valid for $R < |\mathbf{r}_1 - \mathbf{r}_2|$, and this may happen in real systems (the electron clouds extend to infinity), also because n_k , n_l are finite instead of ∞ .

The Total Multipole Moment Operator

The total multipole moment operator represents a sum of the same operators for the individual particles (of course, they all have to be computed in the same coordinate system):

$$\hat{M}_a^{(k,m)}(A) = \sum_{i \in A} \hat{M}_a^{(k,m)}(i).$$

The first thing that 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 be seen in a while when inspecting the formulas for the multipole moments.

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 examples. If $k = 0$, then (because of $P_k^{|m|}$) $m = 0$, and the monopole, therefore, has a single component $M^{(00)}$:

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

Hence,

Monopole

The monopole for a particle is simply its charge.

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

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

Dipole Moment Operator

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

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

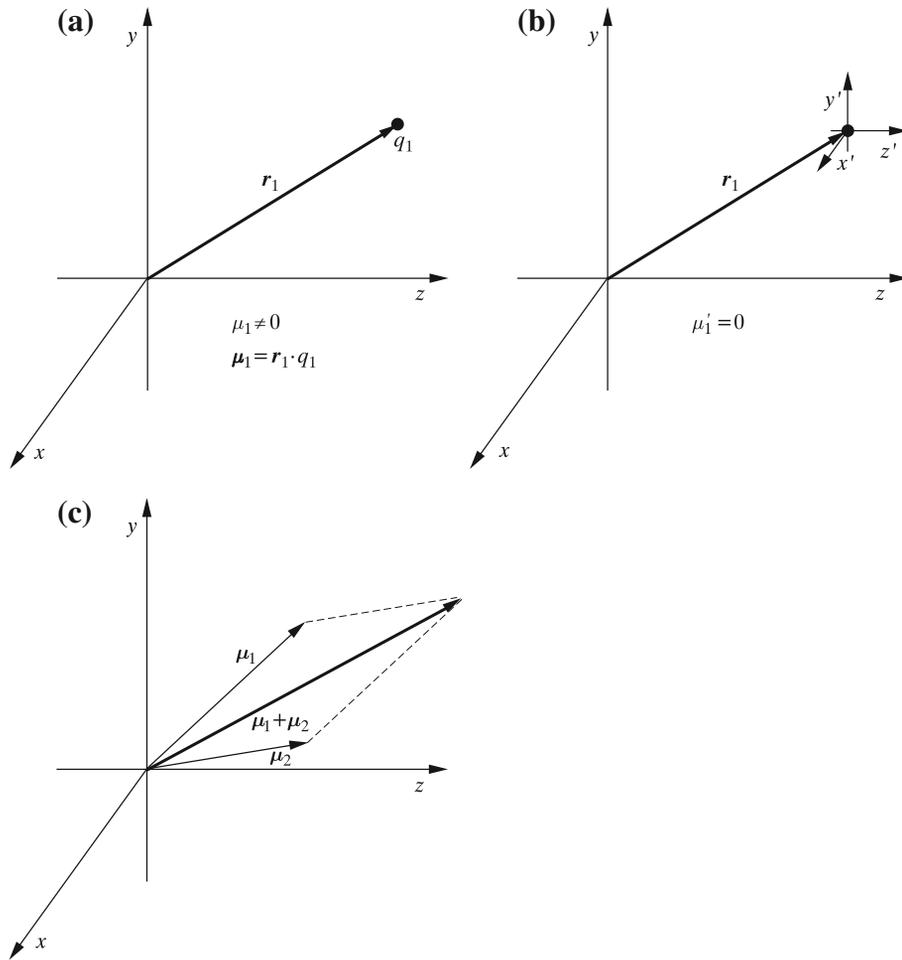


Fig. X.2. The multipole moments (or simply multipoles) in general depend on the choice of the coordinate system. (a) The dipole moment of a pointlike particle with charge q_1 is equal to μ_1 . (b) The dipole moment of the same particle in the coordinate system with the origin on the particle. In such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

After a careful (but a little boring) derivation, we arrive at the table of multipoles up to the octupole, see below. 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 represents a k th-degree polynomial of x , y , and z .

The Multipoles Depend on the Coordinate System Chosen

Evidently any multipole moment value (except monopole) depends on the whim of the participant, because I am free to choose any coordinate system I want, and the z -coordinate of

m	0	± 1	± 2	± 3
k				
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 particle in such a system will 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, but the other moments in general do depend on it.

This is not peculiar for the moments defined by Eq. (X.4) or (X.5), but it represents a property of every term of the form $x^n y^l z^m$. Indeed, $k = n + l + m$ tells us that we are dealing with a 2^k -pole. Let us shift the origin of the coordinate system by the vector \mathbf{L} . Then, the $x^n y^l z^m$ moment computed 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 were equal to zero, then this would indicate the invariance of the moment of the choice of the coordinate system.

Let us take the system ZnCl^+ as an example. In the first approximation, the system may be approximated by two pointlike 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 compute the z -component of the dipole moment³: $M^{(1,0)} = \mu_z = q_1 z_1 + q_2 z_2 = (+2)0 + (-1)5 = -5$. What if we had chosen another coordinate system? Let us check what would happen if the origin of the coordinate system were shifted toward 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,

³ Since we are dealing with point charges, the computation of the multipole moments are reduced to inserting into the multipole operator the values of the coordinates of the corresponding charges.

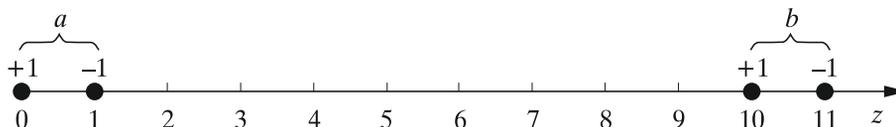


Fig. X.3. An interaction of the *non-pointlike* dipoles contains interactions of higher multipoles.

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 at any shift of the coordinate system. Therefore,

the dipole moment of a molecular ion depends on our arbitrary choice of the coordinate system.

Interaction Energy of Non-pointlike Multipoles

In chemical reasoning about intermolecular interactions, the multipole-multipole (mainly dipole-dipole, like for interactions in water, to cite one example), interaction plays an important role. The dipolar molecules have nonzero dimensions and therefore they represent something else than just pointlike dipoles. Let us clarify that taking a 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 the system b also has two charges $+1$, with $z = 10$ and -1 with $z = 11$

+ - + -

A first idea is that we are dealing with the interaction of two dipoles and nothing else. Let us check whether everything is OK, then. Doing this is very easy because what really interacts are the charges, not dipoles. Thus, the exact interaction of the 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 the 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 formulas 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 equal zero. Since A and B are neutral, then it is irrelevant which coordinate system is chosen to compute 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 confronting 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 compute the dipole-dipole interaction: $-2 \cdot 10^{-3}(-1)(-1) = -0.0020000$. Close! The computed exact 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 nonzero octupole moments (the quadrupoles equal zero) and nonzero higher odd-order multipoles, and we did not take them into account. If somebody computed all the interactions of such multipoles, then we would recover the correct interaction energy with any desired accuracy. But why does such a simple dipolar system also have a nonzero octupole moment? The answer is simple: it is because the dipole is not pointlike.⁴ The conclusion from this story is that the reader has to pay attention whether we are dealing with pointlike or non-pointlike multipole moments.

The table here reports which multipole moments (in the center-of-mass coordinate system) are zero and which are nonzero for a few simple chemical systems. All of this follows from the symmetry of their nuclear framework in the electronic ground state.

	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

⁴ Just think about a multipole component of the form qz^n computed with respect to the center of each subsystem.

Properties of the Multipole Expansion

In practicing the multipole expansion, 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 ?
- 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 makes 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 nonzero,⁵ then, however horrifying it might be, the result of the multipole expansion is in general coordinate-dependent. If, however, the n_k and n_l satisfy $n_k + n_l = \text{const}$, then we may shift both coordinate systems (the same translation for both) however we like and the interaction energy computed stays 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, then the result does not depend on the same translations of both coordinate systems.

This means that in order to maintain the invariance of the energy with respect to equal translations of both coordinate systems, we have to compute in the multipole expansion all terms satisfying $n_k + n_l = n_{\text{max}}$. If, e.g., $n_{\text{max}} = 2$, then we have to compute the term proportional to R^{-1} or 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).

Imagine a scientist calculating the interaction energy of two molecules. As it will be shown later, in his multipole expansion he will have the charges of both interacting *molecules*, their dipole moments, their quadrupole moments, etc. Our scientist is a systematic fellow, so he likely 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, and that makes his decision easier). Then, he will be ready to compute all the individual multipole-multipole interaction contributions. He will make a table of such interactions (rows: the multipole moments of *A*, columns: the multipole moments of *B*) and compute all the entries in his table. Then, many of his colleagues would sum up *all* the entries of the table so as not to waste their effort. This will be an error. The scientists might not suspect that due to this procedure, their result depends on the choice of the coordinate system, which is always embarrassing. However,

⁵ Zero would introduce large errors in most applications.

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

our fellow will make something else. He will sum up the entries corresponding to charge-charge, charge-dipole, dipole-charge, charge-quadrupole, quadrupole-charge, and dipole-dipole, and he will discard the other computed entries. This decision made by the scientist will gain a lot: his interaction energy will not depend on how he translated the a and b coordinate systems.

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

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

Note that each of the computed terms separately depends 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,

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

and 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 somebody still had illusions that the coordinate system dependence is negligible, then this is the time to change this opinion. Evidently, each term depends on what we chose as T , and T can be *anything*! If I were really malicious, then I would get monstrous dependence on T .

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

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

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

Convergence of the Multipole Expansion

At this point, I owe the reader the 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

$$|\mathbf{r}_2 - \mathbf{r}_1| < |\mathbf{R}|, \quad (\text{X.11})$$

where \mathbf{r}_1 denotes the vector pointing the particle 1 from its coordinate system origin, similarly the vector \mathbf{r}_2 .

The reader will convince himself easily if he draws two spheres that are tangent (this is the most dangerous situation) and then considers possible \mathbf{r}_1 and \mathbf{r}_2 vectors. Whatever the \mathbf{r}_1 and \mathbf{r}_2 vectors are, our criterion will be fulfilled. The criterion is, however, even more general than allowing two non-overlapping spheres. It is easy to find such locations of the two particles that are outside the spheres, and yet the convergence criterion is fulfilled. For instance, let us take two intersecting spheres (Fig. X.4c) with the radii ρ_1 and ρ_2 (their centers are on the x -axis), as well as the vectors $\mathbf{r}_1 = (0, \rho_1, 0)$ and $\mathbf{r}_2 = (0, u, 0)$, where $u = \rho_1 + R/10$. Then, $|\mathbf{r}_2 - \mathbf{r}_1| = R/10 < R$; 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

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

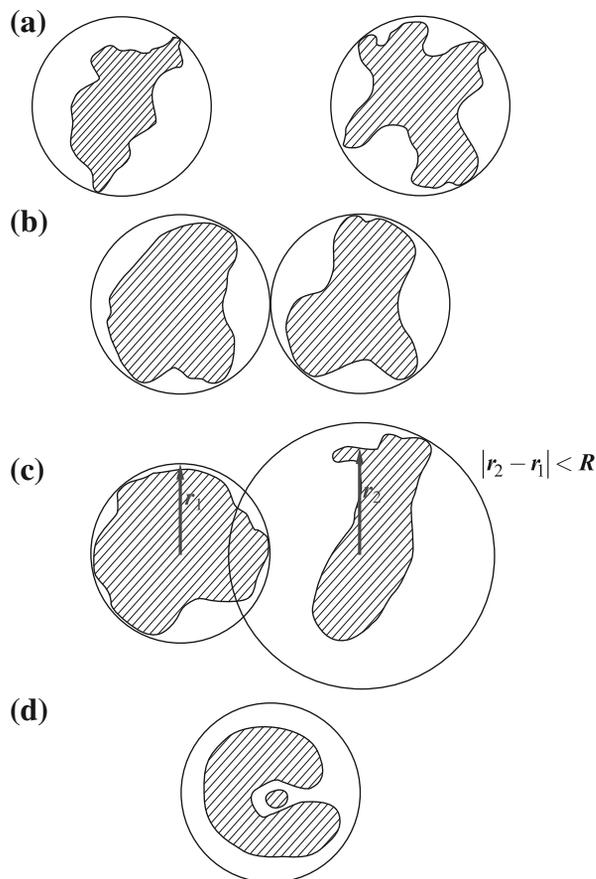


Fig. X.4. Convergence of the multipole expansion. The expansion converges in situations (a–c), and diverges in (d).

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

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

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

However strange it could look, in mathematics we are able to extract very useful information also from divergent series, if they converge *asymptotically*; see p. 249. This is precisely the situation with the multipole expansion applied to the diffuse charge distributions as molecules have. This is why the multipole expansion is useful.⁸ It has also an important advantage to be physically appealing, because thanks to this, we may interpret the interaction energy in terms of properties of the individual interacting molecules (their charges, dipole, quadrupole, etc. moments).

⁸ If the computation were feasible with very high accuracy, then the multipole expansion might be of little importance.

