

Molecular Interactions: The Multipole Expansion

Francisco M. Fernández

INIFTA (UNLP, CCT La Plata-CONICET), División Química Teórica, Diag. 113 y 64 (S/N), Sucursal 4, Casilla de Correo 16(1900) La Plata, Argentina, fernande@quimica.unlp.edu.ar

Received July 26, 2012. Accepted September 12, 2012.

Abstract: This laboratory provides students with the opportunity to reinforce their knowledge of the numerous parameters involved in electrophilic aromatic substitution reactions. These concepts are investigated using a benchtop GC-MS. Students obtain hands-on experience with the coupling of gas-chromatographic analysis and mass-spectral analysis. Each student determines one data point by reacting a pair of compounds with bromine and iron (III) chloride. Individual results are then pooled into composite class data, affording students more available information for analysis than is typical in an organic chemistry laboratory.

1. Introduction

Most textbooks on physical chemistry offer a chapter about molecular interactions and the analysis of the different contributions: charge-dipole, dipole-dipole, and so forth. In order to develop them in the simplest possible way they resort to particular geometries, and rather oversimplified charge distributions such as, for example, the one-dimensional arrangements of three charges to simulate the charge-dipole interaction or four charges to obtain the dipole-dipole one [1]. Even the particular and rather limited interaction between two parallel dipoles is regarded to be too complicated to be explicitly treated [1]. The expressions derived from such oversimplified settings are of dubious utility and they may at most be useful to show the relative order of magnitude of each interaction type with respect to the distance between the centers of the charge distributions [1]. Note, for example, that the average potential energy calculated with the restriction of parallel dipoles does not lead to the correct coefficient of the Keesom interaction [1].

On the other hand, the formal, rigorous and systematic multipole expansion yields all those contributions to the molecular interaction in a quite general way and even reveals the necessity of well known concepts like the dipole moment, quadrupole moment, etc [2]. Unfortunately, the standard derivation of the multipole expansion [2] is rather too complicated for an undergraduate course on physical chemistry.

In view of what has just been said, it would be most useful to derive the multipole expansion, which leads to general expressions for the molecular interactions, in a sufficiently simple way that does not require too complicated mathematics. In this paper we explore such possibility. In Section 2 we obtain the potential produced by an arbitrary charge distribution at a point sufficiently far from its center. In Section 3 we use the results of Section 2 to obtain the different terms that contribute to the interaction between two widely separated arbitrary charge distributions, and in Section 4 we discuss the results and draw conclusions.

2. Potential Due to a Charge Distribution

In what follows we consider a distribution of charges q_i located at positions \mathbf{r}_i from its center O . We are interested in the potential of that charge distribution at a given point P located at \mathbf{R} from the origin O . The Coulomb potential at P is given by

$$V(\mathbf{R}) = \sum_i \frac{q_i}{4\pi\epsilon_0 R_i} \quad (1)$$

where ϵ_0 is the vacuum permittivity, $R_i = |\mathbf{R}_i|$ is the distance from the charge q_i to the point P and $\mathbf{R}_i = \mathbf{R} - \mathbf{r}_i$ is the vector from q_i to P (see Figure 1).

We are interested in the case that the point P is at such great distance from the center O of the charge distribution that $R = |\mathbf{R}| \gg r_i = |\mathbf{r}_i|$ for all i .

For convenience we write $\mathbf{R}_i = \mathbf{R} - \lambda \mathbf{r}_i$ and then set $\lambda = 1$ at the end of the calculation. Note that $R_i^2 = R^2 - 2\lambda \mathbf{R} \cdot \mathbf{r}_i + \lambda^2 r_i^2$, and if we expand

$$\frac{1}{R_i} = \frac{1}{\sqrt{R^2 - 2\lambda \mathbf{R} \cdot \mathbf{r}_i + \lambda^2 r_i^2}} \quad (2)$$

in a Taylor series about $\lambda = 0$ we obtain

$$\frac{1}{R_i} = \frac{1}{R} + \frac{\mathbf{R} \cdot \mathbf{r}_i}{R^3} + \frac{3(\mathbf{R} \cdot \mathbf{r}_i)^2 - R^2 r_i^2}{2R^5} + \dots \quad (3)$$

for $\lambda = 1$. We appreciate that the λ -power series is equivalent to a $1/R$ expansion, so that the larger the value of R the greater the convergence rate of the series.

If we multiply equation (3) by q_i and sum over all values of i in the charge distribution, the first term in the right-hand side gives us

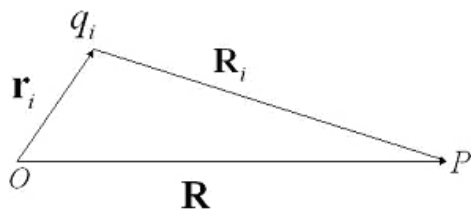


Figure 1. Contribution of charge q_i to the Coulomb potential at point P .

$$\sum_i \frac{q_i}{R} = \frac{q}{R} \quad (4)$$

where q is the net charge of the distribution. For the numerator of the second term we have

$$\sum_i q_i \mathbf{R} \cdot \mathbf{r}_i = \mathbf{R} \cdot \sum_i q_i \mathbf{r}_i \quad (5)$$

where we see that it is convenient to define the vector

$$\boldsymbol{\mu} = \sum_i q_i \mathbf{r}_i \quad (6)$$

that we call the dipole moment of the charge distribution. Note that the dipole moment appears in a natural way when we carry out the multipole expansion.

The third term in the right-hand side of equation (3) gives rise to the quadrupole moment of the charge distribution. A detailed analysis of such term is beyond the scope of this paper that we want to keep as simple as possible. Note, however, that we can derive an expression for the quadrupole just in the same way as we already did for the first two terms. In fact, we have all the necessary ingredients at hand.

If we restrict ourselves to just the first two terms we have

$$V(\mathbf{R}) = \frac{q}{4\pi\epsilon_0 R} + \frac{\mathbf{R} \cdot \boldsymbol{\mu}}{4\pi\epsilon_0 R^3} + \dots \quad (7)$$

If $q \neq 0$ the first term dominates at large distances from the center of the charge distribution and the potential at the point P is mainly due to a point charge located at O . However, if $q = 0$ the potential at the point P is provided by the dipole moment of the charge distribution which results to be the dominant contribution. If the charge distribution is such that both the net charge and the dipole moment vanish then the dominant contribution is given by the quadrupole moment.

In order to appreciate the actual dependence of the different contributions on the inverse of the distance at the point P more clearly we define the unit vector $\mathbf{n} = \mathbf{R}/R$. Thus, equation (7) becomes

$$V(\mathbf{R}) = \frac{q}{4\pi\epsilon_0 R} + \frac{\mathbf{n} \cdot \boldsymbol{\mu}}{4\pi\epsilon_0 R^2} + \dots \quad (8)$$

3. Interaction Between two Charge Distributions

In this section we consider the interaction between a charge distribution about an origin O_A and another one about the origin O_B . We assume that there is a set of charges $q_{A,i}$ located at $\mathbf{r}_{A,i}$ from O_A and another set $q_{B,j}$ at $\mathbf{r}_{B,j}$ from O_B . Let \mathbf{R} be the vector from O_A to O_B and \mathbf{R}_{ij} the vector from $q_{A,i}$ to $q_{B,j}$. It follows from these definitions that $\mathbf{R}_{ij} = \mathbf{R} + \mathbf{r}_{B,j} - \mathbf{r}_{A,i}$ (see Figure 2).

Thus, the interaction between both charge distributions is given by

$$V_{AB}(\mathbf{R}) = \sum_i \sum_j \frac{q_{A,i} q_{B,j}}{4\pi\epsilon_0 R_{ij}} \quad (9)$$

If we write $\mathbf{R}_{ij} = \mathbf{R} - \lambda \mathbf{u}$, where $\mathbf{u} = \mathbf{r}_{A,i} - \mathbf{r}_{B,j}$, we can apply exactly the same procedure followed in the preceding section. The Taylor expansion of $1/R_{ij}$ about $\lambda = 0$ calculated at $\lambda = 1$ gives us

$$\frac{1}{R_{ij}} = \frac{1}{R} + \frac{\mathbf{R} \cdot \mathbf{u}}{R^3} + \frac{3(\mathbf{R} \cdot \mathbf{u})^2 - R^2 u^2}{2R^5} + \dots \quad (10)$$

If we multiply equation (10) by $q_{A,i} q_{B,j}$ and sum over all i and j the first term in the right-hand side gives us

$$\sum_i \sum_j \frac{q_{A,i} q_{B,j}}{R} = \frac{q_A q_B}{R} \quad (11)$$

where q_A and q_B are the net charges of the distributions A and B , respectively. The numerator of the second term leads to

$$\sum_i \sum_j q_{A,i} q_{B,j} \mathbf{R} \cdot (\mathbf{r}_{A,i} - \mathbf{r}_{B,j}) = q_B \mathbf{R} \cdot \boldsymbol{\mu}_A - q_A \mathbf{R} \cdot \boldsymbol{\mu}_B \quad (12)$$

Analogously, the third term in the right-hand side of

$$R^2 u^2 = R^2 (r_{A,i}^2 + r_{B,j}^2 - 2\mathbf{r}_{A,i} \cdot \mathbf{r}_{B,j}) \quad (13)$$

gives us

$$-2(\mathbf{R} \cdot \boldsymbol{\mu}_A)(\mathbf{R} \cdot \boldsymbol{\mu}_B) \quad (14)$$

and the third term in the right-hand side of

$$R^2 u^2 = R^2 (r_{A,i}^2 + r_{B,j}^2 - 2\mathbf{r}_{A,i} \cdot \mathbf{r}_{B,j}) \quad (15)$$

becomes

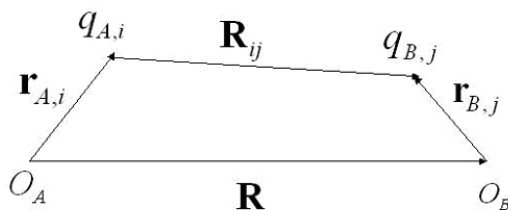


Figure 2. Coulomb interaction between charges $q_{A,i}$ and $q_{B,j}$.

$$-2R^2 \boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B \quad (16)$$

Thus, the truncated series for the interaction potential results to be

$$V_{AB}(\mathbf{R}) = \frac{q_A q_B}{4\pi\epsilon_0 R} + \frac{q_B \mathbf{R} \cdot \boldsymbol{\mu}_A - q_A \mathbf{R} \cdot \boldsymbol{\mu}_B}{4\pi\epsilon_0 R^3} - \frac{R^2 \boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B - 3(\mathbf{R} \cdot \boldsymbol{\mu}_A)(\mathbf{R} \cdot \boldsymbol{\mu}_B)}{4\pi\epsilon_0 R^5} + \dots \quad (17)$$

The first term in the right-hand side of this equation is the interaction between a point charge q_A located at O_A and a point charge q_B at O_B . The second term is the interaction between a dipole at O_A and a charge at O_B and a charge at O_A and a dipole at O_B . The third term is the interaction between two dipoles. For simplicity we omit the remaining terms that involve other multipoles. If, for example, both charge distributions are neutral, then the leading term is the dipole-dipole interaction.

We may rewrite the expression (17) in terms of the unit vector \mathbf{n} defined above as

$$V_{AB}(\mathbf{R}) = \frac{q_A q_B}{4\pi\epsilon_0 R} + \frac{q_B \mathbf{n} \cdot \boldsymbol{\mu}_A - q_A \mathbf{n} \cdot \boldsymbol{\mu}_B}{4\pi\epsilon_0 R^2} - \frac{\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B - 3(\mathbf{n} \cdot \boldsymbol{\mu}_A)(\mathbf{n} \cdot \boldsymbol{\mu}_B)}{4\pi\epsilon_0 R^3} + \dots \quad (18)$$

Note that the dipole-dipole interaction now looks like the one commonly obtained by means of the multipole expansion [2].

If we use the dipole-dipole interaction given by either equation (17) or (18) to calculate the average potential energy of two rotating molecules we obtain the correct form of the Keesom interaction that the approximate expression for two parallel dipoles fails to provide [1].

4. Conclusions

We have tried to show that the derivation of the general multipole expansion for the potential of an arbitrary charge distribution, and for the interaction between two of them is not too difficult for an undergraduate course on physical chemistry. The only required mathematics is the Taylor expansion of a simple function and a few vector properties which students at such level are supposed to be acquaintance with. Many textbooks on physical chemistry already have recourse to the Taylor expansion in order to obtain the necessary expressions for the interactions [1]. However, their results are commonly of too restricted validity because they resort to particular geometries and oversimplified charge distributions [1]. Here, on the other hand, we have derived general expressions without specifying any explicit locations of the point charges.

Another interesting feature of the multipole expansion is that the concepts of dipole moment, quadrupole moment, and, in general, multipole moments appear in a natural and straightforward way. Note, for example, how our derivation of the multipole expansion for the potential of a charge distribution suggests the convenience of defining the quantity that we know as dipole moment. We could have also derived a general expression for the quadrupole from the third term in the right-hand side of equation (10).

References and Notes

1. Atkins, P.; de Paula, J. *Adkins' Physical Chemistry*, 7th ed.; Oxford University Press: Oxford, 2002.
2. Jackson, J. D. *Classical Electrodynamics*, 2nd ed.; John Wiley & Sons: Singapore, 1990.