The Theory of Intermolecular Forces

Second Edition

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Introduction

1.1 The evidence for intermolecular forces

The idea that matter is made up of atoms and molecules was known to the Greeks, though the evidence for it did not become persuasive until the eighteenth and nineteenth centuries, when the ideal gas laws, the kinetic theory of gases, Faraday’s laws of electrolysis, the stoichiometry of most chemical reactions, and a variety of other indications combined to decide the matter beyond doubt. In the twentieth century, further techniques such as X-ray diffraction and, more recently, high-resolution microscopy, have provided more evidence.

Given the idea that matter consists of molecules, however, the notion that there must be forces between them rests on much simpler evidence. The very existence of condensed phases of matter is conclusive evidence of attractive forces between molecules, for in the absence of attractive forces, the molecules in a glass of water would have no reason to stay confined to the glass. Furthermore, the fact that water has a definite density, and cannot easily be compressed to a smaller volume, shows that at short range the forces between the molecules become repulsive.

It follows that the energy of interaction $U$ between two molecules, as a function of the distance $R$ between them, must take the form shown in Fig. 1.1. That is, it must have an attractive region at long range, where the force $-\partial U/\partial R$ is negative, and a steeply repulsive region at close range to account for the low compressibility of condensed materials. There is a separation $R_m$ where the energy is a minimum, and a closer distance $\sigma$ where the energy of interaction goes through zero before climbing steeply. These are conventional notations, as is the symbol $\epsilon$ for the depth of the attractive well. The precise form of the function $U(R)$ will depend on the particular molecules concerned, but these general features will be almost

![Fig. 1.1 A typical intermolecular potential energy function.](image-url)
universal. For some pairs of molecules, in some relative orientations, the interaction energy may be repulsive at all distances, but unless the molecules are both ions with the same sign of charge, there will always be orientations where the long-distance interaction is attractive.

Van der Waals was the first to take these ideas into account in describing the departure of real gases from ideality. He suggested that the volume \( V \) occupied by a gas included a volume \( b \) that was occupied by the incompressible molecules, so that only \( V - b \) remained for the free movement of the molecules; and that the attractive forces between the molecules had the effect of reducing the pressure exerted by a gas on its container, by an amount proportional to the square of the density. Thus the ‘true’ pressure, in the sense of the gas laws, is not the measured pressure \( P \) but \( P + a/V^2 \). The gas law \( PV = RT \) then took the form \((P + a/V^2)(V - b) = RT\), where \( P \) and \( V \) are now the measured pressure and volume rather than the ideal values.

This simple equation gave a remarkably good account of the condensation of gases into liquids, and the values of the constants \( a \) and \( b \) correspond tolerably well with the properties of molecules as we now understand them. Although this approach has been superseded, the forces of attraction and repulsion between molecules are still often called ‘Van der Waals’ forces.

### 1.1.1 Magnitudes

The value of the Van der Waals parameter \( b \) has a clear interpretation in terms of molecular size; but more direct methods, such as X-ray crystallography, provide accurate values for the equilibrium separation in the solid. This is not quite the same as \( R_m \), because there are attractive forces between more distant molecules that compress the nearest-neighbour distance slightly. The depth \( \epsilon \) of the attractive well can be estimated via calorimetric data. One simple order-of-magnitude method is based on *Trouton’s rule*, an empirical observation which states that the enthalpy of vaporization is approximately related to the boiling point at atmospheric pressure \( T_b \) by \( \Delta H_{\text{vap}} \approx 10RT_b \). Although this is an empirical rule, it can be understood quite easily in a general way: the change in Gibbs free energy \( G = H - TS \) between liquid and vapour is zero at the boiling point, so \( \Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}} \). We approximate \( \Delta S \) in terms of the change of volume between liquid and gas, \( \Delta S = R \ln(V_g/V_l) \), as if the liquid were just a highly compressed gas. Typically \((V_g/V_l) \approx 10^3\), which gives \( \Delta S \approx 7R\); the remaining 3\( R \) or so can be accounted for by the fact that liquids are more structured than gases, and so have a lower entropy than is assumed in this simple picture.

Now the energy required to separate a condensed liquid into its constituent molecules is approximately \( \epsilon \) for each pair of molecules that are close together. If each molecule has \( n \) neighbours in the liquid, the total energy for \( N \) molecules is \( \frac{1}{2}Nne \) (where the factor of \( \frac{1}{2} \) is needed to avoid counting each interaction twice). This is approximately the latent heat of evaporation; we should really correct for the zero-point energy of vibration of the molecules in the liquid, but if we assume that the intermolecular vibrations are classical the energy in these vibrations will be the same as the translational energy in the gas. Thus we find that \( \frac{1}{2}Nne \approx 10RT_b \), or \( \epsilon/k_B \approx 20T_b/n \).

Table 1.1 shows the values that result for a few atoms and molecules. The value of the coordination number \( n \) has been assumed here to be the same as in the solid; this is probably a slight overestimate in most cases. The results show that the predictions are quite good, and certainly adequate for estimating the order of magnitude of \( \epsilon \).
The evidence for intermolecular forces

Table 1.1 Pair potential well depths.

<table>
<thead>
<tr>
<th></th>
<th>( T_b/K )</th>
<th>( n )</th>
<th>( (20T_b/n)/K )</th>
<th>( (\epsilon_{\text{exp}}/k_B)/K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>4.2</td>
<td>12</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>Ar</td>
<td>87</td>
<td>12</td>
<td>145</td>
<td>142</td>
</tr>
<tr>
<td>Xe</td>
<td>166</td>
<td>12</td>
<td>277</td>
<td>281</td>
</tr>
<tr>
<td>CH₄</td>
<td>111.5</td>
<td>12</td>
<td>186</td>
<td>180–300</td>
</tr>
<tr>
<td>H₂O</td>
<td>373.2</td>
<td>4</td>
<td>1866</td>
<td>2400 approx.</td>
</tr>
</tbody>
</table>

We see, then, that the strength of intermolecular interactions between small molecules, as measured by the well depth \( \epsilon \), is typically in the region 1–25 kJ mol\(^{-1} \) or 100–2000 K. This is considerably weaker than a typical chemical bond, which has a dissociation energy upwards of 200 kJ mol\(^{-1} \), and this is why intermolecular interactions can be broken easily by simple physical means such as moderate heat, while chemical bonds can only be broken by more vigorous procedures.

1.1.2 Pairwise additivity

In this analysis, we have tacitly assumed that the energy of an assembly of molecules, as in a liquid, can be treated as a sum of pairwise interactions; that is, that the total energy \( W \) of the assembly can be expressed in the form

\[
W = \sum_i W_i + \sum_{i>j} U_{ij},
\]

where \( W_i \) is the energy of isolated molecule \( i \) and \( U_{ij} \) is the energy of interaction between \( i \) and \( j \). We have to be careful to count each pair of molecules only once, not twice, and the sum over pairs can be written in several ways, as shown, the second form being a conventional abbreviation of the first.

This assumption of pairwise additivity is only a first approximation. Eqn (1.1.1) is just the leading term in a series which should include three-body terms, four-body terms, and so on:

\[
U = W - \sum_i W_i^0
= \sum_{i>j} U_{ij} + \sum_{i>j>k} U_{ijk} + \sum_{i>j>k>l} U_{ijkl} + \cdots
= W_{\text{2body}} + W_{\text{3body}} + W_{\text{4body}} + \cdots.
\] (1.1.2)

For instance, if there are three molecules \( A \), \( B \) and \( C \), the pairwise approximation to the total energy is \( U_{AB} + U_{BC} + U_{AC} \), where \( U_{AB} \) is evaluated as if molecule \( C \) were not present, and so on. However, the presence of molecule \( C \) will modify the interaction between the other two
molecules, so there is a three-body correction: \( U = U_{AB} + U_{BC} + U_{AC} + U_{ABC} \). When there are four molecules, we have to include a three-body correction for each set of three molecules, and the error that remains is the four-body correction. We hope that the total contribution \( W_{3\text{body}} \) of the three-body corrections will be small, and the four-body term smaller still. In most circumstances this is a reasonably good approximation, so most effort is concerned with getting the pair interactions right. However, the many-body terms are not small enough to neglect altogether, and we shall need to consider them later, in Chapter 10. In particular, the three-body terms may be much too large to ignore.

Eqn (1.1.2) ignores a further contribution which may need to be taken into account. Usually the geometry of each interacting molecule is distorted in the environment of its neighbours. The most common example is the hydrogen bond A–H···B, where the AH bond is usually longer in the complex than in the isolated molecule. The distortion away from the equilibrium geometry costs energy, but if the interaction with the neighbour is enhanced the overall energy may be lowered. The difference between the energy of the molecule in its distorted geometry and its energy \( W_i^0 \) at equilibrium is called the deformation energy. If the molecules are rigid (high vibrational force constants) the cost of even a small distortion outweighs any improvement in binding energy and the deformation energy is negligible. If there are soft vibrational modes, however, the deformation may be significant and the deformation energy may need to be included. This is not easy to do, as the distortion of each molecule depends on all its neighbours, so the deformation energy is a complicated many-body effect, and in practice it is often neglected completely.

### 1.2 Classification of intermolecular forces

We can identify a number of physical phenomena that are responsible for attraction and repulsion between molecules. Here we give an overview of the main contributions to forces between molecules. All of the important ones arise ultimately from the electrostatic interaction between the particles comprising the two molecules. They can be separated into two main types: ‘long-range’, where the energy of interaction behaves as some inverse power of \( R \), and ‘short-range’, where the energy decreases in magnitude exponentially with distance. This apparently arbitrary distinction has a clear foundation in theory, as we shall see.

The long-range effects are of three kinds: electrostatic, induction and dispersion. The electrostatic effects are the simplest to understand in general terms: they arise from the straightforward classical interaction between the static charge distributions of the two molecules. They are strictly pairwise additive and may be either attractive or repulsive. Induction effects arise from the distortion of a particular molecule in the electric field of all its neighbours, and are always attractive. Because the fields of several neighbouring molecules may reinforce each other or cancel out, induction is strongly non-additive. Dispersion is an effect that cannot easily be understood in classical terms, but it arises because the charge distributions of the molecules are constantly fluctuating as the electrons move. The motions of the electrons in the two molecules become correlated, in such a way that lower-energy configurations are favoured and higher-energy ones disfavoured. The average effect is a lowering of the energy, and since the correlation effect becomes stronger as the molecules approach each other, the result is an attraction.

We shall discuss all these effects in much more detail later. For the moment they are summarized in Table 1.2. Two other effects that can arise at long range are included in the
### Table 1.2 Contributions to the energy of interaction between molecules.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Additive?</th>
<th>Sign</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Long-range</strong> ((U \sim R^{-n}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrostatic</td>
<td>Yes</td>
<td>±</td>
<td>Strong orientation dependence</td>
</tr>
<tr>
<td>Induction</td>
<td>No</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Dispersion</td>
<td>approx.</td>
<td>–</td>
<td>Always present</td>
</tr>
<tr>
<td>Resonance</td>
<td>No</td>
<td>±</td>
<td>Degenerate states only</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Yes</td>
<td>±</td>
<td>Very small</td>
</tr>
<tr>
<td><strong>Short-range</strong> ((U \sim e^{-\alpha R}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exchange-repulsion</td>
<td>approx.</td>
<td>+</td>
<td>Dominates at very short range</td>
</tr>
<tr>
<td>Exchange-induction</td>
<td>approx.</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Exchange-dispersion</td>
<td>approx.</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Charge transfer</td>
<td>No</td>
<td>–</td>
<td>Donor-acceptor interaction</td>
</tr>
</tbody>
</table>

Table: these are resonance and magnetic effects. Resonance interactions occur either when at least one of the molecules is in a degenerate state—usually an excited state—or when the molecules are identical and one is in an excited state. Consequently they do not occur between ordinary closed-shell molecules in their ground states. They will be discussed in Chapter 11. Magnetic interactions involving the electrons can occur only when both molecules have unpaired spins, but in any case are very small. Magnetic interactions involving nuclei can occur whenever there are nuclei with non-zero spin, which is quite common, but the energies are several orders of magnitude smaller still, and are never of any significance in the context of intermolecular forces.

The ‘long-range’ electrostatic, induction and dispersion contributions are so called because they are the ones that survive at large separations. However, they are still present at short distances, even when the molecules overlap strongly. The electrostatic interaction, for example, being the electrostatic interaction between the unperturbed molecular charge distributions, is well defined at any distance, and remains finite unless nuclei come into contact. However, it is usual to describe all of these contributions as power series in \(1/R\), where \(R\) is the molecular separation, and such series evidently diverge as \(R \to 0\), so they are only valid for sufficiently large \(R\). Even where the series converges, it may still be in error, because the series treats each molecule as if it were concentrated at a point, rather than extended in space. This error is called the ‘penetration error’. Furthermore, it is necessary in practice to truncate the series at a finite number of terms, leading to a ‘truncation error’.

Further contributions to the energy arise at short range—that is, at distances where the molecular wavefunctions overlap significantly and electron exchange between the molecules becomes possible. The most important is described as exchange-repulsion or just exchange. It can be thought of as comprising two effects: an attractive part, arising because the electrons become free to move over both molecules rather than just one, increasing the uncertainty in their positions and so allowing the momentum and energy to decrease; and a repulsive part, arising because the wavefunction has to adapt to maintain the Pauli antisymmetry requirement that electrons of the same spin may not be in the same place, and this costs energy. The latter dominates, leading to a repulsive effect overall. It is usual to take these effects together. The remaining effects listed in Table 1.2, namely exchange-induction, exchange-dispersion and
charge transfer, also arise when the wavefunctions overlap; the charge-transfer interaction is often viewed as a separate effect but is better thought of as a part of the induction energy. These terms will be discussed in more detail in Chapter 8.

1.3 Potential energy surfaces

Only in the case of atoms is a single distance sufficient to describe the relative geometry. In all other cases further coordinates are required, and instead of contemplating a potential energy curve like Fig. 1.1, we need to think about the ‘potential energy surface’, which is a function of all the coordinates describing the relative position of the molecules. In the case of two non-linear molecules, there are six of these coordinates (we discuss them below) and the potential energy surface becomes very difficult to visualize. For many purposes, however, we can think in three dimensions: a vertical dimension for the energy, and two horizontal dimensions which are representative of the six or more coordinates that we should really be using. This simplified picture is then like a landscape, with hills and valleys. There are energy minima on the potential energy surface that correspond to depressions in the landscape. In the real landscape such depressions are usually filled with water, to give lakes or tarns; there may be many of them, at different heights. In the quantum-mechanical landscape of the potential-energy surface, there may also be many minima, but there is always one ‘global minimum’ that is lower than any of the others. (Sometimes there are several global minima of equal energy, related to each other by symmetry.) The rest are ‘local minima’: the energy at a local minimum is lower than the energy of any point in its immediate neighbourhood, but if we move further away we can find other points that are lower still.

Just as the depressions in the landscape are filled with water, we might think of the minima in the potential-energy surface as being filled with zero-point energy; and just as lakes may merge into each other, so the zero-point energy may permit molecular systems to move freely between adjacent minima if the barriers between them are not too high. The zero-point energy in molecular complexes is often a substantial fraction of the well depth. In the HF dimer, for example, the well depth \( \epsilon \) (alternatively described as the dissociation energy from the equilibrium geometry, \( D_e \)) is 19.2 kJ mol\(^{-1}\) (Peterson and Dunning 1995), while the dissociation energy \( D_0 \) from the lowest vibrational level to monomers at their lowest vibrational level is only 1062 cm\(^{-1}\) = 12.70 kJ mol\(^{-1}\) (Dayton et al. 1989). Given enough energy, the molecular system can rearrange, passing from one energy minimum to another via a ‘saddle point’ or ‘transition state’ which is the analogue of the mountain pass. The molecular system however can also tunnel between minima, even if the energy of the system is not high enough to overcome the barrier in the classical picture. A well-known example is the ammonia molecule, which can invert via a planar transition structure from one pyramidal minimum to the other. The height of the barrier in this case is 2020 cm\(^{-1}\) or about 24 kJ mol\(^{-1}\). If tunnelling is ignored, the lowest-energy stationary states for the inversion vibration have an energy of 886 cm\(^{-1}\), and there are two of them, one confined to each minimum. When tunnelling is taken into account, these two states can mix. If they combine in phase the resulting state has a slightly lower energy; if out of phase, the energy is slightly higher. The difference in energy—the ‘tunnelling splitting’—is 0.79 cm\(^{-1}\) in this case, and can be measured very accurately by spectroscopic methods. Such tunnelling splittings are a useful source of information about potential energy surfaces.

Along with the minima, then, the barriers constitute the other important features of the surface, corresponding to the mountain passes of the real landscape. To understand the nature
Potential energy surfaces

of the potential energy surface, we need to characterize the minima and the transition states. In mathematical terms, these are both ‘stationary points’, where all the first derivatives of the energy with respect to geometrical coordinates are zero. To distinguish between them, we need to consider the second derivatives. If we describe the energy $U$ in the neighbourhood of a stationary point by a Taylor expansion in the geometrical coordinates $q_i$, it takes the form

$$U = U(0) + \frac{1}{2} \sum_{ij} q_i q_j \left. \frac{\partial^2 U}{\partial q_i \partial q_j} \right|_0 + \cdots ; \quad (1.3.1)$$

the first derivatives are all zero at a stationary point, and we can ignore the higher derivatives if the $q_i$ are small. The matrix of second derivatives is called the ‘Hessian’; its components are

$$H_{ij} = \left. \frac{\partial^2 U}{\partial q_i \partial q_j} \right|_0 . \quad (1.3.2)$$

The eigenvalues of the Hessian are all positive at a minimum; in this case the Hessian is said to be ‘positive definite’. Whatever direction we walk away from a minimum, we find ourselves going uphill. Such a point is said to have ‘Hessian index zero’: that is, the Hessian has no negative eigenvalues there. At a saddle point or mountain pass, precisely one of the eigenvalues is negative—the Hessian index is 1. If we walk along the eigenvector corresponding to that eigenvalue, in either direction, we find ourselves going downhill, but the other eigenvectors take us uphill. Just as in the real landscape, the saddle points provide the routes from one valley or minimum to another. If two or more of the eigenvalues are negative, there are two orthogonal directions that will take us downhill. In this case (in the real landscape) we are at the top of a hill, and all directions lead downhill; in the many-dimensional system there may be other directions that lead uphill. However, it is never necessary to go over the top of the hill to get to the other side; there is always a lower route round the side of the hill (Murrell and Laidler 1968). If we are interested in characterizing the potential-energy surface, then, the most important stationary points are the minima, with Hessian index 0, and the saddle points, with Hessian index 1. Stationary points with higher values of the Hessian index are much less important.

Often there are several equivalent minima with the same energy, related to each other by the symmetry of the system. In the HF dimer, for example, the equilibrium structure is hydrogen-bonded, with only one of the two H atoms in the hydrogen bond. There are two such structures, one with the H atom of molecule 1 forming the hydrogen bond, the other with the H atom of molecule 2 in that role. For reasons of symmetry they have the same energy; they are distinguishable only if we can label the atoms in some way. The two cases are said to be different ‘versions’ of the same structure. In the same way there may be several versions of a transition state, related to each other by symmetry (Bone et al. 1991).

For large systems, comprising many molecules, the number of stationary points increases exponentially with the size of the system, and detailed characterization of the potential energy surface becomes difficult or impossible. In such cases, a qualitative or statistical description of the nature of the ‘energy landscape’ is more useful: are the typical barriers high or low compared with the temperature, or with the energy differences between adjacent minima, and what are the consequences for properties such as the rate of rearrangement to the global minimum? Such questions will not be pursued here, but have been addressed in detail by Wales (2004), Wolynes (1997) and others.
Molecules in Electric Fields

2.1 Molecular properties: multipole moments

Of the contributions to the interaction energy listed in Table 1.2, the electrostatic interaction is often the most important, as we shall see in later chapters. However, all of the contributions to the interaction energy between molecules, except for the unimportant magnetic terms, derive ultimately from the Coulombic interactions between their particles. In order to develop the theory of all these effects, we need to be able to describe the way in which the charge is distributed in a molecule. For most purposes, this is done most simply and compactly by specifying its multipole moments, and while this description has its limitations it provides an essential part of the language that we use to discuss intermolecular forces.

Multipole moments can be defined in two ways. One uses the mathematical language of cartesian tensors, while the other, the spherical-tensor formulation, is based on the spherical harmonics. The two descriptions are very closely related, and in many applications it is possible to use either. For more advanced work, the spherical-tensor approach is more flexible and powerful, but we begin with the cartesian approach because it is somewhat easier to understand. Later we shall use the spherical-tensor and cartesian tensor definitions more or less interchangeably, using whichever is more convenient.

2.1.1 Cartesian definition

The simplest multipole moment is the total charge: \( q = \sum_a e_a \), where \( e_a \) is the charge on particle \( a \) and the sum is taken over all the electrons and nuclei. If the molecule is placed in an electrostatic potential field \( V(r) \), its energy is

\[
U_{es} = \sum_a e_a V(a),
\]

where we are using the vector \( a \) to describe the position of particle \( a \). In a uniform electric field of magnitude \( F_z \) in the \( z \) direction, the electrostatic potential is \( V(r) = V_0 - zF_z \), and the energy becomes

\[
U_{es} = qV_0 - \sum_a e_a a_z F_z,
\]

where \( V_0 \) is an arbitrary constant, the electrostatic potential at the origin. In the second term, we are led to introduce the dipole moment \( \hat{\mu}_z = \sum_a e_a a_z \), and the energy becomes \( U_{es} = -F_z \hat{\mu}_z \). If the electric field also has components \( F_x \) and \( F_y \) in the \( x \) and \( y \) directions, the energy becomes

\[
U_{es} = qV_0 - (\hat{\mu}_x F_x + \hat{\mu}_y F_y + \hat{\mu}_z F_z) = qV_0 - \hat{\mu} \cdot F,
\]

(2.1.1)
Table 2.1 Examples of dipole moments in atomic units, debye and C m. Positive values correspond to positive charge at the left-hand end of the molecule as written.

<table>
<thead>
<tr>
<th></th>
<th>$ea_0$</th>
<th>D</th>
<th>$10^{-30}$ C m</th>
<th>$ea_0$</th>
<th>D</th>
<th>$10^{-30}$ C m</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>0.718</td>
<td>1.826</td>
<td>6.091</td>
<td>H$_2$O</td>
<td>0.730</td>
<td>1.855</td>
</tr>
<tr>
<td>HCl</td>
<td>0.436</td>
<td>1.109</td>
<td>3.70</td>
<td>H$_3$N</td>
<td>0.578</td>
<td>1.47</td>
</tr>
<tr>
<td>CO</td>
<td>-0.0431</td>
<td>-0.1096</td>
<td>-0.3656</td>
<td>(CH$_3$)$_2$CO</td>
<td>1.13</td>
<td>2.88</td>
</tr>
<tr>
<td>OCS</td>
<td>-0.2814</td>
<td>-0.7152</td>
<td>-2.386</td>
<td>C$_5$H$_5$N</td>
<td>0.86</td>
<td>2.19</td>
</tr>
<tr>
<td>HCN</td>
<td>1.174</td>
<td>2.984</td>
<td>9.953</td>
<td>CH$_3$CN</td>
<td>1.539</td>
<td>3.913</td>
</tr>
</tbody>
</table>

where $\hat{\mu}_x = \sum_a e_a a_x$ and $\hat{\mu}_y = \sum_a e_a a_y$. We can write the three components in one equation using ‘tensor notation’:

$$\hat{\mu}_\alpha = \sum_a e_a a_\alpha,$$

where $\alpha$ may stand for $x$, $y$ or $z$. The caret over the symbol $\mu$ is to remind ourselves that this is an operator. If we require the value of the dipole moment in state $|n\rangle$, we construct it by taking the expectation value of this operator:

$$\mu_\alpha = \langle n | \hat{\mu}_\alpha | n \rangle = \int \rho_n(r) r_\alpha \, d^3r,$$

where the second form is expressed in terms of the molecular charge density $\rho(r)$, and again $\alpha$ may stand for $x$, $y$ or $z$. If we integrate over electronic coordinates only (but include the contribution of the nuclear charge) we get the dipole moment for a fixed nuclear configuration. We have to integrate over nuclear coordinates too (vibrational average) to get a result that corresponds to the value that is measured experimentally. For example, the dipole moment of BH at its equilibrium geometry in the ground state has a magnitude of 0.5511 $ea_0$, but the vibrationally averaged value is 0.5345 $ea_0$ (Halkier et al. 1999).

Dipole moment values for some small molecules are listed in Table 2.1; for others see McClellan (1963, 1974, 1989) or Gray and Gubbins (1984). The quantity $ea_0$ is the atomic unit of dipole moment, where $e$ is the elementary charge (the charge on a proton) and $a_0$ is the Bohr radius. Other common units are the debye, D $= 10^{-18}$ esu, and the SI unit, the coulomb metre; 1 atomic unit $= 2.5418 \, D = 8.478 \times 10^{-30}$ C m. See Appendix D for other conversion factors. Atomic units are convenient for describing molecular properties, since the numerical values are typically of order unity.

The most accurate experimental technique for the measurement of dipole moments is the Stark effect in microwave spectroscopy. Unfortunately this does not provide the sign of the moment, and although the sign can usually be determined unambiguously on theoretical grounds, this is not always possible. A well-known example is carbon monoxide, for which the very small dipole moment is in the direction $^{-1}CO^+$, contrary to elementary chemical intuition and to ab initio calculations at the SCF level, though more accurate calculations allowing for the effects of electron correlation give the correct sign. Experimental determination of the
**Fig. 2.1** Quadrupole moments. (a) the angular part of \( \Theta_{zz} = \frac{1}{2} (3 \cos^2 \theta - 1) \), (b) CO\(_2\), (c) HF, (d) HCCH, (d) C\(_6\)H\(_6\), (e) H\(_2\)O.

The next of the multipole moments is the *quadrupole moment*, so called because a quadrupolar charge distribution using charges of equal magnitude needs four of them, two positive and two negative.\(^\dagger\) We define the operator

\[
\hat{\Theta}_{zz} = \sum_a e_a a_z^2 - \frac{1}{2} a_z^2,
\]

where in the last line the vector \( \mathbf{a} \) has been expressed in spherical polar coordinates. The expectation value of this operator for a particular state has the form

\[
\Theta_{zz} = \int \rho(\mathbf{r}) r^2 \left( \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) d^3 \mathbf{r}.
\] (2.1.3)

The angular factor in parentheses is positive when the angle \( \theta \) is less than about 54\(^\circ\) or more than 126\(^\circ\), and is negative between these values, in the region of the \( xy \) plane (see Fig. 2.1a).

To estimate the quadrupole moment for a particular molecule, we can superimpose the angular

\(^\dagger\)There is some diversity of spelling of ‘quadrupole’ in the literature. The Latin prefix for four is ‘quadri-’ (as in quadrilateral, for example) so ‘quadripole’ would be acceptable. However, ‘quadri-’ usually becomes ‘quadru-’ before the letter ‘p’ (as in ‘quadruped’) so ‘quadrupole’ is correct and is the usual spelling. ‘Quadrapole’ is sometimes seen, but this is definitely incorrect; it is presumably formed by analogy with words like ‘quadrangle’, but there the ‘a’ belongs to ‘angle’ and the prefix has lost its final vowel. ‘Octopole’ too occurs with alternative spellings. In this case there is no clearcut rule: ‘octopole’ is more usual, but ‘octapole’ is also acceptable.

\(^\ast\)There is the possibility of confusion about the direction of a dipole moment. As defined here and in virtually all of the recent literature, the direction is from negative to positive charge. However, Debye used a crossed arrow to represent the dipole moment vector, thus: \( \rightarrow \), the arrow pointing from positive to negative charge, and this convention for the direction of the dipole moment may still occasionally be encountered. It causes much confusion and should be avoided.
function on the molecular charge distribution and carry out the integration schematically. For CO₂ (Fig. 2.1b) we see that the negatively charged oxygen atoms are in regions where the angular factor is positive, while the positively charged carbon atom occupies the region near the origin (small r) and contributes little to the quadrupole moment. Accordingly we expect a negative quadrupole moment. The experimental value is $-3.3 \text{ea}_0^2$ (Battaglia et al. 1981). Once again, we are using atomic units, here $\text{ea}_0$. The SI unit is C m², and the electrostatic unit and debye-ångström are also commonly used. $\text{ea}_0^2 = 1.3450 \times 10^{-26}$ esu = 1.3450 D Å = 4.487 $\times 10^{-40}$ C m². For HF (Fig. 2.1c) the H atom is positively charged, so with the origin at the centre of mass, as shown, we expect a positive quadrupole moment, in agreement with the experimental value of $+1.76 \text{ea}_0^2$. In this case, however, the result depends on the choice of origin; see §2.7 for a detailed discussion.

Other interesting examples are acetylene and benzene. Acetylene (Fig. 2.1d) has a small charge separation between C and H, with the H atoms carrying small positive charges. These charges are in regions where $(3 \cos^2 \theta - 1)$ is large and positive, and are at relatively large r. There is also a substantial region of negative charge arising from the $\pi$-bonding orbitals in the region where $(3 \cos^2 \theta - 1)$ is negative. Consequently the quadrupole moment is quite large and positive; its value is $5.6 \text{ea}_0^2$—larger than for CO₂. A similar situation arises in benzene (Fig. 2.1e), but here the H atoms are in the $xy$ plane, where $(3 \cos^2 \theta - 1)$ is negative, and the $\pi$ electrons are in the region where $(3 \cos^2 \theta - 1)$ is positive or small in magnitude. In this case, therefore, the quadrupole moment is negative; its value is $-6.7 \text{ea}_0^2$.

The quadrupole moment has other components besides $\Theta_{zz}$, though they are all either zero or related to $\Theta_{zz}$ in the molecules discussed so far. They are

\[
\Theta_{xx} = \sum_a e_a \left( \frac{3}{2} a_x^2 - \frac{1}{2} a_x^2 \right), \\
\Theta_{yy} = \sum_a e_a \left( \frac{3}{2} a_y^2 - \frac{1}{2} a_y^2 \right), \\
\Theta_{xy} = \sum_a e_a \frac{3}{2} a_x a_y, \\
\Theta_{xz} = \sum_a e_a \frac{3}{2} a_x a_z, \\
\Theta_{yz} = \sum_a e_a \frac{3}{2} a_y a_z.
\]

Notice that $\Theta_{xx} + \Theta_{yy} + \Theta_{zz} = 0$, as a direct consequence of the definition. For linear and axially symmetric molecules, $\Theta_{xy} = \Theta_{xz} = \Theta_{yz} = 0$, while $\Theta_{xx} = \Theta_{yy}$, so that both are equal to $- \frac{1}{2} \Theta_{zz}$. Although there are three non-zero components in this case, namely $\Theta_{xx}$, $\Theta_{yy}$ and $\Theta_{zz}$, the value of any one of them determines the others, so there is only one independent non-zero component. For molecules with $C_{2v}$ symmetry, like water or pyridine, $\Theta_{xy} = \Theta_{xz} = \Theta_{yz} = 0$ again, but $\Theta_{xx}$ and $\Theta_{yy}$ may be non-zero and unequal. In such cases it is usual to take the independent non-zero components to be $\Theta_{zz}$ and $\Theta_{xx} - \Theta_{yy}$. The consequences of molecular symmetry are discussed in more detail in §2.6.

The water molecule has the charge distribution shown in Fig. 2.1f. The H atoms carry positive charges and are in the $yz$ plane, while the lone pairs are directed in the $xz$ plane and contain substantial amounts of negative charge. These facts fit well with the observed
Table 2.2  Examples of quadrupole moments in atomic units, debye ångström and C m². The origin is taken at the centre of mass in each case. For pyridine and H₂O, the z axis is along the C₂ axis and the x axis is perpendicular to the molecular plane.

<table>
<thead>
<tr>
<th></th>
<th>$e a_0^2$</th>
<th>Θ_{zz}</th>
<th>Θ_{xx} - Θ_{yy}</th>
<th>D Å</th>
<th>10^{-40} C m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>-3.3</td>
<td>0.0</td>
<td>4.4</td>
<td>0.0</td>
<td>14.8</td>
</tr>
<tr>
<td>HCCl</td>
<td>+5.6</td>
<td>0.0</td>
<td>7.6</td>
<td>0.0</td>
<td>25.1</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>-6.6</td>
<td>0.0</td>
<td>-8.7</td>
<td>0.0</td>
<td>-29.0</td>
</tr>
<tr>
<td>HF</td>
<td>1.75</td>
<td>0.0</td>
<td>2.36</td>
<td>0.0</td>
<td>7.87</td>
</tr>
<tr>
<td>HCl</td>
<td>2.75</td>
<td>0.0</td>
<td>3.7</td>
<td>0.0</td>
<td>12.3</td>
</tr>
<tr>
<td>H₂O</td>
<td>-0.1</td>
<td>-3.8</td>
<td>-0.13</td>
<td>-5.1</td>
<td>-0.4</td>
</tr>
<tr>
<td>C₅H₅N</td>
<td>-1.9</td>
<td>-9.7</td>
<td>-2.6</td>
<td>-13.0</td>
<td>-8.7</td>
</tr>
</tbody>
</table>

quadrupole moments, which are $Θ_{xx} = -1.86 \ e a_0^2$ and $Θ_{yy} = +1.96 \ e a_0^2$. On the other hand, $Θ_{zz}$ is small, with a value of only $-0.10 \ e a_0^2$. (These values are origin-dependent; the origin here is taken at the centre of mass.) Note again that $Θ_{xx} + Θ_{yy} + Θ_{zz} = 0$. These values and some others are listed in Table 2.2. Note that measurements of quadrupole moment are not very accurate, and different measurements do not always agree. See Gray and Gubbins (1984, Table D.3) for details and a fuller list.

It is convenient to summarize all these definitions in ‘tensor notation’:

$$Θ_{αβ} = \sum_α e_α \left( \frac{3}{2} a_α a_β - \frac{1}{2} a^2 δ_{αβ} \right).$$

(2.1.4)

The subscripts $α$ and $β$ can each be $x$, $y$ or $z$. The quantity $δ_{αβ}$ is the ‘Kronecker delta’: $δ_{αβ} = 1$ if $α = β$ and 0 if $α \neq β$. This provides a much more compact way to write down the definitions, and also provides a powerful notation for manipulating them. Appendix A gives a brief summary of tensor notation, which we shall use extensively. The quadrupole moment tensor has nine components, but it is symmetric ($Θ_{αβ} = Θ_{βα}$) and together with the ‘trace condition’ $Θ_{xx} + Θ_{yy} + Θ_{zz} = 0$ this means that there are only five independent non-zero quadrupole components for a molecule with no symmetry.
3
Electrostatic Interactions between Molecules

3.1 The electric field of a molecule

Suppose that molecule A is located at position A in some global coordinate system. The particles of this molecule are at positions a relative to A, i.e., at positions A + a. We want to evaluate the potential at a point B where we shall in due course put another molecule. In terms of the positions and charges of the particles of molecule A, the potential is

\[ V^A(B) = \sum_a \frac{e_a}{4\pi\varepsilon_0|B - A - a|} = \sum_a \frac{e_a}{4\pi\varepsilon_0|R - a|}, \]  

where \( R = B - A \). (See Fig. 3.1.) We expand this potential as a Taylor series about A, giving

\[ V^A(B) = \sum_a \frac{e_a}{4\pi\varepsilon_0|R - a|} \]

\[ = \sum_a \frac{e_a}{4\pi\varepsilon_0} \left\{ \frac{1}{R} + a_{\alpha} \left( \frac{\partial}{\partial a_{\alpha}} \frac{1}{R - a_{\alpha}} \right)_{a=0} + \frac{1}{2} a_{\alpha} a_{\beta} \left( \frac{\partial^2}{\partial a_{\alpha} \partial a_{\beta}} \frac{1}{R - a_{\alpha}} \right)_{a=0} + \cdots \right\} \]

\[ = \sum_a \frac{e_a}{4\pi\varepsilon_0} \left\{ \frac{1}{R} - a_{\alpha} \left( \frac{\partial}{\partial R_{\alpha}} \frac{1}{R - a_{\alpha}} \right)_{a=0} + \frac{1}{2} a_{\alpha} a_{\beta} \left( \frac{\partial^2}{\partial R_{\alpha} \partial R_{\beta}} \frac{1}{R - a_{\alpha}} \right)_{a=0} - \cdots \right\} \]

\[ = \sum_a \frac{e_a}{4\pi\varepsilon_0} \left\{ \frac{1}{R} - a_{\alpha} \nabla_{\alpha} \frac{1}{R} + \frac{1}{2} a_{\alpha} a_{\beta} \nabla_{\alpha} \nabla_{\beta} \frac{1}{R} - \cdots \right\}. \]  

(3.1.2)

As before, we can replace the second moment \( M_{\alpha\beta} = \sum_a e_a a_{\alpha} a_{\beta} \) by the quadrupole moment \( \frac{2}{3} \Theta_{\alpha\beta} \), because \( 1/R \) satisfies Laplace’s equation and there is no contribution to the potential from the trace \( M_{\alpha\alpha} \). The higher moments are treated similarly. When we do this, we get

\[ \frac{1}{R+b-a} \]

\[ \frac{R}{A} \]

\[ \frac{B}{b} \]

\[ \text{Fig. 3.1 Definition of position vectors in two interacting molecules.} \]
Electrostatic Interactions between Molecules

\[ V^A(B) = \frac{1}{4\pi\varepsilon_0} \left\{ q^A \left( \frac{1}{R} \right) - \hat{\mu}_a^A \nabla_a \left( \frac{1}{R} \right) + \frac{1}{3} \hat{\Theta}_{a\beta}^A \nabla_a \nabla_\beta \left( \frac{1}{R} \right) - \cdots \right\} \]

\[ \equiv T q^A - T_a \hat{\mu}_a^A + \frac{1}{3} T_{a\beta} \hat{\Theta}_{a\beta}^A - \cdots + \frac{(-1)^n}{(2n - 1)!!} T^{(n)}_{a\beta...\nu} \xi_{a\beta...\nu} + \cdots , \]

(3.1.3)

where

\[ 4\pi\varepsilon_0 T = \frac{1}{R}, \]  

(3.1.4)

\[ 4\pi\varepsilon_0 T_a = \nabla_a \frac{1}{R} = -\frac{R_a}{R^3}, \]  

(3.1.5)

\[ 4\pi\varepsilon_0 T_{a\beta} = \nabla_a \nabla_\beta \frac{1}{R} = \frac{3R_aR_\beta - R^2 \delta_{a\beta}}{R^5}, \]  

(3.1.6)

\[ 4\pi\varepsilon_0 T_{a\beta\gamma} = \nabla_a \nabla_\beta \nabla_\gamma \frac{1}{R} \]

\[ = -\frac{15R_aR_\betaR_\gamma - 3R^2(R_a\delta_{\beta\gamma} + R_\beta\delta_{a\gamma} + R_\gamma\delta_{a\beta})}{R^7}, \]  

(3.1.7)

\[ 4\pi\varepsilon_0 T_{a\beta\gamma\delta} = \nabla_a \nabla_\beta \nabla_\gamma \nabla_\delta \frac{1}{R} \]

\[ = \frac{1}{R^9}[105R_aR_\betaR_\gammaR_\delta - 15R^2(R_aR_\beta\delta_{\gamma\delta} + R_\betaR_\gamma\delta_{a\delta} + R_\gammaR_\delta\delta_{a\beta} + R_\betaR_\delta\delta_{a\gamma} + R_\gammaR_\delta\delta_{a\beta}) \]

\[ + 3R^4(\delta_{a\beta}\delta_{\gamma\delta} + \delta_{a\gamma}\delta_{\beta\delta} + \delta_{a\delta}\delta_{\beta\gamma})] \]  

(3.1.8)

and in general

\[ T^{(n)}_{a\beta...\nu} = \frac{1}{4\pi\varepsilon_0} \nabla_a \nabla_\beta \cdots \nabla_\nu \frac{1}{R} . \]  

(3.1.9)

The superscript \((n)\) specifies the number of subscripts, but is normally omitted when the number is obvious. If we wish to avoid ambiguity when dealing with a system of more than two molecules, we can label the \(T\) tensors with the molecular labels: \(T^{AB}\), \(T_{a^B}^{\alpha^B}\), etc. This tends to make the notation rather cumbersome, however, and we omit the labels in the two-molecule case. Notice though that it is important to establish whether we are dealing with \(T^{AB}\) or \(T_{a^B}^{\alpha^B}\), i.e., whether \(R = B - A\), as above, or \(R = A - B\). The definitions above are for the \(T^{AB}\), and show that \(T_{a^B}^{\alpha^B}(n) = (-1)^n T^{AB}(n)\).

Returning to eqn (3.1.3), we see that the potential at \(R\) due to a charge \(q\) at the origin is \(q/4\pi\varepsilon_0 R\); the potential at \(R\) due to a dipole \(\mu\) at the origin is \(-\mu_aT_a = +\mu_aR_a/4\pi\varepsilon_0 R^3 = \mu \cdot R/4\pi\varepsilon_0 R^3\), and so on.

Having found the potential as a function of position \(R\), it is now very easy to determine the electric field, the field gradient and the higher derivatives. Thus from the potential \(qT\) arising from the charge \(q\), we obtain the electric field at \(B\) due to molecule \(A\) as \(F^A_{a^B}(B) = -\nabla_a qT = -qT_a\) and the field gradient \(F^{AB}_{a^B}(B) = -\nabla_a \nabla_\beta qT = -qT_{a\beta}\). For the dipole potential we need to be a little more careful with the suffixes, to avoid clashes; so we write the potential as \(-\mu_aT_a\gamma\).
and then the electric field is \( F^A_a(B) = -\nabla_a(-\mu_y T_y) = +\mu_y T_{ay} \). Similarly the field gradient is \( F^A_{ab}(B) = -\nabla_a \nabla_b(-\mu_y T_y) = +\mu_y T_{aby} \). In this way we find, for the complete field,

\[
F^A_a(B) = -\nabla_a V^A(B) = -T_\alpha q + T_{ab} \hat{\mu}_b - \frac{1}{3} T_{ab\gamma} \hat{\Theta}_{\beta\gamma} + \cdots - \frac{(1)^n}{(2n-1)!!} T^{(n+1)}_{ab\ldots\nu\tau} \hat{\xi}_{\beta\gamma\ldots\nu\tau} - \cdots ,
\]

and for the field gradient,

\[
F^A_{ab}(B) = -\nabla_a \nabla_b V^A(B) = -T_{ab} q + T_{ab\gamma} \hat{\mu}_\gamma - \frac{1}{3} T_{ab\beta\delta} \hat{\Theta}_{\gamma\delta} + \cdots - \frac{(1)^n}{(2n-1)!!} T^{(n+2)}_{ab\ldots\nu\tau} \hat{\xi}_{\gamma\delta\ldots\nu\tau} - \cdots .
\]

This representation is quite compact and economical, but it is rather terse on first acquaintance. We will look at some examples shortly. Notice that due to a point charge (regarding \( T_\alpha \) as a vector function of position) and also the potential due to a point dipole (where we take the scalar product \(-\mu_\alpha T_\alpha\) to obtain a scalar function of position, as required for a potential).

Two important general properties of the \( T \) tensors with two or more suffixes are: (i) invariance with respect to interchange of suffixes, so that for example \( T_{xy} = T_{yx} \); and (ii) tracelessness: \( T_{ayy\ldots y} = 0 \), for any \( y\ldots y \). These results follow from the fact that the differential operators commute, and from the fact that \( \nabla^2(1/R) = 0 \) (provided that \( R \neq 0 \)). It follows from these properties that \( T^{(n)}_{ab\ldots y} \), like \( \xi^{(n)}_{ab\ldots y} \), has \( 2n + 1 \) components. (See p. 18 for the proof.) It also satisfies Laplace’s equation, \( \nabla^2 T^{(n)}_{ab\ldots y} = 0 \), and is proportional to \( R^{-n-1} \) (because it is obtained by differentiating \( R^{-1} \) \( n \) times), so its components must be linear combinations of the irregular spherical harmonics of rank \( n \), \( I_{nm} = r^{-n-1} C_{nm} \). (See Appendix B.) A detailed discussion of the relationship may be found in Tough and Stone (1977). From this and the orthogonality property of the spherical harmonics a further important property follows: if \( T^{(n)}_{ab\ldots y} \) is averaged over all directions of the intermolecular vector \( R \), the result is zero, except for \( n = 0 \), i.e., for \( T = 1/R \).

### 3.2 Multipole expansion in cartesian form

We are now in a position to calculate the electrostatic interaction between a pair of molecules in terms of their multipole moments—the multipole expansion. Molecule \( A \) has its local origin at position \( A \) in the global coordinate system, and molecule \( B \) has its origin at \( B \). We know the potential \( V^A \) at \( B \) due to molecule \( A \) from eqn (3.1.3), and we can write down the energy of a molecule in a given potential from the results of Chapter 2. Combining these formulae gives the interaction operator:

\[
\mathcal{H}' = q^B V^A + \hat{\mu}_a^B V^A_a + \frac{1}{3} \hat{\Theta}_{ab}^B V^A_{ab} + \cdots \\
= q^B \{ T^A q^A - T_a \hat{\mu}_a^A + \frac{1}{3} T_{ab} \hat{\Theta}_{\beta\gamma}^A - \cdots \} + \hat{\mu}_a^B \{ T_a q^A - T_a \hat{\mu}_\beta^A + \frac{1}{3} T_{ab\gamma} \hat{\Theta}_{\gamma\delta}^A - \cdots \} \\
+ \frac{1}{3} \hat{\Theta}_{ab}^B \{ T_{ab} q^A - T_{ab} \hat{\mu}_\gamma^A + \frac{1}{3} T_{ab\beta\delta} \hat{\Theta}_{\gamma\delta}^A - \cdots \}, \\
= T^A q^B + T_a (q^A \hat{\mu}_a^B - \hat{\Theta}_{ab}^A \hat{\Theta}_{\beta\gamma}^B - \hat{\Theta}_{ab\gamma}^A \hat{\Theta}_{\gamma\delta}^B + \frac{1}{3} \hat{\Theta}_{ab}^A \hat{\Theta}_{\gamma\delta}^B - \hat{\Theta}_{ab}^A \hat{\Theta}_{\gamma\delta}^B + \frac{1}{3} \hat{\Theta}_{ab}^A \hat{\Theta}_{\gamma\delta}^B + \cdots .
\]

(3.2.1)
Notice that some relabelling of subscripts has been necessary to avoid clashes. We are again using $T_{\alpha\beta...}$ rather than $T^{AB}_{\alpha\beta...}$ to avoid overloading the notation. For neutral species, the charges are zero, and the leading term is the dipole–dipole interaction:

$$
H' = -T_{\alpha\beta\gamma...} \hat{\mu}_\alpha^A \hat{\mu}_\beta^B - \frac{1}{3} T_{\alpha\beta\gamma}(\hat{\Theta}^A_{\alpha\beta\gamma} \hat{\Theta}^B_{\gamma\delta} - \frac{1}{9} \hat{\Theta}^A_{\alpha\beta\gamma} \hat{\Theta}^B_{\gamma\delta} + \frac{1}{15} \hat{\Omega}^A_{\alpha\beta\gamma\delta} \hat{\mu}^B_{\delta}) + \cdots.
$$

This expression, like the preceding one, is an operator. If we require the electrostatic interaction $U_{cs}$ between two molecules in non-degenerate states, then we need the expectation value of this operator, which we obtain by replacing each multipole operator by its expectation value. Thus for two neutral molecules the result is

$$
U_{cs} = -T_{\alpha\beta\gamma...} \hat{\mu}_\alpha^A \hat{\mu}_\beta^B - \frac{1}{3} T_{\alpha\beta\gamma\delta}(\hat{\Theta}^A_{\alpha\beta\gamma} \hat{\Theta}^B_{\gamma\delta} - \frac{1}{9} \hat{\Theta}^A_{\alpha\beta\gamma} \hat{\Theta}^B_{\gamma\delta} + \frac{1}{15} \hat{\Omega}^A_{\alpha\beta\gamma\delta} \hat{\mu}^B_{\delta}) + \cdots.
$$

Eqns (3.2.2) and (3.2.3) have been derived for a pair of molecules, isolated from any others. However, they are based on the Coulomb interactions between nuclear and electronic charges, which are strictly additive, so we can generalize them to an assembly of molecules by summing over the distinct pairs.

Similar expressions have been derived by a number of authors: for example, Hirschfelder et al. (1954), Jansen (1957, 1958), Buckingham (1967) and Leavitt (1980).

### 3.2.1 Explicit formulae

The formulae just derived are general but somewhat opaque, and for practical application we need more transparent forms. We substitute the explicit expression for $T_{\alpha\beta}$, eqn (3.1.9), to obtain the dipole–dipole interaction in the form

$$
U_{\mu\mu} = -\mu_\alpha^A \mu_\beta^B \frac{3R_\alpha R_\beta - R^2 }{4\pi\varepsilon_0 R^5} \delta_{\alpha\beta} \tag{3.2.4}
$$

$$
= R^2 \mu^A \cdot \mu^B - 3(\mu^A \cdot R)(\mu^B \cdot R) \frac{1}{4\pi\varepsilon_0 R^5} \tag{3.2.5}
$$

It is often convenient to choose coordinates with the $z$ axis along $R$, with the origin at $A$. The direction of $\mu^A$ is specified by polar angles $\theta_A$ and $\varphi_A$ and the direction of $\mu^B$ by $\theta_B$ and $\varphi_B$. (See Fig. 1.4.) Then

$$
\mu^A \cdot R = \mu^A R \cos \theta_A,
$$

$$
\mu^B \cdot R = \mu^B R \cos \theta_B,
$$

$$
\mu^A \cdot \mu^B = \mu^A \mu^B (\sin \theta_A \cos \varphi_A \sin \theta_B \cos \varphi_A + \sin \theta_A \sin \varphi_A \sin \theta_B \sin \varphi_B + \cos \theta_A \cos \theta_B)
$$

$$
= \mu^A \mu^B (\cos \theta_A \cos \theta_B + \sin \theta_A \sin \theta_B \cos(\varphi_B - \varphi_A)),
$$

so that the dipole–dipole interaction becomes

$$
U_{\mu\mu} = - \frac{\mu^A \mu^B}{4\pi\varepsilon_0 R^5} (2 \cos \theta_A \cos \theta_B - \sin \theta_A \sin \theta_B \cos \varphi), \tag{3.2.6}
$$

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

4.2 The induction energy

In the long-range theory it is natural to develop the induction energy using the multipole expansion, and this approach is presented first. If the intermolecular distance is too short, though, the multipole expansion may not converge, even when the molecular wavefunctions do not overlap. One way to deal with this problem is described in §4.2.3; others are discussed in Chapters 7 and 9.

Using the multipole expansion, the operator $\mathcal{H}'$ is given by eqn (3.2.2):

$$\mathcal{H}' = T q^A q^B + T_\alpha (q^A \mu_\alpha^B - \mu_\alpha^A q^B) - T_{\alpha\beta} \mu_{\alpha}^A \mu_{\beta}^B + \cdots.$$  

(We drop the terms involving the quadrupole for the moment.) Substituting in 4.1.13 gives

$$U_{\text{ind}}^B = -\sum_{n \neq 0} \langle 0| T q^A q^B + T_\alpha (q^A \mu_\alpha^B - \mu_\alpha^A q^B) - T_{\alpha\beta} \mu_{\alpha}^A \mu_{\beta}^B + \cdots |0\rangle$$

$$\times \langle n| T q^A q^B + T_\alpha (q^A \mu_\alpha^B - \mu_\alpha^A q^B) - T_{\alpha'\beta'} \mu_{\alpha'}^A \mu_{\beta'}^B + \cdots |0\rangle$$

$$\times (W_n^B - W_0^B)^{-1}.$$

Now we can perform the implied integration over the coordinates of molecule $A$, which just yields the expectation values of the multipole moment operators. We note also that the matrix elements of $q^B$ vanish, because the excited states are orthogonal to the ground state and $q^B$ is just a constant. This gives

$$U_{\text{ind}}^B = -\sum_{n \neq 0} \frac{\langle 0| T q^A \mu_\alpha^B - T_{\alpha\beta} \mu_{\alpha}^A \mu_{\beta}^B + \cdots |n\rangle \langle n| T_\alpha q^A \mu_{\alpha'}^B - T_{\alpha'\beta'} \mu_{\alpha'}^A \mu_{\beta'}^B + \cdots |0\rangle}{W_n^B - W_0^B}$$

$$= -(q^A T_\alpha - \mu_\alpha^A T_{\alpha\beta} + \cdots) \sum_{n \neq 0} \frac{\langle 0| \mu_{\alpha'}^B |n\rangle \langle n| \mu_{\beta'}^B |0\rangle}{W_n^B - W_0^B} (q^A T_{\alpha'} - \mu_{\alpha'}^B T_{\alpha'\beta'} + \cdots). \quad (4.2.1)$$

Now we can recognize here the sum-over-states expression for the polarizability $\alpha_{\alpha\alpha'}$ (see eqn (2.3.2)), so that the induction energy is

$$U_{\text{ind}}^B = -\frac{1}{2} (q^A T_\alpha - \mu_\alpha^A T_{\alpha\beta} + \cdots) \alpha_{\alpha\alpha'}^B (q^A T_{\alpha'} - \mu_{\alpha'}^B T_{\alpha'\beta'} + \cdots). \quad (4.2.2)$$

But the expression $(q^A T_\alpha - \mu_\alpha^A T_{\alpha\beta} + \cdots)$ is merely minus the electric field $F^A_{\alpha}(B)$ at $B$ due to molecule $A$ (eqn (3.1.10)), so the induction energy is $-\frac{1}{2} F^A_{\alpha}(B) F^A_{\alpha'}(B) \alpha_{\alpha\alpha'}^B$, exactly as we would expect from a straightforward classical treatment of the field. The only part played by the quantum mechanical perturbation theory is to provide the formula for the polarizability.

In this derivation, we ignored all terms in the perturbation except for some of the ones involving the dipole operator for molecule $B$. It is clear by analogy or by explicit calculation that we shall have other terms in the induction energy, involving the dipole–quadrupole polarizability, the quadrupole–quadrupole polarizability, and so on, so that the induction energy takes the form

$$U_{\text{ind}}^B = -\frac{1}{2} F^A_{\alpha}(B) F^A_{\alpha'}(B) \alpha_{\alpha\alpha'}^B - \frac{1}{3} F^A_{\alpha}(B) F^A_{\alpha'\beta'}(B) \alpha_{\alpha\alpha'}^B$$

$$- \frac{1}{6} F^A_{\alpha\beta}(B) F^A_{\alpha'\beta'}(B) \alpha_{\alpha\alpha'}^B - \cdots. \quad (4.2.3)$$

The simplest case arises when $A$ is a spherical ion, like Na+. Then the field at $B$ is $-qT_\alpha = qR_\alpha/(4\pi\varepsilon_0 R^3)$. For the case where $A$ is at the origin and $B$ at $(0, 0, z)$ the field is $F_z = q/(4\pi\varepsilon_0 z^2)$ and the induction energy is $q^2 \alpha_{zz}^B/((4\pi\varepsilon_0)^2 z^4)$. In this case, therefore, the energy is proportional to $R^{-4}$. If $A$ is neutral but polar ($\mu \neq 0$), the field is proportional to $R^{-3}$ and the energy to $R^{-6}$. Notice that the induction energy is always negative.
though, the multipole expansion may not converge, even when the molecular wavefunctions do not overlap. One way to deal with this problem is described in §4.2.3; others are discussed in Chapters 7 and 9.

Using the multipole expansion, the operator \( \mathcal{H}' \) is given by eqn (3.2.2):

\[
\mathcal{H}' = T q^A q^B + T_{\alpha} (q^A \hat{\mu}_{\alpha} - \hat{\mu}_\alpha' q^B) - T_{\alpha\beta} \hat{\mu}_\alpha' \hat{\mu}_\beta' + \cdots.
\]

(We drop the terms involving the quadrupole for the moment.) Substituting in 4.1.13 gives

\[
U_{\text{ind}}^B = -\sum_{n \neq 0} \langle 0| T q^A q^B + T_{\alpha} (q^A \hat{\mu}_{\alpha} - \hat{\mu}_\alpha' q^B) - T_{\alpha\beta} \hat{\mu}_\alpha' \hat{\mu}_\beta' + \cdots |0\rangle
\times \langle 0| T q^A q^B + T_{\alpha'} (q^A \hat{\mu}_{\alpha'} - \hat{\mu}_\alpha'' q^B) - T_{\alpha'\beta'} \hat{\mu}_{\alpha'}' \hat{\mu}_{\beta'}' + \cdots |0\rangle
\times (W_n^B - W_0^B)^{-1}.
\]

Now we can perform the implied integration over the coordinates of molecule \( A \), which just yields the expectation values of the multipole moment operators. We note also that the matrix elements of \( q^B \) vanish, because the excited states are orthogonal to the ground state and \( q^B \) is just a constant. This gives

\[
U_{\text{ind}}^B = -\frac{1}{2} \sum_{n \neq 0} \langle 0| T q^A \mu_{\alpha} - \mu_{\alpha}' T_{\alpha\beta} + \cdots |n\rangle \langle n| T q^A \mu_{\alpha}' - \mu_{\alpha}'' T_{\alpha'\beta'} + \cdots |0\rangle
\times (W_n^B - W_0^B)^{-1}.
\]

Now we can recognize here the sum-over-states expression for the polarizability \( \alpha_{\alpha\alpha'} \) (see eqn (2.3.2)), so that the induction energy is

\[
U_{\text{ind}}^B = -\frac{1}{2} (q^A T_{\alpha} - \mu_{\alpha}' T_{\alpha\beta} + \cdots) \alpha_{\alpha\alpha'} (q^A T_{\alpha'} - \mu_{\alpha}' T_{\alpha'\beta'} + \cdots).
\]

But the expression \( (q^A T_{\alpha} - \mu_{\alpha}' T_{\alpha\beta} + \cdots) \) is merely minus the electric field \( F_{\alpha}^B(B) \) at \( B \) due to molecule \( A \) (eqn (3.1.10)), so the induction energy is \(-\frac{1}{2} F_{\alpha}^A(B) F_{\alpha'}^A(B) \alpha_{\alpha\alpha'}^B \), exactly as we would expect from a straightforward classical treatment of the field. The only part played by the quantum mechanical perturbation theory is to provide the formula for the polarizability.

In this derivation, we ignored all terms in the perturbation except for some of the ones involving the dipole operator for molecule \( B \). It is clear by analogy or by explicit calculation that we shall have other terms in the induction energy, involving the dipole–quadrupole polarizability, the quadrupole–quadrupole polarizability, and so on, so that the induction energy takes the form

\[
U_{\text{ind}}^B = -\frac{1}{2} F_{\alpha}^A(B) F_{\alpha'}^A(B) \alpha_{\alpha\alpha'}^B - \frac{1}{3} F_{\alpha}^A(B) F_{\alpha'}^A(B) A_{\alpha\alpha'}^B
- \frac{1}{6} F_{\alpha}^A(B) F_{\alpha'}^A(B) C_{\alpha\beta\alpha'}^B \cdots.
\]

The simplest case arises when \( A \) is a spherical ion, like \( \text{Na}^+ \). Then the field at \( B \) is \(-qT_{\alpha} = qR_{\alpha} / (4\pi\varepsilon_0 R^3) \). For the case where \( A \) is at the origin and \( B \) at \((0,0,z)\) the field is \( F_z = q / (4\pi\varepsilon_0 z^2) \) and the induction energy is \( q^2 \alpha_{zz}^B / (4\pi\varepsilon_0 z^5) \). In this case, therefore, the energy is proportional to \( R^{-4} \). If \( A \) is neutral but polar (\( \mu \neq 0 \)), the field is proportional to \( R^{-3} \) and the energy to \( R^{-6} \). Notice that the induction energy is always negative.
4.2.1 Non-additivity of the induction energy

A very important feature of the induction energy emerges when we consider the case of a molecule surrounded by several others. The induction energy still takes the same form, i.e., $-\frac{1}{2} F_{\alpha}(B) F_{\alpha'}(B) \alpha_{\alpha \alpha'}$, but the field is now the total field due to the other molecules. (The simplest way to view this is to regard the rest of the system as comprising ‘molecule A’. However, the same result can be obtained by working through the perturbation theory using as perturbation the sum of all intermolecular interactions, and again picking out the terms in which only molecule B is excited.) Now consider the cases illustrated in Fig. 4.1. In Fig. 4.1a we have molecule B in the field of a single polar neighbour, so that $F(B) = \frac{2\mu}{4\pi\epsilon_0}R^3$, and the induction energy is $-2\alpha\mu^2/(4\pi\epsilon_0)^2R^6$. In Fig. 4.1b there are two polar neighbours, aligned so that their fields are in the same direction at B. In this case the total field is twice as big as before, $F(B) = \frac{4\mu}{4\pi\epsilon_0}R^3$, and the induction energy is $-8\alpha\mu^2/(4\pi\epsilon_0)^2R^6$, four times as big. In Fig. 4.1c there are again two polar neighbours, but aligned this time so that their fields are in opposite directions at B. Now the total field is zero and so is the induction energy.

This simple example illustrates dramatically the severe non-additivity of the induction energy. Both types of situation may occur. For example, the local environment of an ion in an ionic crystal is often centrosymmetric, so that the electric field has to vanish, and in such cases there is no dipole–dipole contribution to the induction energy. In molecular crystals and liquids, the opposite case is common; for example, in the tetrahedral structure found in ice and (approximately) in liquid water, there are two proton donors and two proton acceptors near each molecule, and the fields of these neighbours tend to add rather than cancel. In the case of induction energy, then, the assumption of pairwise additivity fails totally.

If we can simply add together the fields arising from the neighbouring molecules, the calculation of the induction energy would not present any difficulties, even though it is quadratic in the field. Unfortunately this also may fail. The simplest way to see this is to follow the derivation first given by Silberstein (1917) of the polarizability of a pair of neighbouring atoms. Two spherical atoms, with polarizabilities $\alpha^A$ and $\alpha^B$ are placed a distance $R$ apart on the $z$ axis. An external field $F$ in the $z$ direction polarizes both atoms, inducing a dipole moment in both of them. The induced dipole of each atom produces an additional field at the other, and this must be added to the applied field. So the equations for the induced moments are
\[ \mu^A = \alpha^A (F + 2\mu^B / (4\pi\varepsilon_0 R^3)), \]
\[ \mu^B = \alpha^B (F + 2\mu^A / (4\pi\varepsilon_0 R^3)). \]

These equations are easily solved to give
\[ \mu^A = \alpha^A F \frac{1 + 2\alpha^B / (4\pi\varepsilon_0 R^3)}{1 - 4\alpha^A \alpha^B / (4\pi\varepsilon_0^2 R^6)}, \]
\[ \mu^B = \alpha^B F \frac{1 + 2\alpha^A / (4\pi\varepsilon_0 R^3)}{1 - 4\alpha^A \alpha^B / (4\pi\varepsilon_0^2 R^6)}. \] (4.2.4)

So the effective field experienced by each atom is enhanced, and so is the induction energy. This is the case of a uniform external field, but much the same applies when the field is due to other molecules. It follows that we cannot in general expect to be able to add together the fields due to the static moments of the other molecules in order to calculate the induction energy. It may be a reasonable approximation to do so, especially if the molecules are not very polar or not very polarizable.

A problem that is apparent from eqn (4.2.4) is that if \( R = (4\alpha^A \alpha^B / (4\pi\varepsilon_0)^2)^{1/6} \) the denominators vanish, so that the induced moments and the electrostatic energy become infinite. This is known as the polarization catastrophe. It is a consequence of ignoring the finite extent of the polarizable charge distribution. Typically, the value of \( \alpha / 4\pi\varepsilon_0 \) is comparable to the atomic volume, so the catastrophe arises when the atoms are so close that they overlap. In that case the point-polarizability model fails. One way to avoid this problem will be discussed in §4.2.3, and others in Chapter 8.

In other geometries, the secondary effects of induction can reduce the magnitude of the induction energy. If the external field in the above example is in the \( \hat{z} \) direction rather than the \( \hat{x} \) direction, the equations for the moments become
\[ \mu^A = \alpha^A (F - \mu^B / (4\pi\varepsilon_0 R^3)), \]
\[ \mu^B = \alpha^B (F - \mu^A / (4\pi\varepsilon_0 R^3)), \]
and the induced moments are
\[ \mu^A = \alpha^A F \frac{1 - \alpha^B / (4\pi\varepsilon_0 R^3)}{1 - \alpha^A \alpha^B / (4\pi\varepsilon_0^2 R^6)}, \]
\[ \mu^B = \alpha^B F \frac{1 - \alpha^A / (4\pi\varepsilon_0 R^3)}{1 - \alpha^A \alpha^B / (4\pi\varepsilon_0^2 R^6)}. \] (4.2.5)

However, the electrostatic energy often favours structures in which the induction energy is enhanced rather than reduced, and of course the induction energy itself favours such structures. We return to the question of cooperative induction effects in Chapter 10.

### 4.2.2 Multipole expansion of the induction energy

A more subtle characteristic of the induction energy emerges when we consider the multipole expansion in more detail. It is enough to consider the simplest case of a hydrogen-like atom \( A \) with nuclear charge \( Z \) in the field of a proton \( B \). We take \( Z > 1 \) to avoid resonance effects (see Chapter 11). The perturbation is
\[ \mathcal{H}' = \frac{Z}{R} - \frac{1}{|\mathbf{R} - \mathbf{r}|}, \] (4.2.6)
where \( \mathbf{R} \) is the position of the proton and \( \mathbf{r} \) the position of the electron relative to an origin at the nucleus of atom \( A \). Expressed as a multipole series using eqn (3.3.2), this becomes
The induction energy

\[ \mathcal{H}' = \frac{1}{R} \left[ Z - \sum_{n=0}^{\infty} \left( \frac{r}{R} \right)^n P_n(\cos \theta) \right], \]

where \( r \) and \( \theta \) are polar coordinates for the electron in a coordinate system in which the proton is on the \( z \) axis.

Dalgarno and Lynn (1957a) were able to find an exact expression for the second-order energy of the atom under this perturbation. Their result is

\[ W'' = -\sum_{n=1}^{\infty} \frac{(2n+2)!(n+2)}{n(n+1)(ZR)^{2n+2}}, \]

plus some terms that decrease exponentially as \( R \) increases; the latter describe the penetration term, which we shall discuss in Chapter 8.

Now we can use the standard ratio test to study the convergence of this series. The ratio of successive terms is \( \frac{2n\times(n+3)(2n+3)}{(n+2)(ZR)^2} \), and it becomes infinite as \( n \to \infty \), for any value of \( R \). Consequently the multipole series expansion of the induction energy diverges for any \( R \).

This is a very disturbing result. It suggests that in general the multipole expansion of the interaction energy may not converge. However, Ahlrichs (1976), in a more rigorous treatment of earlier work by Brooks (1952), proved that it is always semi-convergent (asymptotically convergent). Specifically, he showed that the interaction energy can be expressed in the form

\[ U_{AB}(R) = W_{AB}(R) - W_A - W_B = \sum_{\nu=0}^{N} U_{\nu} R^{-\nu} + O(R^{-N-1}), \]

so that the remainder left after truncating the multipole series at any term tends to zero as the intermolecular distance tends to infinity. Ahlrichs also showed that the exchange terms, which arise from overlap of the molecular wavefunctions and which will be discussed in Chapter 8, decrease faster with increasing \( R \) than any power of \( 1/R \). The upshot of all this is that although the multipole expansion cannot be shown to converge at any fixed value of \( R \), and can be shown in some cases to diverge for all \( R \), it gives results that can be made arbitrarily accurate if the intermolecular distance is large enough. In practice, even at distances that are not very large, useful results may be obtained by truncating the multipole series.

4.2.3 Avoiding the multipole expansion

Because of the convergence problems that arise from the use of the multipole expansion, it would be desirable to avoid it. Instead of expressing the interaction with a neighbouring molecule in terms of the multipole expansion, we may write the perturbation in one of the forms (4.1.1–4.1.6). We shall use eqn (4.1.5), which describes the interaction between the charge density of \( A \) and an external potential, due to molecule \( B \) or in general to the rest of the system. If we are considering the induction energy of \( A \), we sum over states in which \( A \) is excited but the rest of the system stays in its ground state, so the operator \( \hat{V}^B(\mathbf{r}) \) becomes the potential \( V(\mathbf{r}) \) at some point \( \mathbf{r} \) in \( A \) due to the rest of the system:

\[ \mathcal{H}' = \int V(\mathbf{r})\hat{\rho}^A(\mathbf{r}) \, d^3\mathbf{r}. \]
When we put this into the perturbation theory, we get

$$U_{\text{ind}}^A = - \sum_{m \neq 0} \int V(\mathbf{r}) \frac{\langle 0 | \hat{\rho}^A(\mathbf{r}) | m \rangle \langle m | \hat{\rho}^A(\mathbf{r'}) | 0 \rangle}{W^A_m - W^A_0} V(\mathbf{r'}) \, d^3 \mathbf{r} \, d^3 \mathbf{r'}$$

$$= \int V(\mathbf{r}) \alpha(\mathbf{r}, \mathbf{r'}; 0) V(\mathbf{r'}) \, d^3 \mathbf{r} \, d^3 \mathbf{r'}.$$  (4.2.11)

In this way we obtain an expression for the induction energy in terms of the static charge density susceptibility. This expression is quite general, within the long-range approximation. By replacing \( V(\mathbf{r}) \) and \( V(\mathbf{r'}) \) by the multipole expansion of the potential due to a neighbouring molecule or set of molecules, we recover the multipole expansion of the induction energy. However, (4.2.11) is more suitable at short distances, where the multipole expansion converges only slowly, if at all. It involves a double integral over position, and is impractical for use in the context of a simulation, where the energy and possibly its derivatives have to be computed at each step, but it can be evaluated quite efficiently to obtain the induction energy of a pair of molecules at particular geometries. We shall explore other solutions to the convergence problem in Chapter 9. We must remember, too, that in the long-range approximation we are ignoring the effects of exchange of electrons between molecules. At short range, these effects become important, and lead to additional terms in the induction energy, which we shall explore in Chapter 8.

4.3 The dispersion energy

4.3.1 Drude model

We turn to the dispersion energy. Because this is a wholly non-classical phenomenon, it may be helpful in understanding it to contemplate a simple model, first introduced by London (1930a) (see London (1937) for a version in English). We represent each atom by a Drude model: a one-dimensional harmonic oscillator in which the electron cloud, mass \( m \), is bound to the nucleus by a harmonic potential with force constant \( k \). The Hamiltonian for each atom takes the form \( \frac{p^2}{2m} + \frac{1}{2} k x^2 \). There is an atomic dipole proportional to the displacement \( x \) of the electrons from the nucleus, and for two adjacent atoms the interaction energy of these dipoles is proportional to the product of the dipole moments. Accordingly the Hamiltonian for the complete system takes the form

$$\mathcal{H} = \frac{1}{2m} (p_A^2 + p_B^2) + \frac{1}{2} k (x_A^2 + x_B^2 + 2c x_A x_B),$$

where \( c \) is some coupling constant. This can be separated into two uncoupled oscillators corresponding to the normal modes \( x_A \pm x_B \): 

$$\mathcal{H} = \frac{1}{4m} (p_A + p_B)^2 + \frac{1}{4} k (1 + c)(x_A + x_B)^2$$

$$+ \frac{1}{4m} (p_A - p_B)^2 + \frac{1}{4} k (1 - c)(x_A - x_B)^2.$$ 

The normal mode frequencies are \( \omega_\pm = \omega_0 \sqrt{1 \pm c} \), where \( \omega_0 = \sqrt{k/m} \) is the frequency of an isolated oscillator.
Now a classical system would have a minimum energy of zero, whether coupled or not. The quantum system however has zero-point energy, and the energy of the coupled system in its lowest state is

\[ \frac{1}{2} \hbar (\omega_+ + \omega_-) = \frac{1}{2} \hbar \omega_0 \left( \sqrt{1 + c} + \sqrt{1 - c} \right) = \frac{1}{2} \hbar \omega_0 \left[ 2 - \frac{1}{4} c^2 - \frac{5}{64} c^4 - \cdots \right], \]

so that there is an energy lowering, compared with the zero-point energy \( \hbar \omega_0 \) of two uncoupled oscillators, of

\[ U_{\text{disp}} = -\hbar \omega_0 \left( \frac{1}{8} c^2 + \frac{5}{128} c^4 + \cdots \right). \]

The interaction between the atoms leads to a correlation between the motion of their electrons, and this manifests itself in a lowering of the energy. Notice that the energy depends on the square of the coupling constant \( c \) and is always negative; regardless of the sign of the coupling, the correlation between the motion of the electrons leads to a lowering of the energy. For interacting dipoles, the coupling \( c \) is proportional to \( R^{-3} \), so the leading term in the dispersion energy is proportional to \( R^{-6} \).

At very large separations, this picture changes slightly because the speed of light is finite. The correlation between the fluctuations in the two molecules becomes less effective, because the information about a fluctuation in the charge distribution of one molecule can only be transmitted to the other molecule at the speed of light. By the time that the other molecule has responded and the information about its response has reached the first molecule again, the electrons have moved, so that the fluctuations are no longer in phase. Detailed calculation (Casimir and Polder 1948, Craig and Thirumachandran 1984) shows that this ‘retardation’ effect becomes important when the separation \( R \) is large compared with the wavelength \( \lambda_0 \) corresponding to the characteristic absorption frequency of the molecule, and the dispersion energy is then reduced by a factor of the order of \( \lambda_0/R \) and becomes proportional to \( R^{-7} \). However, this only occurs at much larger distances than we are concerned with, since \( \lambda_0 \) is typically several thousand ångström. For a fuller discussion see Israelachvili (1992).

4.3.2 Quantum-mechanical formulation

We return to the perturbation-theory expression, eqn (4.1.14). For simplicity we consider first only the dipole–dipole term in \( \mathcal{H}' \):

\[ U_{\text{disp}}^{(6)} = -\sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A 0_B | \hat{p}_{A \alpha} T_{\alpha \beta} \hat{p}_{B \beta} | m_A n_B \rangle \langle m_A n_B | \hat{p}_{A \gamma} T_{\gamma \delta} \hat{p}_{B \delta} | 0_A 0_B \rangle}{W_{m_0}^A + W_{n_0}^B}, \]

\[ = -T_{\alpha \beta} T_{\gamma \delta} \sum_{m_A \neq 0} \sum_{n_B \neq 0} \frac{\langle 0_A | \hat{p}_{A \alpha} | m_A \rangle \langle m_A | \hat{p}_{A \gamma} | 0_A \rangle \langle 0_B | \hat{p}_{B \beta} | n_B \rangle \langle n_B | \hat{p}_{B \delta} | 0_B \rangle}{W_{m_0}^A + W_{n_0}^B}, \tag{4.3.1} \]

where \( W_{m_0}^A = W_m^A - W_0^A \). This is an inconvenient expression to deal with, because although the matrix elements can be factorized into terms referring to \( A \) and terms referring to \( B \), the denominator cannot. There are two commonly used ways to handle it. One was first introduced by London (1930a), and uses the Unsöld or average-energy approximation (Unsöld 1927). Here we first write (4.3.1) as