Molecular Modelling for Beginners

Second Edition

ALAN HINCHLIFFE

The University of Manchester

WILEY

A John Wiley and Sons, Ltd, Publication

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Preface to the Second Edition

It is five years since the first edition was published, and many things have moved on sufficiently to justify this second edition.

Some things never change; I have left the elementary chapters alone and I still believe that Appendix A on relevant mathematical methods is the correct place for you to *start* your studies.

Some topics have matured in the last five years. Density functional theory (and especially the B3LYP choice of functionals) has become the workhorse of modern computational chemistry. I have reworked all the problems and expanded the text as appropriate.

I have also said 'goodbye' to a few of the older topics. For example, everyone can now do chemical drawing, so I do not need to teach it. Thankfully that bane of our lives the Z-matrix has all but disappeared; I still have fond memories of struggling to get cyclic structures symmetrical and so it still gets a page of discussion.

I have completely rewritten the chapters dealing with Monte Carlo and molecular dynamics, the G*n* models, transition states and solvent models. I have also added a completely new chapter called 'Sharing Out the Energy', and I hope you will enjoy reading it.

It is fashionable to have an associated website with any new teaching text, and I have therefore added a website at

http://www.wileyeurope.com/college/hinchliffe

where you will find a number of problem sets and their solutions. Feel free to use them any way you like. I used them in my own teaching. Perhaps you have a corresponding set that you would like to share with the rest of us? Let me know.

I did all the illustrative calculations using either Gaussian 03 or HyperChem; these were done either on a beautiful Sony Vaio laptop or on the University of Manchester's High Performance Computing parallel computer, a Bull Itanium2 system.

As always, I welcome comments and can be reached at: Alan.Hinchliffe@manchester.ac.uk.

Alan Hinchliffe
Manchester, UK

Preface to the First Edition

There is nothing radically new about the techniques we use in modern molecular modelling. Classical mechanics hasn't changed since the time of Newton, Hamilton and Lagrange, the great ideas of statistical mechanics and thermodynamics were discovered by Ludwig Boltzmann and J. Willard Gibbs amongst others and the basic concepts of quantum mechanics appeared in the 1920s, by which time J.C. Maxwell's famous electromagnetic equations had long since been published.

The chemically inspired idea that molecules can profitably be treated as a collection of balls joined together with springs can be traced back to the work of D.H. Andrews in 1930. The first serious molecular Monte Carlo simulation appeared in 1953, closely followed by B.J. Alder and T.E. Wainwright's classic molecular dynamics study of hard discs in 1957.

The Hartrees' 1927 work on atomic structure is the concrete foundation of our everyday concept of atomic orbitals, whilst C.C.J. Roothaan's 1951 formulation of the HF-LCAO model arguably gave us the basis for much of modern molecular quantum theory.

If we move on a little, most of my colleagues would agree that the two recent major advances in molecular quantum theory have been density functional theory, and the elegant treatment of solvents using ONIOM. Ancient civilizations believed in the cyclic nature of time and they might have had a point for, as usual, nothing is new. Workers in solid-state physics and biology actually proposed these models many years ago. It took the chemists a while to catch up.

Scientists and engineers first got their hands on computers in the late 1960s. We have passed the point on the computer history curve where every ten years gave us an order of magnitude increase in computer power, but it is no coincidence the that growth in our understanding and application of molecular modelling has run in parallel with growth in computer power. Perhaps the two greatest driving forces in recent years have been the PC and the graphical user interface. I am humbled by the fact that my lowly 1.2 GHz AMD Athlon office PC is far more powerful than the world-beating mainframes that I used as a graduate student all those years ago, and that I can build a molecule on screen and run a B3LYP/6-311++G(3d,2p) calculation before my eyes (of which more in Chapter 20).

We have also reached a stage where tremendously powerful molecular modelling computer packages are commercially available, and the subject is routinely taught as part of undergraduate science degrees. I have made use of several such packages to produce the screenshots; obviously they look better in colour than the greyscale of this text.

There are a number of classic (and hard) texts in the field; if I'm stuck with a basic molecular quantum mechanics problem, I usually reach for Eyring, Walter and Kimball's *Quantum Chemistry* but the going is rarely easy.

Equally there are a number of beautifully produced elementary texts and software reference manuals that can apparently transform you into an expert overnight. It's a two-edged sword, and we are victims of our own success. One often meets self-appointed experts in the field who have picked up much of the jargon with little of the deep understanding. It's no use (in my humble opinion) trying to hold a conversation about gradients, hessians and density functional theory with a colleague who has just run a molecule through one package or another but hasn't the slightest clue what the phrases or the output mean.

It therefore seemed to me (and to the reviewers who read my new book proposal) that the time was right for a middle course. I assume that you are a 'Beginner' in the sense of Chambers dictionary, *someone who begins; a person who is in the early stages of learning or doing anything*. . . , and I want to tell you how we go about modern molecular modelling, why we do it, and most important of all, explain much of the basic theory behind the mouse clicks. This involves mathematics and physics, and the book neither pulls punches nor aims at instant enlightenment. Many of the concepts and ideas are difficult ones, and you will have to think long and hard about them; if it's any consolation, so did the pioneers in our subject. I have given many of the derivations in full, and tried to avoid the dreaded phrase 'it can be shown that'.

There are various strands to our studies, all of which eventually intertwine. We start off with molecular mechanics, a classical treatment widely used to predict molecular geometries. In Chapter 8, I give a quick guide to statistical thermodynamics (if such a thing is possible), because we need to make use of the concepts when trying to model arrays of particles at nonzero temperatures. Armed with this knowledge, we are ready for an assault on Monte Carlo and molecular dynamics.

Just as we have to bite the bullet of statistical mechanics, so we have to bite the equally difficult one of quantum mechanics, which occupies Chapters 11 and 12. We then turn to the quantum treatment of atoms, where many of the sums can be done on a postcard if armed with knowledge of angular momentum.

The Hartree–Fock and HF-LCAO models dominate much of the next few chapters, as they should. The Hartree–Fock model is great for predicting many molecular properties, but it can't usually cope with bond breaking and bond making. Chapter 19 treats electron correlation and Chapter 20 deals with the very topical density functional theory (DFT). You won't be taken seriously if you have not done a DFT calculation on your molecule. Quantum mechanics, statistical mechanics and electromagnetism all have a certain well-deserved reputation amongst science students; they are hard subjects. Unfortunately all three all feature in this new text. In electromagnetism it is mostly a matter of getting to grips with the mathematical notation (although I have spared you Maxwell's beautiful equations), whilst in the other two subjects it is more a question of mastering hard concepts. In the case of quantum mechanics, the concepts are often in direct contradiction to everyday experience and common sense. I expect from you a certain level of mathematical competence; I have made extensive use of vectors and matrices not because I am perverse, but because such mathematical notation brings out the inherent simplicity and beauty of many of the equations. I have tried to help by giving a mathematical appendix, which should also make the text self-contained.

I have tried to put the text into historical perspective, and in particular I have quoted directly from a number of what I call *keynote papers*. It is interesting to read at first hand how the pioneers put their ideas across, and in any case they do it far better than me. For example, I am not the only author to quote Paul Dirac's famous statement

> The underlying Physical Laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact application of these laws leads to equations much too complicated to be soluble.

I hope you have a profitable time in your studies, and at the very least begin to appreciate what all those options mean next time you run a modelling package!

Alan Hinchliffe
Manchester, UK

1

Electric Charges and their Properties

As far as we can tell, there are four fundamental types of interactions between physical objects. There is the *weak nuclear interaction* that governs the decay of beta particles, and the *strong nuclear interaction* that is responsible for binding together the particles in a nucleus. The familiar *gravitational* interaction holds the Earth very firmly in its orbit round the Sun, and finally we know that there is an *electromagnetic* interaction that is responsible for binding atomic electrons to nuclei and for holding atoms together when they combine to form molecules.

Of the four, the gravitational interaction is the only one we would normally come across in our everyday world. This is because gravitational interactions between bodies always add. The gravitational interaction between two atoms is negligible but when large numbers of fundamental particles such as atoms are aggregated together, the gravitational interaction becomes significant.

You may think it bizarre that there are four types of interaction, yet, conversely, you might wonder why there should be just four. Why not one, three or five? Should there not be a unifying theory to explain why there are four, and whether they are related? As I write, there is no such unifying theory despite tremendous research activity.

1.1 Point Charges

In this chapter I am going to concentrate on electric charges and their properties, since electrons and protons are fundamental building blocks for atoms and molecules.

It turns out that there are two types of electric charge in nature, which we might choose to call type X and type Y (or Red and Blue for that matter, but X and Y will do for

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now). Experimental evidence shows the existence of an electrostatic force between electric charges; the force between two X-type charges is always repulsive, as is the force between two Y-type charges. The force between an X-type and a Y-type is always attractive. For this reason, the early experimenters decided to classify charges as positive or negative, because a positive quantity times a positive quantity gives a positive quantity, a negative quantity times a negative quantity gives a positive quantity whilst a negative quantity times a positive quantity gives a negative quantity. I am sure you know that the best known fundamental particles responsible for these charges are electrons and protons, and you are probably expecting me to tell you that the electrons are the negatively charged particles whilst protons are positively charged. It is actually just a convention that we take: we could just as well have called electrons positive.

Whilst on the subject, it is fascinating to note that the charge on the electron is exactly equal and opposite of that on a proton. Atoms and molecules generally contain exactly the same number of electrons and protons, and so the net charge on a molecule is almost always zero. Ions certainly exist in solutions of electrolytes, but the number of Na^+ ions in a solution of sodium chloride is exactly equal to the number of Cl^- ions and once again we are rarely aware of any imbalance of charge.

A thunderstorm results when nature separates out positive and negative charges on a macroscopic scale. It is thought that friction between moving masses of air and water vapour detaches electrons from some molecules and attaches them to others. This results in parts of clouds being left with an excess of charge, often with spectacular results. It was investigations into such atmospheric phenomena that gave the first clues about the nature of the electrostatic force.

We normally start any study of charges at rest (*electrostatics*) by considering the force between two point charges, as shown in Figure 1.1. The term 'point charge' is a mathematical abstraction; obviously electrons and protons have a finite size. Just bear with me for a few pages, and accept that a point charge is one whose dimensions are small compared to the distance between them. An electron is large if you happen to be a nearby electron, but can normally be treated as a point charge if you happen to be a human being a metre away.

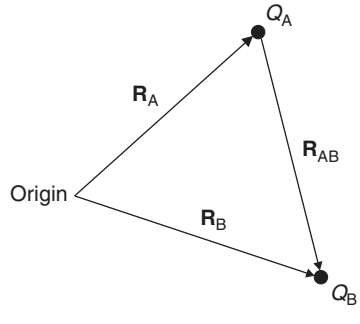

Figure 1.1 *Point charges*

The concept of a point charge may strike you as an odd one, but once we have established the magnitude of the force between two such charges, we can deduce the force between

any arbitrary charge distributions on the grounds that they are composed of a large number of point charges.

In Figure 1.1 we have point charge Q_A at position vector $\mathbf{R}_A$ and Q_B at $\mathbf{R}_B$. From the laws of vector analysis, the vector $\mathbf{R}_{AB} = \mathbf{R}_B - \mathbf{R}_A$ joins Q_A to Q_B, and points from Q_A to Q_B as shown. I have indicated the direction of the vectors with arrows.

1.2 Coulomb's Law

In 1785, Charles Augustin de Coulomb became the first person to give a mathematical form to the force between point charges. He measured the force directly between two very small charged bodies, and was able to show that the force exerted by Q_A on Q_B was

- proportional to the inverse square of the distance between Q_A and Q_B when both charges were fixed;
- proportional to Q_A when Q_B and $\mathbf{R}_{AB}$ were fixed;
- proportional to Q_B when Q_A and $\mathbf{R}_{AB}$ were fixed.

He also noticed that the force acted along the line joining the centres of the two charges, and that the force was either attractive or repulsive depending on whether the charges were different or of the same type. The sign of the product of the charges therefore determines the direction of the force.

A mathematical result of these observations can be written in scalar form as

$$F_{\text{A on B}} \propto \frac{Q_A Q_B}{R_{AB}^2} \tag{1.1}$$

Forces are vector quantities, and Equation (1.1) is better written in vector form as

$$\mathbf{F}_{\text{A on B}} \propto \frac{Q_A Q_B}{R_{AB}^3}\mathbf{R}_{AB}$$

When Coulomb first established his law, he had no means of quantifying charge and so could not identify the proportionality constant. He took it to be unity, and thereby defined charge in terms of the force between charges. Modern practice is to regard charge and force as independent quantities, and because of this a dimensioned proportionality constant is necessary. For a reason that need not concern us, this is taken as $1/4\pi\varepsilon_0$, where the permittivity of free space ε_0 is an experimentally determined quantity with the approximate value $\varepsilon_0 = 8.854 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$. Coulomb's law is therefore

$$\mathbf{F}_{\text{A on B}} = \frac{1}{4\pi\varepsilon_0}\frac{Q_A Q_B}{R_{AB}^3}\mathbf{R}_{AB} \tag{1.2}$$

and it applies to measurements done in free space. If we repeat Coulomb's experiments with the charges immersed in different media, then we find that the law still holds but with a different proportionality constant. We modify the proportionality constant using a quantity ε_r called the *relative permittivity*. In older texts, ε_r is called the *dielectric constant*. Our final statement of Coulomb's law is therefore

$$\mathbf{F}_{\text{A on B}} = \frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{Q_A Q_B}{R_{AB}^3}\mathbf{R}_{AB} \tag{1.3}$$

According to Newton's third law, we know that if Q_A exerts a force $\mathbf{F}_{A\text{ on }B}$ on Q_B, then Q_B should exert an equal and opposite force on Q_A. Coulomb's law satisfies this requirement, since

$$\mathbf{F}_{B\text{ on }A} = \frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{Q_A Q_B}{R_{BA}^3}\mathbf{R}_{BA}$$

(the vector $\mathbf{R}_{BA}$ points in the opposite direction to $\mathbf{R}_{AB}$ and so one force is exactly the negative of the other, as it should be).

1.3 Pair Wise Additivity

Suppose we now add a third point charge Q_C with position vector $\mathbf{R}_C$ as shown in Figure 1.2. Since Q_A and Q_B are point charges, the addition of Q_C cannot alter the force between Q_A and Q_B.

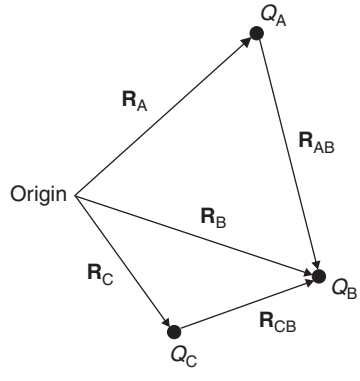

Figure 1.2 *Third charge added*

The total force on Q_B now comprises two terms, the force due to point charge Q_A and the force due to point charge Q_C. This total force is given by

$$\mathbf{F}_B = \frac{Q_B}{4\pi\varepsilon_0}\left(Q_A\frac{\mathbf{R}_{AB}}{R_{AB}^3} + Q_C\frac{\mathbf{R}_{CB}}{R_{CB}^3}\right) \tag{1.4}$$

This may seem at first sight to be a trivial statement: surely all forces act this way. Not necessarily, for I have assumed that the addition of Q_C did not have any effect on Q_A and Q_B (and so did not influence the force between them).

The generic term *pair wise additive* describes things like forces that add as above. Forces between point electric charges are certainly pair wise additive, and so you might imagine that forces between atoms and molecules must therefore be pair wise additive, because atoms and molecules consist of (essentially) point charges. I am afraid that nature is not so kind, and we will shortly meet situations where forces between the composites of electrons and protons that go to make up atoms and molecules are far from being pair wise additive.

1.4 Electric Field

Suppose now we have a point charge Q at the coordinate origin, and we place another point charge q at point P that has position vector $\mathbf{r}$ (Figure 1.3).

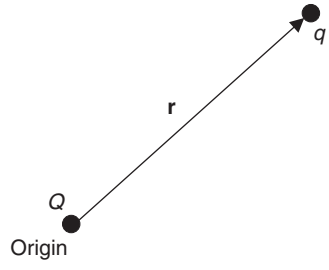

Figure 1.3 *Field concept*

The force exerted by Q on q is

$$\mathbf{F} = \frac{1}{4\pi\varepsilon_0}\frac{Qq}{r^3}\mathbf{r}$$

which I can rewrite trivially as

$$\mathbf{F} = \left(\frac{1}{4\pi\,\varepsilon_0}\frac{Q}{r^3}\mathbf{r}\right)q$$

The point is that the term in brackets is to do with Q and the vector $\mathbf{r}$, and contains no mention of q. If we want to find the force on any arbitrary q at $\mathbf{r}$, we calculate the quantity in brackets once and then multiply by q. One way of thinking about this is to imagine that the charge Q creates a certain field at point $\mathbf{r}$, which determines the force on any other q when placed at position $\mathbf{r}$.

This property is called the *electric field* $\mathbf{E}$ at that point. It is a vector quantity, like force, and the relationship is

$$\mathbf{F}\,(\text{on } q \text{ at } \mathbf{r}) = q\mathbf{E}\,(\text{at } \mathbf{r})$$

Comparison with Coulomb's law, Equation (1.3), shows that the electric field at point $\mathbf{r}$ due to a point charge Q at the coordinate origin is

$$\mathbf{E} = \frac{1}{4\pi\,\varepsilon_0}\frac{Q\mathbf{r}}{r^3} \tag{1.5}$$

$\mathbf{E}$ is sometimes written $\mathbf{E}(\mathbf{r})$ to emphasize that the electric field depends on the position vector $\mathbf{r}$.

Electric fields are vector fields and they are often visualized as *field lines*. These are drawn such that their spacing is inversely proportional to the strength of the field, and their tangent is in the direction of the field. They start at positive charges and end at negative charges, and two simple examples are shown in Figure 1.4. Here the choice of eight lines is quite arbitrary.

Electric fields that do not vary with time are called *electrostatic* fields.

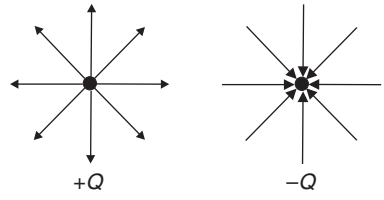

Figure 1.4 *Field lines for point charges*

1.5 Work

Look again at Figure 1.3, and suppose we move point charge q whilst keeping Q fixed in position. When a force acts to make something move, energy is transferred. There is a useful phrase in physical science that is to do with the energy transferred, and it is *work*. Work measures the energy transferred in any change, and can be calculated from the change in energy of a body when it moves through a distance under the influence of a force.

We have to be careful to take account of the energy balance. If a body gains energy, this energy has to come from somewhere, and that somewhere must lose energy. What we do is to divide the universe into two parts: the bits we are interested in called the *system* and the rest of the universe that we call the *surroundings*.

Some texts focus on the work done *by* the system, some concern themselves with the work done *on* the system. According to the law of conservation of energy, one is exactly the equal and opposite of the other, but we have to be clear which is being discussed. I am going to write w_{on} for the work done on our system.

If the system gains energy, then w_{on} will be positive. If the system loses energy then w_{on} will negative.

We also have to be careful about the phrase 'through a distance'. The phrase means 'through a distance that is the projection of the force vector on the displacement vector', and you should instantly recognize a vector scalar product (see Appendix A).

A useful formula that relates to the energy gained by a system (i.e. w_{on}) when a constant force $\mathbf{F}$ moves its point of application through $\mathbf{l}$ is

$$w_{\text{on}} = -\mathbf{F}.\mathbf{l} \tag{1.6}$$

In the case where the force is not constant, we have to divide up the motion into differential elements $\mathrm{d}\mathbf{l}$. The energy transferred is then given by the sum of all the corresponding differential elements $\mathrm{d}w_{\text{on}}$. The corresponding formulae are

$$\begin{aligned} \mathrm{d}w_{\text{on}} &= -\mathbf{F}.\mathrm{d}\mathbf{l} \\ w_{\text{on}} &= -\int \mathbf{F}.\mathrm{d}\mathbf{l} \end{aligned} \tag{1.7}$$

We now move q by an infinitesimal vector displacement $\mathrm{d}\mathbf{l}$, as shown in Figure 1.5, so that it ends up at point $\mathbf{r} + \mathrm{d}\mathbf{l}$. The work done on the system in that differential change is

$$\mathrm{d}w_{\text{on}} = -\mathbf{F}.\mathrm{d}\mathbf{l}$$

If the angle between the vectors $\mathbf{r}_{\text{I}}$ and $\mathrm{d}\mathbf{l}$ is θ, then we have

$$\mathrm{d}w_{\text{on}} = -F\mathrm{d}l\cos\theta$$

and examination of Figure 1.6 shows that $\mathrm{d}l\cos\theta$ is the radial distance moved by charge q, which we will write $\mathrm{d}r$.

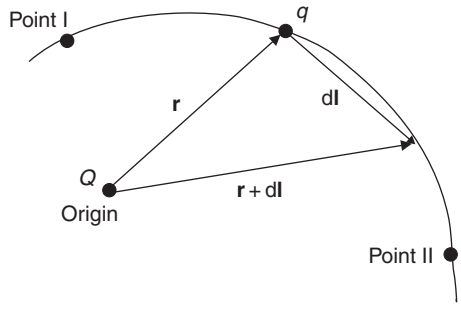

Figure 1.5 *Electrostatic work*

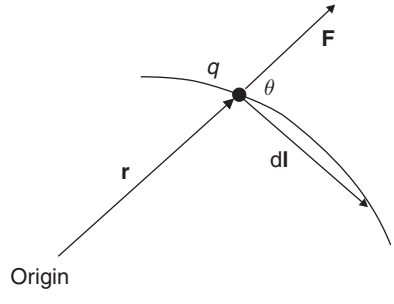

Figure 1.6 *Relationship between vectors*

Hence

$$\mathrm{d}w_{\mathrm{on}} = -\frac{1}{4\pi\varepsilon_0}\frac{Qq}{r^2}\mathrm{d}r$$

The total work done moving from position I to position II is therefore found by integrating

$$\begin{aligned} w_{\mathrm{on}} &= -\frac{1}{4\pi\varepsilon_0}\int_{\mathrm{I}}^{\mathrm{II}}\frac{Qq}{r^2}\mathrm{d}r \\ &= \frac{1}{4\pi\varepsilon_0}Qq\left(\frac{1}{r_{\mathrm{II}}}-\frac{1}{r_{\mathrm{I}}}\right) \end{aligned} \tag{1.8}$$

The work done depends only on the initial and final positions of charge q; it is independent of the way we make the change.

Another way to think about the problem is as follows. The force is radial, and we can divide the movement from position I to position II into infinitesimal steps, some of which are parallel to **F** and some of which are perpendicular to **F**. The perpendicular steps count 0 towards w_{on}, the parallel steps only depend on the change in the (scalar) radial distance.

1.6 Charge Distributions

So far I have concentrated on point charges, and carefully skirted round the question as to how we deal with continuous distributions of charge. Figure 1.7 shows a charge distribution Q_A. The density of charge need not be constant through space, and we normally write $\rho(\mathbf{r})$ for the density at the point whose position vector is $\mathbf{r}$. The charge contained within the volume element $d\tau$ at $\mathbf{r}$ is therefore $\rho(\mathbf{r})d\tau$ and the relationship between $\rho(\mathbf{r})$ and Q_A is discussed in Appendix A. It is

$$Q_A = \int \rho(\mathbf{r})\ d\tau \tag{1.9}$$

In order to find the force between the charge distribution and the point charge Q_B we simply extend our ideas about the force between two point charges; one of the point charges being $\rho(\mathbf{r})d\tau$ and the other Q_B.

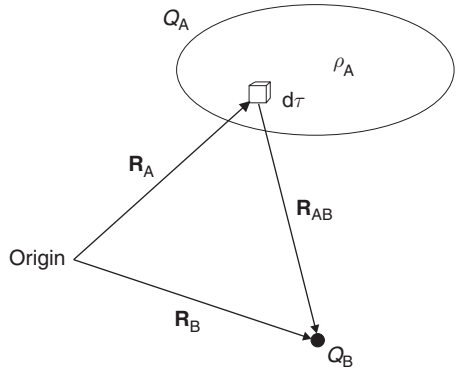

Figure 1.7 *Charge distribution*

The total force is given by the sum of all possible contributions from the elements of the continuous charge distribution Q_A with point charge Q_B. The practical calculation of such a force can be a nightmare, even for simple charge distributions. One of the reasons for the nightmare is that forces are vector quantities; we need to know about both their magnitude and their direction.

In the next section, I am going to tell you about a very useful scalar field called the mutual potential energy U. This field has the great advantage that it is a scalar field, and so we do not need to worry about direction in our calculations.

1.7 Mutual Potential Energy, *U*

Suppose now we start with charge q at infinity, and move it up to a point with vector position $\mathbf{r}$, as shown in Figure 1.3. The work done is

$$w_{on} = \frac{1}{4\pi\varepsilon_0}\frac{Qq}{r} \tag{1.10}$$

and this represents the energy change on building up the charge distribution, with the charges initially at infinite separation. It turns out that this energy change is an important property, and we give it a special name (the *mutual potential energy*) and a special symbol U (occasionally Φ).

Comparison of the equations for force, work and mutual potential energy given above suggests that there might be a link between the force and the mutual potential energy; at first sight, one expression looks like the derivative of the other.

I am going to derive a relationship between force and mutual potential energy. The relationship is perfectly general; it applies to all forces provided that they are constant in time.

1.8 Relationship between Force and Mutual Potential Energy

Consider a body of mass m that moves in (say) the x-direction under the influence of a constant force. Suppose that at some instant its speed is v. The kinetic energy is $\frac{1}{2}mv^2$. You are probably aware of the law of conservation of energy, and know that when I add the potential energy U to the kinetic energy, I will get a constant energy that I will denote ε (sorry about the clash of symbols with electric permittivity, but that is life):

$$\varepsilon = \frac{1}{2}mv^2 + U \tag{1.11}$$

I want to show you how to relate U to the force F. If the energy ε is constant in time, then $\mathrm{d}\varepsilon/\mathrm{d}t = 0$. Differentiation of Equation (1.11) with respect to time gives

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = mv\frac{\mathrm{d}v}{\mathrm{d}t} + \frac{\mathrm{d}U}{\mathrm{d}t}$$

and so, by the chain rule

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = mv\frac{\mathrm{d}v}{\mathrm{d}t} + \frac{\mathrm{d}U}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}t}$$

If the energy ε is constant then its first differential with respect to time is zero, and v is just $\mathrm{d}x/\mathrm{d}t$. Likewise $\mathrm{d}v/\mathrm{d}t$ is the acceleration and so

$$0 = \left(m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} + \frac{\mathrm{d}U}{\mathrm{d}x}\right)\frac{\mathrm{d}x}{\mathrm{d}t} \tag{1.12}$$

Equation (1.12) is true if the speed is zero, or if the term in brackets is zero. According to Newton's second law of motion, mass times acceleration is force, and so

$$F = -\frac{\mathrm{d}U}{\mathrm{d}x} \tag{1.13}$$

which gives us the link between force and mutual potential energy.

When working in three dimensions, we have to be careful to distinguish between vectors and scalars. We treat a body of mass m whose position vector is $\mathbf{r}$. The velocity is $\mathbf{v} = \mathrm{d}\mathbf{r}/\mathrm{d}t$ and the kinetic energy is $\frac{1}{2}m(\mathrm{d}\mathbf{r}/\mathrm{d}t)(\mathrm{d}\mathbf{r}/\mathrm{d}t)$.

Analysis along the lines given above shows that the force $\mathbf{F}$ and U are related by

$$\mathbf{F} = -\mathrm{grad}\ U \tag{1.14}$$

where the gradient of U is discussed in Appendix A and is given in Cartesian coordinates by

$$\text{grad } U = \frac{\partial U}{\partial x}\mathbf{e}_x + \frac{\partial U}{\partial y}\mathbf{e}_y + \frac{\partial U}{\partial z}\mathbf{e}_z \tag{1.15}$$

Here $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ are unit vectors pointing along the Cartesian axes.

1.9 Electric Multipoles

We can define exactly an array of point charges by listing the magnitudes of the charges, together with their position vectors. If we then wish to calculate (say) the force between one array of charges and another, we simply apply Coulomb's law (Equation (1.3)) repeatedly to each pair of charges. Equation (1.3) is exact, and can be easily extended to cover the case of continuous charge distributions.

For many purposes, it proves more profitable to describe a charge distribution in terms of certain quantities called the *electric moments*. We can then discuss the interaction of one charge distribution with another in terms of the interactions between the electric moments.

Consider first a pair of equal and opposite point charges, $+Q$ and $-Q$ separated by distance R (Figure 1.8). This pair of charges is usually said to form an *electric dipole* of magnitude QR. In fact, electric dipoles are vector quantities and a more rigorous definition is

$$\mathbf{p}_e = Q\mathbf{R} \tag{1.16}$$

where the vector $\mathbf{R}$ points from the negative charge to the positive charge.

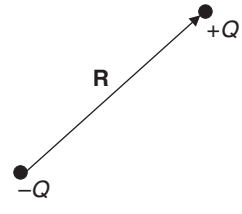

Figure 1.8 *Simple electric dipole*

We sometimes have to concern ourselves with a more general definition, one relating to an arbitrary array of charges such as that shown in Figure 1.9. We have four point charges: Q_1 whose position vector is $\mathbf{R}_1$, Q_2 whose position vector is $\mathbf{R}_2$, Q_3 whose position vector is $\mathbf{R}_3$ and Q_4 whose position vector is $\mathbf{R}_4$. We define the *electric dipole moment* $\mathbf{p}_e$ of these four charges as

$$\mathbf{p}_e = \sum_{i=1}^{4} Q_i\mathbf{R}_i$$

It is a vector quantity with x, y and z Cartesian components

$$\sum_{i=1}^{4} Q_iX_i, \quad \sum_{i=1}^{4} Q_iY_i \quad \text{and} \quad \sum_{i=1}^{4} Q_iZ_i$$

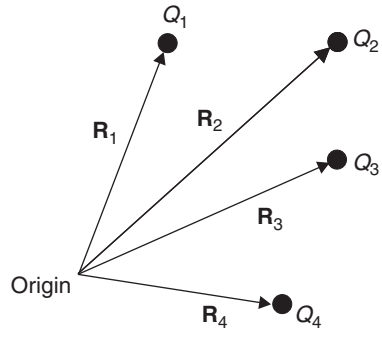

Figure 1.9 *Generalized electric dipole*

This is consistent with the elementary definition given above; in the case of two equal and opposite charges $+Q$ and $-Q$ a distance d apart, the electric dipole moment has magnitude Qd and points from the negative charge to the positive. The generalization to n charges is obvious: we substitute n for 4 in the above definition.

There are several general rules about electric moments of charge distributions, and we can learn a couple of the ones that apply to dipole moments by considering the simple arrays shown in Figure 1.10 and keeping the definitions in mind.

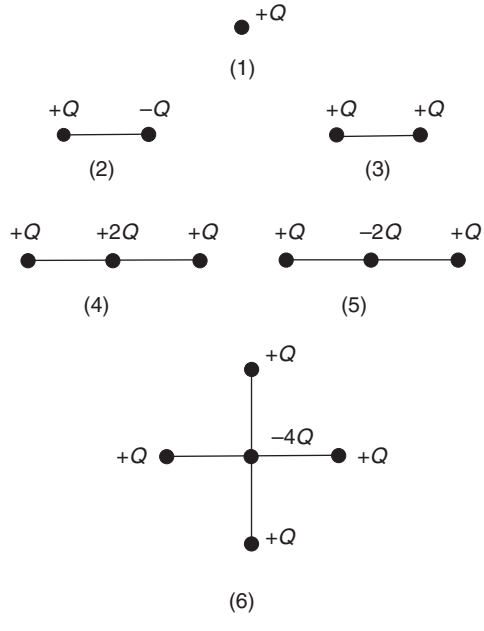

Figure 1.10 *Simple arrays of point charges*

I have joined up the charges with lines in order to focus attention on the charge systems involved; there is no implication of a 'bond'. We do not normally discuss the electric dipole due to a point charge (1). Examination of the charge distributions (2) through (6) and calculation of their electric dipole moment for different coordinate origins suggest the general result; neutral arrays of point charges have a unique electric dipole moment that does not depend on where we take the coordinate origin. Otherwise, we have to state the coordinate origin when we discuss the electric dipole moment.

I can prove this from Equation (1.16), generalized to n point charges:

$$\mathbf{p}_e = \sum_{i=1}^{n} Q_i \mathbf{R}_i \tag{1.17}$$

Suppose that we move the coordinate origin so that each point charge Q_i has a position vector $\mathbf{R}'_i$ where

$$\mathbf{R}_i = \mathbf{R}'_i + \boldsymbol{\Delta}$$

with $\boldsymbol{\Delta}$ a constant vector. From the definition of electric dipole moment we have

$$\mathbf{p}_e = \sum_{i=1}^{n} Q_i \mathbf{R}_i$$

and so, with respect to the new coordinate origin

$$\begin{aligned} \mathbf{p}'_e &= \sum_{i=1}^{n} Q_i \mathbf{R}'_i \\ &= \sum_{i=1}^{n} Q_i \left(\mathbf{R}_i - \boldsymbol{\Delta}\right) \\ &= \mathbf{p}_e - \boldsymbol{\Delta} \sum_{i=1}^{n} Q_i \end{aligned}$$

The two definitions only give the same vector if the sum of charges is zero. We often use the phrase *gauge invariant* to describe quantities that do not depend on the choice of coordinate origin.

Arrays (5) and (6) each have a centre of symmetry. There is a general result that any charge distribution having no overall charge but a centre of symmetry must have a zero dipole moment, and similar results follow for other highly symmetrical arrays of charges.

1.9.1 Continuous Charge Distributions

In order to extend the definition of an electric dipole to a continuous charge distribution such as that shown in Figure 1.7, we first of all divide the region of space into differential elements $\mathrm{d}\tau$. If $\rho(\mathbf{r})$ is the charge density then the change in volume element $\mathrm{d}\tau$ is $\rho(\mathbf{r})\mathrm{d}\tau$. We then treat each of these volume elements as point charges and add (i.e. integrate). The electric dipole moment becomes

$$\mathbf{p}_e = \int \mathbf{r}\rho\left(\mathbf{r}\right)\ \mathrm{d}\tau \tag{1.18}$$

1.9.2 Electric Second Moment

The electric dipole moment of an array of point charges is defined by the three sums

$$\sum_{i=1}^{n} Q_i X_i, \quad \sum_{i=1}^{n} Q_i Y_i \quad \text{and} \quad \sum_{i=1}^{n} Q_i Z_i$$

and we can collect them into a column vector in an obvious way as

$$\mathbf{p}_{\mathrm{e}} = \begin{pmatrix} \sum_{i=1}^{n} Q_i X_i \\ \sum_{i=1}^{n} Q_i Y_i \\ \sum_{i=1}^{n} Q_i Z_i \end{pmatrix} \tag{1.19}$$

The six independent quantities

$$\sum_{i=1}^{n} Q_i X_i^2, \quad \sum_{i=1}^{n} Q_i X_i Y_i, \quad \sum_{i=1}^{n} Q_i X_i Z_i, \ldots, \quad \sum_{i=1}^{n} Q_i Z_i^2$$

are said to define the *electric second moment* of the charge distribution. We usually collect them into a real symmetric 3×3 matrix $\mathbf{q}_{\mathrm{e}}$:

$$\mathbf{q}_{\mathrm{e}} = \begin{pmatrix} \sum_{i=1}^{n} Q_i X_i^2 & \sum_{i=1}^{n} Q_i X_i Y_i & \sum_{i=1}^{n} Q_i X_i Z_i \\ \sum_{i=1}^{n} Q_i Y_i X_i & \sum_{i=1}^{n} Q_i Y_i^2 & \sum_{i=1}^{n} Q_i Y_i Z_i \\ \sum_{i=1}^{n} Q_i Z_i X_i & \sum_{i=1}^{n} Q_i Z_i Y_i & \sum_{i=1}^{n} Q_i Z_i^2 \end{pmatrix} \tag{1.20}$$

The matrix is symmetric because of the obvious equalities of the off-diagonal sums such as

$$\sum_{i=1}^{n} Q_i X_i Y_i \quad \text{and} \quad \sum_{i=1}^{n} Q_i Y_i X_i$$

There are unfortunately many different definitions related to the second (and higher) moments in the literature. There is little uniformity of usage, and it is necessary to be crystal clear about the definition and choice of origin when dealing with these quantities.

Most authors prefer to work with a quantity called the *electric quadrupole moment* rather than the second moment, but even then there are several different conventions. A common choice is to use the symbol $\boldsymbol{\Theta}_{\mathrm{e}}$ and the definition

$$\boldsymbol{\Theta}_{\mathrm{e}} = \frac{1}{2} \begin{pmatrix} \sum_{i=1}^{n} Q_i \left(3X_i^2 - R_i^2\right) & 3\sum_{i=1}^{n} Q_i X_i Y_i & 3\sum_{i=1}^{n} Q_i X_i Z_i \\ 3\sum_{i=1}^{n} Q_i Y_i X_i & \sum_{i=1}^{n} Q_i \left(3Y_i^2 - R_i^2\right) & 3\sum_{i=1}^{n} Q_i Y_i Z_i \\ 3\sum_{i=1}^{n} Q_i Z_i X_i & 3\sum_{i=1}^{n} Q_i Z_i Y_i & \sum_{i=1}^{n} Q_i \left(3Z_i^2 - R_i^2\right) \end{pmatrix} \tag{1.21}$$

Notice that the diagonal elements of this matrix sum to zero and so the matrix has zero trace (the *trace* being the sum of the diagonal elements; see Appendix A). Some authors do not

use the factor of ½ in their definition. Quadrupole moments are gauge invariant provided the electric dipole moment and the charge are both zero.

Figure 1.11 shows an octahedrally symmetrical array of point charges. Each point charge has magnitude Q, apart from the central charge that has magnitude $-6Q$ in order to make the system neutral. The distance between each axial point charge and the central one is a.

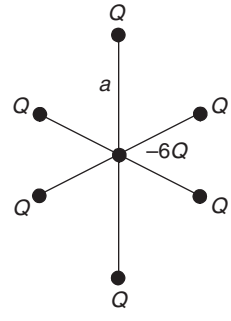

Figure 1.11 *Octahedral charge distribution*

If I choose to direct the Cartesian axes along the symmetry axes, then the second moment matrix is

$$\mathbf{q}_e = Qa^2 \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

whilst the quadrupole moment matrix is zero.

If I now reduce the symmetry of the charge distribution by placing charges $2Q$ along the vertical axis (taken for the sake of argument as the x-axis) and $-8Q$ at the centre (to keep the electrical balance), the second moment matrix becomes

$$\mathbf{q}_e = Qa^2 \begin{pmatrix} 4 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

whilst the quadrupole moment matrix is now

$$\mathbf{\Theta}_e = Qa^2 \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The electric quadrupole moment measures deviations from spherical symmetry. It is zero when the charge distribution has spherical symmetry.

It always has zero trace (because of the definition), but it is not always diagonal. Nevertheless, it can always be made diagonal by a rotation of the coordinate axes.

Finally, consider a linear array formed by the top $(+Q)$, central $(+2Q)$ and lower charges $(-3Q)$. We find

$$\mathbf{q}_e = Qa^2 \begin{pmatrix} -2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \text{ and } \boldsymbol{\Theta}_e = Qa^2 \begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

In cases where the symmetry of the problem determines that the second moment tensor only has one nonzero component, we speak colloquially of *the* second moment (which in this case is $-2Qa^2$).

1.9.3 Higher Electric Moments

The set of ten independent quantities

$$\sum_{i=1}^{n} Q_i X_i^3, \quad \sum_{i=1}^{n} Q_i X_i^2 Y_i, \ldots, \quad \sum_{i=1}^{n} Q_i Z_i^3$$

defines the electric third moment of the charge distribution, and so on. We rarely encounter such higher moments of electric charge in chemistry.

1.10 Electrostatic Potential

Electrostatic forces are vector quantities, and we have to worry about their magnitude and direction. I explained earlier that it is more usual to work with the mutual potential energy U rather than the force $\mathbf{F}$, if only because U is a scalar quantity. In any case we can recover one from the other by the formula

$$\mathbf{F} = -\text{grad } U$$

Similar considerations apply when dealing with electrostatic fields. They are vector fields with all the inherent problems of having to deal with both a magnitude and a direction. It is usual to work with a scalar field called the *electrostatic potential* ϕ. This is related to the electrostatic field $\mathbf{E}$ in the same way that U is related to $\mathbf{F}$:

$$\mathbf{E} = -\text{grad } \phi$$

We will hear more about the electrostatic potential in later sections. In the meantime, I will tell you that the electrostatic potential at field point $\mathbf{r}$ due to a point charge Q at the coordinate origin is

$$\phi(\mathbf{r}) = \frac{Q}{4\pi\varepsilon_0} \frac{1}{r} \tag{1.22}$$

The electric field and the electrostatic potential due to an electric dipole, quadrupole and higher electric moments are discussed in all the elementary electromagnetism texts. The expressions can be written exactly in terms of the various distances and charges involved. For many applications, including our own, it is worthwhile examining the mathematical form of these fields for points in space that are far away from the charge distribution. We then refer to (for example) the 'small' electric dipole and so on.

The electrostatic potential at field point $\mathbf{r}$ due to a small electric dipole $\mathbf{p}_e$ at the coordinate origin turns out to be

$$\phi(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\frac{\mathbf{p}_e.\mathbf{r}}{r^3} \tag{1.23}$$

which falls off as $1/r^2$. It falls off faster with r than the potential due to a point charge because of the cancellation due to plus and minus charges. This is in fact a general rule: the electrostatic potential for a small electric multipole of order l falls off as $r^{-(l+1)}$ so dipole moment potentials fall off faster than those due to point charges, and so on.

1.11 Polarization and Polarizability

In electrical circuits, charges are stored in capacitors, which at their simplest consist of a pair of conductors carrying equal and opposite charges. Michael Faraday (1837) made a great discovery when he observed that filling the space between the plates of a parallel plate capacitor with substances such as mica increased their ability to store charge. The multiplicative factor is called the relative permittivity and is given a symbol ε_r, as discussed above. I also told you that the older name is the dielectric constant.

Materials such as glass and mica differ from substances such as copper wire, in that they have few conduction electrons and so make poor conductors of electric current. We call materials such as glass and mica *dielectrics*, to distinguish them from metallic conductors.

Figure 1.12 shows a two-dimensional picture of a dielectric material, illustrated as positively charged nuclei each surrounded by a localized electron cloud.

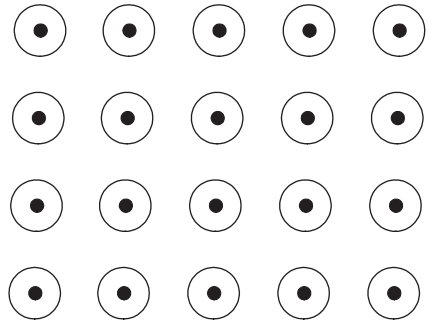

Figure 1.12 *Dielectric slab*

We now apply an electrostatic field, directed from the left to the right. There is a force on each charge, and the positive charges are displaced to the right whilst the negative charges move a corresponding distance to the left, as shown in Figure 1.13.

The macroscopic theory of this phenomenon is referred to as *dielectric polarization*, and we focus on the induced dipole moment $d\mathbf{p}_e$ per differential volume $d\tau$. Because it is a macroscopic theory, no attention is paid to atomic details; we assume that there are a large number of atoms or molecules within the volume element $d\tau$ (or that the effects caused by the discrete particles have somehow been averaged out).

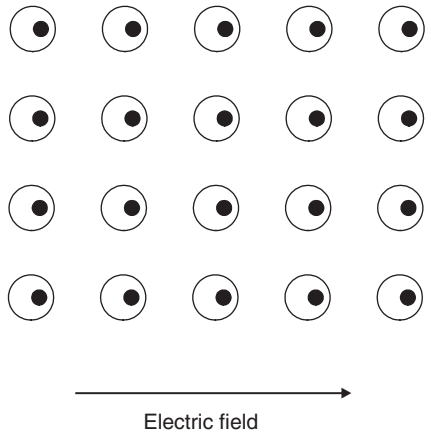

Figure 1.13 *Dielectric with applied field*

We relate the induced electric dipole to the volume of a differential element by

$$\mathrm{d}\mathbf{p}_\mathrm{e} = \mathbf{P}\mathrm{d}\tau \tag{1.24}$$

where the dielectric polarization **P** is an experimentally determined quantity. **P** can depend on the applied field in all manner of complicated ways, but for very simple media and for low field strengths, it turns out that **P** is directly proportional to **E**. We write

$$\mathbf{P} = (\varepsilon_\mathrm{r} - 1)\,\varepsilon_0\mathbf{E} \tag{1.25}$$

where ε_r is the relative permittivity of the dielectric. The polarization acts so as to reduce the field inside a dielectric.

1.12 Dipole Polarizability

At the microscopic level, we concern ourselves with the various electric moments that are induced in each atom or molecule.

Consider the simple case shown in Figure 1.14, where we apply a weak electric field **E** in a direction parallel to a molecule's electric dipole moment. This causes charge redistribution and we can write

$$p_\mathrm{e}\,(\text{induced}) = p_\mathrm{e}\,(\text{permanent}) + \alpha E \tag{1.26}$$

I have distinguished between the permanent electric dipole, the one a molecule has in free space with no fields present, from the induced dipole. I have also used the symbol α for the *dipole polarizability*.

In the general case, the field need not be weak and the induced dipole need not be in the same direction as either the applied field or the permanent dipole moment. This is shown in Figure 1.15. Parameter α cannot be a scalar, since the directions of the applied field and the induced dipole need not be the same.

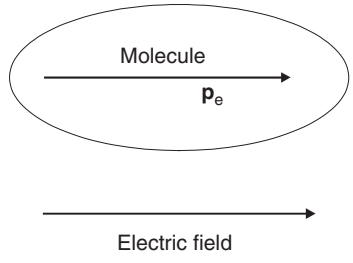

Figure 1.14 *Induced molecular dipole*

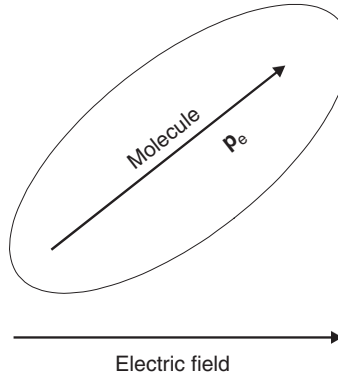

Figure 1.15 *More general case*

The dipole polarizability $\boldsymbol{\alpha}$ is a special type of physical property called a tensor, just like the electric second moment. We can represent $\boldsymbol{\alpha}$ as a 3×3 real symmetric matrix

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{\mathbf{xx}} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \tag{1.27}$$

and I will write the more general expression as

$$\mathbf{p}_e \text{ (induced)} = \mathbf{p}_e \text{ (permanent)} + \alpha.\mathbf{E} + \text{higher order terms} \tag{1.28}$$

The higher order terms are the *hyperpolarizabilities*; they feature in advanced texts of this kind. We are not going to meet them again. We interpret Equation (1.28) as a matrix equation; the $\mathbf{p}$'s are column vectors.

1.12.1 Properties of Polarizabilities

The matrix $\boldsymbol{\alpha}$ can always be written in diagonal form by a suitable rotation of the Cartesian axes (see Appendix A) to give

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{aa} & 0 & 0 \\ 0 & \alpha_{bb} & 0 \\ 0 & 0 & \alpha_{cc} \end{pmatrix}$$

The quantities α_{aa}, α_{bb} and α_{cc} are called the *principal values* of the polarizability tensor. For molecules with symmetry, the principal axes of polarizability correspond to the molecular symmetry axes. For a linear molecule the components that refer to perpendicular axes are equal and usually different from the parallel component and the matrix is usually written

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{aa} & 0 & 0 \\ 0 & \alpha_{bb} & 0 \\ 0 & 0 & \alpha_{bb} \end{pmatrix}$$

1.13 Many-Body Forces

It is instructive to calculate the work done in building up an array of charges such as that shown in Figure 1.9. We will assume that all the charges are point charges and so cannot be polarized. We start with all the charges (n in total) at infinity, and move them in turn from infinity to their position as shown.

Moving Q_1 from infinity to position vector $\mathbf{R}_1$ takes no energy, because no other charges are present.

Moving Q_2 from infinity to position vector $\mathbf{R}_2$ involves an energy change:

$$U_{12} = \frac{1}{4\pi\varepsilon_0}\frac{Q_1 Q_2}{R_{12}}$$

where R_{12} is the length of the vector joining the charges. We now move Q_3 from infinity to position vector $\mathbf{R}_3$. This charge moves in the field due to Q_1 and Q_2, involving an energy cost:

$$U_{13} + U_{23} = \frac{1}{4\pi\varepsilon_0}\frac{Q_1 Q_3}{R_{13}} + \frac{1}{4\pi\varepsilon_0}\frac{Q_2 Q_3}{R_{23}}$$

The total work done U_{tot} is seen to be

$$U_{\text{tot}} = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} U_{ij} \tag{1.29}$$

This expression holds because of the pair wise additivity of the forces between point charges. The expression would not necessarily hold if the charges were themselves charge distributions because the addition of further charges could polarize the existing ones and so alter the forces already calculated.

Whatever the case, U_{tot} will depend on the coordinates of all the charges present:

$$U_{\text{tot}} = U_{\text{tot}}\left(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_n\right) \tag{1.30}$$

and it is always possible to write a formal expansion

$$U_{\text{tot}}\left(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_n\right) = \sum_{\text{pairs}} U^{(2)}\left(\mathbf{R}_i, \mathbf{R}_j\right) + \sum_{\text{triples}} U^{(3)}\left(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k\right) + \cdots + U^{(n)}\left(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_n\right) \tag{1.31}$$

involving distinct pairs, triples, etc. of particles. The $U^{(2)}$ terms are referred to as the pair contributions, the $U^{(3)}$ terms are the three-body terms, and so on. Terms higher than the second are identically zero for the interaction between point charges.

1.14 Problem Set

A set of problems, together with solutions, is available on the associated website.

2

The Forces between Molecules

When molecules are near enough to influence one another, we need to concern ourselves with the balance between the forces of attraction and repulsion. We know that such attractive forces exist, for otherwise there would be nothing to bring molecules together into the solid and liquid states, and all matter would be gaseous. A study of the forces between atomic or molecular species constitutes the subject of *intermolecular forces*.

People have speculated about the nature of intermolecular forces ever since the ideas of atoms and molecules first existed. Our present ideas, that molecules attract at long range but repel strongly at short range, began to emerge in the nineteenth century due to the experimental work of Rudolf J.E. Clausius and Thomas Andrews. It was not until the early twentieth century, when the principles of quantum mechanics became established, that we could truly say that we understood the detailed mechanism of intermolecular forces.

Although we talk about intermolecular *forces*, it is more usual and convenient to focus on the *mutual potential energy*, discussed in Chapter 1. If we start with two argon atoms at infinite separation, then their mutual potential energy at separation R tells us the energy change on bringing the atoms together to that distance from infinity.

Even for the simplest pair of molecules, the intermolecular mutual potential energy will depend on their relative orientations in addition to their separation. Perhaps you can now see why the study of intermolecular forces has taken so much effort by so many brilliant scientists, over very many years.

2.1 Pair Potential

So, to start with, we concern ourselves with two atomic or molecular species A and B, and ask how they interact. No chemical reaction is implied, and I should say straightaway that I am not going to be concerned with bond making and bond breaking in this chapter. That is

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the subject of *valence theory*. In the (unusual) case that the two species A and B concerned are ions, you may think that the problem is more or less solved. We simply calculate their mutual Coulomb potential energy as discussed in Chapter 1:

$$U_{AB} = \frac{1}{4\pi\varepsilon_0}\frac{Q_A Q_B}{R_{AB}} \tag{2.1}$$

You would certainly be on the right lines in this approach except that ions are not point charges and they can be polarized just like any other continuous charge distribution. But as I explained in Chapter 1, we rarely have to concern ourselves with ions, and to get started we will consider the very simple case of a pair of like atoms (such as two argon atoms). We know from experiment that the general form of their mutual potential energy must be that shown in Figure 2.1. This curve is meant to be schematic, and I have been careful not to quantify the axes. It has all the right features but we have yet to discover its precise form. We very often speak about the *pair potential*, and write it $U(R)$, where R is the separation between the two atoms. The zero of $U(R)$, denoted by the horizontal line, is commonly taken to refer to the two atoms at infinity. We often characterize the curve in terms of a small number of parameters; for example, the collision diameter σ being the distance at which $U(R) = 0$, the minimum R_{min} and minus the value of $U(R)$ at R_{min} (often written ε, and as defined is a positive quantity).

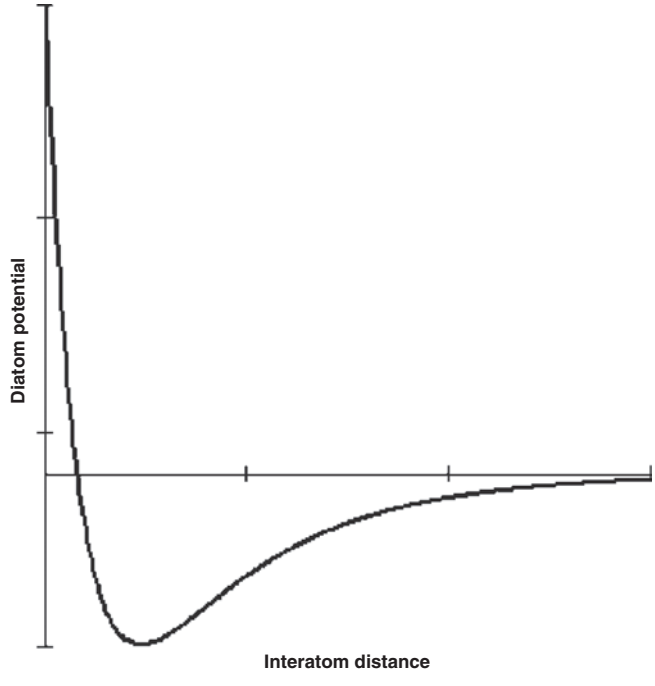

Figure 2.1 *Schematic argon–argon interaction*