Part I

Foundations of electronic and photoelectron spectroscopy
1 Introduction

1.1 The basics

It is convenient to view electrons in atoms and molecules as being in orbitals. This idea is ingrained in chemistry and physics students early on in their studies and it is a powerful concept that provides explanations for a wide variety of phenomena. It is important to stress from the very beginning that the concept of an orbital in any atom or molecule possessing more than one electron is an approximation. In other words, orbitals do not actually exist, although electrons in atoms and molecules often behave to a good approximation as if they were in orbitals.

An orbital describes the spatial distribution of a particular electron. For example, we expect that an electron in a 1s orbital in an atom will, on average, be much closer to the nucleus than an electron in a 2s orbital in the same atom. Qualitatively, we would picture the electron as being represented by a charge cloud with a much greater density near the nucleus for the 1s orbital than the 2s orbital. Similarly, we know that the electron in a 2pz orbital does not have a spherically symmetric distribution, as does an s electron, but instead is distributed in a cylindrically symmetric fashion about the z axis with the charge cloud consisting of lobes pointing along both the +z and −z directions.

Within the constraints of the orbital approximation, electronic spectroscopy is the study of transitions of electrons from one orbital to another, induced by the emission or absorption of a quantum of electromagnetic radiation, i.e. a photon. Each orbital in an atom or molecule has a specific energy, $E_n$, and to induce a transition between these orbitals the photon must satisfy the resonance condition

$$E_2 - E_1 = hν = \frac{hc}{λ} \quad (1.1)$$

where $ν$ and $λ$ are the frequency and wavelength of the radiation, respectively, and $h$ is the Planck constant (see Appendix A). Under normal circumstances, only one electron is involved in the promotion or demotion process, and therefore we say that we are dealing with one-electron transitions. Thus all other electrons remain in their original orbitals, although their energies may have changed as a result of the electronic transition.

In electronic emission spectroscopy, an electron drops to an orbital of lower energy with the concomitant emission of a photon. Owing to the quantization of orbital energies, only photons of certain discrete wavelengths are produced and an emission spectrum can therefore be obtained by measuring the emitted radiation intensity as a function of wavelength. In
absorption, the reverse process operates and an *absorption spectrum* can be obtained by measuring the change in intensity of radiation, such as that produced by a continuum lamp, as a function of wavelength after passing it through a sample.

Photoelectron spectroscopy is essentially a special case of electronic absorption spectroscopy\(^1\) in which the electron is given enough energy to take it beyond any of the bound orbitals: in other words, the electron is able to escape the binding forces of the atom or molecule and is said to have exceeded the *ionization limit*. The minimum energy required to do this is the *ionization energy* for an electron in that particular orbital. Photoionization differs from an absorption transition involving two bound orbitals in that there is more than one photon energy which can bring it about. In fact any photon with an energy high enough to promote an electron above the ionization limit can, in principle, bring about photoionization. Notice that this does not defy the resonance condition: the resonance condition equivalent to the requirement that energy be conserved and is still satisfied because the electron is able to take away any excess energy in the form of electron kinetic energy.

Since there are no discrete absorption wavelengths (only discrete absorption *onsets*), photoelectron spectroscopy is carried out in a very different manner from conventional electronic absorption spectroscopy. As the name implies, it is electron energies rather than photon energies which are measured. For an atom, part of the energy \(h\nu\) provided by the incoming photon is used to ionize the atom. The remainder is partitioned between the atomic cation and the electron kinetic energy and so, from the conservation of energy,

\[
h\nu = IE_i + T_{\text{ion}} + T_e \tag{1.2}
\]

where \(IE_i\) is the ionization energy of an electron in orbital \(i\) and \(T_{\text{ion}}\) and \(T_e\) are the cation and electron kinetic energies, respectively. Given that an electron is very much lighter than an atomic nucleus, conservation of momentum dictates that the ion recoil velocity will be very low and most of the kinetic energy will be taken away by the electron. As a result, \(T_{\text{ion}}\) can usually be neglected and a spectrum can therefore be obtained by fixing \(h\nu\) and measuring the electron current as a function of electron kinetic energy. This is the basic idea of the traditional photoelectron spectroscopy experiment. In the case of atoms, peaks will appear at various electron energies in the spectrum corresponding to ionization of electrons from the various occupied orbitals. A peak at a given \(T_e\) can be converted to an orbital ionization energy using equation (1.2) provided the ionizing photon frequency \(\nu\) is known.

Photoelectron spectroscopy is a good example of the tremendous changes that have taken place in spectroscopic techniques over the past two or three decades. Although conventional photoelectron spectroscopy as outlined above is still important and widely used, a relatively new method of electron spectroscopy, zero electron kinetic energy (ZEKE) spectroscopy, is now capable of extracting the same type of information but at much higher resolution. ZEKE spectroscopy is one of those techniques that has benefited from the introduction of the laser as a spectroscopic light source. There are many other laser-based spectroscopic techniques, some relatively simple and some which are very complicated. Most of the spectroscopic

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\(^1\) To minimize verbosity the term *electronic spectroscopy* will often be used to encompass both ‘normal’ electronic spectroscopy and photoelectron spectroscopy.
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Data presented in this book have been obtained using laser spectroscopy of one form or another, which should indicate its importance in the study of molecules in the gas phase.

However, it is not the aim of this book to describe the wide variety of methods that are available for electronic spectroscopy, although some experimental details are given in Part II. Rather the focus is primarily on the spectra themselves and in particular how they can be interpreted and what they reveal. The underlying principles needed to do this are common to a variety of different spectroscopic techniques, and in this part we develop the basic theoretical background.

1.2 Information obtained from electronic and photoelectron spectra

Before addressing some of the theoretical principles, we want to convince the reader that electronic spectroscopy is worthwhile doing. In particular, what information can be extracted from an electronic or photoelectron spectrum? This will be addressed in some detail when specific examples are met in Part III, but let us outline at this early stage some of the extraordinary range of information that can be deduced.

First and most obviously, information is obtained on orbital energies. In particular, the spectroscopic transition energy can be equated with the difference in energy between the two orbitals involved in an electronic transition (assuming that the orbital energies are unchanged as a result of the electron changing orbitals, which is only approximately true). Photoelectron spectroscopy is even more informative in this regard, since in the upper state the electron has no binding energy and can therefore be regarded as being in an orbital with zero potential energy. Consequently, ionization energies are a direct measure of orbital energies in the neutral atom or molecule, and can therefore be used to construct a molecular orbital diagram.

However, electronic spectroscopy is able to provide much more than just a measure of absolute orbital energies or orbital energy differences. Very often, particularly for molecules in the gas phase, vibrational and rotational structure can be resolved. Vibrational structure leads directly to vibrational frequencies. As will be seen later, not all vibrations need be active in electronic spectra. Excitation of some vibrations may be forbidden because of their symmetries. This may seem unfortunate, but in fact the absence of certain vibrational features can also have the benefit of providing qualitative, and sometimes even quantitative, information on the structure of the molecule, as will be shown later.

Rotational structure tends to be difficult to resolve in electronic spectra, except for small molecules, but when it is obtained it can be highly informative. Accurate equilibrium structures in both upper and lower states may be extracted from a rotational analysis. In addition, the exact details of the rotational structure are not only dependent on molecular structure, but also on the symmetries of the electronic states involved. Consequently, rotationally resolved spectra provide a reliable means of establishing electronic state symmetries. When spectra are of exceptionally high resolution there is even more information that can be extracted, although such ultra-high resolution spectra will not be considered in any detail in this book.
Finally, one should note that some of the laser-based methods of electronic spectroscopy are extremely sensitive, and are therefore able to detect very small quantities of a particular sample. This has many different uses, particularly in analytical chemistry. Furthermore, it is possible to detect and characterize molecules that are extremely unstable or reactive and therefore inevitably have a fleeting presence and/or very low concentrations. Species in this category would include free radicals and molecular ions, and we will show a number of examples in Part III.
2 Electronic structure

2.1 Orbitals: quantum mechanical background

In this and the subsequent chapter the reasoning behind the concept of orbitals in atoms and molecules is outlined. An appreciation of what an orbital is, and what its limitations are, is vital for an understanding of electronic spectroscopy. Some may find this section frustrating in that little justification is given for many of the statements made. However, the theoretical treatment of electronic structure is a complicated subject and is for the most part beyond the scope of this book, although some effort is made to summarize some of the technical issues in Appendix B. For a detailed account, including proof of the statements made below, the reader should consult some of the more advanced texts listed at the end of this chapter.

2.1.1 Wave–particle duality and the Schrödinger equation

An orbital defines the spatial distribution of an electron within an atom or molecule. It arises from the application of quantum mechanical ideas to atomic and molecular structure. Central to the wave mechanical view of quantum mechanics is the identification of a wavefunction, \( \psi \), of a system, which is a solution of the Schrödinger equation

\[
H \psi = E \psi
\]  

(2.1)

This simple-looking and very famous equation is deceptive, for it is more complicated than it first appears. \( H \), the so-called Hamiltonian, is actually a mathematical operator composed of, among other things, second-order differential operators such as \( \frac{d^2}{dx^2} \). On its own it is therefore an abstract mathematical quantity. The detailed form of the Hamiltonian appropriate for describing the electronic structure of atoms and molecules is given in Section 2.1.3. The Hamiltonian is an energy operator which, when it operates on the wavefunction on the left-hand side of equation (2.1), generates an energy, \( E \), multiplied by the wavefunction on the right-hand side. The energy is said to be an observable, i.e. it is a physical property that can, in principle, be measured.

The Schrödinger equation provides the means for describing physical behaviour at the atomic and molecular level. Underlying this description is the implication that all matter possesses wave-like properties, and that this becomes particularly significant when dealing with sub-atomic particles, such as electrons, protons, and neutrons, and collections of these particles in atoms and molecules. The possession of both wave and particle properties is...
known as wave–particle duality. The wave characteristics are represented mathematically by the wavefunction, $\psi$, and it is important to have some feel for what it is that the wavefunction describes. Although oversimplified, it is useful to view the wavefunction as describing the amplitude of a matter wave, such as that associated with an electron, throughout space. If we persist in trying to think of the electron as a particle, then the alternative wave description clearly muddies any effort to specify the precise location of the electron at any instant in time. Instead, we can only specify the probability that the electron will be found at a particular place at a particular instant in time in an experimental measurement. This probabilistic interpretation was made quantitative by Born, who associated the square of the wavefunction, $\psi^2$, evaluated at some point in space, with the probability of the particle being at that point in space at any instant in time.\footnote{Solution of the Schrödinger equation can yield complex wavefunctions in some instances, i.e. $\psi$ may have both real and imaginary parts. Since we only attach a physical interpretation to the square of the wavefunction, rather than the wavefunction itself, this causes no practical problems. It is simply necessary to ensure that the square of the wavefunction is a real quantity, and so for complex wavefunctions $\psi^* \psi$ must be used in place of $\psi^2$, where $\psi^*$ is the complex conjugate of $\psi$.} Since $\psi$ is a continuous function and the particle must be located somewhere in space, we insist that

$$\int \psi^2 \, dV = 1 \quad (2.2)$$

where, although no integration limits have been shown, the implication is that integration is over all accessible space ($V$ is the volume). This is known as the normalization condition.

### 2.1.2 The Born–Oppenheimer approximation

The Schrödinger equation for molecules is complicated, since it must describe not only the motion of a collection of electrons, but also nuclear motion as well. However, there is an important simplification that can be made, which follows from the large mass difference between electrons and nuclei. Given that the mass of a proton is 1836 times larger than that of an electron, electrons in a molecule will generally move at far greater speeds than the nuclei. When the nuclei make small changes in their relative positions, such as during a molecular vibration, the electron cloud almost instantaneously adjusts to the new set of nuclear positions. This means that the electrons are almost completely unaffected by the speed with which the nuclei move. This statement is one version of a very important approximation known as the Born–Oppenheimer approximation.

The utility of the Born–Oppenheimer approximation is that it makes it possible to separate the total energy of a molecule into two terms, namely,

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{kin}} \quad (2.3)$$

where $E_{\text{elec}}$ is the energy consisting of the potential energy due to all electrostatic interactions (see next section) plus the electron kinetic energies, and $E_{\text{kin}}$ is the kinetic energy due to nuclear motions (vibrations and rotations). Since the electronic structure is affected by the nuclear coordinates but not their rate of change, $E_{\text{kin}}$ can be ignored for the time being.
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2.1.3 The Schrödinger equation for many-electron atoms and molecules

If the Born–Oppenheimer approximation is invoked, the Hamiltonian in the Schrödinger equation (2.1), for a molecule with fixed nuclear positions has the general form

$$H = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) - \sum_{i,A} Z_A e^2 \frac{Z_A}{4\pi \varepsilon_0 R_{iA}} + \sum_i \sum_{j \neq i} e^2 \frac{1}{4\pi \varepsilon_0 r_{ij}} + \sum_A \sum_{B \neq A} Z_A Z_B e^2 \frac{1}{4\pi \varepsilon_0 R_{AB}} \tag{2.4}$$

In the above expression we make use of the general relationship from classical electrostatics that the electrostatic potential energy between two particles with charges $q_i$ and $q_j$ separated by distance $r$ is given by $q_i q_j / 4\pi \varepsilon_0 r$, where $\varepsilon_0$ is the permittivity of free space. In this specific case $Z_A$ is used to designate the charge on nucleus $A$ and $e$ is the fundamental charge (an electron has charge $-e$). The quantity $\hbar$ is shorthand notation for $\hbar / 2\pi$.

Although it looks formidable, equation (2.4) has a simple interpretation. Four groups of operators can be identified inside the summations in (2.4). The first group is the total electron kinetic energy operator, which is the sum of kinetic energy operators for each electron. The second summation represents the electron–nuclear electrostatic interactions, where $R_{iA}$ is the electron–nuclear distance, with the subscripts $i$ and $A$ labelling electrons and nuclei respectively. The third term, the first of the double summations, is the operator for electron–electron repulsion, while the fourth is for nuclear–nuclear repulsion. The Hamiltonian is therefore logical in the sense that it is a total energy operator constructed from the summation of kinetic energy operators for each individual electron and the operators describing all electron–nuclear, electron–electron, and nuclear–nuclear electrostatic interactions in the molecule. This is also illustrated in Figure 2.1 for a two-electron diatomic molecule. Had we not invoked the Born–Oppenheimer approximation, the molecular Schrödinger equation would also have to have included terms containing nuclear kinetic energy operators, which would clearly be an added complication.

Despite the simplification brought about by the Born–Oppenheimer approximation, the Schrödinger equation containing the Hamiltonian in (2.4) still cannot be solved exactly for any molecule containing more than one electron. The problem lies with the third term in the Hamiltonian, the electron–electron repulsions. If one were to imagine creating a molecule containing several electrons but these electrons interacted only with the nuclei, i.e. there were no electron–electron repulsions (clearly an imaginary situation!), then equation (2.4) would be rather easy to solve. In this limit the electronic wavefunction is a product of wavefunctions for each individual electron, i.e.

$$\psi = \phi_1(1) \phi_2(2) \ldots \phi_N(N) \tag{2.5}$$

where $N$ is the number of electrons and $\phi_i(i)$ is the wavefunction of electron $i$. The product form of the wavefunction makes it possible to separate the full Schrödinger equation into a series of individual and independent Schrödinger equations, one for each electron, each of...
Figure 2.1  A schematic illustration of the electrostatic potential energies in a two-electron diatomic molecule at some particular instant in time.

which can then be solved exactly after some mathematical effort. Each of the wavefunctions for the individual electrons describes the spatial probability distribution of that electron: in other words $\phi_1$ is a function of the coordinates only of electron 1 and $\phi_1^2$ at any point in space describes the probability that the electron is at that point in space. The individual wavefunctions $\phi_i$ are referred to as orbitals.

2.1.4 The orbital approximation

Electron–electron repulsion destroys the orbital picture given above. This arises because each electron–electron repulsion operator is a function of the coordinates of two electrons, and therefore the position of one electron affects all of the others. Consequently, the true electronic wavefunction in a molecule (or atom) containing two or more electrons is not a product of independent one-electron wavefunctions (orbitals).

This would seem to be unfortunate, since the ability to be able to describe electrons as being in separate orbitals offers a great simplification in the description of electronic structure. Fortunately, all is not lost since it is possible to retain the orbital concept if the following approach is adopted. We know that, strictly speaking, the total electronic wavefunction cannot be expressed exactly as a product of orbital wavefunctions. However, suppose that we in any case choose to express the total wavefunction as such an orbital product. This constraint allows the many-electron Schrödinger equation to be converted
into a new set of equations, known as the Hartree–Fock equations, which allow orbitals and their energies to be calculated. The way in which this is done is outlined in Appendix B.

The Hartree–Fock method allows for most of the electron–electron repulsion, but it treats it in an averaged fashion, i.e. it effectively takes each electron in turn and calculates the repulsive energy for this electron interacting with the time-averaged charge cloud of all the other electrons. In reality, the instantaneous electron–electron interactions tend to keep electrons further apart than is the case in the Hartree–Fock model. This inadequate treatment of electron correlation is the weakness of the Hartree–Fock method, and it is the price paid for clinging on to the concept of orbitals. Nevertheless, it can be used to make rather good calculations of atomic and molecular properties from first principles. Further details on these so-called \textit{ab initio} calculations can be found in Appendix B.

References