1

Principles

1.1 THE ORBITAL MODEL

The great majority of the applications of molecular quantum mechanics to chemistry are based on what is called the orbital model. The planetary model of the atom can be traced back to Rutherford (Born, 1962). It consists of a *point-like* nucleus carrying the whole mass and the whole positive charge $+Ze$ surrounded by N electrons each having the elementary negative charge $-e$ and a mass about 2000 times smaller than that of the proton and moving in a space which is essentially that of the atom.[1] Electrons are point-like elementary particles whose negative charge is distributed in space in the form of a *charge cloud*, with the probability of finding the electron at point r in space being given by

$$|\psi(\mathbf{r})|^2\, d\mathbf{r} = \text{probability of finding in } d\mathbf{r} \text{ the electron in state } \psi(\mathbf{r}) \tag{1.1}$$

The functions $\psi(\mathbf{r})$ are called *atomic* orbitals (AOs, one centre) or *molecular* orbitals (MOs, many centres) and describe the quantum states of the electron. For (1.1) to be true, $\psi(\mathbf{r})$ must be a *regular* (or Q-class) mathematical function (single valued, continuous with its first derivatives,

[1] The atomic volume has a diameter of the order of 10^2 pm, about 10^5 times larger than that of the nucleus.

Methods of Molecular Quantum Mechanics: An Introduction to Electronic Molecular Structure
Valerio Magnasco
© 2009 John Wiley & Sons, Ltd

COPYRIGHTED MATERIAL

quadratically integrable) satisfying the normalization condition

$$\int d\mathbf{r}\, |\psi(\mathbf{r})|^2 = \int d\mathbf{r}\, \psi^*(\mathbf{r})\psi(\mathbf{r}) = 1 \tag{1.2}$$

where integration is extended over the whole space of definition of the variable $\mathbf{r}$ and where $\psi^*(\mathbf{r})$ is the complex conjugate to $\psi(\mathbf{r})$. The last of the above physical constraints implies that ψ must vanish at infinity.[2]

It seems appropriate at this point first to introduce in an elementary way the essential mathematical methods which are needed in the applications, followed by a simple axiomatic formulation of the basic postulates of quantum mechanics and, finally, by their physical interpretation (Margenau, 1961).

1.2 MATHEMATICAL METHODS

In what follows we shall be concerned only with regular functions of the general variable x.

1.2.1 Dirac Notation

$$\begin{cases} \text{Function} & \psi(x) = |\psi\rangle \Rightarrow \text{ket} \\ \text{Complex conjugate} & \psi^*(x) = \langle\psi| \Rightarrow \text{bra} \end{cases} \tag{1.3}$$

The scalar product (see the analogy between regular functions and complex vectors of infinite dimensions) of ψ^* by ψ can then be written in the bra-ket ('bracket') form:

$$\int dx\, \psi^*(x)\psi(x) = \langle\psi|\psi\rangle = \text{finite number} > 0 \tag{1.4}$$

1.2.2 Normalization

If

$$\langle\psi|\psi\rangle = A \tag{1.5}$$

then we say that the function $\psi(x)$ (the ket $|\psi\rangle$) is normalized to A (the *norm* of ψ). The function ψ can then be normalized to 1 by multiplying it by the *normalization factor* $N = A^{-1/2}$.

[2] In an atom or molecule, there must be zero probability of finding an electron infinitely far from its nucleus.

1.2.3 Orthogonality

If

$$\langle \psi | \varphi \rangle = \int \mathrm{d}x \, \psi^*(x) \varphi(x) = 0 \tag{1.6}$$

then we say that φ is orthogonal ($\perp$) to ψ. If

$$\langle \psi' | \varphi' \rangle = S (\neq 0) \tag{1.7}$$

then φ' and ψ' are *not* orthogonal, but can be orthogonalized by choosing the linear combination (Schmidt orthogonalization):

$$\psi = \psi', \qquad \varphi = N(\varphi' - S\psi'), \qquad \langle \psi | \varphi \rangle = 0 \tag{1.8}$$

where $N = (1 - S^2)^{-1/2}$ is the normalization factor. In fact, it is easily seen that, if ψ' and φ' are normalized to 1:

$$\langle \psi | \varphi \rangle = N \langle \psi' | \varphi' - S\psi' \rangle = N(S - S) = 0 \tag{1.9}$$

1.2.4 Set of Orthonormal Functions

Let

$$\{\varphi_k(x)\} = (\varphi_1 \varphi_2 \ldots \varphi_k \ldots \varphi_i \ldots) \tag{1.10}$$

be a set of functions. If

$$\langle \varphi_k | \varphi_i \rangle = \delta_{ki} \quad k, i = 1, 2, \ldots \tag{1.11}$$

where δ_{ki} is the Kronecker delta (1 if $i = k$, 0 if $i \neq k$), then the set is said to be orthonormal.

1.2.5 Linear Independence

A set of functions is said to be linearly independent if

$$\sum_k \varphi_k(x) C_k = 0 \quad \text{with, necessarily, } C_k = 0 \text{ for any } k \tag{1.12}$$

For a set to be linearly independent, it will be sufficient that the determinant of the metric matrix **M** (see Chapter 2) be different from zero:

$$\det \mathbf{M}_{ki} \neq 0 \qquad \mathrm{M}_{ki} = \langle \varphi_k | \varphi_i \rangle \tag{1.13}$$

A set of orthonormal functions, therefore, is a linearly independent set.

1.2.6 Basis Set

A set of linearly independent functions forms a *basis* in the function space, and we can expand any function of that space into a linear combination of the basis functions. The expansion is unique.

1.2.7 Linear Operators

An operator is a rule transforming a given function into another function (e.g. its derivative). A linear operator $\hat{A}$ satisfies

$$\begin{cases} \hat{A}[\psi_1(x) + \psi_2(x)] = \hat{A}\psi_1(x) + \hat{A}\psi_2(x) \\ \hat{A}[c\psi(x)] = c\hat{A}[\psi(x)] \end{cases} \tag{1.14}$$

where c is a complex constant. The first and second derivatives are simple examples of linear operators.

1.2.8 Sum and Product of Operators

$$(\hat{A} + \hat{B})\psi(x) = \hat{A}\psi(x) + \hat{B}\psi(x) = (\hat{B} + \hat{A})\psi(x) \tag{1.15}$$

so that the algebraic sum of two operators is commutative.

In general, the product of two operators is *not* commutative:

$$\hat{A}\hat{B}\psi(x) \neq \hat{B}\hat{A}\psi(x) \tag{1.16}$$

where the inner operator acts first. If

$$\hat{A}\hat{B} = \hat{B}\hat{A} \tag{1.17}$$

then the two operators commute. The quantity

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{1.18}$$

is called the commutator of the operators $\hat{A}, \hat{B}$.

1.2.9 Eigenvalue Equation

The equation

$$\hat{A}\psi(x) = A\psi(x) \tag{1.19}$$

is called the eigenvalue equation for the linear operator $\hat{A}$. When (1.19) is satisfied, the constant A is called the *eigenvalue*, the function ψ the *eigenfunction* of the operator $\hat{A}$. Often, $\hat{A}$ is a differential operator, and there may be a whole spectrum of eigenvalues, each one with its corresponding eigenfunction. The spectrum of the eigenvalues can be either discrete or continuous. An eigenvalue is said to be n-fold degenerate when n different independent eigenfunctions belong to it. We shall see later that the Schroedinger equation for the amplitude $\psi(x)$ is a typical eigenvalue equation, where $\hat{A} = \hat{H} = \hat{T} + V$ is the total energy operator (the Hamiltonian), $\hat{T}$ being the kinetic energy operator and V the potential energy characterizing the system (a scalar quantity).

1.2.10 Hermitian Operators

A Hermitian operator is a linear operator satisfying the so-called 'turnover rule':

$$\begin{cases} \langle\psi|\hat{A}\varphi\rangle = \langle\hat{A}\psi|\varphi\rangle \\ \int \mathrm{d}x\, \psi^*(x)(\hat{A}\varphi(x)) = \int \mathrm{d}x\, (\hat{A}\psi(x))^*\varphi(x) \end{cases} \tag{1.20}$$

The Hermitian operators have the following properties:

(i) *real* eigenvalues;
(ii) *orthogonal* (or anyway orthogonalizable) eigenfunctions;
(iii) their eigenfunctions form a *complete* set.

Completeness also includes the eigenfunctions belonging to the continuous part of the eigenvalue spectrum.

Hermitian operators are $-\mathrm{i}\partial/\partial x$, $-\mathrm{i}\nabla$, $\partial^2/\partial x^2$, ∇^2, $\hat{T} = -(\hbar^2/2m)\nabla^2$ and $\hat{H} = \hat{T} + V$, where i is the imaginary unit ($\mathrm{i}^2 = -1$), $\nabla = \mathbf{i}(\partial/\partial x) + \mathbf{j}(\partial/\partial y) + \mathbf{k}(\partial/\partial z)$ is the gradient vector operator, $\nabla^2 = \nabla \cdot \nabla = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ is the Laplacian operator (in Cartesian coordinates), $\hat{T}$ is the kinetic energy operator for a particle of mass m with $\hbar = h/2\pi$ the reduced Planck constant and $\hat{H}$ is the Hamiltonian operator.

1.2.11 Anti-Hermitian Operators

$\partial/\partial x$ and ∇ are instead anti-Hermitian operators, for which

$$\begin{cases} \left\langle \psi \middle| \dfrac{\partial \varphi}{\partial x} \right\rangle = -\left\langle \dfrac{\partial \psi}{\partial x} \middle| \varphi \right\rangle \\ \langle \psi | \nabla \varphi \rangle = -\langle \nabla \psi | \varphi \rangle \end{cases} \tag{1.21}$$

1.2.12 Expansion Theorem

Any regular (Q-class) function $F(x)$ can be expressed exactly in the *complete* set of the eigenfunctions of any Hermitian operator[3] $\hat{A}$. If

$$\hat{A}\varphi_k(x) = A_k\varphi_k(x), \qquad \hat{A}^\dagger = \hat{A} \tag{1.22}$$

then

$$F(x) = \sum_k \varphi_k(x) C_k \tag{1.23}$$

where the expansion coefficients are given by

$$C_k = \int \mathrm{d}x' \varphi_k^*(x') F(x') = \langle \varphi_k | F \rangle \tag{1.24}$$

as can be easily shown by multiplying both sides of Equation (1.23) by $\varphi_k^*(x)$ and integrating.

Some authors insert an integral sign into (1.23) to emphasize that integration over the continuous part of the eigenvalue spectrum must be included in the expansion. When the set of functions $\{\varphi_k(x)\}$ is *not* complete, *truncation errors* occur, and a lot of the literature data from the quantum chemistry side is plagued by such errors.

1.2.13 From Operators to Matrices

Using the expansion theorem we can pass from operators (acting on functions) to matrices (acting on vectors; Chapter 2). Consider a *finite*

[3] A less stringent stipulation of completeness involves the *approximation in the mean* (Margenau, 1961).

n-dimensional set of basis functions $\{\varphi_k(x)\}k = 1, \ldots, n$. Then, if $\hat{A}$ is a Hermitian operator:

$$\hat{A}\varphi_i(x) = \sum_k \varphi_k(x) A_{ki} = \sum_k |\varphi_k\rangle\langle\varphi_k|\hat{A}\varphi_i\rangle \tag{1.25}$$

where the expansion coefficients now have *two* indices and are the elements of the square matrix **A** (order n):

$$A_{ki} = \langle\varphi_k|\hat{A}\varphi_i\rangle = \int \mathrm{d}x'\, \varphi_k^*(x')(\hat{A}\varphi_i(x')) \tag{1.26}$$

$$\{A_{ki}\} \Rightarrow \mathbf{A} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} = \boldsymbol{\varphi}^\dagger \hat{A} \boldsymbol{\varphi} \tag{1.27}$$

which is called the *matrix representative* of the operator $\hat{A}$ in the basis $\{\varphi_k\}$, and we use matrix multiplication rules (Chapter 2). In this way, the eigenvalue equations of quantum mechanics transform into eigenvalue equations for the corresponding representative matrices. We must recall, however, that a complete set implies matrices of infinite order.

Under a unitary transformation **U** of the basis functions $\boldsymbol{\varphi} = (\varphi_1 \varphi_2 \ldots \varphi_n)$:

$$\boldsymbol{\varphi}' = \boldsymbol{\varphi}\,\mathbf{U} \tag{1.28}$$

the representative **A** of the operator $\hat{A}$ is changed into

$$\mathbf{A}' = \boldsymbol{\varphi}'^\dagger \hat{A} \boldsymbol{\varphi}' = \mathbf{U}^\dagger \mathbf{A} \mathbf{U} \tag{1.29}$$

1.2.14 Properties of the Operator ∇

We have seen that in Cartesian coordinates the vector operator ∇ (the gradient, a vector whose components are operators) is defined as (Rutherford, 1962)

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \tag{1.30}$$

Now, let $F(x,y,z)$ be a scalar function of the space point $P(\mathbf{r})$. Then:

$$\nabla F = \mathbf{i}\frac{\partial F}{\partial x} + \mathbf{j}\frac{\partial F}{\partial y} + \mathbf{k}\frac{\partial F}{\partial z} \tag{1.31}$$

is a vector, the gradient of F.

If $\mathbf{F}$ is a vector of components F_x, F_y, F_z, we then have for the scalar product

$$\nabla \cdot \mathbf{F} = \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} = \operatorname{div} \mathbf{F} \tag{1.32}$$

a scalar quantity, the divergence of $\mathbf{F}$. As a particular case:

$$\nabla \cdot \nabla = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1.33}$$

is the Laplacian operator.

From the vector product of ∇ by the vector $\mathbf{F}$ we obtain a new vector, the curl or rotation of $\mathbf{F}$ (written curl F or rot $\mathbf{F}$):

$$\nabla \times \mathbf{F} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \\ F_x & F_y & F_z \end{vmatrix} = \operatorname{curl} \mathbf{F} = \mathbf{i} \operatorname{curl}_x \mathbf{F} + \mathbf{j} \operatorname{curl}_y \mathbf{F} + \mathbf{k} \operatorname{curl}_z \mathbf{F} \tag{1.34}$$

a vector operator with components:

$$\begin{cases} \operatorname{curl}_x \mathbf{F} = \dfrac{\partial F_z}{\partial y} - \dfrac{\partial F_y}{\partial z} \\ \operatorname{curl}_y \mathbf{F} = \dfrac{\partial F_x}{\partial z} - \dfrac{\partial F_z}{\partial x} \\ \operatorname{curl}_z \mathbf{F} = \dfrac{\partial F_y}{\partial x} - \dfrac{\partial F_x}{\partial y} \end{cases} \tag{1.35}$$

In quantum mechanics, the vector product of the position vector $\mathbf{r}$ by the linear momentum vector operator $-i\hbar\nabla$ (see Section 1.3) gives the angular momentum vector operator $\hat{\mathbf{L}}$:

$$\hat{\mathbf{L}} = -i\hbar\mathbf{r} \times \nabla = -i\hbar \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \end{vmatrix} = \mathbf{i}\hat{L}_x + \mathbf{j}\hat{L}_y + \mathbf{k}\hat{L}_z \tag{1.36}$$

with components

$$\hat{L}_x = -\mathrm{i}\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \quad \hat{L}_y = -\mathrm{i}\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$$
$$\hat{L}_z = -\mathrm{i}\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{1.37}$$

In the theory of angular momentum, frequent use is made of the *ladder* (or shift) operators:

$$\hat{L}_+ = \hat{L}_x + \mathrm{i}\hat{L}_y \text{ (step-up)}, \quad \hat{L}_- = \hat{L}_x - \mathrm{i}\hat{L}_y \text{ (step-down)} \tag{1.38}$$

These are also called raising and lowering operators[4] respectively.

Angular momentum operators have the following commutation relations:

$$\begin{cases} [\hat{L}_x, \hat{L}_y] = \mathrm{i}\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = \mathrm{i}\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = \mathrm{i}\hat{L}_y \\ [\hat{L}_z, \hat{L}_+] = \hat{L}_+, [\hat{L}_z, \hat{L}_-] = -\hat{L}_- \\ [\hat{L}^2, \hat{L}_\kappa] = [\hat{L}^2, \hat{L}_\pm] = 0 \quad \kappa = x, y, z \end{cases} \tag{1.39}$$

The same commutation relations hold for the spin vector operator $\hat{\mathbf{S}}$ (Chapter 5).

1.2.15 Transformations in Coordinate Space

We now give the definitions of the main coordinate systems useful in quantum chemistry calculations (Cartesian, spherical, spheroidal), the relations between Cartesian and spherical or spheroidal coordinates, and the expressions of the volume element $\mathrm{d}\mathbf{r}$ and of the operators ∇ and ∇^2 in the new coordinate systems. We make reference to Figures 1.1 and 1.2.

(i) Cartesian coordinates (x,y,z):

$$x,\ y,\ z \in (-\infty, \infty) \tag{1.40}$$

$$\mathrm{d}\mathbf{r} = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \tag{1.41}$$

[4] Note that the ladder operators are non-Hermitian.

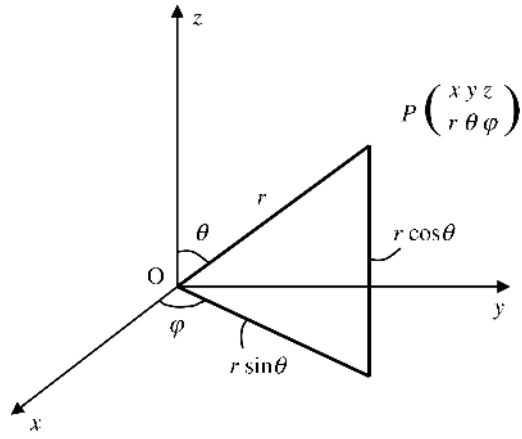


Figure 1.1 Cartesian and spherical coordinate systems

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \tag{1.42}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1.43}$$

(ii) Spherical coordinates (r,θ,φ):

$$r(0,\infty),\ \theta(0,\pi),\ \varphi(0,2\pi) \tag{1.44}$$

$$x = r\sin\theta\cos\varphi,\ y = r\sin\theta\sin\varphi,\ z = r\cos\theta \tag{1.45}$$

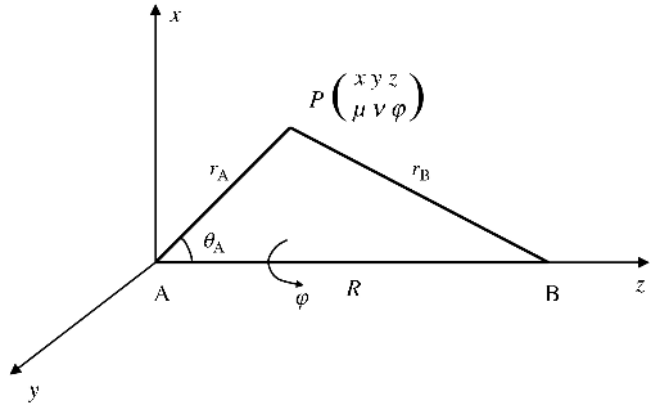


Figure 1.2 Cartesian and spheroidal coordinate systems

$$\mathrm{d}\mathbf{r} = r^2 \mathrm{d}r \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi \tag{1.46}$$

$$\nabla = \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_\varphi \frac{1}{r \sin\theta} \frac{\partial}{\partial \varphi} \tag{1.47}$$

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right] \\ &= \nabla_r^2 - \frac{\hat{L}^2/\hbar^2}{r^2} \end{aligned} \tag{1.48}$$

where $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\varphi$ are unit vectors along r, θ, and φ. In Equation (1.48):

$$\nabla_r^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \tag{1.49}$$

is the radial Laplacian and

$$\begin{cases} \hat{L}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = -\hbar^2 \left[\dfrac{1}{\sin\theta} \dfrac{\partial}{\partial \theta} \left(\sin\theta \dfrac{\partial}{\partial \theta} \right) + \dfrac{1}{\sin^2\theta} \dfrac{\partial^2}{\partial \varphi^2} \right] \\ \quad = -\hbar^2 \left(\dfrac{\partial^2}{\partial \theta^2} + \cot\theta \dfrac{\partial}{\partial \theta} + \dfrac{1}{\sin^2\theta} \dfrac{\partial^2}{\partial \varphi^2} \right) \end{cases} \tag{1.50}$$

is the square of the angular momentum operator (1.36). For the components of the angular momentum vector operator $\hat{L}$ we have

$$\hat{L}_x = -\mathrm{i}\hbar \left(-\sin\varphi \frac{\partial}{\partial \theta} - \cot\theta \cos\varphi \frac{\partial}{\partial \varphi} \right) \tag{1.51}$$

$$\hat{L}_y = -\mathrm{i}\hbar \left(\cos\varphi \frac{\partial}{\partial \theta} - \cot\theta \sin\varphi \frac{\partial}{\partial \varphi} \right) \tag{1.52}$$

$$\hat{L}_z = -\mathrm{i}\hbar \frac{\partial}{\partial \varphi} \tag{1.53}$$

$$\hat{L}_+ = \hbar \exp(\mathrm{i}\varphi) \left(\frac{\partial}{\partial \theta} + \mathrm{i} \cot\theta \frac{\partial}{\partial \varphi} \right) \tag{1.54}$$

$$\hat{L}_- = \hbar \exp(-\mathrm{i}\varphi) \left(-\frac{\partial}{\partial \theta} + \mathrm{i} \cot\theta \frac{\partial}{\partial \varphi} \right) \tag{1.55}$$

(iii) Spheroidal coordinates (μ, ν, φ):

$$\mu = \frac{r_A + r_B}{R} (1 \leq \mu \leq \infty), \quad \nu = \frac{r_A - r_B}{R} (-1 \leq \nu \leq 1), \quad \varphi(0, 2\pi) \tag{1.56}$$

$$x = \frac{R}{2}\sqrt{(\mu^2 - 1)(1 - \nu^2)}\cos\varphi, \quad y = \frac{R}{2}\sqrt{(\mu^2 - 1)(1 - \nu^2)}\sin\varphi,$$
$$z = \frac{R}{2}(\mu\nu + 1) \tag{1.57}$$

$$\mathrm{d}\mathbf{r} = \left(\frac{R}{2}\right)^3 (\mu^2 - \nu^2)\, \mathrm{d}\mu\, \mathrm{d}\nu\, \mathrm{d}\varphi \tag{1.58}$$

$$\nabla = \frac{2}{R}\left[\mathbf{e}_\mu \sqrt{\frac{\mu^2 - 1}{\mu^2 - \nu^2}} \frac{\partial}{\partial\mu} + \mathbf{e}_\nu \sqrt{\frac{1 - \nu^2}{\mu^2 - \nu^2}} \frac{\partial}{\partial\nu} + \mathbf{e}_\varphi \frac{1}{\sqrt{(\mu^2 - 1)(1 - \nu^2)}} \frac{\partial}{\partial\varphi}\right] \tag{1.59}$$

$$\nabla^2 = \frac{4}{R^2(\mu^2 - \nu^2)} \times \left\{\frac{\partial}{\partial\mu}\left[(\mu^2 - 1)\frac{\partial}{\partial\mu}\right] + \frac{\partial}{\partial\nu}\left[(1 - \nu^2)\frac{\partial}{\partial\nu}\right] + \frac{\mu^2 - \nu^2}{(\mu^2 - 1)(1 - \nu^2)} \frac{\partial^2}{\partial\varphi^2}\right\} \tag{1.60}$$

Equations (1.44)–(1.55) are used in atomic (one-centre) calculations, whereas Equations (1.56)–(1.60) are used in molecular (at least two-centre) calculations.

1.3 BASIC POSTULATES

We now formulate in an axiomatic way the basis of quantum mechanics in the form of three postulates.

1.3.1 Correspondence between Physical Obervables and Hermitian Operators

In coordinate space, we have the basic correspondences

$$\begin{cases} \mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z & \Rightarrow \hat{\mathbf{r}} = \mathbf{r} \\ \mathbf{p} = \mathbf{i}p_x + \mathbf{j}p_y + \mathbf{k}p_z & \Rightarrow \hat{\mathbf{p}} = -\mathrm{i}\hbar\nabla \end{cases} \tag{1.61}$$

where i is the imaginary unit ($\mathrm{i}^2 = -1$) and $\hbar = h/2\pi$ is the reduced Planck constant. More complex observables can be treated by repeated

applications of the correspondences (1.61) under the constraint that the resulting quantum mechanical operators must be Hermitian.[5] Kinetic energy and Hamiltonian (*total* energy operator) for a particle of mass m in the potential V are examples already seen. We now give a few further examples by specifying the nature of the potential energy V.

(a) **The one-dimensional harmonic oscillator**
If m is the mass of the oscillator of force constant k, then the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{kx^2}{2} \tag{1.62}$$

(b) **The atomic one-electron problem (the hydrogen-like system)**
If r is the distance of the electron of mass m and charge $-e$ from a nucleus of charge $+Ze$ ($Z = 1$ will give the hydrogen atom), then the Hamiltonian in SI units[6] is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{\mathrm{r}} \tag{1.63}$$

To get rid of all fundamental physical constants in our formulae we shall introduce consistently at this point a system of *atomic units*[7] (au) by posing

$$e = \hbar = m = 4\pi\varepsilon_0 = 1 \tag{1.64}$$

The basic atomic units of charge, length, energy, and time are expressed in SI units as follows:

$$\begin{cases} \text{charge, } e & e = 1.602\,176\,462 \times 10^{-19}\ \mathrm{C} \\ \text{length, Bohr} & a_0 = 4\pi\varepsilon_0\dfrac{\hbar^2}{me^2} = 5.291\,772\,087 \times 10^{-11}\ \mathrm{m} \\ \text{energy, Hartree} & E_\mathrm{h} = \dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{a_0} = 4.359\,743\,802 \times 10^{-18}\ \mathrm{J} \\ \text{time} & \tau = \dfrac{\hbar}{E_\mathrm{h}} = 2.418\,884\,331 \times 10^{-17}\ \mathrm{s} \end{cases} \tag{1.65}$$

[5] The quantities observable in physical experiments must be *real*.

[6] An SI dimensional analysis of the two terms of Equation (1.63) shows that they have the dimension of energy (Mohr and Taylor, 2003): $|\hbar^2\nabla^2/2m| = (\mathrm{kg\,m^2\,s^{-1}})^2\,\mathrm{m^{-2}\,kg^{-1}} = \mathrm{kg\,m^2\,s^{-2}} = \mathrm{J}$; $|Ze^2/4\pi\varepsilon_0 r| = \mathrm{C^2\,(J\,C^{-2}\,m)\,m^{-1}} = \mathrm{J}$.

[7] Atomic units were first introduced by Hartree (1928a).

At the end of a calculation in atomic units, as we always shall do, the actual SI values can be obtained by taking into account the SI equivalents (1.65).

The Hamiltonian of the hydrogenic system in atomic units will then take the following simplified form:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \tag{1.66}$$

From now on, we shall consistently use atomic units everywhere, unless explicitly stated.

(c) **The atomic two-electron system**

Two electrons are attracted by a nucleus of charge $+Z$. The Hamiltonian will be

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} = \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \tag{1.67}$$

where

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \tag{1.68}$$

is the one-electron Hamiltonian (which has the *same* functional form for both electrons) and the last term is the Coulomb repulsion between the electrons (a two-electron operator). $Z = 2$ gives the He atom.

(d) **The hydrogen molecule-ion** H_2^+

This is a diatomic one-electron molecular system, where the electron is simultaneously attracted by the two protons at A and B. The Born–Oppenheimer Hamiltonian (see Chapter 9) will be

$$\hat{H} = \hat{h} + \frac{1}{R} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} = \hat{h}_A + V \tag{1.69}$$

where $\hat{h}_A$ is the one-electron Hamiltonian (1.68) for atom A (with $Z = 1$) and

$$V = -\frac{1}{r_B} + \frac{1}{R} \tag{1.70}$$

is the interatomic potential between the hydrogen atom A and the proton B.

(e) **The hydrogen molecule H_2**

This is a diatomic two-electron molecular system. The Born–Oppenheimer Hamiltonian will be

$$\begin{cases} \hat{H} = \hat{h}_1 + \hat{h}_2 + \dfrac{1}{r_{12}} + \dfrac{1}{R} \\ \quad = \left(-\dfrac{1}{2}\nabla_1^2 - \dfrac{1}{r_{A1}} - \dfrac{1}{r_{B1}} \right) + \left(-\dfrac{1}{2}\nabla_2^2 - \dfrac{1}{r_{A2}} - \dfrac{1}{r_{B2}} \right) + \dfrac{1}{r_{12}} + \dfrac{1}{R} \\ \quad = \hat{h}_{A1} + \hat{h}_{B2} + V \end{cases} \tag{1.71}$$

where $\hat{h}_{A1}$ and $\hat{h}_{B2}$ are the one-electron Hamiltonians (1.68) for atoms A and B (with $Z = 1$) and

$$V = -\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} + \frac{1}{R} \tag{1.72}$$

is the interatomic potential between A and B.

1.3.2 State Function and Average Value of Observables

We assume there is a *state function* (or wavefunction, in general complex) $\Psi(x,t)$ that describes in a probabilistic way the dynamical state of a microscopic system. In coordinate space, Ψ is a regular function of coordinate x and time t such that

$$\begin{aligned} &\Psi(x,t)\Psi^*(x,t)\,\mathrm{d}x \\ &= \text{probability at time } t \text{ of finding at } \mathrm{d}x \text{ the system in state } \Psi \end{aligned} \tag{1.73}$$

provided Ψ is normalized to 1:

$$\int \mathrm{d}x\, \Psi^*(x,t)\Psi(x,t) = 1 \tag{1.74}$$

where integration covers the whole space.

The *average value* of any physical observable[8] A described by the Hermitian operator $\hat{A}$ is obtained from

$$\langle A \rangle = \frac{\int \mathrm{d}x\, \Psi^*(x,t)\hat{A}\Psi(x,t)}{\int \mathrm{d}x\, \Psi^*(x,t)\Psi(x,t)} = \int \mathrm{d}x\, \hat{A}\, \frac{\Psi(x,t)\Psi^*(x,t)}{\int \mathrm{d}x\, \Psi^*(x,t)\Psi(x,t)} \tag{1.75}$$

[8] Its expectation value, that can be observed by experiment.

where integration is extended over all space and $\hat{A}$ acts always on Ψ and not on Ψ^*. The last expression above shows that $\hat{A}$ is *weighted* with the (normalized) probability density $\Psi\Psi^*$.

1.3.3 Time Evolution of the State Function

The state function Ψ is obtained by solving the time-dependent Schroedinger equation:

$$\hat{H}\Psi(x,t) = \mathrm{i}\hbar \frac{\partial \Psi(x,t)}{\partial t} \tag{1.76}$$

a partial differential equation which is second order in the space coordinate x and first order in the time t. This equation involves the Hamiltonian of the system $\hat{H}$, so that the total energy E is seen to play a fundamental role among all physical observables.

If the Hamiltonian $\hat{H}$ does not depend explicitly on t (the case of stationary states), then, following the usual mathematical techniques, the variables in Equation (1.76) can be separated by writing Ψ as the product of a space function $\psi(x)$ and a time function $g(t)$:

$$\Psi(x,t) = \psi(x)g(t) \tag{1.77}$$

giving upon substitution

$$\begin{cases} \hat{H}\psi(x) = E\psi(x) \\ g(t) = g_0 \exp(-\mathrm{i}\omega t) \end{cases} \tag{1.78}$$

where E is the separation constant, g_0 is an integration constant, and $\omega = E/\hbar$. The first part of Equation (1.78) is the eigenvalue equation for the total energy operator (the Hamiltonian) of the system, and $\psi(x)$ is called the amplitude function. This is the Schroedinger equation that we must solve or approximate for the physical description of our systems. The second equation gives the time dependence of the stationary state, while general time dependence is fundamental in spectroscopy. It is immediately evident that, for the stationary state, the probability $\Psi\Psi^* \, \mathrm{d}x$ is independent of time:

$$\Psi(x,t)\Psi^*(x,t) \, \mathrm{d}x = |\Psi(x,t)|^2 \, \mathrm{d}x = |\psi(x)|^2 |g_0|^2 \, \mathrm{d}x \tag{1.79}$$

1.4 PHYSICAL INTERPRETATION OF THE BASIC PRINCIPLES

The explanation of our, so far, unusual postulates is hidden in the nature of the experimental measurements in atomic physics. The experimentally observed *atomicity* of matter (electrons and protons, carrying the elementary negative and positive charge respectively), energy ($h\nu$, Planck), linear momentum (h/λ, De Broglie), and angular momentum ($\hbar$, Bohr) implies some limits in the measurements done at the microscopic level. The direct consequence of the ineliminable interaction between the experimental apparatus and the object of measurement at the subatomic scale was shown by Heisenberg (1930) in his *gedanken Experimente*, and is embodied in his famous uncertainty principle, which for canonically conjugate quantities[9] can be stated in the form

$$\Delta x \Delta p_x \approx h \quad \Delta E \Delta t \approx h \tag{1.80}$$

where h is the Planck constant, Δx is the uncertainty in the measurement of the x-coordinate, and Δp_x is the uncertainty resulting in the simultaneous measurement of the conjugate linear momentum. It can be seen that the corresponding quantum mechanical operators do not commute:

$$[x, \hat{p}_x] = x\hat{p}_x - \hat{p}_x x = \mathrm{i}\hbar \tag{1.81}$$

whereas operators that are not conjugate commute; say:

$$[x, \hat{p}_y] = x\hat{p}_y - \hat{p}_y x = 0 \tag{1.82}$$

This means that we cannot measure with the same arbitrary accuracy two conjugated dynamical variables whose quantum mechanical operators do not commute: the exact determination of the position coordinate of the electron would imply the simultaneous infinite inaccuracy in the determination of the corresponding component of the linear momentum!

As a consequence of Heisenberg's principle, the only possible description of the dynamical state of a microscopic body is a *probabilistic* one, and the problem is now to find the function that describes such a probability. This was achieved by Schroedinger (1926a, 1926b, 1926c, 1926d), who assumed that particle matter (the electron) could be

[9] In the sense of analytical mechanics.

described by the progressive wave in complex form:

$$\Psi = A\exp(\mathrm{i}\alpha) = A\exp[2\pi\mathrm{i}(kx - \nu t)] \tag{1.83}$$

where A is the amplitude and α the phase of a monochromatic plane wave of wavenumber k and frequency ν, which propagates along x. Taking into account the relations of De Broglie and Planck connecting wave-like and particle-like behaviour:

$$k = \frac{p}{h}, \quad \nu = \frac{E}{h} \tag{1.84}$$

the phase of a *matter wave* could be written as

$$\alpha = \frac{1}{\hbar}(px - Et) \tag{1.85}$$

giving the wave equation for the matter particle in the form

$$\Psi = A\exp\left[\frac{\mathrm{i}}{\hbar}(px - Et)\right] = \Psi(x, t) \tag{1.86}$$

which defines Ψ as a function of x and t at constant values of p and E. Then, taking the derivatives of Ψ with respect to x and t, we obtain respectively

$$\frac{\partial\Psi}{\partial x} = \frac{\mathrm{i}}{\hbar}p\Psi \quad \text{whence } \Rightarrow \hat{p} = -\mathrm{i}\hbar\frac{\partial}{\partial x} \tag{1.87}$$

which is our first postulate (1.61) for the x-component of the linear momentum, and

$$\frac{\partial\Psi}{\partial t} = -\frac{\mathrm{i}}{\hbar}E\Psi \quad \text{whence } \Rightarrow \hat{E} = \hat{H} = \mathrm{i}\hbar\frac{\partial}{\partial t} \tag{1.88}$$

the time-dependent Schroedinger Equation (1.76) giving the time evolution of the state function Ψ. Hence, the two correspondences (1.87) and (1.88), connecting linear momentum and total energy to the first derivatives of the function Ψ, necessarily imply the fundamental relations occurring in our axiomatic proposition of quantum mechanics.

As a consequence of our probabilistic description, in doing experiments in atomic physics we usually obtain a *distribution* of the observable eigenvalues, unless the state function Ψ coincides at time t with the eigenfunction φ_κ of the corresponding quantum mechanical operator, in which case we have a 100% probability of observing for A the value A_κ. Such probability distributions fluctuate in time for all observables but the energy, where we have a distribution of eigenvalues (the possible values of

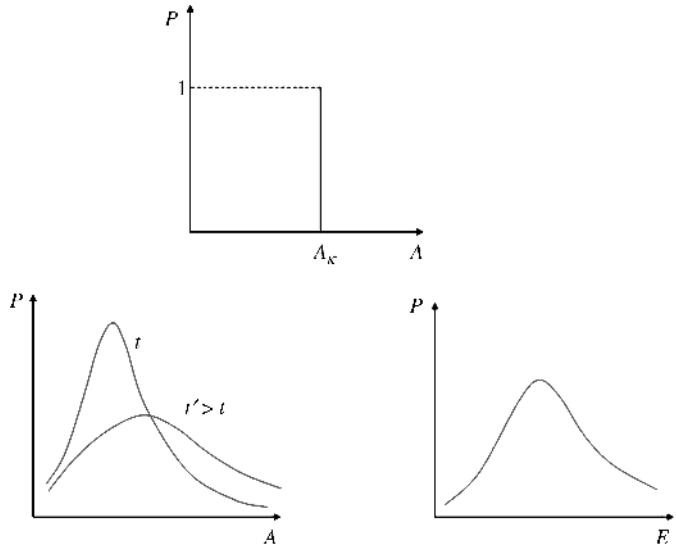


Figure 1.3 Probability distribution of the physical observable A. Top row: definite value for the κth eigenvalue. Bottom row: fluctuation in time of the probability distribution (left) and distribution of energy eigenvalues constant in time (right)

the energy levels) constant in time. These different cases are qualitatively depicted in the plots of Figure 1.3.

The formulation of quantum mechanics of Section 1.3 is the most useful for us, but not the only one possible. For instance, using Dirac's approach, Troup (1968) showed the equivalence between our Schroedinger[10] 'wave mechanics' (the *continuous* approach) and Heisenberg 'matrix mechanics' (the *discrete* approach), giving working examples in both cases (e.g. the harmonic oscillator and the hydrogen atom). However, this matter is outside the scope of the present book.

[10] Based on the Schroedinger (1926a, 1926b, 1926c, 1926d) series of four papers entitled 'Quantisierung als Eigenwertproblem'. The equivalence between matrix and wave mechanics was examined by Schroedinger (1926e) in an intermediate paper.