Methods of Molecular Quantum Mechanics

An Introduction to Electronic Molecular Structure

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This edition first published 2009
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Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ,
United Kingdom

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Library of Congress Cataloging-in-Publication Data

Magnasco, Valerio.
Methods of molecular quantum mechanics : an introduction to electronic molecular structure / Valerio Magnasco.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-68442-9 (cloth) – ISBN 978-0-470-68441-2 (pbk. : alk. paper) 1. Quantum chemistry. 2. Molecular structure. 3. Electrons. I. Title.
QD462.M335 2009
541'.28–dc22
2009031405

A catalogue record for this book is available from the British Library.
ISBN H/bk 978-0470-684429 P/bk 978-0470-684412
Set in 10.5/13pt, Sabon by Thomson Digital, Noida, India.
Printed and bound in Great Britain by TJ International Ltd, Padstow, Cornwall.

To my Quantum Chemistry students

Contents

Preface

The structure of this little textbook is essentially methodological and introduces in a concise way the student to a working practice in the *ab initio* calculations of electronic molecular structure, giving a sound basis for a critical analysis of the current calculation programmes. It originates from the need to provide quantum chemistry students with their own personal instant book, giving at low cost a readable introduction to the methods of molecular quantum mechanics, a prerequisite for any understanding of quantum chemical calculations. This book is a recommended companion of the previous book by the author, *Elementary Methods of Molecular Quantum Mechanics*, published in 2007 by Elsevier, which contains many worked examples, and designed as a bridge between Coulson's *Valence* and McWeeny's *Methods of Molecular Quantum Mechanics*. The present book is suitable for a first-year postgraduate university course of about 40 hours.

The book consists of 12 chapters. Particular emphasis is devoted to the Rayleigh variational method, the essential tool for any practical application both in molecular orbital and valence bond theory, and to the stationary Rayleigh–Schroedinger perturbation methods, much attention being given to the Hylleraas variational approximations, which are essential for studying second-order electric properties of molecules and molecular interactions, as well as magnetic properties. In the last chapter, elements on molecular symmetry and group theoretical techniques are briefly presented. Major features of the book are: (i) the consistent use from the very beginning of the system of atomic units (au), essential for simplifying all mathematical formulae; (ii) the introductory use of density matrix techniques for interpreting the properties of many-body systems so as to simplify calculations involving many-electron wavefunctions; (iii) an introduction to valence bond methods, with an explanation of the origin of the chemical bond; and (iv) a unified presentation of basic elements of atomic and molecular interactions, with particular emphasis on the practical use of second-order calculation techniques. Though many examples are treated in depth in this book, for other problems and their detailed solutions the reader may refer to the previous book by the author. The book is completed by alphabetically ordered bibliographical references, and by author and subject indices.

Finally, I wish to thank my son Mario for preparing the drawings at the computer, and my friends and colleagues Deryk W. Davies and Michele Battezzati for their careful reading of the manuscript and useful discussions. In saying that, I regret that, during the preparation of this book, DWD died on 27 February 2008.

I acknowledge support by the Italian Ministry for Education University and Research (MIUR), under grant number 2006 03 0944 003, and Aracne Editrice (Rome) for the 2008 publishing of what is essentially the Italian version entitled *Elementi di Meccanica Quantistica Molecolare*.

Valerio Magnasco
Genoa, 15 May 2009

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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 $\mathbf{r}$ 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,

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

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quadratically integrable) satisfying the normalization condition

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

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:

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

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* $N = A^{-1/2}$.

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[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 'turn-over rule':

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

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 $-\mathrm{i}\partial/\partial x$, $-\mathrm{i}\nabla, \partial^2/\partial x^2, \nabla^2, \hat{T} = -(\hbar^2/2m)\nabla^2$ 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*

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[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 $\boldsymbol{\varphi} = (\varphi_1\varphi_2\cdots\varphi_n)$:

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

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 d**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):

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

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

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

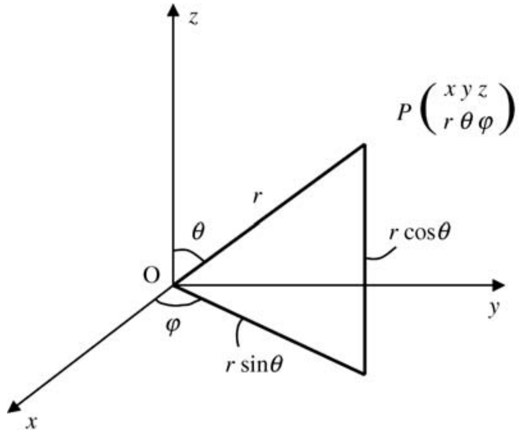

Figure 1.1 Cartesian and spherical coordinate systems

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

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

(ii) Spherical coordinates (r,θ,φ):

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

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

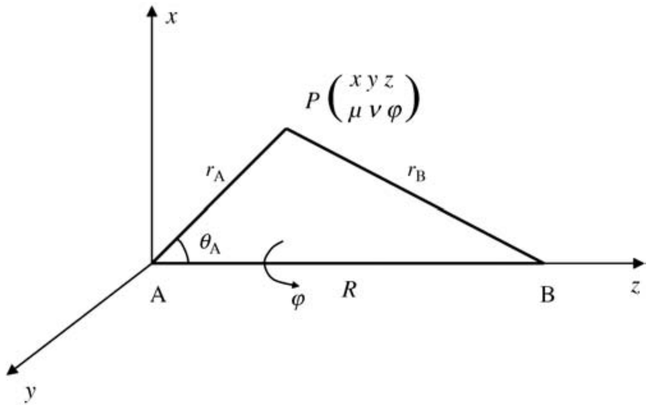

Figure 1.2 Cartesian and spheroidal coordinate systems

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

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

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

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

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

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):

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

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

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

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

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

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

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

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:

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

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[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.