# The Natural Quantum Mechanics



| 1s | z | | 2s | z | | 2px | z | | 2pz | z |
| x and y | | | x and y | | | x | | | x and y | |

| 3s | z | | 3px | z | | 3pz | z |
| x and y | | | x | | | x and y | |

| 3dz² | z | | 3dxy | y | | 3d(x²−y²) | y |
| x and y | | | x | | | x | |

Scale   0   10   20   30   40 $a_0$      0      1      2 nm
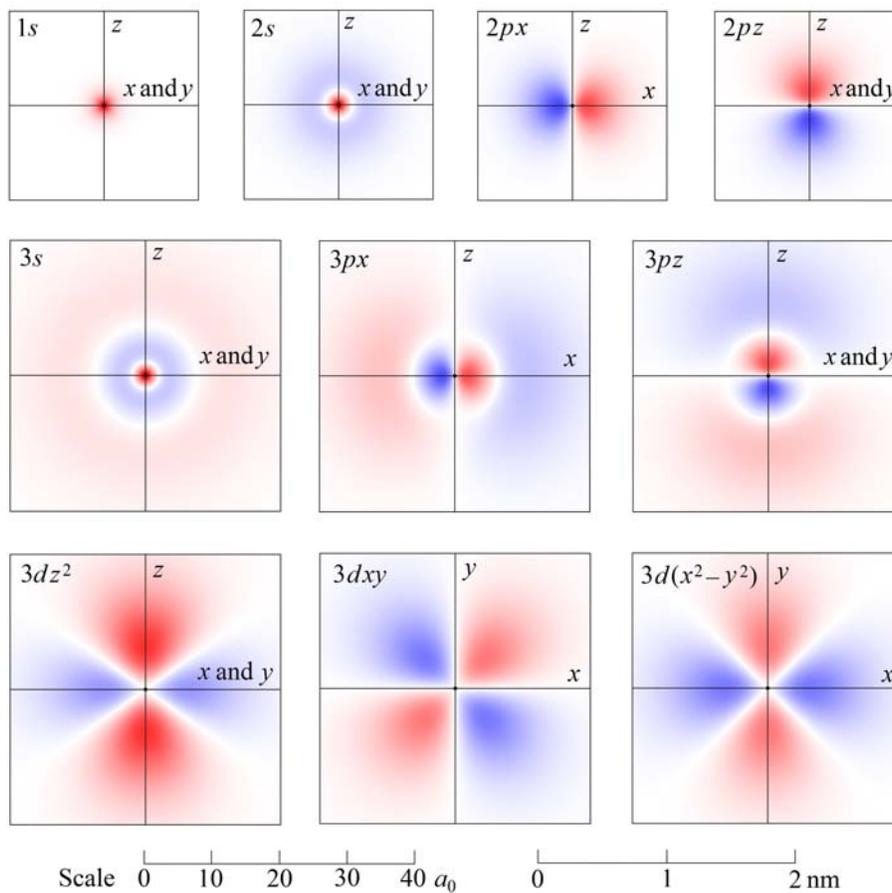
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Quantum mechanics is the centerpiece of modern physics. It is the foundation of modern technologies benefiting everyday life of everybody. For many decades, learning introductory quantum mechanics was hampered by unintelligible paradoxes. However, the advanced quantum physics, quantum field theory, is free from paradoxes. This is because in quantum field theory, both electrons and radiation are treated as continuous fields, while in some introductory quantum mechanics textbooks, electrons are treated as fictitious material points. The split-personality of electrons and radiation is the origin of paradoxes.

Starting from the modern all-fields view that both electrons and radiation are continuous fields, this introductory quantum mechanics textbook is logically consistent and covers all essential applications with no paradoxes. It is designed for freshman and sophomore students majoring in physics, chemistry, solid state electronics, materials science, and molecular biology. The minimal mathematical prerequisite is the high-school advanced-placement calculus or equivalent. It also provides a conceptual bridge to quantum field theory. To improve intuitiveness, two-colored graphs are used to show wavefunctions.

This textbook can be used for a one-semester course or a two-semester course. For students already learned classical physics and partial differential equations but not interested in advanced topics, Chapters 2 through 7 fits a one-semester course. A more complete course takes two semesters.

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# Preface

Quantum mechanics is the centerpiece of modern physics. It underlies much of modern science and technology, including transistors and integrated circuits, light-emitting diodes, solar cells, lasers, all of chemistry, and molecular biology. Ideally, all students majoring in science and engineering should learn quantum mechanics in their freshman or sophomore years. However, teaching and learning quantum mechanics have always been difficult mainly due to the unintelligible paradoxes and controversies. Even grand masters of physics found them annoying. Richard Feynman famously said, "I think I can safely say that nobody understands quantum mechanics".

In the second half of the 20th century, quantum electrodynamics, the relativistic quantum field theory of radiation and matter, was established. It predicted the values of physical quantities such as the anomalous magnetic dipole moment of the electron to better than one part in a trillion. Remarkably, that advanced quantum theory is free from paradoxes and controversies. Leading quantum field theorists including Steven Weinberg and Frank Wilczek commented that the source of paradoxes in elementary quantum mechanics is the relics of classical physics. Quantum field theory has a unified view that both radiation and matter are continuous fields while photons and electrons are quanta of these fields. However, in elementary quantum mechanics, radiation and matter were often treated differently. Radiation was described by Maxwell's equations, where both coordinates $\mathbf{r}$ and time $t$ are field parameters. Neverthelesss, the electron was described as a material point with a trajectory $\mathbf{r}(t)$; where the coordinates $\mathbf{r}$ were treated as dynamic variables. Such a split personality is incompatible with special relativity, where $\mathbf{r}$ and $t$ should be on the same footing. In quantum field theory, the electron is described by a Dirac spinor, a function of $\mathbf{r}$ and $t$, same as electromagnetic fields. Because Schrödinger's wavefunction is a nonrelativistic approximation of Dirac's spinor, it should also be treated as a physical field, with both $\mathbf{r}$ and $t$ are field parameters.

The above arguments were elaborated by Art Hobson in a series of articles published in *American Journal of Physics* and *The Physics Teacher*.[1] Those papers summarize the views of leading quantum field theorists, and propose a better way to teach elementary quantum mechanics by treating electrons not as material points, but as quanta of the continuous wavefunction. The paradoxes and controversies are eliminated.

During the early 21st century, using the scanning tunneling microscope, atomic and molecular wavefunctions are observed and mapped down to sub-

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[1] A. Hobson, "Electrons as field quanta: A better way to teach quantum physics in introductory general physics courses", *Am. J. Phys*, 73 630 (2005); "Teaching Quantum Physics Without Paradoxes", *The Physics Teacher*, 45, 96 (2007); "There are no particles, there are only fields", *Am. J. Phys*, 82 211 (2013).

picometer resolution with negligible disturbance. Even the nodal structures inside the molecular wavefunctions are observed and mapped. Those experiments proved that wavefunctions are physical fields as designated by quantum field theory. No point-like electrons were observed.[2]

Motivated by the experimental discovery and the need of my students to learn quantum mechanics without paradoxes, I tried to teach quantum mechanics based on the all-field concept for several years. This book manuscript is based on the lecture notes. My teaching experience indicated that the all-field concept has additional benefits. The difficult mathematical prerequisites, such as Hilbert space, Lagrangian–Hamiltonian mechanics, and probability theory, can be avoided. Furthermore, by teaching partial differential equations during the early lectures in classical physics, especially acoustics and electromagnetics, the mathematical prerequisite can be as low as high-school advanced-placement calculus. Therefore, it can be a freshman-sophomore course for students with less mathematical training. Nevertheless, it provides many topics in quantum mechanics sufficient for applications in condensed-matter physics, materials science, solid-state electronics, all branches of chemistry, and molecular biology. A conceptual bridge to quantum field theory is also established.

To improve intuitiveness, two-color graphics is extensively used to represent wavefunctions. According to the Wigner theorem, if the Hamiltonian is time-reversal invariant, all wavefunctions are real. By displaying wavefunctions with two colors, for example, red or blue as positive or negative, intuitiveness is greatly improved. Color graphics also improves the understanding of many other physical concepts.

Following is a brief summary of the Chapters.

Chapter 1, A Review of Classical Physics. In Section 1.1, Newtonian mechanics is presented for an easy transition to quantum mechanics. Nevertheless, the naïveté of the material-points concept is emphasized to avoid misunderstandings. Section 1.2 presents wave phenomena, including standing waves, eigenvalues, eigenfunctions, nodal structures, orthogonality, and superposition. For students with no exposure to partial differential equations, this section is a teaching-by-example introduction. Section 1.3 presents Maxwell's theory that light as an electromagnetic wave. The concept of polarization is presented in detail to prepare for a correct explanation of the electron spin. In some textbooks, spin is presented as a property of an single electron designated as a material point, that causes gross misunderstandings. In fact, electron spin is equivalent to polarization of light. Finally, starting with a simple proof of the Euler formula $e^{ix} = \cos x + i \sin x$, the powerfulness of complex numbers in treating wave phenomena is presented with examples in planar geometry and electromagnetism.

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[2]C. J. Chen, *Introduction to Scanning Tunneling Microscopy*, Third Edition, Oxford University Press 2021. Chapter 8, *Imaging Wavefunctions.*

Chapter 2, Wave and Quantum. From the beginning, the correct concept in quantum field theory that electron is a continuous physical field, like electromagnetic fields, is emphasized. The terms electron and photon mean that energy, mass, and electrical charge are quantized when interacting with other fields. There are no material points. The chapter starts with Einstein's theory of quantization of light: when light is generated or converted into other forms, energy is quantized. In free space, light is an electromagnetic wave, not a spray of geometrical points. Similarly, according to quantum field theory, electron is always a field, not a material point. Accordingly, Compton effect is presented in terms of waves. Finally, blackbody radiation is presected in details, including Einstein's 1916 derivation, that shows the true mesaning of quantization.

Chapter 3, The Static Schrödinger Equation. A simple and intuitive derivation of Schrödinger's equation is presented based on the de Broglie postulate and the classical energy integral. Solutions of the harmonic oscillator and the hydrogen atom are presented in real variables. The solutions of the harmonic oscillator are presented using creation and annihilation operators in real variables. It is intuitive and very simple. Quantization of bosons in the occupation-number representation, or the Fock space, is presented to provide a bridge to quantum field theory.

Chapter 4, Many-Electron Systems. Many-electron wavefunctions and the Slater determinants are introduced based on Pauli exclusion principle and the electron spin. The Hartree-Fock method and the density functional theory are presented. Quantization of fermions, formulated by the anti-commutative creation and annihilation operators in the Fock space, is presented. It is intuitive, and the mathematics is simple. It provides another bridge to quantum field theory.

Chapter 5, The Chemical Bond. Four types of chemical bonds are described: the van der Waals bond, the covalent bond, the ionic bond, and the hydrogen bond. A perturbation theory of the covalent bond is described in detail. As an example, the hydrogen molecular ion is treated in detail analytically. The homonucleus diatomic molecules are presented.

Chapter 6, The Dynamic Schrödinger Equation. By presenting the wavefunction as a two-component real field, the dynamic Schrödinger equation is derived from de Broglie's postulate and the classical energy integral. The two-component real wavefunction is invariant under an SO(2) group, which is equivalent to SU(1). The complex wavefunction is introduced with a proof of gauge invariance. The operator algebra initially presented in Chapter 3 for the harmonic oscillator is extended to complex wavefunctions. The applications to angular momentum and Pauli's derivation of energy levels of hydrogen atom are presented. Finally, the wavepacket as a macroscopic particle and the Ehrenfest theorem are presented.

Chapter 7, Perturbation Theories. Both static and dynamic perturbation theories are presented through examples. The interaction of radiation

fields with atomic systems are presented. The golden rule is derived.

Chapter 8, Physics of Semiconductors. The concept of band theory of solids is presented in terms of a tight-bonding model. Three types of band structures are presented. Semiconductors with impurities and the working principles of $p$-$n$ junctions are explained. The principles of transistors, light-emitting diodes, and solar cells are explained.

Chapter 9, Quantum Theory of Light. Using the creation operators and annihilation operators introduced in Chapter 3 and Chapter 4, basic concepts in quantum field theory especially quantum electrodynamics are presented. In the interaction picture, Einstein's three coefficients are derived and explained.

Chapter 10, Dirac Equation and Pauli Equation. Starting from the relativistic energy-momentum equation and the de Broglie postulate, Dirac equation is presented as a physical field. The elementary solution in free space and the existence of positron is presented. The non-relativistic approximation, the Pauli equation is presented. The meaning of spin as an analogy to polarization of light is explained. The Stern-Gerlach experiment is explained in analogy to the experiments of polarization of light.

This textbook can be used for a one-semester course or a two-semester course. For students already learned classical physics and partial differential equations but not interested in advanced issues, Chapters 2 through 7 fits a one-semester course. A more complete course takes two semesters.

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# Chapter 3

# The Static Schrödinger Equation

The year 1905 was Albert Einstein's *annum mirabilis* when he published four papers on *Annalen der Physik* that literally started the modern physics. Similarly, the year 1926 was Erwin Schrödinger's *annum mirabilis* with six papers published on the same journal *Annalen der Physik* that defined non-relativistic quantum mechanics. Thus commented Paul Dirac in 1929: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known". Those papers, belonging to the defining publications of modern science, are still worth reading. Here is a brief summary of the important ones:

The first paper, *Quantization as an Eigenvalue Problem, Part I*, received by *Annalen der Physik* on January 27, 1926, defined a wavefunction $\psi$, which is "everywhere real, single-valued, finite, and continuously differentiable up to the second order". A differential equation of $\psi$ is presented as a variation of the Hamilton-Jacobi equation. By applying that equation to the hydrogen atom, the Rydberg formula was explained.

The second paper, *Quantization as an Eigenvalue Problem, Part II*, presented a parallelism of the relation of quantum mechanics and classical mechanics with the relation of wave optics and geometrical optics. He emphasized that the wave nature of electrons is fundamental, and the particle view is a macroscopic approximation. He also presented an even simpler way to introduce the differential equation of the wavefunction based on de



**Fig. 3.1. Austrian banknote with a portrait of Schrödinger.** It is a rare honor for a scientist to have a portrait printed on a banknote. Note the large value.

Broglie wave. Three further problems were treated: the harmonic oscillator, rigid rotor and non-rigid rotor, all related to molecular physics.

The dynamic Schrödinger's equation was introduced in the sixth paper, received by *Annalen der Physik* on June 23, 1926. By treating radiation as classical electromagnetic waves, its effect to atomic systems was resolved as a perturbation. Tunneling at an atomic scale is also resolved.

We will introduce Schrödinger's equations in three stages. In this Chapter, the static Schrödinger's equation for a single electron is introduced. In Chapter 4, the many-electron version is introduced. In Chapter 6, the dynamic Schrödinger's equation is introduced.

## 3.1 The static Schrödinger equation

The static Schrödinger equation can be derived by applying the de Broglie postulate to the classical energy integral, Eq. 1.11,

$$\frac{\mathbf{p}^2}{2m_e} + V(\mathbf{r}) = E. \tag{3.1}$$

According to de Broglie, the electron is a field. A bound electron is similar to a standing wave $\psi(\mathbf{r})$, satisfying the Helmhotz equation, Eq. 1.120,

$$\nabla^2\psi(\mathbf{r}) + k^2\psi(\mathbf{r}) = 0. \tag{3.2}$$

The wave vector is then

$$k^2 = -\frac{\nabla^2\psi(\mathbf{r})}{\psi(\mathbf{r})}. \tag{3.3}$$

According to the de Broglie's relation, Eq. 2.24,

$$\mathbf{p} = \hbar\mathbf{k}. \tag{3.4}$$

Combining Eq. 3.3 and Eq. 3.4, one finds

$$\mathbf{p}^2 = -\frac{\hbar^2\nabla^2\psi(\mathbf{r})}{\psi(\mathbf{r})}. \tag{3.5}$$

Insert Eq. 3.5 into Eq. 3.1, multiply both sides by $\psi(\mathbf{r})$, a differential equation for wavefunction $\psi(\mathbf{r})$ is obtained,

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{3.6}$$

This is the *the static Schrödinger equation.*

## 3.2  Wavefunctions in a potential well

To illustrate the meanings of the Schrödinger equation and wavefunctions, the problems of electrons in a potential well is analyzed. The similarity to sound waves is explained. The Dirac notations are introduced.

### 3.2.1  One-dimensional potential well

Consider first a one-dimensional potential well of length $L$. Within the well, the potential is zero. Schrödinger's equation is

$$-\frac{\hbar^2}{2m_e}\frac{d^2\psi(x)}{dx^2} = E\psi(x). \tag{3.7}$$

Assuming the wall is infinitely high. The boundary conditions are: at the boundaries, $x = 0$ and $x = L$, the wavefunction must be zero.

Introduce a wave vector $k$ defined as

$$k = \frac{\sqrt{2m_e E}}{\hbar}, \tag{3.8}$$

the Schrödinger's equation Eq. 3.7 becomes

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x). \tag{3.9}$$

The general solution of Eq. 3.9 is

$$\psi(x) = C\sin(kx + \phi), \tag{3.10}$$

where $C$ is a normalization constant, and $\phi$ is a phase angle. Because at $x = 0$, the wavefunction must be zero, one should have $\phi = 0$:

$$\psi(x) = C\sin(kx). \tag{3.11}$$

The boundary condition at the other end, $\psi(L) = 0$, requires that

$$k = \frac{n\pi}{L}, \tag{3.12}$$
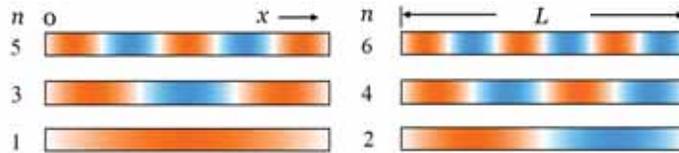


**Fig. 3.2.  Wavefunctions in a one-dimensional potential well.** The wavefunctions are labeled by quantum number $n$, similar to the sound waves in a bugle. See Fig. 1.17.
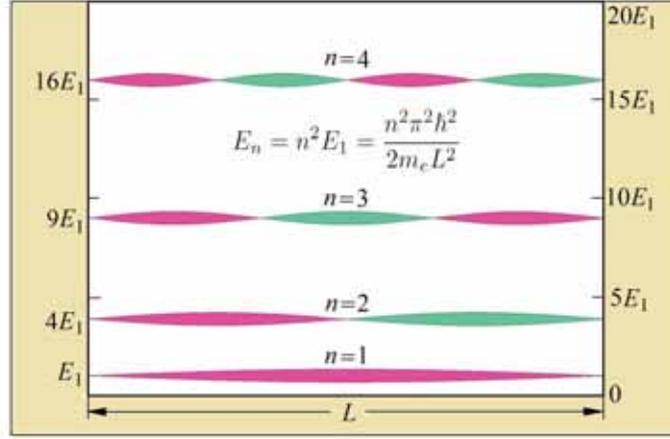
**Fig. 3.3.  Energy levels in a one-dimensional potential well.** The wavefunctions are labeled by quantum number $n$.  The wavefunctions are similar to the vibration of string, see Fig. 1.10.  The energy eigenvalue is proportional to $n^2$.

where $n = 1, 2, 3, \ldots$ is an integer.  The wavefunctions are

$$\psi_n(x) = C \sin\left(\frac{n\pi x}{L}\right). \tag{3.13}$$

The constant $C$ will be determined shortly.  Figure 3.2 shows the wavefunctions. It is similar to the sound waves in a bugle, see Fig. 1.17.

In classical mechanics, as in Eq. 3.1, energy can take any value.  In quantum mechanics, because of condition Eq. 3.12, energy is *quantized*: it can only take discrete values determined by Eqs. 3.8 and 3.12:

$$E_n = n^2 E_1 = \frac{n^2\pi^2\hbar^2}{2m_e L^2}, \tag{3.14}$$

Those allowed values of energy are called the *energy eigenvalues*, adapted from German, the *proper values of energy*.

Because the Schrödinger equation is linear to the wavefunction, the constant $C$ does not affect the determination of energy eigenvalues.  According to Schrödinger, the square of the wavefunction is proportional to the charge density distribution of the electron as a field in space:

$$\rho(x) = -e\psi^2(x). \tag{3.15}$$

Because the total charge of an electron over the space equals to one elementary charge $-e$, the integral over the entire space must equal to 1.  In the current situation, the electron is confined in a well of width $L$,

$$\int_0^L \psi^2(x)dx = 1. \tag{3.16}$$

The average value of the square of sine function over any number of half periods is 1/2. Therefore, for all quantum numbers, the constant is

$$C = \sqrt{\frac{2}{L}}. \tag{3.17}$$

The wavefunctions are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}. \tag{3.18}$$

It is straightforward to show that eigenstates with different quantum numbers $n$ are orthogonal. In fact, using Eq. 3.18,

$$\int_0^L dx \, \psi_n(x) \, \psi_m(x) = \delta_{nm}, \tag{3.19}$$

which is zero when $n \neq m$, and is 1 when $n = m$.

Furthermore, the set of wavefunctions is *complete*. Any function $f(x)$ in the interval $[0, L]$ can be expanded as a sum of those wavefunctions,

$$f(x) = \sum_{n=1}^{\infty} b_n \psi_n(x), \tag{3.20}$$

with coefficients

$$b_n = \int_0^L f(x) \, \psi_n(x) \, dx. \tag{3.21}$$

This is a special case of the Fourier theorem, the proof can be found in any mathematics textbook with Fourier series. Nonetheless, if Eq. 3.20 is true, it is easy to prove that the expression of the coefficients, Eq. 3.21, is correct. In fact, because of the orthonormal relation Eq. 3.19,

$$\int_0^L \psi_n(x) dx \sum_{m=1}^{\infty} b_m \psi_m(x) = \sum_{m=1}^{\infty} \delta_{nm} b_m = b_n. \tag{3.22}$$

### 3.2.2 The Dirac notation

The notations of wavefunctions, Eq. 3.18, and the integrals, Eqs. 3.16 and 3.19, occurs very often in quantum mechanics. In the third edition of *Principles of Quantum Mechanics*, Dirac introduced the bra and ket notations, that greatly simplifies mathematical notations in quantum mechanics. In the real formulation of quantum mechanics, bra and ket are equivalent. A wavefunction can be denoted either as a bra or as a ket. For the case of electrons in a one-dimensional potential well, it is either

$$\langle n| = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \tag{3.23}$$

or

$$|n\rangle = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}. \tag{3.24}$$

A complete bracket represents an integral of two wavefunctions,

$$\langle n|m\rangle = \int_0^L dx \; \psi_n(x) \, \psi_m(x). \tag{3.25}$$

Obviously, the real Dirac notation is symmetric, or *commutative*,

$$\langle n|m\rangle = \langle m|n\rangle. \tag{3.26}$$

The orthogonal and normalizing condition in Dirac notation is

$$\langle n|m\rangle = \delta_{nm}, \tag{3.27}$$

and the completeness of the wavefunctions means that any function $|f\rangle$ in the same interval $[0, L]$ can be expanded as a sum of the wavefunctions,

$$|f\rangle = \sum_{n=1}^{\infty} \langle n|f\rangle |n\rangle. \tag{3.28}$$

A linear operation on a wavefunction is represented by an operator. To differentiate it from an ordinary constant, a hat is added, such as $\hat{o}$. Multiplying the wavefunction with the coordinate, for example $x$ to a one-dimensional wavefunction, is an linear operation. We denote it as $\hat{x}$. A differential operator is defined as

$$\hat{\delta}|f\rangle \equiv \frac{d}{dx}f(x). \tag{3.29}$$

If for all wavefunctions $f$ and $g$, two operators $\alpha$ and $\beta$ satisfying the following relation,

$$\langle \hat{\alpha}f|g\rangle = \langle f|\hat{\beta}g\rangle, \tag{3.30}$$

then we say the operator $\alpha$ is an *adjoint operator* of $\beta$, denoted as

$$\hat{\alpha}^\dagger = \hat{\beta}, \quad \text{or} \quad \hat{\beta}^\dagger = \hat{\alpha}. \tag{3.31}$$

The operator $\hat{x}$ is obviously self-adjoint,

$$\hat{x} = \hat{x}^\dagger. \tag{3.32}$$

However, the differential operator is not. In fact, because

$$\int_{-\infty}^{\infty} \left[ \frac{df(x)}{dx}g(x) + f(x)\frac{dg(x)}{dx} \right] dx = \int_{-\infty}^{\infty} \frac{d}{dx}\left[ f(x)g(x) \right] dx = 0, \tag{3.33}$$

one has

$$\hat{\delta} = -\hat{\delta}^\dagger. \tag{3.34}$$

The Schrödinger equation, Eq. 3.6, can be written as

$$\hat{H}|\psi\rangle = E|\psi\rangle \tag{3.35}$$

by defining an *energy operator* or a Hamiltonian,

$$\hat{H} \equiv -\frac{\hbar^2}{2m_e}\nabla^2 + V(\mathbf{r}). \tag{3.36}$$

The energy operator is self-adjoint. The proof is left as an exercise.

## 3.3   The harmonic oscillator

In quantum mechanics, the harmonic oscillator is of fundamental importance. It describes the oscillation of molecules and solids near its equilibrium point. The electromagnetic wave can be decomposed into a number of simple harmonic oscillators. Using the quantization procedure presented here, the electromagnetic waves can be quantized. It is the basis of quantum electrodynamics, the complete theory of radiation and matter.

From Eqs. 1.26 and 3.6, the Schrödinger equation for a one-dimensional harmonic oscillator is

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{m}{2}\omega^2 x^2\right)\psi(x) = E\psi(x). \tag{3.37}$$

By introducing a dimensionless coordinate $q$ defined as

$$q \equiv \sqrt{\frac{m\omega}{\hbar}}x, \tag{3.38}$$

the Schrödinger equation Eq. 3.37 is simplified to

$$\frac{1}{2}\left(-\frac{d^2}{dq^2} + q^2\right)\hbar\omega\psi(q) = E\psi(q). \tag{3.39}$$

### 3.3.1   Creation operator and annihilation operator

As we have presented in previous sections, the basic concept in quantum mechanics is the wavefunction, and it is governed by a partial differential equation, the Schrödinger equation. In some cases, the process of obtaining solutions of partial differential equations can be greatly simplified with differential operators using algebraic methods. This is especially true for the case of the harmonic oscillator.

In order to find an algebraic solution of the harmonic oscillator, a pair of operators are introduced: an *annihilation operator*,

$$\hat{a} = \frac{1}{\sqrt{2}} \left( q + \frac{d}{dq} \right),$$  (3.40)

and a *creation operator*

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}} \left( q - \frac{d}{dq} \right).$$  (3.41)

From Eqs. 3.32 and 3.34, the creation operator is the adjoint of the annihilation operator. The meanings of these terms well be clarified soon. Those operators greatly simplify the solution of the harmonic oscillator problem, and are the basis of quantum field theory.

By acting on any function $f(q)$, a simple algebra shows that the two operators satisfy a *commutation relation*. One one hand, we have

$$
\begin{aligned}
\hat{a}\hat{a}^\dagger f(q) &= \frac{1}{\sqrt{2}} \left( q + \frac{d}{dq} \right) \frac{1}{\sqrt{2}} \left( q - \frac{d}{dq} \right) f(q) \\
&= \frac{1}{2} \left( q^2 - \frac{d^2}{dq^2} + \frac{d}{dq} q - q \frac{d}{dq} \right) f(q) \\
&= \frac{1}{2} \left( q^2 - \frac{d^2}{dq^2} + 1 \right) f(q).
\end{aligned}
$$  (3.42)

On the other hand, we have

$$
\begin{aligned}
\hat{a}^\dagger \hat{a} f(q) &= \frac{1}{\sqrt{2}} \left( q - \frac{d}{dq} \right) \frac{1}{\sqrt{2}} \left( q + \frac{d}{dq} \right) f(q) \\
&= \frac{1}{2} \left( q^2 - \frac{d^2}{dq^2} - \frac{d}{dq} q + q \frac{d}{dq} \right) f(q) \\
&= \frac{1}{2} \left( q^2 - \frac{d^2}{dq^2} - 1 \right) f(q).
\end{aligned}
$$  (3.43)

Here, the obvious identity is applied:

$$\frac{d}{dq}(q\,f(q)) = q\frac{d}{dq}f(q) + \frac{dq}{dq}f(q) = q\frac{d}{dq}f(q) + f(q).$$  (3.44)

Combining Eqs. 3.42 and 3.43, we find the commutation relation

$$[\hat{a}, \hat{a}^\dagger] \equiv \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1.$$  (3.45)

Through a simple algebra, the Schrödinger equation Eq. 3.39 becomes

$$\left( \hat{a}^\dagger\hat{a} + \frac{1}{2} \right) \hbar\omega\psi(q) = E\psi(q).$$  (3.46)

The verification is left as a Problem.

### 3.3.2    Algebraic solution of the Schrödinger equation

In this Section, we show how to utilize Eq. 3.45 to solve the Schrödinger equation Eq. 3.46. Denoting the wavefunction with Dirac notation $|n\rangle$ (see Section 3.2.2), it is sufficient to solve the following algebraic equation,

$$\hat{a}^{\dagger}\hat{a}|n\rangle = u_n|n\rangle. \tag{3.47}$$

Here the eigenstates are labeled by a number $n$ with eigenvalue $u_n$. By comparing Eq. 3.46 with Eq. 3.47, the energy eigenvalues are

$$E_n = \left(u_n + \frac{1}{2}\right)\hbar\omega. \tag{3.48}$$

As a consequence of Eq. 3.45, if $|n\rangle$ is an eigenstate with eigenvalue $u_n$, then $\hat{a}|n\rangle$ is also an eigenstate,

$$\hat{a}^{\dagger}\hat{a}\,\hat{a}|n\rangle = (\hat{a}\hat{a}^{\dagger} - 1)\hat{a}|n\rangle = (u_n - 1)\,\hat{a}|n\rangle \tag{3.49}$$

with eigenvalue $u_n - 1$. Because $\langle n|\hat{a}^{\dagger}\hat{a}|n\rangle = \langle \hat{a}n|\hat{a}n\rangle$ must not be negative, there must be an eigenstate $|0\rangle$ with a minimum eigenvalue 0,

$$\hat{a}^{\dagger}\hat{a}|0\rangle = 0. \tag{3.50}$$

On the other hand, also as a consequence of Eq. 3.45, if $|n\rangle$ is an eigenstate with eigenvalue $u_n$, then $\hat{a}^{\dagger}|n\rangle$ is also an eigenstate

$$\hat{a}^{\dagger}\hat{a}\hat{a}^{\dagger}|n\rangle = \hat{a}^{\dagger}(\hat{a}^{\dagger}\hat{a} + 1)|n\rangle = (u_n + 1)\hat{a}^{\dagger}|n\rangle \tag{3.51}$$

with eigenvalue $u_n + 1$. Starting with the lowest eigenstate $|0\rangle$, by applying $\hat{a}^{\dagger}$ many times, we have

$$\hat{a}^{\dagger}\hat{a}\left(\hat{a}^{\dagger}\right)^n|0\rangle = n\left(\hat{a}^{\dagger}\right)^n|0\rangle. \tag{3.52}$$

Because the eigenvalue of the zeroth eigenstate $|0\rangle$ of the operator $\hat{a}^{\dagger}\hat{a}$ is zero, and each time a creation operator $\hat{a}^{\dagger}$ is applied, the eigenvalue is added by 1, the eigenvalues of the operator $\hat{a}^{\dagger}\hat{a}$ equals to an integer, the number of times the creation operator applied. Therefore, except for a numerical constant, it is the $n$-th eigenstate of the operator $\hat{a}^{\dagger}\hat{a}$:

$$|n\rangle = C_n\left(\hat{a}^{\dagger}\right)^n|0\rangle. \tag{3.53}$$

The operator $\hat{a}^{\dagger}\hat{a}$ is deservedly called the *particle number operator*,

$$\hat{N} \equiv \hat{a}^{\dagger}\hat{a}, \tag{3.54}$$

because its eigenvalue is the number of energy quanta,

$$\hat{N}|n\rangle = n|n\rangle. \tag{3.55}$$

The normalization constant $C_n$ can be determined as follows. The zeroth-order state is by definition normalized,

$$\langle 0|0 \rangle = 1. \tag{3.56}$$

By applying $\hat{a}^\dagger$ many times, we have

$$\langle 0| \left( \hat{a} \right)^n \left( \hat{a}^\dagger \right)^n |0 \rangle = n!. \tag{3.57}$$

Therefore, $C_n = (n!)^{-1/2}$, and

$$|n \rangle = \frac{1}{\sqrt{n!}} \left( \hat{a}^\dagger \right)^n |0 \rangle. \tag{3.58}$$

Following Eq. 3.48, the energy eigenvalues of the harmonic oscillator is

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega. \tag{3.59}$$

The energy level of the harmonic oscillator is thus quantized, with energy quanta $\hbar \omega$. The operator $\hat{a}^\dagger$ adds an energy quanta to the oscillator, thus named a *creation operator*; the operator $\hat{a}$ removes an energy quanta from the oscillator, thus named an *annihilation operator*.

### 3.3.3 Explicit expressions of wavefunctions

The above algebraic solution provides the simplest approach to find explicit expressions of the wavefunctions. First, from Eqs. 3.50 and 3.40, the zeroth-

**Table 3.1: Wavefunctions of the harmonic oscillator**

| State | Energy | wavefunction |
|-------|--------|--------------|
| $|0\rangle$ | $\frac{1}{2}\hbar\omega$ | $\frac{1}{\sqrt{\sqrt{\pi}}} e^{-q^2/2}$ |
| $|1\rangle$ | $\frac{3}{2}\hbar\omega$ | $\frac{1}{\sqrt{2\sqrt{\pi}}} 2q e^{-q^2/2}$ |
| $|2\rangle$ | $\frac{5}{2}\hbar\omega$ | $\frac{1}{\sqrt{2\sqrt{\pi}}} \left( 2q^2 - 1 \right) e^{-q^2/2}$ |
| $|3\rangle$ | $\frac{7}{2}\hbar\omega$ | $\frac{1}{\sqrt{3\sqrt{\pi}}} \left( 2q^3 - 3q \right) e^{-q^2/2}$ |
| $|4\rangle$ | $\frac{9}{2}\hbar\omega$ | $\frac{1}{\sqrt{24\sqrt{\pi}}} \left( 4q^4 - 12q^2 + 3 \right) e^{-q^2/2}$ |
| $|5\rangle$ | $\frac{11}{2}\hbar\omega$ | $\frac{1}{\sqrt{60\sqrt{\pi}}} \left( 4q^5 - 20q^3 + 15q \right) e^{-q^2/2}$ |

order wavefunction $|0\rangle = \psi_0(q)$ should satisfy

$$\left(q + \frac{d}{dq}\right)\psi_0(q) = 0. \tag{3.60}$$

The solution is

$$\psi_0(q) = C_0 \exp\left(-\frac{q^2}{2}\right). \tag{3.61}$$

The normalization constant $C_0$ can be determined directly by

$$\int_{-\infty}^{\infty} \psi_0^2(q)dq = C_0^2 \int_{-\infty}^{\infty} \exp(-q^2)dq = C_0^2\sqrt{\pi} = 1, \tag{3.62}$$

which gives

$$C_0 = \pi^{-1/4}. \tag{3.63}$$

All wavefunctions of the harmonic oscillator $|n\rangle = \psi_n(q)$ can be obtained from Eqs. 3.41 and 3.58 using Eqs. 3.61 and 3.63:

$$\psi_n(q) = \frac{1}{\sqrt{2^n n!\sqrt{\pi}}}\left(q - \frac{d}{dq}\right)^n \exp\left(-\frac{q^2}{2}\right). \tag{3.64}$$

The first few wavefunctions are listed in Table 3.1, and graphically displayed in Fig. 3.4. The solid curve, a parabola, represents the potential
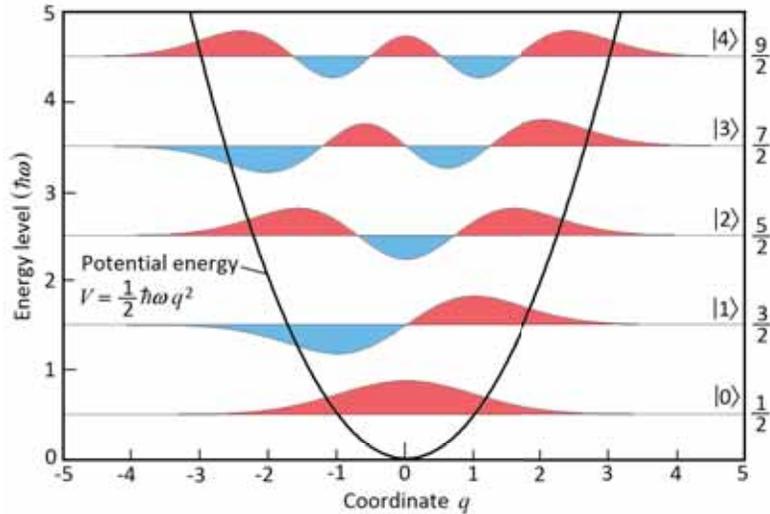


**Fig. 3.4. Energy levels and wavefunctions of a harmonic oscillator.** The solid curve is the potential energy. The wavefunctions of the first five eigenstates are shown. The red shade indicates positive phase, and blue shade indicates negative phase. The $y$-position of the energy eigenvalue is the baseline for the wavefunction.

energy as a function of the normalized coordinate $q$. The horizontal lines represent the energy levels of the eigenstates. For the region inside the potential curve, energy level $E$ is greater than the potential energy. The wavefunction resembles a sinusoidal wave. Outside the potential curve, the energy level is lower than the potential curve. The wavefunction resembles an exponential function decaying into the barrier. The lowest eigenstate has an energy value of $\frac{1}{2}\hbar\omega$. The wavefunction has no node. The energy eigenvalue increases by $\hbar\omega$ each step, while a new node is added. Those nodal structures make the wavefunctions orthogonal to each other.

## 3.4   The hydrogen atom

Hydrogen atom is a central subject of quantum mechanics. The accurate interpretation of the Rydberg formula marked a groundbreaking triumph. Many predictions of relativistic quantum electrodynamics are verified by measurements on the hydrogen atom. The hydrogen wavefunctions are the foundation for the understanding of complex atoms and atomic systems. There are only two real-world systems that the Schrödinger equation has analytic solutions: the hydrogen atom, and the hydrogen molecular ion, $H_2^+$, which is the basis to understand the chemical bond, and how condensed matter is formed. The ground-state wavefunction of hydrogen atom is also the starting point of the treatment of $H_2^+$.

In Gaussian unit system, the potential energy function $V(r)$ is the attractive force from the positively charged proton, see Eq. 1.182,

$$V(\mathbf{r}) = -\frac{e^2}{r}. \tag{3.65}$$

Because the electron mass $m_e$ is much smaller than the proton mass, to a good approximation, the Schrödinger equation Eq. 3.6 is

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi - \frac{e^2}{r}\psi = E\psi. \tag{3.66}$$

**Fig. 3.5.    Hydrogen atom in spherical polar coordinates.** The center of the coordinate system is the positively charged proton. The force and potential energy $V$ only depends on radius $r$. Therefore, it is natural to use spherical polar coordinates, with radius $r$, polar angle $\theta$, and azimuth $\phi$.
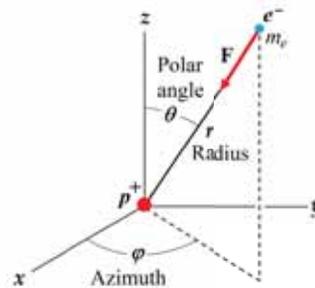
The potential only depends on $r$. It is natural to solve the equation in polar coordinates, similar to the problem of basketball in Section 1.4. In spherical polar coordinates, Eq. 3.66 becomes

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \frac{1}{r^2}\mathbf{L^2}\psi\right] - \frac{e^2}{r}\psi = E\psi. \tag{3.67}$$

where the *angular momentum operator* $\mathbf{L^2}$ is defined as

$$\mathbf{L^2}\psi \equiv -\frac{1}{\sin^2\theta}\left[\frac{\partial^2\psi}{\partial\phi^2} + \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)\right]. \tag{3.68}$$

The solutions of Eq. 3.68 are spherical harmonics, see Sections 1.4.2.

### 3.4.1 The ground state

First, we study the ground state, where the wavefunction $\psi$ only depends on $r$. The Schrödinger equation Eq. 3.67 becomes

$$-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) - \frac{e^2}{r}\psi = E\psi, \tag{3.69}$$

Intuitively, since the electron is being attracted by the positively charged proton, the wavefunction should concentrate near the proton, and decays with distance $r$. Therefore, to resolve Schrödinger's equation Eq. 3.69, we use the following trial function

$$\psi = Ce^{-r/a}, \tag{3.70}$$

where $a$ is a parameter to be determined, and $C$ is a normalization constant. Insert Eq. 3.70 into Eq. 3.69, eliminate the common factor $\psi$, we obtain

$$\frac{\hbar^2}{m_e ar} - \frac{\hbar^2}{2m_e a^2} - \frac{e^2}{r} = E. \tag{3.71}$$

The solution should be valid for all values of $r$. The two terms with common factor $1/r$ must cancel each other. It implies

$$a = \frac{\hbar^2}{m_e e^2}. \tag{3.72}$$

Therefore, the trial function Eq. 3.70 is a valid solution of Eq. 3.69, and the decay length is $a$, given by Eq. 3.72. The rest of Eq. 3.71 provides an expression of the energy eigenvalue

$$E = -\frac{\hbar^2}{2m_e a^2} = -\frac{m_e e^4}{2\hbar^2}. \tag{3.73}$$
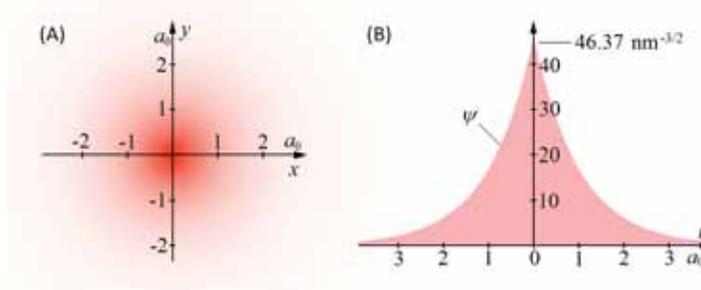
**Fig. 3.6. Wavefunction of ground-state hydrogen atom.** (A) The density plot of the wavefunction. (B) the amplitude profile of the wavefunction.

The parameter $a$ in Eq. 3.72 is the *Bohr radius*,

$$a_0 \equiv \frac{\hbar^2}{m_e e^2} \approx 52.9 \text{ pm.} \tag{3.74}$$

The absolute value of the energy eigenvalue in Eq. 3.73 is the *Rydberg constant*, which agrees well with experimental findings,

$$\text{Ry} \equiv |E_0| = \frac{m_e e^4}{2\hbar^2} = \frac{e^2}{2a_0} \approx 13.6 \text{ eV.} \tag{3.75}$$

In order to determine the normalization constant $C$, we note that according to Schrödinger, the square of the wavefunction is proportional to the charge density distribution of an electron as a field in space,

$$\rho = -e\psi^2, \tag{3.76}$$

requiring that the integration of $\psi^2$ over the entire space is 1,

$$\int_0^\infty 4\pi\psi^2 r^2 dr = \int_0^\infty 4\pi C^2 e^{-2r/a_0} r^2 dr = 1, \tag{3.77}$$

which yields

$$C = \frac{1}{\sqrt{\pi a_0^3}}. \tag{3.78}$$

The ground-state wavefunction of hydrogen atom is then

$$|1s\rangle \equiv \psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}. \tag{3.79}$$

The subscript $1s$ indicates that it is the state of lowest energy and spherically symmetric. A density plot and an amplitude contour of the ground-state wavefunction of hydrogen atom are shown in Fig. 3.6. Wavefunction is the form of existence of the electron. The ground state represents an electron at rest. There is no point charge, and no motion at all. The electrical charge density of the electron is spread out in space around the proton, with the highest charge density in the immediate vicinity of the proton.

### 3.4.2 Energy eigenvalues of excited States

Following the mathematics in Section 1.4, by writing the wavefunction as a product of a radial function $R(r)$ and a spherical harmonics,

$$\psi(\mathbf{r}) = R(r)Y(\theta, \phi), \tag{3.80}$$

the differential equation for the radial function $R(r)$ is

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) - \frac{l(l+1)R(r)}{r^2}\right] + \frac{e^2}{r}R(r) = ER(r), \tag{3.81}$$

where $l$ is the *azimuthal quantum number*, a parameter of the spherical harmonics, see Section 1.4.2. To resolve Eq. 3.81, by intuition, we use the following trial function

$$R(r) = C\,r^b e^{-r/a}, \tag{3.82}$$

where the parameters $a$ and $b$ are to be determined by Eq. 3.81, and $C$ is a normalization constant. Insert Eq. 3.82 into Eq. 3.81, eliminate the common factor $R(r)$, we obtain an algebraic equation

$$-\frac{\hbar^2}{2m_e}\left[\frac{b(b+1)}{r^2} - \frac{l(l+1)}{r^2} + \frac{2(b+1)}{ar} - \frac{1}{a^2}\right] + \frac{e^2}{r} = E. \tag{3.83}$$

To cancel the two terms with $1/r^2$, a sufficient condition is

$$b = l. \tag{3.84}$$

To cancel the two terms with $1/r$, one must have

$$a = (b+1)\frac{\hbar^2}{m_e e^2} = (b+1)a_0. \tag{3.85}$$

The remaining terms in Eq. 3.83 determine the energy eigenvalue

$$E = -\frac{\hbar^2}{2m_e a^2} = -\frac{\text{Ry}}{(b+1)^2}. \tag{3.86}$$

In all those formulas, $(b+1)$ occurs. Define an integer index $n$,

$$n = b + 1, \tag{3.87}$$

which is called the *principle quantum number*. The wavefunction is

$$\psi = Cr^{n-1}e^{-r/na_0}\,Y_{lm}(\theta, \phi). \tag{3.88}$$

The energy eigenvalue only depends on the principle quantum number $n$, perfectly explains the experimentally discovered Rydberg formula,

$$E_n = -\frac{\text{Ry}}{n^2}. \tag{3.89}$$

The length scale of the wavefunction, $a = na_0$, is a useful parameter for further study of the hydrogen wavefunction. It is

$$a = na_0 = \frac{\hbar}{\sqrt{-2m_e E}}. \tag{3.90}$$

Similar to Eq. 3.77, the normalization constant is found to be

$$C = \sqrt{\frac{2^{2n+1}}{\pi(2n+2)!\,(na_0)^{2n+3}}}. \tag{3.91}$$

In Fig. 3.7, we show some interesting cases. Following Section 1.4.2, for $m = l$, the spherical harmonics up to a normalization constant is

$$Y_{ll}^g(\theta, \phi) \propto \sin^l \theta \cos l\phi, \tag{3.92}$$

and

$$Y_{ll}^u(\theta, \phi) \propto \sin^l \theta \sin l\phi. \tag{3.93}$$

The wavefunctions shown in Fig. 3.7 are on the plane $z = 0$, where $\sin \theta = 1$. Using Eqs. 3.84 and 3.87, $l = n - 1$. The explicit expressions are

$$\psi_g \propto r^{n-1} e^{-r/na_0} \cos(n-1)\phi, \tag{3.94}$$

and

$$\psi_u \propto r^{n-1} e^{-r/na_0} \sin(n-1)\phi, \tag{3.95}$$
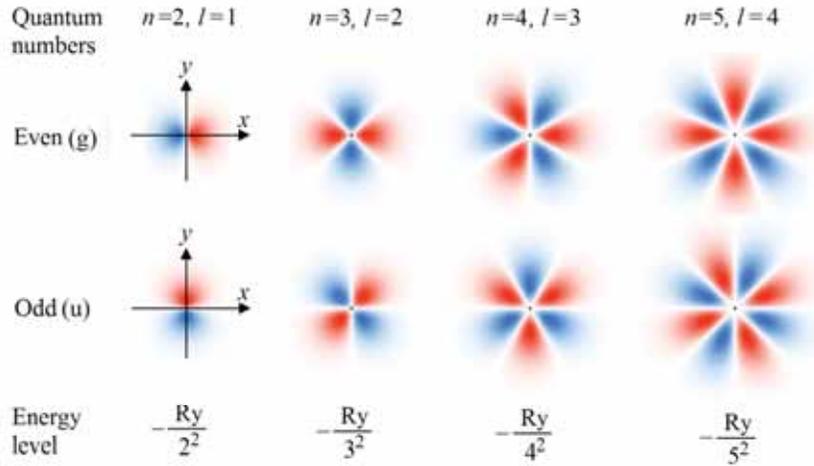


**Fig. 3.7. Wavefunctions of excited-states of hydrogen atom.** Wavefunctions in Eqs. 3.94 and 3.95, standing waves on the horizontal plane $z = 0$. For each principle quantum number, there is an even wavefunction symmetric regarding the $x$-axis, and an wavefunction antisymmetric regarding the $x$-axis. The energy level, Eq. 3.89, depends only on the principle quantum number $n$, explains the Rydberg formula.

where the subscript $g$ and $u$ indicates even and odd with respect to $x$-axis. Those wavefunctions represent standing waves on the $z = 0$ plane. As remarked by Schrödinger, the energy-level quantization in hydrogen atom resembles the nodes of a vibrating string in Section 1.2.1. Especially, it is similar to the resonance frequencies in a basketball in Section 1.4. The electron forms standing waves around the proton. Similar to the vibrating string and the basketball, different patterns of standing waves with different number of nodes are formed, resulting in different energy levels.

### 3.4.3 Wavefunctions

In the previous Subsection, following an elementary mathematical procedure, special solutions of Eq. 3.81 are derived. Due to a high degree of degeneracy, all energy eigenvalues are obtained. Especially, for the cases of $l = n - 1$ and $m = l$, wavefunctions are shown in Figs 3.6 and 3.7. Nevertheless, Eq. 3.81 does have other useful solutions, here we find them.

Inspired by the special solutions, a dimensionless variable $\rho$ is introduced by scaling the radius $r$ using the length $a = na_0$ in Eq. 3.90,

$$\rho = \frac{r}{a}. \tag{3.96}$$

Equation 3.81 becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR(\rho)}{d\rho}\right) + \left[-1 - \frac{l(l+1)}{\rho^2} + \frac{2n}{\rho}\right]R(\rho) = 0. \tag{3.97}$$

In the process of the algebra, Eq. 3.74 is applied to obtain

$$\frac{2m_e a\, e^2}{\hbar^2} = \frac{a}{a_0} = n. \tag{3.98}$$

Analogous to Eqs. 3.82 and 3.84, we make a substitution

$$R(\rho) = \rho^l\, e^{-\rho}\, F(\rho). \tag{3.99}$$

Insert Eq. 3.99 to Eq. 3.97, the differential equation for $F(\rho)$ is obtained:

$$\rho\frac{d^2 F(\rho)}{d\rho^2} + 2(l+1-\rho)\frac{dF(\rho)}{d\rho} + 2(n-l-1)F(\rho) = 0. \tag{3.100}$$

It is the differential equation for associate Laguerre polynomials, well known for mathematicians for two centuries. The general formula is fairly cumbersome. In condensed-matter physics, chemistry and molecular biology, only a few more cases are needed. Here is a complete list.

$$F(r) = 1 - \frac{1}{2}\frac{r}{a_0}, \qquad\qquad n = 2, \quad l = 0; \tag{3.101}$$

$$F(r) = 1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\left(\frac{r}{a_0}\right)^2, \qquad n = 3, \quad l = 0; \tag{3.102}$$

$$F(r) = 1 - \frac{1}{6}\frac{r}{a_0}, \qquad\qquad n = 3, \quad l = 1. \tag{3.103}$$

Those expressions can be verified by directly inserting those polynomials $F(r)$ into Eq. 3.100. It is left as an exercise.

By combining the radial functions in Eq. 3.99, using Eqs. 3.101 through 3.103 and the spherical harmonics in Table 1.4, we found the first nine wavefunctions of the hydrogen atom, listed in Table 3.2, and in Fig. 3.8. In Table 1.4, the first column shows the chemist's name of the wavefunction. The second column is in Dirac notation. The expression of the wavefunction, column 3, is in Cartesian coordinates with Bohr radius $a_0$ as unit. The last column is the average size of the wavefunction, also in unit of $a_0$.
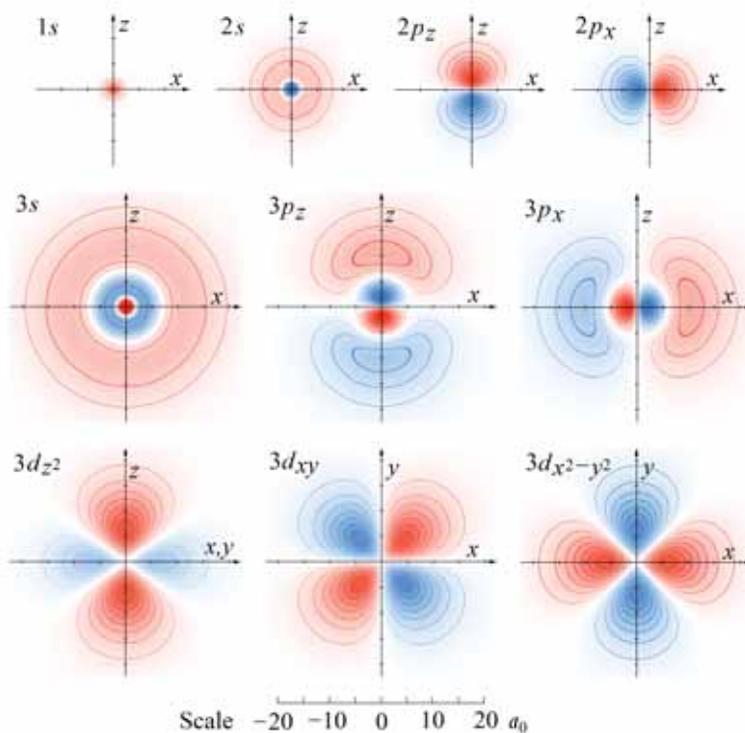


**Fig. 3.8. Hydrogen wavefunctions.** The phase, either positive or negative, is colored as red or blue. The amplitude of the wavefunction is shown by the intensity of color, with several equal-amplitude contours to guide the eyes. All graphs are sized following the Scale at the bottom of the Figure. As shown in the last column of Table 3.2, the sizes of wavefunctions with different principle quantum number $n$ vary dramatically.

**Table 3.2: Wavefunctions of the hydrogen atom**

| Name | State | Wavefunction | $\bar{r}\,(a_0)$ |
|---|---|---|---|
| $1s$ | $\lvert 1s0\rangle$ | $\dfrac{1}{\sqrt{\pi}}\,e^{-r}$ | 1.5 |
| $2s$ | $\lvert 2s0\rangle$ | $\dfrac{1}{2\sqrt{2\pi}}\,(1-\tfrac{1}{2}r)\,e^{-r/2}$ | 6 |
| $2p_x$ | $\lvert 2p1u\rangle$ | $\dfrac{1}{4\sqrt{2\pi}}\,x\,e^{-r/2}$ | 5 |
| $2p_y$ | $\lvert 2p1g\rangle$ | $\dfrac{1}{4\sqrt{2\pi}}\,y\,e^{-r/2}$ | 5 |
| $2p_z$ | $\lvert 2p0\rangle$ | $\dfrac{1}{4\sqrt{2\pi}}\,z\,e^{-r/2}$ | 5 |
| $3s$ | $\lvert 3s0\rangle$ | $\dfrac{1}{3\sqrt{3\pi}}\,(1-\tfrac{2}{3}r+\tfrac{2}{27}r^2)\,e^{-r/3}$ | 13.5 |
| $3p_x$ | $\lvert 3p1u\rangle$ | $\dfrac{2}{27\sqrt{6\pi}}\,(1-\tfrac{1}{6}r)x\,e^{-r/3}$ | 12.5 |
| $3p_y$ | $\lvert 3p1g\rangle$ | $\dfrac{2}{27\sqrt{6\pi}}\,(1-\tfrac{1}{6}r)y\,e^{-r/3}$ | 12.5 |
| $3p_z$ | $\lvert 3p0\rangle$ | $\dfrac{2}{27\sqrt{6\pi}}\,(1-\tfrac{1}{6}r)z\,e^{-r/3}$ | 12.5 |
| $3d_{z^2}$ | $\lvert 3d0\rangle$ | $\dfrac{2}{27\sqrt{6\pi}}\,(z^2-\tfrac{1}{3}r^2)\,e^{-r/3}$ | 10.5 |
| $3d_{xz}$ | $\lvert 3d1u\rangle$ | $\dfrac{2}{27\sqrt{6\pi}}\,xz\,e^{-r/3}$ | 10.5 |
| $3d_{yz}$ | $\lvert 3d1g\rangle$ | $\dfrac{2}{27\sqrt{6\pi}}\,yz\,e^{-r/3}$ | 10.5 |
| $3d_{xy}$ | $\lvert 3d2u\rangle$ | $\dfrac{2}{27\sqrt{6\pi}}\,xy\,e^{-r/3}$ | 10.5 |
| $3d_{x^2-y^2}$ | $\lvert 3d2g\rangle$ | $\dfrac{4}{27\sqrt{6\pi}}\,(x^2-y^2)\,e^{-r/3}$ | 10.5 |

### 3.4.4 Nomenclature of atomic states

The wavefunctions of the hydrogen atom are the foundation of the nomenclature of electron states in many-electron atoms, see Table 3.3.

The principle quantum number $n$ identifies the shells, labeled by $K$, $L$, $M$, etc. The azimuthal quantum number $l$ identifies the subshells. The

Table 3.3: Nomenclature of atomic states

| $n$ | Shell | Maximum electrons | $l$ | Subshell | Maximum electrons |
|---|---|---|---|---|---|
| 1 | K | 2 | 0 | 1s | 2 |
| 2 | L | 8 | 0 | 2s | 2 |
|   |   |   | 1 | 2p | 6 |
| 3 | M | 18 | 0 | 3s | 2 |
|   |   |   | 1 | 3p | 6 |
|   |   |   | 2 | 3d | 10 |

labels, $s$, $p$, $d$ etc., have its origin in atomic spectrum. The spectral lines starting from $l = 0$ states are often sharp, thus named $s$. The spectral lines starting from $l = 1$ states are often intensive, thus named $p$, means principle. The spectral lines starting from $l = 2$ are often diffuse, thus named $d$. Because of spin, see Section 2.5, each wavefunction has two electrons.

### 3.4.5   Degeneracy and wavefunction hybridization

The energy eigenvalues of the hydrogen atom only depends on the principle quantum number $n$. For each principle quantum number, there are $n^2$ different wavefunctions: it is $n^2$-fold degenerate. For $n = 2$, there are four states, $|2s\rangle$, $|2px\rangle$, $|2py\rangle$, and $|2pz\rangle$. Because the Schrödinger equation is linear, any linear superposition of wavefunctions with the same energy eigenvalue is also a good wavefunction with the same energy eigenvalue. Especially, an $s$-wavefunction can make linear superposition with $p$-wavefunctions, to form *hybrid* wavefunctions. This concept is fundamental in chemistry, such
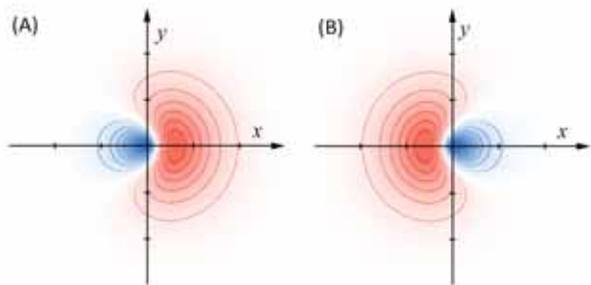


**Fig. 3.9.  Hybrid** $sp1$ **wavefunctions.** The phase of the wavefunction is shown by color, positive in red, negative in blue. The equal-value contours are also shown. The main lobe spans a wide angle. It is difficult to show both on the same figure.

as for carbon and silicon, especially in organic chemistry. Here we show the concept of hybridization using the hydrogen wavefunctions.

Figure 3.9 shows two $sp1$ hybrid wavefunctions. (A) is with a positive $2px$ wavefunction,

$$|2sp1+\rangle = \frac{1}{\sqrt{2}}|2s\rangle + \frac{1}{\sqrt{2}}|2px\rangle, \qquad (3.104)$$

resulting in a wavefunction preferentially concentrated in the $+x$ direction; and (B) is with a negative $2px$ wavefunction,

$$|2sp1-\rangle = \frac{1}{\sqrt{2}}|2s\rangle - \frac{1}{\sqrt{2}}|2px\rangle, \qquad (3.105)$$

resulting in a wavefunction preferentially concentrated in the $-x$ direction. This happens for example in acetylene $C_2H_2$, for both the $\sigma$-bond between the two carbon atoms, and the two C-H bonds.

Figure 3.10 shows three $sp2$ hybrid wavefunctions. The formulas are

$$|2sp2u\rangle = \frac{1}{\sqrt{3}}|2s\rangle + \sqrt{\frac{2}{3}}|2py\rangle, \qquad (3.106)$$

$$|2sp2l\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \frac{1}{\sqrt{2}}|2px\rangle - \frac{1}{\sqrt{6}}|2py\rangle, \qquad (3.107)$$

and

$$|2sp2r\rangle = \frac{1}{\sqrt{3}}|2s\rangle + \frac{1}{\sqrt{2}}|2px\rangle - \frac{1}{\sqrt{6}}|2py\rangle, \qquad (3.108)$$

respectively. It is the basic structure of grapheme and carbon nanotubes. In ethylene, $C_2H_4$, the $sp1$ hybrid wavefunctions are the basis of both the $\sigma$-bond between the two carbon atoms, and the four C-H bonds.
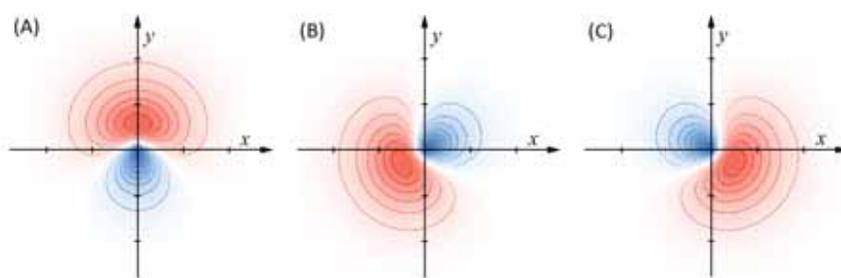


**Fig. 3.10.    Hybrid** $sp2$ **wavefunctions.** The three $sp2$ hybrid wavefunctions are pointing to the three vertices of a regular triangle, 120° apart in the same plane. The phase, positive or negative, is shown by color. The equal-value contours are also shown.
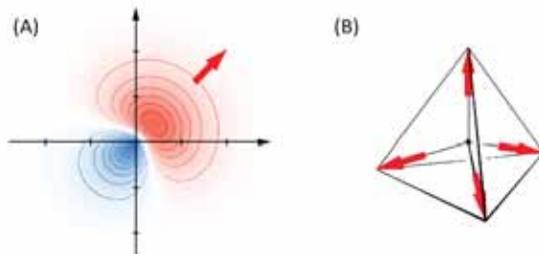
**Fig. 3.11. Hybrid** $sp3$ **wavefunctions.** (A), one of the four hybrid wavefunctions. The other three have the same shape but different orientation, pointing to the four vertices of a regular tetrahedron. (b), a regular tetrahedron.

A prevailing hybridization is the $sp3$ mode, where one $s$-wavefunction is linearly superposed with three $p$-wavefunctions to form four hybrid wavefunctions pointing to the four vertices of a tetrahedron, see Fig. 3.11. A set of sample formula is

$$
\begin{aligned}
|t111\rangle &= \frac{1}{2}\left(|2s\rangle + |2px\rangle + |2py\rangle + |2pz\rangle\right), \\
|t\bar{1}1\bar{1}\rangle &= \frac{1}{2}\left(|2s\rangle - |2px\rangle + |2py\rangle - |2pz\rangle\right), \\
|t\bar{1}\bar{1}1\rangle &= \frac{1}{2}\left(|2s\rangle - |2px\rangle - |2py\rangle + |2pz\rangle\right), \\
|t1\bar{1}\bar{1}\rangle &= \frac{1}{2}\left(|2s\rangle + |2px\rangle - |2py\rangle - |2pz\rangle\right).
\end{aligned}
\tag{3.109}
$$

It is the backbone of all alkanes, including methane, ethane, propane, butane, etc., and the crystalline structures of diamond and silicon.

In some quantum chemistry textbooks, those hybrid wavefunctions are depicted as sharply oriented long and narrow bulbs, to emphasize the directional effect. Often, three or four such long and narrow bulbs are shown in a single drawing. As shown here, the accurate amplitude contours of wavefunctions of $sp$-hybridizations span a broad angle. It is difficult to depict three or four such hybrid wavefunctions on a single graph.

By comparing Fig. 3.4 with the vibrational modes of a string, Fig. 1.30, a striking resemblance is found. As an objective reality, wavefunction is of the same nature as the standing waves in classical physics.

## 3.5   Wavefunctions outside the atomic core

In Section 1.4, the solutions of the wave equation inside a basketball are discussed. Similar solutions of the Schrödinger equation inside a spherical

potential well can be obtained. We leave this as a problem. In this section, a similar but more useful problem is discussed: the solutions of the Schrödinger equation *outside* the atomic core, represented by a potential well determined by the nucleus and the electrond inside the atomic core. Such solutions have applications in solid-state physics to describe the wavefunctions of electronic bands in the space surrounding the atomic cores, the of covalent bonds in chemical physics, and atomic-scale tunneling.

Outside the sphere where $r > r_0$, the potential is zero. The Schrödinger equation Eq. 3.6 becomes

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{3.110}$$

The energy $E$ is negative, see Fig 3.12. Introducing a decay constant $\kappa$,

$$\kappa = \frac{\sqrt{-2m_e E}}{\hbar}, \tag{3.111}$$

Equation 3.110 becomes

$$\nabla^2\psi(\mathbf{r}) - \kappa^2\psi(\mathbf{r}) = 0. \tag{3.112}$$

Following the mathematics in Section 1.4, by writing the wavefunction as a product of a radial function $R(r)$ and a spherical harmonics,

$$\psi(\mathbf{r}) = R(r)Y(\theta, \phi), \tag{3.113}$$

the differential equation for the radial function $R(r)$ is

$$\frac{d}{dr}\left(r^2\frac{dR(r)}{dr}\right) - \left[l(l+1) + \kappa^2 r^2\right]R(r) = 0, \tag{3.114}$$

where the parameter $l$ is an index of the spherical harmonics, see Section 1.4.2. Equation 3.114 is almost identical to Eq. 1.135 except that $-k^2$ is replaced by $\kappa^2$. It is expected that the solutions are similar. By direct insertion, one finds the solutions of Eq. 3.114 are

$$R(r) = k_l(\kappa r), \tag{3.115}$$

where

$$k_0(\rho) = \frac{1}{\rho}e^{-\rho}, \tag{3.116}$$

$$k_1(\rho) = \left(\frac{1}{\rho} + \frac{1}{\rho^2}\right)e^{-\rho}, \tag{3.117}$$

and

$$k_2(\rho) = \left(\frac{1}{\rho} + \frac{3}{\rho^2} + \frac{3}{\rho^3}\right)e^{-\rho}, \tag{3.118}$$
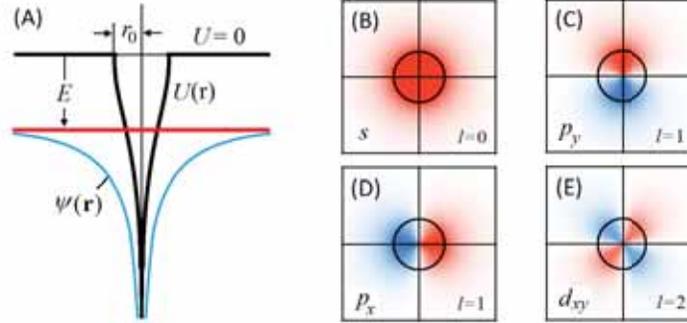
**Fig. 3.12. Wavefunctions outside a spherical potential well.** (A) The energy diagram. (B) through (E), the wavefunctions are specified by the azimuthal quantum number $l$ and the magnetic quantum number $m$, determined by the wavefunctions inside the sphere, which can be understood as the vacuum tails of the wavefunctions inside the sphere. Wavefunctions with the same $l$ but different $m$ are degenerate.

for $l = 0$, 1, and 2, respectively. The general expression is

$$k_l(\rho) = (-\rho)^l \left( \frac{d}{\rho d\rho} \right)^l \frac{e^{-\rho}}{\rho}. \tag{3.119}$$

Although those functions are elementary, due to their origin, they are called *spherical modified Bessel functions*, see Appendix D.

Figure 3.12(A) shows the energy diagram and wavefunctions. A wavefunction inside the sphere $\psi(\mathbf{r})$ is a solution of a Schrödinger equation inside the sphere with potential function $U(r)$. Similar to the acoustic waves in Section 1.4, it is a product of a radial function $R(r)$ and a spherical harmonics $Y(\theta, \phi)$. The spherical harmonics is labeled by an azimuthal quantum number $l$ and a magnetic quantum number $m$.

Outside the sphere, the potential is zero. The wavefunctions are shown in Fig. 3.12 (B) through (E). At the boundary $r = r_0$, their values match those of the wavefunctions inside the sphere. As a vacuum tail of a wavefunction inside the sphere, it decays with radius $r$. Nevertheless, the angular dependence characterized by the spherical harmonics is preserved.

### 3.5.1   *s*-type wavefunction

Here we present an elementary derivation of the *s*-type wavefunction outside an atomic core.

In general, the Schrödinger equation of tip wavefunction outside the atomic core is

$$-\frac{\hbar^2}{2m} \nabla^2 \chi_\nu = E_\nu \, \chi_\nu. \tag{3.120}$$

Consider first a spherically symmetric tip wavefunction, centered at the nucleus of the tip atom at coordinates $\mathbf{r}_0$. For a point in space $\mathbf{r}$, the distance from that point to the center of the tip atom is

$$r = |\mathbf{r} - \mathbf{r}_0|. \tag{3.121}$$

Equation **??** becomes

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}(r\chi_\nu) = E_\nu\chi_\nu. \tag{3.122}$$

Intruducing a decay constant

$$\kappa = \sqrt{\frac{-2mE_\nu}{\hbar}}, \tag{3.123}$$

denoting $u = \kappa r$ and $f(u) = \chi_\nu/u$, Eq. 3.122 becomes

$$\frac{d^2 f(u)}{du^2} = f(u). \tag{3.124}$$

The solutions are

$$f(u) = e^u \quad \text{and} \quad f(u) = e^{-u}. \tag{3.125}$$

The first solution diverges at a large distance. Therefore, the only valid solution is

$$\chi_s(r) = \frac{C_s}{\kappa r}e^{-\kappa r}. \tag{3.126}$$

It is the spherically symmetric wavefunction, or an $s$-type wavefunction.

### 3.5.2 $p$-type wavefunctions

Here we show that the $p$-type wavefunctions outside an atomic core is the partial derivative of the $s$-type wavefunction. This is useful in the treatment of atomic forces in Chapter 5 and tunneling rates in Chapter 7.

Because the $s$-type spherical harmonics is a constant, the wavefunctions outside an atomic core up to a constant is

$$\chi_s(\mathbf{r}) = \frac{1}{\kappa r}e^{-\kappa r}. \tag{3.127}$$

From Eq. 3.110, if $\psi(\mathbf{r})$ is a solution, then a partial derivative of $\psi(\mathbf{r})$ is also a solution,

$$\frac{\partial}{\partial x}\left[-\frac{\hbar^2}{2m_e}\nabla^2\psi(\mathbf{r})\right] = -\frac{\hbar^2}{2m_e}\nabla^2\left[\frac{\partial\psi(\mathbf{r})}{\partial x}\right] = E\left[\frac{\partial\psi(\mathbf{r})}{\partial x}\right]. \tag{3.128}$$

Therefore, the $x$-partial derivative of $\chi_s(\mathbf{r})$

$$\frac{\partial}{\partial x}\left[\frac{1}{\kappa r}e^{-\kappa r}\right] = \frac{x}{r}\left(\frac{1}{\kappa r} + \frac{1}{(\kappa r)^2}\right)e^{-\kappa r} \tag{3.129}$$

is also a valid wavefunctions outside an atomic core. According to Table 1.4, the $px$ type spherical harmonics, $Y_{11}^g(\theta, \phi)$, up to a constant, is

$$Y_{11}^g(\theta, \phi) = \sin\theta\cos\phi = \frac{x}{r}, \tag{3.130}$$

Equation 3.129 is the $px$-type wavefunctions outside an atomic core. Similarly, we have up to a constant,

$$\chi_{px}(\mathbf{r}) = \frac{\partial\chi_s(\mathbf{r})}{\partial x} = \left(\frac{1}{\kappa r} + \frac{1}{(\kappa r)^2}\right) e^{-\kappa r} \sin\theta\cos\phi, \tag{3.131}$$

$$\chi_{py}(\mathbf{r}) = \frac{\partial\chi_s(\mathbf{r})}{\partial y} = \left(\frac{1}{\kappa r} + \frac{1}{(\kappa r)^2}\right) e^{-\kappa r} \sin\theta\sin\phi, \tag{3.132}$$

and

$$\chi_{pz}(\mathbf{r}) = \frac{\partial\chi_s(\mathbf{r})}{\partial z} = \left(\frac{1}{\kappa r} + \frac{1}{(\kappa r)^2}\right) e^{-\kappa r} \cos\theta. \tag{3.133}$$

## 3.6 General properties of wavefunctions

In this Chapter, we presented wavefunctions as the solution of the Schrödinger equation through three example. Here are the general properties of the wavefunctions. Those properties are similar to those in acoustics, see Section 1.2. For simplicity, we use Dirac notations.

### 3.6.1 Normalization

According to Schrödinger, the square of the wavefunction is proportional to the charge density of the electron as a field in space

$$\rho(\mathbf{r}) = -e\psi^2(\mathbf{r}). \tag{3.134}$$

The total charge of an electron is $-e$. Therefore, the wavefunction is normalized over the entire space,

$$\langle\psi|\psi\rangle \equiv \int \psi^2(\mathbf{r})\, d^3\mathbf{r} = 1. \tag{3.135}$$

### 3.6.2 Orthogonality

Wavefunctions with different energy eigenvalues are orthogonal. For two wavefunctions with different energy eigenvalues $E_1 \neq E_2$, the Schrödinger equations are

$$\hat{H}|\psi_1\rangle = E_1|\psi_1\rangle \tag{3.136}$$

and

$$\hat{H}|\psi_2\rangle = E_2|\psi_2\rangle. \tag{3.137}$$

Multiply Eq. 3.136 by $\langle \psi_2 |$ and multiply Eq. 3.137 by $\langle \psi_1 |$, the difference is

$$\langle \psi_1 | \hat{H} | \psi_2 \rangle - \langle \psi_2 | \hat{H} | \psi_1 \rangle = (E_2 - E_1) \langle \psi_1 | \psi_2 \rangle. \tag{3.138}$$

By definition, the right-hand side of Eq. 3.138 is zero. Therefore, if $E_2 - E_1 \neq 0$, one must have

$$\langle \psi_1 | \psi_2 \rangle = 0. \tag{3.139}$$

### 3.6.3 Completeness

If the eigenfunctions of an energy operator are

$$\hat{H} | \psi_n \rangle = E_n | \psi_n \rangle, \quad n = 1, 2, ... \infty, \tag{3.140}$$

For an arbitrary function $|\chi\rangle$, define a coefficient

$$c_n = \langle \chi | \psi_n \rangle, \quad n = 1, 2, ... \infty, \tag{3.141}$$

then the set of eigenfunctions is *complete* means

$$|\chi\rangle = \sum_{n=0}^{\infty} c_n | \psi_n \rangle. \tag{3.142}$$

For the three examples in this Chapter, the series of eigenfunctions are complete. If this is true, then an arbitrary function can be expended into a series of eigenfunctions from that energy operator.

### 3.6.4 Charge density distributions

For a single electron wavefunction, according to Schrödinger, the charge density is proportional to the square of the wavefunction,

$$\rho(\mathbf{r}) = -e\psi^2(\mathbf{r}). \tag{3.143}$$

If the electronic states are degenerate, a linear superposition of wavefunctions of the same energy eigenvalues is also a good wavefunction for that energy eigenvalue. The square of the new wavefunction also represents an electron charge density. Here is an example. The $2px$-state and $2py$-state are degenerate. The wavefunctions from Table 3.2 are

$$\psi_{2px} = \frac{1}{4\sqrt{2\pi}} e^{-r/2} \, r \sin \theta \cos \phi \tag{3.144}$$

and

$$\psi_{2py} = \frac{1}{4\sqrt{2\pi}} e^{-r/2} \, r \sin \theta \sin \phi. \tag{3.145}$$

The charge density distributions are

$$\rho_{2px} = -\frac{e}{32\pi} e^{-r} \, r^2 \sin^2 \theta \cos^2 \phi \tag{3.146}$$

and

$$\rho_{2py} = -\frac{e}{32\pi}e^{-r}\,r^2\sin^2\theta\sin^2\phi, \qquad (3.147)$$

as shown in Fig. 3.13(1) and (2).

Because any linear combination of the wavefunctions Eq. 3.144 and 3.145 is also a good wavefunction, by rotating the coordinate system 45°, the following wavefunctions are legitimate:

$$\psi_{2p1} = \frac{1}{4\sqrt{2\pi}}e^{-r/2}\,r\sin\theta\cos\left(\phi - \frac{\pi}{4}\right) \qquad (3.148)$$

and

$$\psi_{2p2} = \frac{1}{4\sqrt{2\pi}}e^{-r/2}\,r\sin\theta\sin\left(\phi - \frac{\pi}{4}\right). \qquad (3.149)$$

The charge density distributions are

$$\rho_{2p1} = -\frac{e}{32\pi}e^{-r}\,r^2\sin^2\theta\cos^2\left(\phi - \frac{\pi}{4}\right) \qquad (3.150)$$

and

$$\rho_{2p2} = -\frac{e}{32\pi}e^{-r}\,r^2\sin^2\theta\sin^2\left(\phi - \frac{\pi}{4}\right), \qquad (3.151)$$

as shown in Fig. 3.13(3) and (4).

Therefore, the electrical charge density of individual wavefunctions depends on the choice of coordinate system. Nevertheless, the sum of Eqs. 3.146 and 3.147 is coordinate-independent. In a plane $z = 0$, it is

$$\rho_{2p} = -\frac{e}{32\pi}e^{-r}\,r^2, \qquad (3.152)$$

and identical to the sum of Eqs. 3.150 and 3.151.

The charge density of an individual wavefunction may not represent the physical reality. Nevertheless, the sum of electrical charges of *all* wavefunctions of the same energy eigenvalue

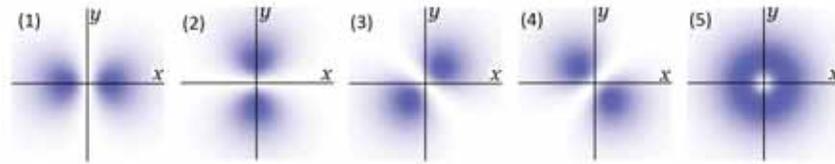$$\rho(\mathbf{r}) = -e\sum\psi^2(\mathbf{r}) \qquad (3.153)$$



**Fig. 3.13. Charge density of the 2p states.** (1) and (2), charge density distributions of the 2px- and 2py-states. (3) and (4), the 2p-states rotated around the z-axis by 45°. (5) The sum of (1) and (2), or the sum of (3) and (4), represents measurable physical reality.

is invariant under a coordinate rotation. Experimental observation provides the total density distribution of all wavefunctions at the same energy level. For example, in the Hartree-Fock approximation of the the sodium atom, the outer valence electron is moving in the field of the $s$-states and the six degenerate $2p$ states. Only the collective effect of the six $2p$ states, forming a spherical symmetric electrical charge, is an observable reality.

This observation hints to a powerful theorem in quantum mechanics: the Hohenberg-Kohn theorem, that at least for the ground state, the total charge density distribution function of the entire system contains complete information about the system, as we shell present in Chapter 4. Nevertheless, the individual wavefunctions, also called orbitals, are necessary and indispensible in the computation and understanding of the atomic system. Take an analogy, although the mechanical phenomena is independent of the choice of coordinate system and invariant under a rotation of the coordinate system, to study and calculate a mechanical process, the choice of a specific coordinate system is necessary.

## 3.7 Quantization of bosons

The creation operator and annihilation operator presented in Section 3.3.1 are the basis of quantum field theory. The energy of a harmonic oscillator is an integer multiple of an elementary energy, $\epsilon = \hbar\omega$, plus the zero-point energy $\epsilon/2$. The zero point energy is not observable. Each chunk of energy, $\epsilon = \hbar\omega$, is identified as a particle. Note that in quantum mechanics, the term particle does not mean a material point which can be represented by a coordinate $\mathbf{r}$ or a trajectory $\mathbf{r}(t)$. The term particle means a chunk of energy, mass, or electricity as an integer multiple of an elementary value. In all cases, the so-called particle is always spread out in space.

### 3.7.1 Bosons and fermions

In quantum mechanics, there are two types of particles, bosons and fermions. For bosons, such as photons, each energy level can have any number of particles. For fermions, such as electrons, each energy level can have at most one particle. In other words, the occupation number of fermions is either zero or one. Here we present the quantization of bosons. The quantization of fermions will be presented in Chapter 4.

### 3.7.2 Fock space of bosons

For a system which can be described by a single harmonic oscillator, as we have presented in Section 3.3.1, the state of an energy level is represented by a non-negative integer, the particle occupation number $n$. An empty

energy level with zero particle, the vacuum, is denoted by $|0\rangle$. An energy level with $n$ particles can be expressed through the creation operator

$$|n\rangle = \frac{1}{\sqrt{n!}} \left(\hat{a}^\dagger\right)^n |0\rangle. \tag{3.154}$$

The number of particles in an energy level can be determined using the particle number operator,

$$\hat{N} \equiv \hat{a}^\dagger \hat{a}, \tag{3.155}$$

because its eigenvalue is the number of energy quanta,

$$\hat{N}|n\rangle = n|n\rangle. \tag{3.156}$$

For a system of $m$ harmonic oscillators, the empty state is defined as

$$|0\rangle \equiv |0, 0, ..., 0\rangle \tag{3.157}$$

where there are $m$ zeros. With a number of creation operators and annihilation operators, a general state is defined as

$$|n_1, n_2, ..., n_m\rangle = \frac{\left(\hat{a}_1^\dagger\right)^{n_1}}{\sqrt{n_1!}} \frac{\left(\hat{a}_2^\dagger\right)^{n_2}}{\sqrt{n_2!}} ... \frac{\left(\hat{a}_m^\dagger\right)^{n_m}}{\sqrt{n_m!}} |0\rangle, \tag{3.158}$$

which has $n_1$ bosons in energy level 1, $n_2$ bosons in energy level 2, and so on. Such a representation of states is called *particle number representation*, and the collection of states such as in Eq. 3.158 is called a *Fock space.* Note that for bosons, all elements in the Fock space are non-negative integers. Examples of applications of the particle-number representation and Fock space to electromagnetic waves are presented in Chapter 9.

# Chapter 4

# Many-Electron Systems

Eyewitnessed the success of Schrödinger's non-relativistic wave equation in condensed-matter physcis, in 1929, Paul Dirac made the following statement in a paper entitled *Quantum Mechanics of Many-Electron Systems*:

> The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between electrons and nuclei.

Analytic solutions of the Schrödinger equation are only available for two natural systems, the hydrogen atom and the hydrogen molecular ion, $H_2^+$. Both are single electron system. For atoms and molecules with two or more electrons, approximations are required. Over the last century, many effective approximate methods have been developed, culminated with two Nobel Prizes in Chemistry to John Pople and Walter Kohn in 1998. Quantum mechanics of many-electron systems is still an active research field. New methods and approximations are intensively pursued. In this Chapter, the principles and some most important approximate methods are presented.

## 4.1   Many-electron Schrödinger equation

Following the argument leading to the single-electron Schrödinger's equation in Chapter 3, a many-electron wave equation can be introduced from the classical energy integral and the de Broglie relation. Because the mass of an nucleus is thousands of times greater than the mass of an electron, in almost all computations, the coordinates of the nuclei are treated as fixed input parameters. The accuracy of such approximation was analyzed mathematically by Born and Oppenheimer in 1927. For a system with $M$ electrons with coordinates $\mathbf{r}_j$ in a potential field formed by $N$ nuclei, the

classical energy integral, similar to that for a single electron, Eq. 3.3, is

$$\sum_{j=1}^{j=M} \left[ \frac{\mathbf{p}_j^2}{2m_e} + v(\mathbf{r}_j) \right] + \sum_{i>j>0}^{i=M} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} = E. \tag{4.1}$$

where the external potential $v(\mathbf{r}_j)$ is the total attractive potential of all nuclei on the $j$-th electron at position $\mathbf{r}_j$,

$$v(\mathbf{r}_j) = -\sum_{l=1}^{l=N} \frac{Z_l\, e^2}{|\mathbf{r}_j - \mathbf{R}_l|}, \tag{4.2}$$

where $\mathbf{R}_l$ is the position of the $l$-th nucleus with atomic number $Z_l$. The second sum in Eq. 4.1 is the repulsive potential between pairs of electrons, and the condition $i > j$ is to avoid double counting.

The wavefunction as a function of the positions of the electrons is

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_M). \tag{4.3}$$

The wave vector associated to the $j$-th electron is

$$k_j^2 = -\frac{1}{\psi} \nabla_j^2 \psi, \tag{4.4}$$

where the Laplacian for the $j$-th electron is

$$\nabla_j^2 = \frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}. \tag{4.5}$$

Using the de Broglie relation,

$$p_j^2 = \hbar^2 k_j^2, \tag{4.6}$$

we obtain the Schrödinger equation for the wavefunction $\psi$,

$$\sum_{j=1}^{j=M} \left[ -\frac{\hbar^2 \nabla_j^2}{2m_e} + v(\mathbf{r}_j) \right] \psi + \sum_{i>j>0}^{i=M} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \psi = E\psi. \tag{4.7}$$

**Table 4.1: Atomic units**

| Quantity | Name | Notation | Value in SI |
|----------|------|----------|-------------|
| Mass | electron mass | $m_e = 1$ | $9.109 \times 10^{-31}$ kg |
| Charge | electron charge | $|e| = 1$ | $1.602 \times 10^{-19}$ C |
| Action | Dirac constant | $\hbar = 1$ | $1.0546 \times 10^{-34}$ J·s |
| Length | Bohr radius $a_0$ | $\hbar^2/m_e e^2$ | 0.05291 nm |
| Energy | hartree | $m_e e^4/\hbar^2$ | 27.211 eV |

By using atomic units, see Table 4.1,

$$\hbar = e = m_e = 1, \tag{4.8}$$

Equation 4.7 is simplified to

$$\sum_{j=1}^{j=M} \left[ -\frac{1}{2}\nabla_j^2 + v(\mathbf{r}_j) \right] \psi + \sum_{i>j>0}^{i=M} \frac{1}{r_{ij}} \psi = E\psi, \tag{4.9}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and Eq. 4.2 becomes

$$v(\mathbf{r}_j) = -\sum_{l=1}^{l=N} \frac{Z_l}{|\mathbf{r}_j - \mathbf{R}_l|}. \tag{4.10}$$

## 4.2 The Hartree-Fock method

Equation 4.9 is complicated. In 1928, Douglas Hartree invented a method to resolve Eq. 4.9 by writing the wavefunction of $M$ electrons as a product of $M$ single-electron wavefunctions,

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_M) = \psi_1(\mathbf{r}_1)\,\psi_2(\mathbf{r}_2)\ldots\psi_M(\mathbf{r}_M). \tag{4.11}$$

Equation 4.9 is then decomposed into $M$ differential equations. The individual wavefunctions, or orbitals, are orthogonal and normalized,

$$\int \psi_i(\mathbf{r})\psi_j(\mathbf{r})\,d^3\mathbf{r} = \delta_{ij}. \tag{4.12}$$

### 4.2.1 The self-consistent field

Take an example of helium atom, where $M = 2$, $N = 1$, and $Z = 2$, and set the nucleus at the origin of the coordinate system, $\mathbf{R} = 0$,

$$\left[ -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \frac{1}{r_{12}} - E \right] \psi_1(\mathbf{r}_1)\,\psi_2(\mathbf{r}_2) = 0, \tag{4.13}$$

where $E$ is the energy eigenvalue to be determined. Multiply Eq. 4.13 by $\psi_2(\mathbf{r}_2)$ and integrate over the space, using Eq. 4.12, one finds

$$\left[ -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + v_{ee}(\mathbf{r}_1) - E_1 \right] \psi_1(\mathbf{r}_1) = 0, \tag{4.14}$$

where

$$E_1 = E + \int d^3\mathbf{r}_2\,\psi_2(\mathbf{r}_2) \left[ \frac{1}{2}\nabla_2^2 + \frac{2}{r_2} \right] \psi_2(\mathbf{r}_2) \tag{4.15}$$

is a new energy eigenvalue for electron 1 to be determined. The integration in Eq. 4.15 is obviously independent of the variable $\mathbf{r}_1$.

The electron-electron repulsion potential in Eq. 4.14 is

$$v_{ee}(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \frac{|\psi_2(\mathbf{r}_2)|^2}{r_{12}}. \tag{4.16}$$

Because the electric charge is defined as $|e| = 1$, the square of the wavefunction of electron 2 is its charge density,

$$\rho_2(\mathbf{r}_2) = |\psi_2(\mathbf{r}_2)|^2, \tag{4.17}$$

the electron repulsion potential in Eq. 4.14 is then

$$v_{ee}(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \frac{\rho_2(\mathbf{r}_2)}{r_{12}}. \tag{4.18}$$

Equation 4.14 has an intuitive explanation. Electron 1 is moving in the potential field of the nucleus and the charge density of electron 2.

Similarly, a differential equation for electron 2 can be derived,

$$\left[ -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + v_{ee}(\mathbf{r}_2) - E_2 \right] \psi_2(\mathbf{r}_2) = 0, \tag{4.19}$$

where $v_{ee}(\mathbf{r}_2)$ is the electron-electron repulsion potential on electron 2 generated by the charge density of electron 1, $\rho_1(\mathbf{r}_1) = |\psi_1(\mathbf{r}_1)|^2$. Equations 4.14 and 4.19 are the one-electron equations for the two-electron system. It can be extended to systems of more than two electrons.

The two equations are correlated to each other. To solve the equation for electron 1, the orbital of electron 2 is required. Those equations are always resolved using *iteration*: By first guess a set of initial orbitals, do the computation, then used the results of the first round of computation as the basis for the second round, and so on, until the results converge. This method, invented by Hartree, is termed *self-consistent field*.

## 4.2.2  Pauli exclusion principle and Slater determinants

As we have presented in Section 3.6.1, because the electrom is a fermion, no two electrons can occupy a single state. The *Pauli exclusion principle* should be applied to the wavefunctions. The standard representation of the exclusion principle, as proposed by John Slater in 1930, is to write the wavefunction as a determinant. For a two-electron system,

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left[ \psi_1(\mathbf{r}_1)\,\psi_2(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\,\psi_2(\mathbf{r}_1) \right]. \tag{4.20}$$

By exchanging any two rows or any two columns, the wavefunction changes sign. Therefore, if any two rows are identical, the Slater determinant becomes zero. The square root of 2 is added for normalization. For general definition and properties of determinates, see Appendix C.

### 4.2.3 The electron spin

As we presented in Section 2.5, each electron wavefunction can have two spin states. Helium is an interesting example to show the effect of spin, see Fig. 4.1. The two electrons can have opposite spin states, one spin up and one spin down, to form a state called parahelium. The two electrons can also have the same spin state, both spin up or both spin down, to form a state called orthohelium. Those types of states cannot make a transition to the other one by optical means. For parahelium, the spin states of the two electrons are different. The spatial wavefunction can be identical. The lowest state is $1s$, similar to the ground state of hydrogen. The energy level is -24.47 eV, almost twice as that of hydrogen, as expected.

### 4.2.4 Exchange interaction

For orthohelium, the wavefunction of the entire atom is a Slater determinant. The Schrödinger equation is

$$\left[ -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + \frac{1}{r_{12}} - E \right] \left| \begin{array}{cc} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) \end{array} \right| = 0. \qquad (4.21)$$

Following the same procedure leading to Eq. 4.14, by multiplying the equation with $\psi_2(\mathbf{r}_2)$ then integrate over $\mathbf{r}_2$, one finds

$$\left[ -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + v_{ee}(\mathbf{r}_1) - E_1 \right] \psi_1(\mathbf{r}_1) = v_{xc}(\mathbf{r}_1)\,\psi_2(\mathbf{r}_1), \qquad (4.22)$$
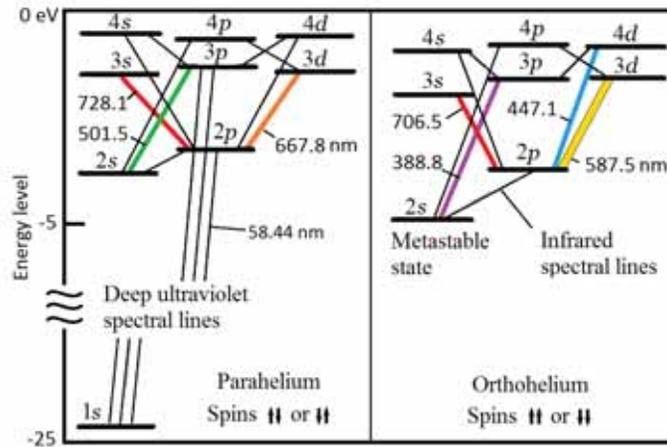


**Fig. 4.1. Energy diagram of helium atom.** For parahelium, the spins of the two electrons are antiparallel, and the spatial wavefunction can be identical. The orbitals of the lowest are $1s$, with no nodes. For orthohelium, the spin states are parallel. One of the spatial orbitals must have a node. The energy level is higher.

where

$$v_{xc}(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \frac{\psi_2(\mathbf{r}_2)\psi_1(\mathbf{r}_1)}{r_{12}} \tag{4.23}$$

is the *exchange potential* that acting to the second orbital. Similarly,

$$\left[ -\frac{1}{2}\nabla_2^2 - \frac{2}{r_2} + v_{ee}(\mathbf{r}_2) - E_2 \right] \psi_2(\mathbf{r}_2) = v_{xc}(\mathbf{r}_2)\, \psi_2(\mathbf{r}_2), \tag{4.24}$$

where the exchange interaction potential is

$$v_{xc}(\mathbf{r}_2) = \int d^3\mathbf{r}_1 \frac{\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)}{r_{12}}. \tag{4.25}$$

With the exchange potentials, Eqs. 4.23 and 4.25, the accuracy is greatly improved, while the computation is much more demanding. The above equations, often called the *Hartree-Fock method*, is widely used in the quantum-mechanical computations of atoms and small molecules.

The two orbitals in Eq. 4.21, $\psi_1$ and $\psi_2$, must be orthogonal. If one of them is an $1s$-state, the other one must have a node. Such an orbital with lowest energy is $2s$, see Fig. 3.8. With a node, the energy level is much higher, see Fig. 4.1. Although the lowest state of orthohelium is about 20 eV higher than the lowest state of parahelium, no optical process can make a transition to a state on parahelium. The ground state of orthohelium can stay for a long time. It is called a metastable state.

The observed spectrum of helium is shown in Fig. 4.2. Seven strongest spectral lines in the visible region are shown. For parahelium, the spectral lines to or from the ground state are in deep ultraviolet region. For orthohelium, the lines are in visible and infrared region.
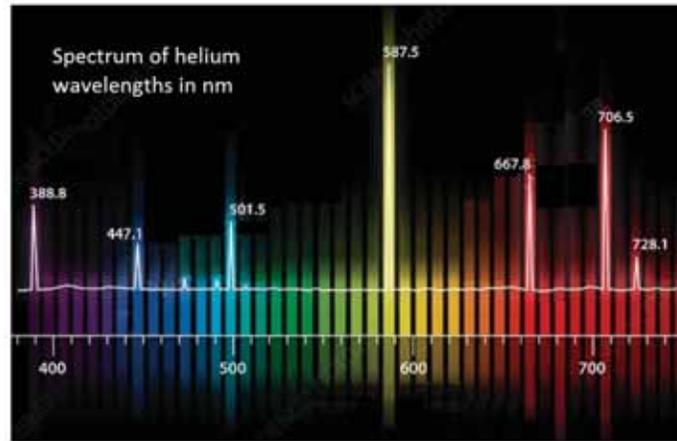


**Fig. 4.2. Observed spectrum of helium atom.** The most intensive spectral lines in the visible range are shown. Wavelengths are in nanometers.
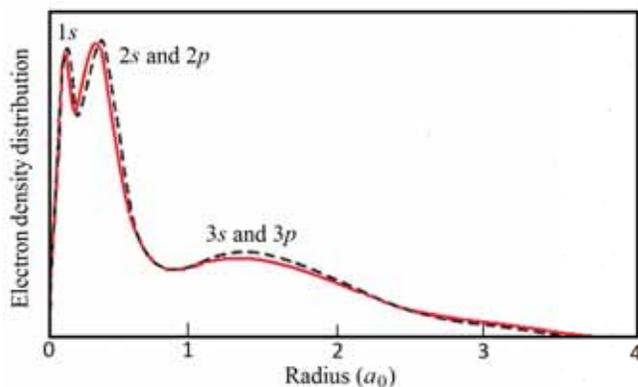
**Fig. 4.3. Density distributions of electrons in argon, theory and experiment.** The electron density distribution is defined by Eq. 4.35. The red curve is from electron diffraction experiments, and the dashed curve is from Hartree-Fock computation.

### 4.2.5 Accuracy of self-consistent computations

According to Schrödinger, the electron density distribution, represented by $\psi^2$, is a measurable physical quantity. Therefore, the accuracy of the Hartree-Fock computations can be verified experimentally. Figure 4.3 shows a comparison of the electron charge density obtained by electron diffraction experiments and the result of Hartree-Fock computation.[1]

The red curve in Fig. 4.3 is the electron distribution measured by electron diffraction experiments. The dashed curve is the result of numerical quantum-mechanical computation. The agreement is satisfactory. The total electron density distribution is the basis of the density functional theory for numerical computations, see Section 4.4.

## 4.3 More complicated atoms

The Hartree-Fock method has been successfully applied to compute the wavefunctions of all atoms. The results are listed in the open literature, in the form of expansions in terms of atomic basis functions.

### 4.3.1 Atomic basis functions

The hydrogen radial wavefunctions are products of a polynomial of $r$ and an exponential function, see Table 3.2. For practical computations, those functional forms are still too complicated. In 1930, John Slater defined a set of base functions as simplified versions of the hydrogen wavefunction, and

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[1]See L. S. Bartell and L. O. Brockway, *The Investigation of Electron Distribution in Atoms by Electron Diffraction*, Physical Review, **90**, 833 (1953).

then widely used in numerical computations involving atoms and molecules. An atomic wavefunction is expressed as a radial function times a spherical harmonics, see Table 1.4. The radial function is expanded as a sum of Slater base functions, abbreviated as SBF, defined as

$$S_n(r) = N_n \, r^{n-1} e^{-\zeta r}, \tag{4.26}$$

where $n$ is the principle quantum number. The normalization constant is

$$N_n = \frac{(2\zeta)^{(n+\frac{1}{2})}}{\sqrt{(2n)!}}. \tag{4.27}$$

The explicit formulas for $n = 1$ through $n = 3$ are

$$S_1(r) = \sqrt{\frac{(2\zeta)^3}{2!}} \, e^{-\zeta r}, \tag{4.28}$$

$$S_2(r) = \sqrt{\frac{(2\zeta)^5}{4!}} \, r \, e^{-\zeta r}, \tag{4.29}$$

and

$$S_3(r) = \sqrt{\frac{(2\zeta)^7}{6!}} \, r^2 e^{-\zeta r}, \tag{4.30}$$

The Slater basis functions are quite similar to the authentic hydrogen wavefunctions, and are widely used to represent atomic orbitals. Nevertheless, the integrals such as in Eqs. 4.16 and 4.23 must be evaluated numerically. Another type of atomic base functions, the *Gaussian basis functions*,



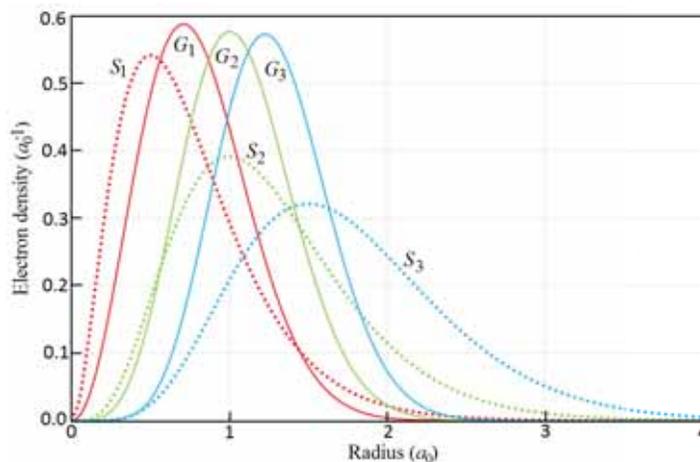**Fig. 4.4. Electron density distributions of several basis functions.** For SBFs, the parameter $\zeta$ is 2.0. For GBFs, the parameter $\alpha$ is 1.0. All electron density distributions are normalized to $r$, such that the area below each curve is 1.

abbreviated as GBF, are more frequently used in calculation of molecules. The radial functions are defined as

$$G_n(r) = \sqrt{\frac{2(4\alpha)^n}{(2n-1)!!}} \sqrt{\frac{2\alpha}{\pi}} r^{n-1} e^{-\alpha r^2}. \tag{4.31}$$

The explicit formulas for $n = 1$ through $n = 3$ are

$$G_1(r) = 2 \left( \frac{8\alpha^3}{\pi} \right)^{\frac{1}{4}} e^{-\alpha r^2}, \tag{4.32}$$

$$G_2(r) = 4 \left( \frac{8\alpha^5}{9\pi} \right)^{\frac{1}{4}} r\, e^{-\alpha r^2}, \tag{4.33}$$

and

$$G_3(r) = 8 \left( \frac{8\alpha^7}{225\pi} \right)^{\frac{1}{4}} r^2\, e^{-\alpha r^2}. \tag{4.34}$$

A significant advantage of the GBF is, all integrals involved have analytic expressions. Numerical computations are greatly simplified.

Electron density plots of those atomic basis functions are shown in Fig. 4.4. To make a fair comparison, the radius dependence of the electron density $\rho(r)$ from a basis function $f(r)$ is expressed as

$$\rho(r)dr = r^2 |f(r)|^2 dr, \tag{4.35}$$

such that the density distribution is normalized in radius $r$,

$$\int_0^\infty \rho(r)dr = 1. \tag{4.36}$$

The SBFs are very close to the hydrogen wavefunctions, and the tails extend more to the space. the GBFs are cut off sharply for large $r$. Therefore, to accurately represent an atomic wavefunction, a larger number of GBFs are required.

A complete orbital is a product of a radial factor and a spherical harmonics. Examples of GBFs in terms of Cartesian coordinates are,

$$g_s(\alpha, r) = \left( \frac{2\alpha}{\pi} \right)^{\frac{3}{4}} e^{-\alpha r^2}, \tag{4.37}$$

$$g_z(\alpha, r) = \left( \frac{128\alpha^5}{\pi^3} \right)^{\frac{1}{4}} z\, e^{-\alpha r^2}, \tag{4.38}$$

and

$$g_{xy}(\alpha, r) = \left( \frac{2048\alpha^7}{\pi^3} \right)^{\frac{1}{4}} xy\, e^{-\alpha r^2}. \tag{4.39}$$

For more details on GBFs, see the monograph *Ab Initio Molecular Orbital Theory* coauthored by John Pople, and many more recent books.

### 4.3.2   The Roothaan-Hartree-Fock method

In 1951, Clemens Roothaan invented a method to compute atomic orbitals by expanding each one as a sum of SBFs, see Eq. 4.26,

$$R_{nl}(r) = \sum_j C_{jln} S_{jl} \tag{4.40}$$

An atomic orbital with principle quantum number $n$ and azimuthal quantum number $l$ is a sum of several SBFs with expansion coefficients $C_{jln}$. Each SBF is described by an integer $n_{jl}$ and an exponent $\zeta_{jl}$, which determine the normalization constant $N_{jl}$, see Eqs. 4.26, and 4.27,

$$S_{jl} = N_{jl}\, r^{n_{jl}-1} e^{-\zeta_{jl} r}. \tag{4.41}$$

The coefficients $C_{jln}$ and the exponents $\zeta_{jl}$ are then computed using the Hartree-Fock equations with a self-consistent procedure, similar to Eqs. 4.22 and 4.24. A table of Roothaan-Hartree-Fock atomic wavefunctions was published as www.ccl.net/cca/data/atomic-RHF-wavefunctions/tables.html.

The published data for atomic wavefunctions is the starting point of understanding their chemical property, and the ab-initio quantum-mechanical computations. Here we show two examples of lithium and carbon.

### 4.3.3   Lithium

Figure 4.5 shows part of the RHF-wavefunction data table for lithium, annotated for easy understanding. Each atomic orbital is a sum of seven Slater basis functions. The electron density distributions as a function of distance, according to Eq. 4.35, are shown in Fig. 4.6.

As shown, the electron density of the $1s$ state of the lithium atom has a small radius, almost one half of that of the ground-state hydrogen. The valence electron $2s$ is loosely attached to the core. With a small ionization energy, the lithium atom can easily loose an electron to become a positive ion with a very small radius, ideal for rechargeable battery.

| $j$ | $n_j l_j$ | $\zeta_j$ | $C_j$: 1s | $C_j$: 2s |
|---|---|---|---|---|
| 1 | 1S | 4.3069 | 0.141279 | -0.022416 |
| 2 | 1S | 2.4573 | 0.874231 | -0.135791 |
| 3 | 3S | 6.7850 | -0.005201 | 0.000389 |
| 4 | 2S | 7.4527 | -0.002307 | -0.000068 |
| 5 | 2S | 1.8504 | 0.006985 | -0.076544 |
| 6 | 2S | 0.7667 | -0.000305 | 0.340542 |
| 7 | 2S | 0.6364 | 0.000760 | 0.715708 |

**Fig. 4.5.   Data for the wavefunctions of lithium.** The data set is adapted from open literature, see Section 4.3.2. Each item is annotated for easy understanding.
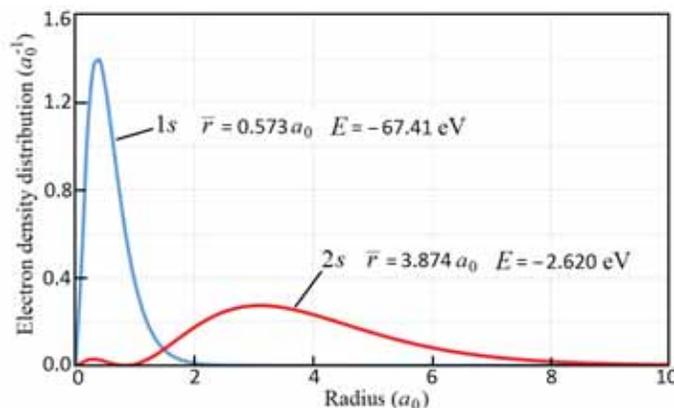
**Fig. 4.6. Density distributions of electrons in lithium.** The electron density distributions defined in Eq. 4.35 as a function of $r$ are shown. Being normalized to $r$, the area below each curve is 1. Not that the $1s$ electrons are tightly bounded to the nucleus. It can easily loose a $2s$ electron to become a positive ion with tiny radius.

### 4.3.4 Carbon

Figure 4.7 shows part of the RHF-wavefunction data table for carbon, annotated for easy understanding. Each carbon atom has two $1s$ orbitals, two $2s$ orbitals, and two $2p$ orbitals.

As shown, the two $2s$ orbitals and the two $2p$ orbitals have similar radius and energy level. Linear combinations of those orbitals could make four hybridized orbitals. It is the basis of organic chemistry and molecular biology, and the strongest chemical bond in diamond. See Chapter 5.

The accuracy of those numerical computations of atoms can be tested directly with experimental observations. First, the energy eigenvalues of each orbitals, including the deepest ones, are the basis of X-ray spectroscopy. Second, using electron diffraction or X-ray diffraction, the charge density distribution in atoms can be measured directly. Both are well-verified. The total electron density distribution function is also the conceptual basis of density functional theory, see Section 4.4.

| $j$ | $n_j l_j$ | $\varsigma_j$ | $C_j$: 1s | $C_j$: 2s | $j$ | $n_j l_j$ | $\varsigma_j$ | $C_j$: 2p |
|---|---|---|---|---|---|---|---|---|
| 1 | 1S | 8.4936 | 0.352872 | −0.071727 | 1 | 2P | 7.0500 | 0.006977 |
| 2 | 1S | 4.8788 | 0.473621 | 0.438307 | 2 | 2P | 3.2275 | 0.070877 |
| 3 | 3S | 15.4660 | −0.001199 | −0.000383 | 3 | 2P | 2.1908 | 0.230802 |
| 4 | 2S | 7.0500 | 0.210887 | −0.091194 | 4 | 2P | 1.4413 | 0.411931 |
| 5 | 2S | 2.2640 | 0.000886 | −0.393105 | 5 | 2P | 1.0242 | 0.350701 |
| 6 | 2S | 1.4747 | 0.000465 | −0.579121 | | | | |
| 7 | 2S | 1.1639 | −0.000119 | −0.126067 | | | | |

**Fig. 4.7. Data for the wavefunctions of carbon.** The data set is adapted from open literature, see Section 4.3.2. Each item is annotated for easy understanding.
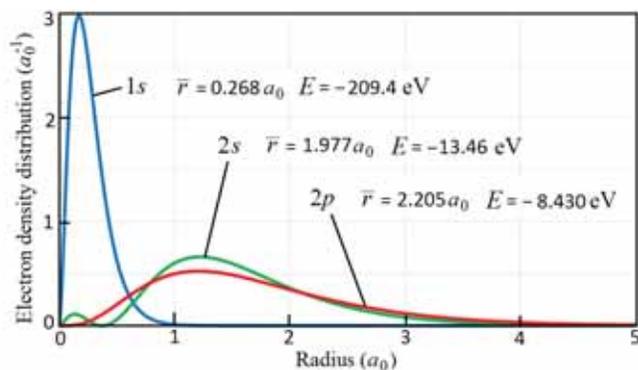
**Fig. 4.8.**   **Density distributions of electrons in carbon.** The electron density distributions defined in Eq. 4.35 as a function of $r$ are shown. Being normalized to $r$, that the area below each curve is 1. The two $2s$ orbitals and the two $2p$ orbitals have similar radius and similar energy level. The linear combinations of those orbitals could make four hybirdized orbitals. It is the basis of organic chemistry and molecular biology, and the strongest chemical bond to form diamond. See Chapter 5.

### 4.3.5   Ionization energy and electron affinity

In this Section, the general idea of how electrons are filling up an atom from a bare nucleus up, and the effect of a variation of the number of electrons could cause is discussed. By starting from a bare nucleus of $Z$ positive charges, the electrons can fill up the wavefunctions from the bottom up. By filling it up with $N$ electrons, the atom becomes neutral. If the number of electrons is not $N$, then the atom becomes a charged ion. The two simplest cases are as follows. If the number of electrons is $N-1$, a positive ion, or a

**Table 4.2: Ionization energy and electron affinity in eV**

| Element | IE | EA | ‖ | Element | IE | EA |
|---------|------|-------|---|---------|-------|-------|
| H  | 13.6  | 0.754 | ‖ | Ne | 21.56 | -     |
| He | 24.6  | -     | ‖ | Na | 5.14  | 0.548 |
| Li | 5.39  | 0.618 | ‖ | Mg | 7.65  | -     |
| Be | 9.326 | -     | ‖ | Al | 5.98  | 0.441 |
| B  | 8.29  | 0.277 | ‖ | Si | 8.15  | 1.385 |
| C  | 11.26 | 1.263 | ‖ | P  | 10.48 | 0.747 |
| N  | 14.53 | -     | ‖ | S  | 10.36 | 2.077 |
| O  | 13.61 | 1.46  | ‖ | Cl | 12.96 | 3.617 |
| F  | 17.42 | 3.40  | ‖ | Ar | 15.76 | -     |

*cation*, is formed. The energy required to remove an electron from a neutral atom is called *ionization energy*. For the case of removing one electron from the neutral atom, it is the first ionization energy. The first ionization energy for alkali metals are small, for example, for Li, it is 5.39 eV. The ionization energy for hydrogen is the Rydberg constant, 13.6 eV, much higher than lithium. Helium is the highest among all atoms, 24.59 eV.

For many atoms, an electron can be attached to form a negative ion, or *anion*, and release some energy, called electron affinity. Therefore, the anion is stable. For example, the electron affinity of hydrogen atom is 0.7542 eV. In other words, in the vacuum, the hydrogen anion is stable. Chlorine has the highest electron affinity of all atoms, 3.61 eV. It is very easy to acquire an electron to become a chlorine anion. For some atoms, no stable anions can be formed, for example the inert gas atoms.

## 4.4 Density functional theory

In Section 3.6.4, we show that because the wavefunctions are subject to superposition, the charge density of individual orbitals is not an intrinsic property of the system. However, the sum of the charge density distributions of wavefunctions at the same energy level is an objective reality. From Section 4.2.5, the total electron density distribution $n(\mathbf{r})$ is a measurable quantity, defined as the sum of squares of all single-electron orbitals,

$$n(\mathbf{r}) = \sum_{j=1}^{j=M} |\psi_j(\mathbf{r})|^2. \tag{4.42}$$

The importance of the total electron charge density is apparent by looking at the many-body Schrödinger equation, Eq. 4.9. Using Dirac notation, by multiply Eq. 4.9 with $\langle\psi|$ then integrate over the space, one obtains

$$\langle\psi| \sum_{j=1}^{j=M} \left[-\frac{1}{2}\nabla_j^2\right] |\psi\rangle + \langle\psi| \sum_{j=1}^{j=M} v(\mathbf{r}_j)|\psi\rangle + \langle\psi| \sum_{i>j>0}^{i=M} \frac{1}{r_{ij}}|\psi\rangle = E. \tag{4.43}$$

Here the first term is the kinetic energy of the electrons,

$$T = \langle\psi| \sum_{j=1}^{j=M} \left[-\frac{1}{2}\nabla_j^2\right] |\psi\rangle. \tag{4.44}$$

The last term is the mutual repulsion energy of the electrons,

$$U = \langle\psi| \sum_{i>j>0}^{i=M} \frac{1}{r_{ij}}|\psi\rangle. \tag{4.45}$$

Those two terms are universal to any electron system. The second term in Eq. 4.43 depends on the external potential that defines the specific nature of the system. By writing the many-body wavefunction as a product of single-electron orbitals, see Eq. 4.11, one obtains

$$V = \langle \psi | \sum_{j=1}^{j=M} v(\mathbf{r}_j) | \psi \rangle = \int n(\mathbf{r}) v(\mathbf{r}) d^3 \mathbf{r}, \qquad (4.46)$$

where the external potential is the attractive potential from all nuclei,

$$v(\mathbf{r}) = - \sum_{l=1}^{l=N} \frac{Z_l}{|\mathbf{r} - \mathbf{R}_l|}. \qquad (4.47)$$

The term $V$ contains all information about the specifics of the system. It has a classical meaning in terms of electrostatics in Maxwell's electromagnetism. And the electron density function $n(\mathbf{r})$ is an experimentally measurable field quantity, for example by electron diffraction.

For a given external potential $v(\mathbf{r})$, following the Schrödinger equation, the ground-state electron charge density $n(\mathbf{r})$ is uniquely defined.

### 4.4.1   The Hohenberg-Kohn theorem

In 1964, Hohenberg and Kohn proved a theorem with mathematical rigor that the reverse is true: At least for the ground state, the electron density distribution Eq. 4.11 *uniquely defines the external potential* $v(\mathbf{r})$. Because the external potential $v(\mathbf{r})$ contains the full information about the system under investigation, *the ground-state electron electron density function $n(\mathbf{r})$ contains full information about the system.*

The proof proceeds by *reductio ad absurdum*. Assume that a different external potential $v'(\mathbf{r})$ gives rise to the same density distribution function $n(\mathbf{r})$. The ground-state energy will become higher, contradicting the definition of the ground state. Therefore, there is only one external potential $v(\mathbf{r})$ corresponding to a given electron distribution function $n(\mathbf{r})$.[2]

### 4.4.2   The Kohn-Sham equations

The Hohenberg-Kohn theorem paves the way to a new set of self-consistent single-electron wave equations, called Kohn-Sham equations, that are much simpler than the Hartree-Fock equations, and often produces better results. Those new single-electron wave equations become widely used in numerical computations in quantum chemistry and solid-state physics.

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[2]For mathematical details of the proof, see the 1998 Nobel lecture of Walter Kohn, or any monograph about the density functional theory.

Similar to Hartree and Hartree-Fock approximations, the Kohn-Sham approximation aims for a series of one-electron orbitals $\varphi_j(\mathbf{r})$, satisfying differential equations resembling the one-electron Schrödinger equation,

$$\left[ -\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) - E_j \right] \varphi_j(\mathbf{r}) = 0, \qquad (4.48)$$

where the index $j$ runs from 1 to the number of electrons in the system $M$. The electron density distribution $n(\mathbf{r})$ is defined as

$$n(\mathbf{r}) = \sum_{j=1}^{j=M} |\varphi_j(\mathbf{r})|^2, \qquad (4.49)$$

similar to Eq. 4.42. There are important differences.

First, in each equation, there is only one unknown function, rather than more than one as in the Hartree-Fock approximation, Eqs. 4.22 and 4.24. Therefore, it is significantly simpler than the Hartree-Fock method, and similar to the original Hartree method, Eq. 4.14 and 4.19.

Second, the form of the effective potential in Eq. 4.48 is much simpler than in the Hartree and Hartree-Fock approximations. It is defined as

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')\, d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}). \qquad (4.50)$$

The first term $v(\mathbf{r})$ is the external potential from the nuclei, as in Eq. 4.47. The second term is the repulsive potential from the entire electron density distribution, *including the electron under consideration.* This is significantly simpler than the Hartree and Hartree-Fock approximation, where the repulsive potential for each electron must be calculated individually, to exclude the electron under consideration. The last term is the exchange and correlation potential as a replacement of Eqs. 4.23 and 4.25. It is central to the Kohn-Sham method, deserving more attention.

In Hartree-Fock approximation, the exchange potential term Eqs. 4.23 and 4.25 must be computed from *all* orbitals of the entire system, and acting on other orbitals. It is the most time-consuming computation. In the Kohn-Sham method, the exchange potential *is simplified to an effective potential acting only on the electron under consideration.*

A further simplification is based on the Hohenberg-Kohn theorem, that the electron density distribution function $n(\mathbf{r})$ contains full information on the system, and certainly contains the information about the exchange and correlation potential. Moreover, from a physical point of view, only the values of the electron density distribution function near the location of the electron under consideration is important. This physical consideration is the origin of the *local density approximation* and *generalized gradient approximation* widely used in practical computations, see following Sections.

### 4.4.3 Local density approximation

In the local density approximation, abbreviated LDC, the exchange and correlation interaction $v_{xc}(\mathbf{r})$ is assumed to be a universal function of $n(\mathbf{r})$ at the position of the electron. There are many different functional dependence in analytic forms or tabulated data, either based on certain theoretical arguments, or determined by semi-empirical trial-and-error methods.

As a classical example, the original expression used by Walter Kohn is a sum of the exchange energy and the correlation energy,

$$v_{xc}(\mathbf{r}) = v_x(\mathbf{r}) + v_c(\mathbf{r}), \tag{4.51}$$

where the exchange energy is

$$v_x(\mathbf{r}) = -\frac{0.458}{r_s}, \tag{4.52}$$

the correlation energy is

$$v_c(\mathbf{r}) = -\frac{0.44}{r_s + 7.8}, \tag{4.53}$$

and the radius of a sphere containing one electron, $r_s$, is defined as

$$\frac{1}{n(\mathbf{r})} = \frac{4\pi r_s^3}{3}. \tag{4.54}$$

### 4.4.4 Generalized gradient approximation

Within the spirit of density functional theory, and the physical intuition that the exchange and correlation interaction mainly depends on the values of electron density distribution function near the position of the electron under consideration, an improvement to the LDC is proposed and practiced. By assuming that the exchange and correlation interaction depends both the local value and the average gradient of the electron density distribution,

$$v_{xc}(\mathbf{r}) = f(n(\mathbf{r}), |\nabla n(\mathbf{r})|), \tag{4.55}$$

the agreement with experimental observations can be further improved. The method is abbreviated as GGA. The explicit form of the function in Eq. 4.55 is still under intensive research.

## 4.5 Quantization of fermions

In Chapter 3, we presented the quantization of bosons. Each energy level can have any number of particles. For fermions, such as electrons, each

energy level can have at most one particle.  The occupation number of fermions is either zero or one. For example, the vacuum state is

$$\Phi_0 = |0, 0, ..., 0\rangle. \tag{4.56}$$

and a state with only one of the energy levels occupied is

$$\Phi_1 = |0, ..., 1, ..., 0\rangle. \tag{4.57}$$

### 4.5.1  Creation and annihilation operators

Let us first look at the system with one energy level.  The state is either empty $|0\rangle$, or full $|1\rangle$.  The creation operator $\hat{b}^\dagger$ and the annihilation operator $\hat{b}$ should have the following properties:

$$\hat{b}^\dagger|0\rangle = |1\rangle, \tag{4.58}$$

means that by applying a creation operator on an empty state, the state becomes full.  And

$$\hat{b}|0\rangle = 0, \tag{4.59}$$

means that no result will be generated by applying an annihilation operator on an empty state.  And

$$\hat{b}|1\rangle = |0\rangle, \tag{4.60}$$

means that by applying an annihilation operator on a full state, the state becomes empty.  And

$$\hat{b}^\dagger|1\rangle = 0. \tag{4.61}$$

means that no result will be generated by applying a creation operator on a full state.

Instead of the commutation relations for the boson creation and annihilation operators, Eq. 3.43, the operators for fermions satisfy the *anticommutation relations*, defined as

$$\{\hat{b}^\dagger, \hat{b}\} \equiv \hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b} = 1. \tag{4.62}$$

and

$$\{\hat{b}^\dagger, \hat{b}^\dagger\} = \{\hat{b}, \hat{b}\} = 0. \tag{4.63}$$

From Eqs. 4.58 through 4.61, we have

$$\left[\hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b}\right]|1\rangle = \hat{b}^\dagger|0\rangle = |1\rangle \tag{4.64}$$

and

$$\left[\hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b}\right]|0\rangle = \hat{b}|1\rangle = |0\rangle. \tag{4.65}$$

Therefore, for any state,

$$\{\hat{b}^\dagger, \hat{b}\} \equiv \hat{b}\hat{b}^\dagger + \hat{b}^\dagger\hat{b} = 1. \tag{4.66}$$

Equations 4.63 are obvious.

### 4.5.2  Matrix representations

In order to have an explicit form of the creation and annihilation operators,[3] we represent the state of each energy level as a two-component vector with elements 1 or 0,

$$|0\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{4.67}$$

and

$$|1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}. \tag{4.68}$$

The creation operator and annihilation operator are two-by-two matrices,

$$\hat{b}^{\dagger} = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix} \tag{4.69}$$

and

$$\hat{b} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}. \tag{4.70}$$

It is easy to verify that they satisfy Eqs. 4.58 through 4.63. For example,

$$\hat{b}\hat{b}^{\dagger} + \hat{b}^{\dagger}\hat{b} = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = 1. \tag{4.71}$$

### 4.5.3  Fock space of fermions

A state of fermions can be constructed by applying creation operators on the vacuum state $|0\rangle$. For example, with states $m$ and $n$ filld, it is

$$|m, n\rangle = \hat{b}^{\dagger}_m \hat{b}^{\dagger}_n |0\rangle. \tag{4.72}$$

Such a representation, called *particle number representation*, is in particular advantageous for fermions. Because most of the electronic states in the system are not active, only those single-electron states involved in the process of interest are under focus, the expression is concise. The collection of all vectors such as in Eq. 4.72 is called a *Fock space*. Note that for fermions, all elements in the Fock space are binary numbers, 0 or 1, identical to those in computer science. Examples of applications of the particle-number representation and Fock space are presented in Chapter 9.

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[3]Bjorken and Drell, *Relativistic Quantum Fields*, McGraw-Hill, 1965, pp. 46-54.