

Lecture 6 : QM + ~~Quantum Mechanics~~ Atomic Structure

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2/2/2006

QM Notation and Representation

- I. * Dirac Notation
- State : abstract state vector $|\psi\rangle$
independent of concrete representation
 - Observable : operator \hat{A}
 - Measurement : $\hat{A} |\psi\rangle \Rightarrow |\psi'\rangle$
 - Time evolution of state : ~~state~~
$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle$$

\hat{H} is Hamiltonian operator, corresponding to total energy.
 \hat{H} can be time-dependent or time-independent.

- II. * Dirac Notation is independent of concrete representation.
But in practical calculation, it is convenient to project Dirac's state vectors and operators to a concrete representation, like a complete set of orthonormal basis of $\{|\vec{r}\rangle\}$, or $\{|\vec{p}\rangle\}$.

Each $|\vec{r}\rangle$ is an eigenstate with eigenvalue of \vec{r} ,
i.e., $\hat{\vec{r}} |\vec{r}\rangle = \vec{r} |\vec{r}\rangle$

Similar thing for the momentum \vec{p} .

- Schrödinger wavefunction $\psi(\vec{r})$ is a projection of the Dirac state vector $|\psi\rangle$ on the ~~coordinates~~ basis $\{|\vec{r}\rangle\}$.

$$\psi(\vec{r}) = \langle \vec{r} | \psi \rangle$$

There is a probabilistic interpretation of $\psi(\vec{r})$ given by Born. $\psi(\vec{r})$ itself ~~means~~ the probability ~~density~~ of finding a particle in the volume element dv at position \vec{r}

is given by: $P(\vec{r}) dv = |\psi(\vec{r})|^2 dv = |\langle \vec{r} | \psi \rangle|^2 dv$

$\psi(\vec{r})$ is the probability amplitude/density. $\psi(\vec{r}) \times \psi^*(\vec{r})$ conjugate.

Different representations are equivalent in principle, but we choose them for our calculation convenience.

In study of atomic structure, besides **energy**, we also care about how electrons move around nucleus, like their orbital status. So, Schrödinger wavefunction $\psi(\vec{r})$ is a good ~~represent~~ choice of representation.

II. * Atomic structure is about how to derive the eigenstate (stationary state) and the energy eigenvalues.

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\vec{r}, t) \psi$$

When $V(\vec{r}, t) \Rightarrow V(\vec{r})$, independent of time,

\Rightarrow eigenvalue equation of energy

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = E \psi(\vec{r})$$

free particle
in external
field.

Forget about those complicated equations, by just remember for an atom system (nucleus + electrons) the eigenstate equation ~~for atoms~~ becomes,

(3)

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(\vec{r}) \right] \psi = E \psi,$$

i.e., use the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ to replace ~~the single electron mass~~ ^{particle} in the previous equation.

Center of mass is assumed at rest, and then ~~we~~ consider the relative motion of electron in the field produced by the nucleus.

1. Coulomb Force between nucleus and electron

replace $V(\vec{r})$ with $-\frac{1}{4\pi\epsilon_0} \cdot \frac{Ze^2}{r}$,

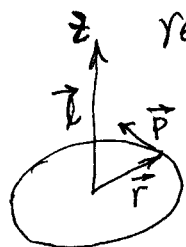
Rydberg
Constant

By solving the eigenvalue equation, we can obtain the eigen-value $E_n = -\frac{Rhc}{n^2}$, $R = \frac{\mu e^4}{8\epsilon_0^2 h^3 c}$ and the eigenstate

$$\psi_{nlm_l}(\vec{r}) = R_{nl}(r) Y_{lm_l}(\theta, \phi)$$

Again, what's the meaning of $\psi_{nlm_l}(\vec{r})$?

— the probability distribution of the electron position relative to the nucleus.



$n,$

$$l, = 0, 1, 2, \dots, n-1 \quad [l^2, H] = 0, \quad [l_z, H] = 0$$

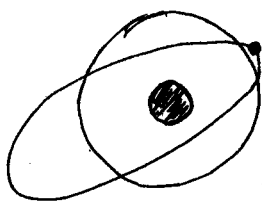
m_l — well-defined z -component

$$\vec{l} = \vec{r} \times \vec{p}$$

(4)

2. Central-Field Approximation

In many-electron atom, there are static electric interactions between electrons. This makes the whole thing very complicated. An ~~approximation~~ way to solve the problem is ~~the~~ the central-field approximation.



$\sum_{i \neq j} \bar{V}_{ij}$ to be a spherical symmetric field.

Pauli exclusion Principle: no two electrons can have the same set of four quantum numbers.

$$\boxed{n, l, m_l, m_s}$$

electron-electron
non-central force
↓
electrons' motions
are correlated
with one another.

↓
remove some of
the degeneracy

Shielding — (closed shells)

penetration — cause states to be non-degenerate.
↓
No energy levels.

3. Electron Spin — Fine structure.

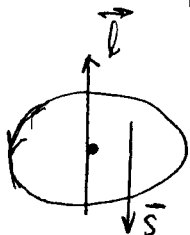
Spin — intrinsic angular momentum, — no corresponding concept in classical mechanics

single electron: $S = 1/2$ $\rightarrow |\vec{S}| = \sqrt{s(s+1)} \hbar = \frac{\sqrt{3}}{2} \hbar$

Spin magnetic moment, $S_z = \pm \frac{\hbar}{2} = m_s \hbar, \therefore m_s = \pm \frac{1}{2}$.

$\vec{\mu}_s = g_s \mu_B \vec{S}, \mu_B = -\frac{e}{2m_e} \hbar$ Bohr magneton.

$\vec{\mu}_l = \mu_B \vec{L}, \vec{J} = \vec{L} + \vec{S}, |\vec{J}| = \sqrt{j(j+1)} \hbar$



Considering the atom as a whole, $j = l+s, l+s-1, \dots, |l-s|$
We change $\vec{S} \rightarrow \vec{S}, \vec{L} \rightarrow \vec{L}, \vec{J} \rightarrow \vec{J}$.
 $\vec{S} = \sum_i \vec{S}_i, \vec{L} = \sum_i \vec{L}_i$

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For atoms with multiple electrons, l_i is not conserved anymore, but the total ~~an~~ orbital angular momentum

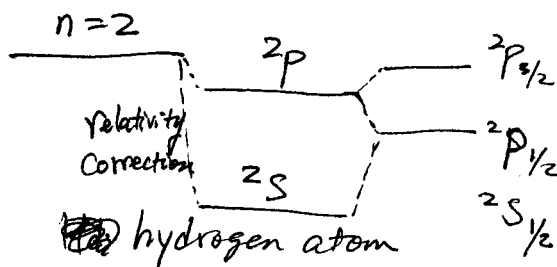
$$\vec{L} = \sum_i \vec{l}_i \text{ is good (Constant of motion)}$$

quantum number

$$\vec{S} = \sum_i \vec{s}_i$$

$$\vec{J} = \vec{L} + \vec{S}$$

Na fine structure



4 ~~the~~ Nuclear influence - Hyperfine Structure + isotope shift.

Nuclear Spin $|\vec{I}| = \sqrt{I(I+1)} \hbar$, $\vec{\mu}_I = g_I \mu_B \vec{I}$.

New Total Angular momentum: $\vec{F} = \vec{J} + \vec{I}$

$$F = J+I, J+I-1, \dots, |J-I|$$

Nuclear quadrupole interaction with electron.

~~Stark effect, Zeeman effect~~

Isotope shift:

Same number of proton, but different neutron numbers.

nuclear spin different

nuclear ~~quadrupole~~ quadrupole different.

mass difference

volume difference

} \Rightarrow cause energy level shift.

\rightarrow Heavier isotope has lower energy.

\rightarrow s electron effect largest, heavier isotope has higher energy.

5. External field —

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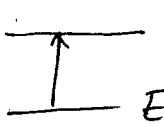
Zeeman effect: $-\vec{\mu} \cdot \vec{B} \rightarrow$ remove degeneracy.
 $m_j = -j, -j+1, \dots, j$

Stark effect: $-\vec{D} \cdot \vec{E} \rightarrow$ cause shift of energy.

~~IV.~~ Atomic transition:

Under the influence of external field (AC), especially radiation, an atom is no longer in stationary state, but becomes a superposition state, and jump occurs — transition.

←


$$i\hbar \frac{\partial \psi}{\partial t} = (\hat{H}_0 + \hat{H}') \psi$$
$$h\nu = E_2 - E_1$$

Selection rules:

$$\Delta n = \text{any}$$

$$\Delta S = 0, \Delta L = 0, \pm 1$$

(for single electron, $\Delta L \neq 0$)

$$\Delta J = 0, \pm 1,$$

$$\Delta M = 0, \pm 1$$

parity must be opposite.

January 30-February 2, 2006

Fundamentals of Atomic and Laser Spectroscopy for Laser Remote Sensing

Professor Xinzhaoh Chu

Reference Books:

1. Corney, A., Atomic and Laser Spectroscopy
2. Softley, T. P., Atomic Spectra
3. Herzberg, G., Atomic Spectra and Atomic Structure
4. Slater, J. C., Quantum Theory of Atomic Structure
5. Schiff, L. I., Quantum Mechanics

Outline

- I. Introduction
- II. Brief Review of Fundamentals of Quantum Mechanics
- III. Eigenvalue Equation versus Schrödinger Equation
- IV. Stationary States
- V. Atomic Structure
- VI. Atomic Transition
- VII. Laser Spectroscopy

I. Introduction

“Fundamentals of Quantum Mechanics” has a threefold purpose: to explain the physical concepts of quantum mechanics, to describe the mathematical formalism of quantum mechanics, and to apply the ideas and methods of quantum mechanics to illustrative examples. The first QM note focused on the first purpose, and shed some light on the second purpose. The “Notation and Representation in QM” note focused on the second purpose. However, they did not touch the applications.

Quantum mechanics (QM) can be applied to nearly every aspect of modern science and technology. To our laser remote sensing class, the main applications of QM lie in the following five aspects:

- Atomic structure and atomic spectra
- Laser spectroscopy
- Molecular structure and molecular spectra
- Scattering and collision theory
- Laser physics and device

The current note is aimed for the first two aspects of QM application as well as getting familiar with the mathematical formalism of QM.

II. Brief Review of Fundamentals of Quantum Mechanics

Before going in further, let us briefly review what we have learned from the previous note. In quantum mechanics, a state of a system is described by an abstract state vector or a concrete wave function, an observable or measurable physical quantity is represented by an operator, and the time evolution of the state is determined by the Schrödinger equation that is the fundamental equation of motion in quantum mechanics.

Any arbitrary state of a system can be expressed in a superposition of a complete set of orthonormal eigenstates. The only possible results of the measurement of a physical observable are one of the eigenvalues. The probability of measurement result occurring in one particular eigenvalue is proportional to the square of the magnitude of the coefficient of this eigenstate in the expansion of the arbitrary state. Uncertainty principle is a fundamental feature in quantum mechanics, and applies to several pairs of physical quantities, e.g., the coordinates and momentum of a particle, or the measurement time length and energy of a particle, cannot be determined to infinite accuracy simultaneously, but possess an indeterminacy to the degree of Planck constant.

III. Eigenvalue Equation versus Schrödinger Equation

The Schrödinger equation is the fundamental equation governing the evolution of the state of a system. A general format of the Schrödinger equation is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\vec{r}, t) \psi. \quad (1)$$

The Schrödinger equation can be considerably simplified when the potential energy $V(\mathbf{r})$ does not depend on the time. It is then possible to express its general solution as a sum of product of functions of \mathbf{r} and t separately. In other words, a particular solution of Eq. (1) can be written as a product: $\psi(\vec{r}, t) = u(\vec{r})f(t)$. A general solution can then be written as a sum of such separated solutions. Substituting the particular solution into Eq. (1), we obtain

$$\frac{i\hbar}{f} \frac{df}{dt} = \frac{1}{u} \left[-\frac{\hbar^2}{2m} \nabla^2 u + V(\vec{r})u \right] \Rightarrow E. \quad (2)$$

Since the left side of Eq. (2) depends only on t and the right side only on \mathbf{r} , both sides must be equal to the same separation constant, which we call E . Then the left side of the equation for f is readily integrated to give

$$f(t) = Ce^{-iEt/\hbar}, \quad (3)$$

where C is an arbitrary constant. The right side of the equation for u becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] u(\mathbf{r}) = Eu(\mathbf{r}). \quad (4)$$

Since Eq. (4) is homogeneous in u , the constant C may be chosen to normalize u . Thus, a particular solution of the Schrödinger equation can be written as

$$\psi(\vec{r}, t) = u(\vec{r})e^{-iEt/\hbar}. \quad (5)$$

Recall the time-derivative operator for the total energy: $E \rightarrow i\hbar(\partial/\partial t)$, it may be applied to the state given by Eq. (5) to give

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi. \quad (6)$$

An equation of the type of Eq. (6) is called an *eigenvalue equation*, and ψ is said to be an *eigenfunction* of the operator that appears on the left, and the constant E that appears on the right is called the corresponding *eigenvalue*.

Eq. (4) is also an eigenvalue equation. It states that u (and hence also ψ) is an eigenfunction of the operator $-(\hbar^2/2m)\nabla^2 + V(\vec{r})$ with the same eigenvalue E . It is, of course, to be expected that ψ is an eigenfunction of this operator if it is an eigenfunction

of the time-derivative operator $i\hbar(\partial/\partial t)$ since the two operators are equivalent not only for separated functions of the form of Eq. (5) but also for more general solutions.

It is worth to point out that Eqs. (4) and (6) are usually called “time-independent Schrödinger equation”. A misunderstanding in QM field is that eigenvalue equations are thought to be a special case of the Schrödinger equation. Time-independent Schrödinger equation is only one of kinds of the eigenvalue equation, i.e., the eigenvalue equation of energy. There exist many other eigenvalue equations, such as the eigenvalue equation for angular momentum, etc. A general expression of an eigenvalue equation is

$$\hat{A}|\psi\rangle = A|\psi\rangle, \quad (7)$$

where \hat{A} is the operator of a physical quantity (observable), A is the eigenvalue of this quantity, and $|\psi\rangle$ is the eigenstate of this operator. When the operator is the Hamiltonian operator, the eigenvalue equation is for the total energy:

$$\hat{H}|\psi\rangle = E|\psi\rangle. \quad (8)$$

When the operator is the angular momentum, the eigenvalue equation is for the angular momentum:

$$\hat{L}^2|\psi\rangle = l^2|\psi\rangle. \quad (9)$$

IV. Stationary States

According to the uncertainty relation, a precise measurement of the total energy of a particle cannot be made in a finite length of time. Thus, if the total energy is to have a definite value, it is essential that the potential energy $V(\mathbf{r})$ be independent of the time. Then the operator $-(\hbar^2/2m)\nabla^2 + V(\vec{r})$, which is equivalent to the total energy operator $i\hbar(\partial/\partial t)$, has eigenfunctions $u(\mathbf{r})$ that need not involve the time. Therefore, the energy-eigenvalue equation can be written as

$$\left[-(\hbar^2/2m)\nabla^2 + V(\vec{r})\right]u_E(\vec{r}) = Eu_E(\vec{r}), \quad (10)$$

where $u_E(\mathbf{r})$ is the eigenfunction corresponding to the eigenvalue E .

An energy eigenfunction, like the one given by Eq. (5) or the one in Eq. (10), is said to represent a *stationary state* of the particle, since $|\psi|^2$ and $|u_E(\mathbf{r})|^2$ are constant in time. The possible eigenvalues of energy depend on detailed situation under consideration. In general, bound states have discrete eigenvalues of energy, while non-bound states (like scattering or collision) have continuous eigenvalue of energy.

The quantum theory of atomic structure discuss below is to derive the discrete stationary states of a bound system – an atom as a whole of nucleus and electrons.

V. Atomic Structure

Atomic structure theory cares about the stationary states of an atom. These stationary states will be achieved by solving the eigenvalue equations of energy and angular momentum under various interactions. Our approach is to consider the interactions within an atom from the major force (like Coulomb force between the nucleus and electrons) to the minor force (like nuclear spin) and the interactions between an atom and external fields (static electric and magnetic fields), and describe how the energy levels of an atom are formed, split, and shifted under these interactions.

1. Coulomb Force in Hydrogen Atom

Hydrogen atom is the simplest atom in the world. We will use it to show how QM works in deriving the energy levels of an atom. The Schrödinger equation given above describes the motion of a single particle in an external field of force. Now we are interested in the motion of two particles (nucleus and electron) that are attracted to each other by a Coulomb force that depends only on the distance between them. The form of the Schrödinger equation to be used for two particles is suggested by the extension from three to six rectangular coordinates, leading to the following equation:

$$i\hbar \frac{\partial}{\partial t} \psi(x_1, y_1, z_1, x_2, y_2, z_2, t) = \left[-\frac{\hbar^2}{2m_1} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) - \frac{\hbar^2}{2m_2} \left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right) + V(x_1, y_1, z_1, x_2, y_2, z_2, t) \right] \psi(x_1, y_1, z_1, x_2, y_2, z_2, t) \quad (11)$$

where m_1 and m_2 represent the masses of two particles. If now the potential energy depends only on the relative coordinates, so that $V = V(x_1 - x_2, y_1 - y_2, z_1 - z_2)$, an important simplification can be made. We define relative coordinates x, y, z and coordinates of the center of mass X, Y, Z by

$$\begin{aligned} x &= x_1 - x_2 & y &= y_1 - y_2 & z &= z_1 - z_2 \\ X &= (m_1 x_1 + m_2 x_2) / M & Y &= (m_1 y_1 + m_2 y_2) / M & Z &= (m_1 z_1 + m_2 z_2) / M \end{aligned} \quad (12)$$

where $M = m_1 + m_2$ is the total mass of the system. Thus, Eq. (11) can be rewritten in terms of the new coordinates

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \right] \psi \quad (13)$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (14)$$

is called the *reduced mass*.

Two separation of Eq. (13) can now be made. First, the time dependence can be separated out as shown in Section III. Second, a separation can be made into a product of functions of the relative coordinates and center-of-mass coordinates. The results are

$$\begin{aligned} \psi(x, y, z, X, Y, Z, t) &= u(x, y, z) U(X, Y, Z) e^{-i(E+E')t/\hbar} \\ -\frac{\hbar^2}{2\mu} \nabla^2 u + Vu &= Eu \\ -\frac{\hbar^2}{2M} \nabla^2 U &= E'U \end{aligned} \quad (15)$$

where ∇^2 operators in the 2nd and 3rd equations imply differentiation with respect to the relative and center-of-mass coordinates, respectively. The second of Eqs. (15) describes the relative motion of the two particles and is the same as the equation for the motion of a single particle that has the reduced mass μ in an external potential energy V . The third of Eqs. (15) tells us that the center of mass of the two-particle system moves like a free particle of mass M .

In the hydrogen atom, we shall be interested in the energy levels E associated with the relative motion. In this case, the reduced mass μ is only slightly smaller than the

electron mass, since atomic nuclei are far more massive than electrons. The Coulomb force between the nucleus and the electron and the Coulomb potential are given by

$$F(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} \text{ and } V(r) = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \quad (16)$$

The boundary conditions implied by Eq. (16) are

$$V \rightarrow 0 \text{ as } r \rightarrow \infty \text{ and } \psi \rightarrow 0 \text{ as } r \rightarrow \infty. \quad (17)$$

The eigenfunction and eigenvalue of the relative motion of the hydrogen atom can be obtained by solving the following eigenvalue equation at the boundary conditions given by Eq. (17):

$$\left[-\frac{\hbar}{2\mu} \nabla^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \right] \psi = E\psi. \quad (18)$$

The consequence of these boundary conditions is that physically meaningful solutions of the Schrödinger equation are not obtainable at any energy E , but only at specific quantized eigen-energies:

$$E = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}, \quad (19)$$

where n is permitted at the integer numbers of 1, 2, 3,

We will not go in details to explain how to solve the eigenvalue equation to obtain the eigenfunction, which can be found in any of the reference books. The eigenfunction of Eq. (18) can be written as a product of a radial function $R_{nl}(r)$ and an angular function $Y_{lm_l}(\theta, \phi)$:

$$\psi_{nlm_l}(\vec{r}) = R_{nl}(r) Y_{lm_l}(\theta, \phi). \quad (20)$$

The radial function is labeled by two quantum numbers n and l , and the angular function is a spherical harmonic function labeled by two quantum numbers l and m_l . Each eigenfunction, defined by the set of quantum numbers n , l , and m_l , must have an associated eigen-energy as defined by Eq. (19). Note, however, Eq. (19) only depends on the quantum number n . There is, for all values of n except $n = 1$, more than one total eigenfunction corresponding to each energy level. This phenomenon is crucially important in spectroscopy and QM and is known as *degeneracy*. The key point here is that the electron can exist in more than one physically distinct state in the atom without changing its total energy.

The quantum number n is called the principal quantum number and it determines the energy level:

$$E = -\frac{Rhc}{n^2} \quad (21)$$

where R is the collection of constants known as the Rydberg constant

$$R = \frac{\mu e^4}{8\epsilon_0^2 \hbar^3 c}. \quad (22)$$

The quantum number l is called the orbital angular momentum quantum number, which is directly related to the magnitude of the orbital angular momentum of the electron:

$$|\vec{l}| = [l(l+1)]^{1/2} \hbar. \quad (23)$$

Classically the angular momentum of a particle is defined by the equation:

$$\vec{l} = \vec{r} \times \vec{p} \quad (24)$$

where \mathbf{r} is the position vector and \mathbf{p} is the linear momentum vector. In quantum mechanics, we obtain operators for the square of the angular momentum as

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2 \quad (25)$$

where the operator for the component is given by

$$\hat{l}_z = \frac{\hbar}{i} \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right]. \quad (26)$$

The orbital angular momentum quantum number l is permitted to take integral values from 0 to $n-1$, i.e.,

$$l = 0, 1, 2, \dots, n-1. \quad (27)$$

States with $l = 0, 1, 2, 3, 4, 5 \dots$ are labeled for historical reasons as s, p, d, f, g, h, \dots respectively and the notation $1s, 2p, 3d$, etc is used for the orbitals, with the first number being the principal quantum number and the letter being the angular momentum quantum number.

The quantum number m_l is called the magnetic quantum number. It characterizes the z -component of the orbital angular momentum vector l_z :

$$l_z = m_l \hbar \quad (28)$$

For every permitted value of l , there are $2l+1$ independent wavefunctions with the magnetic quantum numbers $m_l = -l, -l+1, \dots, +l$. Again, these are degenerate states.

Without considering relativity correction (mass change due to the velocity) and the electron spin, the hydrogen atom energy levels are highly degenerated. For each principal quantum number n , the degeneracy is given by

$$\sum_{l=0}^{n-1} (2l+1) = n^2. \quad (29)$$

The wavefunctions for the atom are generally referred to as orbitals. This word represents an extension of the old ideas of quantum theory (Bohr theory) in which electrons moved in well-defined elliptical orbits around the nucleus. In the modern quantum theory, the orbital trajectory is not precisely specified. The true meaning of the orbitals is seen through the probabilistic interpretation of the wavefunctions. Recall what we explained in the two QM notes: the square of the wavefunction $\psi(\vec{r})$ gives the probability density for the electron at a particular position in space. In the case of an atom, the wavefunction $\psi(\vec{r})$ represents the probability distribution of the electron position relative to the nucleus. So the orbitals corresponding to different quantum number l give the probability distribution of how the electron moves around the nucleus.

2. Central-Field Approximation

The starting-point of calculations on all except the lightest atoms (hydrogen) is the *central-field approximation*. This assumes that each of the atomic electrons moves in a spherically symmetric potential energy $V(r)$ that is produced by the nucleus and all the other electrons. The approximation is a good one if the deviation from the $V(r)$ for one electron produced by close passage of other electrons is relatively small. This is actually the case, since the constant nuclear potential is of the order of Z times as large as the fluctuating potential due to each nearby electron, and the latter varies quite slowly (inversely) with the separation distance. The two principal problems are then the calculation of the central field and the correction of the approximate results obtained from it.

The energy levels of many-electron atoms will have a much more complicated structure compared to hydrogen, because the quantized energies are now determined not only by nucleus-electron Coulomb attraction, but also by the mutual repulsion between the electrons. An energy level for the many-electron case represents the total energy of all N electrons when the atom is in a particular quantum state. In quantum mechanics the wavefunctions and energy levels are obtained by solving the Schrödinger equation, which for a many-electron atom can be written down in the following form:

$$\left[\sum_i \frac{-\hbar^2}{2\mu} \nabla_i^2 + \sum_i V_{iN} + \sum_{i \neq j} V_{ij} \right] \psi = E\psi. \quad (30)$$

The first term in square bracket is the sum of kinetic energy operators for each electron, and the second is the sum of potential energies of nucleus-electron attraction. Whereas both these terms are present for a one-electron atom, the new term (i.e., the third) that must be added is the electron-electron repulsive potential energy, V_{ij} summed over all pairs of electrons ($i \neq j$):

$$V_{iN} = \frac{-Ze^2}{4\pi\epsilon_0 r_i} \text{ and } V_{ij} = \frac{-e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}. \quad (31)$$

Unfortunately, the consequence of this third term is that the equation can no longer be solved exactly. Even for the helium atom with only two electrons, we have a so-called “three-body problem” for which even in classical mechanics there is no analytical solution to the equations of motion of the three interacting particles.

The central-field approximation enables us to gain approximate analytical knowledge of these many-electron atoms while the corrections help us to get close to the truth. First, it is assumed that the total wavefunction describing the positions and momenta of all the electrons can be written as a product of one-electron wavefunctions, each of which describes the position and momentum of just one electron. It is then proposed that each one-electron wavefunction is similar to the eigenfunction (orbitals) we have already described for the hydrogen atom, and is characterized by the same set of quantum numbers. Within the central-field approximation, each electron moves within the time-averaged charge distribution due to all the other electrons, and the one-electron wavefunctions are obtained by solving a one-electron Schrödinger equation with the potential energy in a form that accounts for the average interactions with all other electrons:

$$\left[\frac{-\hbar^2}{2\mu} \nabla_i^2 + V_{iN} + \sum_{i \neq j} \overline{V_{ij}} \right] \phi_i = \epsilon_i \phi_i. \quad (32)$$

The double bar on the electron-electron repulsion operator indicates two averaging processes: an average over all angles so that the angle-dependent potential energy is replaced by a spherically symmetric one, and also the average over all positions of the other electrons. The only variables in the equation are now the coordinates of electron i and the equation is solvable by numerical integration methods.

The complication is that in order to obtain the wavefunction for one electron we need to know the wavefunctions for all the other electrons, so that the average electron-electron repulsion potential can be calculated. These, however, can only be determined by the same procedure that requires a predetermination of the wavefunction for the first

electron. *Catch 22?* A useful procedure to solve this problem is the *self-consistent field* (SCF) method, in which an initial guess is made for the wave functions of the $N-1$ electrons, and the Schrödinger equation solved for the N th electron. This wavefunction is then used as an improved guess for that electron in the calculation of the wavefunction for another electron. The procedure continues iteratively, improving each wavefunction a succession of times until further iterations lead to no further change of the wavefunctions. The total wavefunction is then self-consistent and is assumed to be the best solution. The orbital energy is defined as the SCF one-electron energy calculated as described above. The total energy of all electrons is not exactly equal to the sum of orbital energies because that includes the repulsion between each pair of electrons twice over. Therefore, the total energy is actually given by

$$E_{total} = \sum_i \varepsilon_i - V_{ee}, \text{ and } V_{ee} = \left\langle \sum_{i \neq j} V_{ij} \right\rangle, \quad (30)$$

where the ε_i are the orbital energies for each electron and V_{ee} is the expectation value of the total electron-electron repulsion energy.

3. Pauli Exclusion Principle and Correction to Central-Field Approximation

The electron configuration is the description of which orbitals are occupied by all the electrons in the atom. If electrons were completely independent and the lowest energy state is available to each electron, then the expected Na atom ground state would be $1s^{11}$. This is not the case because electrons in atoms are found to obey the *Pauli exclusion principle*, which states that no two electrons in an atom can have the same set of four quantum numbers n , l , m_l , and m_s . Thus, the $1s$ orbital has quantum numbers $n=1$, $l=0$, and $m_l=0$, and there are two possible values for m_s ($\pm 1/2$); therefore, two electrons can exist in this orbital in one atom, one with $m_s=+1/2$, and another with $m_s=-1/2$. Similarly, we can derive the maximum possible electron numbers in each state. The principle is to fill in the lowest state and then move onto the next lowest state, until all electrons are filled in. For sodium the ground state electron configuration is $1s^2 2s^2 2p^6 3s$.

For an atom with many electrons, like the Na, correction needs to be made to the central-field approximation. There are mainly two effects: *shielding and penetration*. Let us use the Na as an example to explain them. The first 10 electrons of the Na atom act like a potential shielding for the 11^{th} electron outside the shell formed by the first 10 electrons. The 11^{th} electron experiences an attractive force due to the positive nuclear of charge of $+11$, and the repulsive force due to an effective point charge of -11 arising from the first 10 electrons. Thus, the net result is that the 11^{th} electron experiences an overall effective nuclear charge of $Z_{\text{eff}} = +1$. We say that the electron is shielded from the nuclear charge by the inner electrons and the binding energy of this electron (i.e., the energy required to remove it from that orbital to infinity) is almost identical to the binding energy of an electron in the same orbital in the hydrogen atom.

Consider next the configuration $1s^2 2s^2 2p^6 3s$ and $1s^2 2s^2 2p^6 3p$. Although in both cases the $n = 3$ electron spends most of its time outside the core electron distribution, there is a certain probability of the electron penetrating inside the core. This probability is substantially greater for the $2s$ compared to the $2p$ orbital. This will cause the states with the same n but different l numbers to be non-degenerate, i.e., these states will have

The intrinsic spin of an electron leads to this particle acting like a tiny bar magnet, with magnetic moment given by

$$\vec{\mu}_s = g_s \mu_B \vec{s}, \text{ where } \mu_B = -\frac{e\hbar}{2m_e}.$$

g_s is the electronic g-factor – a constant that has been accurately measured to the value of 2.002319314, and μ_B is the Bohr magneton.

The orbital angular momentum possessed by an electron with $l > 0$ leads to a second source of magnetism. The circulating charged particle is an electric current and produces at the center of the orbit a magnetic moment given by

$$\vec{\mu}_l = \mu_B \vec{l}.$$

Just as two bar magnets repel or attract one another according to their relative orientation, the orbital and spin magnetic moments can be lined up in an attractive or repulsive orientation, that is energetically favorable or unfavorable, respectively.

It is convenient to define a total angular momentum vector as the vector sum of the orbital vector and the spin vector:

$$\vec{j} = \vec{l} + \vec{s}.$$

Quantum mechanically, the vector \vec{j} behaves in a very similar way to \vec{l} . In particular, the operators representing j^2 and j_z have the same commutation properties as those representing l^2 and l_z . The magnitude of \vec{j} is restricted to

$$|\vec{j}| = \sqrt{j(j+1)}\hbar,$$

where j is the total angular momentum quantum number, analogous to l . j is restricted to have values of

$$j = l + s, l + s - 1, \dots, |l - s|.$$

The formation of the total angular momentum results in the fine structure of atomic energy levels, as shown in the Na diagram.

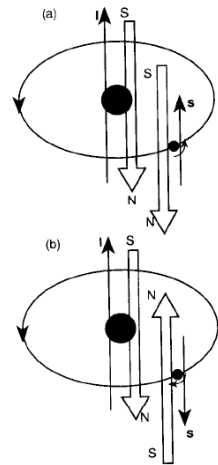
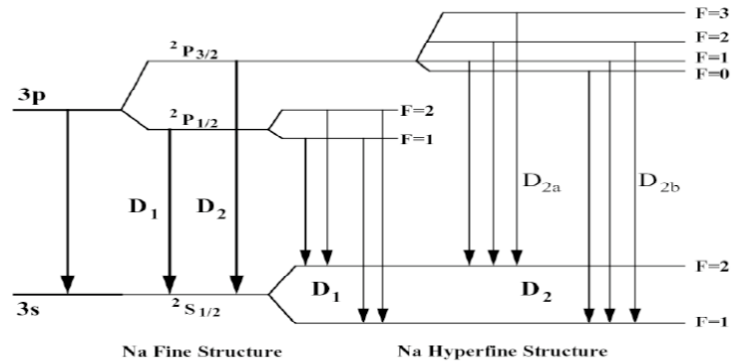


Fig. 2.18 (a) The orbital angular momentum vector \vec{l} and spin angular momentum vector \vec{s} are parallel; hence the two magnetic moments are also parallel (in the opposite direction) and repel resulting in a high energy state. (b) The magnetic moments are antiparallel and there is an attractive low-energy interaction. The north (N) and south (S) poles indicate the analogy with two simple bar magnets.



5. Influences of Nucleus - Hyperfine Structure and Isotope Shift

The nucleus also possesses an intrinsic spin angular momentum given by

$$|\vec{I}| = \sqrt{I(I+1)}\hbar$$

Its corresponding magnetic moment is given by

$$\vec{\mu}_I = g_I \mu_N \vec{I}.$$

The nuclear spin angular momentum interacts with the electron total angular momentum. So it is convenient to define a new total angular momentum:

$$\vec{F} = \vec{J} + \vec{I}$$

The magnitude of \vec{F} is restricted to

$$|\vec{F}| = \sqrt{F(F+1)}\hbar,$$

where F is the new total angular momentum quantum number given by

$$F = J + I, J + I - 1, \dots, |J - I|$$

The magnetic interaction between the nucleus and the electrons results in the hyperfine structure of atomic energy levels, as shown in the Na diagram.

Isotope shift: by mass shift and by field shift

6. Influence of external static electric and magnetic field – Stark and Zeeman Effects

The external static field can further cause the energy level to split and shift.

VI. Atomic Transitions

If a physical system is set up in a certain stationary state, it will remain in that stationary state so long as it is not acted upon by outside forces. Any atomic system in practice, however, frequently gets acted upon by external electromagnetic fields, under whose influence it is liable to cease to be in one stationary state and to make a transition to another.

The transition problem can be solved by using the time-dependent perturbation theory. We will not talk about the details. The results of the transitions are the absorption or emission of photons at specific frequency (wavelength) determined by the energy levels of the stationary states:

$$h\nu = E_2 - E_1.$$

A result of this theory is that to a high degree of accuracy, transitions between two states cannot occur under the influence of EM radiation if the matrix element of the operator with two stationary states is zero. It happens for many atomic systems that the great majority of the matrix elements do vanish. Therefore, there are severe limitations on the possibilities for transitions. These rules are called *selection rules*.

Spontaneous emission can only be explained by the quantization of the radiation field,

$$E = \sum_{\omega} (n_{\omega} + 1/2)\hbar\omega.$$

It is caused by the “zero-field” energy.

VII. Laser Spectroscopy