Study Guide for Quantum Mechanics (TFFY54)

Patrick Norman

Department of Physics, Chemistry and Biology,
Linköping University, SE-581 83 Linköping, Sweden
(Dated: Spring Term 2007)

Abstract

The intention of this document is to define the content of the course. It summarizes the material presented during the lectures and provides a reading guide to our textbook by Bransden and Joachain.
I. INTRODUCTION

A. Reading Guide

1. Chapter 1 gives the historical background that everyone should have a general knowledge about, but it is not of primary concern in this course.

B. Topics

1. Wave–particle dualism

Light and matter, which were separated in classical physics, are united in the Einstein–de Broglie relations

\[ E = \hbar \omega, \quad (1) \]
\[ p = \hbar k, \quad \lambda = \frac{2\pi}{|k|}. \quad (2) \]

2. Dynamical variables and operators

The dynamical variables in (nonrelativistic) classical physics are replaced by operators in quantum mechanics.

<table>
<thead>
<tr>
<th>Quantum Mechanics</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hat{E} = i\hbar \frac{\partial}{\partial t} )</td>
</tr>
<tr>
<td>( \hat{p} = -i\hbar \nabla )</td>
</tr>
<tr>
<td>( \hat{x} = x )</td>
</tr>
<tr>
<td>( \hat{T} = \hat{p}^2/2m )</td>
</tr>
<tr>
<td>( \hat{V} = V(x) )</td>
</tr>
<tr>
<td>( \hat{H} = \hat{T} + \hat{V} )</td>
</tr>
</tbody>
</table>
II. EQUATION OF MOTION FOR MATTER WAVES

A. Reading Guide

1. Sections 2.1–2.4 on the topics of wave–particle dualism, wave function interpretation, and wave packets. The Heisenberg uncertainty principle (Section 2.5) is covered in Lecture 9.

2. Sections 3.1–3.2 on the Schrödinger equation and the conservation of probability. Read also Section 3.3, which is concerned with expectation values, but we are not yet properly acquainted with the representation of the wave function in momentum space.

B. Topics

1. Schrödinger equation

The time propagation of matter waves is governed by the Schrödinger equation, which is a linear differential equation and the superposition principle thus applies. The Schrödinger equation for a particle with mass $m$ reads

$$\text{i} \hbar \frac{\partial \psi(r, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r, t) \quad (3)$$

The Schrödinger equation is of first order in time, and a sufficient initial condition for its solution is thus the wave function at a given time $t_0$.

2. Interpretation of the wave function

The probability to detect the particle in the volume element $dr$ at position $r$, at time $t$, is

$$P(r, t) \, dr = |\psi(r, t)|^2 \, dr. \quad (4)$$

This interpretation was given first by M. Born in 1926.
3. Probability current density and normalization

If the wave function is normalized at a given time $t_0$, i.e.,

$$\int_V |\psi(r, t_0)|^2 \, d\mathbf{r} = 1,$$

it must remain normalized at all times, and we thus have

$$\frac{\partial}{\partial t} \int_V |\psi(r, t)|^2 \, d\mathbf{r} = 0.$$  \hspace{1cm} (6)

This result is proven to be in agreement with the Schrödinger equation, and it then becomes natural to define the probability density $\rho$ and probability current density $\mathbf{j}$ according to

$$\rho(r, t) = |\psi(r, t)|^2,$$  \hspace{1cm} (7)

$$\mathbf{j}(r, t) = \text{Re} \left\{ \psi^*(r, t) \frac{\hat{p}}{m} \psi(r, t) \right\}.$$  \hspace{1.5cm} (8)

We note that the probability current density vanishes for real wave functions.

4. Hermitian operators

An operator $\hat{\Omega}$ is Hermitian, if

$$\int_V \psi^*(r, t) \left[ \hat{\Omega} \psi(r, t) \right] \, d\mathbf{r} = \int_V \left[ \hat{\Omega} \psi(r, t) \right]^* \psi(r, t) \, d\mathbf{r}.$$  \hspace{1cm} (9)

The hermiticity of the Hamiltonian is proven by combining the Schrödinger equation [Eq. (3)] and the normalization condition [Eq. (6)]. It follows directly from Eq. (9) that the expectation value of a Hermitian operator is real.

III. TIME-INDEPENDENT SCHRÖDINGER EQUATION

A. Reading Guide

1. Sections 3.5–3.8 are central in Quantum Mechanics. Section 3.4 is important but postponed until Lecture 9.

2. Chapter 4 contains several examples of solving the time-independent Schrödinger equation. The principles must be clear to everyone, but the details are not at focus in this course.
B. Topics

1. Time-independent Schrödinger equation and stationary states

For conservative systems, \(i.e.,\) in cases when the potential is time-independent, we can find solutions to the Schrödinger equation [Eq. (3)] which are separable in space and time variables. It is straightforward to prove that the time-dependent part is a phase factor and the spatial part must be a solution to the time-independent Schrödinger equation

\[
\hat{H} \psi(r) = E \psi(r).
\]  

Having solved Eq. (10), the time-dependent wave functions that solve Eq. (3) are \(\psi(r, t) = \psi(r) \exp(-iEt/\hbar)\). For these solutions, it is clear that

- \(\hat{H}\) is Hermitian \(\Rightarrow\) \(E\) is real.
- The probability density \(\rho(r, t)\) is time-independent

\[
\rho(r, t) = \rho(r) = |\psi(r)|^2.
\]  

States with time-independent probability density are called stationary. It is clear that stationary states also have time-independent probability current densities.
- Expectation values of operators \(\hat{\Omega}(\hat{x}, \hat{p})\), which have no explicit time-dependence, are time-independent.
- If \(\alpha\) is a real number, then \(\psi(r)\) and \(\psi(r) \exp(i\alpha)\) are solutions to Eq. (10) with the same eigenvalue, and the two wave functions correspond to the same physical state.
- Eigenfunctions in Eq. (10) corresponding to different eigenvalues are orthogonal.

2. General solution to the Schrödinger equation

The eigenfunctions to the Hamiltonian can be used to solve the Schrödinger equation [Eq. (3)] in the general case. Given that the wave functions at time \(t = 0\) is \(\psi(r, 0)\) then the solution to Eq. (3) will be

\[
\psi(r, t) = \sum_E c_E \psi_E(r) e^{-iEt/\hbar},
\]  

where
\[ c_E = \int_V \psi_E^*(\mathbf{r}) \psi(\mathbf{r}, 0) \, d\mathbf{r}. \] (13)

This recipe is based on the fact that the eigenfunctions to the Hamiltonian form a complete set of functions.

IV. POSTULATES IN QUANTUM MECHANICS

A. Reading Guide

1. Sections 5.1–5.3 discusses the postulates in Quantum Mechanics. The exact formulation of these varies from one textbook to another.
### B. Topics

#### 1. Analogies with classical mechanics

<table>
<thead>
<tr>
<th>Classical Mechanics</th>
<th>Quantum Mechanics</th>
</tr>
</thead>
<tbody>
<tr>
<td>A The state of a particle at any given time is given by the two variables $x(t)$ and $p(t)$, i.e., a point in a 2D phase space.</td>
<td>The state of a particle is represented by a state vector $</td>
</tr>
<tr>
<td>B Every dynamical variable $\omega$ is a function of $x$ and $p$: $\omega = \omega(x, p)$</td>
<td>The independent variables $x$ and $p$ in classical mechanics are represented by the Hermitian operators $\hat{x}$ and $\hat{p}$. The operator that corresponds to the dynamical variable $\omega(x, p)$ is the Hermitian operator one obtains by the substitution $\hat{\Omega}(\hat{x}, \hat{p}) = \omega(x \rightarrow \hat{x}, p \rightarrow \hat{p})$</td>
</tr>
<tr>
<td>C A measurement of the variable $\omega$ on a particle in a state given by $x$ and $p$ gives a value $\omega(x, p)$. After the measurement, the state is left unchanged.</td>
<td>A measurement of the variable that corresponds to $\Omega$ on a particle in state $</td>
</tr>
<tr>
<td>D The state variables have a time dependence given by Hamilton’s equations:</td>
<td>The state vector $</td>
</tr>
</tbody>
</table>

\[ \dot{x} = \frac{\partial \mathcal{H}}{\partial p} \]
\[ \dot{p} = -\frac{\partial \mathcal{H}}{\partial x} \]
V. DIRAC’S BRACKET NOTATION

A. Reading Guide

1. Sections 5.1–5.3 on the Dirac bracket notation.

2. Section 5.6 on matrix representations.

B. Topics

1. Inner product

In an \( n \)-dimensional, linear, complex vector space, we define the inner product as the number that fulfills

1. \( \langle \psi_i | \psi_i \rangle \geq 0 \)

2. \( \langle \psi_i | \psi_j \rangle = \langle \psi_j | \psi_i \rangle^* \)

3. \( \langle \psi_i | \alpha \psi_j + \beta \psi_k \rangle = \alpha \langle \psi_i | \psi_j \rangle + \beta \langle \psi_i | \psi_k \rangle \)

2. Basis

Bra and ket vectors have unique expansions in every basis

\[
|\psi\rangle = \sum_i a_i |i\rangle, \quad \langle \psi | = \sum_i a_i^* \langle i | \quad (14)
\]

\[
|\psi\rangle \leftrightarrow \begin{bmatrix} a_1 \\ \vdots \\ a_n \end{bmatrix}, \quad \langle \psi | \leftrightarrow (a_1^*, \ldots, a_n^*) \quad (15)
\]

\[
\langle \psi | \psi' \rangle = (a_1^*, \ldots, a_n^*) \begin{bmatrix} a_1^* \\ \vdots \\ a_n^* \end{bmatrix} \quad (16)
\]

\[
\hat{P}_i = |i\rangle \langle i|, \quad \sum_i \hat{P}_i = \hat{I} \quad (17)
\]
3. **Linear operators**

An operator defines how bra and ket vectors are transformed

\[
\hat{\Omega}\ket{\psi} = \ket{\hat{\Omega}\psi} = \ket{\psi'},
\]

(18)

\[
\bra{\psi}\hat{\Omega}^\dagger = \bra{\hat{\Omega}\psi} = \bra{\psi'},
\]

(19)

where \(\hat{\Omega}^\dagger\) is the adjoint operator of \(\hat{\Omega}\).

1. \(\hat{\Omega}\alpha\ket{\psi} = \alpha\hat{\Omega}\ket{\psi}\)

2. \(\hat{\Omega}\left[\alpha\ket{\psi_i} + \beta\ket{\psi_j}\right] = \left[\alpha\hat{\Omega}\ket{\psi_i} + \beta\hat{\Omega}\ket{\psi_j}\right]\)

4. **Matrix representation**

If \(\hat{\Omega}\ket{\psi} = \ket{\psi'}\), then the components fulfill

\[
\begin{bmatrix}
a'_1 \\
\vdots \\
a'_n
\end{bmatrix}
= 
\begin{bmatrix}
\bra{1}\hat{\Omega}\ket{1} & \cdots & \bra{1}\hat{\Omega}\ket{n} \\
\vdots & \ddots & \vdots \\
\bra{n}\hat{\Omega}\ket{1} & \cdots & \bra{n}\hat{\Omega}\ket{n}
\end{bmatrix}
\begin{bmatrix}
a_1 \\
\vdots \\
a_n
\end{bmatrix}
\]

(20)

5. **Hermitian operators**

An operator is Hermitian if \(\hat{\Omega}^\dagger = \hat{\Omega}\). On the other hand, if \(\hat{\Omega}^\dagger = -\hat{\Omega}\) it is called anti-Hermitian.

6. **Unitary operators**

An operator is unitary if \(\hat{U}\hat{U}^\dagger = \hat{I}\). Unitary operators conserve inner products, and are a generalization of rotation operators.

7. **Diagonalization**

Every Hermitian operator \(\hat{\Omega}\) can be diagonalized by, at least, one unitary change of basis

\[
\ket{\omega_i} = \hat{U}\ket{i} \quad \Rightarrow
\]

\[
\hat{\Omega}\ket{\omega_i} = \omega_i\ket{\omega_i}
\]

(21) (22)
VI. COMPLETE SET OF COMMUTING OBSERVABLES

A. Reading Guide

1. Section 5.4 on commuting observables.
2. Section 5.2 on functions of operators.

B. Topics

1. Simultaneous diagonalization of Hermitian operators

If \( \hat{\Omega} \) and \( \hat{\Lambda} \) commute, i.e.,
\[
[\hat{\Omega}, \hat{\Lambda}] = \hat{\Omega}\hat{\Lambda} - \hat{\Lambda}\hat{\Omega} = 0,
\]
then there exists (at least) one basis that diagonalizes both operators.

The largest set of commuting observables that can be found is called a complete set of commuting observables. The set of corresponding eigenvalues gives a unique specification of the eigenvectors.

2. Functions of operators

We define a function of an operator as the corresponding Taylor series
\[
f(\hat{\Omega}) = \sum_{n=0}^{\infty} a_n \hat{\Omega}^n.
\]

• If \( \hat{U} \) is a unitary operator that diagonalizes \( \hat{\Omega} \) then
\[
f(\hat{\Omega}) = \hat{U} f(\hat{U}^\dagger \hat{\Omega} \hat{U}) \hat{U}^\dagger.
\]

• If the expansion coefficients in the Taylor series are real then
\[
\left[ f(\hat{\Omega}) \right]^\dagger = f(\hat{\Omega}^\dagger).
\]

• If \( \hat{\Omega} \) and \( \hat{\Lambda} \) commute then
\[
e^{\Omega} e^{\Lambda} = e^{\Omega+\Lambda}.
\]

• If \( \hat{\Omega} \) is Hermitian then \( \exp(i\Omega) \) is unitary.
VII. STATE VECTORS

A. Reading Guide

1. Section 5.1 on the inner product for continuous wave functions.

B. Topics

1. Generalization to infinite dimensions

The $n$ dimensional vector space can be used to represent discrete functions $\psi_n(x_i)$ with endpoints $x_1 = a$ and $x_n = b$:

$$|\psi_n\rangle \leftrightarrow \begin{bmatrix} \psi_n(x_1) \\ \vdots \\ \psi_n(x_n) \end{bmatrix}. \quad (28)$$

The basis vectors

$$\langle x_i \rangle \rightarrow (0 \, \cdots \, 1 \, \cdots \, 0) \quad (29)$$

fulfill

$$\langle x_i | x_j \rangle = \delta_{ij} \quad \text{(orthogonal)} \quad (30)$$

$$\sum_{i=1}^{n} |x_i\rangle \langle x_i| = \hat{I} \quad \text{(complete basis).} \quad (31)$$

The function $\psi_n(x_i)$ is represented by a vector

$$|\psi_n\rangle = \sum_{i=1}^{n} |x_i\rangle \langle x_i| \psi_n = \sum_{i=1}^{n} \psi_n(x_i) |x_i\rangle \quad (32)$$

and the inner product between two vectors is

$$\langle \psi_n | \psi'_n \rangle = \sum_{i=1}^{n} \langle \psi_n | x_i \rangle \langle x_i | \psi'_n \rangle = \sum_{i=1}^{n} \psi_n^*(x_i) \psi'_n(x_i). \quad (33)$$

If we wish to represent continuous functions $\psi(x)$, we may think of $\psi_n(x_i)$ as sampled points and let $n \to \infty$. The interval $[a, b]$ is arbitrary and can be considered to be $]-\infty, \infty[$. The inner product becomes

$$\langle \psi | \psi' \rangle = \int_{-\infty}^{\infty} \psi^*(x) \psi'(x) dx. \quad (34)$$
The basis vectors are

\begin{align}
\langle x \rangle & \leftrightarrow \delta_x, \\
\langle k \rangle & \leftrightarrow \frac{1}{\sqrt{2\pi}} e^{ikx}, \\
\langle x \rangle^* & \leftrightarrow \delta_x, \\
\langle k \rangle^* & \leftrightarrow \frac{1}{\sqrt{2\pi}} e^{-ikx},
\end{align}

and these are complete, i.e.,

\begin{align}
\int \langle x \rangle \langle x \rangle^* dx &= \hat{I}, \\
\int \langle k \rangle \langle k \rangle^* dx &= \hat{I}.
\end{align}

What we are used to refer to as the wave function namely \( \psi(x) \) can thus be interpreted as the projection of the state vector on the \( x \)-basis, since

\[ \langle x \rangle^* \psi = \int_{-\infty}^{\infty} \delta_x(y) \psi(y) dy = \psi(x). \]  

VIII. OPERATOR MATRIX ELEMENTS IN BASIS SETS \(|X\rangle\) AND \(|K\rangle\)

A. Reading Guide

1. Section 5.6 on matrix representations.

B. Topics

1. Operators and infinite dimensions

The matrix elements of a linear operator \( \hat{\Omega} \) in the continuous case are denoted \( \Omega_{xx'} \) and introduced as

\[ \langle x \hat{\Omega} \psi \rangle = \int_{-\infty}^{\infty} \langle x \hat{\Omega} | x' \rangle \langle x' \psi \rangle dx' = \int_{-\infty}^{\infty} \Omega_{xx'} \psi(x') dx'. \]

The matrix elements are thus functions from \( R^2 \to C \) and act under integration.

The Hermitian operators \( \hat{x} \) and \( \hat{k} \) are those to which the basis vectors \( |x\rangle \) and \( |k\rangle \) are eigenvectors with eigenvalues \( x \) and \( k \), respectively. The matrix elements of these operators
where $\delta'$ denotes the derivative of the Dirac delta function.

### IX. A FEW RESULTS DUE TO HEISENBERG AND EHRENFEST

#### A. Reading Guide

1. Section 5.4 on the Heisenberg uncertainty relations.
2. Section 3.4 on the Ehrenfest theorem.
3. Section 5.7 on time evolution of a system.
4. Section 5.8 on the Heisenberg picture.

#### B. Topics

1. **Heisenberg’s uncertainty relation**

   If $\hat{\Omega}$ and $\hat{\Lambda}$ are Hermitian operators with

   \[ [\hat{\Omega}, \hat{\Lambda}] = i\hat{\Gamma} \]

   then $\Gamma$ is Hermitian.

   We define standard deviations $\Delta \Omega$ and $\Delta \Lambda$ as

   \[ (\Delta \Omega)^2 = \langle \psi | [\hat{\Omega} - \langle \hat{\Omega} \rangle]^2 | \psi \rangle, \]
   \[ (\Delta \Lambda)^2 = \langle \psi | [\hat{\Lambda} - \langle \hat{\Lambda} \rangle]^2 | \psi \rangle, \]

   and the Heisenberg’s uncertainty relation tells us that

   \[ (\Delta \Omega)^2 (\Delta \Lambda)^2 \geq \frac{1}{4} (\hat{\Gamma})^2. \]
2. **Ehrenfest’s theorem**

An analogy to classical mechanics is obtained by studying the time-development of quantum mechanical expectation values. The Ehrenfest theorem tells us that

\[
\frac{d}{dt} \langle \hat{\Omega} \rangle = \langle \frac{\partial \hat{\Omega}}{\partial t} \rangle + \frac{1}{i\hbar} \langle [\hat{\Omega}, \hat{H}] \rangle. \tag{51}
\]

3. **Time-development of the state vector**

In cases when the Hamiltonian carries no explicit time-dependence, the time evolution of the state vector, as governed by the Schrödinger equation, can be interpreted as a rotation of the state vector in Hilbert space:

\[
|\psi(t)\rangle = e^{i\hat{H}(t-t_0)/\hbar} |\psi(t_0)\rangle, \tag{52}
\]

where the unitary operator

\[
U(t, t_0) = e^{i\hat{H}(t-t_0)/\hbar} \tag{53}
\]

is referred to as the propagator of the system.

4. **Heisenberg picture**

In the Heisenberg picture, state vectors are time-independent while operator matrix elements are time-dependent. State vectors and operators in the Schrödinger and Heisenberg pictures are related by the propagator [Eq. (53)]

\[
|\psi_H\rangle = U^\dagger(t, t_0) |\psi(t)\rangle, \tag{54}
\]

\[
\hat{\Omega}_H(t) = U^\dagger(t, t_0) \hat{\Omega} U(t, t_0), \tag{55}
\]

where the subscript $H$ labels elements in the Heisenberg picture.

X. **SYMMETRY AND CONSERVATION**

A. **Reading Guide**

1. Section 5.10 on symmetry and conservation.
B. Topics

1. Infinitesimal translations

For each operation that leaves the Hamiltonian invariant there is a corresponding dynamical variable that is a constant of the motion and is conserved. Translational symmetry provides an example.

<table>
<thead>
<tr>
<th>Classical Mechanics</th>
<th>Quantum Mechanics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Translation $x \rightarrow x + \epsilon$</td>
<td>$\langle \hat{x} \rangle \rightarrow \langle \hat{x} \rangle + \epsilon$</td>
</tr>
<tr>
<td>$p \rightarrow p$</td>
<td>$\langle \hat{p} \rangle \rightarrow \langle \hat{p} \rangle$</td>
</tr>
<tr>
<td>Invariance $\mathcal{H} \rightarrow \mathcal{H}$</td>
<td>$\langle \hat{H} \rangle \rightarrow \langle \hat{H} \rangle$</td>
</tr>
<tr>
<td>Conservation $\dot{p} = 0$</td>
<td>$\langle \dot{\hat{p}} \rangle = 0$</td>
</tr>
</tbody>
</table>

Define a translation operator $\hat{T}(\epsilon)$ for which the action on position kets is

$$\hat{T}(\epsilon)|x\rangle = |x + \epsilon\rangle.$$  \hspace{1cm} (56)

It is shown that to first order in $\epsilon$ the translation operator is

$$\hat{T}(\epsilon) = \hat{I} - \frac{i\epsilon}{\hbar} \hat{p},$$ \hspace{1cm} (57)

and the requirement that $\langle \hat{H} \rangle$ should be invariant under the translation of a wave function, i.e.,

$$|\psi\rangle \longrightarrow \hat{T}(\epsilon)|\psi\rangle,$$ \hspace{1cm} (58)

then leads to the result

$$[\hat{p}, \hat{H}] = 0 \implies \langle \dot{\hat{p}} \rangle = 0.$$ \hspace{1cm} (59)

2. Finite translations

A finite translation of a state vector is accomplished with the operator

$$\hat{T}(a) = e^{-ia\hat{p}/\hbar}.$$ \hspace{1cm} (60)
XI. HARMONIC OSCILLATOR

A. Reading Guide

1. Section 4.7 with solution to the harmonic oscillator in the $x$-basis. This course is not concerned with the fine details of the solution in the coordinate basis, but the general ideas of solving the time-independent Schrödinger equation should be clear to everyone.

2. Section 5.6 on the harmonic oscillator in the energy basis should be studied in detail.

B. Topics

1. Hamiltonian

The Hamiltonian to the 1D harmonic oscillator is

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2,$$

and, we are interested in solving the eigenvalue problem

$$\hat{H}|n\rangle = E_n|n\rangle.$$  (62)

2. Creation and annihilation operators

An auxiliary operator $\hat{a}$ is introduced as

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \sqrt{\frac{1}{2m\omega\hbar}} \hat{p},$$

and, we can write the Hamiltonian as

$$\hat{H} = \hbar \omega (\hat{a}^\dagger \hat{a} + \frac{1}{2}).$$  (64)

Given the commutation relation

$$[\hat{x}, \hat{p}] = i\hbar$$

we show, first,

$$[\hat{a}, \hat{a}^\dagger] = 1.$$  (66)
and, second,

\[
\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \quad (67)
\]
\[
\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \quad (68)
\]

We refer to \(\hat{a}^\dagger\) and \(\hat{a}\) as creation and annihilation operators, respectively, and we conclude that the energy spectrum is given by \(E_n = \hbar\omega(n + 1/2)\) with \(n = 0, 1, 2, \ldots\).

3. Transition from energy to coordinate basis

If we are interested in the particle probability density, we need to find the projections of the eigenkets on the basis vectors \(|x\rangle\). The ground state must fulfill

\[
\hat{a}|0\rangle = 0, \quad (69)
\]

which, when projected on \(|x\rangle\), implies

\[
\left[ \sqrt{\frac{m\omega}{2\hbar}} \frac{d}{dx} + \frac{\hbar}{2m\omega} \frac{d}{dx} \right] \psi_0(x) = 0. \quad (70)
\]

The solution to this differential equation is

\[
\psi_0(x) = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-m\omega x^2/2\hbar}. \quad (71)
\]

Wave functions corresponding to the excited states are found by the relation

\[
\psi_n(x) = \langle x|n \rangle = \langle x|\left(\hat{a}^\dagger\right)^n|0\rangle. \quad (72)
\]

XII. ROTATIONAL SYMMETRY AND ORBITAL ANGULAR MOMENTUM

A. Reading Guide

1. Sections 6.1 and 6.2 present general operator properties and the connection to rotations. These sections are central.

2. Section 6.4 illustrates how the spherical harmonics are the exact solutions to some “real” problems. This is important.
B. Topics

1. Orbital angular momentum

In accordance with the linear momentum $p$, the orbital angular momentum $L$ is conserved for isolated systems. In quantum mechanics the orbital angular momentum operator takes the form

$$\hat{L} = \hat{\mathbf{r}} \times \hat{\mathbf{p}},$$

or in terms of the Cartesian components

$$\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y,$$
$$\hat{L}_y = \hat{z} \hat{p}_x - \hat{x} \hat{p}_z,$$
$$\hat{L}_z = \hat{x} \hat{p}_y - \hat{y} \hat{p}_x.$$

Given the commutation relations between position and linear momentum operators, it is straightforward to show the relations:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z,$$
$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x,$$
$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y,$$

or, alternatively,

$$\hat{L} \times \hat{L} = i\hbar \hat{L}.$$  

We define an operator corresponding to the square length of the orbital angular momentum as

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

and it easily shown that the following commutation relations hold

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0.$$  

We can thus find eigenstates to $\hat{L}^2$ and any of the components.
2. Rotational invariance

As stated above, for each operation that leaves the Hamiltonian invariant there is a corresponding dynamical variable that is a constant of the motion and is conserved. Rotational symmetry provides an example.

<table>
<thead>
<tr>
<th></th>
<th>Classical Mechanics</th>
<th>Quantum Mechanics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation</td>
<td>( x \rightarrow x \cos \epsilon - y \sin \epsilon )</td>
<td>( \langle \hat{x} \rangle \rightarrow \langle \hat{x} \rangle \cos \epsilon - \langle \hat{y} \rangle \sin \epsilon )</td>
</tr>
<tr>
<td></td>
<td>( y \rightarrow x \sin \epsilon + y \cos \epsilon )</td>
<td>( \langle \hat{x} \rangle \rightarrow \langle \hat{x} \rangle \sin \epsilon + \langle \hat{y} \rangle \cos \epsilon )</td>
</tr>
<tr>
<td></td>
<td>( p_x \rightarrow p_x \cos \epsilon - p_y \sin \epsilon )</td>
<td>( \langle \hat{p}_x \rangle \rightarrow \langle \hat{p}_x \rangle \cos \epsilon - \langle \hat{p}_y \rangle \sin \epsilon )</td>
</tr>
<tr>
<td></td>
<td>( p_y \rightarrow p_x \sin \epsilon + p_y \cos \epsilon )</td>
<td>( \langle \hat{p}_y \rangle \rightarrow \langle \hat{p}_x \rangle \sin \epsilon + \langle \hat{p}_y \rangle \cos \epsilon )</td>
</tr>
<tr>
<td>Invariance</td>
<td>( \mathcal{H} \rightarrow \mathcal{H} )</td>
<td>( \langle \hat{H} \rangle \rightarrow \langle \hat{H} \rangle )</td>
</tr>
<tr>
<td>Conservation</td>
<td>( \hat{L}_z = 0 )</td>
<td>( \langle \hat{L}_z \rangle = 0 )</td>
</tr>
</tbody>
</table>

Let \( \hat{R}(\epsilon \mathbf{e}_z) \) be a rotation operator that rotates a system an angle \( \epsilon \) about the \( z \)-axis. The action of the rotation operator on position kets is

\[
\hat{R}(\epsilon \mathbf{e}_z) |x, y\rangle = |x \cos \epsilon - y \sin \epsilon, x \sin \epsilon + y \cos \epsilon\rangle.
\]  

(83)

It is shown that to first order in \( \epsilon \) the rotation operator is

\[
\hat{R}(\epsilon \mathbf{e}_z) = \mathbf{I} - \frac{i\epsilon}{\hbar} \hat{L}_z,
\]  

(84)

and the requirement that \( \langle \hat{H} \rangle \) should be invariant under the rotation of a wave function, i.e.,

\[
|\psi\rangle \rightarrow \hat{R}(\epsilon \mathbf{e}_z)|\psi\rangle,
\]  

(85)

then leads to the result

\[
[\hat{L}_z, \hat{H}] = 0 \implies \langle \hat{L}_z \rangle = 0.
\]  

(86)

3. Finite rotations

A finite rotation of a state vector is accomplished with the operator

\[
\hat{R}(\phi \mathbf{e}_z) = e^{-i\phi \hat{L}_z/\hbar}.
\]  

(87)
XIII. GENERAL ANGULAR MOMENTUM OPERATORS

A. Reading Guide

1. Sections 6.5 and 6.6 on the solution to the general angular momentum problem in 3D with help of ladder operators should be studied in detail.

B. Topics

1. Ladder operators

The laws for infinitesimal rotations in 3D are expressed in the commutation relation

\[ \hat{J} \times \hat{J} = i\hbar \hat{J} . \] (88)

Given this relation, let us solve the common eigenvalue problem for operators \( \hat{J}^2 \) and \( \hat{J}_z \), i.e.,

\[ \hat{J}^2 |j, m\rangle = j(j + 1)\hbar^2 |j, m\rangle , \] (89)
\[ \hat{J}_z |j, m\rangle = m\hbar |j, m\rangle . \] (90)

Define the auxiliary operator

\[ \hat{J}_+ = \hat{J}_x + i\hat{J}_y \] (91)

and let the adjoint of this operator be denoted by \( \hat{J}_- = \hat{J}_+^\dagger \). The operators \( \hat{J}_\pm \) are referred to as ladder operators. It is then straightforward to show that

\[ [\hat{J}^2, \hat{J}_\pm] = 0 , \] (92)
\[ [\hat{J}_z, \hat{J}_\pm] = \pm \hbar \hat{J}_\pm . \] (93)

With help of the auxiliary operator, one is able to obtain the allowed eigenvalues to the eigenvalue problems in Eqs. (89) and (90). The possible eigenvalues are

\[ j = 0, 1/2, 1, 3/2, \ldots , \] (94)
\[ m = -j, -(j - 1), \ldots , (j - 1), j . \] (95)
2. Matrix representation

Once the actions of the ladder operators on the common eigenkets to $\hat{J}^2$ and $\hat{J}_z$ have been established, it is trivial to determine the matrix representation of an arbitrary operator $\hat{\Omega}(\hat{J}_x, \hat{J}_y, \hat{J}_z)$. These actions are:

$$\hat{J}_\pm |j, m\rangle = \sqrt{j(j+1) - m(m \pm 1)} \hbar |j, m\rangle$$

(96)

XIV. ORBITAL ANGULAR MOMENTUM

A. Reading Guide

1. Section 6.3 solve for common eigenfunctions to $\hat{L}^2$ and $\hat{L}_z$ in the coordinate basis.

The general ideas should be known by everyone, but the details are not central in this course. Here follows an alternative, where the coordinate representations are found from the abstract kets $|l, m\rangle$, and this technique should be clear to everyone.

B. Topics

1. Eigenvalue problem

The solution to the eigenvalue problem for the orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ is obtained from the general analysis by setting $\hat{L} = \hat{J}$ and ignore eigenstates with half-integer values of $j$ and $m$. Hence, for the orbital angular momentum, we have

$$\hat{L}^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle, \quad l = 0, 1, 2, \ldots,$$

$$\hat{L}_z |l, m\rangle = m\hbar |l, m\rangle, \quad m = 0, \pm 1, \pm 2, \ldots.$$  

(97)

2. Eigenstates in the coordinate basis

We find the representation of $|l, m\rangle$ in the coordinate basis by using

$$\hat{L}_+ |l, l\rangle = 0$$

(98)

which implies

$$\left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] Y_{ll}(\theta, \phi) = 0.$$  

(99)
Since \( Y^{ll}_\theta(\theta, \phi) \) is an eigenfunction of \( \hat{L}_z \) with eigenvalue \( l \hbar \), we must have

\[
Y^{ll}_\theta(\theta, \phi) = \frac{1}{\sqrt{2\pi}} e^{il\phi} \Theta^{ll}_\theta(\theta). \tag{100}
\]

Eq. (99) thereby reduces to

\[
\left[ \frac{\partial}{\partial \theta} - l \cot \theta \right] \Theta^{ll}_\theta(\theta, \phi) = 0 \tag{101}
\]

with a solution that is proportional to \((\sin \theta)^l\). The normalized solution becomes

\[
Y^{ll}_\theta(\theta, \phi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l + 1)!}{4\pi}} (\sin \theta)^l e^{il\phi}. \tag{102}
\]

Solutions \( Y^{lm}_\theta(\theta, \phi) \) with \( m < l \) are obtained by operation with the operator \( \hat{L}_- \). The eigenfunctions are orthogonal since they are nondegenerate eigenfunctions to the Hermitian operators \( \hat{L}^2 \) and \( \hat{L}_z \).

XV. STATE SPACE OF ELECTRONS

A. Reading Guide

1. Sections 6.7 and 6.8 on spin angular momentum.

B. Topics

1. State space of the electron

The state space of the electron is a direct product between an infinite-dimensional space, which describes the orbital degrees of freedom, and a two-dimensional space describing the spin degrees of freedom. The basis vectors of the electron state space are

\[
| x, y, z, s_z \rangle = | x, y, z \rangle \otimes | s_z \rangle, \tag{103}
\]

where reference to the magnitude of the spin has been omitted (it is invariant and given by \( s = 1/2 \)) and the possible values of the spin along the \( z \)-axis are given by \( s_z = \pm 1/2 \). The eigenkets in spin space are also referred to as the “spin up” ket \(|+\rangle\) and the “spin down” ket \(|-\rangle\).
The completeness relation for the basis vectors is
\[ \hat{I} = \sum_{s_z = \pm 1/2} \int_V |x, y, z, s_z \rangle \langle x, y, z, s_z| \, dx dy dz, \]  
(104)
and, the orthogonality relation is
\[ \langle x, y, z, s_z | x', y', z', s'_z \rangle = \delta(x - x') \delta(y - y') \delta(z - z') \delta_{s_z s'_z}, \]  
(105)
where the first three \(\delta\)'s are Dirac delta functions and the last is a Kronecker delta function.

A general state vector is
\[ |\psi\rangle = |\psi^+_o \rangle \otimes |+\rangle + |\psi^-_o \rangle \otimes |-\rangle, \]  
(106)
where the subscript \(\text{"o"}\) indicates that the vector belong to the orbital space. The inner product between two state vectors become
\[ \langle \psi_1 | \psi_2 \rangle = \left[ \langle \psi^+_1 o | \otimes |+\rangle + \langle \psi^-_1 o | \otimes |-\rangle \right] \]  
(107)
\[ = \langle \psi^+_1 o | \psi^+_2 o \rangle \langle +|+\rangle + \langle \psi^-_1 o | \psi^-_2 o \rangle \langle +|-\rangle + \langle \psi^-_1 o | \psi^+_2 o \rangle \langle -+\rangle + \langle \psi^+_1 o | \psi^-_2 o \rangle \langle --\rangle \]
\[ = \langle \psi^+_1 o | \psi^+_2 o \rangle + \langle \psi^-_1 o | \psi^-_2 o \rangle, \]
where we have used that the basis kets of the spin space are orthogonal.

2. Operators

The familiar operators in orbital space \(\hat{\Omega}_o\) are modified according to
\[ \hat{\Omega} = \hat{\Omega}_o (\hat{x}, \hat{p}) \otimes \hat{I}_s, \]  
(108)
where \(\hat{I}_s\) is the two-dimensional identity operator in spin space. We refer to such operators as pure orbital operators, since they do not affect spin kets.

Operators that act in spin space take the form
\[ \hat{\Omega} = \hat{I}_o \otimes \hat{\Omega}_s, \]  
(109)
where \(\hat{I}_o\) is the identity operator in orbital space. We refer to such operators as pure spin operators, since they do not affect orbital kets.

Many important systems are described by either pure orbital or pure spin operators (or a combination thereof). In general, however, operators may take the form
\[ \hat{\Omega} = \hat{\Omega}_o \otimes \hat{\Omega}_s. \]  
(110)
Spin operators, apart from $\hat{I}_s$, are found from the general angular momentum analysis by restricting the quantum number $j = 1/2$. We denote these restricted operators and quantum numbers with the letter $s$. An arbitrary spin operator $\hat{\Omega}$ can be expressed by a linear combination of the identity operator and the three angular momentum operators $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ with $j = 1/2$:

$$
\hat{I}_s = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}; \quad \hat{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \quad \hat{S}_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \quad \hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
$$

If the Hamiltonian of an electronic system is separable in orbital and spin degrees of freedom, i.e.,

$$
\hat{H} = \hat{H}_o \otimes \hat{I}_s + \hat{I}_o \otimes \hat{H}_s,
$$

then state vectors factorize according to

$$
|\psi(t)\rangle = |\psi_o(t)\rangle \otimes |\chi_s(t)\rangle.
$$

The time evolutions of $|\psi_o(t)\rangle$ and $|\chi_s(t)\rangle$ are governed by $\hat{H}_o$ and $\hat{H}_s$, respectively. The orbital and spin part of the wave function are thus separated and are statistically independent.

3. Expectation values

The expectation value of an operator becomes

$$
\langle \psi | \hat{\Omega} | \psi \rangle = \langle \psi_o^+ | \hat{\Omega}_o | \psi_o^+ \rangle \langle + | \hat{\Omega}_s | + \rangle + \langle \psi_o^+ | \hat{\Omega}_o | \psi_o^- \rangle \langle + | \hat{\Omega}_s | - \rangle + \langle \psi_o^- | \hat{\Omega}_o | \psi_o^+ \rangle \langle - | \hat{\Omega}_s | + \rangle + \langle \psi_o^- | \hat{\Omega}_o | \psi_o^- \rangle \langle - | \hat{\Omega}_s | - \rangle
$$

For a state that is separable in orbital and spin degrees of freedom, the expectation value simplifies according to

$$
\langle \psi | \hat{\Omega} | \psi \rangle = \langle \psi_o | \hat{\Omega}_o | \psi_o \rangle \langle \chi_s | \hat{\Omega}_s | \chi_s \rangle.
$$

It is customary to normalize the orbital and spin kets individually, and expectation values of pure operators then become particularly simple.
4. Rotations

A finite rotation of the state vector is accomplished with the total angular momentum operator \( \mathbf{J} = \mathbf{L} + \mathbf{S} \). For instance a rotation an angle \( \phi \) about the \( z \)-axis of a system, which is represented by a separable state, is accomplished by the operation

\[
|\psi^R\rangle = e^{-i\phi \hat{J}_z/\hbar} |\psi\rangle = e^{-i\phi \hat{L}_z/\hbar} |\psi_o\rangle \otimes e^{-i\phi \hat{S}_z/\hbar} |\chi_s\rangle.
\]

(116)

XVI. SPIN DYNAMICS

A. Reading Guide

1. Section 6.8 on Pauli spin matrices.

2. Section 6.9 on rotations in spin space.

B. Topics

1. Spin kets

An arbitrary spin ket is written as

\[
|\chi_s\rangle = \alpha |+\rangle + \beta |-\rangle = \alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}
\]

(117)

and it is normalized according to

\[
\langle \chi_s | \chi_s \rangle = (\alpha^* \beta^*) \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = |\alpha|^2 + |\beta|^2 = 1.
\]

(118)

If \( \mathbf{n} \) is a unit vector pointing along the \((\theta, \phi)\)-direction in the laboratory, then the eigenvectors to the operator \( \mathbf{n} \cdot \hat{\mathbf{S}} \) are

\[
|n+\rangle = \begin{pmatrix} \cos(\theta/2) e^{-i\phi/2} \\ \sin(\theta/2) e^{i\phi/2} \end{pmatrix}, \quad |n-\rangle = \begin{pmatrix} -\sin(\theta/2) e^{-i\phi/2} \\ \cos(\theta/2) e^{i\phi/2} \end{pmatrix},
\]

(119)

and

\[
\langle \hat{\mathbf{S}} \rangle = \langle n\pm | \hat{\mathbf{S}} | n\pm \rangle = \pm \frac{\hbar}{2} \mathbf{n}.
\]

(120)
2. Pauli spin matrices

The Pauli spin matrices are introduced as

\[
\hat{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \quad \hat{\sigma}_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}; \quad \hat{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},
\]

i.e.,

\[
\hat{S} = \frac{\hbar}{2} \hat{\sigma}.
\]

The Pauli spin matrices are linearly independent, and together with the identity matrix they form a complete basis for complex \(2 \times 2\) matrices. They have the following properties

1. \([\hat{\sigma}_i, \hat{\sigma}_j]_+ = 0\) for all \(i \neq j\).

2. \([\hat{\sigma}_i, \hat{\sigma}_j] = 2i \hat{\sigma}_k\) with cyclic ordering of indices.

3. \(\hat{\sigma}_i \hat{\sigma}_j = i \hat{\sigma}_k\) with cyclic ordering of indices.

4. \(\text{Tr}(\hat{\sigma}_i) = 0\)

5. \(\hat{\sigma}_i^2 = \hat{I}_s\)

6. \((\hat{A} \cdot \hat{\sigma})(\hat{B} \cdot \hat{\sigma}) = (\hat{A} \cdot \hat{B})\hat{I}_s + i(\hat{A} \times \hat{B}) \cdot \hat{\sigma}\)

3. Rotation operators in spin space

The operator that rotates a spinor an angle \(\theta\) about the \(n\) axis is

\[
\hat{R}(\theta \mathbf{n}) = e^{-i \theta \mathbf{n} \cdot \hat{S}/\hbar} = \cos(\theta/2) \hat{I}_s - i \sin(\theta/2) \mathbf{n} \cdot \hat{\sigma}.
\]

It is clear that the identity operation can be represented by a rotation \(\theta = 4\pi\) in spin space, whereas a rotation \(\theta = 2\pi\) produce a sign change of the spinor.

4. Spin dynamics

The interaction of the electron spin angular momentum and an external, homogeneous, static, magnetic field \(\mathbf{B}\) is described by the Hamiltonian

\[
\hat{H}_s = \frac{g_e}{2m} \hat{S} \cdot \mathbf{B} = \mu_B \hat{\sigma} \cdot \mathbf{B},
\]

26
where $e$ is the elementary charge, $m$ the electron mass, and the electronic $g$-factor has been set equal to 2. The numerical value of the Bohr magneton is

$$
\mu_B = \frac{e\hbar}{2m} = 5.788 \times 10^{-6} \text{ eV/T},
$$

so the interaction energy is small compared to the electronic binding energy in atoms.

Assume that a system at time $t_0$ is in a state given by the spinor $|\chi(t_0)\rangle$. The time-dependence of the spinor is obtained with use of the propagator

$$
|\chi(t)\rangle = e^{-i\hat{H}_s(t-t_0)/\hbar}|\chi(t_0)\rangle,
$$

i.e., a rotation in spin space.

XVII. HYDROGEN ATOM

A. Reading Guide

1. Section 7.5 presents the details of the solution for the radial hydrogen functions $R_{n,l}(r)$. The emphasis is not on these details in this course, but the general aspects should be clear to everyone. For instance, the solution of the radial equation depends parametrically on the $l$ quantum number and impose restrictions on this quantum number. The remainder of this chapter provides other 3D examples for solving the time-independent Schrödinger equation. We are only concerned with the principles of these solutions.

B. Topics

1. Hamiltonian

The Hamiltonian for an electron which is bound to a proton is

$$
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r),
$$

where $m$ is the electron mass and the potential $V(r)$ is given by

$$
V(r) = -\frac{e^2}{4\pi\epsilon r}.
$$

The Hamiltonian is spherically symmetric and thus commutes with the generators of rotations in orbital space, i.e., the components of the orbital angular momentum operator.
Furthermore, the Hamiltonian is a pure orbital operator and thus commutes with pure spin operators. It is therefore possible to find common eigenkets to the set of operators: $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$. These eigenstates are

$$\psi_{n,l,m_l,m_s}(r, \theta, \phi) = R_{n,l}(r)Y_{l,m}(\theta, \phi) \times \begin{cases} 
1, & \text{for } m_s = +1/2 \\
0, & \text{for } m_s = -1/2 
\end{cases}$$

where $Y_{l,m}$ are the spherical harmonics and $R_{n,l}$ are the radial hydrogen wave functions which are solutions to the equation

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{l(l+1)}{r^2} \right) + V(r) \right] R_{n,l}(r) = E_n R_{n,l}(r).$$

The energy $E_n$ is degenerate with respect to quantum numbers $l$, $m_l$, and $m_s$. The numerical value of the energy is $E_n = -13.6/n^2$ (eV), and the quantum numbers are given by

$$n = 1, 2, 3, \ldots,$$

$$l = 0, 1, 2, \ldots, (n-1),$$

$$m_l = -l, -(l-1), \ldots, (l-1), l,$$

$$m_s = \pm 1/2.$$  

2. **Complete set of commuting observables**

The set of operators $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ forms a complete set of commuting observables for the hydrogen atom. This is, however, by no means the only possible set of operators. We could for instance replace the $z$-component of the vector operators for any of the other two components. Another, less trivial, possibility is to choose the set $\hat{H}$, $\hat{J}^2$, $\hat{L}^2$, $\hat{S}^2$, and $\hat{J}_z$, where

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

is the total angular momentum operator. Clearly, different choices of commuting operators lead to a different sets of eigenstates. The sets are all complete so it is an arbitrary choice.
3. Hydrogen atom in weak magnetic fields

Assume that the hydrogen atom is placed in a weak, homogeneous, time-independent, magnetic field directed along the $z$-axis:

$$\mathbf{B} = B_0 \mathbf{e}_z.$$  

(133)

The orbital and spin angular momenta couples to the external field and the Hamiltonian for the electron becomes

$$\hat{H} = \hat{H}_0 + \frac{eB_0}{2m} \hat{L}_z + \frac{geB_0}{2m} \hat{S}_z,$$

(134)

where $H_0$ denotes the Hamiltonian in absence of the field [Eq. (127)]. Since $\hat{L}_z$ and $\hat{S}_z$ are included in the complete set of commuting observables, the Hamiltonian $\hat{H}$ is diagonalized by the same states as before namely $|n, l, m_l, m_s\rangle$ in Eq. (129). The eigenvalues of the Hamiltonian become

$$\hat{H}|n, l, m_l, m_s\rangle = \left[ E_n + \frac{eB_0}{2m} (m_l + 2m_s) \right] |n, l, m_l, m_s\rangle,$$

(135)

where $g$ is set equal to 2. This result is known as the Zeeman splitting of energy levels.

XVIII. ADDITION OF ANGULAR MOMENTA

A. Reading Guide

1. Section 6.10 on addition of angular momenta.

2. Section 8.2 on the spin-orbit contribution to the fine structure splitting of the hydrogen spectrum.

B. Topics

1. Spin-orbit coupling in hydrogen

Even for an isolated system, there are small, but sometimes important, corrections to the Hamiltonian in Eq. (127) due to relativistic effects. Such corrections may be deduced from a relativistic theory and incorporated in an ad hoc manner. A proper set of commuting
observables in the relativistic case is $\hat{H}$, $\hat{J}^2$, and $\hat{J}_z$, i.e., the Hamiltonian is invariant under rotations of the spinor.

The spin-orbit correction to the Hamiltonian is given by

$$\hat{H}_{\text{SO}} = \frac{\hbar \alpha}{2m^2 c} \frac{1}{r^3} \hat{L} \cdot \hat{S},$$  \hspace{1cm} (136)$$

where $m$ is the electron mass, $c$ is the speed of light, and $\alpha$ is the dimensionless fine-structure constant ($\alpha \approx 1/137$). From the relation

$$\hat{L} \cdot \hat{S} = \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2),$$  \hspace{1cm} (137)$$

it is clear that the spin-orbit interaction is diagonalized by the common eigenkets to $\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$, $\hat{S}^2$ which we may denote by $|j, m_j\rangle$.

2. Addition of angular momenta

If an angular momentum (here $\mathbf{J}$) is the sum of two independent angular momenta (here $\mathbf{L}$ and $\mathbf{S}$), we may relate the eigenkets of $\mathbf{J}$ to those of $\mathbf{L}$ and $\mathbf{S}$. The relevant question to ask is; if the magnitude of the independent angular momenta are known, then what are the possible values for the magnitude of the total angular momentum. In other words, given $l$ and $s$, we are to find the set of eigenkets $|j, m_j\rangle$ and thus the possible values for $j$ and $m_j$.

The two sets of eigenkets are related by the unitary transformation

$$|j, m_j\rangle = \sum_{m_l, m_s} |l, m_l, s, m_s\rangle \langle l, m_l, s, m_s|j, m_j\rangle,$$  \hspace{1cm} (138)$$

where $|l, m_l, s, m_s\rangle$ are known as Clebsch–Gordan coefficients. The possible values of $j$ and $m_j$ are found by a few considerations:

- Since $m_j = m_l + m_s$, the maximum value of $m_j$ is $l + s$. This corresponds to a possible value for $j$, and, since there is only one such ket, we have

$$|l+s, l+s\rangle = |l, l, s, s\rangle.$$  \hspace{1cm} (139)$$

The other kets $|l+s, m_j\rangle$ are found by applying the ladder operator $\hat{J}_- = \hat{L}_- + \hat{S}_-$ on the ket $|l, l, s, s\rangle$. 

30
• There are two kets $|l, m_l, s, m_s\rangle$ with $m_j = l + s - 1$, which give rise to two linearly independent kets $|j, l + s - 1\rangle$. One of these two linear combinations must be the ket $|l + s, l + s - 1\rangle$, and the other must thus be $|l + s - 1, l + s - 1\rangle$. The next possible value of $j$ is thus $l + s - 1$.

• The number of $|l, m_l, s, m_s\rangle$ kets must equal the number of $|j, m_j\rangle$ kets. The smallest possible value of $j$ is therefore $|l - s|$, so that

$$ (2l + 1)(2s + 1) = \sum_{j=|l-s|}^{l+s} (2j + 1). \quad (140) $$

In the coordinate basis the $|j, m_j\rangle$ kets take the form

$$ Y_{l\pm1/2, m_j}(\theta, \phi) = \left[ \pm \sqrt{\frac{l\pm m_j+1/2}{2l+1}} Y_{l, m_j-1/2}(\theta, \phi) \right] - \left[ \sqrt{\frac{l\pm m_j+1/2}{2l+1}} Y_{l, m_j+1/2}(\theta, \phi) \right]. \quad (141) $$

3. Fine-structure splitting

The energy shift due to the spin-orbit interaction is one of three contributions to the fine-structure splitting, and the magnitude is calculated with first-order perturbation theory. The unperturbed wave functions are

$$ \psi_{n,j,m_j}^{(0)}(r, \theta, \phi) = R_{n,l}(r) Y_{j,m_j}(\theta, \phi) \quad (142) $$

with quantum numbers that fulfill

$$ n = 1, 2, 3, \ldots, $$

$$ l = 0, 1, 2, \ldots, (n - 1), $$

$$ s = \frac{1}{2} $$

$$ j = |l - s|, l + s, $$

$$ m_j = -j, -(j - 1), \ldots, (j - 1), j. \quad (143) $$

The energy corrections become

$$ \langle \psi_{n,j,m_j}^{(0)} | \hat{H}_{SO} | \psi_{n,j,m_j}^{(0)} \rangle = \frac{\hbar \alpha}{2m^2c} \left\langle \frac{1}{r^3} \right\rangle_R \langle j, m_j \rangle \frac{1}{2} (j^2 - \hat{L}^2 - \hat{S}^2) |j, m_j\rangle, \quad (144) $$

where the radial integration $\langle r^{-3}\rangle_R$ can be carried out analytically. It is clear that the spin-orbit correction vanishes for states with $l = 0$, i.e., so-called $s$-states. For states with $l > 0$
the first-order energy corrections become

\[ \langle \psi^{(0)} | \hat{H}_{SO} | \psi^{(0)} \rangle = \frac{\hbar^3 \alpha}{4m^2 c} \left( \frac{1}{r^3} \right)_{R} \times \begin{cases} 
    l & \text{for } j = l + 1/2 \\
    -(l + 1) & \text{for } j = l - 1/2 
\end{cases} . \] (145)

4. Importance of spin-orbit interaction

In hydrogen the spin-orbit interaction is small in magnitude. For heavier atoms, however, it is significant and perturbation theory is not always applicable.

THE END