

Introduction to Quantum Mechanics

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Preface

This script is based on the lecture Introduction to Quantum Mechanics (FS 2017) for Engineers taught by Pr. Dr. David Norris.

I cannot guarantee neither correctness nor completeness of the script. Please report any mistake directly to me.

Have fun with Quantum Mechanics!

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1 The Wave Function and the Schrödinger Equation

1.1 The Schrödinger Equation

Consider a particle of mass m that moves along the x -axis in a potential $V(x, t)$. The particle's wave function $\Psi(\cdot, \cdot) : \mathbb{R} \times \mathbb{R} \rightarrow \mathbb{C}$ is the solution of the Schrödinger Equation (SE):

$$i\hbar \frac{d}{dt} \Psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x, t) \Psi, \quad (1.1)$$

where $i^2 = -1$ and $\hbar = h/2\pi$ is the normalized Plank's constant. The wave function has a statistical interpretation:

$$\int_a^b \Psi^* \Psi dx = \int_a^b |\Psi|^2 dx = P(x(t) \in [a, b]), \quad (1.2)$$

i.e. probability of finding the particle between a and b at time t ($|\Psi|^2$ is the probability density). To be physically meaningful Ψ must be:

1. square-integrable:

$$\int_{-\infty}^{+\infty} |\Psi|^2 dx < \infty;$$

2. normalized:

$$\int_{-\infty}^{+\infty} |\Psi|^2 dx = 1.$$

Remark. Square-integrability implies (at least in physics):

$$\lim_{x \rightarrow \pm\infty} \Psi = 0, \quad \lim_{x \rightarrow \pm\infty} \frac{\partial \Psi}{\partial x} = 0.$$

Example. The wave function $\Psi = kx$ with $x \in \mathbb{R}$ is not square integrable:

$$\int_{-\infty}^{+\infty} |\Psi|^2 dx = \int_{-\infty}^{+\infty} k^2 x^2 dx = 2 \int_0^{+\infty} k^2 x^2 dx \rightarrow \infty.$$

Example. The wave function $\Psi = kx$ with $x \in [-1, +1]$ is square-integrable and, for appropriate k , normalized:

$$\int_{-\infty}^{+\infty} |\Psi|^2 dx = \int_{-1}^{+1} k^2 x^2 dx = 2 \int_0^1 k^2 x^2 dx = \frac{2}{3} k^2 \stackrel{!}{=} 1 \quad \Rightarrow \quad k = \sqrt{\frac{3}{2}}.$$

1.2 Observables and Expectation Values

Given any observable quantity Q , in QM we have an operator \hat{Q} which can be written as a function of the

- position operator: $\hat{x} = x$ and
- momentum operator $\hat{p} = -i\hbar \frac{\partial}{\partial x}$,

i.e. $\hat{Q} = \hat{Q}(\hat{x}, \hat{p})$. The expectation value of the quantity is

$$\langle Q(x, p) \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{Q}(\hat{x}, \hat{p}) \Psi dx. \quad (1.3)$$

What does that mean? The expectation value of the position of the particle is

$$\langle x \rangle = \int_{-\infty}^{+\infty} x |\Psi|^2 dx.$$

The expectation value of the momentum is therefore

$$\begin{aligned} m \frac{d\langle x \rangle}{dt} &= m \frac{d}{dt} \int_{-\infty}^{+\infty} x |\Psi|^2 dx \\ &= m \int_{-\infty}^{+\infty} x \frac{d}{dt} \Psi^* \Psi dx \\ &= m \int_{-\infty}^{+\infty} x \left(\frac{d}{dt} \Psi^* \Psi + \frac{d}{dt} \Psi \Psi^* \right) dx \\ &= m \int_{-\infty}^{+\infty} x \left(-\frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + V \Psi^* \right) \Psi + \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi \right) \Psi^* \right) dx \\ &= m \int_{-\infty}^{+\infty} x \frac{\hbar^2}{i\hbar 2m} \left(\frac{\partial^2 \Psi^*}{\partial x^2} \Psi - \frac{\partial^2 \Psi}{\partial x^2} \Psi^* \right) dx \\ &= m \int_{-\infty}^{+\infty} \left(-\frac{i\hbar}{2m} \right) x \frac{\partial}{\partial x} \left(\frac{\partial \Psi^*}{\partial x} \Psi - \frac{\partial \Psi}{\partial x} \Psi^* \right) dx \\ &= -\frac{i\hbar}{2} \left(x \left(\frac{\partial \Psi^*}{\partial x} \Psi - \frac{\partial \Psi}{\partial x} \Psi^* \right) \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \left(\frac{\partial \Psi^*}{\partial x} \Psi - \frac{\partial \Psi}{\partial x} \Psi^* \right) dx \right) \\ &= \frac{i\hbar}{2} \left(\int_{-\infty}^{+\infty} \frac{\partial \Psi^*}{\partial x} \Psi dx - \int_{-\infty}^{+\infty} \frac{\partial \Psi}{\partial x} \Psi^* dx \right) \\ &= \frac{i\hbar}{2} \left(\Psi^* \Psi \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{\partial \Psi}{\partial x} \Psi^* dx - \int_{-\infty}^{+\infty} \frac{\partial \Psi}{\partial x} \Psi^* dx \right) \\ &= -i\hbar \int_{-\infty}^{+\infty} \frac{\partial \Psi}{\partial x} \Psi^* dx \\ &= \int_{-\infty}^{+\infty} \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi dx. \end{aligned}$$

Thus, it holds $\hat{p} = -i\hbar \frac{\partial}{\partial x}$.

Example. The kinetic energy operator is given by

$$\hat{T} = \frac{1}{2} m \hat{v}^2 = \frac{1}{2} \frac{\hat{p}^2}{m} = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right) \left(-i\hbar \frac{\partial}{\partial x} \right) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}.$$

Remark. The expectation value is the (average) value we obtain if we measure the observable on a QM-ensemble (many identical particles with the same initial condition).

1.3 Uncertainty Principle

It holds:

$$\sigma_x \cdot \sigma_p \geq \frac{\hbar}{2}, \tag{1.4}$$

where σ_x is the standard deviation in x and σ_p the standard deviation in p .

Remark. The uncertainty principle is an inequality, i.e. $\sigma_x \cdot \sigma_p$ can be larger than $\hbar/2$.

1.4 The Time-independent Schrödinger Equation

Recall the time-dependent Schrödinger Equation (TDSE or SE):

$$i\hbar \frac{d}{dt} \Psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x, t) \Psi. \quad (1.5)$$

Assuming the potential is time independent, i.e. $V(x, t) = V(x)$, and using separation of variables with solutions

$$\Psi(x, t) = \psi(x) \varphi(t) \quad (1.6)$$

we get

$$\begin{aligned} i\hbar \frac{d}{dt} \varphi \psi(x) &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \varphi(t) + V(x) \psi(x) \varphi(t) \\ \underbrace{i\hbar \frac{1}{\varphi(t)} \frac{d}{dt} \varphi}_{\text{LHS, } C_1(t)} &= \underbrace{-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi}{\partial x^2} + V(x)}_{\text{RHS, } C_2(x)} = E \end{aligned}$$

The LHS yields

$$i\hbar \frac{1}{\varphi(t)} \frac{d}{dt} \varphi = E \quad \Rightarrow \quad \varphi(t) = \exp(-iEt/\hbar).$$

The RHS leads to the time-independent Schrödinger Equation (TISE):

$$\hat{H} \psi(x) = E \psi(x), \quad (1.7)$$

where

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_{\text{KE}} + \underbrace{V(x)}_{\text{PE}} \quad (1.8)$$

is the Hamiltonian, i.e. the operator for the total energy. The full wave function is then

$$\Psi_n(x, t) = \psi_n(x) \cdot \exp(-iE_n t/\hbar). \quad (1.9)$$

Remark. This is also called stationary state, since

$$|\Psi_n|^2 = \Psi_n^* \Psi_n = \psi_n^* e^{iE_n t/\hbar} \cdot \psi_n e^{-iE_n t/\hbar} = \psi_n^* \psi_n = |\psi_n|^2.$$

1.5 General Solution to the TDSE

The general solution is a linear combination of Ψ_n 's:

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) \exp(-iE_n t/\hbar). \quad (1.10)$$

Remark. Stationary states are no longer possible, since $|\Psi|^2$ leads to $\exp(i(E_m - E_n)t/\hbar)$ terms.

Remark. The probability that a measurement of energy will yield E_i is $|c_i|^2$.

1.6 Free Particle

Consider a free particle, i.e. $V(x) = 0$. The wave function is

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(k) \exp\left(i\left(kx - \frac{\hbar k^2}{2m} t\right)\right) dk, \quad (1.11)$$

where $g(k)$ is the shape function

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \Psi(x, 0) \exp(-ikx) dx. \quad (1.12)$$

Remark. The shape function is needed to make the solutions square-integrable (physical).

1.7 Confined Particle

Consider a particle in a infinite square well:

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq a, \\ \infty & \text{else,} \end{cases} \quad (1.13)$$

i.e. the particle can only be between 0 and a . The solutions to the TISE are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}. \quad (1.14)$$

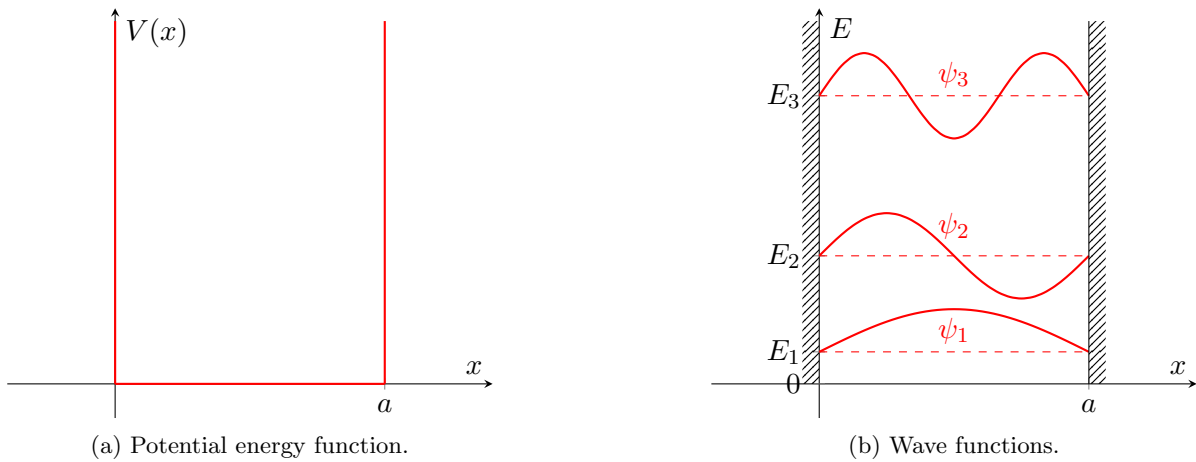


Figure 1: Infinite Square Well.

Remark. The solutions to infinite square well are mutually orthogonal:

$$\int_{-\infty}^{+\infty} \psi_m^* \psi_n dx = \delta_{mn} = \begin{cases} 1 & \text{if } m = n, \\ 0 & \text{if } m \neq n. \end{cases}$$

1.8 Quantum Harmonic Oscillator

Consider a particle in the potential $V(x) = \frac{1}{2}m\omega^2x^2$. The TISE yields

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi. \quad (1.15)$$

To solve for ψ_n we introduce

$$\begin{aligned} \hat{a}_+ &= \frac{1}{\sqrt{2\hbar m\omega}}(-i\hat{p} + m\omega\hat{x}) = \text{raising operator,} \\ \hat{a}_- &= \frac{1}{\sqrt{2\hbar m\omega}}(+i\hat{p} + m\omega\hat{x}) = \text{lowering operator.} \end{aligned} \quad (1.16)$$

Why? To make the TISE easier to solve. In particular, if ψ solves the TISE with energy E , then

$$\begin{aligned} \hat{H}\hat{a}_+\psi &= (E + \hbar\omega)\hat{a}_+\psi, \\ \hat{H}\hat{a}_-\psi &= (E - \hbar\omega)\hat{a}_-\psi, \end{aligned}$$

i.e. $\hat{a}_\pm \psi$ solves the TISE with energy $E \pm \hbar\omega$. From that:

$$\begin{aligned}\hat{a}_+ \psi_n &= \sqrt{n+1} \psi_{n+1}, & \psi_0 &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\frac{m\omega}{2\hbar}x^2\right), & E_n &= \left(n + \frac{1}{2}\right) \hbar\omega, \\ \hat{a}_- \psi_n &= \sqrt{n} \psi_{n-1}, & \psi_n &= \frac{1}{\sqrt{n!}} (\hat{a}_+)^n \psi_0,\end{aligned}$$

where ψ_0 comes from $\hat{a}_- \psi = 0$.

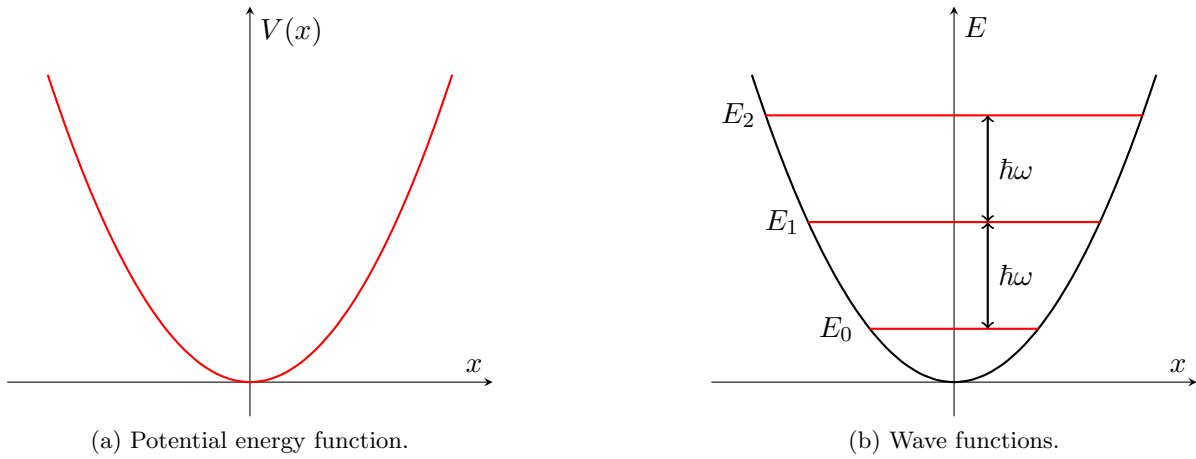


Figure 2: Quantum Harmonic Oscillator.

Remark. In general, for ψ 's for confining potentials:

- If $V(x)$ is symmetric, then ψ_n alternate even/odd;
- ψ_{n+1} has one more node than ψ_n ;
- ψ_n 's are mutually orthogonal, i.e.

$$\int_{-\infty}^{+\infty} \psi_m^* \psi_n dx = \delta_{mn} = \begin{cases} 1 & \text{if } m = n, \\ 0 & \text{if } m \neq n; \end{cases}$$

- ψ_n 's make a complete set of functions, i.e. the general solution is a function of them.
- Orthogonality can be used to obtain the coefficients c_n 's. By integrating

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

we obtain

$$\int_{-\infty}^{+\infty} \psi_m^* \Psi(x, 0) dx = \int_{-\infty}^{+\infty} \psi_m^* \sum_{n=1}^{\infty} c_n \psi_n dx = \sum_{n=1}^{\infty} c_n \int_{-\infty}^{+\infty} \psi_m^* \psi_n dx.$$

Orthogonality then leads to

$$c_m = \int_{-\infty}^{+\infty} \psi_m^* \Psi(x, 0) dx.$$

1.9 Further Examples

To solve the problems with different potential the procedure is as follows:

- Divide the problem into regions and solve the TISE in each region.
- Use boundary conditions to match solutions at interfaces between regions. Typical boundary conditions are: continuity of ψ , ψ has to be finite, continuity of $\frac{\partial\psi}{\partial x}$.
- For $E > V(\pm\infty)$ we have scattering states, for $E < V(\pm\infty)$ we have bound states.

Remark. Recall that for any solution it must hold: $E > V_{\min}$. Otherwise, the wave function is not normalizable.

1.9.1 Finite Potential Step

Consider an incoming incident wave from left and a step of magnitude V_0 :

- $E > V_0$: Reflection (QM behavior) and transmission wave.
- $0 < E < V_0$: Only reflection but penetration (QM behavior) into barriers.
- $E < 0$: No physical solutions.

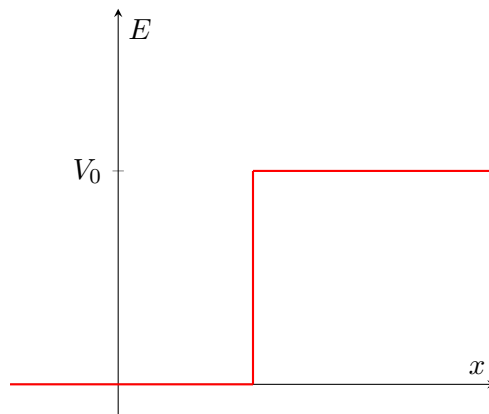


Figure 3: Finite Potential Step.

1.9.2 Finite Potential Well

Consider an incoming incident wave from left and a well of magnitude $-V_0$ and width $2a$:

- $E > 0$: Reflection (QM behavior) and transmission wave.
- $-V_0 < E < 0$: Bound states with some penetration (QM behavior) into barriers.
- $E < -V_0$: No physical solutions.

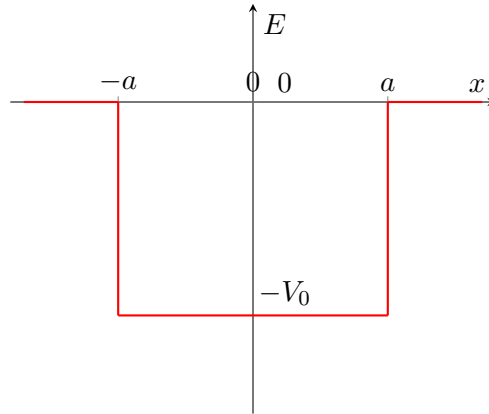


Figure 4: Finite Potential Step.

1.9.3 Finite Potential Barrier

Consider an incoming incident wave from left and a barrier of magnitude V_0 and width $2a$:

- $E > V_0$: Reflection (QM behavior) and transmission as in finite well.
- $0 < E < V_0$: Reflection and transmission (QM behavior) with exponential decay in the barrier.
- $E < 0$: No physical solutions.

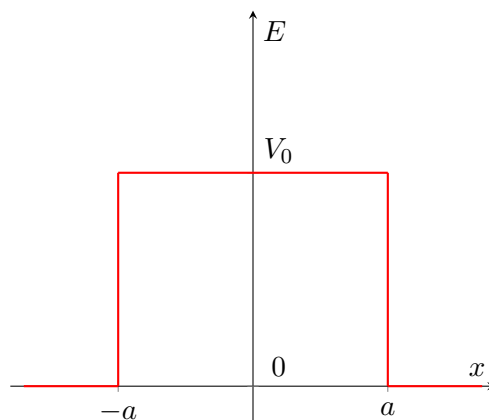


Figure 5: Finite Potential Barrier.

1.9.4 Quantum Mechanical Tunneling

Tunneling denotes the non-classical penetration through a barrier. It can be quantified in terms of the transmission coefficient T , denoting the probability that a particle will be transmitted through the barrier. For tall, wide barrier it reads

$$T = \frac{16E(V_0 - E)}{V_0^2} \exp\left(-4\frac{\sqrt{2m(V_0 - E)}}{\hbar}a\right). \quad (1.17)$$

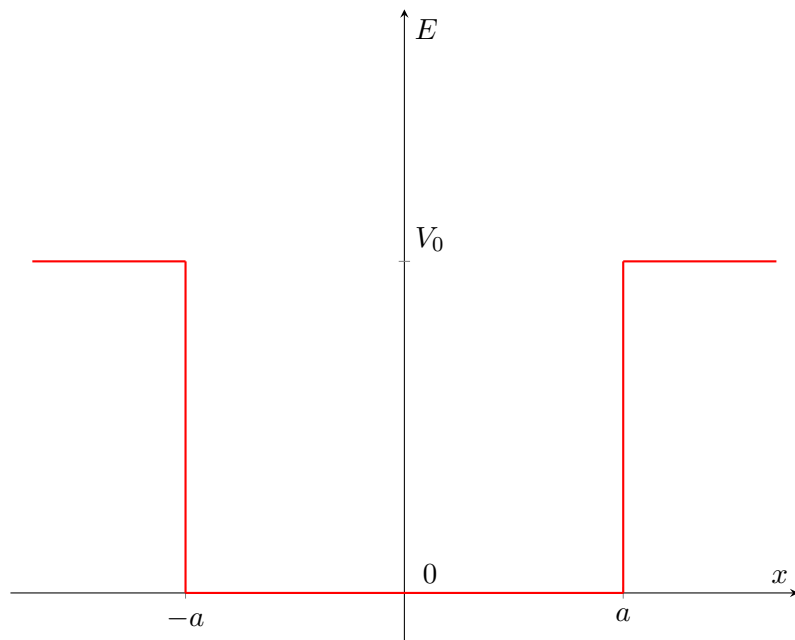
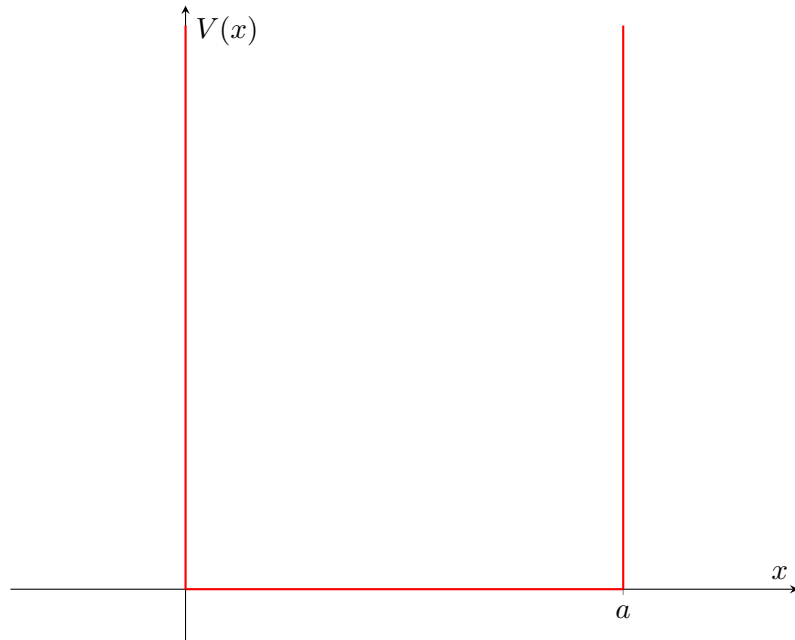
1.10 Quick Checks

Circle True or False.

- T F $\Psi(x, t)$ has no direct physical meaning.
- T F According to the uncertainty principle, if σ_x is very large, then the momentum is well determined.
- T F Any solution of the T.I.S.E. can be normalized.
- T F To obtain the T.I.S.E. from the T.D.S.E., we had to assume that the potential energy function was time-independent.
- T F If we confine an electron inside a finite volume with $V(x) = 0$, its ground state energy can never be exactly zero.
- T F Stationary states have a probability density that does not change with time.
- T F If a particle is described by a wave packet, its energy is always well defined.
- T F $\frac{d}{dt} \int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 0$ arises only for unphysical solutions to the 1D SE.
- T F $\int_{-\infty}^{+\infty} |\Psi(x, t)|^2 dx = 0$ arises only for unphysical solutions to the 1D SE.
- T F It holds $\langle H^2 \rangle = (\sum_i |c_i|^2 E_i)^2$.
- T F It holds $\langle H^2 \rangle = (\sum_i |c_i|^2 E_i^2)$.

1.11 Exercises

1. Given the two square wells as shown below with the same width.
 - (a) Sketch the ground state wavefunction in the corresponding plot.
 - (b) Sketch the first excited state. Assume that V_0 is large.



2. Consider a particle in the infinite square well with an initial wave function:

$$\Psi(x, 0) = A(\psi_1(x) + \psi_2(x)).$$

- (a) Normalize $\Psi(x, 0)$.
- (b) Determine $\Psi(x, t)$ and $|\Psi(x, t)|^2$.
- (c) Compute $\langle x \rangle$.
- (d) Compute $\langle p \rangle$.
- (e) If you measure the energy of this particle, what are the possible values?
- (f) What is the probability of obtaining each of the possible energies?
- (g) Compute $\langle H \rangle$ and compare to E_1 and E_2 .

3. Consider a free particle with an initial normalized wave function:

$$\Psi(x, 0) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \exp(-ax^2),$$

where a is a real positive constant.

- (a) Determine $\Psi(x, t)$.
- (b) Determine $|\Psi(x, t)|^2$.
- (c) Sketch $|\Psi(x, t)|^2$ versus x at $t = 0$ and at a later t . Describe qualitatively what happens to $|\Psi(x, t)|^2$ as a function of time.
- (d) Find σ_x and σ_p .
- (e) Is the uncertainty principle satisfied?
- (f) At what time does the system come closest to the uncertainty principle?

Hint:

$$\int_{-\infty}^{+\infty} e^{-(ax^2+ikx)} dx = \sqrt{\frac{\pi}{a}} e^{-\frac{k^2}{4a}}.$$

4. We prepare a simple harmonic oscillator with the following normalized wavefunction:

$$\Psi(x, 0) = \left(\frac{9\beta^2}{\pi}\right)^{\frac{1}{4}} \exp(-9(\beta x)^2/2),$$

where $\beta = \sqrt{m\omega/\hbar}$. We then immediately measure the energy of the oscillator in this state. What is the probability of getting the ground state energy?

5. Give an example of a quantum mechanical system that has both a discrete and continuous part to its spectrum.

6. At time zero, a system is in a linear combination:

$$\Psi = \sqrt{2}\psi_1 + \sqrt{3}\psi_2 + \psi_3 + \psi_4,$$

where ψ_n represents a normalized eigenstate of the system's Hamiltonian \hat{H} such that

$$\hat{H}\psi_n = n^2\varepsilon\psi_n.$$

If the energy of the system is measured at time zero, what values will be obtained and with what probabilities?

2 Formalism

2.1 Hermitian Operators

In quantum mechanics, operators are linear and Hermitian. An operator \hat{Q} is linear if

$$\hat{Q}(\alpha f(x) + \beta g(x)) = \alpha \hat{Q}f(x) + \beta \hat{Q}g(x), \quad (2.1)$$

where $\alpha, \beta \in \mathbb{R}$. An operator \hat{Q} is Hermitian if

$$\int_{-\infty}^{+\infty} \Psi^* \hat{Q} \Psi \, d^3\vec{r} = \int_{-\infty}^{+\infty} (\hat{Q} \Psi)^* \Psi \, d^3\vec{r} \quad (2.2)$$

or, using Dirac's notation,

$$\langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle.$$

Remark. Note that the two following statements are equivalent:

- $\langle \Psi | \hat{Q} \Psi \rangle = \langle \hat{Q} \Psi | \Psi \rangle$;
- $\langle f | \hat{Q} g \rangle = \langle \hat{Q} f | g \rangle$.

Example. Consider the operator $\hat{Q} = a$, where $a \in \mathbb{R} \setminus \{0\}$. Then,

$$\langle f | \hat{Q} g \rangle = \int_{-\infty}^{+\infty} f^* \hat{Q} g \, dx = \int_{-\infty}^{+\infty} f^* a g \, dx = \int_{-\infty}^{+\infty} a f^* g \, dx = \int_{-\infty}^{+\infty} (a f)^* g \, dx = \langle \hat{Q} f | g \rangle.$$

Thus, $\hat{Q} = a$ is Hermitian.

Example. Consider the operator $\hat{Q} = i$. Then,

$$\langle f | \hat{Q} g \rangle = \int_{-\infty}^{+\infty} f^* \hat{Q} g \, dx = \int_{-\infty}^{+\infty} f^* i g \, dx = \int_{-\infty}^{+\infty} i f^* g \, dx = \int_{-\infty}^{+\infty} (-i f)^* g \, dx = -\langle \hat{Q} f | g \rangle.$$

Thus, $\hat{Q} = i$ is not Hermitian.

2.2 Dirac's Notation

In general,

$$\langle f | g \rangle = \int_{-\infty}^{+\infty} f^* g \, dx \in \mathbb{R}.$$

Why does that make sense?

$\langle f |$ is a row matrix:

$$\langle f | = [c_1^* \quad c_2^* \quad \dots \quad c_n^*]$$

and $|f\rangle$ is a column matrix:

$$|f\rangle = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix}.$$

Thus, it makes sense that

$$\langle f | f \rangle = [c_1^* \quad c_2^* \quad \dots \quad c_n^*] \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = \sum_{i=1}^n |c_i|^2 \in \mathbb{R}.$$

2.3 Quick Checks

Circle True or False.

- T F The momentum operator \hat{p} is not Hermitian, since $\hat{p} \neq \hat{p}^*$.
- T F The Dirac Delta function is not in Hilbert space.
- T F The function $f(x) = \sin(x)$ is in Hilbert space.
- T F The function $f(x) = e^{-x} \sin(x)$ is in Hilbert space.
- T F The function $f(x) = e^{-x^4} \sin(x)$ is in Hilbert space.
- T F Every classical observable can be represented in QM by a Hermitian Operator.
- T F The operator $\hat{A} = \text{diag}(4, 4, 2)$ is Hermitian.
- T F The operator $\hat{A} = \text{diag}(4, 4, i)$ is Hermitian.
- T F For a free particle, the separable solutions to the SE are not in Hilbert space.

2.4 Exercises

1. (a) Show that the sum of two Hermitian operators is Hermitian.
(b) When is the product of two Hermitian operators also Hermitian?

2. Consider a particle in the infinite square well constrained to have $n \leq 3$.
 - (a) Write the general wavefunction in vector notation (as bracket).
 - (b) Write the Hamiltonian of the system in matrix form.

3 Measurements

3.1 Deterministic and Probabilistic Measurements

A measurement of a quantity Q is deterministic iff $\text{Var}[Q] = \sigma_Q^2 = 0$. That is,

$$\begin{aligned}\sigma_Q^2 &= \langle (Q - \langle Q \rangle)^2 \rangle \\ &= \langle \Psi | (\hat{Q} - \langle Q \rangle)^2 \Psi \rangle \\ &= \langle (\hat{Q} - \langle Q \rangle) \Psi | (\hat{Q} - \langle Q \rangle) \Psi \rangle \\ &= \int \left((\hat{Q} - \langle Q \rangle) \Psi \right)^* (\hat{Q} - \langle Q \rangle) \Psi \, d^3\vec{r} \\ &= \int |(\hat{Q} - \langle Q \rangle) \Psi|^2 \, d^3\vec{r} \stackrel{!}{=} 0.\end{aligned}$$

That holds if and only if $(\hat{Q} - \langle Q \rangle) \Psi = 0$, i.e. Ψ satisfies the eigenvalue equation

$$\hat{Q} \Psi = q_Q \Psi, \quad (3.1)$$

where $q_Q = \langle Q \rangle$. In general, an equation of the form

$$\hat{Q} f_q = q f_q$$

is called eigenvalue equation, where q is an eigenvalue of \hat{Q} and f_q is the corresponding eigenfunction.

Example. Consider a particle in the infinite square well with $\Psi = \Psi_1$. We investigate whether measurements of the energy are deterministic:

$$\hat{H} \Psi = \hat{H} \Psi_1 = E_1 \Psi_1.$$

Therefore, measurements are deterministic.

Example. Consider a particle in the infinite square well with $\Psi = \Psi_1$. We investigate whether measurements of the position are deterministic:

$$\hat{x} \Psi = x \Psi_1 \neq q_x \Psi_1.$$

Therefore, measurements are probabilistic.

Example. Consider a particle in the infinite square well with $\Psi = \frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2)$. We investigate whether measurements of the energy are deterministic:

$$\hat{H} \Psi = \hat{H} \left(\frac{1}{\sqrt{2}}(\Psi_1 + \Psi_2) \right) = \frac{1}{\sqrt{2}}(E_1 \Psi_1 + E_2 \Psi_2) \neq q_{\hat{H}} \Psi.$$

Therefore, measurements are probabilistic.

3.2 Commutator

Consider two operators \hat{A} and \hat{B} . The commutator of \hat{A} and \hat{B} is

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (3.2)$$

To evaluate it place a function to the right and then eliminate it.

Remark. If \hat{A} and \hat{B} commute then $[\hat{A}, \hat{B}] = 0$.

Example. Consider $\hat{A} = x$ and $\hat{B} = c$, where $c \in \mathbb{R}$. Then,

$$[\hat{A}, \hat{B}]f(x) = (x\hbar - \hbar x)f(x) = x\hbar f(x) - \hbar x f(x) = 0 \cdot f(x).$$

Thus, $[\hat{A}, \hat{B}] = 0$.

Example. Consider $\hat{A} = x$ and $\hat{B} = \frac{\partial}{\partial x}$, where $c \in \mathbb{R}$. Then,

$$[\hat{A}, \hat{B}]f(x) = \left(x \frac{\partial}{\partial x} - \frac{\partial}{\partial x} x\right) f(x) = x \frac{\partial f(x)}{\partial x} - \frac{\partial(xf(x))}{\partial x} = x \frac{\partial f(x)}{\partial x} - \left(f(x) + x \frac{\partial f(x)}{\partial x}\right) = -f(x)$$

Thus, $[\hat{A}, \hat{B}] = -1$.

3.3 Compatible Observables

Two observables \hat{A} and \hat{B} are called compatible if

$$[\hat{A}, \hat{B}] = 0.$$

Two compatible observables share the same eigenfunctions:

$$\begin{aligned}\hat{A}|\psi_n\rangle &= a_n|\psi_n\rangle, \\ \hat{B}|\psi_n\rangle &= b_n|\psi_n\rangle.\end{aligned}$$

As a consequence, we can determine both observables at the same time.

3.4 Incompatible Observables

Two observables \hat{A} and \hat{B} are called incompatible if

$$[\hat{A}, \hat{B}] \neq 0.$$

Two incompatible observables have different eigenfunctions:

$$\begin{aligned}\hat{A}|\psi_{n,A}\rangle &= a_n|\psi_{n,A}\rangle, \\ \hat{B}|\psi_{m,B}\rangle &= b_m|\psi_{m,B}\rangle.\end{aligned}$$

As a consequence, we cannot determine both observables at the same time.

Example. \hat{x} and \hat{p} are incompatible observables, since $[\hat{x}, \hat{p}] = i\hbar \neq 0$. \hat{x} and \hat{y} are compatible observables, since they commute.

3.5 Generalized Uncertainty Principle

The uncertainty principle for two observables \hat{A} and \hat{B} is

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle\right)^2. \quad (3.3)$$

Example. For $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}$ we obtain

$$\sigma_A^2 \sigma_B^2 \geq \left(\frac{1}{2i} \langle [\hat{x}, \hat{p}] \rangle\right)^2 = \left(\frac{1}{2i} \langle i\hbar \rangle\right)^2 = \left(\frac{1}{2i} i\hbar\right)^2 = \left(\frac{\hbar}{2}\right)^2,$$

which gives the well-known expression $\sigma_{\hat{x}} \sigma_{\hat{p}} \geq \hbar/2$.

3.6 Time-energy Uncertainty Relation

The time-energy uncertainty relation is

$$\sigma_{\hat{H}}^2 \sigma_{\hat{Q}}^2 \geq \left(\frac{\hbar}{2}\right)^2 \left(\frac{d\langle Q \rangle}{dt}\right)^2. \quad (3.4)$$

From that, using

$$\Delta E = \sigma_{\hat{H}}, \quad \Delta t = \frac{\sigma_{\hat{Q}}}{\left|\frac{d\langle Q \rangle}{dt}\right|},$$

we obtain $\Delta E \Delta t \geq \hbar/2$.

Remark. This uncertainty relation cannot be derived from the generalized uncertainty principle.

3.7 Quick Checks

Circle True or False.

- | | | |
|---|---|--|
| T | F | In quantum mechanics, all measurements are probabilistic. |
| T | F | Two Hermitian operators always commute. |
| T | F | If a particle is in a non-stationary state, the measurement of its energy must yield one of several values. |
| T | F | If a quantum mechanical observable is measured, one possible result is always the expectation value of the observable. |
| T | F | An uncertainty relation will exist for any two observables that have operators that do not commute. |
| T | F | \hat{p}_x and \hat{p}_y are compatible observables. |
| T | F | Since $\hat{V} = V(\hat{x})$ and $[\hat{x}, \hat{p}] \neq 0$, the operators \hat{p} and \hat{V} never commute. |

3.8 Exercises

1. An operator \hat{A} , representing observable A , has two normalized eigenstates ψ_1 and ψ_2 with eigenvalues a_1 and a_2 , respectively. Operator \hat{B} , representing observable B , has two normalized eigenstates ϕ_1 and ϕ_2 with eigenvalues b_1 and b_2 respectively. The eigenstates are related by

$$\begin{aligned}\psi_1 &= \frac{1}{5}(3\phi_1 + 4\phi_2) \\ \psi_2 &= \frac{1}{5}(4\phi_1 - 3\phi_2).\end{aligned}$$

- (a) Observable A is measured, and the eigenvalue a_2 is obtained. What is the state of the system immediately after this measurement?
- (b) If observable B is now measured (after the first measurement in part (a)), what are the possible results, and what are their probabilities?
- (c) Right after the measurement of B in part (b), A is measured again. You were not told the outcome of the B measurement before the A measurement. What is the probability of getting a_2 after the three measurements (A , B , and then A)?
- (d) Would your answer in part (c) change if you were told the outcome of the B measurement? How?

2. Determine $[\hat{a}_-, \hat{a}_+]$.

3. Is the ground state of the infinite square well an eigenfunction of momentum? If so, what is its momentum? If not, why not?

4. Below is a set of one-dimensional operators for a particle in an arbitrary potential $\hat{V}(x)$. Identify the largest group of compatible observables.

$$\hat{x}, \quad \hat{p}, \quad \hat{V}(x), \quad \hat{a}_+, \quad \hat{H}.$$

5. Determine eigenvalues and eigenvectors of $\hat{Q} = \frac{\partial}{\partial x}$. Which eigenfunctions of \hat{Q} are in Hilbert space?

4 Quantum Mechanics in 3D

4.1 The 3D Schrödinger Equation

The 3D Schrödinger equation is given by

$$i\hbar \frac{d}{dt} \Psi = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi. \quad (4.1)$$

Similarly as in the 1D, we assume the potential is time-independent. Then, we can use separation of variable and obtain the TISE

$$\hat{H}\psi = E\psi, \quad (4.2)$$

where $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$.

4.2 Hydrogen Atom

For the hydrogen atom the potential is given by Coulomb attraction. That is,

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}.$$

By rewriting the TISE in spherical coordinates we obtain

$$\psi_{n,l,m_l} = R_{n,l}(r)Y_l^{m_l}(\theta, \varphi), \quad (4.3)$$

where $R_{n,l}(r)$ and $Y_l^{m_l}(\theta, \varphi)$ can be found in tables. The energy levels are

$$E_n = -\frac{1}{n^2} \left(\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right) \approx -\frac{13.6 \text{ eV}}{n^2}. \quad (4.4)$$

We can also define the Bohr radius, denoted by a and given by

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 0.0529 \text{ nm}.$$

Remark. Since E_n 's are discrete only the photon energies $E_2 - E_1$, $E_3 - E_1$, ... can be absorbed by the hydrogen atom.

4.3 Angular Momentum

For the angular momentum we use the classic definition:

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \quad \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2.$$

We have seen that \hat{L}_x , \hat{L}_y , and \hat{L}_z do not commute, but they all commute with \hat{L}^2 . The eigenfunctions are the spherical harmonics and the eigenvalues are function of l :

$$\begin{aligned} \hat{L}^2 Y_l^{m_l} &= \hbar^2 l(l+1) Y_l^{m_l}, \\ \hat{L}_z Y_l^{m_l} &= \hbar m_l Y_l^{m_l}, \end{aligned} \quad (4.5)$$

where $l = 0, 1, 2, \dots$ and $m_l = -l, -l+1, \dots, l-1, l$.

4.4 Spin

Due the intrinsic spin of the particle, it acts *as if* it has an inherent rotation about z -axis. Similarly to the angular momentum the eigenvalue problem is:

$$\begin{aligned}\hat{S}^2|s, m_s\rangle &= \hbar^2 s(s+1)|s, m_s\rangle, \\ \hat{S}_z|s, m_s\rangle &= \hbar m_s|s, m_s\rangle.\end{aligned}\tag{4.6}$$

for $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ and $m_s = -s, -s+1, \dots, s-1, s$.

Remark. For an electron: it can occupy different orbitals, so l can vary (s, d, p, \dots orbitals). However, each quantum mechanical particle has a fixed spin s . For an electron $s = \frac{1}{2}$, for a photon $s = 1$.

Therefore, for an electron (or any $\frac{1}{2}$ -spin particle) there are two possible eigenstates:

$$|s, m_s\rangle \rightarrow \begin{cases} |\frac{1}{2}, +\frac{1}{2}\rangle & \text{“spin up”}, \\ |\frac{1}{2}, -\frac{1}{2}\rangle & \text{“spin down”}, \end{cases}\tag{4.7}$$

where up/down refer to the projection of the spin along the z -axis. We can choose these eigenstates as our basis vectors, that is

$$\begin{aligned}|\frac{1}{2}, +\frac{1}{2}\rangle &\rightarrow \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \\ |\frac{1}{2}, -\frac{1}{2}\rangle &\rightarrow \begin{bmatrix} 0 \\ 1 \end{bmatrix}.\end{aligned}\tag{4.8}$$

Then, the general spin state can be written as a linear combination:

$$\begin{aligned}|\chi\rangle &= a|\frac{1}{2}, +\frac{1}{2}\rangle + b|\frac{1}{2}, -\frac{1}{2}\rangle, \\ |\chi\rangle &= a \begin{bmatrix} 1 \\ 0 \end{bmatrix} + b \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \\ |\chi\rangle &= \begin{bmatrix} a \\ b \end{bmatrix}\end{aligned}\tag{4.9}$$

The operators in this basis are given by

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \hat{S}_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \hat{S}_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \hat{S}_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}.$$

Example. Let's work out \hat{S}^2 . We know it is a 2×2 matrix, that is

$$\hat{S}^2 = \begin{bmatrix} c & d \\ e & f \end{bmatrix}.$$

We use the eigenvalue equations:

$$\begin{aligned}\hat{S}^2|\frac{1}{2}, \pm\frac{1}{2}\rangle &= \hbar^2 s(s+1)|\frac{1}{2}, \pm\frac{1}{2}\rangle \\ &= \hbar^2 \frac{1}{2} \left(\frac{1}{2} + 1 \right) |\frac{1}{2}, \pm\frac{1}{2}\rangle \\ &= \frac{3}{4}\hbar^2 |\frac{1}{2}, \pm\frac{1}{2}\rangle.\end{aligned}$$

In matrix notation:

$$\begin{bmatrix} c & d \\ e & f \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \Rightarrow \quad \begin{bmatrix} c \\ e \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 \\ 0 \end{bmatrix}.$$

Thus, $c = \frac{3}{4}\hbar^2$ and $e = 0$. Similarly

$$\begin{bmatrix} c & d \\ e & f \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad \Rightarrow \quad \begin{bmatrix} d \\ f \end{bmatrix} = \frac{3}{4}\hbar^2 \begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

which leads to $d = 0$ and $f = \frac{3}{4}\hbar^2$. Hence,

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}.$$

Example. Consider a particle with spin 2. The possible values of m_s are $\{-2, -1, 0, 1, 2\}$. Therefore, there are 5 eigenstates, given by $|2, \pm 2\rangle$, $|2, \pm 1\rangle$, and $|2, 0\rangle$. In vector form we would have 5-dimensional vectors/matrices.

4.5 Quick Checks

Circle True or False.

- | | | |
|---|---|--|
| T | F | Given a specific shell in a hydrogenic atom, all of the subshells have the same energy. |
| T | F | The orbital shapes that we know from chemistry (s, p, d , etc.) come from the solutions to the angular equation of the hydrogen atom. |
| T | F | For a single-particle system with a spherically symmetric potential, the eigenfunctions of \hat{H} will involve the spherical harmonics. |
| T | F | In our mathematical treatment of the hydrogen atom, the potential energy function only affected the radial equation. |
| T | F | Each spin eigenstate can be represented as a two-dimensional vector. |
| T | F | For an atom with two electrons we can solve the TISE exactly (using separation of variables) if we ignore the interaction between the particles. |
| T | F | For an one-electron atom with the potential $V(r, t) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \cos(\omega t)$ we can solve the TISE exactly. |
| T | F | For an electron, the value of s can be $\pm\frac{1}{2}$. |
| T | F | \hat{L}_x and \hat{L}^2 are compatible observables . |
| T | F | The electron has a spin angular momentum because it is rotating in space. |
| T | F | If we excite an electron in a hydrogen atom, we can change both its s and l . |
| T | F | If we state that the spin of an electron is “up” with respect to the z axis, this means its spin-angular-momentum vector is pointing parallel to the z axis. |
| T | F | An electron cannot be both “spin up” and “spin down”. |

4.6 Exercises

1. If a particle is placed in a sphere of radius ρ where the potential $V(r)$ is described by

$$V(r) = \begin{cases} 0 & \text{for } r \leq \rho, \\ \infty & \text{for } r > \rho, \end{cases}$$

where r is radial coordinate. Write down the angular components to the particle's wave function.

2. A hydrogenic atom consists of a single electron orbiting a nucleus with Z protons. For example, $Z = 1$ for hydrogen itself, $Z = 2$ for helium with one electron removed, $Z = 3$ for lithium with two electrons removed, etc. Determine the Bohr energies $E_n(Z)$, the binding energy $E_1(Z)$, and the Bohr radius $a(Z)$ for a hydrogenic atom.

3. We introduced a specific spin 1/2 basis in lecture, i.e.,

$$|\frac{1}{2}, +\frac{1}{2}\rangle \rightarrow \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad |\frac{1}{2}, -\frac{1}{2}\rangle \rightarrow \begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

where the ket notation represents $|s, m_s\rangle$.

- (a) In this basis, determine the eigenvalues and eigenvectors for \hat{S}_y .
(b) If you measure S_y on the general spin state

$$|\chi\rangle = a \begin{bmatrix} 1 \\ 0 \end{bmatrix} + b \begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

what values would you get and with what probabilities? Check that the probabilities add to one.

Note: a and b do not have to be real.

- (c) If you measure S_y^2 on the same general state, what values would you get and with what probabilities?

4. Consider a particle in the orbital angular momentum

$$\psi = \sqrt{\frac{2}{7}}Y_1^1 + \sqrt{\frac{2}{7}}Y_1^{-1} + \sqrt{\frac{1}{14}}Y_0^0 + \sqrt{\frac{1}{14}}\sum_{i=-2}^2 Y_2^i.$$

- (a) What are the possible values for a measurement of L_z ? What is $\langle L_z \rangle$?
- (b) What are the possible values for a measurement of L^2 ? What is $\langle L^2 \rangle$?

5. (a) Determine $[\hat{L}_z, \hat{r}^2]$ where $\hat{r}^2 = \hat{x}^2 + \hat{y}^2 + \hat{z}^2$.
Hint: Use your knowledge (or cheat sheet) for $[\hat{L}_z, \hat{x}]$, $[\hat{L}_z, \hat{y}]$, $[\hat{L}_z, \hat{z}]$.
- (b) Determine $[\hat{L}_z, \hat{p}^2]$ where $\hat{p}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$.
Hint: Use your knowledge (or cheat sheet) for $[\hat{L}_z, \hat{p}_x]$, $[\hat{L}_z, \hat{p}_y]$, $[\hat{L}_z, \hat{p}_z]$.
- (c) Show that the Hamiltonian \hat{H} commutes with all three components of \hat{L} if the potential is spherically symmetric. Thus, \hat{H} , \hat{L}^2 , \hat{L}_z all commute. What is the significance of this?

5 Systems with Multiple Particles

5.1 Atoms

Consider an atom with Z electrons and Z protons. Then,

$$\hat{H} = \sum_{j=1}^Z \left(\underbrace{\left(-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{|\vec{r}_j|} \right)}_{\hat{H} \text{ of } j\text{-th electron in hydr. state}} + \underbrace{\frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{k=1, k \neq j}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_k|}}_{\text{interaction between electrons}} \right). \quad (5.1)$$

The second term causes a mathematical problem: We can no longer solve the S.E. exactly. First, we neglect this term. Then electrons are each sitting in single-particle hydrogenic state. However, electrons are indistinguishable, therefore we have to consider linear combinations. By assuming there are only two particles, we get:

Spatial:

$$\psi_{\pm} = C (\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)) \quad (5.2)$$

ψ_{\pm} is the two particle state (spatial part of the wave function).

Spin:

$$\chi(s) = \begin{cases} \uparrow\uparrow & \Rightarrow \text{Triplet} \\ \downarrow\downarrow & \Rightarrow \text{Triplet} \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) & \Rightarrow \text{Triplet} \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) & \Rightarrow \text{Singlet} \end{cases} \quad (5.3)$$

The first three states are called triplet (symmetric), the last one singlet (anti-symmetric).

The overall wave function will be the product of spatial and spin parts.

5.2 Fermions and Bosons

A fermion is a QM particle with half-integer spin, a boson is a QM particle with integer spin. Thus, electrons are fermions.

Axiom: The overall wave function for a multiple particle system of identical fermions must be antisymmetric with respect to exchange of any two particles. For bosons, it must be symmetric. So for an electron (fermion), the overall wave function is

$$\psi_+ \cdot (\text{singlet}) \quad \text{or} \quad \psi_- \cdot (\text{triplet}).$$

5.3 Exchange Operator

Define the exchange operator:

$$\hat{P}f(\vec{r}_1, \vec{r}_2) \rightarrow f(\vec{r}_2, \vec{r}_1) \quad (5.4)$$

This operator switches the position of two particles. Note that $[\hat{P}, \hat{H}] = 0$, i.e. \hat{P} and \hat{H} share the same eigenfunctions ψ_+ and ψ_- . The eigenvalues are ± 1 .

5.4 Pauli's Exclusion Principle

There is no way to place two electrons in exactly the same state (i.e. with the same n, l, m_l, m_s) and still have an antisymmetric state.

Motivation: Assume two fermions share the same quantum numbers. Then,

$$\begin{aligned}\psi_+ &= C (\psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2) + \psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2)), \\ &= 2C\psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2) \\ \psi_- &= C (\psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2) - \psi_{n,l,m_l}(\vec{r}_1)\psi_{n,l,m_l}(\vec{r}_2)) \\ &= 0.\end{aligned}$$

In order to obtain a physical solution, we must therefore pick ψ_+ . Thus, the spin must be antisymmetric (singlet) in order to have an antisymmetric wave function; that is

$$\chi_{m_s} = \frac{1}{2}(\uparrow\downarrow - \downarrow\uparrow).$$

With a triplet (in particular $\uparrow\uparrow$ or $\downarrow\downarrow$) the overall wave function cannot be antisymmetric. Therefore, the two electrons cannot share the same quantum numbers.

5.5 Multielectron Atoms

Recall the quantum numbers n, l, m_l, m_s :

- n designates the shell of electron orbital, $n = 1, 2, \dots$;
- l designates the subshell (shape) of electron orbital, $l = 0, \dots, n - 1$;
- m_l designates the orientation of orbital, $m_l = -l, \dots, l$;
- m_s designates the spin of electron (up or down), $m_s = \pm \frac{1}{2}$.

In the hydrogenic states the energies are

$$E_n = -\frac{1}{n^2} \left(\frac{m}{2\hbar^2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right)^2 \right),$$

i.e. subshells are degenerate (e.g. $n = 1, l = 1$ and $n = 1, l = 0$). For multielectron atoms different subshells are not degenerate, due to screening (electron-electron interactions).

5.5.1 Electronic Configuration

To indicate how an atom is filled we can use the electronic configuration.

Example. Determine the electronic configuration:

- Ar, $Z = 18$, $1s^2 2s^2 2p^6 3s^2 3p^6$.
- Cl, $Z = 17$, $1s^2 2s^2 2p^6 3s^2 3p^5$.
- Fe, $Z = 26$, $[\text{Ar}]4s^2 3d^6$.

Exceptions: Cr, Cu.

5.6 Angular Momentum for Multiparticle Systems

Define the new quantum numbers:

- L : total orbital angular momentum, $M_L = \sum_i m_{l_i}$;
- S : total spin angular momentum, $M_S = \sum_i m_{s_i}$;
- J : total angular momentum, combines L and S ;
- $M_J = M_L + M_S$.

Remark. Filled subshells never contribute to L, S, J , since $M_L = \sum_i m_{l_i} = 0$ and $M_S = \sum_i m_{s_i} = 0$, which is the case only for $L = S = 0$. Thus, $J = 0$.

What does combine mean?

Given any two angular momenta in QM:

$$j_1 \text{ and } j_2 \quad \xrightarrow{\text{combine to give}} \quad j.$$

The possible values are

$$j = (j_1 + j_2), (j_1 + j_2 - 1), \dots, |j_1 - j_2|.$$

Example. Let $j_1 = 4, j_2 = 4$. Then $j = 8, 7, 6, 5, 4, 3, 2, 1, 0$.

Example. Let $j_1 = 3, j_2 = \frac{5}{2}$. Then $j = \frac{11}{2}, \frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$.

5.6.1 Term Symbols

For any element we can consider the electronic configuration and determine all the possible combinations of angular momenta. These are labeled by the term symbols:

$${}^{2S+1}L_J, \tag{5.5}$$

where $L = 0 \equiv$ "S", $L = 1 \equiv$ "P", $L = 2 \equiv$ "D", and $L = 3 \equiv$ "F".

Example. What are the possible term symbols for Al? The electronic configuration is $[\text{Ne}]3s^23p^1$. Thus, only one electron will determine the total angular momentum. Since $l = 1$ we have $L = 1$. Similarly, since $s = \frac{1}{2}$ we have $S = \frac{1}{2}$. The possible values of J are then $\frac{3}{2}, \frac{1}{2}$. Therefore, the possible term symbols are

$${}^2P_{\frac{3}{2}}, {}^2P_{\frac{1}{2}}.$$

5.6.2 Hund's Rule

To determine the ground state we can use Hund's Rules:

1. The state with the largest S is the most stable;
2. For states with the same S the largest L is most stable;
3. For states with the same S and L :
 - smallest J is most stable for subshells less or equal than half full;
 - largest J is most stable for subshells more than half full.

5.7 Quick Checks

Circle True or False.

- T F In a multielectron atom with two electrons in $2p$ orbital the possible values of L are 0, 1, 2.
- T F Given a system of two identical particles, the exchange operator \hat{P} always commute with the Hamiltonian operator \hat{H} .
- T F The Pauli exclusion principle applies to both fermions and bosons.
- T F In quantum mechanics, an electron and proton are always distinguishable.
- T F Quantum mechanics allows us to determine the length of the orbital angular momentum vector.
- T F The Pauli's principle applies to particles with $s = \frac{3}{2}$.
- T F The electron configuration of an atom (e.g. $1s^2 2s^2 2p^2$) is enough information to describe its exact energy.
- T F In multielectron atoms, the $3p$ orbitals are lower in energy than the $4s$ orbitals.
- T F In multielectron atoms, the $3d$ orbitals are lower in energy than the $4s$ orbitals.
- T F It is possible to have the following term symbol for a multielectron atomic state: 1D_1 .
- T F The term symbol for $J = 2$, $L = 1$, and $S = 1$ is 1D_1 .
- T F For multielectron atoms, the energy of the single-particle states only depends on n .

5.8 Exercises

1. Answer the following questions:

(a) Which of the following combinations of quantum numbers are allowed for a single-particle hydrogenic state?

- $n = 3, l = 2, m_l = 1, m_s = 0.$
- $n = 2, l = 0, m_l = 0, m_s = -1/2.$
- $n = 7, l = 2, m_l = -2, m_s = 1/2.$
- $n = 3, l = -3, m_l = -2, m_s = -1/2.$
- $n = 0, l = 0, m_l = 0, m_s = 1/2.$

(b) Determine the electronic configurations for the following elements:

- B:
- F:
- P:
- C:
- Cr:
- Ma:
- Fe:
- Cu:
- Kr:

- Using the rules for the addition of angular momenta (i.e. do not worry about exchange symmetry), determine all the possible electronic states for the elements B, C, and N in terms of their possible “term symbols”, i.e. $^{2S+1}L_J$, where S is the total electronic spin, L is the total orbital angular momentum, and J is the total angular momentum.

3. What is the electronic configuration and term symbol for the ground state of Al?

4. Find the ground-state energy for a system of N noninteracting identical particles that are confined to a one-dimensional infinite square well when the particles are (i) bosons and (ii) spin $1/2$ fermions. For the N bosons, also write down the ground-state time-independent wave function.

5. Consider $N = 3$ electrons in the 1D infinite square well of width a .

(a) Give the full Hamiltonian of the system.

For the next questions, you may ignore interactions between the electrons.

(b) Simplify the Hamiltonian accordingly.

(c) Give the ground state energy.

(d) One more electron is added to the system: the system now consists of four electrons. Give the new ground state energy.

(e) One more proton is added to the system: the system now consists of three electrons and one proton. Give the new ground state energy.

6. Given two identical QM particles positioned at \vec{r}_1 and \vec{r}_2 . Explain if the following functions symmetric and antisymmetric with respect to exchange:

(a) $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1| + |\vec{r}_2| + 1$;

(b) $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1| + 2|\vec{r}_2|$;

(c) $f(\vec{r}_1, \vec{r}_2) = -|\vec{r}_1| + |\vec{r}_2| + 1$;

(d) $f(\vec{r}_1, \vec{r}_2) = -|\vec{r}_1| + |\vec{r}_2|$;

(e) $f(\vec{r}_1, \vec{r}_2) = |\vec{r}_1|^2 + |\vec{r}_2|^3$;

(f) $f(\vec{r}_1, \vec{r}_2) = (|\vec{r}_1| - |\vec{r}_2|)^2$;

(g) $f(\vec{r}_1, \vec{r}_2) = \sin(|\vec{r}_1| - |\vec{r}_2|)$.

6 Solids

6.1 Free Electron Model

Solids are treated as a QM box in which electrons are free to move around:

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right)$$

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right).$$

6.1.1 Fermi Energy

The Fermi energy is the energy of the highest occupied level. Consider a solid with N atoms with q valence electrons. Let

$$k_F^2 = \frac{n_x^2 \pi^2}{l_x^2} + \frac{n_y^2 \pi^2}{l_y^2} + \frac{n_z^2 \pi^2}{l_z^2}$$

be the Fermi level. In the k -space each solution occupies a volume of $\frac{\pi^3}{V}$, where $V = l_x l_y l_z$. Thus,

$$(\text{total volume in } k\text{-space}) = (\# \text{ electrons}) \cdot \frac{1}{2} \cdot (\text{volume per state in } k\text{-space}).$$

That is,

$$\frac{1}{8} \frac{4}{3} \pi k_F^3 = \frac{Nq}{2} \frac{\pi^3}{V} \quad \Rightarrow \quad k_F = \left(\frac{3\pi^2 Nq}{V} \right)^{\frac{1}{3}}.$$

The Fermi energy is then

$$E_F = \frac{\hbar^2}{2m} k_F^2 \quad \Rightarrow \quad E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 Nq}{V} \right)^{\frac{2}{3}}.$$

Remark. Often N and V are not given but the ratio N/V can be derived from the density, the atomic weights, and the Avogadro's number. The number of valence electrons q is typically 1 or 2.

6.1.2 Density of States

From above we have that

$$Nq = \frac{V}{3\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{\frac{3}{2}}.$$

The number of one-electron levels per unit state or density of states is then

$$D(E) = \frac{\partial(Nq)}{\partial E} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}}.$$

6.2 Kronig-Penny Model

The free electron model does not work for all solids. In insulators, for example, the electrons feel the periodic potential from the atoms. We simplify further and use the so-called ‘‘Dirac-Comb’’, shown in the Figure 6.

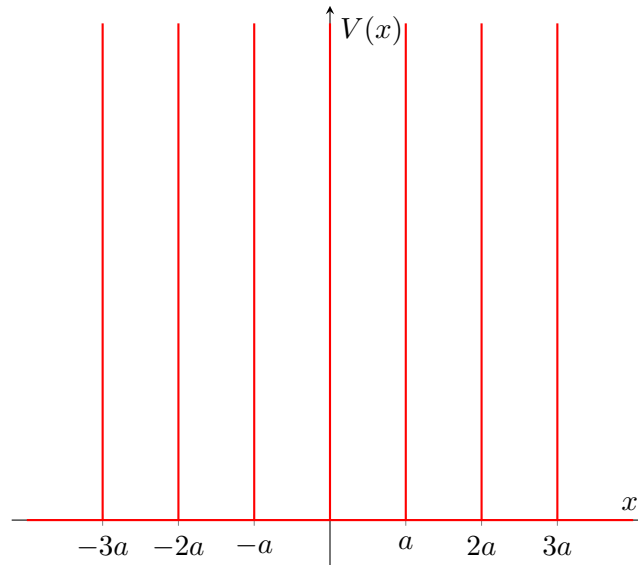


Figure 6: “Dirac-Comb” Potential.

6.2.1 Bloch’s Theorem

For periodic potential $V(x) = V(x + a)$ we have

$$\psi(x + a) = e^{iKa} \psi(x),$$

where K is real and independent of x . By solving the SE we see that gaps arise.

6.2.2 Metals

By definition, they have a partially filled band. So they can conduct electricity. They have empty electronic states that a moving electron can move into.

6.2.3 Insulators and Semiconductors

The highest occupied level is at the top of the “valence band” (V.B.). Then, a band gap separates these filled states with empty “conduction band” (C.B.). To get an insulator/semiconductor to conduct, we need to excite an electron from the V.B. into the C.B. This can be done:

- Optically: photoconductivity if $h\nu > E_{\text{gap}}$.
- Thermally:

$$n_{\text{electrons}} \approx N_i \exp\left(-\frac{E_{\text{gap}}}{k_B T}\right),$$

where $n_{\text{electrons}}$ is the number of free electrons per unit volume and N_i is the effective “intrinsic” carrier concentration.

- Doping (see next).

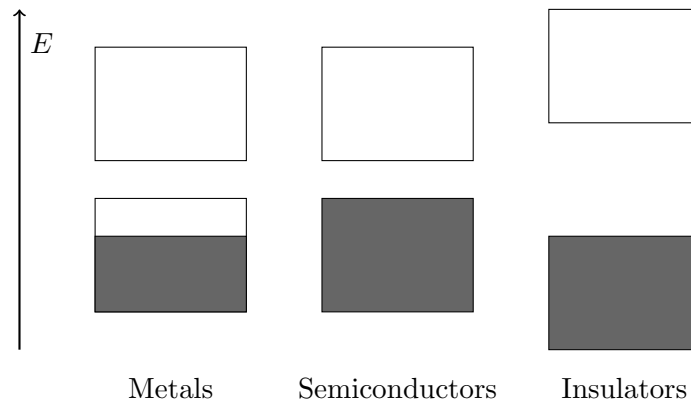


Figure 7: Metals, insulators, and semiconductors.

6.2.4 Doping

Doping consists of adding impurities with one more/less valence electron.

Example. Consider a solid of Si. P has one more valence electron and one more proton. Without the two extra particles the solid has no charge, we can model this system as the hydrogen atom, where the extra electron orbits around the extra proton. Therefore, the electron is not in the C.B. (attractive force). To get free electrons in a doped semiconductor we “ionize the impurity”, i.e. we give energy more than E_d to put the extra electron in C.B. In this case, P is called a “donor” because it has an extra electron to donate to C.B. To quantify how many free electrons we can use

$$n_{\text{electrons}} = N_D \exp\left(-\frac{E_d}{k_B T}\right),$$

where N_D is the concentration of donors. Note that, if $k_B T \gg E_d$ then $n_{\text{electrons}} = N_D$.

6.3 Quick Checks

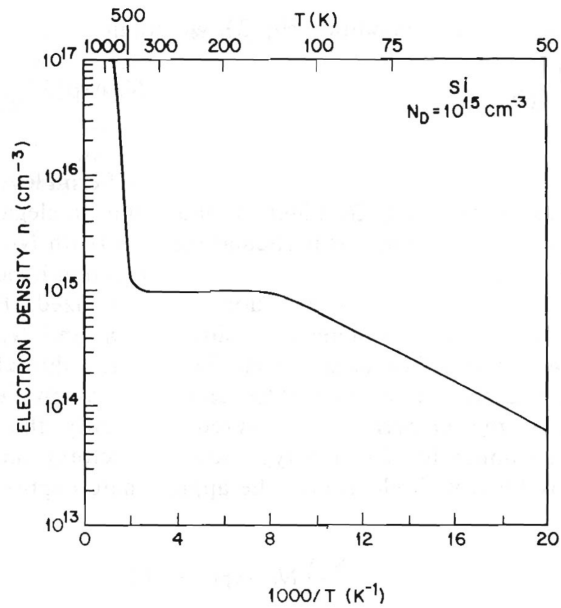
Circle True or False.

- | | | |
|---|---|--|
| T | F | Electronic bands exist in semiconductor and insulators, but not metals. |
| T | F | In metals at $T = 0\text{K}$, the electronic states are filled up to the Fermi level. |
| T | F | Doping is used to enhance the conductivity of solids. |
| T | F | If we add more electrons to a crystalline metallic solid, such that additional electronic states are occupied, the Fermi energy rises. |
| T | F | Bloch's theorem applies to systems that have a potential-energy function that is periodic in space. |
| T | F | The electronic density of states at the Fermi energy affects the ability of a solid to conduct electricity. |
| T | F | Semiconductors have band gaps, but insulators do not. |
| T | F | Bloch's theorem states that the wave function in a solid is the same for each atom in the solid. |

6.4 Exercises

1. Calculate the Fermi energy for non-interacting electrons in a two-dimensional infinite square well. Let σ be the number of free electrons per unit area of the well.

2. (a) For intrinsic (i.e., undoped) silicon, calculate the approximate temperature required to thermally excite free electrons at a concentration of $2 \cdot 10^{17}$ per cm^3 . Silicon is a semiconductor with a band gap of 1.12 eV and an effective intrinsic carrier concentration, n_i , of $1.71 \cdot 10^{19}$ per cm^3 .
- (b) Repeat the above calculation for silicon that is doped with phosphorous at a concentration of 10^{18} per cm^3 . The binding energy of the donor electron on P is 0.045 eV.
- (c) Explain (in words) the temperature dependence of the electron density shown in the plot below for silicon that is doped with donors at a concentration of 10^{15} per cm^3 .



7 Approximate Methods

7.1 Perturbation Theory

7.1.1 Non-degenerate Perturbation Theory

Assume we want to solve

$$\hat{H}\psi_n = E_n\psi_n$$

and we already know the solution to

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

where $\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}'$. Using power series we can write the energies and the wave function as

$$\begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \\ \psi_n &= \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots \end{aligned}$$

By plugging into the TISE we get

$$\begin{aligned} E_n^{(1)} &= \langle \psi_n^{(0)} | \hat{H}' \psi_n^{(0)} \rangle, \\ \psi_n^{(1)} &= \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | \hat{H}' \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}, \\ E_n^{(2)} &= \sum_{m \neq n} \frac{|\langle \psi_m^{(0)} | \hat{H}' \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}. \end{aligned}$$

7.1.2 Degenerate Perturbation Theory

For degenerate states the above equations do not hold. We need to use the degenerate perturbation theory. For two states we obtain

$$E_{\pm}^{(1)} = \frac{1}{2} \left(W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right),$$

where

$$W_{ij} = \langle \psi_i^{(0)} | \hat{H}' \psi_j^{(0)} \rangle.$$

For n -degenerate states $E_n^{(1)}$ are the eigenvalues of the equation

$$W|\psi_n^{(0)}\rangle = E_n^{(1)}|\psi_n^{(0)}\rangle,$$

where W is now a matrix with $W_{ij} = \langle \psi_i^{(0)} | \hat{H}' \psi_j^{(0)} \rangle$.

7.2 Variational Principle

Assume we want to determine the ground state energy for an Hamiltonian \hat{H} , for which we cannot solve the TISE. By the variational principle we can pick any trial function ψ_{trial} , then

$$E_{\text{gs}} \leq \langle \psi_{\text{trial}} | \hat{H} \psi_{\text{trial}} \rangle.$$

That is, the expectation value of \hat{H} is an upper bound for the actual ground state energy.

Remark. A typical approach consists of picking a trial function with some parameter α . Then pick the parameter α that minimizes $\langle \psi_{\text{trial}} | \hat{H} \psi_{\text{trial}} \rangle$ in order to find a better upper bound for the ground state energy.

Example. Consider $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + cx^4$. Give an upper bound for the ground state energy using the trial wave function $\psi_{\text{trial}} = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp(-\alpha^2 x^2/2)$. Then,

$$\begin{aligned} E_{\text{gs}} &\leq \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \exp\left(-\frac{\alpha x^2}{2}\right) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + |x|\right) \exp\left(-\frac{\alpha x^2}{2}\right) dx \\ &\leq \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \left(\frac{\hbar^2}{4m} (\alpha\pi)^{\frac{1}{2}} + \frac{3c\pi^{\frac{1}{2}}}{4\alpha^{\frac{5}{2}}}\right) \\ &\leq \frac{\hbar^2\alpha}{4m} + \frac{3c}{4\alpha^2}. \end{aligned}$$

Since α is adjustable we can find the value that gives the minimum. That is,

$$\frac{d}{d\alpha} \left(\frac{\hbar^2\alpha}{4m} + \frac{3c}{4\alpha^2}\right) = \frac{\hbar^2}{4m} - \frac{3c}{2\alpha^3} = 0 \quad \Rightarrow \quad \alpha_{\text{min}} = \left(\frac{6mc}{\hbar^2}\right)^{\frac{1}{3}},$$

which gives

$$E_{\text{gs}} \leq \frac{3}{8} \left(\frac{6c\hbar^4}{m^2}\right)^{\frac{1}{3}}.$$

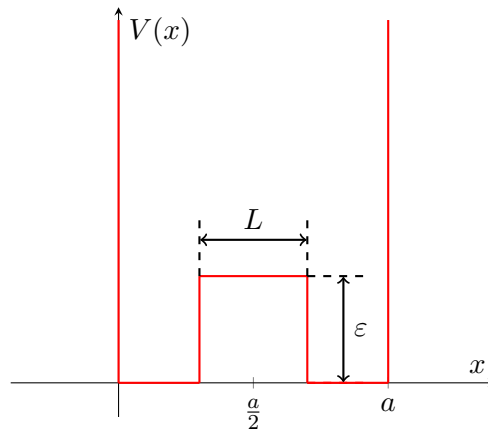
7.3 Quick Checks

Circle True or False.

- | | | |
|---|---|---|
| T | F | The variational principle can be used to estimate the ground state wave function. |
| T | F | Perturbation theory is mostly concerned with the calculation of the ground state energy. |
| T | F | To get a good solution with the variational principle, we should make a good guess at a trial and add many adjustable parameters. |
| T | F | The variational principle allows one to minimize the ground state energy by varying \hat{H}' . |
| T | F | If your trial function has many adjustable parameters, the variational principle guarantees the exact ground state energy. |
| T | F | Perturbation theory assumes non-degenerate states. |
| T | F | The ground state energy is lower-bounded by the minimum of the potential energy V_{\min} . |
| T | F | Any function can be used as trial function for the variational principle. |
| T | F | In general, the accuracy of perturbation theory increases as the “strength” of the perturbation decreases. |
| T | F | Perturbation theory is an alternative way to find the exact solution to the TISE. |

7.4 Exercises

1. A one-dimensional infinite square well has a potential step centered in the middle as shown.



- (a) Calculate the energy of the ground state to first order. Then evaluate it for $L = a/10$.
- (b) Using first-order perturbation theory, determine how much of the $n = 2$ eigenstate from the standard infinite square well (i.e. without the potential step in the middle) is contained in the lowest energy eigenstate of the perturbed infinite square well from (a).

2. Use a Gaussian trial function, $(\alpha/\pi)^{\frac{1}{4}} \exp(-\alpha x^2/2)$, to obtain the lowest upper bound on the ground state energy of the linear potential: $V(x) = C|x|$, where C is a constant.

3. Consider a quantum system with just three linearly independent states. Suppose the Hamiltonian, in matrix form, is

$$\hat{H} = V_0 \begin{bmatrix} 1 - \varepsilon & 0 & 0 \\ 0 & 1 & \varepsilon \\ 0 & \varepsilon & 2 \end{bmatrix},$$

where V_0 is a constant and $\varepsilon \ll 1$ is some small number.

- (a) Write down the eigenvectors and eigenvalues of the unperturbed Hamiltonian ($\varepsilon = 0$).
- (b) Solve for the exact eigenvalues of \hat{H} . Expand each of them as a power series in ε , up to second order.
- (c) Use first- and second-order nondegenerate perturbation theory to find the approximate eigenvalue for the state that grows out of the nondegenerate eigenvector of $\hat{H}^{(0)}$. Compare the exact result, from (a).
- (d) Use degenerate perturbation theory to find the first-order correction to the two initially degenerate eigenvalues. Compare the exact results.

A Probability Theory

Let Y be a discrete random variable (DV) with sample space $\mathcal{Y} = \mathbb{N}$ and probability function $P(Y = y)$. Let X be a continuous random variable (CV) with sample space $\mathcal{X} = \mathbb{R}$ and probability density function $\rho(x)$.

A.1 Normalization

$$\text{DV: } \sum_{y=0}^{+\infty} P(Y = y) = 1$$

$$\text{CV: } \int_{-\infty}^{+\infty} \rho(x) dx = 1$$

A.2 Expected Value

$$\text{DV: } \langle Y \rangle = \sum_{y=0}^{+\infty} yP(Y = y)$$

$$\langle f(Y) \rangle = \sum_{y=0}^{+\infty} f(y)P(Y = y)$$

$$\text{CV: } \langle X \rangle = \int_{-\infty}^{+\infty} x\rho(x) dx$$

$$\langle f(X) \rangle = \int_{-\infty}^{+\infty} f(x)\rho(x) dx$$

Linearity of the expected value:

$$\langle aY + b \rangle = a \cdot \langle Y \rangle + b \quad a, b \in \mathbb{R}$$

$$\langle aX + b \rangle = a \cdot \langle X \rangle + b \quad a, b \in \mathbb{R}$$

A.3 Variance

$$\begin{aligned} \text{Var}(Y) &= \sigma_Y^2 = \langle (Y - \langle Y \rangle)^2 \rangle \\ &= \langle Y^2 - 2\langle Y \rangle Y + \langle Y \rangle^2 \rangle \\ &= \langle Y^2 \rangle - 2\langle Y \rangle \langle Y \rangle + \langle Y \rangle^2 \\ &= \langle Y^2 \rangle - \langle Y \rangle^2 \end{aligned}$$

$$\begin{aligned} \text{Var}(X) &= \sigma_X^2 = \langle (X - \langle X \rangle)^2 \rangle \\ &= \langle X^2 - 2\langle X \rangle X + \langle X \rangle^2 \rangle \\ &= \langle X^2 \rangle - 2\langle X \rangle \langle X \rangle + \langle X \rangle^2 \\ &= \langle X^2 \rangle - \langle X \rangle^2 \end{aligned}$$

$$\text{DV: } \sigma_Y^2 = \sum_{y=0}^{+\infty} (y - \langle Y \rangle)^2 P(Y = y)$$

$$\text{CV: } \sigma_X^2 = \int_{-\infty}^{+\infty} (x - \langle X \rangle)^2 \rho(x) dx$$

B Dirac Delta Function

The Dirac Delta function is given by

$$\delta(x) = \begin{cases} \infty & \text{if } x = 0, \\ 0 & \text{if } x \neq 0. \end{cases}$$

It has the property

$$\int_{-\infty}^{+\infty} \delta(x) dx = 1.$$

If we multiply $f(x)$ by $\delta(x - a)$ it gives by $f(a)$ multiplied by $\delta(x - a)$, i.e.

$$f(x)\delta(x - a) = f(a)\delta(x - a).$$

By integrating we obtain

$$\int_{-\infty}^{+\infty} f(x)\delta(x - a) dx = f(a).$$

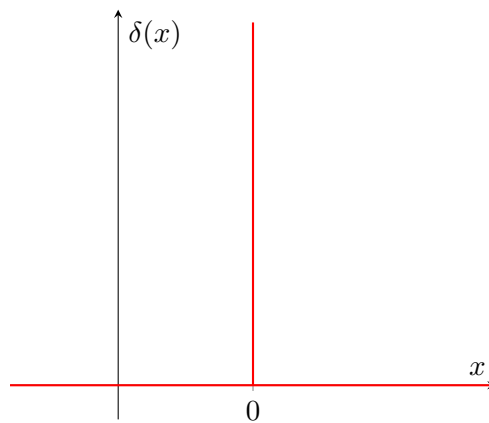


Figure 8: Dirac Delta Function.

Example. Compute the following integral:

$$\int_{-\infty}^{+\infty} x^2 \delta(x - 2) dx = 2^2 = 4.$$

Example. Compute the following integral:

$$\int_{-1}^{+1} x^2 \delta(x - 2) dx = 0,$$

since $\delta(x - 2)$ is always 0 in the interval $[-1, +1]$.