MA3441: Quantum Mechanics I

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Chapter 1

State vectors and operators

1.1 Sum over alternatives

Consider the two-slit experiment with a source S and only slit 1 open. The probability amplitude at a position x on the screen is:

$$\phi_1(x) = \langle x|S\rangle$$

This is read from right to left: "from S to x". $\phi_1(x)$ can be decomposed as:

$$\phi_1(x) = \langle x|1\rangle\langle 1|S\rangle$$

i.e. "from S to 1, and from 1 to x." The probability P_1 at x is then given by:

$$P_1(x) = |\langle x|1\rangle|^2\,|\langle 1|S\rangle|^2$$

Similarly,

$$P_2(x) = |\langle x|2\rangle|^2\,|\langle 2|S\rangle|^2$$

The probability with *both* slits open $P_{1,2}$ is *not* the sum of P_1 and P_2! We sum the probability *amplitudes* to obtain an expression for $\phi_{1,2}(x)$ and then we can find $P_{1,2}(x)$:

$$\begin{aligned}\phi_{1,2}(x) &= \phi_1(x) + \phi_2(x)\\ &= \langle x|1\rangle\langle 1|S\rangle + \langle x|2\rangle\langle 2|S\rangle\\ P_{1,2}(x) &= |\langle x|1\rangle\langle 1|S\rangle + \langle x|2\rangle\langle 2|S\rangle|^2 \neq P_1(x) + P_2(x)\end{aligned}$$

1.2 State space

Consider a vector $\vec{A}$ in an n-dimensional Euclidean space. Let $\{\vec{a}\}_i^n$ be an orthonormal basis set of vectors (i.e. $\vec{a}_i^* \cdot \vec{a}_j = \delta_{ij}$). Then $\vec{A}$ can be expanded in the basis set:

$$\vec{A} = \sum_{i=1}^{n}(\vec{a}_i^* \cdot \vec{A})\vec{a}_i = \sum_{i=1}^{n}(\vec{a}_i, \vec{A})\vec{a}_i$$

where $(\cdot, \cdot)$ is the *inner product*.

Likewise, the state $|\psi\rangle$ of a system can be expanded in a set of 'basis states'. If $|i\rangle$ is a basis set, then for all ψ:

$$\sum_i \langle i|\psi\rangle |i\rangle$$

So $\langle\phi|\psi\rangle$ is in fact the *inner product* of $\langle\phi|$ and $|\psi\rangle$.

1.3 Ket space and bra space

1.3.1 Ket space

In QM, a physical state is represented by a *state vector* in a complex vector space. We call such a vector a *ket*, and denote it by $|\psi\rangle$. The state vector is postulated to contain complete information about the physical state.

The **principle of superposition** states that if $|\psi_1\rangle$ and $|\psi_2\rangle$ are two possible states of a system, then $c_1|\psi_1\rangle + c_2|\psi_2\rangle$, $c_1, c_2 \in \mathbb{C}$ is also a possible state. Furthermore, $|\psi\rangle$ and $c|\psi\rangle$ represent the same state.

1.3.2 Bra space

Bra space is a vector space dual to the ket space. It is postulated that for every ket $|\psi\rangle$ there exists a bra $\langle\psi|$ in this dual space. The bra space is spanned by the basis $\{\langle i|\}$ which corresponds to the ket basis $\{|i\rangle\}$. The correspondence is postulated to be one-to-one: $\langle\psi| \leftrightarrow |\psi\rangle$.

The bra vector dual to $c|\psi\rangle$ is postulated to be $c^*\langle\psi|$.

1.3.3 Properties

- $\langle\psi|\phi\rangle = \langle\phi|\psi\rangle^*$
- $\langle\psi|\psi\rangle \geqslant 0$, with $\langle\psi|\psi\rangle = 0 \Leftrightarrow |\psi\rangle = 0$
- $\langle\phi|c\psi\rangle = c\langle\phi|\psi\rangle$
- $\langle(\langle\phi_1| + \langle\phi_2|)\,|\psi\rangle = \langle\phi_1|\psi\rangle + \langle\phi_2|\psi\rangle$
- $|\psi\rangle$ and $|\phi\rangle$ are said to be *orthogonal* if $\langle\psi|\phi\rangle = 0$.
- The norm of $|\psi\rangle$ is $\langle\psi|\psi\rangle$, so the normalised $|\overline{\psi}\rangle = \frac{1}{\sqrt{\langle\psi|\psi\rangle}}|\psi\rangle$

The dimesionality of the vector space depends on what is being described. For example an electron can be 'spin up', $|\uparrow\rangle$, or 'spin down', $|\downarrow\rangle$. So the spin space of an electron is 2-dimensional. The momentum of a free spinless particle can be anything $-\infty < p < \infty$, so its momentum state space is infinite-dimensional.

1.4 Hilbert space

A complex vector space $\mathcal{H}$ with the following properties is called a *Hilbert space*.

1. $\mathcal{H}$ is complete, i.e there exists a basis set $|i\rangle$ such that $|\psi\rangle = \sum_i \langle i|\psi\rangle |i\rangle$ for all $|\psi\rangle \in \mathcal{H}$.
2. $\mathcal{H}$ is an inner product space [properties described in Section 1.3.3]

1.5 Eigenstates

Let A be a linear operator representing some physical quantity ("observable") of a quantum system.

Let $|\psi\rangle \in \mathcal{H}$, $|\psi'\rangle = A|\psi\rangle$. The dual of $|\psi'\rangle$ is $\langle\psi'| = \langle\psi|A^\dagger$. The values an observable can take are caled its *eigenvalues*. A state $|\psi\rangle \in \mathcal{H}$ for which $A|\psi\rangle = a|\psi\rangle$, $a \in \mathbb{C}$ is called an *eigenstate* of A.

Eigenvectors can be of two general types:

- Non-degenerate: one $|\psi\rangle$ for each a
- Degenerate: more than one $|\psi\rangle$ for each a, excluding trivial case.

Chapter 2

Hermitian and unitary operators

2.1 Hermitian operators

Forming the inner product of ψ (defined in Section 1.5) and some $|\phi\rangle \in \mathcal{H}$, and taking the complex conjugate gives:

$$\langle\phi|A|\psi\rangle^* = \langle\phi|\psi'\rangle^* = \langle\psi'|\phi\rangle$$

But the dual of $|\psi'\rangle$ is $\langle\psi'| = \langle\psi|A^\dagger$. So

$$\langle\phi|A|\psi\rangle^* = \langle\psi|A^\dagger|\phi\rangle.$$

If $\langle\phi|A|\psi\rangle^* = \langle\psi|A^\dagger|\phi\rangle = \langle\psi|A|\phi\rangle$, A is said to be a **Hermitian operator**.

2.1.1 Properties

Theorem: The eigenvalues of a Hermitian operator are real.

Proof: $A|\psi\rangle = a|\psi\rangle \Rightarrow \langle\psi|A|\psi\rangle = a\langle\psi|\psi\rangle$, so a is real if $\langle\psi|A|\psi\rangle$ is real. But $\langle\psi|A|\psi\rangle^* = \langle\psi|A|\psi\rangle$ by hypothesis. QED.

Note that since the eigenvalues of an observable A are the result of measurement, they must be real, and A must be Hermitian.

Theorem: If A is Hermitian and $a_m \neq a_n$, then $\langle\psi_m|\psi_n\rangle = 0$; i.e. the eigenstates are orthogonal.

Proof:

$$A|\psi_m\rangle = a_m|\psi_m\rangle, A|\psi_n\rangle = a_n|\psi_m\rangle$$
$$\langle\psi_n|A|\psi_m\rangle = a_m\langle\psi_n|\psi_m\rangle$$

Taking complex conjugate gives:

$$\langle\psi_n|A|\psi_m\rangle^* = a_m^*\langle\psi_n|\psi_m\rangle$$

But A is Hermitian, so $a_m, a_n \in \mathbb{R}$. Hence,

$$\langle\psi_n|A|\psi_m\rangle = a_m\langle\psi_n|\psi_m\rangle$$

But

$$\langle\psi_n|A|\psi_m\rangle = a_n\langle\psi_n|\psi_m\rangle.$$

Subtracting gives

$$\begin{aligned}(a_m - a_n)\langle\psi_m|\psi_n\rangle &= 0\\ \Rightarrow \langle\psi_m|\psi_n\rangle &= 0\end{aligned}$$

since $a_m \neq a_n$ by hypothesis. QED.

2.1.2 Degenerate eigenvalues

Suppose we have $A|\psi_1\rangle = a|\psi_1\rangle$ and $A|\psi_2\rangle = a|\psi_2\rangle$, but $|\psi_1\rangle \neq |\psi_2\rangle$. It is not necessarily true that $|\psi_1\rangle$ and $|\psi_2\rangle$ are orthogonal, but they can be made orthogonal as follows:

$$\begin{aligned}\text{Let } |\psi_1^{\text{new}}\rangle &= |\psi_1\rangle,\\ |\psi_2^{\text{new}}\rangle &= c_1|\psi_1\rangle + c_2|\psi_2\rangle.\end{aligned}$$

Then, $\langle\psi_1^{\text{new}}|\psi_2^{\text{new}}\rangle = 0$ if $c_1/c_2 = \langle\psi_1|\psi_2\rangle/\langle\psi_1|\psi_1\rangle$.

This procedure can be generalised to multiple degenerate eigenvalues.

2.2 Spectral theorem

Theorem: Let A be a Hermitian operator acting on a finite-dimensional Hilbert space $\mathcal{H}$, and suppose A has eigenvectors: $A|\psi_n\rangle = a_n\psi_n$, $n = 1, 2, \ldots$ which satisfy the orthonormality condition $\langle\psi_m|\psi_n\rangle = \delta_{mn}$. Then for any $|\phi\rangle \in \mathcal{H}$,

$$|\phi\rangle = \sum_{n=1}^{N} |\psi_n\rangle\langle\psi_n|\phi\rangle. \tag{2.1}$$

This is called the 'spectral decomposition' or 'eigenstate expansion' of $|\phi\rangle$. The set $\{a_n\}$ is called the *spectrum* of A.

Note: If $\mathcal{H}$ is infinite-dimensional, A must be a self-adjoint compact operator on $\mathcal{H}$. 'Compact' means discrete eigenvalues, finite number of eigenstates for each eigenvector.

Equation (2.1) allows completeness of eigenvectors $|\psi_n\rangle$ of A to be stated as:

$$\sum_{n=1}^{N} |\psi_n\rangle\langle\psi_n| = \mathbb{1},$$

where $\mathbb{1}$ is the **unit operator.**

2.2.1 Example

A complete set of spin states for an electron is:

$$\begin{aligned}|\uparrow\rangle &= \tbinom{1}{0}, \text{ spin up along } z\text{-axis}\\ |\downarrow\rangle &= \tbinom{0}{1}, \text{ spin down along } z\text{-axis}\end{aligned}$$

and so an arbitrary spin state $|\psi\rangle$ can be expressed as

$$|\psi\rangle = \langle\uparrow|\psi\rangle\begin{pmatrix}1\\0\end{pmatrix} + \langle\downarrow|\psi\rangle\begin{pmatrix}0\\1\end{pmatrix}.$$

Note that

$$\begin{aligned}|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow| &= \begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1&0\end{pmatrix} + \begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0&1\end{pmatrix}\\ &= \begin{pmatrix}1&0\\0&0\end{pmatrix} + \begin{pmatrix}0&0\\0&1\end{pmatrix}\\ &= \begin{pmatrix}1&0\\0&1\end{pmatrix}\\ &= \mathbb{1}.\end{aligned}$$

2.3 Unitary operators

An operator U is called a **unitary operator** if $U^{-1} = U^\dagger$ *or* if $UU^\dagger = U^\dagger U = 1$.

2.3.1 Transformation of orthonormal bases

Let A and B be Hermitian operators acting on a Hilbert space $\mathcal{H}$. Then the eigenstates of A, $\{|\psi_k\rangle\}$, and of B, $\{|\phi_k\rangle\}$, are complete orthonormal sets spanning $\mathcal{H}$.

Problem: Find the operator U such that $U|\phi_k\rangle = |\psi_k\rangle$.

Solution: Multiply by $\langle\phi_k|$ on the right, giving

$$U|\phi_k\rangle\langle\phi_k| = |\psi_k\rangle\langle\phi_k|$$

and sum over k. Since $\{|\phi_k\rangle\}$ is complete, $\sum_{k=1}^{n} |\phi_k\rangle\langle\phi_k| = 1$, and hence:

$$U = \sum_{k=1}^{n} |\psi_k\rangle\langle\phi_k|.$$

U may be written as a matrix. Using completeness of $\{|\phi_k\rangle\}$, we have:

$$\begin{aligned}&\sum_l |\phi_l\rangle\langle\phi_l|U|\phi_k\rangle = |\psi_k\rangle.\\ &\Leftrightarrow \sum_l U_{lk}|\phi_l\rangle = |\psi_k\rangle\end{aligned}$$

where $U_{lk} = \langle\phi_l|U|\phi_k\rangle$.

Theorem: U is unitary.

Proof: $U^\dagger = \sum_k |\phi_k\rangle\langle\psi_k|$, so:

$$\begin{aligned}U^\dagger U &= \sum_{k,l} |\phi_k\rangle \underbrace{\langle\psi_k|\psi_l\rangle}_{\delta_{kl}}\langle\phi_l|\\ &= \sum_k |\phi_k\rangle\langle\phi_k|\\ &= 1.\end{aligned}$$

Similarly, $UU^\dagger = \sum_k |\psi_k\rangle\langle\psi_k| = 1 \Rightarrow U^\dagger = U^{-1}$. QED.

Hence, we can state: A unitary transformation transforms one orthonormal basis into another orthonormal basis in a Hilbert space.

Example: An alternative set of spin states for an electron is:

$$|\uparrow\rangle_x = \tfrac{1}{\sqrt{2}}\left(\begin{smallmatrix}1\\1\end{smallmatrix}\right), \quad |\downarrow\rangle_x = \tfrac{1}{\sqrt{2}}\left(\begin{smallmatrix}1\\-1\end{smallmatrix}\right).$$

A unitary operator that transforms from x-basis to z-basis is:

$$\begin{aligned} U &= |\uparrow\rangle_z\langle\uparrow|_x + |\uparrow\rangle_x\langle\uparrow|_z \\ &= \tfrac{1}{\sqrt{2}}\left(\begin{smallmatrix}1\\0\end{smallmatrix}\right)\left(\begin{smallmatrix}1&1\end{smallmatrix}\right) + \tfrac{1}{\sqrt{2}}\left(\begin{smallmatrix}0\\1\end{smallmatrix}\right)\left(\begin{smallmatrix}1&-1\end{smallmatrix}\right) \\ &= \tfrac{1}{\sqrt{2}}\left(\begin{smallmatrix}1&1\\0&0\end{smallmatrix}\right) + \tfrac{1}{\sqrt{2}}\left(\begin{smallmatrix}0&0\\1&-1\end{smallmatrix}\right) \\ &= \tfrac{1}{\sqrt{2}}\left(\begin{smallmatrix}1&1\\1&-1\end{smallmatrix}\right). \end{aligned}$$

This gives us $U\left[\frac{1}{\sqrt{2}}\left(\begin{smallmatrix}1\\1\end{smallmatrix}\right)\right] = \left(\begin{smallmatrix}1\\0\end{smallmatrix}\right)$ and $U\left[\frac{1}{\sqrt{2}}\left(\begin{smallmatrix}1\\-1\end{smallmatrix}\right)\right] = \left(\begin{smallmatrix}0\\1\end{smallmatrix}\right)$, and $UU^\dagger = \frac{1}{2}\left(\begin{smallmatrix}1&1\\1&-1\end{smallmatrix}\right)\left(\begin{smallmatrix}1&1\\1&-1\end{smallmatrix}\right) = \mathbb{1}$.

2.3.2 Unitary transformations and probability amplitudes

Theorem: Unitary transformations preserve probability amplitudes.

Proof: Let $|a\rangle, |b\rangle \in \mathcal{H}$ and let $|a'\rangle = U|a\rangle$, $|b'\rangle = U|b\rangle$. Then $\langle b'| = \langle b|U^\dagger$, and $\langle b'|a'\rangle = \langle b|U^\dagger U|a\rangle = \langle b|a\rangle$. QED.

2.3.3 Unitary equivalence

Consider the matrix elements of A in ϕ basis.

$$\begin{aligned} \langle\phi_k|A|\phi_l\rangle &= \langle\phi_k|U^\dagger UAU^\dagger U|\phi_l\rangle \\ &= \langle\psi_k|UAU^\dagger|\psi_l\rangle \end{aligned}$$

Hence, A in ϕ-basis $\longrightarrow UAU^\dagger$ in ψ-basis. A and $UAU^\dagger$ are said to be **unitarily equivalent.**

Example:

$$S_x|\uparrow\rangle = \tfrac{\hbar}{2}|\uparrow\rangle_x$$

where $S_x = \frac{\hbar}{2}\left(\begin{smallmatrix}0&1\\1&0\end{smallmatrix}\right)$, the x component of spin angular momentum (discussed in more depth later). We wish to find S_z. Using the operator U which transforms from x-basis to z-basis (calculated in Section 2.3.1):

$$\begin{aligned} S_x|\uparrow\rangle_x &= \tfrac{\hbar}{2}|\uparrow\rangle_x \\ US_xU^\dagger U|\uparrow\rangle_x &= \tfrac{\hbar}{2}U|\uparrow\rangle_x \\ US_xU^\dagger|\uparrow\rangle_z &= \tfrac{\hbar}{2}|\uparrow\rangle_z \\ US_xU^\dagger &= S_z \end{aligned}$$

2.3.4 Spectra of unitarily equivalent observables

Theorem: Unitarily equivalent observables have the same spectra.

Proof: We have $A|\phi_n\rangle = a_n|\phi_n\rangle$ and $U|\phi_n\rangle = |\psi_n\rangle$.
Then,

$$\begin{aligned} AU^\dagger U|\phi_n\rangle &= a_n|\phi_n\rangle \\ UAU^\dagger U|\phi_n\rangle &= a_n U|\phi_n\rangle \\ UAU^\dagger|\psi_n\rangle &= a_n|\psi_n\rangle. \text{ QED.} \end{aligned}$$

2.3.5 Miscellaneous properties

- The elements U_{ij} of a unitary matrix satisfy $|U_{ij}| \leqslant 1$.
- The eigenvalues $\{\lambda_i\}$ of a unitary matrix satisfy $|\lambda_i| = 1$.

Chapter 3

The Schrödinger equation, measurements and entanglement

3.1 The Schrödinger equation

3.1.1 Derivation

By the spectral theorem, a state $|\psi(t)\rangle \in \mathcal{H}$ can be expressed as a superposition of eigenstates of an observable A:

$$|\psi(t)\rangle = \sum_n \langle a_n|\psi(t)\rangle |a_n\rangle$$

And so,

$$\langle\psi(t)|\psi(t)\rangle = \sum_n |\langle a_n|\psi(t)\rangle|^2 = 1.$$

We want $\langle\psi(t+dt)|\psi(t+dt)\rangle$ to equal 1, i.e. probability conservation. This is ensured if $|\psi(t+dt)\rangle$ is obtained from $|\psi(t)\rangle$ by a unitary transformation (as proven in Section 2.3.2):

$$|\psi(t+dt)\rangle = U(dt)|\psi(t)\rangle \quad \text{where } U^\dagger(dt) = U^{-1}(dt)$$

We let $U(dt) = 1 - \frac{i}{\hbar}H\,dt$, where H is self-adjoint (meaning $U^\dagger = 1 + \frac{i}{\hbar}H\,dt$) so that:

$$U^\dagger(dt)U(dt) = U(dt)U^\dagger(dt) = 1 + O(dt)^2,$$

giving:

$$|\psi(t+dt)\rangle = |\psi(t)\rangle\left(1 - \tfrac{i}{\hbar}H\,dt\right).$$

Using the fact that

$$|\psi(t+dt)\rangle - |\psi(t)\rangle = \frac{\partial}{\partial t}|\psi(t)\rangle dt + O(t^2),$$

we see that the time development of the state is determined by the **Schrödinger equation**:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle.$$

3.1.2 The Hamiltonian operator

H is called the system's **Hamiltonian operator.** By definition, H must have dimension of (time)/(angular momentum) = energy. For a single particle interacting with a potential V, for example,

$$H = \frac{1}{2m}\vec{p}\cdot\vec{p} + V(\vec{x}, t)$$

3.2 Quantum measurements

A system is assumed to be in some initial state $|\psi_0\rangle$. It evolves according to the Schrödinger equation: $|\psi_0\rangle \xrightarrow{H} |\psi\rangle$. We wish to measure an observable A. By the spectral theorem, $|\psi\rangle$ can be expanded in terms of A's eigenstates $|\psi_n\rangle$:

$$|\psi\rangle = \sum_n |\psi\rangle\langle\psi_n|\psi\rangle.$$

The only possible result of a measurement of A is one of its eigenstates a_n.

A measurement always causes the system to jump into an eigenstate of A:

$$|\psi\rangle \xrightarrow{\text{measurement}} |\psi_n\rangle.$$

The probability of jumping into $|\psi_n\rangle$ is $|\langle\psi_n|\psi\rangle|^2$. We cannot predict which state $|\psi_n\rangle$ the system will jump into by measurement.

3.2.1 Expectation value

The **expectation value** of an observable A is:

$$\langle A\rangle \equiv \langle\psi|A|\psi\rangle = \sum_n |\langle\psi_n|\psi\rangle|^2 a_n.$$

Proof:

$$\begin{aligned} A|\psi\rangle &= \sum_n A|\psi_n\rangle\langle\psi_n|\psi\rangle \\ &= \sum_n a_n|\psi_n\rangle\langle\psi_n|\psi\rangle \\ \langle\psi|A|\psi\rangle &= \sum_n a_n\langle\psi|\psi_n\rangle\langle\psi_n|\psi\rangle \\ &= \sum_n a_n|\langle\psi_n|\psi\rangle|^2. \text{ QED.} \end{aligned}$$

The experimental interpretation of A is the following: for N identical systems, let a_i be the value of A in the i^{th} system. Then:

$$\langle A\rangle = \lim_{N\to\infty}\frac{1}{N}\sum_{i=1}^{N} a_i$$

Thus, $\langle A\rangle$ has statistical significance for many measurements of one system.

Example: Suppose $|\psi\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$. Then there is a 50/50 chance that a measurement of $|\psi\rangle$ will produce result $|1\rangle$. One measurement cannot establish this 50/50 chance. The probability that state $|1\rangle$ will be found r times in n independent trials is: $\binom{n}{r}p^r q^{n-r}$. For large n, this can be approximated by Stirling's formula to give:

$$P(r) = \frac{1}{\sqrt{2\pi npq}} e^{-\frac{(r-np)^2}{2npq}}$$

This is a normal distribution with width $\sim \frac{1}{2n}$. So as $n \to \infty$, the curve becomes sharper, peaking at the expectation value $\frac{n}{2}$. This is in accord with the law of large numbers, which states that the relative frequency of an event is almost surely close to the probability when the number of trials is sufficiently large.

3.3 Entanglement

A spin-0 particle decays into two spin-$\frac{1}{2}$ particles, e.g. $\pi^0 \to e^- + e^+$. Their state, $|\psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2)$, is called an **entangled state** because it cannot be factorised to the form $|\psi\rangle = |\text{particle 1}\rangle|\text{particle 2}\rangle$. The state predicts correlations between spin measurements. The two particles will *always* have opposite spin when measured along the same quantisation axis. Thus, particle 1 has a 50/50 chance of having spin up along, say, the z-axis. Suppose observer 1 finds spin up. Then although particle 2 may be space-like separated from particle 1, it *must* have spin down.

We may decide which axis to measure the spin along long after the decay. Thus, $|\psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle_1^z|\downarrow\rangle_2^z - |\downarrow\rangle_1^z|\downarrow\rangle_2^z)$ *or* $|\psi\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\rangle_1^{\hat{n}}|\downarrow\rangle_2^{\hat{n}} - |\downarrow\rangle_1^{\hat{n}}|\downarrow\rangle_2^{\hat{n}}\right)$. Measurement of spin up along $\hat{n}$ means that $|\psi\rangle \to |\uparrow\rangle_1^{\hat{n}}|\downarrow\rangle_2^{\hat{n}} \to$ particle 2 *must* have spin down along $\hat{n}$. QM implies possibility of non-local effects, and this has been confirmed by experiment.

3.4 Stern–Gerlach experiment

In the Stern–Gerlach experiment, a beam of silver atoms is emitted from a furnace. $_{47}$Ag's magnetic dipole moment due to a single 5s electron is $\vec{\mu} = 2\frac{e}{2mc}\vec{S}$, where $\vec{S}$ is the electron's spin angular momentum. Its interaction Hamiltonian in the presence of a magnetic field $\vec{B}$ is $-\vec{m}u \cdot \vec{B} = -\frac{e}{mc}\vec{B} \cdot \vec{S}$. This means the beam will split according to spin. If we take the spin-up ensemble and measure the z-component of their spin, S_z, we know the result: $|\uparrow\rangle_z \to |\uparrow\rangle_z$.

The spin state of the spin-up atoms can be expanded in the x-basis set:

$$|\uparrow\rangle_z = \underbrace{{}_x\langle\uparrow|\uparrow\rangle_z}_{1/\sqrt{2}}|\uparrow\rangle_x + \underbrace{{}_x\langle\downarrow|\uparrow\rangle_z}_{1/\sqrt{2}}|\downarrow\rangle_x$$

So if we introduce an x-filter, we do not know the outcome *a priori*! We have $P(|\downarrow\rangle_x) = \frac{1}{2}$ and $P(|\uparrow\rangle_x) = \frac{1}{2}$.

Note: If the $|\uparrow\rangle_x$ beam is again split using a z-filter, we find that half of the particles are spin-up and half are spin-down. The $|\downarrow\rangle_z$ particles are somehow 'regenerated' by the x-filter!

3.5 Time dependence of expectation value

$$\frac{\partial}{\partial t}\langle\psi|A|\psi\rangle = \left(\frac{\partial}{\partial t}\langle\psi|\right)A|\psi\rangle + \langle\psi|\left(\frac{\partial A}{\partial t}|\psi\rangle\right) + \langle\psi|A\left(\frac{\partial}{\partial t}|\psi\rangle\right)$$

Recalling that

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H \quad \text{and} \quad -i\hbar\langle\psi| = \langle\psi|H,$$

we obtain:

$$\frac{\partial}{\partial t}\langle\psi|A|\psi\rangle = \frac{i}{\hbar}\langle\psi|HA|\psi\rangle - \frac{i}{\hbar}\langle\psi|AH|\psi\rangle + \langle\psi|\frac{\partial A}{\partial t}|\psi\rangle$$
$$\frac{\partial}{\partial t}\langle A\rangle = \frac{1}{i\hbar}\langle\psi|[A,H]|\psi\rangle + \langle\psi|\frac{\partial A}{\partial t}|\psi\rangle$$

where $[A,H]$ is the **commutator** of A and H, equal to $AH - HA$.

So the expectation value of A is constant if $\frac{\partial A}{\partial t} = 0$ and A commutes with H, i.e. $[A,H] = 0$.

3.6 Non-commutative observables

Suppose a system has observables A and B, where $[A,B] \neq 0$, for example:

$$A = S_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \quad B = S_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

States of the system can be eigenstates of A or of B:

$$A|a\rangle = a|a\rangle \quad \text{or} \quad B|b\rangle = b|b\rangle$$

The states $|a\rangle$ and $|b\rangle$ are connected by a unitary transformation U: $|b\rangle = U|a\rangle$.

Now suppose we insisted on a simultaneous eigenstate of A and B. Then:

$$AB|a,b\rangle = ab|a,b\rangle$$
$$BA|a,b\rangle = ba|a,b\rangle$$
$$\Rightarrow (AB - BA)|a,b\rangle = 0.$$

Note that this does *not* mean that $AB - BA = 0$!

Chapter 4

Time evolution

4.1 Stationary states

A state of an isolated system with definite energy is called a **stationary state;** it is an eigenstate of H, which is time-independent since the system is isolated. Let $|E_n, t\rangle$ be such a state at time t. Then

$$H|E_n, t\rangle = E_n|E_n, t\rangle$$

for some constant E_n. The Schrödinger equation gives:

$$i\hbar\frac{\partial}{\partial t}|E_n, t\rangle = H|E_n, t\rangle = E_n|E_n, t\rangle$$

Solving this gives:

$$\begin{aligned}|E_n, t\rangle &= e^{-iE_nt/\hbar}|E_n, 0\rangle \\ &= e^{-iE_nt/\hbar}|E_n\rangle.\end{aligned}$$

This describes an eigenstate with energy E_n.

4.2 Expansion of an arbitrary time-dependent state

A state $|\psi(t)\rangle$ can be expanded in terms of the eigenstates $|E_n\rangle$ of H:

$$|\psi(t)\rangle = \sum_n c_n(t)|E_n\rangle$$

for some $c_n(t)$ to be determined. This gives:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \sum_n i\hbar\dot{c}_n|E_n\rangle = \sum_n c_nE_n|E_n\rangle.$$

We take the scalar product of the above with $\langle E_m|$, giving:

$$\sum_n i\hbar\dot{c}_n\langle E_m|E_n\rangle = \sum_n c_nE_n\langle E_m|E_n\rangle.$$

But H is Hermitian, so its eigenvalues are orthogonal: $\langle E_m|E_n\rangle = \delta_{mn}$, so the above equation reads:

$$i\hbar\dot{c}_m = E_mc_m.$$

Solving this (and renaming $m \to n$) gives:

$$\begin{aligned} c_n(t) &= e^{-iE_n t/\hbar} c_n(0) \\ \Rightarrow |\psi(t)\rangle &= \sum_n c_n(0) e^{-iE_n t/\hbar} |E_n\rangle \end{aligned}$$

The initial state $|\psi(0)\rangle$ determines $c_n(0)$:

$$\begin{aligned} \sum_n c_n(0)|E_n\rangle &= |\psi(0)\rangle \\ \Rightarrow c_n(0) &= \langle E_n|\psi(0)\rangle \end{aligned}$$

Had we expanded $|\psi(t)\rangle$ in some other basis $\{|n\rangle\}$ in which H is not diagonal, we would have

$$\begin{aligned} i\hbar \frac{\partial}{\partial t}\langle m|\psi(t)\rangle &= \langle m|H|\psi(t)\rangle \\ &= \sum_n \langle m|H|n\rangle\langle n|\psi(t)\rangle \end{aligned}$$

i.e.

$$i\hbar \dot{c}_m(t) = \sum_n H_{mn} c_n(t),$$

where $c_n(t) = \langle n|\psi(t)\rangle$.

A unitary operator connects the two bases:

$$U|n\rangle = |E_n\rangle$$

Note also that

$$H^*_{mn} = \langle n|H^\dagger|m\rangle = \langle n|H|m\rangle = H_{mn}$$

i.e. H_{mn} is Hermitian.

4.3 Time evolution operator

Recall the Schrödinger equation for a ket state:

$$i\hbar \frac{\partial}{\partial t}|a,t\rangle = H|a,t\rangle \tag{4.1}$$

where $\lim_{t\to t_0} |a,t\rangle \equiv |a\rangle$.

In order to discuss the time evolution $|a\rangle \xrightarrow{\text{time}} |a,t\rangle$ we discuss the time evolution operator $U(t,t_0)$ such that:

$$|a,t\rangle = U(t,t_0)|a\rangle \tag{4.2}$$

which means that $U(t_0,t_0) = 1$.

Substituting (4.2) into (4.1) gives us the Schrödinger equation for the time evolution operator:

$$i\hbar \frac{\partial}{\partial t} U(t,t_0) = HU(t,t_0) \tag{4.3}$$

4.3.1 Properties

Assuming H is Hermitian, we have the following properties:

1. U is unitary.

Proof:

$$\begin{aligned}\frac{\partial}{\partial t}\langle a,t|a,t\rangle &= \frac{\partial}{\partial t}(\langle a,t|)|a,t\rangle + \langle a,t|\left(\frac{\partial}{\partial t}|a,t\rangle\right)\\ &= \frac{i}{\hbar}\langle a,t|H|a,t\rangle - \frac{i}{\hbar}\langle a,t|H|a,t\rangle\\ &= 0.\end{aligned}$$

So $\langle a,t|a,t\rangle$ is time-invariant, i.e. $\langle a,t_0|a,t_0\rangle = \langle a,t|a,t\rangle$. But by the definition of U, this means that:

$$\begin{aligned}\langle a,t_0|a,t_0\rangle &= \langle a,t_0|U^\dagger(t,t_0)U(t,t_0)|a,t_0\rangle\\ \Rightarrow U^\dagger(t,t_0)U(t,t_0) &= 1.\end{aligned}$$

Therefore U is unitary for a finite-dimensional space. Proof for infinite-dimensional space omitted.

2. U has the group property: $U(t_2,t_0) = U(t_2,t_1)U(t_1,t_0)$.

Proof:

$$\begin{aligned}|a,t'\rangle &= U(t',t)|a,t\rangle = U(t',t)U(t,t_0)|a\rangle\\ \Rightarrow U(t',t_0) &= U(t',t)U(t,t_0).\ \text{QED.}\end{aligned}$$

4.3.2 Construction

Case 1: H is time-independent. Then (4.3) has solution:

$$U(t,t_0) = \exp(-iH(t-t_0)/\hbar)$$

Case 2: H is time-dependent, but $[H(t),H(t')] = 0$. Then (4.3) has solution:

$$U(t,t_0) = \exp\left(\frac{i}{\hbar}\int_{t_0}^{t} dt'\, H(t')\right)$$

Case 3: H is time-dependent and $[H(t),H(t')] \neq 0$, e.g.: $H = -\vec{\mu}\cdot\vec{B}(t) = -\frac{eg}{2mc}\vec{S}\cdot\vec{B}(t)$, where $[S_x,S_y] = i\hbar S_z$. If $\vec{B}$ changes direction with time, then $[H(t),H(t')] \neq 0$. Then, from (4.3):

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, H(t')U(t',t_0)$$

Iterating gives:

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, H(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1' \int_{t_0'}^{t_1'} dt_2'\, H(t_1')H(t_2') + ...$$

Which can be simplified to:

$$U(t,t_0) = \mathcal{T}\left(\exp\left(-\frac{1}{\hbar}\int_{t_0}^{t} dt'\, H(t')\right)\right)$$

where $\mathcal{T}$ is the **time-ordering operator**:

$$\mathcal{T}(H(t_1)...H(t_n)) = H(t_i)...H(t_j)...H(t_k) \text{ where } t_i < t_j < t_k.$$

4.4 Schrödinger and Heisenberg pictures

These are two equivalent formulations of quantum dynamics: in the **Schrödinger picture** bras and kets evolve in time, while operators remain fixed. In the **Heisenberg picture** bras and kets remain fixed, and operators evolve in time.

Consider the matrix element of observable X:

$$\begin{aligned}\langle\alpha|X|\beta\rangle &\xrightarrow{\text{time}} \langle\alpha,t|X|\beta,t\rangle \\ &= \langle\alpha|U^\dagger(t,t_0)\, X\, U(t,t_0)|\beta\rangle\end{aligned}$$

U and $U^\dagger$ can be considered equally well as operating on X or on $\langle\alpha|$ and $|\beta\rangle$. We can rewrite this as:

$$X_H(t) = U^\dagger(t,t_0)\, X_S\, U(t,t_0).$$

and note that commutation relations are preserved:

$$[x_S, p_S] = i\hbar \quad \Rightarrow \quad U^\dagger(t,t_0)\,[x_S,p_S]\,U(t,t_0) = [x_H(t), p_H(t)] = i\hbar.$$

4.5 Heisenberg equation of motion

Consider the simplest case: H is constant and self-adjoint, and X_S has no explicit time dependence. Then $U(t,t_0) = e^{-iH(t-t_0)/\hbar}$ and:

$$\begin{aligned}\frac{dX_H}{dt} &= \dot{U}^\dagger X_S U + U^\dagger X_S \dot{U} \\ &= -\frac{1}{i\hbar}U^\dagger H X_S U + \frac{1}{i\hbar}U^\dagger X_S H U \\ &= -\frac{1}{i\hbar}U^\dagger H U U^\dagger X_S U + \frac{1}{i\hbar}U^\dagger X_S U U^\dagger H U \\ &= -\frac{1}{i\hbar}H X_H + \frac{1}{i\hbar}X_H H\end{aligned}$$

$$\text{or simply,} \quad i\hbar\frac{dX_H}{dt} = [X_H, H].$$

This is called the **Heisenberg equation of motion** *for the specified conditions!*

4.5.1 Example

Consider the harmonic oscillator with mass $m = 1$ and frequency ω.

$$H = \frac{1}{2}p^2 + \frac{1}{2}\omega^2$$

Since the oscillator is isolated, $H(t) = H$, a constant. We set $t_0 = 0$ and define the Heisenberg operator:

$$p(t) = U^\dagger(t)\, p\, U(t) = e^{iHt/\hbar}\, p\, e^{-iHt/\hbar}$$
$$x(t) = U^\dagger(t)\, x\, U(t) = e^{iHt/\hbar}\, x\, e^{-iHt/\hbar}$$

Then,

$$e^{iHt/\hbar}[x, p]e^{-iHt/\hbar} = [x(t), p(t)] = i\hbar. \tag{4.4}$$

Problem: find $x(t)$ and $p(t)$.

Solution:

$$i\hbar\dot{p}(t) = [p(t), H]$$
$$i\hbar\dot{x}(t) = [x(t), H]$$

Using (4.4), and the fact that $H(0) = H(t)$, we obtain:

$$i\hbar p(t) = -i\hbar\omega^2 x(t)$$
$$i\hbar x(t) = i\hbar p(t)$$

These equations can be decoupled by defining:

$$a(t) = \frac{p(t) - i\omega x(t)}{\sqrt{2\hbar\omega}}$$
$$\dot{a}(t) = \frac{\dot{p}(t) - i\omega\dot{x}(t)}{\sqrt{2\hbar\omega}} = \frac{-\omega^2 x(t) - i\omega p(t)}{\sqrt{2\hbar\omega}} = -i\omega a(t).$$

From the above differential equation, and defining $p(0) \equiv p$ and $x(0) \equiv x$, we get:

$$a(t) = a(0)e^{-i\omega t} = \frac{p - i\omega t}{\sqrt{2\hbar\omega}}$$

and so:

$$\begin{aligned} p(t) &= \sqrt{\frac{\hbar\omega}{2}}\left(a(t) + a^\dagger(t)\right) \\ &= \frac{1}{2}\left[(p - i\omega x)e^{-i\omega t} + (p + i\omega x)e^{i\omega t}\right] \\ &= p\cos(\omega t) - \omega x \sin(\omega t) \end{aligned}$$

$$\begin{aligned} x(t) &= i\left(\frac{\hbar}{2\omega}\right)^{\frac{1}{2}}\left(a(t) - a^\dagger(t)\right) \\ &= \frac{i}{2\omega}\left[(p - i\omega t)e^{-i\omega t} - (p + i\omega t)e^{i\omega t}\right] \\ &= x\cos(\omega t) + \frac{p}{\omega}\sin(\omega t) \end{aligned}$$

Comment: These results can be obtained by replacing x and p in the classical solution with operators such that $[x, p] = i\hbar$.

Note also that:

$$
\begin{aligned}
[x(t), x(t')] &= \frac{i\hbar}{\omega} \sin\left[\omega(t - t')\right] \\
[x(t), p(t')] &= i\hbar \cos\left[\omega(t - t')\right] \\
[p(t), p(t')] &= i\hbar\omega \sin\left[\omega(t - t')\right]
\end{aligned}
$$

Chapter 5

Wave mechanics

5.1 Coordinate and momentum representations

We introduce the notation:

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

the value of ψ at $\vec{r}$, where $\vec{r}$ is interpreted to be an *eigenstate* of the position operator. Now we take the Fourier transform of ψ:

$$\psi(\vec{r}) = \int \frac{d^3k}{(2\pi)^{3/2}} e^{i\vec{k}\cdot\vec{r}} \hat{\psi}(\vec{k}) \tag{5.1}$$

$$\hat{\psi}(\vec{k}) = \int \frac{d^3\vec{r}}{(2\pi)^{3/2}} e^{-i\vec{k}\cdot\vec{r}} \psi(\vec{r}) \tag{5.2}$$

Now define symbols:

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

$$\langle \vec{r}|\vec{k}\rangle = \frac{e^{i\vec{k}\cdot\vec{r}}}{(2\pi)^{3/2}}$$

$$\langle \vec{k}|\vec{r}\rangle = \langle \vec{r}|\vec{k}\rangle^* = \frac{e^{-i\vec{k}\cdot\vec{r}}}{(2\pi)^{3/2}}$$

which allows us to rewrite (5.1) as:

$$\langle \vec{r}|\psi\rangle = \int d^3k \, \langle \vec{r}|\vec{k}\rangle \langle \vec{k}|\psi\rangle$$

and (5.2) as:

$$\langle \vec{k}|\psi\rangle = \int d^3r \, \langle \vec{k}|\vec{r}\rangle \langle \vec{r}|\psi\rangle,$$

which suggest the completeness relations:

$$\int d^3k \, |\vec{k}\rangle\langle\vec{k}| = \mathbb{1} \quad \text{and} \quad \int d^3r \, |\vec{r}\rangle\langle\vec{r}| = \mathbb{1} \tag{5.3}$$

Note that since $|\psi\rangle \in \mathcal{H}$:

$$\int d^3k \langle \vec{r}|\vec{k}\rangle\langle\vec{k}|\vec{r}'\rangle = \int \frac{d^3k}{(2\pi)^3} e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} = \delta(\vec{r}-\vec{r}')$$

$$\text{and } \int d^3r \langle \vec{k}|\vec{r}\rangle\langle \vec{r}|\vec{k}'\rangle = \int \frac{d^3r}{(2\pi)^3} e^{-i\vec{r}\cdot(\vec{k}-\vec{k}')} = \delta(\vec{k}-\vec{k}').$$

and combining these with (5.3) gives orthogonality relations:

$$\langle \vec{r}|\vec{r}'\rangle = \delta(\vec{r}-\vec{r}') \quad \text{and} \quad \langle \vec{k}|\vec{k}'\rangle = \delta(\vec{k}-\vec{k}')$$

(5.3) can also be expressed as:

$$|\psi\rangle = \int d^3k\, |\vec{k}\rangle\langle \vec{k}|\psi\rangle = \int d^3r\, |\vec{r}\rangle\langle \vec{r}|\psi\rangle$$

All the equations suggest the interpretation that $|\vec{k}\rangle$ and $|\vec{r}\rangle$ are basic vectors in which a state $|\psi\rangle$ can be represented. This suggests that $\langle \vec{r}|\psi\rangle$ and $\langle \vec{k}|\psi\rangle$ are inner products of $|\psi\rangle$ on the $\vec{r}$ and $\vec{k}$ bases:

$$\langle \vec{r}|\psi\rangle = \psi(\vec{r}) = \text{coordinate representation of } |\psi\rangle.$$
$$\langle \vec{k}|\psi\rangle = \hat{\psi}(\vec{k}) = \text{momentum representation of } |\psi\rangle.$$

Note: While $|\psi\rangle \in \mathcal{H}$, the eigenvectors $|\vec{r}\rangle \notin \mathcal{H}$, they are continuous linear functionals on $\mathcal{H}$. A functional on $\mathcal{H}$ is a mapping $f : \mathcal{H} \to \mathbb{C}$.

A linear functional $|w\rangle$ on $\mathcal{H}$ is a mapping:

$$|w\rangle : \mathcal{H} \to \mathbb{C}, \quad |\psi\rangle \mapsto \langle w|\psi\rangle$$

such that:

$$\langle w|\,(|\psi_1\rangle + |\psi_2\rangle)\rangle = \langle w|\psi_1\rangle + \langle w|\psi_2\rangle \quad \text{and} \quad \langle w|\alpha\psi\rangle = \alpha\langle w|\psi\rangle.$$

for any $\alpha \in \mathbb{C}$. The space of linear functionals on a vector space is called its **algebraic dual space.** It is consistent to interpret $|\vec{r}\rangle$ and $|\vec{k}\rangle$ as eigenstates of position and momentum$/\hbar$:

$$\vec{r}_{\text{op}}|\vec{r}\rangle = \vec{r}|\vec{r}\rangle, \quad \vec{k}_{\text{op}}|\vec{k}\rangle = \vec{k}|\vec{k}\rangle, \quad \vec{p}_{\text{op}} \equiv \hbar\vec{k}_{\text{op}}.$$

where $\vec{k}$ is the **wavenumber,** and:

$$\vec{r}_{\text{op}} \equiv x_{\text{op}}\hat{\imath} + y_{\text{op}}\hat{\jmath} + z_{\text{op}}\hat{k}$$
$$\vec{r}_{\text{op}}|\vec{r}\rangle = \vec{r}|\vec{r}\rangle = x\hat{\imath} + y\hat{\imath} + z\hat{k}$$

Also, $x_{\text{op}}|\vec{r}\rangle = x|\vec{r}\rangle$ etc.

5.1.1 Example

In $\vec{r}$ representation,

$$\begin{aligned}
\langle \vec{r}|\vec{P}_{\text{op}}|\vec{r}'\rangle &= \hbar\langle \vec{r}|\vec{k}_{\text{op}}|\vec{r}'\rangle \\
&= \hbar\int d^3k\, \langle \vec{r}|\vec{k}_{\text{op}}|\vec{k}\rangle\langle \vec{k}|\vec{r}'\rangle \\
&= \hbar\int d^3k\, \vec{k}\langle \vec{r}|\vec{k}\rangle\langle \vec{k}|\vec{r}'\rangle \\
&= \hbar\frac{1}{(2\pi)^{3/2}}\int d^3k\, \vec{k}e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} \\
&= \frac{\hbar}{i}\frac{1}{(2\pi)^{3/2}}\vec{\nabla}_r\int d^3k\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} \\
&= \frac{\hbar}{i}\vec{\nabla}_r\delta(\vec{r}-\vec{r}')
\end{aligned}$$

giving us the coordinate representation of $\vec{p}_{\text{op}}$:

$$\frac{\hbar}{i}\vec{\nabla}_r = \frac{\hbar}{i}\left(\hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)$$

Thus,

$$[x_{\text{op}i}, p_{\text{op}j}] = i\hbar\delta_{ij}$$

since

$$[x_i, p_j] = \left[x_i, \frac{\hbar}{i}\frac{\partial}{\partial x_j}\right] = i\hbar\delta_{ij}$$

Likewise, in $\vec{k}$- space,

$$\langle\vec{k}|\vec{p}_{\text{op}}|\vec{k}'\rangle = \hbar\vec{k}'\delta(\vec{k}-\vec{k}') = \hbar\vec{k}\delta(\vec{k}-\vec{k}')$$

so the momentum representation of $\vec{p}_{\text{op}}$ is $\hbar\vec{k} \equiv \vec{p} =$ momentum.

Note also that the de Broglie wavelength is $\lambda = \frac{h}{p}$, so from $|\vec{p}| = \hbar|\vec{k}| = \frac{h}{2\pi}|\vec{k}|$, we get:

$$|\vec{k}| = \frac{2\pi}{\lambda} = \text{wavenumber.}$$

5.2 The Schrödinger wave equation

5.2.1 Derivation

Consider the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle \tag{5.4}$$

For a single particle interacting with a potential V,

$$H = \frac{1}{2m}p_{\text{op}}^2 + V(\vec{r}_{\text{op}}, t). \tag{5.5}$$

So going to the $\vec{r}$ basis, we have:

$$i\hbar\frac{\partial}{\partial t}\langle\vec{r}|\psi(t)\rangle = \langle\vec{r}|H|\psi(t)\rangle = \int d^3r'\,\langle\vec{r}|H|\vec{r}'\rangle\langle\vec{r}'|\psi(t)\rangle$$

We calculate the matrix element:

$$\langle\vec{r}|H|\vec{r}'\rangle = \frac{1}{2m}\langle\vec{r}|p_{\text{op}}^2|\vec{r}'\rangle + \langle\vec{r}|V(\vec{r}_{\text{op}}, t|\vec{r}'\rangle$$

But we know that $\langle\vec{r}|V(\vec{r}_{\text{op}}, t)|\vec{r}'\rangle = V(\vec{r}, t)\delta(\vec{r}-\vec{r}')$, and:

$$\begin{aligned}
\langle\vec{r}|p_{\text{op}}^2|\vec{r}'\rangle &= \int d^3r''\,\langle\vec{r}|p_{\text{op}}|\vec{r}''\rangle\langle\vec{r}''|p_{\text{op}}|\vec{r}'\rangle \\
&= \left(\frac{\hbar}{i}\right)^2\int d^3r''\,\vec{\nabla}_r\delta(\vec{r}-\vec{r}'')\vec{\nabla}_{r''}\delta(\vec{r}''-\vec{r}) \\
&= \hbar^2\int d^3r''\,\vec{\nabla}_r\cdot\vec{\nabla}_{r''}\delta(\vec{r}-\vec{r}'')\delta(\vec{r}''-\vec{r}') \\
&= -\hbar^2\int d^3r''\,\vec{\nabla}_r\cdot\vec{\nabla}_r\delta(\vec{r}-\vec{r}'')\delta(\vec{r}''-\vec{r}') \\
&= -\hbar^2\nabla_r^2\left(\delta(\vec{r}-\vec{r}')\right)
\end{aligned}$$

If we let $\langle \vec{r}|\psi(t)\rangle \equiv \psi(\vec{r},t)$, then we can combine this definition of p_{op}^2 with (5.4) and (5.5) to give:

$$i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t) = \int d^3r' \left(-\frac{\hbar}{2m}\nabla_r^2 + V(\vec{r},t)\right)\delta(\vec{r}-\vec{r}')\psi(\vec{r}',t)$$

or in other words,

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

This is the **Schrödinger wave equation** for a single particle.

This can be generalised to n particles by defining:

$$H = -\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2 + \sum_{i=1}^{n}V(\vec{r},t) + \sum_{i<j=1}^{n}V(|\vec{r}_i-\vec{r}_j|)$$

where $\psi(\vec{r}_1,\ldots,\vec{r}_n,t) = \langle \vec{r}_1,\ldots,\vec{r}_n|\psi(t)\rangle$

5.2.2 Example

Suppose the system is isolated, so H is time-independent. To find eigenstates and eigenvalues ψ_E, consider one such state:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi_E(t)\rangle = E|\psi(t)\rangle$$

$$\Rightarrow |\psi_E(t)\rangle = e^{iEt/\hbar}|\psi_E(0)\rangle \quad \text{(a stationary state)}$$

So,

$$\begin{aligned}\langle \vec{r}|\psi_E(t)\rangle = \psi_E(\vec{r},t) &= \langle \vec{r}|\psi_E(0)\rangle e^{-iEt/\hbar} \\ &= \psi_E(\vec{r})e^{-iEt/\hbar}\end{aligned}$$

We substitute this into the wave equation and get:

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

which is subject to normalisation condition. For bound (i.e. localised) states, this is:

$$\begin{aligned}1 = \langle\psi_E(t)|\psi_E(t)\rangle &= \langle\psi_E(0)|\psi_E(0)\rangle \\ &= \int d^3r\,\langle\psi_E(0)|\vec{r}\rangle\langle\vec{r}|\psi_E(0)\rangle \\ &= \int d^3r\,\psi_E(r)\psi_E(r) = \int d^3r|\psi_E(\vec{r})|^2.\end{aligned}$$

Thus, we are looking for solutions in the Hilbert space of square-integrable functions.

5.2.3 Interpretation

Given the above normalisation, we may interpret $|\psi_E(\vec{r})|^2\,d^3r = |\langle\psi_E(0)|\vec{r}\rangle|^2\,d^3r$ as the probability that a particle initially in definite energy state $|\psi_E(0)\rangle$ will be found in the volume element d^3r at $\vec{r}$. For a general normalised wavefunction $\psi(\vec{r},t) = \langle\vec{r}|\psi(t)\rangle$, we interpret $|\langle\vec{r}|\psi(t)\rangle|^2\,d^3r$ as the probability for finding the system in volume element d^3r at $\vec{r}$ at time t.

5.3 Heisenberg uncertainty principle

Let A, B be Hermitian operators with $[A, B] = i\hbar$, e.g. x and p. Let a system be in state $|\psi\rangle$ such that $\langle\psi|\psi\rangle = 1$, and define:

$$\begin{aligned}(\Delta A)^2 &\equiv \langle\psi|\left(A - \langle\psi|A|\psi\rangle\right)|\psi\rangle \\ &= \langle\psi|A^2|\psi\rangle - \langle\psi|A|\psi\rangle^2 \\ &= \langle A^2\rangle - \langle A\rangle^2.\end{aligned}$$

ΔA is called the **uncertainty** in A and the **Heisenberg uncertainty principle** states that:

$$\Delta A\,\Delta B \geqslant \frac{\hbar}{2}.$$

5.3.1 Comments

1. Let $|n\rangle$ be the eigenstates of A such that:

$$A|n\rangle = A_n|n\rangle.$$

If A is self-adjoint, then the set $\{|n\rangle\}$ is complete. Then for any $|\psi\rangle \in \mathcal{H}$,

$$\begin{aligned}(\Delta A)^2 &= \langle\psi|(A - \langle A\rangle)^2|\psi\rangle \\ &= \sum_n \langle\psi|(A - \langle A\rangle^2)|n\rangle\langle n|\psi\rangle \\ &= \sum_n \langle\psi|(A_n - \langle A\rangle)^2|n\rangle\langle n|\psi\rangle \\ &= \sum_n |\langle n|\psi\rangle|^2 (A_n - \langle A\rangle)^2\end{aligned}$$

This is a weighted sum of deviations of eigenvalues from the expectation value.

If $|\psi\rangle = |m\rangle =$ eigenstate of A, then $\langle A\rangle = \langle\psi|A|\psi\rangle = A_m$, and $\langle n|\psi\rangle = \delta_{mn}$. So,

$$\Delta A = 0 \quad \Rightarrow \Delta B = \infty.$$

2. Since $[A, B] = \hbar$, there are *no* simultaneous eigenstates $|a, b\rangle$ of A and B such that:

$$A|a, b\rangle = a|a, b\rangle \quad \text{and} \quad B|a, b\rangle = b|a, b\rangle$$

due to the Kochen–Specker theorem. If the theorem were *not* true, then there could exist states $|a, b\rangle$ for which $\Delta A = \Delta B = 0$, violating the uncertainty principle.

5.3.2 Proof

Let $\alpha = A - \langle\psi|A|\psi\rangle$ and $\beta = B - \langle\psi|B|\psi\rangle$. Then,

$$\begin{aligned}|\langle\psi|\alpha\beta - \beta\alpha|\psi\rangle|^2 &= |\langle\psi|\alpha\beta|\psi\rangle - \langle\psi|\beta\alpha|\psi\rangle|^2 \\ &\leqslant \left(|\langle\psi|\alpha\beta|\psi\rangle| + |\langle\psi|\beta\alpha|\psi\rangle|\right)^2\end{aligned} \tag{5.6}$$

by triangle inequality.

Now consider:

$$\langle\psi|\alpha\beta|\psi\rangle = \langle\psi|(A - \langle\psi|A|\psi\rangle)(B - \langle\psi|B|\psi\rangle)|\psi\rangle$$

Defining $|B\rangle \equiv (B - \langle\psi|B|\psi\rangle)\psi$, then:

$$\begin{aligned}\langle\psi|\alpha\beta|\psi\rangle &= \langle\psi|(A - \langle\psi|A|\psi\rangle)|B\rangle \\ &= \langle B|(A - \langle\psi|A|\psi\rangle)|\psi\rangle^*\end{aligned}$$

and defining $|A\rangle \equiv A - \langle\psi|A|\psi\rangle)\psi$, so:

$$\langle\psi|\alpha\beta|\psi\rangle = \langle B|A\rangle^* = \langle A|B\rangle.$$

By the Cauchy–Schwarz inequality,

$$\begin{aligned}|\langle\psi|\alpha\beta|\psi\rangle|^2 = |\langle A|B\rangle|^2 &\leqslant \langle A|A\rangle\langle B|B\rangle \\ &= \langle\psi|(A - \langle\psi|A|\psi\rangle)^2|\psi\rangle\langle\psi|(B - \langle\psi|B|\psi\rangle)^2|\psi\rangle \\ &= (\Delta A)^2(\Delta B)^2\end{aligned}$$

So we have:

$$|\langle\psi|\alpha\beta|\psi\rangle|^2 \leqslant (\Delta A)^2(\Delta B)^2 \tag{5.7}$$

and similarly,

$$|\langle\psi|\beta\alpha|\psi\rangle|^2 \leqslant (\Delta A)^2(\Delta B)^2 \tag{5.8}$$

Substituting (5.7) and (5.8) into (5.6) and noting that $\langle\psi|\alpha\beta - \beta\alpha|\psi\rangle = \langle\psi|[A,B]|\psi\rangle = i\hbar$ gives:

$$\begin{aligned}\hbar^2 &\leqslant (2\Delta A\,\Delta B)^2 \\ \Rightarrow \Delta A\,\Delta B &\geqslant \frac{\hbar}{2} \quad \text{QED.}\end{aligned}$$

5.3.3 More comments

1. More generally, the uncertainty principle can be stated as:

$$\Delta A\,\Delta B \geqslant \frac{1}{2}|\langle\psi|[A,B]|\psi\rangle|.$$

2. Consider two particles such that:

$$\begin{aligned}\vec{p} &= \vec{p}_1 + \vec{p}_2 \\ \vec{r} &= \vec{r}_1 - \vec{r}_2\end{aligned}$$

Then $[r_i, p_j] = 0$. Hence, the total momentum and relative coordinates of two particles can be measured to arbitrary precision, *seemingly* violating the uncertainty principle. (Einstein–Podolsky–Rosen, 1935)

5.3.4 Example

$$[x, p] = i\hbar.$$

Consider a particle in an infinite square well. On $[0, 1]$ the particle is free, so $V = 0$ and the Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_E(x) = E\psi_E(x).$$

This, plus boundary conditions, gives:

$$\psi_E(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{px}{\hbar}\right) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

In addition, from Schrödinger equation:

$$E = \frac{p^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2}$$
$$\Rightarrow p = \frac{n\pi\hbar}{L}$$

where $n = \pm 1, \pm 2, \ldots$.

ψ_E is normalised so that:

$$\int_0^L dx\,|\psi_E(x)|^2 = \frac{2}{L}\int_0^L dx\,\sin^2\left(\frac{n\pi x}{L}\right) = 1.$$

This means:

$$\langle x\rangle = \int_0^L dx\,\psi_n^*(x)\,x\,\psi_n(x) = \frac{L}{2},$$

$$\langle x^2\rangle = \int_0^L dx\,\psi_n^*(x)\,x^2\,\psi_n(x) = \frac{L^2}{3}.$$

So:

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 = \frac{L^2}{3} - \frac{L^2}{4} = \frac{L^2}{12}.$$

Also,

$$\langle p\rangle = \int_0^L dx\,\psi_n^*\,p_{\text{op}}\,\psi_n = \frac{\hbar}{i}\int_0^L dx\,\psi_n^*(x)\frac{d}{dx}\psi_n(x) = 0,$$

$$\langle p^2\rangle = -\hbar^2\int_0^L dx\,\psi_n^*(x)\frac{d^2}{dx^2}\psi_n(x) = p^2.$$

So:

$$\Delta p = |p| = \frac{n\pi\hbar}{L}, \quad n = 1, 2, \ldots$$

Combining these, we have:

$$\Delta p\Delta x = \frac{L|p|}{\sqrt{12}} = \frac{n\pi\hbar}{\sqrt{12}} > \frac{\hbar}{2},$$

in agreement with HUP.

5.3.5 Heisenberg uncertainty principle and stability of atoms

Theorem: The Heisenberg uncertainty principle has nothing to do with the stability of atoms.

Proof: Consider the special case of a hydrogenic atom. We are interested in its ground-state energy. Assume the state ψ has spherical symmetry (i.e. no orbital angular momentum).

- Consider:

$$\langle p^2 \rangle \equiv \langle \psi | p^2 | \psi \rangle = \langle p_x^2 \rangle + \langle p_y^2 \rangle + \langle p_z^2 \rangle$$
$$\langle r^2 \rangle \equiv \langle \psi | r^2 | \psi \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$$

- By symmetry, $\langle x \rangle^2 = 0 \Rightarrow (\Delta x)^2 = \langle x^2 \rangle$. Similarly, $(\Delta y)^2 = \langle y^2 \rangle$, $(\Delta z)^2 = \langle z^2 \rangle$.
- Likewise, $(\Delta p_x)^2 = \langle p_x^2 \rangle$, $(\Delta p_y)^2 = \langle p_y^2 \rangle$, $(\Delta p_z)^2 = \langle p_z^2 \rangle$.
- By spherical symmetry, $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle \Rightarrow (\Delta x)^2 = \langle x^2 \rangle = \frac{1}{3}\langle r^2 \rangle$.
- Likewise, $(\Delta p_x)^2 = \frac{1}{3}\langle p^2 \rangle$.
- So, Heisenberg uncertainty principle gives:

$$\langle p^2 \rangle \langle r^2 \rangle \geqslant \frac{9}{4}\hbar^2. \tag{5.9}$$

The intuition applied to (5.9) is that if the electron's most probable distance from the nucleus is R in the state $|\psi\rangle$, its kinetic energy is at least as large as:

$$\left\langle \frac{p^2}{2m} \right\rangle \geqslant \frac{9}{4}\frac{\hbar^2}{2mR^2},$$

using $\langle r^2 \rangle \approx R^2$.

Consequently, for:

$$H = \frac{p^2}{2m} - \frac{Ze^2}{R},$$

we have:

$$\langle \psi | H | \psi \rangle \geqslant \frac{9}{4}\frac{\hbar^2}{2mR^2} - \frac{Ze^2}{R}, \tag{5.10}$$

using $\langle \frac{1}{r} \rangle \approx \frac{1}{R}$.

The right-hand side of (5.10) takes a minimum at $R = \frac{9}{4}\frac{\hbar^2}{Ze^2m}$, so for this $|\psi\rangle$, we have:

$$\langle \psi | H | \psi \rangle \geqslant -\frac{2}{9}Z^2\frac{me^4}{\hbar^2} = -\frac{4}{9}Z^2\,\mathrm{Ry},$$

where 1 Rydberg (Ry) $= \frac{me^4}{2\hbar^2} \approx 13.6\,\mathrm{eV}$.

The exact ground-state energy is actually $-Z^2$ Ry ($\frac{4}{9}$ arises from approximations made).

So far we have established that the Heisenberg uncertainty principle gives a lower bound on ground-state energy of hydrogenic atoms for a particular state $|\psi\rangle$. We will now prove that the Heisenberg uncertainty principle does *not* imply stability, i.e. the intuition in this conclusion is wrong. Remember, the Heisenberg uncertainty principle holds for *any* state $|\psi\rangle$.

Consider a wavefunction ψ consisting of two parts: $\psi = \psi_1 + \psi_2$. ψ_1 has support in a spherically symmetric thin shell of radius R centred at the origin, with $\int |\psi_1|^2 = \frac{1}{2}$; and ψ_2 has support in a spherically symmetric thin shell of mean radius L, with $\int |\psi_2|^2 = \frac{1}{2}$.

$\int \psi_1 \psi_2 = 0$, and $\int |\psi|^2 = 1$. If L is large enough, then:

$$\langle r^2 \rangle = \int r^2 |\psi(r)|^2 \, d^3r \approx \frac{L^2}{2},$$

whereas:

$$\int \frac{1}{r} |\psi(r)|^2 \, d^3r \approx \frac{1}{2R}.$$

Thus, from (5.9), $\langle p^2 \rangle \langle r^2 \rangle \geqslant \frac{9}{4}\hbar^2$, so we conclude that $\langle p^2 \rangle \geqslant \frac{9\hbar^2}{2L^2}$, and hence:

$$\langle \psi | H | \psi \rangle \geqslant \frac{9\hbar^2}{4mL^2} - \frac{Ze^2}{2R}.$$

With this wavefunction, and using *only* the Heisenberg uncertainty principle, we can make the ground-state energy arbitrarily negative by letting $R \to 0$.

Conclusion: The uncertainty principle *alone* does not imply stability, but the result:

$$\left\langle \psi \middle| \frac{p^2}{2m} \middle| \psi \right\rangle \geqslant \frac{9}{8} \frac{\hbar^2}{m \langle \psi | r^2 | \psi \rangle}$$

is correct, where $|\psi\rangle$ is a spherically symmetric state.

The more the electron is localised, the higher its kinetic energy.

Chapter 6

Units

6.1 cgs units

The **cgs system** is based on the centimetre, the gram and the second. The derived unit of force is the **dyne,** where $1\ \text{dyn} = 1\ \text{g cm/s}^2$. The derived unit of energy is the **erg**, where $1\ \text{erg} = 1\ \text{g cm}^2/\text{s}^2 = 10^{-7}$ J.

In cgs units, Planck's constant $\hbar = 1.05 \cdot 10^{-27}$ erg sec, the electron mass $m = 9.11 \cdot 10^{-38}$ g, and the electron charge $e = 4.80 \cdot 10^{-10}$ esu, where esu stands for **electrostatic units**, and is defined such that Coulomb's law reads:

$$\vec{F} = \frac{e_1 e_2}{r^2}\hat{r}$$

when e is in esu (r in cm, F in dyn).

6.2 Atomic units

We can also form a system of units starting from $\hbar$, m and e.

- Length: $\frac{\hbar^2}{me^2}$, the Bohr radius ≈ 0.5 Å.
- Time: $\frac{\hbar^2}{me^4} \approx 10^{-17}$ s.
- Energy: $\frac{me^4}{2\hbar^2} = 1$ Ry, ≈ 13.6 eV.

Hence,

$$\text{atomic velocity} = \frac{\text{length}}{\text{time}} = \frac{\hbar^2/me^2}{\hbar^3/me^4} = \left(\frac{e^2}{\hbar c}\right)c = \alpha c$$

where α is the dimensionless **fine structure constant**, $\approx \frac{1}{137}$. So atomic velocity given by $\frac{c}{137}$ is a good non-relativistic approximation.

But if $Z \gtrsim 90$ in $-\frac{Ze^2}{r}$, then $\alpha \to Z\alpha$, $\alpha c \to Z\alpha c$. Therefore, non-relativistic QM does *not* apply to inner electrons of heavy elements, and the **Dirac equation** must be used.

Chapter 7

Eigenfunctions

7.1 Eigenfunctions of a free particle

In 1D, the Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\,\psi(x),$$

$$\Rightarrow \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}}\,e^{ipx/\hbar},$$

where $E = \frac{p^2}{2m}$, $-\infty < p < \infty$.

Note that:

$$p_{\text{op}}\psi_p = \frac{\hbar}{i}\frac{d}{dx}\psi_p = p\psi_p.$$

Let $k = \frac{p}{\hbar} = \frac{2\pi}{\lambda}$ = wavenumber. Then define:

$$\psi_k(x) = \frac{1}{\sqrt{2\pi}}\,e^{ikx}.$$

Note that:

$$\begin{aligned}\int_{-\infty}^{\infty} dx\,\psi_k(x)\psi_k^*(x) &= \int_{-\infty}^{\infty} dk\left(\frac{1}{\sqrt{2\pi}}\,e^{ikx}\right)\left(\frac{1}{\sqrt{2\pi}}\,e^{-ikx'}\right)\\ &= \int_{-\infty}^{\infty} dk\,\frac{1}{2\pi}\,e^{ik(x-x')}\\ &= \delta(x-x')\end{aligned}$$

i.e. ψ_k are complete.

In 3D,

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\psi(\vec{r}) \Rightarrow \psi_{\vec{p}}(\vec{r}) = \frac{1}{(2\pi\hbar)^{3/2}}\,e^{i\vec{p}\cdot\vec{r}/\hbar}$$

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{(2\pi)^{3/2}}\,e^{i\vec{k}\cdot\vec{r}}$$

Likewise,

$$\int d^3k\, \psi^*_{\vec{k}}(\vec{r})\psi_{\vec{k}}(\vec{r}) = \int \frac{d^3k}{(2\pi)^3}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} = \delta(\vec{r}-\vec{r}'),$$

where δ in this case is the 3D Dirac delta function:

$$\delta(\vec{r}-\vec{r}') = \delta(x-x')\,\delta(y-y')\,\delta(z-z')$$

These functions are not square integrable:

$$\int d^3k |\psi_{\vec{k}}(\vec{r})|^2 = \infty$$

but this may be overcome by confining the particle's location to a box with side length L. Periodic boundary conditions are:

$$\psi_{\vec{k}}\left(-\tfrac{L}{2}, y, z\right) = \psi_{\vec{k}}\left(\tfrac{L}{2}, y, z\right), \text{ etc.}$$
$$\Rightarrow e^{-ik_xL/2} = e^{ik_xL/2},$$

or, $k_xL = 2\pi n_x$, where $n_x = 0, \pm1, \pm2, \ldots$ So we have:

$$k_x = \frac{2\pi n_x}{L} \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}.$$

Normalised eigenfunctions are now:

$$\int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} dy \int_{-L/2}^{L/2} dz\, |\psi_{\vec{k}}|^2 = 1.$$

The particle in infinite space can be regained by taking $L \to \infty$ at end of calculation.

7.2 Minimum wave packet

Consider a free particle in 1D with definite momentum p. The particle's wavefunction is:

$$\psi_p(x,t) = \frac{1}{(2\pi\hbar)^{3/2}} e^{ip/2} e^{-iEt/\hbar}, \text{ where } E = \frac{p^2}{2m}$$

Because of the linearity of the Schrödinger equation, we may consider a superposition of momentum states, i.e. a **wave packet**:

$$\psi(x,t) = \int_{-\infty}^{\infty} dp\, c(p) e^{ip_x/\hbar} e^{-iEt/\hbar}$$

where $c(p)$ is a weighting function. This satisfies the free-particle Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi$$

The particle no longer has a definite momentum. Hence, its position is no longer undefined: $|\psi|^2$ may look like Figure 7.1 at some time t.

Choosing $c(p)$ such that it gives the minimum uncertainty: $\Delta p \Delta x = \frac{\hbar}{2}$ gives us the **minimum wave packet.**

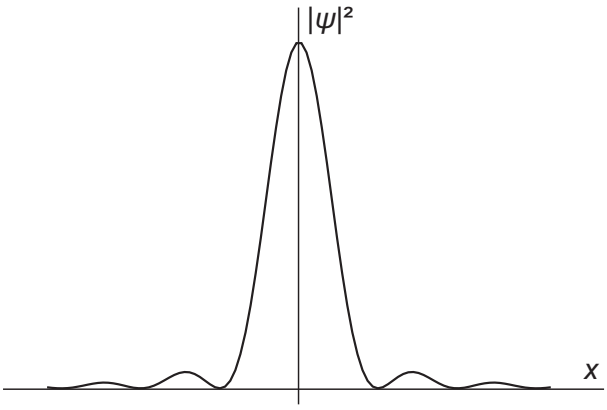


Figure 7.1: A wave packet

Note: Since we are considereing the *initial* wave packet, ψ may subsequently propagate in an arbitrary potential V with the minimum wave packet as its *initial* state.

7.2.1 Construction

$$\alpha = x - \langle x \rangle, \qquad \beta = p - \langle p \rangle,$$

where $\langle x \rangle = \int dx\, |\psi(x)|^2$, etc.

We demand (reason given later) that $\alpha\psi = \gamma\beta\psi$, where $\gamma \in \mathbb{C}$. So,

$$\beta\alpha\psi = \gamma\beta^2\psi$$

$$\Rightarrow \langle \beta\alpha \rangle = \gamma\langle \beta^2 \rangle = \gamma(\Delta p)^2.$$

Taking the complex conjugate, $\langle \alpha\beta \rangle = \gamma^*(\Delta p)^2$. Also, $\alpha^2\psi = \gamma\alpha\beta\psi$. Therefore:

$$\langle \alpha^2 \rangle = (\Delta x)^2 = \gamma\langle \alpha\beta \rangle = |\gamma|^2(\Delta p)^2$$

or simply,

$$\Delta x = |\gamma|\Delta p.$$

In order to obtain the minimum wave packet, we need $\Delta x \Delta p = \frac{\hbar}{2}$,

$$\Rightarrow |\gamma| = \frac{2(\Delta x)^2}{\hbar}$$

Demanding $\alpha\psi = \gamma\beta\psi$ gives:

$$(x - \langle x \rangle)\psi = \gamma\left(\frac{\hbar}{i}\frac{d}{dx} - \langle p \rangle\right)\psi, \text{ or:}$$

$$\frac{d\psi}{dx} = \left(\frac{i(x - \langle x \rangle)}{\hbar\gamma} + \frac{i\langle p \rangle}{\hbar}\right)\psi.$$

By inspection,

$$\psi = N \exp\left(\frac{i(x - \langle x \rangle)^2}{2\gamma\hbar} + \frac{i\langle p \rangle x}{\hbar}\right).$$

This ψ is not normalisable unless γ has a negative imaginary part. In fact,

$$\gamma = \frac{-2i(\Delta x)^2}{\hbar} \tag{7.1}$$

So,

$$\int_{-\infty}^{\infty} dx\, |\psi|^2 = N^2 \int_{-\infty}^{\infty} dx\, \exp\left(-\frac{(x-\langle x\rangle)^2}{|\gamma|\hbar}\right) = 1.$$

$$\Rightarrow N^2\sqrt{\pi\hbar|\gamma|} = 1.$$

Hence, the minimum wave packet is given by:

$$\psi(x) = \left(2\pi(\Delta x)^2\right)^{-1/4} \exp\left[-\frac{(x-\langle x\rangle)^2}{4(\Delta x)^2} + \frac{i\langle p\rangle x}{\hbar}\right],$$

with $\Delta x \Delta p = \frac{\hbar}{2}$ in this state.

Proof of (7.1): We started with $\alpha\psi = \gamma\beta\psi$. So,

$$\langle\alpha^2\rangle = \gamma\langle\alpha\beta\rangle = (\Delta x)^2$$
$$\langle\beta\alpha\rangle = \gamma\langle\beta^2\rangle = \gamma(\Delta p)^2$$

Hence,

$$\gamma\langle\alpha\beta - \beta\alpha\rangle = \gamma\langle[x,p]\rangle = (\Delta x)^2 - \gamma^2(\Delta p)^2 \tag{7.2}$$

$$= (\Delta x)^2 - \frac{\gamma^2\hbar^2}{4(\Delta x)^2} \tag{7.3}$$

We let $\gamma = |\gamma|e^{i\phi}$, where $|\gamma| = 2(\Delta x)^2/\hbar$ as before. Then (7.2) and (7.3) give:

$$2e^{i\phi} = 1 - e^{2i\phi}.$$

Imaginary part gives $2\cos\phi = -\sin 2\phi \Rightarrow \phi = \pm\frac{\pi}{2}$. We choose $\phi = -\frac{\pi}{2}$ since $\frac{\pi}{2}$ does not satisfy corresponding equation for real part. Hence,

$$\gamma = -i|\gamma| = \frac{-2i(\Delta x)^2}{\hbar} \quad \text{QED.}$$

7.2.2 Time development

We found the minimum wave packet:

$$\psi(x) = \left(2\pi(\Delta x)^2\right)^{-1/4} \exp\left[-\frac{(x-\langle x\rangle)^2}{4(\Delta x)^2} + i\frac{\langle p\rangle x}{\hbar}\right] \tag{7.4}$$

where $\Delta x \Delta p = \frac{\hbar}{2}$.

Recall an arbitrary particle state ψ can be expanded in terms of its energy eigenstates:

$$\psi(x,t) = \sum_n c_n e^{-iEnt/\hbar}\psi_n(x).$$

For a free particle,

$$\psi_n = \frac{e^{ikx}}{\sqrt{2\pi}}, \quad k = \frac{p}{\hbar}, \quad E_n = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}.$$

Since $-\infty < k < \infty$, $\sum_n \longrightarrow \int_{-\infty}^{\infty} dk$.

$$\psi(x,t) = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}} c(k) e^{-i\hbar k^2 t/2m} e^{ikx}$$

Note: packet does not have definite energy or momentum.

Assuming particle is in a minimum packet state (7.4) at $t = 0$, how to find $\psi(x,t)$?

Solution: Assume $\langle x \rangle = \langle p \rangle = 0$ at $t = 0$. Then,

$$\psi(x,0) = Ne^{-\frac{x^2}{4(\Delta x)^2}} = \int_{-\infty}^{\infty} \frac{dk}{\sqrt{2\pi}} c(k) e^{ikx},$$

where $N = \left(2\pi(\Delta x)^2\right)^{-1/4}$. Inverse Fourier transform gives:

$$\begin{aligned} c(k) &= N \int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}} e^{-ikx} e^{-\frac{x^2}{4(\Delta x)^2}} \\ &= Ne^{-k^2(\Delta x)^2} \int_{-\infty}^{\infty} \frac{dx}{\sqrt{2\pi}} e^{\left(\frac{x}{2\Delta x} + ik\Delta x\right)^2} \\ &= \frac{2\Delta x\, N}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dy\, e^{-y^2} e^{-k^2(\Delta x)^2} \\ &= \sqrt{2}\Delta x\, N\, e^{-k^2(\Delta x)^2} \end{aligned}$$

Hence,

$$\psi(x,t) = \left[\frac{(\Delta x)^2}{2\pi^2}\right]^{-1/4} \int_{-\infty}^{\infty} dk\, \exp\left[-k^2(\Delta x)^2 - \frac{i\hbar k^2 t}{2m} + ikx\right] \tag{7.5}$$

Note that:

$$-k^2(\Delta x)^2 - \frac{i\hbar k^2 t}{2m} + ikx = -\left[k\left((\Delta x)^2 + \frac{i\hbar t}{2m}\right)^{1/2} - \frac{ix}{2\left((\Delta x)^2 + \frac{i\hbar t}{2m}\right)^{1/2}}\right]^2 - \frac{x^2}{4(\Delta x)^2 + 2i\hbar t/m}$$

Thus, after making the change of variable:

$$k\left((\Delta x)^2 + \frac{i\hbar t}{2m}\right)^{1/2} - \frac{ix}{2\left((\Delta x)^2 + \frac{i\hbar t}{2m}\right)^{1/2}} = \omega, \qquad dk(\ldots) = d\omega$$

(7.5) gives:

$$\psi(x,t) = \frac{\left[\frac{(\Delta x)^2}{2\pi^3}\right]\sqrt{\pi}}{\left[(\Delta x)^2 + \frac{i\hbar t}{2m}\right]^{1/2}} \cdot \exp\left[-\frac{x^2}{4(\Delta x)^2 + \frac{2i\hbar t}{m}}\right]$$

and so:

$$|\psi(x,t)|^2 = \left[2\pi\left((\Delta x)^2 + \frac{\hbar^2 t^2}{4m^2(\Delta x)^2}\right)\right]^{-1/2} \cdot \exp\left[-\frac{x^2}{2\left((\Delta x)^2 + \frac{\hbar^2 t^2}{4m^2(\Delta x)^2}\right)}\right]$$

Comparing this with $|\psi(x,0)|^2$, which is given by:

$$|\psi(x,0)|^2 = \left[2\pi(\Delta x)^2\right]^{-1/2} \cdot \exp\left[-\frac{x^2}{2(\Delta x)^2}\right],$$

we see that the wave packet spreads out with time:

$$[\Delta x(t)]^2 = (\Delta x)^2 + \frac{\hbar^2 t^2}{4m^2(\Delta x)^2}$$

Small Δx initially means rapid spreading. Significant spreading occurs when $t \gtrsim m(\Delta x)^2/\hbar$.

7.2.3 Notes

1. Does minimum packet satisfy:

$$\int_{-\infty}^{\infty} dx\, |\psi(x,t)|^2 = 1$$

for $t > 0$?

Yes. Recall, if a state is normalised it stays normalised. $\frac{d}{dt}\langle\psi(t)|\psi(t)\rangle = 0$ due to hermiticity of H and Schrödinger equation.

2. Does minimum packet preserve minimum uncertainty $\Delta p \Delta x = \frac{\hbar}{2}$?

No. Recall,

$$(\Delta x)^2 \to (\Delta x(t))^2 = (\Delta x)^2 + \frac{\hbar^2 t^2}{4m^2(\Delta x)^2}.$$

At $t = 0$, $\Delta p = \frac{\hbar}{2\Delta x}$, where $(\Delta p)^2 = \langle p^2\rangle - \langle p\rangle^2$ as usual.

At later times, $(\Delta p(t))^2 = \langle\psi(t)|p^2|\psi(t)\rangle - \langle\psi(t)|p|\psi(t)\rangle^2$. But:

$$i\hbar\frac{d}{dt}\langle\psi(t)|p^2|\psi(t)\rangle = \langle\psi(t)|\underbrace{[p^2, H]}_{0}|\psi(t)\rangle = 0.$$

For the same reason,

$$\frac{d}{dt}\left(\langle\psi(t)|p|\psi(t)\rangle\right)^2 = 0.$$

Therefore,

$$\Delta p(t) = \Delta p = \frac{\hbar}{2\Delta x}$$

$$\Rightarrow \Delta p(t)\Delta x(t) = \frac{\hbar}{2}\left(1 + \frac{\hbar^2 t^2}{4m^2(\Delta x)^4}\right)^{1/2},$$

i.e. $\Delta p \Delta x$ increases over time.

4. Spreading is significant when $t \gtrsim m(\Delta x)^2/\hbar$. For example, an α particle has diameter $\sim 10^{-12}$ cm. If it is localised to $\Delta x \sim 10^{-11}$ cm, then the time for significant spreading is $\sim 10^{-18}$ s. At 1 MeV, an α particle has velocity $\sim c/30$, which means it can travel $\sim 10^{-9}$ cm before significant spreading, i.e. ~ 1000 nuclear diameters.

7.2.4 Rydberg atoms

Suppose there is an pulse $\mathrm{Ex}(z,t)$ given by:

$$\mathrm{Ex}(z,t) = \mathrm{Re} \int_{-\infty}^{\infty} dk\, A(k) e^{ikz - i\omega t},$$

where $\omega = ck \Rightarrow \Delta\omega = c\Delta k$. This pulse is concentrated on a narrow band of frequencies.

Suppose this pulse is incident on an alkali atom (i.e. one with a lone s-electron), and is 'tuned' so that it excites the s-electron to a narrow band of states. Then, the exicted s-electron is in a **wave packet state:**

$$\psi(\vec{r},t) = \sum_{n\sim 50,l,m} c_{nlm}\psi_{nlm}(\vec{r}) e^{-iEnt/\hbar}$$

where ψ here is the normal hydrogenic wavefunction.

This describes a Kepler-like orbit about the nucleus. Its radius is large: $\langle r \rangle \sim 1200$ Å (compared to 4 Å for a typical atom.)

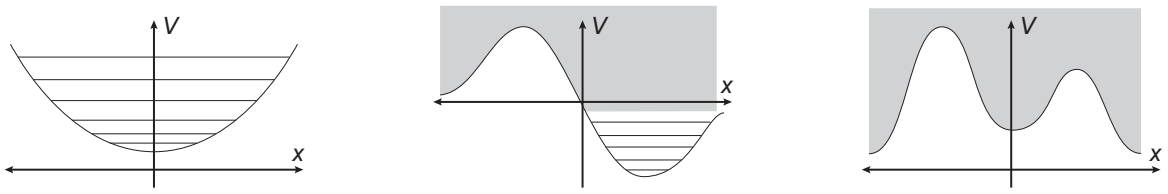
7.3 Energy eigenstates

7.3.1 Classes

Consider an energy eigenstate of a Hamiltonian: $H\psi_E = E\psi_E$. Such eigenstates fall into two classes:

- **Bound states:** localised, discrete states with $\int |\psi_E|^2 < \infty$.
- **Continuum states:** Non-localised 'scattering states'.

Eigenstates for typical potentials are shown in Figure 7.2.



(a) Bound states only (b) Possible bound states (c) No bound states

Figure 7.2: Eigenstates for typical potentials

7.3.2 Notes

1. Recall $H = T + V$. Consider any normalised state $|\psi\rangle$ for which both terms in $\langle\psi|H|\psi\rangle = \langle\psi|T|\psi\rangle + \langle\psi|V|\psi\rangle$ are finite.

Since $\langle T\rangle \geqslant 0$ and $\langle V\rangle \geqslant V_{\min}$, then for any eigenstate $|n\rangle$ with eigenvalues E_n, $E_n \geqslant V_{\min}$.

2. $\Delta x \Delta p \geqslant \hbar/2$ means that the better the localisation, the greater the dispersion in momentum, which means greater kinetic energy, since $(\Delta p)^2 = \langle p\rangle^2$. Hence, the discrete spectrum may be empty for potentials that are too shallow and/or too narrow.

7.3.3 Examples

1. Symmetric well: always has at least one bound state in 1D, but possibly none in >1D.

2. Asymmetric well: may have none in 1D.

3. In 1D, none of the bound states of a potential V are degenerate (to be shown).

4. Wavefunction of a non-degenerate level may be chosen real:

$$H(\mathrm{Re}\,\psi + i\,\mathrm{Im}\,\psi) = E(\mathrm{Re}\,\psi + i\,\mathrm{Im}\,\psi)$$

$\Rightarrow$ two-fold degeneracy if $\mathrm{Re}\,\psi$, $\mathrm{Im}\,\psi \neq 0$. So we choose $\mathrm{Re}\,\psi$.

7.4 Parity

The parity operation P maps:

$$\vec{r} \to -\vec{r}$$
$$\vec{p} \to -\vec{p}$$
$$\vec{L} \to \vec{L}.$$

P maps a right-handed frame to a left-handed frame.

In quantum mechanics, if $[H, P] = 0$ then H and P are simultaneously diagonalisable. Suppose $[H, P] = 0$. Then:

$$H\psi = E$$
$$\Rightarrow H(P\psi) = E(P\psi).$$

If the energy level is non-degenerate, we must have $P\psi = \eta\psi$, where η is a constant. But:

$$P^2\psi = \eta^2\psi = \psi \Rightarrow \eta = \pm 1$$

Therefore,

$$P\psi(\vec{r}) = \psi(-\vec{r}) = \pm\psi(\vec{r})$$

eigenfunctions have definite parity if E is non-denegerate.

Let:

$$\begin{aligned}\psi &= \psi_+ + \psi_- \\ &= \tfrac{1}{2}\left[\psi(\vec{r}) + \psi(-\vec{r})\right] + \tfrac{1}{2}\left[\psi(\vec{r}) - \psi(-\vec{r})\right]\end{aligned}$$

where $P\psi_\pm = \pm\psi_\pm$.

From

$$H\psi = H\psi_+ + H\psi_- = E(\psi_+ + \psi_-),$$

we get:

$$PH\psi = HP\psi = H\psi_+ - H\psi_- = E(\psi_+ - \psi_-).$$

Adding and subtracting these results gives:

$$H\psi_+ = E\psi_+, \quad H\psi_- = E\psi_-.$$

So eigenfunctions of the Schrödinger equation can always be chosen to have definite parity so long as the Hamiltonian is invariant under P, i.e. $[H, P] = 0$.

7.5 1D harmonic oscillator

For the harmonic oscillator, $V = \frac{1}{2}m\omega^2x^2$. The Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x) \tag{7.6}$$

Note that H:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2$$

is invariant under reflection: $x \to -x$, therefore eigenfunctions of H have definite parity, either even or odd.

(7.6) can be solved by power series. Let:

$$\xi = \sqrt{\frac{m\omega}{\hbar}}x.$$

Then

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left(\frac{2E}{\hbar\omega} - \xi^2\right)\psi(\xi) = 0. \tag{7.7}$$

We seek normalisable solutions, i.e. that:

$$\int_{-\infty}^{\infty} |\psi(\xi)|^2\, d\xi < \infty.$$

From (7.7), we know that:

$$\psi'' \underset{|\xi|\to\infty}{\sim} \xi^2\psi$$

$$\Rightarrow \psi \underset{|\xi|\to\infty}{\sim} e^{\pm\xi^2/2}$$

Choose '$-$' and set $\psi = e^{-\xi^2/2} y(\xi)$. Substitute this into (7.7):

$$y'' - 2\xi y' + 2ny = 0, \tag{7.8}$$

where

$$2n \equiv \frac{2E}{\hbar\omega} - 1. \tag{7.9}$$

(7.8) has no singular point at $\xi = 0$, so try:

$$y = \sum_{m=0}^{\infty} a_m \xi^m$$

Substituting this into (7.8):

$$\sum_{m=0}^{\infty} m(m-1) a_m \xi^{m-2} - 2 \sum_{m=0}^{\infty} m a_m \xi^m + 2n \sum_{m=0}^{\infty} a_m \xi^m \tag{7.10}$$

Noting that:

$$\sum_{m=0}^{\infty} (n-m) a_m \xi^m = \sum_{m=2}^{\infty} a_{m-2} (n-m+2) \xi^{m-2}$$

we can rewrite (7.10):

$$\sum_{m=0}^{\infty} m(m-1) a_m \xi^{m-2} + 2 \sum_{m=2}^{\infty} (n-m+2) a_{m-2} \xi^{m-2} = 0.$$

We equate powers of ξ to 0:

$$m(m-1) a_m = 0 \quad \text{and} \quad a_m = \frac{2(m-n-2)}{m(m-1)} a_{m-2} \tag{7.11}$$

a_0 and a_1 are arbitrary.

Even parity solutions: Set $a_1 = 0$. Then:

$$y = \sum_{m=0,2,4,\ldots} a_m \xi^m,$$

and $a_{2m} \sim \frac{1}{m} a_{2m-2}$ for large m.

Consider e^{x^2}, which has power series:

$$1 + x^2 + \frac{x^4}{2!} + \frac{x^6}{3!} + \ldots = \sum_{m=0}^{\infty} c_{2m} x^{2m}$$

Ratio of adjacent terms is:

$$\frac{c_{2m}}{c_{2m-2}} = \frac{(m-1)!}{m!} = \frac{1}{m}$$

So even parity solutions grow as e^{ξ^2}.

Odd parity solutions: Set $a_0 = 0$.

$$y = \sum_{m=1,3,5,\ldots} a_m \xi^m = \xi(a_1 + a_3\xi^2 + \ldots)$$

For large m,

$$\frac{a_{2m+1}}{a_{2m-1}} \sim \frac{1}{m},$$

so that $a_1 + a_3\xi^2 + \ldots \sim e^{\xi^2} \Rightarrow y \sim \xi e^{\xi^2}$.

Since $\psi = e^{-\xi^2/2}y$, this behaviour is not acceptable. Hence the series generated by (7.11) must terminate. This happens if $n = 0, 1, 2, \ldots$

So in order for ψ to be normalisable, E can only assume the discrete values (by (7.9)):

$$E_n = \hbar\omega(n + \tfrac{1}{2}).$$

Eigenfunctions: From (7.11),

Even parity:	**Odd parity:**
$a_0 =$ arbitrary	$a_1 =$ arbitrary
$a_2 = -na_0$	$a_3 = \dfrac{1-n}{3}a_1$
$a_4 = \dfrac{n(n-2)}{6}a_0$	$a_5 = \dfrac{(n-3)(n-1)}{30}a_1$
$\vdots$	$\vdots$

Set $a_0 = a_1 = 1$. Then:

$$y_{\text{even}} = 1 - n\xi^2 + \frac{n(n-2)}{6}\xi^4 - \ldots$$
$$y_{\text{odd}} = \xi - \frac{n-1}{3}\xi^3 + \frac{(n-3)(n-1)}{30}\xi^5 - \ldots$$

Hermite polynomials are conventionally defined by:

$$\textbf{even } n\textbf{:} \quad H_n(\xi) = (-1)^{\frac{n}{2}} \frac{n!}{(\frac{n}{2})!}\, y_{\text{even}}$$
$$\textbf{odd } n\textbf{:} \quad H_n(\xi) = (-1)^{\frac{n-1}{2}} \frac{2(n!)}{(\frac{n-1}{2})!}\, y_{\text{odd}}$$

Thus $H_0 = 1$, $H_1 = 2\xi$, $H_2 = -2 + 4\xi^2$, $H_3 = -12\xi + 8\xi^3$, ..., and H_n is normalised such that ξ^n has coefficient 2^n.

Hence, the general normalisable solution of

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x)$$

is:

$$\psi_n(x) = c_n H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega x^2}{2\hbar}}, \quad n = 0, 1, \ldots$$

and c_n is chosen such that

$$\int_{-\infty}^{\infty} dx\, \psi_n^2 = 1.$$

The generating function for H_n is:

$$F(s,\xi) = e^{-s^2+2s\xi} = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n \tag{7.12}$$

and the H_ns defined by (7.12) satisfy (7.8).

From (7.12) we can get an explicit representation of $H_n(\xi)$:

$$\begin{aligned} H_n(\xi) &= \frac{d^n}{ds^n} e^{-s^2+2s}\Big|_{s=0} \\ &= \frac{d^n}{ds^n} e^{\xi^2} e^{-(s-\xi)^2}\Big|_{s=0} \\ &= (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} \end{aligned}$$

The remaining problem is to find c_n such that

$$\int_{-\infty}^{\infty} dx\, \psi_n^2 = 1.$$

Solution: Use the generating function of H_ns (7.12):

$$F(s,\xi) = e^{-s^2+2s\xi} = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n$$

where:

$$\psi = \sqrt{\frac{m\omega}{\hbar}} x.$$

(7.12) gives:

$$\int_{-\infty}^{\infty} d\xi\, e - s^2 + 2s\xi e^{-t^2+2t\xi} e^{-\xi^2} = \sum_{m,n=0}^{\infty} \frac{s^n t^m}{n!m!} \int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi) H_m(\xi)\, d\xi \tag{7.13}$$

But:

$$\int_{-\infty}^{\infty} d\xi\, e^{-\xi^2+2s\xi+2t\xi} = e^{(s+t)^2} \int_{-\infty}^{\infty} e^{-(\xi-s-t)^2}\, d\xi = \sqrt{\pi} e^{(s+t)^2}$$

Substituting this into (7.13):

$$\sqrt{\pi} e^{2st} = \sqrt{\pi} \sum_{n=0}^{\infty} \frac{(2st)^2}{n!} = \sum_{m,n=0}^{\infty} \frac{s^n t^m}{n!m!} \int_{-\infty}^{\infty} d\xi\, e^{-\xi^2} H_m(\xi) H_n(\xi)$$

Hence,

$$\int_{-\infty}^{\infty} d\xi\, e^{-\xi^2} H_m(\xi) H_n(\xi) = \sqrt{2\pi} 2^n n! \delta_{mn}.$$

Returning to x,

$$\int_{-\infty}^{\infty} d\xi e^{-\frac{m\omega x^2}{\hbar}} H_n^2\left(\sqrt{\frac{m\omega}{\hbar}}x\right) = \sqrt{\frac{\pi\hbar}{m\omega}}2^n n!$$

$$\Rightarrow c_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}}$$

Hence,

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}}$$

$$E_n = \hbar\omega\left(n + \tfrac{1}{2}\right), \quad n = 0, 1, \ldots$$

All n roots of H_n are real; so each ψ_n has n nodes.

7.6 Oscillation theorem

Let $\psi_0, \psi_1, \ldots$ be bound-state wavefunctions in 1D. The function $\psi_n(x)$ corresponding to the n^{th} eigenstate E_n (where $E_0 < E_1 < \ldots$) vanishes n times for finite values of x.