Quantum Mechanics

Problem Sheet 2

Time Dependence, Schrödinger Equation & Wave Mechanics

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Time Dependence and the Schrödinger Equation

2.1

The time-dependent Schrödinger equation (TDSE) for the position wave function $\psi(x,t) \equiv \langle \hat{x}|\psi(t)\rangle$ is:

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \hat{H}\psi(x,t) \tag{1}$$

while the time-independent Schrödinger equation (TISE) for the energy eigenfunction $\psi_n(x)$ is:

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \tag{2}$$

Any wave function $\psi(x,t)$ must satisfy the TDSE but not necessarily the TISE. A wave function that satisfies the TISE is called an energy eigenfunction that only undergoes a phase change under time evolution.

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2.2

Newton's second law is not a classical analogue of the Schrödinger equation.

2.3

(a)

$$P(E \leq 6\varepsilon, t=0) = \sum_{n=1,2} P(E = n^2\varepsilon, t=0) = 0.2^2 + 0.3^2 = 0.13 \tag{3}$$

(b)

$$\begin{aligned}\langle E\rangle &= \sum E_n P(E = n^2\varepsilon, t=0)\\ &= \left(1^2\times 0.2^2 + 2^2\times 0.3^2 + 3^2\times 0.4^2 + 4^2\times 0.843^2\right)\varepsilon\\ &= 13.210\varepsilon\end{aligned} \tag{4}$$

$$\begin{aligned}\left\langle E^2\right\rangle &= \sum E_n^2 P(E = n^2\varepsilon, t=0)\\ &= \left(1^4\times 0.2^2 + 2^4\times 0.3^2 + 3^4\times 0.4^2 + 4^4\times 0.843^2\right)\varepsilon^2\\ &= 196.366\varepsilon^2\end{aligned} \tag{5}$$

so that the rms deviation is:

$$\Delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = 4.675\varepsilon \tag{6}$$

(c) The time evolution of $|\psi(0)\rangle$ is given by:

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle = \sum_n e^{-iE_n t/\hbar} c_n\,|n\rangle \tag{7}$$

so that after a time t, the probability of finding the system in the state $|j\rangle$ is:

$$P(j,t) = |\langle j|\psi(t)\rangle|^2 = \left|\sum_n e^{-iE_n t/\hbar} c_n \langle j|n\rangle\right|^2 = |c_j|^2 \tag{8}$$

which is unchanged because the time-evolution operator only changes the phase of each coefficient c_n.

Thus, the previous results still hold for $t > 0$.

(d) If energy is measured to be 16ε, then the system has 'collapsed' to the state $|\psi\rangle = |4\rangle$. We would only obtain the energy 16ε in any subsequent measurement of energy.

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2.4

Since the Hamiltonian $\hat{H}$ and momentum operator $\hat{p}$ commute, they share a common set of eigenfunctions and it is possible for a particle to have both well-defined energy and momentum. However, $\hat{H}$ and position operator $\hat{x}$ generally do not commute, so that a particle cannot have both well-defined energy and position.

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2.5

$$\begin{aligned}
\langle \hat{x} \rangle &= \int_{-\infty}^{\infty} \psi^*(x,t) x \psi(x,t)\,\mathrm{d}x \\
\left\langle \hat{x}^2 \right\rangle &= \int_{-\infty}^{\infty} \psi^*(x,t) x^2 \psi(x,t)\,\mathrm{d}x \\
\langle \hat{p}_x \rangle &= \int_{-\infty}^{\infty} \psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x,t)\,\mathrm{d}x \\
\left\langle \hat{p}_x^2 \right\rangle &= \int_{-\infty}^{\infty} \psi^*(x,t) \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \psi(x,t)\,\mathrm{d}x \\
\left\langle \hat{H} \right\rangle &= \int_{-\infty}^{\infty} \psi^*(x,t) \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right) \psi(x,t)\,\mathrm{d}x
\end{aligned} \tag{9}$$

where the expectation for energy is given by the equation with the Hamiltonian operator $\hat{H}$.

The probability of finding the particle in (x_1, x_2) is:

$$P(x_1 < x < x_2) = \int_{x_1}^{x_2} |\psi(x,t)|^2 \, \mathrm{d}x \tag{10}$$

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2.6

Any state $|\psi(t)\rangle$ must satisfy the TDSE:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \tag{11}$$

and its bra counterpart:

$$-i\hbar \frac{\partial}{\partial t} \langle\psi(t)| = \langle\psi(t)| \hat{H} \tag{12}$$

We also know that $\hat{Q}|\psi(t)\rangle$, being a state itself, satisfies the TDSE:

$$i\hbar \frac{\partial}{\partial t} \left(\hat{Q} |\psi(t)\rangle\right) = \hat{H}\hat{Q} |\psi(t)\rangle \tag{13}$$

Assuming that $\hat{Q}$ is a time-independent operator, consider the time derivative of its expectation:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \left\langle \hat{Q} \right\rangle &= \frac{\mathrm{d}}{\mathrm{d}t} \left(\langle\psi(t)| \hat{Q} |\psi(t)\rangle \right) \\ &= \left\langle \frac{\partial \psi}{\partial t} \middle| \hat{Q} \middle| \psi \right\rangle + \left\langle \psi \middle| \hat{Q} \middle| \frac{\partial \psi}{\partial t} \right\rangle \\ &= -\frac{1}{i\hbar} \langle\psi|\hat{H}\hat{Q}|\psi\rangle + \frac{1}{i\hbar} \langle\psi|\hat{Q}\hat{H}|\psi\rangle \\ &= \frac{1}{i\hbar} \langle\psi|[\hat{Q},\hat{H}]|\psi\rangle \end{aligned} \tag{14}$$

which immediately gives the desired result.

Now let $\hat{Q} = \hat{x}$ and $[\hat{x}, \hat{H}]$ would be non-zero, so that the expectation of position is not conserved, i.e. constant in time. However, if $\hat{Q} = \hat{p}$, then $[\hat{p}, \hat{H}] = 0$ and the expectation of momentum is conserved.

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Wave Mechanics

2.7

In the region $x < 0$ and $V = 0$, the TISE is:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \tag{15}$$

with the solution:

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \tag{16}$$

where $k \equiv \sqrt{2mE}/\hbar$.

In the region $0 < x$ and $V = V_0 < E$, the TISE is:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V_0\psi = E\psi \tag{17}$$

with the solution:

$$\psi(x) = Ce^{iKx} + De^{-iKx} \tag{18}$$

where $K \equiv \sqrt{2m(E - V_0)}/\hbar$.

The condition of no particle incident from $+\infty$ is $D = 0$.

Continuity of $\psi(x)$ and $\psi'(x)$ at $x = 0$ gives:

$$\begin{aligned} A + B &= C \\ ik(A - B) &= iKC \end{aligned} \tag{19}$$

solving which yields $B = A(k - K)/(k + K)$ and $C = 2Ak/(k + K)$.

Hence, the probability of reflection is the probability of finding the particle travelling to $-\infty$ in the region $x < 0$:

$$\left|\frac{B^2}{A^2}\right| = \left(\frac{k - K}{k + K}\right)^2 \tag{20}$$

Probability of transmission is:

$$\left|\frac{C^2}{A^2}\right| = \frac{4kK}{(k+K)^2} \tag{21}$$

The probability current on the left is:

$$\frac{ih}{2m}\left(\psi\frac{\partial\psi^*}{\partial x} - \psi^*\frac{\partial\psi}{\partial x}\right) = \frac{h}{m}\frac{kK}{k+K} = \frac{h}{2m}\left(\frac{k-K}{k+K}\right) \tag{22}$$

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2.8

For bound states, we have $E < V_0$. Outside the well, the solution is:

$$\psi(x) = \begin{cases} De^{\kappa x} + D'e^{-\kappa x} & x < -a \\ Ce^{-\kappa x} + C'e^{\kappa x} & x > a \end{cases} \tag{23}$$

where $\kappa \equiv \sqrt{2m(V_0 - E)}/\hbar$.

and inside the well, the solution is:

$$\psi(x) = A\cos{(kx)} + B\sin{(kx)} \tag{24}$$

where $k \equiv \sqrt{2mE}/\hbar$.

For odd-parity solutions, we set $A = 0$ and $C = -D$ so that $\psi(x) = -\psi(-x)$. For the wave function to be finite, we also need $C' = D' = 0$. Continuity of $\psi(x)$ and $\psi'(x)$ at $x = \pm a$ gives:

$$\begin{aligned} B\sin{(ka)} &= Ce^{-\kappa a} \\ kB\cos{(ka)} &= -KCe^{-\kappa a} \\ -B\sin{(ka)} &= De^{-\kappa a} = -Ce^{-\kappa a} \\ kB\cos{(ka)} &= KDe^{-\kappa a} = -KCe^{-\kappa a} \end{aligned} \tag{25}$$

These can be solved to give:

$$\cot{(ka)} = -\frac{\kappa}{k} = -\sqrt{\frac{V_0}{E} - 1} = -\sqrt{\frac{W^2}{(ka)^2} - 1} \tag{26}$$

where $W \equiv \sqrt{2mV_0a^2}/\hbar$.

For the square root to be valid, we must have $W > ka$ or $V_0 > E$. But for the cotangent to negative, we must have $ka > \pi/2$. Hence, we require $W > \pi/2$.

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2.9

Consider the potential well:

$$V(x) = \begin{cases} -V_0 & |x| < a \\ 0 & \text{otherwise} \end{cases} \tag{27}$$

The solutions are:

$$\psi(x) = \begin{cases} De^{ikx} + re^{-ikx} & x < -a \\ Ae^{iKx} + Be^{-iKx} & -a < x < a \\ Ce^{-ikx} + te^{ikx} & x > a \end{cases} \tag{28}$$

where $k \equiv \sqrt{2mE}/\hbar$ and $K \equiv \sqrt{2m(V_0 + E)}/\hbar$.

Let us set $D = 1$ and $C = 0$ so that there is no particle incident from $+\infty$. Continuity of $\psi(x)$ and $\psi'(x)$ at $x = \pm a$ gives:

$$\begin{aligned} e^{-ika} + re^{ika} &= Ae^{-iKa} + Be^{iKa} \\ ik(e^{-ika} - re^{ika}) &= iK(Ae^{-iKa} - Be^{iKa}) \\ te^{ika} &= Ae^{iKa} + Be^{-iKa} \\ ikte^{ika} &= iK(Ae^{iKa} - Be^{-iKa}) \end{aligned} \tag{29}$$

These can be solved to give an expression for r:

$$r = \frac{e^{-2ika}\left(e^{4iKa} - 1\right)(k - K)(k + K)}{k^2\left(e^{4iKa} - 1\right) - 2kK\left(1 + e^{4iKa}\right) + K^2\left(e^{4iKa} - 1\right)} \tag{30}$$

Due to the factor $(e^{4iKa} - 1)$, $r = 0$ whenever $Ka = n\pi/2$ for $n \in \mathbb{Z}$. In this case, the particle is completely transmitted through the well and there is zero probability of observing a reflected particle.

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2.10

Given the potential $V(x) = V_\delta \delta(x)$, the solutions are:

$$\psi(x) = \begin{cases} Ae^{ikx} + re^{-ikx} & x < 0 \\ Be^{-ikx} + te^{ikx} & x > 0 \end{cases} \tag{31}$$

where $k \equiv \sqrt{2mE}/\hbar$.

Again, let $B = 0$ so that there is no particle incident from $+\infty$. Continuity of $\psi(x)$ at $x = 0$ gives $A + r = t$. The continuity condition on $\psi'(x)$ is obtained by integrating the TISE around $x = 0$:

$$\begin{aligned} 0 &= \lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V_\delta\delta(x)\psi - E\psi\right]\mathrm{d}x \\ &= -\frac{\hbar^2}{2m}\left[\psi'(0^+) - \psi'(0^-)\right] + V_\delta\psi(0) \end{aligned} \tag{32}$$

which means:

$$ik(A - r + t) = K(A + r) \tag{33}$$

where $K \equiv \sqrt{2m(V_\delta + E)}/\hbar$.

Solving the equations yields $t = 2iAk/(2ik + K)$ and the probability of transmission is:

$$P_{\text{tun}} = \left|\frac{t}{A}\right|^2 = \left|\frac{1}{1 + K/2ik}\right|^2 = \frac{1}{1 + (K/2k)^2} \tag{34}$$

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2.11

Given the definition of the probability current density:

$$\mathbf{J}(\mathbf{r}, t) = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right) \tag{35}$$

we evaluate:

$$\begin{aligned} \psi &= Ae^{i(kz-\omega t)} + Be^{-i(kz-\omega t)} \\ \psi^* &= A^*e^{-i(kz-\omega t)} + B^*e^{i(kz-\omega t)} \\ \nabla\psi &= ik\left[Ae^{i(kz-\omega t)} - Be^{-i(kz-\omega t)}\right]\hat{z} \\ \nabla\psi^* &= -ik\left[A^*e^{-i(kz-\omega t)} - B^*e^{i(kz-\omega t)}\right]\hat{z} \end{aligned} \tag{36}$$

so that:

$$\begin{aligned}\mathbf{J}(\mathbf{r},t) &= \hat{z}\frac{-\hbar k}{2m}\left(-2\left|A\right|^2 + 2\left|B\right|^2\right) \\ &= \frac{\hbar k}{m}\left(\left|A\right|^2 - \left|B\right|^2\right)\hat{z}\end{aligned} \tag{37}$$

The probability is proportional to the speed of the wave packet, and the minus sign is due to opposite directions of the wave packets.

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2.12

A momentum eigenstate, expressed in its position representation, is:

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ipx/\hbar} \tag{38}$$

with its complex conjugate:

$$\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{-ipx/\hbar} \tag{39}$$

For a wave function of the form:

$$\psi(x,0) = \langle x|\psi(0)\rangle = \left(\frac{1}{2\pi\sigma^2}\right)^{1/4}\exp\left(-\frac{x^2}{4\sigma^2} + \frac{ip_0x}{\hbar}\right) \tag{40}$$

its momentum representation is the integral:

$$\begin{aligned}\langle p|\psi(0)\rangle &= \int \langle p|x\rangle\langle x|\psi(0)\rangle \,\mathrm{d}x \\ &= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{1}{2\pi\sigma^2}\right)^{1/4}\int \exp\left[-\frac{x^2}{4\sigma^2} + \frac{i(p_0-p)x}{\hbar}\right]\mathrm{d}x\end{aligned} \tag{41}$$

Consider the change of variable:

$$y = \frac{x}{2\sigma} - \frac{i(p_0-p)\sigma}{\hbar} \tag{42}$$

We have:

$$\begin{aligned}\int \exp\left[-\frac{x^2}{4\sigma^2}+\frac{i(p_0-p)x}{\hbar}\right]\mathrm{d}x &= 2\sigma\int \exp\left[-y^2-\left(\frac{p_0-p}{\hbar}\right)^2\sigma^2\right]\mathrm{d}y \\ &= \exp\left[-\frac{(p_0-p)\sigma}{\hbar}\right]^2 2\sigma\sqrt{\pi}\end{aligned} \tag{43}$$

so that the momentum representation is:

$$\langle p|\psi(0)\rangle = \left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\exp\left[-\frac{(p_0-p)\sigma}{\hbar}\right]^2 \tag{44}$$

Note that $\langle p|\psi(0)\rangle$ just the Fourier transform of $\langle x|\psi(0)\rangle$:

$$\langle p|\psi(0)\rangle = \mathcal{F}\left[\langle x|\psi(0)\rangle\right] = \frac{1}{\sqrt{2\pi\hbar}}\int e^{-ipx/\hbar}\langle x|\psi(0)\rangle\,\mathrm{d}x \tag{45}$$

Consider a momentum eigenstate $|p\rangle$ that satisfies $\hat{p}\,|p\rangle = p\,|p\rangle$. Applying the Hamiltonian operator to $|p\rangle$ gives:

$$\hat{H}\,|p\rangle = \frac{\hat{p}^2}{2m}\,|p\rangle = \frac{p^2}{2m}\,|p\rangle \tag{46}$$

which means that $|p\rangle$ is also an energy eigenstate with the eigenvalue $p^2/2m$.

The time-evolution of a momentum eigenstate $|p\rangle$ is hence given by:

$$|p\rangle \to e^{-i\hat{H}t/\hbar}\,|p\rangle = e^{-ip^2t/2m\hbar}\,|p\rangle \tag{47}$$

We may write $|\psi(0)\rangle$ as a superposition of momentum eigenstates so that its time-evolution is:

$$\begin{aligned}|\psi(t)\rangle &= e^{-i\hat{H}t/\hbar}\,|\psi(0)\rangle \\ &= \int e^{-i\hat{H}t/\hbar}\,|p\rangle\langle p|\psi(0)\rangle\,\mathrm{d}p \\ &= \int e^{-ip^2t/2m\hbar}\,|p\rangle\langle p|\psi(0)\rangle\,\mathrm{d}p\end{aligned} \tag{48}$$

Then the position representation of $|\psi(t)\rangle$ is:

$$
\begin{aligned}
\psi(x,t) &= \langle x|\psi(t)\rangle \\
&= \int \exp\left(-\frac{ip^2t}{2m\hbar}\right)\langle x|p\rangle\langle p|\psi(0)\rangle\,\mathrm{d}p \\
&= \frac{1}{\sqrt{2\pi\hbar}}\left(\frac{2\sigma^2}{\pi\hbar^2}\right)^{1/4}\int \exp\left[-\frac{ip^2t}{2m\hbar}+\frac{ipx}{\hbar}-\frac{(p_0-p)^2\sigma^2}{\hbar^2}\right]\mathrm{d}p \\
&= \left(\frac{2}{\pi}\right)^{1/4}\frac{1}{\sqrt{2\sigma+i\hbar t/m\sigma}}\exp\left[-\frac{4mp_0\sigma^2x-2p_0^2\sigma^2t+i\hbar mx^2}{-2\hbar^2t+4i\hbar m\sigma^2}\right]
\end{aligned} \tag{49}
$$

where the integral can be evaluated using a substitution similar to the previous one.

The square modulus of $\psi(x,t)$ is:

$$
|\psi(x,t)|^2 = \frac{\sigma}{\sqrt{2\pi\hbar^2\,|b(t)|^2}}\exp\left[-\frac{\sigma^2(x-p_0t/m)^2}{2\hbar^2\,|b(t)|^2}\right] \tag{50}
$$

where $b(t)\equiv\sigma^2/\hbar+it/2m$ and $|b(t)|^2=\sigma^4/\hbar^2+t^2/4m^2$.

As time goes on, the wave packet moves to the right and its variance/width increases:

$$
\sigma^2(t) = \sigma^2\left(1+\frac{\hbar^2t^2}{4m^2\sigma^4}\right) \tag{51}
$$

The particle gets 'smeared out' in space with an increasing uncertainty in its position due to an initial uncertainty in its momentum.

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