

Lecture 13: Time-domain quantum mechanics

1. Solving Schrödinger's equation

We start by deriving the general solution for the time-dependent Schrödinger equation (TDSE):

$$\frac{\partial}{\partial t} \psi(t) = -i\mathbf{H} \psi(t) \quad (1)$$

with a static Hamiltonian $\mathbf{H}$. After expanding $\psi(t)$ as a Taylor series around $t = 0$, we get:

$$\psi(t) = \psi(0) + \left. \frac{\partial \psi(t)}{\partial t} \right|_{t=0} t + \frac{1}{2} \left. \frac{\partial^2 \psi(t)}{\partial t^2} \right|_{t=0} t^2 + \frac{1}{6} \left. \frac{\partial^3 \psi(t)}{\partial t^3} \right|_{t=0} t^3 + \dots \quad (2)$$

The derivatives of the wavefunction at time zero are known to us from Schrödinger's equation:

$$\begin{aligned} \left. \frac{\partial \psi(t)}{\partial t} \right|_{t=0} &= -i\mathbf{H} \psi(t) \Big|_{t=0} = (-i\mathbf{H}) \psi(0) \\ \left. \frac{\partial^2 \psi(t)}{\partial t^2} \right|_{t=0} &= \left. \frac{\partial}{\partial t} (-i\mathbf{H} \psi(t)) \right|_{t=0} = (-i\mathbf{H}) \left(\left. \frac{\partial \psi(t)}{\partial t} \right|_{t=0} \right) = (-i\mathbf{H})^2 \psi(t) \Big|_{t=0} = (-i\mathbf{H})^2 \psi(0) \\ \left. \frac{\partial^3 \psi(t)}{\partial t^3} \right|_{t=0} &= \left. \frac{\partial}{\partial t} ((-i\mathbf{H})^2 \psi(t)) \right|_{t=0} = \dots = (-i\mathbf{H})^3 \psi(0) \end{aligned} \quad (3)$$

and so on. The sum in Equation (2) becomes:

$$\psi(t) = \psi(0) + (-i\mathbf{H}t) \psi(0) + \frac{1}{2} (-i\mathbf{H}t)^2 \psi(0) + \dots = \left[\sum_{n=0}^{\infty} \frac{(-i\mathbf{H}t)^n}{n!} \right] \psi(0) \quad (4)$$

We can recognise the Taylor expansion of the exponential function in square brackets. That expansion is actually the definition of the *operator exponential*. With that in place, we get the general solution of the TDSE with a static Hamiltonian:

$$\psi(t) = \left[\sum_{n=0}^{\infty} \frac{(-i\mathbf{H}t)^n}{n!} \right] \psi(0) = \exp(-i\mathbf{H}t) \psi(0) \quad (5)$$

If vector-matrix representations are used for the wavefunction and the Hamiltonian, Dirac brackets appear, and the equations are rewritten as:

$$\frac{\partial}{\partial t} |\psi(t)\rangle = -i\mathbf{H} |\psi(t)\rangle, \quad |\psi(t)\rangle = \exp(-i\mathbf{H}t) |\psi(0)\rangle \quad (6)$$

where the exponential $\exp(-i\mathbf{H}t)$ is called *propagator* because it moves the system forward in time. The case of the time-dependent Hamiltonian is more complicated; it will not be considered in this course because our timetable is very tight.

2. Quantum mechanical treatment of spin precession

As an example of a time-domain solution to Schrödinger's equation, consider a single spin in a magnetic field directed along the Z axis of the laboratory frame. The Hamiltonian is:

$$\mathbf{H} = \omega \mathbf{S}_z, \quad \frac{\partial}{\partial t} |\psi\rangle = -i\omega \mathbf{S}_z |\psi\rangle, \quad \omega = -\gamma B_0 \quad (7)$$

The general solution to this problem is obtained using Equation (5):

$$\exp(-i\omega\mathbf{S}_Z t) = \sum_{n=0}^{\infty} \frac{(-i\omega t)^n}{n!} \mathbf{S}_Z^n = \sum_{n=0}^{\infty} \frac{(-i\omega t)^n}{n!} \begin{pmatrix} (1/2)^n & 0 \\ 0 & (-1/2)^n \end{pmatrix} = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \quad (8)$$

and therefore

$$|\psi(t)\rangle = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} |\psi(0)\rangle \quad (9)$$

If the initial direction of the spin is along the Z axis,

$$|\psi(0)\rangle = |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \Rightarrow |\psi(t)\rangle = \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} \quad (10)$$

and the time dependence of the three projections of our spin is:

$$\begin{aligned} \langle S_X(t) \rangle &= \begin{pmatrix} e^{i\omega t/2} & 0 \end{pmatrix} \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} = 0 \\ \langle S_Y(t) \rangle &= \begin{pmatrix} e^{i\omega t/2} & 0 \end{pmatrix} \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} = 0 \\ \langle S_Z(t) \rangle &= \begin{pmatrix} e^{i\omega t/2} & 0 \end{pmatrix} \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \begin{pmatrix} e^{-i\omega t/2} \\ 0 \end{pmatrix} = 1/2 \end{aligned} \quad (11)$$

So the magnetisation stays on the Z axis. If the initial state is along the X axis:

$$\begin{aligned} |\psi(0)\rangle &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \langle \psi(0) | \mathbf{S}_X | \psi(0) \rangle = 1/2 \\ \langle \psi(0) | \mathbf{S}_Y | \psi(0) \rangle &= \langle \psi(0) | \mathbf{S}_Z | \psi(0) \rangle = 0 \end{aligned} \quad (12)$$

then the corresponding time-dependent solution is

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\omega t/2} & 0 \\ 0 & e^{i\omega t/2} \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\omega t/2} \\ e^{i\omega t/2} \end{pmatrix} \Rightarrow \begin{aligned} \langle \psi(t) | \mathbf{S}_Z | \psi(t) \rangle &= 0 \\ \langle \psi(t) | \mathbf{S}_X | \psi(t) \rangle &= \dots = +\cos(\omega t)/2 \\ \langle \psi(t) | \mathbf{S}_Y | \psi(t) \rangle &= \dots = -\sin(\omega t)/2 \end{aligned} \quad (13)$$

where we see the expected circular precession of the expectation values in the XY plane.

3. Density operator

Consider an ensemble average $\bar{O}$ of an observable quantity O corresponding to a quantum mechanical operator $\mathbf{O}$. Because matrix trace is linear and invariant under cyclic permutations of arguments:

$$\bar{O} = \overline{\langle \psi | \mathbf{O} | \psi \rangle} = \overline{\text{Tr}(\langle \psi | \mathbf{O} | \psi \rangle)} = \overline{\text{Tr}(|\psi\rangle \langle \psi | \mathbf{O})} = \text{Tr}(\overline{|\psi\rangle \langle \psi |} \mathbf{O}) \quad (14)$$

It is apparent that the descriptor carrying the information about the ensemble average is not produced by averaging the wavefunction (that average would be zero because the wavefunction phase is arbitrary), but rather by averaging the projector $|\psi\rangle \langle \psi|$ in which phase multipliers cancel:

$$|e^{i\varphi}\psi\rangle \langle e^{i\varphi}\psi| = e^{i\varphi} e^{-i\varphi} |\psi\rangle \langle \psi| = |\psi\rangle \langle \psi| \quad (15)$$

The quantity $\rho = |\psi\rangle\langle\psi|$ is called *density operator* or *density matrix* (not to be confused with density functional and density matrix in electronic structure theory, those are different things). It is an operator because it acts on a wavefunction and returns another wavefunction:

$$\rho|\varphi\rangle = |\psi\rangle\langle\psi|\varphi\rangle = a|\psi\rangle, \quad a = \langle\psi|\varphi\rangle \quad (16)$$

It is also Hermitian and *idempotent* – its positive integer powers are equal to itself:

$$\rho^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = \rho \quad (17)$$

The physical meaning of ρ follows from the expressions for its matrix elements. The diagonal elements

$$\langle n|\rho|n\rangle = \langle n|\psi\rangle\langle\psi|n\rangle = |c_n|^2 = p_n \quad (18)$$

correspond to the probability of finding the system in a state $|n\rangle$. It follows that, for a single quantum system, the trace of the density matrix is the sum of all probabilities, and therefore equal to 1. The off-diagonal elements indicate the presence of a superposition in the wavefunction:

$$\begin{aligned} |\psi\rangle &= \dots + c_n|n\rangle + c_k|k\rangle + \dots \\ \Downarrow \\ \langle n|\rho|k\rangle &= \langle n|\psi\rangle\langle\psi|k\rangle = c_n c_k^* \end{aligned} \quad (19)$$

When the ensemble average is applied, the trace of ρ indicates the *purity* of the ensemble: when the wavefunctions of the individual systems are identical up to a phase (*pure ensemble*), the trace of the ensemble average density matrix is equal to 1. However, when individual systems have different wavefunctions, the trace of the average density matrix is smaller than 1 (*mixed ensemble*). In the average density matrix, the off-diagonal elements $c_n c_k^*$ acquire the meaning of correlation coefficients between wavefunction components across the ensemble; they are colloquially called *coherences*.

4. Liouville – von Neumann equation

The equation of motion (called *Liouville – von Neumann equation*) for the density operator is obtained from its definition and Schrödinger's equation using the product rule:

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \frac{\partial}{\partial t}(|\psi\rangle\langle\psi|) = \left(\frac{\partial}{\partial t}|\psi\rangle\right)\langle\psi| + |\psi\rangle\left(\frac{\partial}{\partial t}\langle\psi|\right) = \\ &= -i\mathbf{H}|\psi\rangle\langle\psi| + i|\psi\rangle\langle\psi|\mathbf{H} = -i\mathbf{H}\rho + i\rho\mathbf{H} = -i[\mathbf{H}, \rho] \\ \Downarrow \\ \frac{\partial \rho}{\partial t} &= -i[\mathbf{H}, \rho] \end{aligned} \quad (20)$$

The solutions are inherited from Schrödinger's equation: two copies of Eq (6) are multiplied together to assemble $\rho = |\psi\rangle\langle\psi|$. With a time-independent Hamiltonian:

$$\begin{aligned} |\psi(t + \Delta t)\rangle &= \exp(-i\mathbf{H}\Delta t)|\psi(t)\rangle \\ \Downarrow \\ \rho(t + \Delta t) &= \exp(-i\mathbf{H}\Delta t)\rho(t)\exp(+i\mathbf{H}\Delta t) \end{aligned} \quad (21)$$

For the calculation of observables, using the cyclic permutation property of the matrix trace, we obtain:

$$\langle O \rangle = \langle\psi|O|\psi\rangle = \text{Tr}(\langle\psi|O|\psi\rangle) = \text{Tr}(O|\psi\rangle\langle\psi|) = \text{Tr}(O\rho) \quad (22)$$