PHY215-07: Schrodinger equation and transition rates

C.-P. Yuan

March 28, 2025

1 Derivation of the Schrödinger Equation

The Schrödinger equation emerges from unifying wave-particle duality with classical physics principles. Here's the structured argument:

1. **Physical Motivation: Wave-Particle Duality**

- de Broglie Hypothesis : Particles exhibit wave-like behavior with wavelength:

$$\lambda = \frac{h}{p},$$

where p is momentum.

- Wave Function (ψ) : Describes quantum states, with $|\psi(x,t)|^2$ as the probability density.

- Probability Conservation : Governed by the continuity equation:

$$\frac{\partial}{\partial t}|\psi|^2 + \nabla \cdot \vec{J} = 0,$$

where $\vec{J} = \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right)$.

2. **Classical Wave Equation Analogy**

- Plane Wave Ansatz : Assume a monochromatic solution:

$$\psi(x,t) = e^{i(kx-\omega t)},$$

with $k = \frac{2\pi}{\lambda}$ and $\omega = 2\pi f$.

- Energy-Momentum Relation : Substitute $E = \hbar\omega$ and $p = \hbar k$. Hence,

$$\psi(x,t) = e^{\frac{i}{\hbar}(px-Et)}.$$

3. **Postulating the Time-Dependent Schrödinger Equation**

- Operator Correspondence :

$$E \to i\hbar\frac{\partial}{\partial t}, \quad \vec{p} \to -i\hbar\nabla.$$

In terms of components, $\vec{p} = (p_x, p_y, p_z)$ with

$$p_x \to -i\hbar\frac{\partial}{\partial x}.$$

- Hamiltonian Formulation :

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

4. **Justifying the Equation**

- Consistency with de Broglie Waves :

$$\hbar\omega\psi = \left(\frac{\hbar^2k^2}{2m} + V\right)\psi \implies E = \frac{p^2}{2m} + V.$$

- Probability Conservation : Recovers the continuity equation.

5. **Stationary States and Time-Independent Equation**

- Separation of Variables : Assume $\psi(x,t) = \psi(x)e^{-iEt/\hbar}$:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right]\psi(x) = E\psi(x).$$

6. **Experimental Validation**

- Hydrogen Atom : Predicts quantized energy levels matching the Balmer series.

- Tunneling Effect : Explains alpha decay and scanning tunneling microscopy.

- Wave Packet Dynamics : Describes spreading consistent with the uncertainty principle.

7. **Limitations and Extensions**

- Non-Relativistic : Fails at $v \sim c$ (requires Dirac equation).

- Multi-Particle Systems : Generalizes to $\psi(x_1, x_2, \ldots, x_N, t)$.

- Probabilistic Interpretation : Born rule ($|\psi|^2$) is a postulate.

8. **Conclusion**

The Schrödinger equation arises from:

1. Postulating wave-particle duality and probability interpretation.
2. Promoting classical observables to quantum operators.
3. Demanding consistency with energy-momentum relations.
4. Agreement with experimental results in quantum systems.

It serves as the foundational equation of non-relativistic quantum mechanics, unifying particle behavior with wave dynamics.

2 Solve the Schrödinger equation for the deuteron

2.1 Reduction to the effective one-body problem

- The deuteron is a two-body system consisting of a proton and a neutron. We first reduce it to an effective one-body problem by introducing the reduced mass. The reduced mass μ of the system is given by $\mu = \frac{m_p m_n}{m_p + m_n}$, where m_p is the mass of the proton and m_n is the mass of the neutron.

- The Schrödinger equation for a central potential $V(r)$ in spherical coordinates is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V(r)\psi = E\psi$$

- In spherical coordinates,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

- For a spherically symmetric potential $V = V(r)$, the wave function can be written as $\psi(r, \theta, \varphi) = R(r)Y_{lm}(\theta, \varphi)$, where $Y_{lm}(\theta, \varphi)$ are the spherical harmonics and $R(r)$ is the radial part of the wave function. The Schrödinger equation then reduces to the radial equation:

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR}{dr}) - \frac{l(l+1)}{r^2}R\right] + V(r)R = ER$$

2.2 Choice of potential model

- A common choice is the square-well potential as a simple approximation. The square-well potential is given by

$$V(r) = \begin{cases} -V_0, & r < a \\ 0, & r \geq a \end{cases}$$

- Inside the well ($r < a$), the radial Schrödinger equation becomes

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}(r^2\frac{dR}{dr}) + \frac{\hbar^2 l(l+1)}{2\mu r^2}R - V_0 R = ER$$

- Let $u(r) = rR(r)$, then the equation simplifies to

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} - V_0\right]u = Eu$$

- The general solution for $l = 0$ (the ground state is usually $l = 0$ for the deuteron) inside the well is $u(r) = A\sin(kr) + B\cos(kr)$, where $k = \sqrt{\frac{2\mu(V_0+E)}{\hbar^2}}$.

- Outside the well ($r \geq a$), the equation is

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2}u = Eu$$

- For $l = 0$, appropriate for the deuteron ground state, the general solution is $u(r) = Ce^{-\kappa r} + De^{\kappa r}$, where $\kappa = \sqrt{-\frac{2\mu E}{\hbar^2}}$. Since the wave function must be finite as $r \to \infty$, we set $D = 0$.

2.3 Applying boundary conditions

- We need to apply the boundary conditions at $r = a$. The wave function and its derivative must be continuous at $r = a$.

- Continuity of the wave function: $A\sin(ka) + B\cos(ka) = Ce^{-\kappa a}$.

- Continuity of the derivative: $k[A\cos(ka) - B\sin(ka)] = -\kappa Ce^{-\kappa a}$.

- By solving these equations simultaneously, we can find the energy eigenvalues E and the constants A, B, and C.

- Eliminating A, B, and C between these two equations, we obtain the transcendental equation for the eigenvalues:

$$k\cot(ka) = -\kappa.$$

Substituting $k = \sqrt{\frac{2\mu(V_0+E)}{\hbar^2}}$ and $\kappa = \sqrt{-\frac{2\mu E}{\hbar^2}}$ into the above equation, we can solve for E numerically to find the bound-state eigenvalues of the square-well potential for the deuteron-like system.

For the deuteron, the experimental data show that there is only one bound state with a binding energy $E_b = 2.225\,\mathrm{MeV}$. According to the model, the bound-state energy $E = -E_b$. When $a \approx 1.4\,\mathrm{fm}$, the above calculation yields $V_0 \approx 35\,\mathrm{MeV}$.

Another more realistic potential model is the Yukawa potential $V(r) = -V_0 \frac{e^{-\frac{r}{a}}}{r}$, which is more in line with the nature of the nuclear force. Solving the Schrödinger equation with the Yukawa potential is more complicated and usually requires numerical methods or approximation techniques such as the variational method or perturbation theory.

2.4 The role of Reduced Mass

The reduced mass accounts for the relative motion of two interacting particles. It effectively transforms the two-body problem into a single-particle problem with mass μ, simplifying the solution of the Schrödinger equation. In the deuteron:

- The proton and neutron orbit their common center of mass.
- The reduced mass captures the combined inertia of both particles, reflecting how each particle "feels" the other's motion.

- It plays a critical role in determining the relationship between the potential depth V_0 and the observed binding energy E_b.

The reduced mass μ in a two-body system (e.g., proton-neutron in the deuteron) is defined as:

$$\mu = \frac{m_p m_n}{m_p + m_n}$$

where $m_p \approx 938.27\,\mathrm{MeV}/c^2$ (proton mass) and $m_n \approx 939.57\,\mathrm{MeV}/c^2$ (neutron mass). For the deuteron, since $m_p \approx m_n$, we approximate $\mu \approx \frac{m_p}{2} \approx 469\,\mathrm{MeV}/c^2$.

3 Schrödinger equation and transition rates

The Schrödinger equation predicts the energy transition rate between atomic orbitals using time-dependent perturbation theory (also known as Fermi's Golden Rule). For a hydrogen atom transitioning from orbital $n = 2$ to $n = 1$, the steps involve solving the time-dependent Schrödinger equation under the influence of an external perturbation (e.g., electromagnetic radiation). Here's a detailed breakdown:

1. Setup: Time-Dependent Schrödinger Equation

The full Hamiltonian is split into a time-independent part (H_0) and a time-dependent perturbation ($H'(t)$):

$$i\hbar\frac{\partial}{\partial t}\psi(t) = [H_0 + H'(t)]\,\psi(t).$$

For hydrogen, H_0 describes the Coulomb interaction between the electron and proton. The perturbation $H'(t)$ typically represents the interaction with electromagnetic radiation (e.g., a photon field).

2. Perturbation Theory and Transition Probability

Assuming the perturbation is weak and short-lived, the transition probability $P_{i\to f}$ from an initial state $|i\rangle$ (e.g., $n = 2$) to a final state $|f\rangle$ (e.g., $n = 1$) is approximated by Fermi's Golden Rule:

$$P_{i\to f} = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\rho(E_f),$$

where:

- $\langle f|H'|i\rangle$ is the transition matrix element (integral of H' over the initial and final wavefunctions).

- $\rho(E_f)$ is the density of states at energy E_f .

3. Applying to Hydrogen Atom Transitions

For the $n = 2 \to n = 1$ transition:

a. Wavefunctions of Initial and Final States

The stationary states of hydrogen are given by the Schrödinger equation solutions:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi),$$

where $R_{nl}(r)$ is the radial wavefunction and $Y_{lm}(\theta, \phi)$ is the spherical harmonic.

For $n = 2$, possible states are $2s(l = 0)$ and $2p(l = 1)$. For $n = 1$, only $1s(l = 0)$ exists.

Selection Rules: Transitions are allowed only if $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$. Thus, $2p \to 1s$ is allowed, but $2s \to 1s$ is forbidden (electric dipole transition).

b. Transition Matrix Element

The perturbation H' for electromagnetic radiation is often approximated by the electric dipole interaction:

$$H' = -e\mathbf{r} \cdot \mathbf{E}(t),$$

where $\mathbf{E}(t)$ is the electric field of the radiation. Assuming monochromatic radiation with frequency ω, the matrix element becomes:

$$\langle 1s|H'|2p\rangle = -e\mathbf{E}_0 \cdot \int \psi_{1s}^* \mathbf{r} \psi_{2p} \, d^3r.$$

This integral simplifies due to symmetry. For $2p \to 1s$:

$$\int \psi_{1s}^* r \cos\theta \, \psi_{2p_z} \, d^3r \neq 0,$$

where

$$\psi_{2p_z} \propto r e^{-r/(2a_0)} \cos\theta.$$

c. Calculating the Matrix Element

The radial integral involves $R_{21}(r)$ and $R_{10}(r)$:

$$\int_0^\infty r^3 R_{10}(r) R_{21}(r) \, dr = \frac{256}{243} a_0^3,$$

where a_0 is the Bohr radius. The angular integral gives

$$\int Y_{00}^* \cos\theta \, Y_{10} \, d\Omega = \frac{4\pi}{3}.$$

Combining these, the matrix element squared is:

$$|\langle 1s|H'|2p\rangle|^2 = \frac{4e^2 E_0^2 a_0^2}{27}.$$

d. Density of States

For photons,

$$\rho(E_f) = \frac{V}{(2\pi\hbar)^3}\frac{E_f^2}{c^3},$$

where V is the volume and c is the speed of light. However, in practice, this is often combined with the Einstein coefficients or normalized to the radiation intensity.

4. Final Transition Rate

Substituting into Fermi's Golden Rule:

$$P_{2p\to 1s} = \frac{2\pi}{\hbar} \cdot \frac{4e^2E_0^2a_0^2}{27} \cdot \frac{VE_f^2}{(2\pi\hbar)^3c^3}.$$

For spontaneous emission (no external field), E_0^2 is replaced by the vacuum field fluctuations, leading to the Einstein A coefficient:

$$A_{2p\to 1s} = \frac{64\pi^4e^2}{3\epsilon_0 hc^3} \cdot \frac{1}{a_0^3} \cdot \left(\frac{\Delta E}{h}\right)^3,$$

where $\Delta E = E_2 - E_1 = \frac{3}{4} \times 13.6\,\text{eV}$.

5. Key Takeaways

- The Schrödinger equation provides the stationary states (ψ_{nlm}) needed to compute transition matrix elements.

- Time-dependent perturbation theory links these states to transition probabilities via Fermi's Golden Rule.

- Selection rules (derived from symmetry) determine which transitions are allowed.

- For hydrogen, the $2p \to 1s$ transition rate is experimentally confirmed and matches predictions from this framework.

This approach extends to other atoms and molecules, forming the basis for understanding spectroscopic line widths and radiative decay processes.

3.1 The vacuum field fluctuations

The analytical expression for the vacuum field fluctuations driving spontaneous emission arises from quantum electrodynamics (QED). These fluctuations represent the quantum mechanical zero-point energy of the electromagnetic field and play a crucial role in inducing transitions between atomic states. Here's a breakdown of the key equations:

- Vacuum Electric Field Fluctuations

In QED, the vacuum state of the electromagnetic field contains fluctuating electric fields. The root-mean-square (RMS) electric field E_{vac} at frequency ω is given by:

$$\langle E_{\text{vac}}^2 \rangle = \frac{\hbar \omega^3}{4\pi^2 \epsilon_0 c^3}.$$

- This arises from summing the zero-point energy $\frac{1}{2}\hbar\omega$ over all electromagnetic modes and relating energy density $u = \frac{1}{2}\epsilon_0 E^2$ to the mode density $\frac{V k^2 dk}{(2\pi)^3}$, where $k = \omega / c$.

3.1.1 Derivation of DOS

To derive the density of states (DOS) at energy E , denoted D(E) , we quantify the number of quantum states per unit energy interval around E . Below is a step-by-step derivation for a free particle in three dimensions (e.g., electrons in a metal), with generalizations for other dimensions.

1. Basic Setup

- System: A particle confined to a cubic box of volume $V = L^3$.

- Boundary Conditions: Periodic boundary conditions (Born-von Karman), leading to discrete wavevectors $\mathbf{k}$.

- Wavefunction: Plane wave

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}},$$

where

$$\mathbf{k} = \left(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right)$$

and $n_x, n_y, n_z \in \mathbb{Z}$.

2. Counting States in $\mathbf{k}$ -Space

- Volume per $\mathbf{k}$ -point: $\left(\frac{2\pi}{L}\right)^3$.

- Total states in a spherical shell: For a wavevector magnitude k, the number of states in dk is:

$$dN = \frac{\text{Volume of shell}}{(2\pi/L)^3} = \frac{4\pi k^2 dk}{(2\pi/L)^3} = \frac{V k^2 dk}{2\pi^2}.$$

- Spin Degeneracy: If particles have spin s, multiply by $2s+1$ (e.g., electrons: 2).

3. Convert to Energy Space

For a free particle, energy $E=\frac{\hbar^2 k^2}{2m}$. Solve for k:

$$k=\sqrt{\frac{2mE}{\hbar^2}}.$$

Differentiate to relate dk to dE:

$$dk=\frac{m}{\hbar^2 k}dE=\frac{\sqrt{2m}}{\hbar}\cdot\frac{dE}{2\sqrt{E}}.$$

Substitute dk into dN:

$$dN=\frac{V}{2\pi^2}\left(\frac{2mE}{\hbar^2}\right)\cdot\frac{\sqrt{2m}}{\hbar}\cdot\frac{dE}{2\sqrt{E}}.$$

Simplify to get the density of states:

$$D(E)=\frac{dN}{dE}=\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}.$$

For electrons (spin-$\frac{1}{2}$), multiply by 2:

$$D(E)=\frac{Vm^{3/2}}{\sqrt{2}\pi^2\hbar^3}\sqrt{E}.$$

4. Key Dimensions

- 3D: $D(E)\propto\sqrt{E}$ (as derived above).

- 2D: $D(E) = \frac{Am}{2\pi\hbar^2}$ (constant, where $A = L^2$).
- 1D: $D(E) \propto \frac{1}{\sqrt{E}}$.

5. Physical Interpretation

- Free Particles: $D(E)$ increases with $\sqrt{E}$, reflecting more available momentum states at higher energies.
- Interacting Systems: In crystals, $D(E)$ depends on the band structure $E(\mathbf{k})$, leading to features like van Hove singularities.
- Applications: Essential for calculating properties like heat capacity, electrical conductivity, and Fermi-Dirac distributions.

Example: Hydrogen Atom

For bound states (e.g., electrons in atoms), the density of states is discrete:

$$D(E) = \sum_n \delta(E - E_n),$$

where

$$E_n = -\frac{13.6\,\mathrm{eV}}{n^2}.$$

3.1.2 DOS for photons

The density of states (DOS) for photons is derived similarly to free particles but with key differences due to photons being massless bosons with energy $E = \hbar\omega = \hbar ck$, where ω is the angular frequency, c is the speed of light, and $k = |\mathbf{k}|$ is the wavevector magnitude. Below is the result from adapting the previous derivation for photons:

Photon Density of States

1. **3D Photons:** The DOS per unit volume is:

$$D(\omega) = \frac{\omega^2}{\pi^2 c^3}.$$

- Units: $\mathrm{Hz}^{-1} \cdot \mathrm{m}^{-3}$.

2. **Energy Representation:**

Using $E = \hbar\omega$, the DOS becomes:

$$D(E) = \frac{E^2}{\pi^2 \hbar^3 c^3}.$$

Key Differences from Free Particles

- **Dispersion Relation:**

- Free particles: $E = \frac{\hbar^2 k^2}{2m} \to D(E) \propto \sqrt{E}$.
- Photons: $E = \hbar c k \to D(E) \propto E^2$.

- **Spin Degeneracy:** Photons have 2 polarization states (helicity ±1), so the result includes a factor of 2.

- **Volume:** The DOS per unit volume $D(\omega)$ is often used in photon-related problems (e.g., blackbody radiation).

Example Application: Blackbody Radiation

The energy density $u(\omega)$ in thermal equilibrium is:

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \cdot \frac{1}{e^{\hbar\omega/(k_B T)} - 1},$$

where $D(\omega) = \frac{\omega^2}{\pi^2 c^3}$ appears explicitly.