PHY215-07: Schrodinger equation and transition rates

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April 16, 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 :

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

- 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 Orbitals

In atomic physics, the number of electrons that can fill each orbital is determined by the Pauli exclusion principle, which states that no two electrons in an atom can have the same set of quantum numbers. Each orbital is defined by the quantum numbers n, l, and m_l, and can hold a maximum of 2 electrons with opposite spins (governed by the spin quantum number $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$).

– Key Steps to Determine Orbitals and Electrons for $n = 3$ 1. Principal Quantum Number (n) Defines the electron shell. For $n = 3$, the possible values of the angular momentum quantum number (l) are $0, 1, 2$ (corresponding to s, p, d subshells).

2. Orbitals per Subshell (l) - For $l = 0$ (s subshell): Magnetic quantum number $m_l = 0 \rightarrow 1$ orbital. - For $l = 1$ (p subshell): $m_l = -1, 0, +1 \rightarrow 3$ orbitals. - For $l = 2$ (d subshell): $m_l = -2, -1, 0, +1, +2 \rightarrow 5$ orbitals.

Total orbitals for $n = 3$: $1 + 3 + 5 = \mathbf{9}$ orbitals.

3. Electrons per Orbital Each orbital can hold 2 electrons (spin - up and spin - down). Total electrons for $n = 3$: $9 \text{ orbitals} \times 2 \text{ electrons/orbital} = \mathbf{18}$ electrons.

– Common Confusion: Orbitals vs. Electrons - Orbitals: Defined by n, l, m_l. For $n = 3$, there are 9 orbitals (not 18). - Electrons: Each orbital holds 2 electrons (due to spin), so the $n = 3$ shell can hold 18 electrons in total.

– Summary - Each orbital: 2 electrons (spin - paired). - For

$n = 3$: - 9 orbitals (1 s, 3 p, 5 d). - 18 electrons in total (9 orbitals × 2 electrons/orbital).

This follows directly from the quantum numbers and the Pauli exclusion principle, which limits each orbital to two electrons with opposite spins.