MAU34403 - Quantum Mechanics I Brief Notes

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Operators

Non-Commuting Operators

For two operators \hat{A} and \hat{B} to commute, i.e. $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$, the two operators must share a common set of eigenvectors and associated eigenvalues.

Remember the canonical commutation relation

$$[\hat{x}, \hat{p}] = i\hbar.$$

Heisenberg Uncertainty Relations

The uncertainty (variance) in an observable is defined as

$$(\Delta A)^2 = \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2 = \langle \psi_A | \psi_A \rangle.$$

So, $(\Delta A)^2 (\Delta B)^2 = \langle \psi_A | \psi_A \rangle \langle \psi_B | \psi_B \rangle \ge |\langle \psi_A | \psi_B \rangle|^2$ by Cauchy-Schwarz. We can rewrite this as $|\langle \psi_A | \psi_B \rangle|^2 = \frac{1}{2i} (\langle \psi | [\hat{A}, \hat{B}] | \psi \rangle)^2$ so we have

$$\Delta A \Delta B \ge \frac{1}{2} |\langle C \rangle| = \frac{1}{2i} [\hat{A}, \hat{B}].$$

e.g. $\Delta x \Delta p \ge \frac{\hbar}{2}$ and $\Delta E \Delta t \ge \frac{\hbar}{2}$.

$$\frac{d}{dt}\left\langle Q\right\rangle = \frac{i}{\hbar}\left\langle \psi\right|\left[\hat{H},\hat{Q}\right]\left|\psi\right\rangle + \left\langle \frac{\partial\hat{Q}}{\partial t}\right\rangle$$

so we have, combining the two results,

$$\Delta H \Delta Q \ge \frac{1}{2} \left| \frac{1}{i} [\hat{H}, \hat{Q}] \right| = \frac{\hbar}{2} \left| \frac{d}{dt} \langle Q \rangle \right|$$

assuming $\frac{\partial \langle Q \rangle}{\partial d} = 0$ (true for steady-state systems).

One-Dimensional Problems

Potential Step



The potential step is given by $V(x) = \Theta(x)V_0$, where $\Theta(x) = \begin{cases} 1, x > 0 \\ 0, x < 0 \end{cases}$. For $0 < E < V_0$ and x < 0, we have

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

with solutions $\psi(x) = Ae^{ikx} + Be^{-ikx}$, $k = \frac{\sqrt{2mE}}{\hbar}$. The time-dependent solutions are found using the time evolution operator $\hat{U}(t) = e^{iEt/\hbar}$ to get

$$\psi(x,t) = \psi(x)e^{iEt/\hbar} = Ae^{i(kx-i\omega t)} + Be^{-i(kx+i\omega t)}$$

where $E = \hbar \omega$. Letting $v = \frac{E}{k}$, we have two waves; one right-moving and one left-moving.

$$\psi(x,t) = Ae^{ik(x-vt)} + Be^{-ik(x+vt)}$$

For x > 0, we have

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2}(V_0 - E)\psi(x)$$

with solutions $\psi(x) = Ce^{-kx} + De^{kx}$, $k = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$, so the probability of finding the particle behind the potential barrier is nonzero. We set D = 0 to ensure normalisability.

The boundary conditions are:

1) $\psi(x)$ is continuous,

2) $\psi'(x)$ is continuous for finite V(x).

The second condition is found by integrating the Schrödinger equation across the boundary.

$$\int_{x-\varepsilon}^{x+\varepsilon} \frac{d^2\psi}{dx^2} dx = \int_{x-\varepsilon}^{x+\varepsilon} \frac{2m}{\hbar^2} (V(x) - E)\psi(x) dx$$
$$\psi'(x+\varepsilon) - \psi'(x-\varepsilon) \le \frac{4m\varepsilon}{\hbar^2} (V(x) - E)_{\max}$$
$$= 0 \text{ as } \varepsilon \to 0.$$

The probability density is $\rho = \psi^*(x)\psi(x)$, and the probability current density is $J_x = \frac{\hbar}{2mi}(\psi^*\psi' - (\psi'^*)\psi)$, related by

$$\frac{d\rho}{dt} + \frac{dJ_x}{dx} = 0$$

For stationary states, $\frac{d\rho}{dt} = 0$ and $\frac{dJ_x}{dx} = 0$.

Harmonic Oscillator

The harmonic oscillator potential is $V(x) = \frac{1}{2}m\omega^2 \hat{x}^2$ and the TISE is

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

Letting $\xi = \sqrt{\frac{m\omega}{\hbar}}x$ and $\varepsilon = \frac{E}{\hbar\omega}$, we have

$$\frac{d^2\psi}{dx^2} + (2\varepsilon - \xi^2)\psi = 0.$$

For large ξ , we have solutions $\psi = Ae^{-\xi^2/2} + Be^{\xi^2/2}$, where we let B = 0 for normalisability. The exact solutions will be of the form $\psi = \nu(\xi)e^{-\xi^2/2}$. Letting $\nu(\xi) = \sum_{k=0}^{\infty} a_k \xi^k$, we get a recursion relation

$$a_{k+2} = \frac{2k - 2n}{(k+2)(k+1)}a_k$$

where $n = 2\varepsilon - 1$. For large k, we have $a_{k+2} \sim \frac{2}{k}a_k$, so to avoid a non-normalisable term, we need some $a_k = 0$ for $a_{k-2} \neq 0$. We then have 2k - 2n = 0, so the energies are given by $E = \hbar\omega(n + 1/2)$.

The solutions to $\nu(\xi)$ are the Hermite polynomials H_n , so

$$\psi_n(x) = C_n H_n e^{-\xi^2/2}, \quad \xi = \sqrt{\frac{m\omega}{\hbar}} x.$$

Three-Dimensional Problems

Radial Schrödinger Equation

We consider the separable solutions to the Schrödinger equation $\psi(\vec{r}) = R(r)Y_l^m(\theta, \phi)$, so that the TISE becomes

$$\left[-\frac{\hbar^2}{2m}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{L^2}{2mr} + V(r)\right]\psi = E\psi$$

The eigenvalues of the L^2 operator acting on $Y_l^m(\theta, \phi)$ are $l(l+1)\hbar Y_l^m(\theta, \phi)$, so

$$\left[-\frac{\hbar^2}{2m}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right]R(r) = ER(r).$$

Letting U(r) = rR(r), we have the Radial Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{d^2U(r)}{dr^2} + \left[\frac{l(l+1)}{2mr} + V(r)\right]U(r) = EU(r)$$

where we require $U(r) \to 0$ as $r \to \infty$.

Coulomb Potential

The Coulomb potential is $V(r) = -\frac{2e^2}{r}$. For values of r near 0, the TISE becomes

$$\frac{d^2U}{dr^2} - \frac{l(l+1)}{r^2}U = 0$$

which has solutions $U(r) = Ar^{l+1} + Br^{-l}, l \ge 0$. For large r, we have

$$\frac{d^2U}{dr^2} = -\frac{2mE}{\hbar^2}U = \kappa^2 U$$

where $\kappa^2 = -\frac{2mE}{\hbar^2} \implies E \leq 0$. The solutions are $U(r) = Ae^{-\kappa r} + Be^{\kappa r}$, but we let B = 0 to satisfy normalisation.

We have solutions $U(\rho) = \rho^{l+1} e^{-\rho} \omega(\rho)$, $\rho = \kappa r$, and assume

$$\omega(\rho) = \sum_{k=0}^{\infty} a_k \rho^k,$$

which yields the condition

$$a_{k+1} = \frac{2(k+l+1) - \rho_0}{(k+1)(k+2l+2)} a_k$$

where $\rho_0 = \frac{Ze^2\kappa}{|E|} = \sqrt{\frac{2m}{|E|}}\frac{Ze^2}{\hbar}.$

For large k, $a_{k+1} \sim \frac{1}{k}a_k$, so to avoid a e^{ρ} term, we require $a_{k+1} = 0$ for some a_k . Thus, we need $2(k+l+1) - \rho_0 = 0$ which gives us a condition for the energy

$$E_n = -\frac{Z^2 m e^4}{2\hbar^2 n^2}.$$

The solutions for $\omega(\rho)$ are

$$\omega(\rho) = CL_{n-l-1}^{2l+1}(2\rho),$$

which are the associated Laguerre polynomials, $L_{q-p}^{p}(x)$. The ground state wavefunction for this Coulomb potential is

$$\psi_{100}(r) = \sqrt{\frac{Z^3}{\pi a^3}} e^{-Zr/a}.$$

Two-Particle Systems

When interactions between particles is weak and the particles are distinguishable, we can write the state of a two-particle system $|\Psi(1,2)\rangle$ as a sum of direct products of one-particle states $|\psi\rangle = \sum_{i} c_i |q_i\rangle$

$$|\Psi(1,2)\rangle = \sum_{i,j} c_{ij} |q_i^{(1)}\rangle \otimes |q_j^{(2)}\rangle$$

However, if the particles are identical (as is the case for electrons), then $|\Psi(1,2)\rangle = |\Psi(2,1)\rangle$, so we have a symmetric Hamiltonian, such as

$$\hat{\mathcal{H}}(1,2) = \hat{\mathcal{H}}(2,1) = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m}$$

Pauli Exclusion Principle

It is known that for a pair of indistinguishable particles that if they have:

- $\frac{1}{2}$ -integer spin (fermions) they will have antisymmetric states,
- integer spin (bosons) they will have symmetric states.

If the two particles are fermions $(\frac{1}{2}$ -integer spin) then the wavefunction $\Psi_{-}(1,2)$ must be antisymmetric:

$$\Psi_{-}(1,2) = \frac{1}{\sqrt{2}} \left[\psi_{a_1}(\vec{x}_1)\psi_{a_2}(\vec{x}_2) - \psi_{a_1}(\vec{x}_2)\psi_{a_2}(\vec{x}_1) \right].$$

Notice that if the two particles have the same set of quantum numbers, i.e. $a_1 = a_2$, then the wavefunction is zero, so there is zero probability of finding the two particles in the same state. Fermions cannot exist in the same state.

However, bosons (integer spin) prefer to be in the same state (same wavefunction, just with a +).

Exchange Force

The expectation value for the (one-dimensional) separation of fermions (-) and bosons (+) is

$$\left\langle (x_1 - x_2)^2 \right\rangle_{\pm} = \left\langle x^2 \right\rangle_{a_1} - 2 \left\langle x \right\rangle_{a_1} \left\langle x \right\rangle_{a_2} + \left\langle x^2 \right\rangle_{a_2} \mp 2 \left| \left\langle x \right\rangle_{a_1 a_2} \right|^2$$

so, fermions tend to be further apart and bosons tend to be closer together (exchange force).

The Hydrogen Molecule

The Exchange Force tells us that if the spatial part of the wavefunction is symmetric, the electrons will tend to be closer together, which results in a region of negative charge that attracts the protons (covalent bonding). However, we know that the total wavefunction of a two-electron system must be antisymmetric. This discrepancy can be resolved by taking into account electron spin, since an antisymmetric spin wavefunction times a symmetric spatial wavefunction will result in an antisymmetric total wavefunction:

$$\Psi(1,2) = \psi_{nlm}(\vec{x})\chi_{s_z} = A\underbrace{[\psi_{a_1}(\vec{x}_1)\psi_{a_2}(\vec{x}_2) \pm \psi_{a_1}(\vec{x}_2)\psi_{a_2}(\vec{x}_1)]}_{\text{spatial part}}\underbrace{[|\uparrow\rangle_1 |\downarrow\rangle_2 \pm |\downarrow\rangle_1 |\uparrow\rangle_2]}_{\text{spin part}}$$

Helium

The Helium atom is a two-electron system with total nuclear charge $Z = \frac{2}{4\pi\varepsilon_0}$ (= 2 in cgs units). The Hamiltonian is

$$\mathcal{H} = \left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{r_1}\right) + \left(-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_2}\right) + \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|r_1 - r_2|}}_{\text{electron repulsion}}$$

Ignoring the electron repulsion term, this becomes $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$, which has solutions consisting of a combination of Hydrogen atom wavefunctions with Z = 2:

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_{n_1 l_1 m_1}(\vec{r}_1) \psi_{n_2 l_2 m_2}(\vec{r}_2)$$

The energies are in terms of Hydrogen atom energies $E = 4(E_{n_1} + E_{n_2})$. The ground state wavefunction is given by

$$\Psi_0(\vec{r_1}, \vec{r_2}) = \psi_{100}(\vec{r_1})\psi_{100}(\vec{r_2}) = \frac{8}{\pi a^3} e^{-2(r_1 + r_2)/a}$$

and the ground state energy is $E_0 = 8(-13.6 \text{ eV}) = -109 \text{ eV}$. The actual value is closer to -79 eV (See Homework 5, Q1 (ii)).

The ground state wavefunction is symmetric, so we must have an antisymmetric spin state. The total ground state wavefunction, including spin, is given by

$$\Psi_0(\vec{r_1},\vec{r_2}) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a} \left(\left|\uparrow\right\rangle_1 \left|\downarrow\right\rangle_2 - \left|\downarrow\right\rangle_1 \left|\uparrow\right\rangle_2\right).$$

The spin states can also be written as vectors $|\uparrow\rangle = \begin{pmatrix} 1\\ 0 \end{pmatrix}$ and $|\downarrow\rangle = \begin{pmatrix} 0\\ 1 \end{pmatrix}$.