

Quantum mechanics / 4.

- Time dependant Schr. eq.
- Perturbation theory
- Transition probability
- Formal quantum mechanics
- Measurement theory

- Time dependent Schrödinger eq.

Question: time dependence of Ψ

Formally: Schr.:
$$\left. \begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + E_p\Psi &= E\Psi \\ \frac{p^2}{2m} + E_p &= E \end{aligned} \right\} p = \frac{\hbar}{i} \frac{d}{dx}$$

Heisenberg's uncertainty principle

$$\left. \begin{aligned} \Delta x \Delta p &\geq \hbar \\ \Delta E \Delta t &\geq \hbar \end{aligned} \right\} E = i\hbar \frac{\partial \Psi}{\partial t}$$

→ Time dependant Schr. eq.

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + E_p\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Not a wave equation (more like transport, but complex)

Solution: try separation by space and time coordinates

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \psi(x)e^{-\frac{iEt}{\hbar}} \quad \frac{\partial^2 \Psi}{\partial x^2} = \frac{\partial^2 \psi}{\partial x^2} e^{-\frac{iEt}{\hbar}}$$

Substituting:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + E_p\psi = E\psi \quad \leftarrow \text{stationary equation}$$

$\rightsquigarrow E$ is the full energy

Since $\psi \sim e^{iEt/\hbar} = e^{i\omega t}$ the wavefunction oscillates with $\omega = \frac{E}{\hbar}$ (de Broglie!)

E.g.

- Particle moving to direction +x : $\psi(x) = A e^{ikx} \rightsquigarrow$

$$\Psi(x,t) = \psi(x)e^{iEt/\hbar} = A e^{i(kx - \omega t)} \equiv \text{wave moving in the +x direction}$$

Phase velocity of the waves

$$v_{ph} = \frac{\omega}{k} = \frac{E}{p}$$

- Particle in a potential box:

$$\psi(x) = A \sin \frac{n\pi x}{a} = \frac{A}{2i} \left(e^{\frac{i n \pi x}{a}} - e^{-\frac{i n \pi x}{a}} \right)$$

$$\psi(x,t) = A \sin \frac{n\pi x}{a} e^{-\frac{i E t}{\hbar}} =$$

$$= \frac{A}{2i} \left[e^{i \left(\frac{n\pi x}{a} - \frac{E t}{\hbar} \right)} - e^{-i \left(\frac{n\pi x}{a} + \frac{E t}{\hbar} \right)} \right]$$

Two counter-propagating waves \rightarrow standing wave

The solutions $\psi(x,t) = \psi(x) e^{-\frac{i E t}{\hbar}}$ are stationary since: $\psi(x,t) = \psi(x) e^{-\frac{i E t}{\hbar}}$

$$|\psi(x,t)|^2 = \left[\psi^*(x) e^{\frac{i E t}{\hbar}} \right] \left[\psi(x) e^{-\frac{i E t}{\hbar}} \right] = |\psi(x)|^2$$

There exist non-stationary solutions as well!

It can be proven that these are linear combinations of the stationary states:

$$\psi(x,t) = \sum_n C_n \psi_n(x) e^{-\frac{i E_n t}{\hbar}}$$

e.g.

$$\psi(x,t) = C_1 \psi_1 e^{-\frac{i E_1 t}{\hbar}} + C_2 \psi_2 e^{-\frac{i E_2 t}{\hbar}}$$

$$t=0: \psi(x,0) = C_1 \psi_1 + C_2 \psi_2$$

(\leftarrow this and the non-linear condition determines C_1, C_2)

The probability density

$$P(x,t) = |\psi(x,t)|^2 = |C_1 \psi_1|^2 + |C_2 \psi_2|^2 + C_1 C_2^* \psi_1 \psi_2^* e^{-\frac{i(E_1 - E_2)t}{\hbar}} + C_1^* C_2 \psi_1^* \psi_2 e^{\frac{i(E_1 - E_2)t}{\hbar}}$$

i.e. $P(x,t)$ oscillates with angular frequency

$$\omega = \frac{E_1 - E_2}{\hbar}$$

In general: the non-stationary states are the sums of states oscillating with $(E_n - E_{n'})/\hbar$ frequencies

This describes transitions between two stationary states of energy E_1 and E_2

In case of a charged particle, during the transition

P oscillates with $\omega = (E_1 - E_2) / \hbar \rightsquigarrow$

emission or absorption of electromagnetic wave

$$E_1 - E_2 = h\nu \implies \text{Bohr equation}$$

— Why does a system get into a non-stationary state?

Perturbation theory

E.g. Excitation of an electron of an atom
ground state \rightarrow excited state transition

$E_p = \text{atomic potential} + \text{external perturbing potential}$

Soln. eq.: $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + (E_p + K)\psi = i\hbar \frac{\partial\psi}{\partial t}$

$$K = K(t)$$

Can be expanded into series by the powers of the ^{perturbing} potential energy V

$$K=0 \quad \psi_i e^{-\frac{i}{\hbar} E_i t}$$

solutions (atomic wave functions)

$$K \neq 0 \quad \psi = \sum_r C_r(t) \psi_r e^{-\frac{i}{\hbar} E_r t}$$

we look for solution in this form

Substituting ψ into the Soln. eq., making use of

that ψ_r 's are orthonormal \rightarrow set of equations for C_r 's

$$\frac{dC_r}{dt} = -\frac{i}{\hbar} \sum_r K_{rt} C_r e^{i\omega_{rt}}$$

$$K_{rt} = \int \psi_r K(t) \psi_r dx$$

$$\omega_{rt} = \frac{E_r - E_r}{\hbar}$$

Solution with successive approximation

nth approximation

$$C_k^{(n)}(t) = C_k^{(n-1)}(0) - \frac{i}{\hbar} \sum_r \int_0^t K_{kr}(\tau) e^{i\omega_{kr}\tau} C_r^{(n-1)}(\tau) d\tau$$

Weak perturbation: K appears at $t=0$ but the system is for some time in the vicinity of the initial state (i)

$$C_r^{(0)}(t) = \begin{cases} 1 & r=i \\ 0 & r \neq i \end{cases} = \delta_{ri}$$

$$C_k^{(1)}(t) = \delta_{ki} - \frac{i}{\hbar} \int_0^t K_{ki}(\tau) e^{i\omega_{ki}\tau} d\tau$$

Transition probability

$$W(i \rightarrow k) = |C_k(t)|^2 = \frac{1}{\hbar^2} \left| \int_0^t K_{ki}(\tau) e^{i\omega_{ki}\tau} d\tau \right|^2 \quad i \neq k$$

Depends on the "matrix element" K_{ki}

When $K_{ki} = 0 \rightarrow$ forbidden transition (in 1st approximation)

Reason: it is against some conservation principle (e.g. angular momentum)

Selection rules

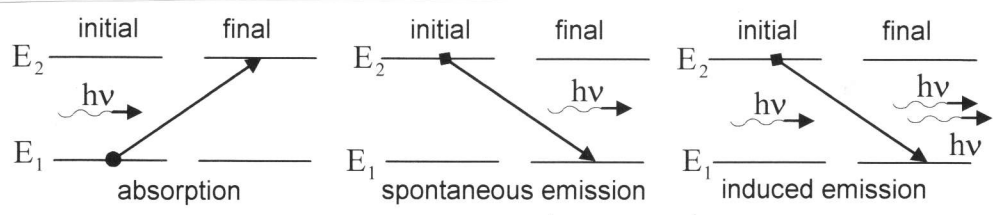
Higher order transitions \rightarrow smaller probabilities

- Selection rules for a harmonic oscillator

$\Delta n = \pm 1$ absorption at a single frequency emission

$\hbar\omega = E_{n+1} - E_n =$ eigenfrequency of the oscillator

- Radiative transitions



lifetime of excited state $\sim 1/W(g \rightarrow g')$ all permitted transitions
 atoms, molecules $\sim 10^{-8}$ sec
 nuclei: $\sim 10^{-8} - 10^{-4}$ sec

Formal quantum mechanics

Schrodinger eq. \rightarrow energy of the system only

Formal theory \rightarrow how to get all the physical information about the system

Schr. eq.: $\left\{ \frac{1}{2m} \left(-\hbar^2 \frac{d^2}{dx^2} \right) + E_p(x) \right\} \psi(x) = E \psi(x)$

OPERATOR \leftarrow acting upon $\psi(x)$
(e.g. derivation, multiplication etc.)

$\hat{H} = \frac{1}{2m} \left(-\hbar^2 \frac{d^2}{dx^2} \right) + E_p(x)$ Hamilton operator

$\hat{H} \psi(x) = E \psi(x)$ where $E = \text{const.}$ (The energy of the system)

\downarrow
This equation holds only for selected $\psi(x)$ functions

These are the eigenfunctions of the \hat{H} operator with E eigenvalues

For any operator

$\hat{A} \psi(x) = a \psi(x)$ eigenvalue equation \rightarrow

$\{ a_1, a_2, a_3, \dots \}$ and $\{ \psi_1, \psi_2, \psi_3, \dots \}$

set of eigenvalues and eigenfunctions

In quantum mechanics the operators representing physical quantities are Hermitian, i.e.:

$$\int \phi_1^* \hat{A} \phi_2 d\tau = \int [\hat{A} \phi_2]^* \phi_1 d\tau$$

Eigenvalues of Hermitian operators are real and their eigenfunctions are

orthogonal. $\int \psi_i^* \psi_k d\tau = \delta_{ik}$

(and form a complete set in the Hilbert space)

H - energy: (Hamilton operator)

$H_{\text{classical}} = \frac{p^2}{2m} + E_p(x)$ full energy

In quantum mechanics $p \rightarrow \hat{p} = -i\hbar \frac{d}{dx}$

$\hat{H}_{\text{q.m.}} = \frac{\hat{p}^2}{2m} + E_p(x)$

In 3 dimensions: $\hat{p}_x \rightarrow -i\hbar \frac{\partial}{\partial x}$ $\hat{p}_y \rightarrow -i\hbar \frac{\partial}{\partial y}$ $\hat{p}_z \rightarrow -i\hbar \frac{\partial}{\partial z}$

$\hat{p} \rightarrow -i\hbar \left[\frac{\partial}{\partial x} \underline{u}_x + \frac{\partial}{\partial y} \underline{u}_y + \frac{\partial}{\partial z} \underline{u}_z \right] = -i\hbar \underline{\nabla}$

$\hat{H} = -\frac{\hbar^2}{2m} \underline{\nabla}^2 + E_p(r)$

I. To any $A(r, p)$ physical quantity there is a corresponding quantum operator with the replacement $p \rightarrow -i\hbar \underline{\nabla}$ $A(r, -i\hbar \underline{\nabla})$

Quantity	Classical def.	Quantum operator
position	\underline{r}	\underline{r}
momentum	\underline{p}	$-i\hbar \underline{\nabla}$
angular momentum	$\underline{r} \times \underline{p}$	$-i\hbar \underline{r} \times \underline{\nabla}$
kinetic energy	$\frac{p^2}{2m}$	$-\left(\frac{\hbar^2}{2m}\right) \underline{\nabla}^2$
total energy	$\frac{p^2}{2m} + E_p(r)$	$-\left(\frac{\hbar^2}{2m}\right) \underline{\nabla}^2 + E_p(r)$

II. When we measure the physical quantity $A(r, p)$ of the system, the measurement results can only be the eigenvalues of the $\hat{A}(r, -i\hbar \underline{\nabla})$ operator

$\hat{A}(r, -i\hbar \underline{\nabla}) \psi = a \psi$

a_1, a_2, a_3, \dots

$\psi_1, \psi_2, \psi_3, \dots$

What happens when the system is not in an eigenstate of \hat{A} , i.e. $\hat{A}\psi \neq a\psi$ (for all ψ)

$\rightarrow A$ is indetermined - ψ can be expanded.

$$\psi = \sum_n c_n \psi_n \quad \text{where} \quad c_n = \int_{\text{space}} \psi_n^* \psi d\tau$$

III. If the system is in state with wavefunction ψ that is not an eigenstate of \hat{A} , then when we measure A , the probability of getting the result a_n is $|c_n|^2$ where $\int_{\text{space}} \psi_n^* \psi d\tau = c_n$ and a_n is the eigenvalue of \hat{A} in state ψ_n .

In such a ψ state only the expectation value of A can be calculated

$$\begin{aligned} A_e &= \int_{\text{space}} \psi^* \hat{A} (\mathbf{r}, i\hbar \nabla) \psi d\tau = \\ &= \int \psi^* \hat{A} \sum_n c_n \psi_n d\tau = \int \psi^* \sum_n c_n \hat{A} \psi_n d\tau = \\ &= \int \psi^* \sum_n c_n a_n \psi_n d\tau = \sum_n c_n a_n \int \psi^* \psi_n d\tau = \\ &= \sum_n c_n a_n c_n^* = \sum_n |c_n|^2 a_n \end{aligned}$$

At each individual measurement we get one of the a_n eigenvalues, however the average of many measurements is A_e . ψ contains all possible information about the system

IV. Evolution of a system in time is described

by $i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$

the time dependent Schrödinger equation

Matrix formalism

Eigenfunctions of \hat{H} are $\psi_1, \psi_2, \psi_3 \dots$ i.e. $\hat{H}\psi_n = E_n\psi_n$

Let A be another physical quantity with \hat{A} operator

$$A_{mn} = \int \psi_m^* \hat{A} \psi_n d\tau \rightarrow \text{matrix elements}$$

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} \dots \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \dots \\ \vdots & & \end{pmatrix}$$

E.g., matrix of $\hat{H} \rightarrow$

Because $\hat{H} \psi_i = E_i \psi_i$ ($i \neq j$)

$$= \int \psi_i^* \hat{H} \psi_j d\tau = E_j \int \psi_i^* \psi_j d\tau = 0$$

$$\begin{pmatrix} E_1 & 0 & 0 \dots \\ 0 & E_2 & 0 \\ 0 & 0 & E_3 \dots \\ \vdots & & \end{pmatrix}$$

(noninteraction)

A state \leftrightarrow state vector

$$\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \end{pmatrix}$$

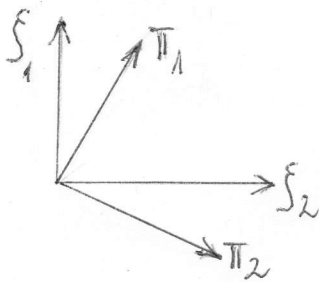
state vector of a state with energy E_i

$$\begin{pmatrix} 0 \\ \vdots \\ \psi_i \\ \vdots \\ 0 \end{pmatrix} \begin{pmatrix} E_1 & & \\ & E_2 & \\ & & \ddots \\ & & & E_i \end{pmatrix} \begin{pmatrix} 0 \\ \vdots \\ \psi_i \\ \vdots \\ 0 \end{pmatrix} = E_i \psi_i$$

E.g.: system with 2 states

$$\hat{x} \quad \begin{cases} \xi_1 \\ \xi_2 \end{cases} \text{ eigenfunctions} \quad \begin{pmatrix} x_{11} & 0 \\ 0 & x_{22} \end{pmatrix}$$

$$\hat{p} \quad \text{in the system of } \xi_1 \text{ and } \xi_2 \quad \begin{pmatrix} p_{11} & p_{12} \\ p_{21} & p_{22} \end{pmatrix} \quad p_{ik} = \int \xi_i^* \hat{p} \xi_k d\tau$$



ξ_1, ξ_2 are orthonormal eigenfunctions
 π_1, π_2 can be expanded as linear combinations of ξ_1 and ξ_2 and vice versa

Measurement: measure $x \rightarrow$ let the system be in ξ_1 state
 but $\xi_1 = a\pi_1 + b\pi_2 \rightarrow p$ is indefinite
 probability of measuring $p_1 = \int \pi_1^* \hat{p} \pi_1 d\tau$
 is $|a|^2$ and $|b|^2$ for p_2 for simultaneous
 measurement of x and p
 \rightarrow Uncertainty relationship

There exist physical quantities with joint system of eigenfunctions $\hat{H}\psi_i = E_i\psi_i$

E.g. energy \hat{H} and angular momentum $\hat{L}\psi_i = L_i\psi_i$

Eigenvalues of \hat{H} (E_i) can be degenerate \rightarrow the same

E_i corresponds to multiple $\psi_i^{(k)}$ -s. (e.g. E_i in 3dim)

Resolution of degeneracy: $\psi_i^{(k)}$ -s differ in some other physical quantity (e.g. angular mom.) while the energy of these states is identical

$$\hat{L}\psi_i^{(k)} = l_i^{(k)}\psi_i^{(k)}$$

the system is characterized by the quantum numbers i, k

$\psi_i^{(k)} = \psi_i \chi_k$ where ψ_i and χ_k are the eigenfunctions of two operators of two different physical quantities (e.g. $i, k \rightarrow$ selected combinations only)

A real system: multiple quantum numbers
e.g. electron in a H atom $\psi_{n, l, m}$ 4 quantum nos

When measuring these quantities \rightarrow eigenvalues
Other physical quantities - no joint set of eigenfunctions
 \rightarrow individual eigenvalues probabilities only.

Operators with joint set of eigenfunctions: are commutative

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \quad \text{i.e.} \quad [\hat{A}, \hat{B}]\psi = 0 \psi$$

For these quantities the uncertainty relationship \downarrow :

$$\Delta A \cdot \Delta B = 0$$

Non-commutative operators

$$\begin{aligned} \text{e.g. } (\hat{p}_x \cdot \hat{x} - \hat{x} \cdot \hat{p}_x)\psi &= (-i\hbar \frac{\partial}{\partial x} x + i\hbar x \frac{\partial}{\partial x})\psi = \\ &= -i\hbar \left(\psi + x \frac{\partial \psi}{\partial x} \right) + i\hbar x \frac{\partial \psi}{\partial x} = -i\hbar \psi \neq 0 \end{aligned}$$

They do not have a joint set of eigenfunction \rightarrow
uncertainty relationship \uparrow $\Delta x \cdot \Delta p_x \geq \hbar$