

Review of Fundamentals

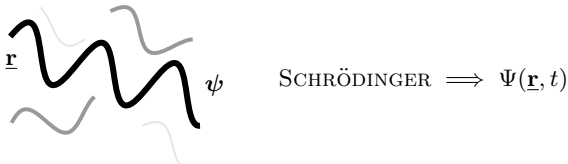
Classical Theory:



$$\text{Hamiltonian: } H = T_{\text{KIN}} + V_{\text{POT}} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad i = \{1, 2, \dots, n\}$$

Quantum Theory:



$$\text{Hamiltonian: } \underline{p}_i \rightarrow -i\hbar\nabla_i$$

General Linear Operators:

$$\Omega(af + bg) = a\Omega(f) + b\Omega(g)$$

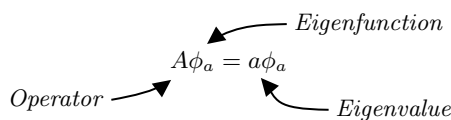
The Postulates of Quantum Mechanics:

I The state of a system is described by a complex wavefunction $\Psi(\mathbf{r}, t)$. If normalised properly,

$$\int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1,$$

then $|\Psi(\mathbf{r}, t)|^2 d\mathbf{r}$ is the probability of finding the particle between $\mathbf{r} \rightarrow \mathbf{r} + d\mathbf{r}$ at time t .

II Observable quantities are described by linear hermitian operators. A linear Hermitian operator has real eigenvalues, and its eigenfunctions may be chosen to obey an orthonormality relation.



III If we measure an observable A when the wavefunction is ψ , the possible outcomes are the eigenvalues a . We measure a with probability...

$$\mathbb{P}(a) = \left| \int_{-\infty}^{\infty} \phi_a \psi d\mathbf{r} \right|^2.$$

A consequence of this is that the expectation value of our measurement is

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^* A \psi d\mathbf{r}.$$

IV When we make the measurement and find the answer a , the wavefunction instantly collapses to the associated eigenfunction ϕ_a ...

$$\psi(\mathbf{r}, t) \xrightarrow[a]{\text{MEASURE}} \phi_a(\mathbf{r}, t)$$

IV In the absence of measurement, a state ψ , varies with time according to the Schrödinger equation...

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

Hamiltonian

The Formal Structure of Quantum Mechanics

The Adjoint of an Operator:

Given the operator A , its adjoint A^\dagger is defined such that...

$$\int \phi^* A \psi d\mathbf{r} = \int (A^\dagger \phi)^* \psi d\mathbf{r}.$$

$$(A + B)^\dagger = A^\dagger + B^\dagger \quad (cA)^\dagger = c^* A^\dagger$$

$$(A^\dagger)^\dagger = A \quad (AB)^\dagger = B^\dagger A^\dagger$$

Self-Adjoint Operators:

"Hermitian Operators"

An operators A is self-adjoint if $A^\dagger = A$.

$$\dots \implies \langle A \rangle = \langle A \rangle^*_{\text{Real Eigenvalues}}$$

$$[A, B] = 0 \xrightarrow{\text{IFF}} (AB)^\dagger \equiv AB$$

$$(AB + BA)^\dagger \equiv AB + BA \quad [i(AB - BA)]^\dagger \equiv i(AB - BA)$$

Gram-Schmidt Orthogonalisation:

Consider a pair of normalised eigenfunctions, ϕ_a and ϕ_b , which share the same eigenvalue a such that...

$$A\phi_\alpha = a\phi_\alpha \quad \text{and} \quad B\phi_\beta = a\phi_\beta \quad \text{with} \quad \int \phi_\alpha^* \phi_\beta d\mathbf{r} = S \neq 0.$$

$$\text{G-S} \implies \phi_{\beta'} = \phi_\beta - S\phi_\alpha \xrightarrow{\dots} \phi_{\beta'} = \frac{\phi_\beta}{\sqrt{1 - |S|^2}}$$

Completeness:

(Discrete Case)

Assuming that the hermitian operator A has a discrete set of eigenvalues $\{a\}$, which for convenience are not degenerate, the eigenfunctions $\phi_a(\mathbf{r})$ of A have two important properties...

(1) The eigenfunctions of A are normalisable.

$$\implies \int \phi_a^* \phi_{a'} d\mathbf{r} = \delta_{aa'}$$

(2) The eigenfunctions form a complete set.

$$\xrightarrow{\text{Superposition}} \Psi(\mathbf{r}, t) = \sum_a c_a(t) \phi_a(\mathbf{r})$$

" $\{\phi_a\}$ is a complete, orthonormal, basis set."

Closure:

$$\sum_a \phi_a^*(\mathbf{r}') \phi_a(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}') \implies \text{III: } \langle A \rangle = \sum_a |c_a|^2 a$$

From sifting property
 $f(\mathbf{r}) = \int \delta(\mathbf{r} - \mathbf{r}') f(\mathbf{r}') d\mathbf{r}$

The Uncertainty Principle:

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2$$

Variance $\implies \Delta A$ is the uncertainty

The general Heisenberg uncertainty principle is...

$$(\Delta A)^2 (\Delta B)^2 \geq -\frac{1}{4} \langle [A, B] \rangle^2.$$

$$[x, p_x] = i\hbar \implies \Delta x \Delta p_x \geq \hbar/2$$

Time Evolution:

$$\text{IV: } i\hbar \frac{\partial \psi}{\partial t} = H\psi \implies \psi(\mathbf{r}, t) = \sum_E a_E \phi_E(\mathbf{r}) \exp\left(\frac{-iEt}{\hbar}\right)$$

The Ehrenfest Theorem:

$$\frac{d}{dt} \langle A \rangle = \frac{1}{i\hbar} \langle [A, H] \rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle$$

Dirac Bracket Notation:

$$\int \psi^* A \phi \, d\mathbf{r} = \langle \psi | A | \phi \rangle \quad \int \phi_m^* A \phi_n \, d\mathbf{r} = \langle m | A | n \rangle$$

$$\text{Orthonormality:} \quad \int \phi_m^* \phi_n \, d\mathbf{r} = \langle m | n \rangle = \delta_{mn} \quad \text{Hermitian:} \quad \langle m | A | n \rangle = \langle m | A | n \rangle^*$$

$$\Rightarrow |\psi\rangle = \sum_a c_a |a\rangle$$

Closure Rule:

$$\sum_a P_a = \sum_a |a\rangle \langle a| = \mathbb{1}$$

Projection Operator
 $P_a |\psi\rangle = |a\rangle \langle a | \psi \rangle = c_a |a\rangle$

The Particle Density Operator:

$$\rho(\mathbf{r}', t) = |\psi(\mathbf{r}', t)|^2 = \int \psi^*(\mathbf{r}, t) \delta(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}, t) \, d\mathbf{r} = \langle \delta(\mathbf{r} - \mathbf{r}') \rangle$$

$$\delta(\mathbf{r} - \mathbf{r}') = \delta(x - x') \delta(y - y') \delta(z - z')$$

Many Particle Systems:

$$H(1, 2) = H_1(1) + H_2(2) + H'(1, 2)$$

$$\text{Non-Interacting: } H'(1, 2) = 0 \quad \text{Interacting: } H'(1, 2) \neq 0$$

Non-Interacting:

$$H(1, 2, \dots, N) = \sum_{i=1}^N H_i(i) \Rightarrow \Phi(1, 2, \dots, N) = \prod_{i=1}^N \phi_{E_i}^{(i)}$$

$$E = E_1 + E_2 + \dots + E_N = \sum_{i=1}^N E_i$$

Systems of Two Identical Particles:

$$\text{Two Identical Particles} \Rightarrow H(1, 2) \equiv H(2, 1)$$

Binary Exchange Operator:

$$\mathcal{P}\Psi(1, 2) = \Psi(2, 1) \quad \mathcal{P}^2\Psi(1, 2) = \Psi(1, 2)$$

$$\mathcal{P}\Phi = \lambda\Phi \xRightarrow{\mathcal{P}^2=1} \lambda = \pm 1$$

Binary Identical Particles Eigenfunctions:

$$\mathcal{P}\Phi_+(1, 2) = +\Phi(1, 2) \quad \mathcal{P}\Phi_-(1, 2) = -\Phi(1, 2)$$

$$\underbrace{\Phi_+(1, 2) \equiv \Phi_+(2, 1)}_{\text{Symmetric}} \quad \underbrace{\Phi_-(1, 2) \equiv -\Phi_-(2, 1)}_{\text{Asymmetric}}$$

Suppose we have a state Ψ , which is a linear combination of a symmetric and an anti-symmetric function such that...

$$\Psi = a\Psi_S + b\Psi_A,$$

then the observable probability density is...

$$|\Psi|^2 = \underbrace{|a|^2 |\Psi_S|^2}_{\text{Symmetric}} + \underbrace{|b|^2 |\Psi_A|^2}_{\text{Symmetric}} + \underbrace{a^* b \Psi_S^* \Psi_A}_{\text{Asymmetric}} + \underbrace{a b^* \Psi_S \Psi_A^*}_{\text{Asymmetric}}$$

Thus, for $|\Psi|^2$ to be symmetric under interchange as it is observable $\Rightarrow a = 0$ or $b = 0$.

"In general, a state of identical particles must be either symmetric or asymmetric."

General Exchange Operator:

$$\mathcal{P}_{\alpha\beta}\Psi(\dots, \alpha, \dots, \beta, \dots) = \Psi(\dots, \beta, \dots, \alpha, \dots)$$

$$\mathcal{P}_{\alpha\beta}\Phi_{\pm}(\dots, \alpha, \dots, \beta, \dots) = \pm \Phi_{\pm}(\dots, \beta, \dots, \alpha, \dots)$$

For the negative eigenvalue $\lambda = -1$ of P , the wavefunction is asymmetric and the particle is a fermion (1/2-integer spin). For the positive eigenvalue $\lambda = +1$, the wavefunction is symmetric and the particle is a boson (integer spin).

Symmetric and Asymmetric Construction:

$$\Phi_A(1, 2) = \frac{1}{\sqrt{2}} [\Phi(1, 2) - \Phi(2, 1)] = -\Phi_A(2, 1)$$

$$\Phi_S(1, 2) = \frac{1}{\sqrt{2}} [\Phi(1, 2) + \Phi(2, 1)] = +\Phi_S(2, 1)$$

Fermion Wavefunctions:

Suppose a non-interacting fermion system, where $\Phi(1, 2) = \phi_a(1)\phi_b(2)$, the asymmetrical wavefunction is...

$$\Phi_A(1, 2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)]$$

In general, for N fermions, we can write an asymmetric wavefunction as a slater determinant...

$$\Phi_A = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & \cdots & \phi_a(N) \\ \phi_b(1) & \phi_b(2) & \cdots & \phi_b(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N) \end{vmatrix}$$

If two rows are identical, the determinant is zero. This physically means that two particles in the same state has no wavefunction... \Rightarrow THE EXCLUSION PRINCIPLE

Boson Wavefunctions:

Suppose a non-interacting boson system, the symmetrical wavefunction is...

$$\Phi_S(1, 2) = \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]$$

In general, for N bosons, we can write a symmetric wavefunction as a slater permanent... $- \rightarrow +$

$$\Phi_S = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_a(2) & \cdots & \phi_a(N) \\ \phi_b(1) & \phi_b(2) & \cdots & \phi_b(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(1) & \phi_N(2) & \cdots & \phi_N(N) \end{vmatrix}_+$$

Many Particle Density Operator:

$$\rho(\mathbf{r}', t) = \sum_{i=1}^N \rho_i(\mathbf{r}', t) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}') \right\rangle = \langle \varrho(\mathbf{r}') \rangle$$

Angular Momentum and Spin

Angular Momentum:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \times \begin{bmatrix} p_x \\ p_y \\ p_z \end{bmatrix} = \begin{bmatrix} yp_z - zp_y \\ zp_x - xp_z \\ xp_y - yp_x \end{bmatrix} = \begin{bmatrix} L_x \\ L_y \\ L_z \end{bmatrix}$$

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x} \quad p_y \rightarrow -i\hbar \frac{\partial}{\partial y} \quad p_z \rightarrow -i\hbar \frac{\partial}{\partial z}$$

$$\mathbf{L}^2 = \mathbf{L} \cdot \mathbf{L} = L_x^2 + L_y^2 + L_z^2$$

Angular Momentum Eigenfunctions:

$$\mathbf{L}^2 Y(\vartheta, \varphi) = W Y(\vartheta, \varphi)$$

The solutions are spherical harmonics, which are simultaneous eigenstates of both \mathbf{L}^2 and L_z ...

$$\mathbf{L}^2 Y_\ell^m(\vartheta, \varphi) = \ell(\ell+1)\hbar^2 Y_\ell^m(\vartheta, \varphi)$$

Operator \rightarrow \leftarrow Quantum Number (ℓ, m)

$$L_z Y_\ell^m(\vartheta, \varphi) = m\hbar Y_\ell^m(\vartheta, \varphi)$$

$$\ell = 0, 1, 2, 3, \dots \quad m = -\ell, \dots, 0, \dots, +\ell$$

Commutator Rules:

$$[L_x, L_y] = i\hbar L_z \quad [L_y, L_z] = i\hbar L_x \quad [L_z, L_x] = i\hbar L_y$$

$$[\mathbf{L}^2, L_k] = 0 \quad k = x, y, z$$

Generalised Angular Momentum Algebra:

$$[j_x, j_y] = i\hbar j_z \quad [j_y, j_z] = i\hbar j_x \quad [j_z, j_x] = i\hbar j_y$$

$$[\underline{j}^2, j_k] = 0 \quad k = x, y, z$$

We introduce a generalised simultaneous eigenstate $|\lambda_j m\rangle \dots$

$$\underline{j}^2 |\lambda_j m\rangle = \lambda_j |\lambda_j m\rangle \quad \text{and} \quad j_z |\lambda_j m\rangle = m\hbar |\lambda_j m\rangle$$

Non-hermitian raising and lowering operators are introduced to show there is a maximum value of $m \dots$

$$j_+ = j_x + ij_y \quad j_- = j_x - ij_y$$

$$j_+ |\lambda_j m\rangle = \hbar \sqrt{j(j+1) - m(m+1)} |\lambda_j m+1\rangle$$

$$j_- |\lambda_j m\rangle = \hbar \sqrt{j(j+1) - m(m-1)} |\lambda_j m-1\rangle$$

Eigenvalue of $j_z^2 \rightarrow (m\hbar)^2 \leq \lambda_j$

Eigenvalue of $\underline{j}^2 = j_x^2 + j_y^2 + j_z^2 \geq j_z^2$

Using the raising and lowering operators, it is shown that the eigenvalues of j_z run from $m = \{-j, -j+1, \dots, j-1, j\}\hbar$. There are two physical solutions for this...

- j is an integer $\Rightarrow m$ is an integer BOSON
- j is 1/2-integer $\Rightarrow m$ is in 1/2-integer FERMION

Spin:

A general angular momentum system, such as a nucleus and electron, can be comprised of both orbital angular momentum ℓ and spin angular momentum $s \dots$

- $\ell = 0, 1, 2, \dots$
- $s = 1/2 \dots$

$$\underline{s}^2 |s m_s\rangle = s(s+1)\hbar^2 |s m_s\rangle \quad s_z |s m_s\rangle = m_s \hbar |s m_s\rangle$$

$$m_s = -s, -s+1, \dots, s-1, s \Rightarrow ||m_s|| = (2s+1)$$

Spin 1/2: $s = \frac{1}{2} \Rightarrow m_s = -\frac{1}{2}, \frac{1}{2}$

$$|\chi\rangle = a \left| \frac{1}{2} \frac{1}{2} \right\rangle + b \left| \frac{1}{2} -\frac{1}{2} \right\rangle = a|\alpha\rangle + b|\beta\rangle \equiv a \begin{bmatrix} 1 \\ 0 \end{bmatrix} + b \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} a \\ b \end{bmatrix}$$

Complex Vectors \rightarrow

$$\langle \chi | = [a^* \quad b^*] \xrightarrow{\text{NORM}} \langle \chi | \chi \rangle = [a^* \quad b^*] \begin{bmatrix} a \\ b \end{bmatrix} = |a|^2 + |b|^2 = 1$$

We can introduce the matrix operators...

$$\underbrace{\begin{bmatrix} \langle \alpha | s_z | \alpha \rangle & \langle \alpha | s_z | \beta \rangle \\ \langle \beta | s_z | \alpha \rangle & \langle \beta | s_z | \beta \rangle \end{bmatrix}}_{s_z = [\dots]} \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} \frac{\hbar}{2} a \\ -\frac{\hbar}{2} b \end{bmatrix}$$

$$s_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad s_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad s_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

Spin 1: $s = 1 \Rightarrow m_s = -1, 0, 1$

$$|\chi\rangle = a|1 \ 1\rangle + b|1 \ 0\rangle + c|1 \ -1\rangle = \begin{bmatrix} a \\ b \\ c \end{bmatrix}$$

Total Wave Function:

$$\phi(\mathbf{r}) = \phi_{\frac{1}{2}}(\mathbf{r})|\alpha\rangle + \phi_{-\frac{1}{2}}(\mathbf{r})|\beta\rangle = \begin{bmatrix} \phi_{\frac{1}{2}}(\mathbf{r}) \\ \phi_{-\frac{1}{2}}(\mathbf{r}) \end{bmatrix}$$

The Variational Principle

Introduction:

The variational principle is used for...

- Finding upper bounds for the ground state energy eigenvalue.
- With modifications, finding upper bounds to excited state energy eigenvalues.
- In general, approximating energy eigenvalues and eigenfunctions, usually the ground state.

The Variational Principle:

$$W = \frac{\int \phi^* H \phi d\mathbf{r}}{\int \phi^* \phi d\mathbf{r}} \geq E_0$$

To apply this, suppose ϕ depends on a set of variational parameters $\{a_1, a_2, \dots, a_r\} \dots$

$$W = \frac{\int \phi^* H \phi d\mathbf{r}}{\int \phi^* \phi d\mathbf{r}} \rightarrow W(a_1, a_2, \dots, a_r)$$

To determine the lowest upper bound, differentiate the functional Rayleigh ratio W with respect to $\{a\} \dots$

$$\frac{\partial W}{\partial a_1} = \frac{\partial W}{\partial a_2} = \dots = \frac{\partial W}{\partial a_r} = 0$$

"The accuracy will always depend on the choice of the trial wavefunction, which should at least have the right symmetry and obey the boundary conditions"

Excited States:

$$\phi = \sum_{i>m-1} c_i \phi_{E_i}$$

$$\langle \phi | H | \phi \rangle \geq E_m \langle \phi | \phi \rangle \Rightarrow \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \phi^* H \phi d\mathbf{r}}{\int \phi^* \phi d\mathbf{r}} \geq E_m$$

The Rayleigh-Ritz Method:

"Variational technique for finding upper bounds to multiple eigenenergies at once"

$$\phi = \sum_{i=1}^r a_i \phi_i \quad S_{ij} = \langle \phi_i | \phi_j \rangle$$

$$\begin{bmatrix} H_{11} & H_{12} & \dots & H_{1r} \\ H_{21} & H_{22} & \dots & H_{2r} \\ \vdots & \vdots & \ddots & \vdots \\ H_{r1} & H_{r2} & \dots & H_{rr} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_r \end{bmatrix} = \epsilon \begin{bmatrix} S_{11} & S_{12} & \dots & S_{1r} \\ S_{21} & S_{22} & \dots & S_{2r} \\ \vdots & \vdots & \ddots & \vdots \\ S_{r1} & S_{r2} & \dots & S_{rr} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_r \end{bmatrix}$$

$$(\mathbf{H} - \epsilon \mathbf{S}) \underline{\mathbf{a}} = 0$$

If we chose an orthonormal basis, everything but the diagonals would be zero... $\Rightarrow S_{ij} = \delta_{ij} \Rightarrow \mathbf{S} = \mathbb{1}$

$$\mathbf{H} \underline{\mathbf{a}} = \epsilon \underline{\mathbf{a}}$$

If the basis isn't orthonormal, we can transform the system...

$$\tilde{\mathbf{H}} = \mathbf{S}^{-1/2} \mathbf{H} \mathbf{S}^{-1/2} \quad \tilde{\underline{\mathbf{a}}} = \mathbf{S}^{1/2} \underline{\mathbf{a}}$$

The Hylleraas-Undheim Theorem:

If the r eigenvalues ϵ_r from a Rayleigh-Ritz calculation with E_r being the true corresponding eigenvalues, then...

$$E_i \leq \epsilon_i \quad \forall i \quad \text{"All upper bounds"}$$

The Simple Hückle Method:

Not important for our year :)

Matrix Element	Hückle Symbol	Physics
H_{ii}	α_i	Coulomb Integral
H_{ij}	β_{ij}	Resonance Integral

"Describes small molecules"

Time-Independent Perturbation Theory

Basic Elements:

Perturbation theory is widely used in physics, particularly in Quantum mechanics. It requires:

- Good knowledge of an unperturbed "base" system.
- A small change (perturbation) is made to the system.
- We want to know what happens to the energy eigenstates.
- The spectrum is discrete.

⇒ TIPT

Derivation:

Let the unperturbed system have Hamiltonian H_0 with orthonormal eigenstates $\{\phi_i\}$ and eigenvalues $\{E_i\}$...

$$H_0\phi_i = E_i\phi_i$$

Let the perturbation be described by $\lambda H'$, where λ is a real parameter. The full Hamiltonian is...

$$H = H_0 + \lambda H'$$

Then to solve $H\phi = E\phi$, a power series in λ is used...

$$\phi = \sum_{n=0}^{\infty} \lambda^n \phi^{(n)} \quad E = \sum_{n=0}^{\infty} \lambda^n E^{(n)}$$

This produces solutions to various orders...

$$\lambda^0 : (H_0 - E^{(0)})\phi^{(0)} = 0$$

$$\lambda^1 : (H_0 - E^{(0)})\phi^{(1)} + (H' - E^{(1)})\phi^{(0)} = 0$$

$$\lambda^2 : (H_0 - E^{(0)})\phi^{(2)} + (H' - E^{(1)})\phi^{(1)} - E^{(2)}\phi^{(0)} = 0$$

Zeroth Order Energy Shift:

The zeroth order must be a chosen eigensolution of the unperturbed Hamiltonian, such that $H_0\phi_m = E_m\phi_m$...

$$\phi^{(0)} = \phi_m \quad E^{(0)} = E_m$$

First Order Energy Shift:

$$E^{(1)} = H'_{mm} = \langle \phi_m | H' | \phi_m \rangle \equiv \int \phi_m^* H' \phi_m \, d\mathbf{r}$$

↖ Matrix Element

Second Order Energy Shift:

$$E^{(2)} = - \sum_{n \neq m} \frac{|H'_{nm}|^2}{E_n - E_m}$$

Summary:

$$H = H_0 + H'$$

$$H_0\phi_m = E_m\phi_m \quad H'_{nm} \equiv \int \phi_n^* H' \phi_m \, d\mathbf{r}$$

$$E_m \rightarrow E_m + H'_{mm} - \sum_{n \neq m} \frac{|H'_{nm}|^2}{E_n - E_m}$$

1st Order ↗ ↖ 2nd Order

$$\phi_m \rightarrow \phi_m - \sum_{n \neq m} \frac{H'_{nm}}{E_n - E_m} \phi_n$$

↖ 1st Order

Accuracy of Low-Order Perturbation Theory:

The above summary is accurate if...

(a) "Small Perturbations"

$$|c_k^{(1)}| = \left| \frac{H'_{km}}{E_k - E_m} \right| \ll 1 \quad \forall k \implies |H'_{km}| \ll |E_k - E_m|$$

(b) if H' is of low order, such as a constant, then perturbation theory is accurate without satisfying (a).

Degenerate Perturbation Theory:

"Becomes more complex and solving the energy shift maps to an eigenproblem"

Time-Dependent Perturbation Theory

Basic Theory:

$$H = H_0 + H'(\mathbf{r}, t)$$

Let the unperturbed eigenstates be $H_0\phi_n = E_n\phi_n$, where $\langle \phi_n | \phi_m \rangle = \delta_{nm}$. The unperturbed solution to the Schrödinger equation becomes...

$$\psi_n = \phi_n e^{-iE_n t/\hbar} \implies i\hbar \frac{\partial \psi_n}{\partial t} = H_0 \psi_n$$

The solution to the perturbed system is thus...

$$\psi(\mathbf{r}, t) = \sum_n a_n(t) \psi_n(\mathbf{r}, t) = \sum_n a_n(t) \phi_n(\mathbf{r}) e^{-iE_n t/\hbar}$$

By solving the total Schrödinger equation for $H = H_0 + H(\mathbf{r}, t)$, various orders are found again...

$$\dot{a}_f^{(0)} = 0$$

$$\dot{a}_f^{(r+1)} = (i\hbar)^{-1} \sum_n a_n^{(r)} H'_{fn} e^{i\omega_{fn} t} \quad \omega_{fn} = \frac{E_f - E_n}{\hbar}$$

Zeroth and First Order Equations:

"i : initial, j : final"

$$a_n^{(0)} = \delta_{ni} \quad a_f^{(1)}(t) = (i\hbar)^{-1} \int_0^t H'_{fi} e^{i\omega_{fi} t'} dt'$$

$$\Psi(\mathbf{r}, t) = \phi_i(\mathbf{r}) e^{-iE_i t/\hbar} + \sum_{f \neq i} a_f^{(1)}(t) \phi_f(\mathbf{r}) e^{-iE_f t/\hbar}$$

Higher Order:

"Long integral... For each increase in order, an increase in the indirect energy jump transition length is considered."

Transition Probabilities:

If H' is "small" and we consider the perturbation only acting for a "short enough" time \implies 1st order result is enough...

$$\psi(\mathbf{r}, t) = \sum_n \left[a_n^{(0)}(t) + a_n^{(1)}(t) \right] \phi_n(\mathbf{r}) e^{-iE_n t/\hbar}$$

The initial wavefunction $\psi(\mathbf{r}, 0) = \phi(\mathbf{r}) \implies a_n^{(0)}(t) = \delta_{ni}$...

$$\psi(\mathbf{r}, t) = \left[1 + a_i^{(1)}(t) \right] \phi_i(\mathbf{r}) e^{-iE_i t/\hbar} + \sum_{n \neq i} a_n^{(1)}(t) \phi_n(\mathbf{r}) e^{-iE_n t/\hbar}$$

Thus, the probability to measure the system initially in state ϕ_i to be in state ϕ_f is...

$$\left| a_f^{(1)}(t) \right|^2 = \left| (i\hbar)^{-1} \int_0^t H'_{fi}(t') e^{i\omega_{fi} t'} dt' \right|^2$$