

Quantum Mechanics II Lecture 2

1 Introduction

- **Degenerate Perturbation Theory:** Discusses systems where degeneracy occurs in the unperturbed Hamiltonian.

2 Two-Fold Degeneracy

Two-Fold Degeneracy:

- Only two states are degenerate.
- Suppose:

$$H^{(0)} \psi_a^{(0)} = E^{(0)} \psi_a^{(0)}, \quad H^{(0)} \psi_b^{(0)} = E^{(0)} \psi_b^{(0)}, \quad \langle \psi_a^{(0)} | \psi_b^{(0)} \rangle = \delta_{a,b}$$

Theorem 1. Superposition of States:

- Any state can be written as a linear combination:

$$\psi^{(0)} = \alpha \psi_a^{(0)} + \beta \psi_b^{(0)}$$

- This is also an eigenstate of $H^{(0)}$.

Proof. Note that

$$\begin{aligned} \langle \psi^{(0)} | H^{(0)} | \psi^{(0)} \rangle &= (\alpha^* \langle \psi_a^{(0)} | + \beta^* \langle \psi_b^{(0)} |) H^{(0)} (\alpha \psi_a^{(0)} + \beta \psi_b^{(0)}) \\ &= \alpha^* \alpha \langle \psi_a^{(0)} | H^{(0)} | \psi_a^{(0)} \rangle + \alpha^* \beta \langle \psi_a^{(0)} | H^{(0)} | \psi_b^{(0)} \rangle \\ &\quad + \beta^* \alpha \langle \psi_b^{(0)} | H^{(0)} | \psi_a^{(0)} \rangle + \beta^* \beta \langle \psi_b^{(0)} | H^{(0)} | \psi_b^{(0)} \rangle \\ &= \alpha^* \alpha E^{(0)} + \beta^* \beta E^{(0)} = E^{(0)} \end{aligned}$$

The last equality holds, since $H^{(0)}$ is diagonal in the degenerate subspace. \square

Perturbation Theory:

Hamiltonian:

$$H = H^{(0)} + \lambda H'$$

where λ is the perturbation parameter.

Eigenvalue Equation:

$$H \psi = E \psi$$

Assumptions:

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

$$\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots$$

Diagonalization:

- To find “good states” that diagonalize H , assume:

$$\psi^{(0)} = \alpha \psi_a^{(0)} + \beta \psi_b^{(0)}$$

- Combine them:

$$H^{(0)} \psi^{(0)} + \lambda (H' \psi^{(0)} + H^{(0)} \psi^{(1)}) + \dots = E^{(0)} \psi^{(0)} + \lambda [E^{(1)} \psi^{(0)} + E^{(0)} \psi^{(1)}] + \dots$$

First-Order Approximation:

- At the first order of λ :

$$H^{(0)} \psi^{(1)} + H' \psi^{(0)} = E^{(1)} \psi^{(0)} + E^{(0)} \psi^{(1)}$$

Solution:

- Solve for $\psi^{(1)}$ and $E^{(1)}$ using the above equation.

Matrix Representation of the Perturbed Hamiltonian:

- The unperturbed Hamiltonian $H^{(0)}$ is diagonal in the degenerate subspace.
- The first-order perturbation H' is represented by the matrix W in the basis of degenerate states:

$$W = \begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix}$$

where

$$W_{ij} = \langle \psi_i^{(0)} | H' | \psi_j^{(0)} \rangle.$$

Eigenvalue Equation in Matrix Form:

- The eigenvalue problem for the perturbed system is written as:

$$W \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E^{(1)} \begin{bmatrix} \alpha \\ \beta \end{bmatrix}.$$

- Using the determinant condition:

$$\det(W - E^{(1)} I) = 0,$$

where I is the identity matrix.

Solution for Eigenvalues:

- The eigenvalues $E^{(1)}$ are obtained by solving the characteristic equation:

$$\det \begin{bmatrix} W_{aa} - E^{(1)} & W_{ab} \\ W_{ba} & W_{bb} - E^{(1)} \end{bmatrix} = 0.$$

- This results in:

$$(W_{aa} - E^{(1)}) (W_{bb} - E^{(1)}) - W_{ab} W_{ba} = 0.$$

- Solving for $E^{(1)}$:

$$E_{\pm}^{(1)} = \frac{W_{aa} + W_{bb}}{2} \pm \sqrt{\left(\frac{W_{aa} - W_{bb}}{2}\right)^2 + W_{ab} W_{ba}}.$$

References:

- See Chapter 4, Eq. (4.15) for the “Spin” problem as an example application.

Boxed Final Answer for Eigenvalues:

$$E_{\pm}^{(1)} = \frac{W_{aa} + W_{bb}}{2} \pm \sqrt{\left(\frac{W_{aa} - W_{bb}}{2}\right)^2 + W_{ab}W_{ba}}$$

Example 1. (Spin)

- The perturbation matrix W is:

$$W = \begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix}.$$

- Define $\Delta W = W_{bb} - W_{aa}$ and $W_{ab} = W_{ba}^*$.

Rotated Basis:

- The rotated basis is defined by the angle θ and phase ϕ :

$$\cos \theta = \frac{\Delta W}{\sqrt{(\Delta W)^2 + |W_{ab}|^2}}, \quad W_{ab} = |W_{ab}| e^{-i\phi}.$$

Good States:

- The “good states” $\psi_+^{(0)}$ and $\psi_-^{(0)}$ are:

$$\psi_+^{(0)} = \begin{pmatrix} \cos \frac{\theta}{2} e^{i\frac{\phi}{2}} \\ \sin \frac{\theta}{2} e^{-i\frac{\phi}{2}} \end{pmatrix}, \quad \psi_-^{(0)} = \begin{pmatrix} \sin \frac{\theta}{2} e^{-i\frac{\phi}{2}} \\ -\cos \frac{\theta}{2} e^{i\frac{\phi}{2}} \end{pmatrix}.$$

Orthogonality Check:

- Verify the orthonormal properties:

$$\langle \psi_+^{(0)} | \psi_-^{(0)} \rangle = 0, \quad \langle \psi_+^{(0)} | \psi_+^{(0)} \rangle = 1, \quad \langle \psi_-^{(0)} | \psi_-^{(0)} \rangle = 1.$$

Expectation Values:

- Compute the expectation values of the perturbation H' in the good states:

$$\langle \psi_+^{(0)} | H' | \psi_+^{(0)} \rangle = \bar{W} + \Delta W, \quad \langle \psi_-^{(0)} | H' | \psi_-^{(0)} \rangle = \bar{W} - \Delta W,$$

where $\bar{W} = \frac{W_{aa} + W_{bb}}{2}$.

Summary:

- The “good states” $\psi_+^{(0)}$ and $\psi_-^{(0)}$ are linear combinations of the degenerate states $\psi_a^{(0)}$ and $\psi_b^{(0)}$ that diagonalize the perturbation matrix W .
- The first-order corrections to the energy levels are given by:

$$E^{(1)} = \bar{W} \pm \Delta W,$$

where $\Delta W = \sqrt{\left(\frac{W_{aa} - W_{bb}}{2}\right)^2 + W_{ab}W_{ba}}$.

Boxed Final Answer:

$$\boxed{\psi_+^{(0)} = \begin{pmatrix} \cos \frac{\theta}{2} e^{i\frac{\phi}{2}} \\ \sin \frac{\theta}{2} e^{-i\frac{\phi}{2}} \end{pmatrix}, \quad \psi_-^{(0)} = \begin{pmatrix} \sin \frac{\theta}{2} e^{-i\frac{\phi}{2}} \\ -\cos \frac{\theta}{2} e^{i\frac{\phi}{2}} \end{pmatrix}}$$

3 Higher-Order Degeneracy

N -fold degeneracy = N -states with the same energy. Use the basis $\{\psi_1, \psi_2, \dots, \psi_N\}$ to express H' as a matrix,

$$W_{ij} \equiv \langle \psi_i | H' | \psi_j \rangle$$

Example. (6.2) 3D cubic well

$$V(x, y, z) = \begin{cases} 0 & x, y, z \in [0, a] \\ \infty & \text{otherwise} \end{cases}$$

unperturbed states

$$\psi_{n_x, n_y, n_z}^{(0)} = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right),$$

$$E_{n_x, n_y, n_z}^{(0)} = \frac{\hbar^2}{2m} \left(\frac{\pi}{a}\right)^2 (n_x^2 + n_y^2 + n_z^2).$$

Ground State Energy:

$$E_0^{(0)} = \frac{\pi^2 \hbar^2}{2m a^2} (1 + 1 + 1) = \frac{3\pi^2 \hbar^2}{2m a^2}$$

First Excited States:

$$\begin{aligned} \psi_a &= \psi_{112}, \quad \psi_b = \psi_{121}, \quad \psi_c = \psi_{211} \\ E_1^{(0)} &= \frac{\pi^2 \hbar^2}{2m a^2} (2^2 + 1 + 1) = \frac{3\pi^2 \hbar^2}{m a^2} \end{aligned}$$

Perturbation:

- A perturbation H' is introduced as:

$$H' = \begin{cases} V_0, & x, y \in [0, \frac{a}{2}] \\ 0, & \text{elsewhere} \end{cases}$$

First-Order Correction to Energy:

- The first-order correction to the energy is given by:

$$E_0^{(1)} = \langle \psi_{111}^{(0)} | H' | \psi_{111}^{(0)} \rangle$$

- Explicitly, this becomes:

$$\boxed{E_0^{(1)} = \left(\frac{2}{a}\right)^3 V_0 \left(\int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a} x\right) dx \right)^2 \int_0^a \sin^2\left(\frac{\pi}{a} z\right) dz}$$

- Since the integral evaluates to a non-zero value, $E_0^{(1)} \neq 0$.

Perturbation Matrix Element W_{aa}

Definition:

$$W_{aa} = \langle \psi_a | H' | \psi_a \rangle$$

where $\psi_a = \psi_{112}$.

Expression:

$$W_{aa} = \left(\frac{2}{a}\right)^3 V_0 \int_0^a dx \sin^2\left(\frac{\pi}{a}x\right) \int_0^a dy \sin^2\left(\frac{\pi}{a}y\right) \int_0^a dz \sin^2\left(\frac{2\pi}{a}z\right)$$

Simplified:

$$W_{aa} = \frac{1}{6} V_0 \neq 0$$

Perturbation Matrix Element W_{ab}

Definition:

$$W_{ab} = \langle \psi_a | H' | \psi_b \rangle$$

where $\psi_a = \psi_{112}$ and $\psi_b = \psi_{121}$.

Expression:

$$W_{ab} = \left(\frac{2}{a}\right)^3 V_0 \int_0^a dx \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{\pi}{a}x\right) \int_0^a dy \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}y\right) \int_0^a dz \sin\left(\frac{2\pi}{a}z\right) \sin\left(\frac{\pi}{a}z\right)$$

Simplified:

$$W_{ab} = 0$$

Key Observations:

- H' does not couple ψ_a and ψ_b because $W_{ab} = 0$.
- Similarly, $W_{ac} = 0$, indicating that H' does not couple ψ_a and ψ_c .

Perturbation Matrix Element W_{bc}

Definition:

$$W_{bc} = \langle \psi_b | H' | \psi_c \rangle$$

where $\psi_b = \psi_{121}$ and $\psi_c = \psi_{211}$.

Expression:

$$W_{bc} = \left(\frac{2}{a}\right)^3 V_0 \int_0^a dx \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}x\right) \int_0^a dy \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}y\right) \int_0^a dz \sin^2\left(\frac{\pi}{a}z\right)$$

Simplified:

$$W_{bc} = \frac{16}{9\pi^2} V_0 \neq 0$$

Matrix Representation of W

$$W = \begin{bmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{bmatrix}$$

Substitution:

$$W = \begin{bmatrix} \frac{1}{6}V_0 & 0 & 0 \\ 0 & \frac{1}{6}V_0 & \frac{16}{9\pi^2}V_0 \\ 0 & \frac{16}{9\pi^2}V_0 & \frac{1}{6}V_0 \end{bmatrix}$$

Diagonalization of W :

- The diagonal elements represent the unperturbed energy levels.
- The off-diagonal elements represent the coupling between states.

Eigenvalues:

- The eigenvalues of W give the first-order corrections to the energy levels.

Good States:

- The eigenstates of W correspond to “good states” that diagonalize the perturbation.

$$W = \begin{bmatrix} \frac{1}{6}V_0 & 0 & 0 \\ 0 & \frac{1}{6}V_0 & \frac{16}{9\pi^2}V_0 \\ 0 & \frac{16}{9\pi^2}V_0 & \frac{1}{6}V_0 \end{bmatrix}$$

The eigenstates ψ_2 and ψ_3 are written as column vectors:

$$\psi_2 = \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} e^{-i\phi} \end{pmatrix}, \quad \psi_3 = \begin{pmatrix} \sin \frac{\theta}{2} e^{i\phi} \\ -\cos \frac{\theta}{2} \end{pmatrix}$$

Derivation:

1. Rotation Angle θ :

- The angle θ is defined as:

$$\cos \theta = \frac{1 - \lambda}{\sqrt{1 + \lambda^2}}$$

- This expression arises from the perturbation theory, where λ is a parameter related to the perturbation strength.

1. Phase Factor ϕ :

- The phase ϕ is determined by the perturbation matrix elements. Here, it is given as:

$$\omega_{12}^a = s_{12}^b \cdot \sqrt{2}$$

- If k is zero, then $\phi = 0$.
-

Orthonormality of Eigenstates

The eigenstates ψ_2 and ψ_3 are orthonormal:

- Normalization:**

$$\langle \psi_2 | \psi_2 \rangle = 1, \quad \langle \psi_3 | \psi_3 \rangle = 1$$

- Orthogonality:**

$$\langle \psi_2 | \psi_3 \rangle = 0$$

Explicit Check:

Normalization of ψ_2 :

$$\langle \psi_2 | \psi_2 \rangle = \left| \cos \frac{\theta}{2} \right|^2 + \left| \sin \frac{\theta}{2} e^{-i\phi} \right|^2 = \cos^2 \frac{\theta}{2} + \sin^2 \frac{\theta}{2} = 1$$

Normalization of ψ_3 :

$$\langle \psi_3 | \psi_3 \rangle = \left| \sin \frac{\theta}{2} e^{i\phi} \right|^2 + \left| -\cos \frac{\theta}{2} \right|^2 = \sin^2 \frac{\theta}{2} + \cos^2 \frac{\theta}{2} = 1$$

Orthogonality:

$$\langle \psi_2 | \psi_3 \rangle = \cos \frac{\theta}{2} \left(-\cos \frac{\theta}{2} \right) + \sin \frac{\theta}{2} e^{-i\phi} \left(\sin \frac{\theta}{2} e^{i\phi} \right) = -\cos^2 \frac{\theta}{2} + \sin^2 \frac{\theta}{2} = 0$$

Linear Combinations of Original States

The eigenstates ψ_2 and ψ_3 can be expressed as linear combinations of the original degenerate states $\psi_2^{(0)}$ and $\psi_3^{(0)}$:

$$\psi_2^{(0)} = \frac{1}{\sqrt{2}} \psi_2 + \frac{1}{\sqrt{2}} \psi_3, \quad \psi_3^{(0)} = \frac{1}{\sqrt{2}} \psi_2 - \frac{1}{\sqrt{2}} \psi_3$$

The eigenstates ψ_2 and ψ_3 are written as column vectors:

$$\psi_2 = \begin{pmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} e^{-i\phi} \end{pmatrix}, \quad \psi_3 = \begin{pmatrix} \sin \frac{\theta}{2} e^{i\phi} \\ -\cos \frac{\theta}{2} \end{pmatrix}$$

Derivation:

1. Rotation Angle θ :

- The angle θ is defined as:

$$\cos \theta = \frac{1 - \lambda}{\sqrt{1 + \lambda^2}}$$

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1. Phase Factor ϕ :

- The phase ϕ is determined by the perturbation matrix elements. Here, it is given as:

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- If k is zero, then $\phi = 0$.
-

Orthonormality of Eigenstates

The eigenstates ψ_2 and ψ_3 are orthonormal:

- Normalization:**

$$\langle \psi_2 | \psi_2 \rangle = 1, \quad \langle \psi_3 | \psi_3 \rangle = 1$$

- Orthogonality:**

$$\langle \psi_2 | \psi_3 \rangle = 0$$

Explicit Check:

Normalization of ψ_2 :

$$\langle \psi_2 | \psi_2 \rangle = \left| \cos \frac{\theta}{2} \right|^2 + \left| \sin \frac{\theta}{2} e^{-i\phi} \right|^2 = \cos^2 \frac{\theta}{2} + \sin^2 \frac{\theta}{2} = 1$$

Normalization of ψ_3 :

$$\langle \psi_3 | \psi_3 \rangle = \left| \sin \frac{\theta}{2} e^{i\phi} \right|^2 + \left| -\cos \frac{\theta}{2} \right|^2 = \sin^2 \frac{\theta}{2} + \cos^2 \frac{\theta}{2} = 1$$

Orthogonality:

$$\langle \psi_2 | \psi_3 \rangle = \cos \frac{\theta}{2} \left(-\cos \frac{\theta}{2} \right) + \sin \frac{\theta}{2} e^{-i\phi} \left(\sin \frac{\theta}{2} e^{i\phi} \right) = -\cos^2 \frac{\theta}{2} + \sin^2 \frac{\theta}{2} = 0$$

Linear Combinations of Original States

The eigenstates ψ_2 and ψ_3 can be expressed as linear combinations of the original degenerate states $\psi_2^{(0)}$ and $\psi_3^{(0)}$:

$$\psi_2^{(0)} = \frac{1}{\sqrt{2}} \psi_2 + \frac{1}{\sqrt{2}} \psi_3, \quad \psi_3^{(0)} = \frac{1}{\sqrt{2}} \psi_2 - \frac{1}{\sqrt{2}} \psi_3$$

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Chap 6.2 Degenerate Perturbation theory

6.2.1 Two-fold degeneracy

Only two states

Suppose $\begin{cases} H^{(0)}|\psi_a^{(0)}\rangle = E^{(0)}|\psi_a^{(0)}\rangle \\ H^{(0)}|\psi_b^{(0)}\rangle = E^{(0)}|\psi_b^{(0)}\rangle \end{cases}$, $= \begin{cases} |\psi_a^{(0)}\rangle \\ |\psi_b^{(0)}\rangle \end{cases}$

[Note] Any state can be written as $|\psi^{(0)}\rangle = \alpha|\psi_a^{(0)}\rangle + \beta|\psi_b^{(0)}\rangle$
is also an eigenstate of $H^{(0)}$

$(P_{100})f = \langle \psi^{(0)} | H^{(0)} | \psi^{(0)} \rangle$
superscripts are coefficients
 $= [\alpha^* \langle \psi_a^{(0)} | + \beta^* \langle \psi_b^{(0)} |] H^{(0)} [\alpha |\psi_a^{(0)}\rangle + \beta |\psi_b^{(0)}\rangle]$

$= (\alpha^* \langle \psi_a^{(0)} | + \beta^* \langle \psi_b^{(0)} |) H^{(0)} (\alpha |\psi_a^{(0)}\rangle + \beta |\psi_b^{(0)}\rangle)$

↑ 投影背景墙面。注意保护，严禁书写的！

$= (1\alpha^2 + 1\beta^2) E^{(0)} = E^{(0)} \times$
We want to solve $H|\psi\rangle = E|\psi\rangle$
with $H = H^{(0)} + \lambda H'$
Assume $\begin{cases} \psi = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \\ \psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots \end{cases}$
to find "Good states": $\psi^{(0)} = \alpha|\psi_a^{(0)}\rangle + \beta|\psi_b^{(0)}\rangle$
to diagonalize H'
Put them together, we have
 $H^{(0)}\psi^{(0)} + \lambda(H'|\psi^{(0)}\rangle + H^{(0)}\psi^{(1)}) + \dots$
 $= E^{(0)}\psi^{(0)} + \lambda(E^{(1)}\psi^{(0)} + E^{(0)}\psi^{(1)} + \dots)$
At the 1st order of λ , we have
 $H^{(0)}\psi^{(0)} + H'\psi^{(0)} = E^{(0)}\psi^{(0)} + F^{(0)}\psi^{(0)}$

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$\langle \psi_a^{(0)} | H^{(0)} | \psi^{(1)} \rangle + \langle \psi_a^{(0)} | H' | \psi^{(0)} \rangle$
 $= E^{(0)} \langle \psi_a^{(0)} | \psi^{(0)} \rangle + E^{(0)} \langle \psi_a^{(0)} | \psi^{(1)} \rangle$
 $\Rightarrow \langle \psi_a^{(0)} | H' | \psi^{(0)} \rangle = E^{(0)} \langle \psi_a^{(0)} | \psi^{(1)} \rangle$
 $\Rightarrow \langle \psi_a^{(0)} | H' | (\alpha|\psi_a^{(0)}\rangle + \beta|\psi_b^{(0)}\rangle) \rangle = E^{(0)} \langle \psi_a^{(0)} | (\alpha|\psi_a^{(0)}\rangle + \beta|\psi_b^{(0)}\rangle)$
 $\Rightarrow \alpha \langle \psi_a^{(0)} | H' | \psi_a^{(0)} \rangle + \beta \langle \psi_a^{(0)} | H' | \psi_b^{(0)} \rangle = E^{(0)} \alpha$
Where we have defined $W_{ij} = \langle \psi_i | H' | \psi_j \rangle$
Similarly, $\langle \psi_b^{(0)} | H' | \psi^{(1)} \rangle$ 1st order perturbation equation
 $\Rightarrow \alpha W_{ba} + \beta W_{bb} = \beta E^{(0)}$

$\Rightarrow \begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E^{(0)} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \begin{bmatrix} E^{(0)} - \alpha \\ E^{(0)} - \beta \end{bmatrix}$
 $\Rightarrow \begin{bmatrix} W_{aa} - E^{(0)} & W_{ab} \\ W_{ba} & W_{bb} - E^{(0)} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = 0$
For non-trivial α, β , let $\begin{vmatrix} W_{aa} - E^{(0)}, W_{ab} \\ W_{ba}, W_{bb} - E^{(0)} \end{vmatrix} = 0$
 $\Rightarrow E^{(1)} = \frac{W_{aa} + W_{bb}}{2} \pm \sqrt{\frac{(W_{aa} - W_{bb})^2}{4} + W_{ab}W_{ba}}$
The Matrix of H' spanned by $|\psi_a^{(0)}\rangle$ and $|\psi_b^{(0)}\rangle$
is $\begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix}$, the degenerate perturbation theory is to diagonalize it.
Problem 6.6 Find the eigen states of W
See Chap 4, Eq. [4.15] "Spin"

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For $E_+ \Rightarrow \psi_+^{(0)} = \begin{pmatrix} \cos\theta \\ \sin\frac{\theta}{2}e^{i\phi} \end{pmatrix}$

$E_- \Rightarrow \psi_-^{(0)} = \begin{pmatrix} \sin\frac{\theta}{2} \\ -\cos\frac{\theta}{2}e^{i\phi} \end{pmatrix} = \begin{pmatrix} \sin\frac{\theta}{2}e^{-i\phi} \\ -\cos\frac{\theta}{2} \end{pmatrix}$

where $\cos\theta = \frac{\Delta W}{\sqrt{(\Delta W)^2 + W_{ab}W_{ba}}}$, $W_{ab} = W_{ba}e^{-i\phi}$

Check the orthonormal properties $\begin{cases} \langle \psi_+^{(0)} | \psi_+^{(0)} \rangle = 1 \\ \langle \psi_+^{(0)} | \psi_-^{(0)} \rangle = 0 \\ \langle \psi_-^{(0)} | \psi_+^{(0)} \rangle = 0 \\ \langle \psi_-^{(0)} | \psi_-^{(0)} \rangle = 1 \end{cases}$

Expectation values $\begin{cases} \langle \psi_+^{(0)} | H' | \psi_+^{(0)} \rangle = W_{aa} \langle \psi_+^{(0)} | \psi_+^{(0)} \rangle \\ \langle \psi_+^{(0)} | H' | \psi_+^{(0)} \rangle = (\cos\theta, \sin\frac{\theta}{2}e^{-i\phi}) W_{aa} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \langle \psi_+^{(0)} | \psi_+^{(0)} \rangle \\ + (\cos\theta, \sin\frac{\theta}{2}e^{-i\phi}) \Delta W \begin{pmatrix} \cos\theta & -\cos\theta \\ \sin\frac{\theta}{2}e^{-i\phi} & -\sin\frac{\theta}{2}e^{-i\phi} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \langle \psi_+^{(0)} | \psi_+^{(0)} \rangle \end{cases}$

$\Rightarrow \langle \psi_+^{(0)} | H' | \psi_+^{(0)} \rangle = \bar{W} + \Delta W (\cos\theta, \sin\frac{\theta}{2}e^{-i\phi})$
 $\times \begin{pmatrix} \cos\theta & \sin\theta & \sin\frac{\theta}{2} \\ \sin\theta & \cos\frac{\theta}{2}e^{i\phi} & -\cos\theta & \sin\frac{\theta}{2}e^{i\phi} \\ \sin\theta & -\cos\frac{\theta}{2}e^{i\phi} & \cos\theta & \sin\frac{\theta}{2}e^{i\phi} \end{pmatrix}$
 $= \bar{W} + \Delta W$
Similarly, $\langle \psi_-^{(0)} | H' | \psi_-^{(0)} \rangle = \bar{W} - \Delta W$
 $\langle \psi_+^{(0)} | H' | \psi_-^{(0)} \rangle = 0$

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6.2.2 Higher-order degeneracy

N -fold degeneracy = N states with the same energy

Use the basis $\{4_1, 4_2, \dots, 4_N\}$ to express H' (perturbation) as a matrix, $W_{ij} = \langle 4_i | H' | 4_j \rangle$

$\Rightarrow N \times N$ Matrix, then diagonalize (W)

Example 6.2 3D cubical well

Potential energy $V(x, y, z) = \begin{cases} 0, & x, y, z \in [0, a] \\ \infty, & \text{elsewhere} \end{cases}$

(Unperturbed 21804 states)

$\Psi_{h_1 h_2 h_3}^{(0)} = \left(\frac{2}{a}\right)^3 V_0 \sin\left(\frac{h_1 \pi}{a} x\right) \sin\left(\frac{h_2 \pi}{a} y\right) \sin\left(\frac{h_3 \pi}{a} z\right)$

h_1, h_2, h_3 positive integers

$E_n^{(0)} = \frac{\hbar^2}{2m} \left(\frac{\pi^2}{a^2}\right) (h_1^2 + h_2^2 + h_3^2)$

Ground State $E_0^{(0)} = \frac{\hbar^2 \pi^2}{2ma^2} (1+1)$

1st excited states (degenerate)

$4_1 = 4_{111}, 4_2 = 4_{121}, 4_3 = 4_{211}$

$E_1^{(0)} = \frac{\hbar^2 \pi^2}{2ma^2} (2^2 + 1) = 3 \frac{\hbar^2 \pi^2}{2ma^2}$

Perturbation $H' = \begin{cases} V_0, & x, y \in [0, a] \\ 0, & \text{elsewhere} \end{cases}$

1st order correction to energy

$E_1^{(1)} = \langle 4_{111} | H' | 4_{111} \rangle$

$= \left(\frac{2}{a}\right)^3 V_0 \left[\int_0^a \sin^2\left(\frac{\pi}{a} x\right) dx \times \int_0^a \sin^2\left(\frac{\pi}{a} z\right) dz \right] = \frac{V_0}{4}$

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For the 1st excited states

$W_{aa} = \langle 4_{111} | H' | 4_{111} \rangle = \langle 4_{111} | H' | 4_{111} \rangle$

$= \left(\frac{2}{a}\right)^3 V_0 \int_0^a dx \sin^2\left(\frac{\pi}{a} x\right) \int_0^a dy \sin^2\left(\frac{\pi}{a} y\right) \int_0^a dz \sin^2\left(\frac{\pi}{a} z\right)$

$\times \int_0^a dz \sin^2\left(\frac{\pi}{a} z\right) = \frac{1}{4} V_0$

Similarly, $W_{bb} = W_{cc} = W_{aa}$

$W_{ab} = \langle 4_{111} | H' | 4_{111} \rangle$

$= \left(\frac{2}{a}\right)^3 V_0 \int_0^a dx \sin^2\left(\frac{\pi}{a} x\right) \int_0^a dy \sin^2\left(\frac{\pi}{a} y\right) \int_0^a dz \sin^2\left(\frac{\pi}{a} z\right)$

$\times \int_0^a dz \sin^2\left(\frac{\pi}{a} z\right) = 0$

H' does not couple 4_{111} and 4_{111}

$H' | 4_{111} \rangle \rightarrow | 4 \rangle, \langle 4_{111} | 4 \rangle = 0$

Similarly, $W_{bc} = 0, H'$ does not couple 4_{111} and 4_{111}

$W_{bc} = \langle 4_{111} | H' | 4_{111} \rangle = \frac{1}{4} V_0 \int_0^a dx \sin^2\left(\frac{\pi}{a} x\right) \int_0^a dy \sin^2\left(\frac{\pi}{a} y\right)$

$\times \int_0^a dz \sin^2\left(\frac{\pi}{a} z\right) + \int_0^a dx \sin^2\left(\frac{\pi}{a} x\right) \int_0^a dz \sin^2\left(\frac{\pi}{a} z\right)$

$= \frac{11}{48} V_0 \neq 0 = \frac{V_0}{4}$

H' couples 4_{111} and 4_{111}

$W_{bc} = H_{bc}^T$

To summarize $H = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \frac{V_0}{4} & 0 \\ 0 & 0 & \frac{V_0}{4} \end{bmatrix}$

The eigen states $| 4 \rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix}$

$E_1^{(0)} = \frac{V_0}{4} \rightarrow | 4 \rangle$

$E_1^{(1)}, E_2^{(1)} \leftarrow \text{degenerate} \rightarrow \frac{V_0}{4} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \Rightarrow E_1 = E_1^{(0)} + \begin{cases} \frac{V_0}{4} (1, 1, 1) \\ \frac{V_0}{4} (-1, -1, 1) \end{cases}$

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Eigen states of $E_1^{(0)}$ and $E_2^{(1)}$

$4_2 = \begin{pmatrix} 0 & e^{i\phi} \\ \sin\theta e^{i\phi} & 0 \end{pmatrix}, 4_3 = \begin{pmatrix} 0 & e^{i\phi} \\ -\cos\theta e^{i\phi} & 0 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$

$\cos\theta = \frac{1-1}{\sqrt{2}} = 0 \Rightarrow \omega_2^{(0)} = \omega_3^{(0)} = \sqrt{\frac{1}{2}}$

K is real $\Rightarrow \phi = 0$

$4_2^{(0)} = \frac{1}{\sqrt{2}} 4_1 + \frac{i}{\sqrt{2}} 4_1, 4_3^{(0)} = \frac{1}{\sqrt{2}} 4_1 - \frac{i}{\sqrt{2}} 4_1$

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