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THIS CAN SERVE AS SUMMARY

Chapter 6 Time-Independent Perturbation Theory

6.1 Nondegenerate perturbation Theory

6.1.1 General Formulation

solved: $H^0\psi_n^0 = E_n^0\psi_n^0$. $\langle\psi_n^0|\psi_m^0\rangle = \delta_{nm}$

to solve: $H\psi_n = E_n\psi_n$

$H = H^0 + \lambda H'$. H': perturbation

$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \cdots$

$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$

$(H^0+\lambda H')[\psi_n^0+\lambda\psi_n^1+\lambda^2\psi_n^2+\cdots] = (E_n^0+\lambda E_n^1+\lambda^2E_n^2+\cdots)[\psi_n^0+\lambda\psi_n^1+\lambda^2\psi_n^2+\cdots]$

$\Downarrow$

$H_0\psi_n^0 + \lambda(H^0\psi_n^1 + H'\psi_n^0) + \lambda^2(H_0\psi_n^2 + H'\psi_n^1) + \cdots = E_n^0\psi_n^0 + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0) + \cdots$

$$\begin{cases} H^0\psi_n^0 = E_n^0\psi_n^0 \\ H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0 & [6.7] \\ H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0 \end{cases}$$

6.1.2 First-Order Theory

$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$.

$\langle\psi_n^0|H^0\psi_n^1\rangle + \langle\psi_n^0|H'\psi_n^0\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle + E_n^1\langle\psi_n^0|\psi_n^0\rangle$.

But $\langle\psi_n^0|H^0\psi_n^1\rangle = \langle H^0\psi_n^0|\psi_n^1\rangle = \langle E_n^0\psi_n^0|\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^1\rangle$.

$\Rightarrow \boxed{E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle}$ [6.9]

- the first-order correction to the energy is the expectation value of the perturbation in the unperturbed state

$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$

$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$

- the unperturbed wave functions constitute a complete set, so ψ_n^1 (like any other function) can be expressed as a linear combination of them

$\psi_n^1 = \sum_{m\neq n} c_m^{(n)}\psi_m^0$.

- There is no need to include $m=n$ in the sum, ...

$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0$.

$\sum_{m\neq n}(E_m^0 - E_n^0)c_m^{(n)}\psi_m^0 = -(H' - E_n^1)\psi_n^0$.

$(E_i^0 - E_n^0) C_i^{(n)} = -\langle \psi_i^0 | H' | \psi_n^0 \rangle$

$\sum_{m \neq n} (E_m^0 - E_n^0) C_m^{(n)} \langle \psi_i^0 | \psi_m^0 \rangle = -\langle \psi_i^0 | H' | \psi_n^0 \rangle + E_n^1 \langle \psi_i^0 | \psi_n^0 \rangle$

if $l \neq n$. $(E_i^0 - E_n^0) C_i^{(n)} = -\langle \psi_i^0 | H' | \psi_n^0 \rangle$

$C_m^{(n)} = \dfrac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}$

$\Rightarrow \boxed{\psi_n^1 = \sum_{m \neq n} \dfrac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0}$

non degenerate

6.1.3 Second-Order Energies

$H^0 \psi_n^2 + H' \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$

$\langle \psi_n^0 | H^0 \psi_n^2 \rangle + \langle \psi_n^0 | H' \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$.

But $\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle$.

$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle$.

But $\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} C_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0$.

so $E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} C_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle = \sum_{m \neq n} \dfrac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0}$.

$\Rightarrow \boxed{E_n^2 = \sum_{m \neq n} \dfrac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$

6.2 Degenerate Perturbation Theory

6.2.1 Twofold Degeneracy

Suppose that $H^0 \psi_a^0 = E^0 \psi_a^0$ $\quad H^0 \psi_b = E^0 \psi_b^0$ and $\langle \psi_a^0 | \psi_b^0 \rangle = 0$.

$\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$. $\quad H^0 \psi^0 = E^0 \psi^0$

to solve : $H\psi = E\psi$.

$$\begin{cases} H^0 \psi^0 = E^0 \psi^0 \\ H^0 \psi^1 + H' \psi^0 = E^0 \psi^1 + E^1 \psi^0 \end{cases}$$

$H^0 \psi^1 + H' \psi^0 = E^0 \psi^1 + E^1 \psi^0$

$\langle \psi_a^0 | H^0 \psi^1 \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle$

But $\langle \psi_a^0 | H^0 \psi^1 \rangle = \langle H^0 \psi_a^0 | \psi^1 \rangle = E^0 \langle \psi_a^0 | \psi^1 \rangle$.

$\langle \psi_a^0 | H' \psi^0 \rangle = E^1 \langle \psi_a^0 | \psi^0 \rangle$. 代入 $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$

But $\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1$.

or, more compactly, $\alpha W_{aa} + \beta W_{ab} = \alpha E^1$. where $W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle$. $(i, j = a, b)$.

Similarly, $\alpha W_{ba} + \beta W_{bb} = \beta E^1$.

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$\alpha W_{ba}+\beta W_{bb}=\beta E'$

$\alpha W_{ab}W_{ba}+\beta W_{ab}W_{bb}=\beta W_{ab}E'$.

using $\beta W_{ab}=\alpha E'-\alpha W_{aa}$

$\alpha W_{ab}W_{ba}+\alpha E'W_{bb}-\alpha W_{aa}W_{bb}=(\alpha E'-\alpha W_{aa})E'$

$\alpha[W_{ab}W_{ba}-(E'-W_{aa})(E'-W_{bb})]=0$

If $\alpha\neq 0$. $(E')^2-E'(W_{aa}+W_{bb})+(W_{aa}W_{bb}-W_{ab}W_{ba})=0$.

note that $W_{ba}=W_{ab}^*$

$\Rightarrow E'_\pm=\frac{1}{2}[W_{aa}+W_{bb}\pm\sqrt{(W_{aa}-W_{bb})^2+4|W_{ab}|^2}]$

• $\alpha=0,\ \beta=1$.

$\alpha W_{aa}+\beta W_{ab}=\alpha E' \Rightarrow W_{ab}=0$. $\alpha W_{ba}+\beta W_{bb}=\beta E'_0 \Rightarrow E_1=W_{bb}$

$E_+^{1}=W_{bb}=\langle\psi_b^0|H'|\psi_b^0\rangle$

• $\alpha=1,\ \beta=0$.

$\alpha W_{ba}+\beta W_{bb}=\beta E'\Rightarrow W_{ba}=0$. $\alpha W_{aa}+\beta W_{ab}=\alpha E' \Rightarrow E_1=W_{aa}$

$E'_-=W_{aa}=\langle\psi_a^0|H'|\psi_a^0\rangle$.

Theorem: Let A be a Hermitian operator that commutes with H'. If ψ_a^0 and ψ_b^0 are eigenfunctions of A with distinct eigenvalues. $A\psi_a^0=\mu\psi_a^0$, $A\psi_b^0=\nu\psi_b^0$, and $\mu\neq\nu$. then $W_{ab}=0$ (and hence ψ_a^0 and ψ_b^0 are the "good" states to use in perturbation theory).

Proof: By assumption, $[A,H']=0$, so

$$\langle\psi_a^0|[A,H']\psi_b^0\rangle=0$$
$$=\langle\psi_a^0|AH'\psi_b^0\rangle-\langle\psi_a^0|H'A\psi_b^0\rangle$$
$$=\langle A\psi_a^0|H'\psi_b^0\rangle-\langle\psi_a^0|H'\nu\psi_b^0\rangle$$
$$=(\mu-\nu)\langle\psi_a^0|H'\psi_b^0\rangle=(\mu-\nu)W_{ab}.$$

But $\mu\neq\nu$, so $W_{ab}=0$. QED

Moral: / seldom necessary (x.

112 121 211 $\quad W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$

6.2.2 Higher-Order Degeneracy

Example. $V(x,y,z) = \begin{cases} 0, & \text{if } 0<x<a,\ 0<y<a, \text{ and } 0<z<a. \\ \infty, & \text{otherwise} \end{cases}$

$\psi^0_{n_x n_y n_z}(x,y,z) = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{a}y\right)\sin\left(\frac{n_z\pi}{a}z\right) \qquad E^0_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2ma^2}(n_x^2+n_y^2+n_z^2).$

Notice that the ground state (ψ_{111}) is nondegenerate; its energy is $E_0^0 \equiv 3\frac{\pi^2\hbar^2}{2ma^2}$.

But the first excited state is (triply) degenerate: $\psi_a \equiv \psi_{112}$, $\psi_b \equiv \psi_{121}$, and $\psi_c \equiv \psi_{211}$, all share the energy $E_1^0 \equiv 3\frac{\pi^2\hbar^2}{ma^2}$.

- Now let's introduce the perturbation

$H' = \begin{cases} V_0, & \text{if } 0<x<\frac{a}{2} \text{ and } 0<y<\frac{a}{2} \\ 0, & \text{otherwise} \end{cases}$

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

* $E_0^1 = \langle \psi_{111} | H' | \psi_{111} \rangle = \left(\frac{2}{a}\right)^3 V_0 \underbrace{\int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}x\right)dx}_{\frac{a}{4}} \underbrace{\int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}y\right)dy}_{\frac{a}{4}} \underbrace{\int_0^{a} \sin^2\left(\frac{\pi}{a}z\right)dz}_{\frac{a}{2}} = \frac{1}{4}V_0.$

- $W_{aa} = \left(\frac{2}{a}\right)^3 V_0 \overbrace{\int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}x\right)dx}^{\frac{a}{4}} \overbrace{\int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}y\right)dy}^{\frac{a}{4}} \overbrace{\int_0^{a} \sin^2\left(\frac{2\pi}{a}z\right)dz}^{\frac{a}{2}} = \frac{1}{4}V_0$ $\quad$ 11122

$W_{bb} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}x\right)dx \int_0^{\frac{a}{2}} \sin^2\left(\frac{2\pi}{a}y\right)dy \int_0^{a} \sin^2\left(\frac{\pi}{a}z\right)dz = \frac{1}{4}V_0.$ $\quad$ 1 22 1

$W_{cc} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin^2\left(\frac{2\pi}{a}x\right)dx \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}y\right)dy \int_0^{a} \sin^2\left(\frac{\pi}{a}z\right)dz = \frac{1}{4}V_0.$ $\quad$ 2 1 1

x	y	z
1	2	1
2	1	1

$W_{ab} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin^2\left(\frac{\pi}{a}x\right)dx \int_0^{\frac{a}{2}} \sin\left(\frac{\pi}{a}y\right)\sin\left(\frac{2\pi}{a}y\right)dy \int_0^{a} \sin\left(\frac{2\pi}{a}z\right)\sin\left(\frac{\pi}{a}z\right)dz = 0.$ $\quad W_{ac} = 0.$

$W_{bc} = \left(\frac{2}{a}\right)^3 V_0 \int_0^{\frac{a}{2}} \sin\left(\frac{\pi}{a}x\right)\sin\left(\frac{2\pi}{a}x\right)dx \int_0^{\frac{a}{2}} \sin\left(\frac{2\pi}{a}y\right)\sin\left(\frac{\pi}{a}y\right)dy \int_0^{a} \sin^2\left(\frac{\pi}{a}z\right)dz = \frac{16}{9\pi^2}V_0.$

Thus. $W = \frac{V_0}{4}\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & k \\ 0 & k & 1 \end{vmatrix}$ $\qquad k \equiv \left(\frac{8}{3\pi}\right)^2 \approx 0.7205.$ $\quad$ 11

The characteristic equation for $\frac{4W}{V_0}$.

$(1-w^3) - k^2(1-w) = 0.$

eigenvalues: $w_1 = 1$; $w_2 = 1+k \approx 1.7205$; $w_3 = 1-k \approx 0.2795$

- To first order in λ, then $E_1(\lambda) = \begin{cases} E_1^0 + \lambda\frac{V_0}{4} \\ E_1^0 + \lambda(1+k)\frac{V_0}{4} \\ E_1 + \lambda(1+k)\frac{V_0}{4}. \end{cases}$

where E_1^0 is the (common) unperturbed energy. The perturbation lifts the degeneracy, splitting E_1^0 into three distinct energy levels. Notice that if we had naively applied nondegenerate perturbation theory to this problem, we would have concluded that the first-order correction is the same for all three states, and equal to $\frac{V_0}{4}$ — which is actually correct only for the middle state.

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Meanwhile, the "good" unperturbed states are linear combinations of the form:

$\psi^0 = \alpha\psi_a + \beta\psi_b + \gamma\psi_c$.

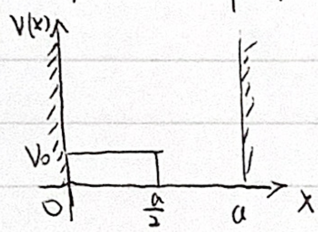
$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & k \\ 0 & k & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = w\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

For $w=1$, we get $\alpha=1$, $\beta=\gamma=0$. for $w=1\pm k$, we get $\alpha=0$, $\beta=\pm\gamma=\frac{1}{\sqrt{2}}$.

Thus the "good" states are

$$\psi^0 = \begin{cases} \psi_a \\ \frac{1}{\sqrt{2}}(\psi_b+\psi_c) \\ \frac{1}{\sqrt{2}}(\psi_b-\psi_c). \end{cases}$$

Example. The unperturbed wave functions for the infinite square well are $\psi_n^0(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$



$H' = V_0$

$\cancel{E_n' = \langle\psi_n^0|V_0|\psi_n^0\rangle = V_0\langle\psi_n^0|\psi_n^0\rangle} = V_0$.

$E_n' = \frac{2V_0}{a}\int_0^{\frac{a}{2}} \sin^2\left(\frac{n\pi}{a}x\right) dx = \frac{V_0}{2}$.