7) We now look at what happens to our stationary-state perturbation theory in case of degeneracy -- i.e. when more than one distinct quantum state $\psi_k^{(0)}$ exhibits the same energy $E_k^{(0)}$. Generally, the perturbation removes the degeneracy -- i.e. $E_k^{(0)} \rightarrow$ several distinct E_k's, just as many as the original # degenerate states.

[Suppose the level w/ unperturbed energy $E_k^{(0)}$ is K-fold degenerate, i.e. $\exists$ K fcns $\psi_{kN}^{(0)}$, $1 \leqslant N \leqslant K$, such that: $\mathcal{H}_0 \psi_{kN}^{(0)} = E_k^{(0)} \psi_{kN}^{(0)}$. (29)]

REMARKS

1. We can assume the $\psi_{kN}^{(0)}$ have been made orthonormal: $\langle \psi_{kM}^{(0)} | \psi_{kN}^{(0)} \rangle = \delta_{MN}$. This can be done by Schmidt orthogonalization (see QM 507 Prob. 33).
2. We assume levels $n \neq k$ are not degenerate, i.e. $\mathcal{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ produces just one $\psi_n^{(0)}$ for each $E_n^{(0)}$ when $n \neq k$.
3. We will calculate the perturbed E_k & ψ_k for the initially degenerate level only. The E_n & ψ_n for the nondegenerate levels $n \neq k$ follow (with just minor adjustments) from the already done nondegenerate theory.

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8) Do the calculation -- as much as possible -- in same way as before. So...

(1) Let $\mathcal{H}_0 \rightarrow \mathcal{H} = \mathcal{H}_0 + V$; write Schrodinger Eqtn: $\mathcal{H} \psi_k = E_k \psi_k$.

Expand perturbed k^{th} state: $\psi_k = \sum_{N=1}^{K} c_{Nk} \psi_{kN}^{(0)} + \sum_{n \neq k} a_{nk} \psi_n^{(0)}$.

all the degenerate states participate

Put this ψ_k into S.Eq. to get...

$$\rightarrow \sum_N (E_k - E_k^{(0)}) c_{Nk} \psi_{kN}^{(0)} + \sum_{n \neq k} (E_k - E_n^{(0)}) a_{nk} \psi_n^{(0)} =$$

$$= \sum_N c_{Nk} V \psi_{kN}^{(0)} + \sum_{n \neq k} a_{nk} V \psi_n^{(0)}. \qquad (30)$$

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(2) Operate through Eq. (30) by $\langle \psi_{kM}^{(0)} |\ \ \rangle$ and invoke orthonormality. Then...

Lifting of Degeneracy in $\mathcal{O}(V)$.

$$\boxed{(E_k - E_k^{(0)})\, c_{Mk} = \sum_N c_{Nk} V_{MN} + \sum_{n\neq k} a_{nk} V_{Mn}}, \tag{31}$$

w/ $V_{MN} = \langle \psi_{kM}^{(0)} | V | \psi_{kN}^{(0)} \rangle$ ∫ coupling within deg. level k, $V_{Mn} = \langle \psi_{kM}^{(0)} | V | \psi_n^{(0)} \rangle$ ∫ coupling out of k to level n.

Eq.(31) is the counterpart of Eq.(5), p. SS2, for the nondegenerate case.

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(3) Treat Eq.(31) by the λ expansion as before: $V \to \lambda V$ (w/ $\lim_{\lambda\to 1}$ understood), and:

$$\left[\begin{array}{l} E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 \underline{E_k^{(2)} + \cdots}\,; \\ a_{nk} = \cancel{a_{nk}^{(0)}}^{\,0} + \lambda a_{nk}^{(1)} + \lambda^2 a_{nk}^{(2)} + \cdots \end{array}\right. \tag{32a}$$

The choice $a_{nk}^{(0)} \equiv 0$ ($n \neq k$) ensures that in 0th order: $\Psi_k^{(0)} = \sum_N c_{Nk} \psi_{kN}^{(0)}$, is at most a linear comb^n of the deg. levels $\psi_{kN}^{(0)}$.

To first order in λ (i.e. $\mathcal{O}(V)$), Eq.(31) requires...

$$E_k^{(1)} c_{Mk} = \sum_N c_{Nk} V_{MN}, \quad \text{w/} \quad \boxed{\sum_{N=1}^{K} (V_{MN} - E_k^{(1)} \delta_{MN})\, c_{Nk} = 0.} \tag{32b}$$

Eq.(32) applies entirely <u>within</u> the sublevels N of the degenerate level k. There are nontrivial solutions for the c_{Nk} only if the ( ) is singular, i.e.

$$\det(V_{MN} - E_k^{(1)} \delta_{MN}) = \det \begin{pmatrix} V_{11} - E_k^{(1)} & V_{12} & V_{13} & \cdots \\ V_{21} & V_{22} - E_k^{(1)} & V_{23} & \cdots \\ V_{31} & V_{32} & V_{33} - E_k^{(1)} & \\ \vdots & \vdots & & \ddots \end{pmatrix} = 0. \tag{33}$$

$1 \leq M, N \leq K$
(the determinant is $K \times K$)

<u>This gives a K^{th} order eqtn for the pert$^{\text{b}}$n $E_k^{(1)}$ $\Rightarrow$ K solutions $E_{kL}^{(1)}$, $1 \leq L \leq K$.</u>

EXAMPLE $K = 2$, i.e. two-fold initial degeneracy for level $E_k^{(0)}$.

$$\text{Eq.(33)} \Rightarrow \det \begin{pmatrix} V_{11} - E_k^{(1)} & V_{12} \\ V_{12}^* & V_{22} - E_k^{(1)} \end{pmatrix} = 0 \Rightarrow \ldots\ \underline{\underline{E_{k\pm}^{(1)}}} = \left(\frac{V_{11}+V_{22}}{2}\right) \pm \sqrt{\left(\frac{V_{11}-V_{22}}{2}\right)^2 + |V_{12}|^2}. \tag{34}$$

The $E_{k\pm}^{(1)}$ here are generally different (unless $V_{22} = V_{11}$ & $V_{12} = 0$), so the degeneracy is "lifted": one of ψ_{kN} now belongs to $E_k^{(0)} + E_{k+}^{(1)}$, the other to $E_k^{(0)} + E_{k-}^{(1)}$.

Degenerate Wavefunctions to $\mathcal{O}(V)$.

(4) Suppose the degeneracy is lifted in $\mathcal{O}(V)$ in the general case, i.e. the solutions $E_{kL}^{(1)}$, $1 \leq L \leq K$, to Eq. (33) are all <u>different</u>. Then go back to Eq. (32b), viz.

$$\rightarrow \sum_{N=1}^{K} (V_{MN} - E_{kL}^{(1)} \delta_{MN}) C_{Nk}^{(L)} = 0 \quad \begin{cases} 1 \leq M \leq K \text{ (degree of degeneracy)}; \\ L = 1, 2, \ldots, K, \text{ w/ each } E_{kL}^{(1)} \text{ distinct.} \end{cases} \tag{35}$$

Now, for each value of L, we can (in principle) solve explicitly for a set of K coefficients $C_{Nk}^{(L)}$, w/ L fixed and index N running over $1, 2, \ldots, K$. These sets of $\{C_{Nk}^{(L)}\}$ specify K <u>new</u> zeroth order wavefcns in level k as

$$\rightarrow \phi_{kL}^{(0)} = \sum_{N=1}^{K} C_{Nk}^{(L)} \psi_{kN}^{(0)}, \quad \text{for each of } L = 1, 2, \ldots, K. \tag{36}$$

These levels will become nondegenerate <u>within</u> level k, when $\mathcal{O}(V)$ appears.

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(5) Now go back to Eq. (30) and write the perturbed level wavefcn ψ_k as:

$$\rightarrow \psi_{kL} = \phi_{kL}^{(0)} + \sum_{n \neq k} [a_{nk}^{(1)} + a_{nk}^{(2)} + \ldots] \psi_n^{(0)}, \quad \text{w/ } L = 1, 2, \ldots, K \tag{37}$$

(This is the same as ψ_k in (30), except for the particular choice of $\phi_{kL}^{(0)}$). Evidently we need the $a_{nk}^{(1)}$ to get ψ_{kL} to $\mathcal{O}(V)$. To get the $a_{nk}^{(1)}$, go back to Eq. (30) and operate through by $\langle \psi_m^{(0)} | \;\rangle$, $m \neq k$. Then...

$$\rightarrow (E_k - E_m^{(0)}) a_{mk} = \sum_N C_{Nk}^{(L)} V_{mN} + \sum_{n \neq k} a_{nk} V_{mn}; \tag{38}$$

... and to 1st order (i.e. $\mathcal{O}(V)$)...

$$(E_k^{(0)} - E_m^{(0)}) a_{mk}^{(1)} = \sum_N C_{Nk}^{(L)} V_{mN} \Rightarrow \boxed{a_{nk}^{(1)} = \frac{\left(\sum_N C_{Nk}^{(L)} V_{nN}\right)}{E_k^{(0)} - E_n^{(0)}}}. \tag{39}$$

The perturbed wavefcn in level k, to $\mathcal{O}(V)$ is then

$$\left[\!\left[\psi_{kL} \simeq \phi_{kL}^{(0)} + \sum_{n \neq k} \left[\left(\sum_N C_{Nk}^{(L)} V_{nN}\right) / (E_k^{(0)} - E_n^{(0)}) \right] \psi_n^{(0)}; \; L = 1, 2, \ldots, K \right]\!\right]. \tag{40}$$

Compare with: $\psi_k = \psi_k^{(0)} + \sum_{n \neq k} [V_{nk} / (E_k^{(0)} - E_n^{(0)})] \psi_n^{(0)}$, for nondeg. case [Eq. (23)].

Perturbed energy to $\mathcal{O}(V^2)$. SUMMARY

(6) Now to $\mathcal{O}(V)$, the K sublevels in level k (previously degenerate) have become distinct, with wavefcns ψ_{kI} per Eq.(40), and energies $E_k^{(0)} + E_{kI}^{(1)} \ldots$ with the $E_{kI}^{(1)}$ being the K distinct solutions to the det( )=0 Eq.(33). The lifting of the degeneracy in $\mathcal{O}(V)$ depends on the $E_{kI}^{(1)}$ being all different.

The $\mathcal{O}(V^2)$ correction to the energy E_k can be gotten from Eq.(31) by inserting the λ-series of Eq.(32a) and picking off the λ^2 terms. We get...

$$\rightarrow E_{kI}^{(2)} C_{Mk}^{(I)} = \sum_{n \neq k} a_{nk}^{(1)} V_{Mn}, \quad a_{nk}^{(1)} = \Big(\sum_N C_{Nk}^{(I)} V_{nN}\Big) \Big/ \big(E_k^{(0)} - E_n^{(0)}\big). \tag{41}$$

[compare with Eq.(26b) for nondeg. case: $E_k^{(2)} = \sum_{n \neq k} a_{nk}^{(1)} V_{kn}$, $a_{nk}^{(1)} = V_{nk}/(E_k^{(0)} - E_n^{(0)})$]. So we need to know the coefficients $C_{Mk}^{(I)}$ explicitly before proceeding. That can be done on a case-by-case basis, and we won't go farther with this calc$^{\underline{n}}$.

$\boxed{\text{SUMMARY}}$ (of degenerate perturbation theory).

1. Start with: $\mathcal{H}_0 \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}$. One level, $m=k$, is K-fold degenerate w/ wavefcns $\{\psi_{kN}^{(0)}\}$.
2. Let $\mathcal{H}_0 \rightarrow \mathcal{H} = \mathcal{H}_0 + \lambda V$, so k^{th} energy is perturbed: $E_k^{(0)} \rightarrow E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \ldots$
   Represent k^{th} state wavefcn by: $\psi_k = \sum_{N=1}^{K} C_{Nk} \psi_{kN}^{(0)} + \sum_{n \neq k} [0 + \lambda a_{nk}^{(1)} + \ldots] \psi_n^{(0)}$.
3. $\mathcal{O}(V)$ energy corrections $E_k^{(1)}$ within state k require: $\sum_{N=1}^{K} (V_{MN} - E_k^{(1)} \delta_{MN}) C_{Nk} = 0$.
   So: $\det(V_{MN} - E_k^{(1)} \delta_{MN}) = 0 \Rightarrow$ K solutions for $E_k^{(1)} \rightarrow E_{kI}^{(1)}$, $I = 1, 2, \ldots, K$.
4. The energy degeneracy is "lifted" in $\mathcal{O}(V)$ by $E_k^{(0)} \rightarrow E_k^{(0)} + E_{kI}^{(1)}$ if the solutions $E_{kI}^{(1)}$ are all distinct. Then, for each of $I = 1, 2, \ldots, K$ we can (in principle) find a set of $\{C_{Nk}^{(I)}, N = 1, 2, \ldots, K\}$ such that: $\sum_{N=1}^{K} (V_{MN} - E_{kI}^{(1)} \delta_{MN}) C_{Nk}^{(I)} = 0$.
5. There are now K distinct wavefcns: $\psi_{kI} = \sum_N C_{Nk}^{(I)} \psi_{kN}^{(0)} + \sum_{n \neq k} a_{nk}^{(1)} \psi_n^{(0)}$, in state k, where to $\mathcal{O}(V)$: $a_{nk}^{(1)} = \big(\sum_N C_{Nk}^{(I)} V_{nN}\big) / \big(E_k^{(0)} - E_n^{(0)}\big)$, $n \neq k$. Calculation of $E_k^{(2)}$, etc. now proceeds as for nondegenerate states, but need to know the $C_{Nk}^{(I)}$.
6. If degeneracy is not lifted in $\mathcal{O}(V)$, consult Higher Authority. Or punt...