OFTEN, IT IS POSSIBLE TO GUESS "GOOD" SOLUTIONS [SEE LATER: FINE STRUCTURE OF HYDROGEN], BY USING THEOREM :

> IF A IS AN HERMETIAN OPERATOR COMMUTING WITH $H^{(0)}$ AND H', AND IF $\psi_a^{(0)}$ AND $\psi_b^{(0)}$, THE DEGENERATE EIGENFUNCTIONS OF $H^{(0)}$, ARE ALSO EIGENFUNCTIONS OF A, WITH DISTINCT EIGENVALUES :
>
> $$A\psi_a^{(0)} = \mu\,\psi_a^{(0)} \quad , \quad A\psi_b^{(0)} = \nu\,\psi_b^{(0)} \quad , \quad \mu \neq \nu$$
>
> THEN $W_{ab} = 0$ AND THUS $\psi_a^{(0)}$ AND $\psi_b^{(0)}$ ARE THE "GOOD" SOLUTIONS TO USE IN <u>NON</u>-DEGENERATE PERTURBATION THEORY

[FOR PROOF : SEE p. 260 IN GRIFFITHS]

A MORE ELEGANT METHOD

REWRITE ⇨ EQS. AS

EIGENVALUE

$$\boxed{\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{(1)}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}}$$

EIGENVECTOR a
[COEFFICIENTS OF UNPERTURBED HAMILTONIAN]

MATRIX EQUATION:

$$W a = E^{(1)} a$$

ZERO VECTOR

$$(W - E^{(1)} I)\, a = \emptyset \qquad \text{WITH} \qquad I = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ \vdots & 1 & & \vdots \\ & & 1 & \\ \vdots & & \ddots & \vdots \\ 0 & \cdots & & 1 \end{pmatrix}$$

BY ASSUMPTION, EIGENVECTOR a IS NON-ZERO, MEANING $(W - E^{(1)} I)$ MUST BE SINGULAR, i.e., ITS DETERMINANT MUST BE ZERO:
[NOT INVERTIBLE]

GRIFFITHS, p. 450

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

"CHARCTERISTIC" OR "SECULAR EQUATION"

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

$$[E^{(1)}]^2 - E^{(1)}(W_{aa} + W_{bb}) + (W_{aa} W_{bb} - W_{ab} W_{ba}) = 0$$

SAME AS EQ. *

ONE COULD PLUCK THESE ENERGY/ SOLUTIONS BACK INTO MATRIX EQUATION

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

TO FIND "GOOD" EIGENFUNCTIONS [COEFFICIENTS]; THESE ZERO-ORDER SOLUTIONS FORM A NEW BASIS TO FIND HIGHER ORDER CORRECTIONS USING NON-DEGENERATE PERTURBATION THEORY

NOTE: IF DEGENERACY IS NOT ENTIRELY REMOVED IN 1. ORDER APPROXIMATION, IT COULD BE REMOVED BY INCLUDING HIGHER ORDER TERMS; SEE L. SCHIFF, QUANTUM MECHANICS, 3rd ed. (1968)

USUAL STRATEGY IN DEGENERATE PERTURBATION THEORY

SOLVE SECULAR EQUATION:

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

FOR EIGENVALUES [FIRST ORDER ENERGY SHIFTS]

DIAGONALIZATION OF PERTURBATION HAMILTONIAN IN DEGENERATE SUBSPACE

$\Downarrow$

PLUCK SOLUTIONS BACK INTO MATRIX EQUATION:

$$\begin{pmatrix} W_{aa} & W_{ab} & \cdots \\ W_{ba} & W_{bb} & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \vdots \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha \\ \beta \\ \vdots \end{pmatrix}$$

TO FIND "GOOD" ZERO-ORDER WAVEFUNCTIONS

$\Downarrow$

USE THESE AS A NEW BASIS TO FIND HIGHER-ORDER CORRECTIONS USING NON-DEGENERATE PERTURBATION THEORY

SINCE THESE ARE THE "CORRECT" SOLUTIONS, MATRIX IS ALREADY DIAGONAL

THE EXPLICIT EXPRESSIONS FOR HIGHER-ORDER CORRECTIONS ARE GIVEN IN: C.E. SOLIVEREZ, AMERICAN JOURNAL OF PHYSICS, VOL. 35, p. 624-627 (1967)

[SEE DANIEL SCHRÖDER LECTURE NOTES ON MATRIX ALGEBRA]

EXAMPLE

IMPLIES 3 DIFFERENT QUANTUM NUMBERS

INFINITE SQUARE-WELL POTENTIAL IN 3D : $V(x,y,z) = \begin{cases} \phi & 0 \le x \le a,\ 0 \le y \le a,\ 0 \le z \le a \\ \infty & \text{ELSE} \end{cases}$

STATIONARY STATES :

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

FORM AN ORTHONORMAL SET, BUT THESE ARE NOT THE "GOOD" SOLUTIONS

$$E^{(0)}_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

G.S. 111

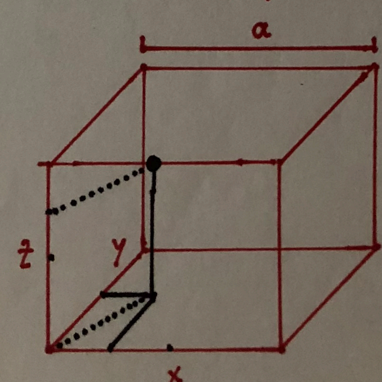
FIRST EXCITED STATE IS TRIPLY-DEGENERATE :

$$E^{(0)}_{\substack{1.\text{EXC.}\\ \text{STATE}}} = 3 \frac{\pi^2 \hbar^2}{ma^2} \quad ; \quad \psi_a^{(0)} = \psi_{112}^{(0)},\ \psi_b^{(0)} = \psi_{121}^{(0)},\ \psi_c^{(0)} = \psi_{211}^{(0)}$$

INTRODUCE δ- PERTURBATION AT $\left(\frac{a}{4}, \frac{a}{2}, \frac{3}{4}a\right)$:

$$H' = a^3 V_0\, \delta\left(x - \frac{a}{4}\right) \delta\left(y - \frac{a}{2}\right) \delta\left(z - \frac{3}{4}a\right)$$

FIND FIRST-ORDER ENERGY CORRECTIONS OF TRIPLY-DEGENERATE FIRST EXCITED STATES



SPECIFIC TASKS:

(i) DETERMINE MATRIX W

HINT:

$$W = \begin{pmatrix} W_{aa} & W_{ab} & -4V_0 \\ W_{ba} & W_{bb} & \emptyset \\ W_{ca} & W_{cb} & 4V_0 \end{pmatrix}$$

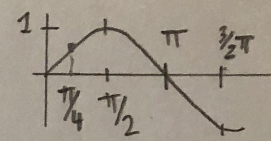
$[\det(W - E^{(1)} I) = \emptyset]$

(ii) SOLVE SECULAR EQUATION; RECALL

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = aei + bfg + cdh - ceg - bdi - afh$$

(iii) FIND FIRST-ORDER ENERGY CORRECTIONS, $E^{(1)}$

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



$\boxed{\psi_a^{(0)} = \psi_{112}^{(0)}}$

$$W_{aa} = \left(\frac{2}{a}\right)^3 a^3 V_0 \iiint \sin^2\left(\frac{\pi x}{a}\right) \sin^2\left(\frac{\pi y}{a}\right) \sin^2\left(\frac{2\pi z}{a}\right) \delta\left(x-\frac{a}{4}\right) \delta\left(y-\frac{a}{2}\right) \delta\left(z-\frac{3a}{4}\right) dx\,dy\,dz$$

$$= 8 V_0 \left(\frac{1}{2}\right)(1)(1) = 4 V_0$$

$\boxed{\psi_b^{(0)} = \psi_{121}^{(0)}}$

$$W_{bb} = 8 V_0 \iiint \sin^2\left(\frac{\pi x}{a}\right) \sin^2\left(\frac{2\pi y}{a}\right) \sin^2\left(\frac{\pi z}{a}\right) \delta\left(x-\frac{a}{4}\right) \delta\left(y-\frac{a}{2}\right) \delta\left(z-\frac{3a}{4}\right) dx\,dy\,dz$$

$$= 8 V_0 \left(\frac{1}{2}\right)(0)\left(\frac{1}{2}\right) = 0$$

$\boxed{\psi_c^{(0)} = \psi_{211}^{(0)}}$

$$W_{cc} = \ldots\ldots = 4 V_0$$

$\boxed{\psi_a^{(0)} = \psi_{112}^{(0)}, \ \psi_b^{(0)} = \psi_{121}^{(0)}}$

$$W_{ab} = 8 V_0 \iiint \sin^2\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi y}{a}\right) \sin\left(\frac{2\pi y}{a}\right) \sin\left(\frac{2\pi z}{a}\right) \sin\left(\frac{\pi z}{a}\right) \delta\left(x-\frac{a}{4}\right) \delta\left(y-\frac{a}{2}\right) \delta\left(z-\frac{3a}{4}\right) dx\,dy\,dz$$

$$= 8 V_0 \sin^2\left(\frac{\pi}{4}\right) \sin\left(\frac{\pi}{2}\right) \sin(\pi) \sin\left(\frac{3}{2}\pi\right) \sin\left(\frac{3}{4}\pi\right) = 0$$

$$W_{ac} = \ldots\ldots = -4 V_0$$

$$W_{bc} = \ldots = 0$$

SOLVE SECULAR EQUATION

$$W = 4V_0 \begin{pmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix} \qquad W_{ab} = W_{ba}^*$$

SOLUTION OF SECULAR EQUATION FOR MATRIX $\frac{1}{4V_0} W$:

$$\det\left(\frac{W}{4V_0} - \lambda I\right) = \begin{vmatrix} 1-\lambda & 0 & -1 \\ 0 & -\lambda & 0 \\ -1 & 0 & 1-\lambda \end{vmatrix} = 0$$

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = aei + \underbrace{bfg}_{=0} + \underbrace{cdh}_{=0} - ceg - \underbrace{bdi}_{=0} - \underbrace{afh}_{=0}$$

THUS: $(1-\lambda)(-\lambda)(1-\lambda) - (-1)(-\lambda)(-1) = 0$

$$-\lambda(1-\lambda)^2 + \lambda = 0$$

$$\lambda\left[1 - (1-\lambda)^2\right] = 0$$

$\Rightarrow \lambda_1 = 0$ OR $(1-\lambda)^2 = 1$

$$1 - \lambda = \pm 1 \quad \Rightarrow \lambda_2 = 0 \ , \ \lambda_3 = 2$$

FIRST-ORDER ENERGY CORRECTIONS (FROM MATRIX W) ARE : $\lambda V_0 4 = \underline{\underline{0, 0, 8V_0}}$

[DEGENERACY ONLY PARTIALLY REDUCED]

"GOOD" UNPERTURBED STATES : $\psi^{(0)} = \alpha \psi_{\substack{a\\112}}^{(0)} + \beta \psi_{\substack{b\\121}}^{(0)} + \gamma \psi_{\substack{c\\211}}^{(0)}$

$$\begin{pmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \lambda \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

FIRST, $\boxed{\lambda = 2}$

$$\begin{pmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = 2 \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

YIELDS :

$$\alpha - \gamma = 2\alpha \rightarrow \alpha = -\gamma$$
$$0 = 2\beta \rightarrow \beta = 0$$
$$-\alpha + \gamma = 2\gamma \rightarrow \gamma = -\alpha$$

GIVES : $\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} \alpha \\ 0 \\ -\alpha \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{pmatrix}$ OR $\boxed{\psi_{\lambda=2}^{(0)} = \frac{1}{\sqrt{2}} \psi_a^{(0)} - \frac{1}{\sqrt{2}} \psi_c^{(0)}}$

$\alpha^2 + (-\alpha)^2 = 1$

$2\alpha^2 = 1$

PROPER NORMALIZATION

SECOND, $\boxed{\lambda = 0}$

$$\begin{pmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \emptyset \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix}$$

YIELDS:

$$\alpha - \gamma = 0 \rightarrow \alpha = \gamma$$

$0 = 0 \rightarrow$ UNDETERMINED; COULD BE $\beta = 0$, OR $\beta = \ldots$

$$-\alpha + \gamma = 0 \rightarrow \alpha = \gamma$$

THE REMAINING TWO EIGENVECTORS MUST BE ORTHOGONAL TO $\psi^{(0)}_{\lambda_1 = 2}$;

THIS IS FULFILLED BY:

$$\begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = \begin{pmatrix} \alpha \\ 0 \\ \alpha \end{pmatrix} \text{ AND } \begin{pmatrix} 0 \\ \beta \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} 1/\sqrt{2} \\ 0 \\ 1/\sqrt{2} \end{pmatrix} \text{ AND } \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \text{[NORMALIZED]}$$

$$\left\{ \begin{array}{l} \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{pmatrix} = 0 \\ \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0 \\ \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0 \end{array} \right.$$

OR: $\boxed{\psi^{(0)}_{\lambda_2 = 0} = \frac{1}{\sqrt{2}} \psi_a^{(0)} + \frac{1}{\sqrt{2}} \psi_c^{(0)}}$ $\quad \boxed{\psi_{\lambda_3 = 0} = \psi_b^{(0)}}$

[NEXT STEP: USE THESE AS A BASIS TO FIND $E^{(2)}$ FROM NON-DEGENERATE P.T.]

web.pa.msu/people/nmoore/TIPT.pdf

FOR EXAMPLE, UP TO SECOND ORDER IN DEGENERATE PERTURBATION THEORY, WE DERIVE:

"GOOD" BASIS

$$E_{nm} = E_n^{(0)} + \lambda \langle nm^{(0)} | H' | nm^{(0)} \rangle$$

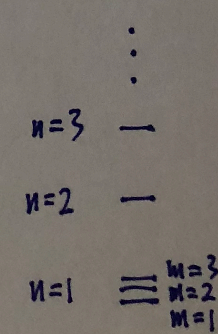
LABELS DEGENERACY

$$- \lambda^2 \sum_{n' \neq n} \sum_{m'=1}^{d_{m'}} \frac{|W_{n'm'nm}|^2}{E_{n'}^{(0)} - E_n^{(0)}} + \mathcal{O}(\lambda^3)$$

WITH $W_{n'm'nm} = \langle n'm'^{(0)} | H' | nm^{(0)} \rangle$

"GOOD" BASIS

WHICH IS ESSENTIALLY THE SAME RESULT AS THAT FROM NON-DEGENERATE PERTURBATION THEORY, BUT WITH THE SINGULAR TERMS EXCLUDED FROM THE SUMMATION



PERTURBATION OF HYDROGEN

SPECTROSCOPY OF HYDROGEN ATOM PLAYED CRUCIAL ROLE FOR DEVELOPMENT OF QUANTUM MECHANICS AND FOR PERTURBATION THEORY IN PARTICULAR

ENERGY LEVELS OF H CAN NOW BE MEASURED WITH 15 DIGITS PRECISION, PROVIDING ONE OF THE BEST TESTS FOR QUANTUM THEORY

OVERVIEW:

PERTURBATIONS CAUSED BY INTERNAL FIELDS
[BETWEEN PROTON + ELECTRON]

- FINE STRUCTURE
  - RELATIVISTIC CORRECTION
  - SPIN-ORBIT COUPLING
- HYPERFINE STRUCTURE

PERTURBATIONS CAUSED BY EXTERNAL FIELDS

- STARK EFFECT [EXT. $\vec{E}$-FIELD]
- ZEEMAN EFFECT [EXT. $\vec{B}$-FIELD]

⇨ PRESENTATIONS