Degenerate Perturbation Theory —

Consider a case like the H-atom for which the eigen energies are degenerate (n^2 for H-atom eg $2s + 3 \times 2p$) If we calculate 2nd order perturbed energy & the perturbing potential V "connects" states that are degenerate (eg $\langle 2s|V|2p\rangle \neq 0$) then since $E_{2s} = E_{2p}$ we have a zero in the denominator.

The problem essentially is that even for λ very small the wavefunction makes a finite shift - ie $\partial_\lambda \Psi$ does not exist.

Anology — If we have a flat surface it doesn't matter which directions we take for x & y. However the smallest inequality makes particular directions for x & y prefered. In some sense if we had initially selected x & y congruent with the not-yet-applied inequality there would be no discontinuous change in x & y directions when that inequality is applied.

→ we need the "right" set of degenerate eigenfunctions that will be congruent with the applied perturbation. Then there will be no discontinuous change.

The solution is easy. Form the matrix: $\langle i|V|j\rangle$ where $|j\rangle$ run over the degenerate eigenfunctions. ("subspace"). Find the eigenvectors/values of this matrix. The eigenvalues will be E_{1j} the eigenvectors (call them $|\alpha\rangle$) will automatically NOT "connect" thru V ie $\langle\alpha|V|\beta\rangle \propto \delta_{\alpha\beta}$

Note: things can still go wrong if the matrix $\langle i|V|j\rangle$ has degenerate eigenvalues — the eigenvectors $|\alpha\rangle$ will not be uniquely defined. In some higher order we may discover the "right" combination consider: $\begin{bmatrix} V \end{bmatrix}\begin{bmatrix} a \end{bmatrix} = E_a\begin{bmatrix} a \end{bmatrix}$ & $\begin{bmatrix} V \end{bmatrix}\begin{bmatrix} b \end{bmatrix} = E_b\begin{bmatrix} b \end{bmatrix}$

we know $\begin{bmatrix} b \end{bmatrix}^{\dagger}\begin{bmatrix} a \end{bmatrix} = 0$ since $E_a \neq E_b$ — 2nd order safe

consider $|\alpha\rangle = \sum a_i |i\rangle$ $\quad |\beta\rangle = \sum b_i |i\rangle$

$$\langle \beta | V | \alpha \rangle = \sum_j \sum_i b_j^* \underbrace{\langle j | V | i \rangle a_i}_{E_a a_j} = E_a \begin{bmatrix} b \end{bmatrix}^{\dagger}\begin{bmatrix} a \end{bmatrix} = 0$$

similarly if $\begin{bmatrix} a \end{bmatrix}$ is normalized $\langle \alpha | V | \alpha \rangle = E_a$ ← first order shift

Eg: 2d particle in box with $V = \lambda\, \delta(x - \frac{L}{3})\, \delta(y - \frac{L}{4})$

$E = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2)$ $\qquad |n_x n_y\rangle = \frac{2}{L}\sin\left(\frac{n_x \pi x}{L}\right)\sin\left(\frac{n_y \pi y}{L}\right)$

$|12\rangle$ & $|21\rangle$ are degenerate.

$$\langle 12 | V | 12 \rangle = \lambda \left(\frac{2}{L}\right)^2 \underbrace{\sin^2\left(\frac{\pi}{3}\right)}_{3/4} \underbrace{\sin^2\left(\frac{2\pi}{4}\right)}_{1} = \lambda\left(\frac{2}{L}\right)^2 \frac{3}{4}$$

$$\langle 21 | V | 21 \rangle = \lambda \left(\frac{2}{L}\right)^2 \underbrace{\sin^2\left(\frac{2\pi}{3}\right)}_{3/4} \underbrace{\sin^2\left(\frac{\pi}{4}\right)}_{\frac{1}{2}} = \lambda\left(\frac{2}{L}\right)^2 \frac{3}{8}$$

$$\langle 12 | V | 21 \rangle = \lambda \left(\frac{2}{L}\right)^2 \underbrace{\sin\left(\frac{\pi}{3}\right)\sin\left(\frac{2\pi}{3}\right)}_{3/4} \underbrace{\sin\left(\frac{2\pi}{4}\right)}_{1} \underbrace{\sin\left(\frac{\pi}{4}\right)}_{1/\sqrt{2}} = \lambda\left(\frac{2}{L}\right)^2 \frac{3}{4}\frac{1}{\sqrt{2}}$$

$$\begin{bmatrix} V \end{bmatrix} = \lambda\left(\frac{2}{L}\right)^2 \frac{3}{4}\begin{bmatrix} 1 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{2} \end{bmatrix} \longrightarrow \det\begin{bmatrix} 1-x & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{2}-x \end{bmatrix} = (1-x)(\tfrac{1}{2}-x) - \frac{1}{2}$$

$$= x\left(x - \frac{3}{2}\right) \rightarrow \underset{a}{0} \; \& \; \underset{b}{\frac{3}{2}}$$

$\begin{bmatrix} a \end{bmatrix} = \begin{bmatrix} 1 \\ -\sqrt{2} \end{bmatrix}$ $\qquad$ take $b \perp$: $\begin{bmatrix} \sqrt{2} \\ 1 \end{bmatrix}$

$$|\alpha\rangle = \frac{2}{L}\left\{ \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right) - \sqrt{2}\,\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\right\}$$

→ has a node @ $(x,y) = \left(\frac{L}{3}, \frac{L}{4}\right)$

$$|\beta\rangle = \frac{2}{L}\left\{ \sqrt{2}\,\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right) + \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\right\}$$

→ is near max @ $(x,y) = \left(\frac{L}{3}, \frac{L}{4}\right)$

[max @ (.326, .287)]

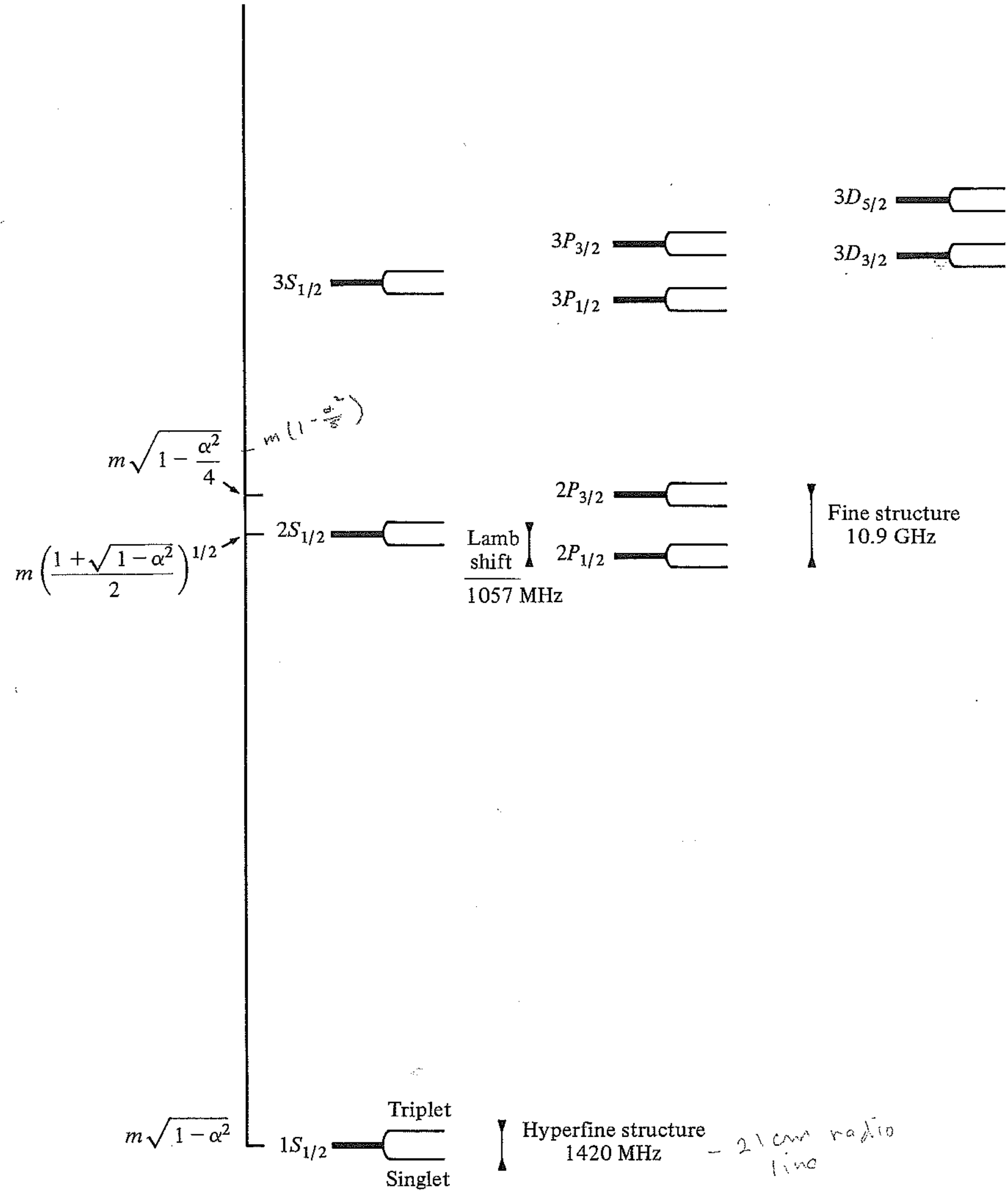

Figure 2-2 Low-lying energy levels of hydrogen.