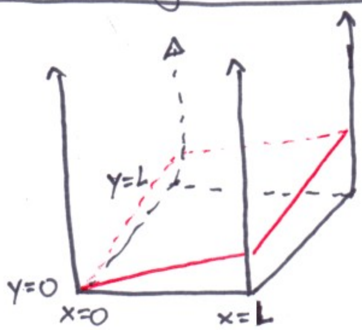
Example of degenerate perturbation theory: ∞ 2D square well



$$V_0 = \begin{cases} 0 & \text{inside} \\ \infty & \text{outside} \end{cases}$$

$$\langle \vec{r} | \varphi^{(0)}_{n_x,n_y} \rangle = \left(\sqrt{\frac{2}{L}} \sin \frac{n_x \pi x}{L} \right) \left(\sqrt{\frac{2}{L}} \sin \frac{n_y \pi y}{L} \right)$$

$$E^{(0)}_{n_x n_y} = \frac{h^2}{8mL^2} \left(n_x^2 + n_y^2 \right)$$

Perturbation: $\hat{H} = \hat{H}_0 + \lambda E^{(0)}_{11} \dfrac{\hat{x}}{L} \dfrac{\hat{y}}{L}$

Note that $E^{(0)}_{12} = E^{(0)}_{21}$ $\Rightarrow$ we must use degenerate perturbation theory for the first excited state.

The exact energies (two of them) are given by $E_2 = E^{(0)}_{12} + \lambda E^{(1)}_2 + \cdots$

We must solve

$$\begin{pmatrix} \langle \varphi^{(0)}_{12} | \hat{H}_1 | \varphi^{(0)}_{12} \rangle & \langle \varphi^{(0)}_{12} | \hat{H}_1 | \varphi^{(0)}_{21} \rangle \\ \langle \varphi^{(0)}_{21} | \hat{H}_1 | \varphi^{(0)}_{12} \rangle & \langle \varphi^{(0)}_{21} | \hat{H}_1 | \varphi^{(0)}_{21} \rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)}_2 \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

$$\downarrow$$

$$\rightarrow \quad \frac{E^{(0)}_{11}}{L^2} \begin{pmatrix} \langle \varphi^{(0)}_{12} | \hat{x}\hat{y} | \varphi^{(0)}_{12} \rangle & \langle \varphi^{(0)}_{12} | \hat{x}\hat{y} | \varphi^{(0)}_{21} \rangle \\ \langle \varphi^{(0)}_{21} | \hat{x}\hat{y} | \varphi^{(0)}_{12} \rangle & \langle \varphi^{(0)}_{21} | \hat{x}\hat{y} | \varphi^{(0)}_{21} \rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)}_2 \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

One of the matrix elements we need is

$$\langle \varphi^{(0)}_{12} | \hat{x}\hat{y} | \varphi^{(0)}_{12} \rangle = \int \langle \varphi^{(0)}_{12} | \vec{r} \rangle \underbrace{\langle \vec{r} | \hat{x}\hat{y} | \varphi^{(0)}_{12} \rangle}_{\text{operate } \hat{x} \text{ then } \hat{y} \text{ to the left, giving } xy \langle \vec{r} | \varphi^{(0)}_{12} \rangle} \xrightarrow{\text{Mathematica}} = \frac{L^2}{4}$$

$\uparrow$

$\int |\vec{r}\rangle\langle\vec{r}| \, d\vec{r}$

$$= \frac{4}{L^2} \int_0^L \int_0^L xy \sin^2 \frac{\pi x}{L} \sin^2 \frac{2\pi y}{L} \, dx \, dy = \frac{4}{L^2} \int_0^L y \sin^2 \frac{2\pi y}{L} dy \int_0^L x \sin^2 \frac{2\pi x}{L} dx$$

Because of the symmetry of $\hat{H}_0$ & $\hat{H}_1$, we then have

$$\langle \varphi_{21}^{(0)} | \hat{x}\hat{y} | \varphi_{21}^{(0)} \rangle = \frac{L^2}{4}$$

We also need

$$\langle \varphi_{12}^{(0)} | \hat{x}\hat{y} | \varphi_{21}^{(0)} \rangle = \int \langle \varphi_{12}^{(0)} | \vec{r} \rangle \, xy \, \langle \vec{r} | \varphi_{21}^{(0)} \rangle \, d\vec{r}$$

$$= \frac{4}{L^2} \int_0^L x \sin\frac{\pi x}{L} \sin\frac{2\pi x}{L} \, dx \int_0^L y \sin\frac{2\pi y}{L} \sin\frac{\pi y}{L} \, dy$$

$$\xrightarrow{\text{Mathematica}} = \alpha L^2 \quad \text{where } \alpha \equiv \frac{2^8}{81\pi^4} \cong 0.320$$

From the symmetry (& also from the requirement that $\lambda \hat{H}_1$ be Hermitian), this also equals $\langle \varphi_{21}^{(0)} | \hat{x}\hat{y} | \varphi_{12}^{(0)} \rangle$

So, our eigenvalue equation becomes

$$E_{11}^{(0)} \begin{pmatrix} \frac{1}{4} & \alpha \\ \alpha & \frac{1}{4} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_2^{(1)} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \Rightarrow \begin{vmatrix} \frac{E_{11}^{(0)}}{4} - E_2^{(1)} & \alpha E_{11}^{(0)} \\ \alpha E_{11}^{(0)} & \frac{E_{11}^{(0)}}{4} - E_2^{(1)} \end{vmatrix} = 0$$

$$\Rightarrow \quad \frac{E_{11}^{(0)}}{4} - E_2^{(1)} = \pm \alpha E_{11}^{(0)} \quad \Leftrightarrow \quad E_2^{(1)} = E_{11}^{(0)} \left(\frac{1}{4} \pm \alpha \right)$$

$\Rightarrow$ First order correction to energy is $\lambda E_2^{(1)} = \lambda E_{11}^{(0)} \left(\frac{1}{4} \pm \alpha \right)$.

This is about the scale of correction we might have guessed from $\lambda \hat{H}_1 = \lambda E_{11}^{(0)} \frac{\hat{x}}{L} \frac{\hat{y}}{L}$

If desired, we can also find the zeroth order approximation to the exact eigenstates:

$$E_{11}^{(0)} \begin{pmatrix} \frac{1}{4} & \alpha \\ \alpha & \frac{1}{4} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E_{11}^{(0)} \left(\frac{1}{4} \pm \alpha\right) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

Top line: $\frac{c_1}{4} + \alpha c_2 = \left(\frac{1}{4} \pm \alpha\right) c_1 \iff c_2 = \pm c_1 \Rightarrow$ After normalizing,

$\lambda E_2^{(1)} = \underbrace{\lambda E_{11}^{(0)} \left(\frac{1}{4} + \alpha\right)}_{\equiv \lambda E_{2+}^{(1)}}$ is the first-order energy correction for $\frac{1}{\sqrt{2}}\left(|\varphi_{12}^{(0)}\rangle + |\varphi_{21}^{(0)}\rangle\right)$

and

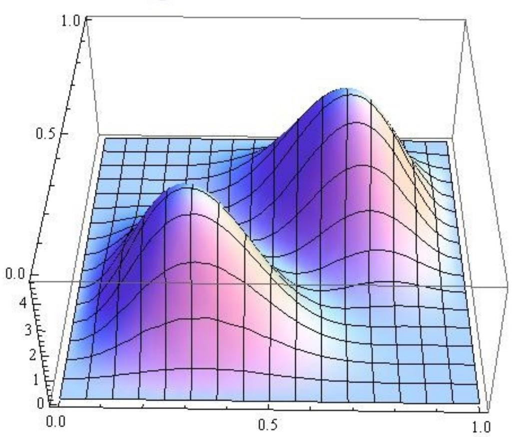
$\lambda E_2^{(1)} = \underbrace{\lambda E_{11}^{(0)} \left(\frac{1}{4} - \alpha\right)}_{\equiv \lambda E_{2-}^{(1)}}$ is the first-order energy correction for $\frac{1}{\sqrt{2}}\left(|\varphi_{12}^{(0)}\rangle - |\varphi_{21}^{(0)}\rangle\right)$

In the position basis, $\lambda E_{2+}^{(1)} \longleftrightarrow \frac{1}{\sqrt{2}}\left(\langle \vec{r}|\varphi_{12}^{(0)}\rangle + \langle \vec{r}|\varphi_{21}^{(0)}\rangle\right)$

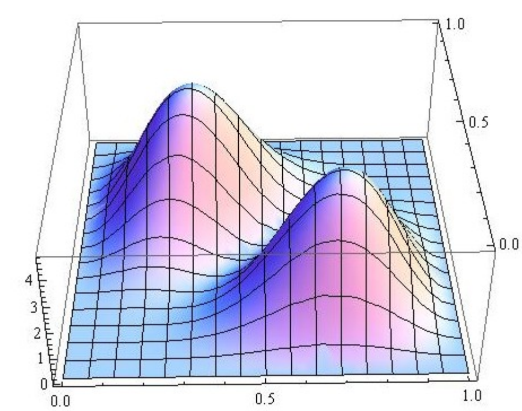
$$= \frac{1}{\sqrt{2}} \frac{2}{L}\left(\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L} + \sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\right) \equiv \psi_+$$

$$\lambda E_{2-}^{(1)} \longleftrightarrow \frac{1}{\sqrt{2}} \frac{2}{L}\left(\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L} - \sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\right) \equiv \psi_-$$

We can understand why these states have different energies by looking at the probability densities:



$|\psi_+|^2$



$|\psi_-|^2$

We see that $|\psi_-|^2$ avoids having much probability density near $x = y = L$, which is the region of highest energy when the perturbation is turned on. Note that both ψ_+ and ψ_- are exact eigenstates of $\hat{H}_0$ (with energy $E_{12}^{(0)}$). As we showed above, they are the zeroth order approximation to the eigenstates of $\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$.