- Consider a two-dimensional Harmonic Oscillator

The Hamiltonian is:

$$\hat{H}_0 = \frac{1}{2m}(\hat{P}_x^2 + \hat{P}_y^2) + \frac{1}{2}m\omega^2(\hat{x}^2 + \hat{y}^2) \equiv \hat{H}_{0x} + \hat{H}_{0y}$$

The eigenvalue equation

$$\hat{H}_0 |\Phi_{n,m}\rangle = E^0_{n,m} |\Phi_{n,m}\rangle$$

with $\quad E^0_{n,m} = E^0_n + E^0_m = \hbar\omega(n+m+1)$

and $\quad |\Phi_{n,m}\rangle = |\phi_n\rangle|\phi_m\rangle$

is satisfied by:

$$E^0_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 1, 2, ..$$

$$\langle x|\phi_n\rangle = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\hbar\pi}\right)^{1/4} \exp\left(-\frac{m\omega}{2\hbar}x^2\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}}\,x\right)$$

with $\quad \int_{-\infty}^{\infty} \phi_n^*(x)\,\phi_k(x)\,dx = \delta_{nk}$

and $\quad \sum_{n=0}^{\infty} \phi_n^*(x')\,\phi_n(x) = \delta(x-x')$

The spectrum is:

$n+m+1$	n	m
1	0	0
2	1	0
2	0	1
3	2	0
3	1	1
3	0	2
4	3	0
4	2	1
4	1	2
4	0	3

Each eigenvalue $E^0_{n,m}$ is $n+m+1$ times <u>degenerate</u>.

Moreover:

$$\langle x, y | \Phi_{n,m} \rangle = \phi_n(x)\, \phi_m(y) \qquad n,m = 0,1,2,\dots$$

Consider now the perturbation:

$$\lambda \hat{V} = \lambda \hat{x} \hat{y}$$

If we define:

$$\hat{x} = \frac{1}{\sqrt{2}\beta}(\hat{a} + \hat{a}^+) \qquad \beta^2 = \frac{m\omega}{\hbar}$$

$$\hat{y} = \frac{1}{\sqrt{2}\beta}(\hat{b} + \hat{b}^+)$$

$$[\hat{a}, \hat{a}^+] = \hat{1} = [\hat{b}, \hat{b}^+]$$

Then:

$$\hat{H}_0 = \hbar\omega(\hat{a}^+\hat{a} + \hat{b}^+\hat{b} + \hat{1})$$

Moreover:

$$\left.\begin{aligned} \hat{a}|\phi_n\rangle &= \sqrt{n}\,|\phi_{n-1}\rangle \\ \hat{a}^+|\phi_n\rangle &= \sqrt{n+1}\,|\phi_{n+1}\rangle \\ \hat{a}^+\hat{a}|\phi_n\rangle &= n|\phi_n\rangle \end{aligned}\right\} \text{The same is valid for } b$$

Consider the second level of energy:

$$E^0_{10} = E^0_{01} = 2\hbar\omega$$

which is two-fold degenerate. We want to diagonalize $\hat{V}$ in the degenerate subspace spanned by $\{|\Phi_{10}\rangle, |\Phi_{01}\rangle\}$:

$$\hat{V} \doteq \begin{bmatrix} \langle\Phi_{10}|\hat{x}\hat{y}|\Phi_{10}\rangle & \langle\Phi_{10}|\hat{x}\hat{y}|\Phi_{01}\rangle \\ \langle\Phi_{01}|\hat{x}\hat{y}|\Phi_{10}\rangle & \langle\Phi_{01}|\hat{x}\hat{y}|\Phi_{01}\rangle \end{bmatrix} = \frac{\hbar}{2m\omega}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \equiv V$$

The matrix elements are easily calculated algebraically.

For example:

$$\langle\Phi_{10}|\hat{x}\hat{y}|\Phi_{01}\rangle = \frac{1}{2\beta^2}\langle\Phi_{10}|\hat{a}\hat{b} + \hat{a}^+\hat{b} + \hat{a}\hat{b}^+ + \hat{a}^+\hat{b}^+|\Phi_{01}\rangle$$

$$= \frac{1}{2\beta^2} \langle \Phi_{10} | \hat{a}^+ \hat{b} | \Phi_{01} \rangle = \frac{1}{2\beta^2}$$

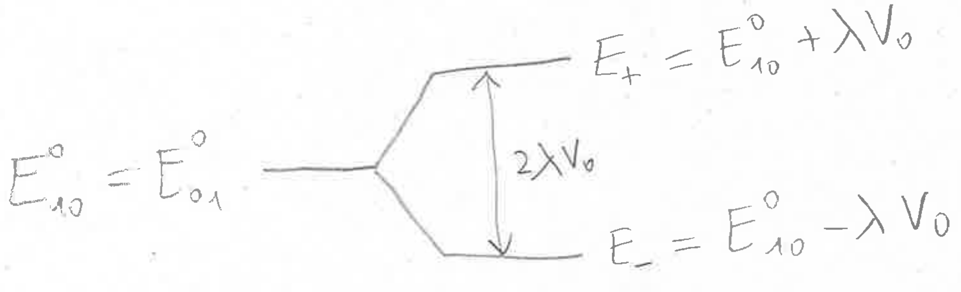
the eigenvalues $\alpha_\pm$ of the matrix

$$V = \begin{bmatrix} 0 & \frac{\hbar}{2m\omega} \\ \frac{\hbar}{2m\omega} & 0 \end{bmatrix} \equiv \begin{bmatrix} 0 & V_0 \\ V_0 & 0 \end{bmatrix}$$ are found as usual:

$$\det \begin{bmatrix} -\alpha & V_0 \\ V_0 & -\alpha \end{bmatrix} = \alpha^2 - V_0^2 = (\alpha - V_0)(\alpha + V_0) = 0 \Rightarrow$$

$$\Rightarrow \alpha_\pm = \pm V_0$$

This means that the original degenerate energy level is no longer degenerate:



The eigenvectors $|\varphi_\pm\rangle$ are easily found

$$|\varphi_\pm\rangle = \frac{1}{\sqrt{2}} \left(|\Phi_{10}\rangle \pm |\Phi_{01}\rangle \right)$$

* The Stark effect *

Consider an Hydrogen atom described by the Hamiltonian (written with respect to the relative coordinates $\underline{r} = \underline{r}_1 - \underline{r}_2$)

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

The corresponding Schrödinger equation is:

$$\hat{H}_0 |\psi_{n\ell m}\rangle = E_n^0 |\psi_{n\ell m}\rangle$$

where

$$\langle \underline{r} | \psi_{n\ell m}\rangle = R_{n\ell}(r) Y_{\ell m}(\theta,\phi) \quad ; \quad \mu = \frac{\overset{\text{nucleus mass}}{M} \cdot \overset{\text{electron mass}}{m}}{M + m}$$

and

$$E_n^0 = -\left(\frac{1}{2}\mu c^2 \alpha^2\right)\frac{1}{n^2} \qquad \alpha \equiv \frac{e^2}{4\pi\epsilon_0}\frac{1}{\hbar c} \qquad \ell > 0$$

Now, suppose to apply to the atom a static electric field parallel to the z-axis of strength $\mathcal{E}$. It introduces a perturbation:

$$\lambda \hat{V} = e\mathcal{E} z = e\mathcal{E} r\cos\theta$$

For simplicity, let us denote the states $|\psi_{n\ell m}\rangle$ simply as:

$$|\psi_{n\ell m}\rangle = |n\,\ell\,m\rangle$$

If $n=2$, we have 3 states.

$$|2,0,0\rangle;\ |2\,1\,1\rangle,\ |2\,1\,0\rangle,\ |2\,1,-1\rangle$$

To diagonalize $\lambda\hat{V}$ in this subspace, we have to calculate the matrix elements:

$$\langle 2\,\ell\,m|\,r\cos\theta\,|2\,\ell'm'\rangle$$

Since $\lambda\hat{V}$ is independent of ϕ, then:

$$\langle 2\,\ell m|r\cos\theta|2\,\ell'm'\rangle = \langle 2\,\ell m|r\cos\theta|2\,\ell'm\rangle\,\delta_{mm'}$$

Therefore, we can write:

$\langle 2\ell m|z|2\ell'm'\rangle =$

	211	21-1	210	200
211	X	0	0	0
21-1	0	X	0	0
210	0	0	X	
200	0	0		X

However, the diagonal element are zero by symmetry because:

$$\langle 2\ell m|z|2\ell m\rangle = \int_{-\infty}^{\infty} dx\,dy\,dz\,\underbrace{|\psi_{2\ell m}|^2}_{\text{even function in } z}\,\overset{\text{odd function}}{z} = 0$$

and

$$Y_{\ell m}(-\underline{r}) = (-1)^{\ell}\,Y_{\ell m}(\underline{r}) \Rightarrow |Y_{\ell m}(-\underline{r})|^2 = (-1)^{2\ell}|Y_{\ell m}(\underline{r})|^2$$

$$= |Y_{\ell m}(\underline{r})|^2$$

So, the only nonzero elements are:

$\langle 200|z|210\rangle$ and the c.c.

Since

$$\psi_{200} = (2a_0)^{-3/2}\, 2\left(1-\frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}}\, Y_{00}\,; \quad Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$\psi_{210} = (2a_0)^{-3/2}\, 3^{-1/2}\left(\frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}\, Y_{10}\,; \quad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

Therefore:

$(z = r\cos\theta)$

$$\int \psi_{200}\, z\, \psi_{210}\, dx\,dy\,dz =$$

$$= \frac{1}{(2a_0)^3}\frac{2}{\cancel{\sqrt{3}}}\frac{\cancel{\sqrt{3}}}{\cancel{4}_{2}\pi}\underbrace{\int_0^{2\pi} d\phi}_{=2\pi}\underbrace{\int_0^{\pi}\cos^2\theta\sin\theta\, d\theta}_{=\frac{2}{3}} \quad *$$

$$* \; \underbrace{a_0^3\int_0^\infty \left(\frac{r}{a_0}\right)^3\left(1-\frac{r}{2a_0}\right)\frac{r}{a_0}\, e^{-r/a_0}\, d\left(\frac{r}{a_0}\right) a_0}$$

$$= a_0^4\int_0^\infty x^4\,(1 - x/2)\, e^{-x}\, dx = a_0^4\,(-36)$$

$$= -3a_0$$

Therefore, we have to diagonalize an effective 2x2 matrix:

$$\underbrace{e\mathcal{E}\begin{bmatrix} \langle 200|z|200\rangle & \langle 200|z|210\rangle \\ \langle 210|z|200\rangle & \langle 210|z|210\rangle \end{bmatrix}}\begin{bmatrix} \alpha_1 \\ \alpha_2 \end{bmatrix} = E^1 \begin{bmatrix} \alpha_1 \\ \alpha_2 \end{bmatrix}$$

$$= -3a_0\mathcal{E}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

This is the same matrix as the previous example! ⇒

$$\Rightarrow \quad E^1_{\pm} = \pm 3e\mathcal{E}a_0$$

and

$$|\psi_{\pm}\rangle \doteq \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ \pm 1 \end{bmatrix}$$

Therefore, we have a partial removal of the degeneracy: