Example: Stark effect for Hydrogen

perturbation term

$-\vec{d}\cdot\vec{E}$ – electric field acting on atomic dipole ($\vec{d}$)

we will write $\vec{d} = -e\cdot\vec{r}$ and convert to operator

$\hat{H}_1 = e\,\hat{\vec{r}}\cdot\vec{E}$, next we direct $\vec{E}$ along 'z'

$$\hat{H}_1 = e\cdot\underbrace{\hat{\vec{r}}}_{x\vec{e}_x + y\vec{e}_y + z\vec{e}_z}\cdot E_z\vec{e}_z = e\,\hat{z}\cdot E_z$$

unit vector along z

not a coordinate, nucleus charge

as a brief reminder $\hat{H}_0 = -\frac{\hbar^2}{2\mu}\cdot\hat{\vec{p}}^{\,2} - \frac{Ze^2}{r}$

with eigenstates $|n,\ell,m\rangle$ which are also eigen states of $\hat{\vec{L}}^2$ and $\hat{L}_z$ operators

$\hat{\vec{L}} = \hat{\vec{r}}\times\hat{\vec{p}}$

so $$\hat{H}_0|n,\ell,m\rangle = E_n|n,\ell,m\rangle$$
$$L_z|n,\ell,m\rangle = \hbar m|n,\ell,m\rangle$$
$$\hat{\vec{L}}_z^2|n,\ell,m\rangle = \hbar^2\ell(\ell+1)|n,\ell,m\rangle$$

let's find Energy correction to the ground level $|1, 0, 0\rangle$

there is no degeneracy so it should be easy.

$$E_1^{(1)} = \langle 1,0,0|\hat{H}_1|1,0,0\rangle = eE_z\langle 1,0,0|\hat{z}|1,0,0\rangle$$

let's do a more general case

$$\langle n',l',m'|z|n,l,m\rangle = ?$$

$$[\hat{L}_z, \hat{z}] = 0$$

$$\Rightarrow \langle n',l',m'|\hat{L}_z\hat{z}|n,l,m\rangle = \langle n',l',m'|\hat{z}\hat{L}_z|n,l,m\rangle$$

$\hat{L}_z^\dagger = \hat{L}_z$

$$\hbar m'\langle n',l',m'|z|n,l,m\rangle = \hbar m\langle n',l',m'|\hat{z}|n,l,m\rangle$$

$$\Rightarrow \boxed{\langle n',l',m'|\hat{z}|n,l,m\rangle = 0, \text{ if } m'\neq m}$$

$\Rightarrow E_1^{(1)} = 0$ so we need to calculate 2nd order correction

which is tedious
$$E_1^{(2)} = \sum_{n\neq 1,\, l,\, m=0} \frac{e^2E_z^2|\langle n,l,0|\hat{z}|1,0,0\rangle|^2}{E_1 - E_n^{(0)}} \sim -E_z^2$$

note m=0

note (−)

Now let's find $E_2^{(1)}$ correction

$E(n=2)$ is degenerate, there are 4 states

$$\left.\begin{array}{ll} n=2,\ \ell=0,\ m=0 & \leftarrow |a\rangle \\ n=2,\ \ell=1,\ m=0 & \leftarrow |b\rangle \\ -1 & \leftarrow |c\rangle \\ +1 & \leftarrow |d\rangle \end{array}\right\}\ \text{labels}$$

So we need to solve

$$\begin{pmatrix} V_{aa} & V_{ab} & V_{ac} & V_{dd} \\ V_{ba} & V_{bb} & V_{bc} & V_{bd} \\ V_{ca} & V_{cb} & V_{cc} & V_{cd} \\ V_{da} & V_{db} & V_{dc} & V_{dd} \end{pmatrix} \begin{pmatrix} C_a \\ C_b \\ C_c \\ C_d \end{pmatrix} = E^{(1)} \begin{pmatrix} C_a \\ C_b \\ C_c \\ C_d \end{pmatrix}$$

where $V_{cd} = \langle c | \hat{H}_1 | d \rangle$

this looks scary but recall that $\hat{H}_1 \sim \hat{z}$

so $V \sim \langle \ldots, m' | \hat{z} | \ldots, m \rangle = 0$ for $m' \neq m$

$$\begin{pmatrix} V_{aa} & V_{ab} & & \\ V_{ab} & V_{bb} & & \\ & & V_{cc} & \\ & & & V_{dd} \end{pmatrix}$$

This is easier but we still need to calculate a lot of matrix elements

One way is brute force calculation

$$|n, \ell, m\rangle \longleftrightarrow |\Psi_{n,\ell,m}(r,\theta,\varphi)\rangle = R_{n\ell}(r)\cdot Y_{\ell m}(\theta,\varphi)$$

$$\hat{z} = r\cdot\cos\theta$$

for example: $V_{ab} = \int_0^\infty r^2 dr \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin\theta\, R_{20}^*(r)\, Y_{00}^*(\theta,\varphi)\, r\cdot\cos\theta\cdot R_{21}(r)\, Y_{10}(\theta,\varphi)$

above is quite scary and we need to do it several times.

It would be nice to find some physics trick

We not the following property of the parity $\hat{\Pi}$

$$\hat{\Pi}^+ \hat{z}\hat{\Pi} = -\hat{z} \quad \text{or} \quad \{\hat{\Pi},\hat{z}\} = 0 \;;\; \hat{\Pi}^+ = \hat{\Pi}$$

also $\hat{\Pi}|n,\ell,m\rangle = (-1)^\ell |n,\ell,m\rangle$ anti-commutator

$$\langle n',\ell',m'|\hat{\Pi}\hat{z}|n\ell m\rangle = \langle n',\ell',m'|-\hat{z}\hat{\Pi}|n,\ell,m\rangle$$

$$(-1)^{\ell'}\langle n',\ell',m'|\hat{z}|n,\ell,m\rangle = -(-1)^\ell\langle n',\ell',m'|\hat{z}|n,\ell,m\rangle$$

$\hat{\Pi}^+$ ''

$$\langle n',\ell',m'|\hat{z}|n,\ell,m\rangle \neq 0 \quad \text{if} \quad \underline{(-1)^{\ell'+\ell+1} = 1}$$

we take ⟨ ⟩ for different parity states

recall $|a\rangle \longleftrightarrow \ell = 0$ $\Rightarrow$ $\hat{V}$ - diagonal terms $= 0$

$|b\rangle, |c\rangle, |d\rangle \longleftrightarrow \ell = 1$

$$\hat{V} = \begin{pmatrix} 0 & V_{ab} & & \\ V_{ba} & 0 & & 0 \\ & & 0 & \\ & 0 & & 0 \end{pmatrix}$$

also recall that
H_1 is Hermitian $\Longleftrightarrow$ $V_{ab} = V_{ba}^*$
but $\hat{z}$ is real so V_{ab} is real

We used physics as much as we could, now we need to do the math.

$$V_{ab} = eE_z \cdot \langle 2,0,0 | \hat{z} | 2,1,0 \rangle =$$

$$= eE_z \int_0^\infty r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\varphi \; R_{20}^*(r) \, Y_{00}^*(\theta,\varphi) \, r \cdot \cos\theta \, R_{21}(r) \, Y_{10}(\theta,\varphi)$$

charge of nucleus

$$= eE_z \int_0^\infty r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\varphi \cdot 2\left(\frac{Z}{2a_0}\right)^{3/2} \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}} \sqrt{\frac{1}{4\pi}} \cdot r \cdot \cos\theta$$

$$\cdot \frac{2}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{2a_0} e^{-\frac{Zr}{2a_0}} \cdot \sqrt{\frac{3}{4\pi}} \cos\theta$$

$\left\{ \text{convinient variable } \rho = \frac{Zr}{2a_0} \rightarrow dr = \frac{2a_0}{Z} d\rho \right\}$

$$V_{ab} = eE_z \cdot 4 \cdot \cancel{\frac{1}{\sqrt{3}}} \cancel{\frac{\sqrt{3}}{4\pi}} \left(\frac{Z}{2a_0}\right)^3 \left(\frac{2a_0}{Z}\right)^4 \int_0^\infty d\rho \int_0^\pi \sin\theta \, d\theta \underbrace{\int_0^{2\pi} d\varphi}_{2\pi} (1-\rho) e^{-2\rho} \rho^4 \cos^2\theta$$

$$= eE_z \, 2 \cdot \frac{2a_0}{Z} \int_0^\infty \rho^4 (1-\rho) e^{-2\rho} d\rho \int_0^\pi \underbrace{\sin\theta \cos^2\theta \, d\theta}_{\int_0^\pi \cos^2\theta \, d(-\cos\theta) = -\frac{\cos^3\theta}{3}\Big|_0^\pi = \frac{2}{3}}$$

$$= \frac{eE_z}{3} 8 \frac{a_0}{Z} \underbrace{\int_0^\infty \rho^4 (1-\rho) e^{-2\rho} d\rho}$$

we can take it by parts
but there is a nice trick

$$\int_0^\infty \rho^4 (1-\rho) e^{-2\rho} d\rho = \Big/ 2\rho = x \Big/ = \int_0^\infty \frac{x^4}{2^4} \left(1 - \frac{x}{2}\right) e^{-x} \frac{dx}{2}$$

$$= \frac{1}{2^5} \left[\underbrace{\int_0^\infty x^4 e^{-x} dx}_{\Gamma(5)} - \frac{1}{2} \underbrace{\int_0^\infty x^5 e^{-x} dx}_{\Gamma(6)} \right]$$

where gamma function $\Gamma(z) = \int_0^\infty x^{z-1} e^{-x} dx = (z-1)!$

$$\int_0^\infty d\rho \,\cdots\cdots = \frac{1}{2^5}\left[\Gamma(5) - \frac{1}{2}\Gamma(6)\right] = \frac{1}{32}\left(4! - \frac{5!}{2}\right) =$$

$$= \frac{1}{32}\left(24 - \frac{120}{2}\right) = \frac{1}{32}\,36 = \frac{9\cdot 4}{8\cdot 4} = -\frac{9}{8}$$

finally we are ready to have V_{ab} in a close form

$$V_{ab} = \frac{e E_z}{3}\, 8\, \frac{a_0}{Z}\cdot\left(-\frac{9}{8}\right) = \boxed{-\frac{3 E_z a_0}{Z} = V_{ab}}$$

Z ← # protons

We could have guess $\sim E_z a_0$ from dimentionality

what a pain, imagine we would have to do it for every V matrix element. Physics saves time

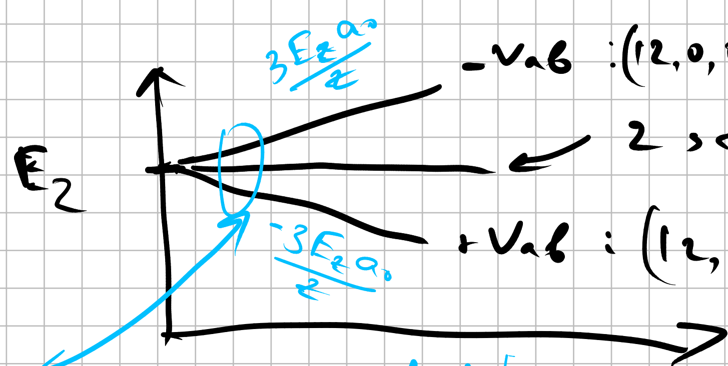
Now we are ready to find $E_2^{(1)}$, i.e changes in energy

$$\begin{pmatrix} 0 & V_{ab} & & \\ V_{ab} & 0 & & \\ & & 0 & \\ & & & 0 \end{pmatrix}\begin{pmatrix} c_a \\ \vdots \\ c_d \end{pmatrix} = E^{(1)}\begin{pmatrix} c_a \\ \vdots \\ c_d \end{pmatrix}$$

$$\det\begin{pmatrix} -E_2^{(1)} & V_{ab} & 0 & \\ V_{ab} & -E_2^{(1)} & & \\ & & -E_2^{(1)} & \\ & 0 & & -E_2^{(1)} \end{pmatrix} = \left(-E_2^{(1)}\right)^2\left(E_2^{(1)2} - V_{ab}^2\right) = 0$$

4 possible solutions

$$E_2^{(1)} = 0,\ 0,\ +V_{ab},\ -V_{ab}$$



$-V_{ab}$: $(|2,0,0\rangle - |2,1,0\rangle)/\sqrt{2}$

2 states not moving $|2,1,\pm 1\rangle$

$+V_{ab}$: $(|2,0,0\rangle + |2,1,0\rangle)/\sqrt{2}$

degeneracy lifted!

eigenstates

$E_2^{(1)} = 0 \rightarrow$ $|c\rangle = |2,1,-1\rangle$
$|d\rangle \quad |2,1,+1\rangle$

what is the state with $E_2^{(1)} = V_{ab}$

$$\begin{pmatrix} 0 & V_{ab} & 0 & 0 \\ V_{ab} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_a \\ c_b \\ c_c \\ c_d \end{pmatrix} = V_{ab} \begin{pmatrix} c_a \\ c_b \\ c_c \\ c_d \end{pmatrix}$$

$$\begin{pmatrix} V_{ab} \cdot c_b \\ V_{ab} \cdot c_a \\ 0 \\ 0 \end{pmatrix} \begin{matrix} = \\ = \\ = \\ = \end{matrix} \begin{pmatrix} V_{ab} \cdot c_a \\ V_{ab} \cdot c_b \\ V_{ab} \cdot c_c \\ V_{ab} \cdot c_d \end{pmatrix} \Rightarrow \vec{C}^T = \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix} \cdot \frac{1}{\sqrt{2}}$$

$c_a = c_b$

normalization of $|\psi\rangle$

$$E_2^{(1)} = V_{ab} : |\psi\rangle \Rightarrow \frac{|a\rangle + |b\rangle}{\sqrt{2}} = \frac{|2,0,0\rangle + |2,1,0\rangle}{\sqrt{2}}$$

similarly

$$E_2^{(1)} = -V_{ab} : |\psi\rangle = \frac{|a\rangle - |b\rangle}{\sqrt{2}} = \frac{|2,0,0\rangle - |2,1,0\rangle}{\sqrt{2}}$$

Let's think about how high electric field is allowed so we are still in perturbation regime.

one way was to say $E_2^{(1)} \ll \min(E_2 - E_m)$

but this boring.

Physisist way : $E_{external} \ll E_{seen}$ internal by electron

electric field

$$E_{ext} = E_z \ll k\frac{Ze}{a_0^2} \approx E_{internal}$$

coulomb constant

$$\ll \frac{ke}{a_0^2} = \frac{9 \cdot 10^9 \left[\frac{V \cdot m}{C}\right] \cdot 1.6 \cdot 10^{-19} [C]}{(5 \cdot 10^{-11})^2 [m^2]}$$

$Z=1$ for hydrogen

$a_0 = 5 \cdot 10^{-11} m$

Bohr radius

$$\simeq 5.8 \cdot 10^{11} \, [V/m]$$

$$\boxed{E_{ext} \ll 5.8 \cdot 10^{11} \frac{V}{m}}$$

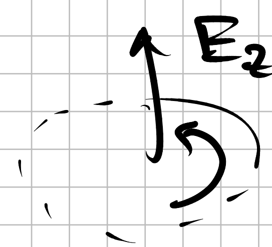
wow! looks like we do not need to worry about being outside of perturbation

Side note about leftover degeneracy:

Degeneracy is consequence of some symmetry.

$-\vec{d}\,\vec{E}$ took away symmetry along $\vec{e}_z$ direction

But we still have rotational symmetry around $\vec{e}_z$



thus unlifted degeneracy.