

# 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

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

$$\hat{H}_1 = e \cdot \vec{r} \cdot E_z \hat{e}_z = e \hat{z} \cdot E_z$$

$$\hat{x}\hat{e}_x + \hat{y}\hat{e}_y + \hat{z}\hat{e}_z$$

unit vector along z

not a coordinate, nucleus charge

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

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

$$\text{so } \hat{H}_0 |n, l, m\rangle = E_n |n, l, m\rangle$$

$$\hat{L}_z |n, l, m\rangle = \hbar m |n, l, m\rangle$$

$$\hat{L}^2 |n, l, m\rangle = \hbar^2 l(l+1) |n, l, m\rangle$$

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

Let's find Energy correction to the ground level  $|1, 0, 0\rangle$  there is no degeneracy so it should be easy.

$$E_1^{(1)} = \langle 1, 0, 0 | \hat{H} | 1, 0, 0 \rangle = e E_2 \langle 1, 0, 0 | \hat{z} | 1, 0, 0 \rangle$$

let's do a more general case

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

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

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

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

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

$$\Rightarrow E_1^{(1)} = 0$$

so we need to calculate 2nd order correction

which is tedious

$$E_1^{(2)} = \sum_{n \neq 1, l, m=0} \frac{e^2 E_2^2 |\langle n, l, 0 | \hat{z} | 1, 0, 0 \rangle|^2}{E_1 - E_n^{(0)}} \sim -E_2^2$$

note  $m=0$ 
note  $\rightarrow$

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

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

$$\left. \begin{array}{l} n=2, l=0, m=0 \quad \leftarrow |a\rangle \\ n=2, l=1, m=0 \quad \leftarrow |b\rangle \\ \quad \quad \quad \quad \quad \leftarrow |c\rangle \\ \quad \quad \quad \quad \quad \leftarrow |d\rangle \end{array} \right\} \text{labels}$$

So we need to solve

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

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

this looks scary but recall that  $\hat{H}_1 \sim \hat{z}^2$

so  $V \sim \langle \dots, m' | \hat{z}^2 | \dots, m \rangle = 0$  for  $m' \neq m$

$$\begin{pmatrix} V_{aa} & V_{ab} & 0 & 0 \\ V_{ab} & V_{bb} & 0 & 0 \\ 0 & 0 & V_{cc} & 0 \\ 0 & 0 & 0 & V_{dd} \end{pmatrix}$$

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

One way is brute force calculation

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

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

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

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

It would be nice to find some physics trick

We note the following property of the parity  $\hat{\Pi}$

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

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

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

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

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

we take  $\langle \rangle$  for different parity states

recall  $|a\rangle \leftrightarrow \ell=0$   
 $|b\rangle, |c\rangle, |d\rangle \leftrightarrow \ell=1 \Rightarrow \hat{V}$ -diagonal terms = 0

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

also recall that  $H_1$  is Hermitian  $\Leftrightarrow V_{ab} = V_{ba}^*$   
 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.

$$\begin{aligned} V_{ab} &= eE_z \langle 2, 0, 0 | \hat{z} | 2, 1, 0 \rangle = \\ &= eE_z \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi R_{20}^*(r) Y_{00}^*(\theta, \phi) r \cos\theta R_{21}(r) Y_{10}(\theta, \phi) \\ &= eE_z \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \cdot 2 \left(\frac{z}{2a_0}\right)^{3/2} \left(1 - \frac{zr}{2a_0}\right) e^{-\frac{zr}{2a_0}} \sqrt{\frac{1}{4\pi}} \cdot r \cos\theta \\ &\quad \cdot \frac{2}{\sqrt{3}} \left(\frac{z}{2a_0}\right)^{3/2} \frac{zr}{2a_0} e^{-\frac{zr}{2a_0}} \cdot \sqrt{\frac{3}{4\pi}} \cos\theta \end{aligned}$$

charge of nucleus

convenient variable  $\rho = \frac{zr}{2a_0} \rightarrow dr = \frac{2a_0}{z} d\rho$

$$V_{ab} = eE_2 \cdot 4 \cdot \frac{1}{\sqrt{3}} \cdot \frac{\sqrt{3}}{4\pi} \left(\frac{z}{2a_0}\right)^3 \left(\frac{2a_0}{z}\right)^4 \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\varphi \int_0^\infty d\rho (1-\rho) e^{-2\rho} \rho^4 \cos^2\theta$$

$$= eE_2 \cdot 2 \cdot \frac{2a_0}{z} \int_0^\infty \rho^4 (1-\rho) e^{-2\rho} d\rho \int_0^\pi \underbrace{\sin\theta \cos^2\theta d\theta}_{\int_0^\pi \cos^2\theta d(-\cos\theta) = -\frac{\cos^3\theta}{3} \Big|_0^\pi = \frac{2}{3}}$$

$$= \frac{eE_2}{3} \cdot 8 \frac{a_0}{z} \int_0^\infty \rho^4 (1-\rho) e^{-2\rho} d\rho$$

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

$$\int_0^\infty \rho^4 (1-\rho) e^{-2\rho} d\rho = \int_0^\infty \frac{x^4}{2^5} (1 - \frac{x}{2}) e^{-x} \frac{dx}{2}$$

$$= \frac{1}{2^5} \left[ \int_0^\infty x^4 e^{-x} dx - \frac{1}{2} \int_0^\infty x^5 e^{-x} dx \right]$$

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

$$\int_0^{\infty} dy \dots = \frac{1}{2^5} [\Gamma(5) - \frac{1}{2} \Gamma(6)] = \frac{1}{32} (4! - \frac{5!}{2}) =$$

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

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

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

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

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

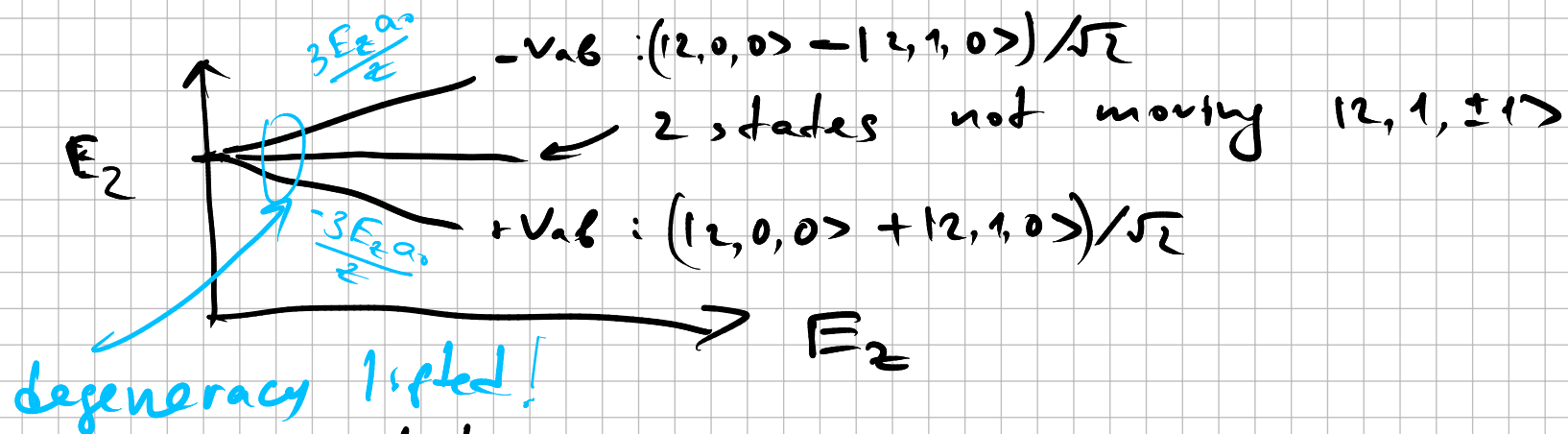
Now we are ready to find  $E_2^{(1)}$ , i.e. changes  
in energy

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

$$\det \begin{pmatrix} -E_2^{(n)} & V_{ab} & 0 \\ V_{ab} & -E_2^{(n)} & 0 \\ 0 & 0 & -E_2^{(n)} - E_2^{(n')} \end{pmatrix} = (-E_2^{(n)})^2 (E_2^{(n)2} - V_{ab}^2) = 0$$

4 possible solutions

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



eigen states

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



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

$$\begin{pmatrix} 0 & V_{ab} & 0 & 0 \\ V_{ab} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_b \\ c_c \\ c_d \end{pmatrix} = V_{ab} \begin{pmatrix} c_1 \\ c_b \\ c_c \\ c_d \end{pmatrix}$$

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

$c_a = c_b$   
 ↑ 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  $E_2^{(1)} \ll \min(E_2 - E_n)$

but this boring.

Physicist way:  $E_{\text{external}} \ll E_{\text{seen by electron}}^{\text{internal}}$   
electric field

$$E_{\text{ext}} = E_2 \ll \frac{kze}{a_0^2} \approx E_{\text{internal}}$$

Coulomb constant

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

$z=1$   
for hydrogen

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

Bohr radius

$$\approx 5.8 \cdot 10^{11} \text{ [V/m]}$$

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

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.

