

# Physics 531 - Lecture 2: The Stark Shift in Hydrogen

In the next few lectures we will consider perturbations to the "exact" nonrelativistic hydrogen atom due to other "internal" and "external" forces.

In this lecture we consider the energy level shifts due to an applied uniform static electric field,  $\vec{E}$ .

Assuming the nucleus (center of mass) is fixed, the force on the electron

$$\vec{F} = -e\vec{E} = -\vec{\nabla} V_{\text{int}} \quad \leftarrow \text{interaction potential}$$

$$V_{\text{int}} = -\vec{x} \cdot \vec{F} = -(-e\vec{x}) \cdot \vec{E} = -\vec{d} \cdot \vec{E}$$

↑  
electron position relative to nucleus

where  $\vec{d} = -e\vec{x} =$  ~~electron~~ dipole moment of atom

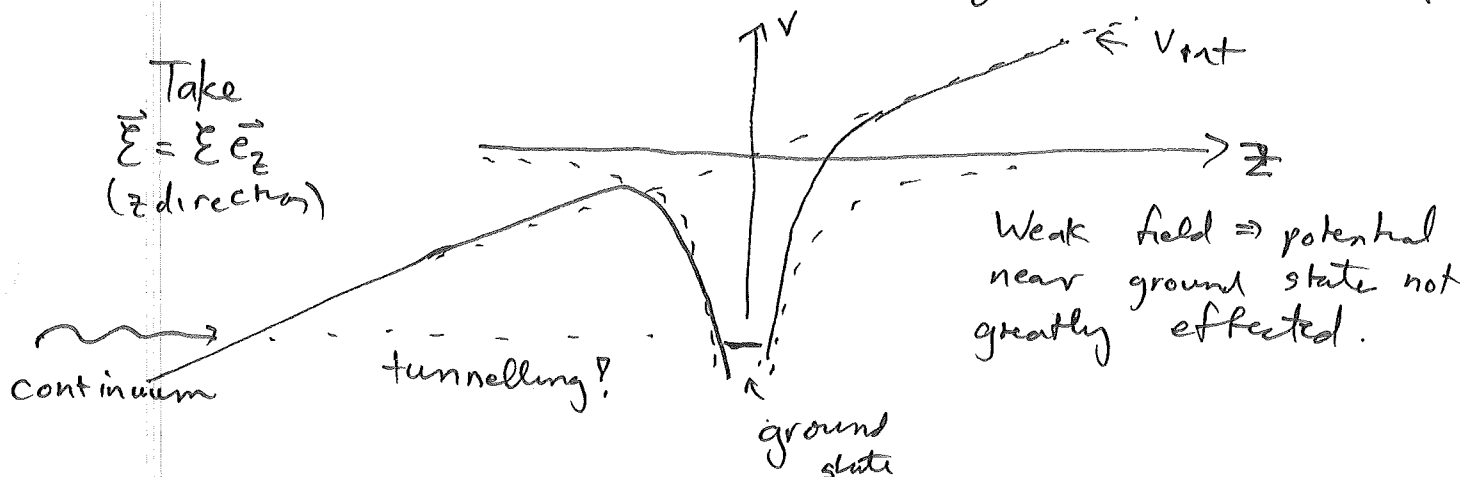
Quantize  $\Rightarrow$  Interaction Hamiltonian  $\hat{H}_{\text{int}} = -\hat{\vec{d}} \cdot \vec{E}$

where  $\hat{\vec{d}} =$  atomic dipole operator  $= -e\hat{\vec{x}}$

Total potential of electron in hydrogen  $= -\frac{e^2}{r} - \hat{\vec{d}} \cdot \vec{E}$

~~Weak~~ Perturbation  $\Rightarrow$  |applied  $\vec{E}$ |  $\ll$  internal field

Internal field of atom  $\sim \frac{e}{a_0^2} \cong 10^9$  Volts/cm



However, no matter how small  $\vec{E}$ , the bound electron can tunnel to freedom!

Formally, this means that the perturbation series never converges. Nonetheless, when  $|\vec{E}| \ll \frac{e^2}{a_0}$ , the states are effectively stable and we get good approximation

Shift on atomic ground state:

According to ~~perturb~~ perturbation theory, the first order shift on the ground ~~is~~ state,  $1s$ , is

$$E_{1s}^{(1)} = \langle 1s | \hat{H}_{int} | 1s \rangle = - \underbrace{\langle 1s | \hat{d} | 1s \rangle}_{\text{mean dipole of the } 1s\text{-state}} \cdot \vec{E}$$

However,  $\langle 1s | \hat{d} | 1s \rangle = 0$ . This follows from symmetry

Parity and electric dipole: The eigenstates  $|n, l, m\rangle$  are eigenstates of the parity operator  $\hat{\Pi}$  since

$\vec{L}$  is invariant under  $\vec{x} \Rightarrow -\vec{x}$ ,  $\vec{p} \Rightarrow -\vec{p}$

$$\therefore \hat{\Pi} |n, l, m\rangle = (-1)^l |n, l, m\rangle$$

However  $\hat{d} = -e\hat{x}$  is odd under parity:  $\hat{\Pi} \hat{d} \hat{\Pi}^\dagger = -\hat{d}$

$\Rightarrow \hat{d}$  has matrix elements only between states of opposite parity.

Formally, consider

$$\begin{aligned} \langle n'l'm' | \hat{d} | nlm \rangle &= \underbrace{\langle n'l'm' | \hat{\Pi}^\dagger}_{(-1)^{l'}} \underbrace{\hat{\Pi} \hat{d} \hat{\Pi}^\dagger}_{-\hat{d}} \underbrace{\hat{\Pi}}_{(-1)^l} | nlm \rangle \\ &= (-1)^{l+l'} \langle n'l'm' | \hat{d} | nlm \rangle \end{aligned}$$

Selection rule

$\Rightarrow$  Matrix element of  $\hat{d}$  vanishes unless  $l+l'$  odd

Thus, in order to see shift of ground state, we must go to second order

$$E_{1s}^{(2)} = \sum_{n'l'm' \neq 100} \frac{|\langle n'l'm' | \hat{H}_{int} | 100 \rangle|^2}{E_{1s} - E_{n'}}$$

Let us ~~take~~ take  $\vec{E}$  in the z-direction, and write the interaction Hamiltonian in a.u.

$$\hat{H}_{int} = e\mathcal{E}\hat{z} \Rightarrow \mathcal{E}\hat{z}$$

where  $\hat{z}$  in units  $a_0$   
 $\mathcal{E}$  in units  $e/a_0^2$   
 $\hat{H}_{int}$  in units  $e^2/a_0$

$$\Rightarrow E_{1s}^{(2)} = \mathcal{E}^2 \sum_{\substack{n'l'm' \neq \\ 100}} \frac{|\langle n'l'm' | \hat{z} | 100 \rangle|^2}{E_{1s} - E_{n'}} \quad , \quad E_n = -\frac{1}{2n^2} \text{ in a.u.}$$

$$= -2\mathcal{E}^2 \sum_{n'l'm' \neq 100} \frac{|\langle n'l'm' | \hat{z} | 100 \rangle|^2}{1 - \frac{1}{n'^2}}$$

Aside:  $\langle n'l'm' | \hat{z} | 100 \rangle = \int d^3x \psi_{n'l'm'}^*(r, \theta, \phi) z \psi_{100}(r, \theta, \phi)$

Using  $z = r \cos \theta$   $\psi_{n'l'm}(r, \theta, \phi) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta, \phi)$

$$\langle n'l'm' | \hat{z} | 100 \rangle = \int dr u_{n'l'}(r) r u_{10}(r) \int d\Omega Y_{l'm'}^*(\theta, \phi) \cos \theta Y_{00}(\theta, \phi)$$

Double aside:  $Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$   $Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$

$$\Rightarrow \langle n'l'm' | \hat{z} | 100 \rangle = \frac{1}{\sqrt{3}} \int dr u_{n'l'}(r) r u_{10}(r) \int d\Omega Y_{l'm'}^* Y_{10}$$

Define as  $\delta_{n'l'}$  new selection rule  $\rightarrow \delta_{l'1} \delta_{m'0}$

$$\therefore E_{1s}^{(2)} = -2\mathcal{E}^2 \sum_{n' \neq 1} \frac{|\langle n'10 | \hat{z} | 100 \rangle|^2}{1 - \frac{1}{n'^2}}$$

$$= -2\mathcal{E}^2 \sum_{n' \neq 1} \frac{|d_{n'1}|^2}{1 - \frac{1}{n'^2}}$$

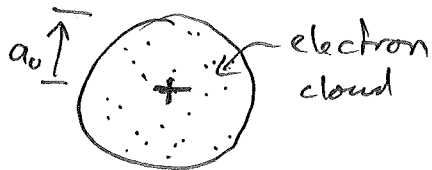
It turns out that the exact <sup>2<sup>nd</sup></sup> order Stark shift can be calculated using parabolic coordinates (more at the end of lecture) - See Bethe - Salpeter "One and Two electron atoms".

Result: In a.u.  $E_{1s}^{(2)} = -\frac{9}{4} \mathcal{E}^2$

Restoring units  $E_{1s}^{(2)} = -\frac{9}{4} \left(\frac{\mathcal{E}}{\mathcal{E}_0}\right)^2 E_0$ ,  $\mathcal{E}_0 = \frac{e}{a_0^2}$ ,  $E_0 = \frac{e^2}{a_0^3}$  Hartree

$\Rightarrow E_{1s}^{(2)} = -\frac{9}{4} a_0^3 \mathcal{E}^2$  (C.g.s) units  $\mathcal{E}^2 = \frac{\text{Energy}}{\text{Volume}}$

Physical picture: Induced dipole of polarizable particle

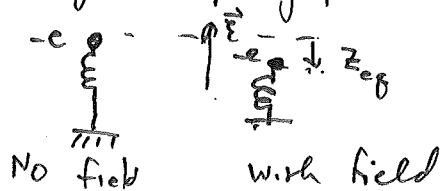


Unperturbed Hydrogen



Induced dipole, first order in  $\vec{E}$

Charge on spring picture:



Balance of electric and restoring force  
 $m\omega^2 z_{eq} = -e\mathcal{E}$

$\Rightarrow z_{eq} = \frac{-e}{m\omega} \mathcal{E}$

Induced dipole  $\vec{d} = -e\vec{x}_{eq} = \frac{e^2}{m\omega^2} \vec{\mathcal{E}} = \alpha \vec{\mathcal{E}}$

Atomic (linear) polarizability  $\alpha = \frac{e^2}{m\omega^2}$

Total potential energy stored in charge

$$U = \underbrace{\frac{1}{2} m \omega^2 z_{\text{eq}}^2}_{\text{in spring}} - \underbrace{\vec{d}_{\text{ind}} \cdot \vec{E}}_{\text{interaction of dipole with } \vec{E}}$$

$$= -\frac{1}{2} m \omega^2 \left( \frac{e}{m \omega^2} \vec{E} \right)^2 - \frac{e^2}{m \omega^2} \vec{E}^2 = -\frac{1}{2} \frac{e^2}{m \omega^2} \vec{E}^2$$

$$\boxed{U = -\frac{1}{2} \vec{d}_{\text{ind}} \cdot \vec{E}}$$

half that of a permanent dipole

Quantum Mechanically

Induced dipole (mean value)  $\langle \psi_{1s} | \hat{d} | \psi_{1s} \rangle$

To first order  $|\psi_{1s}\rangle = |\psi_{1s}^{(0)}\rangle + \epsilon |\psi_{1s}^{(1)}\rangle$

$$\Rightarrow \langle \hat{d} \rangle_{\text{induced}} = \frac{\epsilon \langle \psi_{1s}^{(0)} | \hat{d} | \psi_{1s}^{(1)} \rangle + \epsilon \langle \psi_{1s}^{(1)} | \hat{d} | \psi_{1s}^{(0)} \rangle}{1 + \epsilon^2 \langle \psi_{1s}^{(0)} | \psi_{1s}^{(1)} \rangle} \rightarrow \text{neglect to this order}$$

With  $|\psi_{1s}^{(0)}\rangle = |100\rangle$

$$|\psi_{1s}^{(1)}\rangle = -\sum_{n'l'm' \neq 100} |n'l'm'\rangle \frac{\langle n'l'm' | \hat{d} | 100 \rangle \vec{E}}{E_1 - E_{n'}} = -\vec{E} \cdot \sum_{n' \neq 1} \frac{\langle n'10 | \hat{d} | 100 \rangle}{E_1 - E_{n'}} |n'10\rangle$$

$$\Rightarrow \langle \hat{d} \rangle_{\text{induced}} = \left( -2 \sum_{n' \neq 1} \frac{|\langle 100 | \hat{d}_z | n'10 \rangle|^2}{(E_{1s} - E_{n'})} \right) \vec{E}$$

Atomic polarizability  $\alpha$

$$-\frac{1}{2} \langle \hat{d} \rangle_{\text{ind}} \cdot \vec{E} = -\frac{1}{2} \alpha \vec{E}^2 = \left( + \sum_{n' \neq 1} \frac{|\langle 100 | \hat{d}_z | n'10 \rangle|^2}{E_{1s} - E_{n'}} \right) \vec{E}^2$$

$$= E_{1s}^{(2)} \quad (\text{as expected})$$

Same basic physics, only expression for  $\alpha$  changes.

## Perturbation to the first excited state, $n=2$

The  $n=2$  state in Hydrogen is 4-fold degenerate (ignoring spin)

$$\{ |2s, 0\rangle; |2p, -1\rangle, |2p, 0\rangle, |2p, +1\rangle \} \text{ Degenerate Perturbation}$$

$\uparrow$   
m quantum #

$$\text{Hamiltonian: } \hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad \hat{H}_{\text{int}} = \epsilon \hat{z} \text{ (a.u.)}$$

Selection rule for matrix element

$$\langle n'l'm' | \hat{z} | nlm \rangle = 0 \text{ unless } \begin{cases} l'+l \text{ odd} \\ \Delta m = 0 \end{cases}$$

$\Rightarrow$  Only one nonzero matrix element

$$\langle 2s, 0 | \hat{z} | 2p, 0 \rangle = \frac{1}{\sqrt{3}} \int dr r \underbrace{u_{20}(r) u_{20}(r)}_{= -3\sqrt{3}} \int d\Omega \underbrace{Y_{10}^* Y_{10}}_{= 1}$$

$\downarrow$   
 $\frac{4\pi}{3} r Y_{10}(\theta, \phi)$

$$\Rightarrow \langle 2s, 0 | \hat{z} | 2p, 0 \rangle = -3 \text{ (a.u.)}$$

We must ~~diagonalize~~ diagonalize the ~~the~~ matrix representation of  $\hat{H}$  in the 4-dimensional subspace spanned by  $n=2$

We order the basis, so the coupled states are neighbors

$$\hat{H} = \begin{bmatrix} E_2^{(0)} & \epsilon & & \\ \epsilon & E_2^{(0)} & & \\ & & E_2^{(0)} & 0 \\ & & 0 & E_2^{(0)} \end{bmatrix} \begin{matrix} |2s, 0\rangle \\ |2p, 0\rangle \\ |2p, +1\rangle \\ |2p, -1\rangle \end{matrix}$$

Where  $E_2^{(0)} = -\frac{1}{8}$        $\epsilon = -3\epsilon$  a.u.

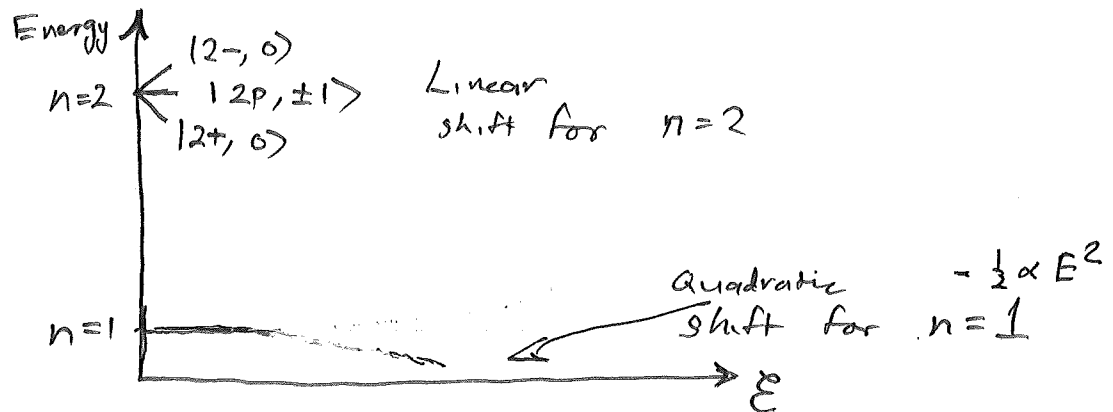
The matrix is block-diagonal.  
 We must diagonalize the  $2 \times 2$   $m=0$  block

$$\hat{H} = \begin{bmatrix} E_2^{(0)} & \epsilon \\ \epsilon & E_2^{(0)} \end{bmatrix} = E_2^{(0)} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \epsilon \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

Eigenstates  $\left| 2_{\pm}, 0 \right\rangle = \frac{1}{\sqrt{2}} \left( \left| 2s, 0 \right\rangle \pm \left| 2p, 0 \right\rangle \right)$  Like  $\hat{\sigma}_x$

Eigenvalues  $E_2^{(\pm)} = E_2^{(0)} \pm \epsilon = -\frac{1}{8} \pm 3\epsilon$

The shift here is linear in the applied field  
 (Linear Stark shift)



The splitting of degenerate levels due to a perturbation is a generic result. The original degeneracy stemmed from the spherical symmetry for a  $\frac{1}{r}$  potential. The perturbation breaks this symmetry, but leaves axial symmetry

$\Rightarrow$  Hamiltonian still commutes with  $\hat{L}_z$

$\Rightarrow m$  is still a good quantum #.

Note:  $L_z \Rightarrow L_z$  under parity  $\Rightarrow$  energy depends only on  $|m|$ .

Perturbed eigenstates: "Hybrid orbitals"

The "new - eigenstates" within the  $n=2$  manifold

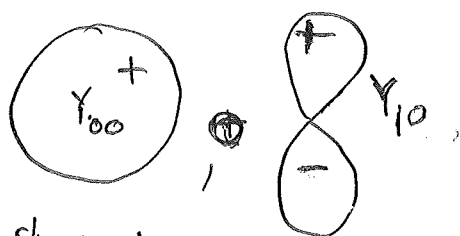
$$|2\pm, 0\rangle \equiv \frac{1}{\sqrt{2}}(|2s, 0\rangle \pm |2p, 0\rangle)$$

Are still eigenstates of  $\hat{H}^{(0)}$ , but they have "broken symmetry"; they are no longer eigenstates of parity. As such they have a permanent dipole moment  $\Rightarrow$  Linear energy shift with  $\mathcal{E}$

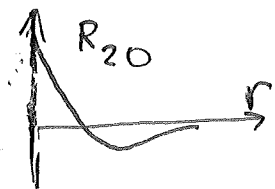
In chemical physics, linear combinations of orbitals within a degenerate manifold are known as "hybrid orbitals"

We can see the permanent dipole by sketching the angular distribution of  $|2\pm\rangle$  at a fixed  $r_0$

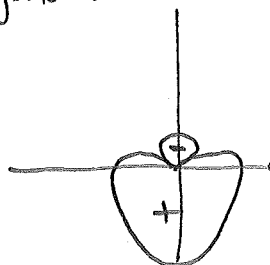
$$f_{\pm}(\theta) = \frac{1}{\sqrt{2}} \left( R_{20}(r_0) \frac{1}{\sqrt{4\pi}} \pm R_{2\pm 1}(r_0) \sqrt{\frac{3}{4\pi}} \cos\theta \right)$$



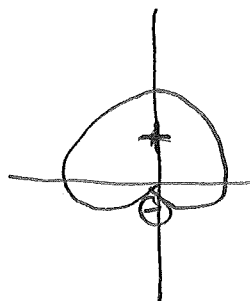
$\pm$  show phase of electron wavefunction, not charge



Hybrids:



$|2-\rangle$



$|2+\rangle$

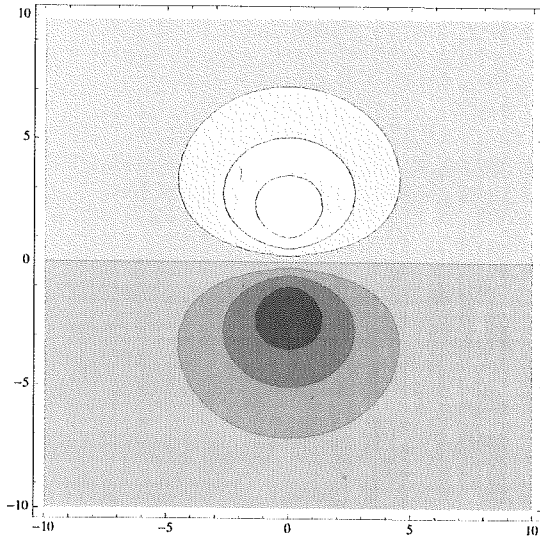


# Hybrid orbitals: x-y plane

$$\text{psi2s}[x, z] := 1 / (2 * \text{Sqrt}[2 \text{ Pi}]) (1 - \text{Sqrt}[x^2 + z^2] / 2) \text{Exp}[-\text{Sqrt}[x^2 + z^2] / 2] :$$

$$\text{psi2p0}[x, z] := 1 / (4 * \text{Sqrt}[2 \text{ Pi}]) \text{Exp}[-\text{Sqrt}[x^2 + z^2] / 2] z :$$

ContourPlot[psi2p0[x, z], {x, -10, 10}, {z, -10, 10}]

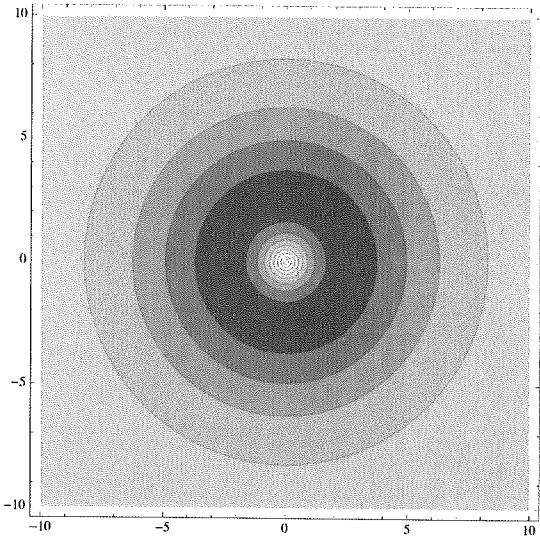


$\psi_{2p_0}$

$\psi_{2s}(x, z)$

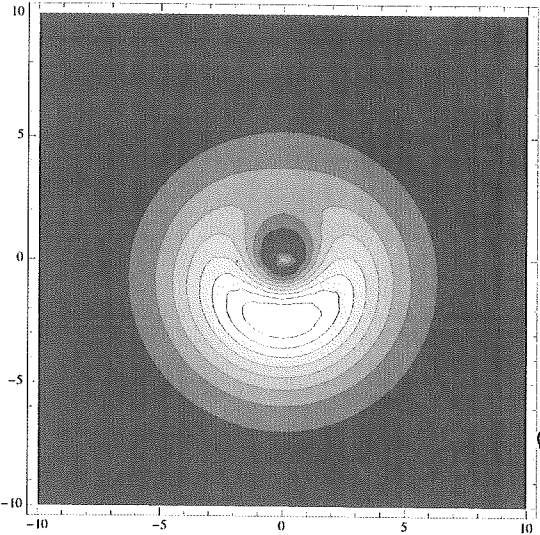
$\psi_{2p_{m=0}}(x, z)$

ContourPlot[psi2s[x, z], {x, -10, 10}, {z, -10, 10}]



$\psi_{2s}$

ContourPlot[(psi2p0[x, z] + psi2s[x, z])^2 / 2, {x, -10, 10}, {z, -10, 10}, PlotRange -> All]



$\frac{1}{\sqrt{2}} (\psi_{2s} + \psi_{2p_0})$

$\uparrow \langle \vec{d} \rangle$

induced dipole

$$\Delta E = -\frac{1}{2} \langle \vec{d} \rangle \cdot \vec{E} < 0$$

Energy shift

## Stark shift using parabolic coordinates

Though the addition of a uniform electric field along z-axis breaks spherical symmetry, it does not break axial symmetry

⇒ Hydrogen + Stark separable in Parabolic coords

⇒ The parabolic q-numbers still good w/ addition  $\vec{E}$

$$H_{int} = \vec{E} \cdot \vec{z} = eE(\xi - \eta)$$

Separate, for two parabolic wave eqns:  $\psi(\xi, \eta, \phi) = f(\xi)g(\eta)e^{im\phi}$

$$\left[ \frac{d}{d\xi} \left( \xi \frac{d}{d\xi} \right) + \left( \frac{1}{2} E \xi - \frac{m^2}{4\xi} + \nu_1 - \frac{1}{4} E \xi^2 \right) \right] f = 0$$

$$\left[ \frac{d}{d\eta} \left( \eta \frac{d}{d\eta} \right) + \left( \frac{1}{2} E \eta - \frac{m^2}{4\eta} + \nu_2 + \frac{1}{4} E \eta^2 \right) \right] g = 0$$

perturbation

where  $\nu_1 + \nu_2 = Z$

Can apply perturbation theory to these diff' eqns

Bethe-Salpeter ⇒

- First order:  $E_{n_1, n_2}^{(1)} = \frac{3}{2} n(n_1 - n_2) E$
- 2<sup>nd</sup> order:  $E_{n_1, n_2, m}^{(2)} = \frac{-1}{16} E^2 n^4 (17n^2 - 3(n_1 - n_2) - 9m^2 + 19)$

Notes: • First order shift does depend on m  
since  $n = n_1 + n_2 + |m| + 1$

• Ground state  $n_1 = n_2 = 0$  ⇒  $E^{(1)} = 0$   
 $m=0, n=1$   $E^{(2)} = \frac{-3}{2} E^2$

• Hybrid  $n=2$  ⇒ Eigenstates with parabolic  
 $m=0, n_1=1, n_2=0, n_1=0, n_2=1$