Physics 531 - Lecture 4: The Stark Shift

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, \( \bar{E} \).

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

\[ \bar{F} = -e \bar{E} = -\vec{V}_{\text{int}} \]

\( \vec{V}_{\text{int}} = -\vec{r} \cdot \bar{F} = -(-e \vec{r}) \cdot \bar{E} = -\vec{r} \cdot \bar{E} \)

where \( \vec{r} \) is the electron position relative to nucleus.

Electron position relative to nucleus

Quantize \( \Rightarrow \) Interaction Hamiltonian

\[ \hat{H}_{\text{int}} = -\vec{J} \cdot \bar{E} \]

where \( \vec{J} \) is the atomic dipole operator, \( -e \hat{\vec{r}} \).

Total potential of electron in hydrogen

\[ -\frac{e^2}{r} - \vec{J} \cdot \bar{E} \]

Weak Perturbation \( \Rightarrow \) applied \( |\bar{E}| \ll \) internal field

Internal field of atom \( \sim \frac{e}{a_0^2} \approx 10^9 \text{ Volts/cm} \)

Take

\[ \bar{E}_2^2 = E_2^2 \bar{E}_z^2 \]

(z direction)

Potential

Weak field = potential near ground state not greatly affected

Tunnelling?

Continuum

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

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

**Shift on atomic ground state:**

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

$$E^{(1)}_{1s} = \langle 1s | \hat{A} \hat{n} | 1s \rangle = -\langle 1s | \hat{A} | 1s \rangle \cdot \bar{E}$$

mean dipole of the 1s state.

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

$$\hat{\Pi}$$ is invariant under $\hat{x} \rightarrow -\hat{x}$, $\hat{p} \rightarrow -\hat{p}$

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

However, $\hat{d} = -e \hat{r}$ is odd under parity: $\hat{\Pi} \hat{d} \hat{\Pi} = -\hat{d}$

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

Formally, consider

$$\langle n' l' m' | \hat{d} | n l m \rangle = \langle n' l' m' | \hat{\Pi} \hat{\Pi} \hat{d} \hat{\Pi} \hat{\Pi} | n l m \rangle$$

$$= (-1)^{l'+l} \langle n' l' m' | \hat{d} | n l m \rangle$$

**Electron rule:** 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

\[ E^{(2)}_{1s} = \sum_{n' \neq 1} \frac{1}{E_{1s} - E_{n'}} \left| \langle 1s | \mathcal{H}_{\text{int}} | 1s \rangle \right|^2 \]

Let us take \( \mathcal{E} \) in the \( z \)-direction, and write the interaction Hamiltonian in a.u.

\[ \mathcal{H}_{\text{int}} = e^2 \mathcal{E} \frac{\hat{z}}{\hbar^2} \Rightarrow \mathcal{E} \frac{\hat{z}}{\hbar^2} \]

where \( e^2 \) in units \( e_0^2 \)

\[ \mathcal{H}_{\text{int}} \text{ in units } e^2 / \hbar^2 \]

\[ \Rightarrow E^{(2)}_{1s} = \mathcal{E}^2 \sum_{n' \neq 1} \frac{\left| \langle n' | \mathcal{H}_{\text{int}} | 1s \rangle \right|^2}{E_{1s} - E_{n'}} \]

\[ = -2 \mathcal{E}^2 \sum_{n' \neq 1} \frac{\left| \langle n' | \hat{z} | 1s \rangle \right|^2}{1 - \frac{1}{n'^2}} \]

Aside: \( \langle n' | \hat{z} | 1s \rangle = -\mathcal{E} \sum_{m' \neq 0} \phi_{n'm'}^* \phi_{1m} \) \( \mathcal{E} \sum_{m' \neq 0} \phi_{n'm'}^* \phi_{1m} = \sum_{n' \neq 1} \langle n' | \hat{z} | 1s \rangle \]

Using \( \mathcal{E} = \mathcal{E} \cos \theta \)

\[ \mathcal{E} \sum_{m' \neq 0} \phi_{n'm'}^* \phi_{1m} = \sum_{n' \neq 1} \langle n' | \hat{z} | 1s \rangle \]

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

\[ \Rightarrow \langle n' | \hat{z} | 1s \rangle = \mathcal{E} \sum_{m' \neq 0} \phi_{n'm'}^* \phi_{1m} \]

Define new selection rule \( \mathcal{E} \sum_{m' \neq 0} \phi_{n'm'}^* \phi_{1m} \rightarrow \mathcal{E} \sum_{m' \neq 0} \phi_{n'm'}^* \phi_{1m} \]

\[ \Rightarrow E^{(2)}_{1s} = -2 \mathcal{E}^2 \sum_{n' \neq 1} \frac{\left| \langle n' | \hat{z} | 1s \rangle \right|^2}{1 - \frac{1}{n'^2}} \]

\[ = -2 \mathcal{E}^2 \sum_{n' \neq 1} \frac{\left| \mathcal{E} \phi_{n'm'}^* \phi_{1m} \right|^2}{1 - \frac{1}{n'^2}} \]
It turns out that the exact 2nd 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. \[ E_{15}^{(2)} = -\frac{9}{4} \frac{e^2}{\ell^2} \]

Restoring units \[ E_{15}^{(2)} = -\frac{9}{4} \left( \frac{\ell}{\ell_0} \right)^2 E_0 \]

\[ E_0 = \frac{e^2}{\ell_0} \text{ Hartree} \]

\[ E_{15}^{(2)} = -\frac{9}{4} a_0^3 \frac{\ell^2}{\text{volume}} \]

Physical picture: Induced dipole of polarizable particle

Unperturbed Hydrogen

Induced dipole, first order in \( \ell^2 \)

Charge on spring picture:

\[ \frac{e}{\ell} = \frac{-e}{\ell + \ell_0} \]

No field without field

Induced dipole \( \vec{d} = -e \vec{\chi}_0 = \frac{e^2}{m_0 \ell_0^2} \vec{\ell} = \alpha \vec{\ell} \)

Atomic (linear) polarizability \( \alpha = \frac{e^2}{m_0 \ell_0^2} \)
Total potential energy stored in charge

\[ U = \frac{1}{2} m v^2 \frac{Z^2}{r^2} - d_{\text{ind}} \cdot \vec{E} \]

\[ = -\frac{1}{2} m v^2 \left( \frac{e}{m} \right)^2 \frac{Z^2}{r^2} - \frac{e^2}{m v^2} \frac{Z^2}{r^2} = -\frac{1}{2} \frac{e^2}{m} \varepsilon^2 \]

\[ U = -\frac{1}{2} d_{\text{ind}} \cdot \vec{E} \]

half that of a permanent dipole

Quantum Mechanically

Induced dipole (mean value) \[ \langle \hat{d} \rangle \]

To first order \[ 1 \langle \hat{d} \rangle = \langle \hat{d} \rangle^{(0)} + \varepsilon \langle \hat{d} \rangle^{(1)} \]

\[ \Rightarrow \langle \hat{d} \rangle = \varepsilon \langle \hat{d} \rangle^{(0)} \frac{\langle \hat{d} \rangle^{(1)}}{1 + \varepsilon^2 \langle \hat{d} \rangle^{(0)}} \]

\[ \text{With } \langle \hat{d} \rangle^{(0)} = |100\rangle \]

\[ \langle \hat{d} \rangle^{(1)} = \sum_{n' \neq 1} \frac{\langle 100 | \hat{d} | n'10 \rangle}{E_{1s} - E_{n'}} \]

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

Atomic polarizability \( \alpha \)

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

\[ = E_{1s}^{(2)} \] (as expected)

Some basic physics, only expression for \( \alpha \) changes.
Perurbation to the first excited state, \( n = 2 \)

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

\[ |12s, 0\rangle, \ 12p_{-1}\rangle, \ 12p_{0}\rangle, \ 12p_{+1}\rangle \]

Degenerate

Hamiltonian: \( \hat{H} = \hat{H}_0 + \hat{H}_{\text{int}} \), \( \hat{H}_{\text{int}} = E \hat{Z} \) (a.u.)

Selection rule for matrix element

\[ \langle n'\ell'm' \| \hat{H} \| n\ell m \rangle = 0 \text{ unless } \ell' + \ell \text{ odd, } \Delta m = 0 \]

\[ \Rightarrow \text{ Only one non-zero matrix element} \]

\[ \langle 2s, 0 \| \hat{H} \| 12p, 0 \rangle = \frac{1}{\sqrt{3}} \int dr \ r \ Y_0^*(\theta, \phi) Y_{20}^* Y_{10}\int \sin \theta d\theta = -3\sqrt{3} \]

\[ \Rightarrow \langle 2s, 0 \| \hat{H} \| 12p, 0 \rangle = -3 \text{ (a.u.)} \]

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

We order the basis, so the coupled states are neighbors

\[ \hat{H} = \begin{bmatrix} E_2^{(0)} & \epsilon & 0 & 12s, 0 \rangle \\ \epsilon & E_2^{(0)} & 0 & 12p, 0 \rangle \\ 0 & 0 & E_2^{(0)} & 12p, +1 \rangle \\ 12p, -1 \rangle & 0 & 0 & E_2^{(0)} \end{bmatrix} \]

Where \( E_2^{(0)} = -\frac{1}{8} \) \( \epsilon = -3 \) (a.u.)
The matrix is block diagonal. We must diagonalize the $2 \times 2$ $m=0$ block:

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

**Eigenstates:**

$$
| E^{(\pm)} \rangle = | E_2^{(o)} \pm \epsilon \rangle = \frac{1}{\sqrt{2}} (| 12s, 0 \rangle \pm | 12p, 0 \rangle)
$$

**Eigenvalues:**

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

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 number.

Note: $L_z = L_x$ under parity $\Rightarrow$ energy depends only on $|m|$. 
Perturbed eigenstates: "Hybrid orbitals"

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

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

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 $\tilde{E}$.

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 $r_0$.

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

$\pm$ show phase of electron wave function, not charge.

**Hybrids:**

$$|1s\rangle \uparrow$$

$$|2\pm\rangle \uparrow$$

$$|2\mp\rangle \downarrow$$
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 \( \vec{E} \)

\[ H_{\text{int}} = \vec{E} \cdot \vec{z} = e \vec{E} (\hat{\xi} - \hat{\eta}) \]

Separate, for two parabolic wave eqns:

\[
\begin{align*}
\left[ \frac{d}{d\xi} \left( \frac{d f}{d\xi} \right) + \left( \frac{1}{2} E \xi - \frac{m^2}{4 \xi} + \nu_1 - \frac{1}{4} \xi \eta^2 \right) \right] f &= 0 \\
\left[ \frac{d}{d\eta} \left( \frac{d g}{d\eta} \right) + \left( \frac{1}{2} E \eta - \frac{m^2}{4 \eta} + \nu_2 + \frac{1}{4} \eta \xi^2 \right) \right] g &= 0
\end{align*}
\]

where \( \nu_1 + \nu_2 = \xi \eta \)

Can apply perturbation theory to these shifted eqns

Bethe-Salpeter ⇒

- First order: \( E_{n_1, n_2}^{(1)} = \frac{3}{2} n (n_1 - n_2) \) &
- Second order: \( E_{n_1, n_2, m}^{(2)} = -\frac{1}{16} \xi^2 n^4 \left( 17 n^2 - 3 (n_1 - n_2) \right) \)

\( \Rightarrow -9 m^2 + 19 \)

Notes:

- First order shift does depend on \( m \)

since \( n = n_1 + n_2 + 1 \mid m \mid + 1 \)

- Ground State \( n_1 = n_2 = 0 \) ⇒ \( E^{(1)} = 0 \)

- Hybrid \( n = 2 \) ⇒ Eigenstates with parabolic

\( m = 0, n_1 = 1, n_2 = 0; \quad n_1 = 0, n_2 = 1 \)