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

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

\[
V_{\text{int}} = -\vec{r} \cdot \vec{F} = -(-e \vec{r}) \cdot \vec{E} = -\vec{r} \cdot \vec{E}
\]

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

Quantize \( \Rightarrow \) Interaction Hamiltonian

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

where \( \hat{\vec{d}} = \text{atomic dipole operator} = -e \hat{\vec{r}} \)

Total potential of electron in hydrogen

\[
-\frac{\alpha^2}{r} - \vec{d} \cdot \vec{E}
\]

Perturbation \( \Rightarrow \) applied \( \vec{E} \ll \) internal field

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

\[
\vec{E}' = \vec{E} e_{\vec{E}}
\]

(\( e_{\vec{E}} \) direction)

\( \vec{r} \)

continuum

tunnelling?

\( \vec{r} \)

\( \vec{r} \)

ground state

Weak field \( \Rightarrow \) potential near ground state not greatly affected.
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 $|\bar{E}| < \frac{e^2}{q_0}$, 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 state, $1s$, is

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

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

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

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

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

However $\hat{d} = -e\vec{x}$ is odd under parity: $\hat{p} \hat{d} \hat{p} = -\hat{d}$

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

Formally, consider

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

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

**Selection 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

\[ E_{15}^{(2)} = \sum_{n \neq m} \frac{\langle n' l' m' l' \mid H_{\text{int}} \mid 1 0 0 \rangle^2}{E_{15} - E_n} \]

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

\[ \hat{H}_{\text{int}} = e \hat{z} \Rightarrow \hat{z} \\
\]

\[ \Rightarrow E_{15}^{(2)} = e^2 \sum_{n' \neq m, l = 100} \frac{\langle n' l' m' l' \mid 1 0 0 \rangle^2}{E_{15} - E_n} \]

\[ = -2e^2 \sum_{n' \neq m, l = 100} \frac{\langle n' l' m' l' \mid 1 0 0 \rangle^2}{1 - \frac{1}{n'^2}} \]

Aside: \( \langle n' l' m' l' \mid 1 0 0 \rangle = \int d\theta d\phi \frac{U_{n' l' m'}}{r} Y_{l' m'}(\theta, \phi) \)

Using \( z = r \cos \theta \) \( U_{n' l' m'}(r, \theta, \phi) = \frac{U_{n' l'}(r)}{r} Y_{l' m'}(\theta, \phi) \)

\[ \Rightarrow \langle n' l' m' l' \mid 1 0 0 \rangle = \int d\theta d\phi \frac{U_{n' l'}(r)}{r} U_{10}(\theta, \phi) \int d\Omega Y_{l' m'}^{*}(\theta, \phi) \cos \theta Y_{10}(\theta, \phi) \]

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

\[ Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta \]

\[ \Rightarrow \langle n' l' m' l' \mid 1 0 0 \rangle = \frac{1}{\sqrt{3}} \int d\theta d\phi \frac{U_{n' l'}(r)}{r} U_{10}(\theta, \phi) \int d\Omega Y_{l' m'}^{*}(\theta, \phi) Y_{10}(\theta, \phi) \]

Define new selection rule: \( \delta_{n'1} \Rightarrow S_{m'0} \)

\[ \Rightarrow E_{15}^{(2)} = -2e^2 \sum_{n' \neq 1} \frac{\langle n' 1 0 1 \mid 1 0 0 \rangle^2}{1 - \frac{1}{n'^2}} \]

\[ = -2e^2 \sum_{n' \neq 1} \frac{\frac{d{n'}^2}{n'^2}}{1 - \frac{1}{n'^2}} \]
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. \[ E_{1s}^{(2)} = -\frac{9}{4} \xi^2 \]

Restoring units \[ E_{1s}^{(2)} = -\frac{9}{4} \left( \frac{\xi}{\xi_0} \right)^2 E_0, \quad \xi_0 = \frac{e^2}{\alpha_0} \text{ Hartree} \]

\[ \Rightarrow \quad E_{1s}^{(2)} = -\frac{9}{4} \alpha_0^3 \xi^2 \] (c.g.s) units \[ \xi^2 = \frac{\text{Energy}}{\text{Volume}} \]

Physical picture: Induced dipole of polarizable particle

Unperturbed Hydrogen

\[ a_0 \]

electron cloud

Induced dipole, first order in \( \xi \)

Charge on spring picture: \( -e \quad \xi \quad \frac{9}{4} \xi^2 \quad e \cdot \xi_0 \)

No field with field

Induced dipole \( \vec{d} = -e \vec{x} \xi_0 = \frac{e^2}{m_0} \xi = \alpha \vec{\xi} \)

Atomic (linear) polarizability \( \alpha = \frac{e^2}{m_0} \)
Total potential energy stored in charge
\[ U = \frac{1}{2} \frac{e^2}{\varepsilon_{0} \varepsilon} \left( \frac{1}{m \omega} \hat{\varepsilon} \right)^2 - \frac{1}{2} \frac{e^2}{m \omega} \hat{\varepsilon}^2 = -\frac{1}{2} \frac{e^2}{m \omega} \hat{\varepsilon}^2 \]
\[ U = -\frac{1}{2} \hat{d}_{ind} \cdot \hat{\varepsilon} \]

Half that of a permanent dipole

**Quantum Mechanically**

**Induced dipole (mean value)** \( \langle \tilde{d}_{1s} | \tilde{d}^\dagger | \tilde{\psi}_{1s} \rangle \)

To first order \( | \tilde{\psi}_{1s} \rangle = | \tilde{\psi}_{1s}^{(0)} \rangle + \epsilon | \tilde{\psi}_{1s}^{(1)} \rangle \)

\[ \langle \tilde{d} \rangle = \frac{\epsilon \langle \tilde{\psi}_{1s}^{(0)} | \tilde{d}^\dagger | \tilde{\psi}_{1s}^{(1)} \rangle + \epsilon \langle \tilde{\psi}_{1s}^{(1)} | \tilde{d}^\dagger | \tilde{\psi}_{1s}^{(0)} \rangle}{1 + \epsilon^2 \langle \tilde{\psi}_{1s}^{(0)} | \tilde{\psi}_{1s}^{(1)} \rangle} \]

**With**
\[ | \tilde{\psi}_{1s}^{(0)} \rangle = | 100 \rangle \]
\[ | \tilde{\psi}_{1s}^{(1)} \rangle = -\sum_{n' \neq 100}^{\infty} \langle n' 100 | \tilde{d}^\dagger | 100 \rangle \frac{\epsilon}{E_{1s} - E_{n'}} \]

\[ \Rightarrow \langle \tilde{d} \rangle_{induced} = \frac{-2 \sum_{n' \neq 1}^{\infty} \langle 100 | \tilde{d}^\dagger | n' 10 \rangle^2}{E_{1s} - E_{n'}} \frac{\epsilon}{(E_{1s} - E_{n'})} \]

**Atomic polarizability** \( \alpha \)

\[ -\frac{1}{2} \langle \tilde{d} \rangle_{ind} \cdot \hat{\varepsilon} = -\frac{1}{2} \alpha \varepsilon^2 = \left( \sum_{n' \neq 1}^{\infty} \frac{1}{E_{1s} - E_{n'}} \frac{\langle 100 | \tilde{d}^\dagger | n' 10 \rangle^2}{E_{1s} - E_{n'}} \right) \varepsilon^2 \]

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

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)

\[ 1s_2, 0^+, 1p_0, -1^-, 1p_0, 0^-, 1p_0, +1^+ \]

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

Selection rule for matrix element

\[ \langle n'l'm' | \hat{Z} | nlm \rangle = 0 \] unless \( l' + l \) odd

\[ \Delta m = 0 \]

\[ \Rightarrow \] Only one nonzero matrix element

\[ \langle 2s, 0 | \hat{Z} | 2p, 0 \rangle = \frac{1}{\sqrt{3}} \int dr \rho \frac{1}{2} Y_{20}^*(\theta, \phi) Y_{10} \]

\[ \frac{1}{\sqrt{3}} \int \rho \; Y_{10} \; (e^4) \]

\[ = -3 \sqrt{3} = 1 \]

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

We must now diagonalize 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

\[
\begin{pmatrix}
E_2^{(o)} & E & 0 & 12s, 0 \\
E & E_2^{(o)} & 0 & 12p, 0 \\
0 & 0 & E_5^{(o)} & 12p, +1 \\
0 & 0 & 0 & E_5^{(o)}
\end{pmatrix}
\]

Where \( E_2^{(o)} = -\frac{1}{8} \) \( E = -3E_5^{(o)} \) a.u.
The matrix is block-diagonal. We must diagonalize the $2 \times 2$ $m=0$ block

\[ \hat{H} = \begin{bmatrix} E_z^{(0)} & E_x^{(0)} \\ E_x^{(0)} & E_z^{(0)} \end{bmatrix} = E_2^{(0)} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \epsilon \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \]

Eigenstates

\[ |12, \pm 0 \rangle = \frac{1}{\sqrt{2}} (|12s, 0 \rangle \pm |12p, 0 \rangle) \]

Eigenvalues

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

The shift here is linear in the applied field ($\text{Linear Stark shift}$)

The splitting of degenerate levels due to a perturbation is a generic result. The original degeneracy stemmed from the spherical symmetry for a $1/r$ 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: $L_z \Rightarrow L_\perp$ under parity $\Rightarrow$ energy depends only on $|m|$. 
Perturbed eigenstates: "Hybrid orbitals"

The "new eigenstates" within the n=2 manifold

\[ |2\pm, 0\rangle = \frac{1}{\sqrt{2}} (|1s, 0\rangle \pm |2p, 0\rangle) \]

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 \( E \)

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 \( r_0 \)

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

\[ Y_{00}, Y_{10}, Y_{11}, Y_{12}, \ldots \]

\[ + \text{ show phase of electron wave function; not charge} \]

Hybrids:

\[ |2\pm\rangle \quad |2\pm\rangle \]
Hybrid orbitals: $x$-$y$ plane

\[
\psi_{2s}(x, y) = \frac{1}{\sqrt{2\pi}} \psi_{2s}(x) \psi_{2s}(y)
\]

\[
\psi_{2p_0}(x, y) = \frac{1}{\sqrt{2\pi}} \psi_{2p_0}(x) \psi_{2p_0}(y)
\]

\[
\psi_{2p_0}(x, y) = \frac{1}{\sqrt{2\pi}} \psi_{2p_0}(x) \psi_{2p_0}(y)
\]

\[
\psi_{2p_0}^\ast(x, y) = \frac{1}{\sqrt{2\pi}} \psi_{2p_0}^\ast(x) \psi_{2p_0}^\ast(y)
\]

\[
\langle \Delta \rangle = -\frac{1}{2} \langle \Delta \rangle \cdot \hat{E} < 0
\]

Energy shift

$\psi_{2s}$, $\psi_{2p_0}$

Induced dipole
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 $\ell$-numbers will good w/ addition $E$

\[ H_{int} = \hat{E} \xi = eE (\xi - \eta) \]

Separate, for two parabolic wave eqns: \[ \psi(\xi, \eta, \phi) = f(\xi) g(\eta) e^{i m \phi} \]

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

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

Where \( \nu_1 + \nu_2 = E \)

Can apply perturbation theory to these differential equations

Bethe-Salpeter \( \Rightarrow \)

- First Order: \( E^{(1)}_{n_1 n_2} = \frac{3}{2} n (n_1 - n_2) E \)

- 2nd Order: \( E^{(2)}_{n_1 n_2 m} = \frac{-1}{16} E^2 n^4 \left( 12 n^2 - 3 (n_1 - n_2) \right) \text{ for } -9m^2 + 1 \)

Notes:
- First order shift does depend on $m$ since $n = n_1 + n_2 + 1 m + 1$
- Ground state: $n_1 = n_2 = 0 \Rightarrow E^{(1)} = 0$
  \( E^{(2)} = -\frac{3}{2} E^2 \)
- Hybrid: $n = 2 \Rightarrow$ Eigenstates with parabolic
  \( m = 0, n_1 = 1, n_2 = 0, n = 0, n_2 = 1 \)