The Stark effect in the Hydrogen Atom

We know H_0 for the unperturbed Hydrogen atom;

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + U(r)$$

where:

$$U(r) = \begin{cases} -\frac{Ze^2}{R}\left[\frac{3}{2} - \frac{1}{2}(\frac{r}{R})^2\right] & ; r \leq R \\ -\frac{Ze^2}{r} & ; r > R \end{cases}$$

Suppose we introduce a constant external electric field $\vec{E}$:

$$\vec{E} = E\hat{e}_3 \quad ; \quad H_1 = -\vec{d}\cdot\vec{E} = -d_3 E$$

where H_1 corresponds to the dipole moment of the atom.

Stark effect: Shifting and splitting of spectral lines of atoms and molecules due to the presence of an external electric field $\vec{E}$.

$$H_1 = -d_3 E = ezE = e(r\cos\theta)E$$

Dipole operator and basis vectors
In spherical polar coordinates:

$$(x+iy) = r\sin\theta(\cos\phi + i\sin\phi) = r\sin\theta e^{i\phi}$$
$$(x-iy) = r\sin\theta e^{-i\phi}$$

We know;

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta \qquad Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$$

$$z = r\cos\theta = r\sqrt{\frac{4\pi}{3}}Y_{1,0} \qquad (\mu = 0)$$

$\therefore$ For x, y directions($\mu = \pm 1$)

$$r\sin\theta e^{\pm i\phi} = \mp r\sqrt{\frac{8\pi}{3}}Y_{1,\pm1}$$

The dipole operator $\vec{d} = -e\vec{r}$ corresponds to:

$$d_0 = d_z = -ez = -e\left(r\sqrt{\frac{4\pi}{3}}Y_{1,0}\right)$$

$$d_\pm = \mp\frac{dx \pm idy}{\sqrt{2}} \implies d_\pm = \pm\mp\frac{e}{\sqrt{2}}(x \pm iy)$$

$$d_\pm = \pm\frac{e}{\sqrt{2}}\left(\mp r\sqrt{\frac{8\pi}{3}}Y_{1,\pm1}\right) \implies d_\pm = -er\sqrt{\frac{4\pi}{3}}Y_{1,\pm1}$$

$$\therefore d_\mu = -e\sqrt{\frac{4\pi}{3}} r Y_{1,\mu} \quad ; \quad \mu = -1, 0, 1$$

We define the Spherical basis vectors: $\hat{e}_{\pm 1} = \mp \frac{\hat{e}_x \pm i\hat{e}_y}{\sqrt{2}}$; $\hat{e}_0 = \hat{e}_z$

$$\therefore E_\mu = \vec{E} \cdot \hat{e}_\mu^*$$

$$E_{+1} = -\frac{1}{\sqrt{2}}(E_x + iE_y) \qquad E_{-1} = \frac{1}{\sqrt{2}}(E_x - iE_y) \qquad E_0 = E_z$$

$$\vec{d} \cdot \vec{E} = \sum_\mu d_\mu^* E_\mu = d_0^* E_0 + d_{-1}^* E_{-1} + d_{+1}^* E_{+1} = d_x E_x + d_y E_y + d_z E_z$$

The electric field induces a dipole moment by polarizing the cloud, then interacts with the induced moments.

Quadratic Stark effect for Non-degenerate Hydrogen-like atoms)
The first order approximation gives;

$$\langle nlm \mid H_1 \mid n'l'm' \rangle = E^{(1)} = 0$$

by parity.

Selection rule (Parity): Under spatial inversion ($r \to -r$)

$$\psi(-r) = (-1)^l \psi(r)$$

$$\therefore |\psi(-r)|^2 = |\psi(r)|^2 \quad \text{(even)}$$

However $d(-r) = -d(r) \implies H_1(-r) = -H_1(r)$ (odd)

$$\therefore \langle \psi_a \mid H_1 \mid \psi_a \rangle = \int \text{even} \times \text{odd} \times \text{even} = 0$$

First order approximation is hence zero.

$$E^{(1)} = \langle nlm \mid H_1 \mid nlm \rangle = 0$$

No linear Stark effect for non-degenerate states.

The second-order perturbation is:

$$\Delta E^{(2)} = \sum_{nlm \neq n'l'm'} \frac{\langle nlm \mid H_1 \mid n'l'm' \rangle \langle n'l'm' \mid H_1 \mid nlm \rangle}{E_{nl} - E_{n'l'}}$$

Applying the previous expansion of our perturbed Hamiltonian:

$$\Delta E^{(2)} = \sum_{nl} \sum_{\mu\nu} E_\mu E_\nu^* \sum_m \frac{\langle nlm \mid d_\nu \mid n'l'm' \rangle \langle n'l'm' \mid d_\mu^* \mid nlm \rangle}{E_{nl} - E_{n'l'}}$$

Due to angular momentum conservation, matrix elements involving d_ν and d_μ^* are non-zero iff the indices match.

$$\Delta E^{(2)} = \sum_{n,l} \sum_{\mu} E_\mu E_\mu^* \sum_m \frac{|\langle nlm \mid d_\mu \mid n'l'm' \rangle|^2}{E_{nl} - E_{n'l'}}$$

$$\Delta E^{(2)} = \frac{E^2}{3} \times \sum_{nlm} \frac{|\langle nlm \mid \vec{d} \mid n'l'm' \rangle|^2}{E_{nl} - E_{n'l'}}$$

where $\vec{d} = \sum_\mu d_\mu$

$$\Delta E^{(2)} = -\frac{1}{2}\alpha E^2 \quad ; \quad \alpha = -\frac{2}{3} \sum_{nlm} \frac{|\langle nlm \mid \vec{d} \mid n'l'm' \rangle|^2}{\underbrace{E_{nl} - E_{n'l'}}_{\text{always negative}}}$$

$$\therefore \alpha \implies \text{always +ve}$$

Angular momentum conservation ($\mu = \nu$)

$$Y_l^m(\theta, \phi) = P_l^m(\cos\theta) \cdot e^{im\phi}$$

$$\langle nlm \mid d_\nu \mid n'l'm' \rangle \propto \int_0^{2\pi} \int_0^{\pi} (Y_l^m)^* (Y_1^\nu)(Y_{l'}^{m'}) \sin\theta d\theta d\phi$$

$$= \int_0^{2\pi} (e^{im\phi})^* (e^{i\nu\phi})(e^{im'\phi}) d\phi \int_0^{\pi} (P_l^m(\cos\theta))^* P_1^\nu(\cos\theta) P_{l'}^{m'}(\cos\theta) \sin\theta d\theta d\phi$$

$$\underbrace{e^{i(-m+\nu+m')\phi}}_{\Downarrow}$$

$$\therefore m = m' + \nu$$

Similarly, you define $d_\mu^* \implies m = m' + \mu$

$$\therefore \mu = \nu$$

The atom starts is state m, to get to a state m', it interacts with a field component carrying angular momentum ν.

The second-order energy correction describes a virtual process

$$m \to m' \to m' \to m$$

$$\langle nlm \mid H_1 \mid n'l'm' \rangle \langle n'l'm' \mid H_1 \mid nlm \rangle$$

To get back to the original state, the atom must interact with the field component in the exact reverse manner.

$$\therefore -\mu \implies -\nu \implies \mu = \nu$$

The external electric field E exerts a force on the electron, distorting it. This creates an induced dipole moment d_{ind}.

$$d_{ind} = \alpha E$$

$$\therefore E \simeq -d_{ind} \cdot \vec{E} = -(\alpha E) \cdot \vec{E} = -\alpha E^2$$

The electric field relaxes the system by allowing the electron to shift into a more favorable position (polarization), effectively binding it slightly tighter in the direction of the field.

When the electric field turns on:-
1) Elastic cost The field pulls the electron away from the nucleus, Modelled like a spring

$$U_{elastic} = \frac{1}{2}kx^2$$

2) Interaction gain As the e^- move a distance x in the direction opposite to the field, it creates a dipole $\vec{d} = -e\vec{x}$

$$U_{interaction} = -\vec{d} \cdot \vec{E} = -(ex)E$$

$$\therefore E_{total} = \frac{1}{2}kx^2 - exE$$

For force balance:

$$ex = \frac{kx^2}{E}$$

$$E_{total} = -\frac{1}{2}exE \implies \text{system pays energy to strecth}$$

Linear Stark Effect for the Degenerate n=2 Hydrogen atom
For $n = 2$, we have the following bases:-

$$\begin{aligned} |1\rangle &= |2s, 0\rangle \quad \text{Parity even} \\ |2\rangle &= |2p, 0\rangle \quad \text{Parity odd} \\ |3\rangle &= |2p, +1\rangle \quad \text{Parity odd} \\ |4\rangle &= |2p, -1\rangle \quad \text{Parity odd} \end{aligned}$$

We define the Perturbation matrix W_{ij}

$$W = \langle i|H_1|j\rangle = \langle i|ezE|j\rangle = E \cdot e\langle i|z|j\rangle \implies 4 \times 4 \text{ matrix}$$

for diagonal elements $i = j$, the integral is $|\psi|^2(\text{even}) * z(\text{odd})$ is odd.

$\therefore$ All diagonal elements are zero. Hence, no first-order shift is an isolated state.
The operator Z cannot change the angular momentum along z

$$\therefore \quad [Z, L_z] = 0 \quad \implies \quad \Delta m = 0$$

This constraint restricts the system from changing the quantum number m during interactions, implying any state with 3, 4 in them are zero since:

$$m = +1 \implies |3\rangle \quad m = -1 \implies |4\rangle]$$

$\therefore$ The only non-zero terms are the states with the same m but opposite parity, $|2s\rangle$ and $|2p\rangle$ with $m = 0$. Specifically Δ_{12} and Δ_{21}

$$\Delta_{12} = \langle 2s, 0 \mid H_1 \mid 2p, 0\rangle$$

$\therefore$ Our 4×4 matrix is now effectively 2×2

$$\begin{pmatrix} 0 & \Delta_{12} \\ \Delta_{21} & 0 \end{pmatrix} \implies \text{off diagonal terms [tunneling]} \quad [2s, 2p \text{ are bad labels}]$$

To calculate the matrix term, start by defining

$$H_1 = -\vec{d} \cdot \vec{E} = -(-ez)E = ezE$$

$$\langle 1 \mid H_1 \mid 2 \rangle = \langle 2 \mid H_1 \mid 1 \rangle = -e\sqrt{\frac{4\pi}{3}} E \langle 2s, m = 0 \mid rY_{10} \mid 2p, m = 0 \rangle$$

$$H_{12} = \int \psi_{2s}^* (ezE) \psi_{2p} d\tau = eE \int \psi_{2s}^* z \psi_{2p} d\tau$$

$$= eE \int \psi_{2s}^* (r\cos\theta) \psi_{2p} (r^2 \sin\theta dr d\theta d\phi)$$

We know;

$$\psi_{2s} = Y_{00} = \frac{1}{\sqrt{4\pi}}; \text{ and } \psi_{2p} = Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$I_{ang} = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \left(\frac{1}{\sqrt{4\pi}}\right) \cos\theta \left(\sqrt{\frac{3}{4\pi}} \cos\theta\right)$$

$$I_{ang} = \frac{1}{\sqrt{3}}$$

The radial wavefunction for 2s and 2p states are:

$$R_{2s}(r) = \frac{1}{\sqrt{8} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$R_{2p}(r) = \frac{1}{\sqrt{24} a_0^{3/2}} \left(\frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\int_0^{\infty} R_{2s} R_{2p} \cdot r^3 dr = N \int_0^{\infty} [2 - x][x][a_0 x]^3 (a_0 dx) e^{-x}$$

$$\text{where } x = \frac{r}{a_0} \quad , \quad N = \frac{1}{8\sqrt{3} a_0^3}$$

Solving ; we get : $I_{rad} = -3\sqrt{3} a_0$

$$\therefore \quad H_{12} = eE \cdot \ (I_{ang})(I_{rad})$$

$$H_{12} = -3ea_0 E$$

$\therefore$ We have the matrix elements, $\Delta_{12} = \Delta_{21} = -3ea_0 E$ The nonzero result comes because the $2s$ wavefunction overlaps differently with the positive and negative lobes of the $2p$ wavefunction when weighted by z.

Diagonalizing: Rotating our matrix to find the "Hybrid states" where the flipping stops.

$$\psi_{\pm} = \frac{1}{\sqrt{2}}(|2s\rangle \pm |2p\rangle) = \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$$

Linearity signifies that the atom in its new hybrid state acts like a permanent electric dipole. Since $2s$ and $2p$ have the same energy, the electric field can easily mix them, the new wavefunction being:-

$$\psi_{\pm} = \frac{1}{\sqrt{2}}(|2s\rangle \pm |2p\rangle)$$

$\therefore$ Solving for eigenvalues $\implies \det(W - \lambda I) \implies \lambda = \pm\Delta_{12}$

$$\therefore E^{(1)}_{1,2} = \pm 3ea_0E$$

If W_{ij} a non-zero $\implies$ perturbation acts like a tunnel, it allows e^- to flow back and forth between $2s$ and $2p$. The 'tunneling' creates a hybrid superposition.

If W_{ii} is non-zero: perturbation pushes the energy up or down without changing the shape.

Remarks

1. Tunneling: When we observe our dipole at the limit $z \to -\infty$. Considering the Coulomb potential, it creates a barrier of finite width. Hence, our Hamiltonian describes a system where the electrons aren't bounded, allowing quantum tunneling leading to ionization of the Hydrogen Atom.
The stationary states developed via perturbation theory correspond to metastable states with a finite lifetime. The reason perturbation theory is a valid approximation is that for weak fields, the probability of tunneling is exponentially small, making the lifetime long enough to treat the state as stationary.
2. Laplace-Runga-Lenz Vector: In our analytical work, we have used spherical coordinates since its efficient for calculations of lower perturbations. However, the problem of the Stark effect in the Hydrogen atom is exactly separable if one uses Parabolic coordinates. This separation is possible due to the $SO(4)$ symmetry of the Hydrogen atom related to the Laplace-Runge-Lenz vector.
3. Lamb Shift: In our analytical work, we have assumed perfect degeneracy between the l states. Therefore, the Linear Stark effect is only observed in the Strong Field Limit, where the Stark interaction energy is much larger than the Lamb shift. For weak fields, the states remain non-degenerate; the effect is Quadratic.