Stark Effect

Hamiltonian: \[ H_{\text{ext}} = -\vec{d} \cdot \vec{E} \]
\[ \vec{d} = e \cdot \vec{x} \] \[ \text{spin-indep. Electric dipole moment.} \]
\[ \text{(EDM)} \]

Notes:
- Any atomic state with non-zero \( \vec{J} \) but can have \( \vec{d} \).
- But a state must be degenerate with another state of opposite parity for it to have \( \vec{d} \).

Fact #1: Because parity (\( P \)) is a good symmetry of the atomic system (i.e. \([\hat{H}, \hat{P}] = 0\)) no atomic stationary state (satisfying \( \hat{H} |\psi\rangle = E |\psi\rangle \)) can have an EDM

Proof: \[ [[\hat{H}, \hat{P}] = 0 \implies |\psi\rangle \text{ has definite } P \quad (P|\psi\rangle = \pm |\psi\rangle) \]
then \[ \langle \psi | \hat{d} | \psi \rangle = \langle \psi | P^{-1} \hat{J} P \hat{P} \cdot \hat{J} | \psi \rangle \]
\[ = (\pm 1)^2 \langle \psi | P^{-1} \hat{J} P | \psi \rangle \]
\[ = (\pm 1)^2 \langle \psi | \hat{J} | \psi \rangle = -\langle \psi | \hat{J} | \psi \rangle = 0. \]

Fact #2: Exception:
For an atomic state to have non-zero EDM, it must be degenerate with another state with opposite parity.

e.g. Hydrogen
\[ \begin{array}{c|c}
\text{S} & \text{P} \\
\hline
2s & 2p \\
1s \\
\end{array} \]

Pictorially:
\[ \text{Mathematically:} \]
Let \( |\psi\rangle = \frac{1}{\sqrt{2}} (|2s\rangle + |2p\rangle) \) (is also c-state of \( \hat{P} \))

Then \[ \langle \psi | \hat{d} | \psi \rangle = \left( \frac{1}{\sqrt{2}} \right)^2 \times 2 \langle 2s | \hat{d} | 2p \rangle \neq 0 \]
Electric Polarizability

Fact #3: For most atomic systems, the effect of an external $E$-field is 2nd order. This is because at 1st order, diagonal elements are zero.

$$\delta E = \langle \psi | -E \cdot \hat{d} | \psi \rangle$$

$$= -E \cdot \langle \psi | \hat{d} | \psi \rangle = 0.$$ 

But at 2nd order,

$$\delta E = \sum_n \frac{\langle \psi | -E \cdot \hat{d} | n \rangle \langle n | -E \cdot \hat{d} | \psi \rangle}{E_n - E_n}$$

Qualitatively, the first factor of $-E \cdot \hat{d}$ serves to polarize the state $|n\rangle$ giving it an induced EDM (though its coupling to $|n\rangle$),

The second factor of $-E \cdot \hat{d}$ couples to this induced EDM shifting the energy.

This picture motivates us to define the polarizability

$$\hat{\chi}_{\text{ind}} = \alpha \hat{E}$$

Induced EDM Polarizability Applied Field

⇒ Energy shift: $\delta E = \int -\hat{d} \cdot d\hat{E}$

$$= \int -\alpha \hat{E} \cdot d\hat{E}$$

$$= -\frac{1}{2} \alpha \hat{E}^2$$

more generally, pol. tensor: $d_{ij} = \sigma_{ij} E_j$

Compute energy shift to second order, and read off the electric polarizability.
Example: Polarizability of Hydrogen atom in ground state.

\[ \hat{\alpha}_{\text{ext}} = -\vec{\alpha} \cdot \vec{E} = e|E_r r_0^3 \theta \]

**First order:**

\[ SE = \langle 1s | -\vec{\alpha} \cdot \vec{E} | 1s \rangle = 0 \quad \text{(Parity)} \]

1s state has no EDM.

**Second order:**

\[ SE = \sum_{n \neq 1} \frac{\langle 1s | -\vec{\alpha} \cdot \vec{E} | n \rangle \langle n | -\vec{\alpha} \cdot \vec{E} | 1s \rangle}{E_{n=1} - E_n} \quad \text{[sum over both bound and continuum states]} \]

**Approximation:**

\[ E_n \approx E_2 \]

\[ \begin{align*}
SE &= \frac{1}{E_{n=1} - E_{n=2}} \sum_n \langle 1s | -\vec{\alpha} \cdot \vec{E} | n \rangle \langle n | -\vec{\alpha} \cdot \vec{E} | 1s \rangle \\
&\quad \text{ok to include } n=1 \text{ in sum because matrix element vanishes anyway.}
\end{align*} \]

Use completeness relation: \( \sum_n \langle n | n \rangle = 1 \)

\[ = \frac{1}{E_{n=1} - E_{n=2}} \langle 1s | (\vec{\alpha} \cdot \vec{E})^2 | 1s \rangle \]

Recall \( E_{n=1} - E_{n=2} = E_{n=1} - \frac{3}{4} E_{n=1} = \frac{1}{4} E_{n=1} \)

\[ = \frac{1}{\frac{3}{4} E_{n=1}} \langle 1s | (\vec{\alpha} \cdot \vec{E})^2 | 1s \rangle \]

Now compute matrix element.
Matrix element calculation:

\[
\langle 1s \mid (\vec{a} \cdot \vec{E})^2 \mid 1s \rangle
\]

\[
= e^2 |E|^2 \langle 1s \mid (r \cos \theta)^2 \mid 1s \rangle
\]

\[
= e^2 |E|^2 \int d^3r \, R_{1s}(r)^2 \, r^2 \, Y_{l=0}^{m=0}(\Omega_r)^2 \cos^2 \theta
\]

\[
= e^2 |E|^2 \int_0^{\infty} (dr \, r^2) \left[ 2 \left( \frac{1}{a} \right)^3 e^{-r/a} \right]^2 \int_0^\pi \sin \theta \left( \frac{1}{2\pi} \right)^2 \cos^2 \theta
\]

\[
= e^2 |E|^2 \int_0^{\infty} (dr \, r^2) \int_0^{2\pi} d\phi \int_0^{1/a} dz \int_{-\frac{1}{2}a^3}^{\frac{1}{2}a^3} d\delta
\]

\[
\frac{1}{4\pi \epsilon_0} \frac{1}{2a}
\]

Therefore energy shift is

\[
\delta E = \frac{1}{\frac{3}{4} \varepsilon_{r+1}} |E|^2 a^2
\]

\[
= \frac{4}{3} \left( \frac{4\pi \epsilon_0}{e^2} \right) (-2a) |E|^2 a^2
\]

\[
= \frac{4\pi \epsilon_0}{e^2} \frac{9}{3} a^3 |E|^2
\]

Comparing with \( \delta E = \frac{1}{2} \alpha \times E^2 \), we read off polarizability \( \alpha \):

\[
\alpha = \frac{4\pi \epsilon_0}{e^2} \frac{16}{3} a^3 = \frac{4\pi \epsilon_0}{e^2} \left( 0.76 \times 10^{-24} \text{ cm}^3 \right)
\]