# Physics 492 - Quantum II

## Lecture 21: Time Independent Perturbation Theory (Continued)

Recap: We seek solutions to the T.I.S.E

$$\hat{H} = \hat{H}_0 + \epsilon \hat{H}_1 \quad , \quad \hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$$

For bound states, where $\epsilon \hat{H}_1$ is a "perturbation" and $\hat{H}_0 |\phi_n^{(0)}\rangle = E_n^{(0)} |\phi_n^{(0)}\rangle$ are know solutions. We expand in a power series in $\epsilon$

$$|\phi_n\rangle = |\phi_n^{(0)}\rangle + |\delta\phi_n\rangle \quad , \quad |\delta\phi_n\rangle = \sum_{k=1}^{\infty} \epsilon^k |\phi_n^{(k)}\rangle$$

$$E_n = E_n^{(0)} + \delta E_n \quad , \quad \delta E_n = \sum_{k=1}^{\infty} \epsilon^k E_n^{(k)}$$

- First order $E_n^{(1)} = \langle \phi_n^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle$

$$|\phi_n^{(1)}\rangle = \sum_{m\neq n}' |\phi_m^{(0)}\rangle \frac{\langle \phi_m^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

Perturbation when

$$|\langle \phi_m^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle| \ll |E_n^{(0)} - E_m^{(0)}|$$

$$\forall n, m$$

No degeneracies!

Consider ~~solutions~~ now the second order corrections. Typically we go to $2^{nd}$ order when first order shifts vanish (more on this below).

The second order contribution to the T.I.S.E.

$$E_n^{(2)} |\phi_n^{(0)}\rangle = \left(\hat{H}_0 - E_n^{(0)}\right) |\phi_n^{(2)}\rangle + \left(\hat{H}_1 - E_n^{(1)}\right) |\phi_n^{(1)}\rangle$$

Project with $\langle \phi_n^{(0)}|$

$$\Rightarrow E_n^{(2)} \langle \phi_n^{(0)} | \phi_n^{(0)} \rangle = \langle \phi_n^{(0)} | \left(\hat{H}_0 - E_n^{(0)}\right) | \phi_n^{(2)} \rangle + \langle \phi_n^{(0)} | \left(\hat{H}_1 - E_n^{(1)}\right) | \phi_n^{(1)} \rangle$$

$$\Rightarrow E_n^{(2)} = \langle \phi_n^{(0)} | \hat{H}_1 | \phi_n^{(1)} \rangle$$

(Having used $\langle \phi_n^{(0)} | \phi_n^{(0)} \rangle = 1$ and $\langle \phi_n^{(0)} | \hat{H}_0 = E_n^{(0)} \langle \phi_n^{(0)} |$)

Plug in for $|\phi_n^{(1)}\rangle$

$$\boxed{\Rightarrow E_n^{(2)} = \sum_{m \neq n}{}' \frac{\langle \phi_n^{(0)} | \hat{H}_1 \overbrace{| \phi_m^{(0)} \rangle \langle \phi_m^{(0)} |}^{\text{"intermediate state"}} \hat{H}_1 | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}}$$

$$E_n^{(2)} = \sum_{m \neq n}{}' \frac{|\langle \phi_m^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

So for $|\vec{\mathcal{E}}| \ll 10^{9}$ Volts/cm, perturbation theory is good.

Consider shift to ground state of H, 1s

$$\Rightarrow E^{(1)}_{1s} = \langle 1s | \hat{V}_{int} | 1s \rangle = e \vec{\mathcal{E}} \cdot \langle 1s | \hat{\vec{r}} | 1s \rangle$$

$$\vec{r} = r \left( \cos\theta \, \vec{e}_z + \sin\theta ( \cos\phi \, \vec{e}_x + \sin\phi \, \vec{e}_y ) \right)$$

$$\psi_{1s}(r,\theta,\phi) = R_{1s}(r) \, Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}} R_{1s}(r)$$

spherically symmetric

$$\Rightarrow \langle 1s | \hat{\vec{r}} | 1s \rangle = 0$$

$$\Rightarrow E^{(1)}_{1s} = 0$$ No first order shift!

(Aside: More generally, $\langle n\,l\,m | \vec{r} | n\,l\,m \rangle = 0$ for any $l\ m$ because of "inversion symmetry" $\vec{r} \Rightarrow -\vec{r}$ )

Since the first order shift vanishes, we must consider second order corrections. This is the lowest nonvanishing contribution.

## Example: The Stark Effect

An important application of perturbation theory is effect of an externally applied field to ~~the~~ matter. Here we study static fields, e.g. a static $\vec{E}$ field applied to an atom. The shift in the energy levels is known as the Stark effect.

Consider the force of an external electric field $\vec{\mathcal{E}}$ on an electron: $\vec{F} = -e\vec{\mathcal{E}}$

$\Rightarrow$ Interaction potential

$$\hat{V}_{int} = -\vec{r}\cdot\vec{F} = e\vec{r}\cdot\vec{\mathcal{E}}$$
$$= -\vec{d}\cdot\vec{\mathcal{E}}$$

$\leftarrow$ electric dipole

Total potential for the electro in Hydrogen

$$\hat{V} = \frac{e}{r} - \vec{d}\cdot\vec{\mathcal{E}}$$

Is this a perturbation? Require externally applied field $|\vec{\mathcal{E}}|$ must smaller that internal field experienced by the electron

$$\mathcal{E}_{internal} \cong \frac{e}{a_0^2} \quad (a_0 = \text{Bohr radius})$$

$$= 10^9 \ \frac{\text{Volts}}{\text{cm}} \quad \text{Huge!}$$

$$E_{1s}^{(2)} = \sum_{\substack{n',l',m' \\ \neq 0,0,0}} \frac{|\langle n',l',m'| \hat{V}_{int} | 1s\rangle|^2}{E_{1s} - E_{n'l'}}$$

$$= \sum_{n',l',m'} \frac{|\langle n',l',m'| \hat{\vec{d}} |1s\rangle \cdot \vec{\mathcal{E}}|^2}{E_{1s} - E_{n'l'}}$$

where $\vec{d} = -e\vec{r}$

Take $\vec{\mathcal{E}}$ is z-direction (irrelevant since spherical symmetric state)

$$\Rightarrow \boxed{E_{1s}^{(2)} = \left(\sum_{n',l',m'} \frac{e^2 |\langle n'l'm'| \hat{z} | 1s\rangle|^2}{E_{1s} - E_{n'l'}}\right) \mathcal{E}^2}$$

"Quadratic Stark effect". Energy shift quadratic function of applied field

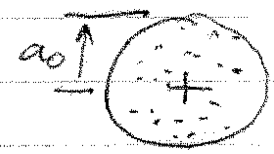
More advanced knowledge → "Selection rules" for dipole matrix elements $\langle n'l'm'| \hat{d}_z | 1s\rangle$, vanishes unless $l' = 1$ $m' = 0$ ⇒ Can do sum

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

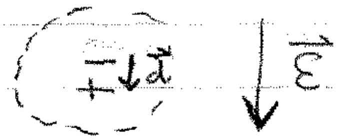
← Field energy

← Hartree

Physical picture: Induced dipole of polarizable particle

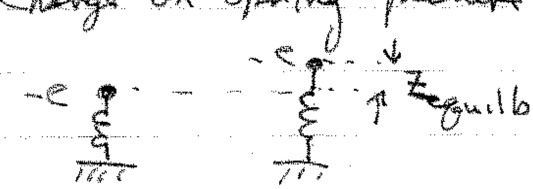



Unperturbed Hydrogen




Induced dipole interacts with $\vec{\mathcal{E}}$ (second order process)

Charge on spring picture




Balance restoring force

$$m\omega^2 z_{eq} = e\,\mathcal{E}_z$$

$$\Rightarrow \quad z_{eq} = \frac{e}{m\omega^2}\mathcal{E}_z$$

$$\Rightarrow \text{Induced dipole moment} \quad \vec{d}_{ind} = \underbrace{\frac{e^2}{m\omega^2}}_{\alpha}\vec{\mathcal{E}}$$

$$\alpha = \text{Polarizability} = \frac{e^2}{m\omega^2}$$

Total potential energy: $\frac{1}{2}m\omega^2 z_{eq}^2 - \vec{d}_{ind}\cdot\vec{\mathcal{E}}$

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

$$= -\frac{1}{2}\frac{e^2}{m\omega^2}\mathcal{E}_z^2 = \boxed{-\frac{1}{2}\alpha\,\mathcal{E}_z^2}$$

$$= -\frac{1}{2}\vec{d}_{ind}\cdot\vec{\mathcal{E}}$$

$\Uparrow$

half the potential is stored in "spring"

## Quantum Mechanically

Induced dipole: $\langle \tilde{\Phi} | \hat{\vec{d}} | \tilde{\Phi} \rangle$ where

$$|\tilde{\Phi}\rangle = \left( |\phi^{(0)}_{1s}\rangle + |\phi^{(1)}\rangle \right) / \|\tilde{\Phi}\|$$

$$|\phi^{(0)}\rangle = |1s\rangle \qquad |\phi^{(1)}\rangle = e\mathcal{E}\sum_{n'} \frac{|n'10\rangle\langle n'10|z|100\rangle}{E_{1s} - E_{n'p}}$$

To lowest order: $$\langle \hat{\vec{d}} \rangle = \frac{\langle \Phi^{(0)}_{1s} | \hat{\vec{d}} | \phi^{(1)} \rangle + \langle \phi^{(1)} | \hat{\vec{d}} | \phi^{(0)} \rangle}{1 + \cancel{\langle \phi^{(1)} | \phi^{(1)} \rangle} \to \text{neglect}}$$

$$\Rightarrow \langle \hat{\vec{d}} \rangle \equiv \vec{d}_{induced} = -2e^2 \sum_{n'} \frac{\langle 100|\hat{z}|n'10\rangle\langle n'10|\hat{z}|n10\rangle}{E_{1s} - E_{n'p}} \hat{e}_z$$

$$\vec{d}_{ind} = \alpha\vec{\mathcal{E}} \Rightarrow \boxed{\alpha = +2e^2 \sum_{n'} \frac{\langle 100|\hat{z}|n'10\rangle\langle n'10|\hat{z}|100\rangle}{E_{n'p} - E_{1s}}}$$

Polarizability (scalar here)

$$E^{(2)}_{1s} = -\frac{1}{2}\alpha\mathcal{E}^2 \quad \checkmark$$

Compare to classical picture:

Oscillator strength $$f_{nn'} \equiv \frac{|\langle n'10| z |100\rangle|^2}{\left(\frac{\hbar}{2m\omega}\right)}$$

Majority of oscillator strength in the $1s \rightarrow 2p$ transition