Applications of the perturbation theory : H-atom

Basic structure (unperturbed Hamiltonian)

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{r}$$

Coulumb interaction

$p \longleftrightarrow e$

Corrections (perturbations)

- H-atom interactions with the outside world
  - magnetic field (Zeeman effect)
  - electric field (Stark effect)
  - neighboring atoms (Van-der-Waals interaction)
- Relativistic corrections
  - Correction to the kinetic energy.
  - Spin
    - fine structure (spin-orbit coupling)
    - hyperfine structure ($\bar{e}$-nuclear spin coupling)
  - QED correction (Lamb shift) (wait for later)

H-atom in magnetic field

as we showed before for $\vec{B} = B\vec{e}_z$

$$\hat{H} = \frac{p^2}{2m_e} - \frac{e^2}{r} + \frac{e}{2m_e c} B\hat{L}_z + \underbrace{\frac{e^2}{8m_e c^2} |B|^2 (x^2+y^2)}_{\text{neglect}}$$

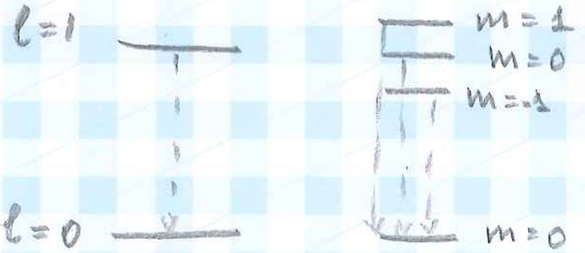
$$\vec{\mu}_{orb} = \frac{-e}{m_e c} \vec{L}$$

If no electron spin is taken into account

$$\hat{V} = -\vec{\mu}_{orb} \cdot \vec{B} = \frac{eB}{m_e c} \cdot \hat{L}_z$$

$[\hat{V}, \hat{L}^2] = [\hat{V}, \hat{L}_z] = 0$ → can use same wavefunctions $|n, l, m\rangle$

$$E^{(1)}_{nlm} = \langle nlm | \hat{V} | nlm \rangle = \frac{e\hbar}{2m_e c} B m$$



Zeeman effect

if looking at optical transitions

one spectral line splits into three

normal Zeeman effect

Spins must be included!

$$\hat{V} = -\frac{eB_z}{2m_e c} (\hat{L}_z + 2\hat{S}_z)$$

Such treatment is valid for strong magnetic field (i.e its effect overpowers spin - orbit coupling)

Wavefunctions $|n l m_l s m_s\rangle$

Paschen - Bach regime

$$E^{(1)}_{nlm_l s m_s} = -\frac{e\hbar}{2m_e c} B (m_l + 2m_s)$$

Application of the perturbation theory for H atom

H-atom in an electric field

As we derived earlier $\hat{V} = -\vec{d}\vec{\mathcal{E}} = -e\vec{r}\vec{\mathcal{E}}$

With no other preferred directions it make sense to choose $\vec{\mathcal{E}}$ along z-axis

$\hat{V} = -e\mathcal{E}z$ since $z \propto Y_{10}(\theta,\varphi)$

$\hat{V}$ transforms as T_0^1 component of vector operator

Electron spin is not coupled, so the $s_z = \pm\frac{1}{2}$ are not resolved $\longrightarrow$ can be ignored.

Ground state $1S$ $n=1$ $l=0$ $m=0$ - no degeneracy

can follow "simple" Pert. theory prescription

$$E^{(1)}_{n=1} = -e\mathcal{E}\,\langle 1,0,0|z|1,0,0\rangle = 0$$

$$E^{(2)}_{n=1} = e^2\mathcal{E}^2 \sum_{|e\rangle \neq |1,0,0\rangle} \frac{|\langle 1,0,0|z|e\rangle|^2}{E^{(0)}_{n=1} - E^{(0)}_{e}}$$

estimate: $\left(E^{(0)}_{e} - E^{(0)}_{n=1}\right) > E^{(0)}_{n=2} - E^{(0)}_{n=1} = \frac{3}{4}E^{(0)}_{n=1}$

$$-E^{(2)}_{n=1} < \frac{e^2\mathcal{E}^2}{\frac{3}{4}|E^{(0)}_{n=1}|} \sum_{|e\rangle} \langle 1,0,0|z|e\rangle\langle e|z|100\rangle$$

↑ can add $|1,0,0\rangle$ as well now!

$$-E^{(2)}_{n=1} \leq -\frac{4e^2\mathcal{E}^2}{3|E^{(0)}_{n=1}|}\langle 1,0,0|z^2|1,0,0\rangle$$

s - spherically-symmetric state $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = \frac{\langle r^2\rangle}{3}$

$$\langle r^2\rangle = \int_0^\infty r^2 R_{10}(r)^2 r^2 dr = \frac{4}{a_0^3}\int_0^\infty r^2 e^{-2r/a_0} r^2 dr =$$

$$= \frac{a_0^2}{8}\int_0^\infty x^4 e^{-x}dx = \frac{a_0^2}{8}\Gamma(5) = 3a_0^2$$

Quadratic Stark effect

$$|E^{(0)}_{n=1}| = \frac{e^2}{2a_0}$$

$$-E^{(2)}_{n=1} < \frac{4}{3}\cancel{e}\mathcal{E}^2\,\frac{2a_0}{\cancel{e^2}}\cdot a_0^2 = \frac{8}{3}a_0^3\mathcal{E}^2$$

Polarizability $\Delta E = -\frac{1}{2}\alpha\mathcal{E}^2$

Exact calculations $E^{(2)} = -\frac{9}{4}a_0^3\mathcal{E}^2$ | $\alpha = \frac{9}{2}a_0^3$

Any excited state of the H-atom is degenerate → need to find the right basis

$n=2 \rightarrow 4$ states $\underbrace{|2,1,1\rangle, |2,1,0\rangle, |2,1,-1\rangle}_{l=1}$ & $\underbrace{|2,0,0\rangle}_{l=0}$

$\hat{V} = -e\mathcal{E}z$ again

Need to evaluate $\langle 2,l,m|\hat{V}|2,l',m'\rangle$ elements.

Because of the Wigner-Eckert theorem only terms with $\Delta m = 0$ are non-vanishing

$$V = \begin{array}{c} \begin{array}{cccc} |100\rangle & |110\rangle & |11,1\rangle & |1,-1\rangle \end{array} \\ \left(\begin{array}{cc|cc} 0 & 3ea_0\mathcal{E} & 0 & 0 \\ 3ea_0\mathcal{E} & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{array}\right) \end{array}$$

Diagonal matrix elements must be zero

$$V_{\substack{lm\\lm}} \propto \int Y_{lm}^2 \cos\theta \, d\Omega = 0$$

Y_{lm}^2: even under $z \rightarrow -z$, $\cos\theta \rightarrow -\cos\theta$

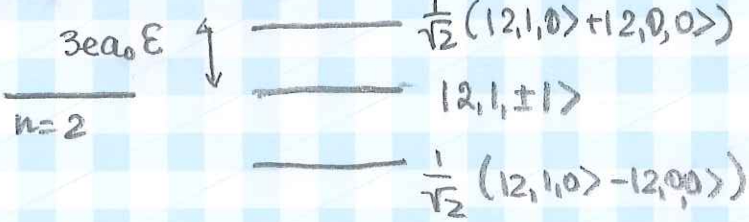
$\cos\theta$: odd under $z \rightarrow -z$, $\cos\theta \rightarrow -\cos\theta$

States $|2,1,1\rangle$ and $|2,1,-1\rangle$ are not affected by electric field – no first-order shift

Effective two-level system

$$E^{(1)}_{\substack{n=2\\m=0}} = \pm 3ea_0\mathcal{E} \qquad |\pm\rangle = \frac{1}{\sqrt{2}}\left(|2,1,0\rangle \pm |2,0,0\rangle\right)$$

E-field partially breaks the degeneracy



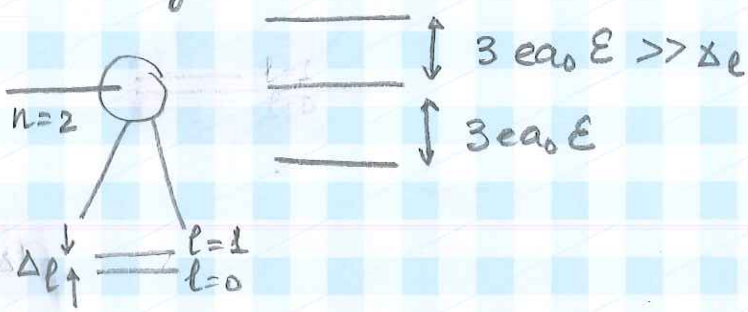
Linear Stark effect

But in reality the states $|2,1,0\rangle$ and $|2,0,0\rangle$ are never <u>exactly</u> degenerate (spin-orbit coupling, QED)

Can we still use the degenerate Pert. Theory?

Depends on the relative strengths of the two corrections

Strong $\mathcal{E}$-field



Linear Stark effect is working

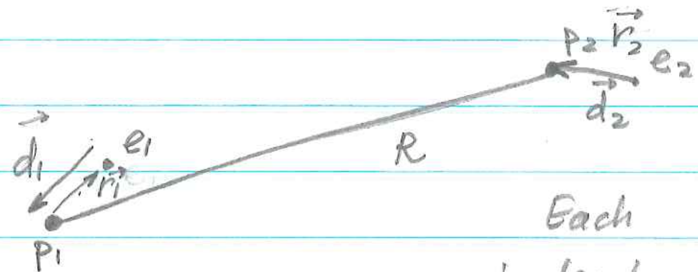
if necessary, can then calculate small corrections to the new basis

Weak $\mathcal{E}$-field

——— $|2,1,m\rangle$

——— $|2,0,0\rangle$ ← apply quadratic Stark effect

Van-der-Waals interaction:
"residual" Coulomb Interaction b/w two H-atoms



Each atom has an instantaneous dipole moment, creating fluctuating electric field

$$\mathcal{E} \sim -\, d/R^3$$

$$\Delta E = -\frac{1}{2}\alpha \mathcal{E}^2 \sim -a_0^3 \cdot \frac{d^2}{R^6} \sim a_0^3 \frac{(e a_0)^2}{R^6}$$

$$\Delta E \approx -e^2\, a_0^5/R^6$$

Short-range ($\sim 1/R^6$) weak atom-atom attraction

Perturbation theory

$$\hat{H}_0 = \frac{\hat{p}_1}{2m} + \frac{\hat{p}_2}{2m} - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$

$$\hat{V} = e^2\left(\frac{1}{R} + \frac{1}{|\vec{R}+\vec{r}_2-\vec{r}_1|} - \frac{1}{|\vec{R}+\vec{r}_2|} - \frac{1}{|\vec{R}-\vec{r}_1|}\right)$$

$$R \gg r_1, r_2 \qquad \frac{1}{\sqrt{1+x}} \approx 1 - \frac{x}{2} + \frac{3x^2}{8} - \ldots$$

$$\frac{1}{|\vec{R}+\vec{r}_2|} = \frac{1}{R} - \frac{\vec{r}_2\vec{R}}{R^3} + \frac{1}{2R^5}\left(3(\vec{r}_2\vec{R})^2 - R^2 r_2^2\right) - \ldots$$

$$\hat{V} = \frac{1}{R} +$$

$$+ \frac{1}{R} - \frac{(\bar{r}_2 - \bar{r}_1)\bar{R}}{R^3} + \frac{1}{2R^5}\left\{3\left[(\bar{r}_2 - \bar{r}_1)\bar{R}\right]^2 - R^2(r_2 - r_1)^2\right\}$$

$$- \frac{1}{R} + \frac{\bar{r}_2 \bar{R}}{R^3} + \frac{1}{2R^5}\left[3(\bar{r}_2 \cdot \bar{R})^2 - R^2 r_2^2\right]$$

$$- \frac{1}{R} + \frac{\bar{r}_1 \bar{R}}{R^3} - \frac{1}{2R^5}\left[3(\bar{r}_1 \bar{R})^2 - R^2 r_1^2\right]$$

Only second-order terms survive

$$\hat{V} = e^2 \frac{x_1 x_2 + y_1 y_2 - 2 z_1 z_2}{R^3}$$

no first-order correction

Second-order correction

$$\Delta E^{(2)} = \frac{e^4}{R^6} \sum_{k \neq 1} \frac{|\langle k^{(0)} | x_1 x_2 + y_1 y_2 - 2 z_1 z_2 | 0^{(0)} \rangle|^2}{E^{(0)}_{n=1} - E^{(0)}_k}$$

$$-\Delta E^{(2)} < \frac{e^4}{R^6} \frac{1}{\frac{3}{4}|E^{(0)}_{n=1}|} \sum_{k \neq 0} |\langle k^{(0)} | x_1 x_2 + y_1 y_2 - 2 z_1 z_2 | 0 \rangle|^2$$

$$= \frac{8 e^2 a_0}{3 R^6} \sum_{k \neq 0} |\langle k | V' | 0 \rangle|^2 \approx \frac{8 e^2 a_0}{3 R^6} \langle 0 | V'^2 | 0 \rangle$$

$$V'^2 = x_1^2 x_2^2 + y_1^2 y_2^2 + 4 z_1^2 z_2^2 + \text{(cross-terms)}$$

using $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} \langle r^2 \rangle = a_0^2$

$$-\Delta E^{(2)} \leq \frac{8 e^2}{3 R^6} a_0 \frac{6}{9} \langle r^2 \rangle^2 = 16 e^2 \frac{a_0^5}{R^6}$$