H-atom in $\vec{B}$ field: $\vec{B} = B_0 \hat{e}_z$ $\qquad$ $H = \frac{1}{2\mu}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 + \ldots$

μ - reduced mass

$\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$ for constant $\vec{B}$

$\frac{\vec{p}^2}{2\mu} - \frac{e^2}{r}$

$$H = H_0 + \frac{e}{2\mu c}(\vec{B} \times \vec{r}) \cdot \vec{p} + \frac{e^2}{8\mu c^2}(\vec{B} \times \vec{r})(\vec{B} \times \vec{r})$$

vector identities: $(\vec{B} \times \vec{r}) \cdot \vec{p} = \vec{B} \cdot (\vec{r} \times \vec{p}) = \vec{B} \cdot \vec{L}$ $\qquad$ $\vec{L}$ - ang momentum

$$(\vec{B} \times \vec{r})(\vec{B} \times \vec{r}) = \vec{B}^2 \vec{r}^2 - (\vec{B} \cdot \vec{r})^2 = B^2(x^2 + y^2)$$

$$\vec{B}^2 \vec{r}^2 - (\vec{B} \cdot \vec{r})(\vec{B} \cdot \vec{r})$$

$$\longrightarrow H = H_0 + \underbrace{\frac{e}{2\mu c}\vec{B} \cdot \vec{L}}_{\to \frac{e}{2\mu c} B \cdot L_z} + \frac{e^2 B^2}{8\mu c^2}(x^2 + y^2)$$

ignores 2 effects: Both nucleus & electron have spin ½ & magnetic moments

work w/ Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^2 \otimes \mathbb{C}^2$

forms of $\vec{r}$ $\qquad$ electron spin $\qquad$ nucleus/proton spin

modifications of H

$$\cancel{\frac{e g_N}{2 m_N c}\vec{B} \cdot \vec{S}_N} + \frac{e g}{2 m_e c}\vec{B} \cdot \vec{S}_E$$

$g_N \sim 5.5$ / nucleon spin $\qquad$ $g \sim 2$ / electron spin

But $m_{proton} \sim 2000\, m_e$, so can drop nucleon spin

$$H = H_0 + \frac{e}{2 m_e c}\vec{B} \cdot (\vec{L} + g\vec{S}) + \frac{e^2 B^2}{8 m_e c^2}(x^2 + y^2)$$

for $\vec{B} = B_0 \hat{e}_z$ $\qquad$ $\mu \simeq m_e$ b/c $\frac{1}{\mu} = \frac{1}{m_e} + \cancel{\frac{1}{m_p}}$

$g \sim 2$ $\quad \vec{B} \cdot (\vec{L} + 2\vec{S})$

$\vec{L} + 2\vec{S} \neq \vec{J}$

for $B \sim 1$ Tesla $\sim 10^4$ gauss, $\quad$ B & B^2 terms lead to small corrections paramagnetism - materials develop a net magnetic moment $\vec{\mu}$ in presence of $\vec{B}$ magnetic field.

$\vec{\mu}$ is aligned w/ $\vec{B}$

$$E = -\vec{\mu}\cdot\vec{B} < 0$$

attracted to large fields

$\vec{\mu} \propto \vec{B}$

diamagnetism - $\vec{\mu}$ is antialigned w/ $\vec{B}$

$$E = -\vec{\mu}\cdot\vec{B} > 0 \qquad \vec{\mu} \propto -\vec{B}$$

H-atom in a state $|\psi\rangle = |n, l, m_l, m_s\rangle$

$$\Delta E_\psi = \underbrace{\frac{eB}{2m_e c}}_{\substack{\text{1st order perturbation theory} \\ \text{1st order in } B}} \langle\psi| L_z + g S_z |\psi\rangle + \underbrace{\frac{e^2B^2}{8m_e c^2}}_{\substack{\text{"1st order in perturbation theory"} \\ \text{2nd order in } B}} \langle\psi| x^2+y^2 |\psi\rangle$$

$$+ \sum_{\psi\neq\psi'} \frac{|\langle\psi| \frac{eB}{2m_e c}(L_z + 2S_z)|\psi'\rangle|^2}{E_\psi - E_{\psi'}} + O(B^3)$$

2nd order perturbation theory

$$H = H_0 + \lambda H_1 \qquad \Delta E_\psi = \langle\psi|H_1|\psi\rangle + \sum_{\psi\neq\psi'} \frac{|\langle\psi|H_1|\psi'\rangle|^2}{E_\psi - E_{\psi'}}$$

When term linear in B is nonzero, it is larger than B^2 term & dominates physics

Ground State of Hydrogen $|n=1, l=0, m_l=0, m_s=\pm\tfrac{1}{2}\rangle$

$$\Delta E_{gnd} = \frac{egB}{2m_e c} \langle 1,0,0,m_s| \underbrace{S_z}_{\pm\hbar/2} |1,0,0,m_s\rangle$$

$$= \pm \frac{egB}{4m_e c} \qquad g=2 \qquad + \quad S_z = +\hbar/2$$

$$= \pm \frac{eB}{2m_e c} \qquad - \quad S_z = -\hbar/2$$

Zeeman Effect splitting of atomic energy levels in a magnetic field

Electrons have dipole moment

$$\vec{\mu} = -\frac{eg}{2m_e c}\vec{S}$$

$m_s = -\frac{1}{2} \rightarrow \mu_z > 0$ lower energy

$m_s = \frac{1}{2} \rightarrow \mu_z < 0$ higher energy

Stat Mech: probability $\sim e^{-E/kT}$ for state of energy E

$$\langle \mu_z \rangle = \underset{\text{\# of atoms}}{N} \cdot \underset{g=2}{\left(\frac{-e\hbar}{m_e c}\right)} \cdot \underset{\text{spin}}{\frac{\hbar}{2}} \cdot \underbrace{\left(e^{-\frac{eB\hbar}{2m_e ckT}} - e^{+\left(\frac{eB\hbar}{2m_e ckT}\right)}\right)}_{\text{probability}} \cdot \underbrace{\left(e^{-\frac{eB\hbar}{2m_e ckT}} + e^{+\left(\frac{eB\hbar}{2m_e ckT}\right)}\right)^{-1}}_{\text{normalization}}$$

$$= N\frac{e^2\hbar^2}{2m_e c} \tanh\left(\frac{eB\hbar}{2m_e ckT}\right)$$

① positive $\rightarrow$ paramagnetic

② B is very small $\langle \mu_z \rangle \sim B/T$ (Curie's law)

if $\langle \psi | L_z + gS_z | \psi \rangle \neq 0$

what if $\underbrace{\langle \psi | L_z + \overbrace{gS_z}^{\text{total spin op. for all electrons}} | \psi \rangle}_{\text{0 for ground state of He}} = 0$ eg ground state of Helium - or any noble gas

$(1s)^2$ electron spin wave fn $|S=0\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle)$

$S_z |s=0\rangle$