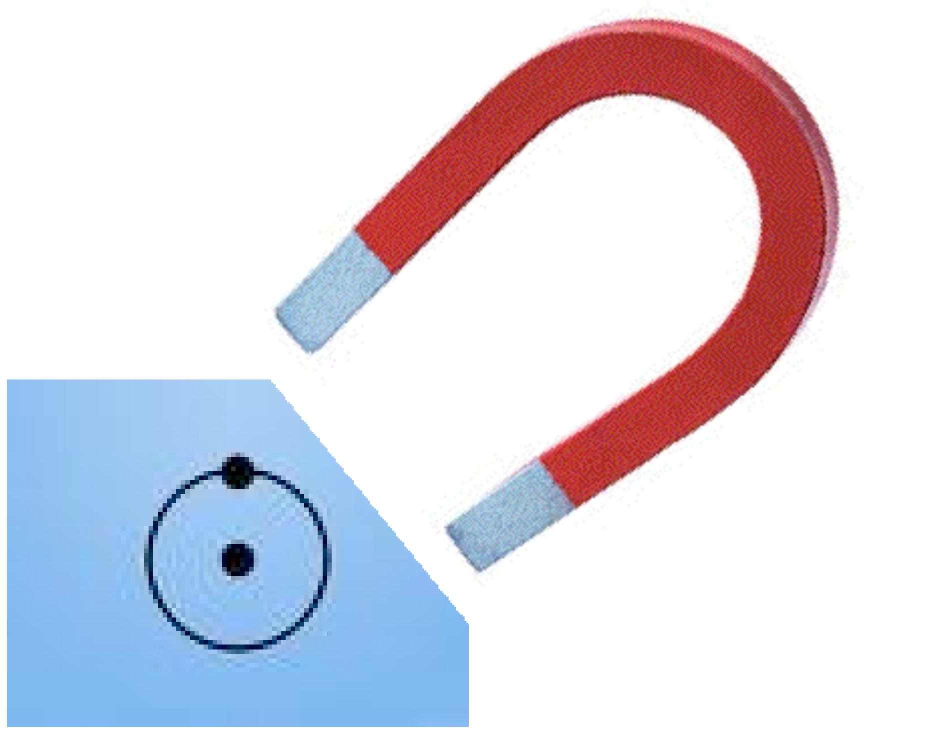


Lecture 31:
The Hydrogen Atom 2:
Dipole Moments

Phy851 Fall 2009

Electric Dipole Approximation

- The interaction between a hydrogen atom and an electric field is given to leading order by the Electric Dipole approximation:

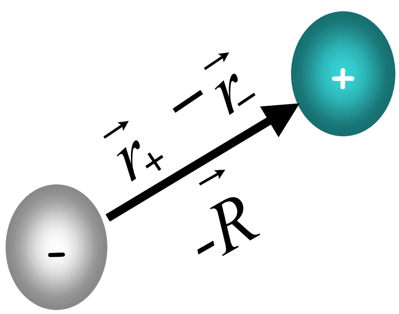
$$V_E = -\vec{D}\cdot\vec{E}(r_{CM})$$

`Semi-Classical' Approx:

•Electric field is classical

•COM motion is classical

- The dipole moment of a pure dipole:
  - Vector quantity
  - Points from - to +.
  - Magnitude is charge _ distance



$$\vec{d} = |q|(\vec{r}_+ - \vec{r}_-)$$

- For Hydrogen atom this gives:

$$\vec{D} = -|e|\vec{R}$$

$\vec{D} = e\vec{R}$

$(e = -1.6\times10^{-19}\,C)$

Dipole Moment Operator

- The electric dipole moment is an operator in $\mathcal{H}^{(R)}$, which means that its value depends on the state of the relative motion:

$$\vec{D} = -|e|\vec{R}$$

$$V_E = -\vec{D}\cdot\vec{E}(r_{CM}) \qquad V_E = |e|\vec{R}\cdot\vec{E}(r_{CM}) = -e\vec{R}\cdot\vec{E}$$

- Choosing the z-axis along the electric field direction gives:

$$V_E = |e|\, Z\, E(r_{CM})$$

- Expanding onto energy eigenstates gives:

$$V_E = \sum_{n=1}^{\infty}\sum_{n'=1}^{\infty}\sum_{\ell=0}^{n-1}\sum_{\ell'=0}^{n'-1}\sum_{m=-\ell}^{\ell}\sum_{m'=-\ell'}^{\ell'} |n\ell m\rangle (V_E)_{n\ell m;n'\ell'm'} \langle n'\ell'm'|$$

$$(V_E)_{n\ell m;n'\ell'm'} = d_{n\ell m;n'\ell'm'} E(r_{CM})$$

$$d_{n\ell m;n'\ell'm'} = \langle n\ell m|\, |e| Z\, |n'\ell'm'\rangle$$

Dipole-Moment Matrix Elements

$$Z_{n\ell m;n'\ell'm'} = \langle n\ell m | R\cos\Theta | n'\ell'm' \rangle$$

- Separate radial and angular Hilbert spaces:

$$d_{n\ell m;n'\ell'm'} = |e| \langle n\ell | R | n'\ell' \rangle^{(R)} \langle \ell m | \cos\Theta | \ell' m' \rangle^{(\Omega)}$$

$$\| \quad \int d\phi\, d(\cos\theta) \left[Y_\ell^m(\theta,\phi)\right]^* \cos\theta \, Y_{\ell'}^{m'}(\theta,\phi)$$

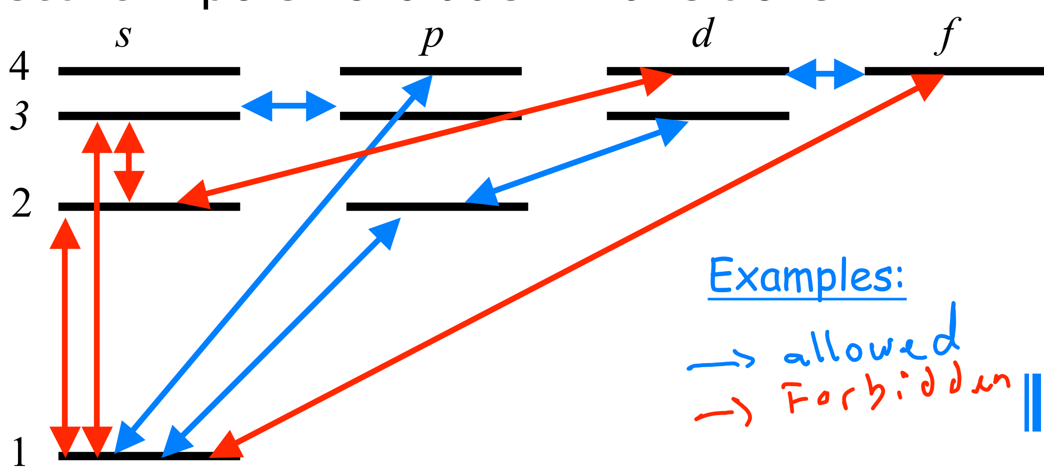
- SELECTION RULES:
  - Arfken, 3rd ed., 12.213

$$\langle \ell m | \cos\Theta | \ell' m' \rangle^{(\Omega)} = \delta_{m,m'} \left(\sqrt{\frac{(\ell+1)^2 - m^2}{4(\ell+1)^2 - 1}}\,\delta_{\ell,\ell'+1} + \sqrt{\frac{\ell^2 - m^2}{4\ell^2 - 1}}\,\delta_{\ell,\ell'-1} \right)$$

- The important thing to remember is that

$$d_{n\ell m;n'\ell'm'} \propto \delta_{m,m'}\delta_{\ell,\ell'\pm 1}$$

- Electric Dipole *Forbidden Transitions*



Examples:

→ allowed

→ Forbidden

Charged particle in a Magnetic Field

- EM fields are described by both a scalar potential, _ and vector potential, *A*

- To include such EM fields, we can make the transformation:

$$\vec{P} \rightarrow \vec{P} - q\vec{A}(\vec{R})$$

- Here *q* is the charge and *A*(*R*) is the vector potential

---

- The Hamiltonian of an electron then becomes:
  - Units of *B* are Gauss (G):

$$H = \frac{1}{2m_e}\left[\vec{P} - e\vec{A}(\vec{R})\right]^2 + e\Phi(\vec{R})$$

- This is known as the 'minimal coupling Hamiltonian'

Vector potential of a uniform B-field

- For a uniform B-field, $\vec{B}(\vec{r}) = \vec{B}_0$ we have:

$$\vec{A}(\vec{r}) = -\frac{1}{2}\vec{r} \times \vec{B}_0$$

- Proof:

$$\vec{B}(\vec{r}) = \vec{\nabla} \times \vec{A}(\vec{r})$$

$$\vec{B}(\vec{r}) = -\frac{1}{2}\vec{\nabla} \times \left(\vec{r} \times \vec{B}_0\right)$$

$$= -\frac{1}{2}\left[\vec{r}\left(\vec{\nabla} \cdot \vec{B}_0\right) - \vec{B}_0\left(\vec{\nabla} \cdot \vec{r}\right) - \left(\vec{r} \cdot \vec{\nabla}\right)\vec{B}_0 + \left(\vec{B}_0 \cdot \vec{\nabla}\right)\vec{r}\right]$$

$$= -\frac{1}{2}\left[0 - 3\vec{B}_0 - 0 + \vec{B}_0\right]$$

$$= \vec{B}_0$$

$$\left[\vec{P} + \frac{e}{2}\vec{R} \times \vec{B}_0\right]^2 = P^2 + \frac{e}{2}\left[\vec{P} \cdot \vec{R} \times \vec{B}_0 + \vec{R} \times \vec{B}_0 \cdot \vec{P}\right] + \frac{e^2}{4}\left(\vec{R} \times \vec{B}_0\right)^2$$

$$= P^2 - e\vec{L} \cdot \vec{B}_0 + \frac{e^2}{4}\left[R^2 B_0^{\,2} - \left(\vec{R} \cdot \vec{B}_0\right)^2\right]$$

An electron in a uniform B-field

- Putting this in the Hamiltonian gives:

$$H = \frac{P^2}{2m_e} - \frac{e}{2m_e}\vec{L}\cdot\vec{B}_0 + \frac{e^2}{8m_e}B_0^2 R_\perp^2 + e\Phi(\vec{R})$$

- Choosing *B* along the z-axis gives:

$$H = \frac{P^2}{2m_e} - \frac{eB_0}{2m_e}L_z + \frac{e^2 B_0^2}{8m_e}\left(X^2 + Y^2\right) + e\Phi(\vec{R})$$

$$-\frac{e}{2m_e}L_z B_0$$

"Paramagnetic term"

•Generates linear Zeeman effect

$$\frac{e^2 B_0^2}{8m_e}\left(X^2 + Y^2\right)$$

"Diamagnetic term"

•Generates quadratic Zeeman effect

Paramagnetic Term: Magnetic Dipole Interaction

- A loop of current, *I*, and area, *a*, creates a magnetic dipole:

$$\mu = I a$$

- The orbital motion of a single electron constitutes a current
  - For a circular orbit we have

$$I = -\frac{e v}{2\pi r}, \quad a = \pi r^2 \qquad I a = -\frac{e v r}{2}$$

- An electron therefore has a magnetic dipole moment associated with its orbital motion

$$-\frac{e v r}{2} = -\frac{e}{2m_e} m_e v r = -\frac{e}{2m_e} \vec{p} \times \vec{r} = \frac{e}{2m_e} \vec{r} \times \vec{p}$$

$$\vec{\mu} = \frac{e}{2m_e} \vec{L}$$

- The paramagnetic term is therefore the energy of the orbital dipole moment in the uniform field:

$$V_B = -\vec{\mu} \cdot \vec{B}_0$$

$$V_B = -\frac{eB_0}{2m_e} L_z$$

Dipole Energy scale

$$\langle n\ell m | V_B | n\ell m \rangle = -\frac{eB_0}{2m_e}\hbar m$$

- The energy shift between different *m* states is very small compared to Hydrogen level spacing

- Order of magnitude:

$$\frac{\langle V_B \rangle}{B_0} \sim \frac{e\hbar}{m_e} = 10^{-19-34+30}\,\frac{J}{T} = 10^{-23}\,\frac{J}{T}$$

- Strongest man-made B-fields ~40 T

$$\langle V_B \rangle \leq 10^{-22} J \quad << \quad |E_1| \left(2.18 \times 10^{-18} J\right)$$

Diamagnetic Term

- An electron in a uniform field will naturally undergo circular motion in the plane perpendicular to the field
  - Cyclotron motion

- Thus the *B*-field induces a current

- This leads to an *induced* magnetic moment, which must be proportional to B_0

$$\vec{\mu}_{induced} \propto \vec{B}_0$$

- The energy of this magnetic moment in the uniform *B* field therefore scales as B^2

$$E = -\vec{\mu}_{induced} \cdot \vec{B}_0 \propto B_0^2 \qquad V_{B^2} = \frac{e^2 B_0^2}{8m_e}\left(X^2 + Y^2\right)$$

- Order of magnitude:

$$\frac{\left\langle V_{B^2} \right\rangle}{B_0^2} \sim \frac{e^2 a_0^2}{8m_e} = 10^{-38-20+30}\,\frac{J}{T^2} = 10^{-28}\,\frac{J}{T^2}$$

$$\left\langle V_{B^2} \right\rangle \leq 10^{-26} J \quad << \quad \left\langle V_B \right\rangle (10^{-22} J) \quad << \quad \left| E_1 \right| (10^{-18} J)$$

  - The diamagnetic term can be neglected unless the B-field is very strong

Zeeman Effect

- The Hamiltonian of a Hydrogen atom in a uniform B-field is
  - Can neglect diamagnetic term

$$H = H_0 - \frac{eB}{2\mu} L_z \qquad H_0 \left| n\ell m \right\rangle = E_n \left| n\ell m \right\rangle$$

- Eigenstates are unchanged

$$H \left| n, \ell, m \right\rangle = E \left| n, \ell, m \right\rangle$$

- Energy eigenvalues now depend on m:

$$E_{n,m} = -\frac{\hbar^2}{2\mu a_0^2} \frac{1}{n^2} - \frac{eB}{2\mu} m$$

- The additional term is called the Zeeman shift
  - We already know that it will be no larger than 10^{-22} J~10^{-4}eV
  - E.g. 100 G field:
    - E_{Zeeman}~10^{-25} J
    - $E_{Zeeman}/E_I \sim 10^{-25+18} \sim 10^{-7}$

- To get the correct Zeeman shift, we will also need to include spin.
  - We will do this next semester using perturbation theory and the Wigner-Ekert Theorem