Lecture 31: The Hydrogen Atom 2: Dipole Moments

Phy851 Fall 2009
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

For Hydrogen atom this gives:

\[ \vec{D} = -|e|\vec{R} \]

\[ \vec{D} = e\vec{R} \]

\( e = -1.6 \times 10^{-19} \text{C} \)
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:

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

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

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

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

- Expanding onto energy eigenstates gives:

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

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

$$d_{n\ell m; n'\ell' m'} = \langle n\ell m | \vec{r} \times \vec{z} | n'\ell' m' \rangle$$
Dipole-Moment Matrix Elements

\[ Z_{n\ell m; n'\ell ' m'} = \langle n\ell m \left| R \cos \Theta \right| n'\ell ' m' \rangle \]

- Separate radial and angular Hilbert spaces:

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

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

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

- The important thing to remember is that

\[ d_{n\ell m; n'\ell ' m'} \propto \delta_{m,m'} \delta_{\ell,\ell'+1} \]

- Electric Dipole *Forbidden Transitions*

![Diagram showing allowed and forbidden transitions for different energy levels](Diagram.png)

**Examples:**
- \( \rightarrow \) allowed
- \( \rightarrow \) Forbidden
Charged particle in a Magnetic Field

- EM fields are described by both a scalar potential, \( \Phi \) and vector potential, \( A \).

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

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

- 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:

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

\[
\vec{B}(\vec{r}) = -\frac{1}{2} \vec{\nabla} \times (\vec{r} \times \vec{B}_0)
\]

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

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

\[
= \vec{B}_0
\]

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

\[
= P^2 - e\vec{L} \cdot \vec{B}_0 + \frac{e^2}{4} \left[ R^2 B_0^2 - (\vec{R} \cdot \vec{B}_0)^2 \right]
\]
An electron in a uniform B-field

• Putting this in the Hamiltonian gives:

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

• Choosing \( B \) along the z-axis gives:

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

\[-\frac{e}{2m_e} L_z B_0 \quad \text{“Paramagnetic term”} \quad \text{• Generates linear Zeeman effect} \]

\[ \frac{e^2B_0^2}{8m_e} \left( X^2 + Y^2 \right) \quad \text{“Diamagnetic term”} \quad \text{• Generates quadratic Zeeman effect} \]
Paramagnetic Term: Magnetic Dipole Interaction

- A loop of current, \( I \), and area, \( a \), creates a magnetic dipole:
  \[ \mu = Ia \]

- The orbital motion of a single electron constitutes a current
  - For a circular orbit we have
  \[
  I = -\frac{ev}{2\pi r}, \quad a = \pi r^2 \quad Ia = -\frac{evr}{2}
  \]

- An electron therefore has a magnetic dipole moment associated with its orbital motion
  \[
  -\frac{evr}{2} = -\frac{e}{2m_e} m_e v r = -\frac{e}{2m_e} \vec{p} \times \vec{r} = \frac{e}{2m_e} \vec{r} \times \vec{p}
  \]
  \[
  \vec{\mu} = \frac{e}{2m_e} \vec{L}
  \]

- 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 \( \sim 40 \) T

\[ \langle V_B \rangle \leq 10^{-22} J \ll |E_1| (2.18 \times 10^{-18} J) \]
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 $B_0$

$$\mu_{\text{induced}} \propto B_0$$

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

$$E = -\vec{\mu}_{\text{induced}} \cdot \vec{B}_0 \propto B_0^2$$

$$V_{B^2} = \frac{e^2 B_0^2}{8m_e} (X^2 + Y^2)$$

- Order of magnitude:

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

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

- 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
  \[ H = H_0 - \frac{eB}{2\mu} L_z \]
  \[ H_0 |n\ell m\rangle = E_n |n\ell m\rangle \]
- Eigenstates are unchanged
  \[ H |n, \ell, m\rangle = E |n, \ell, m\rangle \]
- 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~\( 10^{-4} \text{eV} \)
  - E.g. 100 G field:
    - \( E_{\text{Zeeman}} \sim 10^{-25} \) J
    - \( E_{\text{Zeeman}}/E_I \sim 10^{-25+18} \sim 10^{-7} \)
- 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