Lecture 20: Electromagnetic Interactions, Continued

Monday, March 02, 2020

Last time, we said that, neglecting spin, gauge invariance restricts the Hamiltonian to have the form

$$H = \frac{\left(\vec{\mathbf{p}} - \frac{e}{c}\vec{\mathbf{A}}\right)^2}{2m} + e\Phi$$

Now we want to study how atoms interact with the electromagnetic field considering this Hamiltonian. Let's assume that the wavelength of the radiation is much larger than the Bohr radius ($\lambda >> a_0$) and use the multipole expansion with static fields. In electrostatics, the electric field only depends on the scalar potential Φ, so

$$\Delta E_E \approx \int |\psi(x)|^2 e\Phi(x)\,\mathrm{d}^3x$$

since, to first order, $\Delta E \approx \langle nlm| H_I |nlm\rangle$. We can Taylor expand the perturbation as:

$$e\Phi(\vec{\mathbf{x}}, 0) = e\Phi(\vec{\mathbf{0}}, 0) + e\vec{\mathbf{x}}\vec{\partial}\Phi(\vec{\mathbf{0}}, 0) + ex_ix_j\partial_i\partial_j\Phi(\vec{\mathbf{0}}, 0) + \cdots$$

We can ignore the first term, since in the static case, this is a constant, so it will not effect the Hamiltonian (as long as gravity is not involved):

$$\Delta E_E = e\langle nlm| \vec{\mathbf{x}} |nlm\rangle \left(-\vec{\mathbf{E}}(0)\right) = \langle nlm| \vec{\mathbf{d}} \cdot \vec{\mathbf{E}} |nlm\rangle$$

where $\vec{\mathbf{d}} = -e\vec{\mathbf{x}}$. We know that both ls can't be $l = 0$, since $\vec{\mathbf{d}}$ is an $l = 1$ operator and $1 \otimes 0 = 1$, which is orthogonal to $l = 0$. The next term is

$$ex_ix_j\partial_i\partial_j\Phi = (?)_{ij}\partial_iE_j$$

x_ix_j is symmetric so it is not irreducible. We need to subtract the trace:

$$\begin{aligned}
&= \left[e\left(x_ix_j - \frac{1}{3}\delta_{ij}\vec{\mathbf{x}}^2\right) + \frac{e}{3}(\delta_{ij}\vec{\mathbf{x}}^2)\right]\partial_iE_j \\
&= Q_{ij}\partial_iE_j + \frac{e}{3}\delta_{ij}\vec{\mathbf{x}}^2\partial_iE_j
\end{aligned}$$

but the second term is $\frac{e}{3}\vec{\mathbf{x}}\vec{\partial}\cdot\vec{\mathbf{E}}(0)$ which vanishes due to Gauss' law. Therefore

$$H = \int \vec{\mathbf{d}} \cdot E + Q_{ij}\partial_iE_j$$

with $Q_{ij} = e\left(x_ix_j - \frac{1}{3}\delta_{ij}\vec{\mathbf{x}}^2\right)$ defining the quadrupole moment.

Say we wanted to evaluate a particular quadrupole moment, $\langle nlm| Q_{xx} |nlm\rangle$. First, we need to convert this into spherical coordinates with indices $-1, 0, 1$:

$$Q_{xx} = \hat{\mathbf{e}}_x^a\hat{\mathbf{e}}_x^bQ_{ab}$$

where

$$\begin{aligned}
\hat{\mathbf{e}}_1 &= -\frac{1}{\sqrt{2}}\left[\hat{\mathbf{e}}_x + \imath\hat{\mathbf{e}}_y\right] \\
\hat{\mathbf{e}}_{-1} &= \frac{1}{\sqrt{2}}\left[\hat{\mathbf{e}}_x - \imath\hat{\mathbf{e}}_y\right]
\end{aligned}$$

We can solve for $\hat{\mathbf{e}}_x = \frac{1}{\sqrt{2}}\left[-\hat{\mathbf{e}}_1 + \hat{\mathbf{e}}_{-1}\right]$. From here, we can (abuse notation to) say $\hat{\mathbf{e}}_x^1 = -\frac{1}{\sqrt{2}}$ and $\hat{\mathbf{e}}_x^{-1} = \frac{1}{\sqrt{2}}$. We can now write Q_{xx} as

$$Q_{xx} = \left[-\frac{1}{\sqrt{2}}\right]^2\left[Q_{1,1} + Q_{-1,-1} - Q_{1,-1} - Q_{-1,1}\right]$$

Each of the indices transform as $l = 1$, and the indices are the m's. Therefore, Q_{11} transforms as $\lvert 11; 11\rangle$, $Q_{1,-1}$ transforms as $\lvert 11; 1, -1\rangle$, and so on. We can therefore write

$$\langle nlm\rvert Q_{xx} \lvert nlm\rangle = \frac{1}{2} \langle nlm\rvert Q_{11} + Q_{-1,-1} - Q_{1,-1} - Q_{-1,1} \lvert nlm\rangle$$

The first two terms must have vanishing expectation values, since $m = 1 + 1 + m$ or $m = -1 - 1 + m$ don't add up. We can write $Q_{1,-1}$ as

$$\lvert 1, 1; 1, -1\rangle = \sum_{J,M} \lvert JM\rangle \langle JM\vert 1, 1; 1, -1\rangle$$

and $Q_{-1,1}$ as

$$\lvert 1, -1; 1, 1\rangle = \sum_{J,M} \lvert JM\rangle \langle JM\vert 1, -1; 1, 1\rangle$$

From here, we could derive the nonzero matrix elements. However, we don't really need to do this entire decomposition, since we know that if Q_{ij} is symmetric and traceless, it must transform as $l = 2$. Therefore the $l = 0$ matrix element must be zero, since $2 \otimes 0 = 2$ and $l = 1 \neq l = 2$ (the states are orthogonal). However, for $l = 1$, we have $2 \otimes 1 = 3 \oplus 2 \oplus 1 \oplus 0$, so there are nonzero matrix elements.

Next, let's find what the magnetic part of the energy shift is.

$$H = \frac{\left(\vec{\mathbf{p}} - \frac{e}{c}\vec{\mathbf{A}}\right)^2}{2m} \to -\frac{e}{2m}\left[\vec{\mathbf{p}} \cdot \vec{\mathbf{A}} + \vec{\mathbf{A}} \cdot \vec{\mathbf{p}}\right] + \frac{e^2}{2mc^2}\vec{\mathbf{A}}^2$$

The second term is repressed by an additional factor of $\frac{1}{c}$, so let's only consider a non-relativistic case. If we expand $\vec{\mathbf{A}}$, $\vec{\mathbf{A}}(0)$ doesn't depend on x, so it commutes with $\vec{\mathbf{p}}$:

$$H = -\frac{e}{2mc}\left[2\vec{\mathbf{p}} \cdot \vec{\mathbf{A}}(0, t) + p_i x_j \partial_j A_i + (\vec{\mathbf{x}} \cdot \vec{\partial}) A_i p_i\right]$$

The lowest order energy shift is proportional to the matrix elements

$$\langle nlm\rvert \vec{\mathbf{p}} \cdot \vec{\mathbf{A}}(0, t) \lvert nlm\rangle$$

$$\langle\vec{\mathbf{p}}\rangle = \left\langle \frac{\mathrm{d}\vec{\mathbf{x}}}{\mathrm{d}t} \right\rangle = \frac{1}{\imath\hbar} \langle E\rvert [x, H] \lvert E\rangle = \frac{1}{\imath\hbar}\left[\langle x\rangle (E - E)\right] = 0$$

so the first term in the multipole expansion vanishes.

A Short Diversion (Nugget)

$$\langle p\rvert [x, p] \lvert p\rangle = \imath\hbar \langle p\vert p\rangle = \imath\hbar$$

but

$$\langle p\rvert [x, p] \lvert p\rangle = \langle p\rvert xp - px \lvert p\rangle = \langle p\rvert x \lvert p\rangle (p - p) = 0$$

Great.

The next term in the expansion is

$$\langle nlm\rvert p_i x_j \partial_j A_i(0) + x_j \partial_j A_i(0) p_i \lvert nlm\rangle = \langle nlm\rvert p_i x_j \partial_j A_i + x_j p_i \partial_j A_i \lvert nlm\rangle$$

We can write

$$p_i x_j = x_j p_i - [p_i, x_j] = x_j p_i - \imath\hbar\delta_{ij}$$

so we can rewrite our operator as

$$2x_j p_i \partial_j A_i + \imath\hbar(\vec{\partial} \cdot \vec{\mathbf{A}})$$

When we're done, this needs to be proportional to the magnetic field, since we must be gauge invariant. We'll finish this in the next lecture.