We have the following Quantized Hamiltonian:

\[ H = H_A + H_R + H_I \]

\[ H_A = \sum_i \frac{p_i^2}{2m_i} + \sum_{i,j} g_i g_j \frac{1}{\pi E_0 |\mathbf{F}_i - \mathbf{F}_j|} \]

\[ H_R = \frac{1}{2} \left( \int dw \left( E_0 \Delta \mathbf{E}_1 \cdot \Delta \mathbf{E}_1 + \Delta \mathbf{B} \cdot \Delta \mathbf{B} \right) \right) = \sum_{\kappa \lambda} \hbar \omega_{\kappa \lambda} (\Delta \mathbf{a}^\dagger_{\kappa \lambda} \Delta \mathbf{a}_{\kappa \lambda} + \frac{1}{\hbar}) \]

\[ H_I = -\sum_i \frac{q_i}{m_i} \Delta \mathbf{p}_i \Delta \mathbf{A}(\mathbf{r}_i) + \sum_i \frac{q_i^2}{2m_i} \Delta \mathbf{A}^2(\mathbf{r}_i) \]

Our goal now is to write \( H_I \) in a more convenient form using \( \mathbf{E}_1, \mathbf{r}, \mathbf{B}, \) and where \( \Delta \mathbf{p} \) means something intuitive.

In general, the wavelength of radiation is much larger than the size of the atom

\[ \Rightarrow \text{look at multipole expansions.} \]

A similar case from classical \( E \cdot M \) is polarizable media. Remember: in a neutral bulk medium, the local charge density is given by

\[ \nabla \cdot \mathbf{P}(\mathbf{r}) \]
This was derived for classical fields by describing the microscopic charge distribution in terms of a polarization density and magnetization density. Take the sourced Maxwell eqns:

\[ \nabla \cdot \hat{E} = \frac{n_F(t)}{\varepsilon_0} \]

\[ \frac{1}{\mu_0} \nabla \times \hat{B} - \varepsilon_0 \frac{\partial \hat{E}}{\partial t} = \mathbf{h}(F, t) \]

where \( n_F(t) \) and \( \mathbf{h}(F, t) \) are microscopic charge & current densities.

We (or perhaps Jackson) wrote

\[ n(F, t) = \rho(F, t) - \nabla \cdot \hat{P}(F, t) \]

\[ \mathbf{h}(F, t) = \mathbf{J}(F, t) + \nabla \times \mathbf{M}(F, t) + \frac{\partial \hat{P}}{\partial t} \]

\( \rho(F, t) \) is the "macroscopic" or "free" charge

\( \mathbf{J}(F, t) \) " " " " current density.

\( \hat{P}(F, t) \) is the local polarization density

\( \mathbf{M}(F, t) \) " " " " magnetization density

This gives

\[ \nabla \cdot \hat{E} = \rho(F, t) - \nabla \cdot \hat{P}(F, t)/\varepsilon_0 \]

\[ \frac{1}{\mu_0} \nabla \times \hat{B} - \varepsilon_0 \frac{\partial \hat{E}}{\partial t} = \mathbf{J}(F, t) + \nabla \times \mathbf{M} + \frac{\partial \hat{P}}{\partial t} \]

or

\[ \nabla \cdot \hat{D} = \rho \]

\[ \nabla \times \hat{H} - \frac{\partial \hat{D}}{\partial t} = \mathbf{J}(F, t) \]

\( \hat{D} = \varepsilon_0 \hat{E} + \hat{P} \), \( \hat{H} = \frac{1}{\mu_0} \hat{B} + \mathbf{M} \)

For neutral systems, \( \rho = 0 \), \( \mathbf{J} = 0 \)

It turns out that the Hamiltonian can be transformed to be quantized in terms of \( \hat{D} \rightarrow \) leads to a useful form.
For charge distributions well localized around a point $\mathbf{R}$, the multipole expansion for $P_a(r)$ and $M_a(r)$ can be written approximately

$$
\sum_{i} \text{ particles in atom} \quad P_a(r) = \left( \sum_{i} q_i \mathbf{r}_i \right) \delta(r-R_a) + \left( \sum_{i=1}^{n} \frac{1}{3} q_i \left( \mathbf{r}_i \mathbf{r}_i - \frac{1}{3} r_i^2 \right) \mathbf{\nabla}_i \right) \delta(r-R_a) + \cdots
$$

$$
M_a(r) = \left( \sum_{i} \frac{1}{2} q_i \mathbf{r}_i \times \mathbf{p}_i \right) \delta(r-R_a) + \cdots
$$

Where $\sum_{i} q_i \mathbf{r}_i \equiv \mathbf{d}$ is the electric dipole moment

$$
\sum_{i} \frac{1}{2} q_i \left( \mathbf{r}_i \mathbf{r}_i - \frac{1}{3} r_i^2 \right) \equiv \mathbf{Q}
$$

is the (tensor) quadrupole moment

$$
\sum_{i} \frac{1}{2} q_i \mathbf{r}_i \times \mathbf{p}_i \equiv \mathbf{M}_L
$$

is the magnetic dipole

For bulk media, we would sum a bunch of terms like the above for each atom in the media, but we will be applying this to a single atom.

$\Rightarrow \mathbf{R}$ is the center of mass of the atom, $\mathbf{r}_i$ are the positions relative to $\mathbf{R}$

the components of $\mathbf{Q}$ are

$$
Q_{\alpha\beta} = \sum_{i} \frac{1}{2} q_i \left( r_i r_{\beta} - \delta_{\alpha\beta} r_i^2 \right)
$$

where $\alpha, \beta$ are cartesian coordinates indices.
Turning to Quantized Fields:
We saw that in the Coulomb gauge, \( \hat{E} \) was
conjugate to \( \hat{A} \) (like \( x \) and \( p \)). The following
unitary transformation

\[
\hat{U} = \exp\left[-i \frac{1}{\hbar} \int dV \, \hat{P}(r) \cdot \hat{A}(r)\right]
\]

transforms the particle and photon space such that

\[
\begin{align*}
\hat{E}' &= \hat{U} \hat{E} \hat{U}^\dagger = \hat{E} - \frac{\hat{P}}{e_0} \\
\hat{A}' &= \hat{A} \\
\hat{P}' &= \hat{P} \\
\hat{B}' &= \hat{B} \\
\hat{D}' &= e_0 \hat{E}' + \hat{P}' = \hat{U}(e_0 \hat{E} + \hat{P}) \hat{U}^\dagger = e_0 \hat{E} - \frac{\hat{P}}{e_0} \hat{E}
\end{align*}
\]

Note that \( \hat{D}' \) and \( e_0 \hat{E} \) are the same
operator (as expected because they are conjugate
to \( \hat{A} \) ) but the corresponding state space
is different \( |\psi'\rangle = \hat{U} |\psi\rangle \).

If one transforms the Hamiltonian on
pg. 0, using the \textcolor{red}{\textbf{approx.}} on pg. 2,
we get:

\[
\text{See: Photons \& Atoms}
\]
\[ \sum_i \frac{q_i}{m_i} \hat{p}_i \cdot \hat{A}(r) \rightarrow - \int dV \hat{M}(r) \cdot \hat{B}(r) = - \hat{\mu}_L \cdot \hat{B}(R) + \text{magnetic dipole} \]

\[ \frac{1}{2m_i} \frac{q_i^2}{2} \left| \hat{A}(r_i) \right|^2 \rightarrow \frac{1}{2m_i} \left( \frac{\hat{r}_i \times \hat{B}(R)}{2} \right)^2 \]

non-linear magnetic term

first part of \( H_R \)

\[ \frac{1}{2} \int dV \varepsilon_0 \left| \hat{E}_\perp \right|^2 \rightarrow \frac{1}{2} \int dV \varepsilon_0 \left| \hat{E}_\perp \right|^2 \]

\[ \frac{1}{2} \varepsilon_0 \left| \hat{E}_\perp \right|^2 = \varepsilon_0 \left| \frac{\hat{D}' - \hat{\mathcal{P}}}{\varepsilon_0} \right|^2 = \frac{\left| \hat{D}' \right|^2}{2 \varepsilon_0} - \frac{\hat{D}' \cdot \hat{\mathcal{P}}}{\varepsilon_0} + \frac{1}{2} \frac{\hat{\mathcal{P}}^2}{\varepsilon_0} \]

For convenience, use \( \hat{E} = \frac{\hat{D}'}{\varepsilon_0} \)

\[ \rightarrow \frac{1}{2} \int dV \varepsilon_0 \left| \hat{E}_\perp \right|^2 - \hat{\mathcal{D}} \cdot \hat{E}(R) - \sum_{\alpha \beta} \frac{Q_{\alpha \beta}}{\varepsilon_0} \frac{\partial \hat{E}_\alpha (R)}{\partial \beta} + \text{self energy term} \]

part of \( H_R \)

So the new Hamiltonian, to lowest orders, is

\[ H_A = \sum_i \frac{\hat{p}_i^2}{2m_i} + V_{\text{coul}} \rightarrow \text{unchanged \ (except} \hat{\mathcal{P}} \text{ means something different)} \]

\[ H_R = \sum_{\alpha \lambda} \frac{k_{\alpha \lambda}}{\hbar} (\hat{a}_{\alpha \lambda}^+ \hat{a}_{\alpha \lambda} + \frac{1}{2}) \rightarrow \text{unchanged} \]

\[ H_T = - \hat{\mathcal{D}} \cdot \hat{E}(R) - \hat{\mu}_L \cdot \hat{B}(R) - \sum_{\alpha \beta} \frac{Q_{\alpha \beta}}{\varepsilon_0} \frac{\partial \hat{E}_\alpha (R)}{\partial \beta} \]

\[ + \sum_i \frac{q_i^2}{2m_i} \left( \frac{\hat{r}_i \times \hat{B}(R)}{2} \right)^2 \]
\[ H_\| = \hat{a} \cdot \hat{E}(\vec{r}) - \hat{\mu}_L \cdot \hat{B}(\vec{r}) - \sum Q_{\alpha\beta} \frac{\partial}{\partial x_\beta} \hat{E}_\alpha(\vec{r}) \]

\[ - \hat{\mu}_S \cdot \hat{B}(\vec{r}) + \frac{e^2}{2m} \sum_i (\hat{r}_i \times \hat{B}(\vec{r}))^2 \]

where \[ \hat{a} = -e \sum_i \hat{r}_i \]

\[ Q_{\alpha\beta} = -\frac{1}{2} e \sum_i \left( r_{\alpha\beta} + \frac{\varepsilon_{\alpha\beta\gamma} r_\gamma}{3} \right) \]

\[ \hat{\mu}_L = -\frac{e}{2m} \sum_i \hat{r}_i \times \hat{p}_i = \frac{e}{2m} \hat{L} \]

\[ \hat{\mu}_S = \frac{e}{m} \hat{S} \]

Here we assume that the nucleus is so massive it is at the center of mass, and the sum is therefore only over the electrons. Also, we’ve added the intrinsic spin of the electron (derivable from Dirac eqn.).

Note also that if we have applied fields (produced from current or charge distributions outside our volume such that the fields are not free) we add a classical field to the operators,

\[ \hat{E} + \hat{E}_{ex} \]

\[ \hat{B} + \hat{B}_{ex} \]

Homework: estimate the sizes of these.

See Bill’s lecture notes regarding Einstein A and B coefficients.