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We have the following Quantized Hamiltonian

$$H = H_A + H_R + H_I$$

$$H_A = \sum_i \frac{\hat{\vec{p}}_i^{\,2}}{2m_i} + \sum_{i\neq j} \frac{q_i q_j}{8\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

$$H_R = \frac{1}{2}\int dV\left(\epsilon_0\, \hat{\vec{E}}_\perp \cdot \hat{\vec{E}}_\perp + \frac{\hat{\vec{B}}\cdot\hat{\vec{B}}}{\mu_0}\right) = \sum_{k\lambda} \hbar\omega_{k\lambda}\left(\hat{a}^\dagger_{k\lambda}\hat{a}_{k\lambda} + 1/2\right)$$

$$H_I = -\sum_i \frac{q_i}{m_i}\,\hat{\vec{p}}_i \cdot \hat{\vec{A}}(\vec{r}_i) + \sum_i \frac{q_i^2}{2m_i}\,\vec{A}^2(\vec{r}_i)$$

(note: in the Coulomb gauge, $\hat{p}\cdot A + \vec{A}\cdot\hat{p} = 2\hat{p}\cdot\vec{A}$ because $\nabla\cdot\vec{A} = 0$)

Our goal now is to write H_I ~~the~~ in a more convenient form using $\hat{\vec{E}}_\perp$, $\hat{r}$, $\hat{\vec{B}}$, and where $\vec{p}$ means something intuitive.

In general, the wavelength of radiation is much larger than the size of the atom $\Rightarrow$ look at multipole expansions.

A similar case from classical E+M is polarizable media. Reminder: in a neutral bulk medium, the local charge density is given by

$$\nabla\cdot \underline{P}(\vec{r})\,,$$ where $\underline{P}(r)$ is the polarization density.

This was derived for classical fields ~~[illegible]~~ by describing the microscopic charge distribution in terms of a polarization density and magnetization density. Take the sourced Maxwell eqns:

see Jackson E+M

$$\nabla \cdot \vec{E} = \frac{\eta(\vec{r},t)}{\epsilon_0} \qquad \frac{1}{\mu_0}\nabla \times \vec{B} - \epsilon_0 \frac{\partial \vec{E}}{\partial t} = h(\vec{r},t)$$

Where $\eta(\vec{r},t)$ and $h(\vec{r},t)$ are microscopic charge & current densities.

We (or perhaps Jackson) wrote

$$\eta(\vec{r},t) = \rho(\vec{r},t) - \nabla \cdot \vec{P}(\vec{r},t)$$

$$h(\vec{r},t) = \vec{J}(\vec{r},t) + \nabla \times \vec{M}(\vec{r},t) + \frac{\partial}{\partial t}\vec{P}(\vec{r},t)$$

$\rho(\vec{r},t)$ is the "macroscopic" or "free" charge
$\vec{J}(\vec{r},t)$ " " " " " current density.
$\vec{P}(\vec{r},t)$ is the local polarization density
$\vec{M}(\vec{r},t)$ " " " magnetization density

This gives
$$\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0}(\vec{r},t) - \nabla \cdot \vec{P}(\vec{r},t)/\epsilon_0$$
$$\frac{1}{\mu_0}\nabla \times \vec{B} - \epsilon_0 \frac{\partial \vec{E}}{\partial t} = \vec{J}(\vec{r},t) + \nabla \times \vec{M} + \frac{\partial \vec{P}}{\partial t}$$

or
$$\nabla \cdot \vec{D} = \rho \qquad \nabla \times \vec{H} - \frac{\partial \vec{D}}{\partial t} = \vec{J}(\vec{r},t)$$

$$D = \epsilon_0 \vec{E} + \vec{P}, \qquad \vec{H} = \frac{1}{\mu_0}\vec{B} + \vec{M}$$

for globally neutral systems, $\rho = 0$, $J = 0$

It turns out that the Hamiltonian can be transformed to be quantized in terms of $\vec{D}$ → leads to a useful form.

For local charge distributions well localized around a point $\vec{R}$, the multipole expansion for $\vec{P}(\vec{r})$ and $\vec{M}(\vec{r})$ can be written approximately

$\sum_i \rightarrow$ particles in atom a

$$\vec{P}_a(\vec{r}) = \left(\sum_i q_i \vec{r}_i\right)\delta(\vec{r}-\vec{R}_a) - \left(\sum_i \frac{1}{2} q_i \left(\vec{r}_i\vec{r}_i - \frac{\mathbb{1} r_i^2}{3}\right)\cdot\nabla_{\vec{r}}\right)\delta(\vec{r}-\vec{R}_a) + \cdots$$

$$\vec{M}_a(\vec{r}) = \left(\sum_i \frac{1}{2}\frac{q_i}{m_i}\,\vec{r}_i\times\vec{p}_i\right)\delta(\vec{r}-\vec{R}_a) + \cdots$$

Where $\boxed{\sum_i q_i \vec{r}_i \equiv \vec{d}}$ is the electric dipole moment

$\boxed{\sum_i \frac{1}{2} q_i \left(\vec{r}_i\vec{r}_i - \frac{\mathbb{1} r^2}{3}\right) \equiv \overleftrightarrow{Q}}$ is the (2nd rank tensor) quadrupole moment $\quad \mathbb{1} = \hat{x}\hat{x} + \hat{y}\hat{y} + \hat{z}\hat{z}$

$\boxed{\sum_i \frac{1}{2}\frac{q_i}{m_i}\,\vec{r}_i\times\vec{p}_i \equiv \vec{\mu}_L}$ 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. $\left(\sum_a \vec{P}_a\right)$

at $\vec{R}_a$ e.g. $\vec{P} = \sum_a \vec{P}_a$

$\Rightarrow$ $\vec{R}$ is the center of mass of the atom, $\vec{r}_i$ are the positions of electrons/nucleus relative to $\vec{R}$

the components of $\overleftrightarrow{Q}$ are

$$Q_{\alpha\beta} = \sum_i \frac{1}{2} q_i \left(r_\alpha r_\beta - \delta_{\alpha\beta}\frac{r^2}{3}\right)$$

where α, β are cartesian coordinates indices.

see Photons & Atoms, Cohen-Tannoudji et al.

Turning to Quantized Fields:

We saw that in the Coulomb gauge, $\hat{E}$ was conjugate to $\hat{A}$ (like $\hat{x}$ & $\hat{p}$). The following unitary transformation

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

(equivalent to a gauge transform)

transforms the particle and photon space such that

$$\hat{\vec{E}}' = \hat{U}\hat{\vec{E}}\hat{U}^{\dagger} = \hat{\vec{E}} - \hat{\vec{P}}/\epsilon_0$$

$$\hat{\vec{D}}' = \epsilon_0\vec{E}' + \underline{P}' = \hat{U}(\epsilon_0\hat{\vec{E}} + \hat{\vec{P}})\hat{U}^{\dagger} = \epsilon_0\hat{\vec{E}} - \hat{\vec{P}} + \hat{\vec{P}}$$

$$= \epsilon_0\vec{E}$$

$$\hat{\vec{p}}' = \hat{U}\hat{\vec{p}}\hat{U}^{\dagger}$$

$\hat{\vec{A}}' = \hat{\vec{A}}$, $\hat{\vec{r}}' = \hat{\vec{r}}$

$\hat{\vec{P}}' = \hat{\vec{P}}$ $\quad\hat{\vec{B}}' = \hat{\vec{B}}$

(Note that $\hat{\vec{D}}'$ and $\epsilon_0\vec{E}$ are the same operator (as expected because they are conjugate to $\vec{A}$) but the corresponding state space is different $|\psi'\rangle = \hat{U}|\psi\rangle$.)

If one transforms the Hamiltonian on pg. 0, using the ~~dipole~~ multipole approx. on pg. 2,

we get:

$$\sum_i \frac{q_i}{m_i} \hat{\vec{p}}_i \cdot \hat{\vec{A}}(\vec{r}) \xrightarrow{\text{algebra}} -\int dV\, \vec{M}(\vec{r}) \cdot \vec{B}(\vec{r}) = -\vec{\mu}_L \cdot \vec{B}(\vec{R}) + \cdots$$

magnetic dipole

$$\sum_i \frac{q_i^2}{2m_i} |\hat{\vec{A}}(\vec{r}_i)|^2 \xrightarrow{\text{algebra}} \sum_i \frac{q_i^2}{2m_i} \left(\frac{\vec{r}_i \times \vec{B}(\vec{R})}{2} \right)^2 + \cdots$$

non-linear magnetic term

$$\overbrace{\frac{1}{2}\int dV\, \epsilon_0 |\hat{\vec{E}}_\perp|^2}^{\text{first part of } H_R} \longrightarrow \frac{1}{2}\int dV\, \epsilon_0 |\hat{\vec{E}}'|^2$$

$$\frac{1}{2}\epsilon_0 |\hat{\vec{E}}'|^2 = \frac{\epsilon_0}{2}\left| \frac{\hat{\vec{D}}' - \hat{\vec{P}}}{\epsilon_0} \right|^2 = \frac{|\hat{\vec{D}}'|^2}{2\epsilon_0} - \frac{\hat{\vec{D}}' \cdot \hat{\vec{P}}}{\epsilon_0} + \frac{|\hat{\vec{P}}|^2}{2\epsilon_0}$$

For convenience, use $\hat{\vec{E}} = \dfrac{\hat{\vec{D}}'}{\epsilon_0}$

$$\longrightarrow \underbrace{\frac{1}{2}\int dV\, \epsilon_0 |\hat{\vec{E}}|^2}_{\text{part of } H_R} - \vec{d} \cdot \hat{\vec{E}}(\vec{R}) - \sum_{\alpha\beta} Q_{\alpha\beta} \frac{\partial}{\partial \beta} \hat{E}_\alpha(\vec{R}) + \cdots$$

$$+ \int \frac{dV}{2} \left| \frac{\hat{\vec{P}}}{2\epsilon_0} \right|^2$$

Self energy term that I'll ignore.

So the new Hamiltonian, to lowest orders, is

$$H_A = \sum_i \frac{\hat{\vec{p}}_i^{\,2}}{2m_i} + V_{coul} \longrightarrow \text{unchanged}$$

(except $\hat{\vec{p}}$ means something different)

$$H_R = \sum_{k\lambda} \hbar\omega_{k\lambda} \left(\hat{a}^\dagger_{k\lambda} \hat{a}_{k\lambda} + 1/2 \right) \longrightarrow \cancel{\text{unchanged}}$$

$\boxed{\text{not unchanged, but the changed part has moved to } H_I}$

$$H_I = -\vec{d} \cdot \hat{\vec{E}}(\vec{R}) - \vec{\mu}_L \cdot \hat{\vec{B}}(\vec{R}) - \sum_{\alpha\beta} Q_{\alpha\beta} \frac{\partial}{\partial \beta} \hat{E}_\alpha(\vec{R})$$

$$+ \sum_i \frac{q_i^2}{2m_i} \left(\frac{\hat{\vec{r}}_i \times \hat{\vec{B}}(\vec{R})}{2} \right)^2$$

$$\boxed{\begin{aligned} H_I = & -\hat{\vec{d}}\cdot\hat{\vec{E}}(\hat{\vec{R}}) - \hat{\vec{\mu}}_L\cdot\hat{\vec{B}}(\hat{\vec{R}}) - \sum_{\alpha\beta}\hat{Q}_{\alpha\beta}\frac{\partial}{\partial x_\beta}\hat{E}_\alpha(\hat{\vec{R}}) \\ & - \hat{\vec{\mu}}_S\cdot\hat{\vec{B}}(\hat{\vec{R}}) + \frac{e^2}{2m}\sum_i\left(\hat{\vec{r}}_i\times\hat{\vec{B}}(\hat{\vec{R}})\right)^2 \\ \text{where } & \vec{d} = -e\sum_i\hat{\vec{r}}_i \qquad Q_{\alpha\beta} = -\tfrac{1}{2}e\sum_i\left(r_\alpha r_\beta - \delta_{\alpha\beta}\frac{r^2}{3}\right) \\ & \hat{\vec{\mu}}_L = -\frac{e}{2m}\sum_i\hat{\vec{r}}_i\times\hat{\vec{p}}_i = \frac{e}{2m}\hat{\vec{L}} \qquad \hat{\vec{\mu}}_S = -\frac{e}{m}\hat{\vec{S}} \end{aligned}}$$

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,

$$\hat{\vec{E}} + \vec{E}_{ex}$$
$$\hat{\vec{B}} + \vec{B}_{ex}$$

Homework $\Rightarrow$ estimate the sizes of these.

See Bill's lecture notes regarding Einstein A + B coefficients.