CHM 502 - Classical & Quantum Light

Prof. Marissa Weichman

In all of our treatment of light-matter interactions thus far, we have considered light as a *classical* monochromatic, oscillating electromagnetic field:

$$\hat{H}'(t) = \vec{\mu} \cdot \vec{E}(t) \tag{1}$$

$$\vec{E}(t) = \vec{E} \cdot \cos(\omega t + \eta) \tag{2}$$

One can of course extend this treatment to consider atomic or molecular systems interacting with pulsed laser light:

$$\vec{E}(t) = \vec{E} \cdot \cos(\omega t + \eta) \cdot e^{-(t-t_0)^2/\Delta t^2} \tag{3}$$

or with multiple laser pulses

$$\vec{E}(t) = \vec{E}_1 \cdot \cos(\omega_1 t + \eta_1) \cdot e^{-(t-t_1)^2/\Delta t^2} + \vec{E}_2 \cdot \cos(\omega_2 t + \eta_2) \cdot e^{-(t-t_2)^2/\Delta t^2} \tag{4}$$

Regardless, all of these cases treat the field of light classically.

I want to take this lecture to briefly introduce a quantum mechanical description of light, as discrete photons populating particular optical modes. We'll use this quantum optics picture to revisit spontaneous emission, and also discuss the Jaynes-Cummings model of matter interacting with quantum light.

1 Quantum light

It will turn out that we can describe photons, as quantized states of a harmonic oscillator Hamiltonian. Let's first take a moment to recall the harmonic oscillator ladder formalism. Remember that we motivate the ladder operators by trying to factor the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 = \hbar\omega \underbrace{\left[\sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}\right]}_{\hat{a}^\dagger} \cdot \underbrace{\left[\sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}\right]}_{\hat{a}} + \frac{1}{2}\hbar\omega \tag{5}$$

$$\equiv \hbar\omega\left[\hat{a}^\dagger\hat{a} + \frac{1}{2}\right] \tag{6}$$

The trick here is that we will be able to write down a Hamiltonian for the quantum radiation field that has this same form. It will look like a sum over the individual Hamiltonians of a basis of harmonic oscillators:

$$\hat{H}_{\text{rad}} = \sum_{\vec{k},\lambda} \hbar\omega_{\vec{k},\lambda}\left[\hat{a}^\dagger_{\vec{k},\lambda}\hat{a}_{\vec{k},\lambda} + \frac{1}{2}\right] \tag{7}$$

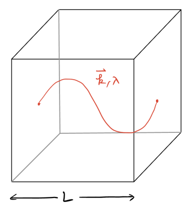
Let's break down the components of this expression:

- We are working in a basis of radiation "modes" here that are described by wavevector $\vec{k}$ and polarization state λ. The way to think about these modes, is that we define a cubic region of space with sides of length L, and volume $V = L^3$. The wavevector $\vec{k}$ is discretized such that:

$$\vec{k} = [k_x, k_y, k_z] = \left[\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L}\right] \tag{8}$$

$$n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots \tag{9}$$

  Meanwhile, we take the polarization state label $\lambda = 1, 2$, since the polarization vector must be perpendicular to $\vec{k}$, so for a given $\vec{k}$, the space of polarization states is spanned by a basis of just two orthogonal polarizations.



- $\hat{a}^\dagger_{\vec{k},\lambda}$ and $\hat{a}_{\vec{k},\lambda}$ are the creation and annihilation operators, respectively, for a photon with wavevector $\vec{k}$ and polarization state λ:

$$\hat{a}^\dagger_{\vec{k},\lambda} |n_{\vec{k},\lambda}\rangle = (n_{\vec{k},\lambda} + 1)^{1/2} |n_{\vec{k},\lambda} + 1\rangle \tag{10}$$

$$\hat{a}_{\vec{k},\lambda} |n_{\vec{k},\lambda}\rangle = n^{1/2}_{\vec{k},\lambda} |n_{\vec{k},\lambda} - 1\rangle \tag{11}$$

$$\hat{a}^\dagger_{\vec{k},\lambda}\hat{a}_{\vec{k},\lambda} |n_{\vec{k},\lambda}\rangle = n_{\vec{k},\lambda} |n_{\vec{k},\lambda}\rangle \tag{12}$$

  where we can think of $\hat{a}^\dagger_{\vec{k},\lambda}\hat{a}_{\vec{k},\lambda}$ as the photon occupation number operator for the $\vec{k}, \lambda$ mode.

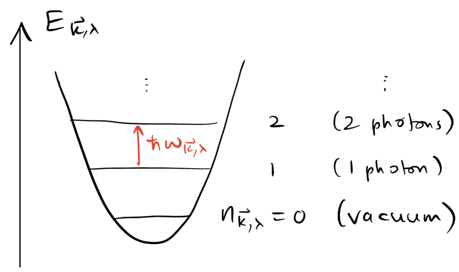
- We label the quantum states of the radiation field by the photon occupation number of all modes. These are also known as Fock states. We take each of these photon modes to be independent of one another:

$$|n_{k_1,\lambda_1}, n_{k_2,\lambda_2}, \ldots, n_{k_i,\lambda_i}, \ldots\rangle = |n_{k_1,\lambda_1}\rangle |n_{k_2,\lambda_2}\rangle \ldots |n_{k_i,\lambda_i}\rangle \ldots \tag{13}$$

It should make a certain intuitive sense that photons can be described as harmonic oscillator levels, since we know that the harmonic oscillator has evenly spaced energy levels separated by $\hbar\omega$. Similarly, the addition of each photon of a given $\vec{k}, \lambda$ will add a constant energy to the system, $\hbar\omega_{k,\lambda}$.

Aside: We've just stated that Eqn. 7 is the Hamiltonian for quantized light without much motivation. The connection to the harmonic oscillator Hamiltonian can be motivated starting from Maxwell's equations, but it takes a bit of time to work this out. There are many textbooks that cover this topic: see Cohen-Tannoudji's "Photons and Atoms: Introduction to Quantum Electrodynamics," Loudon's "The Quantum Theory of Light," or Keeling's notes on "Light-Matter Interactions and Quantum Optics."

Here, we'll just take a moment to try to motivate this connection at a very high level.



Classically, the total energy of the electromagnetic field radiation field in our volume V is given by

$$E_{rad} = \frac{1}{2} \int_{cav} dV \left[\epsilon_0 |\vec{E}(\vec{r},t)|^2 + \frac{1}{\mu_0} |\vec{B}(\vec{r},t)|^2 \right] \tag{14}$$

This expression for energy is a sum of the squares of the electric and magnetic fields, just as the harmonic oscillator Hamiltonian is a sum of squares of position and momentum. Position and momentum have a special relationship as conjugate variables, which gives them a certain commutation relation and makes them convenient to work with within the ladder operator formalism. It turns out that the electric field and magnetic field have a similar relationship as conjugate variables. The fact that the radiation Hamiltonian is written as a sum of their squares is what enables us to draw a connection to harmonic oscillator Hamiltonian.

Again, to work with this, you expand the electromagnetic fields in terms of basis waves labeled by $\vec{k}, \lambda$. In the end, you can write the expression for the electric field operator in terms of raising and lowering operators (in the Coulomb gauge) as:

$$\hat{E}(\vec{r}) = i \sum_{k,\lambda} \hat{e}_{k,\lambda} \sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}} \left[\hat{a}_{k,\lambda} e^{i\vec{k}\cdot\vec{r}} - \hat{a}^\dagger_{k,\lambda} e^{-i\vec{k}\cdot\vec{r}} \right] \tag{15}$$

It also can be useful to talk about the vector potential operator $\hat{A}$, which is closely related to the electric field, and can be written in terms of the ladder operators as:

$$\hat{A}(\vec{r}) = \sum_{k,\lambda} \frac{\hat{e}_{k,\lambda}}{\omega_{k,\lambda}} \sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}} \left[\hat{a}_{k,\lambda} e^{i\vec{k}\cdot\vec{r}} + \hat{a}^\dagger_{k,\lambda} e^{-i\vec{k}\cdot\vec{r}} \right] \tag{16}$$

where $\hat{e}_{k,\lambda}$ is the polarization unit vector for the field.

2 Quantum light interacting with matter

We've talked now about the Hamiltonian for the quantum field of radiation itself. How do we treat the coupling of a quantum electromagnetic field to matter? There are several commonly used ways to write down the light-matter interaction Hamiltonian, in various gauges and with various approximations.

The total energy of the system can be expressed as:

$$\hat{H} = \hat{H}_{\text{mol}} + \hat{H}_{\text{rad}} + \hat{H}_{\text{int}} \tag{17}$$

where $\hat{H}_{\text{mol}}$ is the molecular Hamiltonian in the absence of the field. We also have already written down that the radiation Hamiltonian is:

$$\hat{H}_{\text{rad}} = \sum_{\vec{k},\lambda} \hbar\omega_{\vec{k},\lambda} \left[\hat{a}^{\dagger}_{\vec{k},\lambda} \hat{a}_{\vec{k},\lambda} + \frac{1}{2} \right] \tag{18}$$

And now we take the light-matter interaction term to be that of the minimal coupling quantum electrodynamics (QED) Hamiltonian here, though we won't derive it here:

$$\begin{aligned} \hat{H}_{\text{int}} &= -\sum_i \frac{e_i}{m_i} \hat{p}_i \cdot \hat{A}(\vec{r}_i) && (19) \\ &= -\sum_i \sum_{\vec{k},\lambda} \frac{e_i}{m_i} \hat{p}_i \cdot \left[\frac{\hat{e}_{k,\lambda}}{\omega_{k,\lambda}} \sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}} \left[\hat{a}_{k,\lambda} \cancel{e^{i\vec{k}\cdot\vec{r}}} + \hat{a}^{\dagger}_{k,\lambda} \cancel{e^{-i\vec{k}\cdot\vec{r}}} \right] \right] && (20) \end{aligned}$$

where i is a sum over all particles (nuclei and electrons) in the molecule, e_i, m_i, and $\hat{p}_i$ are the charge, mass, and momentum of the n^{th} particle. $\hat{A}(\vec{r}_i)$ is the vector potential at its spatial location, $\vec{r}_i$, and we've swapped in its expression from Eqn. 16. We will take the *long-wavelength approximation* and treat the field as spatially uniform on the length scale of a single molecule, dropping the $e^{\pm i\vec{k}\cdot\vec{r}}$ terms.

As we did in TDPT, we'll use the eigenfunctions and eigenenergies of the uncoupled systems as a reference, and look at how $\hat{H}_{\text{int}}$ drives transitions between the original eigenstates. For simplicity, we'll consider interactions with just one mode of radiation, $\vec{k}, \lambda$, and label the quantum states of this total system as:

$$\begin{aligned} |\Psi\rangle &= |\psi_{\text{mol}}\rangle \, |\psi_{\text{rad}}\rangle && (21) \\ &\equiv |\alpha\rangle \, |n_{k,\lambda}\rangle && (22) \end{aligned}$$

where α is a quantum number that labels the molecular state, and $n_{k,\lambda}$ is the photon occupation quantum number.

The energy of these eigenstates is given by

$$E = E_{\text{mol}} + \hbar\omega_{k,\lambda} n_{k,\lambda} \tag{23}$$

2.1 Absorption and emission of light

In a first example, let's consider how we can drive transitions with quantum light within Fermi's Golden Rule:

$$\Gamma_{f\leftarrow i} \propto \left| \langle f|\hat{H}_{\text{int}}|i\rangle \right|^2 \tag{24}$$

So let's evaluate the $\langle f|\hat{H}_{\text{int}}|i\rangle$ matrix element for a transition between states $|\alpha\rangle \, |n\rangle$ and $|\alpha'\rangle \, |n'\rangle$:

$$\langle\alpha'| \langle n'| \, \hat{H}_{\text{int}} \, |\alpha\rangle \, |n\rangle = -\sum_i \frac{e_i}{m_i \omega_{k,\lambda}} \sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}} \; \langle\alpha'|\hat{p}_i \cdot \hat{e}_{k,\lambda}|\alpha\rangle \; \langle n'|\hat{a}_{k,\lambda} + \hat{a}^{\dagger}_{k,\lambda}|n\rangle \tag{25}$$

Let's consider the two inner products in this expression separately. The final radiation term is straightforward to evaluate using what we know of ladder operators:

$$\langle n'|\hat{a}_{k,\lambda} + \hat{a}^{\dagger}_{k,\lambda}|n\rangle = \sqrt{n}\delta_{n',n-1} + \sqrt{n+1}\delta_{n',n+1} \tag{26}$$

The light-matter interaction term $\langle \alpha'|\hat{p}_i \cdot \hat{e}_{k,\lambda}|\alpha\rangle$ is more subtle to evaluate, but it turns out we can manipulate it to look like the $\vec{\mu} \cdot E$ terms we are more familiar with. Consider first the following commutator of the position of particle i with the total molecular Hamiltonian:

$$[\hat{H}_{\text{mol}}, \hat{r}_i] = \left[\sum_i \frac{\hat{p}_i^2}{2m_i} + V(r_1, r_2, \dots), \hat{r}_i\right] \tag{27}$$

$\hat{r}_i$ should commute with all other $\hat{r}_j$ and with $\hat{p}_{j\neq i}$. Therefore:

$$[\hat{H}_{\text{mol}}, \hat{r}_i] = \left[\frac{\hat{p}_i^2}{2m_i}, \hat{r}_i\right] \tag{28}$$

$$= \frac{\hat{p}_i}{2m_i}[\hat{p}_i, \hat{r}_i] + [\hat{p}_i, \hat{r}_i]\frac{\hat{p}_i}{2m_i} \tag{29}$$

$$= \frac{\hat{p}_i}{2m_i} \cdot -(i\hbar) + (-i\hbar) \cdot \frac{\hat{p}_i}{2m_i} = -\frac{i\hbar}{m_i}\hat{p}_i \tag{30}$$

$$\rightarrow \hat{p}_i = \frac{im_i}{\hbar}[\hat{H}_{\text{mol}}, \hat{r}_i] \tag{31}$$

We can now return to our light-matter interaction term and evaluate the following:

$$-\sum_i \frac{e_i}{m_i}\langle \alpha'|\hat{p}_i \cdot \hat{e}_{k,\lambda}|\alpha\rangle = -\sum_i \frac{e_i}{m_i} \cdot \frac{im_i}{\hbar}\langle \alpha'|\,[\hat{H}_{\text{mol}}, \hat{r}_i] \cdot \hat{e}_{k,\lambda}\,|\alpha\rangle \tag{32}$$

$$= \sum_i \frac{e_i}{i\hbar}\left[\langle \alpha'|\,\hat{H}_{\text{mol}} \cdot \hat{r}_i \cdot \hat{e}_{k,\lambda}\,|\alpha\rangle - \langle \alpha'|\,\hat{r}_i \cdot \hat{e}_{k,\lambda} \cdot \hat{H}_{\text{mol}}\,|\alpha\rangle\right] \tag{33}$$

$$= \sum_i \frac{e_i}{i\hbar}\left[E_{\alpha'}\langle \alpha'|\,\hat{r}_i \cdot \hat{e}_{k,\lambda}\,|\alpha\rangle - E_\alpha\langle \alpha'|\,\hat{r}_i \cdot \hat{e}_{k,\lambda}\,|\alpha\rangle\right] \tag{34}$$

$$= \frac{(E_{\alpha'} - E_\alpha)}{i\hbar}\langle \alpha'|\sum_i e_i\hat{r}_i \cdot \hat{e}_{k,\lambda}\,|\alpha\rangle \tag{35}$$

$$= \frac{(E_{\alpha'} - E_\alpha)}{i\hbar}\langle \alpha'|\,\hat{\mu} \cdot \hat{e}_{k,\lambda}\,|\alpha\rangle \tag{36}$$

$$\equiv \frac{(E_{\alpha'} - E_\alpha)}{i\hbar}\hat{\mu}_{\alpha'\alpha} \tag{37}$$

And just like that we've recovered our usual transition dipole matrix element. Returning to Eqn. 25, we can now write:

$$\langle \alpha'|\,\langle n'|\,\hat{H}_{\text{int}}\,|\alpha\rangle\,|n\rangle = \frac{(E_{\alpha'} - E_\alpha)}{i\hbar\omega_{k,\lambda}}\sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}}\hat{\mu}_{\alpha'\alpha}\left[\sqrt{n}\,\delta_{n',n-1} + \sqrt{n+1}\,\delta_{n',n+1}\right] \tag{38}$$

We can first consider the case of resonant absorption of one photon, taking $n' = n - 1$ and $\hbar\omega_{k,\lambda} = E_{\alpha'} - E_\alpha$. Under these conditions we find

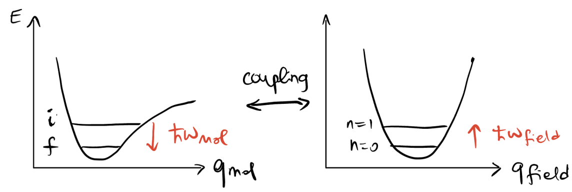
$$\left|\,\langle \alpha'|\,\langle n'|\,\hat{H}_{\text{int}}\,|\alpha\rangle\,|n\rangle\,\right|^2 \propto n \cdot \left|\hat{\mu}_{\alpha'\alpha} \cdot \sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}}\hat{e}_{k,\lambda}\right|^2 \tag{39}$$

This rate is therefore linear in the quanta of photons, n in the relevant mode.

We can also look at the emission rate of one photon, taking $n' = n + 1$ to account for the creation of a new photon particle, finding:

$$\left| \langle \alpha' | \langle n' | \hat{H}_{\text{int}} | \alpha \rangle | n \rangle \right|^2 \propto (n+1) \cdot \left| \hat{\mu}_{\alpha'\alpha} \cdot \sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}} \hat{e}_{k,\lambda} \right|^2 \tag{40}$$

This looks much the same as the absorption rate, however note that even when the original state has *no photons present*, $n = 0$, there is still a rate of photon emission. This is the spontaneous emission rate. We can interpret the term $\sqrt{\frac{\hbar\omega_{k,\lambda}}{2\epsilon_0 V}}$ as the intensity of the electric field of this "vacuum" state of the quantum field, which is still able to couple to our molecule even with no photons present.



2.2 The Jaynes-Cummings model

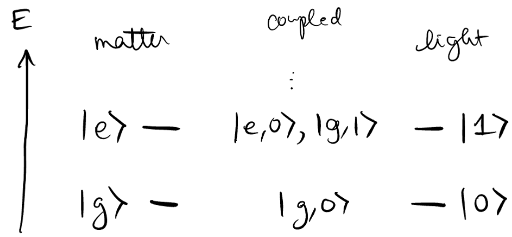
So far we've made the assumption that interactions with the quantum field of light perturb the populations of eigenstates of the bare molecular and radiation Hamiltonians. We can also consider what happens when light-matter interactions are strong enough that they significantly change the eigenstates and eigenenergies of the coupled system. Let's briefly discuss the Jaynes-Cummings model, a very simple model system describing the coupling of a two-level system to a single $\vec{k}, \lambda$ mode of the quantized radiation field Consider a two-level molecular system with states $|g\rangle, |e\rangle$, and two Fock states of the quantized radiation field, $|0\rangle$ and $|1\rangle$. We can combine these ket labels to describe the coupled system:

$$\text{0 excitations} \qquad |g\rangle |0\rangle \tag{41}$$
$$\text{1 excitation} \qquad |g\rangle |1\rangle, \; |e\rangle |0\rangle \tag{42}$$
$$\text{2 excitations} \qquad |e\rangle |1\rangle, \; |g\rangle |2\rangle \tag{43}$$
$$\text{etc.} \tag{44}$$

Here, we are going to take the near-resonant case where the photon energy $\hbar\omega_{\text{rad}}$ is close to the energy gap of the two level-system $\hbar [\omega_e - \omega_g] \equiv \hbar\omega_{eg}$. In this case, the manifold of 1-excitation states, $|g, 1\rangle$ and $|e, 0\rangle$ become near-degenerate.

The Hamiltonian for this system is easy to write down:

$$\hat{H}_{\text{JC}} = \hat{H}_{\text{mol}} + \hat{H}_{\text{rad}} + \hat{H}' \tag{45}$$
$$= \hbar\omega_g |g\rangle \langle g| + \hbar\omega_e |e\rangle \langle e| + \hbar\omega_{\text{rad}} \left[\hat{a}^\dagger \hat{a} + \frac{1}{2} \right] + \hat{H}' \tag{46}$$
$$= \begin{bmatrix} \hbar\omega_g + \hbar\omega_{\text{rad}} & 0 \\ 0 & \hbar\omega_e \end{bmatrix} + \hat{H}' \tag{47}$$



Where in the last step we have written out the Hamiltonian in just the basis of 1-excitation states, $|g,1\rangle$ and $|e,0\rangle$

The light-matter coupling perturbation $\hat{H}'$ is going to add off-diagonal terms and mix these states together. The strength of this coupling is often labeled g, which comes from the usual interaction of the molecular transition dipole with the field:

$$\langle g,1|\,\hat{H}'\,|e,0\rangle = \langle e,0|\,\hat{H}'\,|g,1\rangle = \hbar g \tag{48}$$

$$\hbar g = \vec{\mu}_{eg}\cdot\vec{E} = \vec{\mu}_{eg}\cdot\hat{e}\cdot\sqrt{\frac{\hbar\omega_{\rm rad}}{2\epsilon_0 V}} \tag{49}$$

where $\hat{e}$ is the unit vector describing the polarization of the field, while $\sqrt{\frac{\hbar\omega_{\rm rad}}{2\epsilon_0 V}}$ is the vacuum field strength, pulled more or less exactly from Eqn. 38.

Aside: The close observer will note that this perturbation should actually be time-dependent and oscillate at the radiation mode frequency. A full derivation uses the rotating wave approximation to get rid of this time-dependence. See the nice review paper on this topic by Törmä and Barnes if you are curious how this is done.

In any event, $\hat{H}'$ is usually written as:

$$\hat{H}' = \hbar g\left[\hat{\sigma}^\dagger\hat{a} + \hat{\sigma}\hat{a}^\dagger\right] \tag{50}$$

$$\hat{\sigma}^\dagger|g\rangle = |e\rangle; \qquad \hat{a}^\dagger|0\rangle = |1\rangle \tag{51}$$

$$\hat{\sigma}|e\rangle = |g\rangle; \qquad \hat{a}|1\rangle = |0\rangle \tag{52}$$

where we use our photon ladder operators again, while transitions from ground to excited state and vice versa are provided by the matrices

$$\sigma^\dagger = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}; \qquad \sigma = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \tag{53}$$

And so, finally, one can write

$$\hat{H}_{\rm JC} = \begin{bmatrix} \hbar\omega_g + \hbar\omega_{\rm rad} & \hbar g \\ \hbar g & \hbar\omega_e \end{bmatrix} \tag{54}$$

One can diagonalize this system to find its new eigenvectors and energy eigenvalues, exactly the same as we did for statically perturbed two-level systems:

$$E_\pm = \frac{1}{2}\left[\hbar\omega_g + \hbar\omega_e\right] + \hbar\omega_{\text{rad}} \pm \frac{1}{2}\sqrt{\left[\Delta E - \hbar\omega_{\text{rad}}\right]^2 + \Omega^2} \tag{55}$$

$$\Delta E \equiv \hbar\omega_e - \hbar\omega_g \tag{56}$$

$$\Omega = 2\hbar g \tag{57}$$

The splitting between these states is given by $\sqrt{\left[\Delta E - \hbar\omega_{\text{rad}}\right]^2 + \Omega^2}$, which is simply equal to Ω when the light-matter detuning is zero.

The new eigenvectors of the system are:

$$|+\rangle = \cos\Theta\,|e,0\rangle + \sin\Theta\,|g,1\rangle \tag{58}$$

$$|-\rangle = -\sin\Theta\,|e,0\rangle + \cos\Theta\,|g,1\rangle \tag{59}$$

$$\Theta \equiv \frac{1}{2}\tan^{-1}\left[\frac{2\hbar g}{\hbar\omega_{\text{rad}} - \Delta E}\right] \tag{60}$$

where Θ is the mixing angle. Again, when when the light-matter detuning is zero, the situation simplifies, and $\sin\Theta = \cos\Theta = 1/\sqrt{2}$. These new, mixed light-matter states are often referred to as "polaritons" when the system is on resonance: