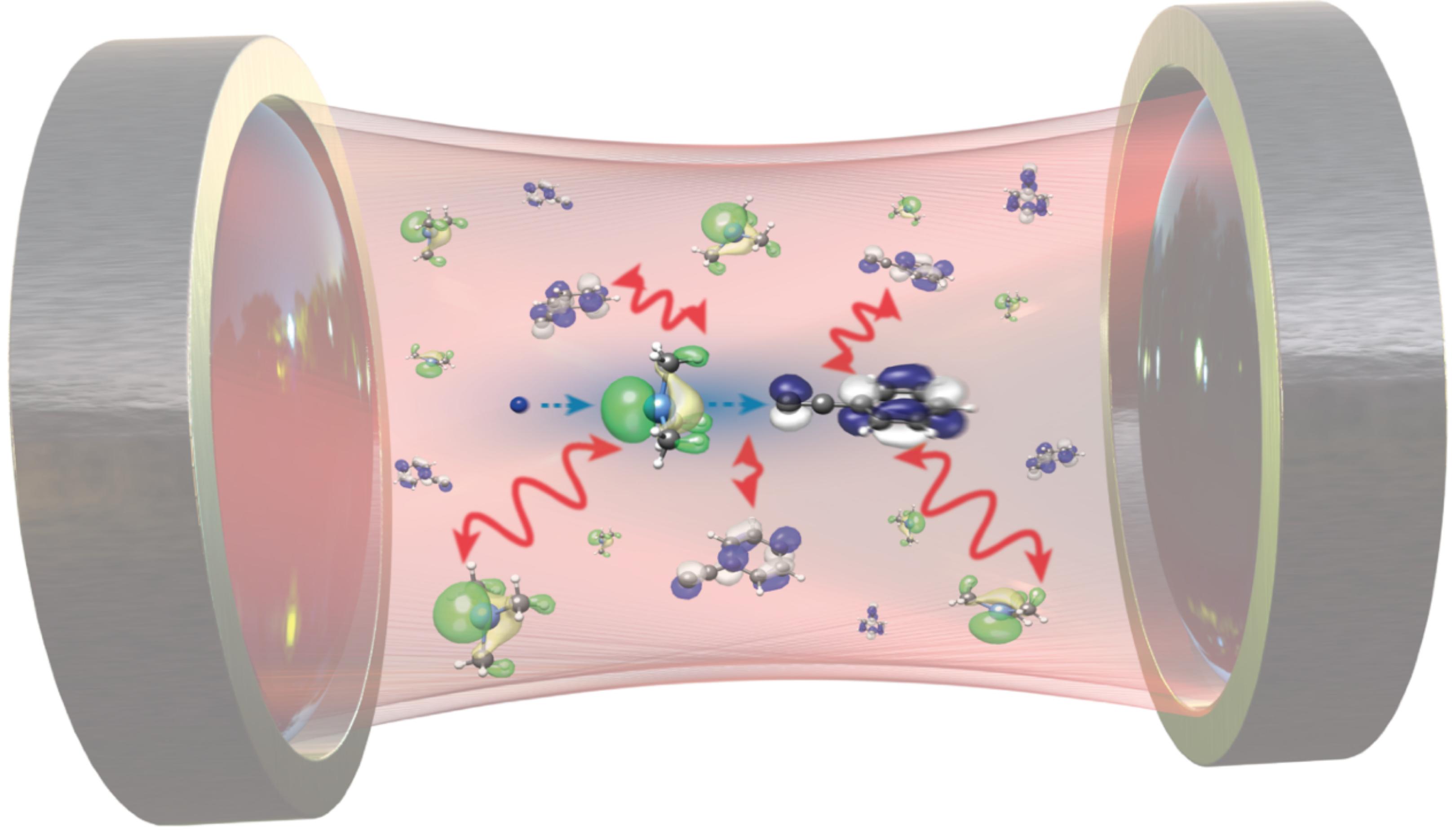
Dominik Sidler, January 2025

Polaritonic / QED Chemistry

Lecture 2: Quantum Optics



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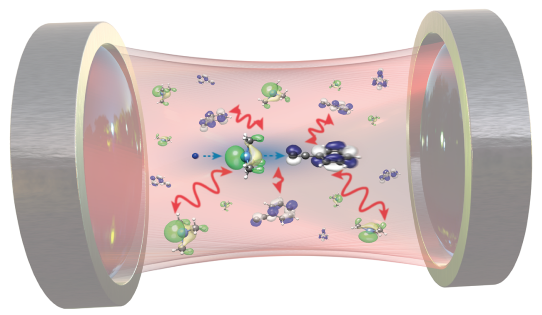
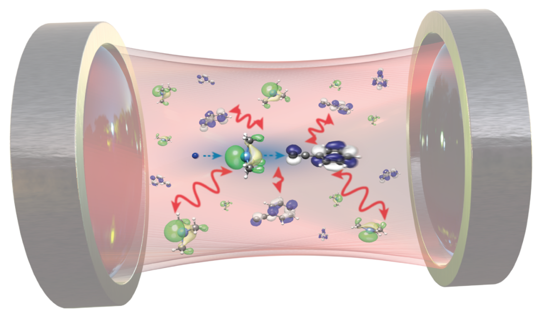
Lecture Outline



1. Repeat quantum mechanics: Notation and important concepts with toy examples.
2. Introduce Jaynes-Cummings model that provides simplest, analytically solvable model for strong (quantized) light-matter interaction.
3. Discuss model extensions numerically (Rabi model) and analytically (Tavis-Cummings model).
4. Understand concept of „collective“ strong coupling.

Quantum Mechanics Repetition



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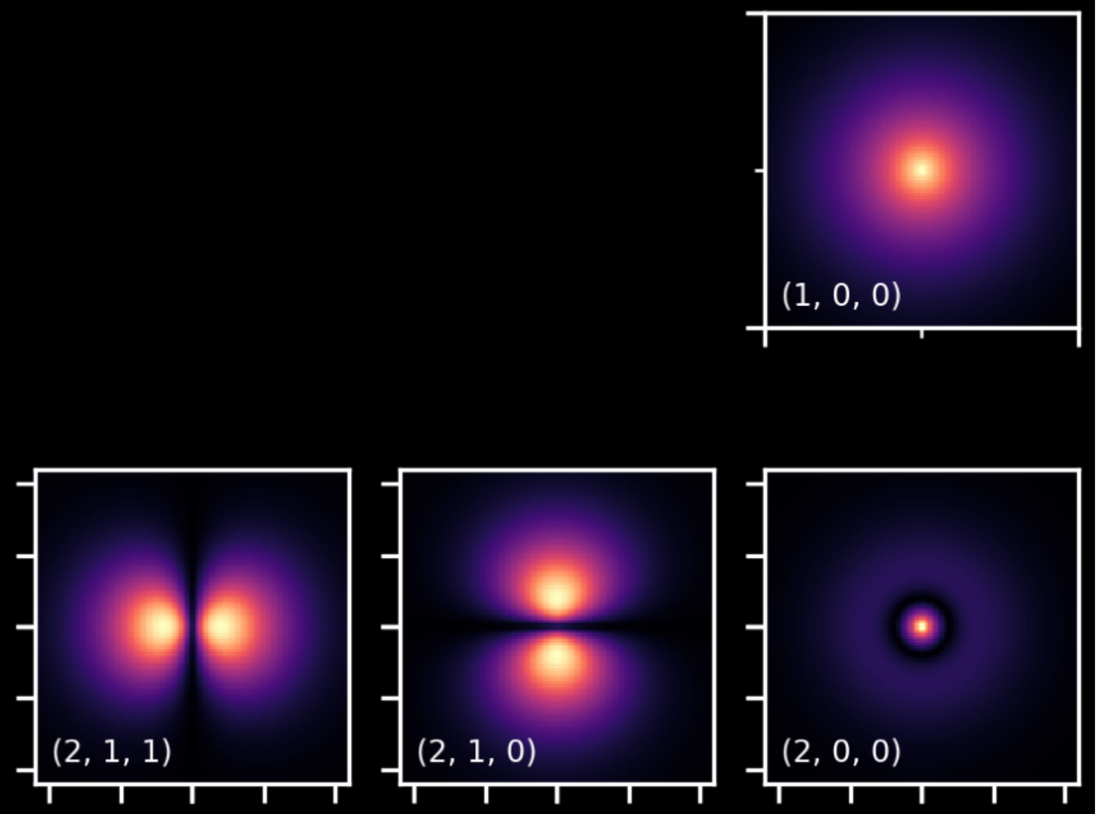
Hydrogen Wave Function

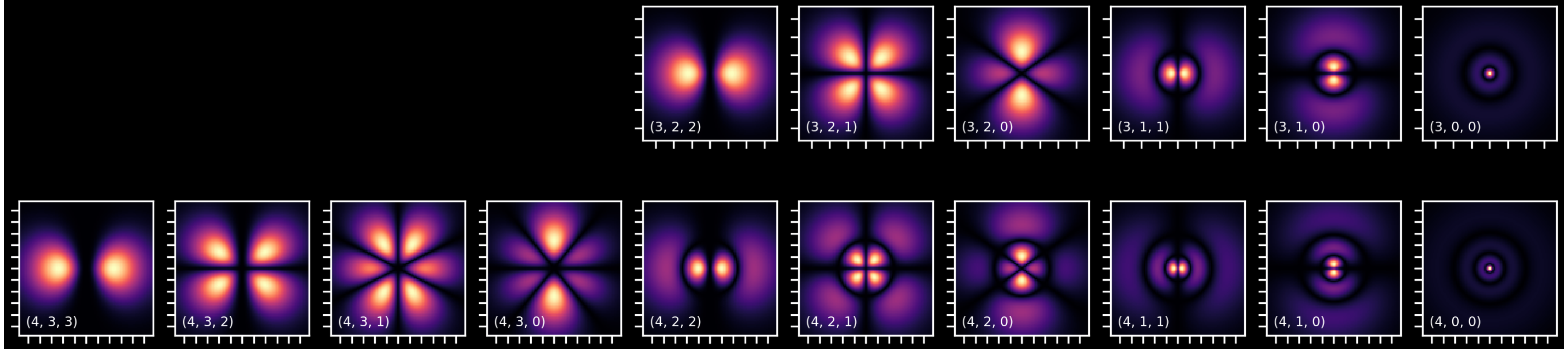
Probability Density

$$\psi_{nlm}(r,\theta,\phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}}\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1} \cdot Y_l^m(\theta,\phi)$$

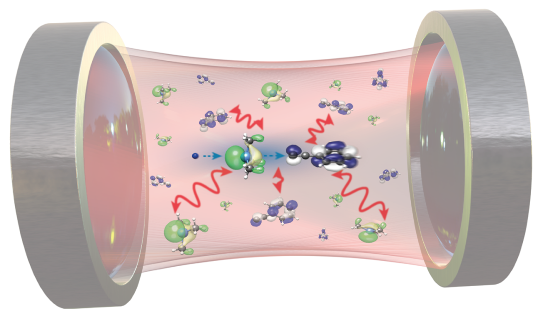


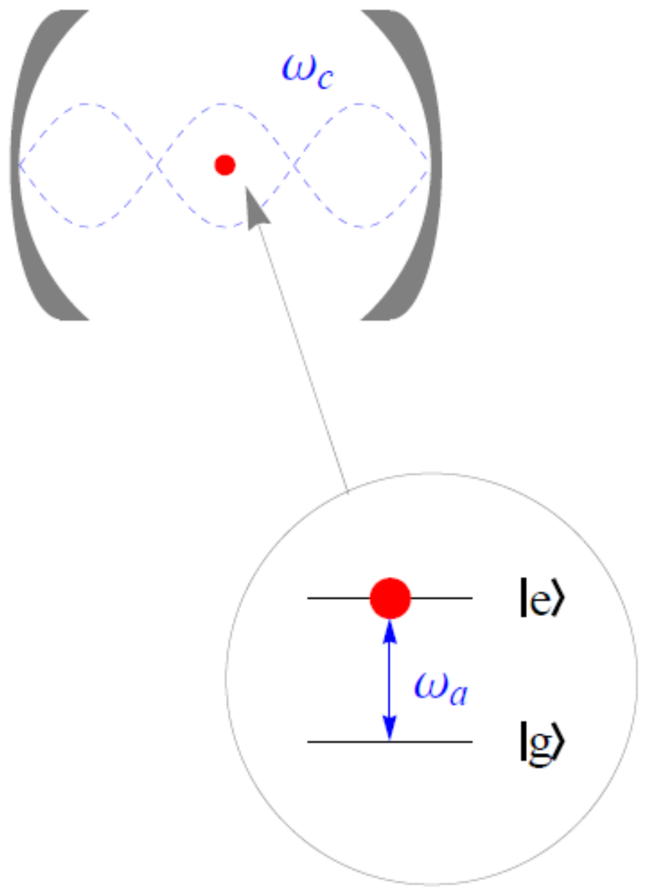
NOTE:

1. The distance between two major ticks in the plot is $5\,a_0$.
2. The numbers in the brace are the three quantum numbers $(n,\, l,\, m)$.



Jaynes-Cummings (JC) model





Strong Coupling - Vacuum Rabi Oscillations

$$\hat{H} = \hat{H}_{\text{field}} + \hat{H}_{\text{atom}} + \hat{H}_{\text{int}}$$

$$\hat{H}_{\text{field}} = \hbar\omega_c \hat{a}^\dagger \hat{a}$$ Angular (photon) mode frequency ω_c

$$\hat{H}_{\text{atom}} = \hbar\omega_a \frac{\hat{\sigma}_z}{2}$$ $\hat{\sigma}_z = |e\rangle\langle e| - |g\rangle\langle g|$ matter excitation frequency ω_a

$$\hat{H}_{\text{int}} = \frac{\hbar\Omega}{2}\hat{E}\hat{S}.$$ $\hat{E} = E_{\text{ZPF}}\left(\hat{a} + \hat{a}^\dagger\right)$

Polarization Operator $\hat{S} = \hat{\sigma}_+ + \hat{\sigma}_-,$

raising / lowering operator of **2-level matter representation** $\hat{\sigma}_+ = |e\rangle\langle g|,\ \hat{\sigma}_- = |g\rangle\langle e|,$

Schrödinger picture: $H_{\text{S}} = H_{0,\text{S}} + H_{1,\text{S}}$ Interaction picture: $H_{0,\text{I}}(t) = \mathrm{e}^{\mathrm{i}H_{0,\text{S}}t/\hbar} H_{0,\text{S}} \mathrm{e}^{-\mathrm{i}H_{0,\text{S}}t/\hbar} = H_{0,\text{S}}$

$$H_{1,\text{I}}(t) = \mathrm{e}^{\mathrm{i}H_{0,\text{S}}t/\hbar} H_{1,\text{S}} \mathrm{e}^{-\mathrm{i}H_{0,\text{S}}t/\hbar}$$

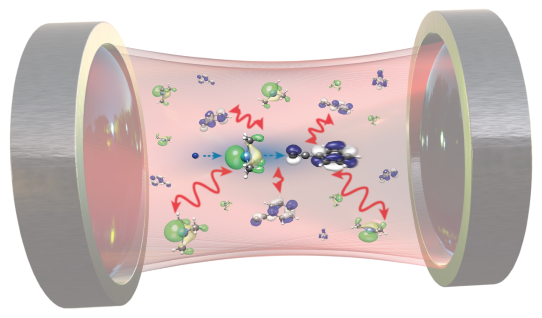
$$\hat{H}_0 = \hat{H}_{\text{field}} + \hat{H}_{\text{atom}}$$

$$\hat{H}_{\text{int}}(t) = \frac{\hbar\Omega}{2}\left(\cancel{\hat{a}\hat{\sigma}_- e^{-i(\omega_c+\omega_a)t}} + \cancel{\hat{a}^\dagger\hat{\sigma}_+ e^{i(\omega_c+\omega_a)t}} + \hat{a}\hat{\sigma}_+ e^{i(-\omega_c+\omega_a)t} + \hat{a}^\dagger\hat{\sigma}_- e^{-i(-\omega_c+\omega_a)t}\right)$$

Rotating wave approximation (RWA): Discard quickly oscillating states that couple energetically far separated state (mix only little for moderate **light-matter coupling strength Ω**)

Schrödinger picture + RWA (**Jaynes-Cummings model**) $\boxed{\hat{H}_{\text{JC}} = \hbar\omega_c \hat{a}^\dagger \hat{a} + \hbar\omega_a \frac{\hat{\sigma}_z}{2} + \frac{\hbar\Omega}{2}\left(\hat{a}\hat{\sigma}_+ + \hat{a}^\dagger\hat{\sigma}_-\right)}$

Solution of JC model



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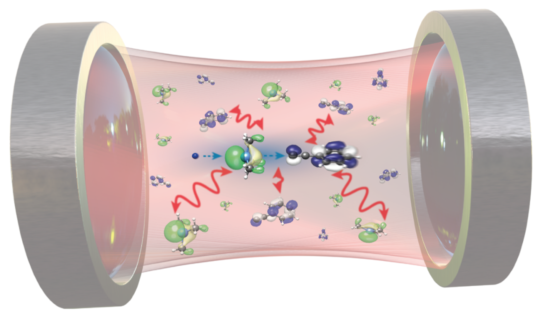
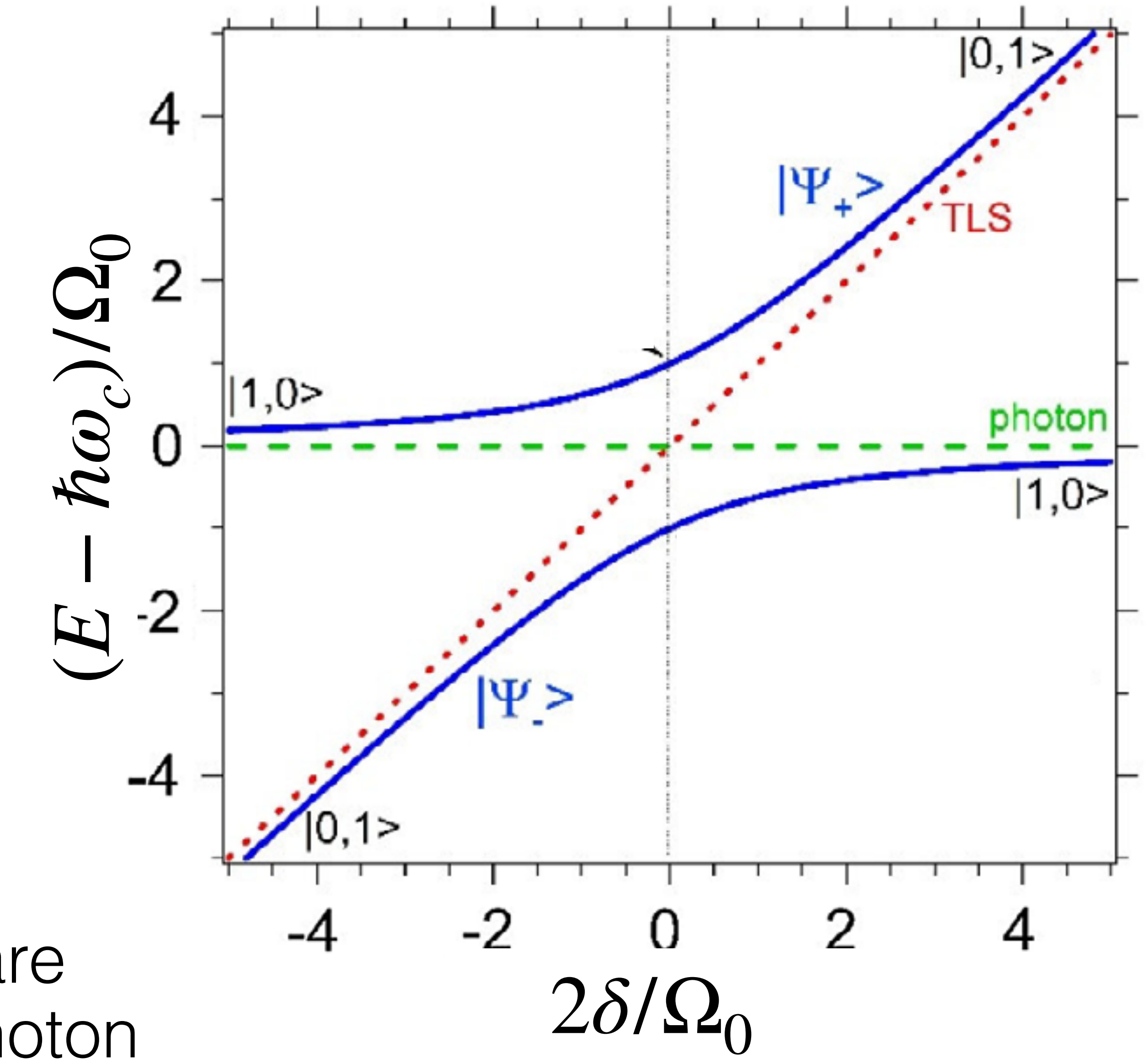
$$\hat{H}_{\mathrm{JC}} = \hbar\omega_c \hat{a}^\dagger \hat{a} + \hbar\omega_a \frac{\hat{\sigma}_z}{2} + \frac{\hbar\Omega}{2}\left(\hat{a}\hat{\sigma}_+ + \hat{a}^\dagger \hat{\sigma}_-\right)$$

JC Summary / Properties



$$\hat{H}_{\mathrm{JC}} = \hbar\omega_c \hat{a}^\dagger \hat{a} + \hbar\omega_a \frac{\hat{\sigma}_z}{2} + \frac{\hbar\Omega}{2}\left(\hat{a}\hat{\sigma}_+ + \hat{a}^\dagger\hat{\sigma}_-\right)$$



Detuning $\delta = \omega_a - \omega_c$

Vacuum Rabi frequency (splitting): $\Omega_n(\delta) = \sqrt{\delta^2 + \Omega^2(n+1)}$

Excited state energy eigenvalues (Jaynes-Cummings ladder)

$$E_\pm(n) = \hbar\omega_c\left(n + \frac{1}{2}\right) \boxed{\pm \frac{1}{2}\hbar\Omega_n(\delta),}$$

bare photon excitation

bare matter

$$|\psi_{1n}\rangle := |n, e\rangle$$

$$|\psi_{2n}\rangle := |n+1, g\rangle$$

$$\alpha_n := \tan^{-1}\left(\frac{\Omega\sqrt{n+1}}{\delta}\right).$$

Lower polariton (eigenstates) $|n,-\rangle = \sin\left(\frac{\alpha_n}{2}\right)|\psi_{1n}\rangle - \cos\left(\frac{\alpha_n}{2}\right)|\psi_{2n}\rangle$

Upper polariton (eigenstates) $|n,+\rangle = \cos\left(\frac{\alpha_n}{2}\right)|\psi_{1n}\rangle + \sin\left(\frac{\alpha_n}{2}\right)|\psi_{2n}\rangle$

Time-evolution:

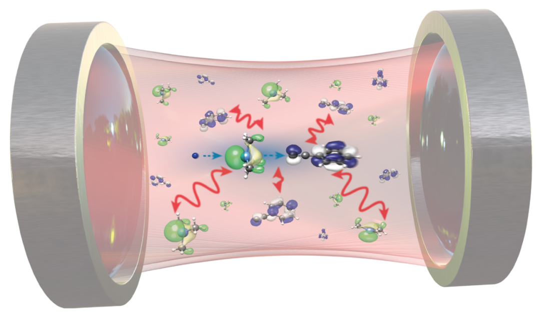
Excited initial state (represented in eigenstates): $|\psi_{\mathrm{tot}}(0)\rangle = \sum_n C_n |n,e\rangle = \sum_n C_n \left[\cos\left(\frac{\alpha_n}{2}\right)|n,+\rangle + \sin\left(\frac{\alpha_n}{2}\right)|n,-\rangle\right]$

Vacuum Rabi Oscillations:
(back to Schrödinger picture)

$$|\psi_{\mathrm{tot}}(t)\rangle = e^{-i\hat{H}_{\mathrm{JC}}t/\hbar}|\psi_{\mathrm{tot}}(0)\rangle = \sum_n C_n \left[\cos\left(\frac{\alpha_n}{2}\right)|n,+\rangle e^{-iE_+(n)t/\hbar} + \sin\left(\frac{\alpha_n}{2}\right)|n,-\rangle e^{-iE_-(n)t/\hbar}\right]$$

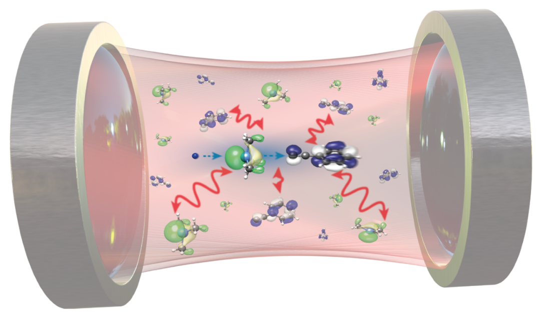
https://en.wikipedia.org/wiki/Jaynes%E2%80%93Cummings_model

Python Exercise 2



Polaritons / Rabi Model (beyond RWA)

Quantum Rabi Model



Difference to JC model

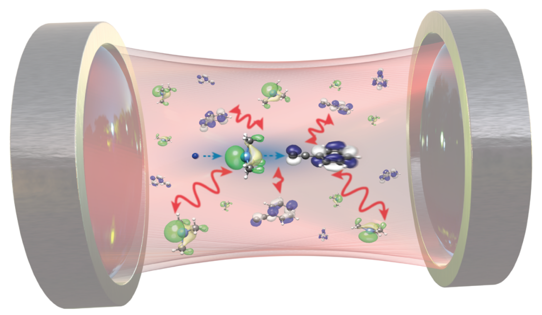
Including counter-rotating terms destroys block-diagonal nature of JC-Hamiltonian in terms of **bare** matter and **bare** photon basis set.

=> Eigenstates of Rabi model require numerical solution, i.e., diagonalization of entire Hamiltonian matrix.

In practice, numerical convergence for relatively small bare matter basis set sizes.

Remark: Discarding counter-rotating terms, i.e., the (A^2)-operator or „dipole self-energy“, removes many physically / chemically relevant effects that could be decisive in real chemical systems! (see upcoming lessons / active area of research)

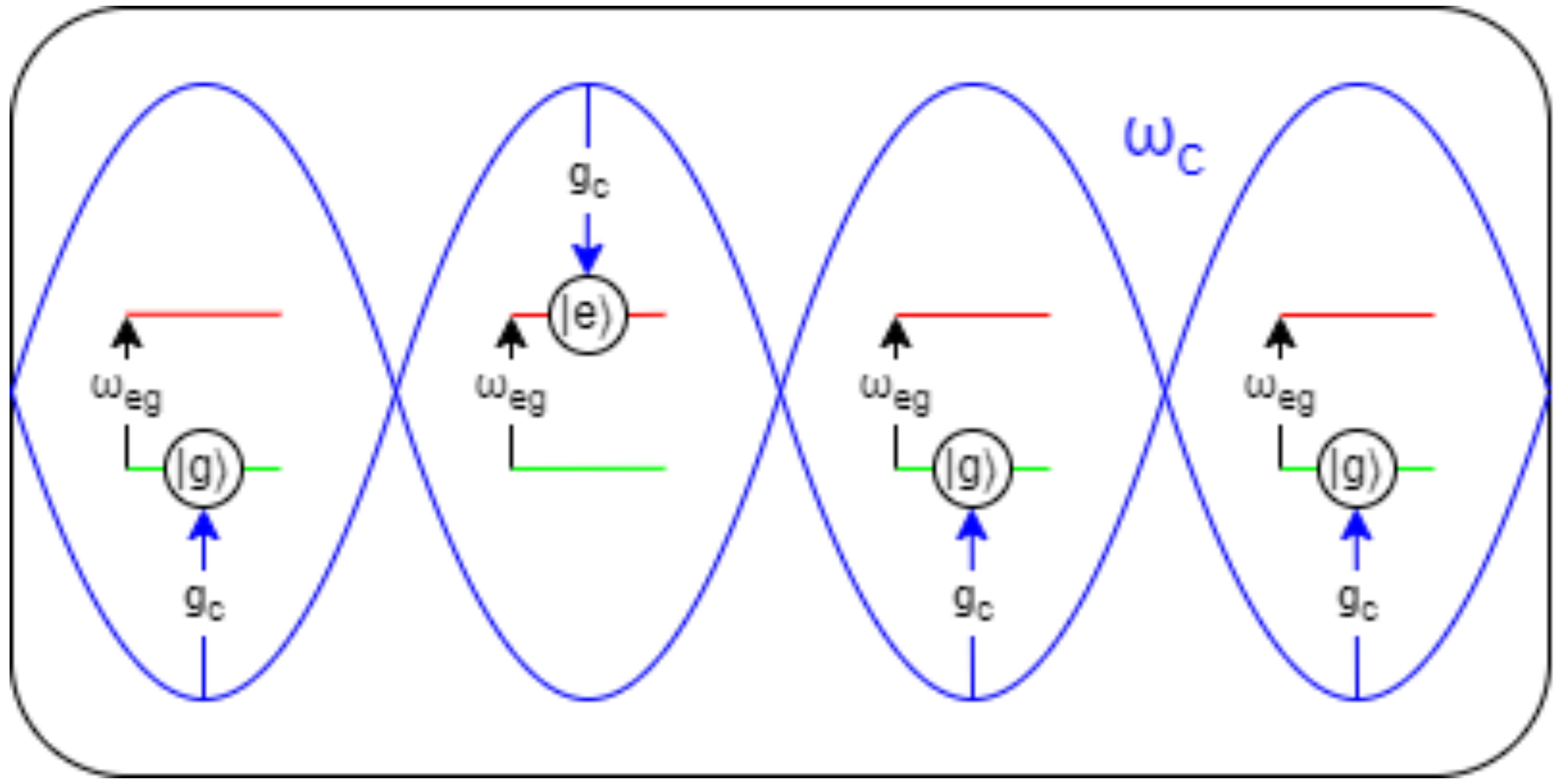
Collective Light-Matter Coupling



Tavis-Cummings Model (many emitters)

$$\hat{H}_{TC} = \hbar\omega_c a^\dagger a + \frac{\hbar\omega_a}{2} S_z + \frac{\hbar\Omega}{2}(a^\dagger S_- + a S_+)$$

$$S_\pm = \sum_{i=1}^{N} \sigma_\pm^{(i)} \qquad S_z = \sum_{i=1}^{N} \sigma_z^{(i)}$$

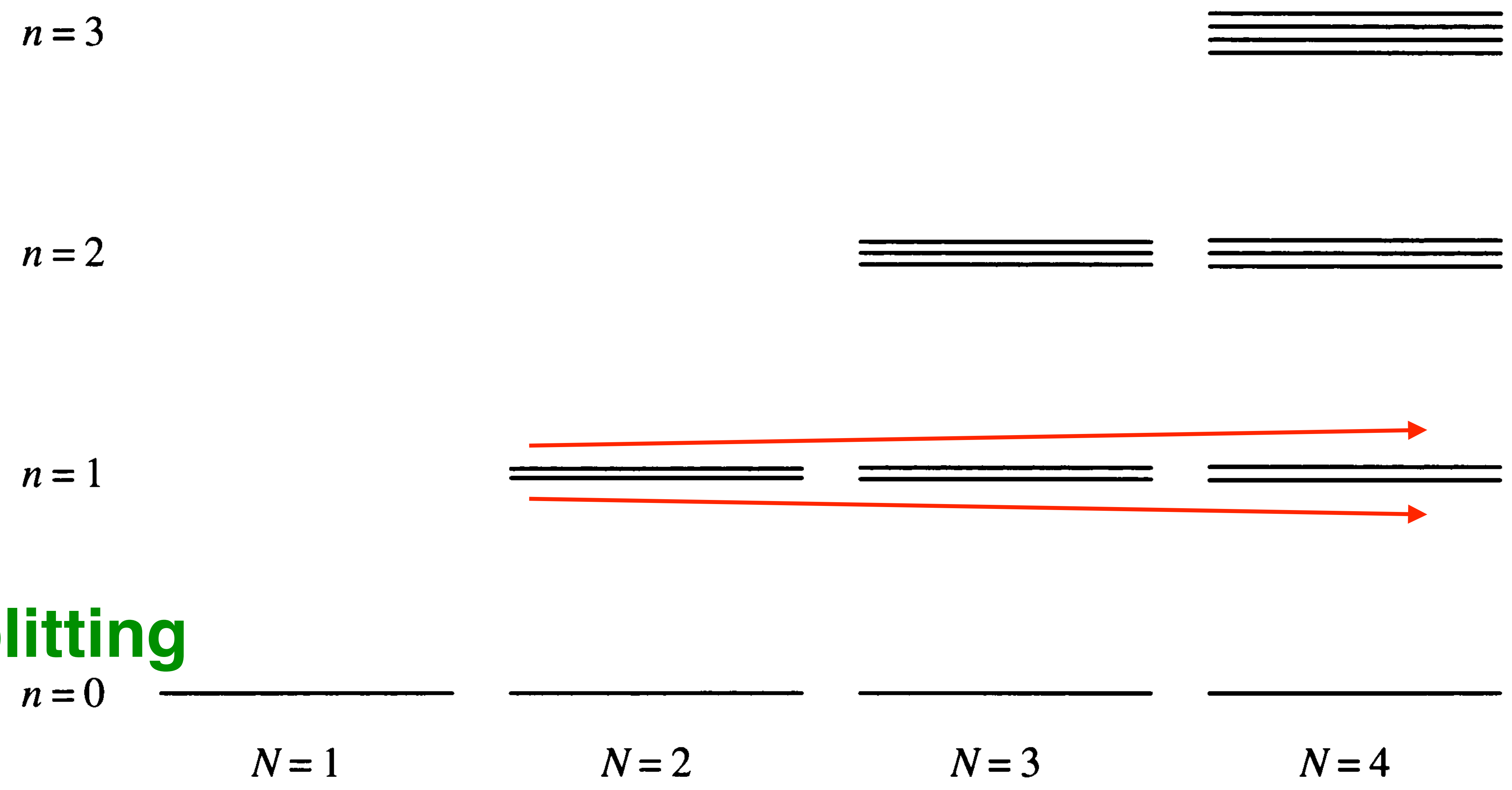


Primakoff transformation (spin to bosonic Fock operator representation) + assume large ensembles of molecules, e.g. $N \lesssim N_A = 6.022 \times 10^{23}$

$$S_+ = b^\dagger(N - b^\dagger b)^{1/2} \overset{N \gg 1}{\approx} b^\dagger\sqrt{N},\; S_- = (N - b^\dagger b)^{1/2} b \overset{N \gg 1}{\approx} b\sqrt{N},\; S_z = b^\dagger b - \frac{N}{2}$$

TC resembles approximately two coupled harmonic oscillators:

$$\hat{H}_{TC} \sim \hbar\omega_c a^\dagger a + \frac{\hbar\omega_a}{2}\left(-\frac{N}{2} + b^\dagger b\right) + \frac{\hbar\Omega}{2}\boxed{\sqrt{N}}(a^\dagger b + a b^\dagger)$$

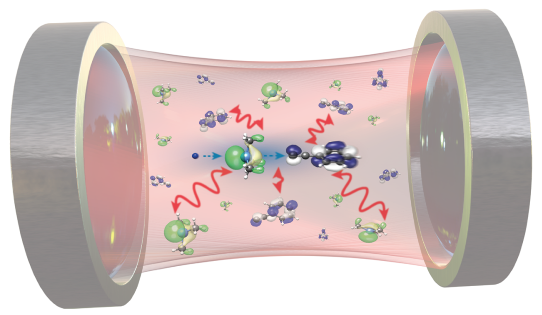


Collective coupling strength $\Omega \mapsto \sqrt{N}\Omega$ introduces **collective Rabi-splitting**

$$E_{TC}(n,j) \sim \left(n - \frac{N}{2}\right)\omega_c - \frac{n}{2}\delta + \boxed{j\sqrt{\hbar^2\Omega^2 N + \delta^2}},\; -n/2 \le j \le n/2,\; 0 \le n < N,\; \Delta j = \in \mathbb{Z}$$

B. M. Garraway, https://www.jstor.org/stable/41148867

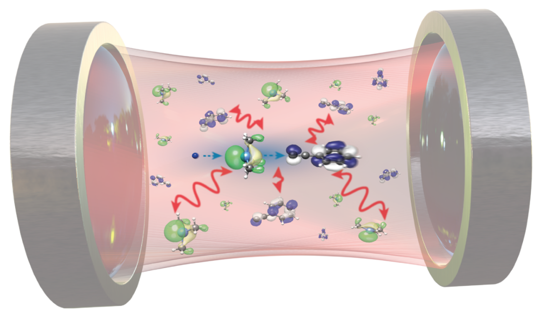
Common (misleading) conclusions from JC / TC models



1. Cavity-modifications of the groundstate are minuscule, and would only appear, when going beyond RWA approximation. Ground-state chemistry should virtually not be affected by optical cavities.
2. In typical experimental setups, a macroscopic amount of molecules is collectively coupled $N \ggg 1$. While this suggests that the collective coupling strength / Rabi splitting $\Omega\sqrt{N}$ may be significant, the coupling between a single molecule and the cavity field must be vanishingly small $\Omega \approx 0$. This suggests that chemistry should not change locally under collective strong coupling.

However: Experiments proof the contrary! What is going on?

Overview of Standard 2-level Models



Model	Counter-rotating terms?	Number of two-level systems
Jaynes-Cummings	no	1
Tavis-Cummings	no	N
Rabi	yes	1
Dicke	yes	N

Remark: Collective models (Dicke and TC) are fare more complex than what we discussed for our approximate solution. More accurate / extensive treatments reveal for example **dark states** that do not couple to the cavity field. Or the models entail phase transitions (e.g. supper-radiant phase) and quantum entanglement etc. In particular, the relevance / existence of a super-radiant phase in real systems is heavily disputed and an active field of research.

Summary and Conclusion

1. JC model reveals vacuum Rabi splitting (and oscillations) for strongly coupled light and matter. Rabi splitting is a typical experimental observable, which can be fitted to the JC/TC model for interpretation.
2. Counter-rotating light-matter interaction are often discarded in models (and also some ab-initio descriptions). Warning: This is believed to remove many physically/chemically relevant effects (active area of research)
3. Increasing the number of 2-level emitters, increases the Rabi-splitting. Light-matter coupling strength can collectively be increased.