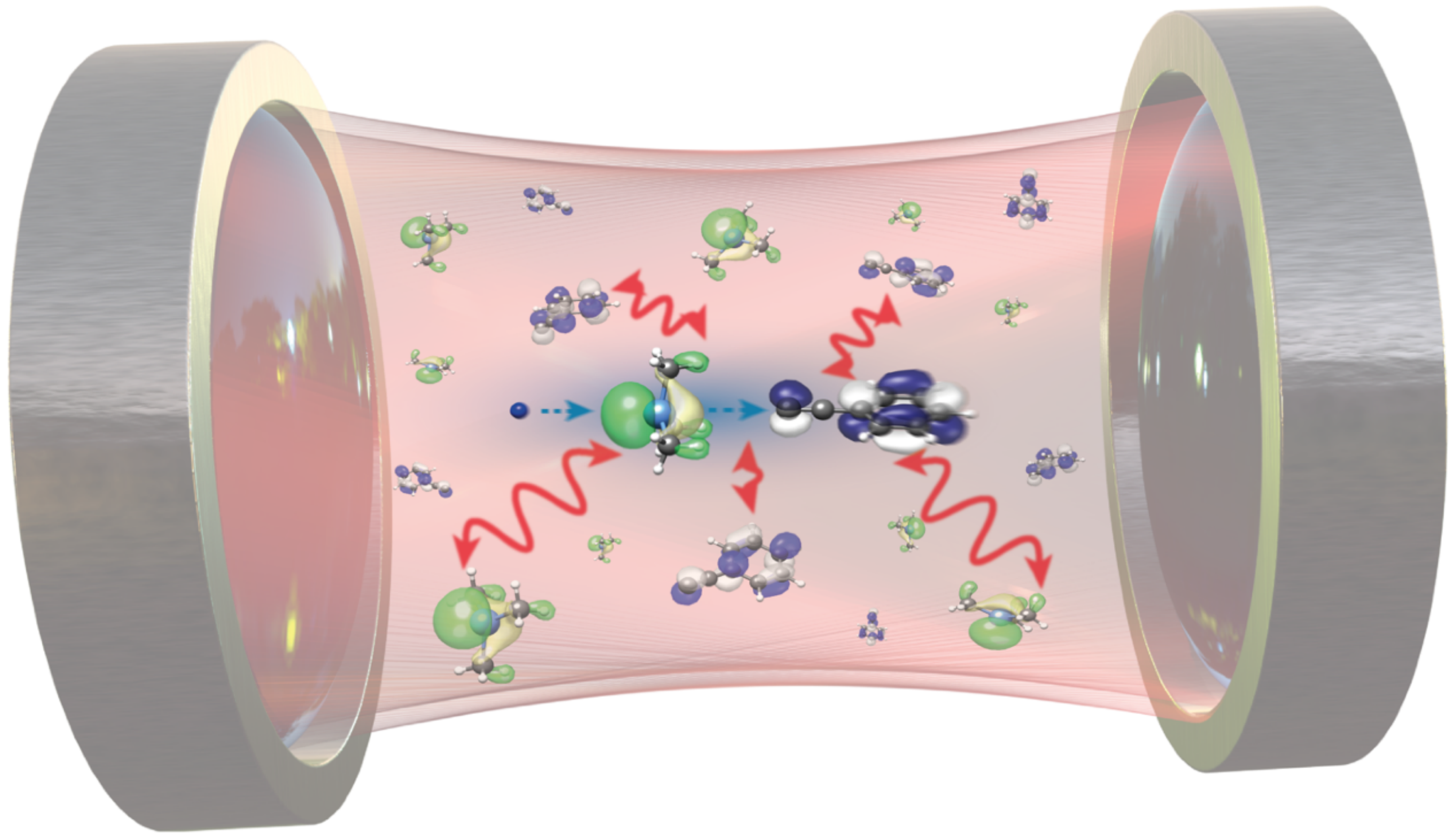
Dominik Sidler, 2025

Polaritonic / QED Chemistry

Lecture 4: Pauli-Fierz Theory



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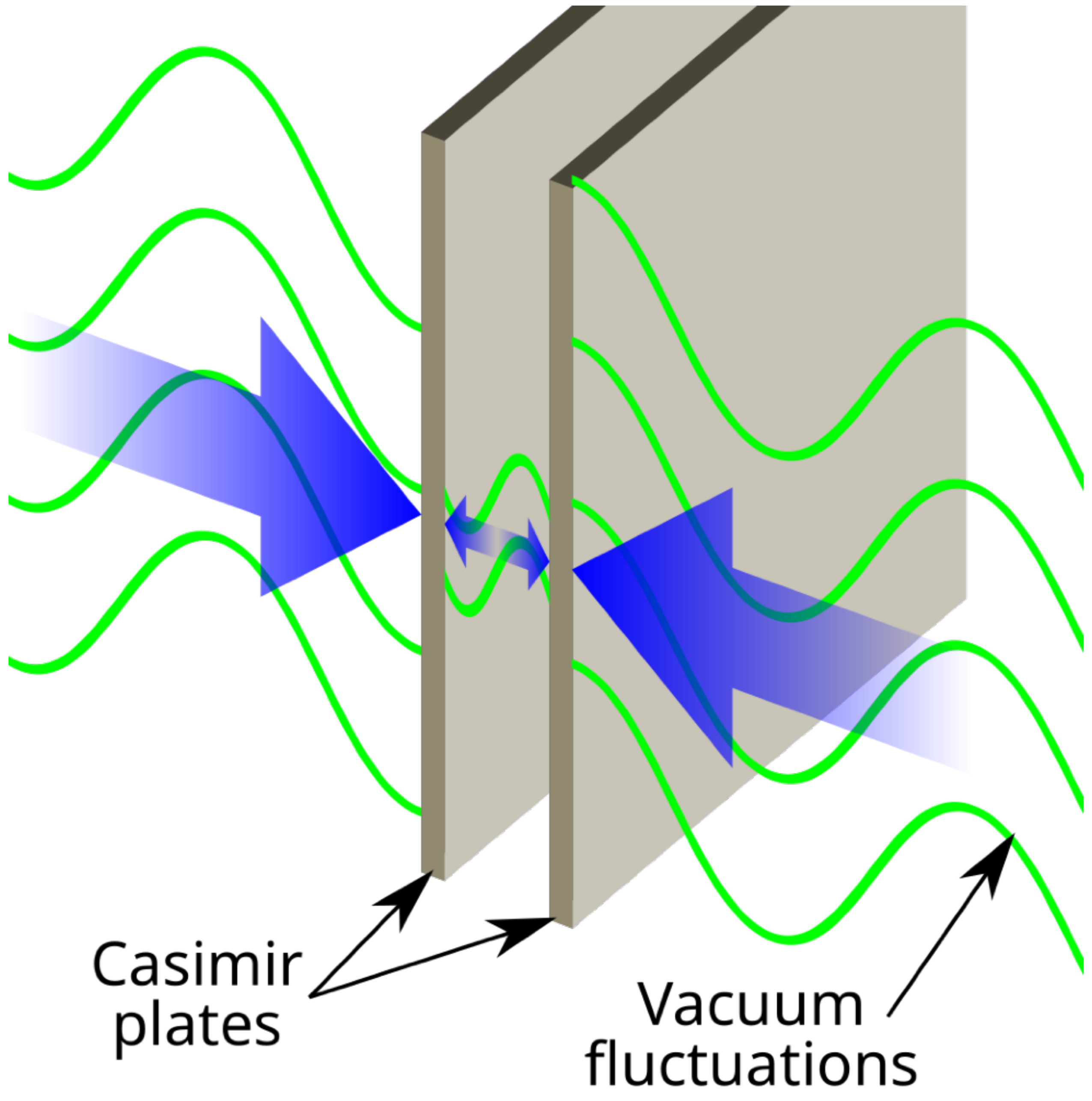
Why Quantum Light in Cavities?

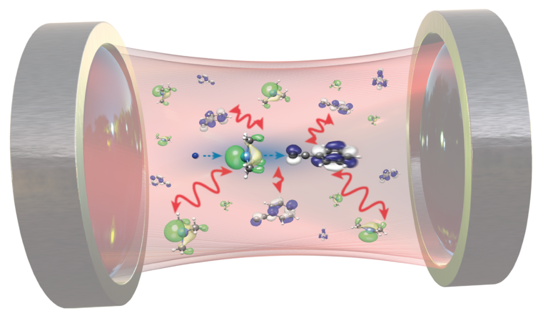
Famous Example: Casimir Forces



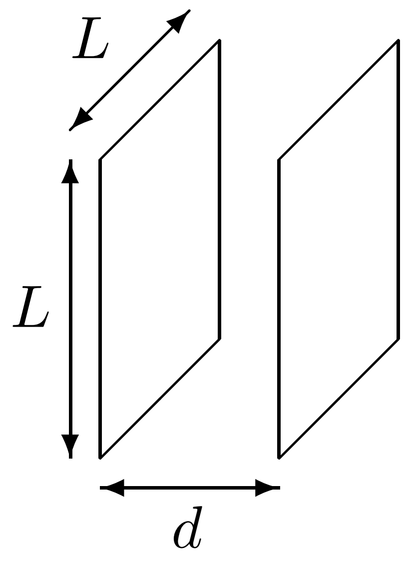
Breaks isotropy of space / vacuum field is restructured that introduces **attractive force on metal plates.**

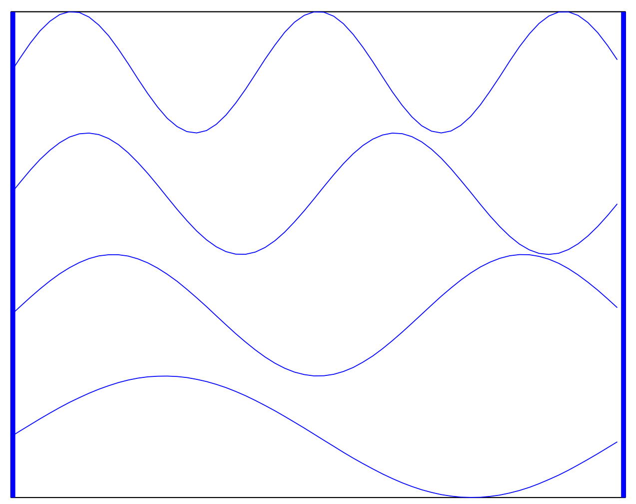
2 *For example: S. Scheel and S. Y. Buhmann, „Macroscopic quantum electrodynamics - concepts and applications“, arXiv:0902.3586, (2009)*

Casimir Force - and More



Why should matter care about the <u>quantum nature</u> of the fields in an optical cavity?





$L^2 d$ with $L \gg d$

$$E_0 = \sum_\lambda \hbar\omega_\lambda \left(\hat{N} + \frac{1}{2}\right) \overset{\text{vacuum}}{=} \sum_\lambda \frac{1}{2}\hbar\omega_\lambda \rightarrow \infty$$

Remark: Regularization of photon modes required to avoid divergence (typically UV cutoff).

Metall mirrors are assumed perfect conductors
-> Boundary condition: **electric field perpendicular to plates must be zero**!

Discretization of allowed field modes: $k_z = n\pi/d, n \in \mathbb{N}.$

Casimir force on mirrors (derivation see Scheel and Buhmann): $\frac{F}{L^2} = -\frac{\pi^2 \boxed{\hbar} c}{240\, d^4}$ Pure quantum (vacuum field) effect

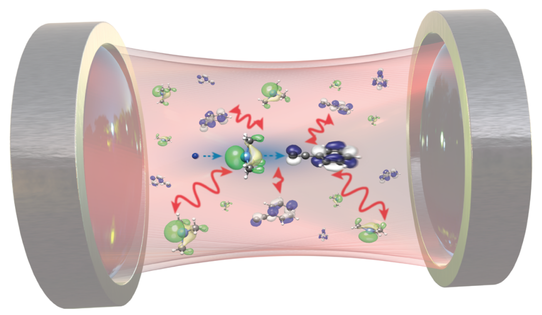
Geometry of mirrors (space) relevant:

geometry	Casimir force
planar	$-\frac{\pi^2 \hbar c L^2}{240 d^4}$
cylinder	$-\frac{0.02712 \hbar c z}{R^3}$
sphere	$\boxed{+}\frac{0.045 \hbar c}{R^2}$

Remark: Purcell effect: Enhancement of spontaneous emission rate in optical cavity (cavity changes density of state in Fermi's golden rule). Typically, **sign of weak coupling**, i.e, no Rabi-splitting, but different line broadening. Not covered in lecture, but if you want to know more, suitable as topic to present in student talks.

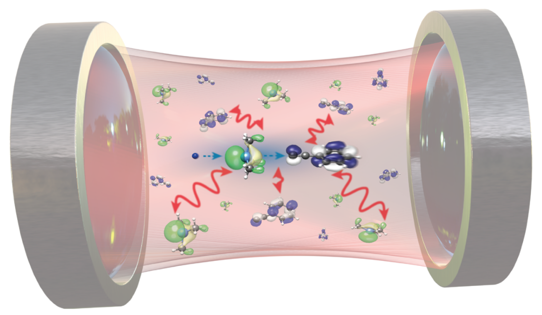
S. Scheel and S. Y. Buhmann, „Macrscopic quantum electrodynamics - concepts and applications", <u>arXiv:0902.3586</u>, (2009)

Lecture Outline



1. Quantization of vector potential for free space (**minimal coupling Pauli-Fierz Hamiltonian**)
2. Simplified representations (**few mode picture, long-wavelength / dipole approximation, length vs. velocity form**).
3. **Zero-transverse electric field condition.**
4. Relevance of **dipole self-energy**
5. Towards a practical solution strategy (**cavity Born-Oppenheimer partitioning**)

Quantization of Vector Potential I



Definitions

Energy of electro-magnetic field (classical) $E_{\text{ph}} = \frac{\epsilon_0}{2}\int \left(\boldsymbol{E}^2(\boldsymbol{r}t) + c^2\boldsymbol{B}^2(\boldsymbol{r}t)\right) \mathrm{d}\boldsymbol{r}$

In the following we use different definition of magnetic field

$\boldsymbol{B} \mapsto \frac{\boldsymbol{B}}{c}$ to be consistent with (Chem. Rev. Ref.).

Does not change physics!

Quantization of the field:

$$\hat{H}_{\text{ph}} = \sum_{\lambda=1}^{2} \int \hbar\omega_{\boldsymbol{k}} \hat{a}^\dagger(\boldsymbol{k}, \lambda)\hat{a}(\boldsymbol{k}, \lambda)\, \mathrm{d}\boldsymbol{k}$$

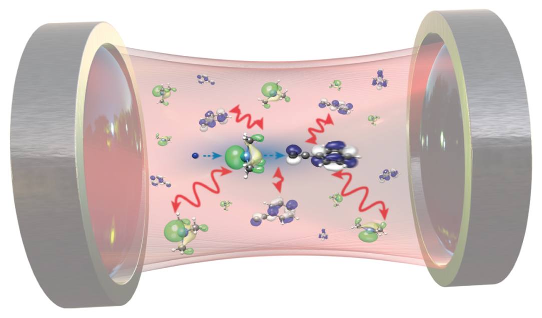
Helicity of light (left vs. right) circular polarization

momentum of light is related to frequency $\omega_{\boldsymbol{k}} = c|\boldsymbol{k}|$

Bosonic (spin-1) photon commutator relation for annihilation and creation Op. $[\hat{a}(\boldsymbol{k}', \lambda'), \hat{a}^\dagger(\boldsymbol{k}, \lambda)] = \delta_{\lambda'\lambda}\delta^3(\boldsymbol{k} - \boldsymbol{k}')$

M. Ruggenthaler, D. Sidler and A. Rubio, Chem. Rev., 123, 11191, (2023)

Quantization of Vector Potential II



Motivation (Not a derivation! Proper way from Dirac eq. beyond the scope of this lecture)

Classical vector potential $-\nabla^2 \boldsymbol{A}(\boldsymbol{r}) = (\nabla \times \nabla \times \cancel{-\nabla\nabla\cdot})\boldsymbol{A}(\boldsymbol{r}) = \boldsymbol{k}^2\boldsymbol{A}(\boldsymbol{r})$

Vector Identity

Coulomb Gauge choice $A \mapsto A_\perp$

$$\left(\frac{1}{c^2}\partial_t^2 - \nabla^2\right)\boldsymbol{A}_\perp(\boldsymbol{r}t) = 0$$

Maxwell's equations + Fourier transform in t = Wave equation

Quantized vector potential

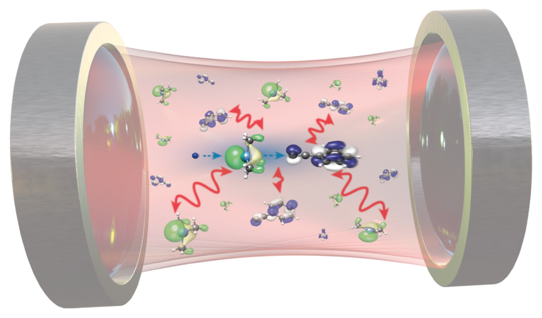
$$\hat{\boldsymbol{A}}_\perp(\boldsymbol{r}) = \sqrt{\frac{\hbar c^2}{\epsilon_0 (2\pi)^3}} \sum_{\lambda=1}^{2} \int \frac{1}{\sqrt{2\omega_{\boldsymbol{k}}}} \left(\hat{a}(\boldsymbol{k},\lambda)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{\epsilon}(\boldsymbol{k},\lambda) + \hat{a}^\dagger(\boldsymbol{k},\lambda)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{\epsilon}^*(\boldsymbol{k},\lambda)\right) \mathrm{d}\boldsymbol{k}$$

$$\boldsymbol{\epsilon}(\boldsymbol{k},\lambda)\cdot\boldsymbol{k} = \boldsymbol{\epsilon}(\boldsymbol{k},1)\cdot\boldsymbol{\epsilon}(\boldsymbol{k},2) = 0 \qquad \nabla\cdot\hat{\boldsymbol{A}}_\perp(\boldsymbol{r}) = 0$$

Quantized magnetic field: $\hat{\boldsymbol{B}}(\boldsymbol{r}) = \frac{1}{c}\nabla \times \hat{\boldsymbol{A}}_\perp(\boldsymbol{r})$

M. Ruggenthaler, D. Sidler and A. Rubio, Chem. Rev., 123, 11191, (2023)

Quantized Electric Field



Motivation (Not a derivation! Proper way from Dirac eq. beyond the scope of this lecture)

Classical electric field from Maxwell's equation $\boldsymbol{E}(\boldsymbol{r}t) = -\nabla\phi(\boldsymbol{r}t) \boxed{-\frac{1}{c}\partial_t} \boldsymbol{A}(\boldsymbol{r}t) \; = E_{\parallel} + E_{\perp}$ ← **transverse electric field** (time-dependent)

↑ **longitudinal electric field** (static Coulomb interaction)

Quantized transverse electric field:

$$\hat{\boldsymbol{E}}_{\perp}(\boldsymbol{r}) = \sqrt{\frac{\hbar}{\epsilon_0(2\pi)^3}} \sum_{\lambda=1}^{2} \int \frac{\boxed{\mathrm{i}\omega_{\boldsymbol{k}}}}{\sqrt{2\omega_{\boldsymbol{k}}}} \left(\hat{a}(\boldsymbol{k},\lambda)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{\epsilon}(\boldsymbol{k},\lambda) \boxed{-} \hat{a}^{\dagger}(\boldsymbol{k},\lambda)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{\epsilon}^{*}(\boldsymbol{k},\lambda)\right) \mathrm{d}\boldsymbol{k}$$

$$\hat{\boldsymbol{A}}_{\perp}(\boldsymbol{r}) = \sqrt{\frac{\hbar \boxed{c^2}}{\epsilon_0(2\pi)^3}} \sum_{\lambda=1}^{2} \int \frac{\boxed{1}}{\sqrt{2\omega_{\boldsymbol{k}}}} \left(\hat{a}(\boldsymbol{k},\lambda)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{\epsilon}(\boldsymbol{k},\lambda) \boxed{+} \hat{a}^{\dagger}(\boldsymbol{k},\lambda)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\boldsymbol{\epsilon}^{*}(\boldsymbol{k},\lambda)\right) \mathrm{d}\boldsymbol{k}$$

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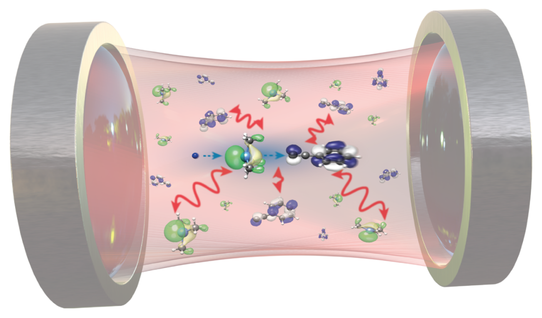
Coupling Light and Matter



Classically

Classical Maxwell's equations in Coulomb gauge:

$$-\nabla^2\phi(\boldsymbol{r}t) = \frac{\rho(\boldsymbol{r}t)}{\epsilon_0} \longleftarrow \text{Charge density distribution}$$

$$\left(\frac{1}{c^2}\partial_t^2 - \nabla^2\right)\boldsymbol{A}_\perp(\boldsymbol{r}t) = \mu_0 c\,\boldsymbol{J}_\perp(\boldsymbol{r}t) \longleftarrow \text{Current density distribution}$$

….. Interaction energy: $E_{\text{int}} = -\frac{1}{c}\int \boldsymbol{J}(\boldsymbol{r}t)\cdot\boldsymbol{A}(\boldsymbol{r}t)\,\mathrm{d}\boldsymbol{r} + \int \rho(\boldsymbol{r}t)\phi(\boldsymbol{r}t)\,\mathrm{d}\boldsymbol{r}$

Classical Coulomb potential
(**Hartree potential**)

$$\phi(\boldsymbol{r}t) = \int \frac{\rho(\boldsymbol{r}'t)}{4\pi\epsilon_0|\boldsymbol{r}-\boldsymbol{r}'|}\,\mathrm{d}\boldsymbol{r}'$$

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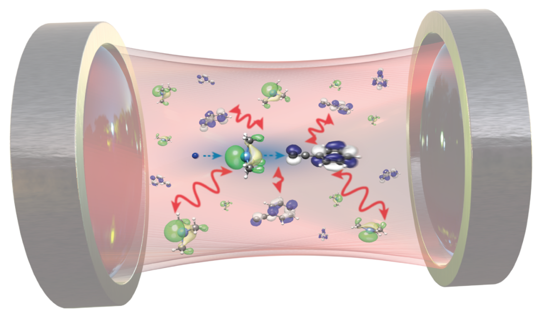
Coupling Light and Matter



....Quantized (Pauli-Fierz Hamiltonian, initial guess known since 1938)

Transverse electron interaction

Transverse Zeeman interaction for electron-spin

$$\hat{H}_{\mathrm{PF}} = \sum_{l=1}^{N_e} \frac{1}{2m}\left(-i\hbar\nabla_{\boldsymbol{r}_l} + \frac{|e|}{c}\hat{\mathbf{A}}_{\perp}(\boldsymbol{r}_l)\right)^2 + \frac{|e|\hbar}{2m}\boldsymbol{\sigma}_l\cdot\hat{\boldsymbol{B}}(\boldsymbol{r}_l)$$

Photon field renormalizes mass of charged particle: Bare masses appear, which are smaller than **physically masses,** measured and used for standard QM, e.g. $m_{\mathrm{e}} = m + m_{\mathrm{ph}}$

Details not covered in lecture, but if you want to know more, suitable as topic to present in student talks.

$$+ \frac{1}{2}\sum_{l\neq m}^{N_e} \frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}_l - \boldsymbol{r}_m|}$$

← Electron-electron longitudinal interaction

$$+ \sum_{l=1}^{N_n} \frac{1}{2M_l}\left(-i\hbar\nabla_{\boldsymbol{R}_l} - \frac{Z_l|e|}{c}\hat{\mathbf{A}}_{\perp}(\boldsymbol{R}_l)\right)^2 - \frac{Z_l|e|\hbar}{2M_l}\boldsymbol{S}_l\cdot\hat{\boldsymbol{B}}(\boldsymbol{R}_l)$$

← Transverse Zeeman interaction for nuclear-spin

Transverse nuclear interaction

$$+ \frac{1}{2}\sum_{l\neq m}^{N_n} \frac{Z_l Z_m e^2}{4\pi\epsilon_0|\boldsymbol{R}_l - \boldsymbol{R}_m|}$$

Longitudinal nuclear-nuclear interaction

$$- \sum_{l=1}^{N_e}\sum_{m=1}^{N_n} \frac{Z_m e^2}{4\pi\epsilon_0|\boldsymbol{r}_l - \boldsymbol{R}_m|} + \sum_{\lambda=1}^{2}\int \hbar\omega_{\boldsymbol{k}}\hat{a}^{\dagger}(\boldsymbol{k},\lambda)\hat{a}(\boldsymbol{k},\lambda)\,\mathrm{d}\boldsymbol{k}$$

← Transverse electric field energy

Longitudinal electron-nuclear interaction

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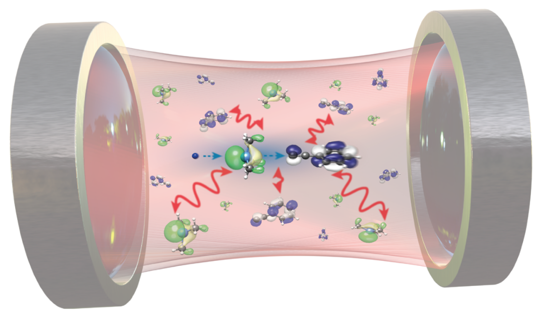
Pauli-Fierz Hamiltonian



General Properties

1. **Schrödinger equation** to solve. Formalism of standard quantum mechanics applicable.
2. Possesses **groundstate**. Can be shown that system with a groundstate in standard QM also has a ground state in non-relativistic QED (Pauli-Fierz theory).
3. **Difference** between standard QM and non-relativistic QED: **Excited states have finite life-time** (spontaneous emission intrinsically allowed). They form a continuum (mode continuum) and all **dissipation and decoherence** channels (nuclei / photons) are explicitly included by construction.
4. **Theory fundamentally non-perturbative** (in contrast to relativistic QED).
5. **Unfeasible to work in practice**, since **all (continuum) light and all matter is described microscopically:** Too many degrees of freedom even for simplest system. Furthermore, how to add external driving fields or temperature baths without including them microscopically?

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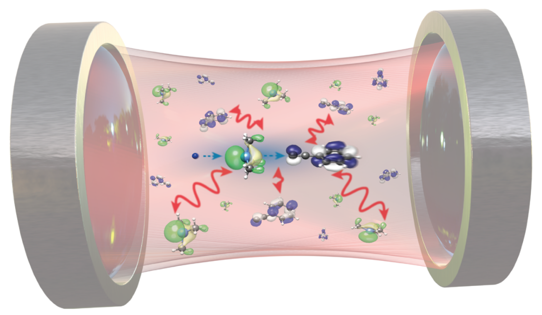
Approximations



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Approximations / assumptions:
- **Linear polarization**
- **Dipole (long-wavelength) approximation** $exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = 1$
- Discretize mode continuum and approximate coupling to cavity by **single effective mode** (bare mass turns into **physical mass** known from standard QM).

From now on, we always work with physical masses as you are used to in chemistry!

Velocity gauge / form (still Coulomb gauge condition applies):

$$\hat{H}'_{\mathrm{PF,v}} = -\sum_{l=1}^{N_e}\frac{\hbar^2}{2m_e}\left(\nabla_{r_l} + |e|\lambda q_\alpha\right)^2 + \frac{1}{2}\sum_{l\neq m}^{N_e}\frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}_l-\boldsymbol{r}_m|} - \sum_{l}^{N_e}\sum_{m}^{N_n}\frac{Z_m e^2}{4\pi\epsilon_0|\boldsymbol{r}_l-\boldsymbol{R}_m|} - \sum_{l=1}^{N_n}\frac{\hbar^2}{2M_{\mathrm{nuk},l}}\left(\nabla_{\boldsymbol{R}_l} - Z_l|e|\lambda q_\alpha\right)^2 + \frac{1}{2}\sum_{l\neq m}^{N_n}\frac{Z_l Z_m e^2}{4\pi\epsilon_0|\boldsymbol{R}_l-\boldsymbol{R}_m|} - \frac{\hbar^2}{2}\frac{\partial^2}{\partial q_\alpha^2} + \frac{\omega_\alpha^2}{2}q_\alpha^2$$

PZW-Transform

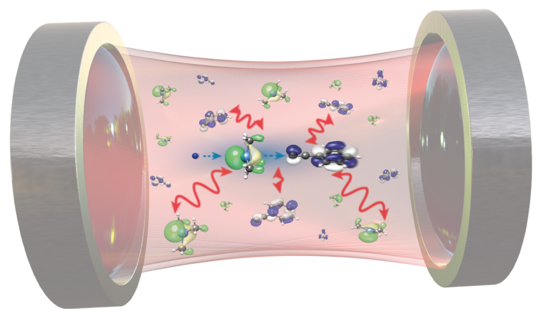
Length gauge / form (still Coulomb gauge condition applies):

$$\boxed{\hat{H}'_{\mathrm{PF,l}} = -\sum_{l=1}^{N_e}\frac{\hbar^2}{2m_e}\nabla_{r_l}^2 + \frac{1}{2}\sum_{l\neq m}^{N_e}\frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}_l-\boldsymbol{r}_m|} - \sum_{l}^{N_e}\sum_{m}^{N_n}\frac{Z_m e^2}{4\pi\epsilon_0|\boldsymbol{r}_l-\boldsymbol{R}_m|} - \sum_{l=1}^{N_n}\frac{\hbar^2}{2M_{\mathrm{nuk},l}}\nabla_{\boldsymbol{R}_l}^2 + \frac{1}{2}\sum_{l\neq m}^{N_n}\frac{Z_l Z_m e^2}{4\pi\epsilon_0|\boldsymbol{R}_l-\boldsymbol{R}_m|} - \frac{\hbar^2}{2}\frac{\partial^2}{\partial q_\alpha^2} + \frac{\omega_\alpha^2}{2}\left(\boxed{q_\alpha - \frac{\lambda_\alpha}{\omega_\alpha}\cdot\boldsymbol{R}}\right)^2},$$

Field-mode q_α couples to the **total electric dipole moment**: $\boldsymbol{R} = -\sum_{l=1}^{N_e}|e|\boldsymbol{r}_l + \sum_{l=1}^{N_n}Z_l|e|\boldsymbol{R}_l$

Dipole self-energy $\frac{(\boldsymbol{\lambda_\alpha}\cdot\boldsymbol{R})^2}{2}$ plays a crucial since it introduces a long-range all-to-all interaction for the matter, still it is in many implementations / calculations discarded.

Dipole Self-Energy and Zero Transverse E-field



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Zero transverse E-Field condition: $\hat{H}'_{\mathrm{PF},1}\Psi_n = E_n\Psi_n$ $\boxed{\langle \hat{\boldsymbol{E}}_\perp \rangle_n = 0}$

$$\boxed{\hat{\boldsymbol{E}}_\perp = \hat{\boldsymbol{E}}^l_\perp = \boldsymbol{\lambda}_\alpha \omega_\alpha \hat{q}_\alpha - \boldsymbol{\lambda}(\boldsymbol{\lambda}\cdot\hat{\boldsymbol{R}}) = \frac{\hat{\boldsymbol{D}}}{\epsilon_0} - \frac{\hat{\boldsymbol{P}}}{\epsilon_0}}$$

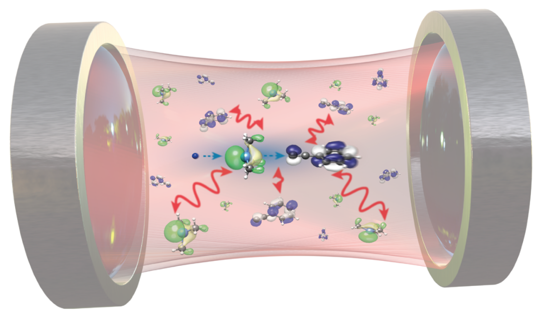
Dipole self-energy necessary to have groundstate (stable electronic structure): $\hat{V}_{DSE} = \frac{(\boldsymbol{\lambda_\alpha}\cdot\boldsymbol{R})^2}{2}$

„Proof“:

Suppose $\hat{V}_{DSE} = \frac{(\lambda_\alpha \hat{r}_i)^2}{2} = 0$ thus transverse light-matter interaction solely given by: $\hat{V}_{\mathrm{displacement}} = -\omega_\alpha \hat{q}_\alpha \lambda_\alpha \hat{r}_i$

Thus: $|\psi>_{r_0} = \frac{e^{-(r_i-r_0)^2}}{\sqrt{<\psi|\psi>}}$ $\lim_{r_0\to\infty} <\psi|\hat{V}_{\mathrm{displacement}}|\psi>_{r_0} = \boxed{-\infty}$ Matter dissociates always in basis set limit!!!

Born-Huang / Born-Oppenheimer Partitioning



Towards a Numerical Solution Procedure

$$\hat{H}'_{\text{PF}} = -\sum_{l=1}^{N_e}\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}_l} + \frac{1}{2}\sum_{l\neq m}^{N_e}\frac{e^2}{4\pi\epsilon_0|\boldsymbol{r}_l-\boldsymbol{r}_m|} - \sum_{l}^{N_e}\sum_{m}^{N_n}\frac{Z_m e^2}{4\pi\epsilon_0|\boldsymbol{r}_l-\boldsymbol{R}_m|} - \sum_{l=1}^{N_n}\frac{\hbar^2}{2M_l}\nabla^2_{\boldsymbol{R}_l} + \frac{1}{2}\sum_{l\neq m}^{N_n}\frac{Z_l Z_m e^2}{4\pi\epsilon_0|\boldsymbol{R}_l-\boldsymbol{R}_m|} + \boxed{\sum_{\alpha=1}^{M_p}}\left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial q_\alpha^2} + \frac{\omega_\alpha^2}{2}\left(q_\alpha - \frac{\boldsymbol{\lambda}_\alpha}{\omega_\alpha}\cdot\boldsymbol{R}\right)^2\right],$$

$$E\Psi(\underline{\boldsymbol{r}},\ \underline{\boldsymbol{R}},\ \underline{q}) = \hat{H}'_{\text{PF}}\Psi(\underline{\boldsymbol{r}},\ \underline{\boldsymbol{R}},\ \underline{q})$$

$$\Psi(\underline{\boldsymbol{r}}, \underline{\boldsymbol{R}}, \underline{q})$$

$$\sum_{i=0}^{\infty}\chi_i(\underline{\boldsymbol{R}}, \underline{q})\psi_i(\underline{r}; \{\underline{\boldsymbol{R}}, \underline{q}\})$$

Cavity Born-Oppenheimer Partitioning

$\chi_i(\underline{\boldsymbol{R}}, \underline{q})$ Polaritonic Nuclear/Ion-Photon Wave Function

$\psi_i(\underline{r}; \{\underline{\boldsymbol{R}}, \underline{q}\})$ Conditional Electronic Wave Function

Considered good for **vibrational strong coupling**

$$\sum_{i=0}^{\infty}\chi_i(\underline{\boldsymbol{R}})\psi_i(\underline{r}, \underline{q}; \{\underline{\boldsymbol{R}}\})$$

Polaritonic Energy Surface Partitioning

$\chi_i(\underline{\boldsymbol{R}})$ Nuclear/Ionic Wave Function

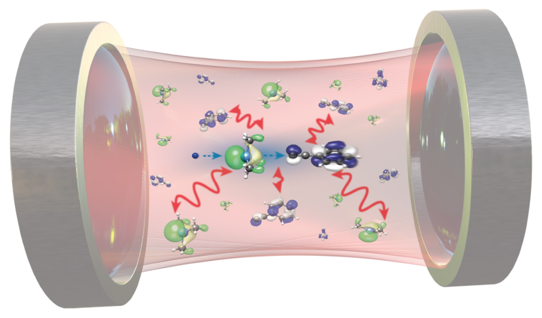
$\psi_i(\underline{r}, \underline{q}; \{\underline{\boldsymbol{R}}\})$ Polaritonic Conditional Electron-Photon Wave Function

Considered good for **electronic strong coupling**

However, so far **no approximation** made by different partitioning!

M. Ruggenthaler, D. Sidler and A. Rubio, Chem. Rev., 123, 11191, (2023)

Cavity Born-Oppenheimer Approach

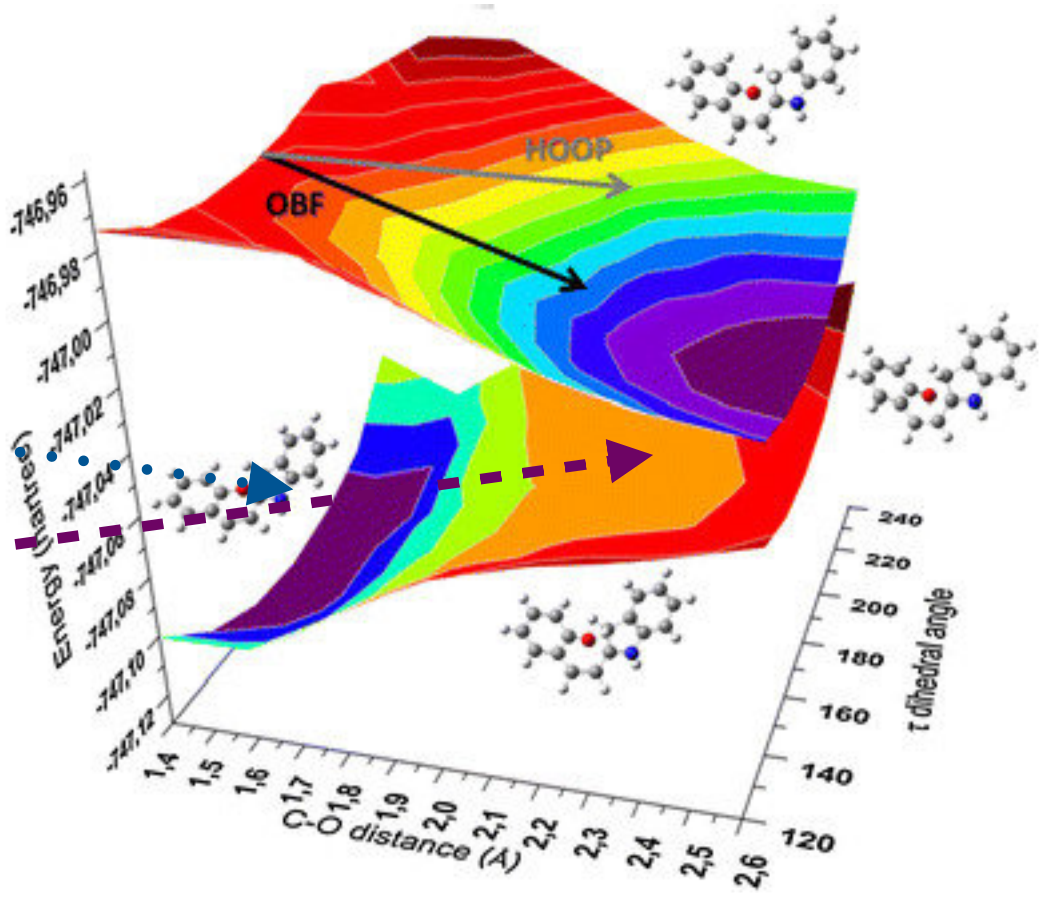


$$\sum_{i=0}^{\infty} \chi_i(\underline{\mathbf{R}}, \underline{q})\psi_i(\underline{r}; \{\underline{\mathbf{R}}, \underline{q}\})$$

Dressed electronic structure problem
parametric dependency on nuclear and displacement field coordinates:

$$E_i(\underline{\mathbf{R}},\ \underline{q})\psi_i(\underline{\mathbf{r}};\ \{\underline{\mathbf{R}},\ \underline{q}\}) = \hat{H}'_{\mathrm{PF}}(\underline{\mathbf{R}},\ \underline{q})\psi_i(\underline{\mathbf{r}};\ \{\underline{\mathbf{R}},\ \underline{q}\})$$

Interpretation: Nuclei and displacement-field „evolve" on cavity-modified electronic **potential energy surfaces (PES)**. If polaritonic system in thermal equilibrium and $E_1 - E_0 \gg k_B T$, chemistry determined „solely" by ground-state PES $E_0(\underline{\boldsymbol{R}}, \underline{\boldsymbol{q}})$.



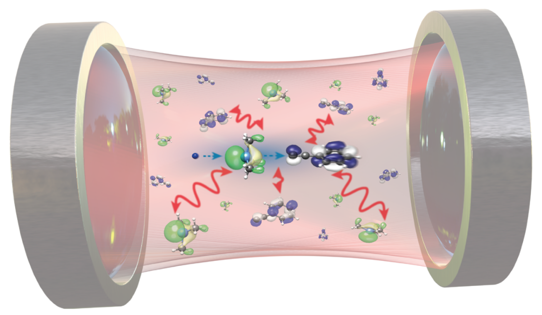
If $E_1 - E_0 \approx k_B T$, **non-adiabatic coupling** elements $i \neq j \neq 0$ between PES start to play a role, i.e. electronically excited PES.

Nuclear / displacement field problem:

$$E\chi_i(\underline{\mathbf{R}},\ \underline{q}) = E_i(\underline{\mathbf{R}},\ \underline{q})\chi_i(\underline{\mathbf{R}},\ \underline{q}) + \sum_{j=0}^{\infty} \int \mathrm{d}\underline{\mathbf{r}}\, \psi_i^*(\underline{\mathbf{r}};\ \{\underline{\mathbf{R}},\ \underline{q}\})$$

$$\left(\sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l}\nabla^2_{\mathbf{R}_l} + \sum_{\alpha=1}^{M_p} -\frac{\hbar^2}{2}\frac{\partial^2}{\partial q_\alpha^2}\right)\psi_j^*(\underline{\mathbf{r}};\ \{\underline{\mathbf{R}},\ \underline{q}\})\chi_j(\underline{\mathbf{R}},\ \underline{q})$$

Summary & Conclusion



1. **Pauli-Fierz Hamiltonian** treats light and matter on an equal footing.
2. **Long-wavelength / dipole approximation** allows effective cavity mode representation (no explicit microscopic representation of mirrors required). Method of choice for ab-inito / quantum chemistry implementations.
3. **Velocity gauge** typically suitable for solids, **length gauge** typically suitable for molecules.
4. **Dipole self-energy necessary** to make theory stable, i.e., otherwise no ground-state, no basis set limit, and thus no self-consistent (ab-initio) solution possible.
5. **cavity Born-Oppenheimer partitioning** allows to solve / simulate the (cavity-modified) electronic structure problem separated from the (still quantized) nuclear / displacement-field problem.