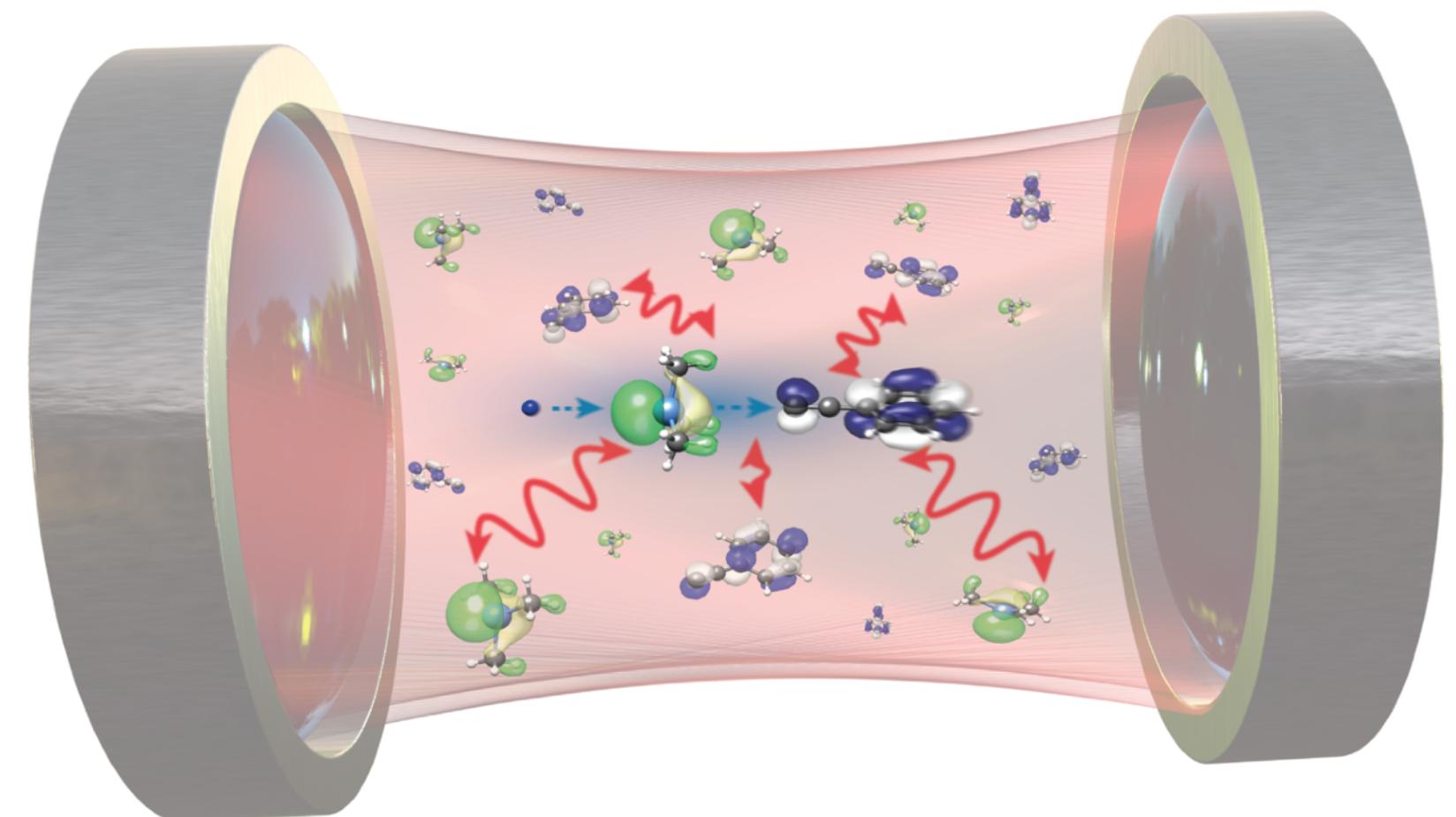
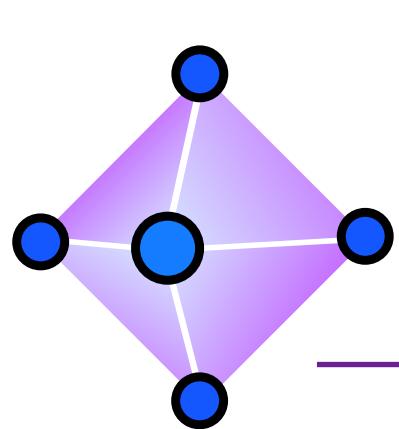


Dominik Sidler, 2025

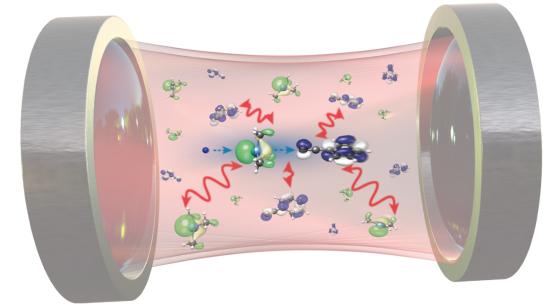
Polaritonic / QED Chemistry

Lecture 5: Vibrational Strong Coupling





Repetition: Born-Huang / Born-Oppenheimer Partitioning



Towards a Numerical Solution Procedure

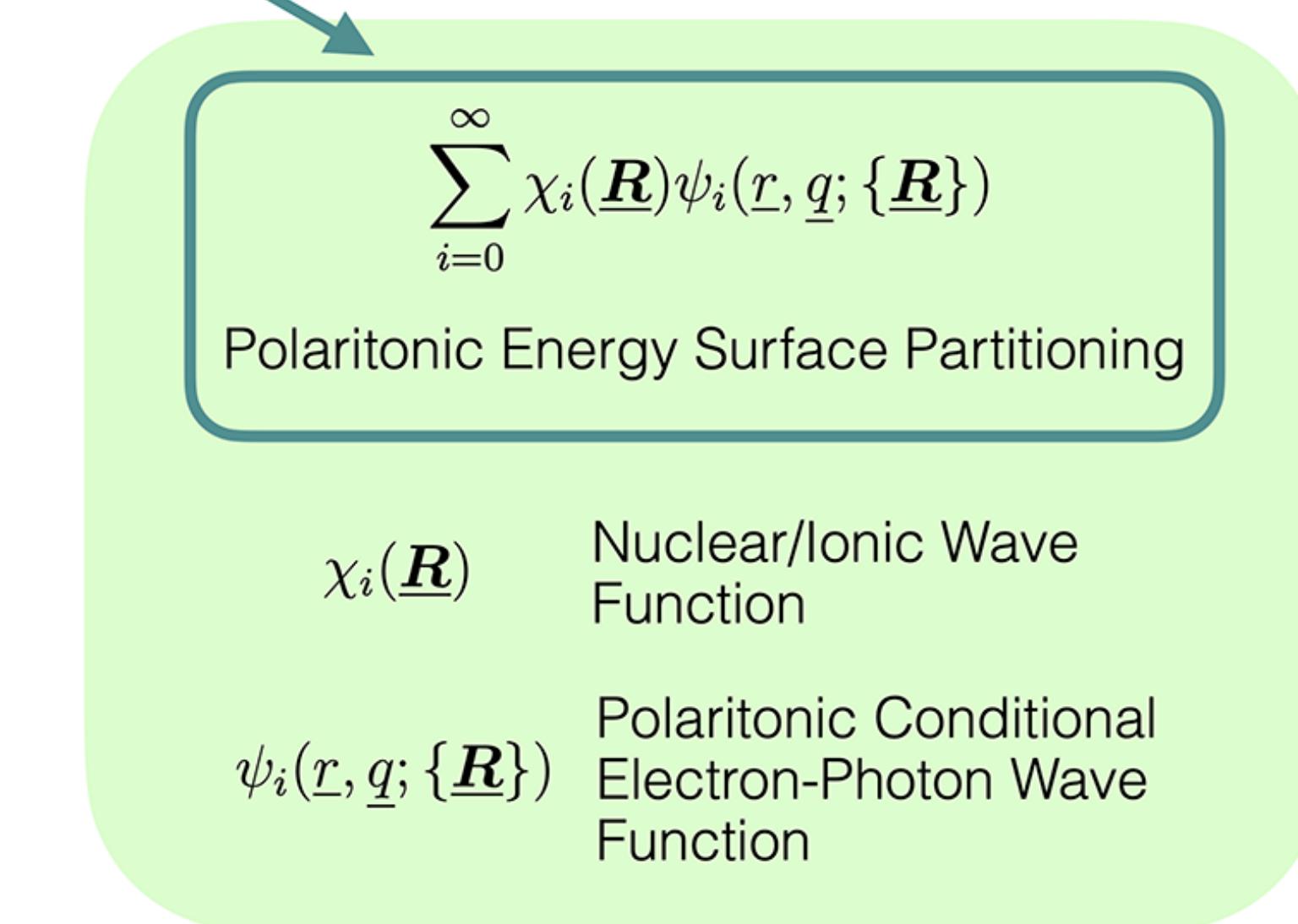
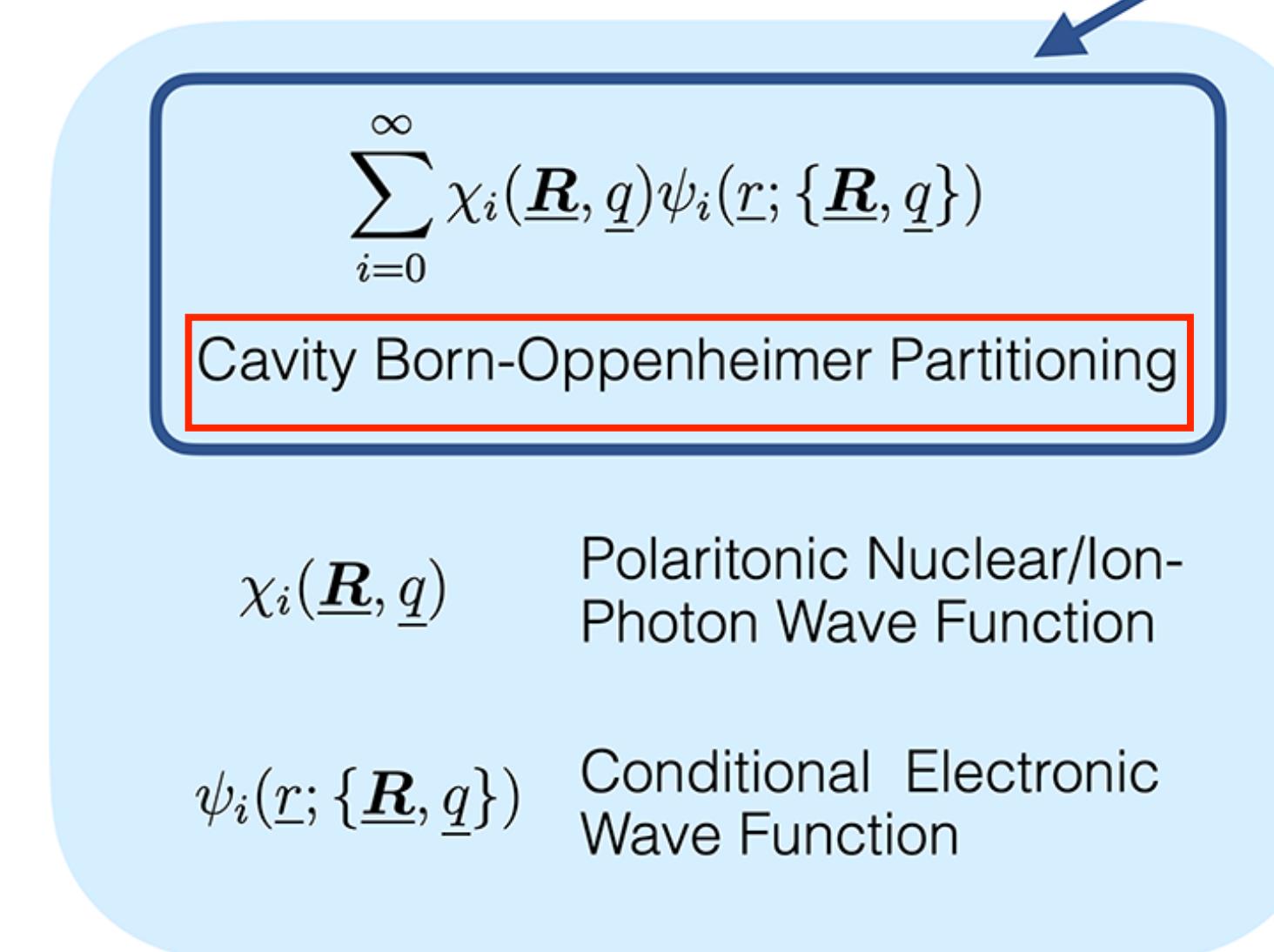
$$\hat{H}'_{\text{PF}} = - \sum_{l=1}^{N_e} \frac{\hbar^2}{2m} \nabla_{\underline{r}_l}^2 + \frac{1}{2} \sum_{l \neq m}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\underline{r}_l - \underline{r}_m|} - \sum_l^{N_e} \sum_m^{N_n} \frac{Z_m e^2}{4\pi\epsilon_0 |\underline{r}_l - \underline{R}_m|} - \sum_{l=1}^{N_n}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

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

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

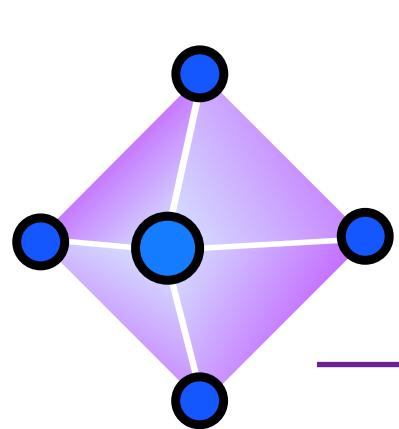
$$\hat{X} + \hat{x} = \frac{\lambda_{\alpha}}{\omega_{\alpha}} \cdot \sum_{l=1}^{N_n} Z_l |e| \underline{R}_l - \frac{\lambda_{\alpha}}{\omega_{\alpha}} \cdot \sum_{l=1}^{N_e} |e| \underline{r}_l$$

Considered
good for **vibrational**
strong coupling

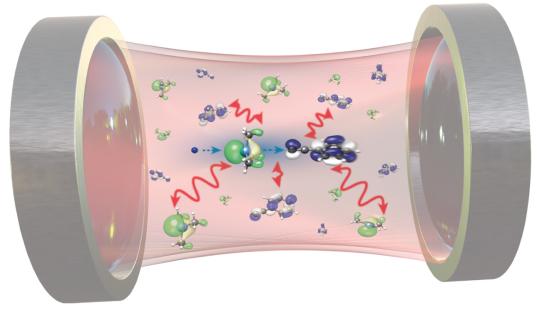


Considered
good for **electronic**
strong coupling

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



Repetition: Cavity Born-Oppenheimer Approach



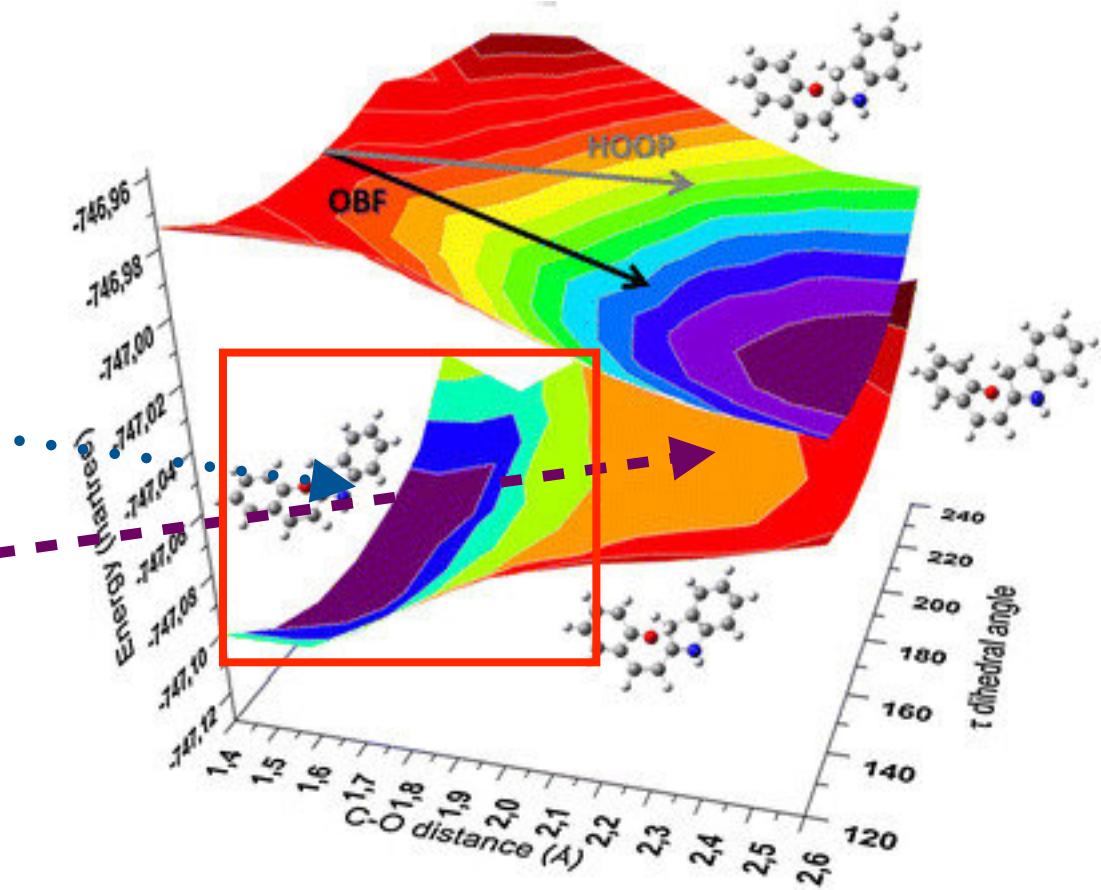
$$\sum_{i=0}^{\infty} \chi_i(\underline{R}, \underline{q}) \psi_i(\underline{r}; \{\underline{R}, \underline{q}\})$$

Dressed electronic structure problem

parametric dependency on nuclear and displacement field coordinates:

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

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 $E_0(\underline{R}, \underline{q})$.



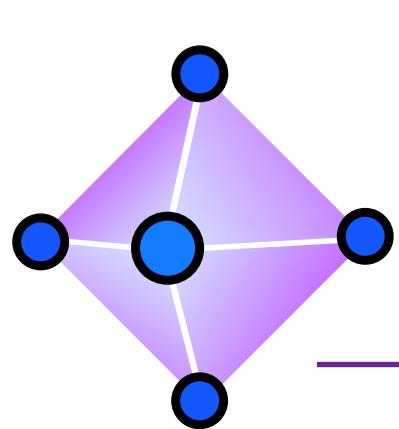
If $E_1 - E_0 \approx k_B T$, **non-adiabatic coupling** elements $i \neq j \neq 0$ between PES start to play a role, i.e. electronically excited PES.

Nuclear / displacement field problem:

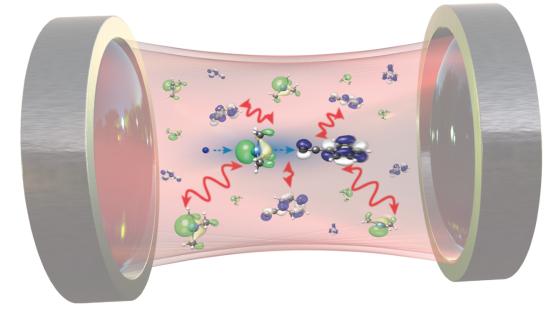
$$E\chi_i(\underline{R}, \underline{q}) = E_i(\underline{R}, \underline{q}) \chi_i(\underline{R}, \underline{q}) + \sum_{j=0}^{\infty} \int d\underline{r} \psi_j^*(\underline{r}; \{\underline{R}, \underline{q}\})$$

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

Today we assume: $E_1 - E_0 \gg k_B T$, i.e., vibrations and displacement field properties „solely“ affected by the electronic structure of the (cavity-modified) **ground-state PES** $E_0(\underline{R}, \underline{q})$



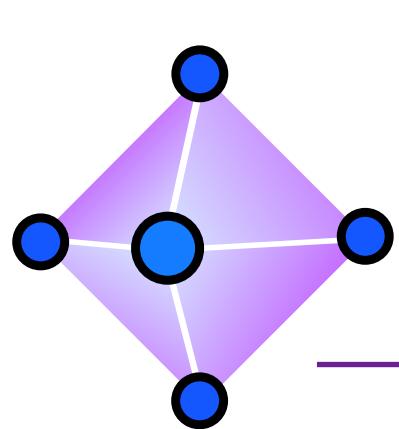
Lecture Outline



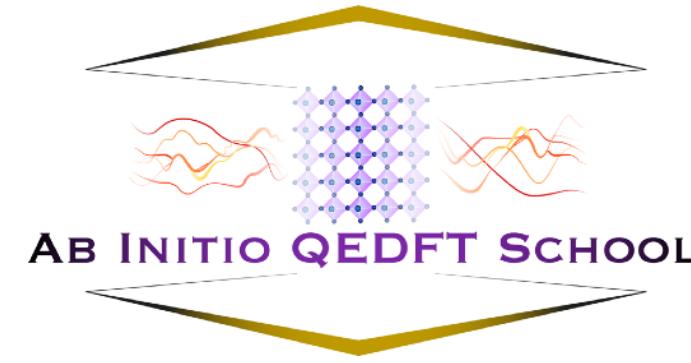
Aim: cavity Born-Oppenheimer molecular dynamics simulation for vibrational strong coupling.

1. Ab-initio Born-Oppenheimer MD applied on **illustrative model** Hamiltonian:
 1. Dressed **electronic** properties (cavity-modified **polarizability** and **forces**).
 2. classical **nuclear-displacement** field dynamics.
2. **MD simulation at finite temperature** (numerical time-propagation on a computer, Langevin equation of motion).
3. Assignment of **mandatory exercise 5** over the extended Easter break. Simulating an ensemble of CO₂ (model) molecules under **collective VSC**.

Remark: Notation of photon modes inconsistent throughout the lecture. $\hat{q}_\alpha \leftrightarrow \hat{q}_\beta$ used interchangeably.



Ab initio solution strategies



Cavity Born-Oppenheimer (CBO) Equations

Stationary Schrödinger equation

$$\hat{H}\Psi_i(\mathbf{r}, \mathbf{R}, \mathbf{q}) = E_i\Psi_i(\mathbf{r}, \mathbf{R}, \mathbf{q})$$

$$\hat{X} = \frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_n} Z_l |e| \mathbf{R}_l$$

cavity Born-Oppenheimer partitioning

$$\Psi_i(\mathbf{r}, \mathbf{R}, \mathbf{q}) = \sum_{j=1}^{\infty} \chi_{ij}(\mathbf{R}, \mathbf{q}) \psi_j(\mathbf{r}, \{\mathbf{R}, \mathbf{q}\})$$

$$\hat{x} = -\frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_e} |e| \mathbf{r}_l$$

Dressed electronic
Schrödinger equation

$$\hat{H}^e(\mathbf{R}, q_\alpha) := \hat{H}_m^e(\mathbf{R}, q_\alpha) + \frac{1}{2}\hat{x}^2 + \hat{x}X - \omega_\alpha \hat{x}q_\alpha,$$

$$\hat{H}^e(\mathbf{R}, q_\alpha)\psi_j(\mathbf{r}, \{\mathbf{R}, \mathbf{q}\}) = \epsilon_j(\mathbf{R}, \mathbf{q})\psi_j(\mathbf{r}, \{\mathbf{R}, \mathbf{q}\})$$

Non-adiabatically coupled nuclear-photon eigenvalue problem

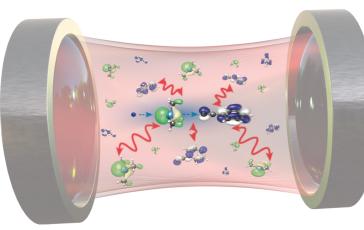
$$\begin{aligned} \hat{H}^{\text{npt}} &:= \hat{H}_m^n + \frac{\hat{p}_\alpha^2}{2} + \frac{\omega_\alpha^2}{2} \left(\hat{q}_\alpha - \frac{\hat{X}}{\omega_\alpha} \right)^2 \\ [\hat{H}^{\text{npt}} + \epsilon_k(\mathbf{R}, \mathbf{q})] \chi_{ik}(\mathbf{R}, \mathbf{q}) + \sum_{j=1}^{\infty} \left(\int d\mathbf{r} \psi_k^*(\mathbf{r}, \{\mathbf{R}, \mathbf{q}\}) [\hat{T}^n + \hat{T}^{\text{pt}}] \psi_j(\mathbf{r}, \{\mathbf{R}, \mathbf{q}\}) \chi_{ij}(\mathbf{R}, \mathbf{q}) \right) &= E_i \chi_{ik}(\mathbf{R}, \mathbf{q}) \end{aligned}$$

Cavity Born-Oppenheimer approximation (neglect non-adiabatic couplings)

$$\left[\hat{H}^{\text{npt}} + \epsilon_k(\mathbf{R}, \mathbf{q}) + \left(\int d\mathbf{r} \psi_j^*(\mathbf{r}, \{\mathbf{R}, \mathbf{q}\}) [\hat{T}^n + \hat{T}^{\text{pt}}] \psi_j(\mathbf{r}, \{\mathbf{R}, \mathbf{q}\}) \right) \right] \chi_{ik}(\mathbf{R}, \mathbf{q}) = E_i \chi_{ik}(\mathbf{R}, \mathbf{q})$$

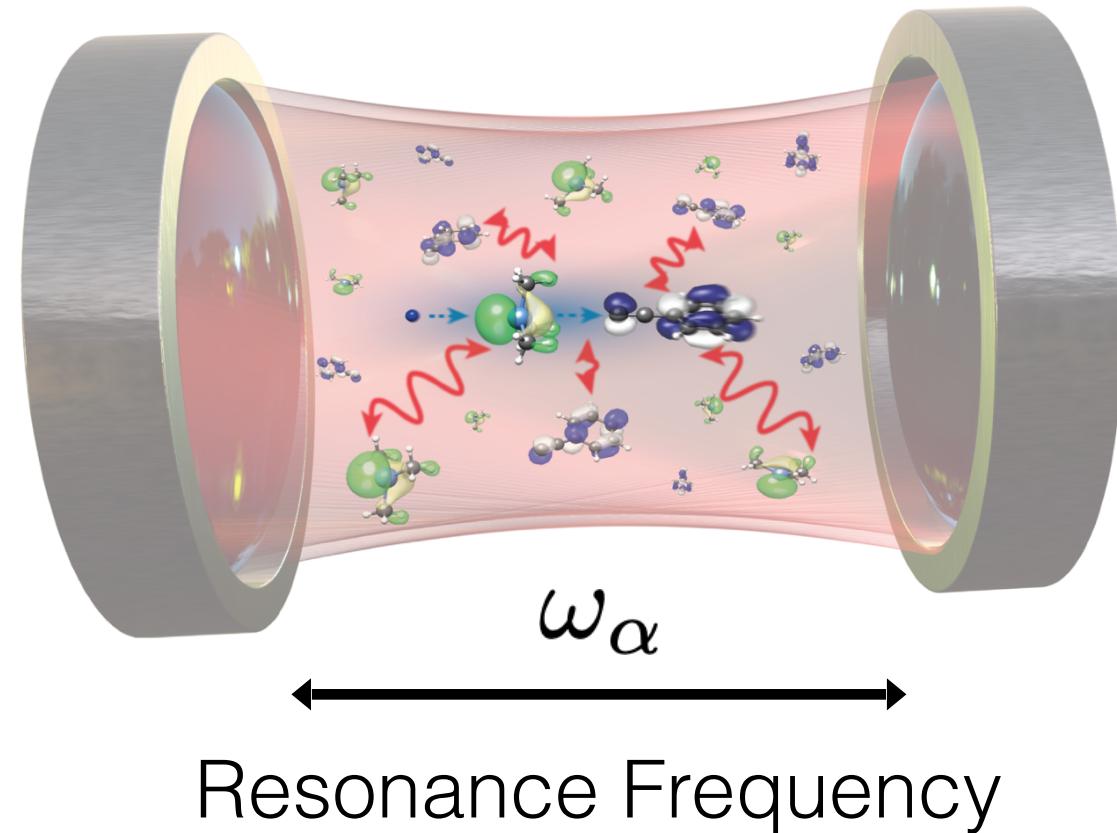
Classical groundstate cavity Born-Oppenheimer approximation

$$H^{\text{npt}} + \epsilon_0(\mathbf{P}, \mathbf{p}, \mathbf{R}, \mathbf{q}) = E_0$$



Ab-initio Insights into VSC

Simplest Case: Classical Cavity Born-Oppenheimer Approximation



$$\hat{H}'_{\text{PF}} = \underbrace{- \sum_{l=1}^{N_e} \frac{\hbar^2}{2m} \nabla_{r_l}^2 + \frac{1}{2} \sum_{l \neq m}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_m|} - \sum_l \sum_m^{N_n} \frac{Z_m e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{R}_m|} - \sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_{\mathbf{R}_l}^2 + \frac{1}{2} \sum_{l \neq m}^{N_n} \frac{Z_l Z_m e^2}{4\pi\epsilon_0 |\mathbf{R}_l - \mathbf{R}_m|}}_{\text{Quantized Matter}} + \sum_{\alpha=1}^{M_p} \left[-\frac{\hbar^2}{2} \frac{\partial^2}{\partial q_\alpha^2} + \frac{\omega_\alpha^2}{2} \left(q_\alpha - \frac{\lambda_\alpha}{\omega_\alpha} \cdot \mathbf{R} \right)^2 \right],$$

Quantized Light — Light-Matter Interaction —

Quantized electronic structure:

Classical nuclei & displacement field:

Classical nuclei \mathbf{R} and fields \mathbf{q}

$$\hat{H}^e := \hat{H}_m^e + \sum_{\alpha=1}^M \left(\frac{1}{2} \hat{x}_\alpha^2 + \hat{x}_\alpha X_\alpha - \omega_\alpha \hat{x}_\alpha q_\alpha \right)$$

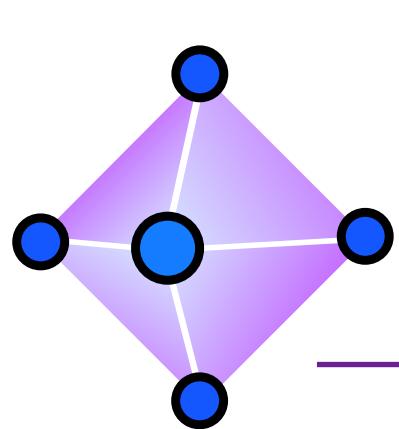
Ab-initio MD

$$H^{\text{npt}} := H_m^n + \sum_{\alpha=1}^M \left(\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2} \left(q_\alpha - \frac{X_\alpha}{\omega_\alpha} \right)^2 + \langle \psi_0 | \hat{H}_e(\underline{\mathbf{R}}, \underline{q}) | \psi_0 \rangle \right)$$

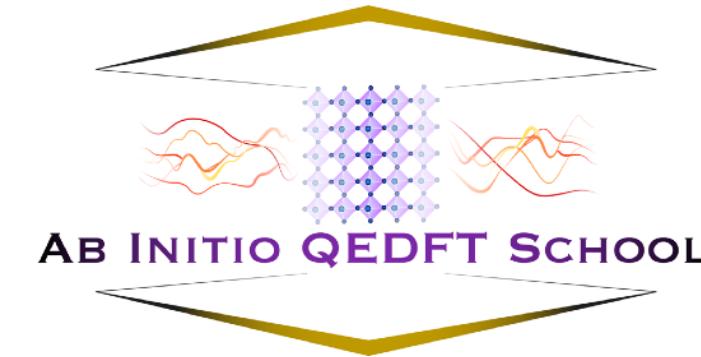
$$\hat{X} + \hat{x} = \frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_n} Z_l |e| \mathbf{R}_l - \frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_e} |e| \mathbf{r}_l$$

Groundstate PES

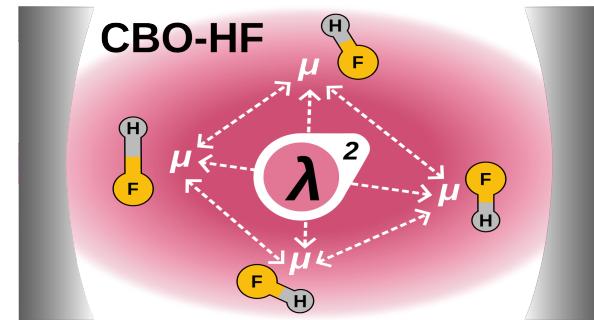
Slightly different definition to previous slide!



Dressed Electronic Problem



Dilute Gas Limit



$$\hat{H}^e := \hat{H}_m^e + \sum_{\alpha=1}^M \left(\frac{1}{2} \hat{x}_{\alpha}^2 + \hat{x}_{\alpha} X_{\alpha} - \omega_{\alpha} \hat{x}_{\alpha} q_{\alpha} \right)$$

Slater determinant Ansatz between N molecules
(Hartree-Fock mean-field)

$$|\Psi\rangle = |\chi_1\rangle \otimes \cdots \otimes |\chi_N\rangle$$

and solve for Ground-state energy

$$\min E_{HF} = \min \langle \psi_{HF} | \hat{H}^e | \psi_{HF} \rangle$$

More details in lecture 6

Mean-field ansatz becomes exact in **dilute gas limit**: **Assume** non-overlapping electronic structure between molecules and zero intermolecular Coulomb Hartree energy!

$$E_{HF} = \sum_{n=1}^N \langle \chi_n | \hat{H}_n^e + \sum_{\alpha=1}^M \left[\frac{1}{2} \hat{x}_{n,\alpha}^2 + \hat{x}_{n,\alpha} X_{\alpha} - \omega_{\alpha} \hat{x}_{n,\alpha} q_{\alpha} \right] | \chi_n \rangle \\ + \frac{1}{2} \sum_{n,m}^N \sum_{\alpha=1}^M \langle \chi_n | \hat{x}_{n,\alpha} | \chi_n \rangle \langle \chi_m | \hat{x}_{m,\alpha} | \chi_m \rangle - \underbrace{\frac{1}{2} \sum_{n,m}^N \sum_{\alpha=1}^M \langle \chi_n | \hat{x}_{n,\alpha} | \chi_m \rangle \langle \chi_m | \hat{x}_{m,\alpha} | \chi_n \rangle}_{\text{Self-consistent coupling to total electronic dipole operator}}$$

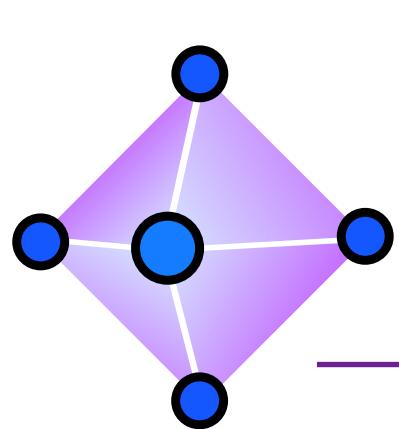
Bare single molecular electronic structure can be solved at arbitrary accuracy using a variational procedures (e.g. full CI)!

$$\hat{H}_m^e = \sum_{n=1}^N \hat{H}_n^e \quad \hat{x}_{n,\alpha} = - \frac{\lambda_{\alpha}}{\omega_{\alpha}} \cdot |e| \mathbf{r}_n$$

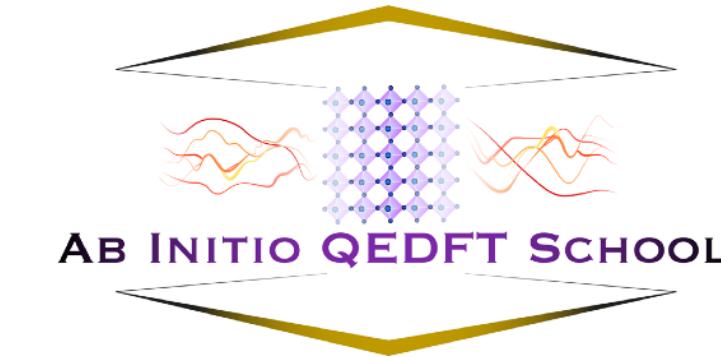
Self-consistent coupling to total electronic dipole operator

HF equations reduce to **N coupled cavity Hartree-equations**

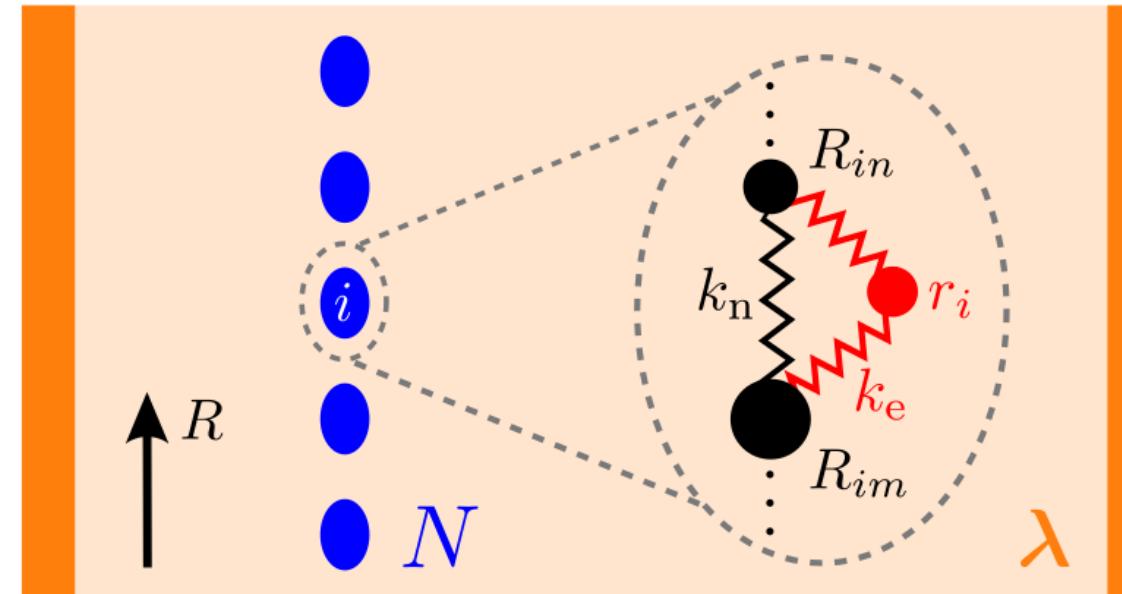
$$\left(\hat{H}_n(\mathbf{R}_n) + \sum_{\alpha=1}^M \left[\frac{p_{\alpha}^2}{2} + \frac{\omega_{\alpha}^2}{2} \left(q_{\alpha} - \frac{X_{\alpha}}{\omega_{\alpha}} \right)^2 + \left(X_{\alpha} - q_{\alpha} \omega_{\alpha} + \sum_{m \neq n}^N \langle \chi_m | \hat{x}_{m,\alpha} | \chi_m \rangle \right) \hat{x}_{n,\alpha} + \frac{\hat{x}_{n,\alpha}^2}{2} \right] \right) \chi_n(\mathbf{z}_1, \dots, \mathbf{z}_{N_e}) = \epsilon_n \chi_n(\mathbf{z}_1, \dots, \mathbf{z}_{N_e})$$



Effective Harmonic Model under VSC



Illustrative Example for Dilute Gas Limit



$$\hat{H}_m = \sum_{i=1}^N \left[\sum_{n=1}^{N_n} \left(\frac{\hat{P}_{in}^2}{2M_n} + \frac{k_e}{2} (\hat{R}_{in} - \hat{r}_i)^2 \right) + \frac{\hat{p}_i^2}{2} + V_i(\hat{\mathbf{R}}_i) \right]$$

$$\hat{H} = \hat{H}_m + \frac{1}{2} \left[\hat{p}_\beta^2 + \omega_\beta^2 \left(\hat{q}_\beta - \frac{\hat{X} + \hat{x}}{\omega_\beta} \right)^2 \right]$$

Harmonic Model Assumptions:

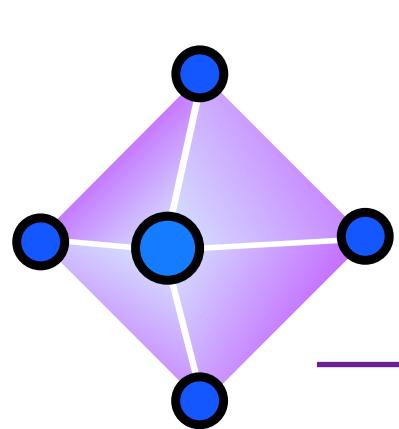
1. Ensemble of N molecules i .
2. One quantized effective electron \hat{r}_i per molecule, which couples harmonically to nuclei of molecule i .
3. N_n classical nuclei R_{in} per molecule that couple harmonically.
4. Molecules are charge neutral.
5. Single cavity-mode q_α couples strongly.
6. Dilute gas approximation based on CBOA partitioning.

cavity Hartree-equations (cH) for dilute N-electron problem:

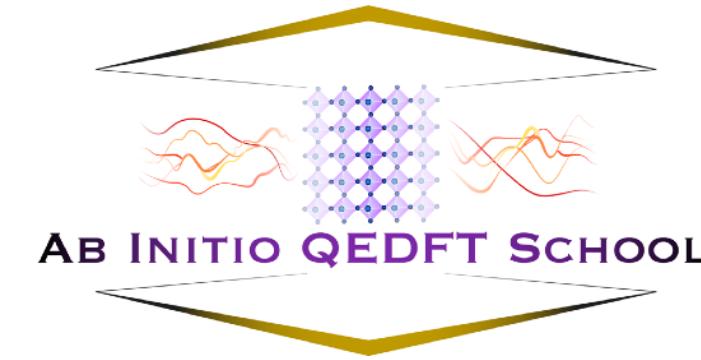
$$\left(\frac{\hat{p}_i^2}{2} - \sum_{n=1}^{N_n} k_e R_{in} \hat{r}_i + N_n k_e \frac{\hat{r}_i^2}{2} \right) + \left(X - q_\alpha \omega_\alpha + \sum_{j \neq i}^N \langle \psi_j | \hat{x}_j | \psi_j \rangle \right) \hat{x}_i + \frac{\hat{x}_i^2}{2} \Big) \psi_i = \varepsilon_i \psi_i$$

Harmonic effective single electron coupled to N_n nuclei

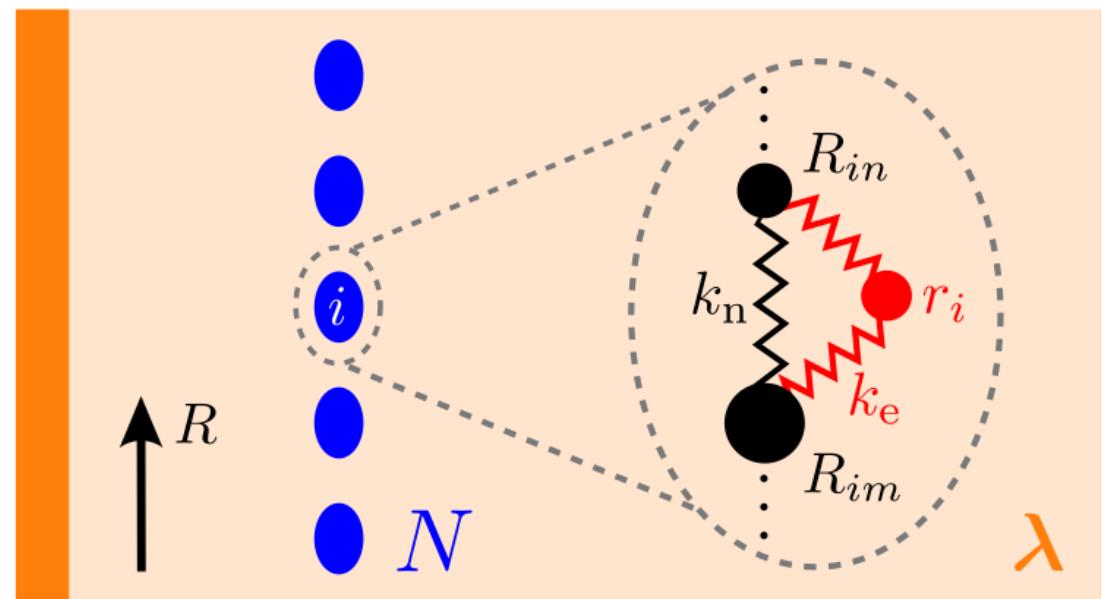
Collective light-matter coupling



Effective Harmonic Model under VSC



Analytic Solution of N Coupled Cavity Hartree Equations



$$\left(\frac{\hat{p}_i^2}{2} - \sum_{n=1}^{N_n} k_e R_{in} \hat{r}_i + N_n k_e \frac{\hat{r}_i^2}{2} \right) + \left(X - q_\alpha \omega_\alpha + \sum_{j \neq i}^N \langle \psi_j | \hat{x}_j | \psi_j \rangle \right) \hat{x}_i + \frac{\hat{x}_i^2}{2} \right) \psi_i = \varepsilon_i \psi_i$$

Harmonic effective single electron coupled to N_n nuclei

Collective light-matter coupling

N shifted harmonic oscillators:

$$\left[\frac{\hat{p}_i^2}{2} + \nu_{1,i} \hat{r}_i + \frac{\nu_2^2}{2} \hat{r}_i^2 \right] \psi_i(r_i) = \epsilon_i \psi_i(r_i),$$

$$\nu_{1,i} := -k_e \sum_{n=1}^{N_n} R_{in} + Z_e \lambda (-X + \omega_\alpha q_\alpha + Z_e \mu_i) \quad \mu_i := \lambda \sum_{j \neq i}^N \langle \psi_j | \hat{r}_j | \psi_j \rangle$$

$$\nu_2 := \sqrt{\lambda^2 Z_e^2 + N_n k_e}$$

See blackboard

Energies:

$$\begin{aligned} \epsilon_i^l &= \left\langle \left(\hat{b}_i^\dagger \hat{b}_i + \frac{1}{2} - \eta_i^2(\mathbf{R}, q_\alpha) \right) \nu_2 \right\rangle_l \\ &= \left(l + \frac{1}{2} - \eta_i^2(\mathbf{R}, q_\alpha) \right) \nu_2 \\ \eta_i(\mathbf{R}, q_\alpha) &= \frac{\nu_{1,i}}{\sqrt{2\nu_2^3}} \end{aligned}$$

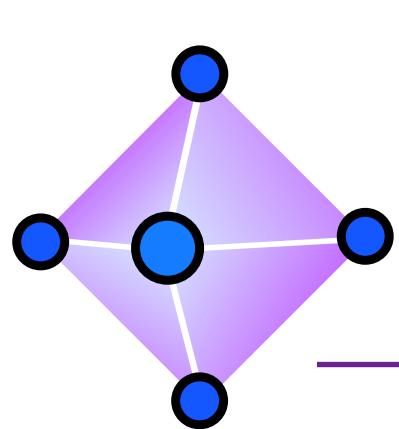
$$\hat{b}_i^\dagger = \hat{a}_i^\dagger + \eta_i, \quad \hat{b}_i = \hat{a}_i + \eta_i$$

Analytic electronic position:

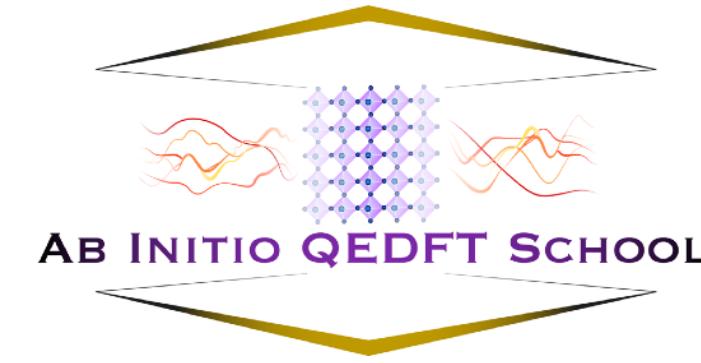
$$\hat{r}_i = \sqrt{1/2\nu_2} (\hat{a}_i^\dagger + \hat{a}_i)$$

$$E_\perp = \lambda(\omega_\alpha q_\alpha - X - \langle x \rangle)$$

$$\begin{aligned} \langle \hat{r}_i \rangle_0 &= -\sqrt{\frac{1}{2\nu_2}} (\eta_i + \eta_i^*) = -\frac{\nu_{1,i}}{\nu_2^2} \\ &= \frac{1}{\nu_2^2} \left(k_e \sum_{n=1}^{N_n} R_{in} + Z_e \lambda \left(X - \omega_\alpha q_\alpha - \lambda Z_e \left(\sum_j^N \langle \hat{r}_j \rangle_0 - \langle \hat{r}_i \rangle_0 \right) \right) \right) \\ &= \frac{1}{N_n} \left(\sum_{n=1}^{N_n} R_{in} + \frac{\lambda Z_e}{k_e} \left(X + \langle x \rangle_0 - \omega_\alpha q_\alpha \right) \right) \\ &= \frac{1}{N_n} \left(\sum_{n=1}^{N_n} R_{in} - \frac{E_\perp Z_e}{k_e} \right) \end{aligned}$$



Molecular Polarizability in a Cavity



Blackboard: Collectively-induced Local Polarizability Modifications

Static electronic polarizability for ensemble of N (interacting) molecules:

$$\alpha = \frac{\partial \langle d \rangle}{\partial E_{\text{ext}}} = \sum_i^N Z_e \frac{\partial \langle \hat{r}_i \rangle}{\partial E_{\text{ext}}}. \quad \text{with } \hat{H}_{\text{tot}} = \hat{H} - \hat{d}E_{\text{ext}}$$

Harmonic **bare matter** polarizability for N **non-interacting** molecules:

$$\alpha = N \underbrace{\frac{Z_e^2}{N_n k_e}}_{\alpha_i},$$

$$\tilde{\alpha}_i = \frac{\partial \langle d_i \rangle}{\partial E_{\text{ext}}} \quad \text{with } \hat{H}_{\text{tot}} = \hat{H} - \hat{d}E_{\text{ext}}$$

Static electronic polarizability for **single molecule in ensemble** of N molecules:

$$\tilde{\alpha}(N, \lambda) = \alpha \gamma^2(N, \lambda),$$

$$\tilde{\alpha}_i(N, \lambda) = \alpha_i \boxed{\gamma^2(N, \lambda)},$$

Self-consistent solution within a cavity including external electric field E_{ext}

$$\gamma^2(N, \lambda) = \frac{1}{1 + \lambda^2 N \alpha_i}, \quad 0 < \gamma^2 \leq 1.$$

Perturbative solution for external electric field perturbation E_{ext} within a cavity

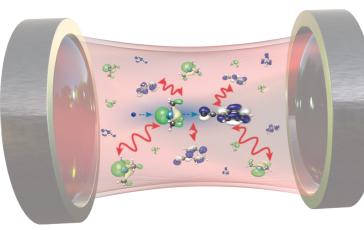
$$\tilde{\alpha}^{\text{pert}}(N, \lambda) = N \tilde{\alpha}_i^{\text{pert}}(N, \lambda).$$

$$\tilde{\alpha}_i^{\text{pert}}(N, \lambda) = \alpha_i \boxed{\gamma^2(1, \lambda)}$$

$$\alpha_i \gamma^2(1, \lambda_{\text{TC}}) \xrightarrow{N \gg 1} \alpha_i,$$

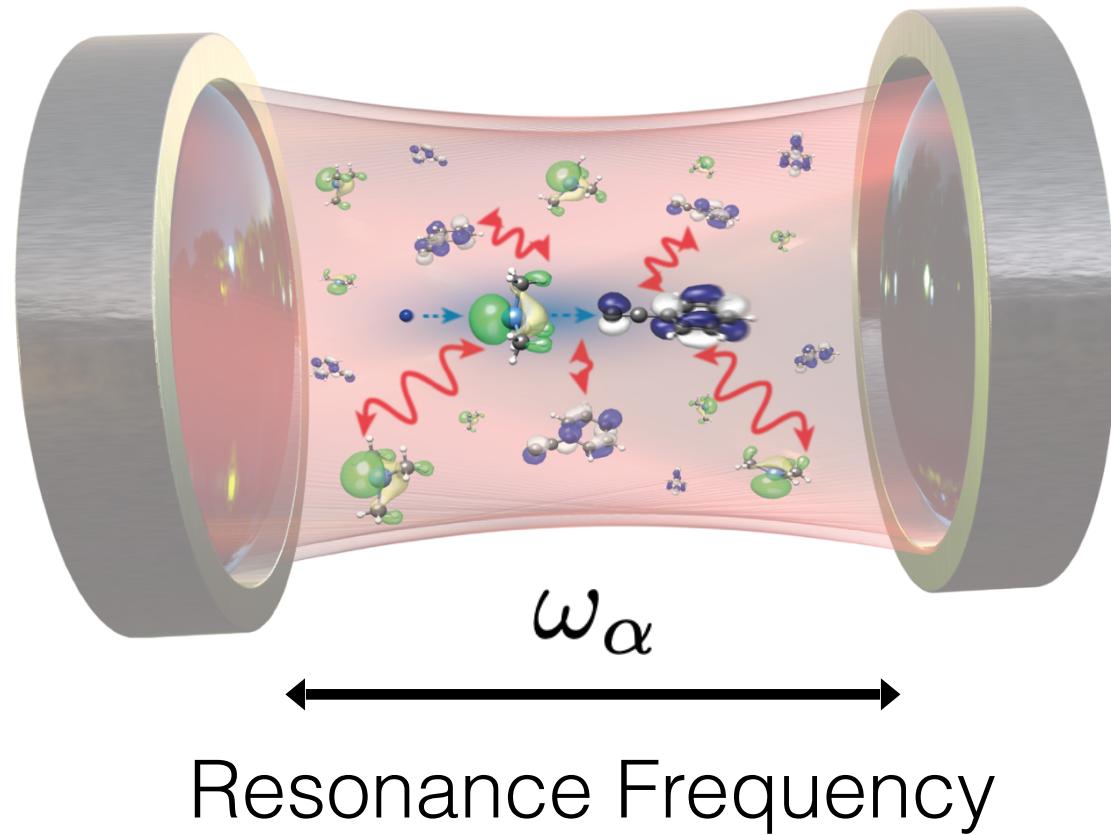
Collective Rabi splitting dependency!

Local Rabi splitting dependency!



Ab-initio Insights into VSC

Simplest Case: Classical Cavity Born-Oppenheimer Approximation



$$\hat{H}'_{\text{PF}} = \underbrace{- \sum_{l=1}^{N_e} \frac{\hbar^2}{2m} \nabla_{r_l}^2 + \frac{1}{2} \sum_{l \neq m}^{N_e} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{r}_m|} - \sum_l \sum_m^{N_n} \frac{Z_m e^2}{4\pi\epsilon_0 |\mathbf{r}_l - \mathbf{R}_m|} - \sum_{l=1}^{N_n} \frac{\hbar^2}{2M_l} \nabla_{\mathbf{R}_l}^2 + \frac{1}{2} \sum_{l \neq m}^{N_n} \frac{Z_l Z_m e^2}{4\pi\epsilon_0 |\mathbf{R}_l - \mathbf{R}_m|}}_{\text{Quantized Matter}} + \sum_{\alpha=1}^{M_p} \left[-\frac{\hbar^2}{2} \frac{\partial^2}{\partial q_\alpha^2} + \frac{\omega_\alpha^2}{2} \left(q_\alpha - \frac{\lambda_\alpha}{\omega_\alpha} \cdot \mathbf{R} \right)^2 \right],$$

— Quantized Light — Light-Matter Interaction

Quantized electronic structure:

Classical nuclei &
displacement field:

Classical nuclei \mathbf{R} and fields \mathbf{q}

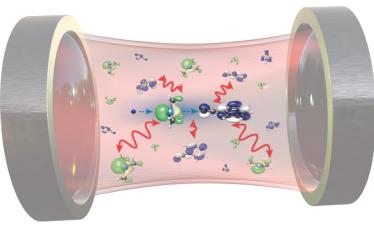
$$\hat{H}^e := \hat{H}_m^e + \sum_{\alpha=1}^M \left(\frac{1}{2} \hat{x}_\alpha^2 + \hat{x}_\alpha X_\alpha - \omega_\alpha \hat{x}_\alpha q_\alpha \right)$$

Ab-initio MD

$$H^{\text{npt}} := H_m^n + \sum_{\alpha=1}^M \left(\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2} \left(q_\alpha - \frac{X_\alpha}{\omega_\alpha} \right)^2 + \langle \psi_0 | \hat{H}_e(\underline{\mathbf{R}}, \underline{q}) | \psi_0 \rangle \right)$$

$$\hat{X} + \hat{x} = \frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_n} Z_l |e| \mathbf{R}_l - \frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_e} |e| \mathbf{r}_l$$

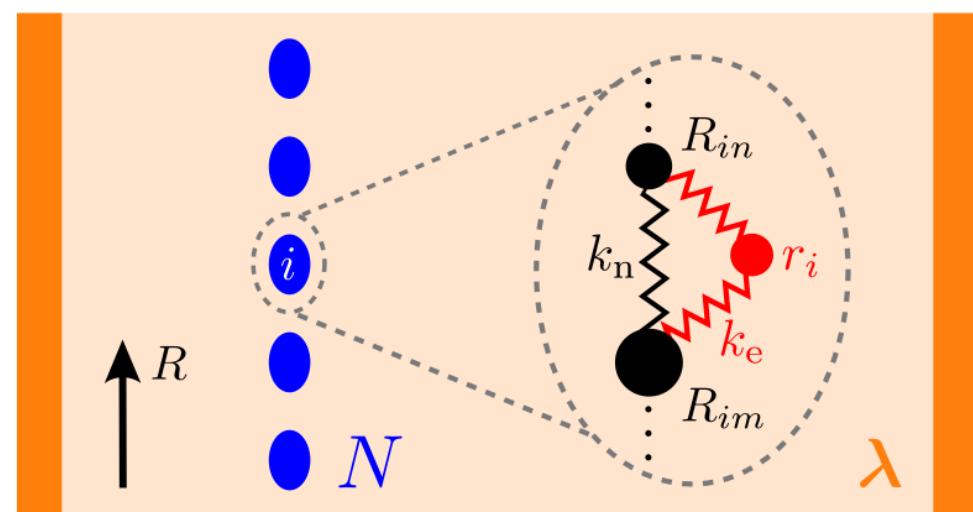
Groundstate PES



Groundstate Ab-initio MD

Blackboard: Classical Hamiltonian Equations of Motion

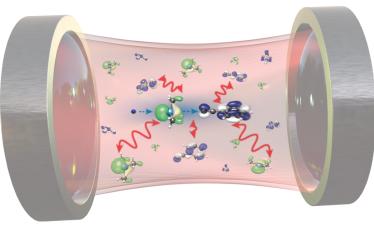
Nuclear-displacement field Hamiltonian for harmonic model:



$$\begin{aligned}\hat{H}^{\text{npt},l} := & \sum_{i=1}^N \left[\sum_{n=1}^{N_n} \left(\frac{\hat{P}_{in}^2}{2M_n} + \frac{k_e}{2} \hat{R}_{in}^2 \right) + V_i(\hat{\mathbf{R}}_i) \right] \\ & + \frac{\hat{p}_\beta^2}{2} + \frac{\omega_\beta^2}{2} \left(\hat{q}_\beta - \frac{\hat{X}}{\omega_\beta} \right)^2 \\ & + \underbrace{\langle \Psi_l | \hat{H}^e(\mathbf{R}, q_\beta) | \Psi_l \rangle}_{=E_l^e(\mathbf{R}, q_\beta)}.\end{aligned}$$

Classical Hamiltonian equations of motion for electronic groundstate:

$$\begin{aligned}\frac{dR_{in}}{dt} &= \frac{\partial H^{\text{npt},0}}{\partial P_{in}} & \frac{dP_{in}}{dt} &= - \frac{\partial H^{\text{npt},0}}{\partial R_{in}} \\ \frac{dq_\beta}{dt} &= \frac{\partial H^{\text{npt},0}}{\partial p_\beta} & \frac{dp_\beta}{dt} &= - \frac{\partial H^{\text{npt},0}}{\partial q_\beta}\end{aligned}$$



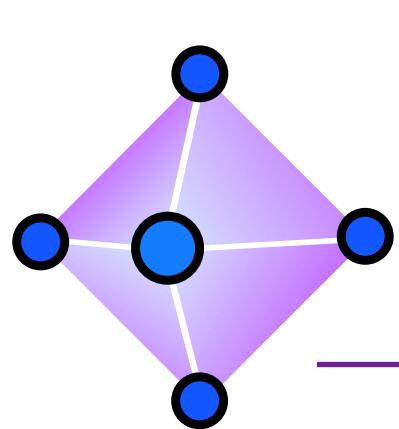
Groundstate Ab-initio MD

Remark: Classical Forces from Approximate Electronic Structure

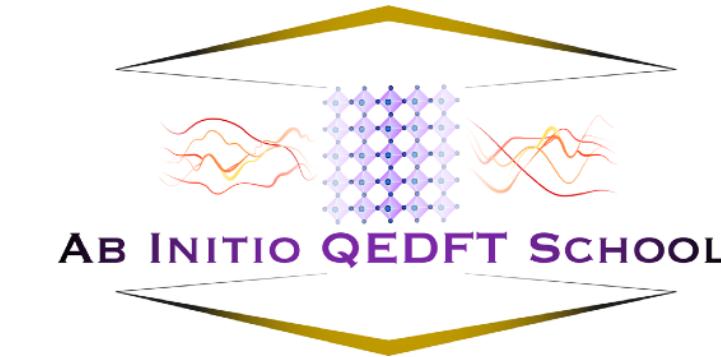
$$\begin{aligned}\frac{dE}{d\mathbf{R}} &= \frac{d}{d\mathbf{R}} \langle \psi | \hat{H} | \psi \rangle \\ &= \left\langle \frac{d\psi}{d\mathbf{R}} \middle| \hat{H} \middle| \psi \right\rangle + \left\langle \psi \middle| \hat{H} \middle| \frac{d\psi}{d\mathbf{R}} \right\rangle + \left\langle \psi \middle| \frac{d\hat{H}}{d\mathbf{R}} \middle| \psi \right\rangle \\ &= \underbrace{E \left\langle \frac{d\psi}{d\mathbf{R}} \middle| \psi \right\rangle}_{0 \text{ for complete basis set}} + E \left\langle \psi \middle| \frac{d\psi}{d\mathbf{R}} \right\rangle + \boxed{\left\langle \psi \middle| \frac{d\hat{H}}{d\mathbf{R}} \middle| \psi \right\rangle}.\end{aligned}$$

Pulay force: in practice (numerics) non-vanishing because basis sets not complete!

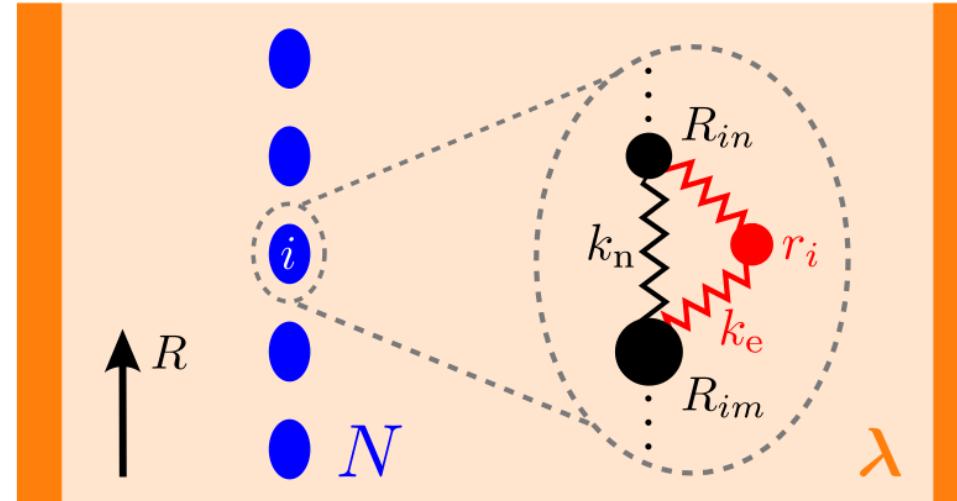
Hellmann-Feynman theorem: Applicable for complete basis sets and variational methods (e.g. Hartree-Fock, DFT, etc.).
See also next lecture.



Effective Harmonic Model under VSC



Classical Equations of Motion

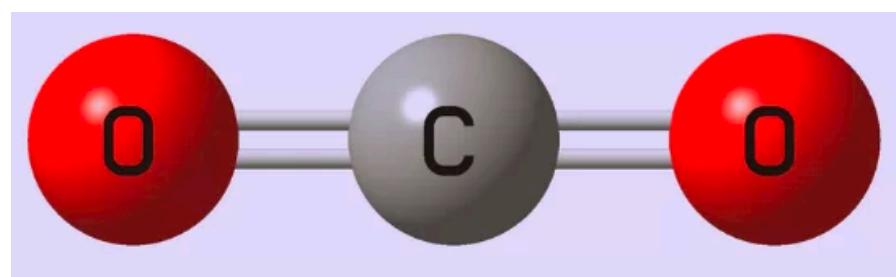


Hellmann-Feynman theorem

$$\begin{aligned} M_n \ddot{R}_{in} &= -\frac{d}{dR_{in}} \langle \hat{H} \rangle_l = -\langle \left(\frac{d}{dR_{in}} \hat{H} \right) \rangle_l \\ &= -\frac{d}{dR_{in}} V(\mathbf{R}_i) - k_e(R_{in} - \langle \hat{r}_i \rangle_l) \\ &\quad + \omega_\alpha \left(q_\alpha - \left(\frac{X + \langle \hat{x} \rangle_l}{\omega_\alpha} \right) \right) \lambda Z_n. \end{aligned}$$

$$\begin{aligned} \langle \hat{r}_i \rangle_0 &= -\frac{d}{dR_{in}} V(\mathbf{R}_i) - k_e \left(R_{in} - \sum_{m=1}^{N_n} \frac{R_{im}}{N_n} \right) && \text{bare matter} \\ E_\perp &= \lambda \left(\omega_\beta q_\beta - X - \langle x \rangle \right) + \left(Z_n - \frac{Z_e}{N_n} \right) E_\perp. && \text{cavity} \end{aligned}$$

no coupling for neutral atoms



Example: Nuclear-displacement field dynamics of **harmonic CO₂** in 1D with one effective harmonic electron under VSC

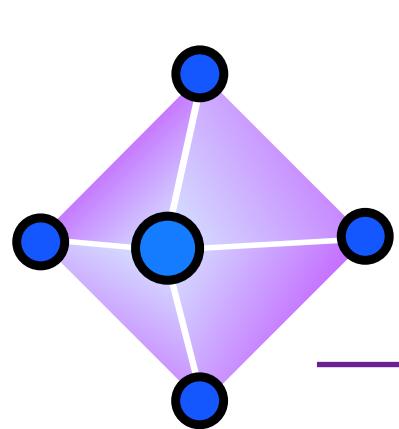
$$H_{\text{CO}_2}^i = \frac{P_{i1}^2}{2M_O} + \frac{P_{i2}^2}{2M_C} + \frac{P_{i3}^2}{2M_O} + \frac{k_n}{2}(R_{i1} - R_{i2})^2 + \frac{k_n}{2}(R_{i2} - R_{i3})^2,$$

$$M = 2M_O + M_C.$$

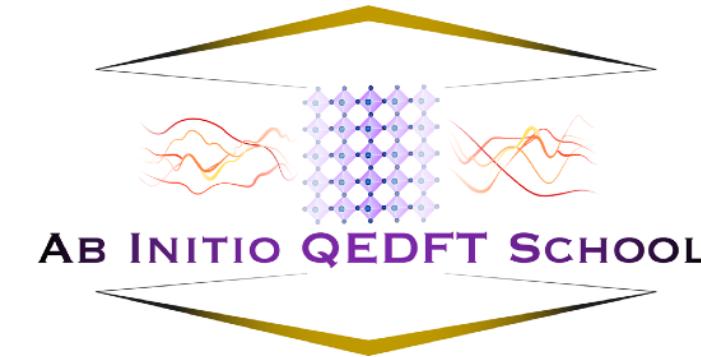
$$\begin{aligned} \rho_{t,i} &= \frac{1}{\sqrt{M}} (M_O R_{i1} + M_C R_{i2} + M_O R_{i3}), \\ \rho_{s,i} &= \frac{1}{\sqrt{2}} \left(\sqrt{M_O} R_{i1} - \sqrt{M_C} R_{i3} \right), \\ \rho_{a,i} &= \frac{\sqrt{M_O M_C}}{\sqrt{M}} (R_{i1} - 2R_{i2} + R_{i3}), \end{aligned}$$

Normal mode transformation

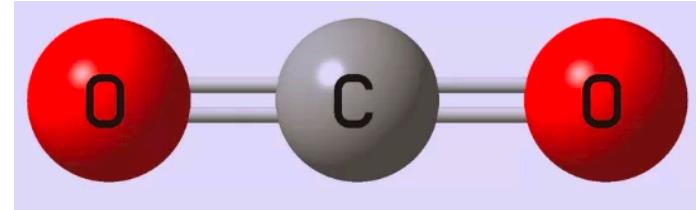
$$\begin{aligned} \ddot{\rho}_{t,i} &= 0, \\ \ddot{\rho}_{s,i} &= - \underbrace{\frac{k_n}{M_O}}_{=k_s} \rho_{s,i}, \\ \ddot{\rho}_{a,i} &= - \underbrace{\frac{M k_n}{M_O M_C}}_{=k_a} \rho_{a,i}. \end{aligned}$$



Harmonic CO₂ under VSC

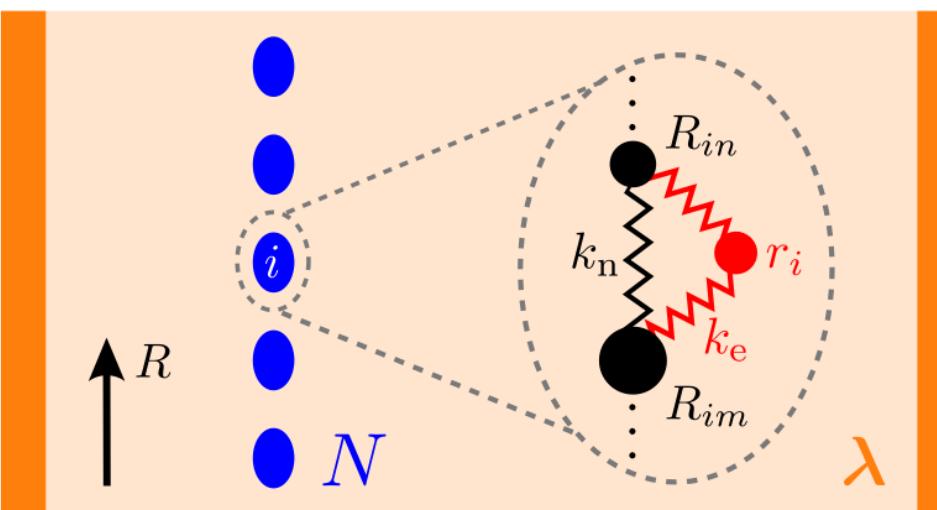


Normal Mode Dynamics



Coupling to the cavity:

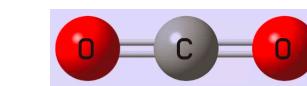
$$E_{\perp} = \lambda \gamma^2 (\omega_{\beta} q_{\beta} + \boxed{\lambda \epsilon_a \rho_a})$$



Local dynamics:

$$\begin{aligned}\ddot{\rho}_{t,i} &= 0, \\ \ddot{\rho}_{s,i} &= -k_s \rho_{s,i}, \\ \ddot{\rho}_{a,i} &= -\boxed{k_a \rho_{a,i}} - \boxed{2(\epsilon_a \lambda \rho_a + \omega_{\beta} q_{\beta}) \epsilon_a \gamma^2 \lambda},\end{aligned}$$

$$2Z_O + Z_C = Z_e. \quad \epsilon_a = \frac{\sqrt{M}(Z_C - Z_O)}{3\sqrt{M_C}\sqrt{M_O}}.$$



Collective dynamics:

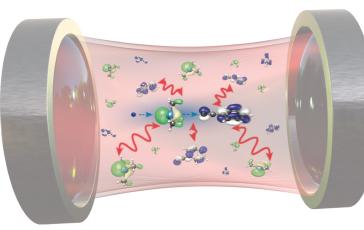
$$\begin{aligned}\ddot{\rho}_t &= 0, \\ \ddot{\rho}_s &= -k_s \rho_s, \\ \ddot{\rho}_a &= -\underbrace{(k_a + 2N\epsilon_a^2 \lambda^2 \gamma^2)}_{=\tilde{k}_a} \rho_a - \frac{2N\epsilon_a \lambda}{\omega_{\beta}} \tilde{\omega}_{\beta}^2 q_{\beta}, \\ \ddot{q}_{\beta} &= -\underbrace{\omega_{\beta}^2 \gamma^2}_{=\tilde{\omega}_{\beta}^2} q_{\beta} - \gamma^2 \omega_{\beta} \epsilon_a \lambda \rho_a.\end{aligned}$$

Hellmann-Feynman

Properties:

- detuning of cavity mode
- only IR active mode couple (linear response picture applies for harmonic model).
- different local and collective matter resonances?

Things get messy... We will need an exercise:-)



Groundstate Ab-initio MD

Numerical Integration (Time-Propagation) of Newton's Equations of Motion

Example: Verlet Integrator properties:

- Simple implementation
- Stable, i.e., approaches correct solution in (some) limit.
- time-reversible (forward / backward propagation possible).
- Symplectic, i.e., system properties should be maintained over long simulation times (e.g. conservation of energy).

$$\text{Newton's eom: } \ddot{\mathbf{r}}(t) = \frac{F(r(t))}{M}$$

Velocity Verlet Integrator (different one implemented in exercise 5, details do not matter):

Intermediate velocity update:

$$\dot{\mathbf{r}}\left(t + \frac{\Delta t}{2}\right) = \dot{\mathbf{r}}(t) + \frac{1}{2}\ddot{\mathbf{r}}(t)\Delta t$$

Position update:

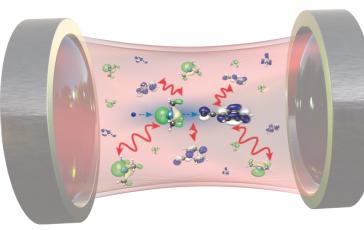
$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \dot{\mathbf{r}}\left(t + \frac{\Delta t}{2}\right)\Delta t$$

Acceleration update / force calculation:

$$\ddot{\mathbf{r}}(t + \Delta t) = \frac{F(r(t + \Delta t))}{M}$$

Final velocity update:

$$\dot{\mathbf{r}}(t + \Delta t) = \dot{\mathbf{r}}\left(t + \frac{\Delta t}{2}\right) + \frac{1}{2}\ddot{\mathbf{r}}(t + \Delta t)\Delta t$$



Groundstate Ab-initio MD

Blackboard: Thermal Equilibrium - Langevin Equations of Motion - Observables in MD

Canonical equilibrium dynamics at temperature T, **Langevin equation of motion** (eom):

$$M\ddot{R} = F - \gamma_T M\dot{R} + \sqrt{2M\gamma_T k_b T} S$$

Gaussian random noise (uncorrelated)

$$\langle S(t) \rangle_t = 0 \quad \langle S(t)S(t') \rangle_t = \delta(t - t')$$

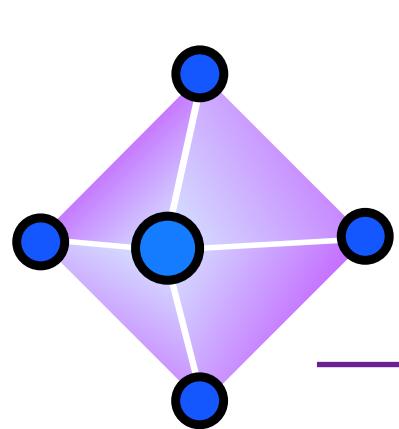
Friction coefficient γ_T

Simulating / calculating (canonical) **ensemble averages from time-averages**:

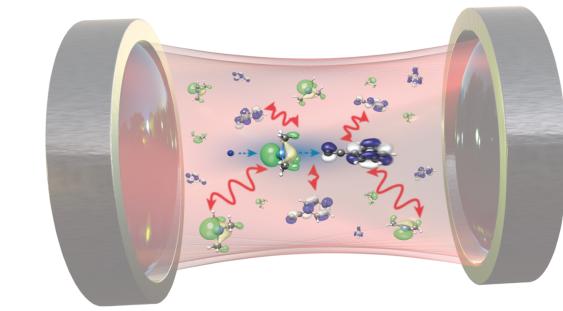
$$\langle O \rangle_T = \frac{\int O(p, r) e^{-\frac{H(p, r)}{k_B T}} dp dr}{\int e^{-\frac{H(p, r)}{k_B T}} dp dr} \stackrel{\text{ergodicity}}{=} \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t O(p(t'), r(t')) dt'$$

↑
Canonical dynamics from Langevin eom

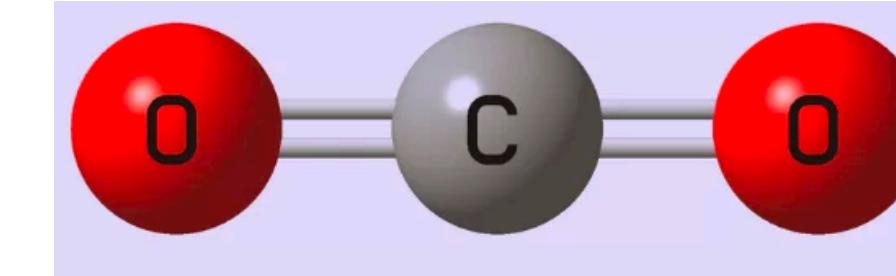
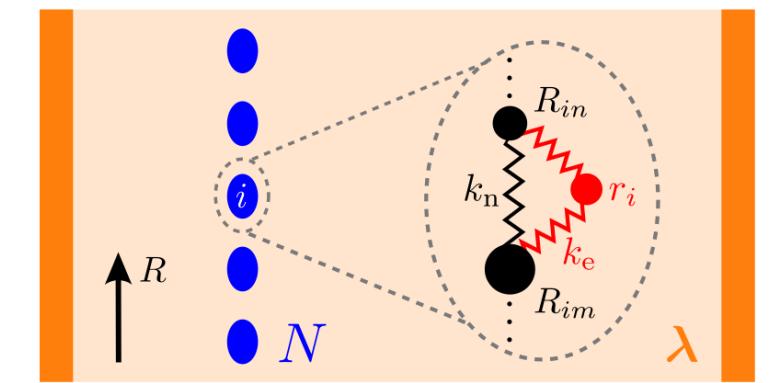
Now we are ready for an ab-initio MD exercise under VSC!



Exercise 5



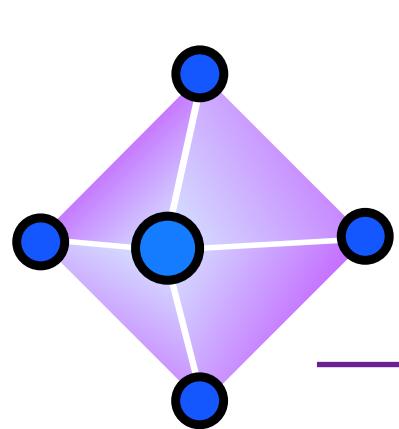
Groundstate Cavity Born-Oppenheimer Molecular Dynamics



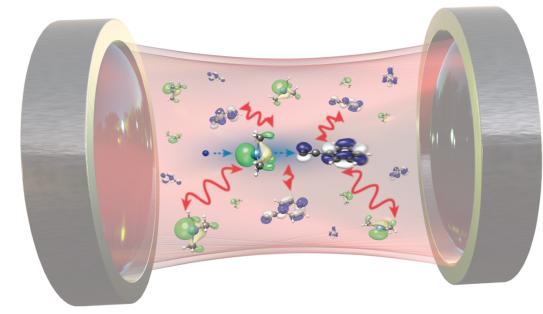
To obtain the **credit points** for the UZH Polaritonic / QED chemistry lecture, please submit a **PDF report** with your answers to this exercise by email (dominik.sidler@psi.ch or dominikurs.sidler@uzh.ch). The report should **not be longer than 3 computer written pages** (including the figures). So please be concise! The deadline to hand-in the report is **Sunday, 4th of May**. The answers will briefly be discussed afterwards, during the lecture. To support collaborative research work, you are **allowed to hand-in joint reports**. However, maximally **two authors per report** are allowed!

Notice that there is **no lecture** on three consecutive Mondays (14th April, 21st April and 28th April), which should give you plenty of time to finish your report. If you have questions, you may ask them next week, during or after the lecture.

The report will not be graded, but I expect a serious attempt to answer the questions. Notice, the **final literature talk assignment** (topics will be distributed on the 5th of May), which is also **mandatory** to receive the credit points.



Summary and Conclusion



Cavity Born-Oppenheimer molecular dynamics simulation for vibrational strong coupling.

1. Groundstate ab-initio Born-Oppenheimer MD applied on **illustrative harmonic model** Hamiltonian:
 - A. **Dressed electronic properties:** **Outlook: Solving general electronic problems numerically.**
 - Solving a **shifted quantum-harmonic oscillator** analytically.
 - **Local changes (!) of molecular polarizability** from collective (!) strong coupling. **Non-perturbative solution** of electronic structure required, including external electric fields.
 - Classical forces from Hellmann-Feynman theorem applied on groundstate electronic structure.
 - B. Classical **nuclear-displacement** field dynamics:
 - **Hamiltonian equations of motion.**
 - Fully harmonic model reveals that only **IR active vibrational modes couple to cavity**. (Not necessary the case for more complex (realistic) electronic structure).
2. **MD simulation at finite temperature: Langevin equations of motion, ensemble average from ergodic hypothesis in MD.**
3. **Exercise 5: Todo:** Investigate de-tuning and scaling under VSC.