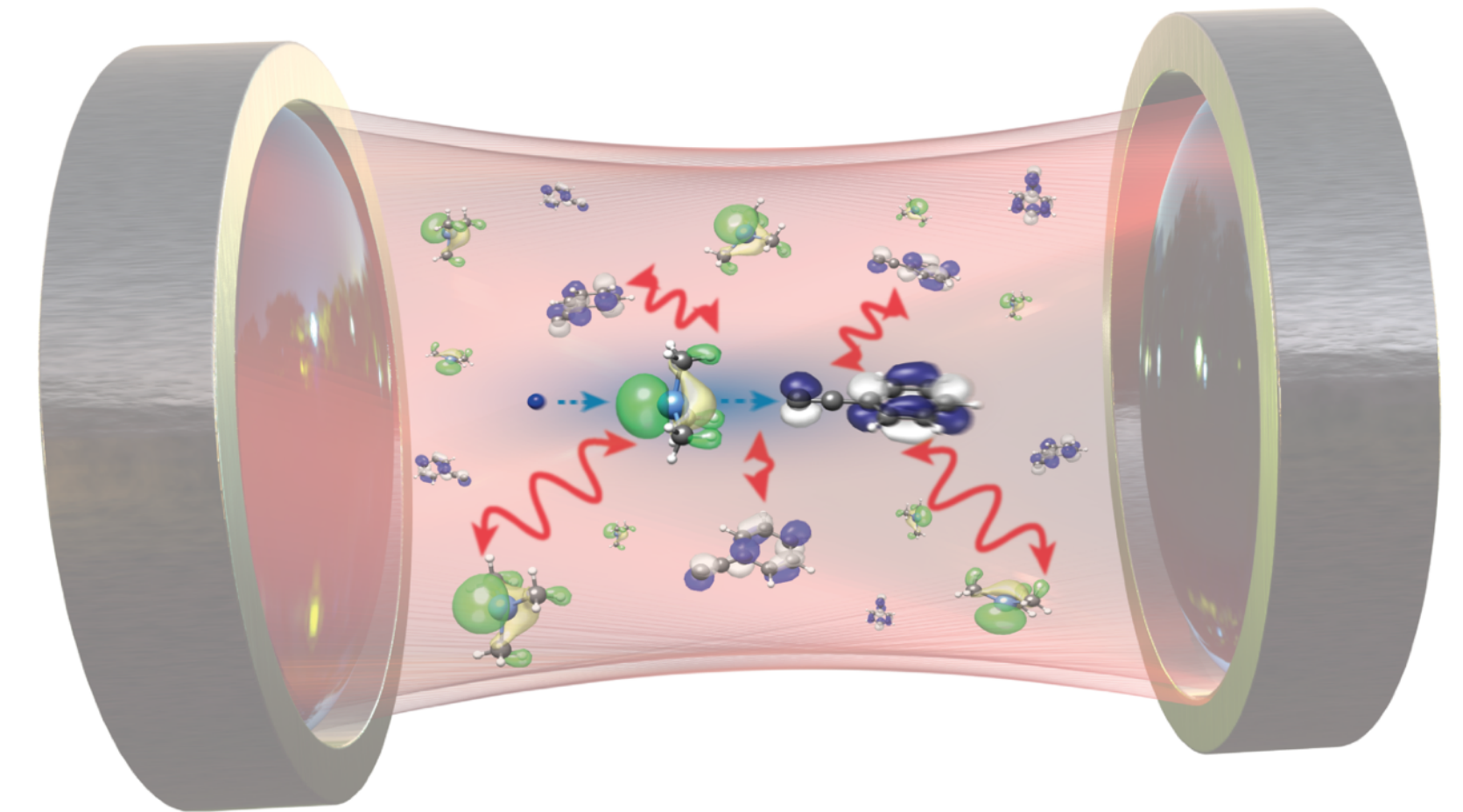
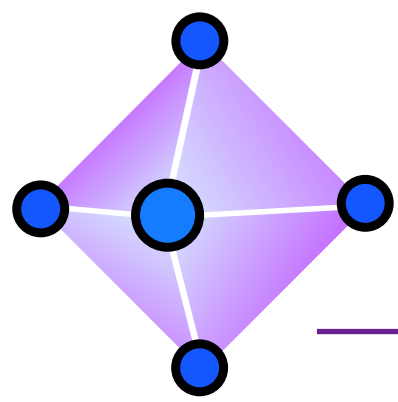


Dominik Sidler, 2025

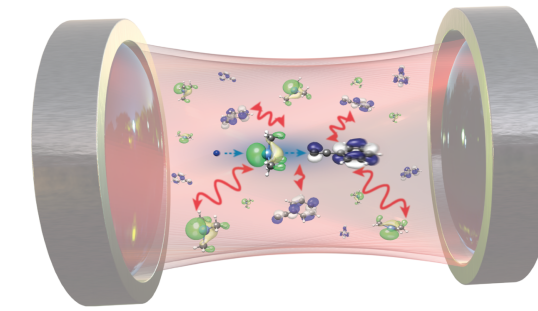
Polaritonic / QED Chemistry

Lecture 6: cavity Hartree-Fock

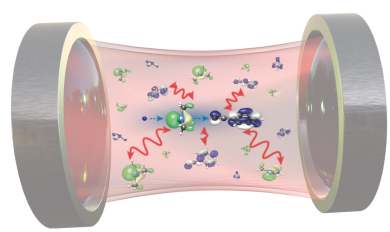




Lecture Outline

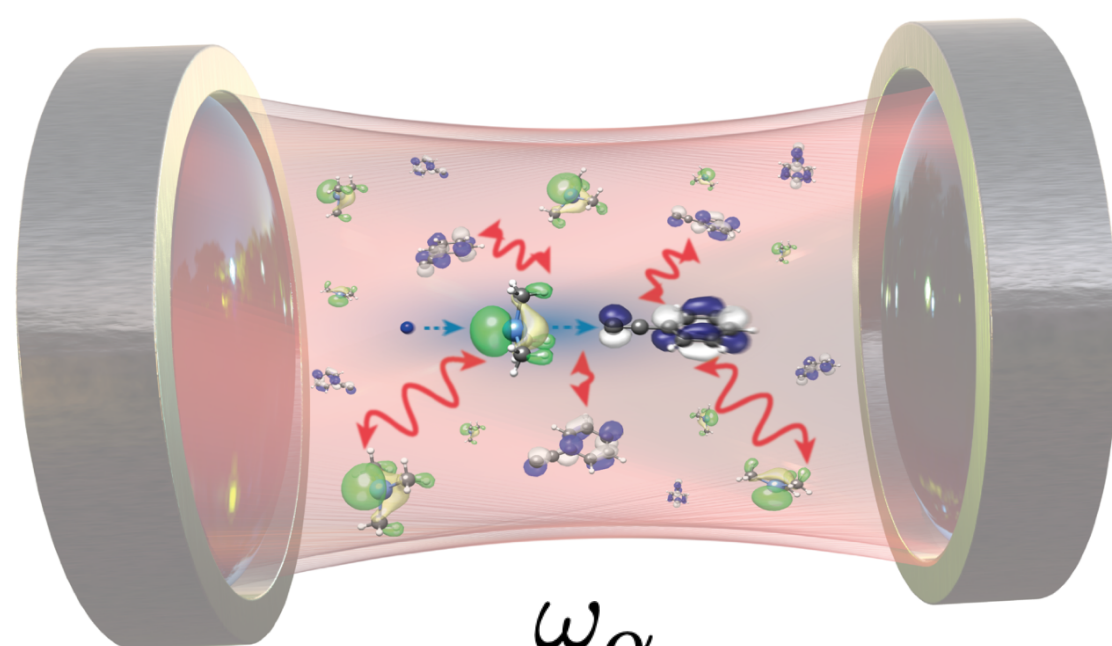


- A. Introduce **Hartree-Fock method** to solve complex electronic structure problems (based on M. Reiher's lecture notes „Quantenchemie“):
1. **Pauli-Principle.**
 2. Orbital integrals: **Hartree** and **exchange energy**.
 3. Hartree-Fock equations to **determine orbitals**.
 4. Finite-**basis set** representation: Roothaan-Hall equations.
- B. Consequences / interpretation **in a cavity** (DSE vs. Coulomb):
5. Modified intermolecular **long-range interactions**.
 6. **Dilute gas limit** (cavity-Hartree equations): Instability, degeneracy and polarization glass.



Ab-initio Insights into VSC

Simplest Case: Classical Cavity Born-Oppenheimer Approximation



ω_α
Resonance Frequency

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

Quantized Light
Light-Matter Interaction

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

Quantized electronic structure:

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

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

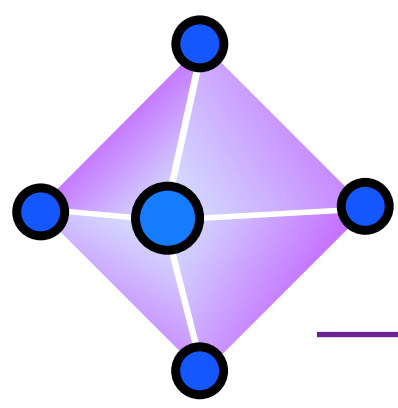
Classical nuclei & displacement field:

Ab-initio MD

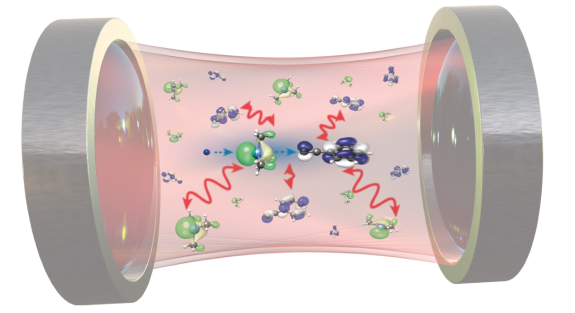
$$H^{\text{npt}} := H_m^n + \sum_{\alpha=1}^M \left(\frac{p_\alpha^2}{2} + \frac{\omega_\alpha^2}{2} \left(q_\alpha - \frac{X_\alpha}{\omega_\alpha} \right)^2 + \langle \psi_0 | \hat{H}_e(\underline{\mathbf{R}}, \underline{\mathbf{q}}) | \psi_0 \rangle \right)$$

Groundstate PES

Slightly different definition to previous slide!

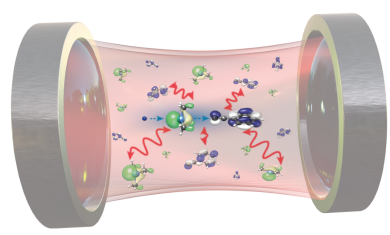


Pauli-Principle



- Total wave-function is **antisymmetric** with respect to the exchange of two identical **Fermionic** particles (e.g. electrons).
- Total wave-function is **symmetric** with respect to the exchange of two identical **Bosonic** particles (e.g. photons).

Notice that CBOA partitioning leaves us with a purely fermionic problem for the dressed electronic structure (i.e. photons appear only parametrically). Remark: Grouping the electrons with the photons instead, is also successfully pursued in practice (e.g. H. Koch group), but will not be the focus of this lecture.



Hartree-Fock Energy

Blackboard

Slater-Determinant Ansatz (approximation) enforces Pauli-principle for the exchange of electrons.

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$

Molecular orbitals ϕ_i to be determined.

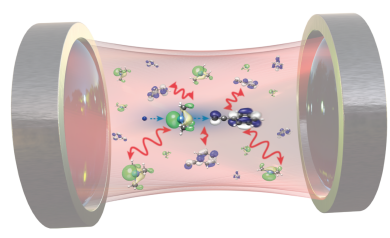
Hartree-Fock energy (closed shell: 2N electrons distributed on N orbitals):

$$E_{HF} = 2 \sum_i^N \langle \phi_i | \hat{h}(\mathbf{r}_1) | \phi_i \rangle + \sum_{i < j}^N \left(2 \langle \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) | \hat{g}(\mathbf{r}_1, \mathbf{r}_2) | \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \rangle - \langle \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) | \hat{g}(\mathbf{r}_1, \mathbf{r}_2) | \phi_j(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \rangle \right)$$

one-electron integrals
(Kinetic, matter, and cavity)

cavity Hartree-interaction
(Coulomb + DSE)

cavity exchange-interaction
(Coulomb + DSE)



Hartre-Fock Energy

General Notation in Terms of Spin Orbitals

So far we have neglected that an **electron can possess spin up and down configurations**, which makes them distinguishable. Therefore, the electron spin must be considered for the Pauli principle! The resulting HF energy can generally be written (i.e. for **open and closed shell systems**) by using **spin orbitals** $\phi_i(\tau)$ that combine spin and spatial information. However, for open shell systems, the solution strategy is more involved, which is why we **restrict our considerations to closed shell systems throughout this lecture**.

$$\langle \Psi | \hat{H}^e | \Psi \rangle = \langle \Psi | \sum_i^{N_e} \left\{ \frac{\hat{p}_i^2}{2} - \frac{1}{2} \sum_l^{N_N} \frac{Z_n}{|\hat{\mathbf{r}}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_j^{N_e} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \right\} + \left(\frac{1}{2} \hat{x}^2 + \hat{x}X - \omega_\beta \hat{x}q_\beta \right) | \Psi \rangle$$

$$= \sum_i^{N_e} \int d\tau \phi_i^*(\tau) (\hat{h}^m(\tau) + \hat{h}^l(\tau)) \phi_i(\tau)$$

1-Electron Integrals

Kinetic energy dominates short range

$$+ \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \int d\tau_1 \int d\tau_2 \phi_i^*(\tau_1) \phi_j^*(\tau_2) \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \phi_i(\tau_1) \phi_j(\tau_2)$$

Coulomb Hartree

Coulomb (longitudinal interaction)
dominates intermediate range

$$- \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \int d\tau_1 \int d\tau_2 \phi_i^*(\tau_1) \phi_j^*(\tau_2) \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \phi_i(\tau_2) \phi_j(\tau_1)$$

Coulomb Exchange

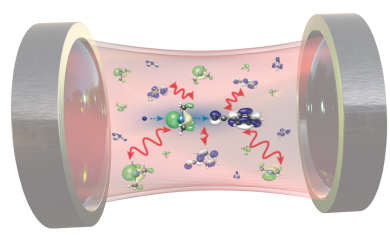
$$+ \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \int d\tau \phi_i^*(\tau) \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} \phi_i(\tau) \int d\tau \phi_j^*(\tau) \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} \phi_j(\tau)$$

DSE Hartree (cavity)

Dipole-self-energy (transversal interaction)
dominates long range

$$- \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \left| \int d\tau \phi_i^*(\tau) \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} \phi_j(\tau) \right|^2$$

DSE Exchange (cavity)



Closed Shell Hartree-Fock Equations

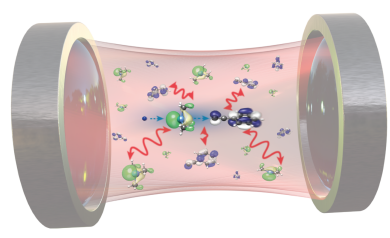
Blackboard

Determine spatial orbitals from **minimizing HF energy variationally** subject to orthogonality constraints.

$$\delta E_{HF} = 0, \langle \phi_i | \phi_j \rangle = \delta_{ij}$$

Problem „equivalent“ to solving the **canonical Hartree-Fock equations**. **Fock operator** \hat{f} is composed of **local** 1-electron operator \hat{h} and local 2-electron operator \hat{J} , as well as **non-local** (!) 2-electron operator \hat{K} (see blackboard for definitions). The orbital energies are defined as ϵ_{ii} and do not sum up to the Hartree-Fock energy (double counting).

$$\hat{f}\phi_i = [2\hat{h} + 2\hat{J} - \hat{K}]\phi_i = \epsilon_{ii}\phi_i$$

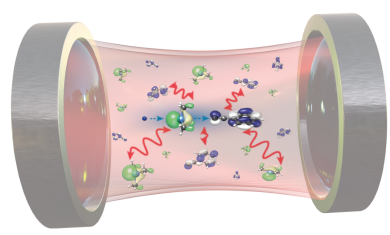


Self-Consistent Field (SCF) Method

Iterative algorithm to solve HF-Equations:

1. Guess initial orbitals $\{\phi_i^{(0)}\}$ (e.g. use core Hamiltonian by setting $\hat{J} = \hat{K} = 0$).
2. Calculate Fock-operator from orbitals $\hat{f}^{(n)} = \hat{f}^{(n)}[\{\phi_i^{(n)}\}]$.
3. Solve Hartree-Fock equations: $\hat{f}^{(n)}\phi_i^{(n+1)} = \epsilon_{ii}^{(n+1)}\phi_i^{(n+1)}$ and get new set of orbitals $\{\phi_i^{(n+1)}\}$.
4. Repeat step 2 and 3 until convergence, i.e., that the new orbitals are not significantly different to previous orbitals.

Remark: Convergence can be tricky in practice. Different numerical procedures known to speed up convergence.



HF Representation on a Computer

Blackboard: Roothaan-Hall Equations

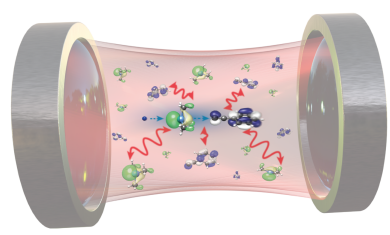
Spatial orbitals ϕ_i represented in terms of **finite basis set** χ_μ of size m .

$$\phi_i(\mathbf{r}) = \sum_{\mu=1}^{\infty} c_{\mu}^{(i)} \chi_{\mu}(\mathbf{r}) \approx \sum_{\mu=1}^m c_{\mu}^{(i)} \chi_{\mu}(\mathbf{r})$$

Recursive Roothaan-Hall equations turn search for orbitals into **search for** corresponding **coefficients** $c_{\mu}^{(i)}$.

$$f(\mathbf{c}) \cdot \mathbf{c} = \mathbf{S} \cdot \mathbf{c} \cdot \epsilon$$

Lowest N orbital energies define **occupied orbitals** for system of $2N$ closed shell electrons. **$N-m$ orbitals are called virtual (unoccupied).**



B: Consequences Inside a Cavity

So far **Hartree-Fock theory** was **generic** inside / outside of a cavity.

What are now the physical / chemical consequences of the cavity-modified electronic structure problem?
(Ongoing research)

Local integrals



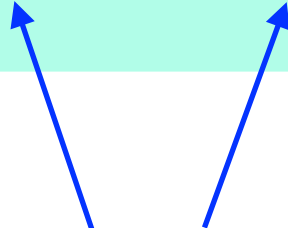
$$\begin{aligned}
 & + \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \int d\tau \phi_i^*(\tau) \lambda \cdot \hat{r} \phi_i(\tau) \int d\tau \phi_j^*(\tau) \lambda \cdot \hat{r} \phi_j(\tau) \\
 & - \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \left| \int d\tau \phi_i^*(\tau) \lambda \cdot \hat{r} \phi_j(\tau) \right|^2
 \end{aligned}$$

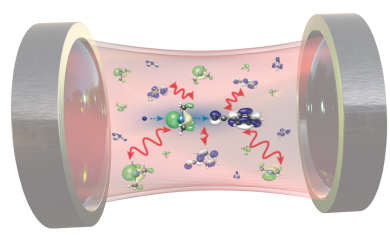
DSE Hartree (cavity)

DSE Exchange (cavity)

Dipole-self-energy (transversal interaction)
dominates long range interaction

Non-local integrals





Basis Set Choice

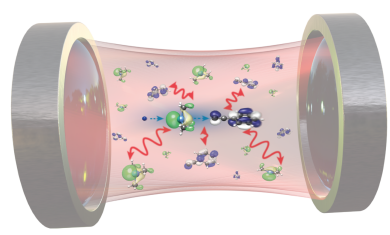
Open Research Question: Consequences of **DSE non-local integrals**?

Typical form of basis function in quantum chemistry: **Slater-type orbitals** (or computationally more common **Gaussian-type** orbitals):

$$\chi_{\mu}(r, \theta, \phi) \propto Y_{l_{\mu}, m_{\mu}}(\theta, \phi) r^{n_{\mu}-1} e^{-\zeta_{\mu} r} \quad \chi_{\mu}(r, \theta, \phi) \propto Y_{l_{\mu}, m_{\mu}}(\theta, \phi) r^{n_{\mu}-1} e^{-\zeta_{\mu} r^2}$$

Orbitals (in particular Gaussians) are very **localized in space**. Difficult to represent delocalized inter-molecular electronic structure (large diffuse basis set required). To save computational time, not all electron-integrals in Fock equation are evaluated, by applying different **truncation schemes**. Quantum chemistry basis sets, and algorithm are designed for Coulomb interaction and not long-range (!) dipole-self energy interactions!

Do we need novel (compression) algorithms and move to grid basis set representations in polaritonic chemistry to capture collective effects accurately?



Hartre-Fock Energy

General Notation in Terms of Spin Orbitals τ_i Instead of Spatial Orbitals r_i

Hartree-Fock Energy

$$\langle \Psi | \hat{H}^e | \Psi \rangle = \langle \Psi | \sum_i^{N_e} \left\{ \frac{\hat{p}_i^2}{2} - \frac{1}{2} \sum_l^{N_N} \frac{Z_n}{|\hat{r}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_j^{N_e} \frac{1}{|\hat{r}_i - \hat{r}_j|} \right\} + \left(\frac{1}{2} \hat{x}^2 + \hat{x}X - \omega_\beta \hat{x}q_\beta \right) | \Psi \rangle$$

$$= \sum_i^{N_e} \int d\tau \phi_i^*(\tau) (\hat{h}^m(\tau) + \hat{h}^l(\tau)) \phi_i(\tau)$$

1-Electron Integrals

Kinetic energy dominates short range

$$+ \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \int d\tau_1 \int d\tau_2 \phi_i^*(\tau_1) \phi_j^*(\tau_2) \frac{1}{|\hat{r}_1 - \hat{r}_2|} \phi_i(\tau_1) \phi_j(\tau_2)$$

Coulomb Hartree

Coulomb (longitudinal interaction) dominates intermediate range

$$- \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \int d\tau_1 \int d\tau_2 \phi_i^*(\tau_1) \phi_j^*(\tau_2) \frac{1}{|\hat{r}_1 - \hat{r}_2|} \phi_i(\tau_2) \phi_j(\tau_1)$$

Coulomb Exchange

$$+ \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \int d\tau \phi_i^*(\tau) \lambda \cdot \hat{r} \phi_i(\tau) \int d\tau \phi_j^*(\tau) \lambda \cdot \hat{r} \phi_j(\tau)$$

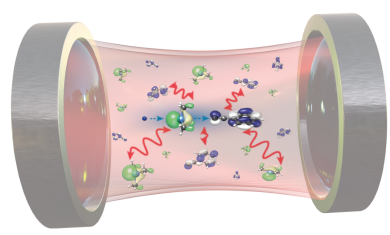
DSE Hartree (cavity)

Dipole-self-energy (transversal interaction) dominates long range

$$- \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \left| \int d\tau \phi_i^*(\tau) \lambda \cdot \hat{r} \phi_j(\tau) \right|^2$$

DSE Exchange (cavity)

? Dilute Gas ?



Ab-initio Insights into VSC

Cavity Hartree Equations (cH)

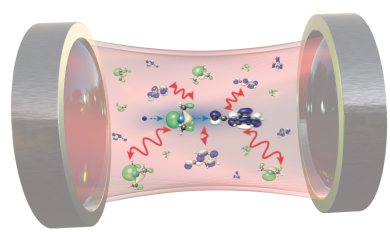
$$\hat{X}_\alpha + \hat{x}_\alpha = \frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_n} Z_l |e| \mathbf{R}_l - \frac{\lambda_\alpha}{\omega_\alpha} \cdot \sum_{l=1}^{N_e} |e| \mathbf{r}_l$$

Cavity Hartree equations in the dilute gas limit:

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

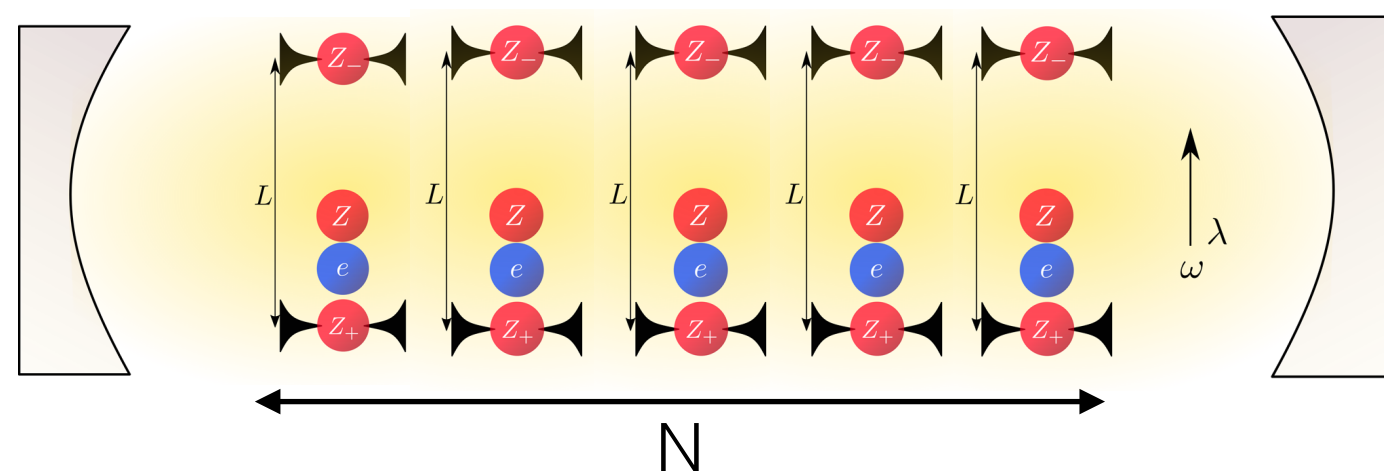
Self-consistent coupling to total
electronic dipole operator

See also lecture and exercise 5 (solution of effective harmonic model).



Beyond Harmonic Electrons

MD at Finite Temperature Based on cH (Dilute Gas)

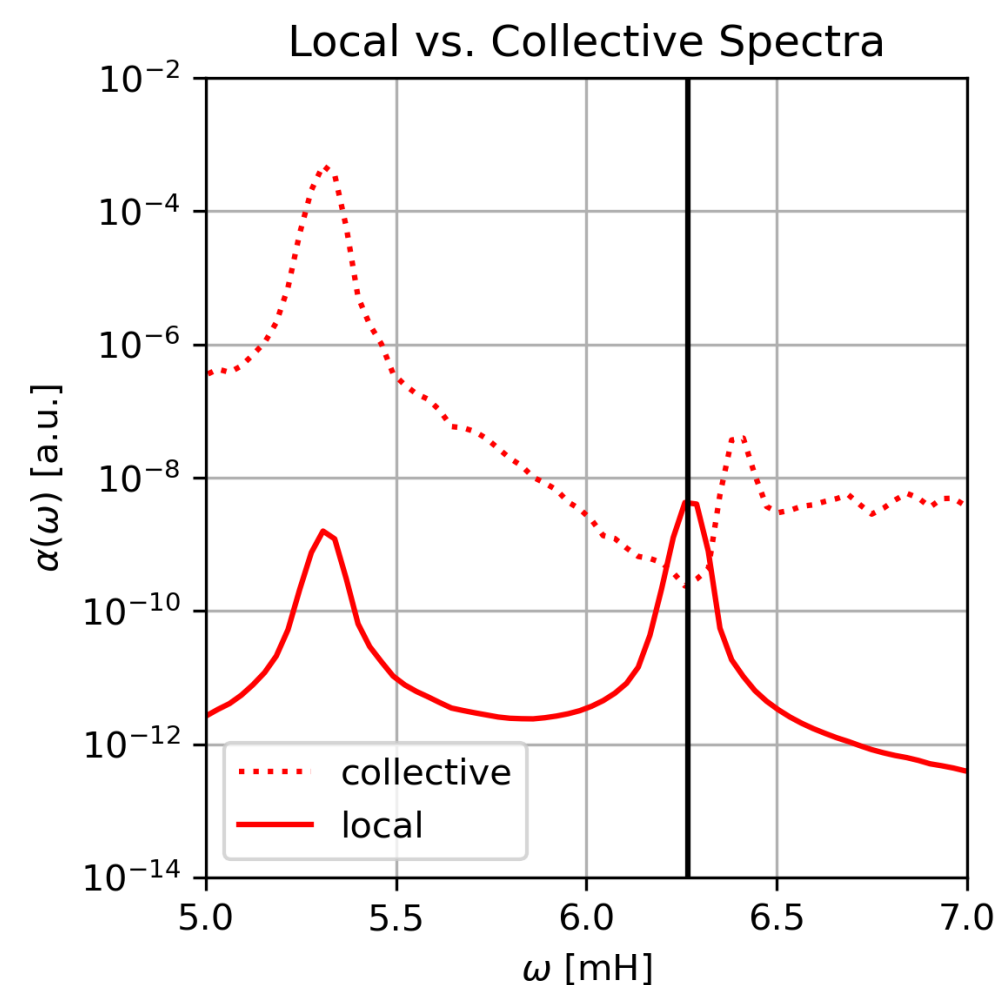


Shin-Metiu model (double-well)

$$\hat{H}_n = \frac{\hat{p}^2}{2M} + \frac{\hat{p}^2}{2} + \frac{1}{|L/2 - \hat{R}|} + \frac{1}{|L/2 + \hat{R}|} - \frac{\text{erf}(|\hat{R} - \hat{r}|/R_f)}{|\hat{R} - \hat{r}|} - \frac{\text{erf}(|\hat{r} - L/2|/R_r)}{|\hat{r} - L/2|} - \frac{\text{erf}(|\hat{r} + L/2|/R_l)}{|\hat{r} + L/2|}.$$

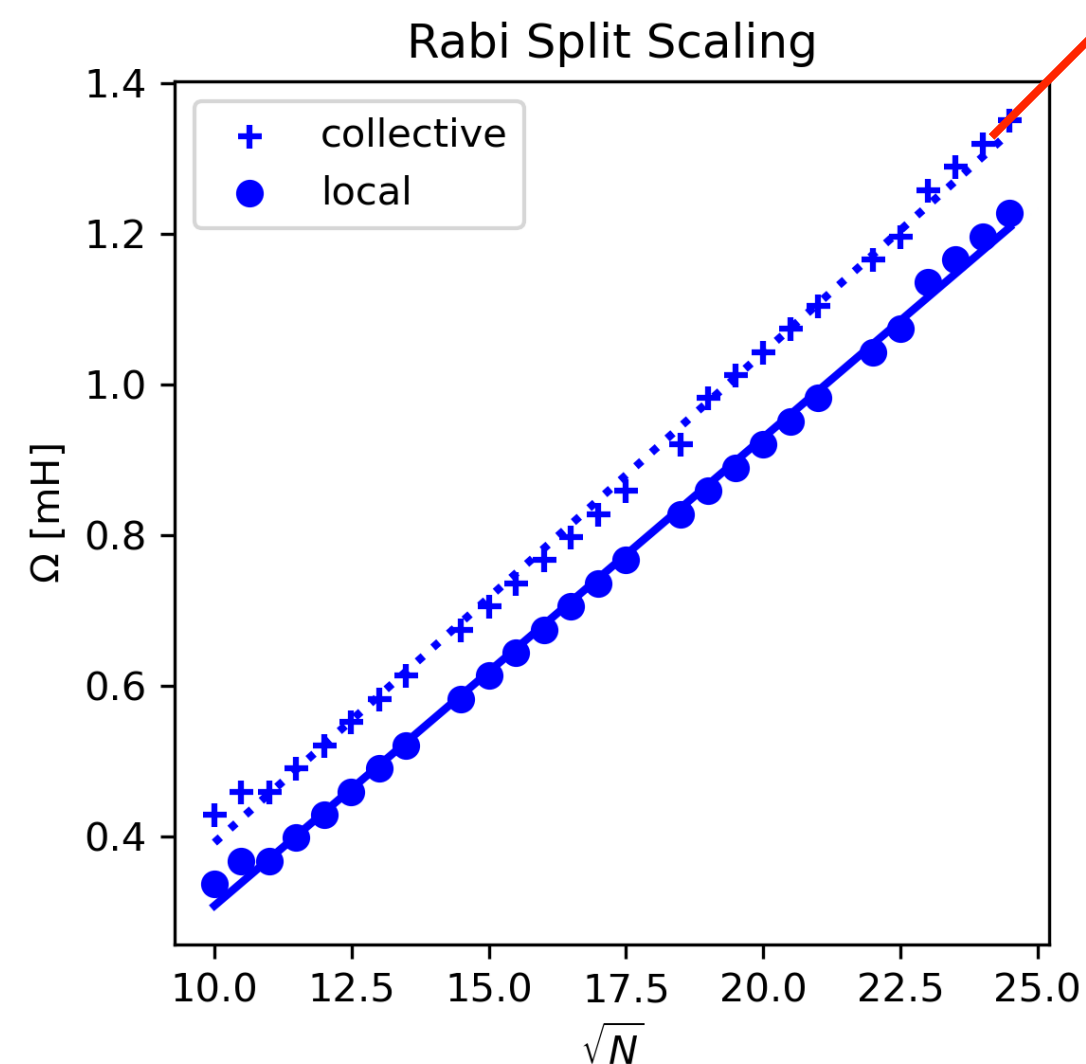
IR spectra

(aligned vs. rotated molecules)



Collective Rabi split scaling

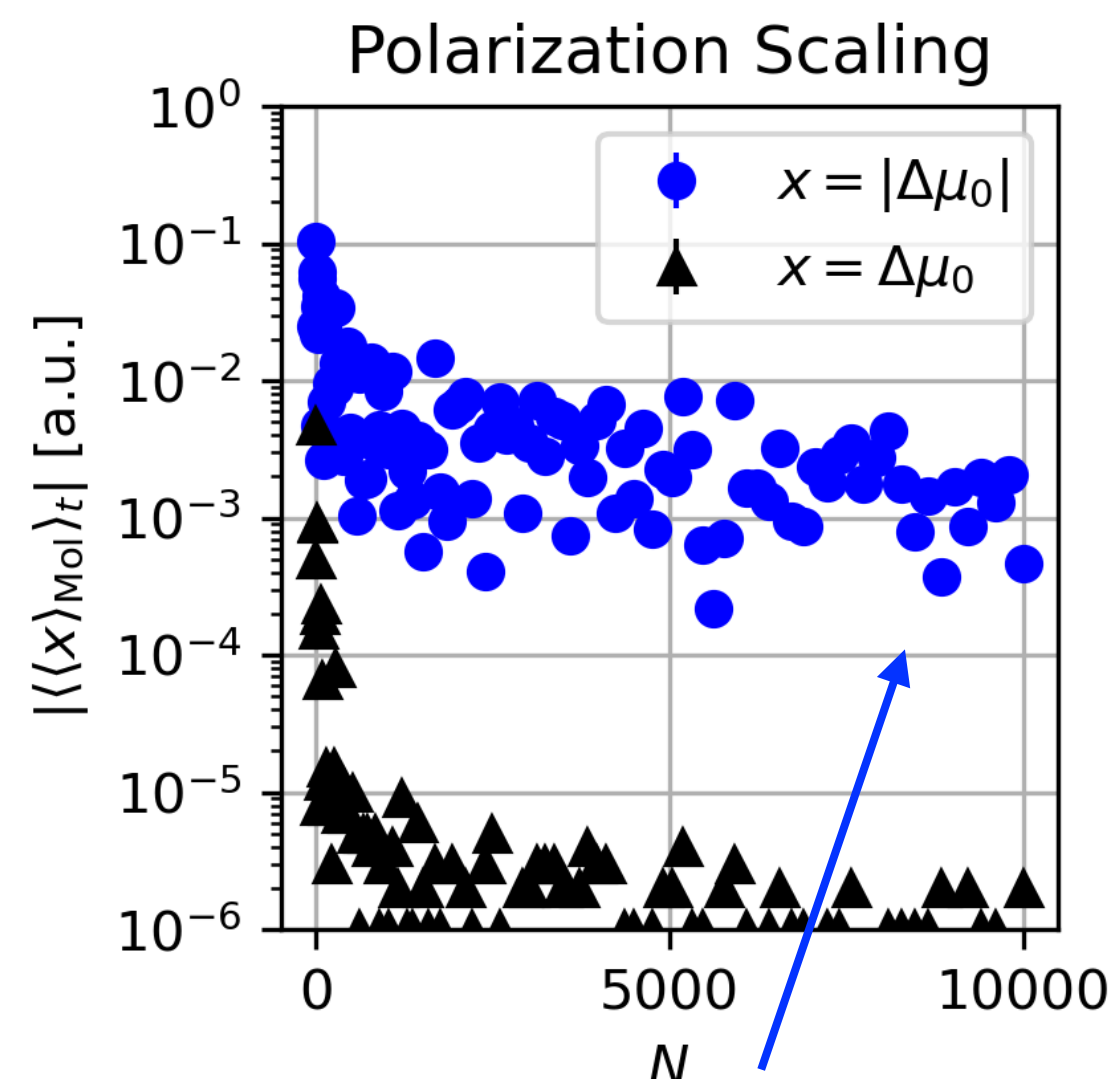
Convergence issue / instability (numerics / physics)



Collective degeneracy? (active research)

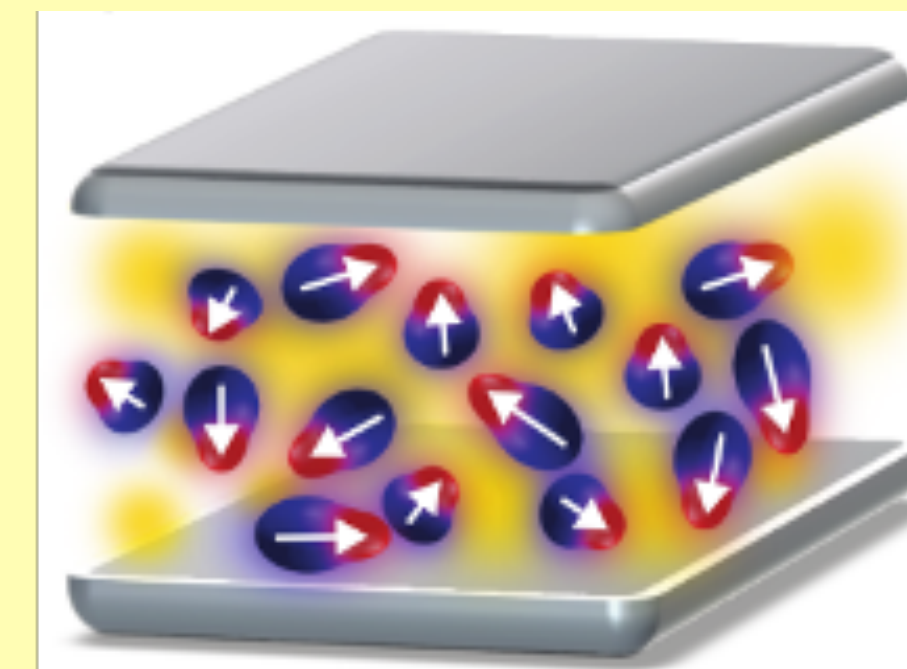
Cavity-induced local polarization

$$\Delta\mu_0 = \langle \hat{\mu}_i \rangle_{0,\lambda=0} - \langle \hat{\mu}_i \rangle_{0,\lambda}$$



Collectively-induced local (!) polarization

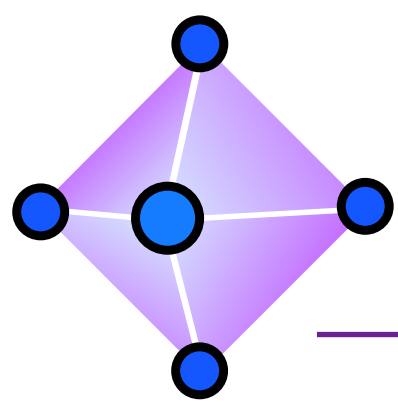
„Polarization glass hypothesis“



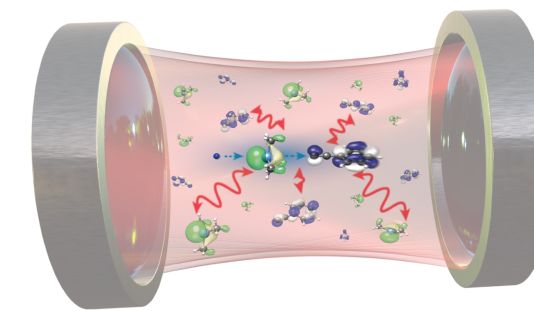
$$E_{\text{cH}}[\Delta\mu_0] = 0$$

$$\text{Var}_{\text{cH}}[\Delta\mu_0] \neq 0.$$

D. Sidler et al., J. Phys. Chem. Lett. 15, 19, 5208, (2024)



Summary & Conclusion



- A. **Cavity Hartree-Fock method** (one way) to solve cavity-modified electronic structure problem starting from **Slater-determinant ansatz**:
1. **Pauli-principle** introduces exchange energy.
 2. **Molecular orbitals** determined from **HF equations**.
 3. **Iterative** (self-consistent field) **algorithm**
 4. Finite-**basis set** representation: Roothaan-Hall equations (non-linear!). Search for coefficients.
- B. Consequences / interpretation in a cavity (**DSE vs. Coulomb**):
5. **Dipole self-energy** expected to be significant for intermolecular **long-range interactions** (exact conditions open question). Potentially different basis sets and (novel) numerical approximation schemes required to capture those effects.
 6. **Dilute gas limit** (cavity-Hartree equations): Instability, degeneracy and polarization glass.

Outlook: Beyond dilute gas limit / cavity-modified electron correlation effects.