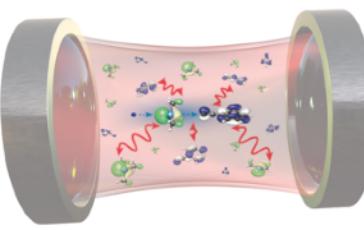


Literature Suggestions for Final Presentations

Talks should be approx. 12-15 minutes + 5 minutes for discussion. Two presentations will take place in the second last week and 4 during the last week. Please let me know by email your 3 favorite choices until tomorrow evening. I will then assign the manuscripts.

1. Quantum Hall effect in a Cavity:
 1. Experiment: <https://www.science.org/doi/abs/10.1126/science.abl5818>
 2. Theory (mathematical): <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.131.196602> (also look at Supporting Information)
2. No groundstate without dipole self-energy: <https://iopscience.iop.org/article/10.1088/1361-6455/aa9c99/meta>
3. Cavity-modified reaction rates:
 1. Ab-initio correlations: <https://www.nature.com/articles/s41467-022-35363-6>
 2. Polaritonic rate model: <https://www.nature.com/articles/s41467-021-21610-9>
4. Collective vs. local effects for electronic strong coupling: <https://pubs.acs.org/doi/full/10.1021/acs.jpclett.0c03436>
5. cavity-Coupled Cluster: <https://journals.aps.org/prx/abstract/10.1103/PhysRevX.10.041043>
6. Chiral Cavity:
 1. Idea: <https://journals.aps.org/prx/abstract/10.1103/PhysRevX.13.031002>
 2. Role of degenerate states: <https://pubs.aip.org/aip/jcp/article/161/24/244101/3327789>
7. Machine learning / Monte Carlo: <https://arxiv.org/abs/2503.15644>
8. Multiconfigurational approach (CASSCF): <https://arxiv.org/pdf/2503.16417.pdf>
9. Thermal control (experiment): <https://www.nature.com/articles/s41586-023-06596-2>
10. Self-alignment by Casimir force (experiment): <https://www.science.org/doi/full/10.1126/sciadv.adn1825>
11. Further experiments (see slide 5 in lecture 1)
12. Your own choice (please let me know in advance to confirm your choice)



Typical Structure of a Research Article

How to Approach the Task Efficiently:

Example: <https://pubs.acs.org/doi/epdf/10.1021/acs.jctc.3c00092>

Numerically Exact Solution for a Real Polaritonic System under Vibrational Strong Coupling in Thermodynamic Equilibrium: Loss of Light–Matter Entanglement and Enhanced Fluctuations

Dominik Sidler,* Michael Ruggenthaler,* and Angel Rubio*



Cite This: *J. Chem. Theory Comput.* 2023, 19, 8801–8814



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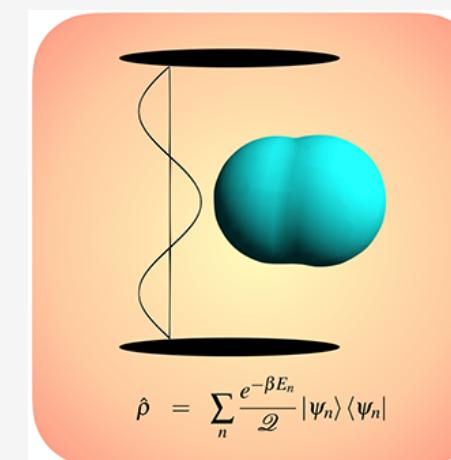
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: The first numerically exact simulation of a full ab initio molecular quantum system (HD^+) under strong ro-vibrational coupling to a quantized optical cavity mode in thermal equilibrium is presented. Theoretical challenges in describing strongly coupled systems of mixed quantum statistics (bosons and Fermions) are discussed and circumvented by the specific choice of our molecular system. Our numerically exact simulations highlight the absence of zero temperature for the strongly coupled matter and light subsystems, due to cavity-induced noncanonical conditions. Furthermore, we explore the temperature dependency of light–matter quantum entanglement, which emerges for the ground state but is quickly lost already in the deep cryogenic regime. This is in contrast to predictions from the Jaynes–Cummings model, which is the standard starting point to model collective strong-coupling chemistry phenomenologically.

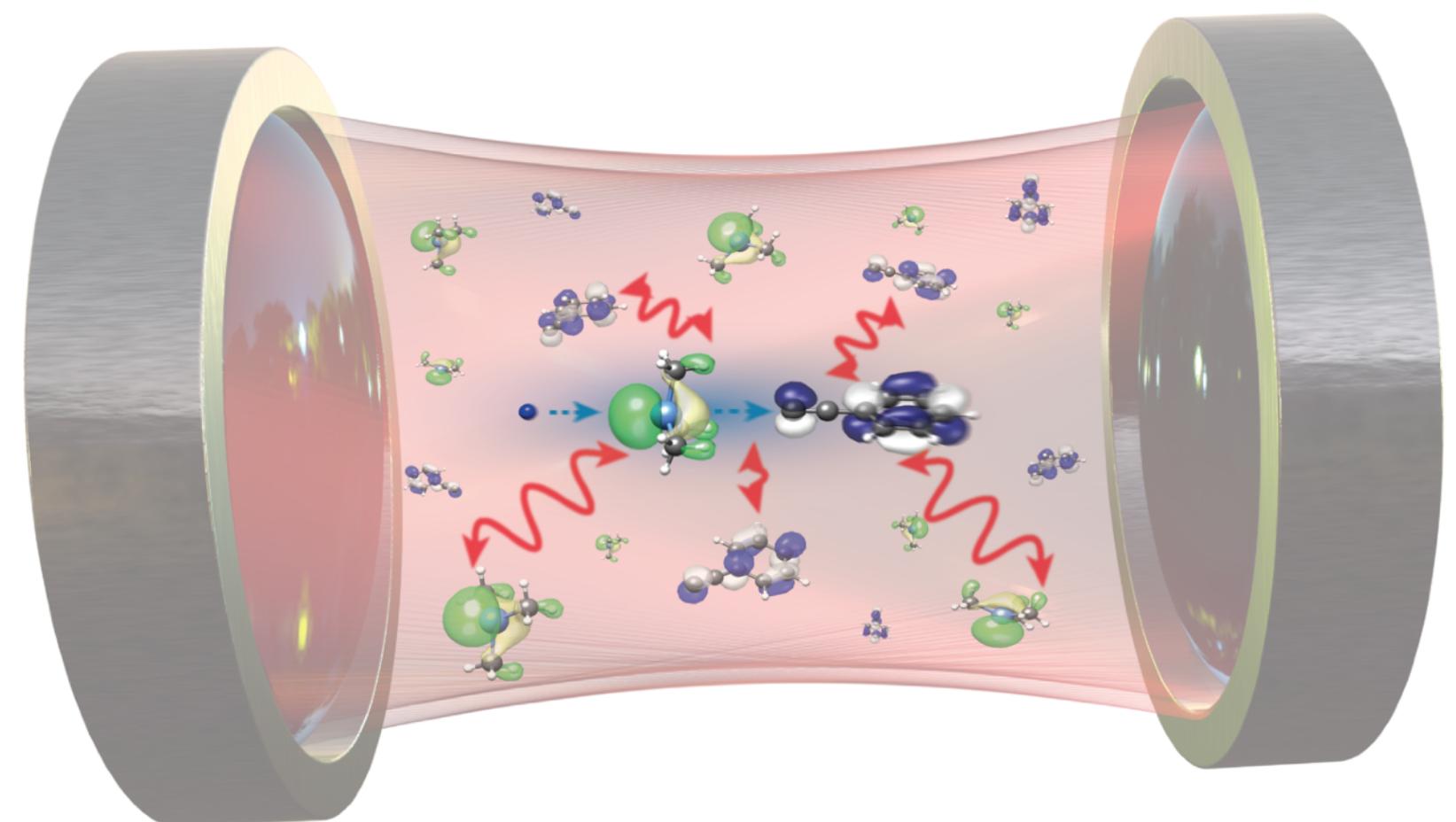
Moreover, we find that the fluctuations of matter remain modified by the quantum nature of the thermal and vacuum-field fluctuations for significant temperatures, e.g., at ambient conditions. These observations (loss of entanglement and coupling to quantum fluctuations) have implications for the understanding and control of polaritonic chemistry and materials science, since a semiclassical theoretical description of light–matter interaction becomes reasonable, but the typical (classical) canonical equilibrium assumption for the nuclear subsystem remains violated. This opens the door for quantum fluctuation-induced stochastic resonance phenomena under vibrational strong coupling, which have been suggested as a plausible theoretical mechanism to explain the experimentally observed resonance phenomena in the absence of periodic driving that has not yet been fully understood.

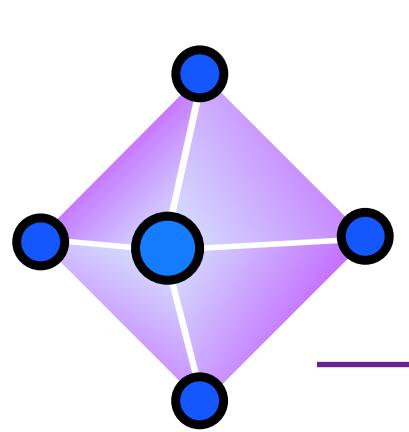


Dominik Sidler, 2025

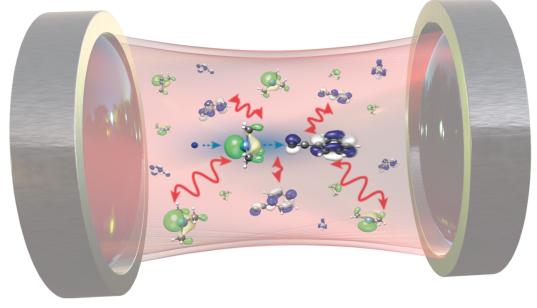
Polaritonic / QED Chemistry

Lecture 7: Configuration Interaction /
Collective Electron Correlations

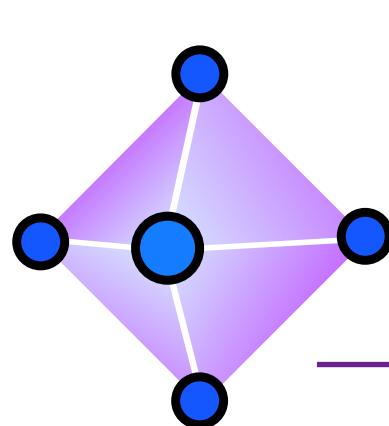




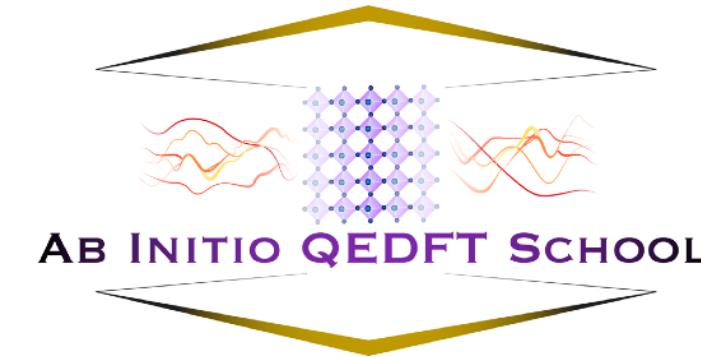
Lecture Outline



1. Electron **correlations** outside a cavity.
2. Correlation effects for electronic **strong coupling of few molecules**.
3. Electron correlations under **collective strong coupling** (VSC).
4. Mapping to a **spin glass** problem.



Motivation: Correlation effects



Correlation is related to the interaction between particles of a quantum system. The correlation energy is a measure of how much the movement of one particle is influenced by the presence of all the other particles.

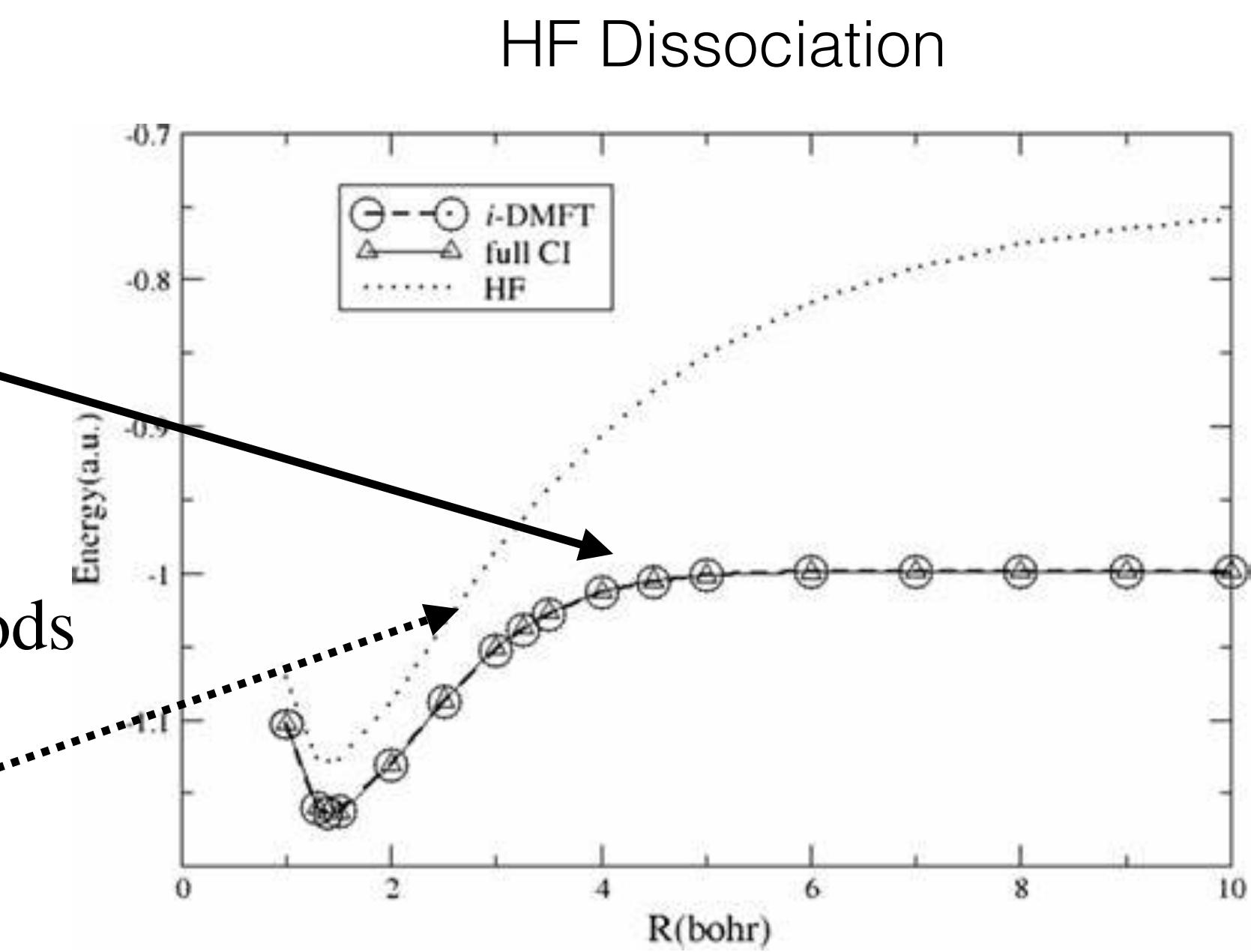
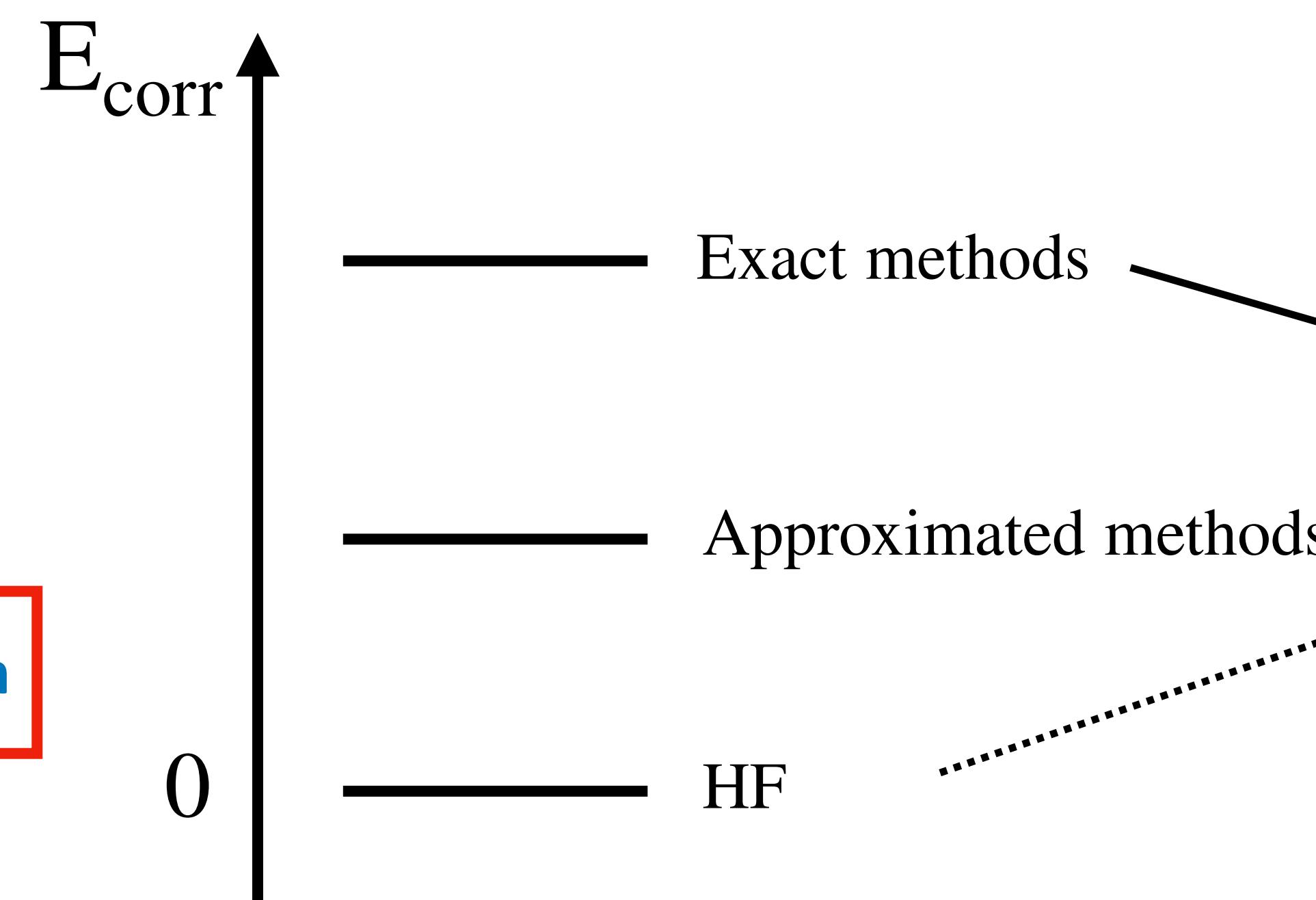
$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$$

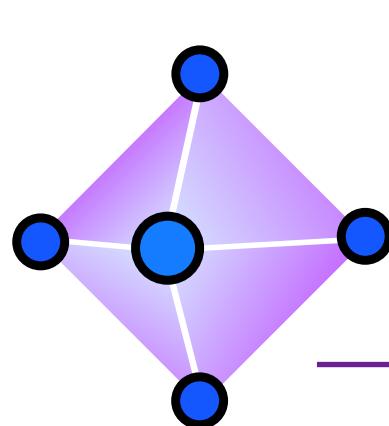
Correlated methods

DFT

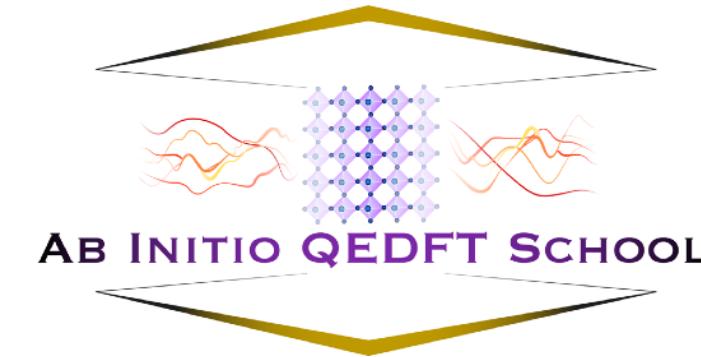
Wave function

Exchange-correlation functionals





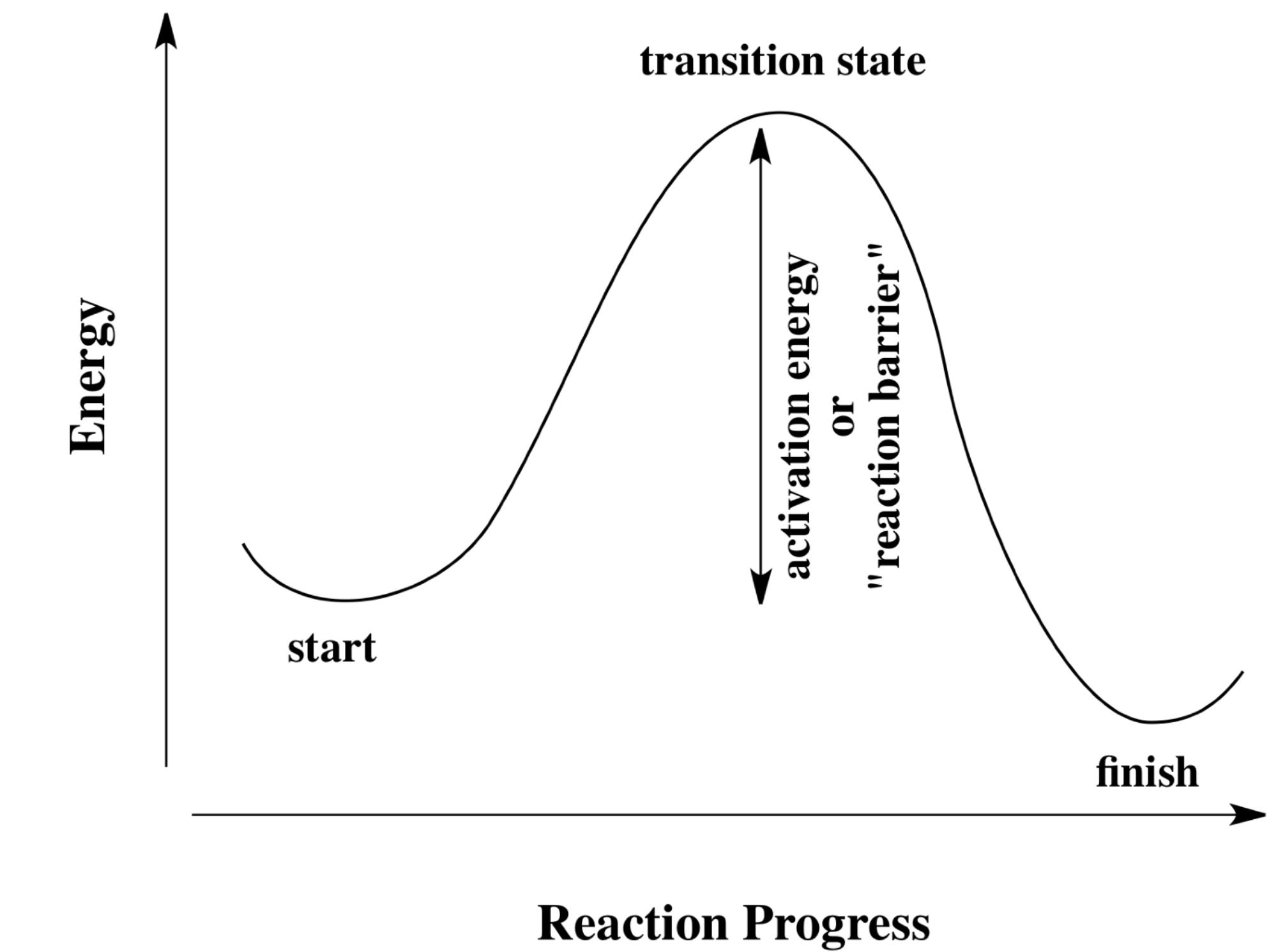
Motivation: Importance of (Coulomb) correlation in quantum chemistry

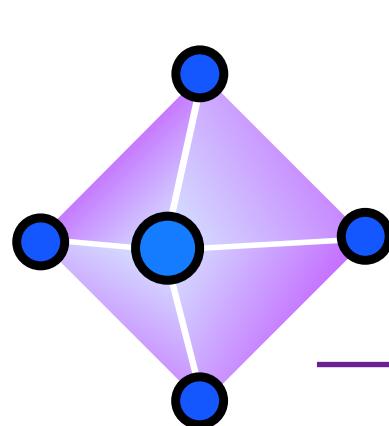


In absolute terms the correlation energy is a small percentage of the total energy.

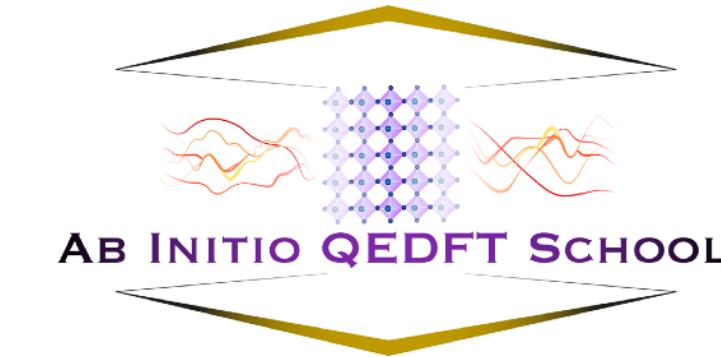
However its size is around tens of kcal/mol that is on the same order of magnitude of the reaction barriers of the reactions commonly used in chemistry.

The inclusion of correlation is then crucial in particular if we want to look at the energetic and at the reactivity of molecules.



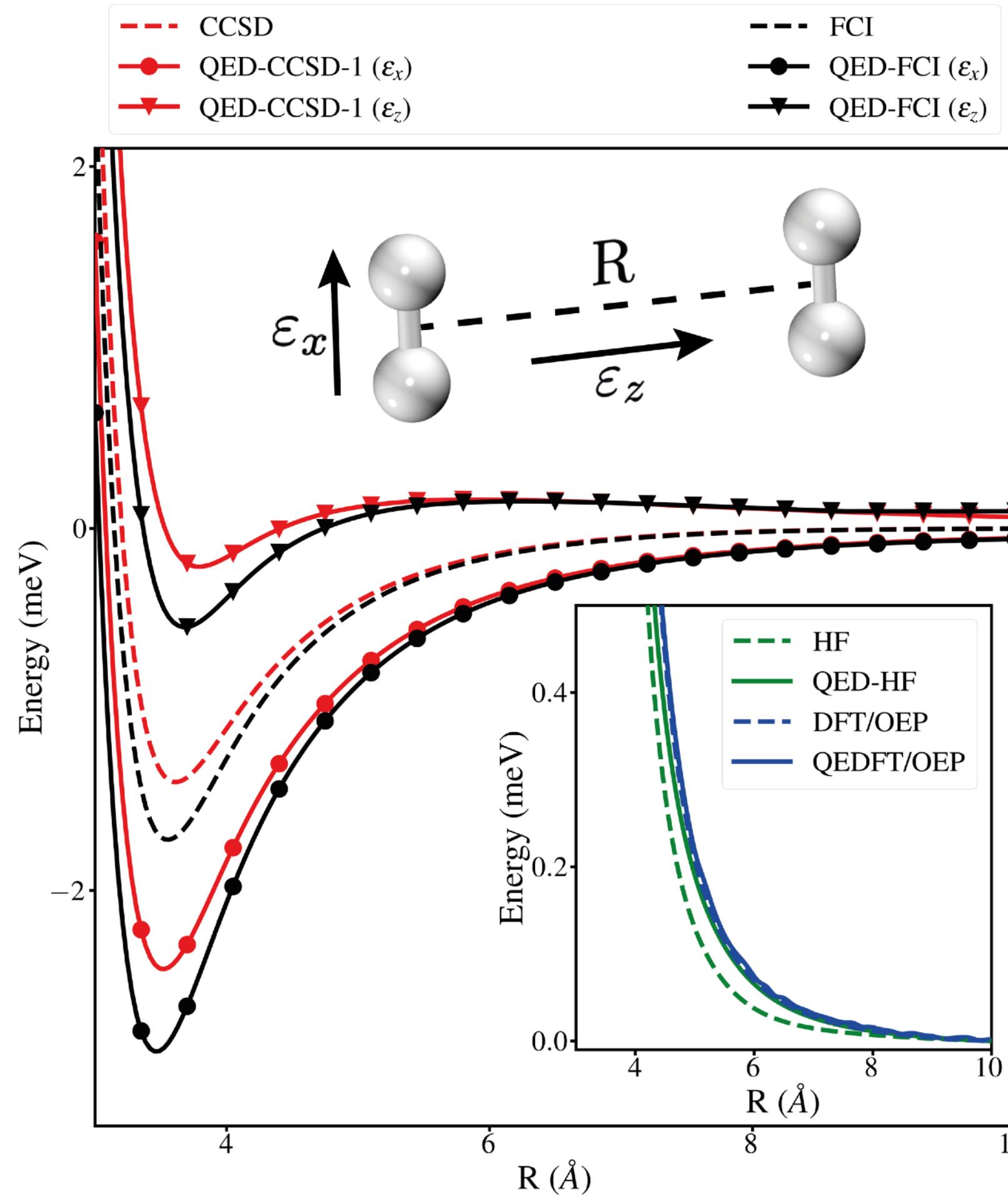


Few (!) molecular electronic strong coupling

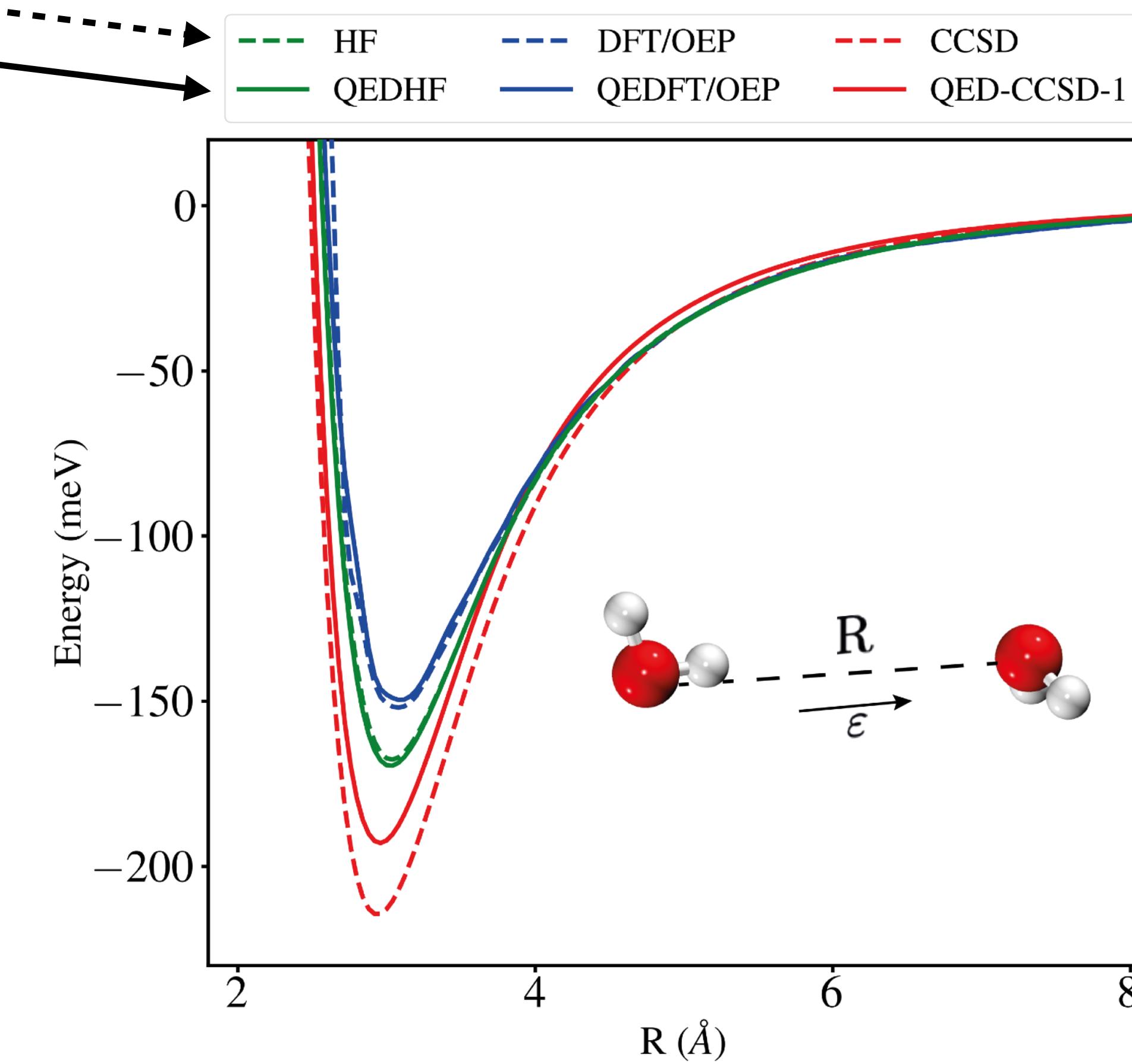


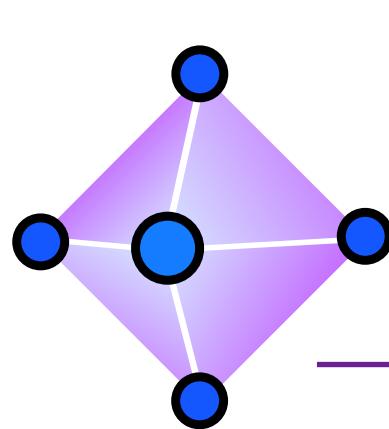
Different computational methods inside/outside a cavity

van der Waals

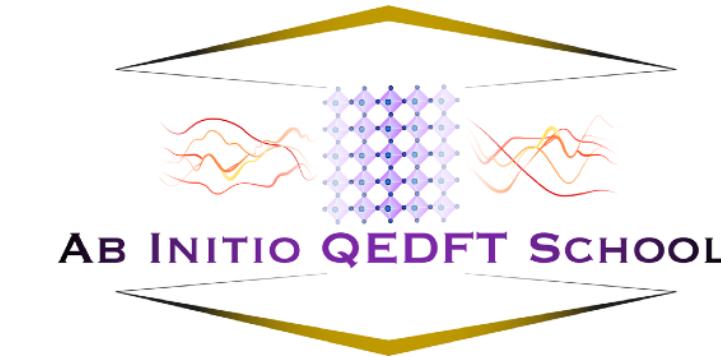


Hydrogen Bonds





Correlated methods based on the wave function



Weak correlation effects



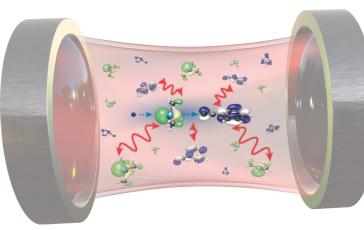
Perturbation theory

$$H = H^{(0)} + V$$

**Strong correlation effects
under collective strong coupling**



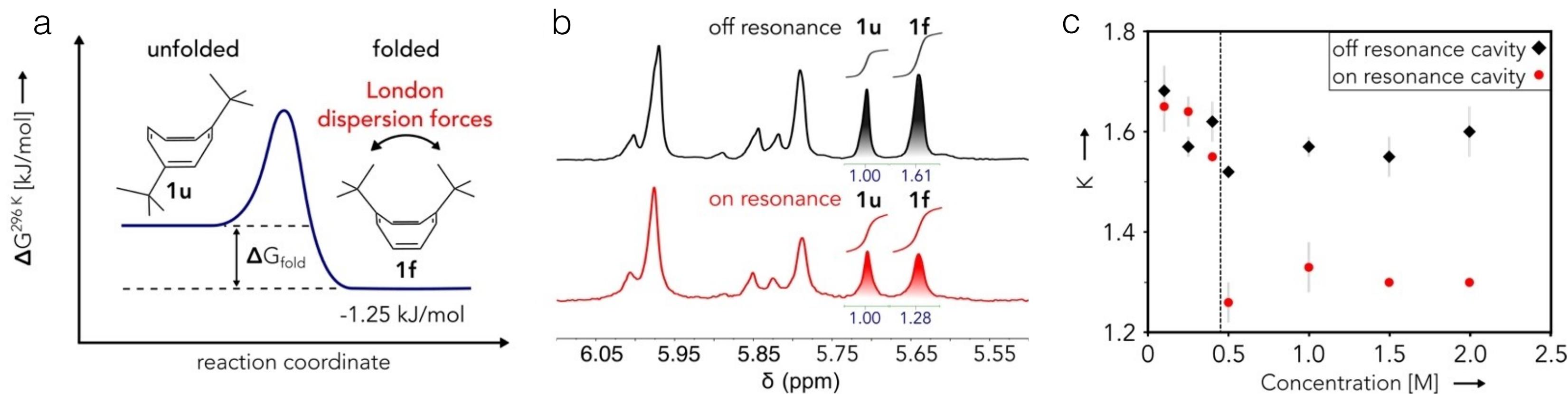
- Configuration Interaction (CI)
- Coupled Cluster (CC)
- Multi-configurational Self-Consistent Field (MCSCF)
- :



Experiment: „Mysteries of VSC“

Insights to Cavity-modified Dispersion Effects from NMR

On resonance: C-H vibrational stretching mode strongly coupled at 2970 cm⁻¹



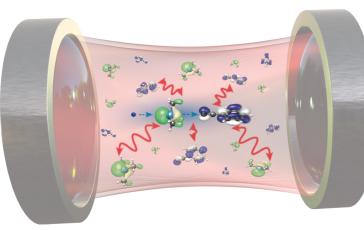
$$\text{Coupling } \lambda \propto \frac{1}{\sqrt{V}} \ll 1$$

- A. VSC influences London dispersion force-equilibrium constant (**local chemical change**).
B. Broadening but no chemical shift (**on average no changes of electronic structure**).

Local vs. Collective Mystery

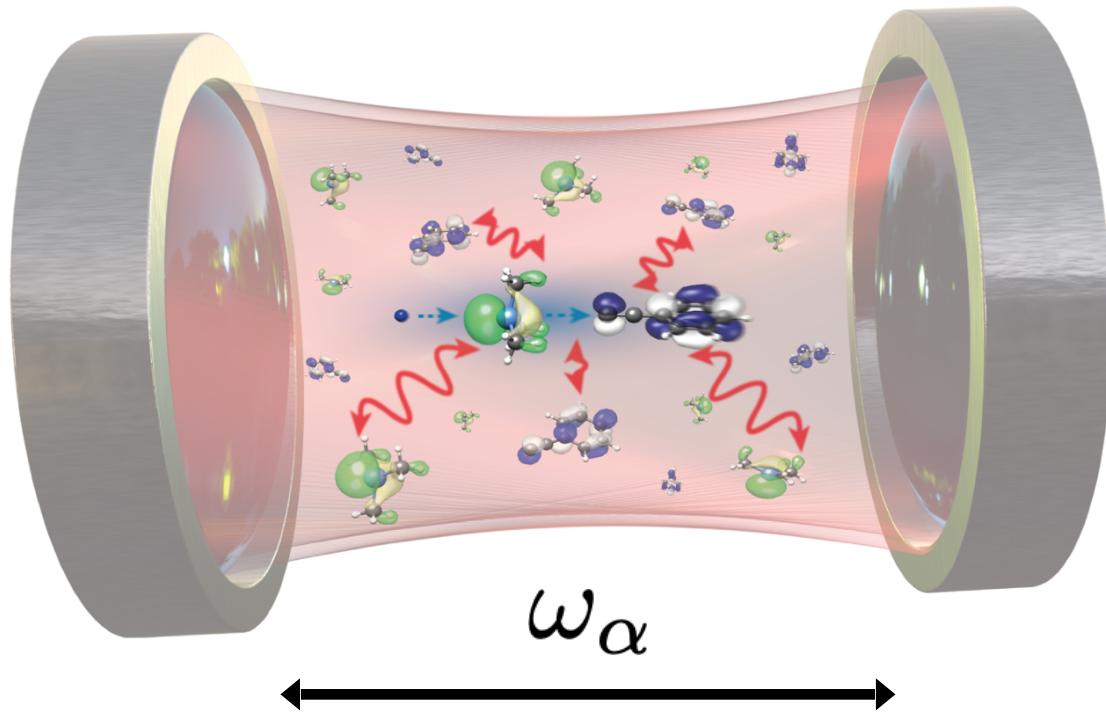
- C. **Phase-like transition** for equilibrium constant at **resonance**.

Resonance Mystery

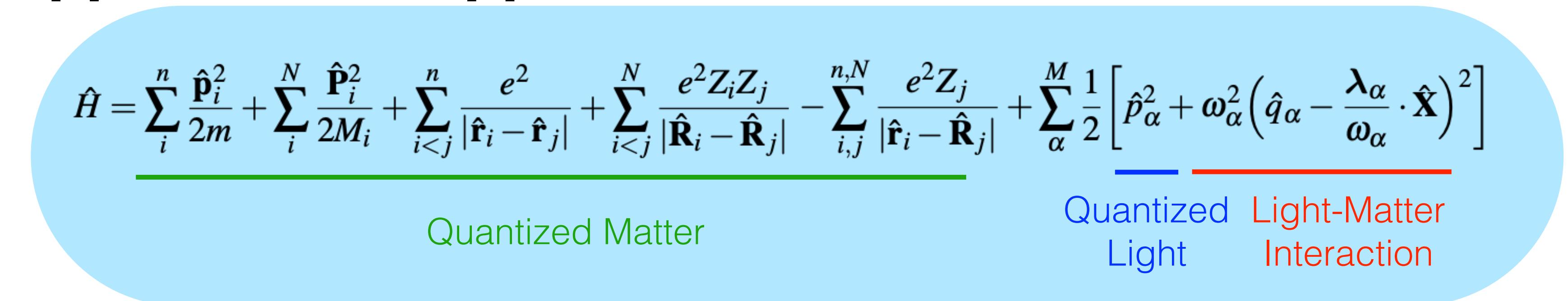


Repetition: Ab-initio Insights into VSC

Cavity Born-Oppenheimer Approximation



Resonance Frequency



Cavity Born-Oppenheimer partitioning

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

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

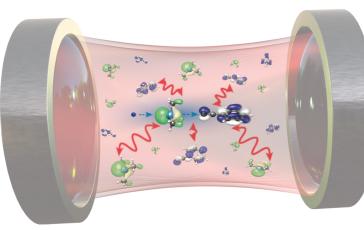
Electrons:

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

Ab-initio MD

Nuclei & displacement field:

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



Repetition: Hartree-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

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

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

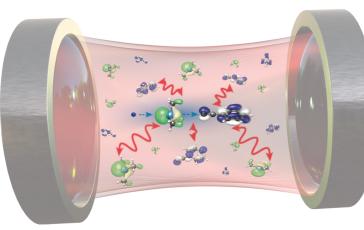
Coulomb (longitudinal interaction)
dominates intermediate range

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

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

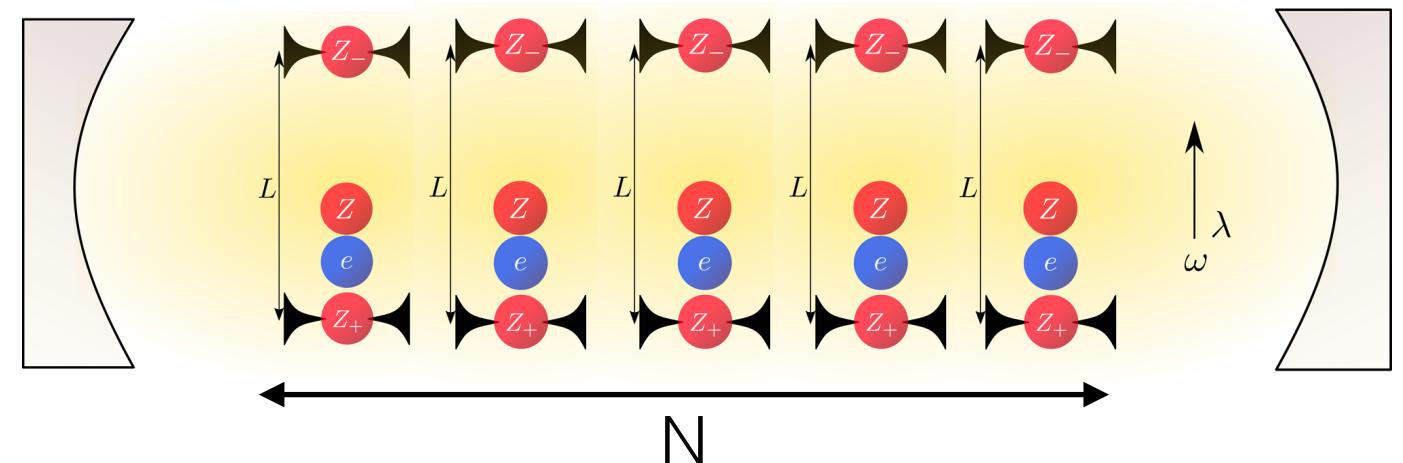
$$- \frac{1}{2} \sum_i^{N_e} \sum_j^{N_e} \left| \int d\tau_i \phi_i^*(\tau) \lambda \cdot \hat{r} \phi_j(\tau) \right|^2 \text{DSE Exchange (cavity)}$$

? Dilute Gas ?



Repetition: Inter-molecular DSE Effects in Dilute Gas Limit

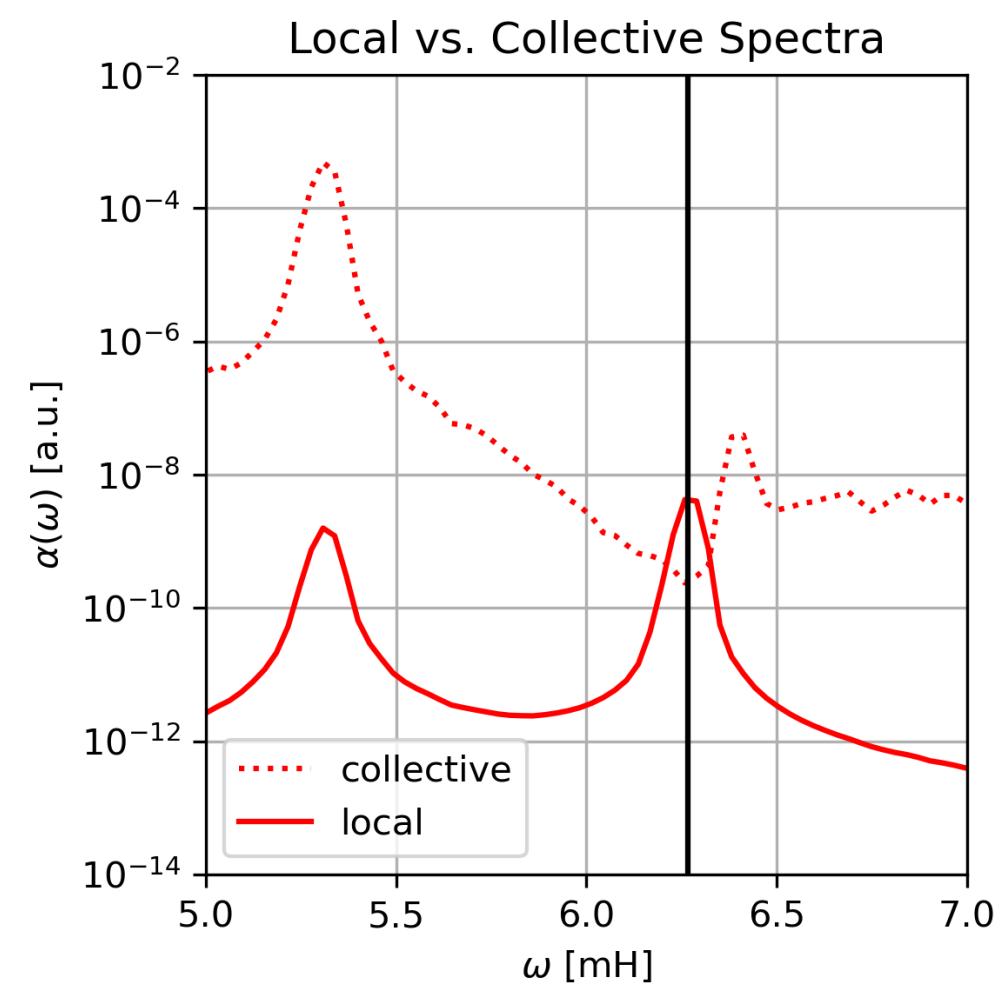
cavity-Hartree MD at Finite Temperature



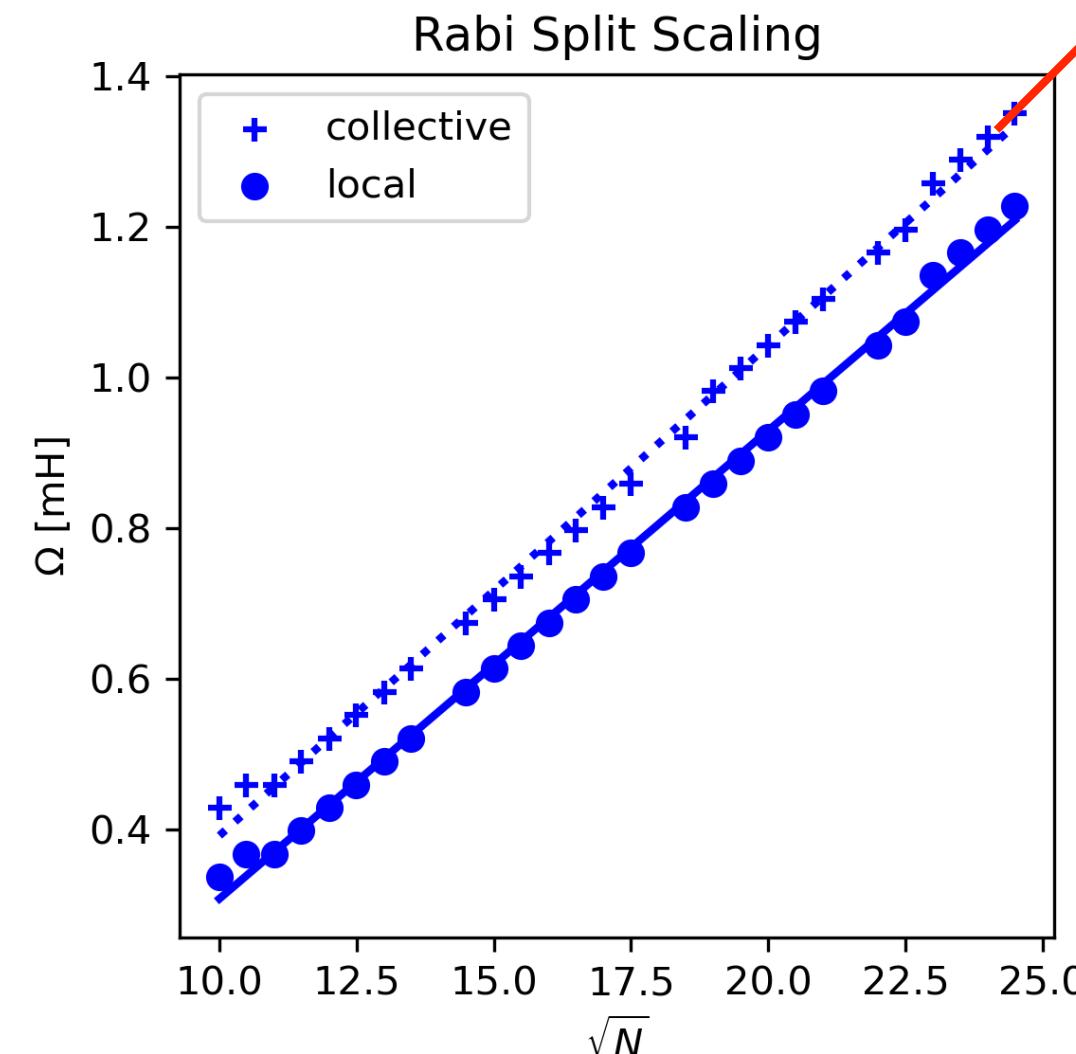
Shin-Metiu model (double-well)

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

IR spectra
(aligned vs. rotated molecules)



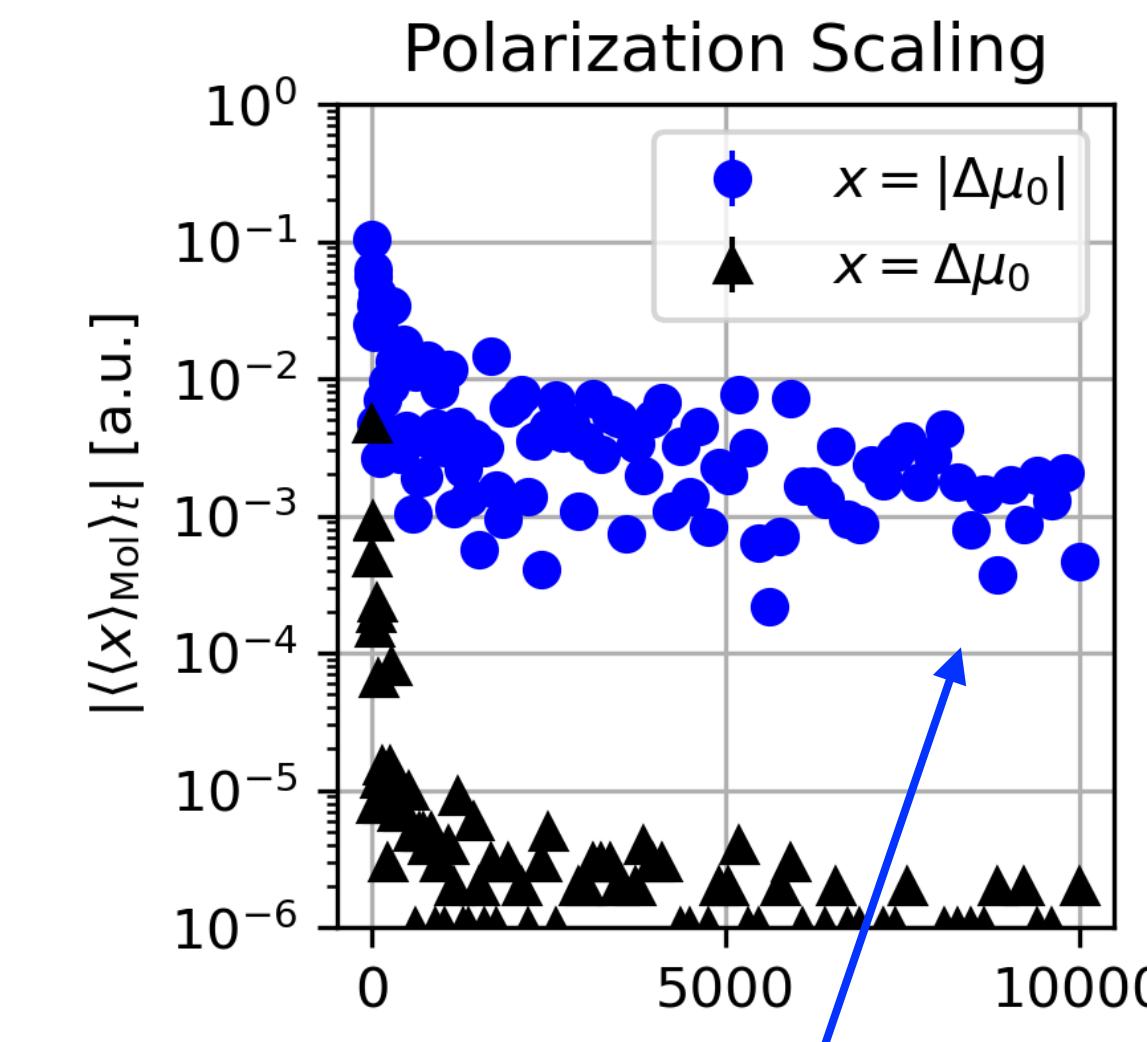
Collective Rabi split scaling
Convergence issue / instability
(numerics / physics)



Collective degeneracy?
(active research)

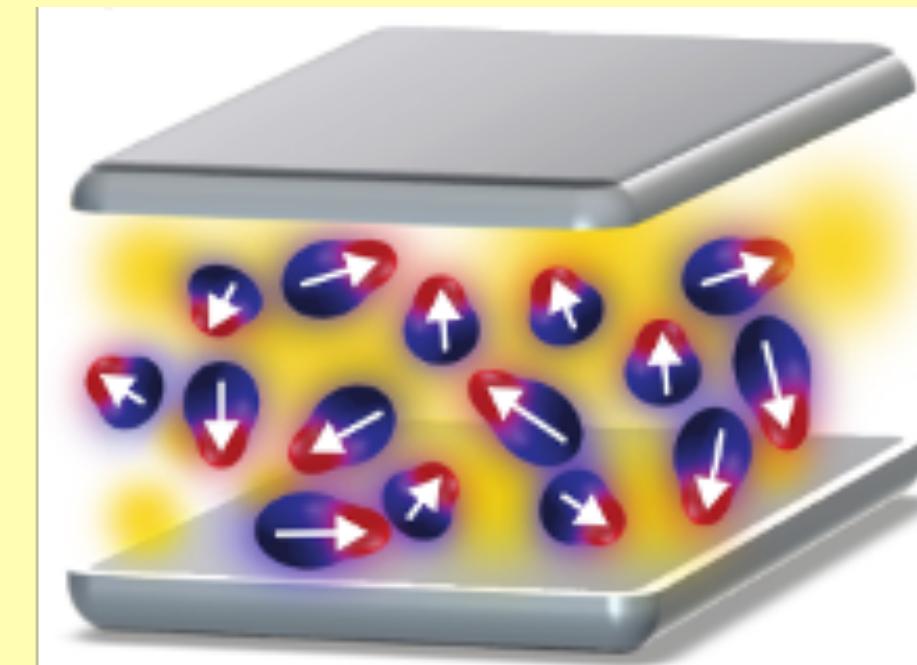
Cavity-induced local polarization

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



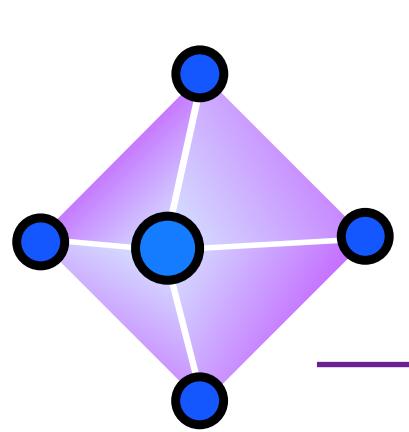
Collectively-induced
local (!) polarization

„Polarization glass hypothesis“

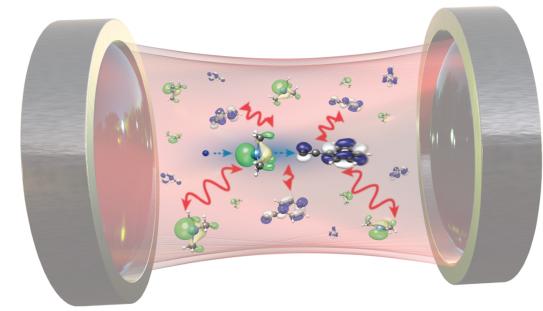


$$E_{\text{cH}}[\Delta\mu_0] = 0$$

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



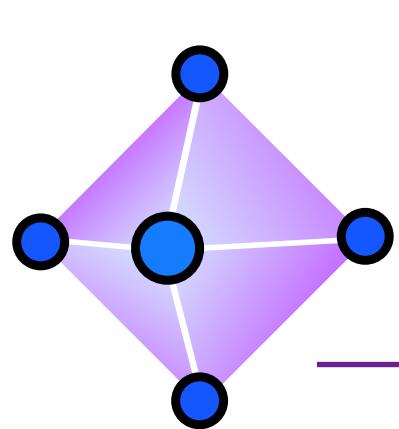
Configuration Interaction (CI)



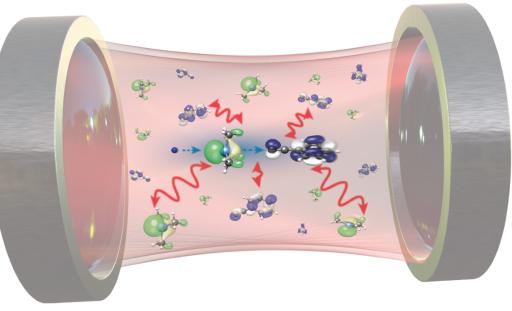
Blackboard: Beyond Hartree-Fock / Electron Correlations

unpublished

$$\begin{aligned}\langle \Psi | \hat{H}^e | \Psi \rangle &= \langle \Psi | \sum_i^{N_e N} \left\{ \frac{\hat{\mathbf{p}}_i^2}{2} - \frac{1}{2} \sum_l^{N_n N} \frac{Z_l}{|\hat{\mathbf{r}}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_j^{N_e N} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \right\} + \left(\frac{1}{2} \hat{x}^2 + \hat{x}X - \omega_\beta \hat{x}q_\beta \right) | \Psi \rangle \\ &= \sum_i^{N_e N} \int d\boldsymbol{\tau} \phi_i^*(\boldsymbol{\tau}) \left(\hat{h}^m + \hat{h}^l \right) \phi_i(\boldsymbol{\tau}) \\ &\quad + \frac{1}{2} \sum_i^{N_e N} \sum_j^{N_e N} \int d\boldsymbol{\tau}_1 \int d\boldsymbol{\tau}_2 \phi_i^*(\boldsymbol{\tau}_1) \phi_j^*(\boldsymbol{\tau}_2) \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \phi_i(\boldsymbol{\tau}_1) \phi_j(\boldsymbol{\tau}_2) \\ &\quad - \frac{1}{2} \sum_i^{N_e N} \sum_j^{N_e N} \int d\boldsymbol{\tau}_1 \int d\boldsymbol{\tau}_2 \phi_i^*(\boldsymbol{\tau}_1) \phi_j^*(\boldsymbol{\tau}_2) \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \phi_i(\boldsymbol{\tau}_2) \phi_j(\boldsymbol{\tau}_1) \\ &\quad + \frac{1}{2} \sum_i^{N_e N} \sum_j^{N_e N} \int d\boldsymbol{\tau} \phi_i^*(\boldsymbol{\tau}) \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} \phi_i(\boldsymbol{\tau}) \int d\boldsymbol{\tau} \phi_j^*(\boldsymbol{\tau}) \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} \phi_j(\boldsymbol{\tau}) \\ &\quad - \frac{1}{2} \sum_i^{N_e N} \sum_j^{N_e N} \left| \int d\boldsymbol{\tau} \phi_i^*(\boldsymbol{\tau}) \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} \phi_j(\boldsymbol{\tau}) \right|^2\end{aligned}$$

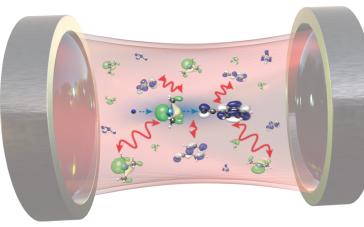


HF energy asymptotically ($N \rightarrow \infty$) exact (outside cavity)



Blackboard: Why we consider CI singles sufficient for collective effects.

unpublished



Correlations

Configuration Interaction (CI) Singles

CI wave-function Ansatz:

$$|\Phi_c\rangle = c_0|\Psi_0\rangle + \sum_c^N \sum_t^\infty c_c^t |\Psi_c^t\rangle,$$

For Coulomb 2-body interaction known:

- single excitations affect charge distribution / polarization.
- double excitations change correlation energy. However, HF energy asymptotically exact.

$$\langle \Psi_d^u | \hat{H}^e | \Psi_c^t \rangle = (E_0 + \epsilon_t - \epsilon_c) \delta_{d,c} \delta_{u,t} + 2(ud|ct) - (ut|cd).$$

$$(ud|ct) = (ud|ct)_C + (ud|ct)_{DSE}. \quad \begin{aligned} (ud|ct)_{DSE} &= \langle \chi_u | \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} | \chi_d \rangle \langle \chi_c | \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} | \chi_t \rangle \\ (ud|ct)_C &= \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_u^*(\mathbf{r}_1) \chi_d(\mathbf{r}_1) |\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|^{-1} \chi_c^*(\mathbf{r}_2) \chi_t(\mathbf{r}_2), \end{aligned}$$

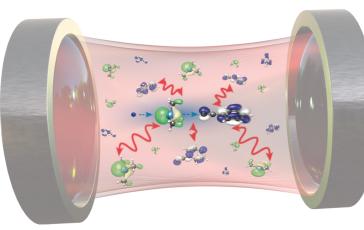
CI-singles energies:

$$\begin{aligned} \mathcal{E}_c &= \langle \Phi_c | \hat{H}^e | \Phi_c \rangle \\ &= \frac{1}{c_0^2 + \sum_{ct} (c_c^t)^2} \left(c_0^2 E_0 + \sum_c^N \sum_d^N \sum_t^\infty \sum_u^\infty c_c^t c_d^u [(E_0 + \epsilon_t - \epsilon_c) \delta_{d,c} \delta_{u,t} + 2(ud|ct) - (ut|cd)] \right). \end{aligned}$$

Explore lowest lying CI-singles energies / degeneracies in asymptotic limit...

$$E_0 \stackrel{?}{=} \mathcal{E}_0 \leq \mathcal{E}_1 \leq \dots$$

unpublished



Collective DSE Correlations

Mapping on a spin glass

$$(ud|ct) = (ud|ct)_C + (ud|ct)_{\text{DSE}}.$$

$$(ud|ct)_{\text{DSE}} = \langle \chi_u | \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} | \chi_d \rangle \langle \chi_c | \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} | \chi_t \rangle$$

$$(ud|ct)_C = \int d\mathbf{r}_1 d\mathbf{r}_2 \chi_u^*(\mathbf{r}_1) \chi_d(\mathbf{r}_1) |\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|^{-1} \chi_c^*(\mathbf{r}_2) \chi_t(\mathbf{r}_2),$$

Definition: Quasi-dilute gas condition:

$$c, d, s, u \in S_{\text{quasi-dilute}} = \{(ud|ct)_C \rightarrow 0 \wedge (ud|ct)_{\text{DSE}} \neq 0\}.$$

Correlation Energy:

$$\begin{aligned} \mathcal{E}_c &= E_0 + E_c^C + E_c^{\text{DSE}} \\ &\approx E_0 + E_c^{\text{C,intra}} + E_c^{\text{C,inter}} + E_c^{\text{DSE,inter}} \\ &\stackrel{\text{quasi dilute}}{\approx} E_0 + E_c^{\text{C,intra}} + E_c^{\text{DSE,inter}}, \end{aligned}$$

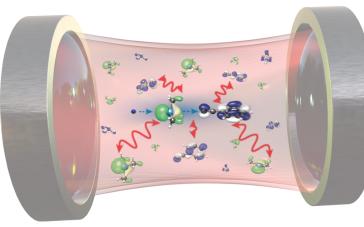
Assumption:

- Bipartite partitioning of coefficients $c, d, t, u \in S = S_{\text{quasi-dilute}} \cup \overline{S}_{\text{quasi-dilute}}$.

unpublished

$$\mathcal{E}_c = \langle \Phi_c | \hat{H}^e | \Phi_c \rangle = \frac{1}{c_0^2 + \sum_{ct} (c_c^t)^2} \left(c_0^2 E_0 + \sum_c^N \sum_d^N \sum_t^\infty \sum_u^\infty c_c^t c_d^u [(E_0 + \epsilon_t - \epsilon_c) \delta_{d,c} \delta_{u,t} + 2(ud|ct) - (ut|cd)] \right).$$

$$\sum_c^N \sum_d^N \sum_t^\infty \sum_u^\infty c_c^t c_d^u 2(ud|ct)_{\text{DSE}} = \underbrace{\left(\sum_c^N \sum_t^\infty c_c^t \langle \chi_c | \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} | \chi_t \rangle \right)^2}_{\rightarrow 0} + \sum_c^N \sum_t^\infty \left(c_c^t \langle \chi_c | \boldsymbol{\lambda} \cdot \hat{\mathbf{r}} | \chi_t \rangle \right)^2. \Rightarrow \text{Diagonal DSE contributions to inter-molecular correlation energy}$$



Collective DSE Correlations

Mapping on a spin glass

unpublished

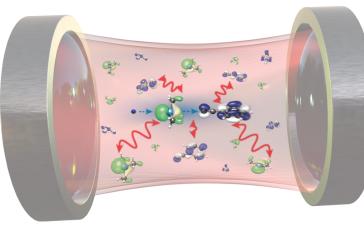
$$\begin{aligned} E_c^{\text{DSE,intra}} &= \frac{1}{c_0^2 + \sum_{ct} (c_c^t)^2} \left[\sum_{c,t \in S_{\text{quasi-dilute}}} (c_c^t)^2 \underbrace{(\epsilon_t - \epsilon_c + (\langle \chi_c | \lambda \cdot \hat{r} | \chi_t \rangle)^2 - (tt|cc)_{\text{DSE}})}_{-\mathcal{K}_{cc}^{tt}} \right. \\ &\quad \left. - \sum_{c,d,t,u \in S_{\text{quasi-dilute}}} c_c^t c_d^u \underbrace{(ut|cd)_{\text{DSE}}(1 - \delta_{cd}\delta_{tu})}_{\mathcal{K}_{cd}^{tu}} \right] \\ &= - \sum_{c,d,t,u \in S_{\text{quasi-dilute}}} c_d^u c_c^t \frac{\mathcal{K}_{cd}^{tu}}{c_0^2 + \sum_{ct} (c_c^t)^2} \\ &= - \sum_{i,j}^{N_S} s_i s_j \mathcal{J}_{ij} \end{aligned}$$

Polarization of cavity introduces
random (!) interactions with
respect to molecular orientation.

Focus on highly degenerate HF ground-state for sufficient collective strong coupling („polarization glass“), i.e., $\langle \mathcal{J}_{ii} \rangle \approx 0$.

DSE Correlation Spin Glass:

$$E_{\text{corr}}^{\text{DSE}} = - \sum_{i < j}^{N_J} s_i s_j J_{ij}, \quad \sum_i s_i^2 = 1, \quad \langle J_{ii} \rangle = 0,$$



DSE Correlation Spin Glass

Summary

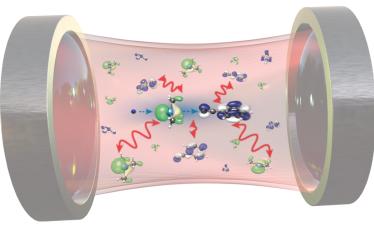
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Prerequisites:

1. „Polarization-ordering“ for sufficiently strong collective light-matter coupling. **Collectively-degenerate electronic ground-state.**
2. **Quasi-dilute gas limit** with sufficient density of states (DSE inter-molecular correlations dominate over Coulomb correlations).
3. Source of **randomness**: E.g., molecular orientations with respect to cavity polarization.
4. Random DSE **fluctuations** must be **sufficiently strong** $\propto T_c$ (critical temperature) for phase transition into a spin glass ($T < T_c$).

DSE Correlation Spin Glass:

$$E_{\text{corr}}^{\text{DSE}} = - \sum_{i < j}^{N_J} s_i s_j J_{ij}, \quad \sum_i s_i^2 = 1, \quad \langle J_{ii} \rangle = 0,$$



Summary and Conclusion

1. Coulombic **electron correlations** crucial to capture reactivity / dispersion effects.
2. **Post-HF** simulation methods required (e.g. CI).
3. **Few-molecule strong coupling** simulation show significant impact on electron correlations due to cavity.
4. **Collective strong coupling:**
 1. **HF energy is asymptotically exact** (at least in free space)!
 2. **CI-singles appear sufficient** to investigate dressed electronic problem / degenerate groundstate.
 3. **Quasi-dilute gas approximation** reveals a **spin glass-like** structure of the cavity-mediated intermolecular **correlation energy**.

Implications -> Next lecture