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MICCoM Workshop & Hands-on tutorials

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Computational Spectroscopy

A modular strategy for innovation

pyCDFT **Diabatic states**

Electronic & structural properties at finite T from first principles MD

Electronic structure of strongly correlated sites from quantum embedding

Quantum vibronic coupling from path-integral

Free energy landscapes from advanced sampling

Opto- electronic spectroscopy from Many Body Perturbation Theory (MBPT)

Coherence properties from spin-Hamiltonians, pyZFS, **and generalized cluster expansion**

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Structural models derived with the aid of DFT and first principles molecular dynamics (FPMD)

$$M_I \ddot{R}_I = F_I$$
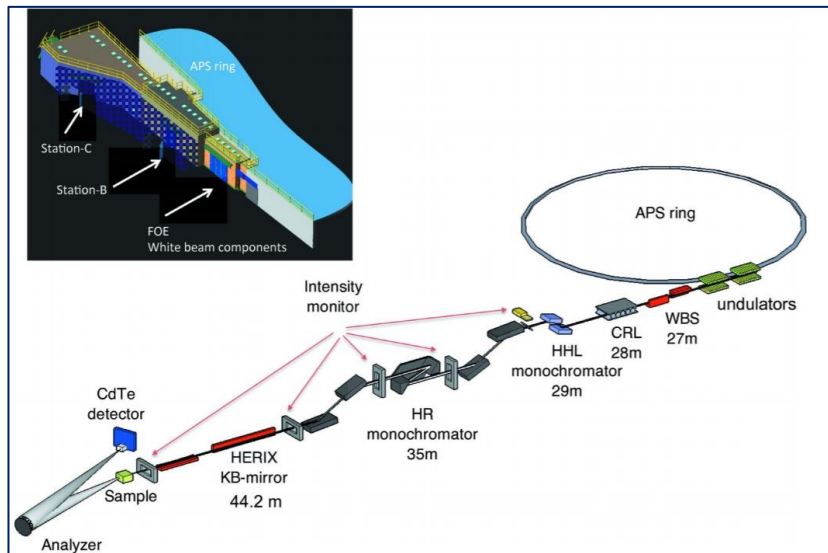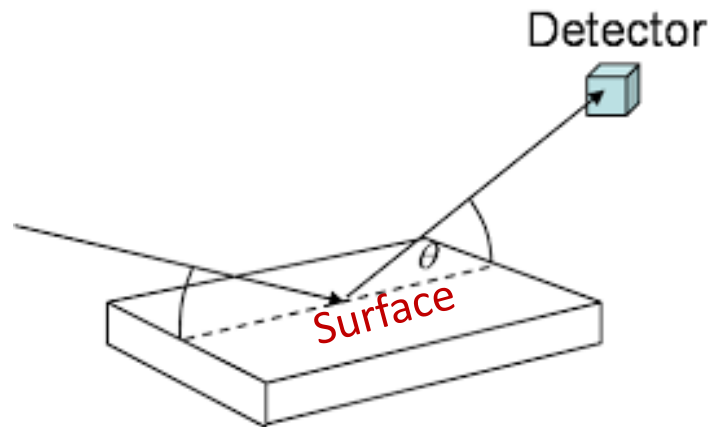$$F_I = -\nabla_I \; E \left(\{ R_I(t) \} \right)$$

↑

E from **DFT**

Spectroscopic signatures

Computational spectroscopy is key

- To validate atomistic structural models by comparing with experiments

- To understand & predict light-matter & external field interaction processes
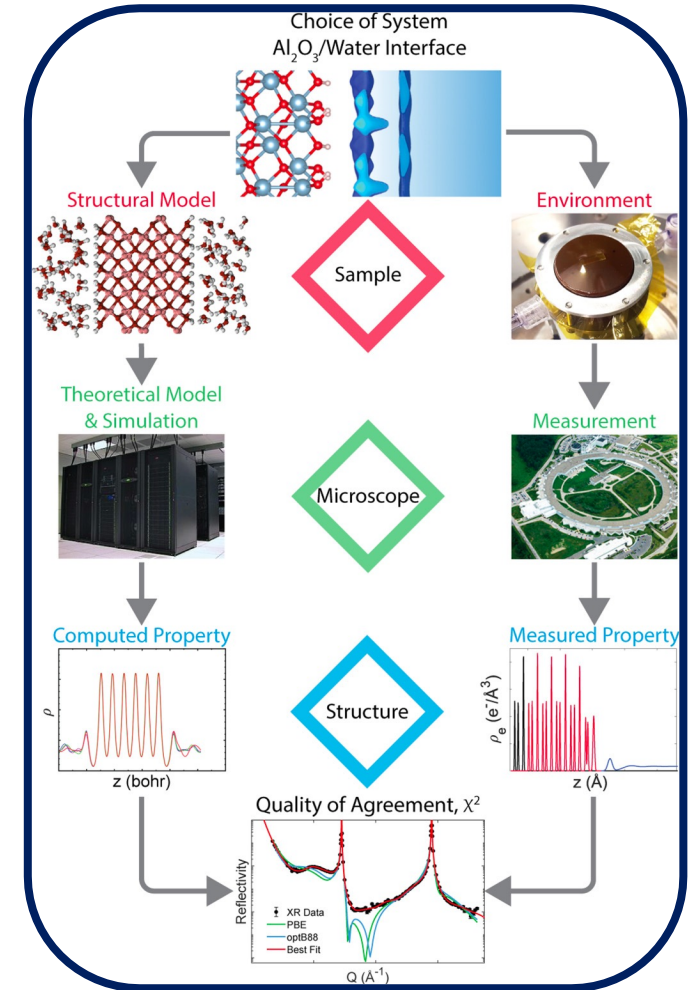
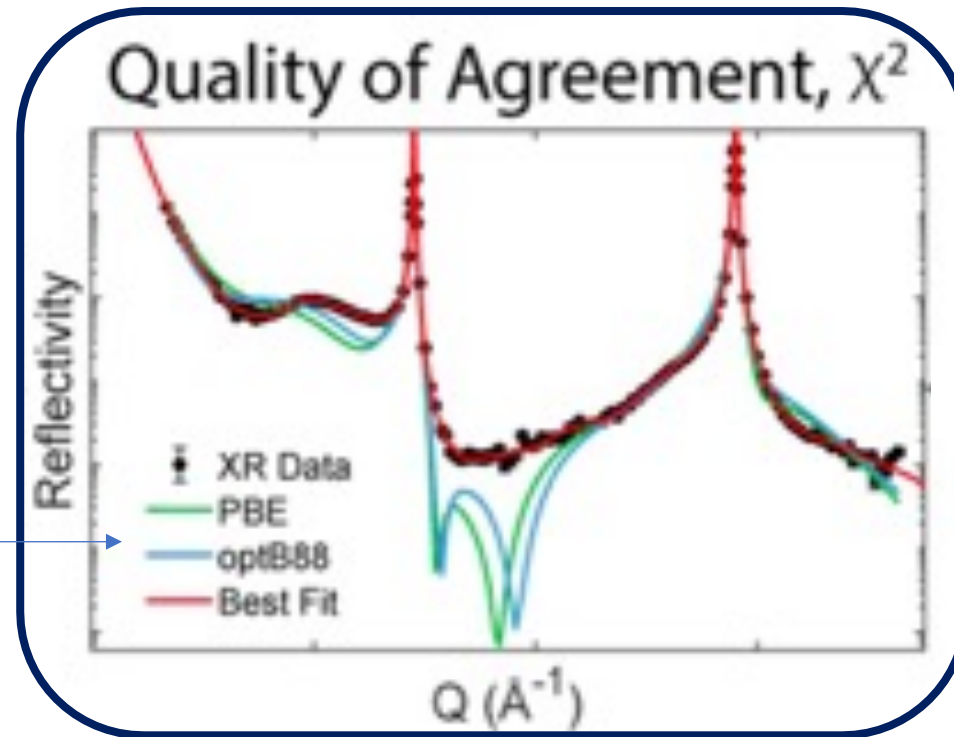# Structural models derived with the aid of DFT and first principles molecular dynamics

Experimental validation of structural models

**Validation of FPMD of oxide/water interfaces with X-ray reflectivity data**

K.Harmon , .. P.Fenter & GG, PRM 2020

Structural models derived with the aid of DFT and first principles molecular dynamics

Different density functionals

K.Harmon , .. P.Fenter & GG, PRM 2020

Structural models derived with the aid of DFT and first principles molecular dynamics (FPMD)

$$M_I \ddot{R}_I = F_I$$

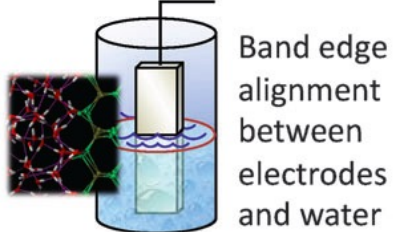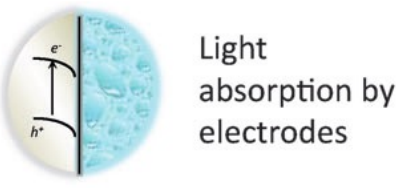$$F_I = -\nabla_I \; E(\{R_I(t)\})$$

↑

E from **DFT**
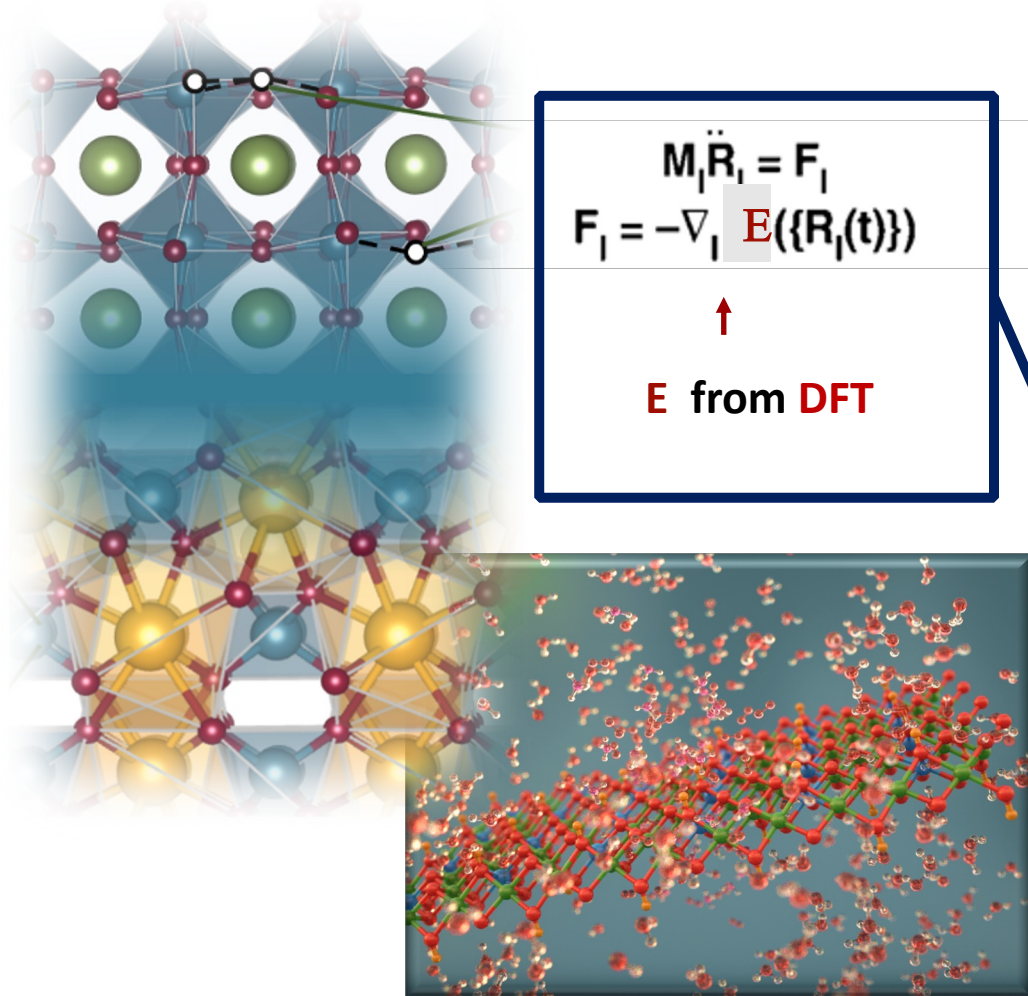
Spectroscopic signatures

Computational spectroscopy is key

- **To validate atomistic structural models by comparing with experiments**

- **To understand & predict light-matter & external field interaction processes**

Spectroscopy on MD samples using Many Body Perturbation Theory

- **Development of post-DFT theories for spectroscopic characterization of materials is key to prediction and design of new systems & properties**

Processes of interest		Band edge alignment between electrodes and water		Light absorption by electrodes
Experiments	Photoemission spectroscopy	GW	UV-vis and ellipsometry spectroscopy	BSE

Spectroscopic Characterization

Many Body Perturbation Theory

- Photoemission
- Absorption
- X-ray photoemission
- Photoluminescence
- Deep level transient spectroscopy
- Ultrafast spectroscopy
- Non-radiative recombination

H. Wilson, F. Gygi, and GG, PRB 2008; H.Wilson, D.Lu, F.Gygi and GG, PRB 2009; H. V. Nguyen, T.A. Pham, D.Rocca and GG PRB (R) 2012;D.Rocca, D.Lu and GG, JCP 2010; T.A.Pham, H,V.Nguyen, D.Rocca and GG, PRB 2013; M.Govoni & GG, JCTC, 2015 & 2018; P.Scherpelz, I.Hamada, M.Govoni and GG, JCTC 2017; R.McAvoy, M.Govoni and GG, JCTC 2018; Nguyen et al. PRL 2019; Ma He et al, JCTC 2019 and JCTC 2020; S.Dong, M.Govoni & GG, Chem.Sci. 2021; H.Yang, A.Kundu, M.Govoni and GG, JCTC 2021

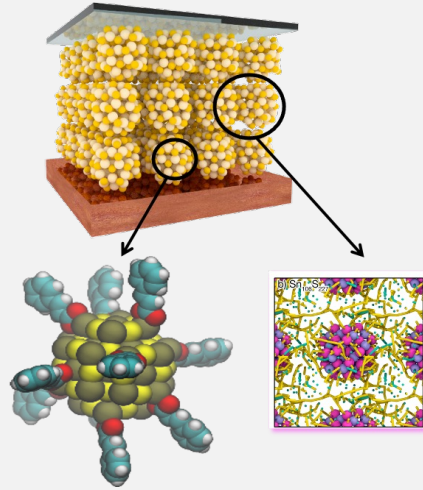# Computational Spectroscopy

Why is it useful?
Why is it interesting?
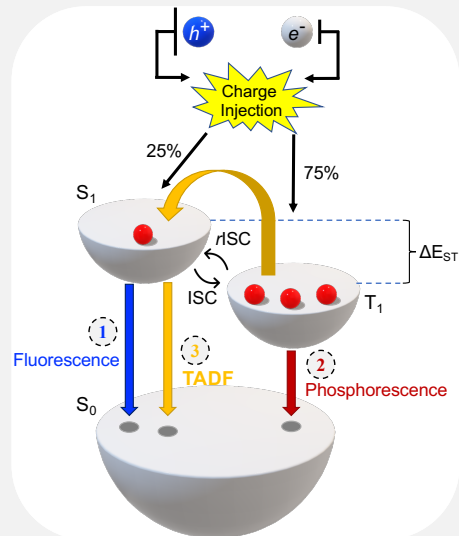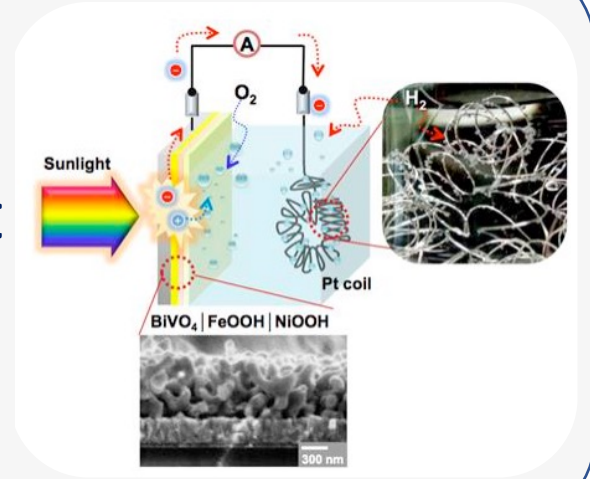**Which problems does it help us solve?**

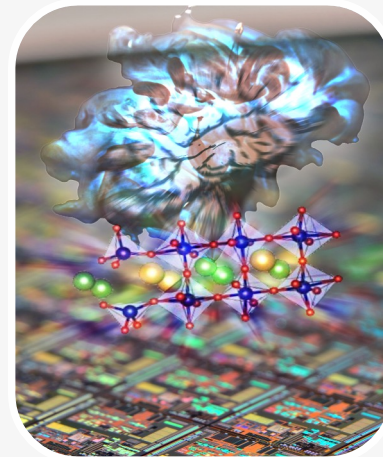# Multi-faceted processes and complex materials

Can we design easy to make and cheap **solar cells** using colloidal quantum dots?

How can we trigger desired photo-reactions to **generate clean fuel** at the interface of photo-absorbers, catalysts and water?
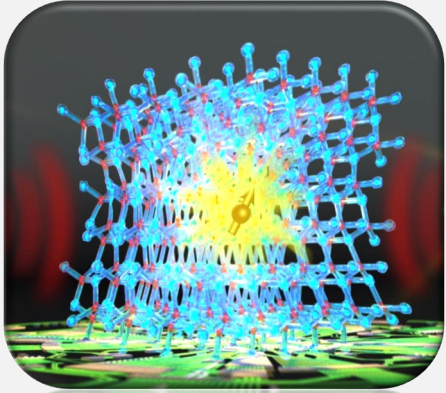

How do we design energy-efficient **all organic** light emitting diodes (**OLEDs**)?

Which materials are suitable for energy-efficient **neuromorphic platforms** and **low power electronics** ?

Multi-faceted processes and complex materials

Can we predict solid state and molecular systems to realize **spin-qubit for quantum technologies**?
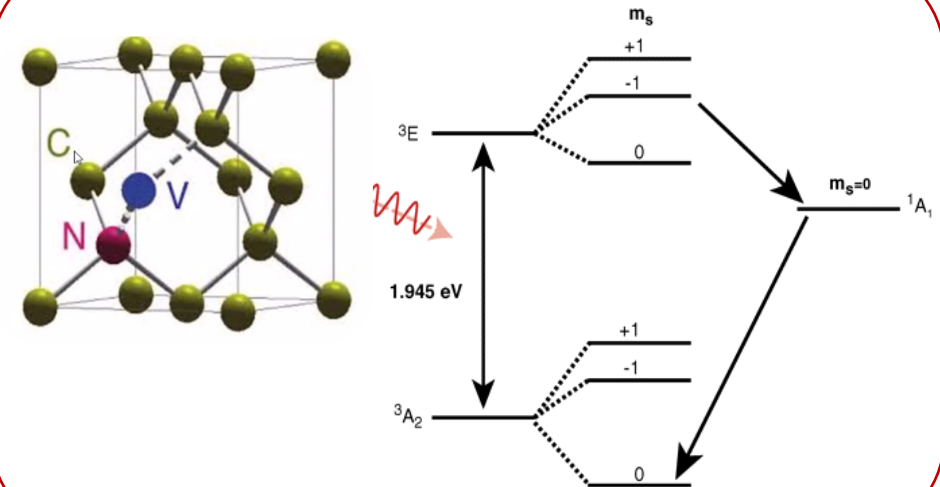
⟶

Harness the power of quantum information:
- Computing
- Sensors
- Communications

- Use electronic states of defects as **two-level systems**

- Optically address the two-level systems

   *Optical transition from ground to an excited state, followed by a spin-selective decay path with nonradiative transitions between states of differing spin multiplicity

Multi-faceted processes and complex materials
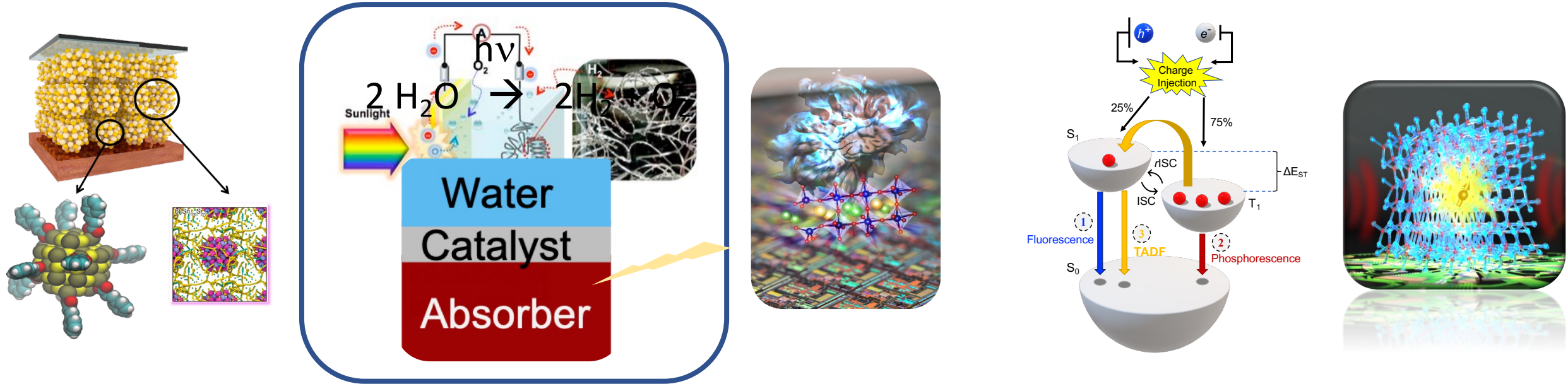
- Heterogeneous systems with **interfaces**, **defects** and complex **building blocks**

- Interaction of matter & **light** and matter & **external fields**

A difficult problem with many components
Simulations and predictions of numerous properties
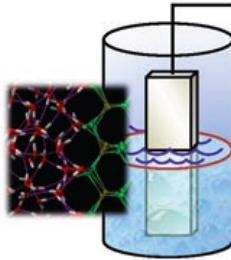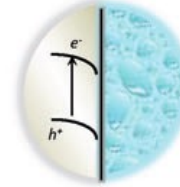
- Reasonable model of (salty) **water** (FPMD)

- Atomistic model of solid/liquid interfaces (FPMD) & their electronic properties (**band offsets** and **Schottky barriers**)

- **Charge transport** @interfaces

Absorption spectra of the solar absorber
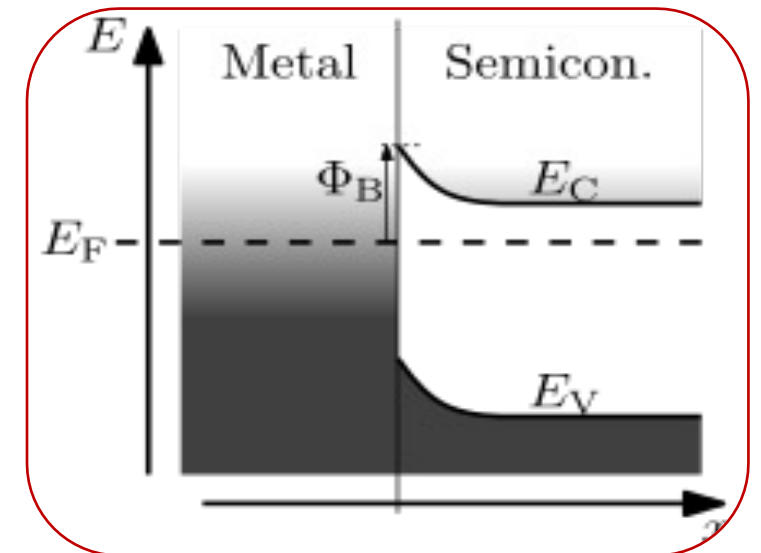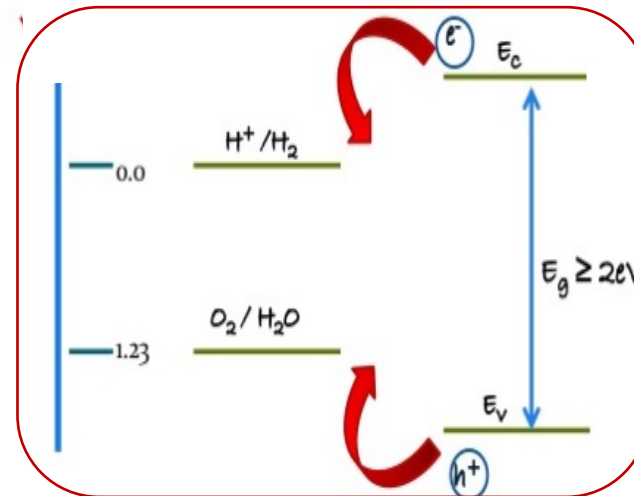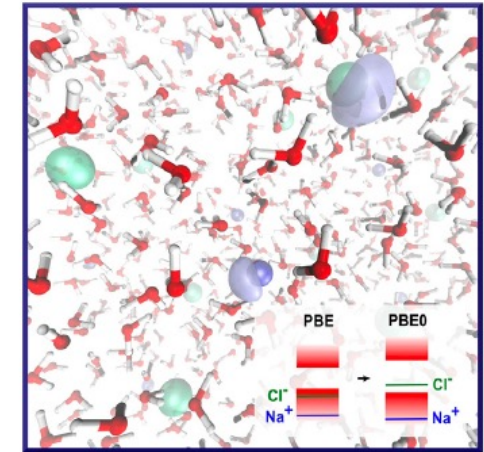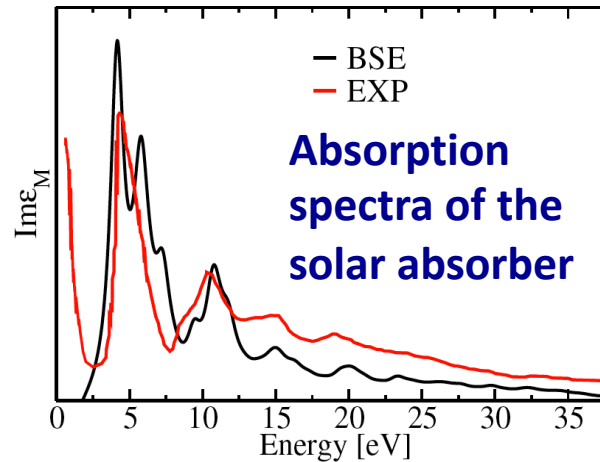
Spectroscopy on MD samples

Use first principles MD trajectories and compute electronic properties from **many body perturbation** theory → Electronic properties at finite T w/statistical errors

Processes of interest	Band edge alignment between electrodes and water	Light absorption by electrodes
Experiments	Photoemission spectroscopy GW	UV-vis and ellipsometry spectroscopy BSE
Theory	Single particle Green's functions $G^{(1)}$: poles represent energies to add or remove an electron from a solid or molecule	Two particle correlation function L: poles correspond to neutral excitation energies of interacting electrons
Equations	Dyson's equation: relates $G^{(1)}$ to self energy Σ (effective potential of interacting electrons)	Bethe Salpeter equation: relates L to the variation of Σ with respect to $G^{(1)}$

Solution of the Hedin's equations

$$\left(\hat{T} + \hat{V}_{ion} + \hat{V}_H + \hat{V}_{xc}\right)|\psi_n\rangle = \varepsilon_n|\psi_n\rangle \quad \text{DFT}$$

$$\left(\hat{T} + \hat{V}_{ion} + \hat{V}_H + \hat{\Sigma}(E_n^{QP})\right)|\psi_n^{QP}\rangle = E_n^{QP}|\psi_n^{QP}\rangle \quad \text{MBPT}$$

Σ expressed in terms of the **dynamically screened Coulomb potential**

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \int \frac{d\omega}{2\pi} G(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r},\mathbf{r}';\omega')$$

$$G(\mathbf{r},\mathbf{r}';\omega) = \langle\mathbf{r}|\frac{1}{\omega - H}|\mathbf{r}'\rangle$$

$$W(\mathbf{r},\mathbf{r}';\omega) = \int d\mathbf{r}'' \epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)v_c(\mathbf{r}'',\mathbf{r}')$$

Use an expression in terms of
Kohn-Sham electronic
states from density-density
response functions
or
From DFT calculations in
electric field

$$E_n^{QP} = \varepsilon_n^{KS} + \langle\psi_n^{KS}|\hat{\Sigma}(E_n^{QP}) - \hat{V}_{xc}|\psi_n^{KS}\rangle$$

L. Hedin, Phys. Rev. 139, A796 (1965)

Back to basics of the classical world: Maxwell equations for the total field

- Maxwell equations: Q = -e; n = density

$$\nabla \cdot \mathbf{E} = 4\pi Q n$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E}(t) = -\frac{1}{c}\frac{\mathrm{d}\mathbf{B}}{\mathrm{d}t}$$

$$\nabla \times \mathbf{B}(t) = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\mathrm{d}\mathbf{E}}{\mathrm{d}t}$$

$$\boxed{\nabla \cdot \mathbf{j} = -Q\frac{\mathrm{d}n}{\mathrm{d}t}}$$
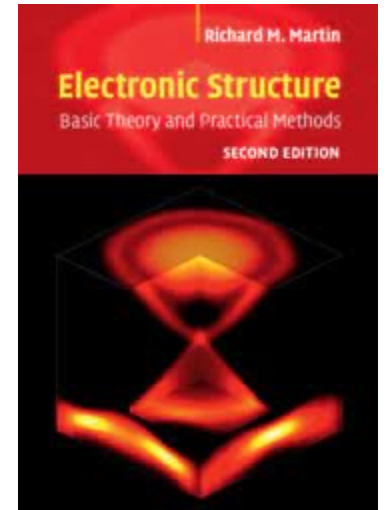
- Internal and External charges and currents:
  - $n = n_{\mathrm{int}} + n_{\mathrm{ext}}$; $j = j_{\mathrm{int}} + j_{\mathrm{ext}}$
- Polarization : defined to *within an additive constant* (one computes *polarization differences*)

$$\boxed{\mathbf{P}(\mathbf{r},t) = \int^{t} \mathrm{d}t'\mathbf{j}_{\mathrm{int}}(\mathbf{r},t')} \quad \boxed{\nabla \cdot \mathbf{P}(\mathbf{r},t) = -Q n_{\mathrm{int}}(\mathbf{r},t)}$$

Maxwell equations for the external field

- $D = E + 4\pi P$ D = external field, **independent of the material**

$$\nabla \cdot \mathbf{D} = 4\pi Q n_{\text{ext}} \qquad \nabla \times \mathbf{E}(t) = -\frac{1}{c}\frac{\mathrm{d}\mathbf{B}}{\mathrm{d}t}$$

$$\nabla \cdot \mathbf{B} = 0 \qquad \nabla \times \mathbf{B}(t) = \frac{4\pi}{c}\mathbf{j}_{\text{ext}} + \frac{1}{c}\frac{\mathrm{d}\mathbf{D}}{\mathrm{d}t}$$

- Relation between current and total field and density and total field

$$\mathbf{j}_{\text{int}}(\mathbf{r}, t) = \int \mathrm{d}\mathbf{r}' \int^{t} \sigma(\mathbf{r}, \mathbf{r}', t - t')\mathbf{E}(\mathbf{r}', t') \qquad \mathbf{j}_{\text{int}}(\mathbf{r}, \omega) = \int \mathrm{d}\mathbf{r}' \sigma(\mathbf{r}, \mathbf{r}', \omega)\mathbf{E}(\mathbf{r}', \omega)$$

$$\mathbf{D}(\mathbf{r}, \omega) = \int \mathrm{d}\mathbf{r}' \epsilon(\mathbf{r}, \mathbf{r}', \omega)\mathbf{E}(\mathbf{r}', \omega) \qquad \mathbf{E}(\mathbf{r}, \omega) = \int \mathrm{d}\mathbf{r}' \epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)\mathbf{D}(\mathbf{r}', \omega)$$

- Response to the total field E

$$\epsilon(\mathbf{r}, \mathbf{r}', \omega) = 1\delta(\mathbf{r} - \mathbf{r}') + \frac{4\pi i}{\omega}\sigma(\mathbf{r}, \mathbf{r}', \omega)$$

- Response to the external field D $\rightarrow$ $\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$

Response in terms of scalar potentials

- $E = -\nabla V(r)$: **field derived from potential** → in Fourier space: $E(q) = i\, q\, V(q)$ is longitudinal (|| to q)

$$\epsilon^{-1}(\mathbf{q},\mathbf{q}',\omega) = \frac{\delta V_{\text{total}}^{C}(\mathbf{q},\omega)}{\delta V_{\text{ext}}(\mathbf{q}',\omega)}$$

$$\epsilon(\mathbf{q},\mathbf{q}',\omega) = \frac{\delta V_{\text{ext}}(\mathbf{q},\omega)}{\delta V_{\text{total}}^{C}(\mathbf{q}',\omega)}$$

External potential   Coulomb potential

- How do we compute the dielectric response?

  - Derive an expression of the direct and inverse dielectric response in terms of single particle (Kohn-Sham) electronic states ψ_i from density response functions

Static density response function

- Response of the electrons to a variation of the total potential at r'

$$\chi_n^0(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta V_{\text{eff}}(\mathbf{r}')} = 2 \sum_{i=1}^{\text{occ}} \sum_{j}^{\text{empty}} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j}$$

Definition   Perturbation theory

$$\chi_n^0(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{\text{occ}} \psi_i^*(\mathbf{r}) G_0^i(\mathbf{r}, \mathbf{r}') \psi_i(\mathbf{r}')$$

Independent particle Green function

$$G_0^i(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i}^{\infty} \frac{\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')}{\epsilon_i - \epsilon_j}$$

Response in terms of scalar potentials

- $E = -\nabla V(r)$: **field derived from potential** → in Fourier space: $E(q) = i q V(q)$ is longitudinal (|| to q)

$$\epsilon^{-1}(\mathbf{q}, \mathbf{q}', \omega) = \frac{\delta V_{\text{total}}^C(\mathbf{q}, \omega)}{\delta V_{\text{ext}}(\mathbf{q}', \omega)}$$

$$\epsilon(\mathbf{q}, \mathbf{q}', \omega) = \frac{\delta V_{\text{ext}}(\mathbf{q}, \omega)}{\delta V_{\text{total}}^C(\mathbf{q}', \omega)}$$

External potential

Coulomb potential

$$\epsilon^{-1} = 1 + \frac{V_C \chi^0}{1 - (V_C + f_{xc})\chi^0}$$

- How do we compute the dielectric response?

  - Derive an expression of the direct and inverse dielectric response in terms of single particle (Kohn-Sham) electronic states ψ_i from density response functions

Calculation of dielectric matrices

Within the RPA approximation ($f_{xc} = 0$)

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \delta_{\mathbf{G},\mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}|^2} \frac{4}{N_k \Omega} \sum_{\mathbf{k},v,c} \frac{\langle v,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c,\mathbf{k}+\mathbf{q}\rangle \langle c,\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v,\mathbf{k}\rangle}{E_{v,\mathbf{k}} - E_{c,\mathbf{k}+\mathbf{q}}}$$

Similarity transformation to a Hermitian matrix:

$$\tilde{\epsilon}_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \frac{|\mathbf{q}+\mathbf{G}|}{|\mathbf{q}+\mathbf{G}'|}\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$$

Eigenvalues of the dielectric matrix are real and greater than or equal to 1

Direct, straightforward calculation of dielectric matrices is prohibitive for large systems

Spectral decomposition

- Represent polarizability by its eigenvalue decomposition and truncate sum over eigenvalues to an *appropriate, small number*

$$\tilde{\chi}_0 = \sum_{i=1}^{N} \tilde{\phi}_i \lambda_i \tilde{\phi}_i^H \longrightarrow \tilde{\chi} = \sum_{i=1}^{N} \tilde{\phi}_i \frac{\lambda_i}{1 - \lambda_i} \tilde{\phi}_i^H$$

RPA

- Once this eigenvalue decomposition is known, computing ε is trivial

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{\phi}_i \left(1 - \lambda_i\right) \tilde{\phi}_i^H \qquad \tilde{\epsilon}^{-1} = \sum_{i=1}^{N} \tilde{\phi}_i \left(\frac{\lambda_i}{1 - \lambda_i} + 1\right) \tilde{\phi}_i^H$$

H.Wilson, F.Gygi and G.Galli, PRB 2008; H.Wilson, D.Lu, F.Gygi & GG, PRB 2009

- Compute eigenvalues and eigenvectors using Density Functional Perturbation Theory[*](DFPT) → avoid costly calculation of empty single particle states

(*) S. Baroni, et al., Rev. Mod. Phys., 73:515, 2001.

# Calculations of dielectric matrices: spectral decomposition & DFPT

$$\tilde{\epsilon}^{-1} = \sum_{i=1}^{\text{Neig}} \tilde{\phi}_i \left(\frac{\lambda_i}{1-\lambda_i} + 1 \right) \tilde{\phi}_i^H$$

- Calculation of empty electronic states, calculation and storage of full dieletric matrix and inversion of $\tilde{\epsilon}$ are avoided

- Scaling: $N_{eig}N_{pw}N_v^2$ (instead of $N_{pw}^2N_vN_c$)

- Efficient evaluation of $\tilde{\epsilon}^{-1}$ at different **q** points and at different MD steps is possible

H. Wilson, F. Gygi, and G. G., PRB 2008; H.Wilson, D.Lu, F.Gygi and G.G., Phys.Rev.B 2009; V. H. Nguyen, S. de Gironcoli, Phys.Rev.B 2009, M.Govoni & GG, J. Chem. Theory Comput., (2015)

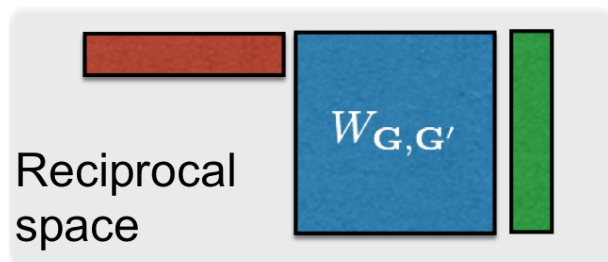# Low rank decomposition of the screened Coulomb interaction W

In **Hartree-Fock**

$$\langle \psi_i \psi_j | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_k \psi_l \rangle$$

Reciprocal space
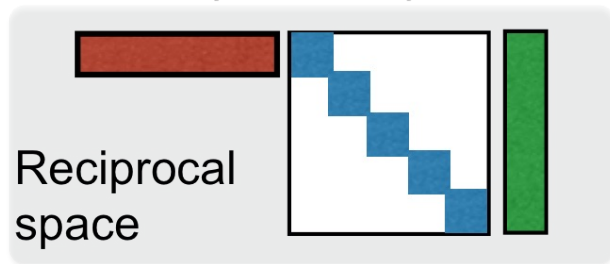
In **GW**

$$\langle \psi_i \psi_j | W(\mathbf{r}, \mathbf{r}') | \psi_k \psi_l \rangle$$

Reciprocal space

Example : 64 water molecules

Direct space   size~$(250)^3$ x $(250)^3$

Difficult to truncate

Reciprocal space   size~$(1'000'000)$ x $(1'000'000)$

Could be truncated, full matrix

Eigenpotential space   size~$(1'000)$ x $(1'000)$

$$W = \sum_\alpha |\alpha\rangle \lambda_\alpha \langle\alpha|$$ **Low-rank decomposition**

 $W_{\mathbf{G},\mathbf{G}'}$ $\longrightarrow$ **Separable form**
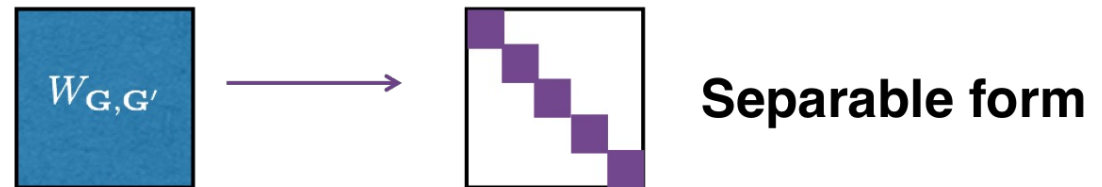
Summary of GW algorithm

- Iterative diagonalization of the dielectric matrix [+] $\rightarrow$

- Low rank decomposition of W

- DFPT [*] based projection techniques to compute G

- Eigenpotentials of $\widetilde{\epsilon}$ as basis set also at finite frequency [++]

- Lanczos algorithm to compute frequency dependence of dielectric matrix in parallel

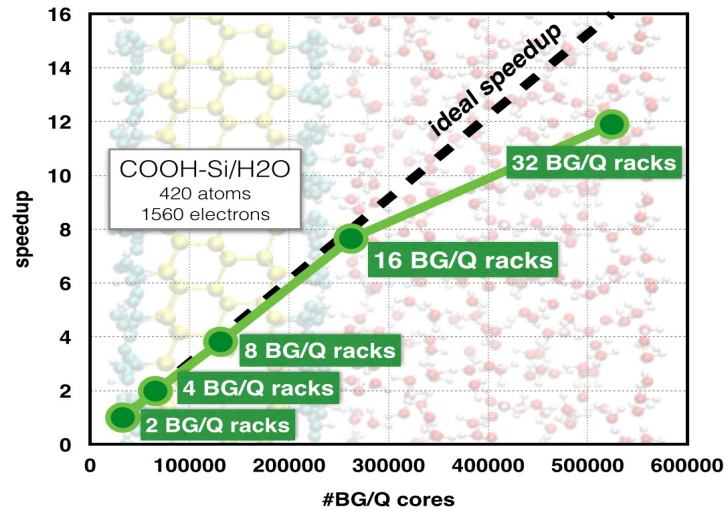- Contour deformation technique for frequency integration [&]

(*) S. Baroni, et al., Rev. Mod. Phys., 73:515, 2001.

(+) H. Wilson, F. Gygi, and G. G., PRB 2008; H.Wilson, D.Lu, F.Gygi and G.G., Phys.Rev.B 2009
(++) H. V. Nguyen, T.A. Pham, D.Rocca and GG Phys. Rev. B (R) 2012; T.A.Pham, H,V.Nguyen, D.Rocca and GG, Phys.Rev.B 2013
(&) M.Govoni & GG, J. Chem. Theory Comput., (2015) & J.Chem.Theory Comp. (2018).

West coupling

$$\hat{W} = v_c + v_c \chi v_c$$

...ations over **empty states** using DFPT

W made **separable** using the eigenvectors of the dielectric matrix as basis set; number of eigenpotentials controls the accuracy of the method.

Greatly reduced **pre-factors** of O(N^4) scaling

16
14
12
10
8
6
4
2
0

speedup

COOH-Si/H2O
420 atoms
1560 electrons

$K_{v,v'}^{1}$ ideal

16 BG/Q racks

8 BG/Q racks

4 BG/Q racks

2 BG/Q racks

0   100000   200000   300000   400000   500000   600000

#BG/Q cores

$$\hat{H} = \hat{H}_o + \Delta V(r)$$

$$\Delta\rho(r) = \sum \varphi_v^{o*}(r) \times [\varphi_v(r) - \varphi_v^o(r)]$$

$$\Delta V(r) = \int v_c(\mathbf{r}, \mathbf{r}') \rho_v^{v'}(r') dr'$$

$$\tau_v^{v'}(r) = \int \hat{W}(\mathbf{r}, \mathbf{r}') \varphi_{v'}^*(r) \varphi_v(r)$$

$$= \Delta V + \int v_c(r, r') \Delta\rho(r')$$

Range of applicability
Ordered and disordered solids, defective materials, liquids, molecular crystals, nanostructures, interfaces

QUANTUMESPRES

Govoni&GG, JCTC 2015, JCTC 2018

〈WEST!〉

West is available for download under the GPL. Get West!

www.west-code.o...

http://qboxcode.org/   http://www.west-code.org/

Absorption of light: solving the Bethe Salpeter equation (BSE)

Quantum Liouville equation

$$i\frac{d\hat{\rho}(t)}{dt} = \left[\hat{H}(t), \hat{\rho}(t)\right]$$

$$\hat{H}(t)\phi(\mathbf{r},t) = \left[-\frac{1}{2}\nabla^2 + v_H(\mathbf{r},t) + v_{ext}(\mathbf{r},t)\right]\phi(\mathbf{r},t)$$
$$+ \int \Sigma(\mathbf{r},\mathbf{r}',t)\phi(\mathbf{r}',t)d\mathbf{r}'$$

$$\Sigma_{COH}(\mathbf{r},\mathbf{r}') = \frac{1}{2}\delta(\mathbf{r}-\mathbf{r}')W_p(\mathbf{r}',\mathbf{r})$$
$$\Sigma_{SEX}(\mathbf{r},\mathbf{r}',t) = -\sum_v \phi_v(\mathbf{r},t)\phi_v^*(\mathbf{r}',t)W(\mathbf{r}',\mathbf{r})$$

BSE

Screened Coulomb interaction

- The quantum Liouville equation is solved within linear response theory
- Explicit calculation of empty electronic states is avoided by using iterative diag. of ε

D. Rocca, D. Lu, and G. Galli, *JCP* (2010)
D. Rocca, Y. Ping, R. Gebauer, and G. Galli, PRB (2012)

D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, *JCP* (2008)
B. Walker, R. Gebauer, A. M. Saitta, and S. Baroni, PRL (2006)

Addressing existing drawbacks

Develop efficient and scalable algorithms to go beyond the random phase approximation (RPA), which are 'easily' applicable to hybrid DFT wavefunctions and lead to improved efficiency

Strategy:

RPA: $f_{\mathrm{xc}} = \dfrac{\delta v_{\mathrm{xc}}[n]}{\delta n} \approx 0$

- A finite field algorithm to compute the density-density response function
- DFT calculations performed by Qbox exploiting:
  - Fast hybrid functional calculations with controllable accuracy
  - Client-server mode

He Ma, M. Govoni, G.Galli & F.Gygi JCTC 2019, PRL 2019
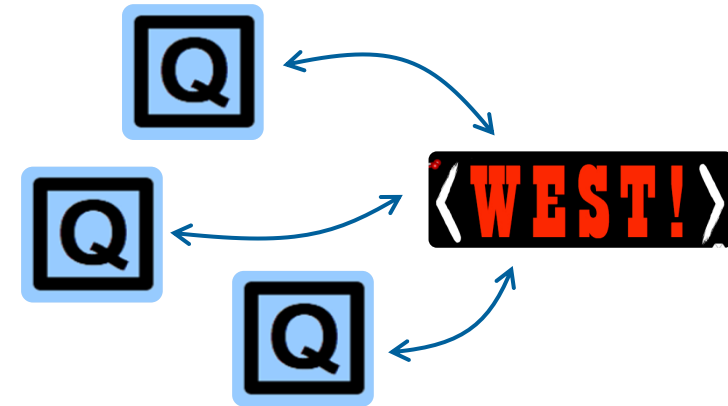
Finite temperature optical spectra

We developed an efficient solver of the Bethe-Salpeter Equation (BSE), based on a finite field approach (unique to WEST)[*]:

- **WEST-Qbox coupling** to avoid direct calculation of dielectric matrices and overcome commonly used approximations (e.g., Random Phase Approximation)

- **Reduced workload** by harnessing orbital localization w/ the recursive bisection method (unique to Qbox)
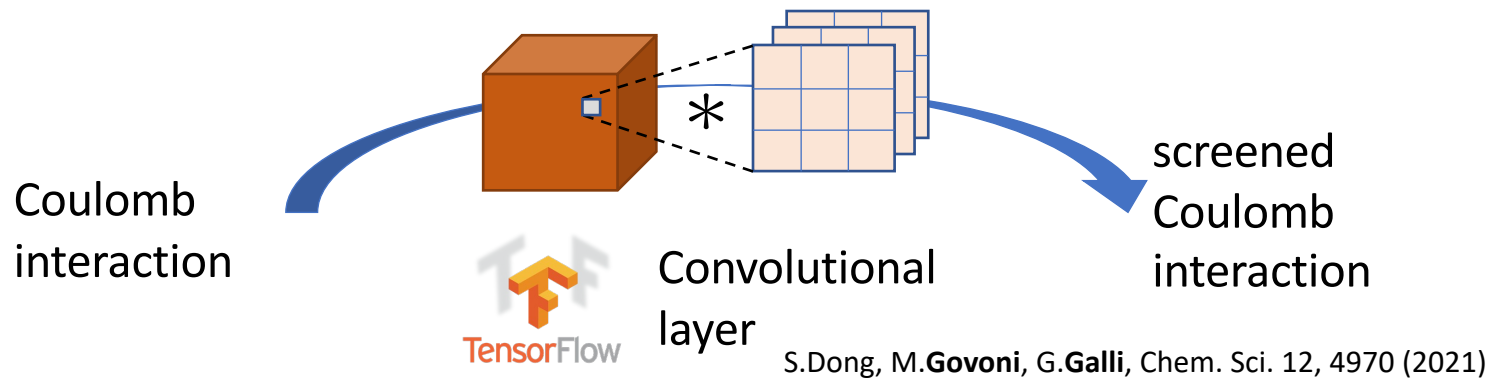
We computed **optical spectra** at finite T (e.g. liquid water and ice), where BSE is solved for several snapshots extracted from MD trajectories.

[*]L. Nguyen, H.Ma, **M.Govoni, F.Gygi, G.Galli**, *PRL* 122, 237402 (2019)
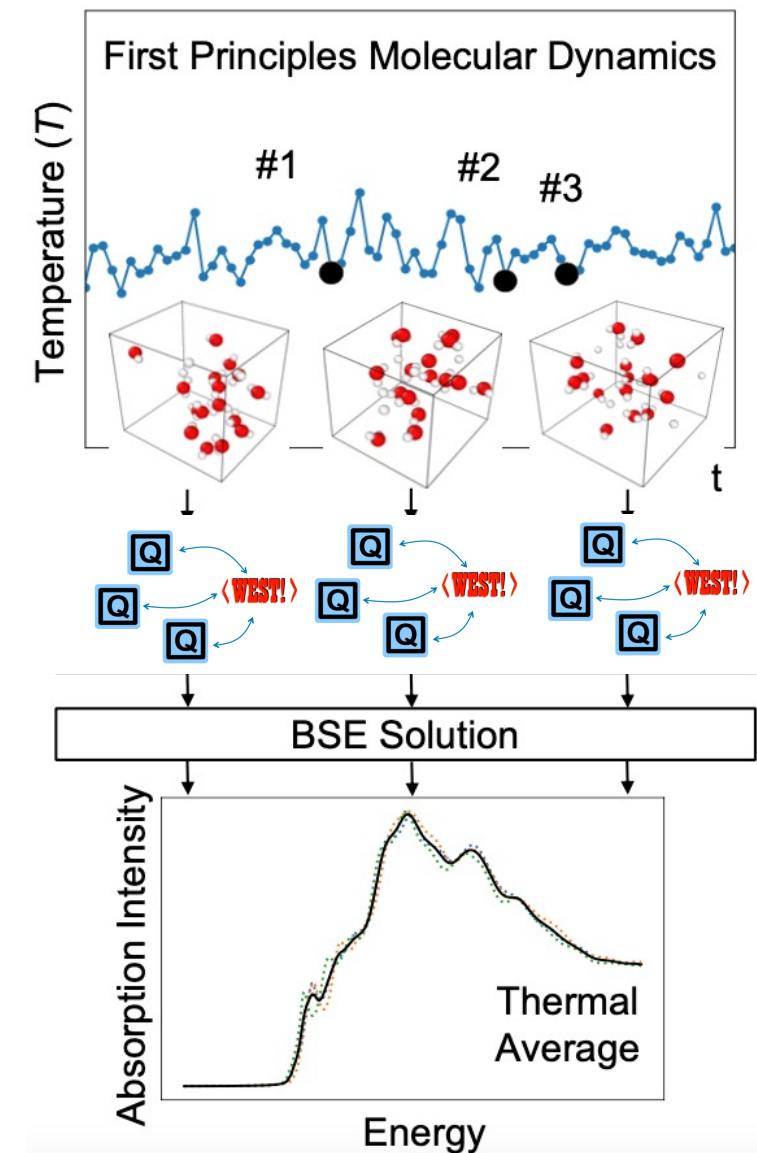
Data driven approach to obtain the dielectric screening

- Identified a **machine learning** protocol to avoid redundant calculations of the dielectric screening
- "Learn" on-the-fly and use a data-driven model for the dielectric response → speedup 100x

Coulomb interaction

*

Convolutional layer

screened Coulomb interaction

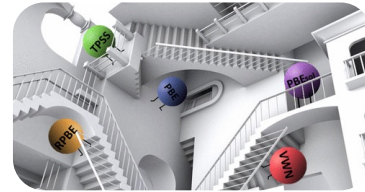S.Dong, M.**Govoni**, G.**Galli**, Chem. Sci. 12, 4970 (2021)

- A strategy to represent physical quantities in electronic structure theory using ML

- **Future work: use similar concept to derive improved density functionals for interfaces**
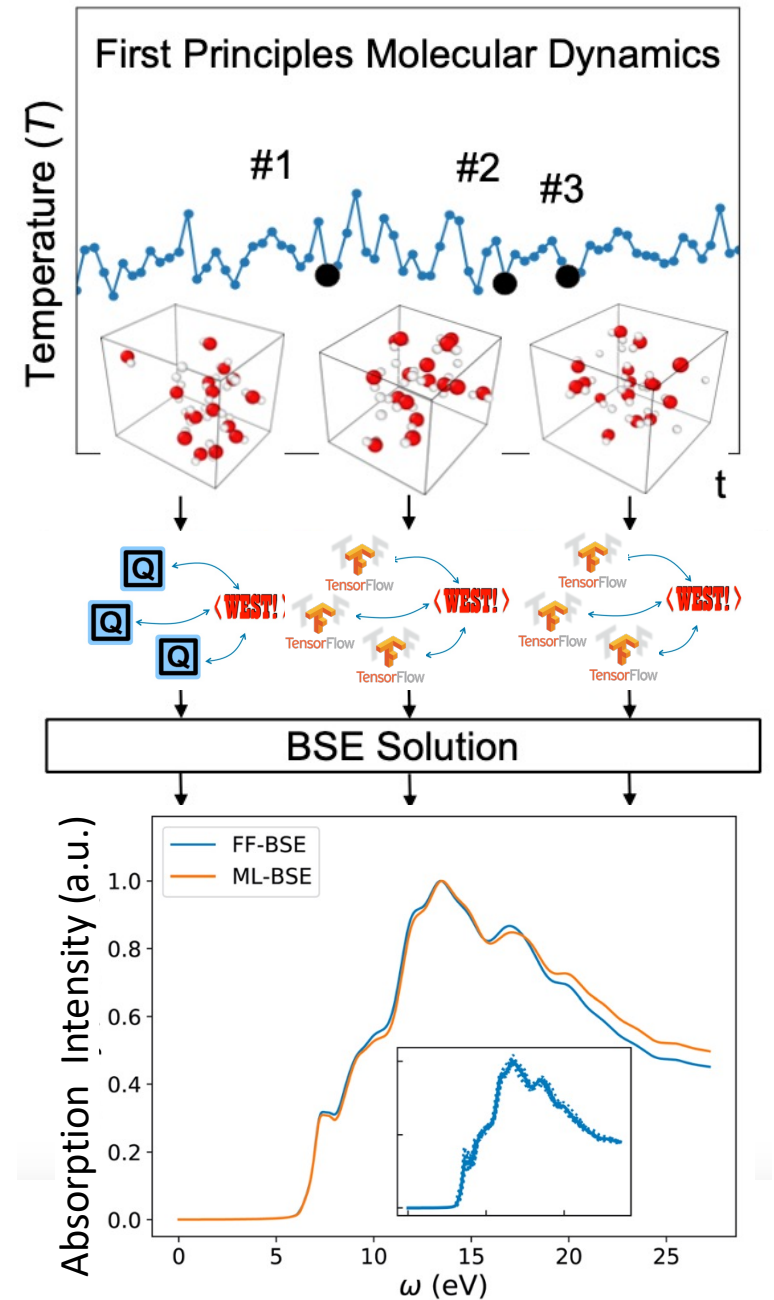
Some open questions

- 'Everything' relies on 'DFT ground states': which DFT?
  - Which functional for interfaces?

- How do we optimize geometries of excited states and deal with conical intersections?

- Can we 'recycle' quantities that are computed many times in electronic structure calculations? Can we 'learn' them and 'extrapolate' them? (e.g. dielectric matrices) ?

- What's the future of Many-Body-Perturbation-Theory?
  - Self-consistency? 'Additional' diagrams ? Use instead quantum chemistry methods for excited states also in the solid state? Role of Quantum Monte Carlo (QMC)?