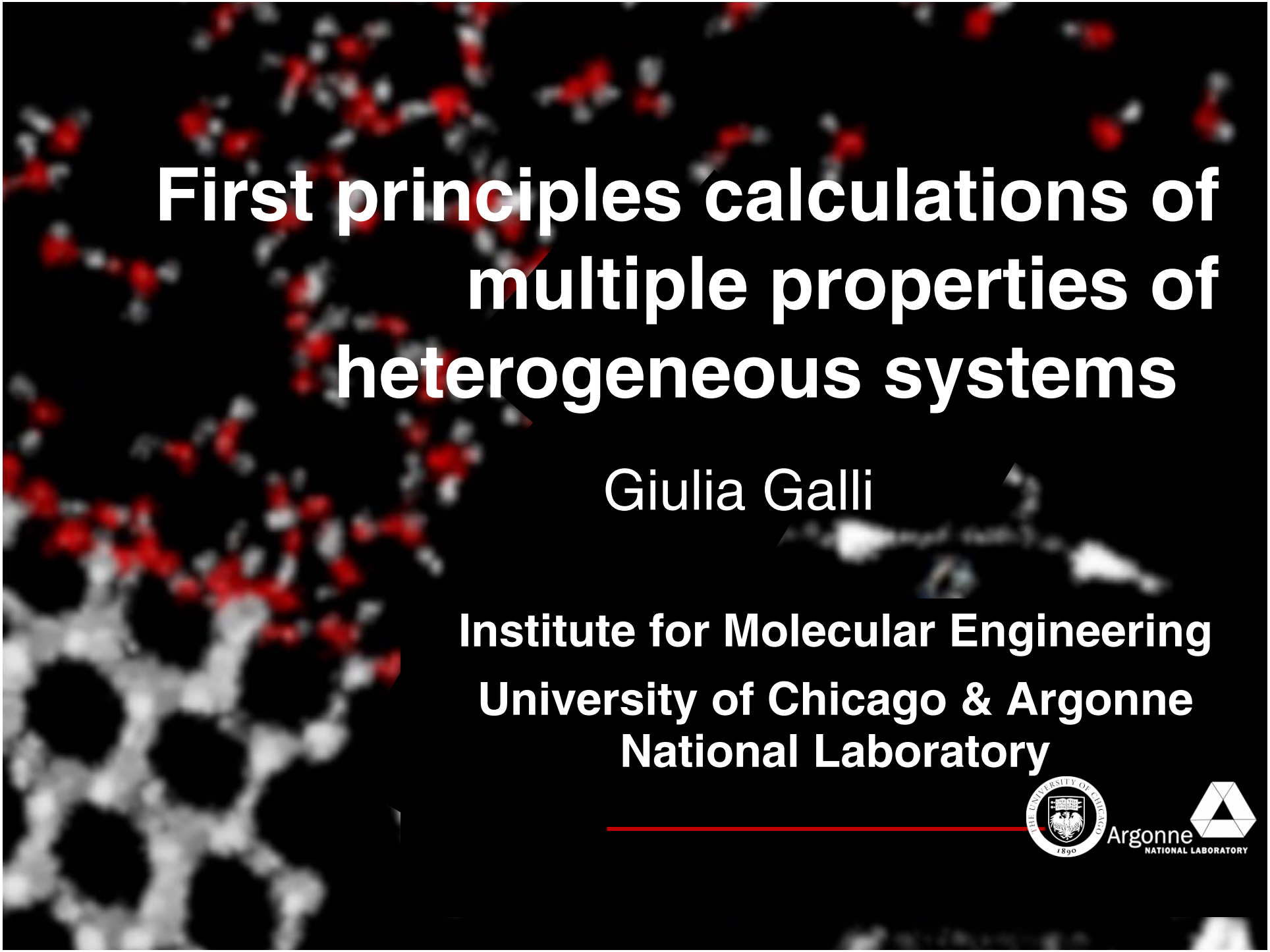
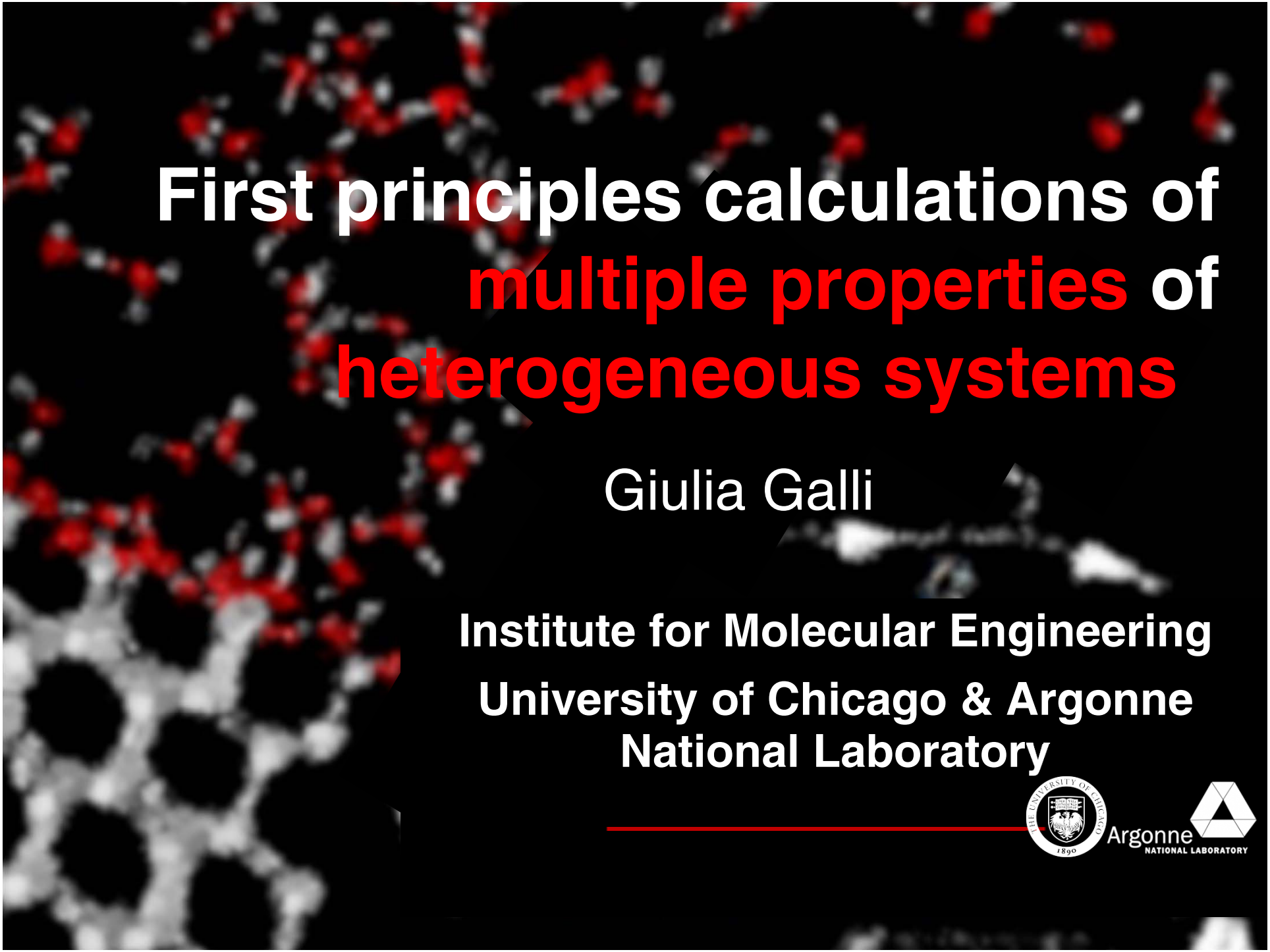


First principles calculations of multiple properties of heterogeneous systems

Giulia Galli

Institute for Molecular Engineering

University of Chicago & Argonne National Laboratory

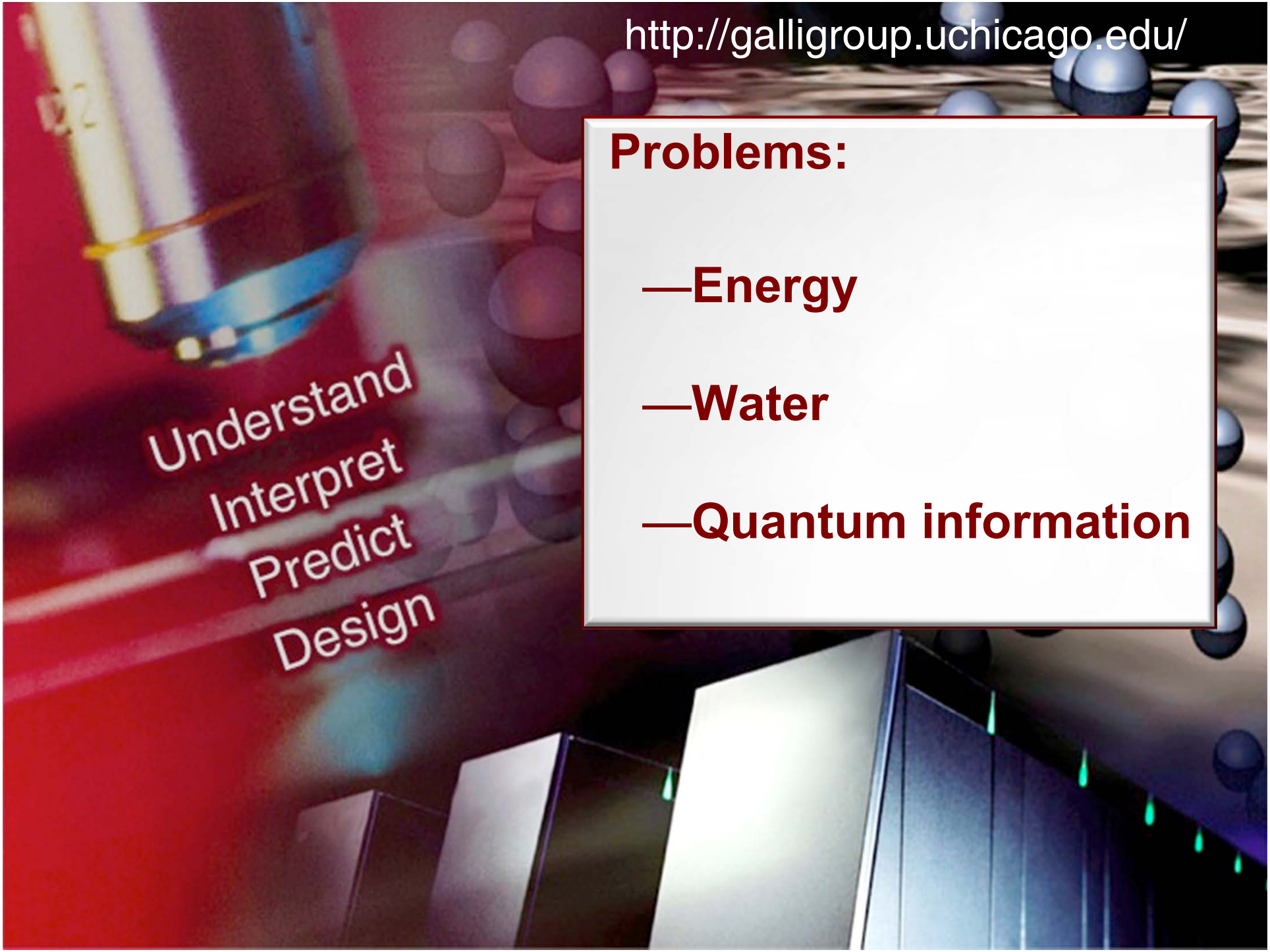


First principles calculations of multiple properties of heterogeneous systems

Giulia Galli

Institute for Molecular Engineering

University of Chicago & Argonne National Laboratory


http://galligroup.uchicago.edu/
Understand
Interpret
Predict
Design
Problems:
—Energy
—Water
—Quantum information

Solids, liquids, nanostructures and combinations thereof

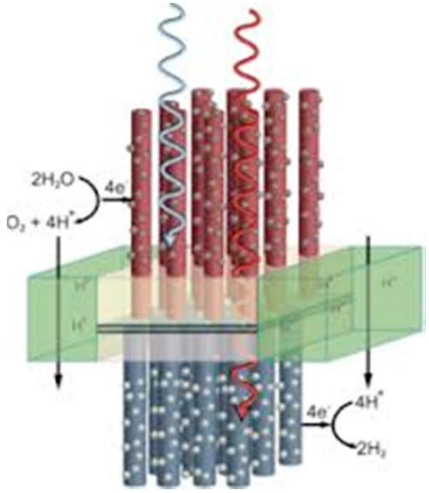
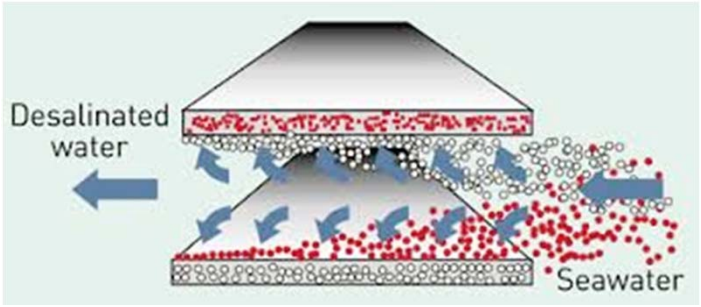
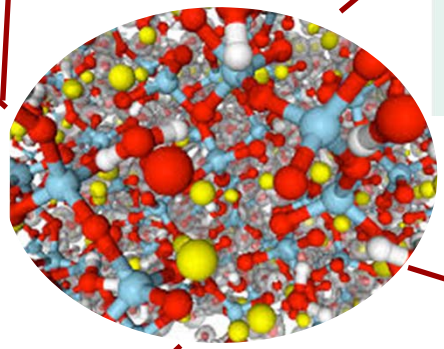
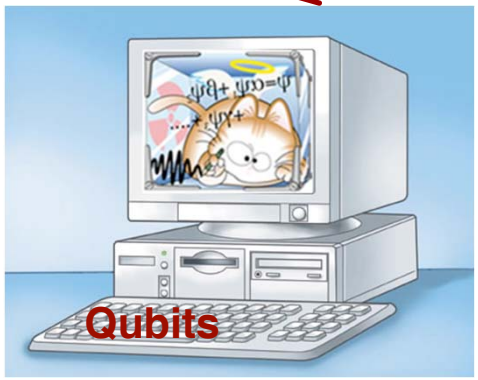


Photo-electrochemical cells

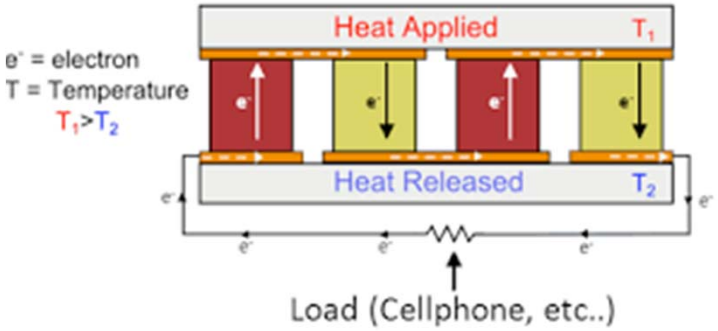
Clean Water

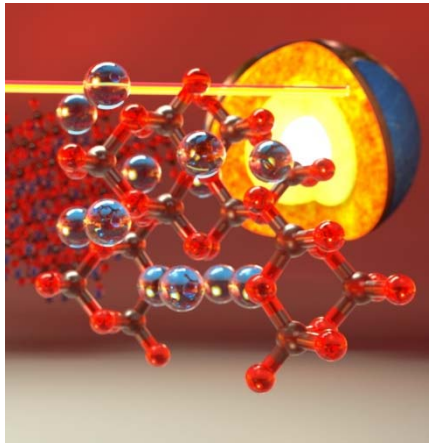






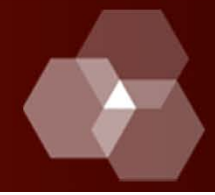
Thermoelectric generators





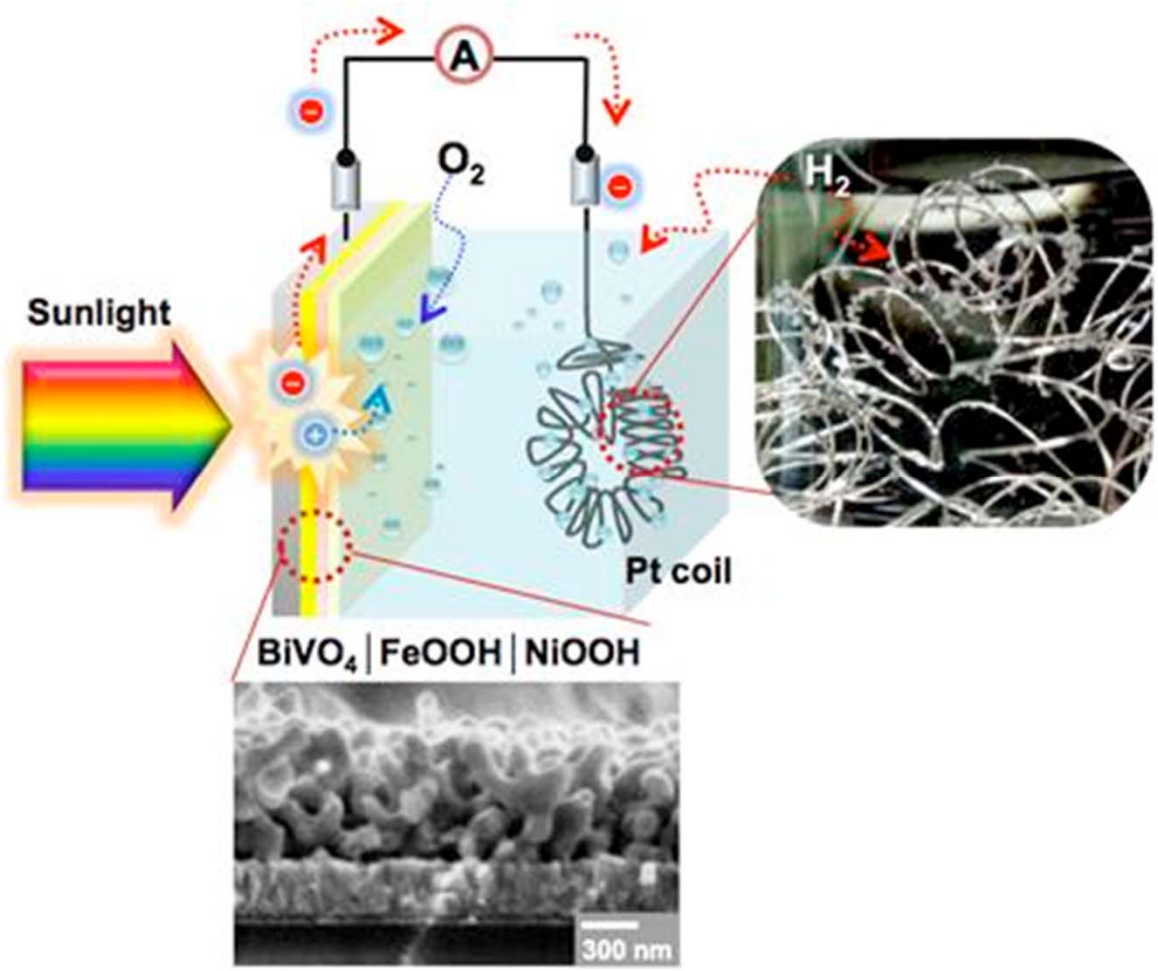
Carbon in the Earth

Heterogeneous systems



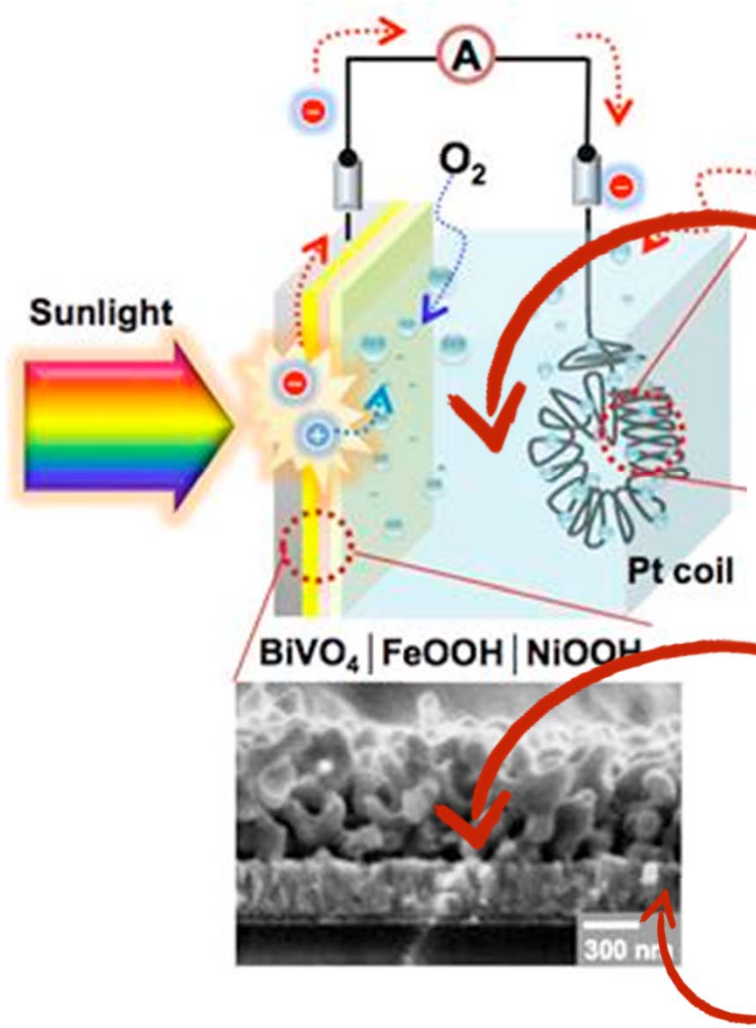
- **Interfaces**
- **Defects**
- **‘Mixed’ correlations**

Artificial photosynthesis



K.S.Choi's group, UW Madison, Science 2014; T.W.Kim, Y. Ping, GG & KS Choi Nat. Comm. 2015

Artificial photosynthesis



Finite T processes

Defective liquid (solvated ions in water)

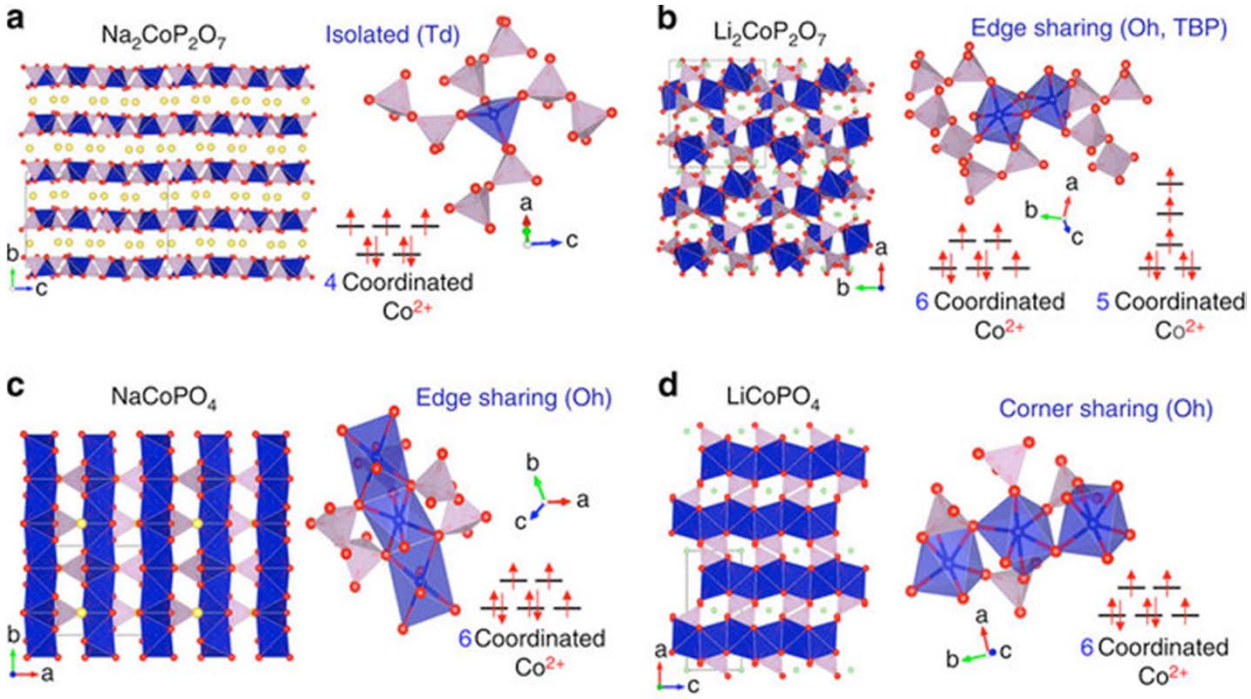
Three-way interface: catalyst/photo-absorber/water (hard/soft-matter interfaces)

Defective photo-absorber (oxide)

K.S.Choi's group, UW Madison, Science 2014; T.W.Kim, Y. Ping, GG & KS Choi Nat. Comm. 2015

Which level of correlation?

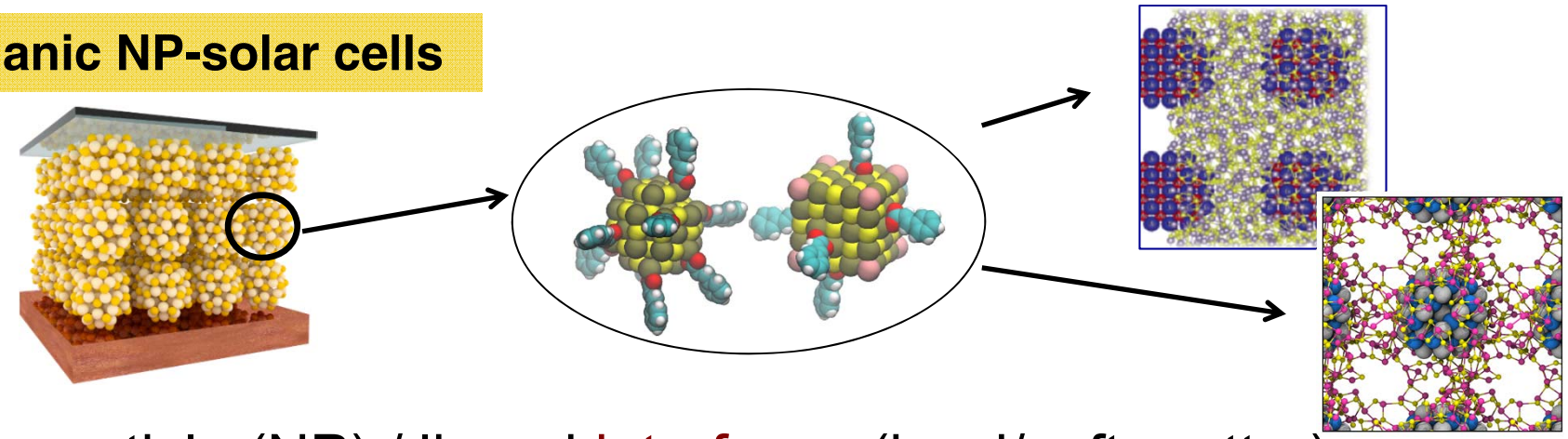
- **$BiVO_4$: how correlated is this (defective solid)?**
- **IrO_2**
- **NiOOH**
- **Ni(Fe)OOH**
- **Co based catalysts**



H.Kim et al. Nat. Comm. 2015

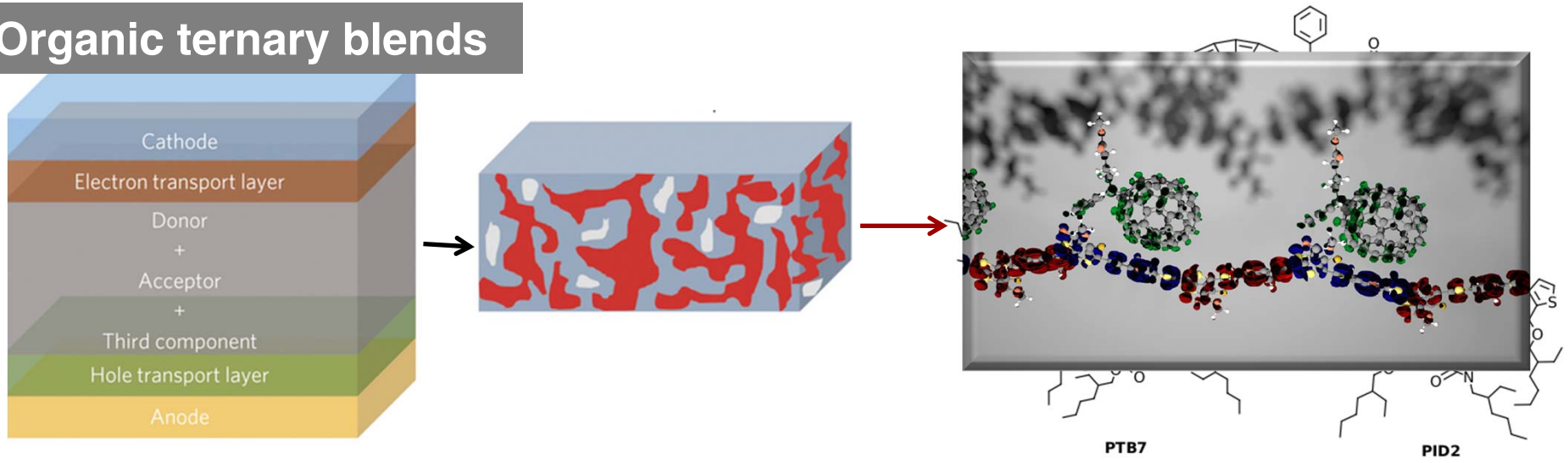
Inorganic & organic solar cells

Inorganic NP-solar cells



- Nanoparticle (NP) / ligand interfaces (hard/soft-matter)
- Polymer/polymer/fullerene interfaces(soft/soft-matter)

Organic ternary blends



Thermoelectrics

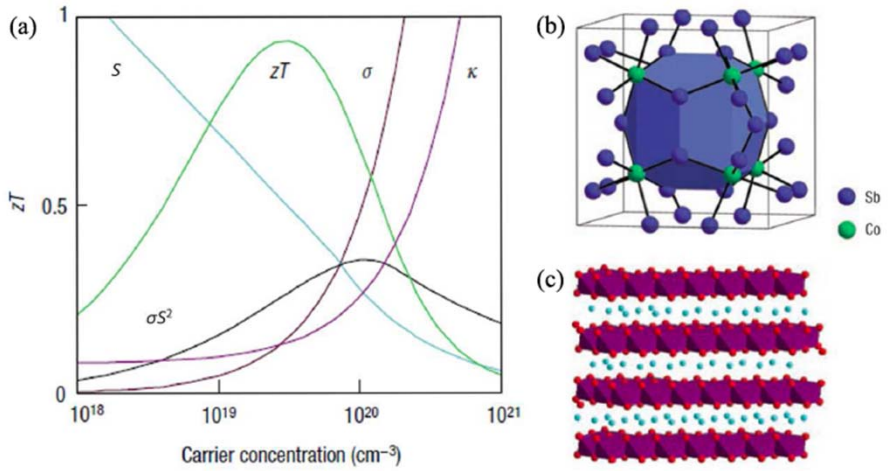
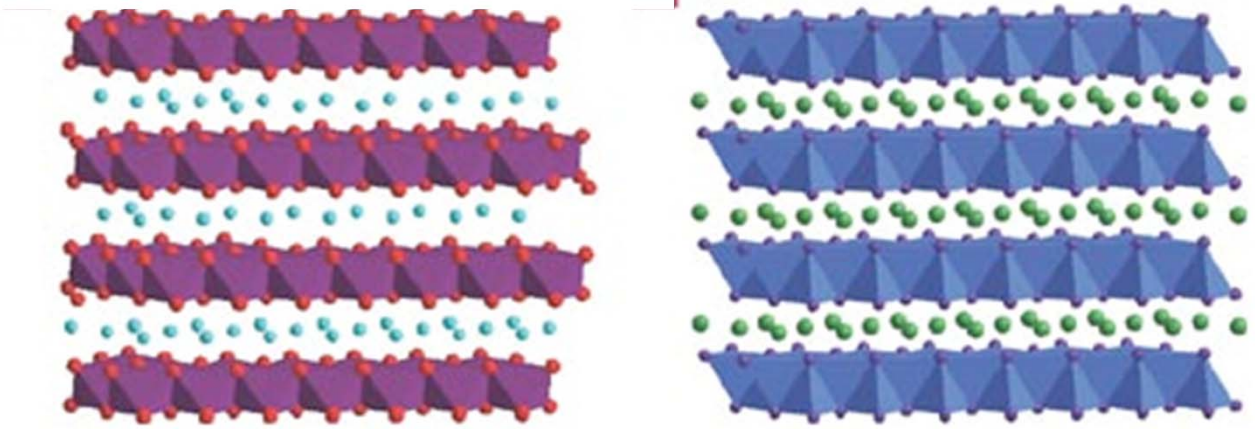


Fig. 1. (color online) (a) A schematic diagram showing the dependence of thermoelectric properties on carrier concentration. (b) The skutterudite $CoSb_3$ structure with large void space shown in blue. (c) Atomic structure of Na_xCoO_2 containing ordered layers (polyhedra) separated by disordered cation monolayers. Adapted from Ref. [3].

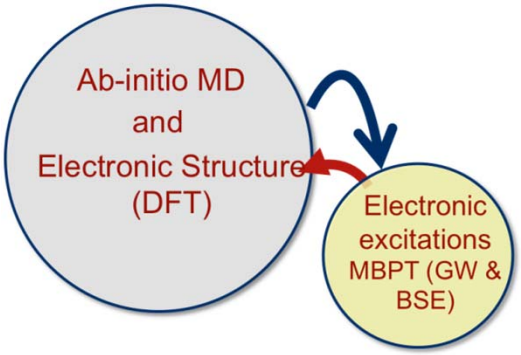
Snyder & Toberer, Nature Mat. 2008



NaxCoO2 and b, CaxYb1–xZn2Sb2 structures both contain ordered layers (polyhedra) separated by disordered cation monolayers, creating electron-crystal phonon-glass structures.

Outline

- Structural models
- The basic role of electronic structure underlying multiple properties of materials
- Large scale calculations and the importance of scalable algorithms
  - —Large scale GW
- ‘Improved’ energy functionals from approximate self-energies
- Transport from first principles

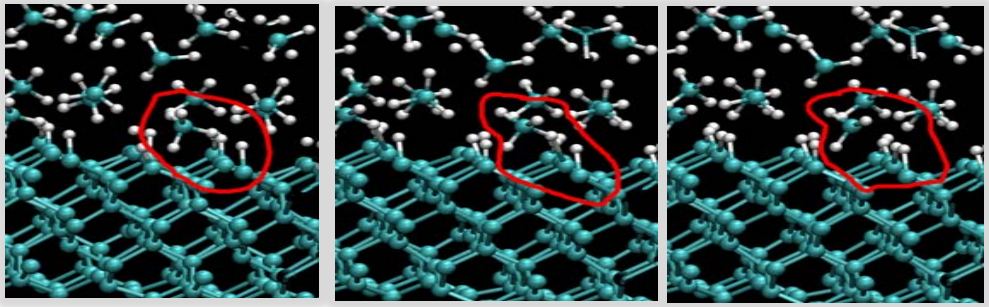


Outline

- Structural models
- The basic role of electronic structure underlying multiple properties of materials
- Large scale calculations and the importance of scalable algorithms
  - —Large scale GW
- ‘Improved’ energy functionals from approximate self-energies
- Transport from first principles

Structural models

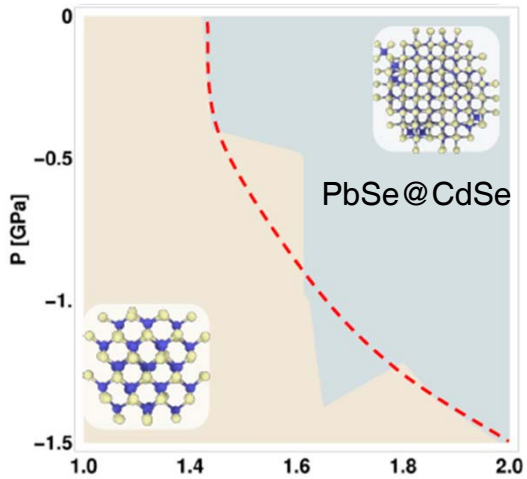
First principles molecular dynamics



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

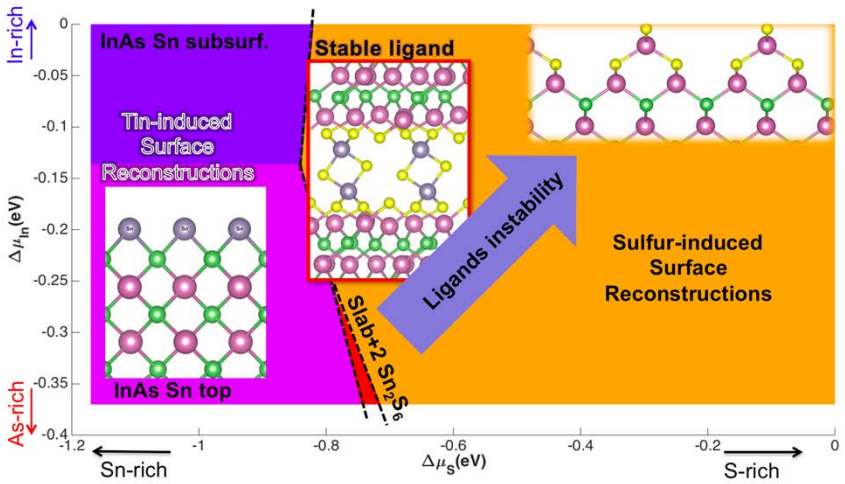
E from Density Functional Theory

Classical MD & advanced sampling



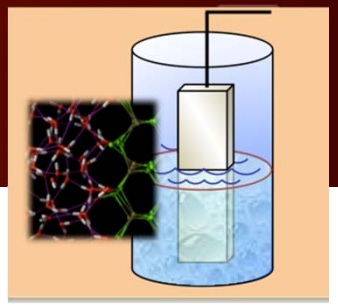
F.Giberti, M.Voros et al. 2016

Ab initio thermodynamics



E.Scalise, S.Wipperman et al. 2016

Interfaces

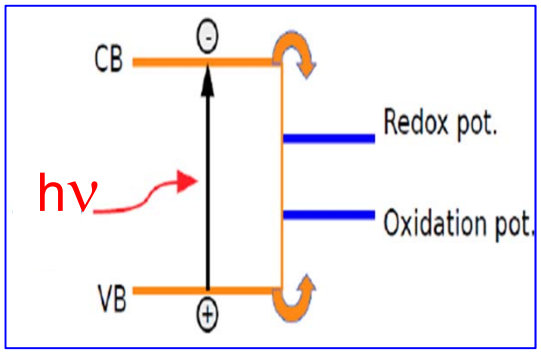


First principles molecular dynamics

Use trajectories to compute complex electronic properties from **hybrid DFT** or **many body perturbation** theory → Electronic properties at finite T w/statistical errors

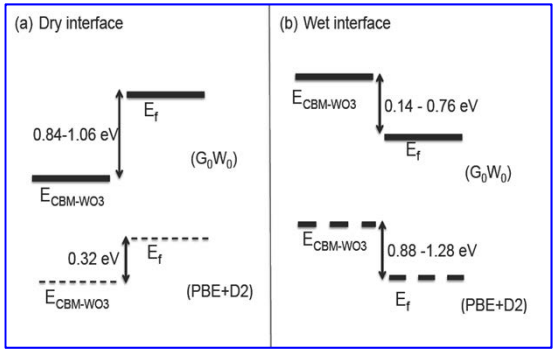
Electronic energy level alignments @ interfaces

Absorber **Water**



T.A.Pham, D. Lee, E.Schwegler, and GG JACS 2014

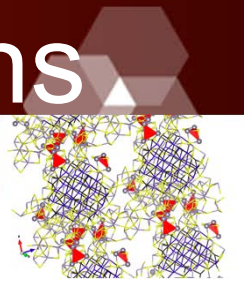
Absorber **Catalyst**



Y.Ping, W.A.Goddard III and GG JACS Comm. 2015

T.A.Pham, Y.Ping & GG, Nature Materials 2017

Interfaces & multiple configurations

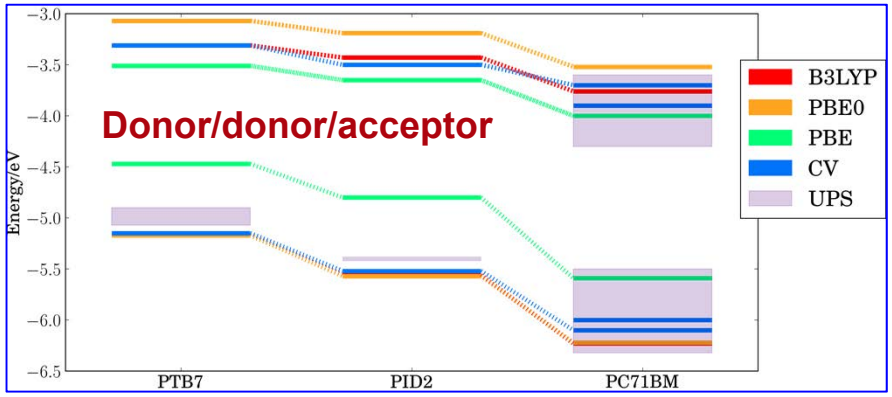


Classical MD & advanced sampling

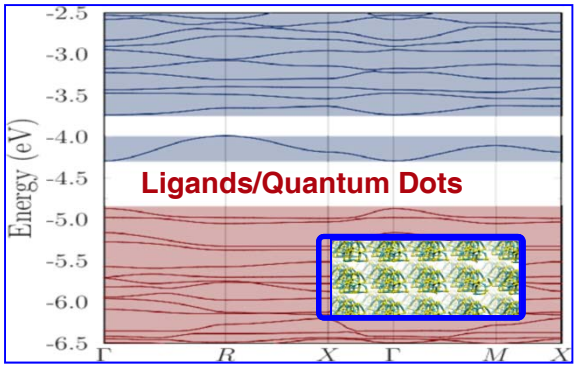
Ab initio thermodynamics

Use **configurations** to compute complex electronic properties from **hybrid DFT** or **many body perturbation** theory → Electronic properties at finite T w/statistical errors

Electronic energy level alignments @ interfaces



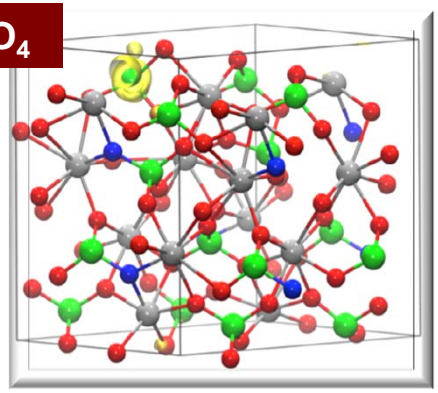
M.Goldey et al. 2016 (submitted)



M.Voros, G.Zimanyi and GG ACS Nano 2015;
M.Voros et al. 2016 (submitted)

Defects

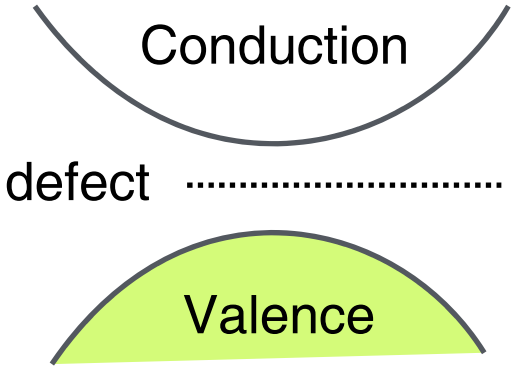
Defects in $BiVO_4$

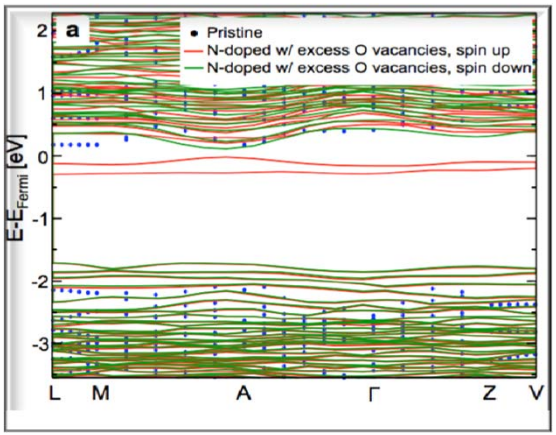


Defects (ions) in water

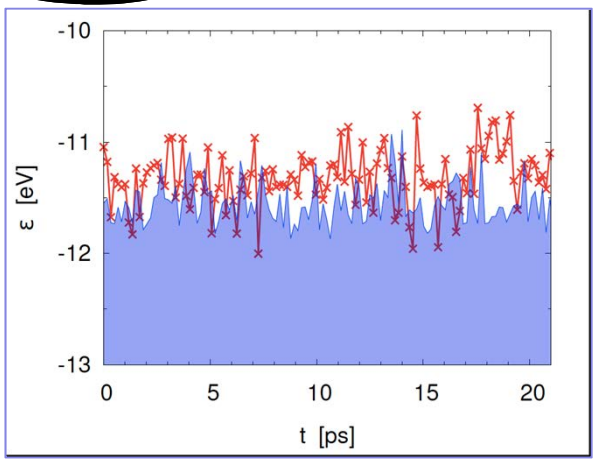
Use trajectories to compute complex electronic properties from **hybrid DFT** or **many body perturbation** theory → Electronic properties at finite T w/statistical errors

Electronic signatures and activity of defects





T.W.Kim, Y. Ping, GG & KS Choi Nat. Comm. 2015

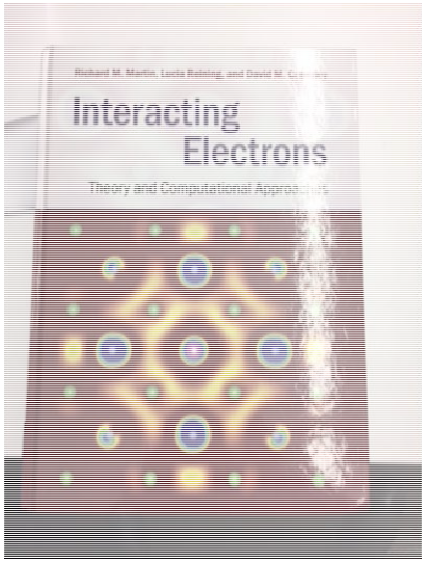


Al Gaiduk et al. JACS-Comm. 2016

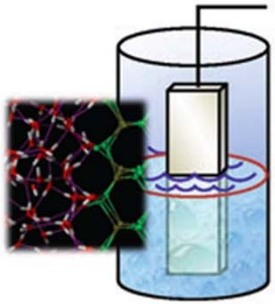
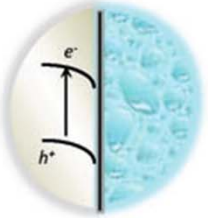
Outline

- Structural models
- The basic role of electronic structure underlying multiple properties of materials
- Large scale calculations and the importance of scalable algorithms

  —Large scale GW
- ‘Improved’ energy functionals from approximate self-energies
- Transport from first principles



Photoemission and absorption

Processes of interest	 Band edge alignment between electrodes and water	 Light absorption by electrodes
Experiments	Photoemission spectroscopy	UV-vis and ellipsometry spectroscopy
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 $G^{(1)}$

Y.Ping, D.Rocca and GG, Chem.Soc.Rev.2013

GW calculations w/o virtual states

$$(T + V_{ext} + V_H)\psi_n(r) + \int dr' \Sigma(r, r', E_n)\psi_n(r') = E_n\psi_n(r)$$

$$\Sigma(r, r', i\omega) = \frac{1}{2\pi} \int d\omega' G(r, r', i(\omega - \omega'))W(r, r', i\omega')$$

Algorithms(*) and parallel codes that allow for:

Calculations for **several hundreds of electrons for tens/hundreds of samples** → change in the type of problems we can tackle and type of questions we can answer

(*) H.Wilson, F.Gygi and G.Galli, PRB 2008; H. V. Nguyen, T.A. Pham, D.Rocca and GG Phys. Rev. B – Rapid Comm. 2012
T.A.Pham, H,V.Nguyen, D.Rocca and GG, Phys.Rev.B 2013; M.Govoni and GG JCTC 2015; **WEST : http://www.west-code.org**

(+) D.Rocca, D.Lu and GG, JCP 2010; Y.Ping, D.Rocca and GG, Chem. Soc. Rev. 2013

(&) M.Voros, A.Gali, D.Rocca,GG and G.Zimanyi Phys. Rev. B 2013; S.Wipperman, M.Voros, A.Gali, G.Zymanyi and GG Phys. Rev. Lett. 2013

Hedin equations

Hedin proposed to express Σ in terms of the **dynamically screened Coulomb potential**, instead of the bare Coulomb potential

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

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

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

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

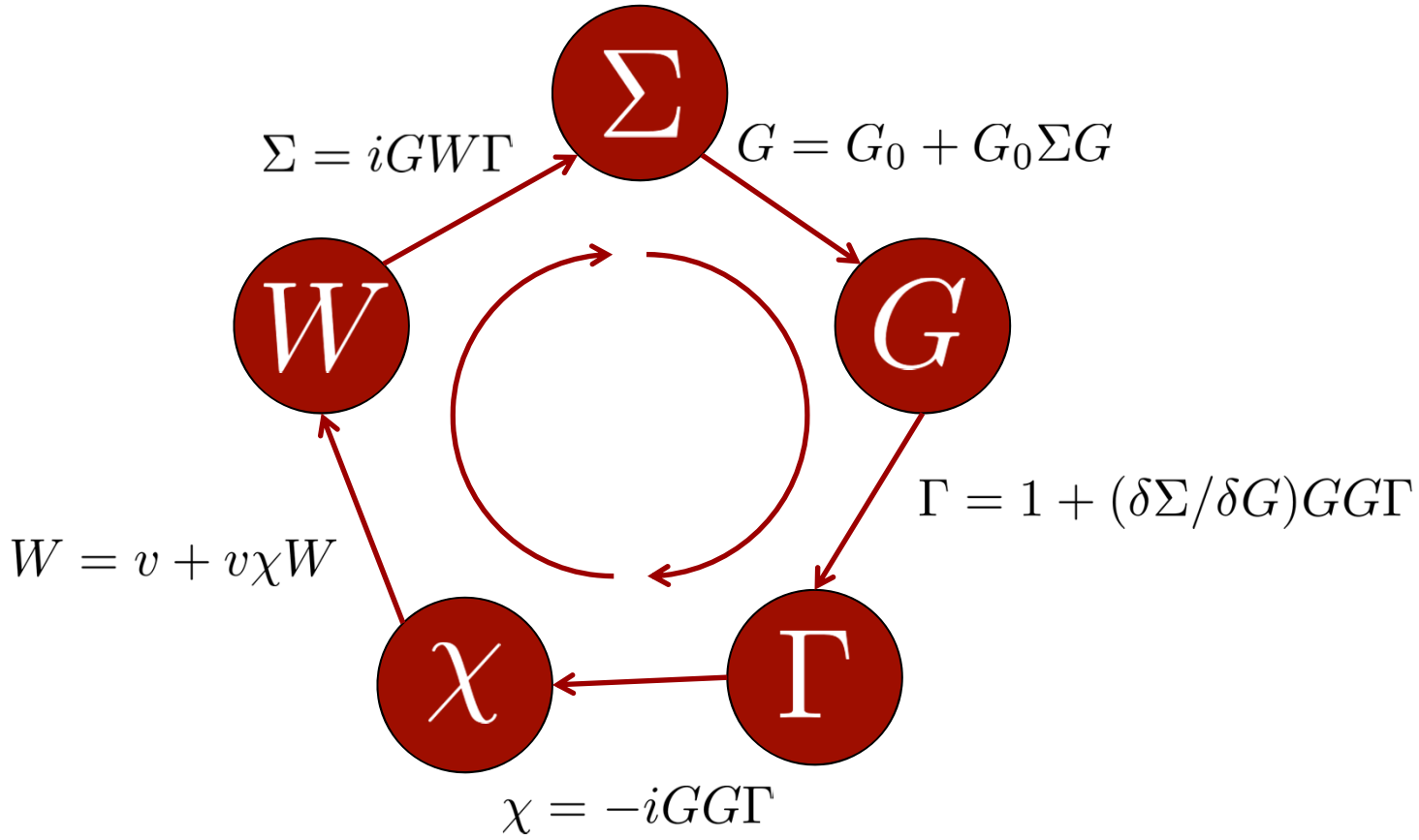
$$W(\mathbf{r},\mathbf{r}';\omega)=\int d\mathbf{r}''\,\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)v_c(\mathbf{r}'',\mathbf{r}')$$

What is its physical meaning ?

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

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

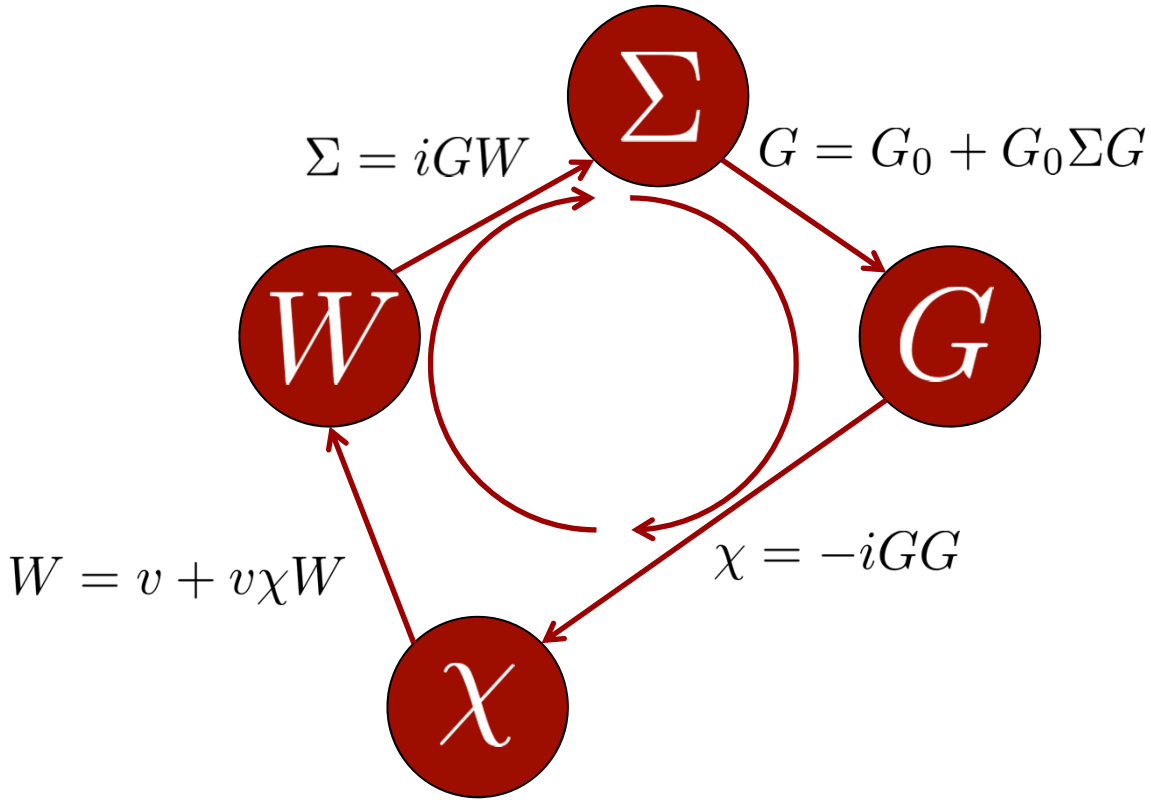
Hedin's idea to solve Dyson equations



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

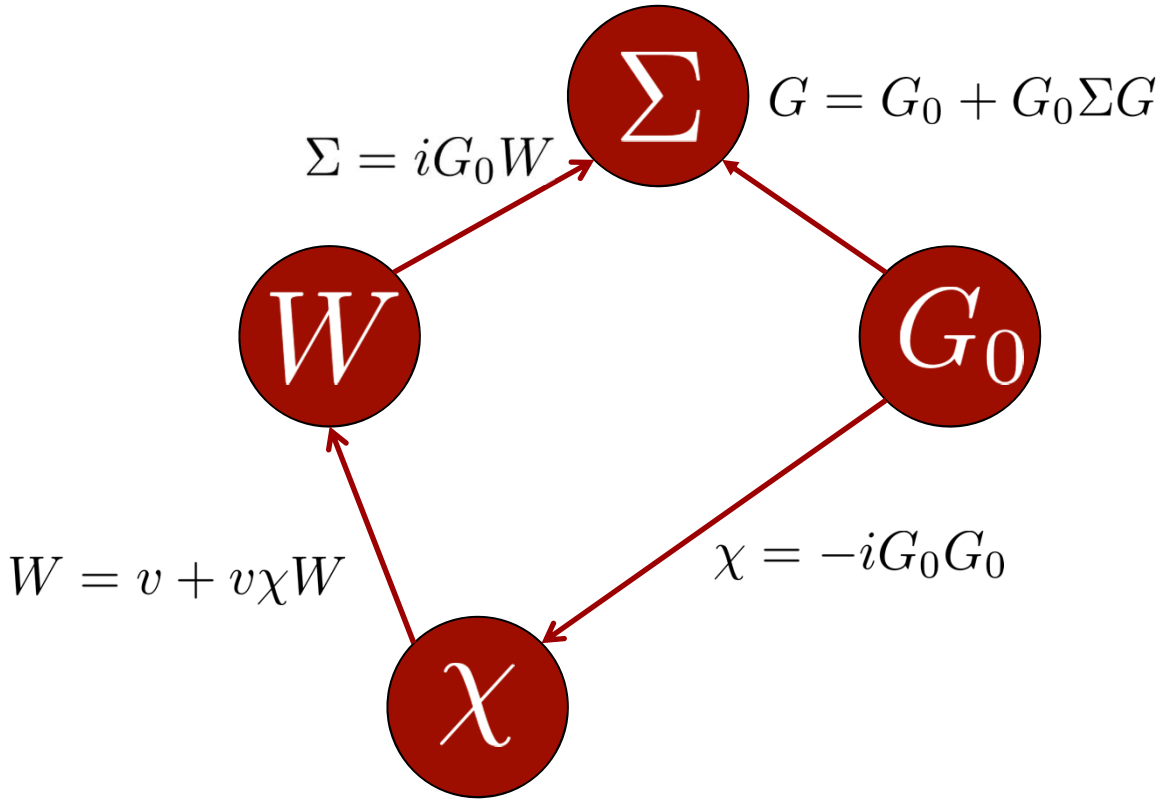
"[…] Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, **there is not much new in principle in this paper**. […]"

The GW approximation



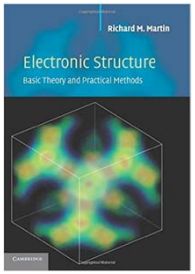
Lars Hedin, Phys. Rev. 139, A796 (1965)

The G_0W_0 approximation



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

Maxwell equations for the total field



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

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

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

$$\nabla \cdot \mathbf{j} = -Q\frac{\mathrm{d}n}{\mathrm{d}t}$$

- **Internal and External charges and currents:**
  - **$n = n_{int} + n_{ext}$; $j = j_{int} + j_{ext}$**
- **Polarization : defined to *within an additive constant* (one computes *polarization differences*)**

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

Maxwell equations for the external field

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

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

Response in terms of scalar potentials

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

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

External potential

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

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

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

Density response function in Fourier space

- **Response to specific Fourier components:**

$$\Delta V_{\text{eff}}(\mathbf{r}) = \Delta V_{\text{eff}} e^{i\mathbf{q}\mathbf{r}} \quad \text{and} \quad n(\mathbf{q}') = \int d\mathbf{r} n(\mathbf{r}) e^{i\mathbf{q}'\mathbf{r}}$$

$$\Downarrow$$

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

$$\langle \psi_i | e^{i\mathbf{q}\cdot\mathbf{r}} | \psi_j \rangle$$

- **Homogeneous system: χ^0 differs from 0 only for q = q'**

- **Non interacting electrons: the variation of the total potential equals the variation of the external potential ➔ χ^0 is the response to an external perturbation**
- **Mean field theory (Kohn-Sham): internal fields vary**

Density response within KS theory

- **Electrons are independent particles in the potential V_{eff} :**

$$\chi_n^0(\mathbf{q},\mathbf{q}') = \frac{\delta n(\mathbf{q}')}{\delta V_{\rm eff}(\mathbf{q})} = 2\sum_{i=1}^{\rm occ}\sum_{j}^{\rm empty}\frac{M_{ij}^*(\mathbf{q})M_{ij}(\mathbf{q}')}{\epsilon_i-\epsilon_j}$$

$$\langle\psi_i|e^{i\mathbf{q}\cdot\mathbf{r}}|\psi_j\rangle$$

- **Response to the external field:**

$$\chi(\mathbf{r},\mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta V_{\rm ext}(\mathbf{r}')} \quad \chi(\mathbf{q},\mathbf{q}') = \frac{\delta n(\mathbf{q})}{\delta V_{\rm ext}(\mathbf{q}')}$$

- **Relationship between response to the total (χ^0) and the external field (χ):**

$$\chi = \chi^0[1-\chi^0 K]^{-1} \qquad \chi^{-1} = [\chi^0]^{-1} - K$$

Random Phase Approximation: $f_{xc} = 0$

$$K(\mathbf{q},\mathbf{q}') = \frac{\delta V_{\rm int}(\mathbf{q})}{\delta n(\mathbf{q}')} = \frac{4\pi}{q^2}\delta_{\mathbf{q},\mathbf{q}'} + \frac{\delta^2 E_{\rm xc}[n]}{\delta n(\mathbf{q})\delta n(\mathbf{q}')} \equiv V_C(q)\delta_{\mathbf{q},\mathbf{q}'} + f_{\rm xc}(\mathbf{q},\mathbf{q}')$$

Dynamical response

- **Time dependence of Kernel:**

$$K(\mathbf{q},\mathbf{q}',t-t') = \frac{\delta V_{\rm int}(\mathbf{q},t)}{\delta n(\mathbf{q}',t')} = \frac{4\pi}{q^2}\delta_{\mathbf{q},\mathbf{q}'}\delta(t-t') + \frac{\delta^2 E_{\rm xc}[n]}{\delta n(\mathbf{q},t)\delta n(\mathbf{q}',t')}$$

↓ FT

$$K(\mathbf{q},\mathbf{q}',\omega) = V_C(q)\delta_{\mathbf{q},\mathbf{q}'} + f_{\rm xc}(\mathbf{q},\mathbf{q}',\omega)$$

- **Generalization of the relationship between response to the total (χ^0) and the external field (χ):**

$$\chi(\omega) = \chi^0(\omega)[1-\chi^0(\omega)K(\omega)]^{-1}$$

- **Kramers-Kronig relations:**

$$\Re\chi(\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\Im\chi(\omega')}{\omega-\omega'}$$

$$\Im\chi(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\Re\chi(\omega')}{\omega-\omega'}$$

Response in terms of scalar potentials

- **E = - ∇V(r) : field derived from potential →**
  in Fourier space: E(q) = i q V(q) is longitudinal (// to q)

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

External potential

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

Coulomb potential

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

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

Dielectric matrices, functions & tensors

- **In a crystal q = k+G where k is in the first Brillouin zone and G is a reciprocal lattice vector**

$$\epsilon^{-1}(\mathbf{q},\mathbf{q}',\omega) = \delta(\mathbf{q}-\mathbf{q}') + V_C(\mathbf{q})\chi(\mathbf{q},\mathbf{q}',\omega)$$

$$\downarrow$$

Matrices

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{k},\omega) \quad \epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{k},\omega)$$

- **Optical excitations→ long wavelengths → G, G' =0 → macroscopic dielectric function :**

$$\epsilon(\mathbf{k},\omega) = \frac{\delta V_{\text{ext}}(\mathbf{k},\omega)}{\delta V^C_{\text{total}}(\mathbf{k},\omega)} = \frac{1}{\epsilon^{-1}_{00}(\mathbf{k},\omega)}$$

$$\epsilon(\mathbf{k},\omega) \approx \epsilon_{00}(\mathbf{k},\omega)$$

Local fields neglected

- **Dielectric tensors:**

$$\epsilon(\mathbf{k},\omega) = \lim_{|\mathbf{k}|\to 0} \hat{\mathbf{k}}_\alpha \epsilon_{\alpha\beta}(\mathbf{k},\omega)\hat{\mathbf{k}}_\beta$$

- **In a cubic crystal:**

$$\epsilon_{\alpha\beta} = \epsilon\delta_{\alpha\beta}$$

Calculation of dielectric matrices

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

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

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***

$$\tilde{\chi}_0 = \sum_{i=1}^{N} \tilde{\phi}_i \lambda_i \tilde{\phi}_i^H \xrightarrow[\text{RPA}]{} \tilde{\chi} = \sum_{i=1}^{N} \tilde{\phi}_i \frac{\lambda_i}{1-\lambda_i} \tilde{\phi}_i^H$$

- **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.

DFPT and Sternheimer equation

SCF

$$H_{\mathrm{SCF}} = -\frac{\Delta}{2} + V_{\mathrm{SCF}}$$

$$(H_{\mathrm{SCF}} - \epsilon_v) P_c |\Delta\psi_v\rangle = -P_c V_i^{\mathrm{pert}} |\psi_v\rangle$$

NSCF

$$\Delta n(\mathbf{r}) = 4\Re \sum_v \psi_v^*(\mathbf{r}) \Delta\psi_v(\mathbf{r}) \longrightarrow \epsilon = 1 - v\chi_0$$

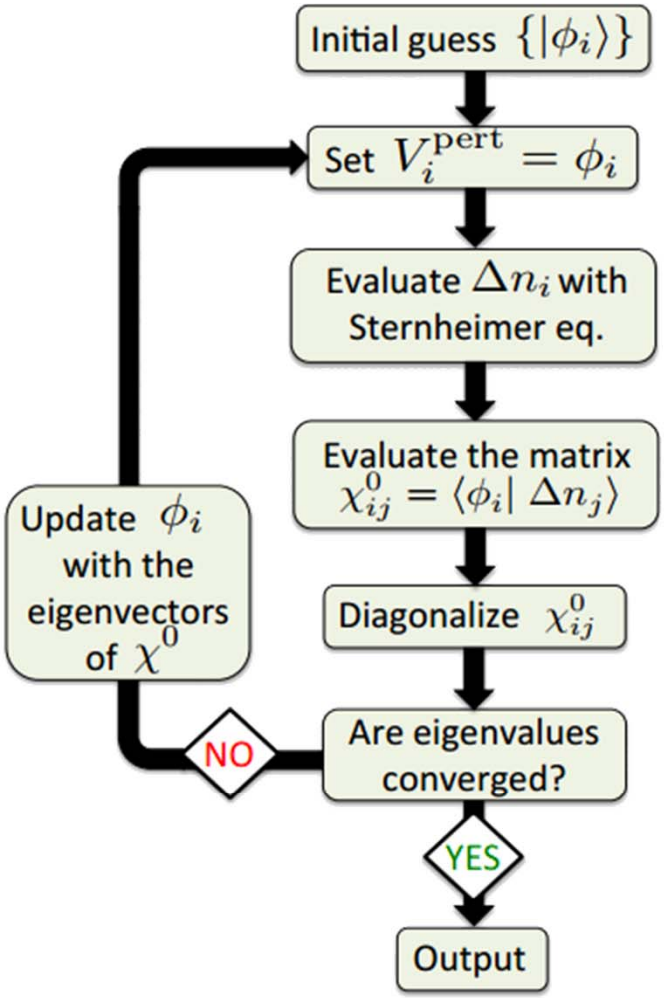
$$\epsilon^{-1} = 1 + v\chi$$

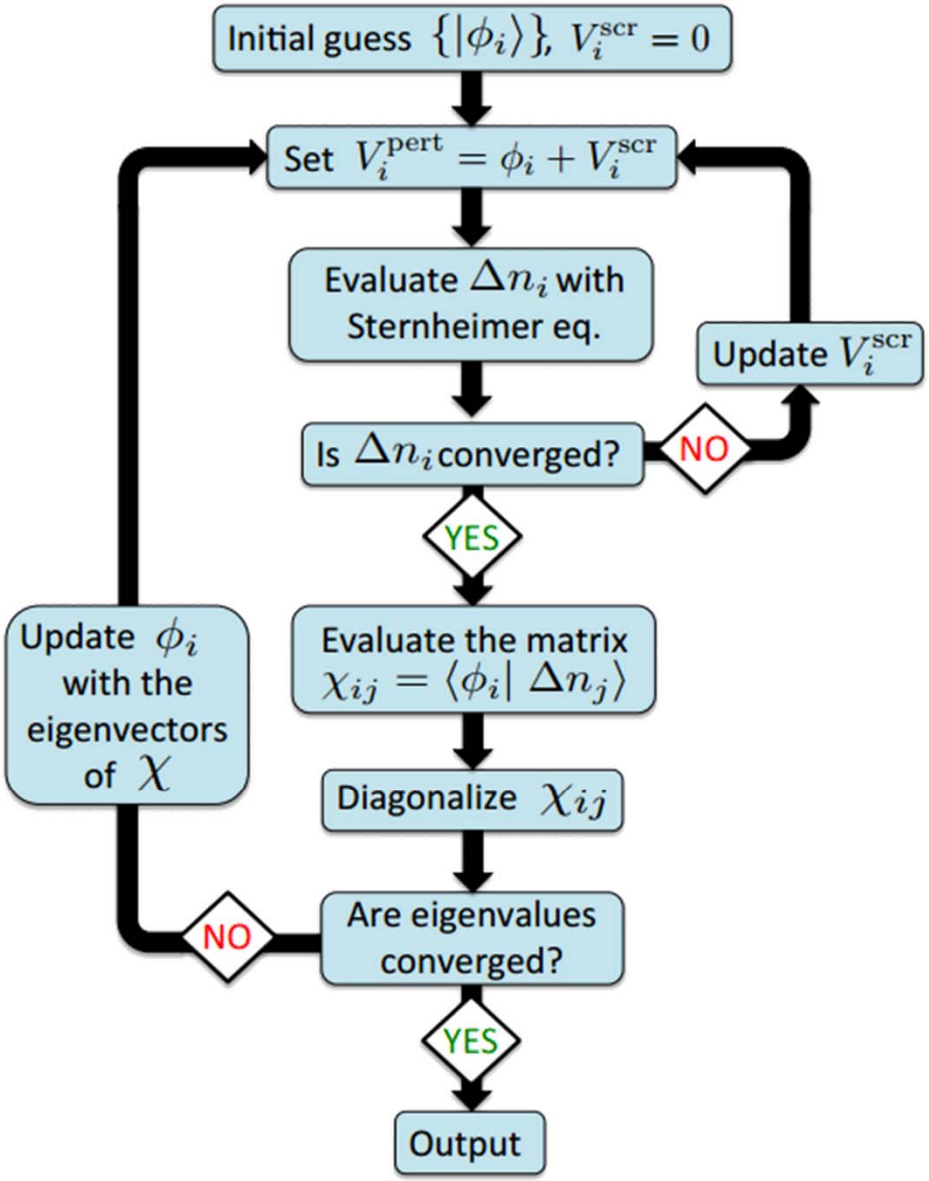
$$\Delta V_{\mathrm{SCF}}(\mathbf{r}) = \Delta V_{\mathrm{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{\Delta n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \left.\frac{dv_{xc}[n]}{dn}\right|_{n=n(\mathbf{r})} \Delta n(\mathbf{r})$$

The Sternheimer equation is solved non-self-consistently.

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

DFPT and Sternheimer equation





M.Govoni & GG, J. Chem. Theory Comput. (2015)

Iterative procedure based on Density Functional Perturbation Theory

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

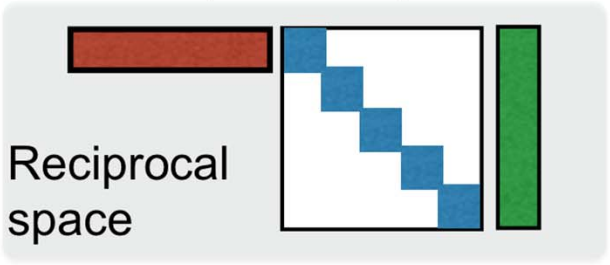
- Calculation of empty electronic states, calculation and storage of full dieletric matrix and inversion of ε are avoided
- Scaling: $N_{eig} N_{pw} N_v^2$ (instead of $N_{pw}^2 N_v N_c$)
- Efficient evaluation of ε^{-1} at different **q** points and at different MD steps is possible
- Incorporation of XC kernel is in principle straightforward

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 (r,r')

In **Hartree-Fock**

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



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)

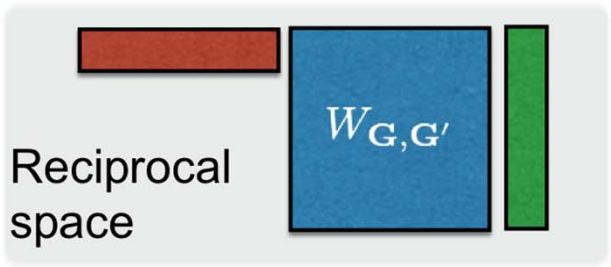
Could be truncated, full matrix

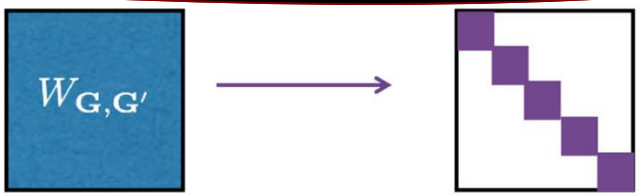
Eigenpotential space size~(1'000) x (1'000)

In **GW**

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

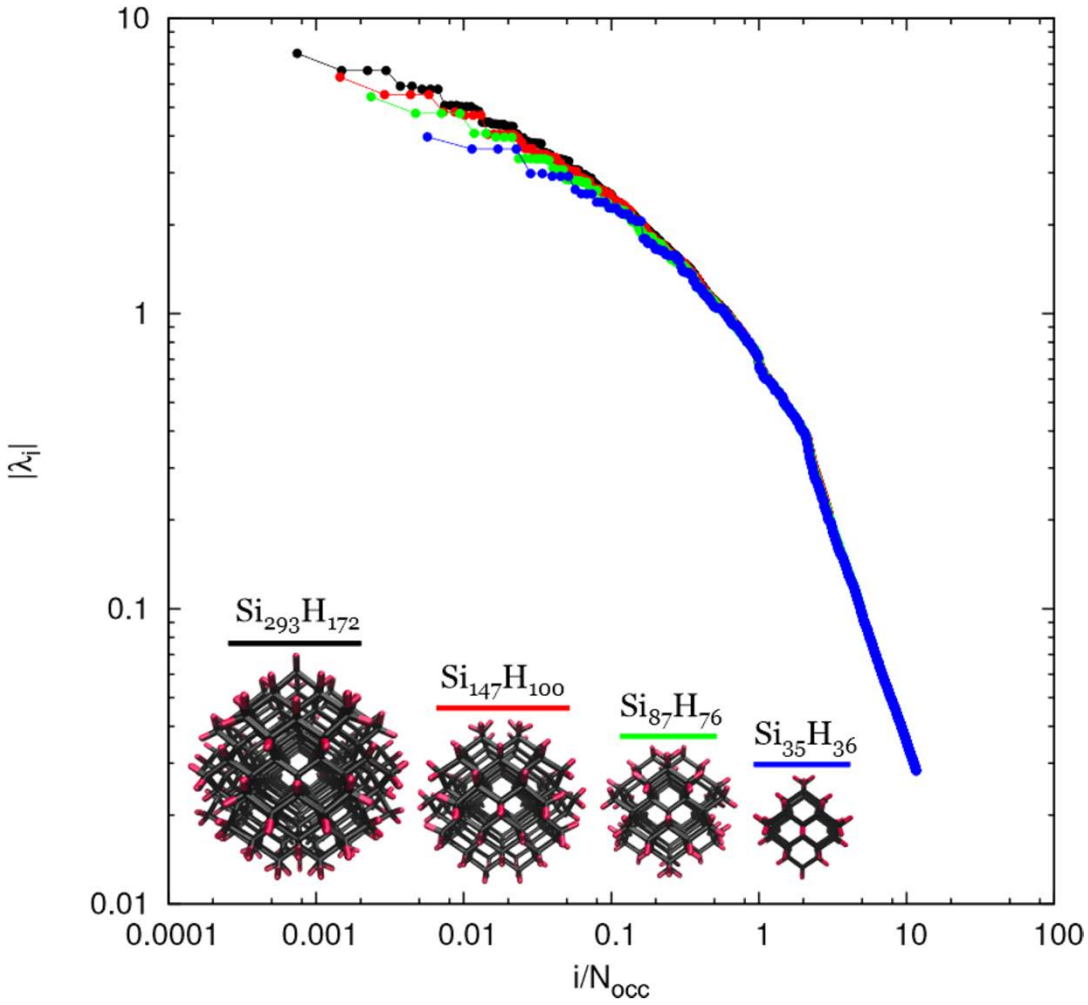
$$W = \sum_{\alpha} |\alpha\rangle \lambda_\alpha \langle\alpha|$$ **Low-rank decomposition**





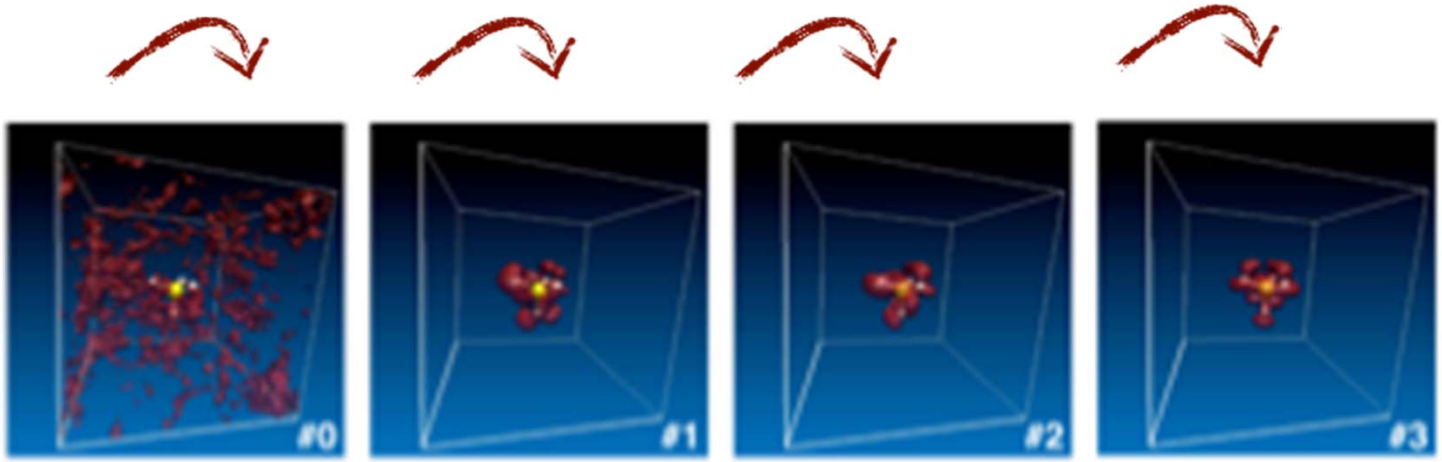
Separable form

Number of eigenpotentials



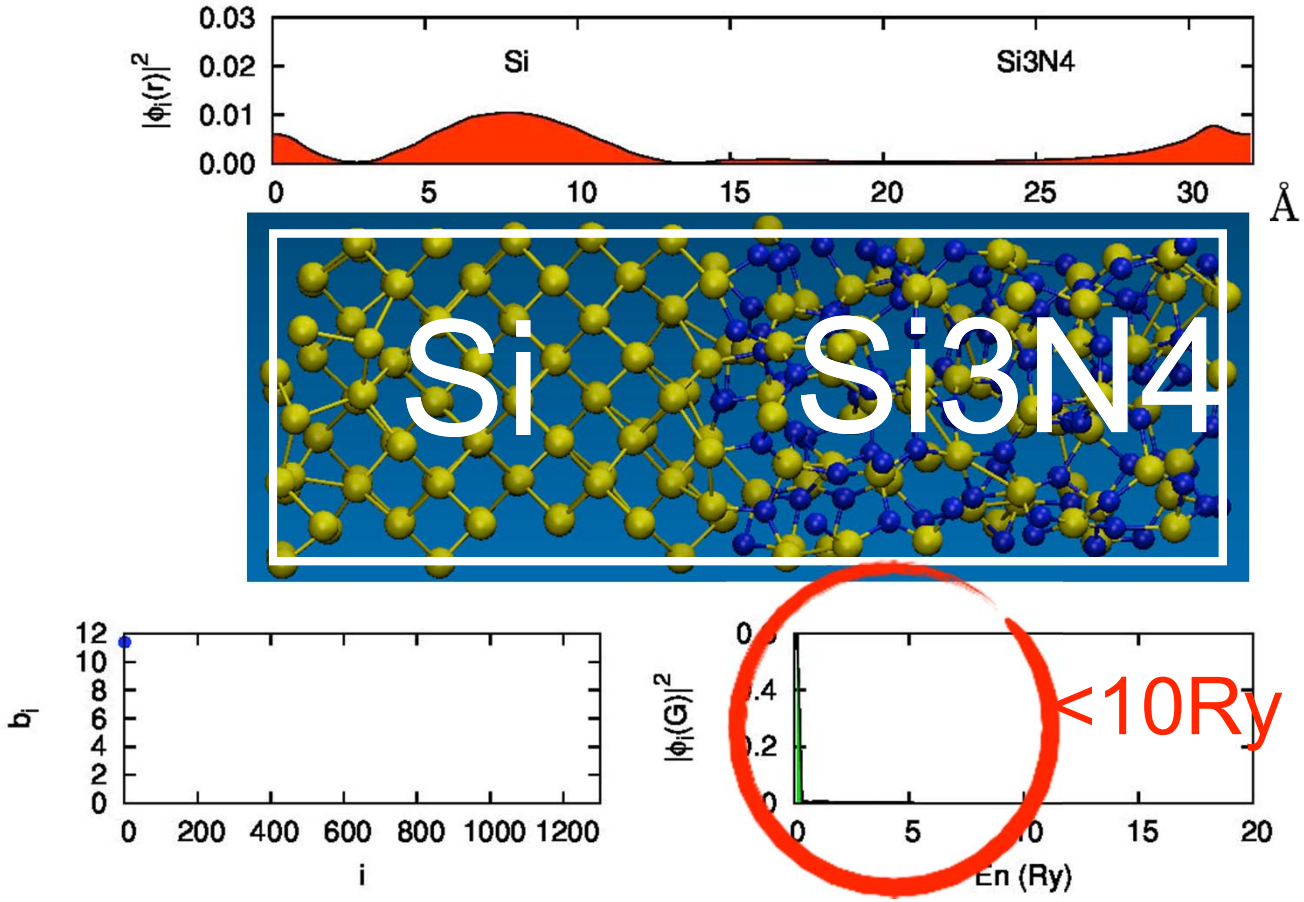
M.Govoni & GG, J. Chem. Theory Comput., 2015

Convergence of eigenpotentials

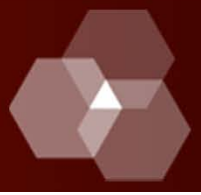


Character and localization of eigenpotentials

No. electrons = 1152; $[E_{cut}]_{wfs}$ = 70 Ry; $[E_{cut}]_{\rho}$ = 280 Ry



Summary of GW algorithm



- Iterative diagonalization of the dielectric matrix
- Low rank decomposition of W
- DFPT based projection techniques to compute G
- Eigenpotentials of ε as basis also at finite frequency
- Lanczos algorithm to obtain frequency dependence in parallel
- Contour deformation technique for frequency integration

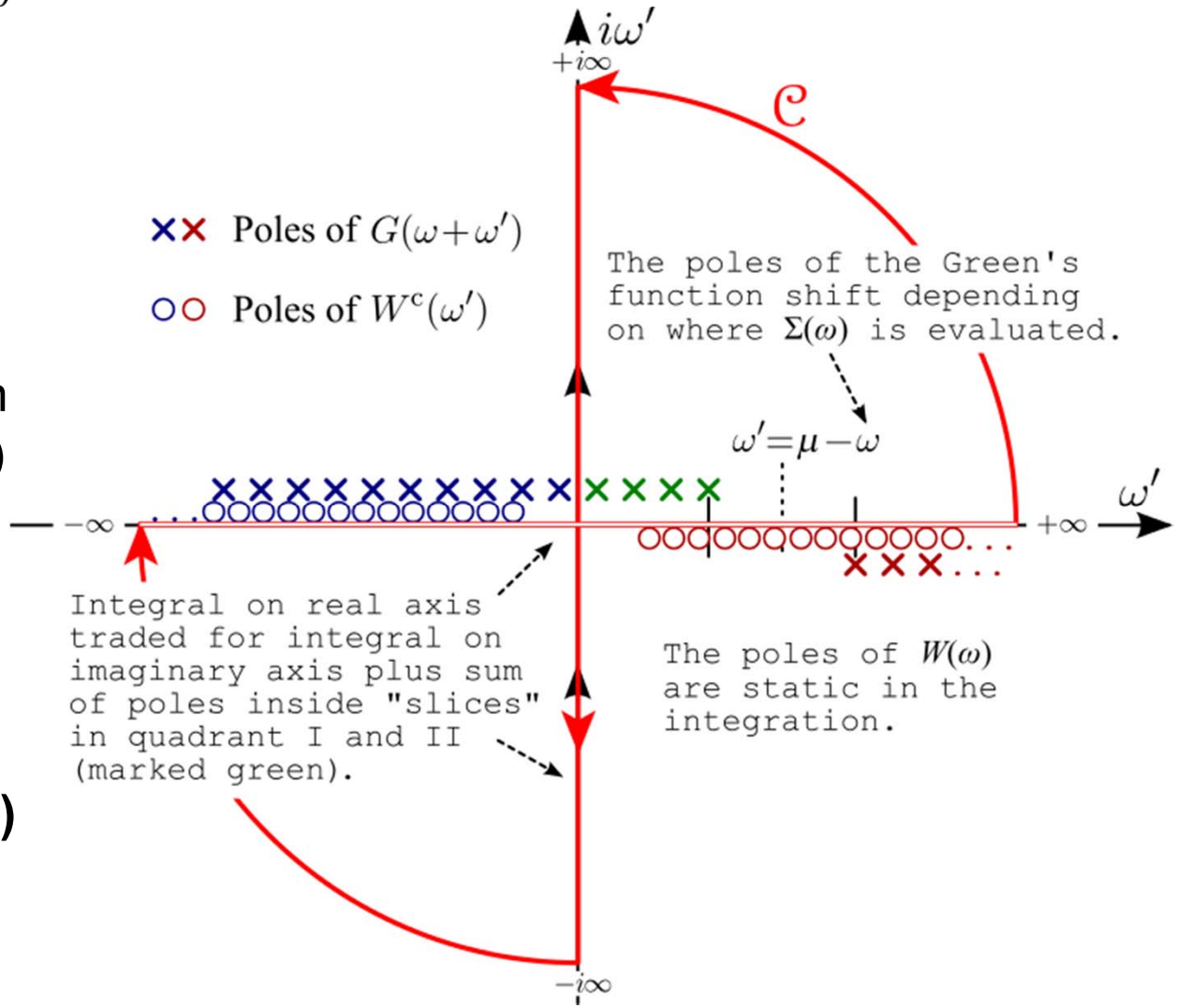
Frequency dependence

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = i\int \frac{\mathrm{d}\omega'}{2\pi} G(\mathbf{r},\mathbf{r}',\omega+\omega')W_{\mathrm{RPA}}(\mathbf{r},\mathbf{r}',\omega')$$

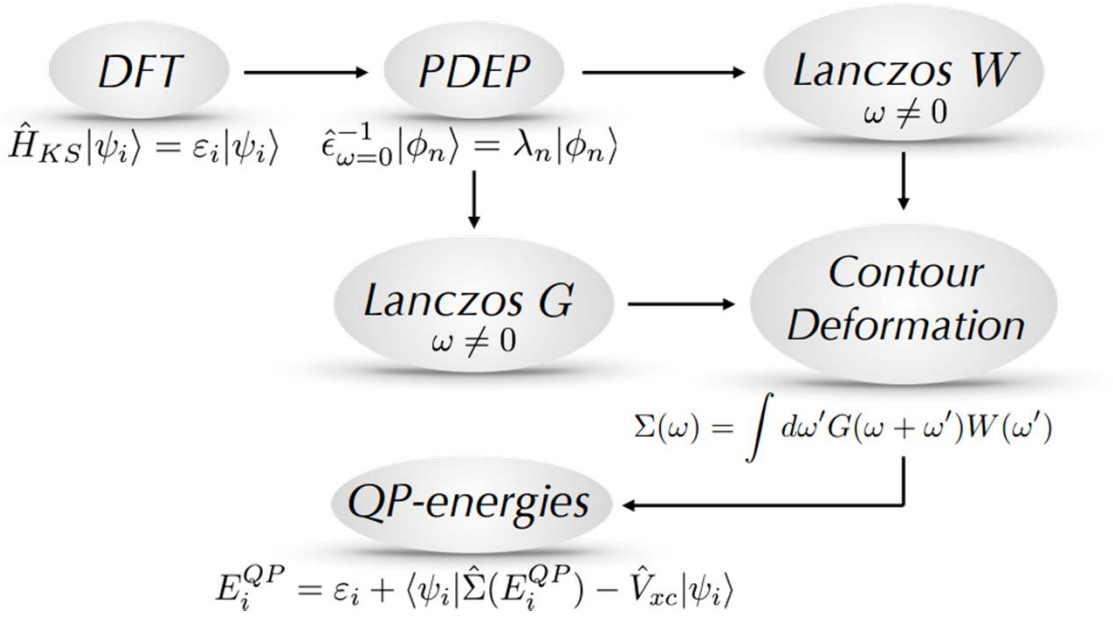
Frequency dependence of *G* and *W* are introduced via Lánczos techniques

Convolution:

- Real-axis integration (exact, dense mesh)
- Analytical continuation
- Plasmon-pole approximation
- **Contour deformation (exact)**



Summary of GW algorithm



- Eliminated summations 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

Electron self-energy: challenging to compute

DFT+MBPT

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

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

W requires the inversion of the dielectric matrix

G requires the inversion of the Hamiltonian

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

H eigenstates are used to expand operators	Achieving convergence may be challenging even for small systems
Non-separable forms for the dielectric matrix are used	Large matrices need to be stored and inverted
The **frequency** dependence of the screened interaction is often approximated (PP)	Accuracy of frequency models often difficult to calibrate

1

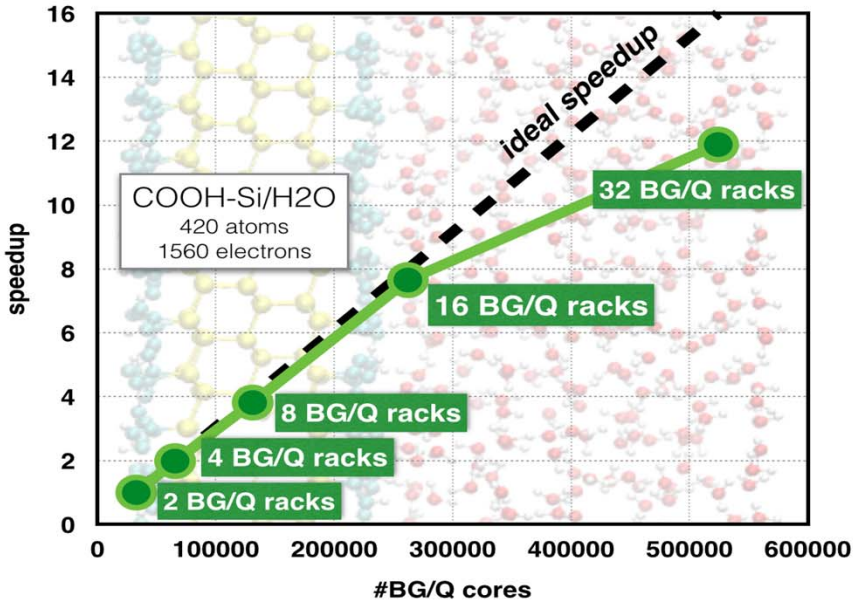
2

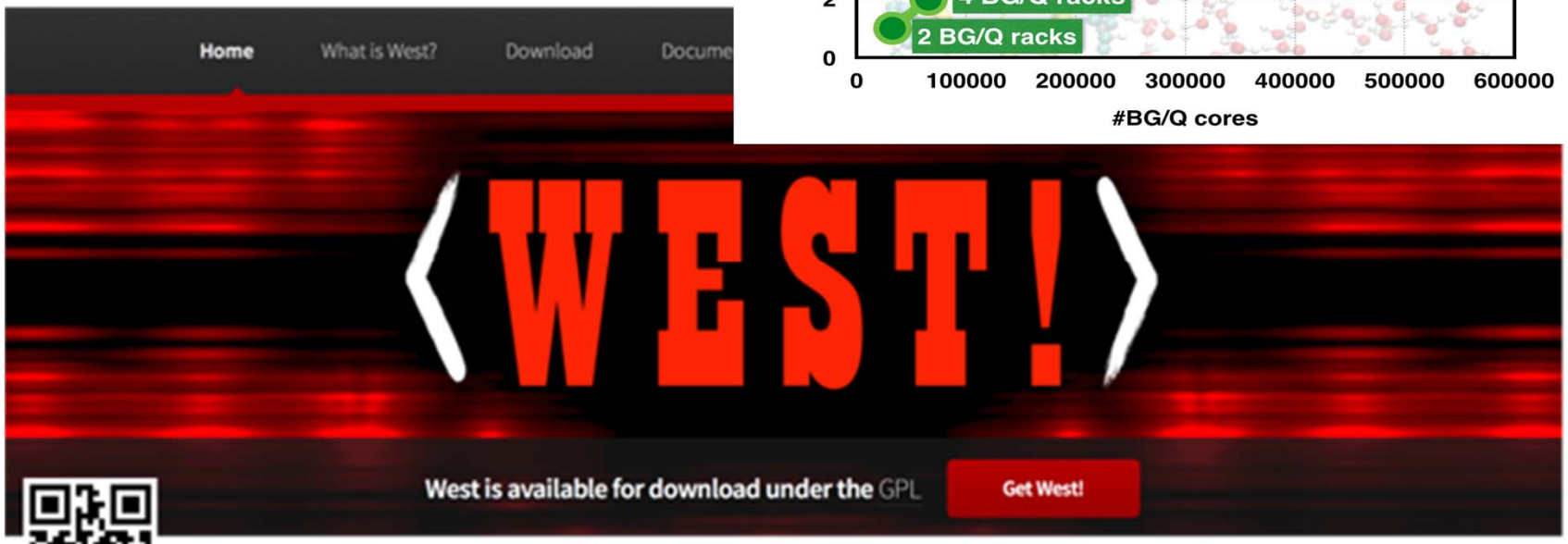
3

Implementation of GW algorithm

Range of applicability

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



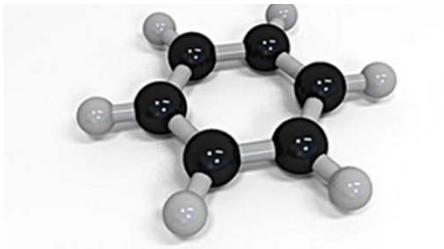


www.west-code.org

scalable to > 500,000 cores

Validation: Data Collections

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

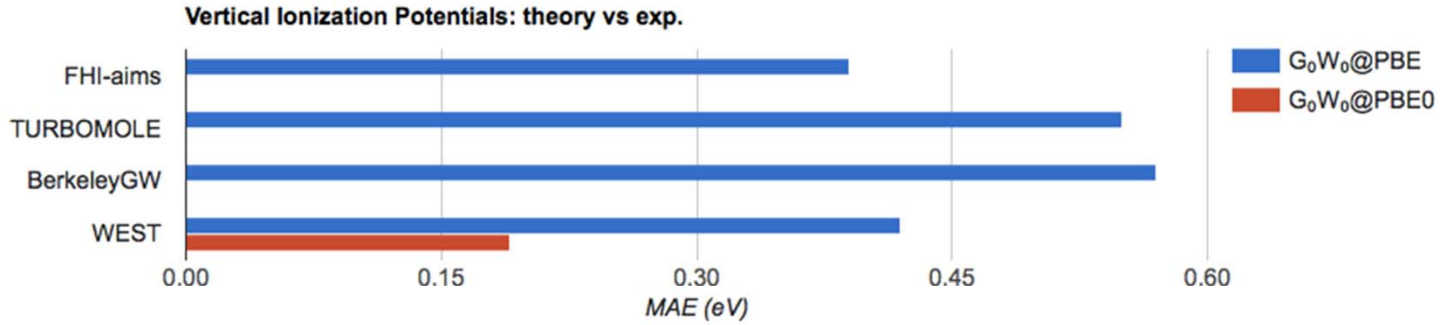


GW100

Benchmark of G_0W_0 on 100 molecules[1-2]. The results obtained with WEST are compared with those of other all emectron and pseudopotential codes.

Access the Data Collection

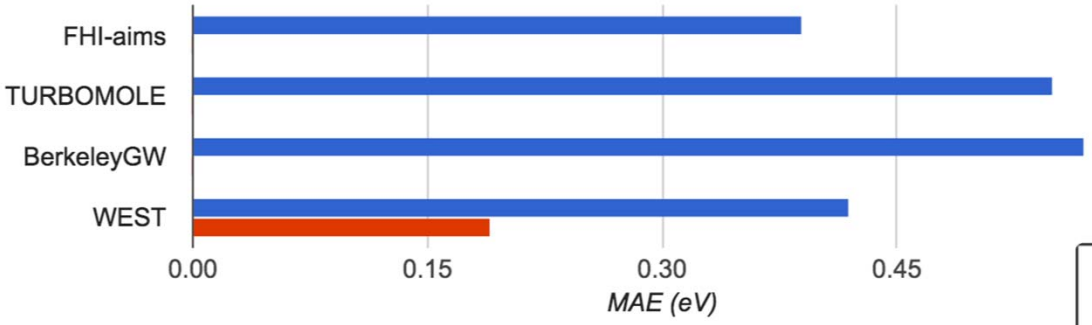
A paper descibing the results obtained with WEST is in preparation.



- [01] M. Schlipf, and F. Gygi, *Optimization algorithm for the generation of ONCV pseudopotentials*, Comput. Phys. Comm. 196, 36 (2015).
- [02] M.J. van Setten, F. Caruso, S. Sharifzadeh, X. Ren, M. Scheffler, F. Liu, J. Lischner, L. Lin, J.R. Deslippe, S.G. Louie, C. Yang, F. Weigend, J.B. Neaton, F. Evers, and P. Rinke, *GW100: Benchmarking G_0W_0 for Molecular Systems*, J. Chem. Theory Comput. 11, 5665 (2015).
- [03] M. Govoni *et al.*, in preparation (2016).
- [04] P.J. Linstrom and W.G. Mallard, Eds., NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov.

MICCoM

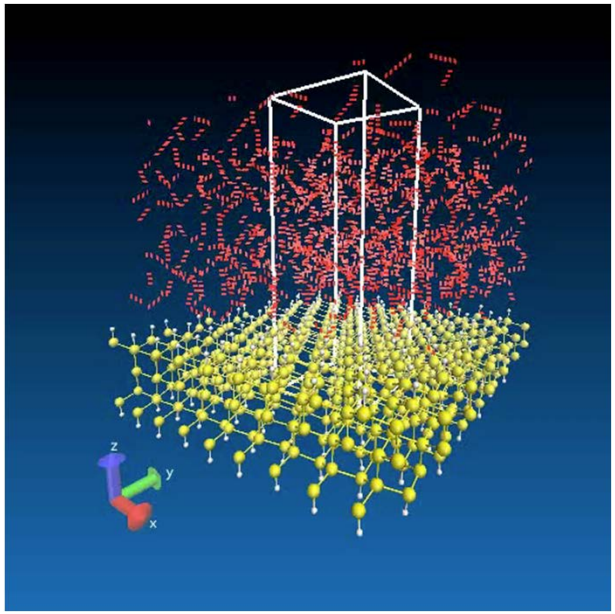
Validation and comparison with other codes



- **Good agreement with AE and PS codes**
- WEST does not require basis-set extrapolation
- WEST implements Full Frequency (no PP)

MAD (eV)		FHI-aims		TURBOMOLE		WEST	BerkeleyGW	
		16P	EXTRA	w/ RI	w/o RI		GPP	FF
FHI-aims	16P	—	0.14	0.05	0.00	0.15	0.62	0.29
	EXTRA	0.14	—	0.19	0.14	0.13	0.50	0.35
Turbomole	w/ RI	0.05	0.19	—	0.05	0.18	0.67	0.26
	w/o RI	0.00	0.14	0.05	—	0.16	0.67	0.29
WEST		0.15	0.13	0.18	0.16	—	0.53	0.17
BerkeleyGW	GPP	0.62	0.50	0.67	0.67	0.53	—	0.88
	FF	0.29	0.35	0.26	0.29	0.17	0.88	—

Applications to interfaces



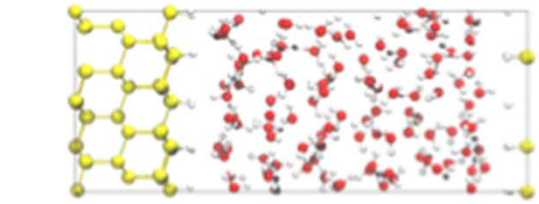
U.S. DEPARTMENT OF ENERGY INCITE LEADERSHIP COMPUTING

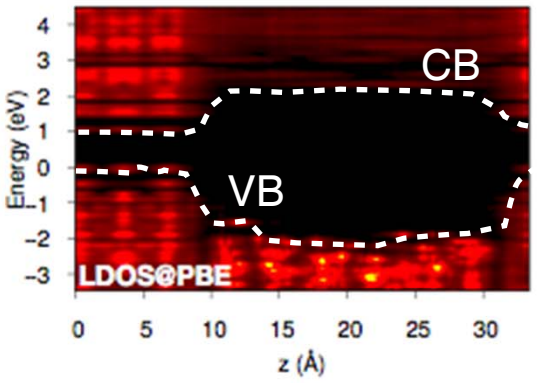
Qbox & WEST

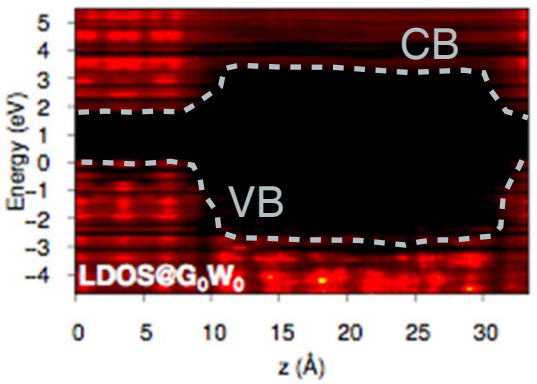
$$D(E,z) = \sum_n |\psi(z)|^2 \delta(E - \varepsilon_n)$$

Ecut = 85 Ry

H-Si/H2O

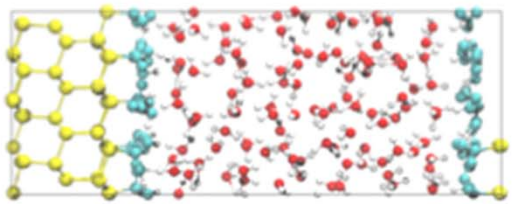


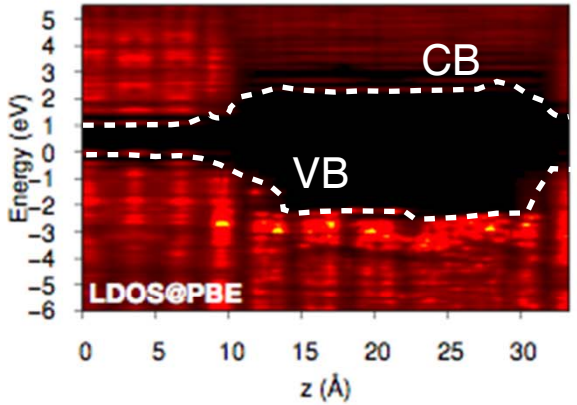


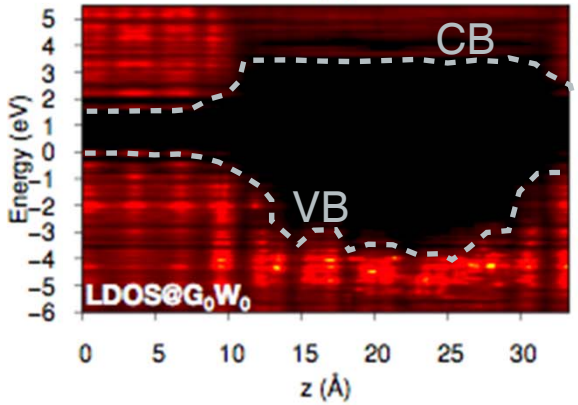


420 atoms 1176 electrons

COOH-Si/H2O



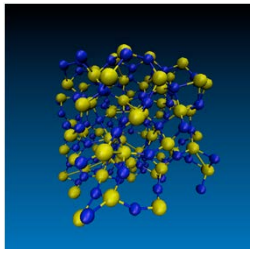


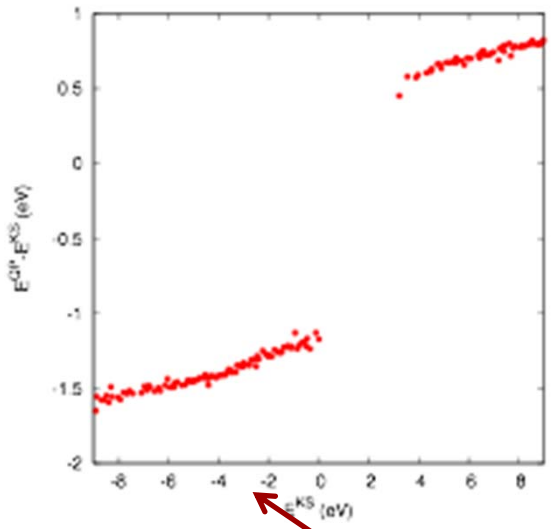


492 atoms 1560 electrons

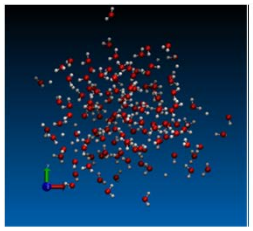
Applications to disordered systems

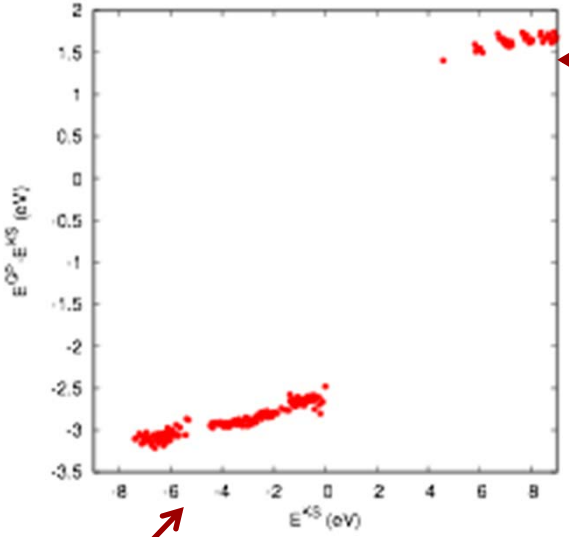
Amorphous Si_3N_4





Liquid water



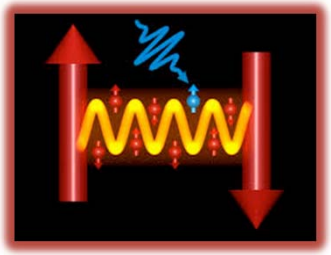


States above CBM

States below the gap

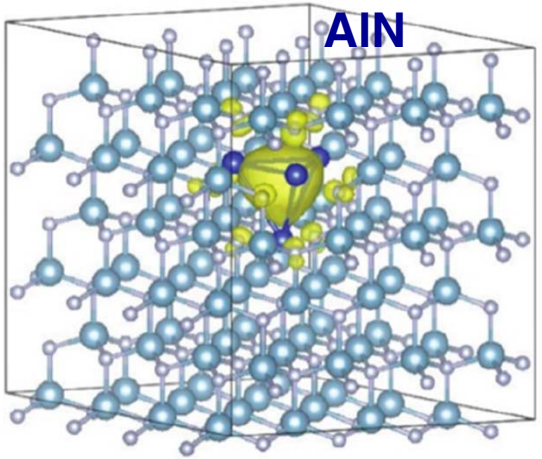
Applications to spin defects

- Manipulating spins with light to design (i) novel computing technologies and (ii) new generation of nanoscale sensors

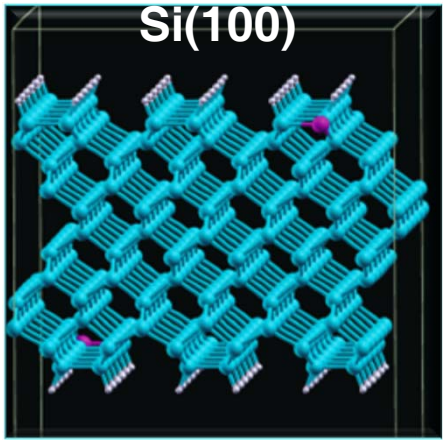


  - Determination of “good” qubits from combined experimental and computational studies
  - Identification of key spin-spin correlations from computation

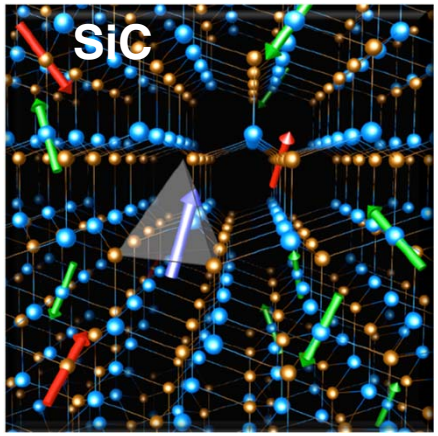
Electronic properties of spin defects



Seo, Govoni &GG Sci. Rep. 2016



Scherpelz, Govoni & GG 2016 (work in progress)



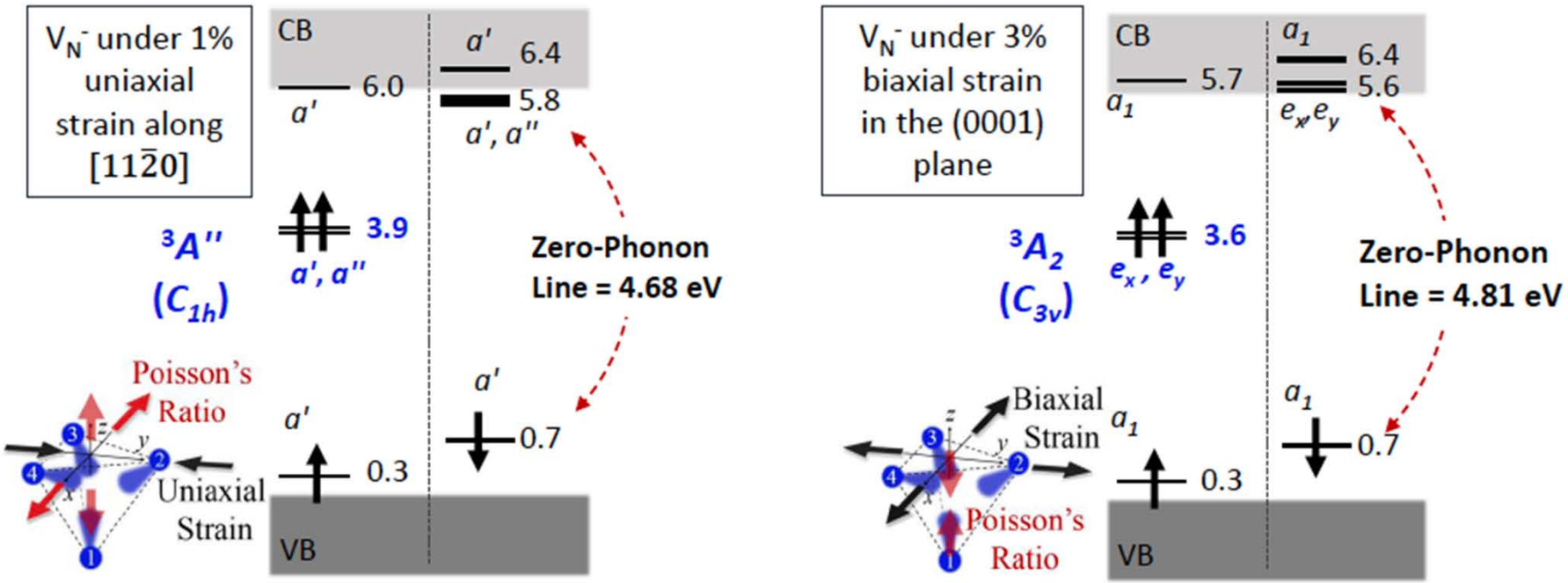
Seo,Falk,Klimov,Miao,, GG, Awschalom, Nat. Comm. 2016

Calculations at DFT and MPBT level

- **Using a combined (hybrid) density functional theory and G_0W_0 many-body perturbation framework, we predicted localized spin-triplet states in *w*-AlN under strain.**

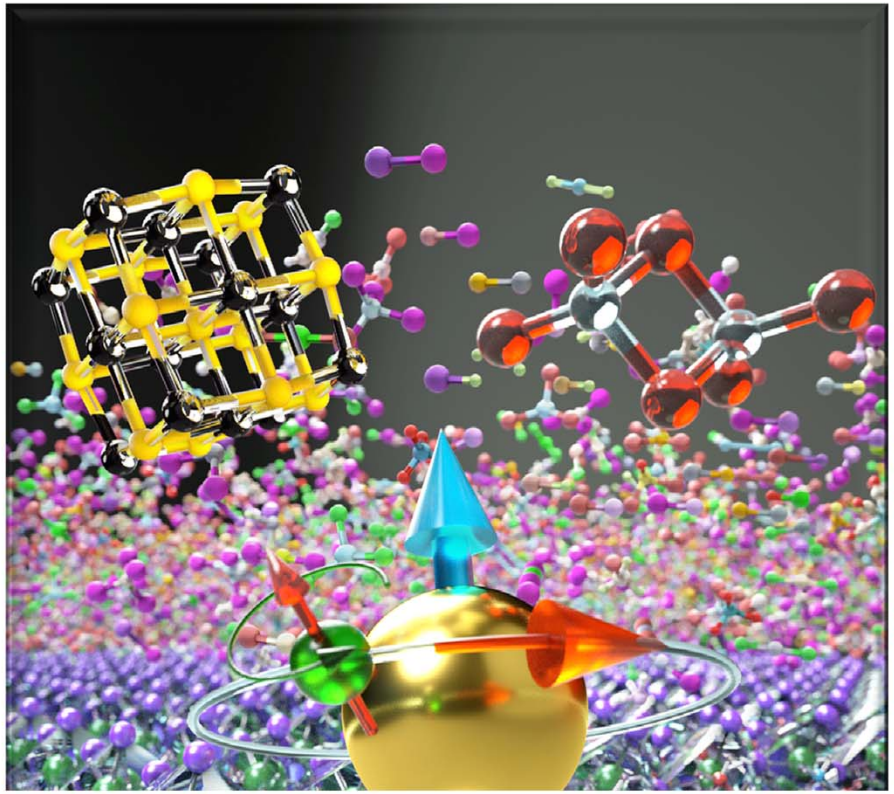
1) Al-vacancy related defects are not suitable as qubits.

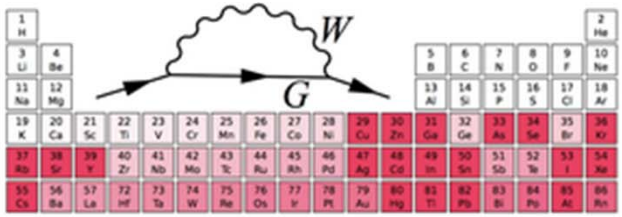
2) We found that negatively charged N-vacancy (V_N^-) have $^3A''$ and $^3A_2$ spin-triplet ground states under uniaxial and biaxial strain, respectively.



Hosung Seo et al. Sci.Rep. & Nat. Comm. 2016

GW calculations w/spin-orbit coupling





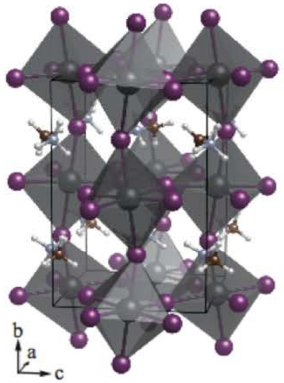
GWSOC81

Benchmark of G_0W_0 with spin-orbit coupling (SOC) on 81 molecules.

P. Scherpelz, M.Govoni, I.Hamada and GG, JCTC 2016

GW calculations w/spin-orbit coupling

$CH_3NH_3PbI_3$

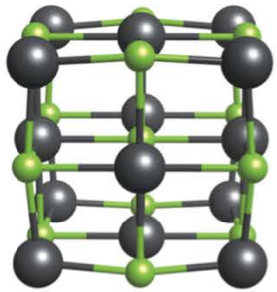


Egap (eV)	DFT	G0W0
wo/ SOC	1.48 (1.50)*	2.84 (2.55)*
w/ SOC	0.44 (0.58)*	1.51 (1.32)*

In good agreement with previous theoretical results

* Filip, Giustino, Phys. Rev. B 2014

$Pb_{14}Se_{13}$



Egap (eV)	DFT	G0W0
wo/ SOC	0.87	3.08
w/ SOC	0.59	2.77

Error cancellation does not hold for PbSe nanoparticles

GW calculations w/spin-orbit coupling

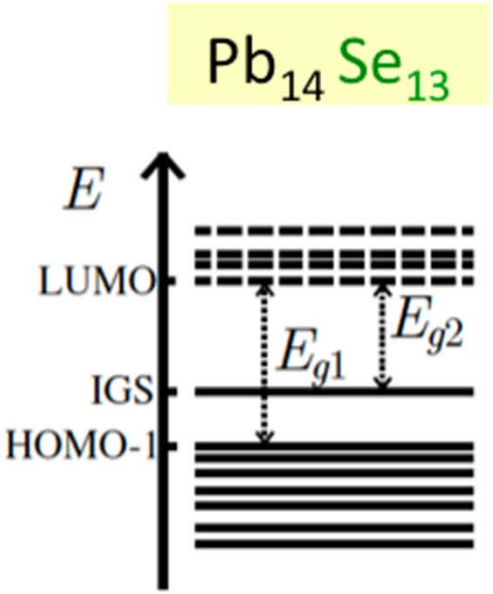
Choice of Pseudopotentials

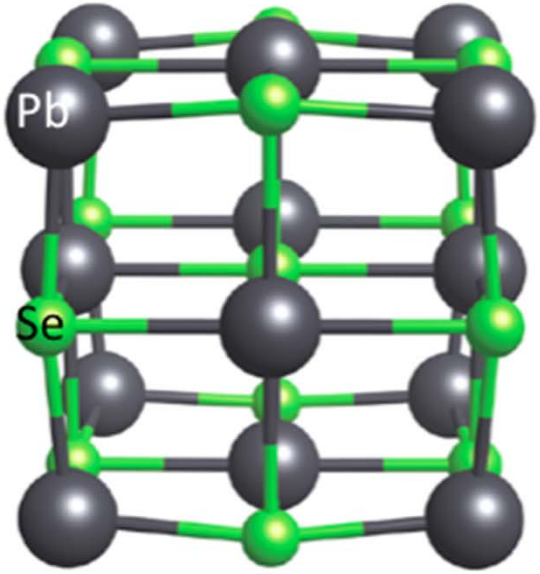
Computed Band Gap (eV) of Solid $CH_3NH_3PbI_3$ As Determined with SR and FR Calculations, for Different Pseudopotential Configurations

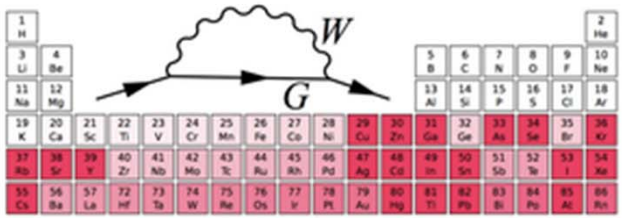
pseudo. set	functional	I config.	Pb config.	DFT E_g	G_0W_0 E_g
SR					
ONCV (I^{25+})	PBE	4s4p4d5s5p	5d6s6p	1.50	2.27
SG15 (I^{17+})	PBE	4d5s5p	5d6s6p	1.49	2.84
SG15 (I^{7+})	PBE	5s5p	5d6s6p	1.48	2.26
GTH	PBE	5s5p	5d6s6p	1.46	2.17
GTH	PBE	5s5p	6s6p	1.44	2.22
SG15-based (I^{17+})	LDA	4d5s5p	5d6s6p	1.36	2.86
SG15-based (I^{7+})	LDA	5s5p	5d6s6p	1.37	2.39
GTH	LDA	5s5p	6s6p	1.32	2.18
ref 51	LDA	4d5s5p	5d6s6p	1.50	2.55
ref 51	LDA	5s5p	5d6s6p	1.42	2.16
FR					
ONCV (I^{25+})	PBE	4s4p4d5s5p	5d6s6p	0.46	0.85
SG15 (I^{17+})	PBE	4d5s5p	5d6s6p	0.44	1.51
SG15 (I^{7+})	PBE	5s5p	5d6s6p	0.43	0.87
SG15-based (I^{17+})	LDA	4d5s5p	5d6s6p	0.32	1.41
SG15-based (I^{7+})	LDA	5s5p	5d6s6p	0.32	0.98
ref 51	LDA	4d5s5p	5d6s6p	0.58	1.32
ref 51	LDA	5s5p	5d6s6p	0.52	0.98

Further testing of PPs for GW calculations is in progress

Spin-orbit coupling: fully relativistic GW calculations







GWSOC81

Benchmark of G_0W_0 with spin-orbit coupling (SOC) on 81 molecules.

Coming Soon

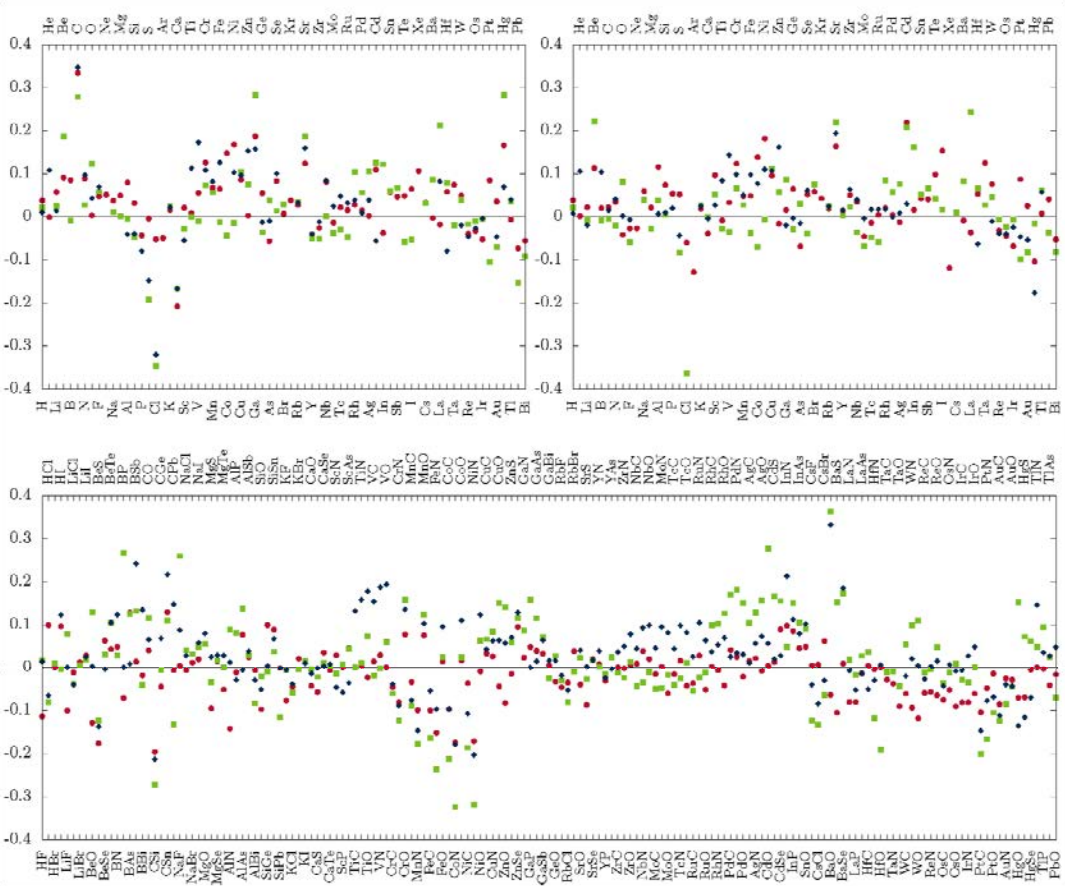
Peter Scherpelz et al. JCTC 2016 (accepted)

The SG15 collection of norm-conserving pseudopotentials

- SG15: A collection of Optimized Norm-Conserving Vanderbilt (ONCV) potentials from H to Bi
- Automatic optimization of parameters using the Nelder-Mead simplex algorithm
- Optimization criteria: reproduce FLAPW lattice constants, using a moderate plane-wave cutoff (60 Ry)
- D. Hamann's ONCV program (http://mat-simresearch.com)
- FLEUR FLAPW code (http://www.flapw.de)
- PPs available in QSO (XML) and UPF (Quantum ESPRESSO) formats at http://www.quantum-simulation.org

M. Schlipf, F.Gygi *Comput. Phys. Comm.* **196**, 36 (2015)

The SG15 collection of norm-conserving pseudopotentials

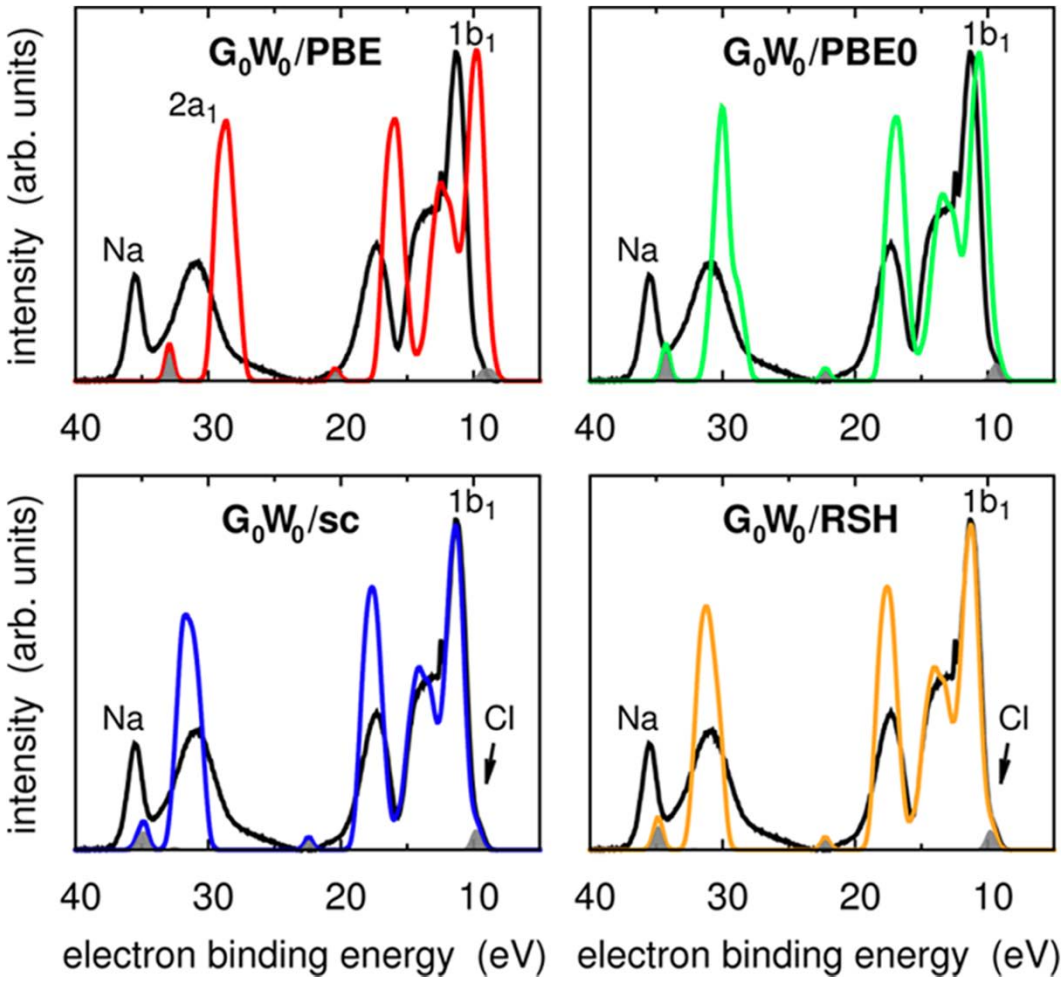


- Over 600 compounds tested
- lattice constant error < 0.4%
- FLAPW, GBRV, PSLib(PAW), SG15 have similar accuracy

M. Schlipf, F.Gygi *Comput. Phys. Comm.* **196**, 36 (2015)

Does the starting point (input DFT) matter?

Example: Photoelectron spectra of aqueous solutions



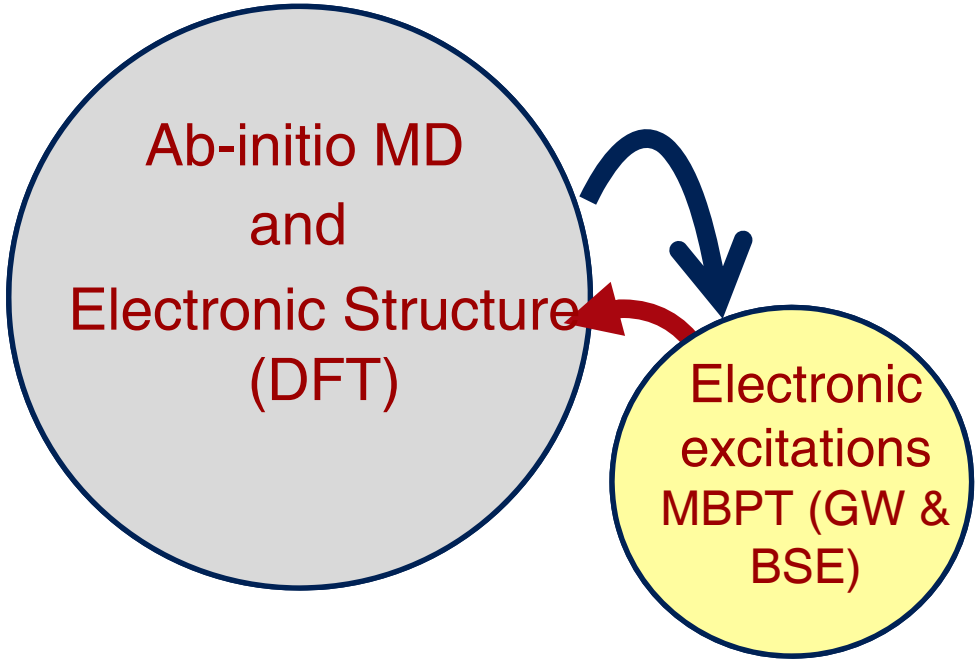
Outline

- Structural models
- The basic role of electronic structure underlying multiple properties of materials
- Large scale calculations and the importance of scalable algorithms

  —Large scale GW

- ‘Improved’ energy functionals from approximate self-energies
- Transport from first principles

Hybrid functionals



Development of hybrid functionals

- Efficient screening of gaps and band positions in bulk materials
- Improved input for G_0W_0 calculations

J.Skone, M.Govoni and GG, PRB 2014; J.Skone et al. 2016; N.Brawand, M.Voros, M.Govoni and GG, PRX 2016

Dielectric dependent hybrid functionals

Global DDH

$$v_{xc}^{hyb}(\mathbf{r},\mathbf{r}') = \epsilon_\infty^{-1} v_x(\mathbf{r},\mathbf{r}') + (1-\epsilon_\infty^{-1}) v_x(\mathbf{r}) + v_c(\mathbf{r})$$

$$W(\mathbf{r},\mathbf{r}') \approx \frac{\epsilon_\infty^{-1}}{|\mathbf{r}-\mathbf{r}'|}$$

Mixing fraction of local and exact exchange is the static dielectric constant, determined self-consistently

Range-separated (RS) DDH

$$\begin{aligned} v_{xc}^{hyb}(\mathbf{r},\mathbf{r}') &= \epsilon_\infty^{-1} v_x^{\mathrm{lr-ex}}(\mathbf{r};\mu) + \beta v_x^{\mathrm{sr-ex}}(\mathbf{r},\mathbf{r}';\mu) \\ &\quad + (1-\epsilon_\infty^{-1}) v_x^{\mathrm{lr}}(\mathbf{r};\mu) + (1-\beta) v_x^{\mathrm{sr}}(\mathbf{r};\mu) + v_c(\mathbf{r}) \end{aligned}$$

Range separation parameter μ is, e.g. the Thomas-Fermi screening length (depends on # of VE)

$$W(\mathbf{r},\mathbf{r}') \approx \frac{\epsilon_\infty^{-1}}{|\mathbf{r}-\mathbf{r}'|} + (\beta - \epsilon_\infty^{-1}) \frac{\mathrm{erfc}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

Qbox
http://qboxcode.org/

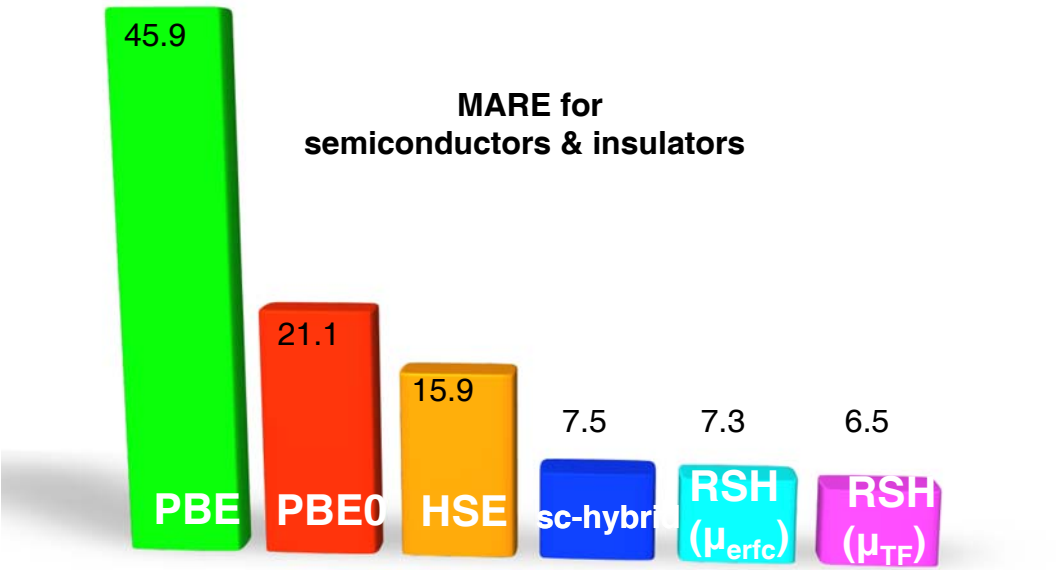
QUANTUM ESPRESSO
http://quantum-espresso.org

CRYSTAL
http://www.crystal.unito.it/

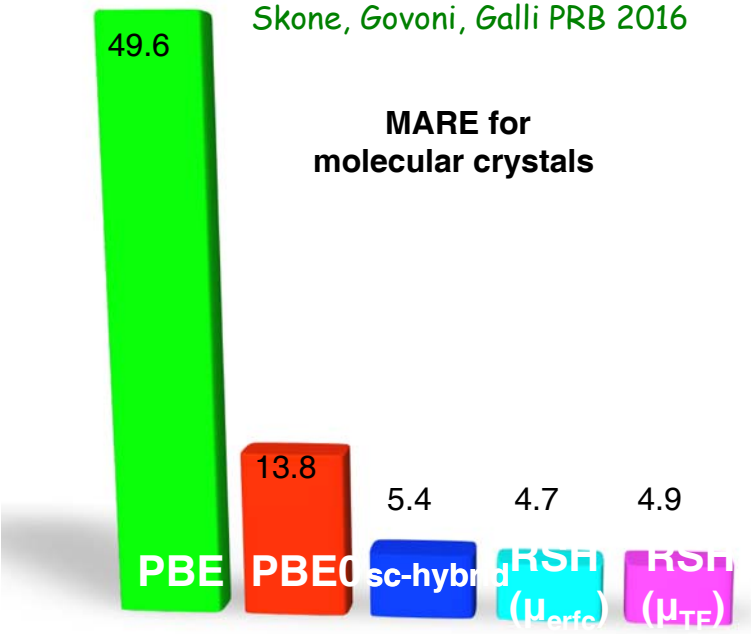
NSF

Performance of DDH functionals

Electronic Gaps of solids



Skone, Govoni, Galli PRB 2016



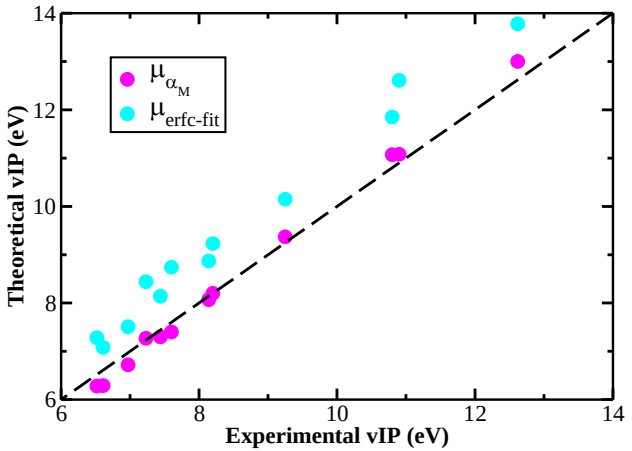
Vertical Ionization Potentials of molecules

μ_{α_M} yields similar values to the OT-RSH* tuning procedure.

$$\mu_{\alpha_M} = \left(\frac{1}{\alpha_M}\right)^{\frac{1}{3}}$$

Molecular polarizability

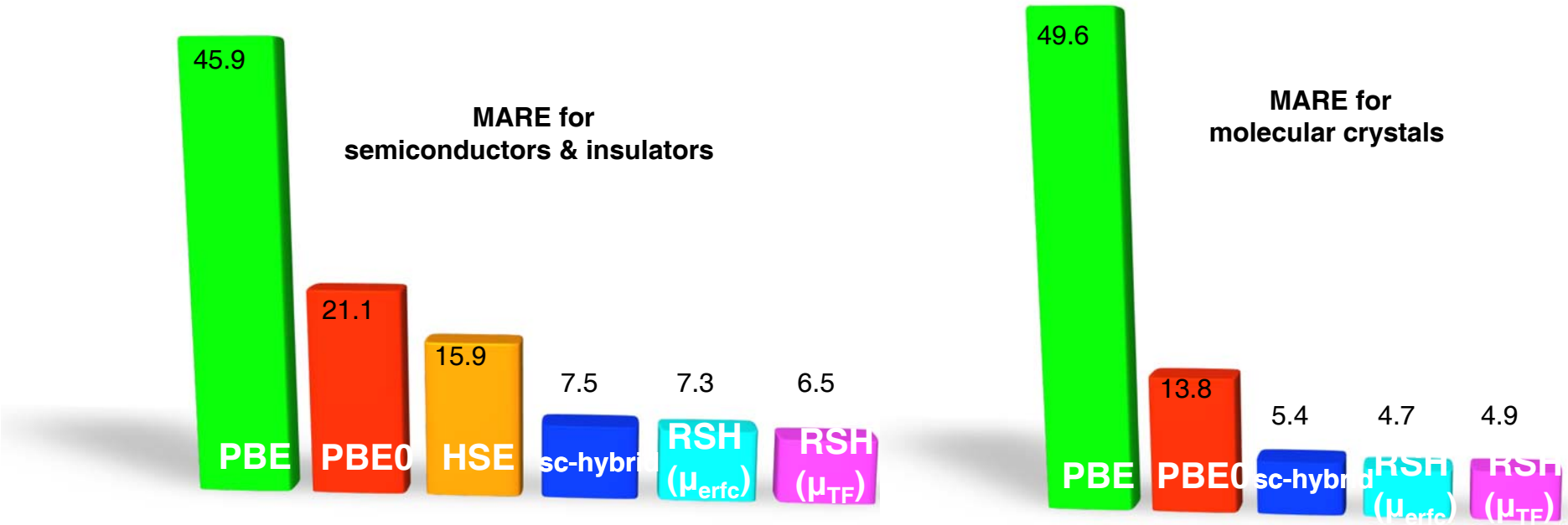
*Refaely-Abramson et. al. PRL **109**, 226405 (2012)
*Kronik et. al. *JCTC* **8**, 1515 (2012)



Performance of DDH functionals

Electronic Gaps

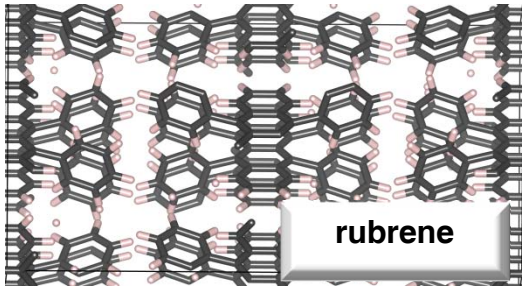
Skone, Govoni, Galli PRB 2016



Ionization Potential

	surface	PBE	PBE0	schybrid	RSH μ_{TF}	Exp.*
vIP (eV)	(100)	3.85	4.45	4.69	4.68	4.85

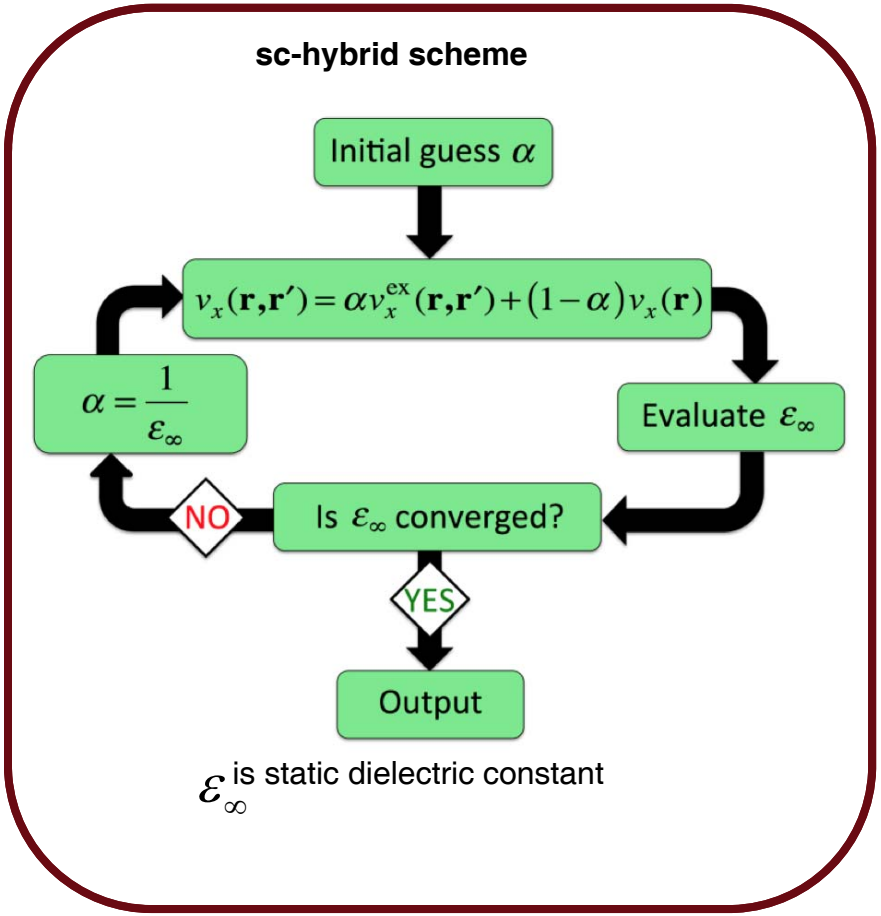
* Nakayama, et al. *App. Phys. Lett.* **93**, 173305 (2008).

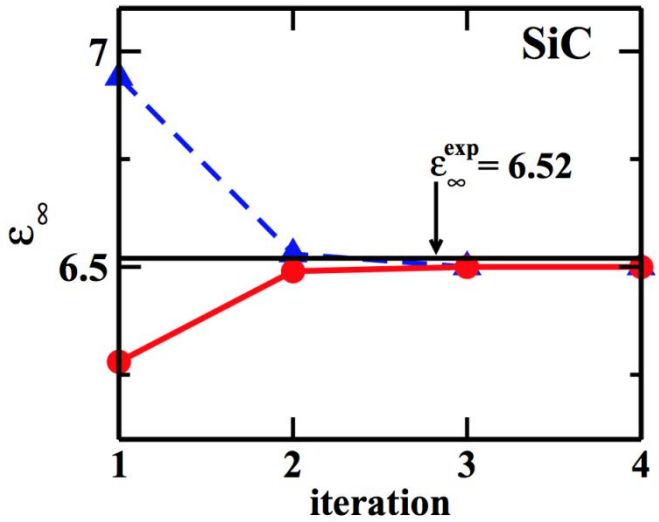


Self-consistent determination of ϵ_∞^{-1}

$$v_{xc}^{hyb}(\mathbf{r},\mathbf{r}') = \epsilon_\infty^{-1} v_x(\mathbf{r},\mathbf{r}') + (1-\epsilon_\infty^{-1}) v_x(\mathbf{r}) + v_c(\mathbf{r})$$

- The fraction of Hartree-Fock exchange is equal to the inverse dielectric constant (ϵ_∞^{-1}) and is determined self-consistently.





- **No empirical input**
- Insensitive to hybrid starting point
- Accurate determination of electronic dielectric constants

Skone, Govoni, and Galli. *PRB.* **89**, 195112 (2014)

Screening parameter (μ) for solids

Valence density based

The Wigner-Seitz radius

$$\frac{4\pi r_s^3}{3} = n^{-1}$$

$$\mu_{WS} = \frac{1}{r_s} = \left(\frac{4\pi n}{3}\right)^{1/3}$$

The Thomas-Fermi screening length:

$$W(r) = \epsilon_\infty^{-1} + (1 - \epsilon_\infty^{-1})\frac{e^{-rk_{TF}}}{r}$$

where $k_{TF} = 2\left(\frac{3n}{\pi}\right)^{1/6}$

$$\mu_{TF} = \frac{1}{2}k_{\mathrm{TF}} = \left(\frac{3n}{\pi}\right)^{1/6}$$

Extract from fit of the dielectric function

$$\mu_{\text{erfc-fit}}: \quad \epsilon^{-1}(\mathbf{G}^2) = \epsilon_\infty + (1 - \epsilon_\infty)\left(1 - \mathrm{e}^{-\mathbf{G}^2/4\mu^2}\right)$$

Generalization of dielectric dependent functionals to finite systems

The dielectric constant and the volume of molecules and nanostructures are ill-defined

$$v_{xc}(\mathbf{r},\mathbf{r}') = \alpha^{\mathrm{SX}}\Sigma_{\mathrm{X}}(\mathbf{r},\mathbf{r}') + (1-\alpha^{\mathrm{SX}})v_x(\mathbf{r}) + v_c(\mathbf{r})$$

$$\Sigma_{\mathrm{X}}(\mathbf{r},\mathbf{r}') = -\sum_{j}^{N}\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')v(\mathbf{r},\mathbf{r}')$$

$$\Sigma_{\mathrm{SX}}(\mathbf{r},\mathbf{r}') = -\sum_{j}^{N}\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')W(\mathbf{r},\mathbf{r}')$$

$$\alpha_i^{\mathrm{SX}} = \frac{\langle\phi_i|\Sigma_{\mathrm{SX}}|\phi_i\rangle}{\langle\phi_i|\Sigma_{\mathrm{X}}|\phi_i\rangle}$$

$$\alpha^{\mathrm{SX}} \rightarrow \epsilon_{\infty}^{-1}$$

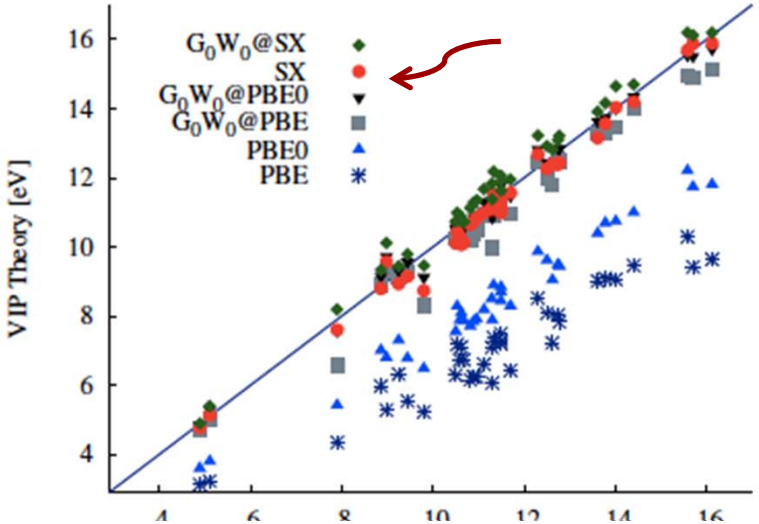
Dielectric matrix using spectral decomposition techniques (no virtual states, no direct diagonalization, no inversion necessary)

http://www.west-code.org

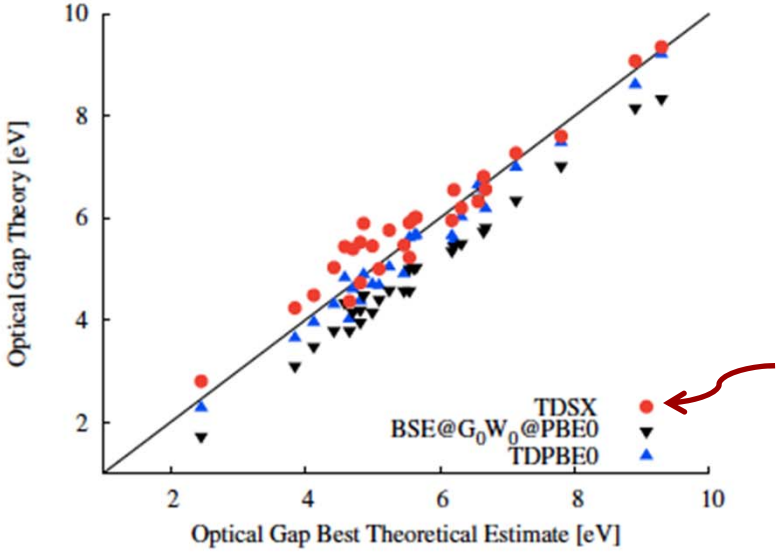
J.Skone, M.Govoni and GG, PRB 2014 and PRB 2016; N.Brawand et al. PRX 2016

Photoemission and optical data

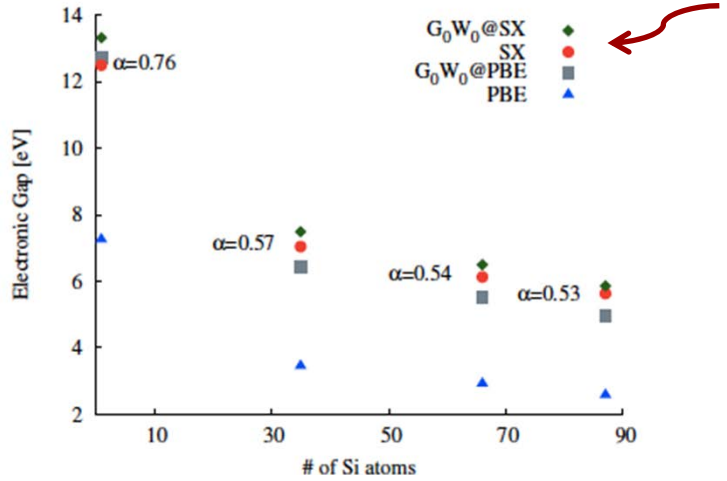
Molecules: Ionization Potentials

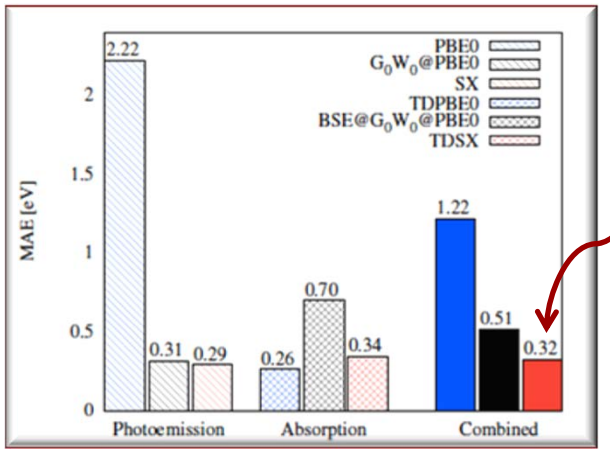


Optical gaps



Si Nanoparticles: electronic gaps





Excellent combined performance for photoemission & absorption

Results are statistically significant

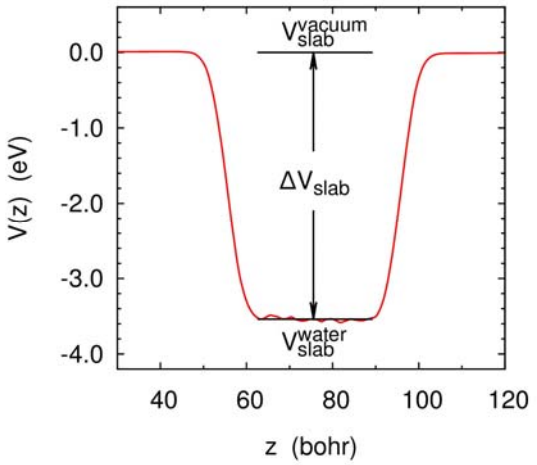
Photoelectron spectra of salts in water

- Trajectories from ab initio MD with hybrid functionals (*)
- GW calculations of energy levels starting from wfs determined with dielectric hybrid functionals (+)
- Intensities computed from Im(Σ)

$$\sum_{i}^{\text{occ.}} f_i(E;E_i,\Gamma_i)\frac{d\sigma_i(h\nu)}{d\Omega} \qquad f_i(E;E_i,\Gamma_i)=\frac{1}{\pi}\frac{\Gamma_i}{(E-E_i)^2+\Gamma_i^2},$$

- Band offsets with vacuum used to obtain spectra on an absolute energy scale (include calculations of water surface)

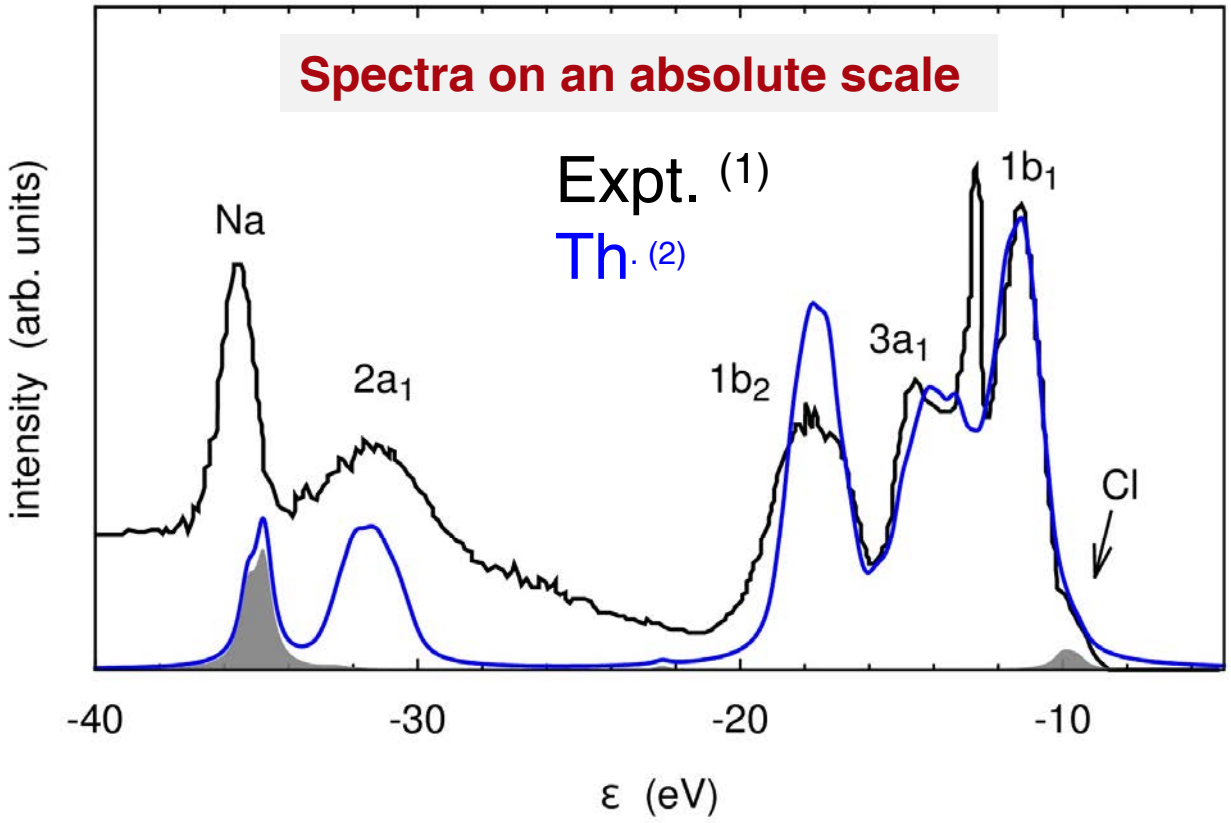
$$\tilde{\varepsilon}_i = \varepsilon_i - \Delta V_{\text{slab}} - V_{\text{bulk}}$$



(*) F.Gygi, PRL 2009; (+) J.Skone, M.Govoni and GG, PRB 2014 & PRB 2016

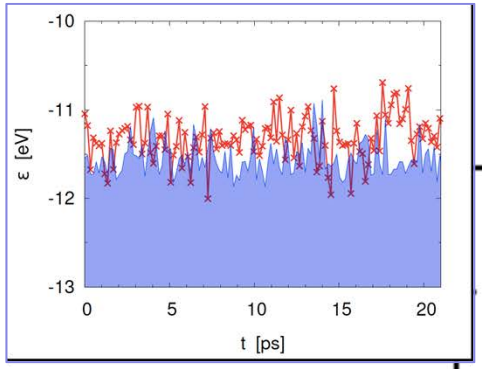
Photoelectron spectra of salts in water

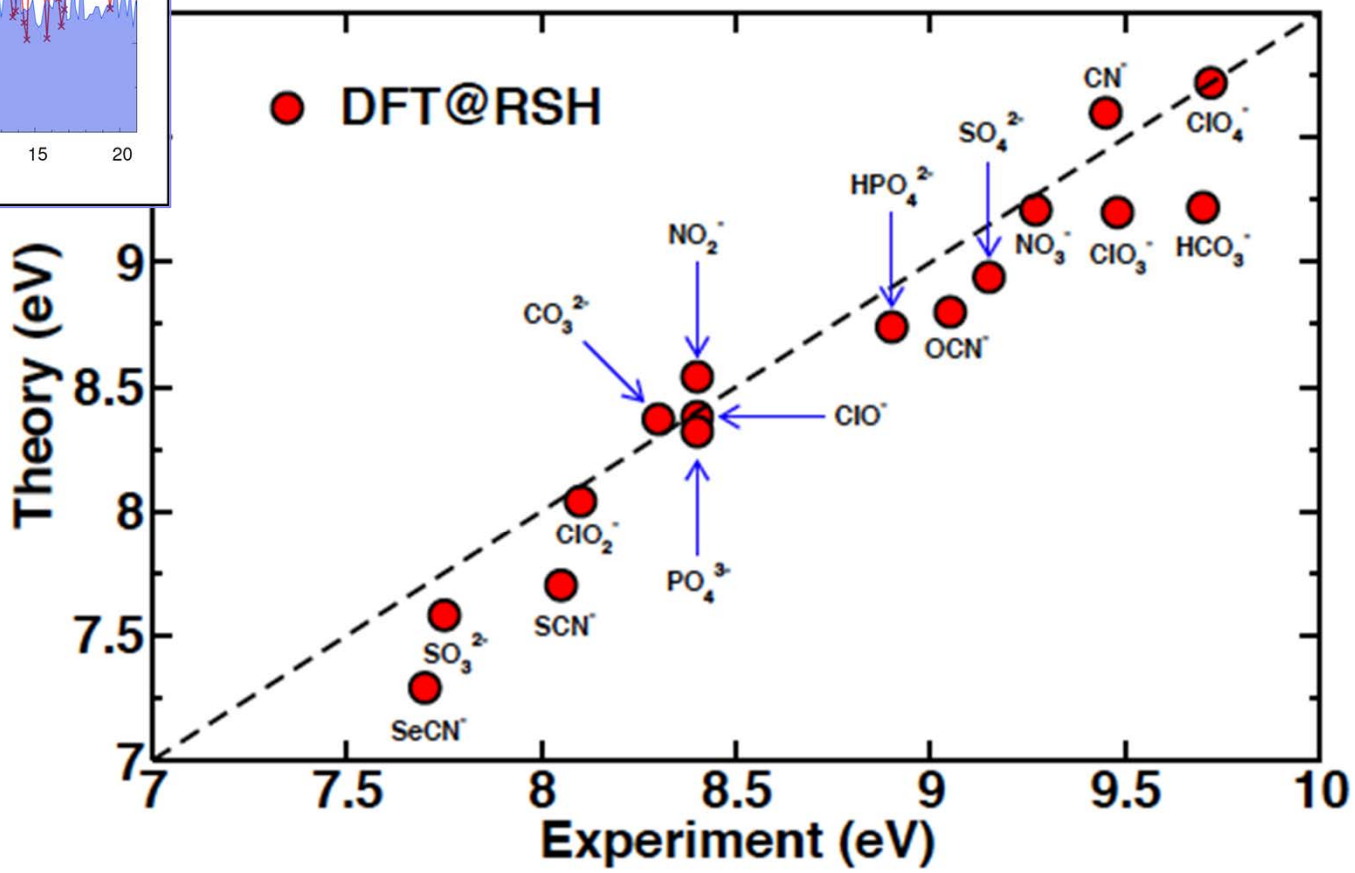
$(NaCl)_{aq}$ 0.9 M solution: G_0W_0@DDH-hybrid



(1) R. Seidel, T. Thürmer & B. Winter, *JPCL* **2,** 633 (2011)& B. Winter and R.Siedel 2016
(2) A.Gaiduk, M.Govoni, J.K. Skone, R.Seidel. B.Winter and GG, JACS Comm. 2016

Electronic levels of anions in water

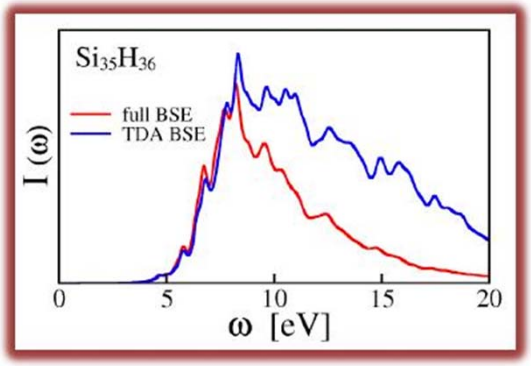




T.A.Pham et al. 2017 (submitted)

Absorption, multi-excitons, …

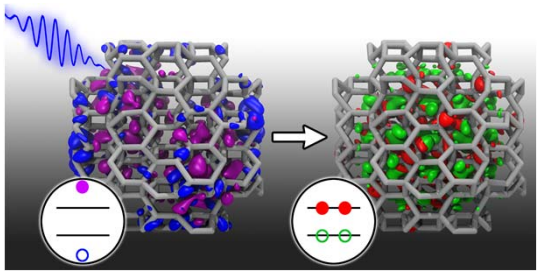
Similar ideas used :



To simulate **photo-absorption**, solving the Bethe-Saltpeter eq.

Rocca *et al.*, J. Chem Phys. 133, 164109 (2010)
Ping *et al.*, Chem Soc. Rev. 42, 2437 (2013)

To simulate **carrier recombinations** (electronic/thermal)

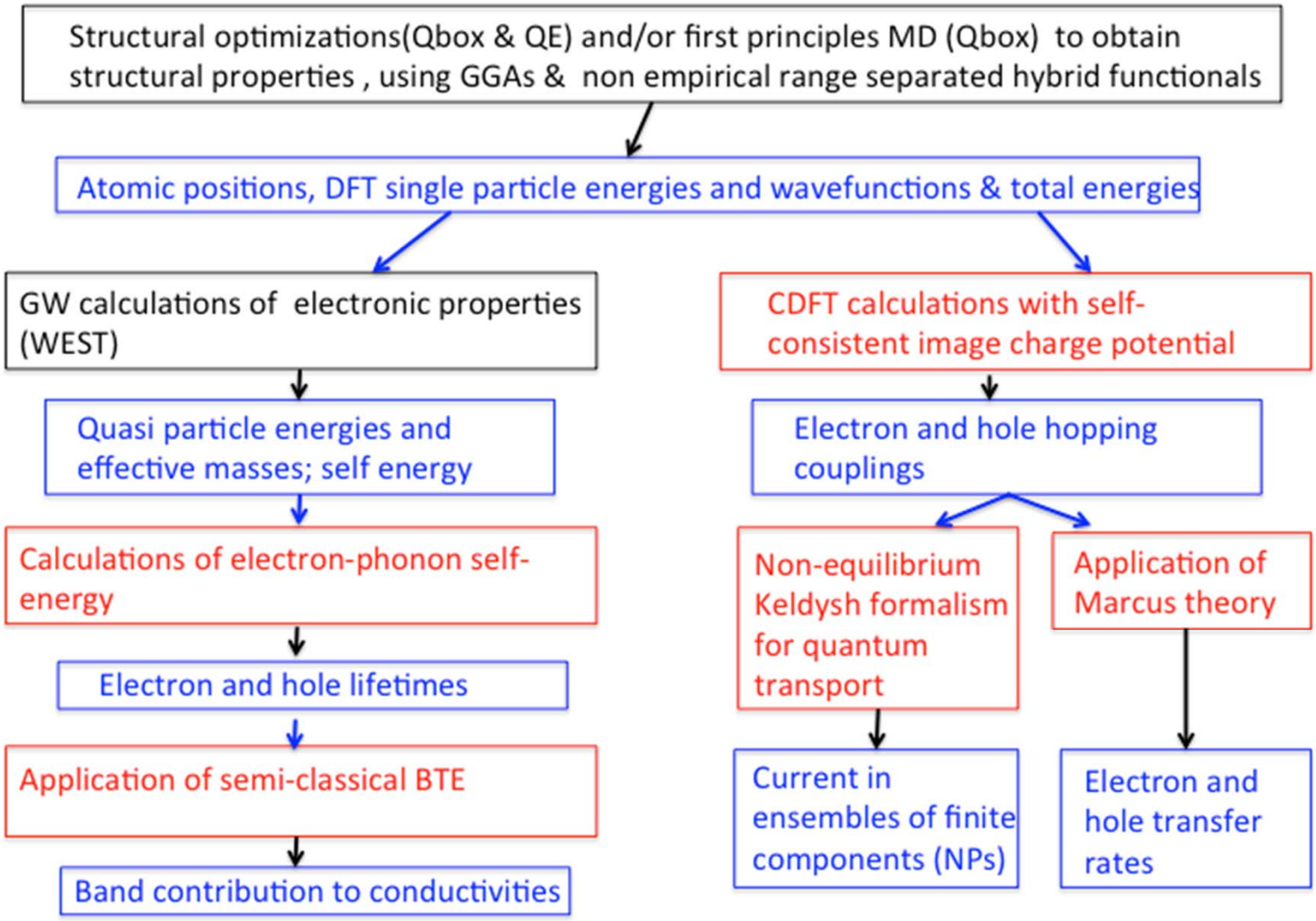


Govoni *et al.*, Nat. Photonics 6, 672-679 (2012)

Wipperman *et al.*, PRL 110, 046804 (2013)

They may also be used in conjunction with **DMFT**

Transport


Structural optimizations(Qbox & QE) and/or first principles MD (Qbox) to obtain structural properties , using GGAs & non empirical range separated hybrid functionals
Atomic positions, DFT single particle energies and wavefunctions & total energies
GW calculations of electronic properties (WEST)
Quasi particle energies and effective masses; self energy
Calculations of electron-phonon self-energy
Electron and hole lifetimes
Application of semi-classical BTE
Band contribution to conductivities
CDFT calculations with self-consistent image charge potential
Electron and hole hopping couplings
Non-equilibrium Keldysh formalism for quantum transport
Application of Marcus theory
Current in ensembles of finite components (NPs)
Electron and hole transfer rates

Transport

Boltzmann Transport Equation (approximate solutions):

$$\sigma_{\alpha\beta} = -2e\sum_n \int_\Omega \frac{d^3k}{(2\pi)^3} v_{n\vec{k}\alpha}\left(-e\frac{\partial f^0_{n\vec{k}}}{\partial \epsilon_{n\vec{k}}} v_{n\vec{k}\beta}\tau_{n\vec{k}}\right)$$

With e-e and e-phonon contributions to lifetimes):

$$\sum^{Fan}_{n\vec{k}}(i\omega, T) = \sum_{n'\vec{q}\lambda} \frac{|g^{\vec{q}\lambda}_{nn'\vec{k}}|^2}{N_q} \times \left[\frac{N_{\vec{q}\lambda}(T)+1-f_{n'\vec{k}-\vec{q}}}{\omega-\epsilon_{n'\vec{k}-\vec{q}}-\omega_{\vec{q}\lambda}-i0^+} + \frac{N_{\vec{q}\lambda}(T)+f_{n'\vec{k}-\vec{q}}}{\omega-\epsilon_{n'\vec{k}-\vec{q}}+\omega_{\vec{q}\lambda}-i0^+}\right].$$

Transfer rates from Marcus theory for hopping transport:

$$k_{et} = \frac{2\pi}{\hbar}|t_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\lambda+\Delta G\ )^2}{4\lambda k_B T}\right)$$

Currents from non equilibrium Keldish formalism

$$I_{r,r'} = \frac{4e}{\hbar}\int \frac{dE}{2\pi} t_{r,r'} Re(G^<(r,r',E)) \quad (5)$$

$$G\hat{}r\ (r, r\hat{}', E) = \sum\_k \text{▒}(\varphi\_k\hat{}\ *\ (r)\varphi\_k\ (r\hat{}'))/(E - E\_k \pm i\delta)$$

Acknowledgements

U.S. DEPARTMENT OF ENERGY

U.S. DEPARTMENT OF ENERGY INCITE LEADERSHIP COMPUTING

Argonne NATIONAL LABORATORY

LDRD support

NERSC

ASCR Leadership Computing Challenge ALCC

MICCoM http://miccom-center.org