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Dielectric Response of Molecular and Condensed Systems From Ab Initio Calculations

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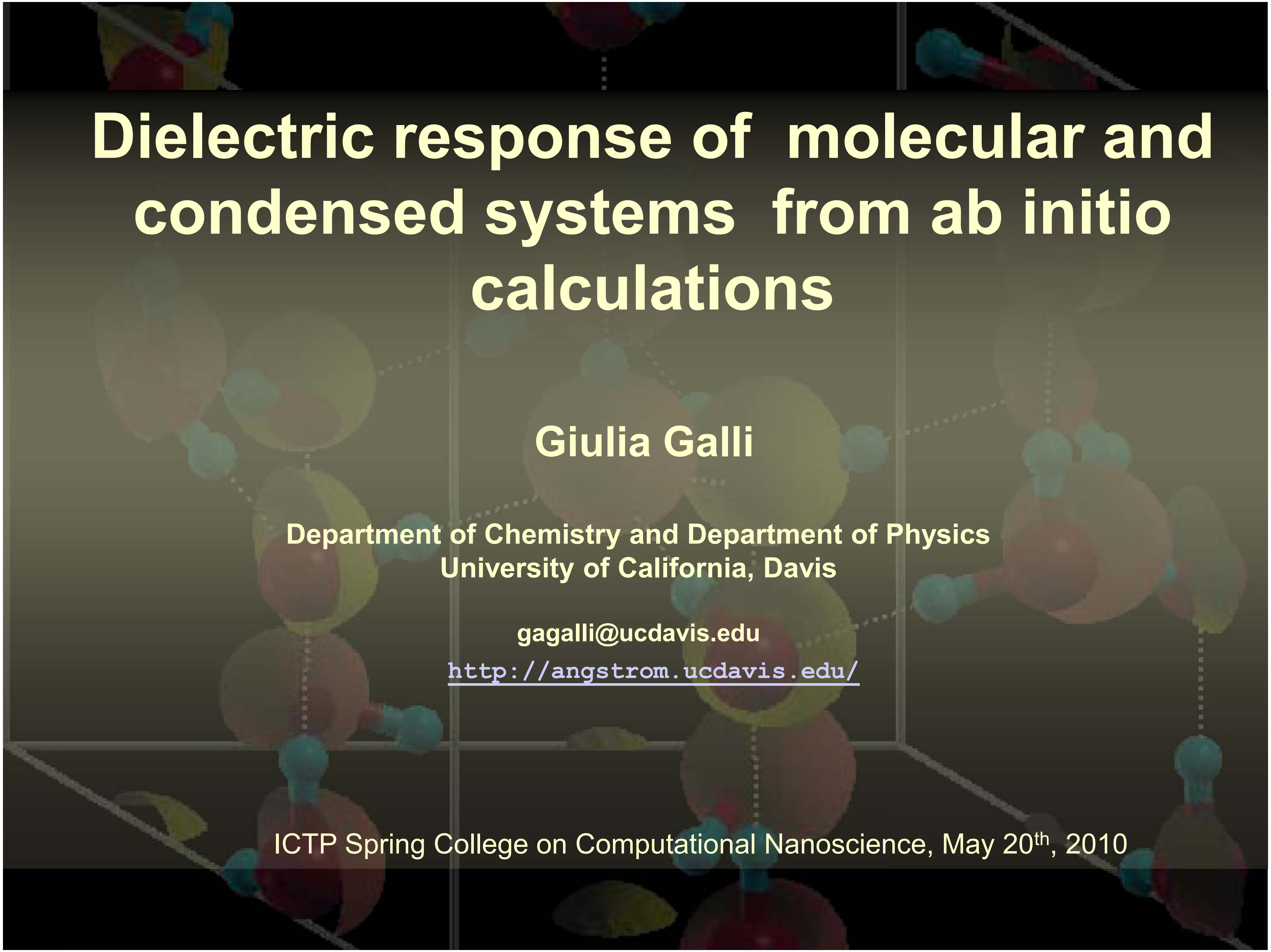

Dielectric response of molecular and condensed systems from ab initio calculations

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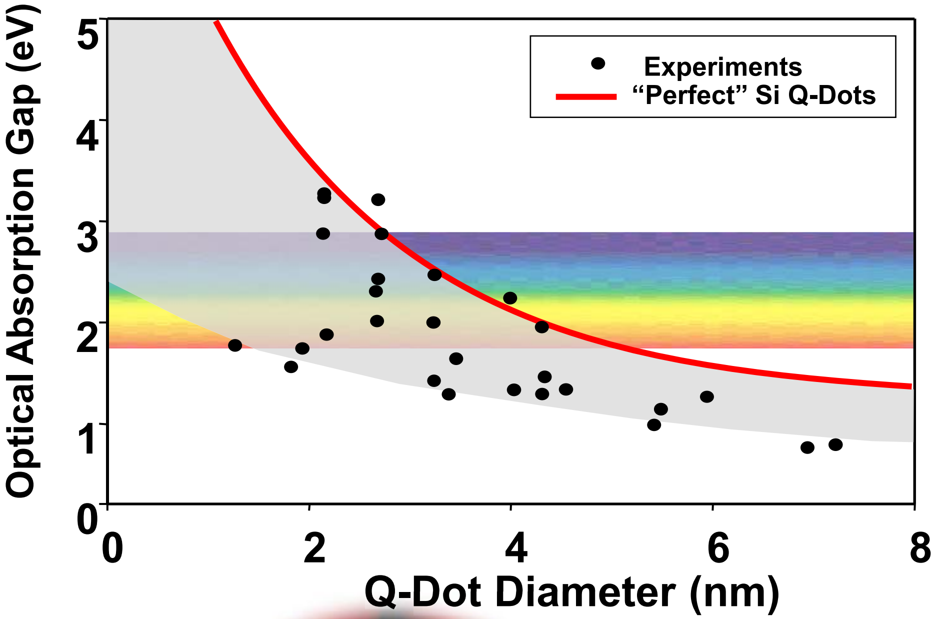
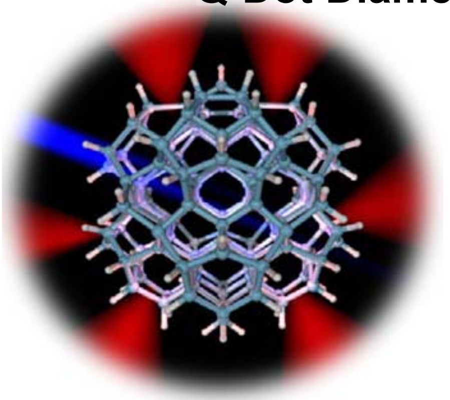
ICTP Spring College on Computational Nanoscience, May 20th, 2010

Optical properties of Si nanocrystals



Key influence of surface structure and passivation on opto-electronic properties

Key role of first principles approach in elucidating interplay between structure and `function`



A.Puzder et al. JACS 2003;A Puzder et al, PRL 2003;E Draeger et al, PRL 2003; F.Reboredo et al., JACS 2003; D.Prendergast et al., JACS 2004; F.Reboredo et al. Nanolett. 2004 and JPC-B 2005; L. Dal Negro et al., APL 2006 and IEEE 2006; S.Hamel et al., APL 2008

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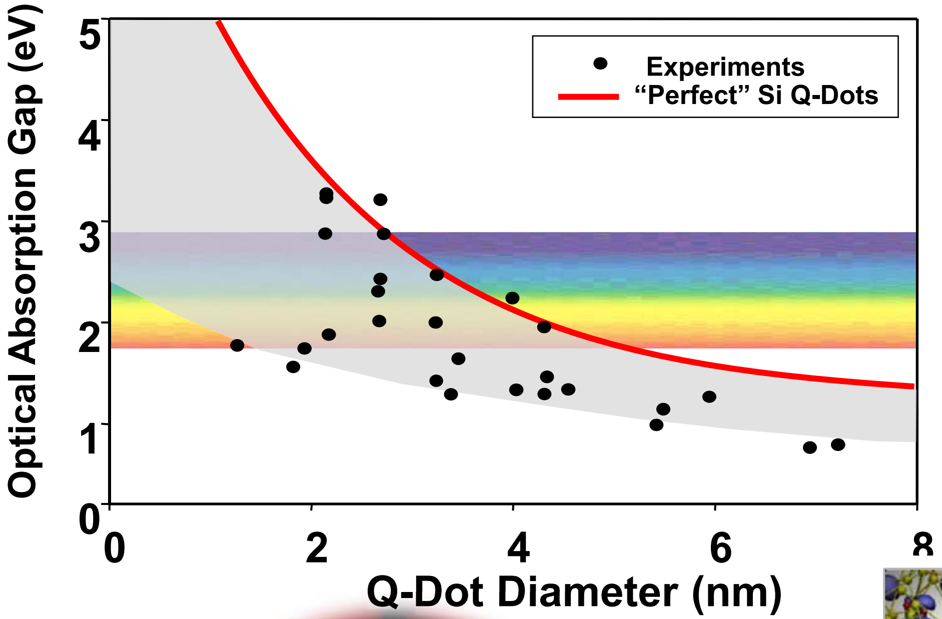

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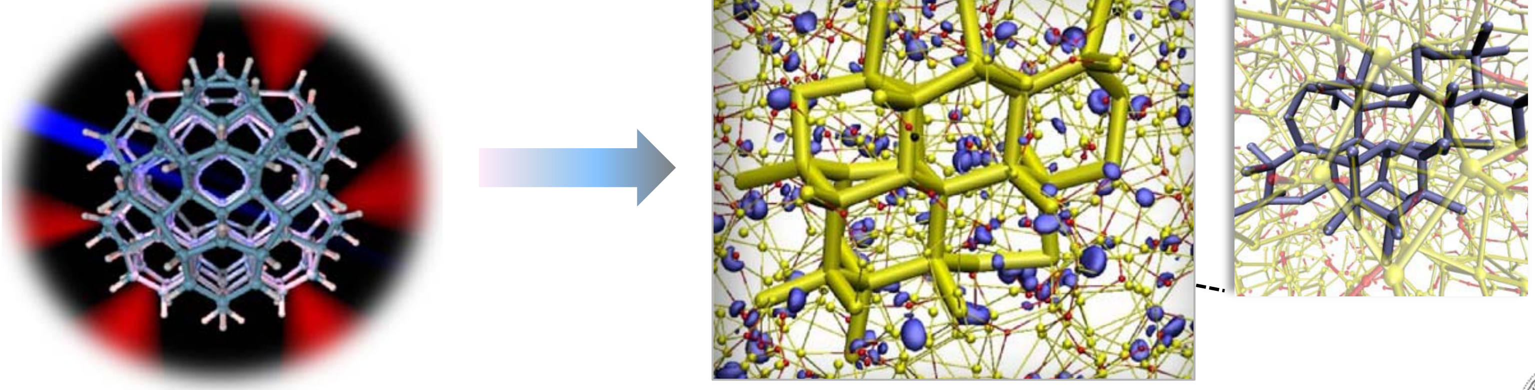

T.Li, D.Donadio, F.Gygi and G.Galli (2010)

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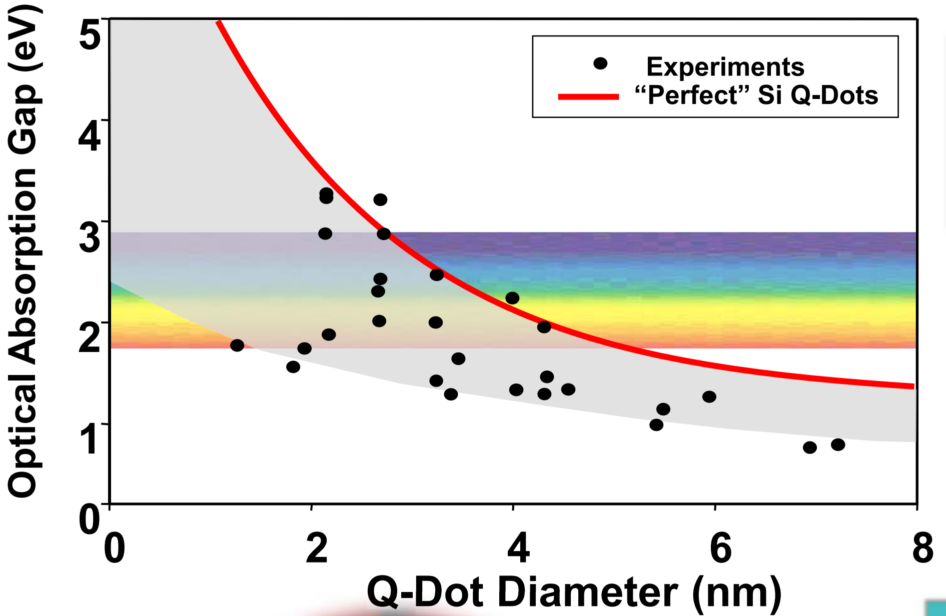

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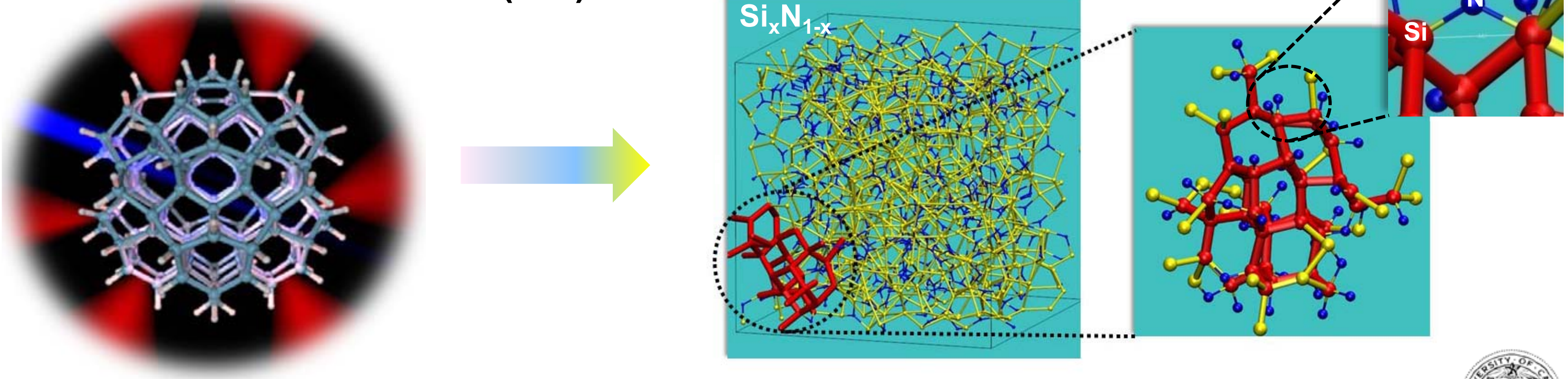

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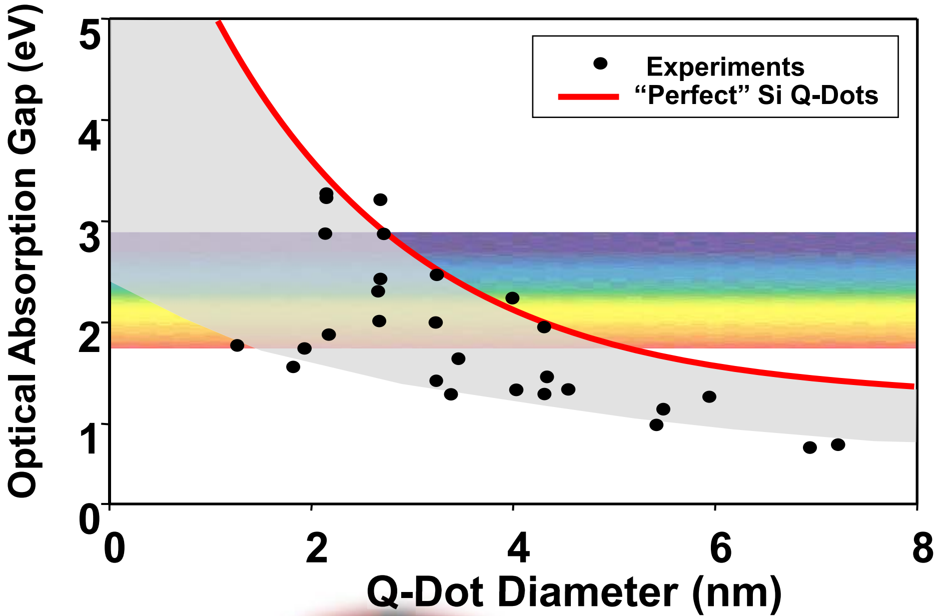

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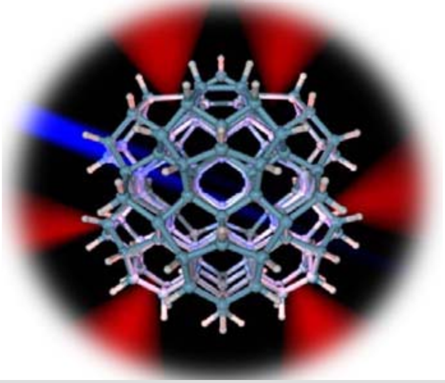
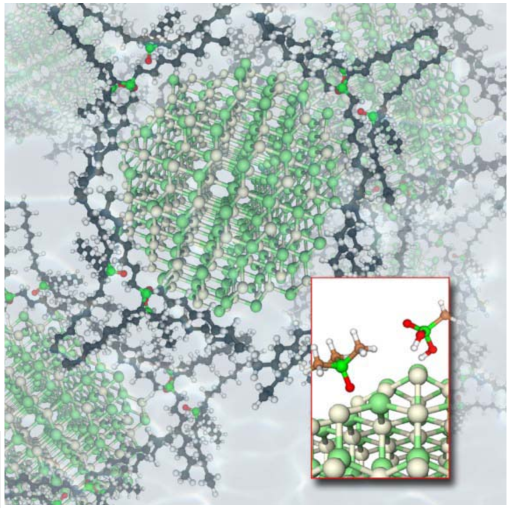


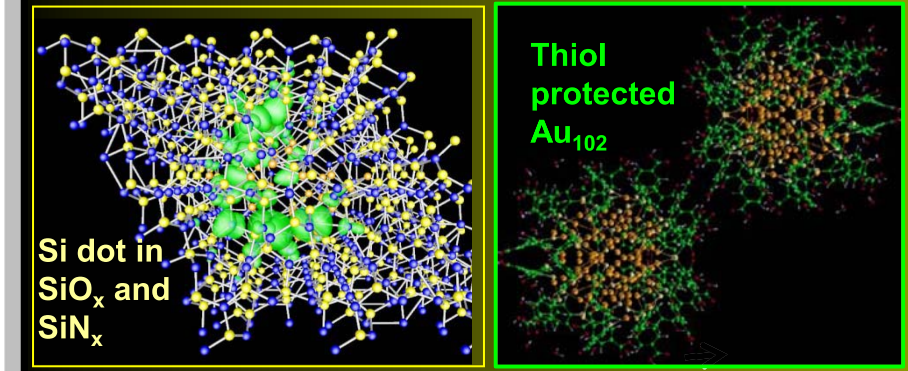


A. Puzder, A. Williamson, F.Gygi G. G. PRL. 04; A. Puzder, A. Williamson, N.Zaitseva, G. G., L.Manna and A.P.Alivisatos, Nanoletters 04

Nanostructures in realistic environments

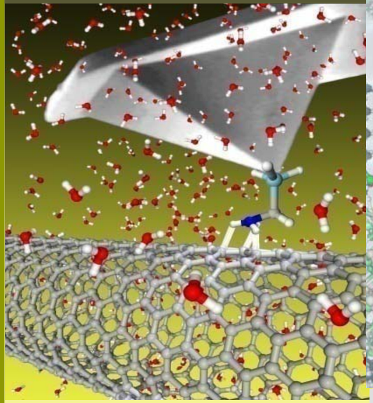
- Nanoparticles embedded in solid matrices
- Nanoparticles in solutions
- Arrays, assemblies of nanostructures

Inorganic and inorganic/organic interfaces



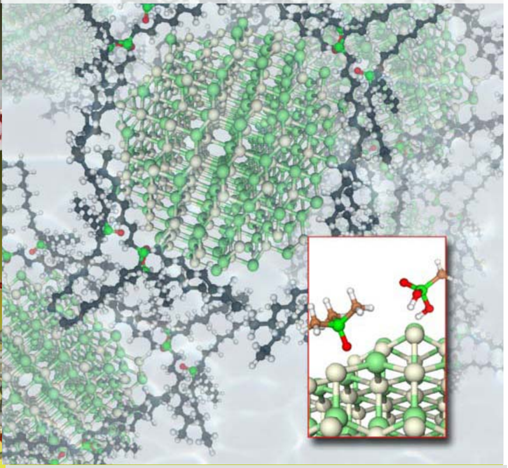
T.Li, D.Donadio, F.Gygi and G.G. (2010); Y.Li, F.Gygi and G.G. ACS Nano 2008

CNT/AFM tip in solvent



LeMieux et al. Nature Nanotech. 2007

CdSe in solution



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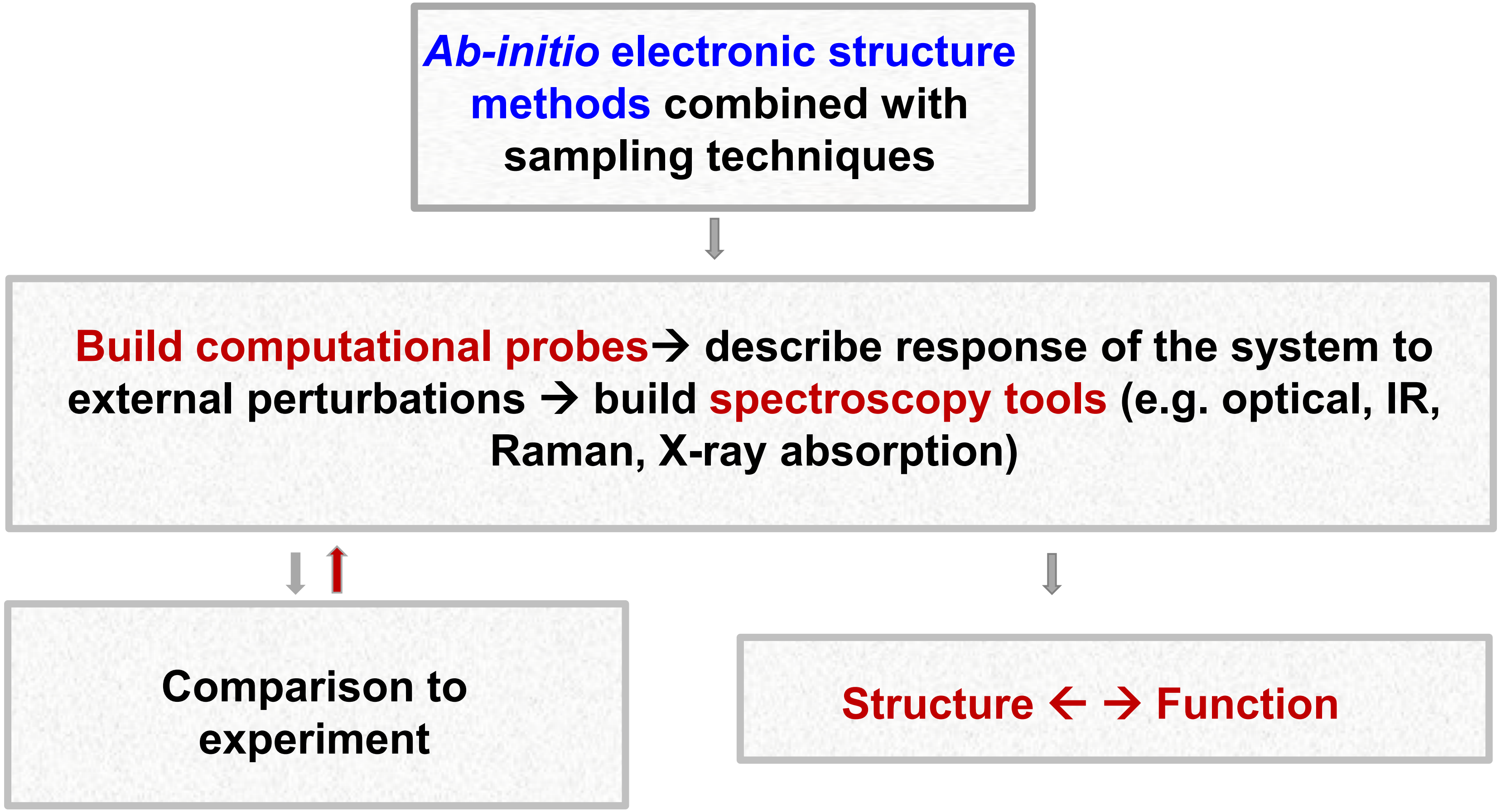
Nanostructured materials:
Complex, large condensed systems

Predictive modeling of multiple properties with controllable accuracy



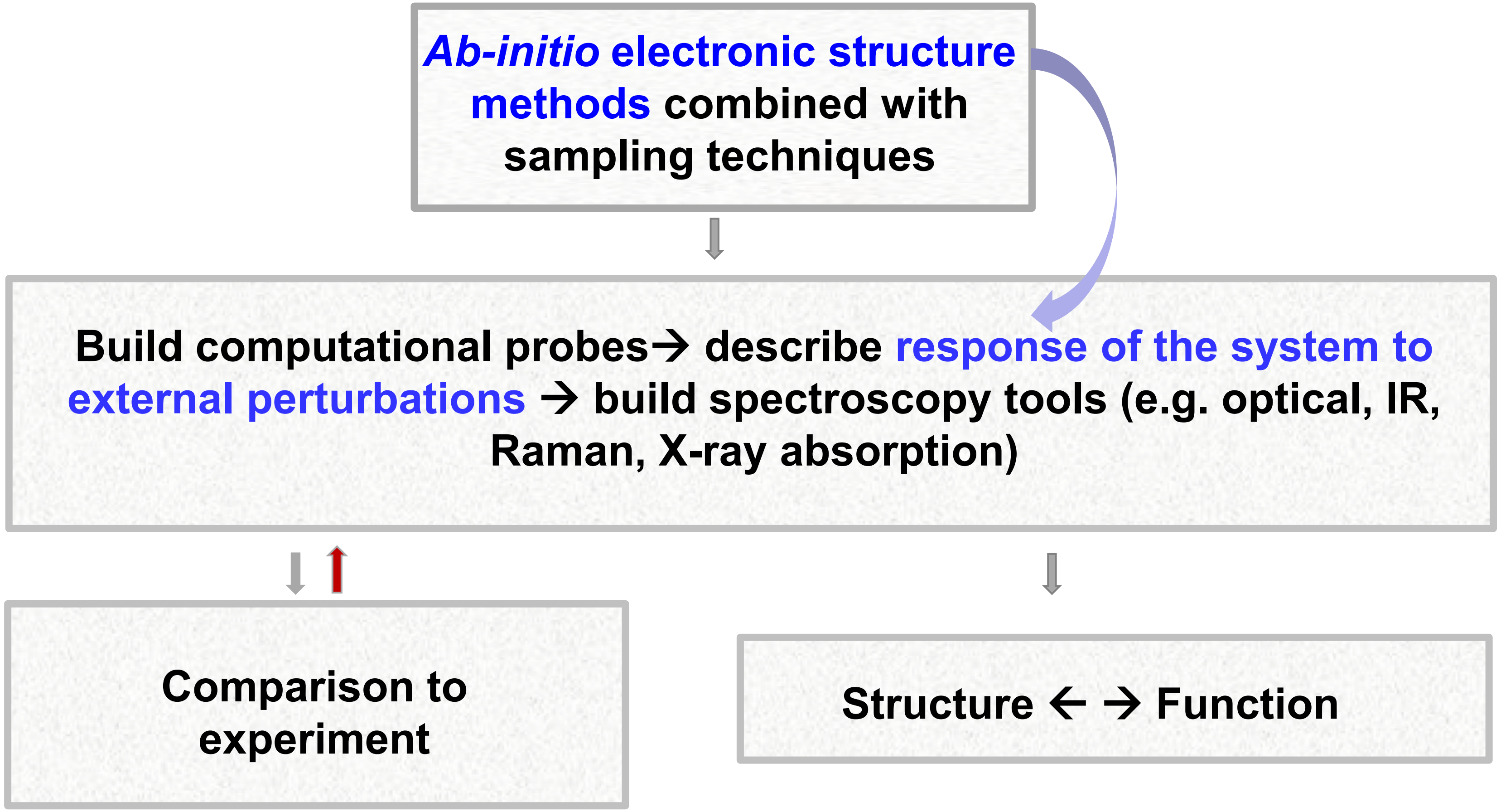
Ab-initio electronic structure methods combined with sampling techniques

Build computational probes → describe response of the system to external perturbations → build **spectroscopy tools** (e.g. optical, IR, Raman, X-ray absorption)

Comparison to experiment

Structure ← → Function

Predictive modeling of multiple properties with controllable accuracy



Ab-initio electronic structure methods combined with sampling techniques

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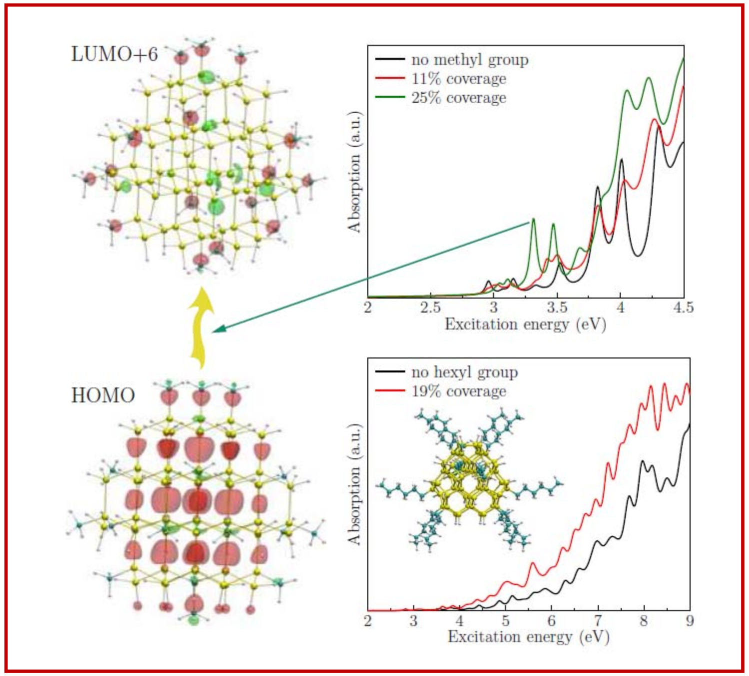
High energy excitations of Si nanoparticles



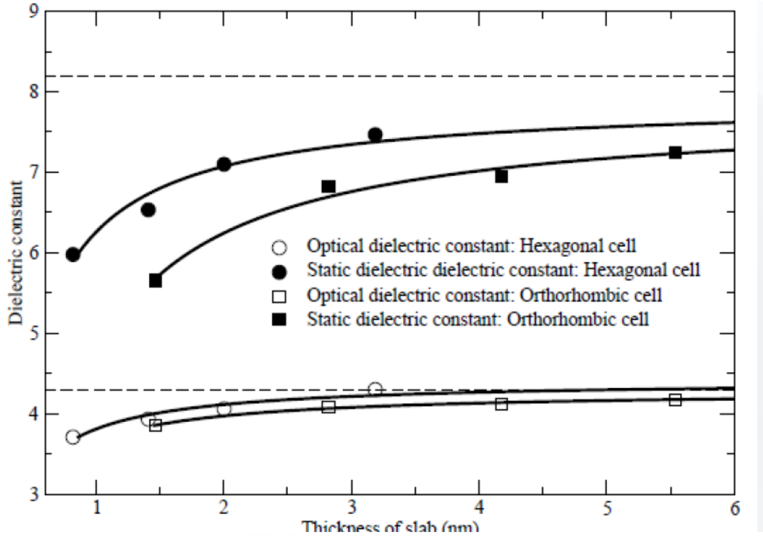
A.Gali, M.Voros, D.Rocca, G.Zimanyi and G.G., Nanolett. 2009, and MRS Bulletin 2010

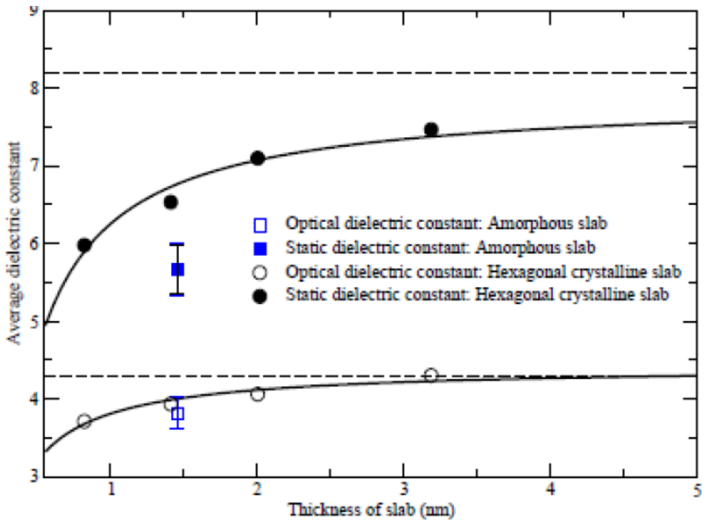
Time-dependent density functional (TDDFT) calculations of excitation spectra:

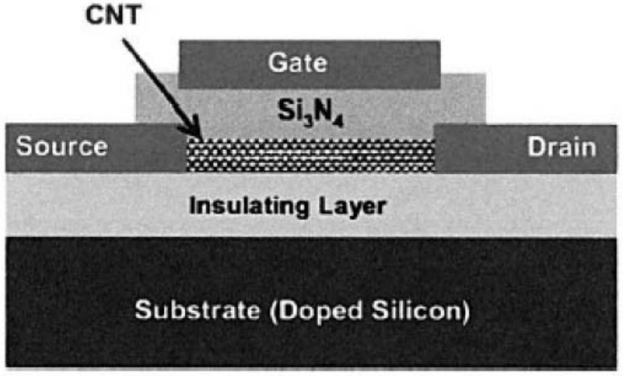
- Surface reconstruction may change excitation spectra both at low and high energies above the gap
- Absorption may be enhanced non-linearly by the presence of alkyl groups, and by the interaction between NPs.
- Insight into interpretation of experiments on Multi-Electron-Generation in colloidal NPs.

Nanoscale interfaces in electric fields: high-κ dielectrics

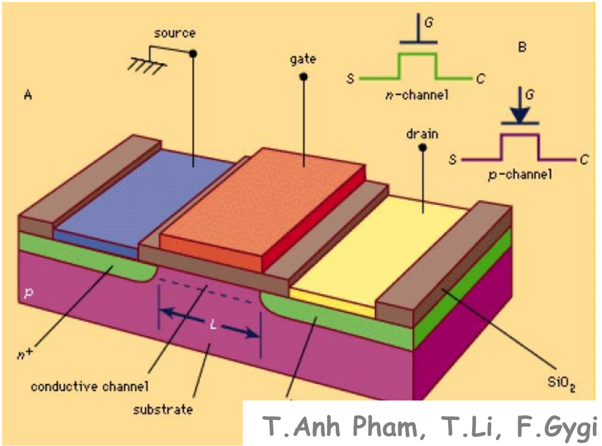
Dielectric properties of ordered and disordered silicon nitride films as a function of thickness





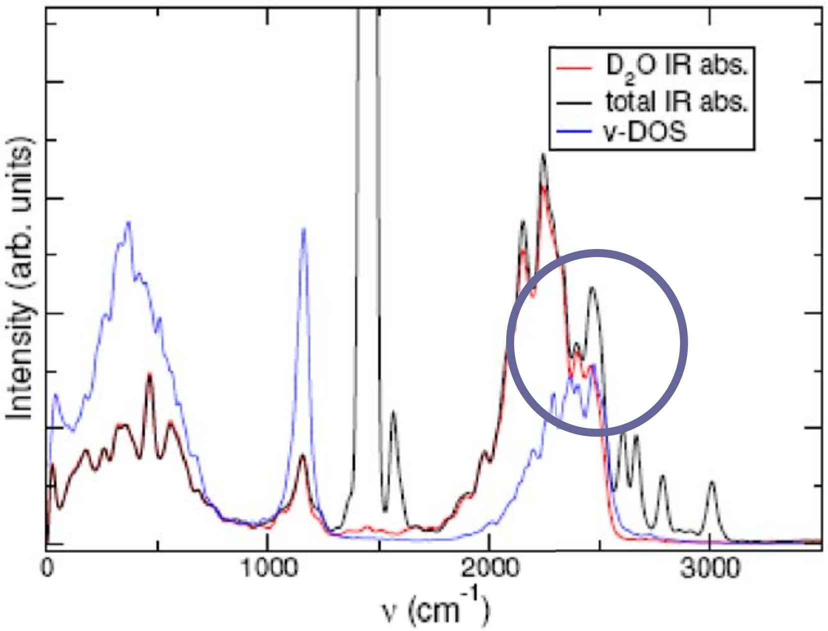


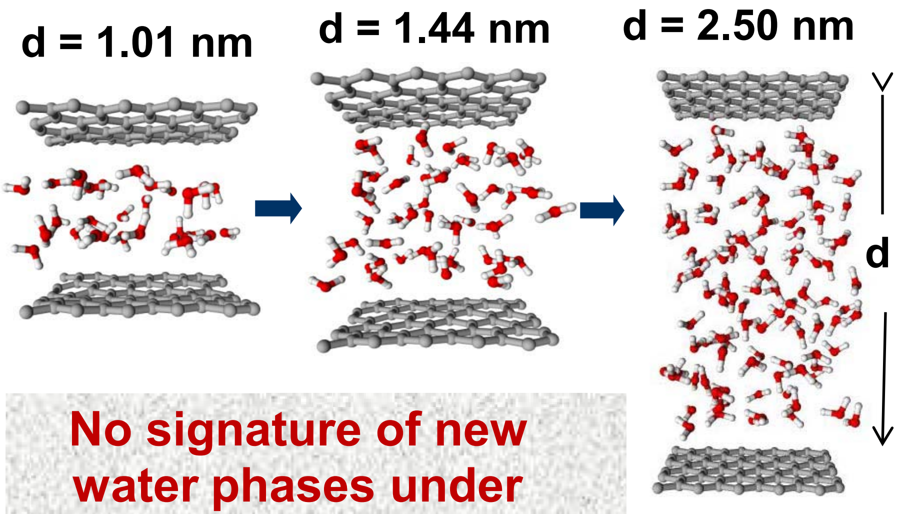
. Schematic cross-section view of top-gate nanotube transistor.



T.Anh Pham, T.Li, F.Gygi and G.G., APL 2010 and in preparation

Water confined at the nanoscale: Infrared spectra





No signature of new water phases under confinement

IR spectra and power spectra show remarkable differences highlighting the importance of electronic effects

Subtle electronic interactions present also in the case of highly hydrophobic substrates

Important implications for the interpretation of "hydrophobic effect(s)"

M.Sharma, D.Donadio, E.Schwegler, G.G., NL 2008; D.Donadio, G.Cicero, E.Schwegler, M.Sharma, G.Galli, JPC-B 2009

Dielectric response of molecules and condensed systems

- In general, *ab-initio* calculations of **excited state properties** of condensed systems and nanostructures involve evaluation of dielectric matrices $\varepsilon^{-1}(r_1,r_2;\omega) \longrightarrow \varepsilon^{-1}_{G,G'}(q,\omega)$

For example to obtain: photoemission spectra ($\Sigma = iGW\,; W = \varepsilon^{-1}v$)

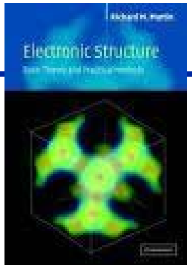
absorption spectra ($\Im$[$1/\varepsilon^{-1}_{0,0}(q=0,\omega)$]); electron energy loss spectra (-$\Im$[$\varepsilon^{-1}_{0,0}(q,\omega)$])…..

- Likewise, calculations of **long range correlation effects** (e.g. RPA correlation energies) involve knowledge of dielectric response functions.

Outline

- Basic Concepts: Response functions

  R.M.Martin: Electronic Structure



- Approximate yet accurate dielectric matrices from eigenvalue decomposition, using Density Functional Perturbation Theory

  Hugh Wilson, Deyu Lu and Francois Gygi

- Interpretation of dielectric eigenmodes: water and ice

  Deyu Lu and Francois Gygi

- RPA correlation energies: binding of organic crystals (benzene, methane) and SAM on surfaces

  Yan Li , Deyu Lu, Viet Nguyen and Dario Rocca

- Solution of Bethe-Salpeter Equations (BSE): Si clusters and charge transfer excitations

  Dario Rocca and Deyu Lu

Maxwell equations in terms of total field E

- 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:
  - $n = n_{int} + n_{ext}$; $\mathbf{j} = \mathbf{j}_{int} + \mathbf{j}_{ext}$

- **Polarization** : defined to *within an additive constant* (one computes *polarization differences*)

$$\mathbf{P}(\mathbf{r}, t) = \int^{t} \mathrm{d}t' \, \mathbf{j}_{\rm int}(\mathbf{r}, t'),$$

$$\nabla \cdot \mathbf{P}(\mathbf{r}, t) = -Q n_{\rm int}(\mathbf{r}, t).$$

Maxwell equations in terms of external field D

- **D = E +** 4π **P** **D = external field**, independent of the material

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

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

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

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

$$\mathbf{D}(\mathbf{r},\omega) = \int d\mathbf{r}'\,\epsilon(\mathbf{r},\mathbf{r}',\omega)\cdot\mathbf{E}(\mathbf{r}',\omega) \quad \text{or} \quad \mathbf{E}(\mathbf{r},\omega) = \int d\mathbf{r}'\,\epsilon^{-1}(\mathbf{r},\mathbf{r}',\omega)\mathbf{D}(\mathbf{r}',\omega).$$

- **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 (V_{xc} excluded)

- **How do we use electronic structure, theory and calculations to obtain 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=r'**

$$\chi_n^0(\mathbf{r},\mathbf{r}') = \underbrace{\frac{\delta n(\mathbf{r})}{\delta V_{\mathrm{eff}}(\mathbf{r}')}}_{\text{Definition}} = \underbrace{2\sum_{i=1}^{\mathrm{occ}}\sum_{j}^{\mathrm{empty}} \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j}}_{\text{Perturbation theory}}$$

$$\Downarrow$$

$$\chi_n^0(\mathbf{r},\mathbf{r}') = \sum_{i=1}^{\mathrm{occ}} \psi_i^*(\mathbf{r})\underbrace{G_0^i(\mathbf{r},\mathbf{r}')}_{\text{Independent particle Green function}}\psi_i(\mathbf{r}'), \qquad G_0^i(\mathbf{r},\mathbf{r}') = \sum_{j\neq i}^{\infty} \frac{\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')}{\varepsilon_i - \varepsilon_j}$$

Density response function in Fourier space

- Response to **specific Fourier components:**

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

$$\Downarrow$$

$$\chi_n^0(\mathbf{q},\mathbf{q}') = \frac{\delta n(\mathbf{q}')}{\delta V_{\mathrm{eff}}(\mathbf{q})} = 2\sum_{i=1}^{\mathrm{occ}}\sum_{j}^{\mathrm{empty}} \frac{M_{ij}^*(\mathbf{q})\boxed{M_{ij}(\mathbf{q}')}}{\varepsilon_i - \varepsilon_j}, \longleftarrow \langle\psi_i|e^{i\mathbf{q}\cdot\mathbf{r}}|\psi_j\rangle$$

- **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 function within Kohn-Sham theory

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

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

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

- Response to the external field:

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

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

$$\chi = \chi^0[1-\chi^0 K]^{-1} \quad \text{or} \quad \chi^{-1} = [\chi^0]^{-1} - K$$

$$\downarrow$$

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

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

Dynamical response

- **Time dependence of Kernel:**

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

$$\Big\downarrow \ \textbf{FT}$$

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

- **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:** ⟶

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

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

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**)

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

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

External potential

Coulomb potential (V_{xc} excluded)

- **How do we use electronic structure, theory and calculations to obtain 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**

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

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

Dielectric matrices, dielectric function, dielectric tensors

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

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

$$\downarrow$$

Matrices

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

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

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

- **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)

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

Similarity transformation to an 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

Iterative calculations of dielectric matrices

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

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i \lambda_i \tilde{\mathbf{v}}_i^H = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i (\lambda_i - 1) \tilde{\mathbf{v}}_i^H + I$$

- **Compute eigenvalues and eigenvectors using Density Functional Perturbation Theory**[*] **(DFPT) →** avoid costly calculation of empty single particle states
  - Compute **charge density variation** from solution of Sternheimer equation (1st order perturbation theory)

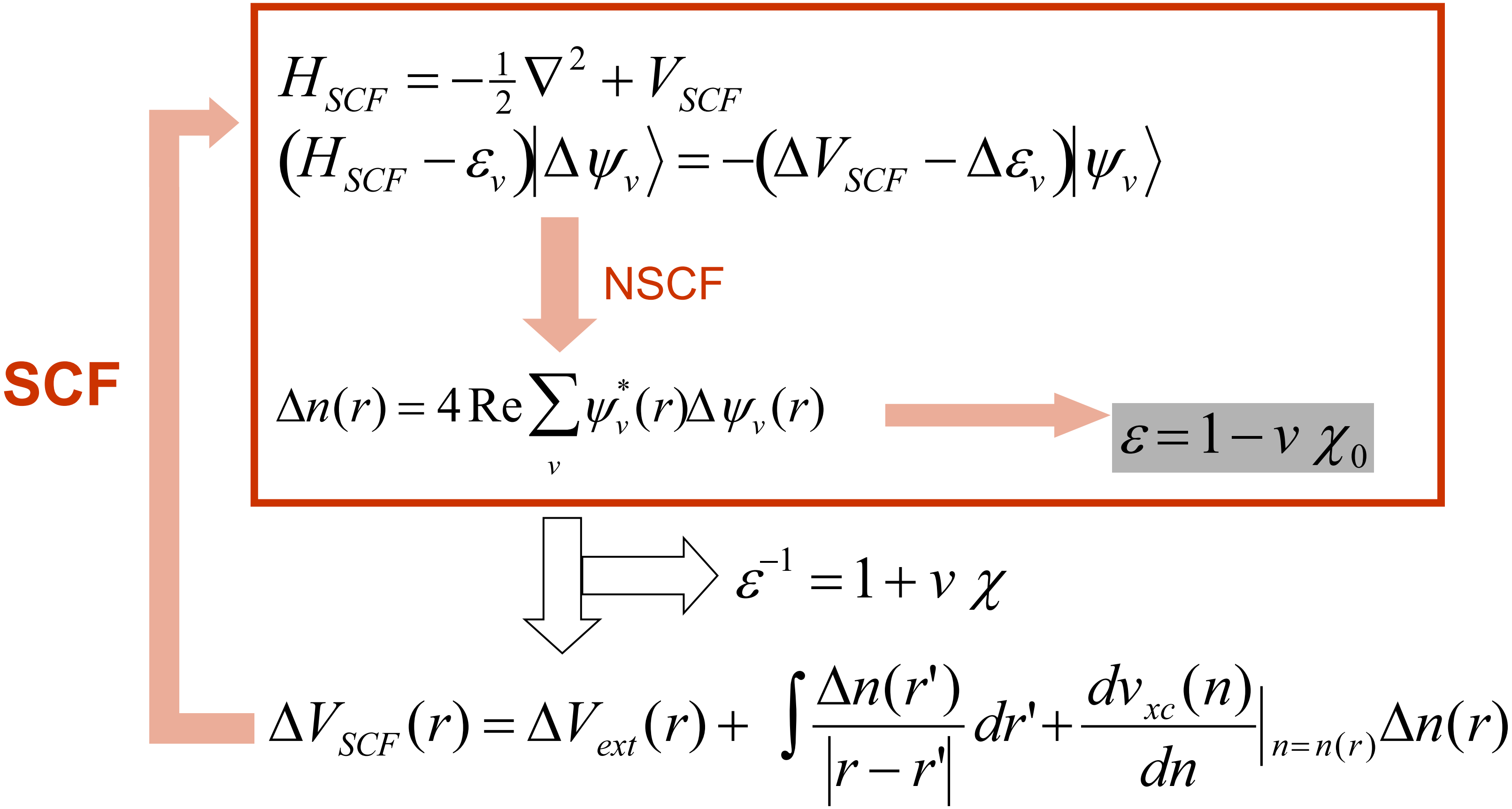
$$\Delta n(\mathbf{r}) = 4\,\mathrm{Re} \sum_{v} \psi_v^*(\mathbf{r}) \Delta \psi_v(\mathbf{r}).$$

  - The action of (ε-I) on any trail potential is then obtained from:

$$(\epsilon - I)\Delta V_{\mathrm{SCF}} = -v_c \chi_0 \Delta V_{\mathrm{SCF}} = -v_c \Delta n.$$

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

DFPT and Sternheimer equation



$$H_{SCF} = -\tfrac{1}{2}\nabla^2 + V_{SCF}$$

$$\left(H_{SCF} - \varepsilon_v\right)\left|\Delta\psi_v\right\rangle = -\left(\Delta V_{SCF} - \Delta\varepsilon_v\right)\left|\psi_v\right\rangle$$

NSCF

$$\Delta n(r) = 4\,\mathrm{Re}\sum_v \psi_v^*(r)\Delta\psi_v(r)$$

$$\varepsilon = 1 - v\,\chi_0$$

SCF

$$\varepsilon^{-1} = 1 + v\,\chi$$

$$\Delta V_{SCF}(r) = \Delta V_{ext}(r) + \int \frac{\Delta n(r')}{|r - r'|} dr' + \frac{dv_{xc}(n)}{dn}\bigg|_{n=n(r)} \Delta n(r)$$

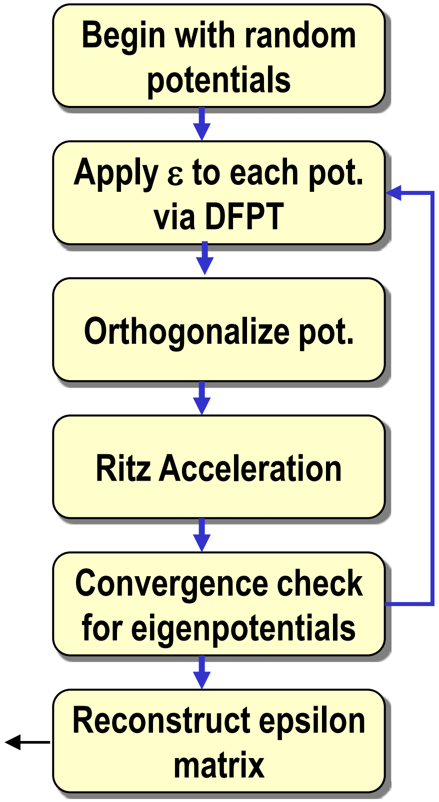
The Sternheimer equation is solved non-self-consistently.

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

Iterative procedure based on Density Functional Perturbation Theory

$$\tilde{\epsilon} = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i \lambda_i \tilde{\mathbf{v}}_i^H = \sum_{i=1}^{N} \tilde{\mathbf{v}}_i (\lambda_i - 1) \tilde{\mathbf{v}}_i^H + I$$

- 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 (eventually) at different MD steps is possible
- Incorporation of XC kernel is straightforward


Begin with random potentials

Apply ε to each pot. via DFPT

Orthogonalize pot.

Ritz Acceleration

Convergence check for eigenpotentials

Reconstruct epsilon matrix

$$\tilde{\varepsilon} = I + \sum_i \tilde{\mathbf{v}}_i^* (\lambda_i - 1) \tilde{\mathbf{v}}_i$$

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.

Power method

$A \in R^{nxn}$ symmetric

$X=[x_1, \ldots, x_n] \in R^{nxn}$ eigenvectors of A

$A\, x_i = \lambda\, x_i$

assume $|\lambda_1|<|\lambda_2|<\cdots<|\lambda_n|$

start from a normalized random vector $q^{(0)}$

1) $z^{(k)} = Aq^{(k-1)}$

2) $q^{(k)} = \dfrac{z^{(k)}}{\left\| z^{(k)} \right\|}$

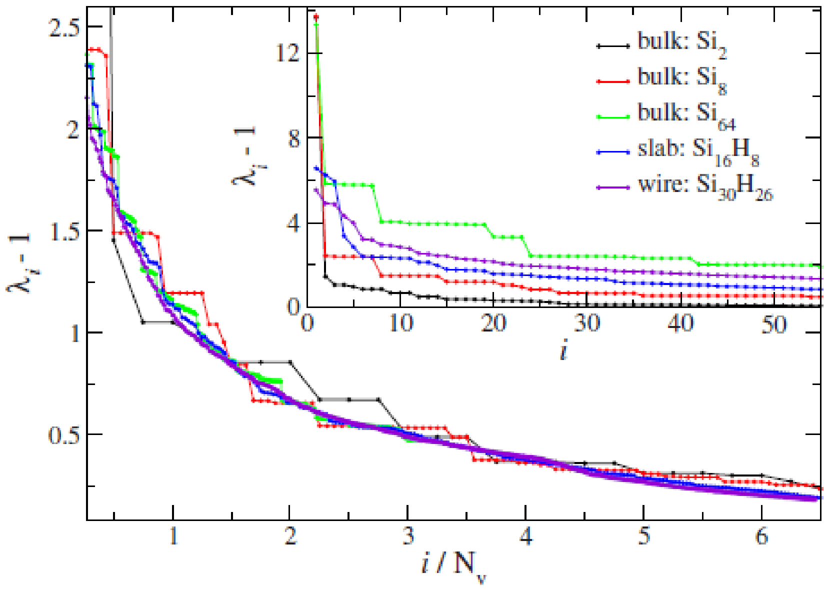
3) $\lambda^{(k)} = \left(q^{(k)}\right)^T Aq^{(k)}$

repeat 1), 2), 3), until converged

- The sequence $q^{(k)}$ converges to the eigenvector x_n
- The sequence $\lambda^{(k)}$ converges to λ_n
- The power method finds the largest eigenvalue of a matrix and its associated eigenvector, if λ_n is a dominant eigenvalue

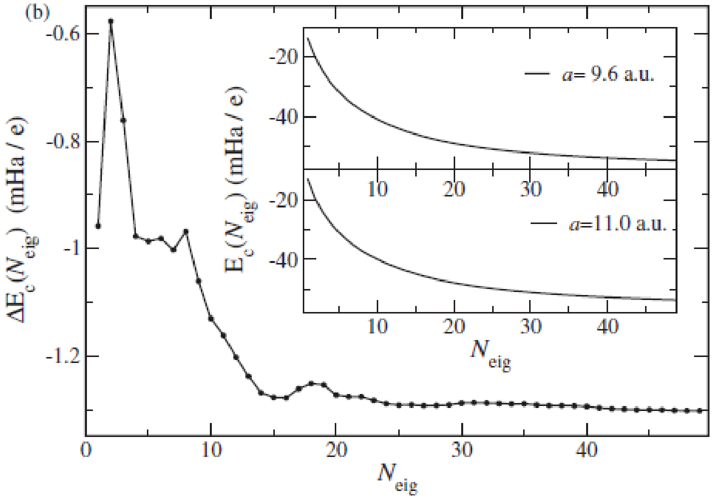
Well behaved decay of dielectric matrix eigenvalues for a broad class of systems

$$\tilde{\varepsilon} = I + \sum_i \tilde{\mathbf{v}}_i^{*} (\lambda_i - 1)\tilde{\mathbf{v}}_i$$

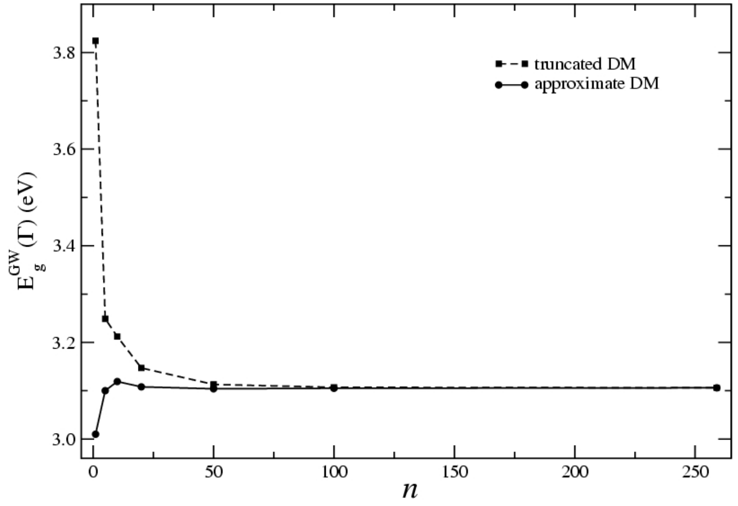


H. Wilson, D.Lu, F. Gygi, and G. G., Phys.Rev.B 2009

Bulk Si RPA Correlation energy

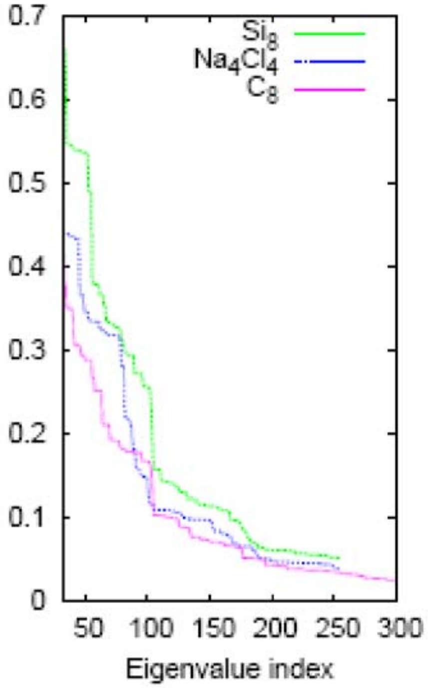


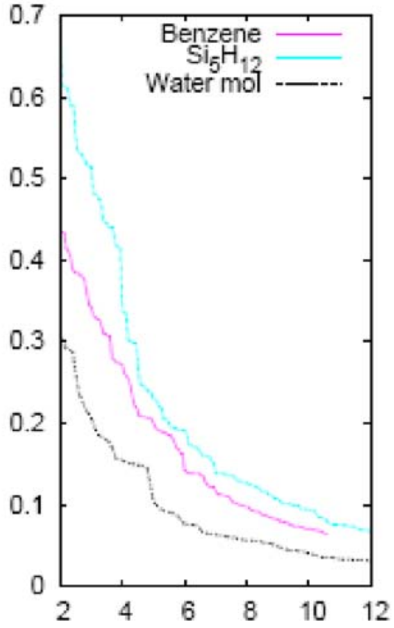
Bulk Si GW gap at Γ

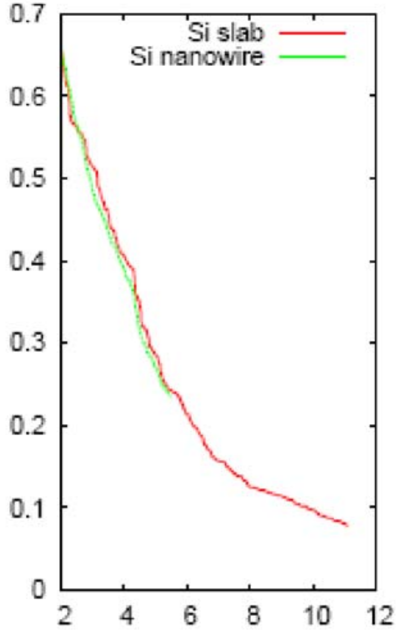


Well behaved decay of dielectric matrix eigenvalues for a broad class of systems

$$\tilde{\varepsilon} = I + \sum_i \tilde{\mathbf{v}}_i^{*}(\lambda_i - 1)\tilde{\mathbf{v}}_i$$



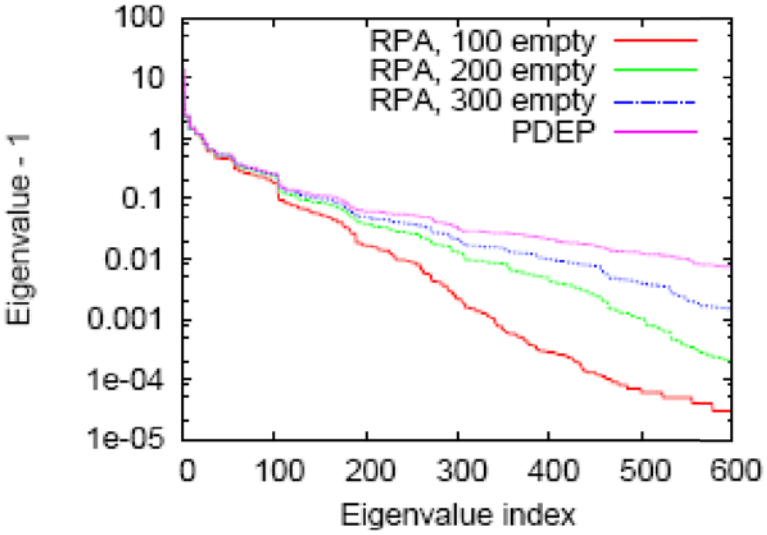


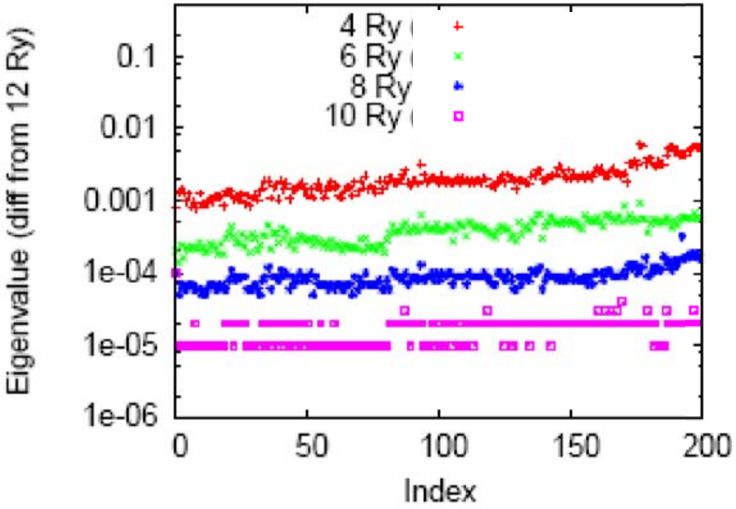


H. Wilson, D.Lu, F. Gygi, and G. Galli Phys. Rev.B 2009

Sensitivity of dielectric matrix calculations to number of empty states and energy cutoff

$$\tilde{\varepsilon} = I + \sum_i \tilde{\mathbf{v}}_i^{*} (\lambda_i - 1) \tilde{\mathbf{v}}_i$$



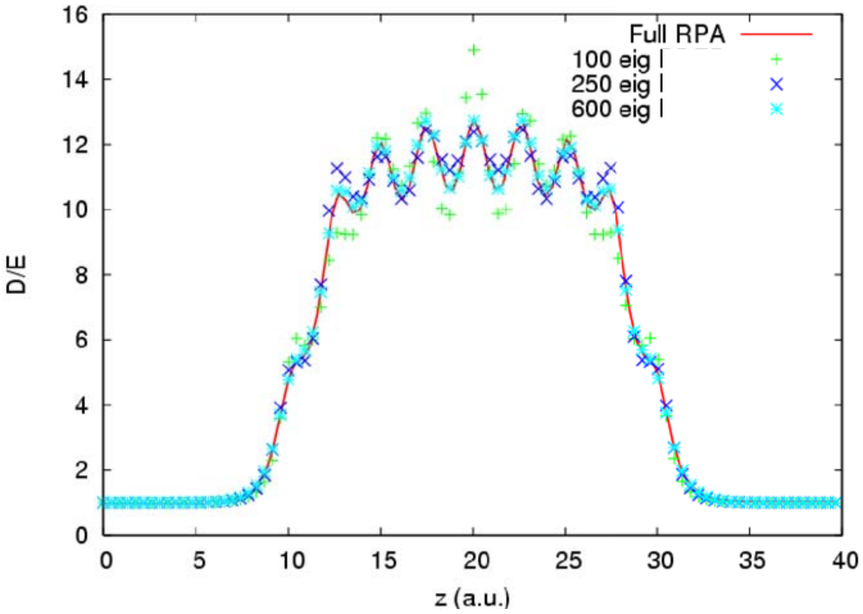


H. Wilson, D.Lu, F. Gygi, and G. Galli, PRB 2009

Well behaved decay of dielectric matrix eigenvalues for a broad class of systems

$$\tilde{\varepsilon} = I + \sum_i \tilde{\mathbf{v}}_i^{\,*} (\lambda_i - 1)\tilde{\mathbf{v}}_i$$

Average electric field inside a hydrogenated Si slab

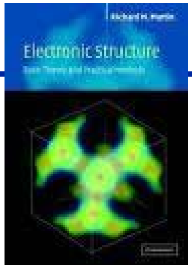


H. Wilson, D.Lu, F. Gygi, and G. G., Phys.Rev.B 2009; S.Hamel, A.Williamson, F.Gygi, GG, Appl.Phys.Lett. 2008

Outline

- Basic Concepts: Response functions

  R.M.Martin: Electronic Structure



- Approximate yet accurate dielectric matrices from eigenvalue decomposition, using Density Functional Perturbation Theory

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- Interpretation of dielectric eigenmodes: water and ice

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- RPA correlation energies: binding of organic crystals (benzene, methane) and SAM on surfaces

  Yan Li , Deyu Lu, Viet Nguyen and Dario Rocca

- Solution of Bethe-Salpeter Equations (BSE): Si clusters and charge transfer excitations

  Dario Rocca and Deyu Lu

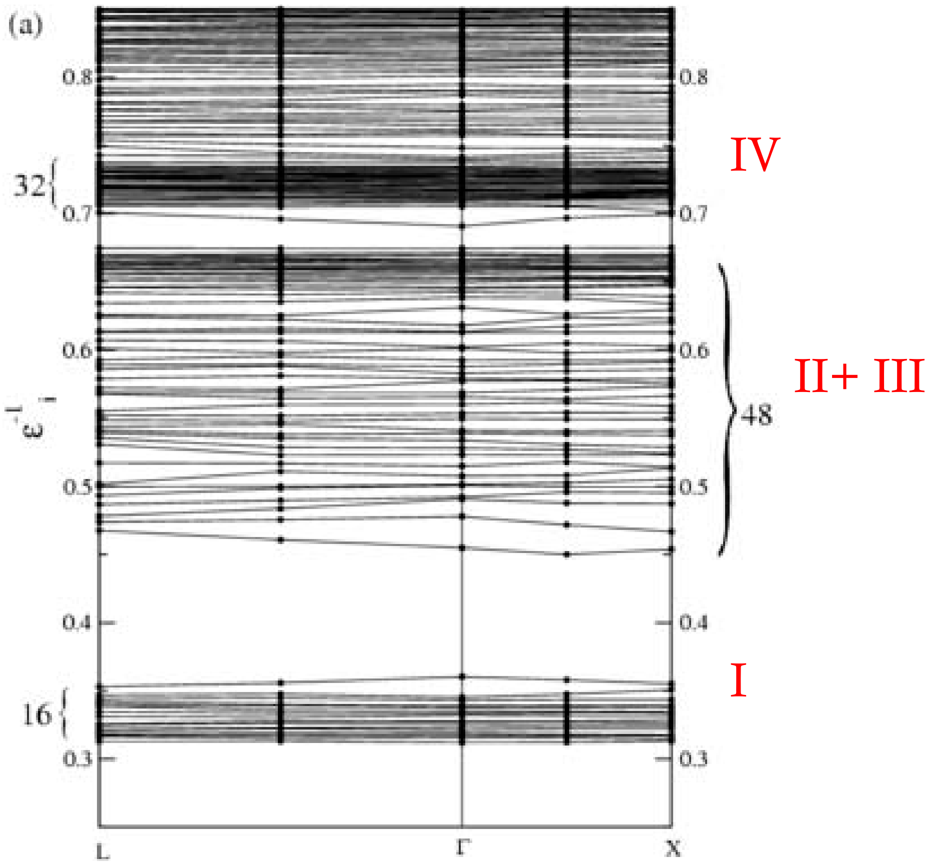
Water: Dielectric band structure

liquid water: 16 molecules

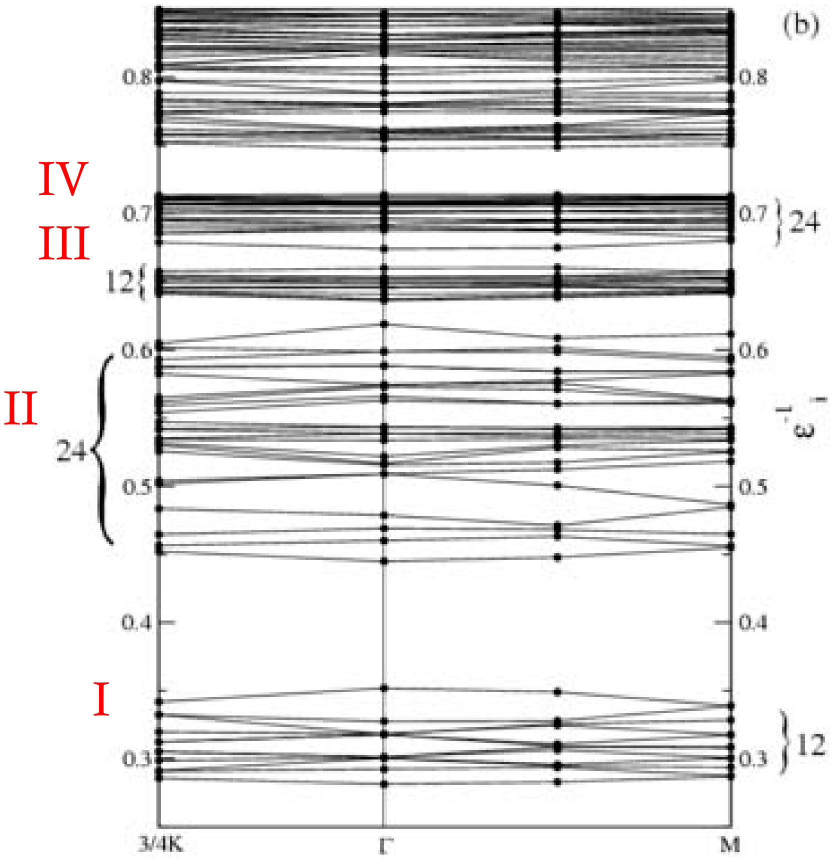
$\varepsilon_M=1.72$ (this work); $\varepsilon_M\approx1.8$ (exp)*

ice Ih: 12 molecules

$\varepsilon_M=1.78$ (this work); $\varepsilon_M\approx1.7$ (exp)*



* Chem. Rev., 105:3197, 2005



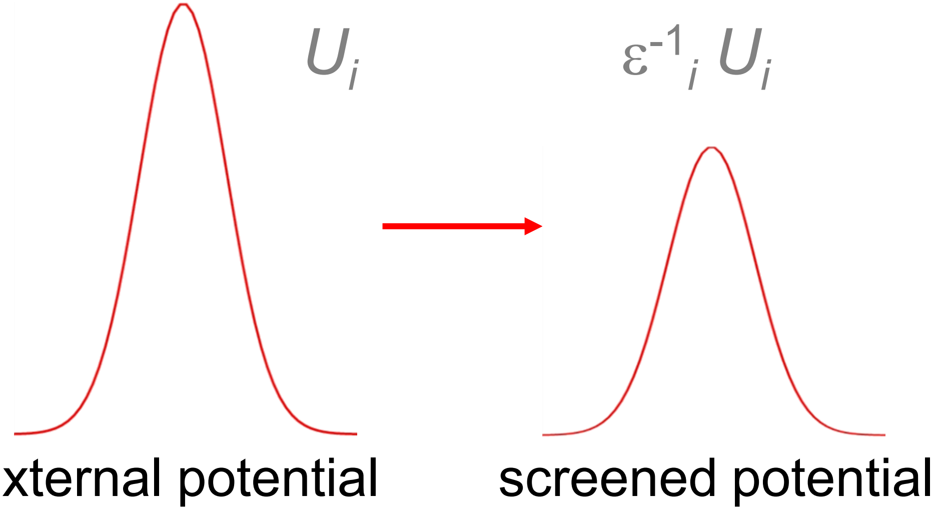
* Proc. R. Soc. Lond. A, 349:467, 1976

Localized screening modes

Eigenmode decomposition:

$$\tilde{\varepsilon}^{-1}(q)\left|U_i(q)\right\rangle = \varepsilon_i^{-1}\left|U_i(q)\right\rangle$$

$$\tilde{\varepsilon}^{-1}(q) = \sum_i \left|U_i(q)\right\rangle \varepsilon_i^{-1}\left\langle U_i(q)\right|$$

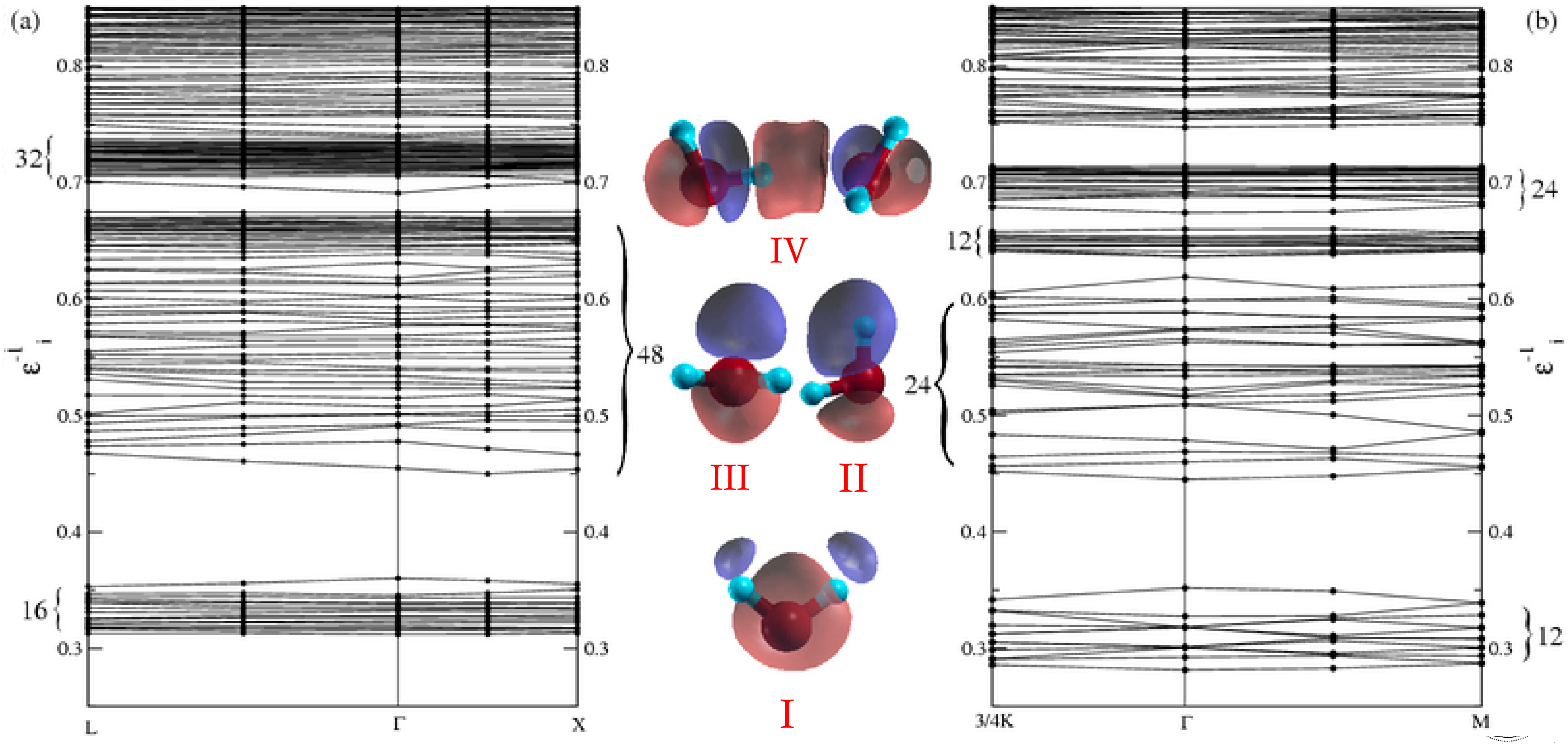


Localization:

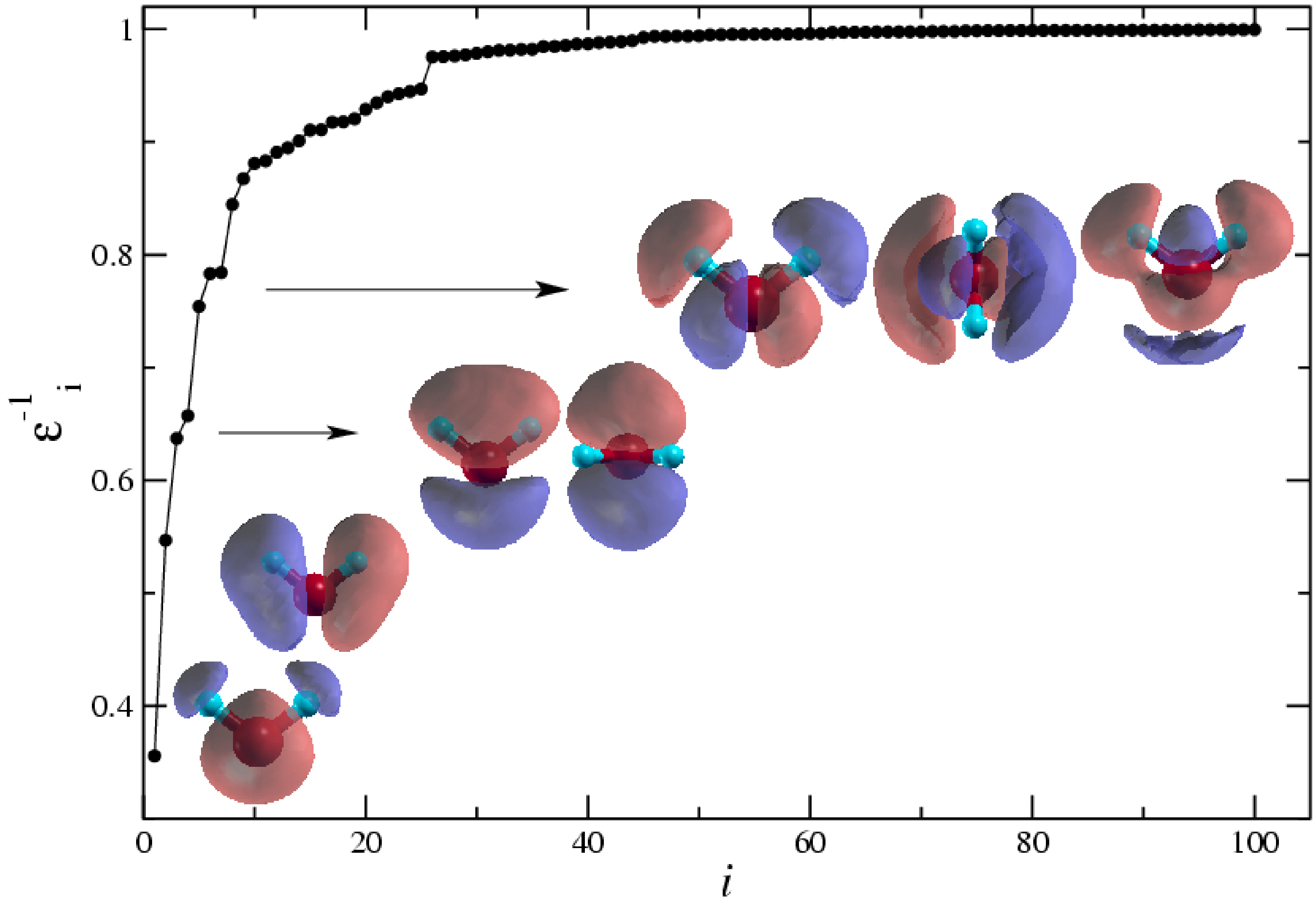
From eigenstates extended in the periodic cell to **maximally localized screening modes**

Dielectric band structure and localized screening modes

Are the lowest Maximally Localized Dielectric Modes (MLDM) related to the Dielectric Eigenmodes of (DEM) of the gas phase molecule?

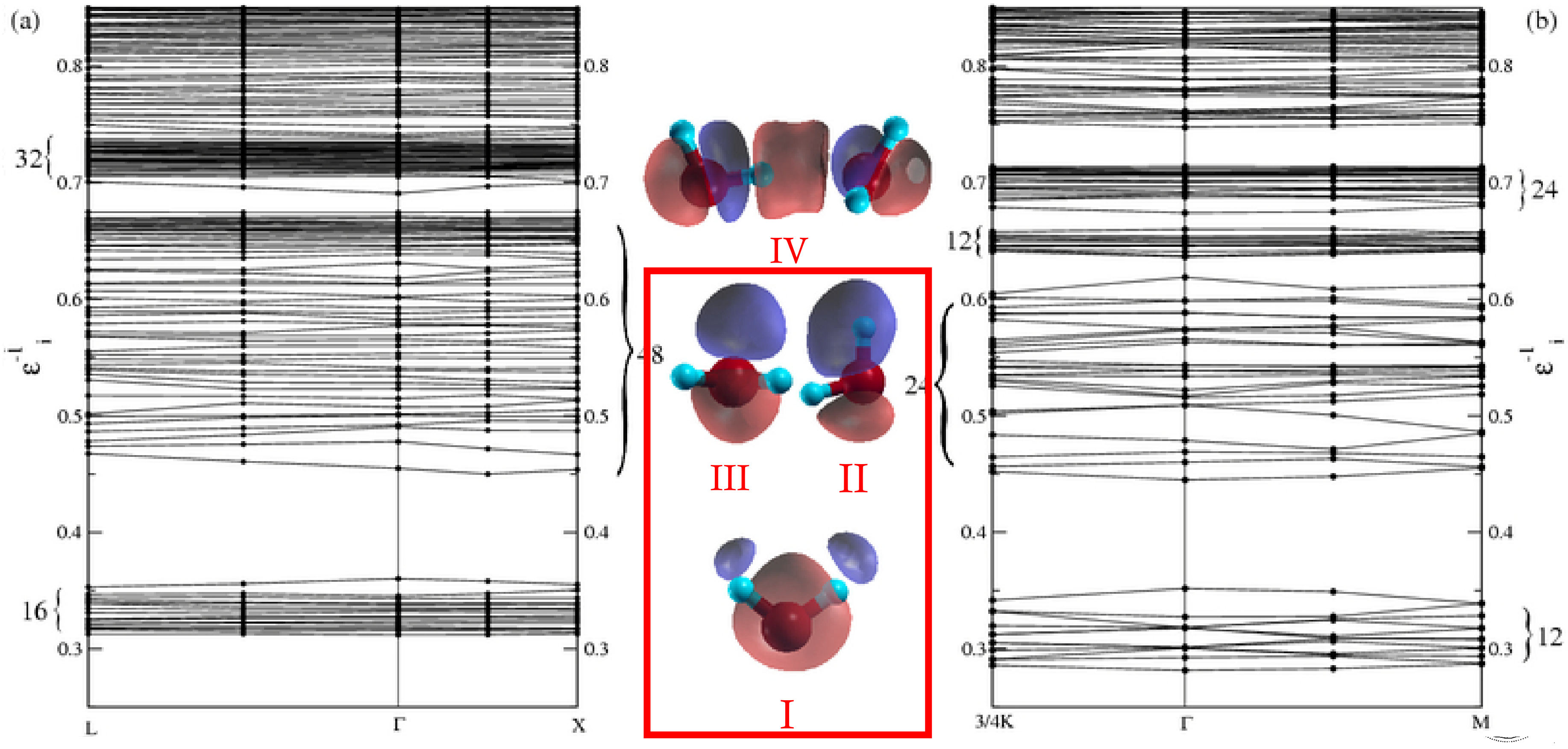


The dielectric eigenmodes of the water molecule



Dielectric band structures and localized screening modes

The lowest Maximally Localized Dielectric Modes (MLDM) are related to the Dielectric Eigenmodes of (DEM) of the **monomer** and **dimer**



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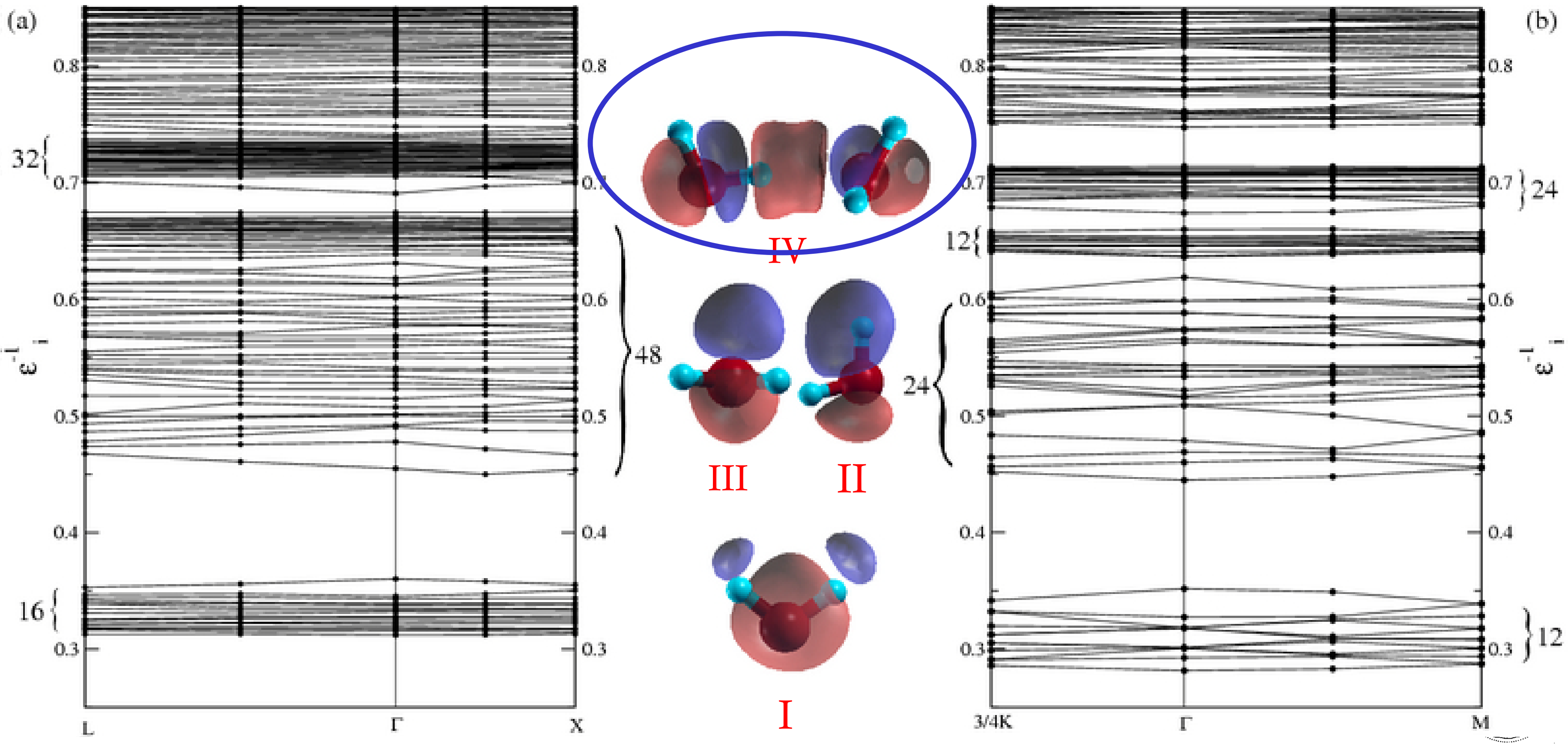
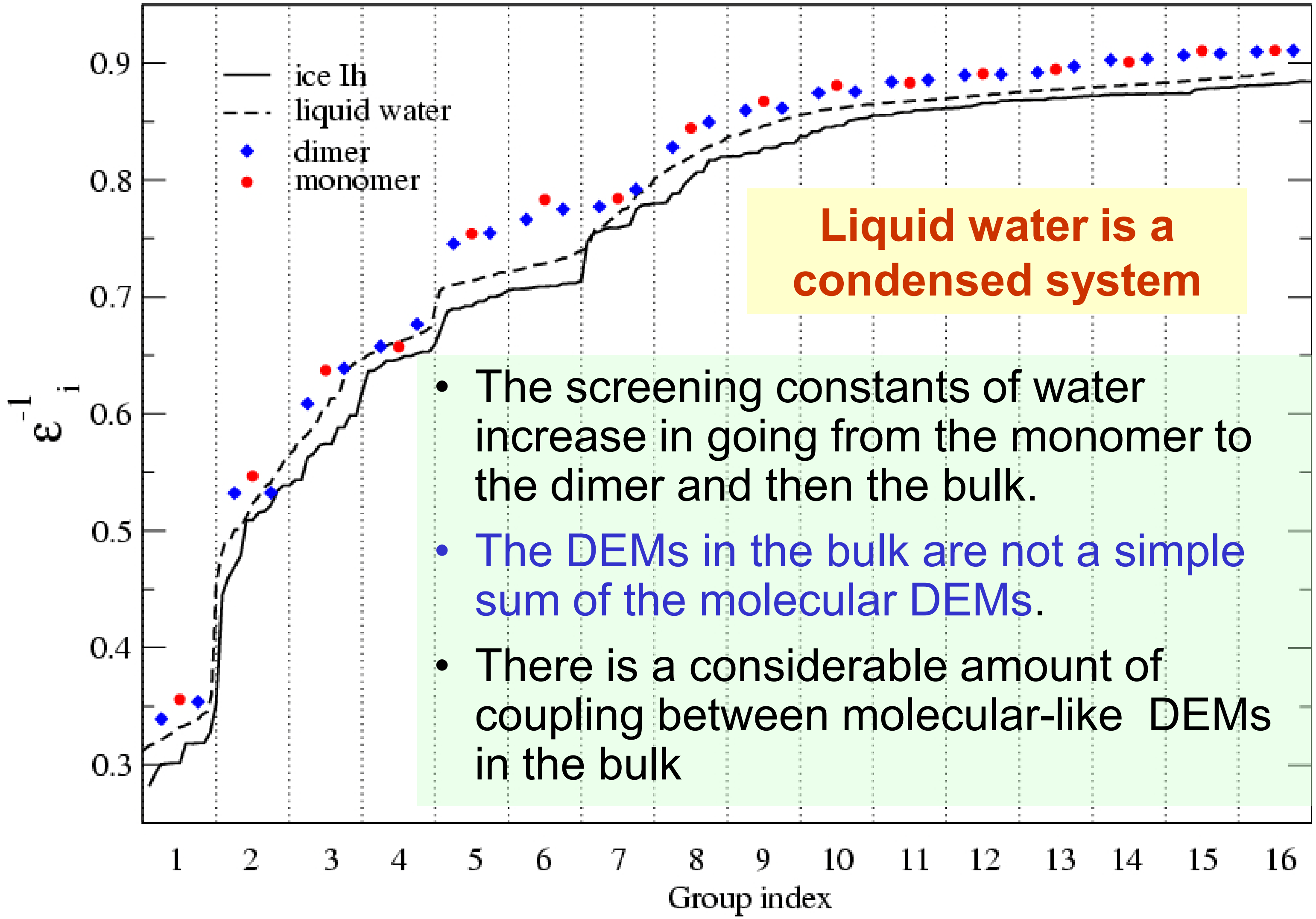


Water: Dielectric response in the gas phase and in the bulk



Liquid water is a condensed system

- The screening constants of water increase in going from the monomer to the dimer and then the bulk.
- The DEMs in the bulk are not a simple sum of the molecular DEMs.
- There is a considerable amount of coupling between molecular-like DEMs in the bulk

D.Lu, F.Gygi and G.Galli, Phys Rev. Lett. 2008

Approximate dielectric matrices for GW calculations

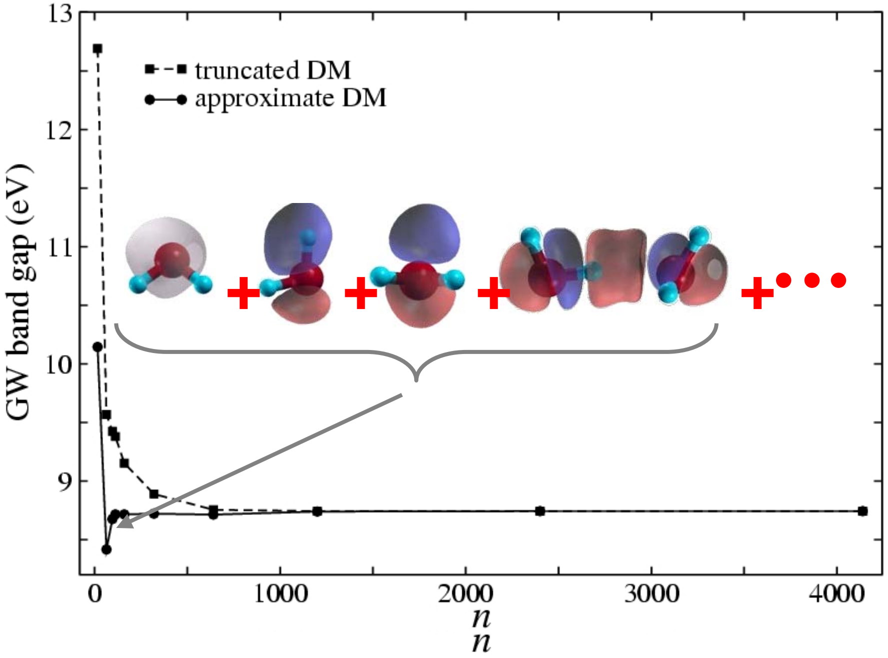
$$\tilde{\varepsilon}^{-1}(q) = \sum_{i=1}^{n} \left|U_i(q)\right\rangle \varepsilon_i^{-1} \left\langle U_i(q)\right| + \sum_{i=n+1}^{N} \left|V_i(q)\right\rangle \varepsilon_i^{-1} \left\langle V_i(q)\right|$$

exact DEMs

model dielectric response

D. Penn, *Phys. Rev., 128: 2093,1962.*

Plasmon Pole model: W. von der Linden and P. Horsch, PRB, 37, 8351,1988



$$E_n = \epsilon_n^{KS} + \langle \Sigma_{GW}(E_n)\rangle_n - \langle V_{xc}\rangle_n$$

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

QP band gap: 8.7 eV(this work);

8.6 eV (theory)[1]; 8.7±0.5 eV (exp)[2]

D.Lu, F.Gygi and G.Galli, Phys Rev. Lett. 2008

[1] Garbuio *et al.*, Phys. Rev. Lett., 97:137402, 2006.
[2] Bernas *et al.*, Chem. Phys. 222:151, 1997.

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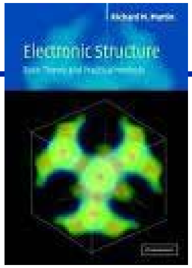

Electronic Structure

- Approximate yet accurate dielectric matrices from eigenvalue decomposition, using Density Functional Perturbation Theory

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  Deyu Lu and Francois Gygi

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  Dario Rocca and Deyu Lu

Correlation energy in terms of response functions

$E_{xc} = E_x + E_c$

- Exact expression for E_c

$$E_c = -\frac{1}{2\pi}\int_0^1 d\lambda \int_0^\infty du \,\mathrm{Tr}\,\{v_c[\chi_\lambda(iu) - \chi_0(iu)]\}$$

- Kohn-Sham response function

$$\chi_0(\mathbf{r},\mathbf{r}';iu) = \sum_{i,j}(f_i - f_j)\frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j + iu}$$

- Dyson-like equation

$$\chi_\lambda = \chi_0 + \chi_0[\lambda v_c + f_\lambda^{xc}]\chi_\lambda$$

$f_\lambda^{xc}(iu)$ unknown!

In RPA, $f_\lambda^{xc}(iu) = 0$

D. C. Langreth and J.P. Perdew, Sol. State. Commun., 17:1425, 1975; D. C. Langreth and J.P. Perdew, *Phys. Rev. B*, 15:2884, 1977; Time-dependent density functional theory, M. Marques, *et al.*, Ch. 28, Springer, 2006.

Adiabatic Connection

- Fictitious Hamiltonian

$$H(\lambda) = T + V_\lambda + \lambda V_{ee} \qquad n_\lambda(\mathbf{r}) \equiv n(\mathbf{r}) \quad \forall \lambda \in [0,1]$$

KS system: $V_{\lambda=0} = V_{KS} = V_{ext} + V_H + V_{xc}$ Real system: $V_{\lambda=1} = V_{ext}$

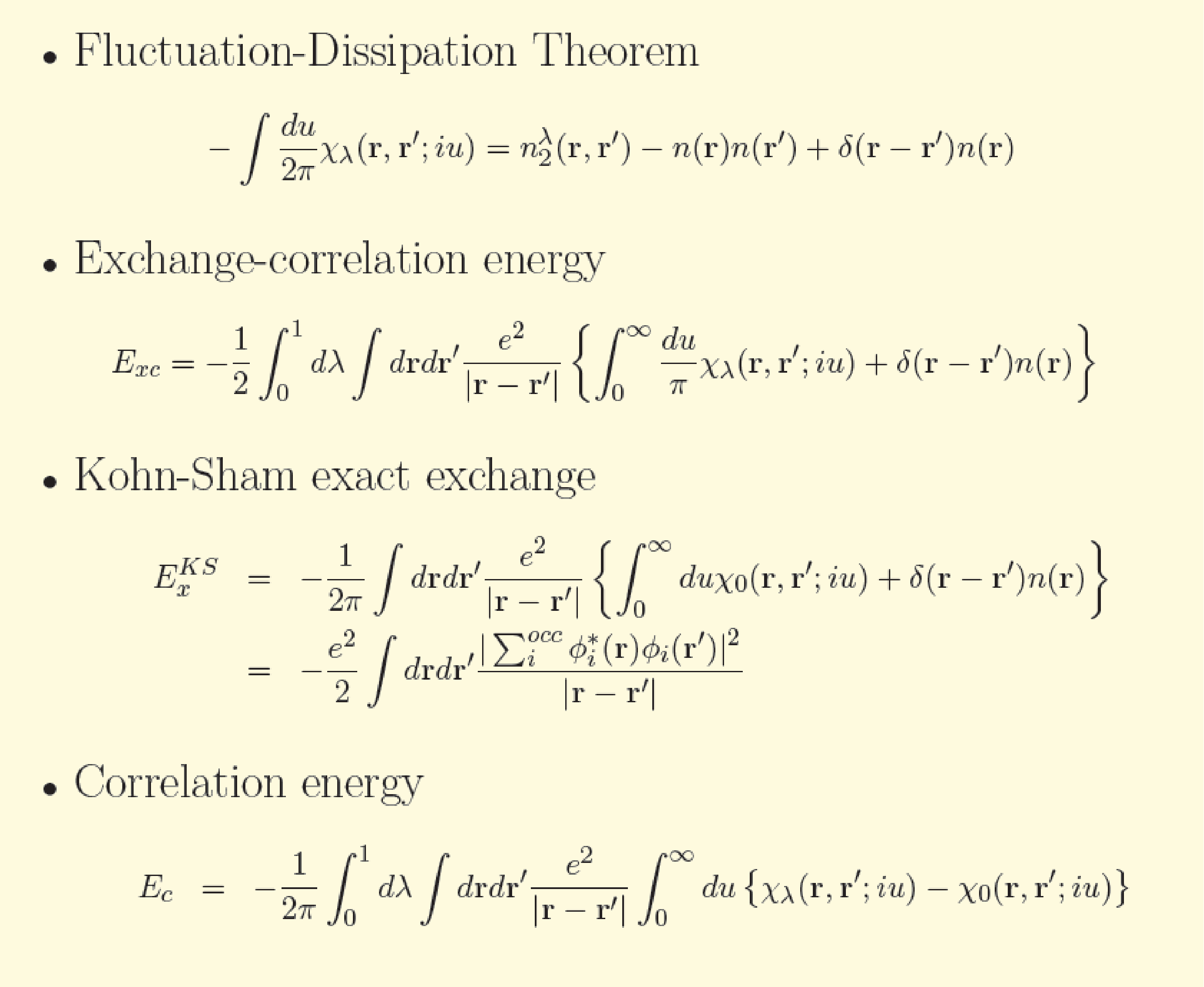
- Hellmann-Feynman theorem

$$\frac{dE(\lambda)}{d\lambda} = \langle \Psi^\lambda | V_{ee} | \Psi^\lambda \rangle + \langle \Psi^\lambda | \frac{\partial V_\lambda}{\partial \lambda} | \Psi^\lambda \rangle$$

- Integrating over λ

$$\begin{aligned} E_H + E_{xc} &= \int_0^1 d\lambda \, \langle \Psi^\lambda | V_{ee} | \Psi^\lambda \rangle \\ &= \frac{1}{2} \int_0^1 d\lambda \int d\mathbf{r} d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n_2^\lambda(\mathbf{r}, \mathbf{r}') \end{aligned}$$

Fluctuation dissipation theoreom



- Fluctuation-Dissipation Theorem

$$-\int \frac{du}{2\pi}\chi_\lambda(\mathbf{r},\mathbf{r}';iu) = n_2^\lambda(\mathbf{r},\mathbf{r}') - n(\mathbf{r})n(\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})$$

- Exchange-correlation energy

$$E_{xc} = -\frac{1}{2}\int_0^1 d\lambda \int d\mathbf{r}d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left\{\int_0^\infty \frac{du}{\pi}\chi_\lambda(\mathbf{r},\mathbf{r}';iu) + \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})\right\}$$

- Kohn-Sham exact exchange

$$\begin{aligned} E_x^{KS} &= -\frac{1}{2\pi}\int d\mathbf{r}d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left\{\int_0^\infty du\chi_0(\mathbf{r},\mathbf{r}';iu) + \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})\right\} \\ &= -\frac{e^2}{2}\int d\mathbf{r}d\mathbf{r}'\frac{|\sum_i^{occ}\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \end{aligned}$$

- Correlation energy

$$E_c = -\frac{1}{2\pi}\int_0^1 d\lambda \int d\mathbf{r}d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty du\left\{\chi_\lambda(\mathbf{r},\mathbf{r}';iu) - \chi_0(\mathbf{r},\mathbf{r}';iu)\right\}$$

Correlation and dielectric response function

RPA Correlation energy in terms of dielectric matrix eigenvalues:

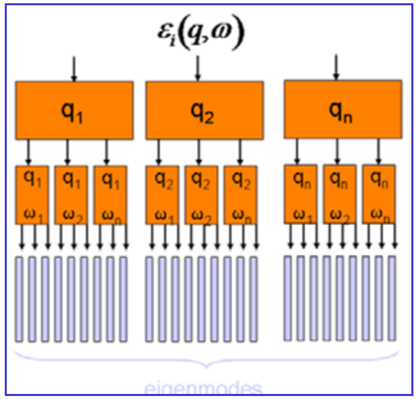
$\varepsilon = 1 - v_c \chi_0$

Scaling (*$N_v^2 N_{eig} N_{pw}$*) *enables* calculation for large systems.

$$E_c = \frac{1}{2\pi} \int_0^\infty du \sum_q \sum_i \{Log[\varepsilon_i(q,iu)] - \varepsilon_i(q,iu) + 1\}$$

Solve frequency dependent Sternheimer equation to obtain eigenvalues ε_i– use a so called BiConjugate Gradient Stabilized (Bi-CGSTAB) technique[1]

Efficient parallelization is possible



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[1] H. A. van der Vorst, "Bi-CGSTAB: A Fast and Smoothly Converging Variant of Bi-CG for the Solution of Nonsymmetric Linear Systems", SIAM J. Sci. Stat. Comput., 13, 631-664, (1992)—thanks to Z. Bai.

Correlation energy calculations for molecular crystals and SAM on surfaces

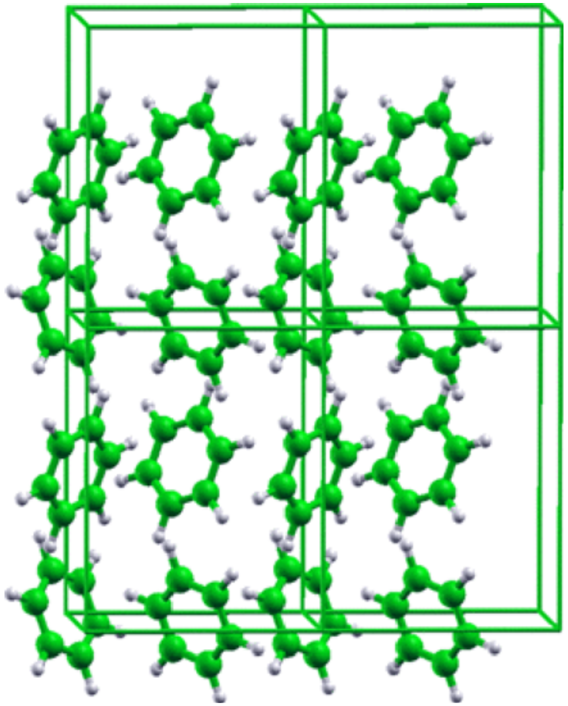
- No integration over coupling constant needed
- No extrapolation as a function of energy cutoff and k-pts sampling
- No empty state calculation
- No dielectric matrix inversion

Benzene Crystal

- One of the simplest organic crystals bound by vdW forces

- Experimental lattice constants (4K) [1]:
  - Four monomers per cell (120 e$^-$)
  - Pbca symmetry
    a=7.360 Å, b=9.375Å,
    c=6.70 Å, $\alpha=\beta=\gamma=90°$

- LDA overestimates the equilibrium density by 13%; PBE underestimates the equilibrium density by 27% and severely under-binds[2].

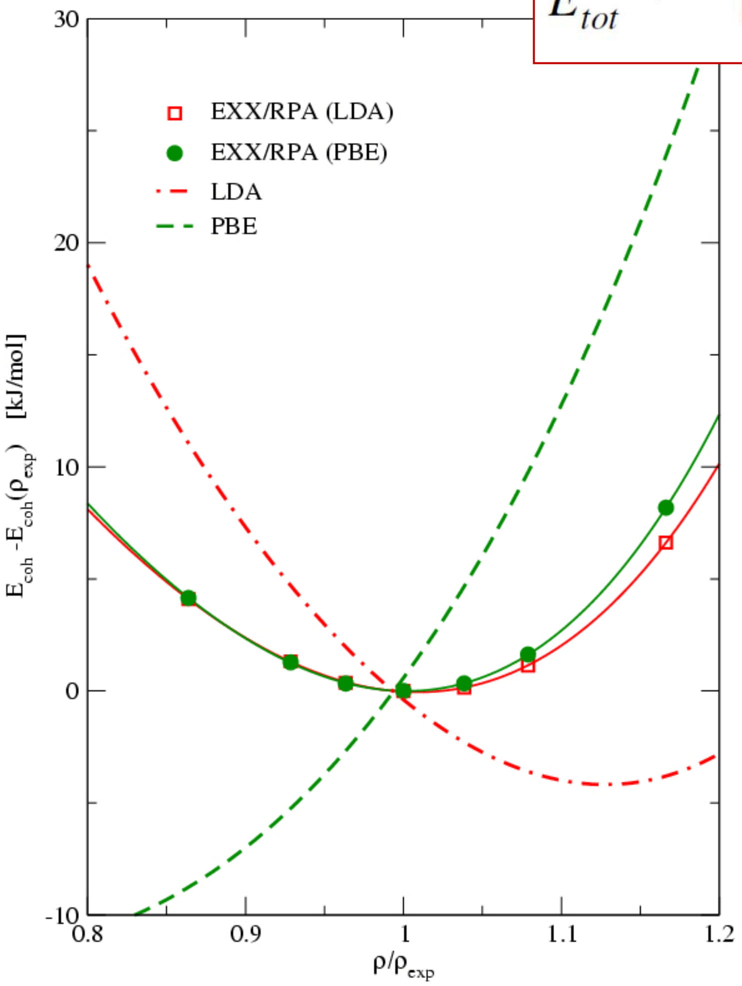


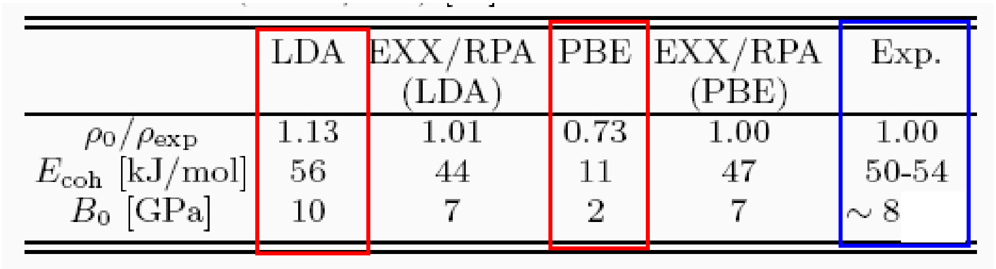
[1] W. David, R. Ibberson, G. Jerey, and J. Ruble, *Physica B*, 180-181, 597, 1992.

$$E_{tot}^{EXX/RPA}[\{\phi_i\}] = T_s + E_{ext} + E_H + E_x^{EXX}[\{\phi_i\}] + E_c^{RPA}[\{\phi_i\}]$$

Benzene crystal binding curve

$$E_{tot}^{EXX/RPA}[\{\phi_i\}] = T_s + E_{ext} + E_H + E_x^{EXX}[\{\phi_i\}] + E_c^{RPA}[\{\phi_i\}]$$





	LDA	EXX/RPA (LDA)	PBE	EXX/RPA (PBE)	Exp.
ρ_0/ρ_{exp}	1.13	1.01	0.73	1.00	1.00
E_{coh} [kJ/mol]	56	44	11	47	50-54
B_0 [GPa]	10	7	2	7	~ 8

Exp.: (1) W. David, R. Ibberson, G. Jeffrey, and J. Ruble, *Physica B*, 180-181: 597, 1992; (2) J. Chickos and W. Acree, Jr., J. Phys. Chem. Ref. Data, 31:537, 2002.

D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.*, 102, 206411, 2009.

Benzene crystal

1 kJ/mol ~ 10 meV

	EXX/RPA@LDA	EXX/RPA@PBE	QC methods	Exp.
E_{coh} (kJ/mol)	43	47	51-56	50-54
ρ_0/ρ_{exp}	1.01	1.00	--	1.0

Exp. values [J. S. Chickos *et al*., JPC Ref. Data 31, 537 (2002)] have been corrected for

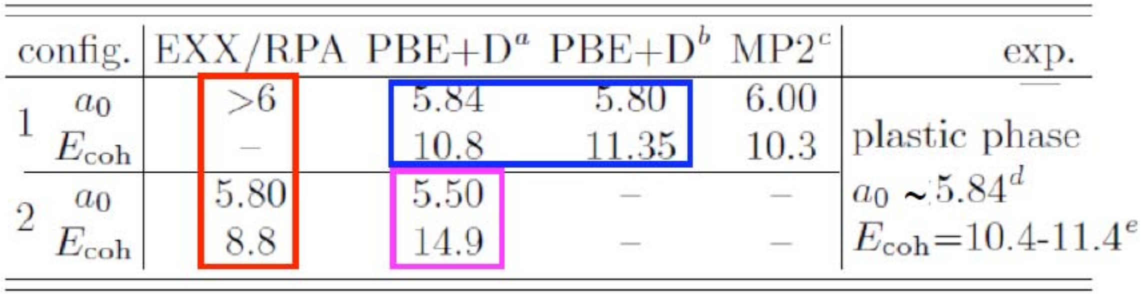
- **Temperature effects** (2RT=4.2 kJ/mol at 250 K)
- **Zero-point energy** (2.8 kJ/mol). [M. Nakamura *et al.*, JCP. 51, 3146 (1969).]

QC results: see Li *et al*., JPCA 114, 1944 (2010) for details.

- EXX/RPA greatly improves over LDA and PBE results.
- Cohesive energy from EXX/RPA@LDA is smaller (by 3kJ/mol) than EXX/RPA@PBE.
- **EXX/RPA** has similar accuracy as quantum chemistry methods.

D. Lu, Y. Li, D. Rocca and G. Galli, *Phys. Rev. Lett.*, 102, 206411, 2009.

EXX/RPA (PBE) results for methane



config.		EXX/RPA	PBE+D[a]	PBE+D[b]	MP2[c]	exp.
1	a_0	>6	5.84	5.80	6.00	
	E_{coh}	–	10.8	11.35	10.3	plastic phase
2	a_0	5.80	5.50	–	–	$a_0 \sim 5.84$[d]
	E_{coh}	8.8	14.9	–	–	E_{coh}=10.4-11.4[e]

a: This work from PBE ground state. Dispersion corrections were evaluated with Grimme2006 parametrization scheme. [S. Grimme, *J. Comp. Chem.* 27, 1787 (2006)].

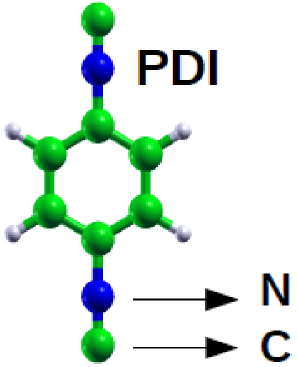
b: T. Kerber, M. Sierka, and J. Sauer, *J. Comput. Chem*. 29, 2088 (2008).

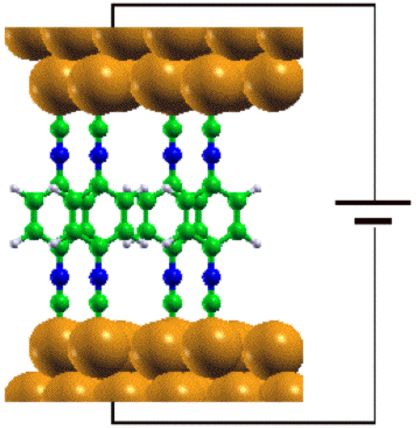
c: A. B. Kunz, *J. Phys. : Condens. Matter*. 6, L233 (1994)

d: a_0 = 5.84 Å was measured at 29K.

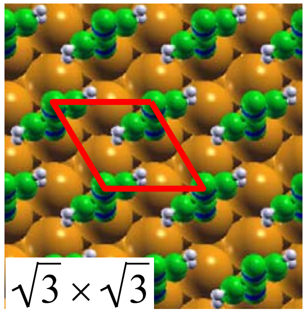
e: The measured heat of sublimation (in kJ/mol) is corrected for temperature effects ZPE is not included.

PDI SAM on Au(111) surface: Is Isocyanide group a good linker?

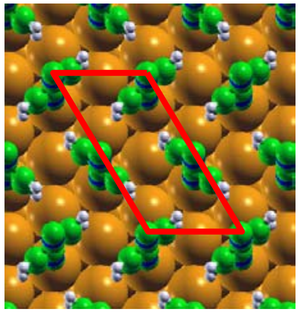




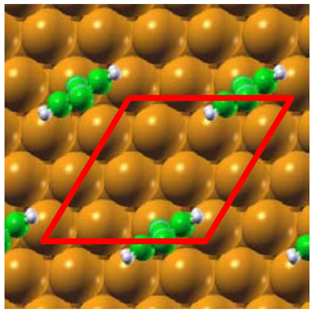
- **The presence of the triple bond in the isocyanide group may effectively connect the $p\pi$ electrons in the aromatic moiety and the $d\pi$ electrons on the gold surface.**
- **However, no ordered monolayers of PDI or BPDI has been observed in either AFM or STM experiments.**
- **DFT (LDA or GGA) does not describe well vdW interactions among SAMs.**



full coverage:
1 PDI / 3 Au



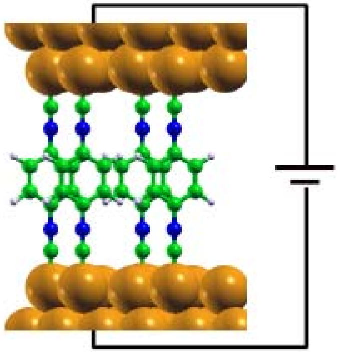
full coverage:
Herringbone



low coverage (1/3):
1 PDI / 9 Au

Which arrangement is more stable?

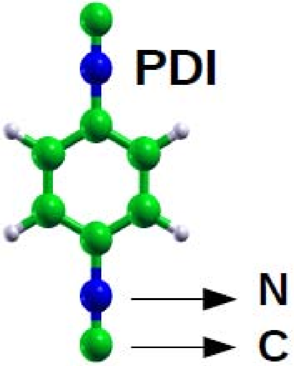
Self-assembled monolayers on metal surfaces



- **Experimentally**, no closely-packed SAM structures of PDI (or PDI derivatives) have been observed.
- **DFT/PBE** calculations predicted repulsive inter-molecular interactions for full-coverage PDI/Au(111).

  Y. Li *et al.*, JPCC 112, 6413 (2008).
- **MP2** calculations predicted more attractive interactions between the PDI dimer than the benzene dimer.

  R. Steele *et al.*, PCCP 12, 82-96 (2010).



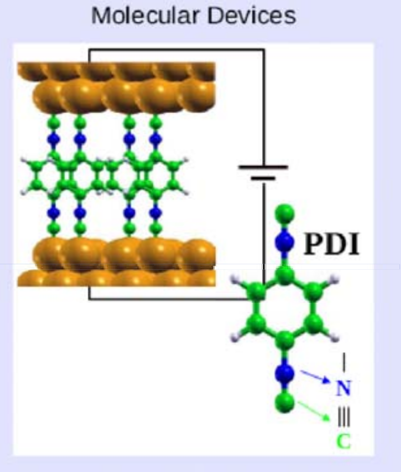
Is there a significant contributions of dispersion interactions to the cohesive energy of PDI SAMs on Au(111) ?

RPA vdW energy in PDI SAM

- **EXX/RPA greatly resuces the under-binding found in PBE for PDI SAMs at high packing density.**
- **Contrary to the case of methane, PBE+D agrees reasonably well with EXX/RPA.**
- **The adsorption energy of the gas phase and the high coverage herringbone structure are nearly identical.**
- **The lack of ordering in experiments may arise from the close competition between vdW interactions at high density and stronger surface binding at low density.**

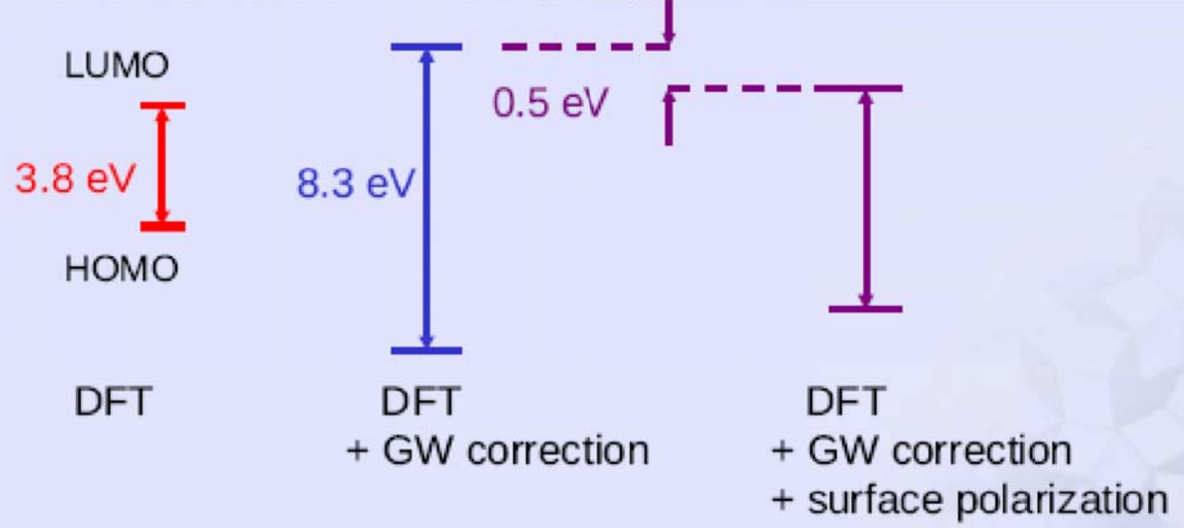
Y. Li, D. Lu, V. Nguyen and G. Galli, *JPC-A 2010*

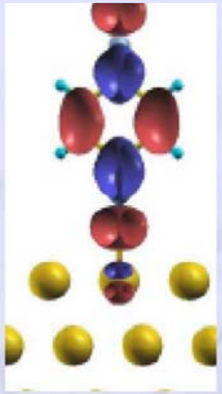
Organics on metals are usually `difficult` cases for DFT/GGA



Define the GW-corrected adsorbate energy level as

$$\varepsilon^{Ad}_{GW}(j) = \varepsilon^{Ad}_{DFT}(j) + \Delta\Sigma^{SAM}_{GW} + \int_{z>z_{I_L}} [V_{im}(z) - V_{xc,DFT}(z)]\rho^{SAM}_{DFT}(j)$$

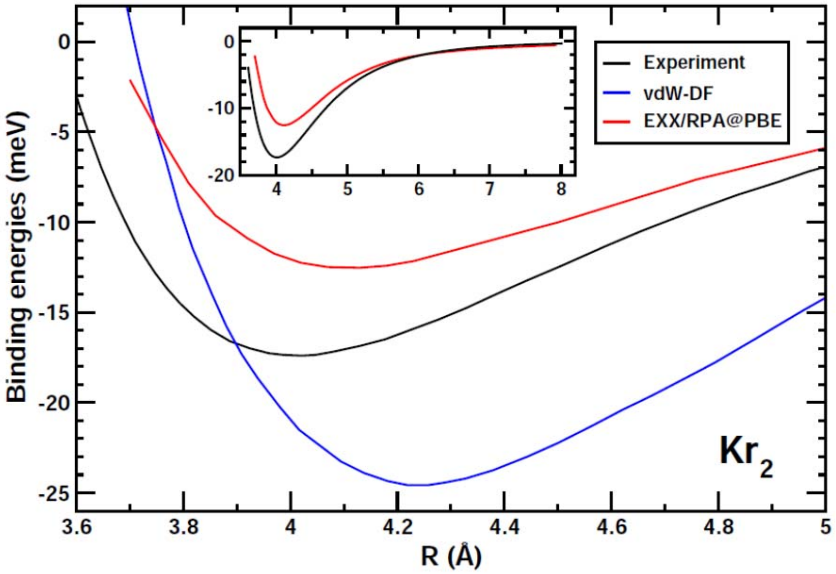


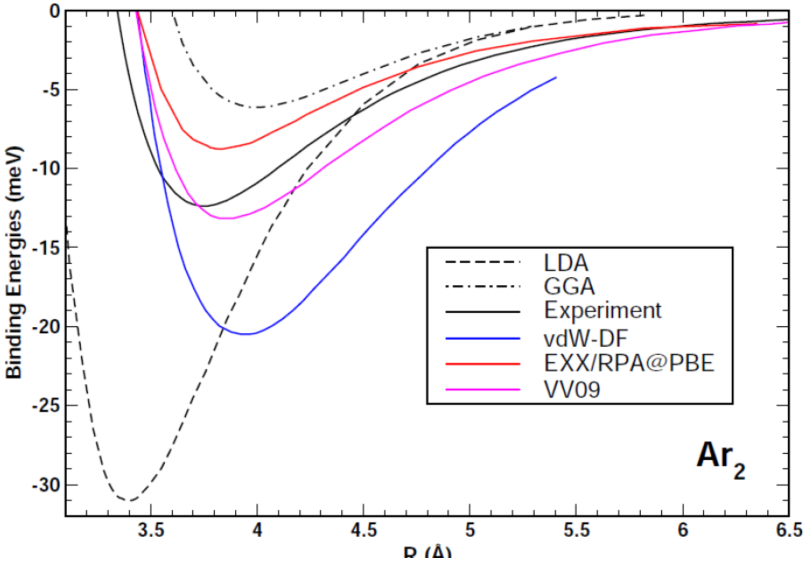


The energy of the lowest unoccupied molecular level is shifted upward by 1.5-2.0 eV in GW calculations, compared with DFT results → this qualitatively changes the picture of electron transport

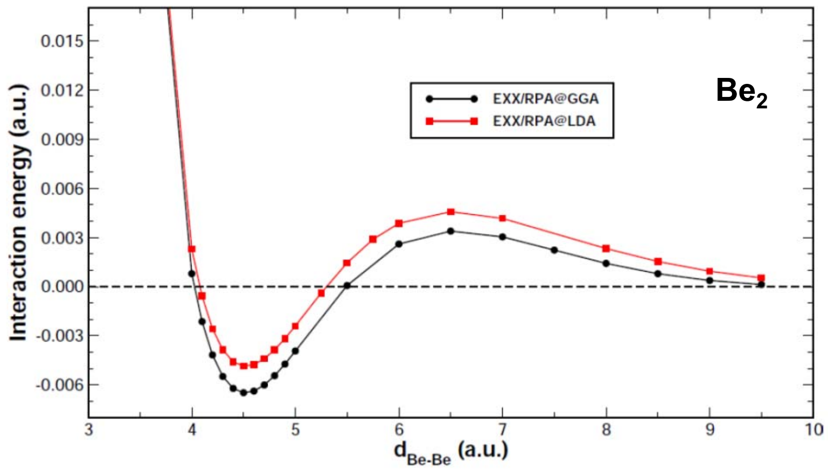
Y.Li, D.Lu, S.Swanson, J.C. Scott, G.G. J.Phys.Chem. C 2008; Y.Li, D.Lu and G.G. submitted

EXX/RPA and van der waals energy functionals





Lack of self-consistency may be a serious issue in Exx/RPA calculations

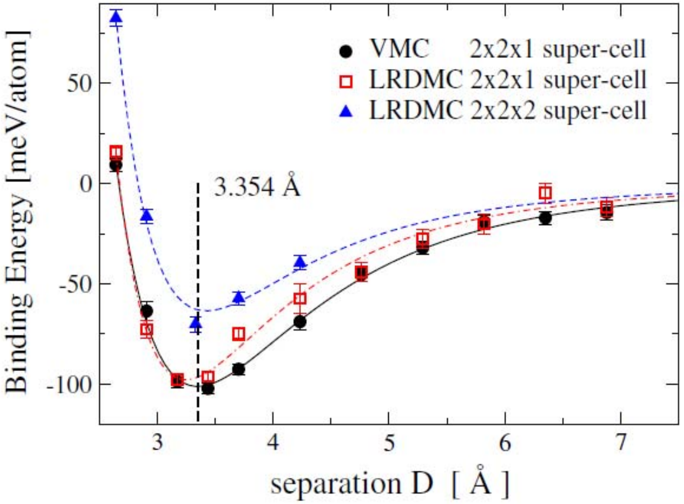


V.Nguyen and GG JCP 2010

Graphite: Quantum Monte Carlo calculations

- Good agreement with most recent experiments for graphite binding energy (56 +/- 5 meV): phonon contributions taken into account at the DFT level.
- At large interlayer separations: $E \sim D^{-4.2}$ → conventional van der Waals interaction from the semiconducting sp^2 bands dominate the unusual asymptotic form arising from in plane polarization of the single semi--metallic band.

Benchmark for other theoretical methods developed to describe dispersion forces

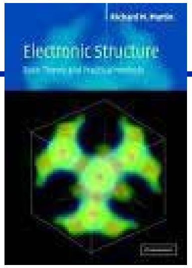


L.Spanu, S.Sorella, G.G. PRL 2009

Outline

- Basic Concepts: Response functions

  R.M.Martin: Electronic Structure



- Approximate yet accurate dielectric matrices from eigenvalue decomposition, using Density Functional Perturbation Theory

  Hugh Wilson, Deyu Lu and Francois Gygi

- Interpretation of dielectric eigenmodes: water and ice

  Deyu Lu and Francois Gygi

- RPA correlation energies: binding of organic crystals (benzene, methane) and SAM on surfaces

  Yan Li , Deyu Lu and Dario Rocca

- Solution of Bethe-Salpeter Equations (BSE): Si clusters and charge transfer excitations

  Dario Rocca and Deyu Lu

Perturbative approach using density matrices

Quantum Liouville equation

$$i\frac{d\hat{\rho}(t)}{dt} = \left[\hat{H}(t), \hat{\rho}(t)\right] \longrightarrow \rho(\mathbf{r},\mathbf{r}',t) = \sum_v \phi_v^*(\mathbf{r},t)\phi_v(\mathbf{r}',t)$$

$$\swarrow$$

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

Apply external electric field, use first order perturbation theory and linearize equation with respect to external potential

$$v'_{ext}(\mathbf{r},\omega) = -\mathbf{E}(\omega)\cdot\mathbf{r}$$

Perturbative approach using density matrices

1^{st} Order perturbation theory; linearized Quantum Liouville equation

$$\begin{aligned}\frac{d\hat{\rho}'(t)}{dt} &= \mathcal{L}\cdot\hat{\rho}'(t) + \left[\hat{v}'_{ext}(t),\hat{\rho}^0\right],\\ \mathcal{L}\cdot\hat{\rho}'(t) &= \left[\hat{H}^0,\hat{\rho}'(t)\right] + \left[\hat{v}'_H[\hat{\rho}'](t),\hat{\rho}^0\right] + \left[\hat{\Sigma}'[\hat{\rho}'](t),\hat{\rho}^0\right],\end{aligned}$$

$$\Big\downarrow$$

Fourier Transform

$$\boxed{(\omega-\mathcal{L})\cdot\hat{\rho}'(\omega) = \left[\hat{v}'_{ext}(\omega),\hat{\rho}^0\right].}$$

Solve for $\hat{\rho}'(\omega)$, ➔ **dipole moment :** $d_i(\omega) = \sum_j \alpha_{ij}(\omega)E_j(\omega)$ **=** $\mathrm{Tr}\left(\hat{r}_i\hat{\rho}'(\omega)\right)$

Solve equation using techniques based on Density Functional Perturbation Theory; obtain polarizability→ absorption coefficient proportional to the Trace of the polarizability tensor.

B.Walker et al., Phys.Rev.Lett. 2006; D.Rocca et al. J.Chem.Phys. 2008

Many body perturbation theory to obtain optical spectra

Quantum Liouville equation

$$i\frac{d\hat{\rho}(t)}{dt} = \left[\hat{H}(t), \hat{\rho}(t)\right] \longrightarrow \rho(\mathbf{r},\mathbf{r}',t) = \textstyle\sum_v \phi_v^*(\mathbf{r},t)\phi_v(\mathbf{r}',t)$$

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

$$\Sigma(\mathbf{r},\mathbf{r}') = v_{xc}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$$

TDDFT in the adiabatic approximation

$$\Sigma_{HF}(\mathbf{r},\mathbf{r}',t) = -\sum_v \phi_v(\mathbf{r},t)\phi_v^*(\mathbf{r}',t)v(\mathbf{r},\mathbf{r}')$$

TD-HF

$$\Sigma_{COH}(\mathbf{r},\mathbf{r}') = \frac{1}{2}\delta(\mathbf{r}-\mathbf{r}')W_p(\mathbf{r}',\mathbf{r})$$

$$\Sigma_{SEX}(\mathbf{r},\mathbf{r}',t) = -\sum_v \phi_v(\mathbf{r},t)\phi_v^*(\mathbf{r}',t)\underset{\uparrow}{W}(\mathbf{r}',\mathbf{r})$$

Statically screened Bethe-Salpeter Equation (BSE)

Screened Coulomb interaction

Optical properties of solids and nanostructures

- We have solved the BSE by replacing the KS exchange-correlation potential by screened exact exchange, in the quantum Liouville equations (1st order perturbation theory)
- We have used the techniques proposed by B.Walker et al. (PRL 06) and D.Rocca et al. (JCP 08) to solve the time dependent equations.
- We have computed the static dielectric screening iteratively, by using eigenvalue decompositions (H.Wilson et al., PRB 08 and PRB 09).

⇓

•Full spectrum at a computational cost comparable to several Hartree-Fock ground state calculations

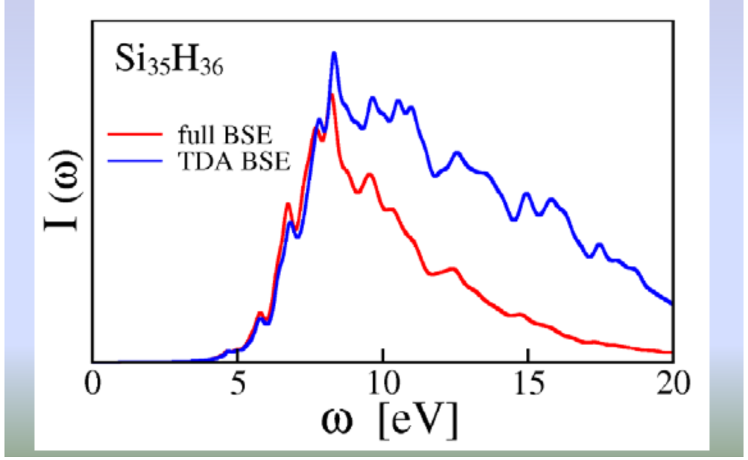
•Calculations of empty electronic states, full dielectric matrix, inverse of dielectric matrix (and basis set approximations) avoided

•Method suitable for large basis sets and large systems

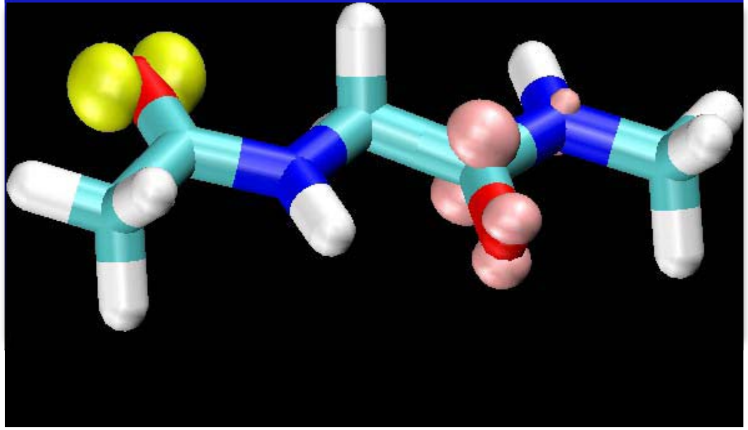
D.Rocca, D.Lu and G.G., submitted (2009)

Optical properties of solids and nanostructures, including excitonic effects

Systems of size comparable to experiments, e.g. Si dots in the few nm range



Charge transfer excitations: e.g. in dipeptides



Iterative solutions of the Bethe-Salpeter Equation:

- Full spectrum at a computational cost comparable to several Hartree-Fock ground state calculations
- Calculations of empty electronic states, full dielectric matrix, inverse of dielectric matrix (and basis set approximations) avoided
- Method suitable for large basis sets and large systems

D.Rocca, D.Lu and G.G., submitted (2009)

Open Source Codes

Qbox: http://eslab.ucdavis.edu/software/qbox

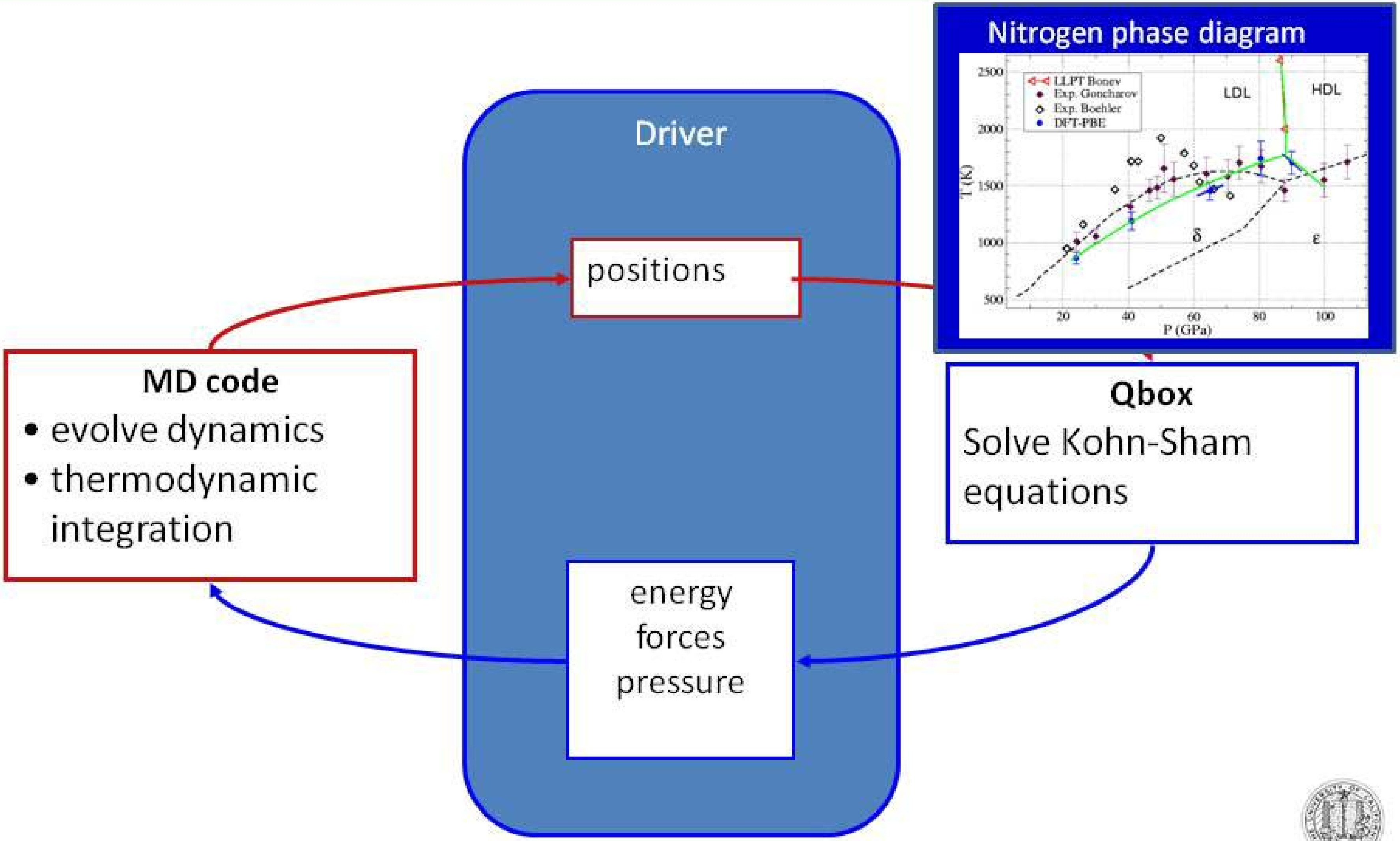
ESlab : http://eslab.ucdavis.edu

The database of pseudopotentials: http://fpmd.ucdavis.edu

The XML standards site for electronic structure:
http://www.quantum-simulation.org

Quantum Espresso: http://quantum.espresso.org

Use of Qbox in client-server mode



Driver

positions

energy
forces
pressure

MD code

- evolve dynamics
- thermodynamic integration

Nitrogen phase diagram

Qbox

Solve Kohn-Sham equations

http://eslab.ucdavis.edu/software/qbox/

Exciting opportunities in theoretical and computational materials science

- Development of advanced materials is a key element for creating new technologies for, e.g. efficient and sustainable energy supplies
- It is an exciting time to make a difference!

-Agreement with experiment is never a sufficient condition to judge simulation results; in certain instances it may be misleading

-Distinction between theory and numerical techniques is essential and increasingly overlooked

- **Verification and validation**
- **Theoretical and algorithmic advances**
- **Connection with experiment**

http://angstrom.ucdavis.edu/

Ab-initio Nanoscience Group for Simulations and Theoretical Research On Materials

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Yan Li

Dario Rocca

Hugh Wilson

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In collaboration with Francois Gygi