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Structure and Dynamics of Hydrogen-Bonded Systems

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Effect of Proton Disorder on the Excited State Properties of Ice

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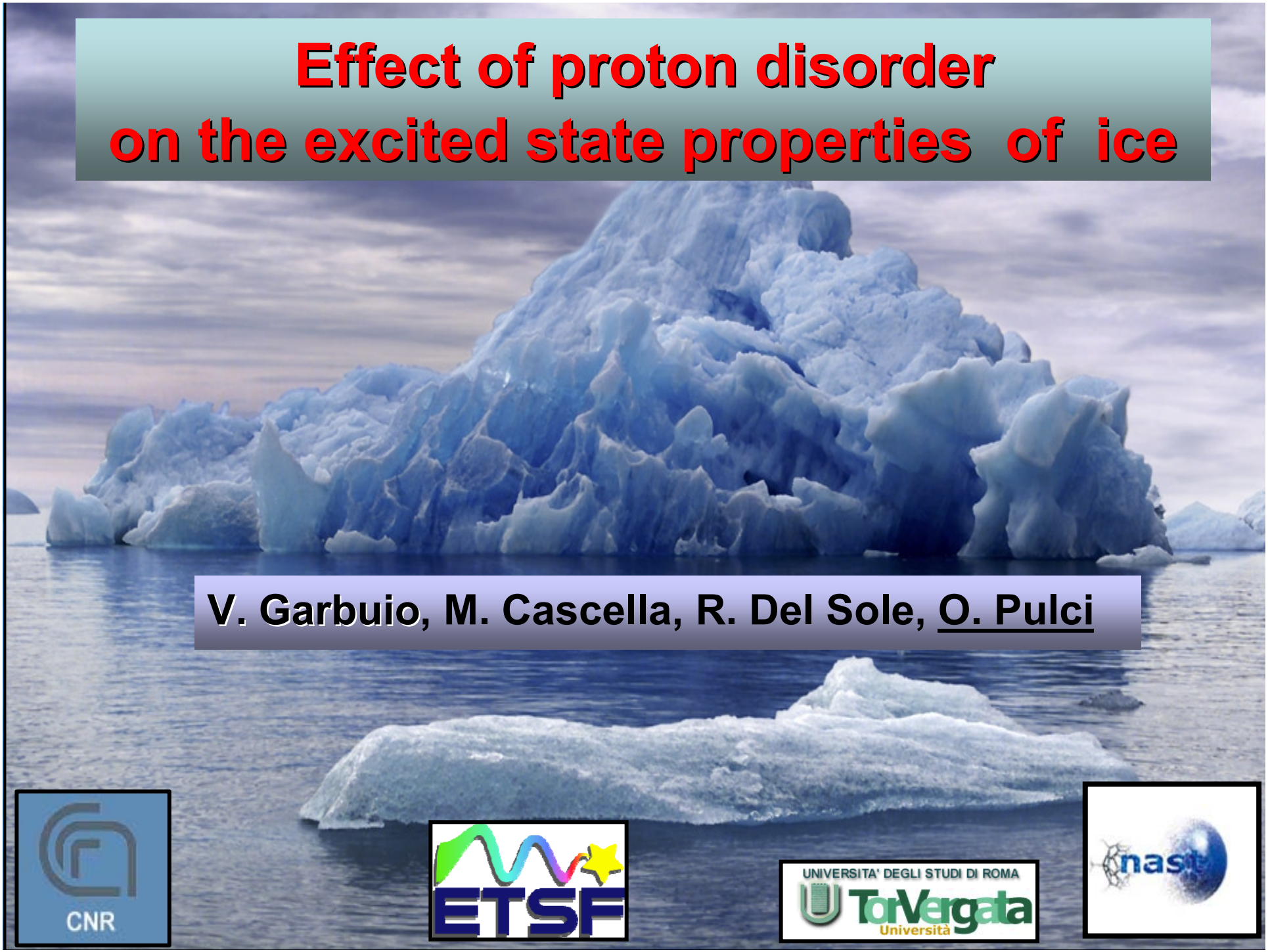
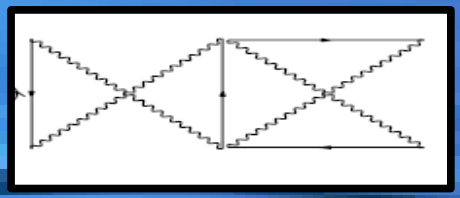
Effect of proton disorder on the excited state properties of ice

V. Garbuio, M. Cascella, R. Del Sole, O. Pulci

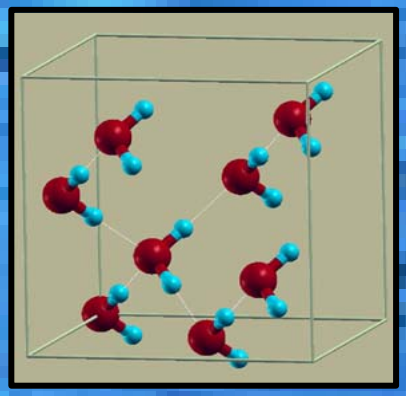


OUTLINE:

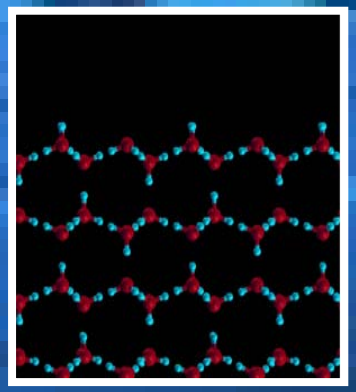
- Theoretical approaches



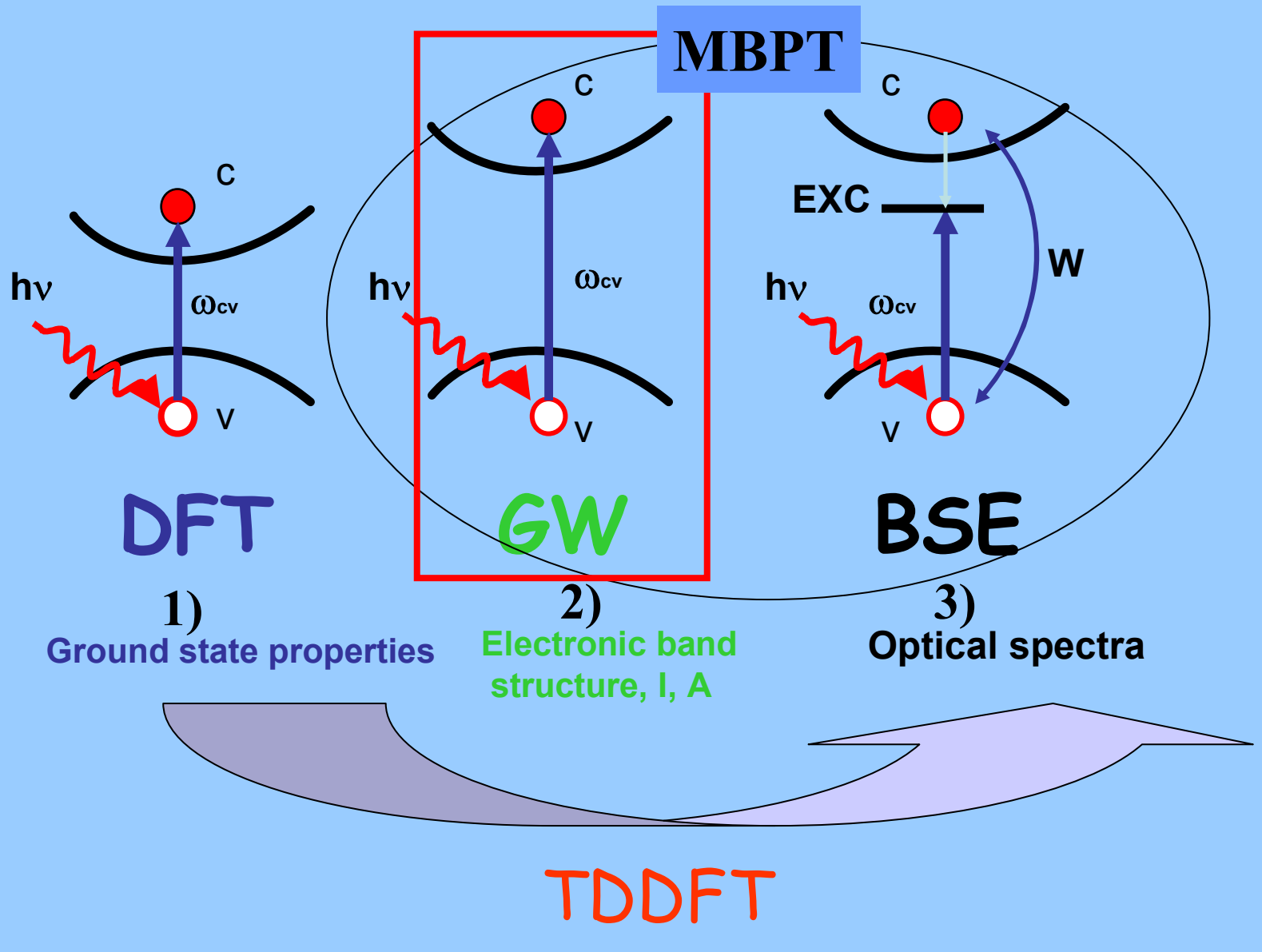
- Ice Ic(bulk)



- Ice Ih surface



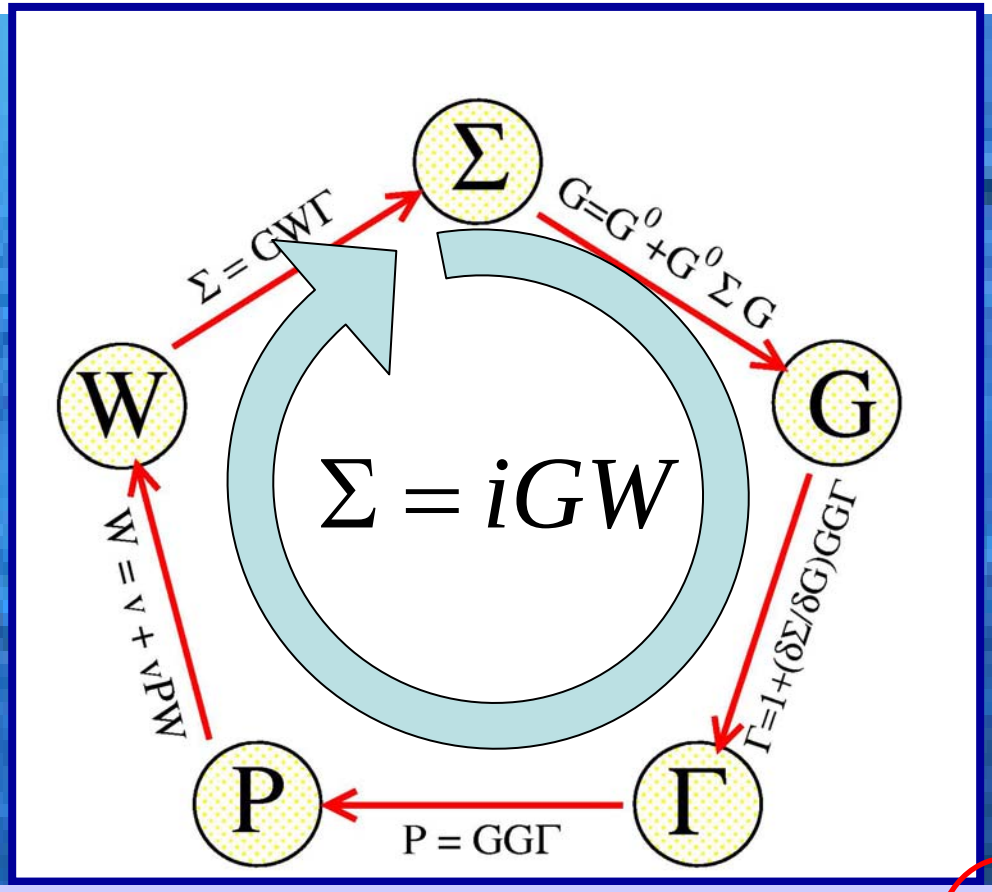
Theoretical approaches



Quasi-particle equation: (Step 2)

Lars Hedin 1965

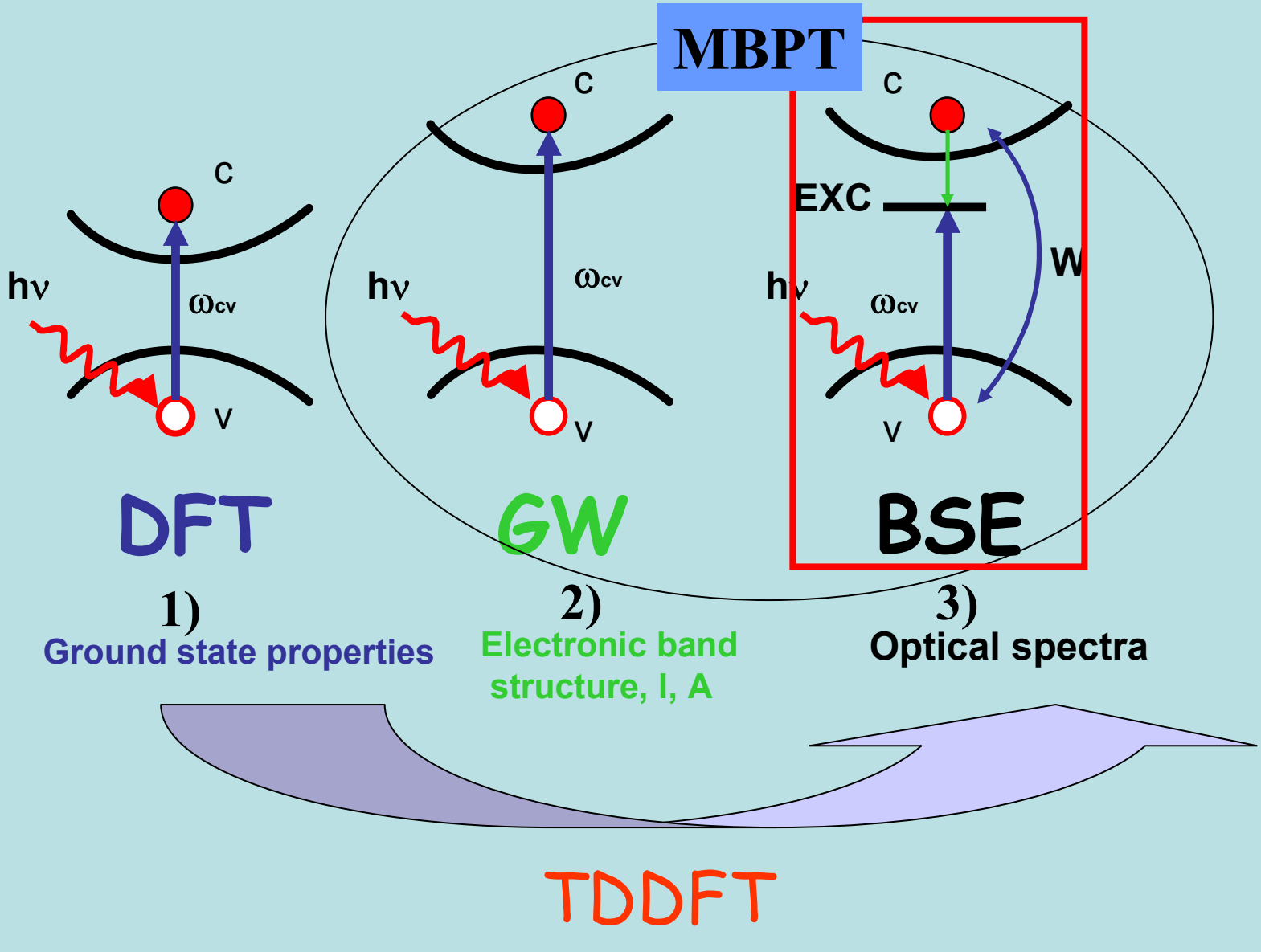
$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H)\Psi_i^{QP}(\vec{r},\omega) + \int \Sigma(\vec{r},\vec{r'},\omega)\Psi_i^{QP}(\vec{r'},\omega)d\vec{r'} = E_i^{QP}(\omega)\Psi_i^{QP}(\vec{r},\omega)$$



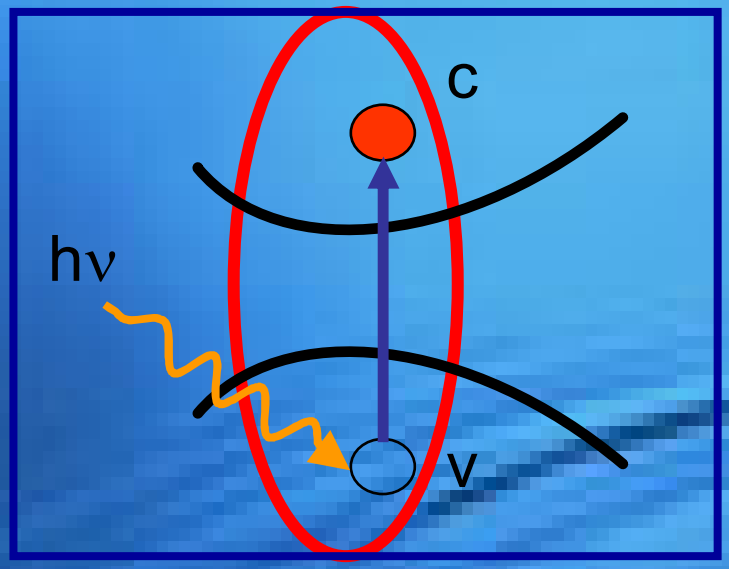
G: single particle Green's function
W: screened Coulomb interaction

$$W = \varepsilon^{-1}V$$

Theoretical approaches

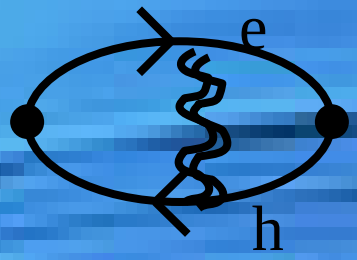


Step 3: calculation of optical spectra within the Bethe Salpeter Equation



Absorption spectra

A photon excites an electron from an occupied state to a conduction state

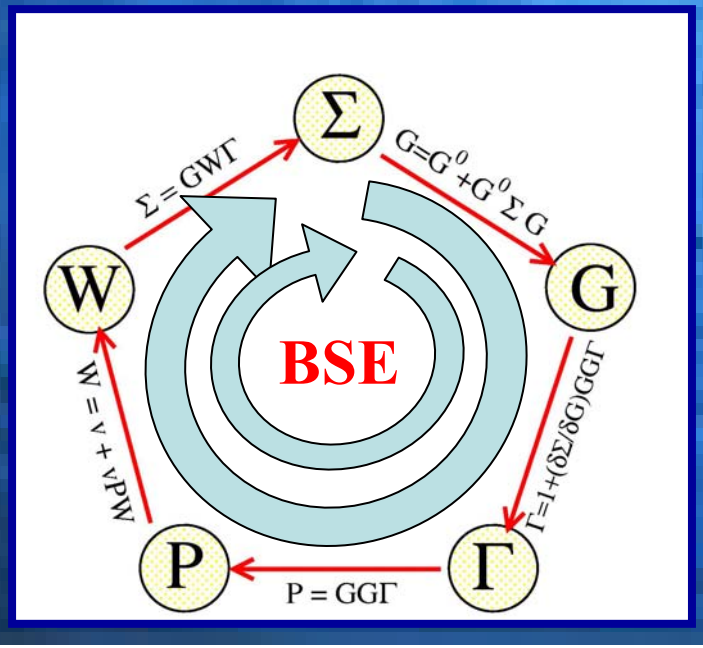


$$\overline{{}^4P} = {}^4P_{IQP} + {}^4P_{IQP}\ {}^4\Xi\ {}^4\overline{P}$$

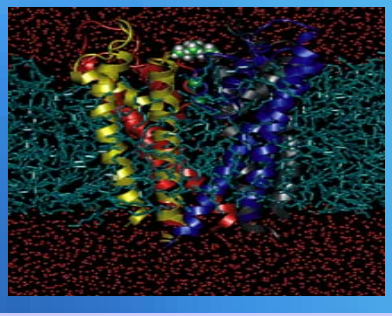
Bethe Salpeter Equation (BSE)

Kernel: $\Xi = \bar{v} - W$

- e-h exchange
- bound excitons



Applicable to:

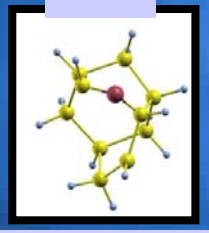


Biological systems

Ab-initio: *(NOT "one puts nothing in, one gets nothing out"!!)*

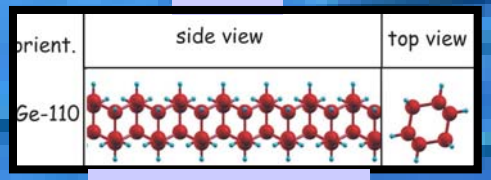
- **Generality, transferability 0D-3D**
- **Detailed physical informations**
- **Complex theory+large comp.cost**

0-D



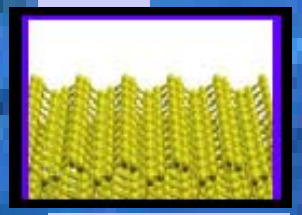
Nanoclusters

1-D



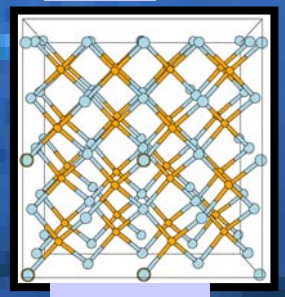
Nanowires

2-D



Surfaces

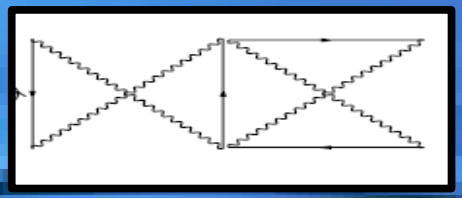
3-D



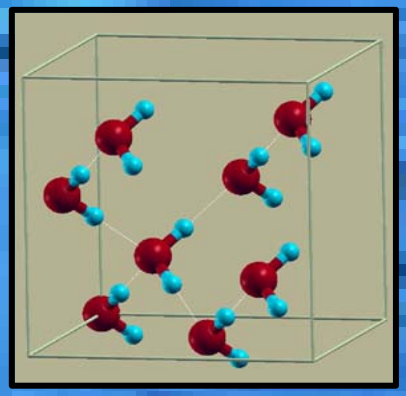
bulks

OUTLINE:

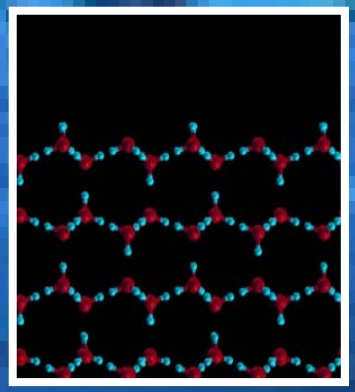
- Theoretical approaches



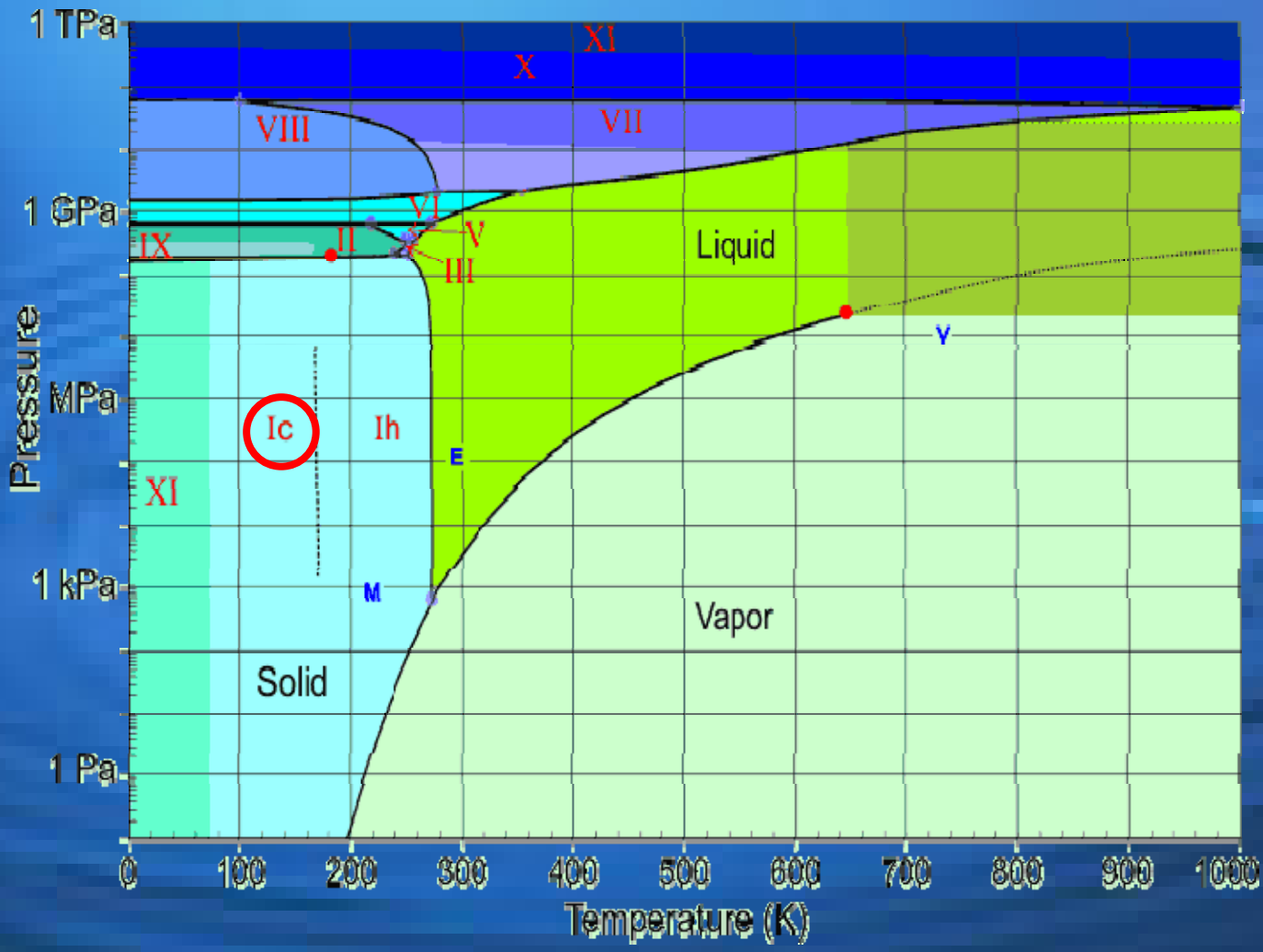
- Ic Ice (bulk)



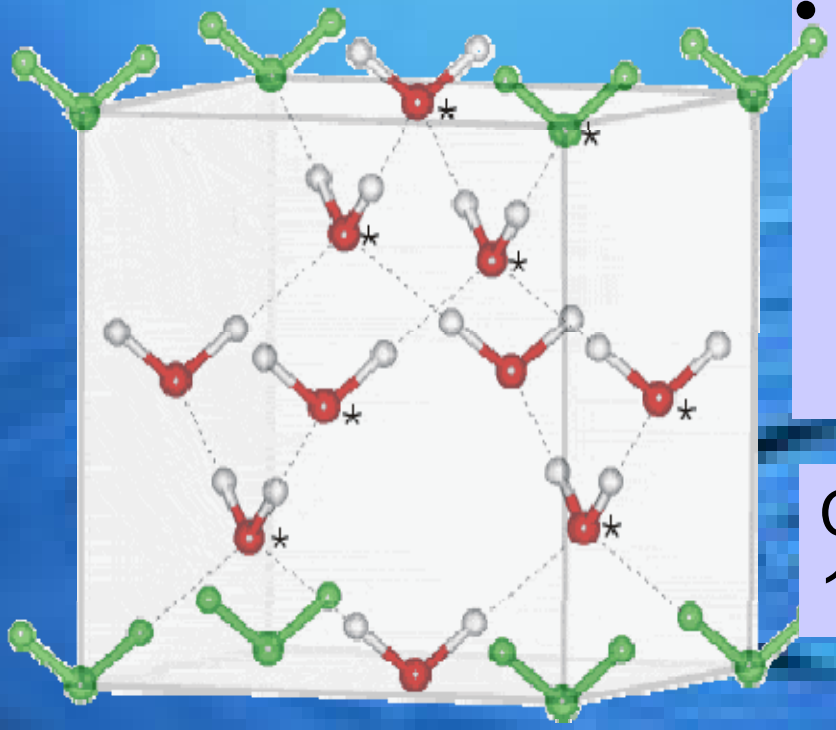
- Ice Ih surface



H_2O phase diagram



Cubic ice (Ic)



- It is a metastable form of ice that can be formed, by condensation of water vapor, at ambient pressure but low temperatures

Cubic ice (Ic) – diamond lattice
153 K down to 113 K

Studied within DFT and Tight-binding

G. Pastori Parravicini et al., *Phys. Rev.* **B 8**, 3009 (1973)
L. Resca et al., *phys. stat. sol. b* **81**, 129 (1977)
W. Y. Ching et al., *Ferroelectrics* **153**, 25 (1994)

Proton disorder:

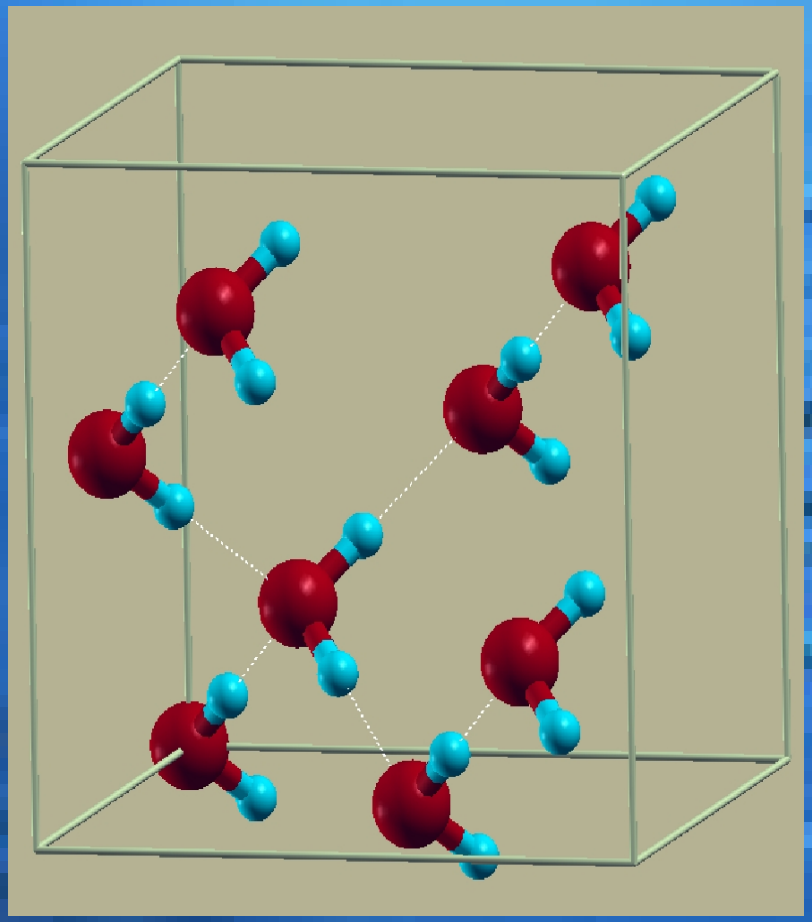
obeying Pauling ice rules

- Each oxygen is covalently bonded to two hydrogens at distance of about 1.8 a.u. (molecular solid)
- Each oxygen atom is hydrogen bonded to two hydrogens belonging to surrounding molecules
- Only one hydrogen atom lies along each O-O axis
- All possible configurations satisfying the preceding conditions are equivalent

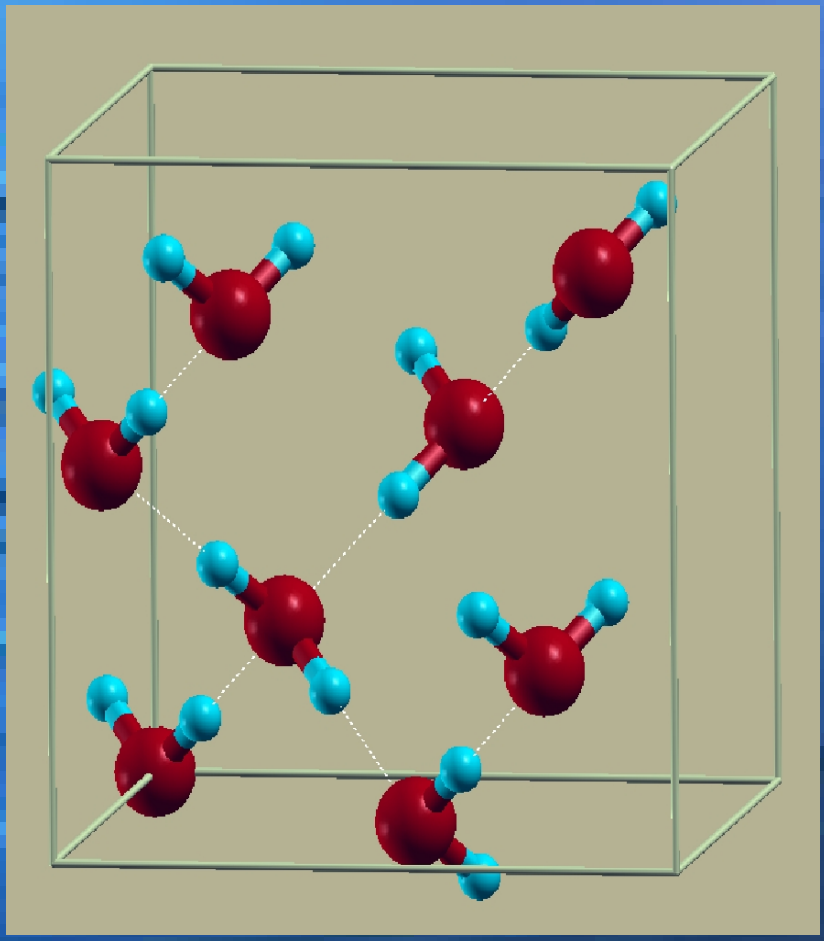
L. Pauling, *J. Am. Chem. Soc*. **57**, 2680 (1935)

Simulation unit cell

- **Polar ordered Ic**

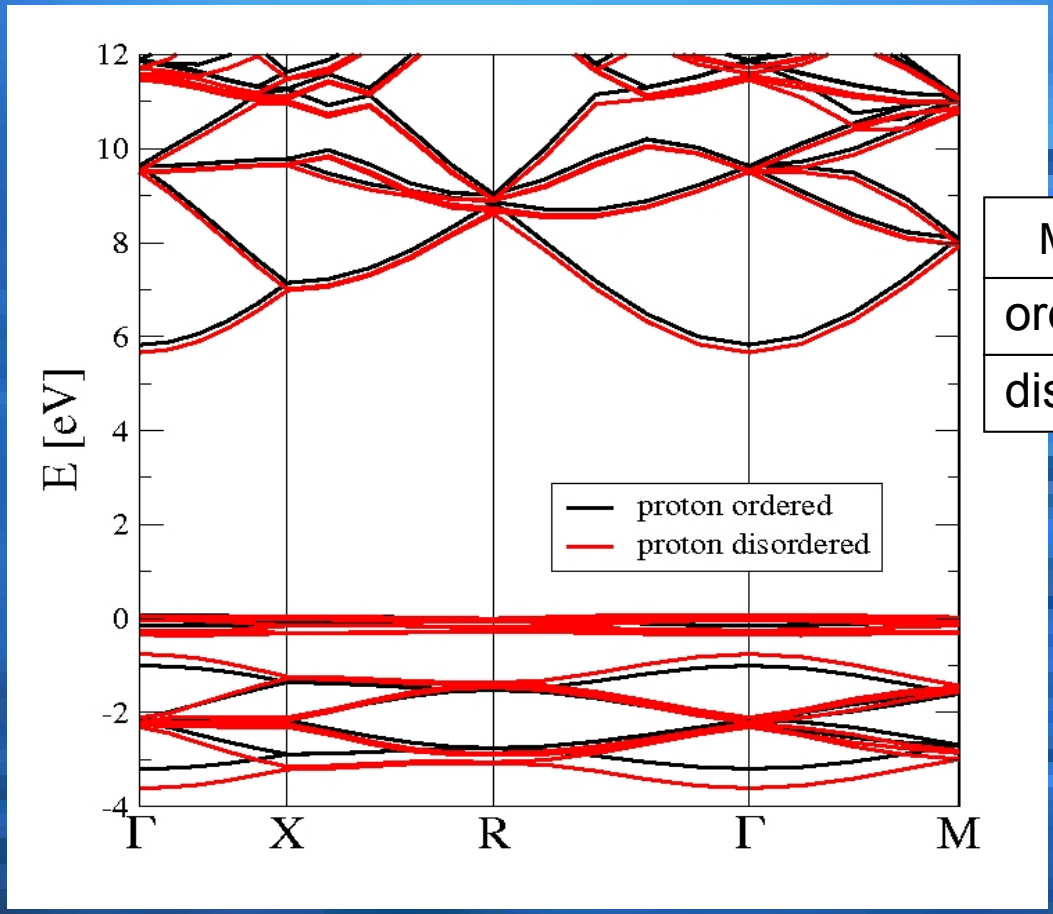


- **Disordered Ic**



More stable (ΔE=-0.05 eV/supercell)

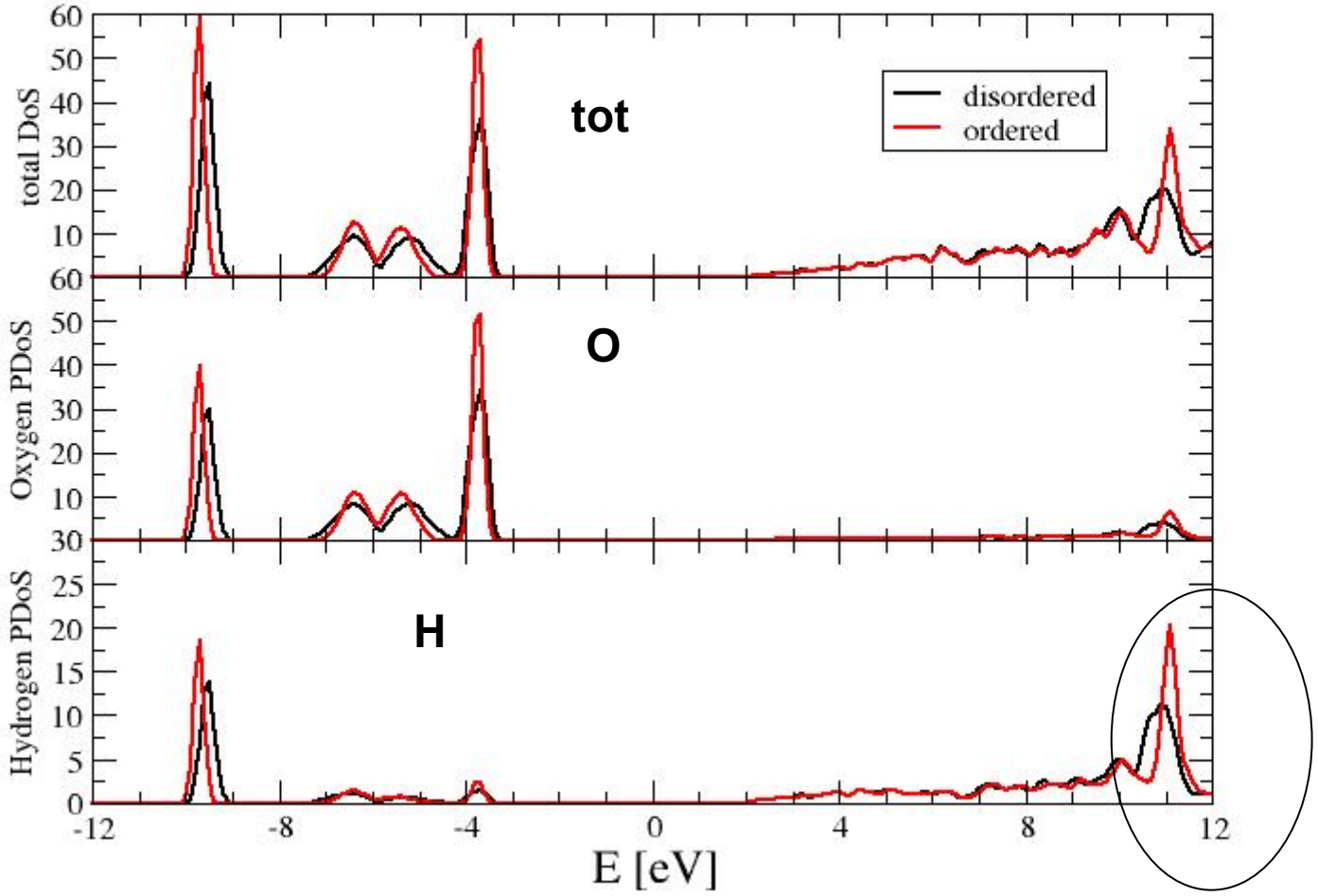
Electronic band structure



Min. gap	DFT gap	GW gap
ordered	5.76 eV	9.5 eV
disordered	5.61 eV	9.0 eV

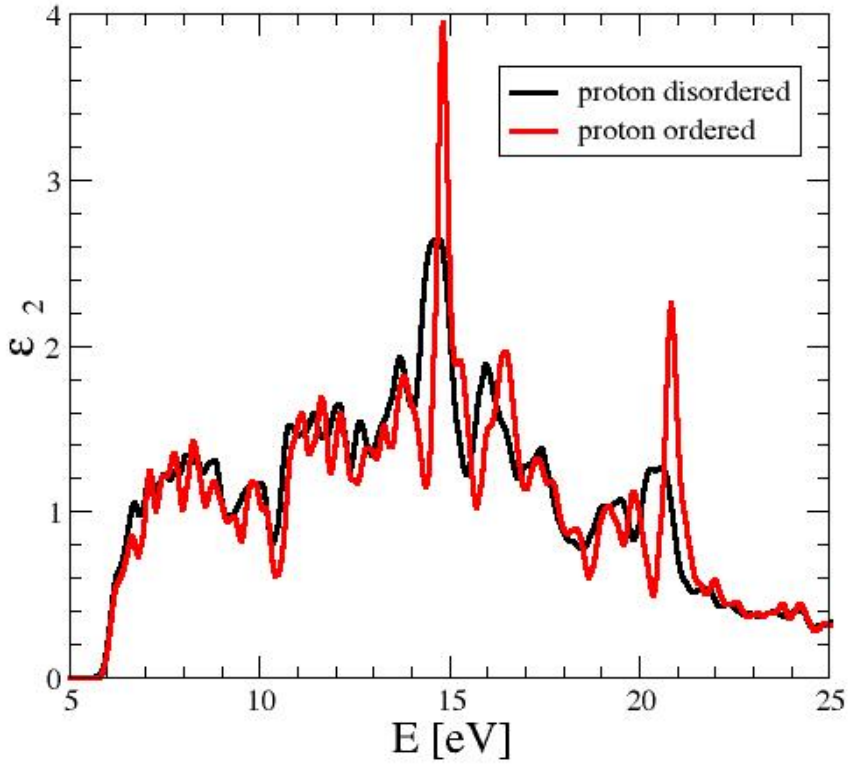
NB: ordered phase has indirect gap

PDOS


total DoS
tot
disordered
ordered
Oxygen PDoS
O
Hydrogen PDoS
H
E [eV]

Optical absorption spectra

DFT ‘Fermi Golden rule’ (DFT-RPA-NLF)



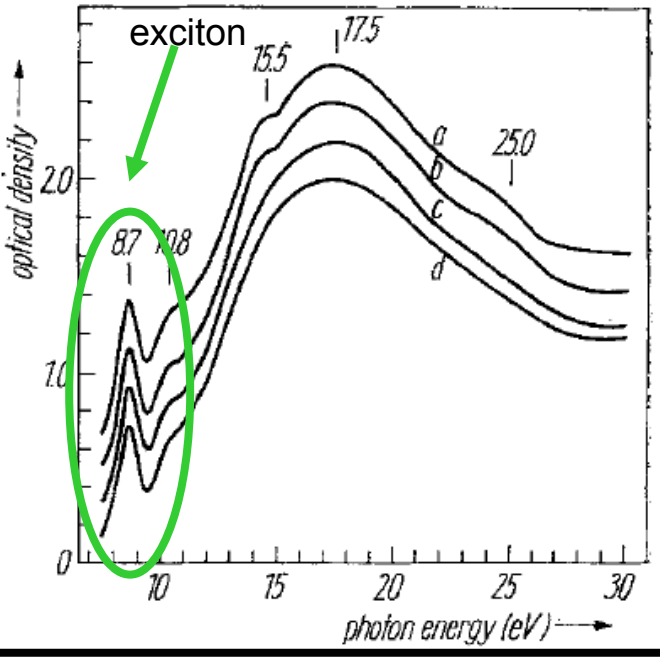
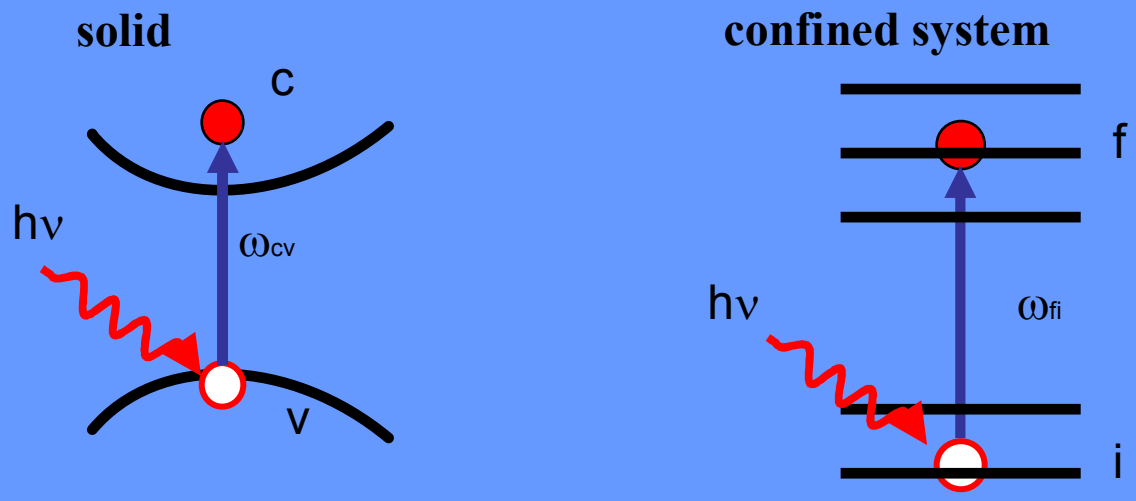


Fig. 3. The absorption spectra of cubic (a, b) and amorphous (c, d) ice. After Watanabe et al. [4]. Ice formed and measured at: (a) $T = -120$, (b) -133, (c) -166, (d) -196 °C

Optical spectra: independent particle approach



sum over independent transitions

(application of Fermi's Golden Rule to an **independent** particle system)

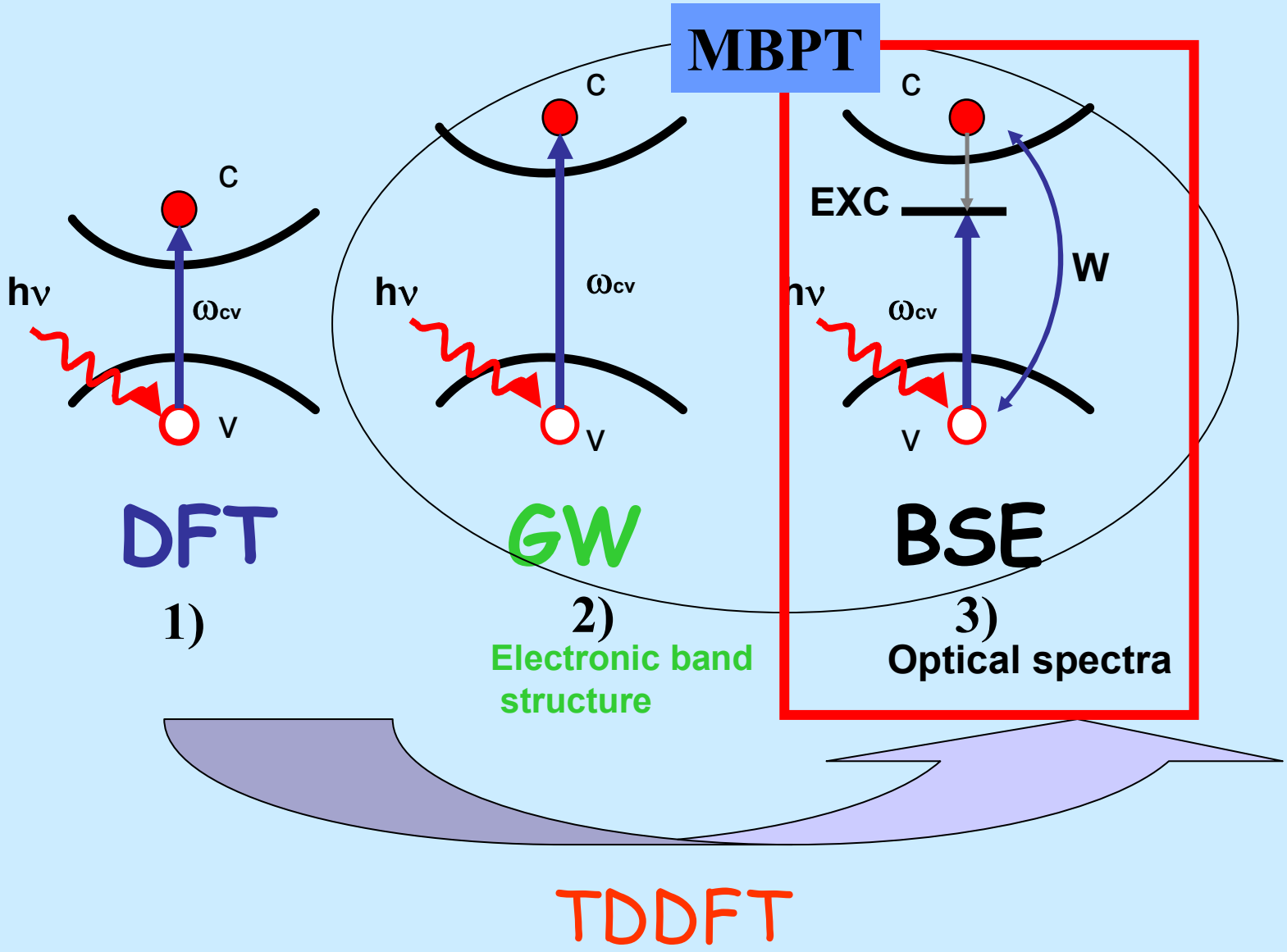
$$\mathrm{ABS}^{\mathrm{RPA}}(\omega) \propto \sum_{vc} \left| \langle \varphi_c | \hat{D} | \varphi_v \rangle \right|^2 \delta(\omega - (\varepsilon_c - \varepsilon_v))$$ Fermi's Golden Rule

Optical Absorption

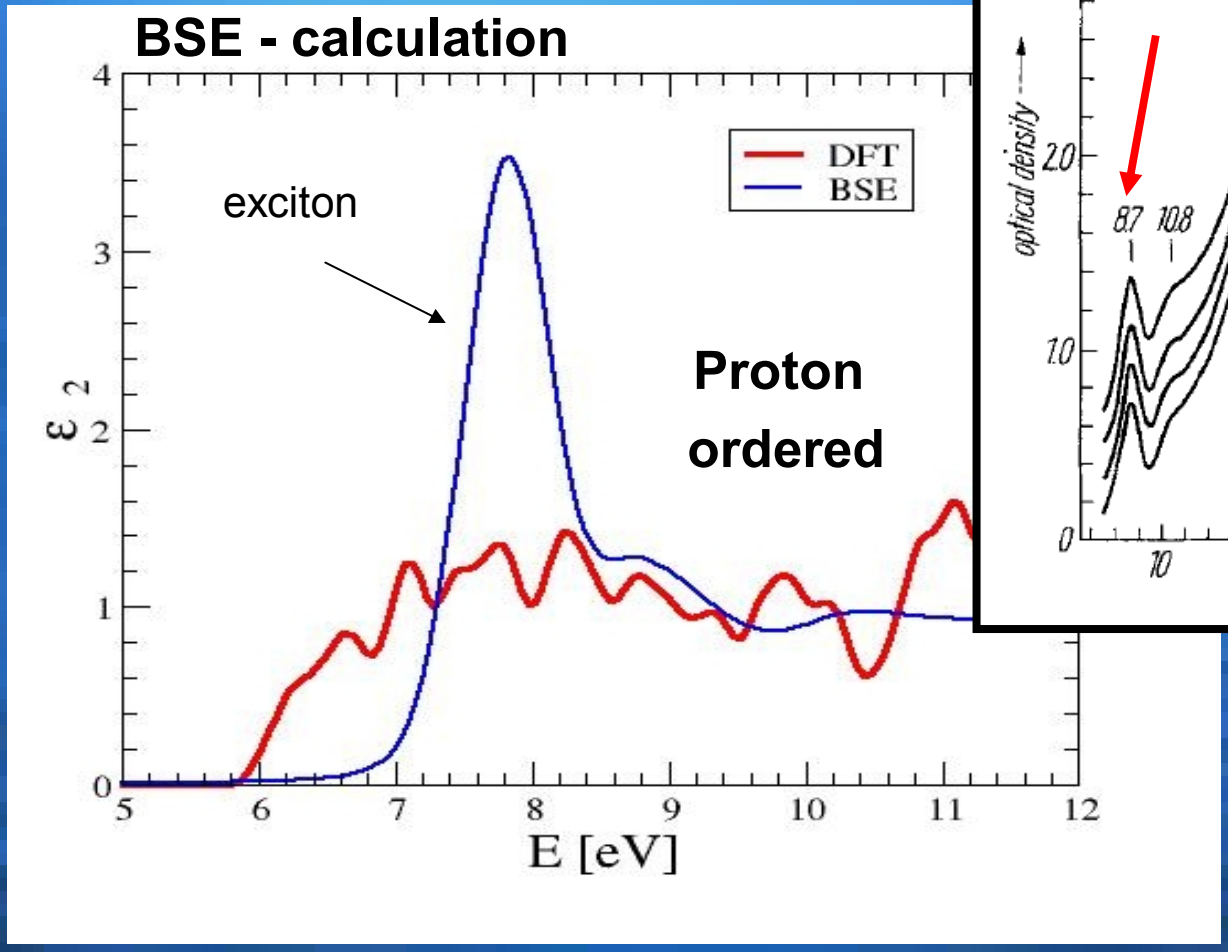
DFT wavefunctions

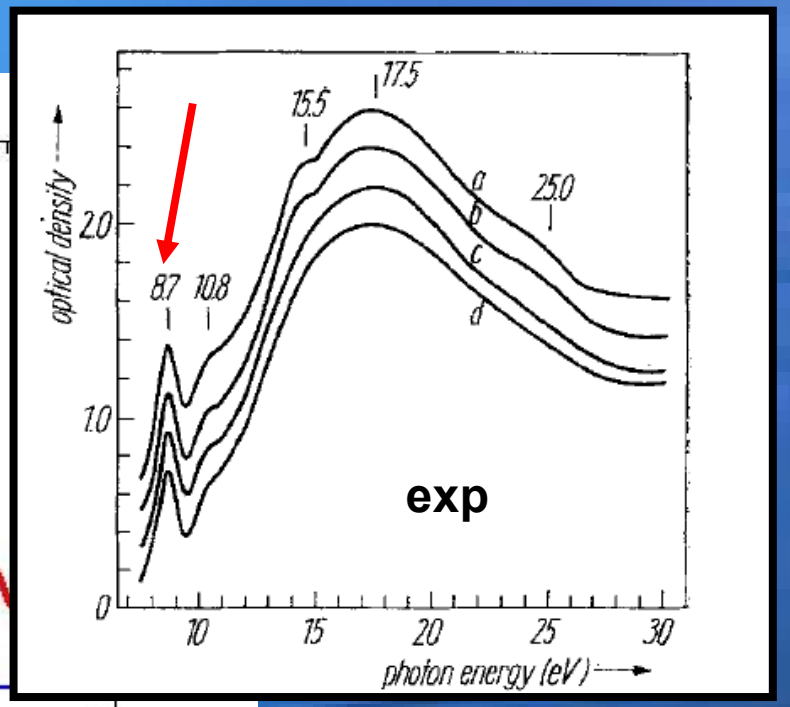
DFTenergies

Theoretical approaches



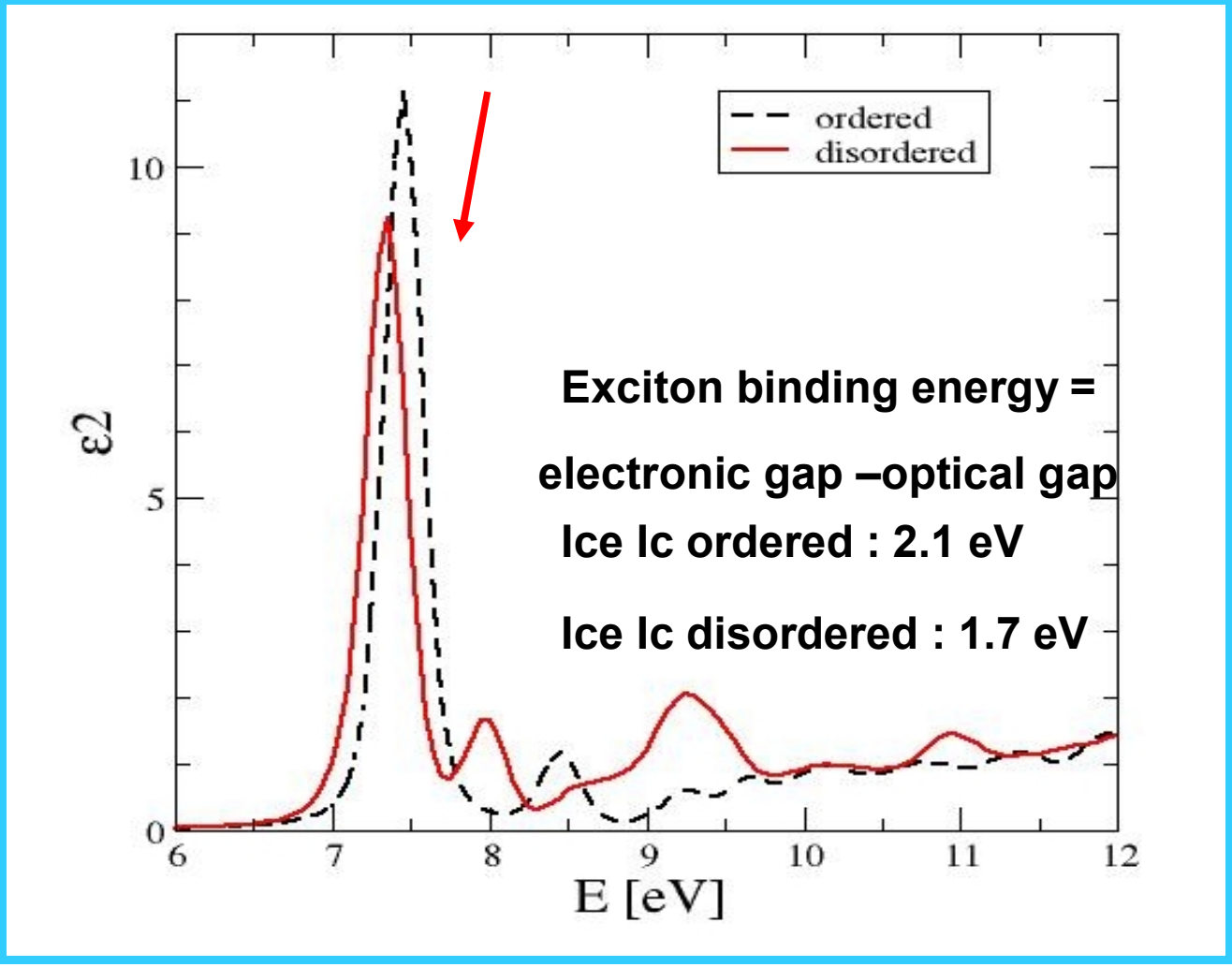
Many-Body effects on the Optical absorption spectrum

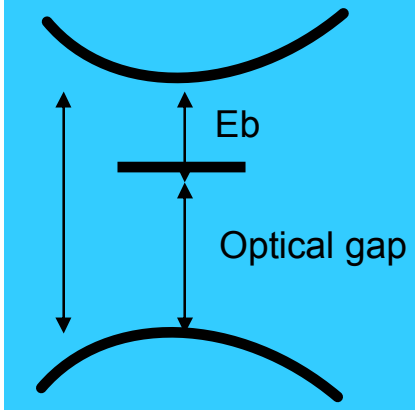




Effect of disorder on the optical absorption spectrum

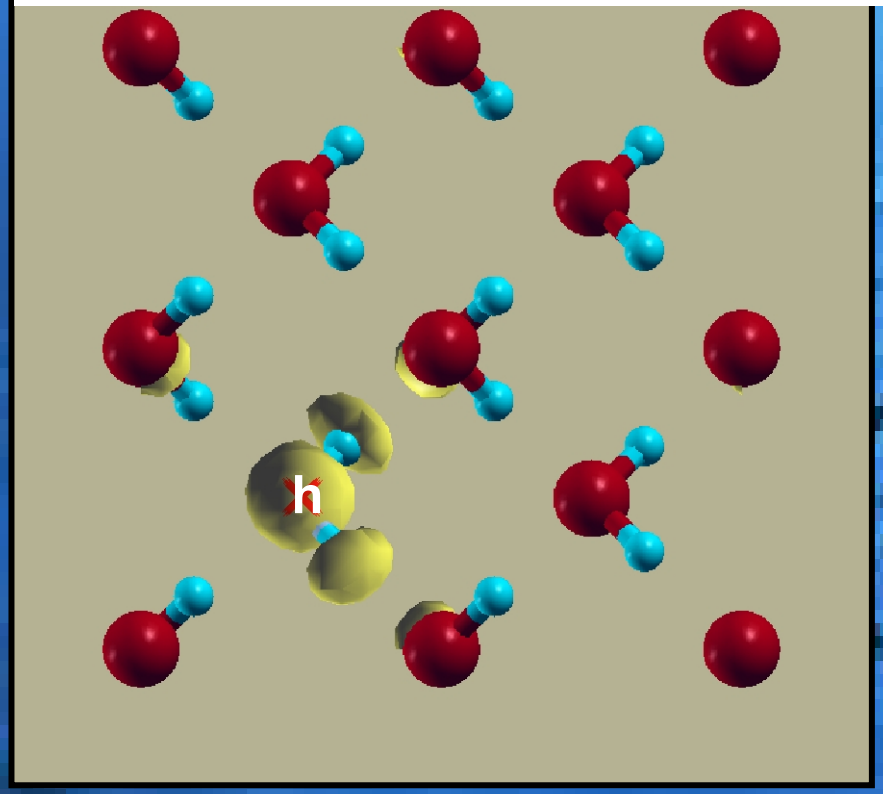
BSE - calculation



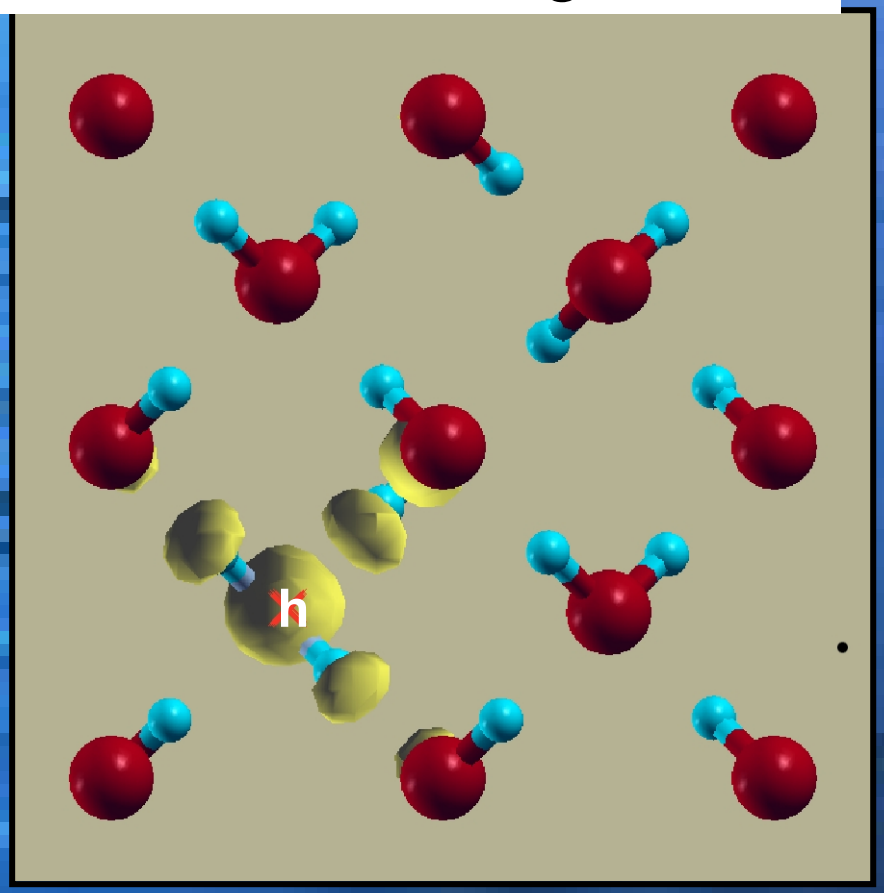


EXCITON WF

e-h pair localized on the 1st shell: short range order

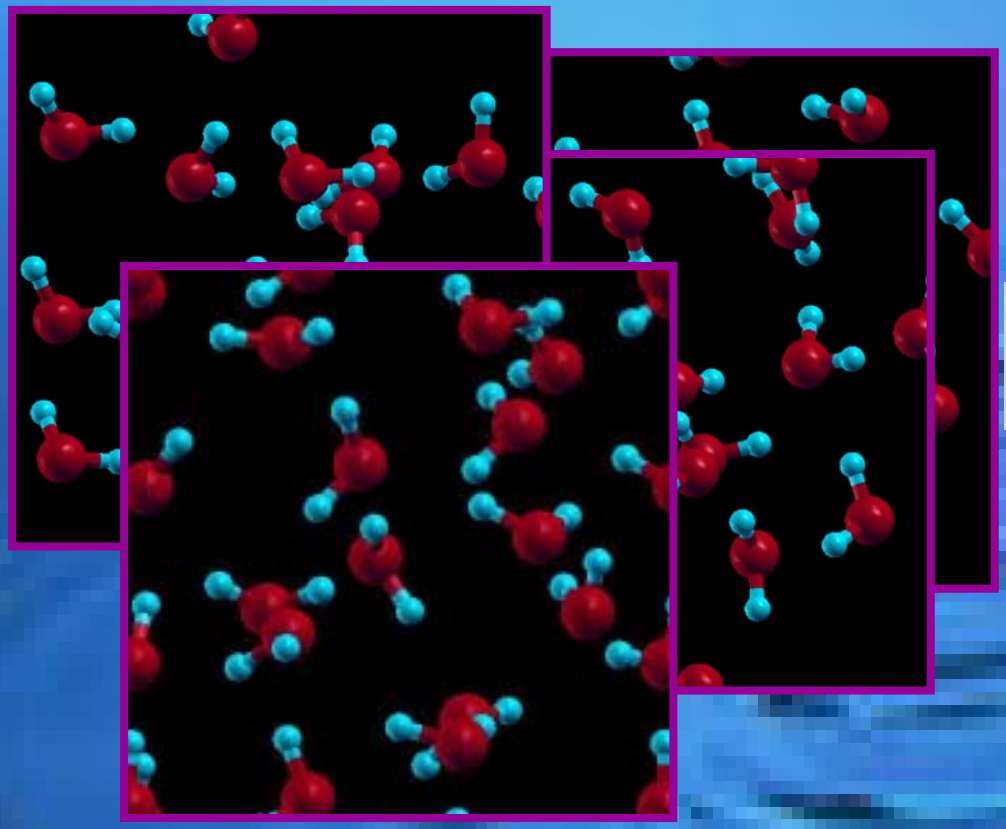


ordered



disordered

Increasing the disorder… liquid water



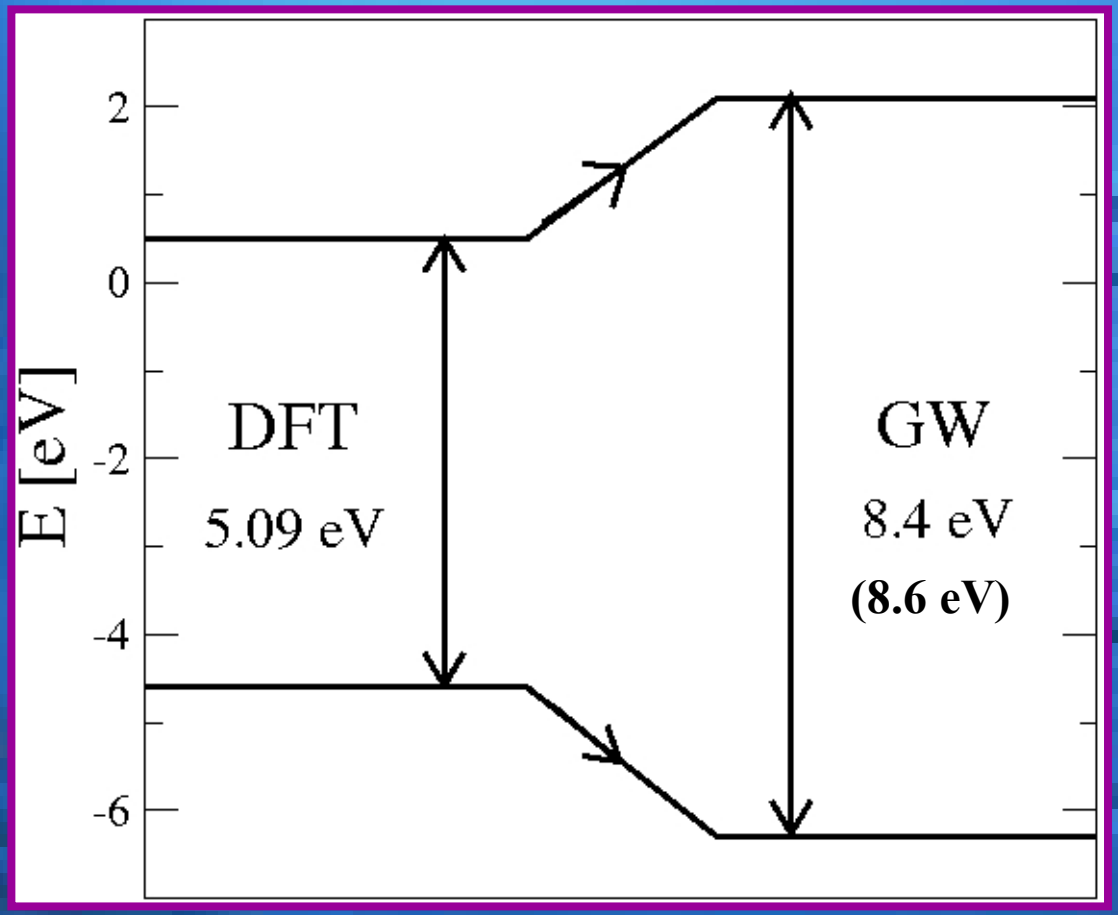
20 molecular dynamics snapshots and average of results.

Configurations of 17 molecules in a box with 15 a.u. side obtained with classical molecular dynamics simulations*

* TIP3P; 40ns simulation run; snapshots every 2ns, NVTensamble Performed by Michele Cascella (EPFL)

Electronic gap

V. Garbuio, M. Cascella, L. Reining, R. Del Sole and O. Pulci, PRL 97, 137402 (2006)



GGA: Egap=5.09 eV

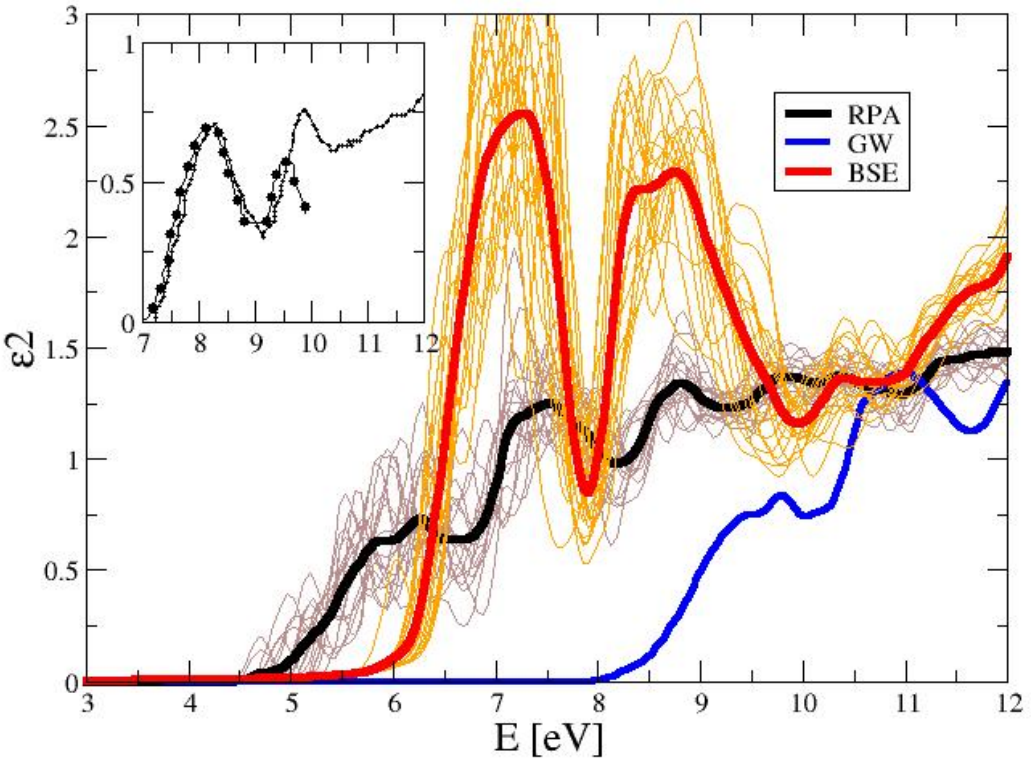
LDA: Egap=4.85 eV

Experimental gap:
8.7 ± 0.5 eV

Bernas *et al.*, Chem. Phys. **222**, 151 (1997)

Exc-absorption spectra

Calculations done on 20 snapshots



*Exp:Painter L.R. *et al.*, PRL 21, 282 (1968) - Kerr G.D. *et al.*, PRA 5, 2523 (1972)

V. Garbuio, M. Cascella, L. Reining, R. Del Sole and O. Pulci, PRL 97, 137402 (2006)
For a review see V. Garbuio, M. Cascella, O. Pulci, J. Phys.: Condens. Matter 21, 033101 (2009)

increasing disorder

Minimum gap	Ice Ic ord	Ice Ic disord	Liquid water **
DFT	5.76 eV	5.61 eV	5.09 eV
Electronic gap (GW)	9.5 eV	9.0 eV	8.6 eV
“Optical” gap	7.4 eV	7.3 eV	7.2 eV

~

Disorder effects:

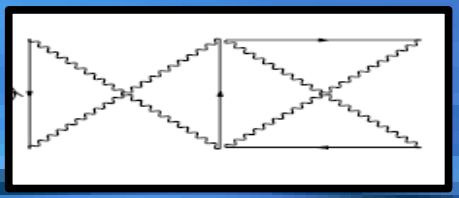
Shrinking of the electronic gap

Bound exciton almost not affected

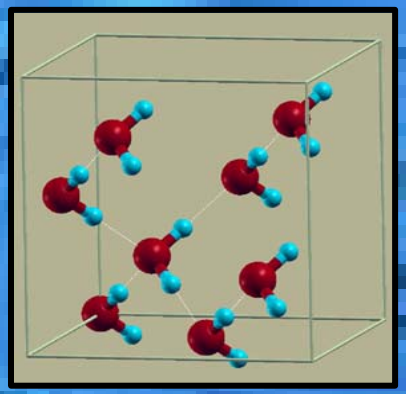
Cancellation effect

OUTLINE:

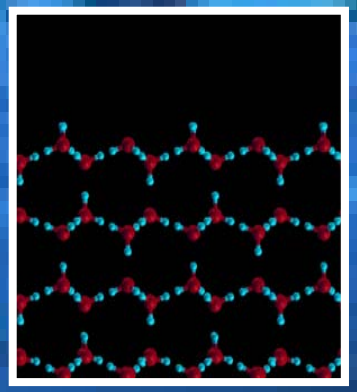
- Theoretical approaches



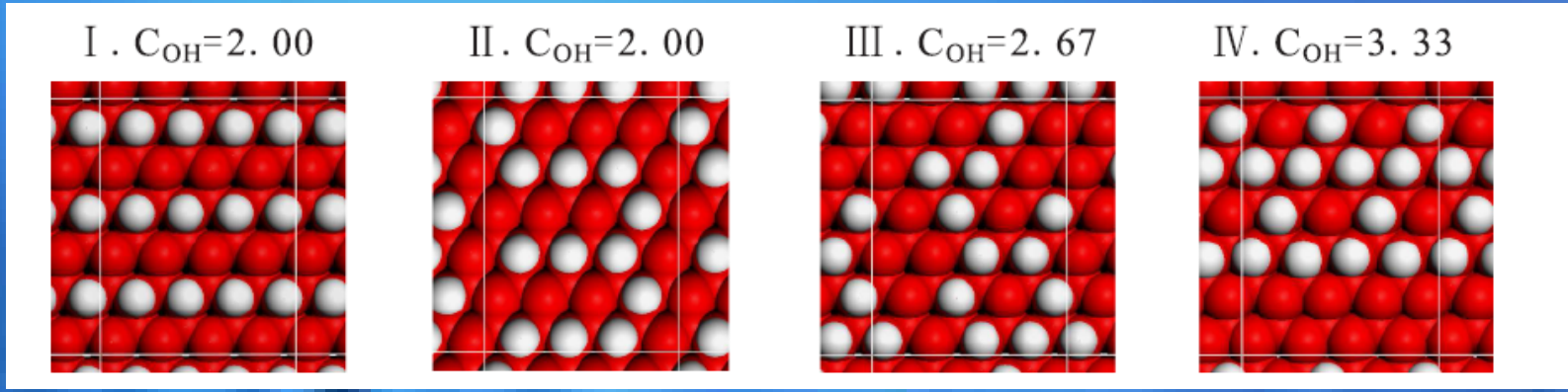
- Ic Ice (bulk)



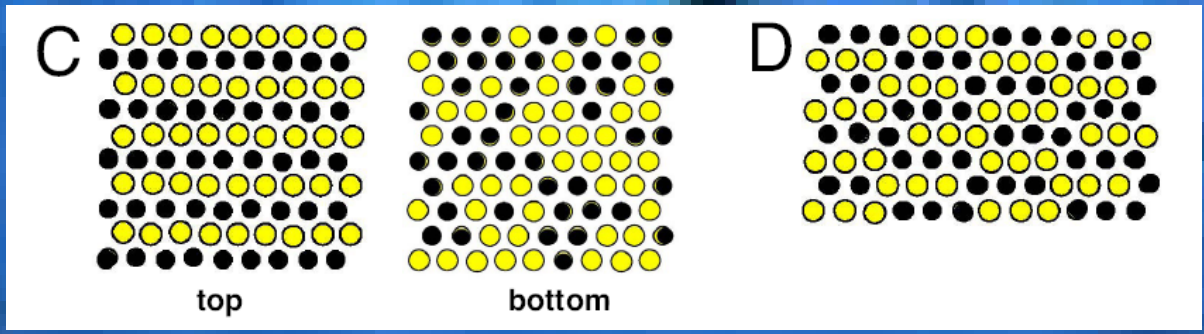
- Ice Ih surface



..and the surface??

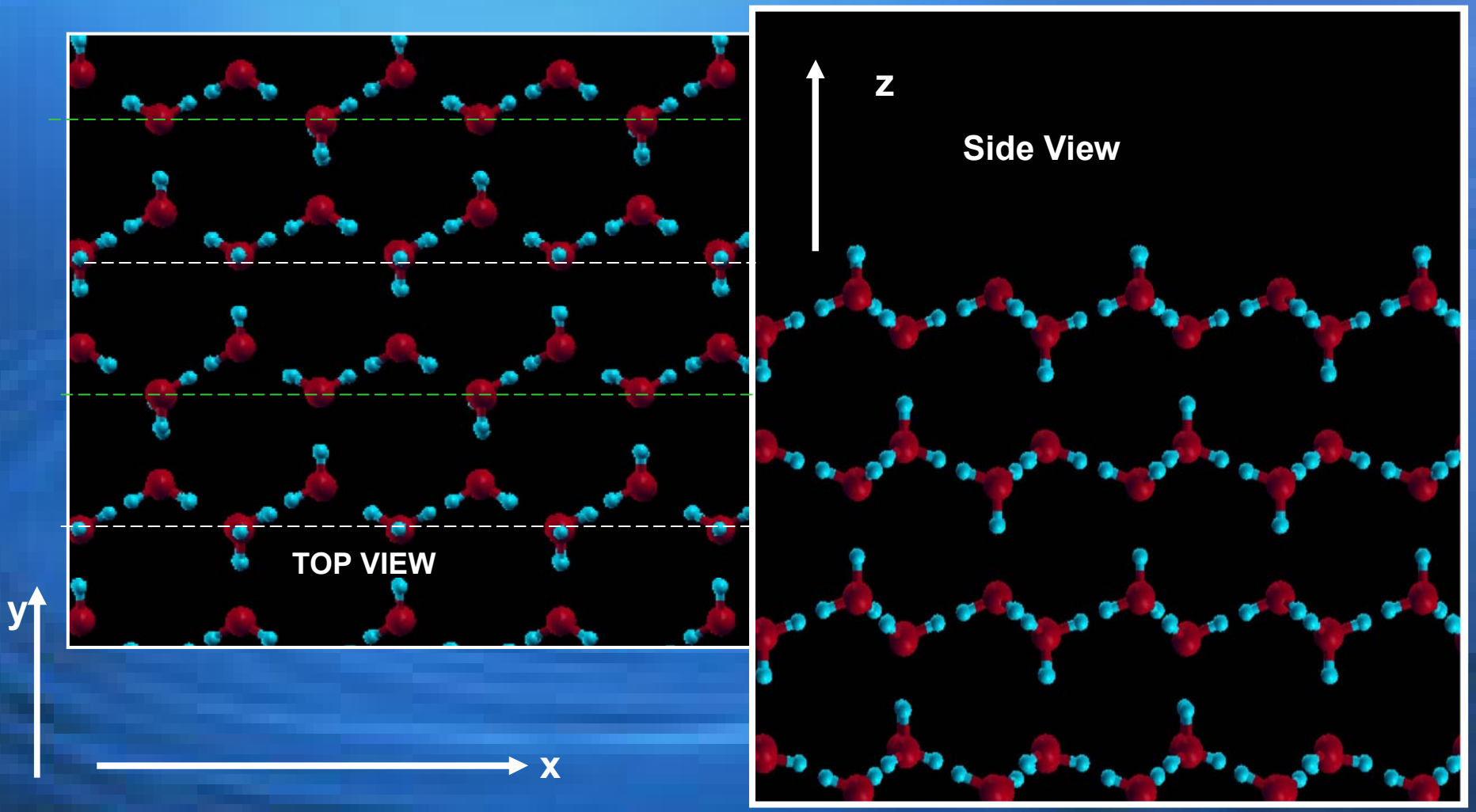


D. Pan et al., *Phys. Rev. Lett.* 101, 155703 (2008)



V.Buch et al., *Proc. Natl Acad. Sci. USA* 105, 5969 (2008)

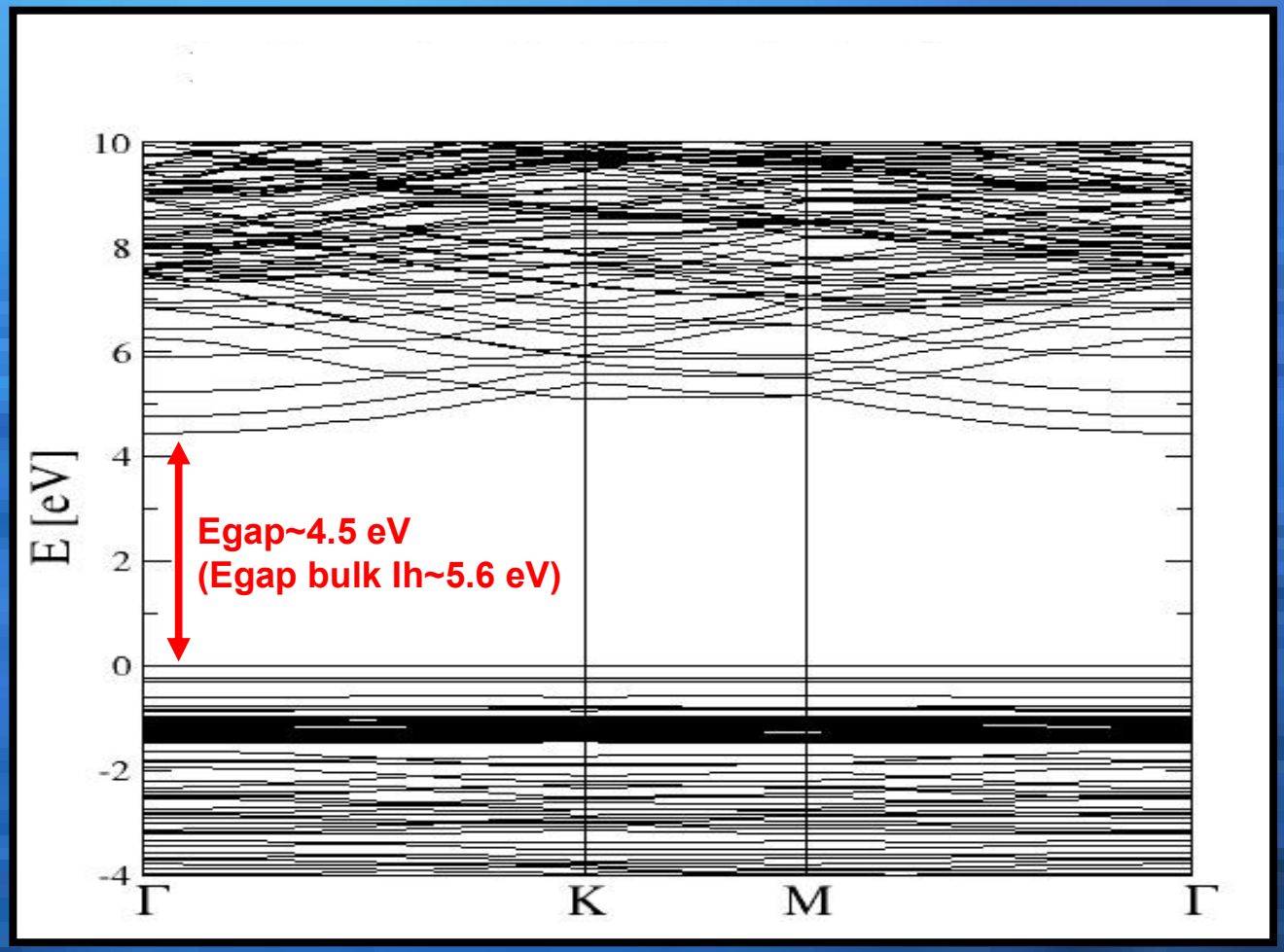
Ice Ih(0001) surface



From F. Baletto, C. Cavazzoni, S. Scandolo, PRL 2005

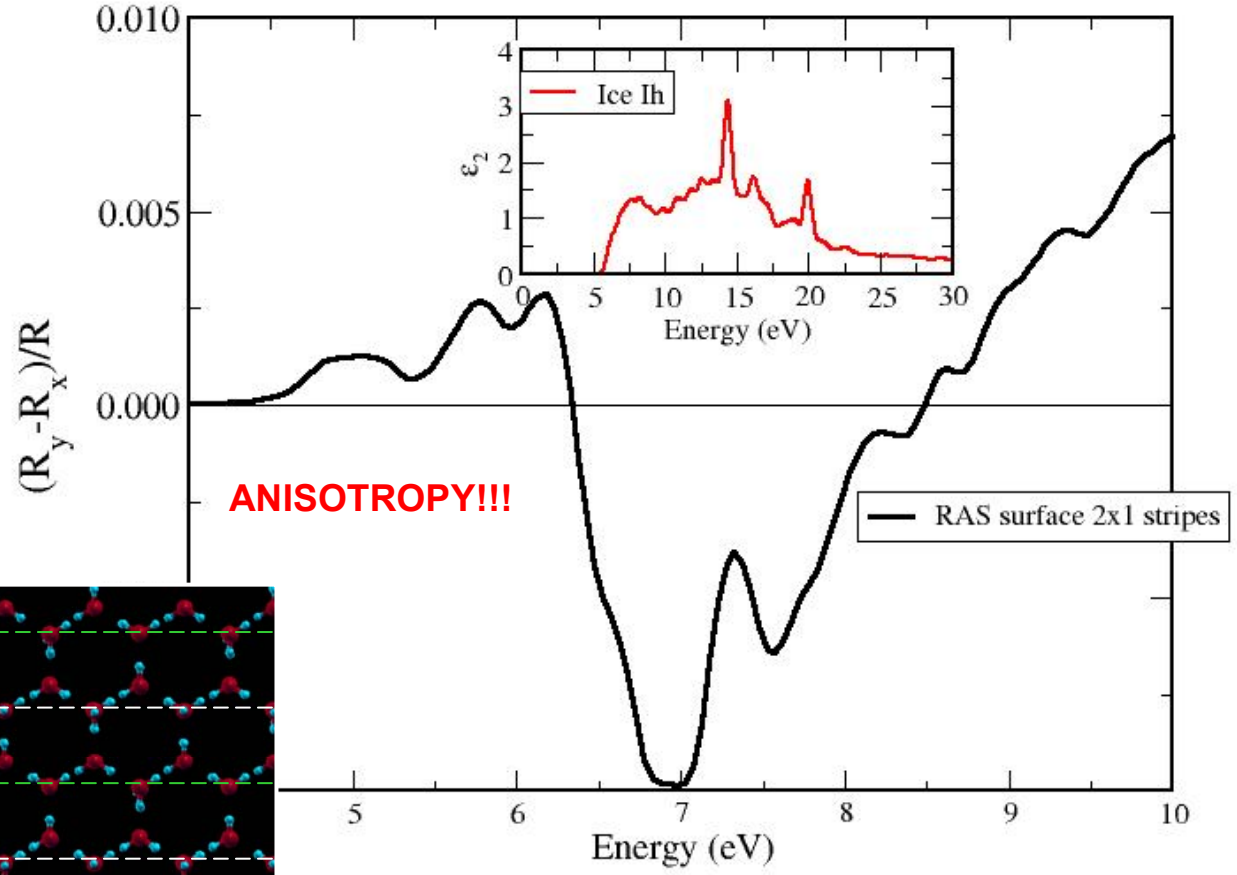
8 molecules per bilayer, 4 bilayers, 96 atoms

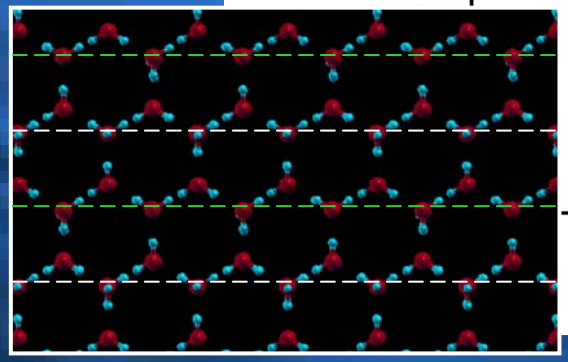
DFT-band structure



Can optics help in understanding the surface geometry?

Preliminary results for the Striped surface





DFT/PW91

Conclusions & perspectives

- Electronic and optical properties of bulk ice Ic slightly modified by proton disorder: differences in density of states, band structures, electronic gap, and optical absorption spectrum
- “Similar” behavior of liquid water
- Effect of disorder: shrinking of the electronic gap not followed by bound exciton that remains almost unaffected.
- Optics *may* probe the order of Ice surfaces

Thanks to:

- Viviana Garbuio (Roma2)
- Rodolfo Del Sole (Roma2)

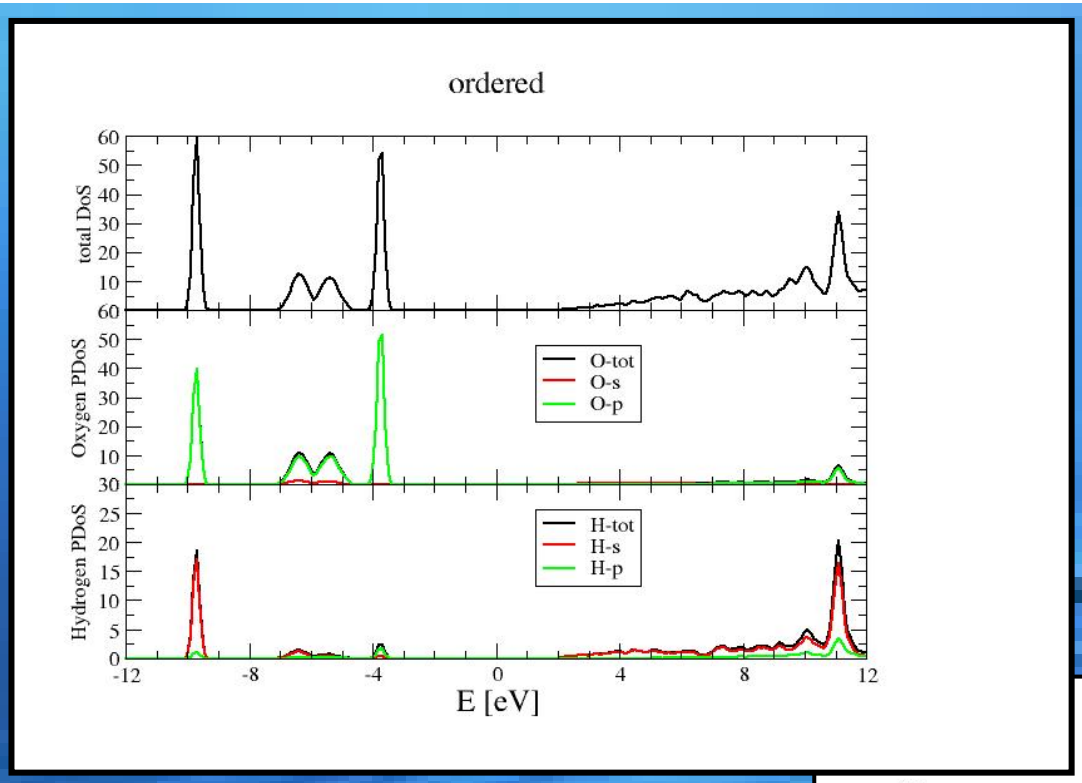
- Michele Cascella (Uni Berne)

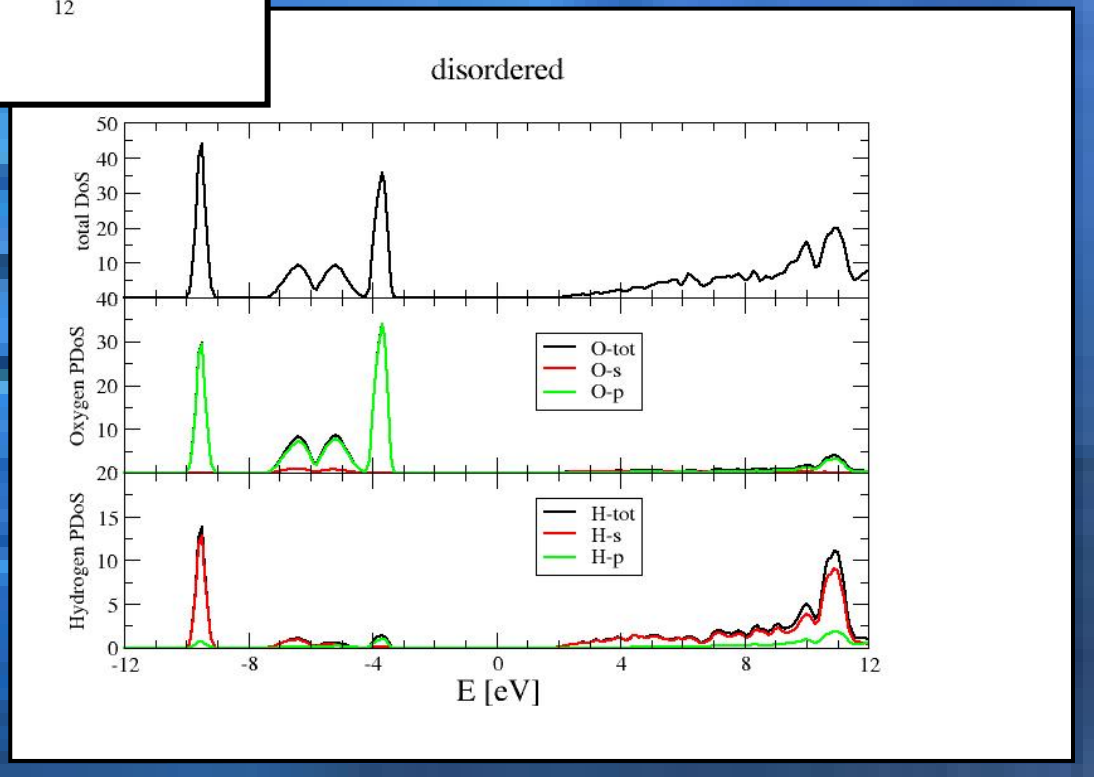
- Erio Tosatti (ICTP, Trieste)
- Sandro Scandolo (ICTP, Trieste)

Thank you for your attention

http://www.etsf.eu

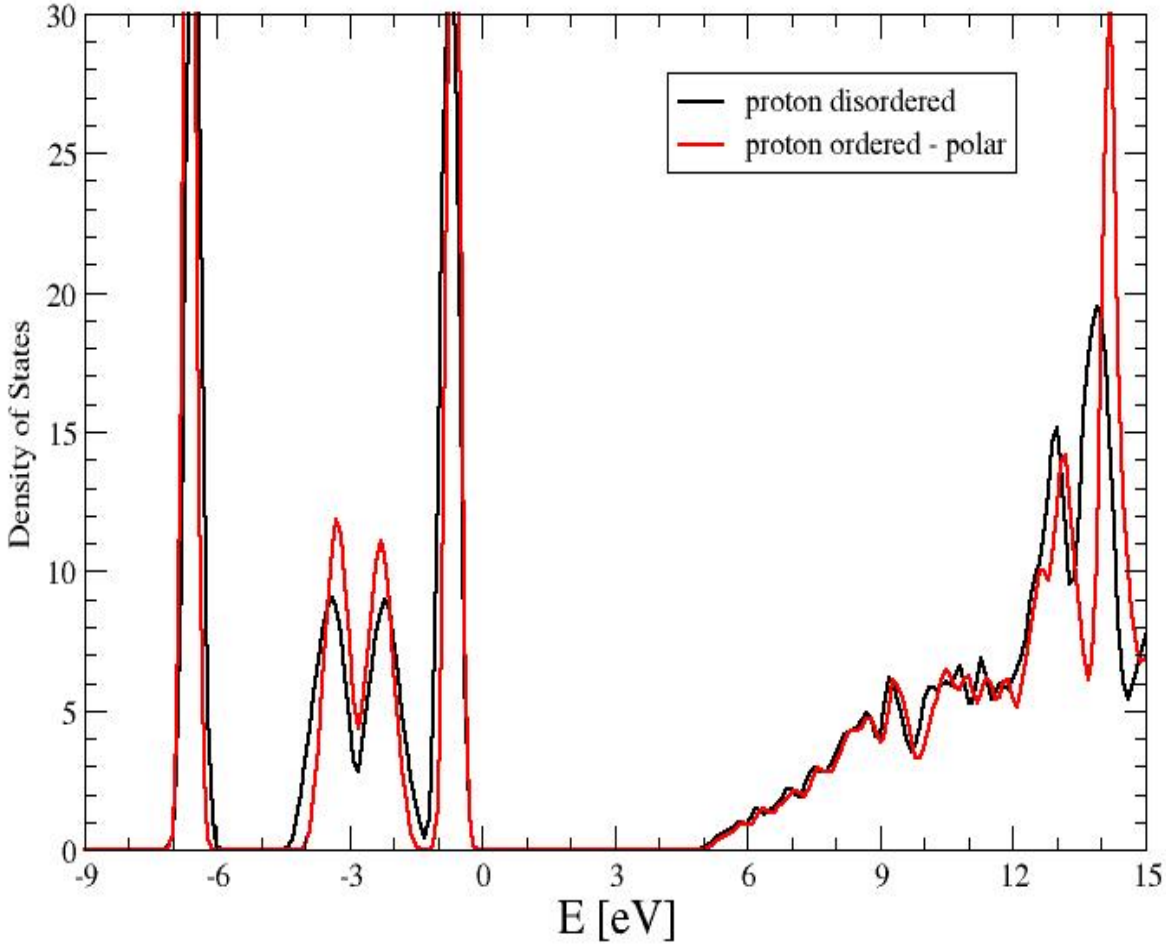
PDOS


ordered
total DoS
Oxygen PDoS
O-tot
O-s
O-p
Hydrogen PDoS
H-tot
H-s
H-p
E [eV]


disordered
total DoS
Oxygen PDoS
O-tot
O-s
O-p
Hydrogen PDoS
H-tot
H-s
H-p
E [eV]

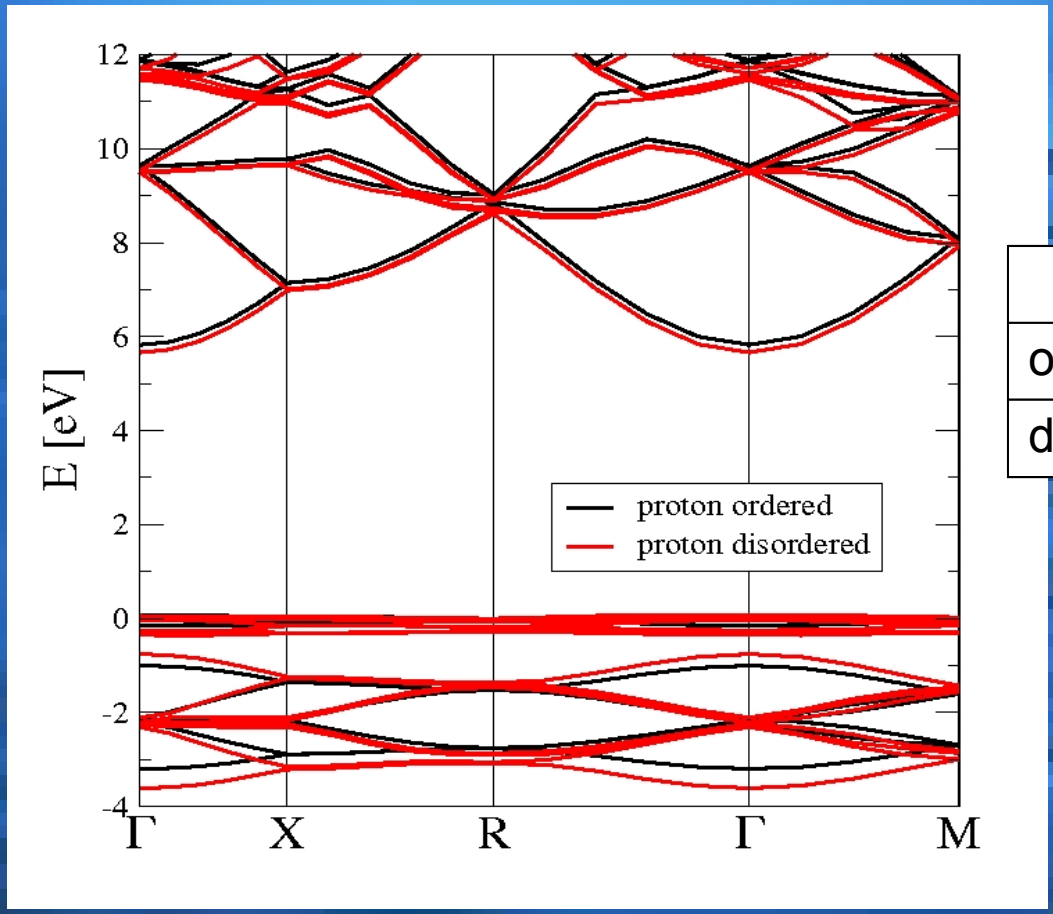
Density of States

DFT calculation



Gap at Gamma

DFT calculation



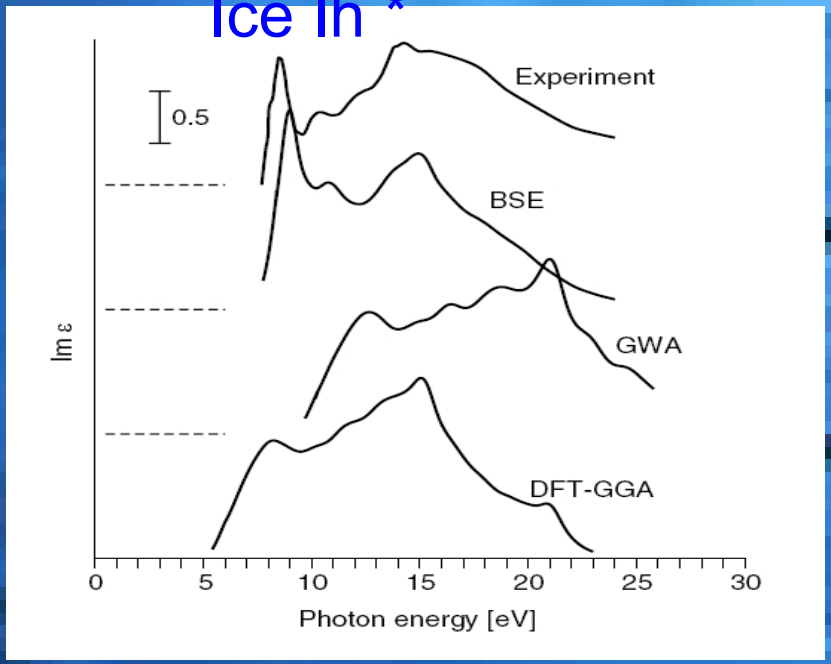
Electronic gap at G

	DFT gap	GW gap
ordered	5.76	
disordered	5.61	

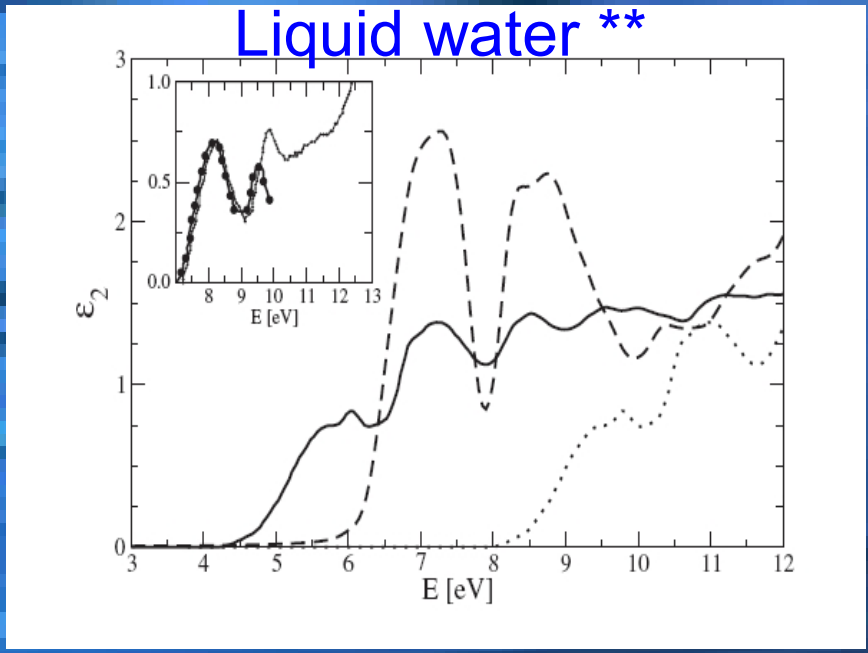
Other phases

	Ice Ic ord	Ice Ic disord	Ice Ih disord	Liquid water **
DFT gap	5.76 eV	5.61 eV	5.6 eV	5.1 eV
GW gap	9.6 eV	9.1 eV	10.1 eV	8.4 eV
Optical gap	7.4 eV	7.3 eV	6.9 eV	6.0 eV

Ice Ih *



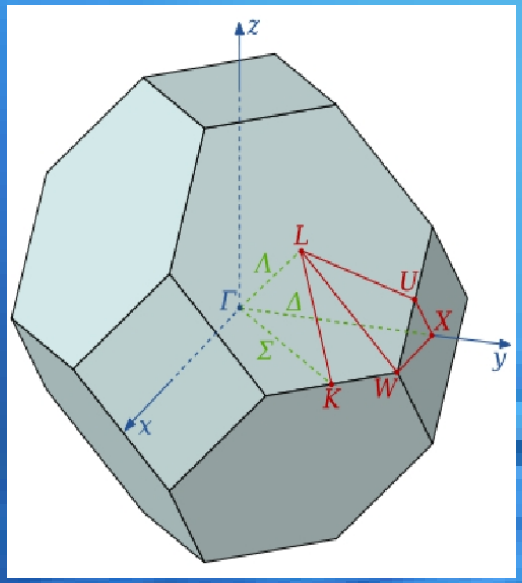
Liquid water **



* P. H. Hahn et al., *Phys. Rev. Lett.* **94**, 037404 (2005)

** V. Garbuio et al., *Phys. Rev. Lett.* **97**, 137402 (2006)

Electronic gap

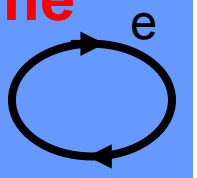


Proton ordered

	DFT gap	GW gap
☝	5.97	9.6
K	9.44	13.0
L	8.86	12.7
X	9.56	13.2
W	9.73	13.2

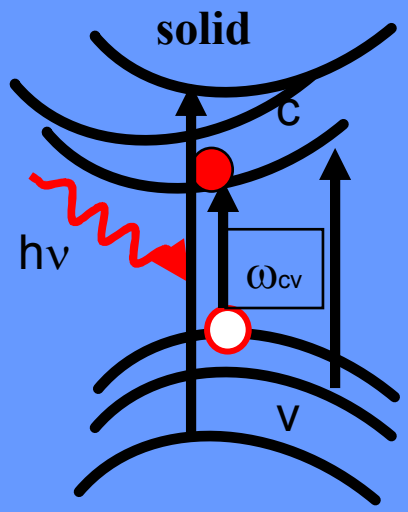
Proton disordered : DFT gap at G = 5.61

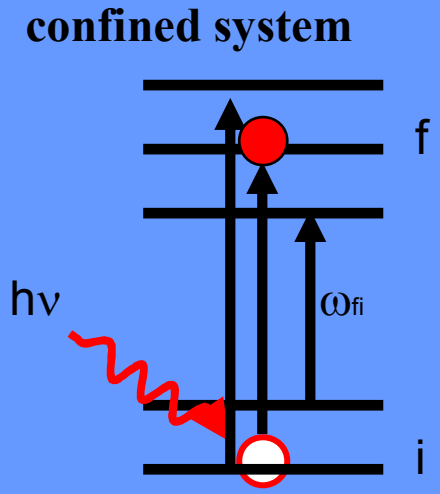
Optical properties within single quasiparticle scheme



Random Phase Approx. = **sum over independent transitions**

(application of Fermi's Golden Rule to an **independent** particle system)





Optical Absorption

$$\mathrm{ABS}^{\mathrm{RPA}}(\omega) \propto \sum_{vc} \left| \langle \varphi_c | \hat{D} | \varphi_v \rangle \right|^2 \delta(\omega - (\varepsilon_c - \varepsilon_v))$$

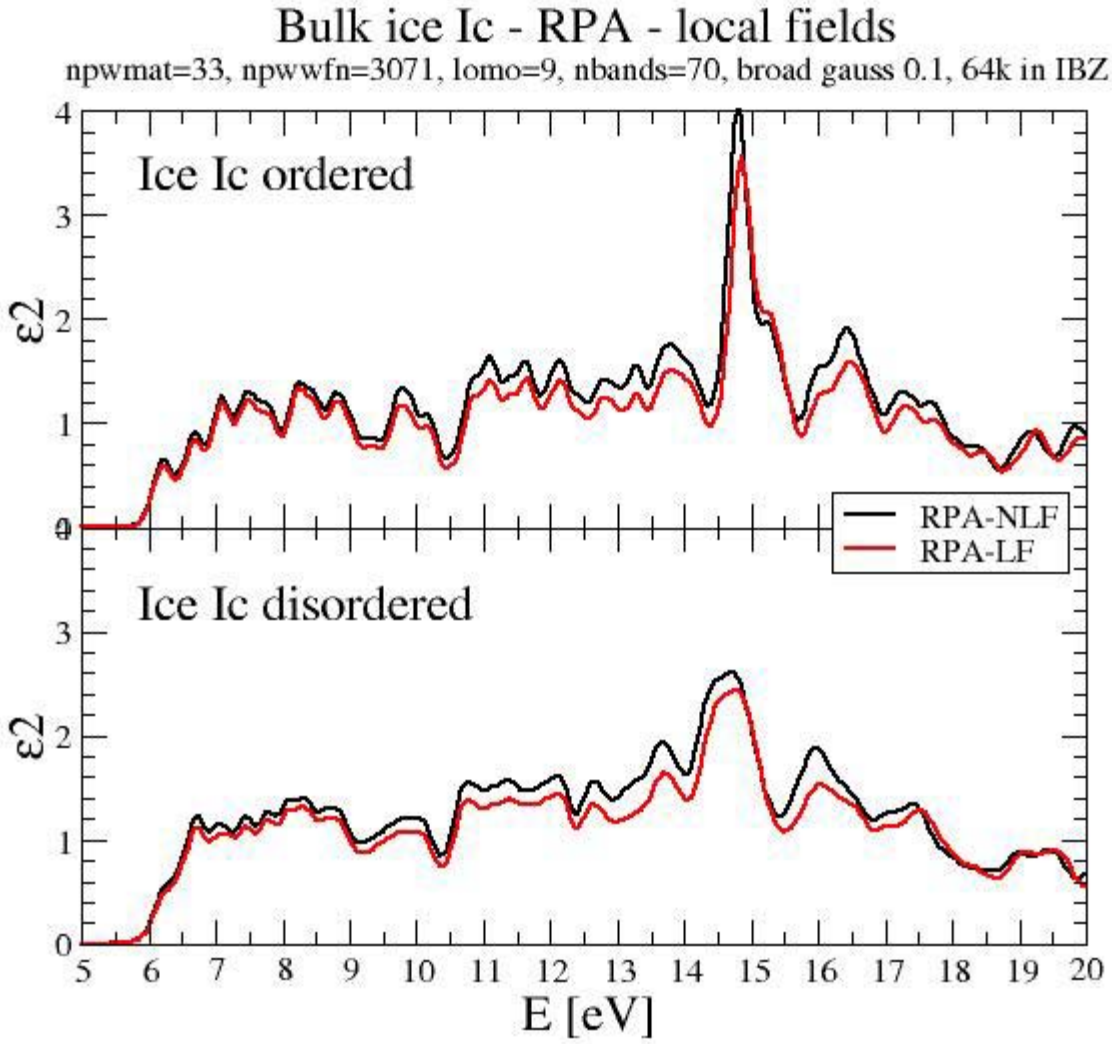
Fermi's Golden Rule

sum over independent transitions

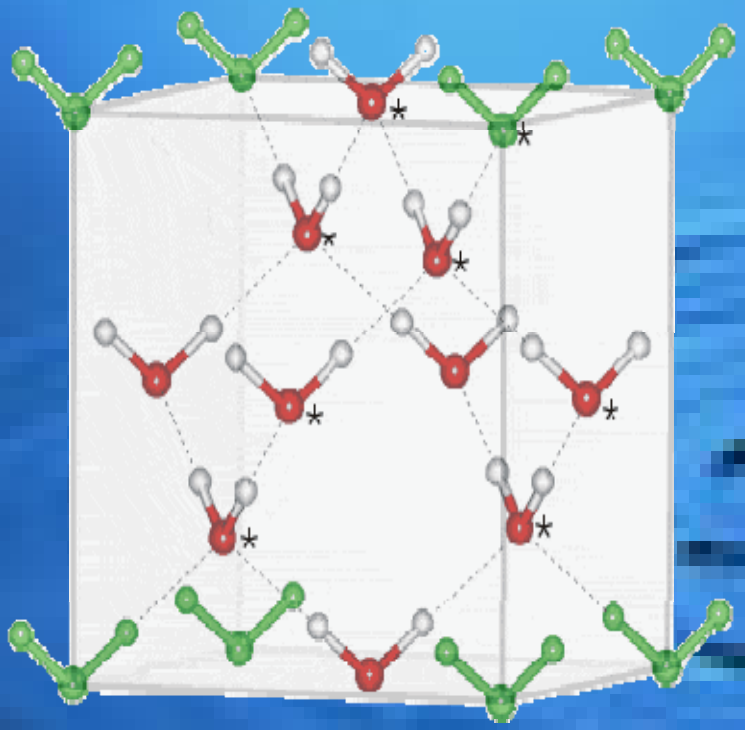
DFT wavefunctions

GW energies

LOCAL FILEDS EFFECTS



Cubic ice

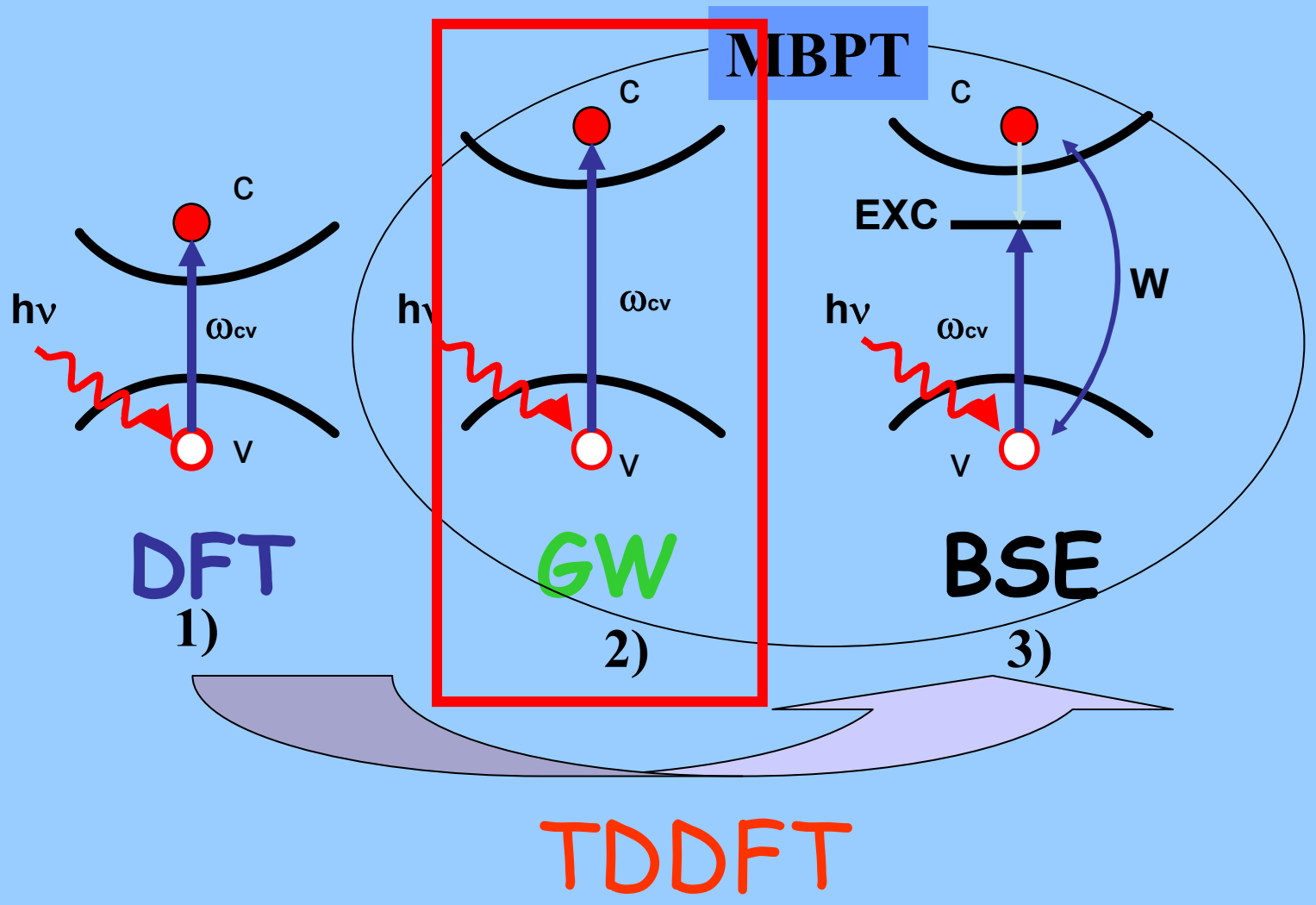


- It is a metastable form of ice that can be formed, by condensation of water vapor, at ambient pressure but low temperatures

Studied within DFT and Tight-binding

G. Pastori Parravicini et al., *Phys. Rev.* **B 8**, 3009 (1973)
L. Resca et al., *phys. stat. sol. b* **81**, 129 (1977)
W. Y. Ching et al., *Ferroelectrics* **153**, 25 (1994)

DFT, GW and Excitonic Effects

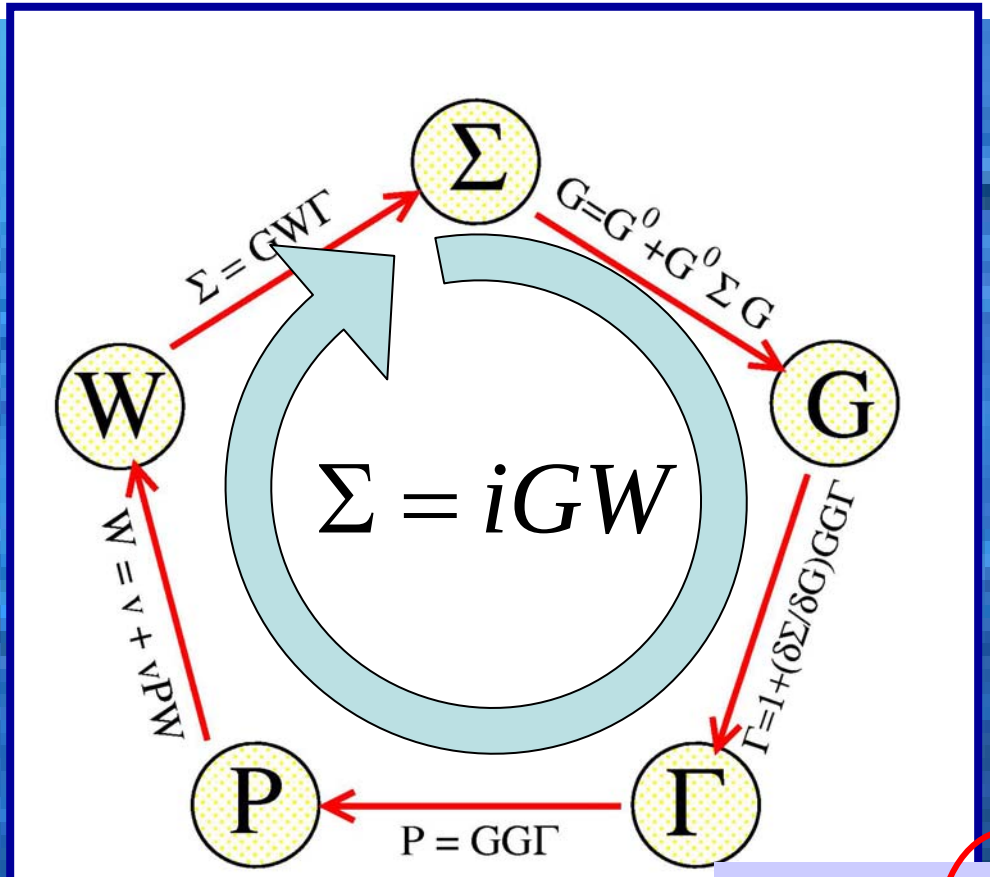


Assess the accuracy/ability of MBPT versus the more conventional (and efficient) TDDFT

Quasi-particle equation: (Step 2)

Lars Hedin 1965

$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H)\Psi_i^{QP}(\vec{r},\omega) + \int \Sigma(\vec{r},\vec{r'},\omega)\Psi_i^{QP}(\vec{r'},\omega)d\vec{r'} = E_i^{QP}(\omega)\Psi_i^{QP}(\vec{r},\omega)$$



G: single particle Green's function
W: screened Coulomb interaction

$$W = \varepsilon^{-1}V$$

GW approximation

$$W = \varepsilon^{-1} V$$

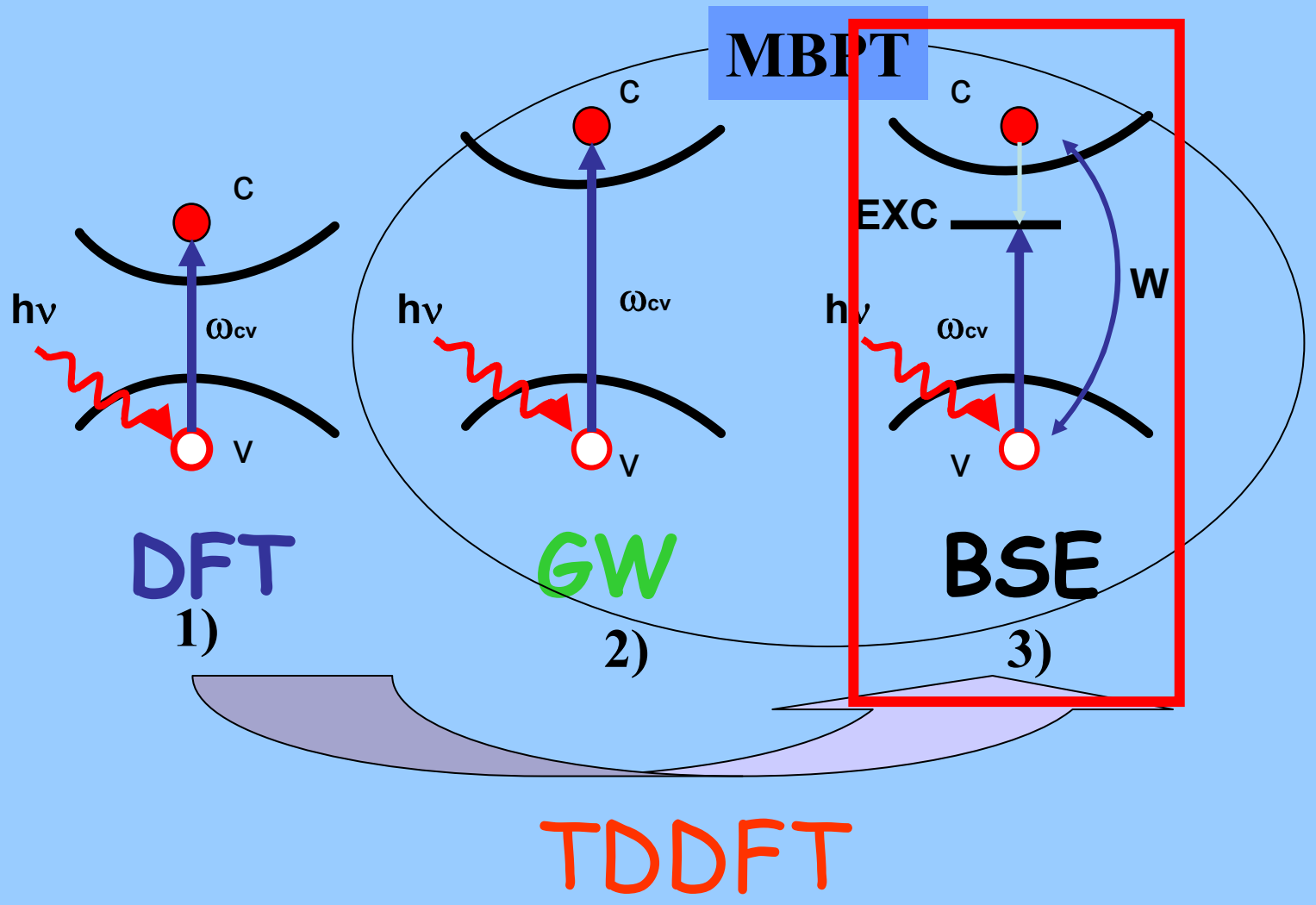
$$\varepsilon_{G,G'}(q,\omega)$$

Has to be inverted!!!!
(limit: 16000x16000)

Empty states summation:
~100-1000 empty states have to be included

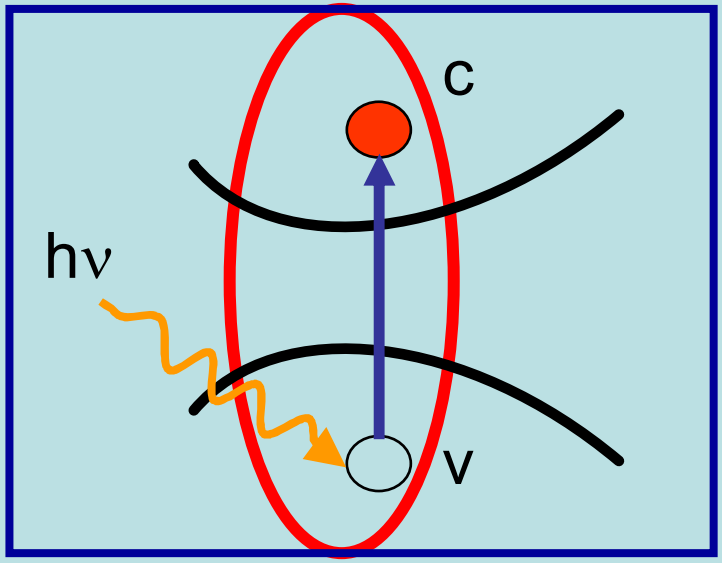
Electronic gaps (I-A) in good agreement with exp.

DFT, GW and Excitonic Effects



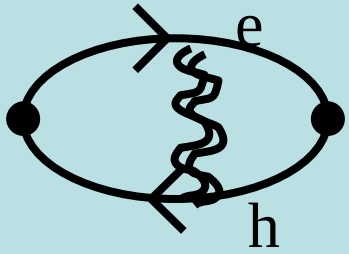
Assess the accuracy/ability of MBPT versus the more conventional (and efficient) TDDFT

Step 3: calculation of optical spectra within the Bethe Salpeter Equation



Absorption spectra

A photon excites an electron from an occupied state to a conduction state



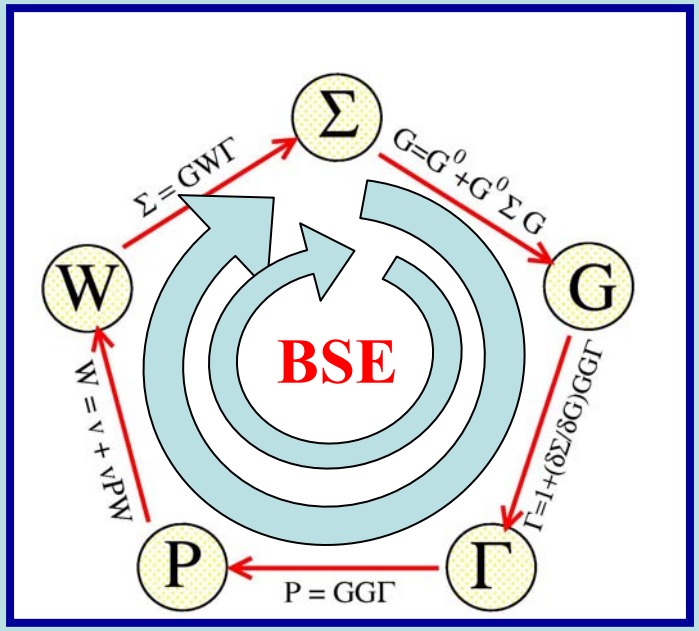
$$\overline{{}^4P} = {}^4P_{IQP} + {}^4P_{IQP}\ {}^4\Xi\ {}^4\overline{P}$$

Bethe Salpeter Equation (BSE)

Kernel: $\Xi = \bar{v} - W$

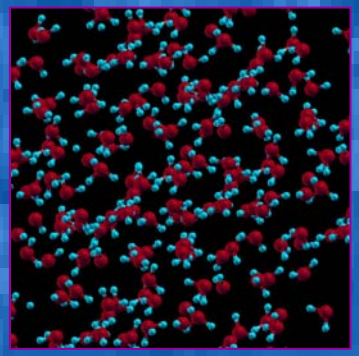
e-h exchange

bound excitons

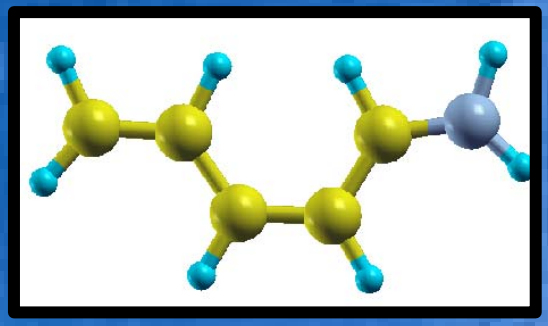


Examples:

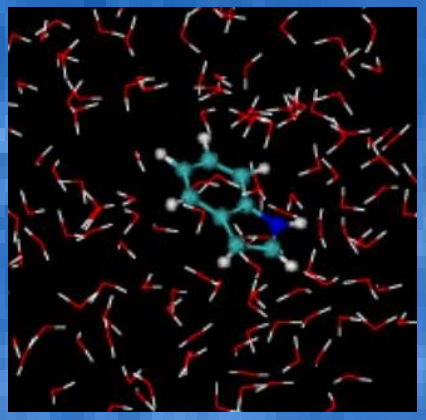
- Optical spectra of water



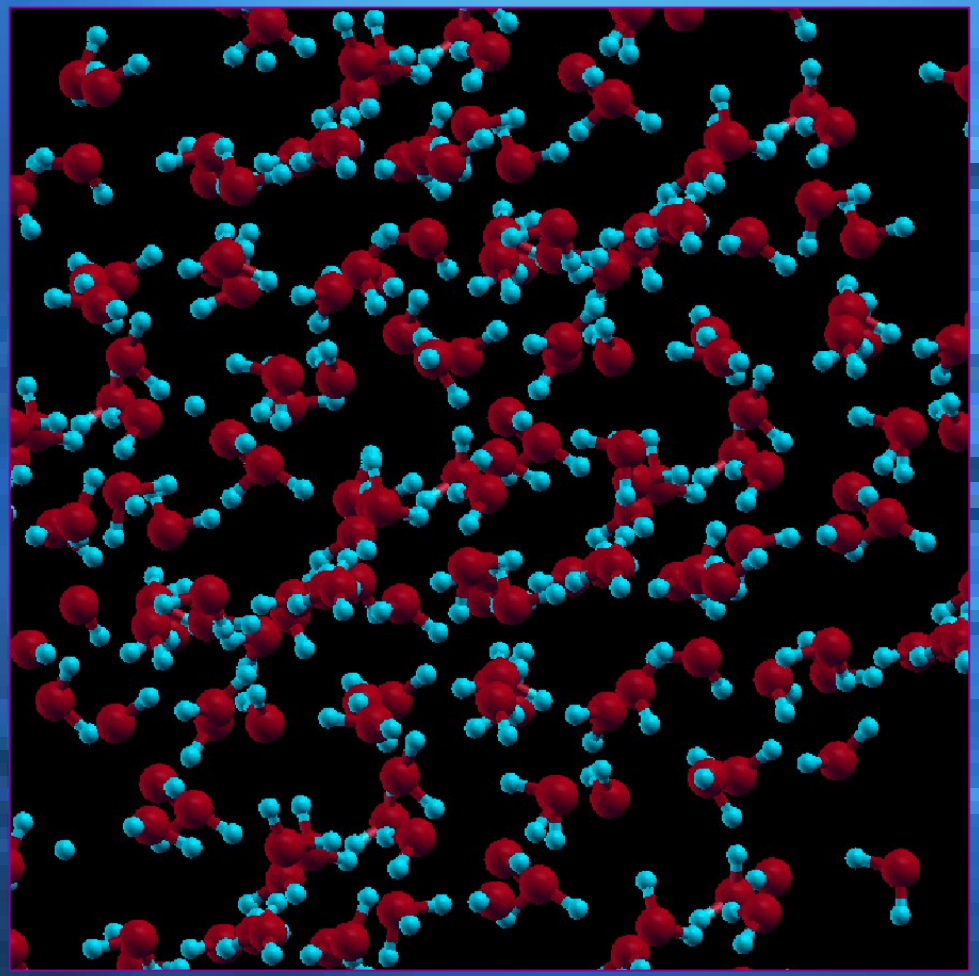
- Minimal Base Schiff Model



- indole in water solution: a QM/MM approach



the solvent! water



Liquid water is a disordered system

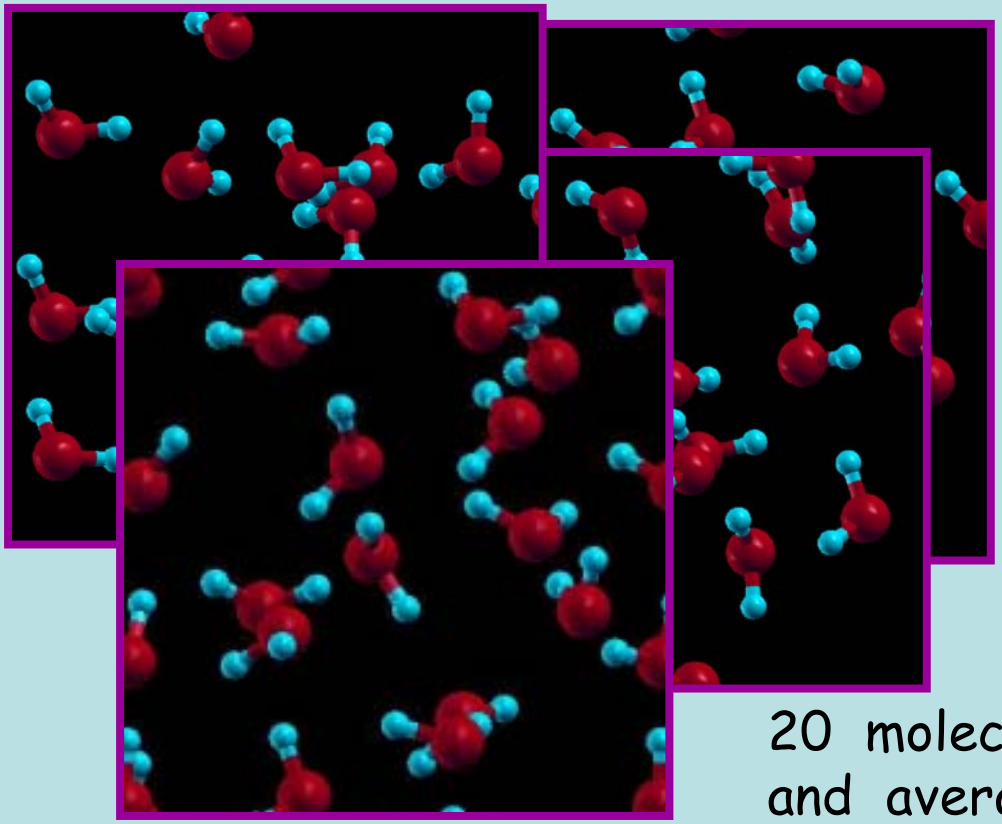
↓

huge unit cell

impossible to study within MBPT the optical absorption of such a large system!!

The "sample"

Relatively small cell



Liquid water is a disordered system

↓

~~Huge unit cell~~

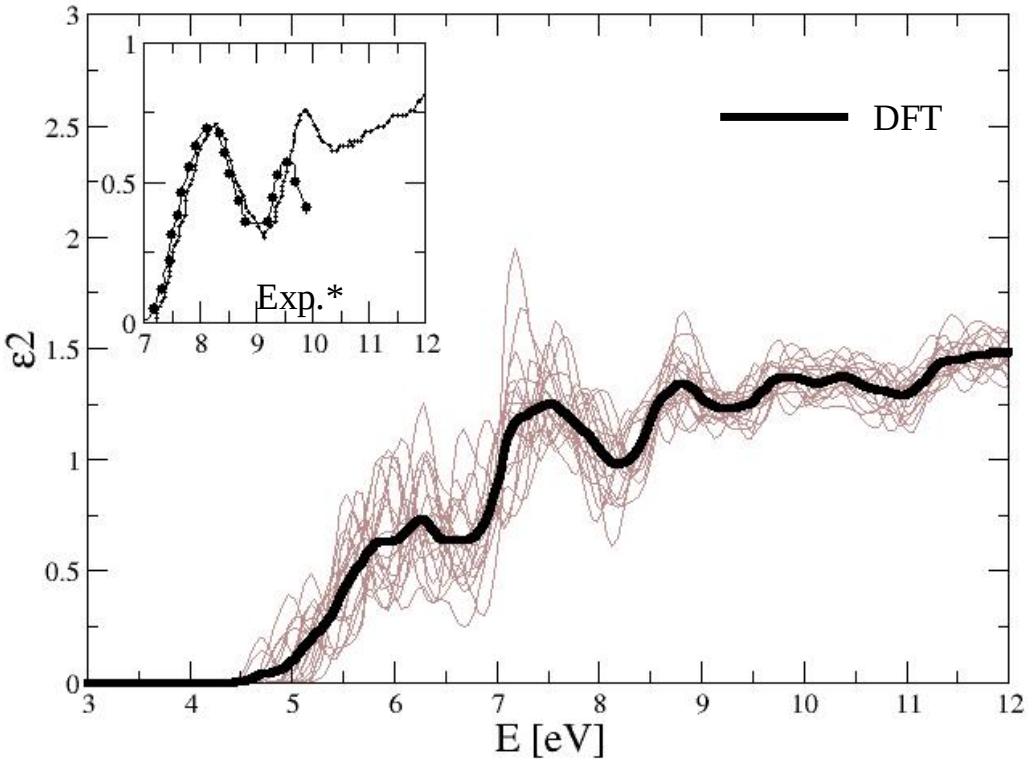
↓

20 molecular dynamics snapshots and average of results.

Configurations of 17 molecules in a box with 15 a.u. side obtained with classical molecular dynamics simulations*

* TIP3P; 40ns simulation run; snapshots every 2ns, NVTensamble Performed by Michele Cascella (EPFL)

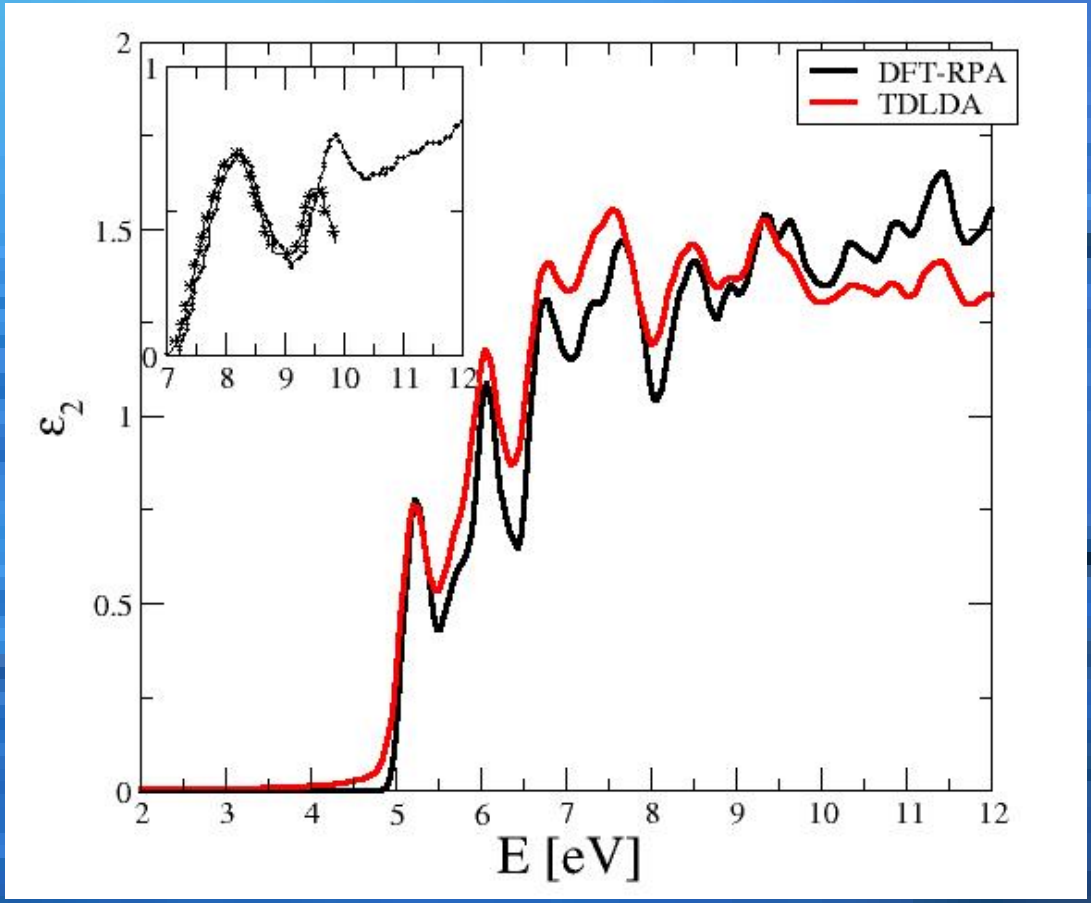
DFT-absorption spectra



*Exp:Painter L.R. *et al.*, PRL **21,** 282 (1968) - Kerr G.D. *et al.*, PRA **5,** 2523 (1972)

TDLDA does not work for H_2O

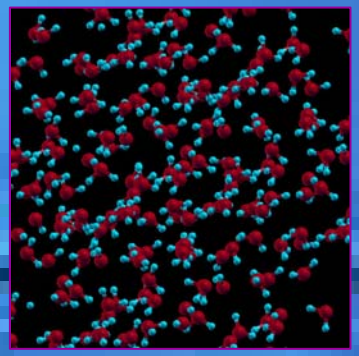
1-snapshot Optical absorption spectra



TDLDA: No improvement with respect to DFT

Examples:

- Optical spectra of water



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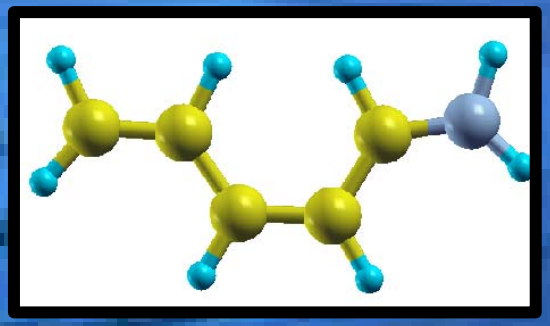
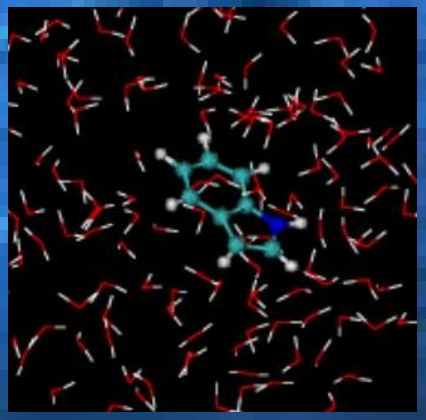
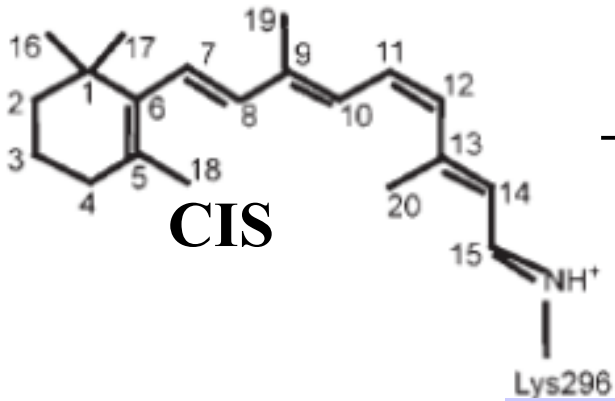


- indole in water solution: a QM/MM approach

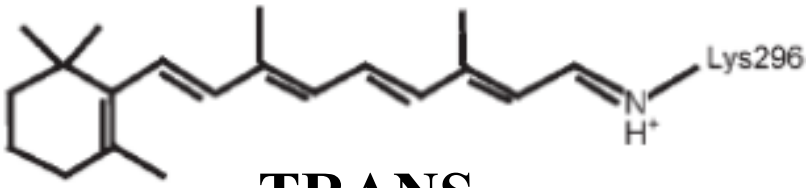


Retinal



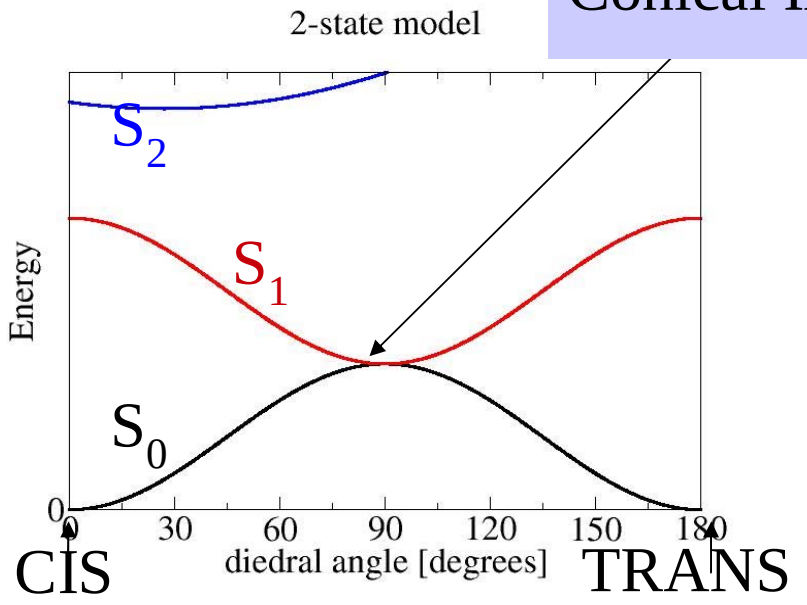
CIS

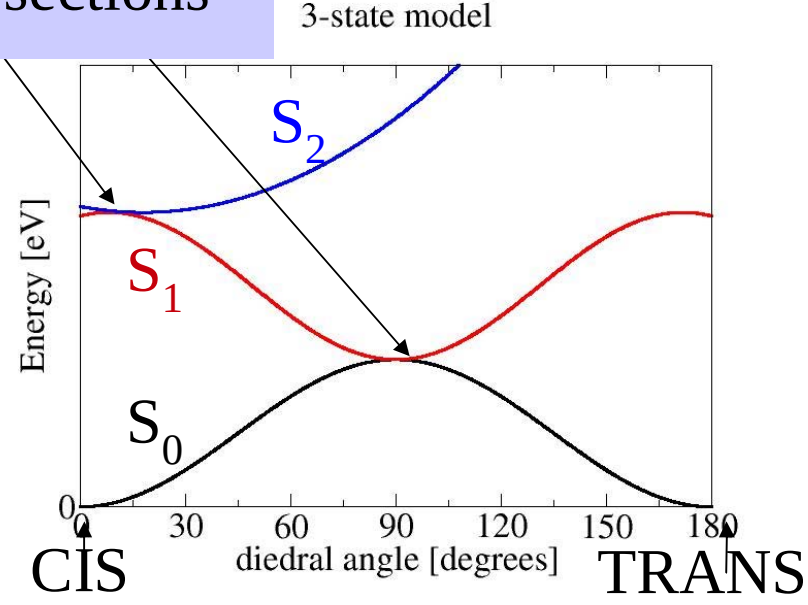
$h\nu$



TRANS

Conical Intersections

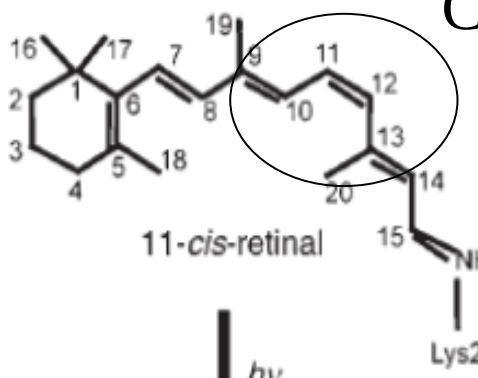


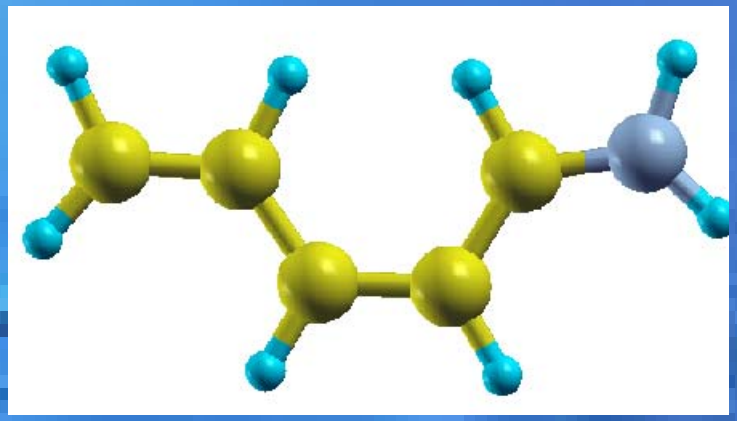


Kobayashi, Saito, Ohtani, *Lett. to Nature*, **414**, 531 (2001)

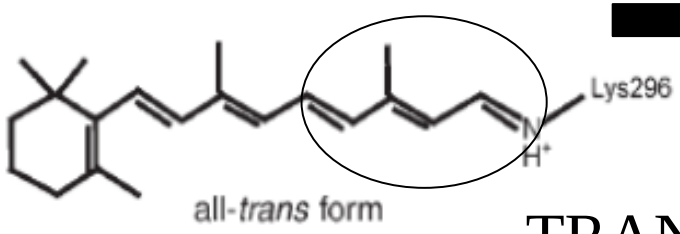
MINIMAL BASE MODEL $(C_5H_6)NH^+_2$

CIS

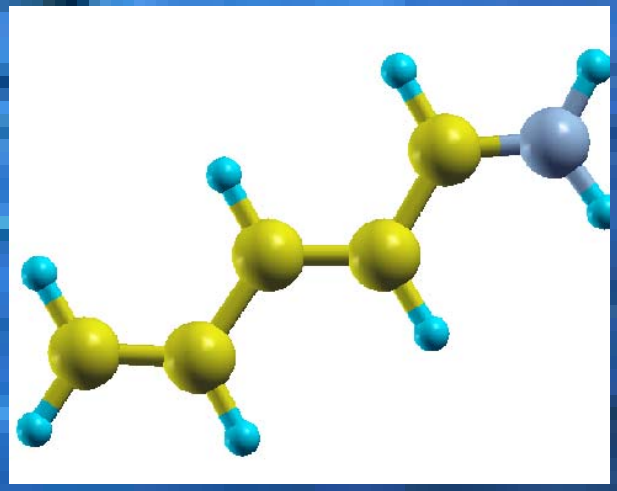




hv



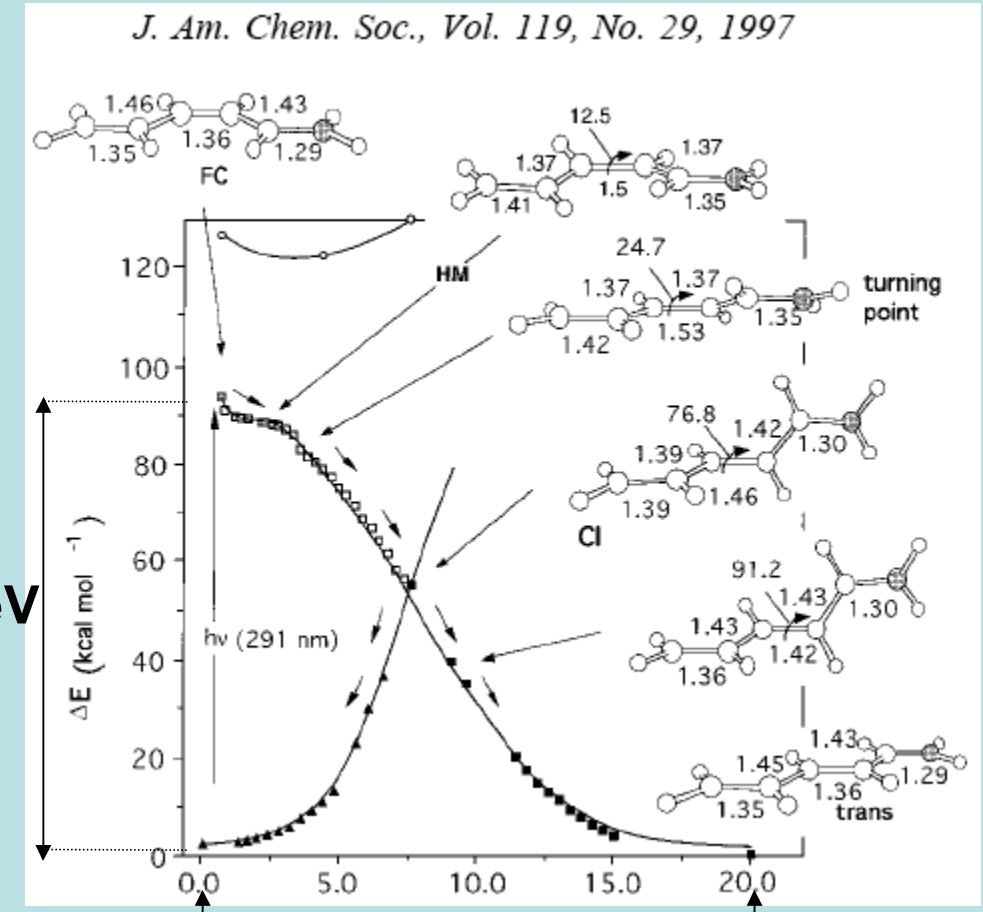
TRANS



Multireference Moller-Plesset calculations (mc-scf)

Along Minimum Energy Paths (MEP) (steepest descent)

M. Garavelli, P. Celani, F. Bernardi, M. A. Robb, and M. Olivucci



E~4 eV

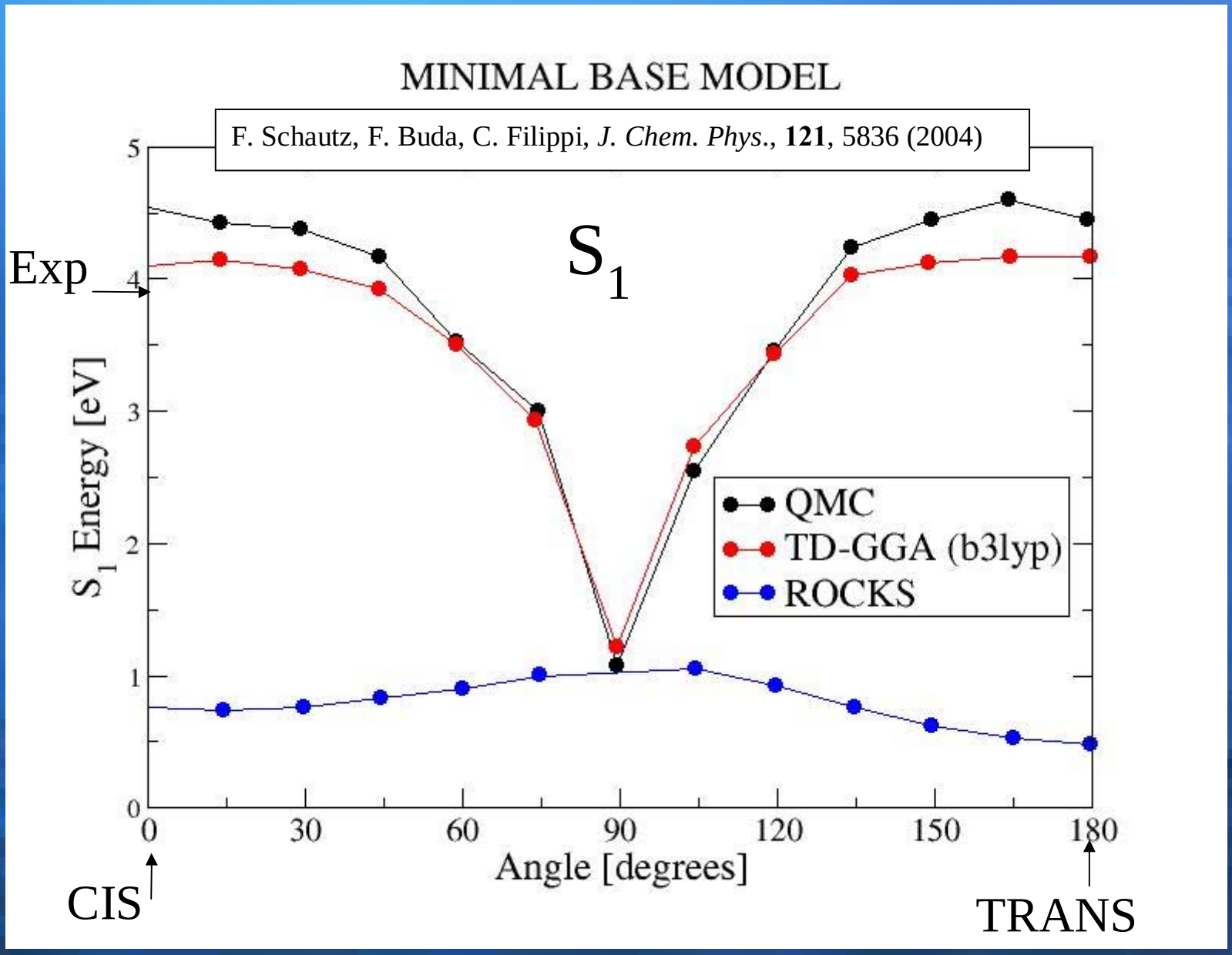
○ → S_2 geometry

□ → S_1 geometry

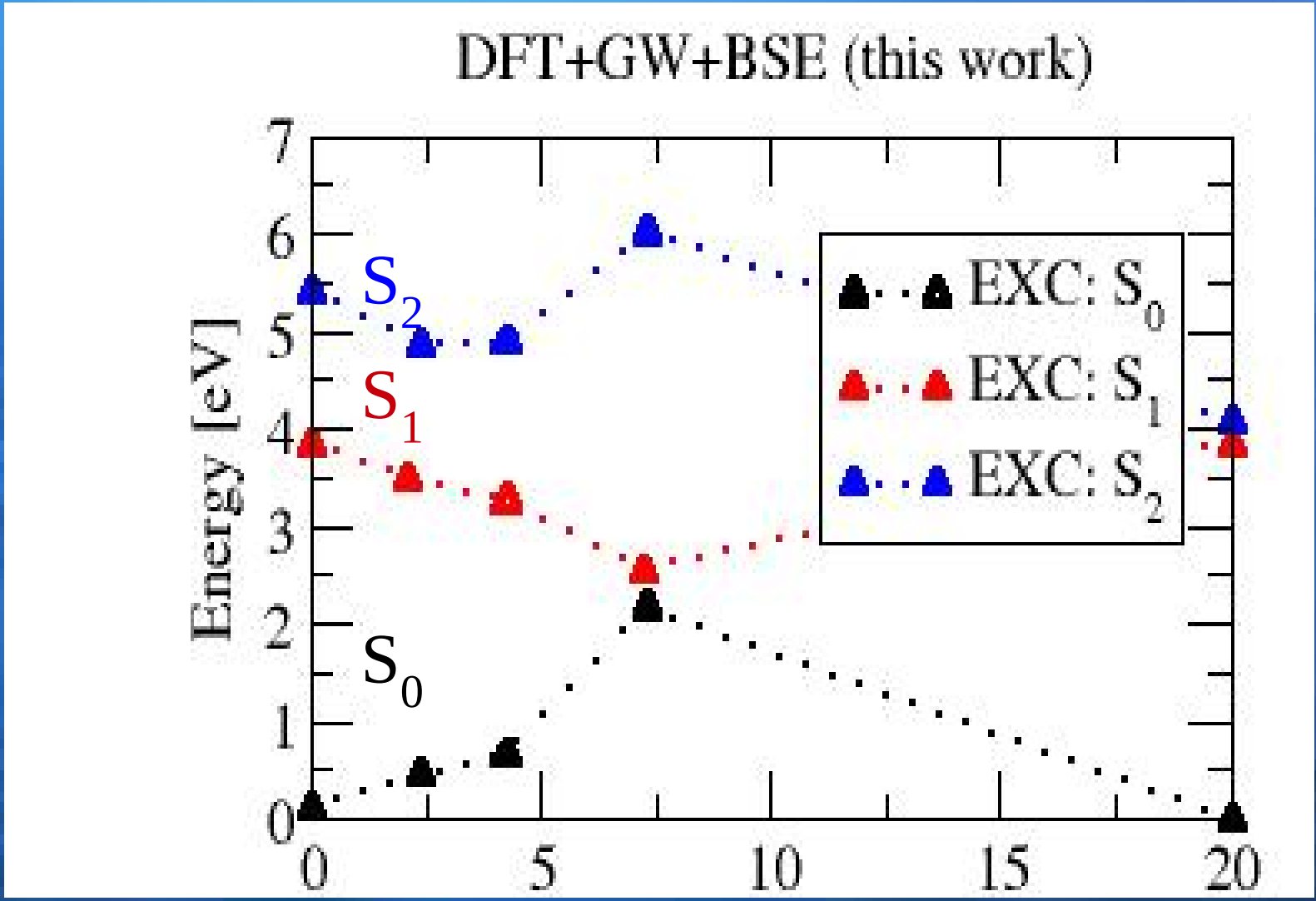
■ ▲ } S_0 geometry

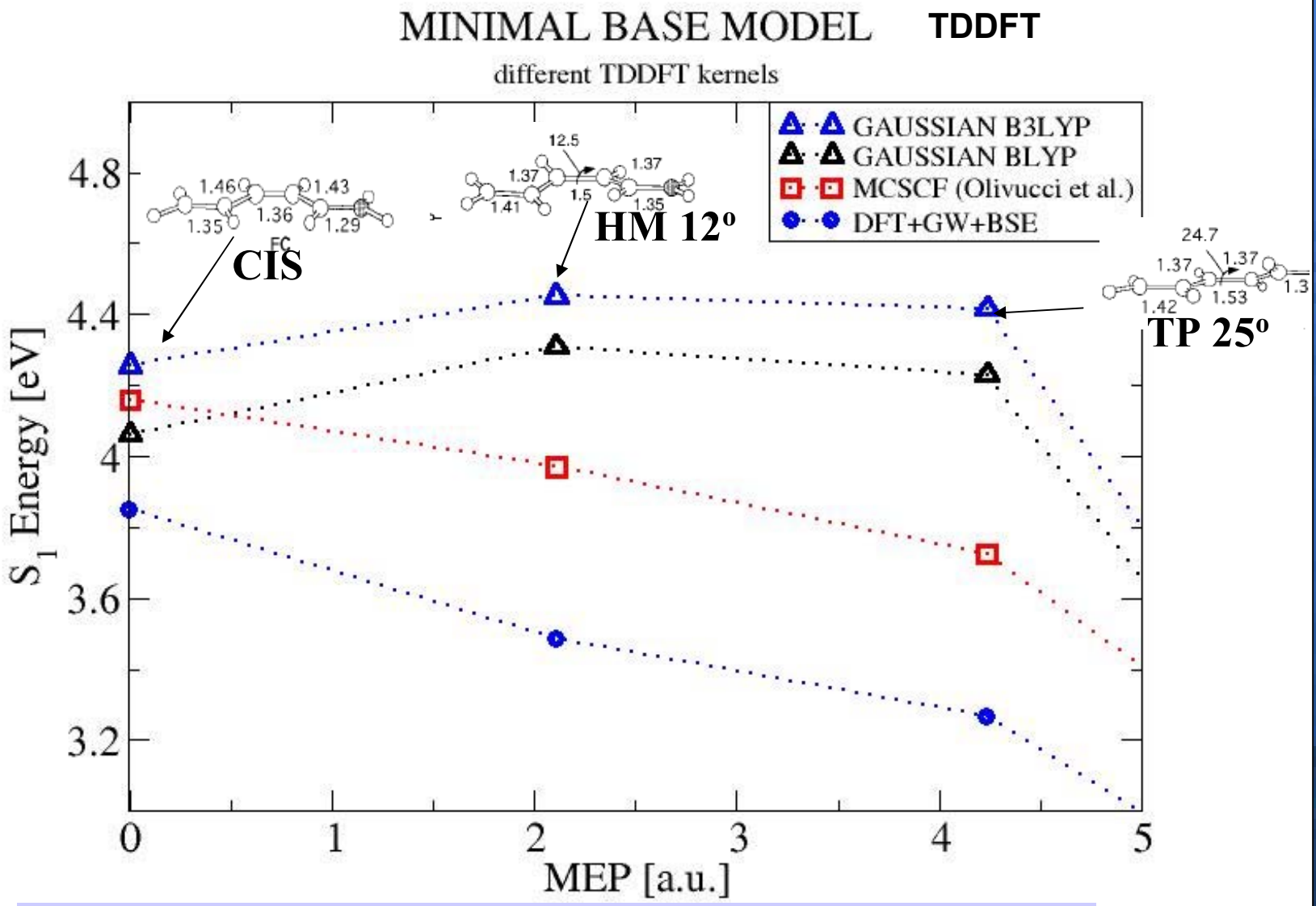
CIS TRANS

…some further theoretical works

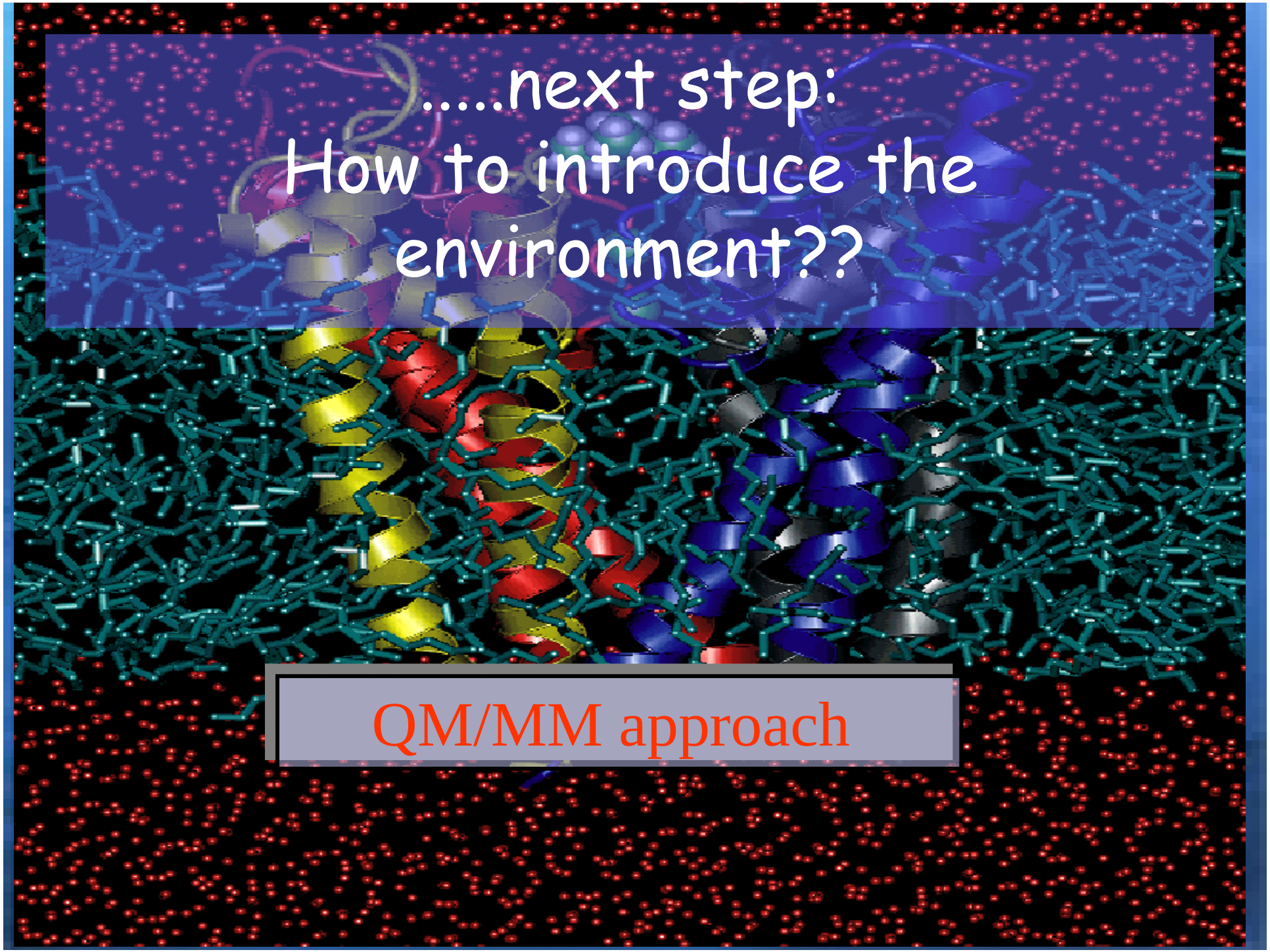


MBPT RESULTS



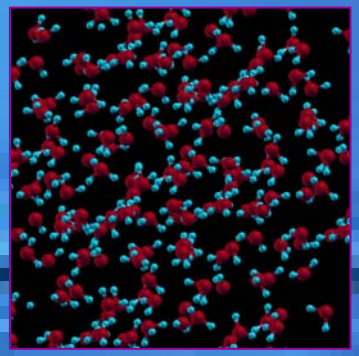


A. Mosca Conte, L. Guidoni, R. Del Sole, and O.P. in preparation

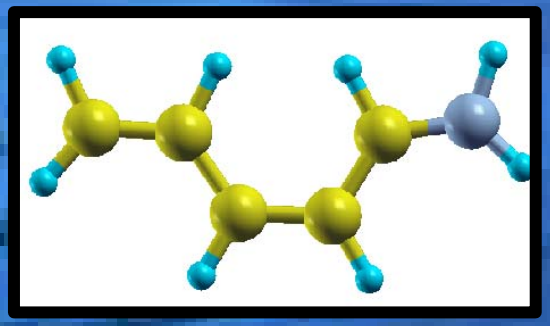

.....next step:
How to introduce the environment??
QM/MM approach

Examples:

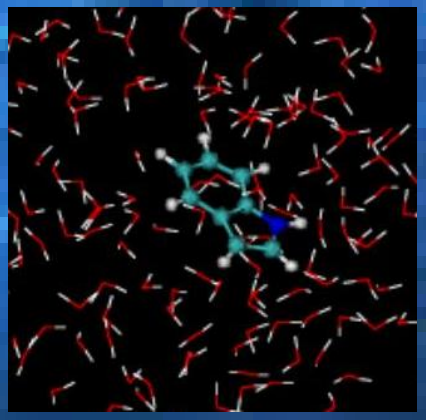
- Optical spectra of water



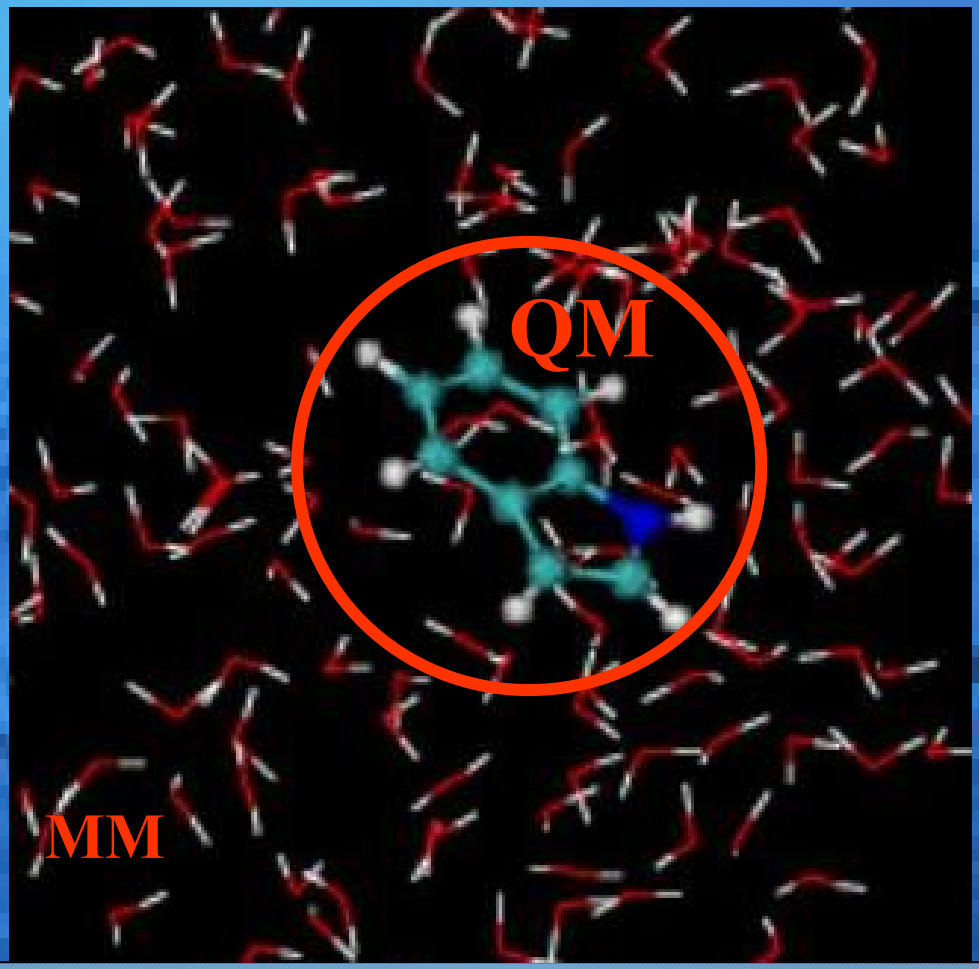
- Minimal Base Schiff Model



- indole in water solution: a QM/MM approach



QM/MM Method+MBPT



Application to indole in water solution

Ground-state properties: **DFT/MM:**

$$\left[T + U^{QM/MM}(\mathbf{r}) + V_{HXC}(\mathbf{r})\right]\psi_{nk}^{KS}(\mathbf{r}) = \varepsilon_{nk}^{KS}\psi_{nk}^{KS}(\mathbf{r})$$

$$U^{QM/MM}(\mathbf{r}) = \sum_{i=1}^{nat(QM)} \frac{Z_{(QM)i}^{ion}}{\left|\mathbf{r} - \mathbf{R}_{(QM)i}\right|} + \sum_{j=1}^{nat(MM)} \frac{q_{(MM)j}^{eff}}{\left|\mathbf{r} - \mathbf{R}_{(MM)j}\right|}$$

Excited state properties: **MBPT/MM**

$$\left[T + V_H(\mathbf{r}) + U^{QM/MM}(\mathbf{r})\right]\psi_{nk}(\mathbf{r}) + \int dr'^3\, \Sigma(\mathbf{r},\mathbf{r}',\varepsilon_{nk}^{QP})\psi_{nk}(\mathbf{r}') = \varepsilon_{nk}^{QP}\psi_{nk}(\mathbf{r})$$

1st perturbation:

P (polarization)

ε^{QP} (QP energies)

W (screened potential)

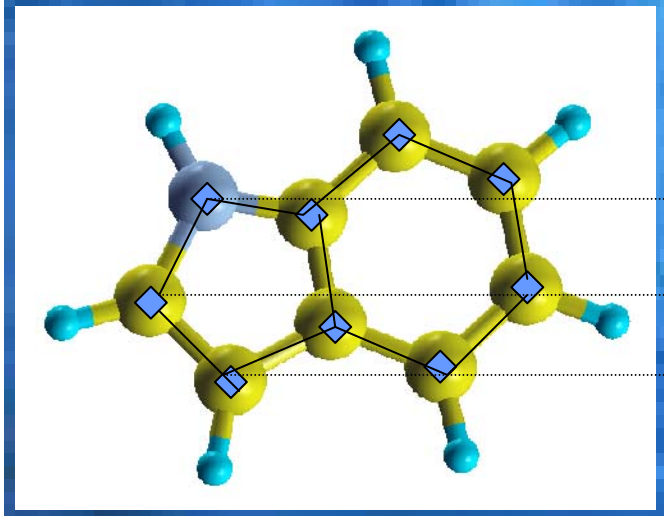
BSE (electron-hole interaction)

SOLVENT SHIFT

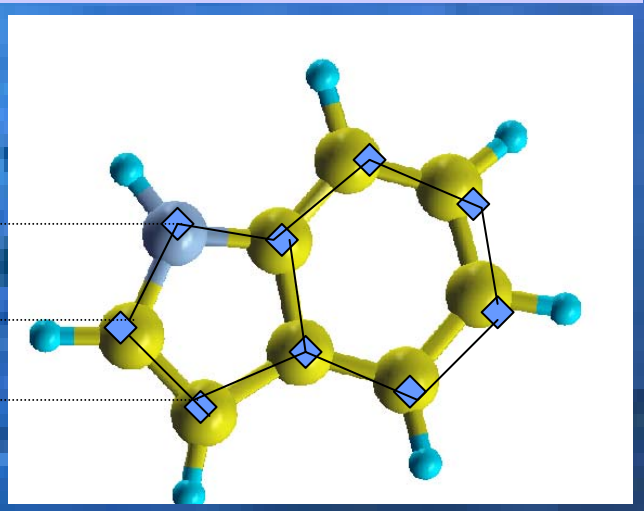
Solvent shift: shift of the optical absorption from vapor phase to solution (environment dependent)

Exp. solvent shift of indole in water: redshift ~ 0.2 eV

IN VAPOR PHASE

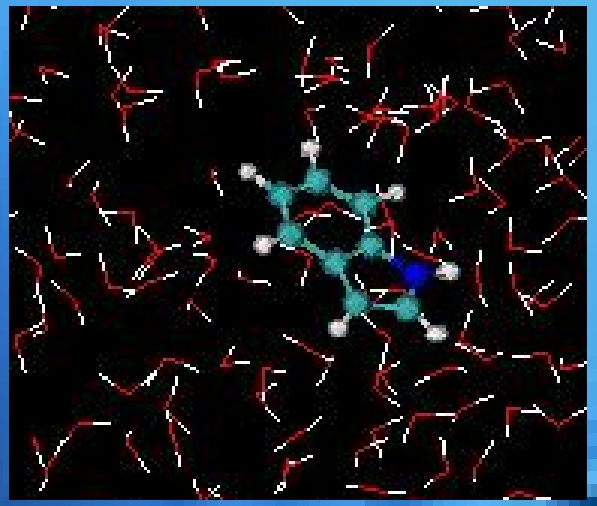


IN WATER (13.08 ps)



Slight distortion of the rings due to the presence of water

Calculating absorption spectra in solution by QM/MM

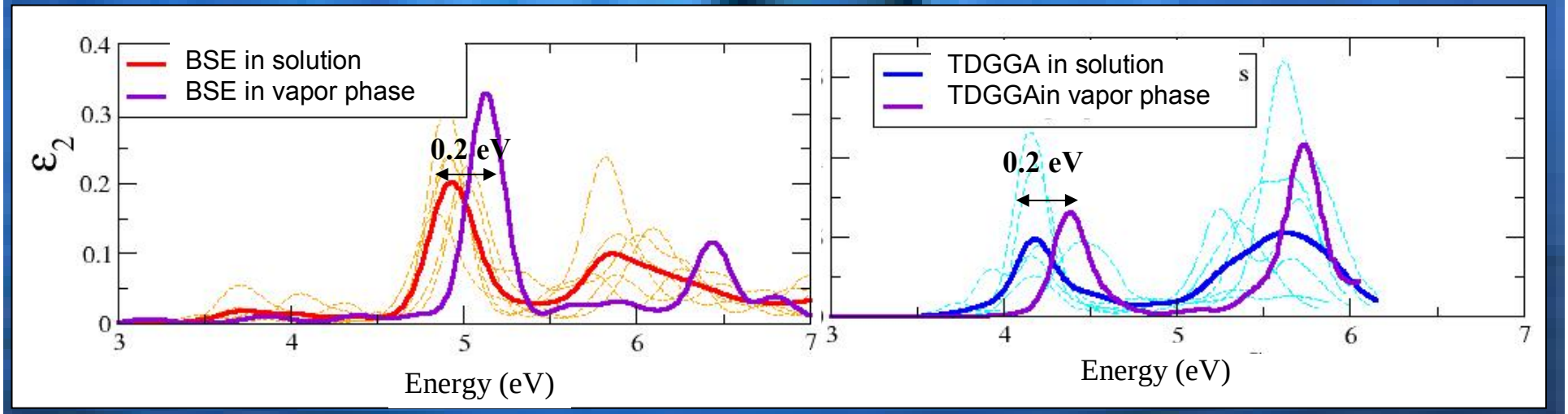


indole in water solution

Extracting snapshots and calculate excitation energies and oscillator strengths within the MM external field.

2000 water molecules
Shift GW is found ~ the same for all the snapshots

averaging over 6 snapshots the optical spectra



A. Mosca Conte, E. Ippoliti, R. Del Sole, P. Carloni, and O. Pulci, JCTC 5, 1822 (2009)

Conclusions

- Electronic gap of water: 8.4-8.6 eV (exp: 8.7 ± 0.5 eV)
- Optical absorption spectrum of water – important excitonic effects!!!

- MBPT on Base Schiff Model for retinal: agreement with post-Hartree Fock and QMC

- QM/MM scheme +MBPT: indole in water solvatochromism in good agreement with experiments

- heavy calculations, GW is the bottleneck

This scheme opens the way to further applications (other biorelevant molecular environment, such as proteins)

In collaboration with:

Viviana Garbuio (Roma Tor Vergata)
Adriano Mosca Conte (Roma Tor Vergata)
Rodolfo Del Sole (Roma Tor Vergata)

Lucia Reining (LSI, Ecole Polytechnique Palaiseau)

Michele Cascella (EPFL Lausanne)

Emiliano Ippoliti (SISSA, Trieste)
Paolo Carloni (SISSA, Trieste)
Leonardo Guidoni (Univ. Aquila, and Roma1)

Codes used:
CPMD Car-Parrinello
Espresso PWSCF http://www.pwscf.org
GW, EXC, DP: http://www.nanoquanta.eu

Development of theory

training

Undergraduates
PhD Students
Post Docs
Other colleagues
exp + Industry!

Marie Curie Fellowships

Development of codes

Distribution:
ABINIT
FHI
OCTOPUS
Yambo
DP+EXC
TOSCA

Research

Carrying on Projects for users


X. Gonze
Université catholique de Louvain
Université Catholique
Louvain
C-O. Almbladh
Lunds Universitet
Lund
R. Godby
University of York
M. Scheffler
Fritz-Haber-Institut
Berlin
BEAMLINES:
Optics (O. Pulci)
EELS (F. Sottile)
X-ray (J. Rehr)
Transport (P. Bokes)
Time-resolved excitations (M. Marques)
Photoemission (C. Verdozzi)
Raman (G. Rignanese) new
E.K.U. Gross
Freie Universität
Berlin
L. Reining
Laboratoire des Solides Irradiés
Paris
San Sebastián
Roma
F. Bechstedt
Universität Jena
Friedrich-Schiller-Universität
Jena
A. Rubio
Universidad del País Vasco
San Sebastián
G. Onida
Universitá degli Studi
Milano
R. Del Sole
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Istituto Nazionale per la Fisica della Materia
Roma


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PARIS
(Reining)
YORK
(Godby)
LOUVAIN
(Gonze)
ROME
(Del Sole)
S.SEBASTIAN
(Rubio)
ETSF
MILAN
(Onida)
BERLIN FU
(Gross)
BERLIN FHI
(Scheffler)
LUND
(von Barth)
JENA
(Bechstedt)

Calculation details

Liquid water

Average over 20 classical MD snapshots
32 water molecules - 8 k-points (no G)
GGA-PW91 pseudo - E_cut=50 Ry
600 cond. states

Σ_x: 19933/20163 pw - Σ_c: 13997/20163 pw
Haydock - resonant – W diagonal

Ice Ic

2 molecules/cell - 2176 k-points
GGA-PW91 pseudo - E_cut=60 Ry
500 cond. states

S_x: 3215/3414 pw - S_c: 721/3414 pw
Haydock - resonant - W_diag

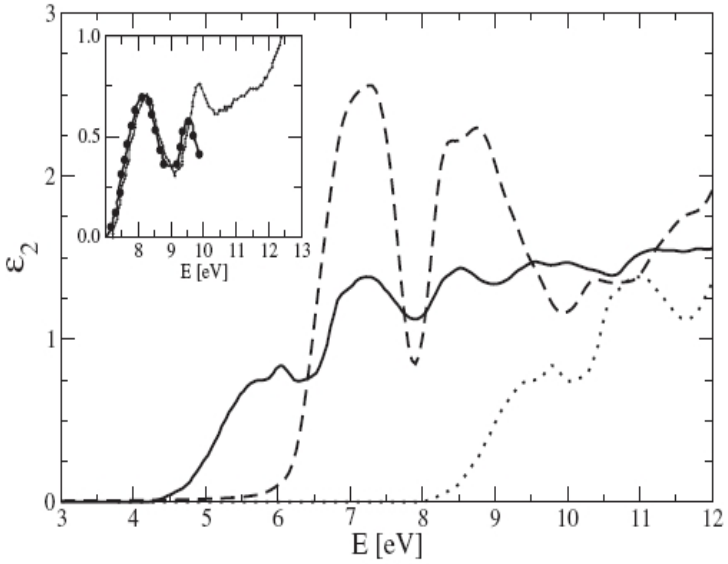
Codes:

PWscf code: http://pwscf.org
GW-Nanoquanta code
BSE-EXC code: http://bethe-salpeter.org
Dp code: www.dp-code.org

Other phases

Average gap	Ice Ic ord	Ice Ic disord	Liquid water **
DFT	5.76 eV	5.61 eV	5.1 eV
GW	9.6 eV	9.1 eV	8.4 eV
Optical	7.4 eV	7.3 eV	7.2 eV

Liquid water **



Disorder effect

Shrinking of the electronic gap

Bound exciton not affected

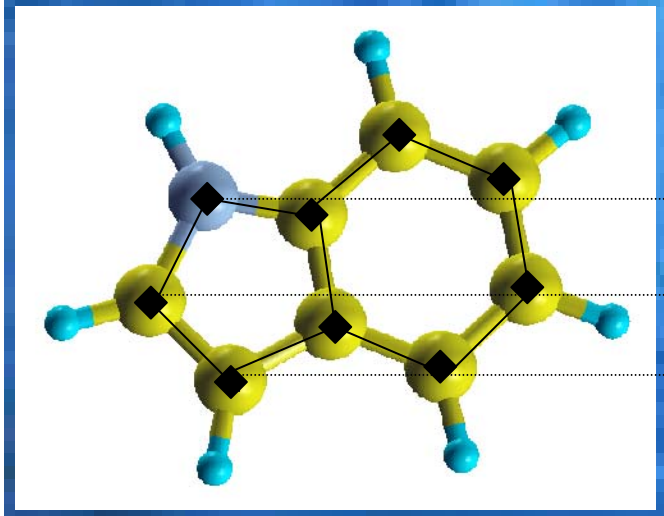
** V. Garbuio et al., *Phys. Rev. Lett.* **97**, 137402 (2006)

SOLVENT SHIFT

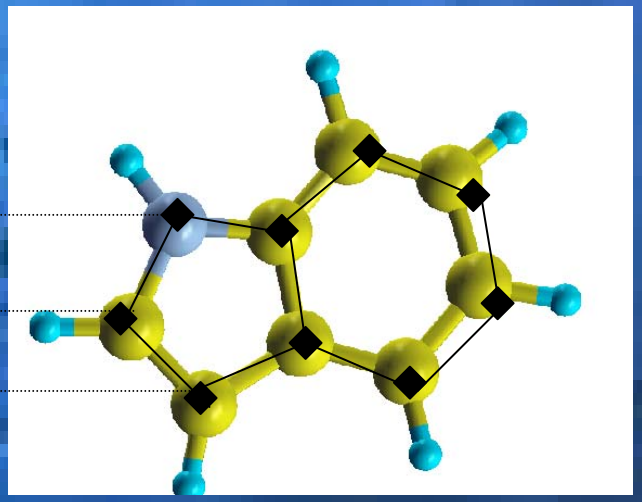
Solvent shift: shift of the optical absorption from vapor phase to solution

Exp. solvent shift of indole in water: redshift ~ 0.2 eV

IN VAPOR PHASE



IN WATER (13.08 ps)



Slight distortion of the rings due to the presence of water

K-points

It has been shown [41, 10] that the choice of the Γ point (k=(0,0,0)) as a single sampling point has a particularly slow convergence with respect to cell size. The interaction between neighboring cells leads to a k dependence of the electronic bands related to cos(kr). In order to minimize this effect, it is necessary to consider a finite set of k-points which zero the cosine for at least the nearest-neighbor cells. To this aim, we sampled the first Brillouin zone with 8 k-points:

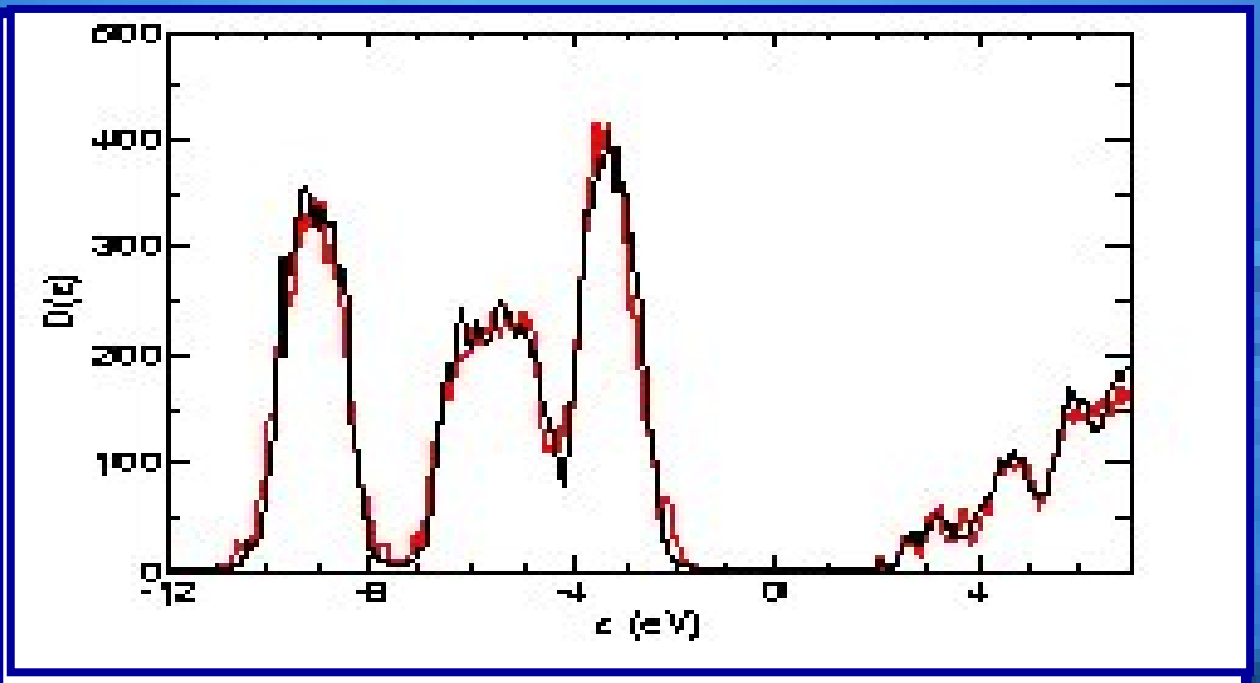
$$k_1 = \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right), \; k_2 = \left(-\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right), \; k_3 = \left(\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}\right), \; k_4 = \left(\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}\right)$$

and those obtained by inversion, in units of $2\pi/a$.

10 – D. Prendergast *et al.*, J. Chem. Phys **123**, 014501 (2005)

41- R. Makov *et al.*, Phys. Rev. B **53**, 15513 (1996)

K-points

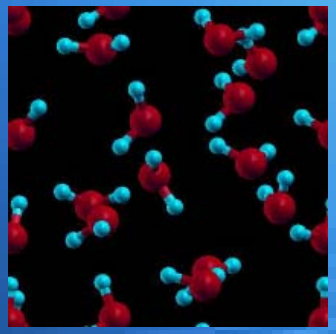


1 k-point, 256 molecules

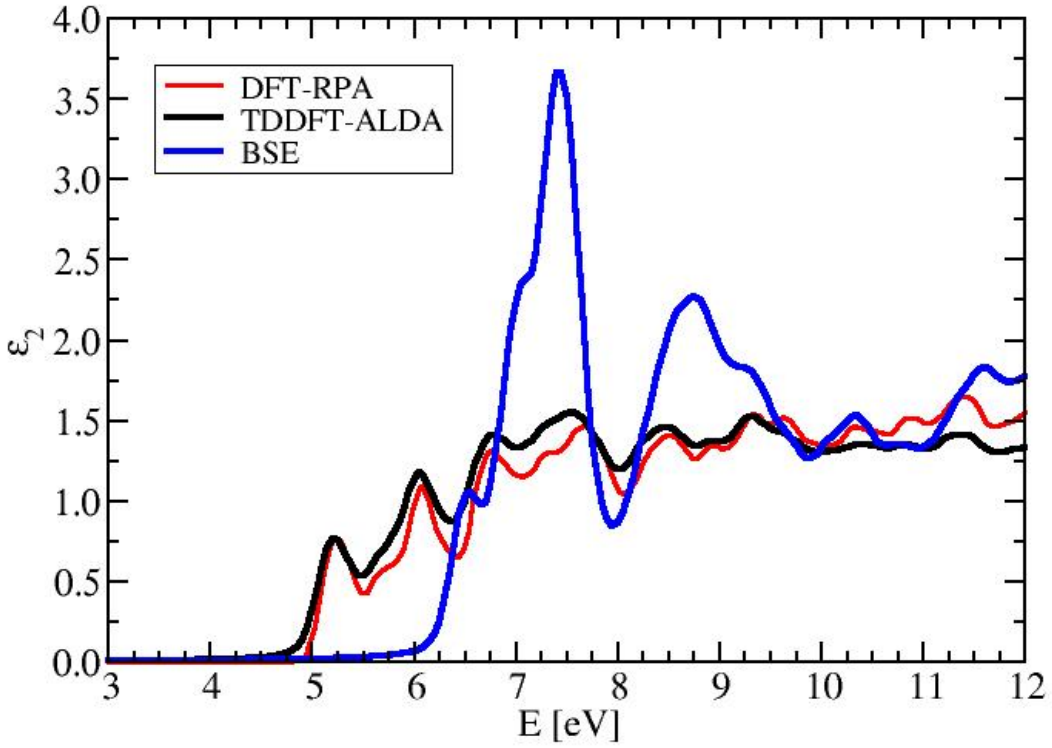
8 k-points, 32 molecules

[10] – D. Prendergast, J.C. Grossman, G. Galli., J. Chem. Phys 123, 014501 (2005)

5) ALDA does not work for liquid H_2O

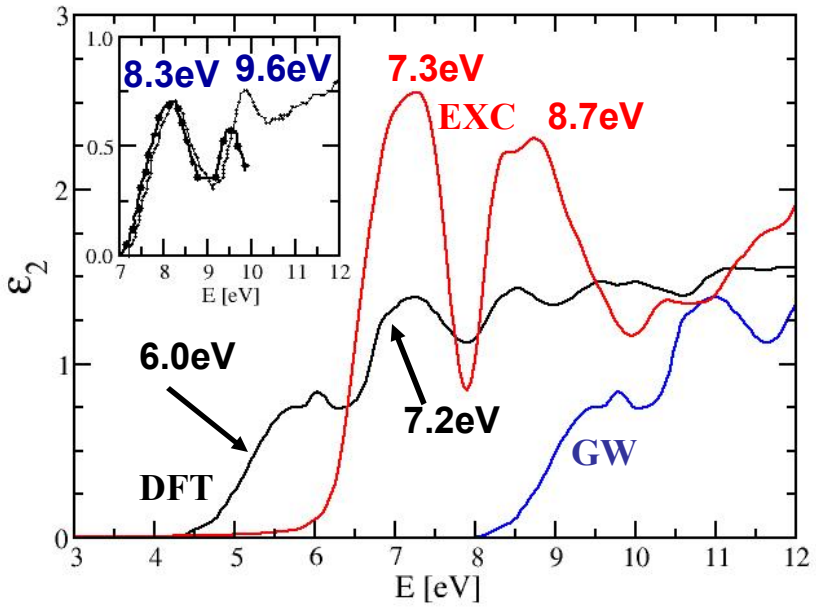


1-snapshot Optical absorption spectra

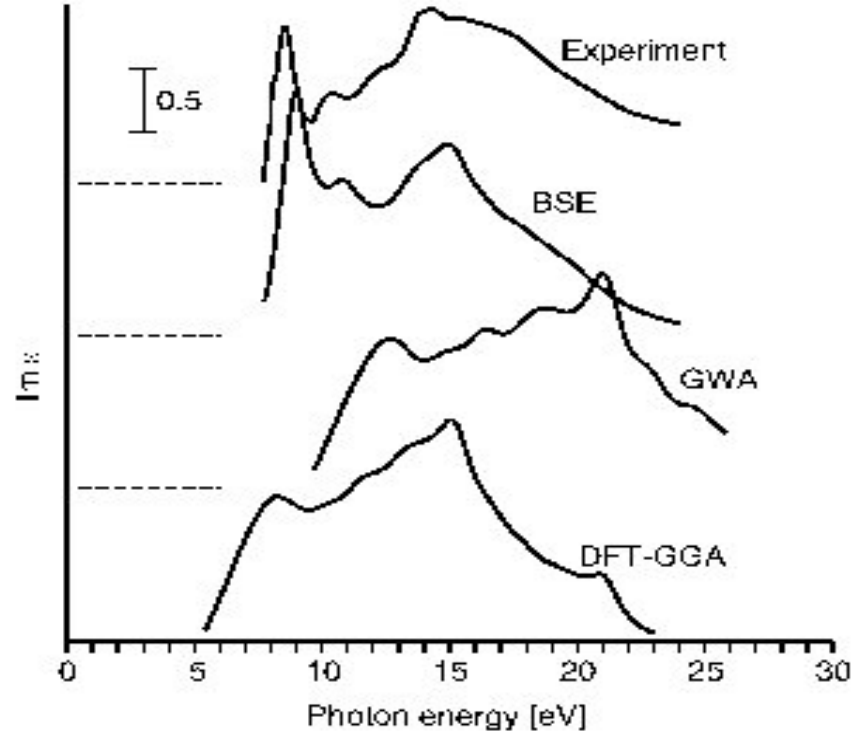


ALDA: No improvement with respect to DFT

Water



Ice



Hahn P.H. *et al.*, PRL. 94, 037404 (2005)

Exciton binding energy: 2.4 eV liquid water

3.2 eV ice

5.3 eV gas phase

RORO kernel

L. Reining, V. Olevano, A. Rubio, G. Onida, Phys. Rev. Lett. 88, 066404 (2002)

$$f_{xc}(r,r') \cong -\frac{\alpha}{4\pi\,|r-r'|}$$

Right Long-range behavior of the kernel

α constant $\alpha = 4.615\varepsilon_{\infty}^{-1} - 0.213$

Does not work for strongly bound excitons

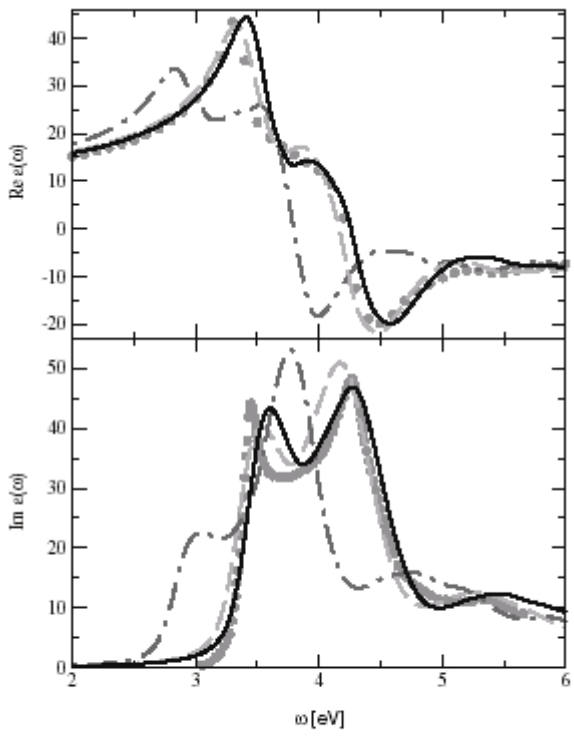


FIG. 1. Silicon, optical absorption (bottom), and refraction index (top panel) spectra. Dots: experiment. Dot-dashed curve: TDLDA result. Dashed curve: result obtained through the Bethe-Salpeter method. Continuous curve: TDDFT result using the long-range kernel derived in this work.

WHY are biomolecules so difficult?

***BSE*:Size problems!**
- **DISK QUOTA (>100Gb)**
- **Memory / CPUtime**

optical properties:
number of transitions (~65000)

GW:
- **number of plane waves (> 300000),**
- **number of empty bands (>1000)**

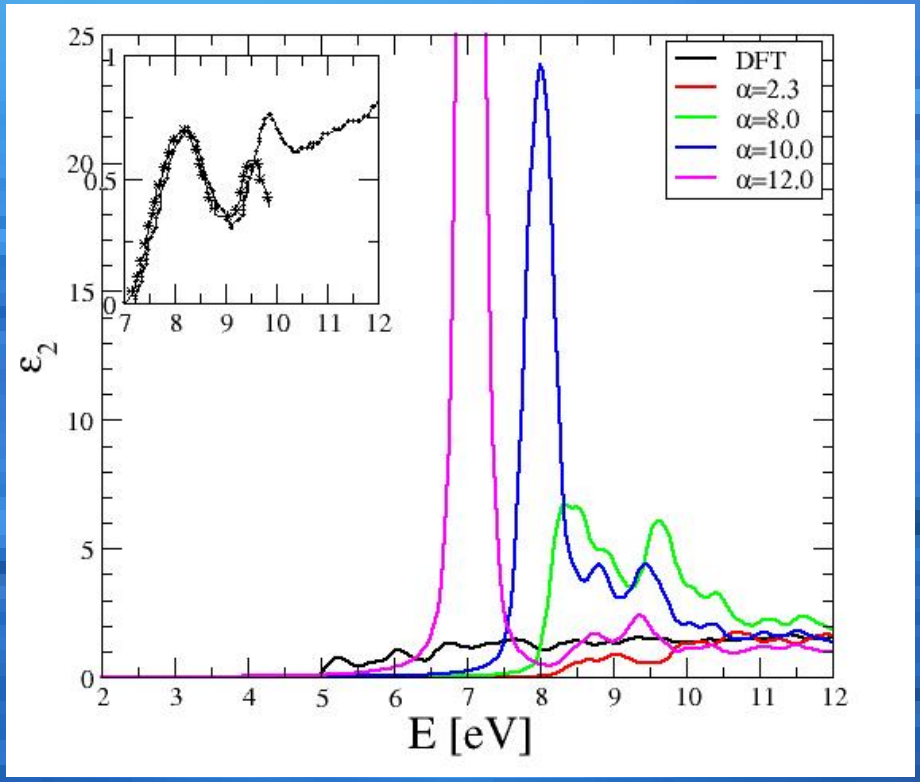
supercell: large enough to include the biomolecule AND vacuum

DFT

large!!!

TDDFT-roro-absorption spectra

V. Garbuio, M. Cascella, O. Pulci, in preparation



$$f_{xc}(r,r') \cong -\frac{\alpha}{4\pi\,|r-r'|}$$

Details of calculations

1st level – DFT (fhi98md code - Berlin)

8 k-points, 600 conduction bands, energy cut-off 50 Ry

2nd level – GW corrections (Godby-Reining code)

Σ_x - 19933/20163 plane waves

Σ_c - 13997/20163 plane waves

GW corrections independent on the configuration!!!

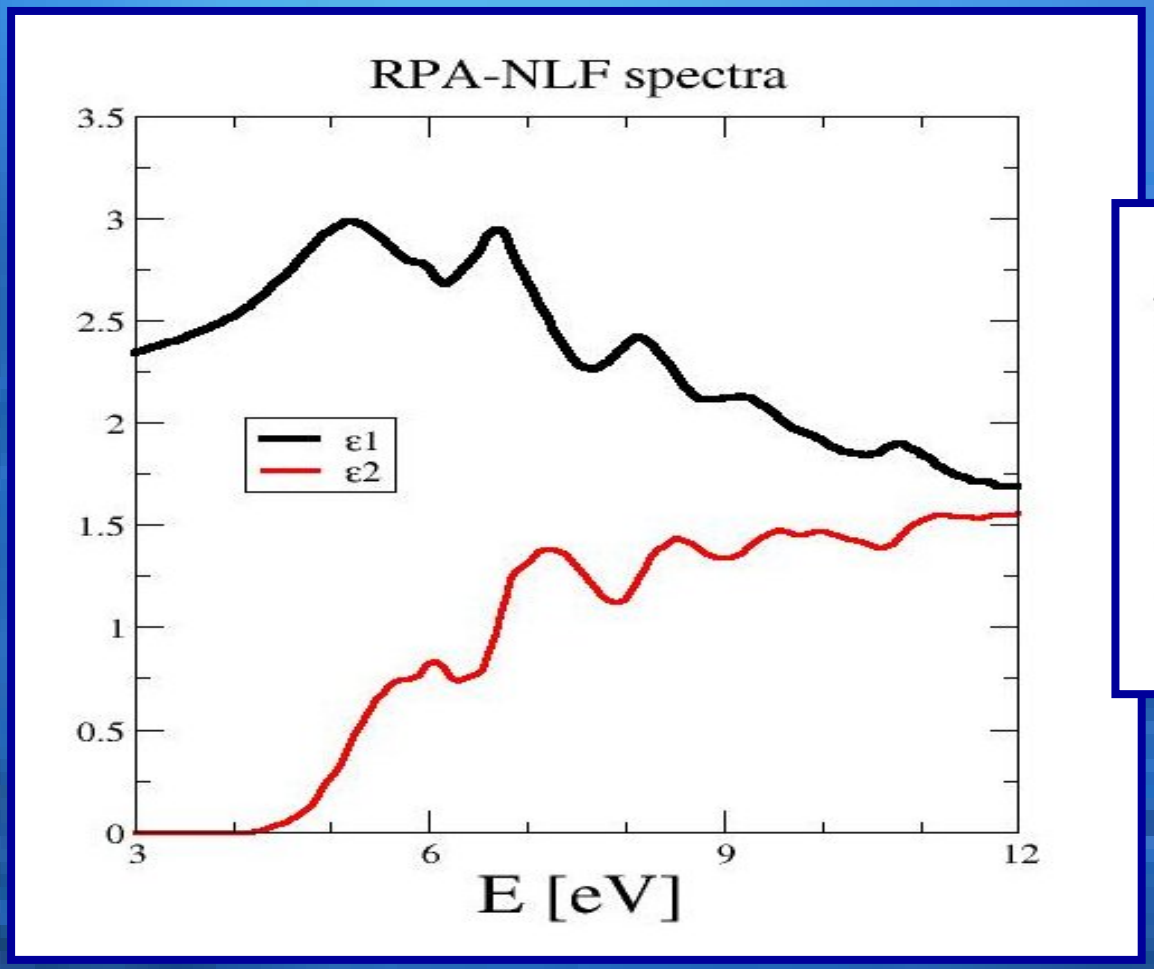
3rd level – excitonic effects (Exc code- Palaiseau)

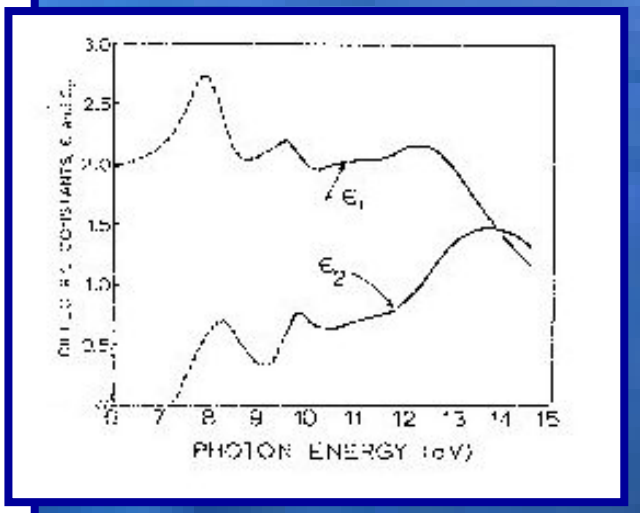
Haydock – 200 iterations – 100 conduction states - 48 valence states

Screen: energy cut-off 50 Ry, 13997/20163 plane waves

Absorption spectra independent on the "screen configuration"!!!

V. Garbuio et al., in preparation





*Kerr *et al.*, PRA **5**, 2523 (1972)

Looking for the Kernel!!

$$\hat{P} = \hat{P}_0 + \hat{P}_0(\bar{V} - W)\hat{P}$$

Bethe Salpeter

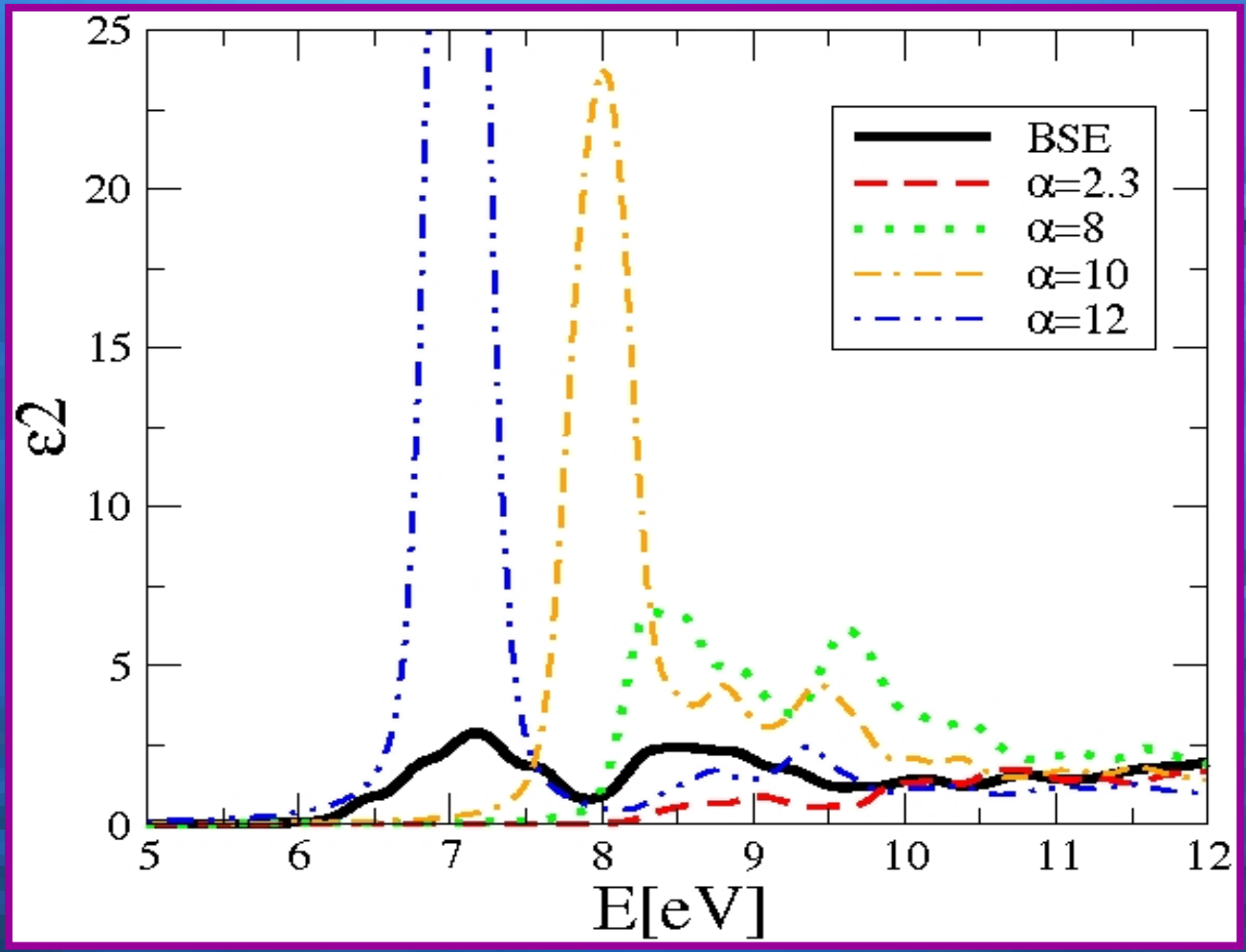
$$\chi = \chi^0_{KS} + \chi^0_{KS}(V + f_{xc})\chi$$

TDDFT

f_{xc} contains gap opening and e-h attraction

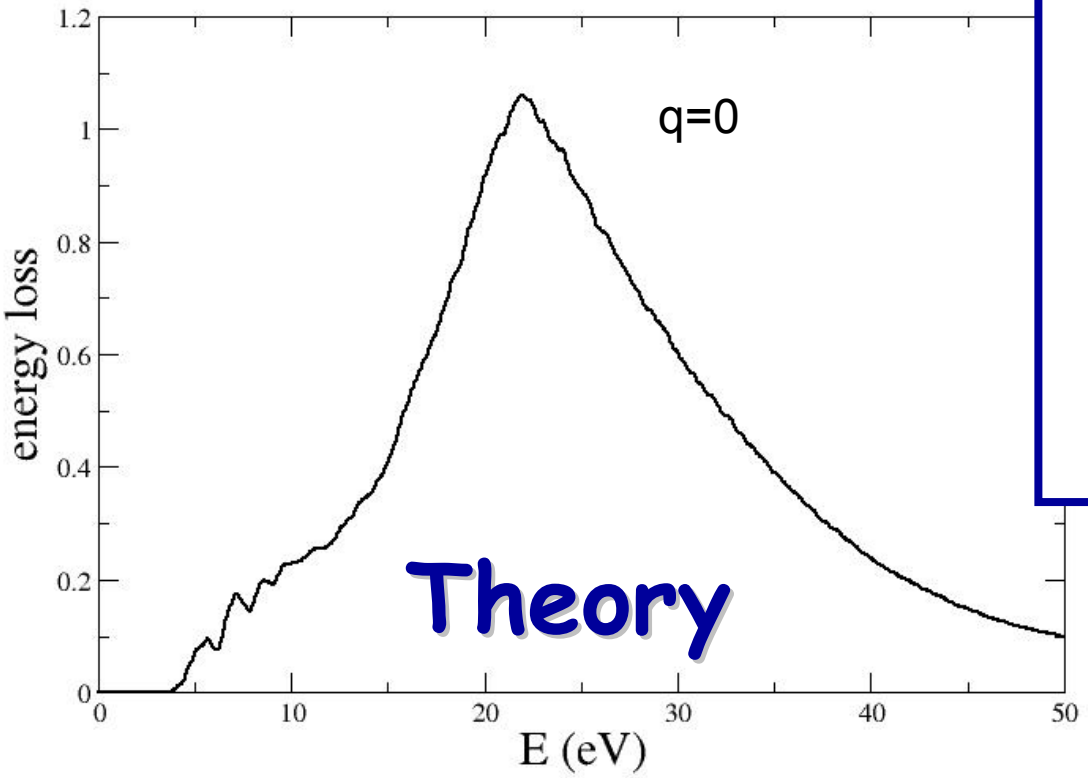
TDDFT-roro-absorption spectra

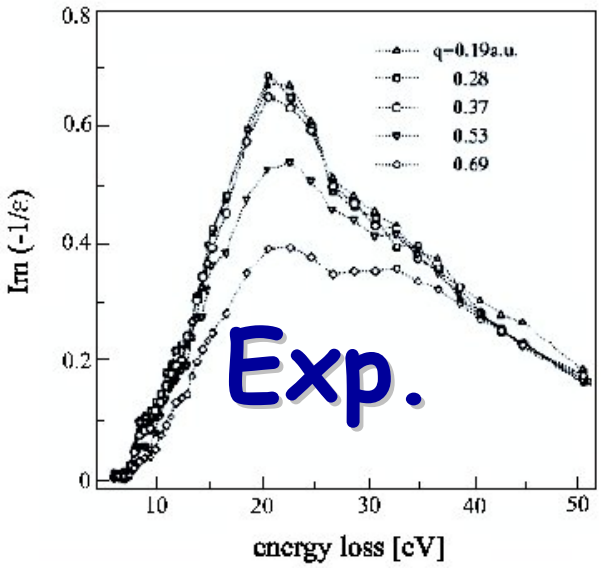
V. Garbuio, M. Cascella, O. Pulci, in preparation



$$f_{xc}(r,r') \cong -\frac{\alpha}{4\pi\,|r-r'|}$$

DFT energy loss

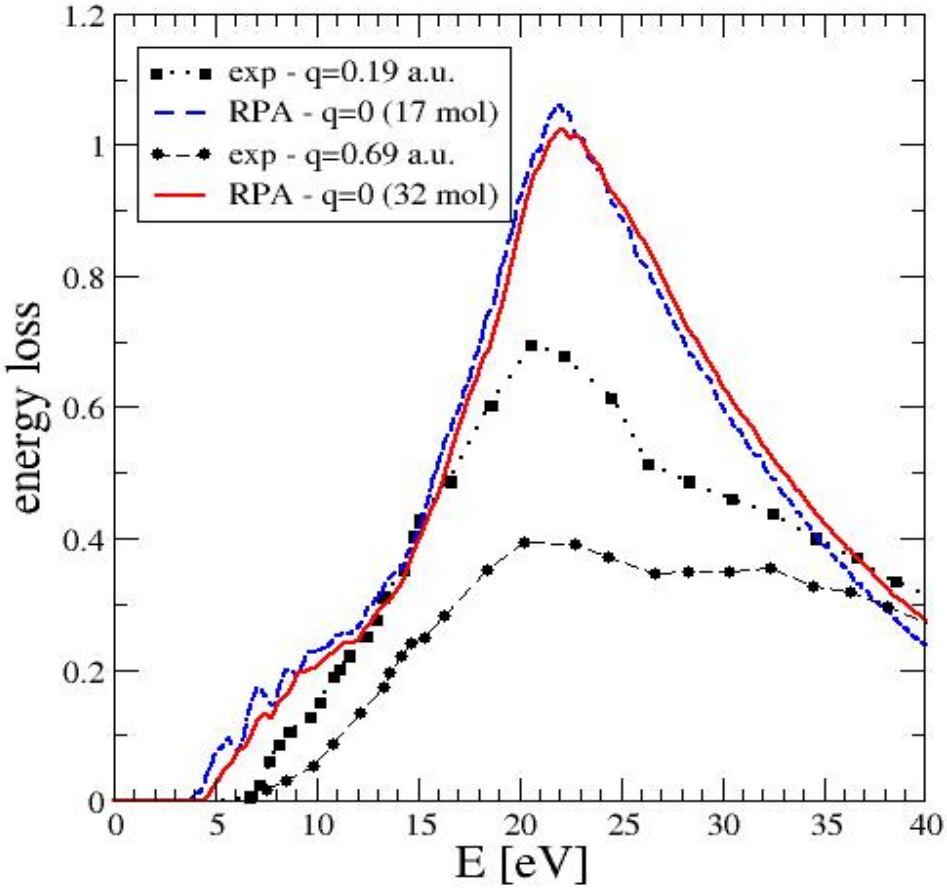




*Hayashi *et al.*, J.Chem.Phys. **108**, 823 (1997)

V. Garbuio et al., in preparation

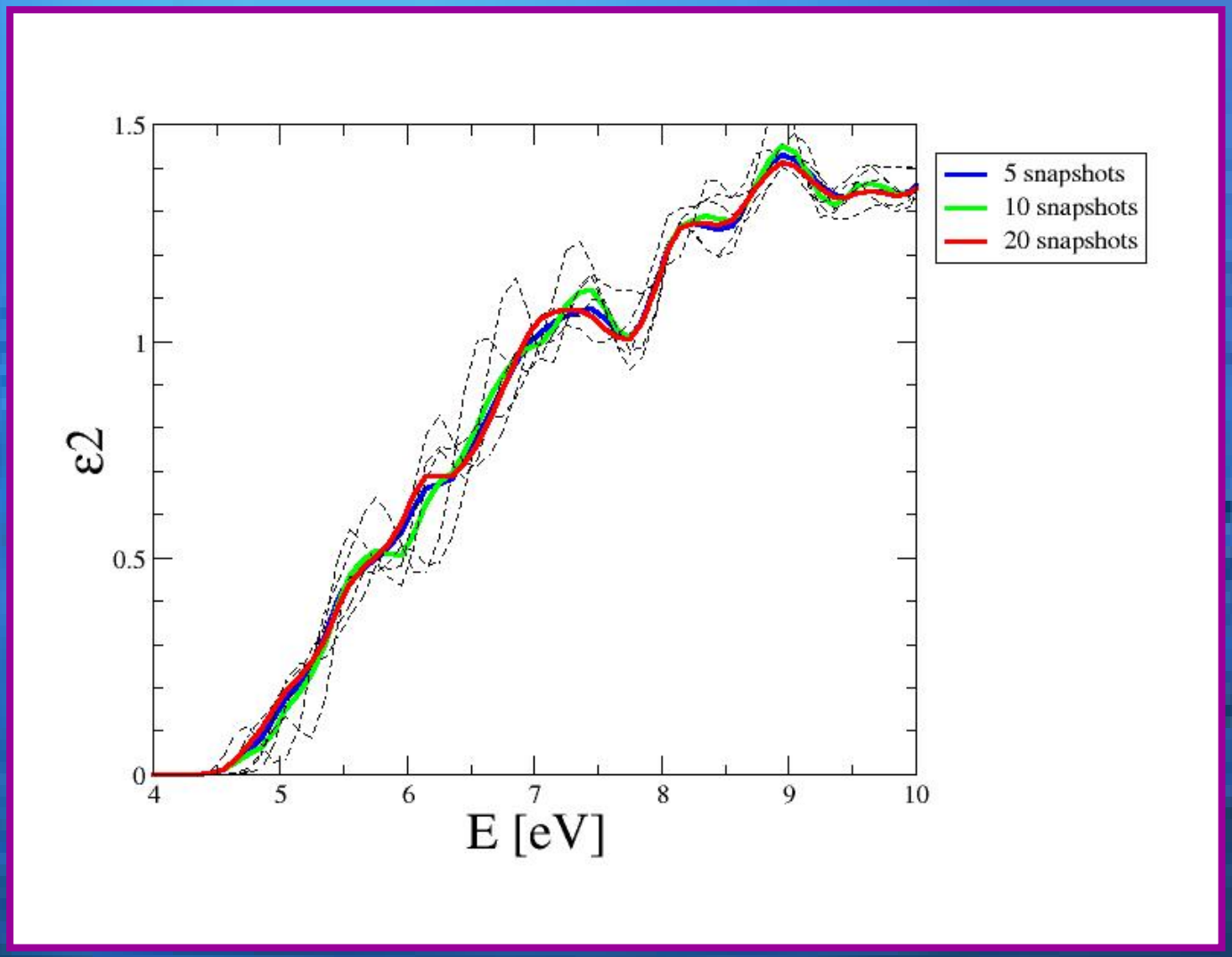
EELS



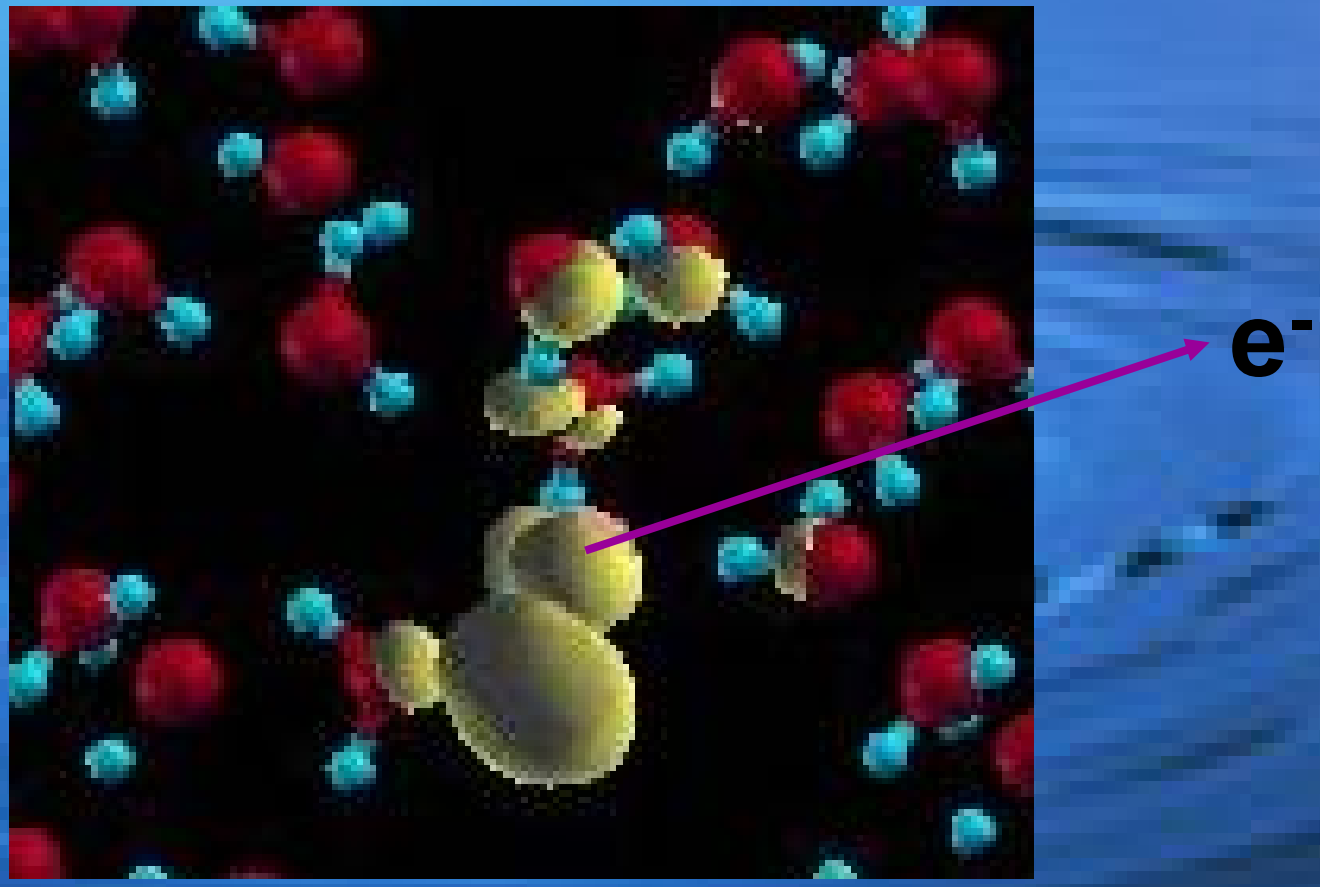
32 molecules GGA
vs. 17 LDA

Exp: Hayashi *et al.*, J.Chem.Phys. **108**, 823 (1997)

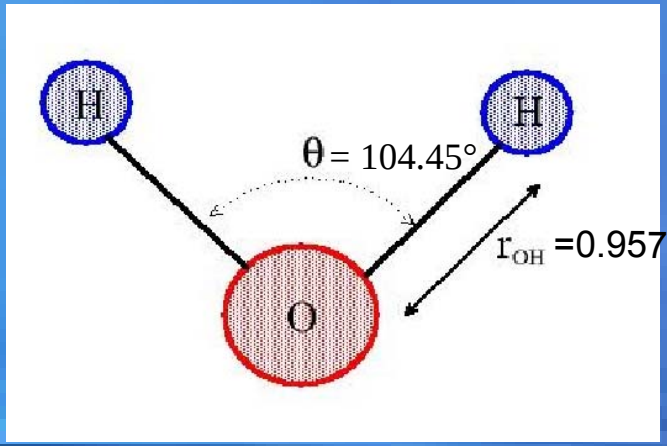
Size problem



Excitonic wavefunction



Importance of water



- essential for life
- it is the major constituent of earth surface
- present in confined geometries in many biological systems
- present both pure and as a solvent in many industrial processes

and chemical and biological reactions

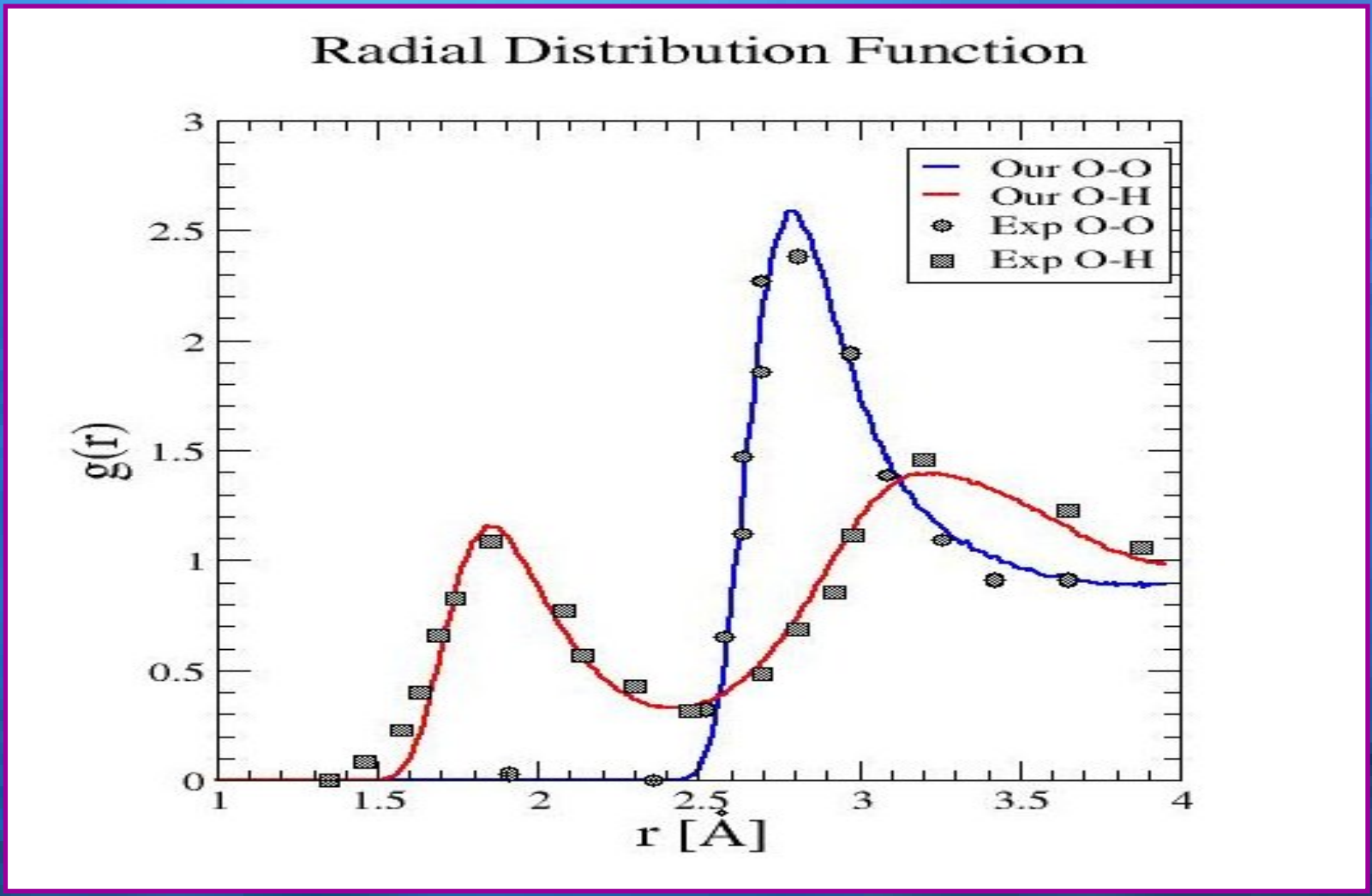
In principle also total energy

e.g. Galitskii and Migdal 1958

$$E=\frac{1}{2}\int dx\,\lim_{t'\to t^+}\left[\frac{\partial}{\partial t}-ih(x)\right]G(x,t,x',t')_{x'\to x},$$

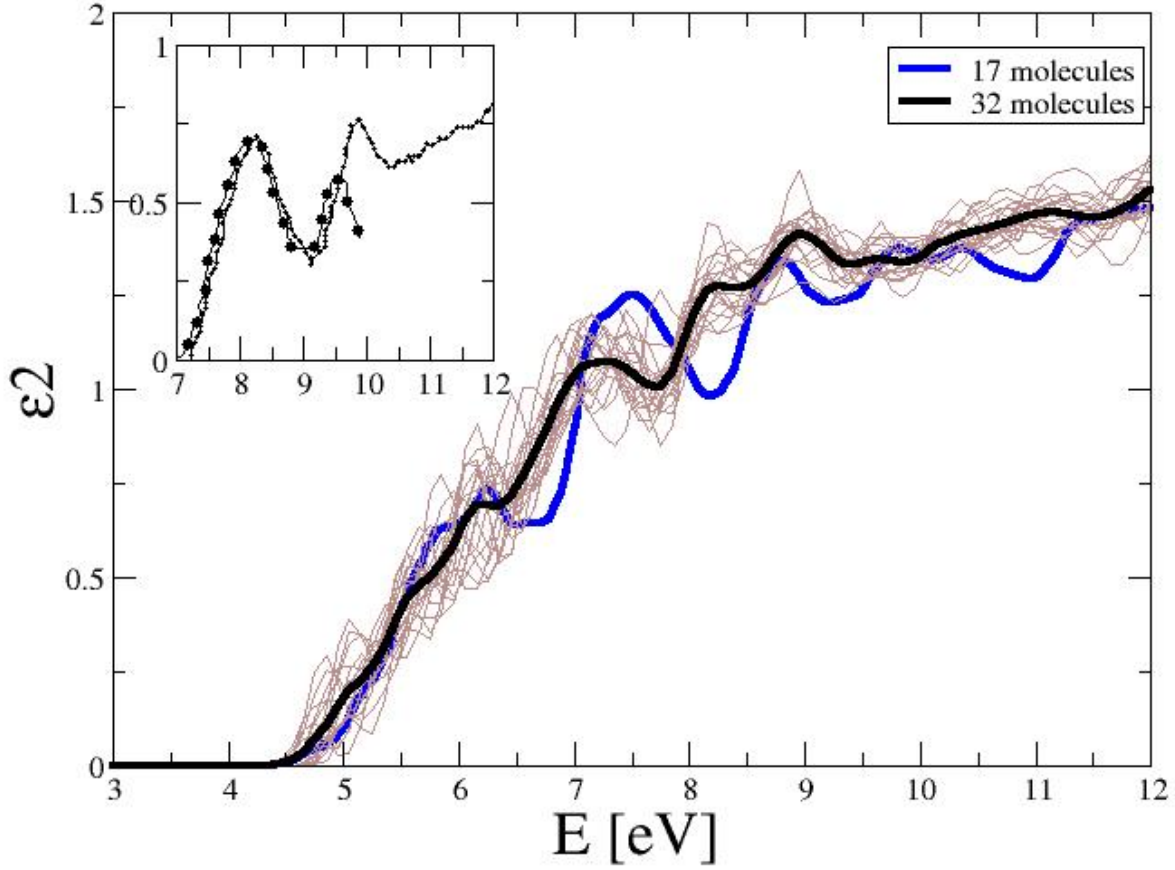
……so we can calculate whatever we want

Radial distribution functions



EXP: Soper *et al.*, J. Chem. Phys. **106**, 247 (1997)

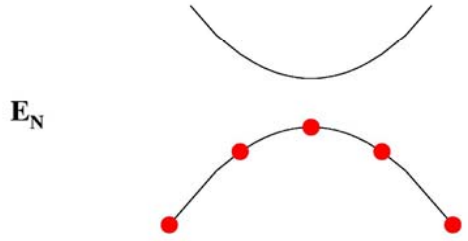
RPA-NLF: 17 vs. 32 molecules



V. Garbuio et al., in preparation

DFT

Ground State properties (Total energy):



$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H + V_{xc})\phi_j^{KS}(\vec{r}) = \varepsilon_j^{KS}\phi_j^{KS}(\vec{r})$$

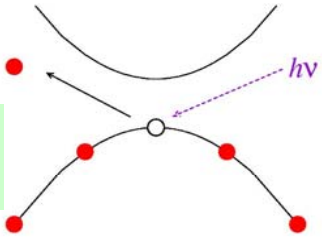
Ground state

Kohn-Sham eq.

•MBPT

Green's function

1 particle excitations (photoemission)



$$E_N - E_{N-1,j} = \varepsilon_j^{QP}$$

$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H)\Psi_j^{QP}(\vec{r}) + \int \Sigma(\vec{r},\vec{r'},\varepsilon_j^{QP})\Psi_j^{QP}(\vec{r'})d\vec{r'} = \varepsilon_j^{QP}\Psi_j^{QP}(\vec{r})$$

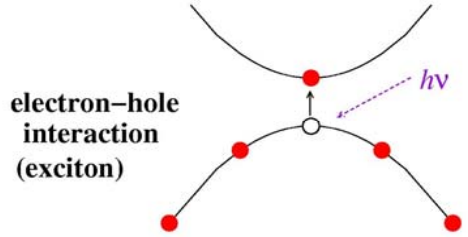
Charged excitations

Quasi-particle eq.

•MBPT

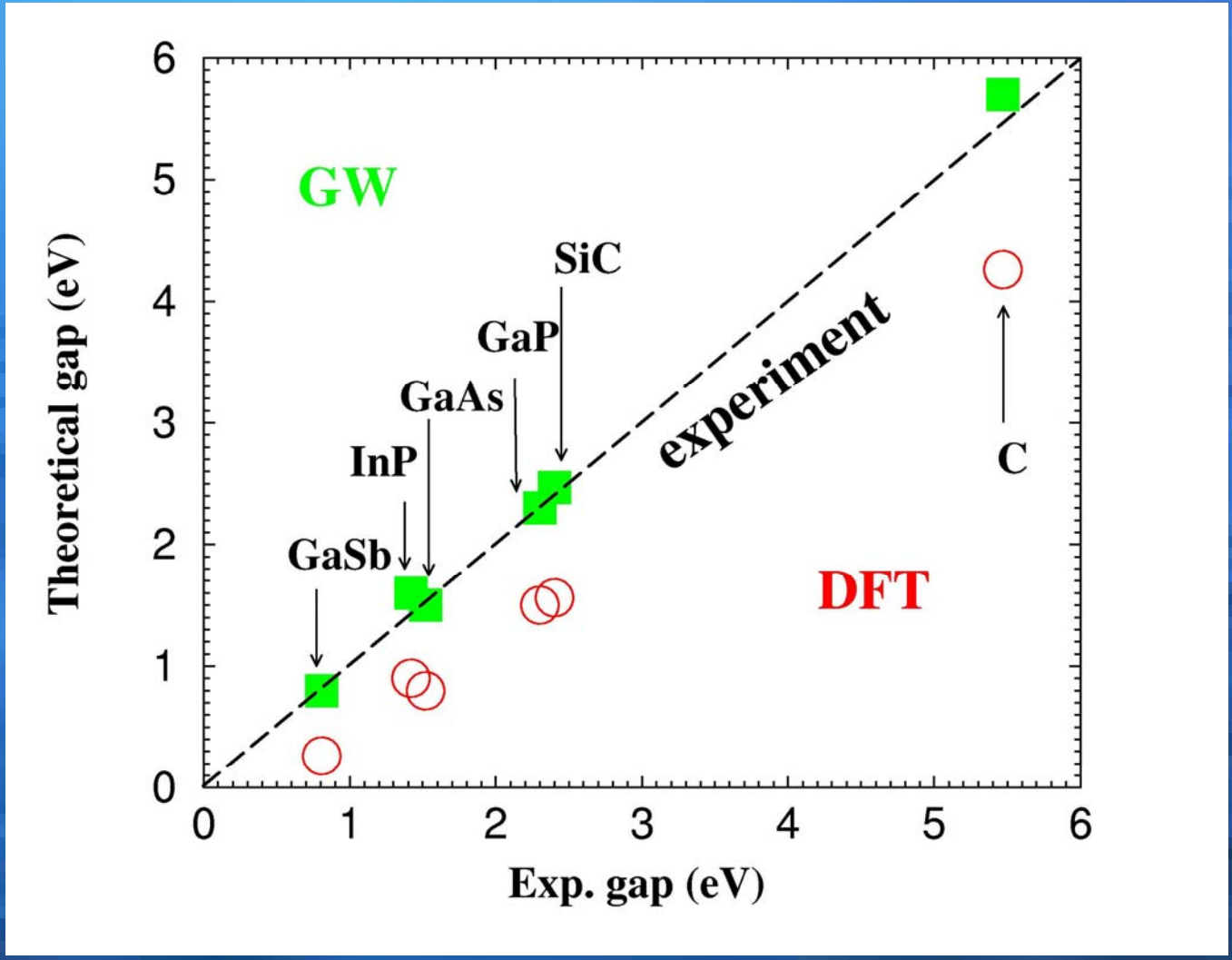
Green's function

2 particle excitations (absorption)



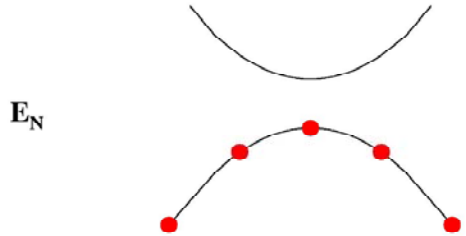
Neutral excitations

DFT vs GW gaps



DFT

Ground State properties (Total energy):



$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H + V_{xc})\phi_j^{KS}(\vec{r}) = \varepsilon_j^{KS}\phi_j^{KS}(\vec{r})$$

Ground state

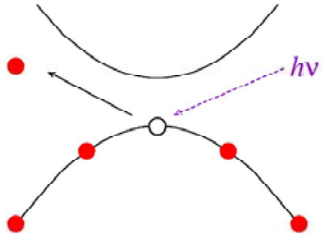
Kohn-Sham eq.

•MBPT

GW

1 particle excitations (photoemission)

$$E_N - E_{N-1,j} = \varepsilon_j^{QP}$$

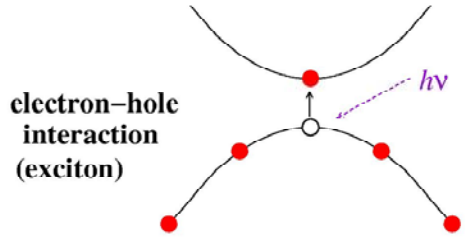


$$(-\frac{1}{2}\nabla^2 + V^{ext} + V^H)\Psi_j^{QP}(\vec{r}) + \int \Sigma(\vec{r},\vec{r'},\varepsilon_j^{QP})\Psi_j^{QP}(\vec{r'})d\vec{r'} = \varepsilon_j^{QP}\Psi_j^{QP}(\vec{r})$$

Charged excitations

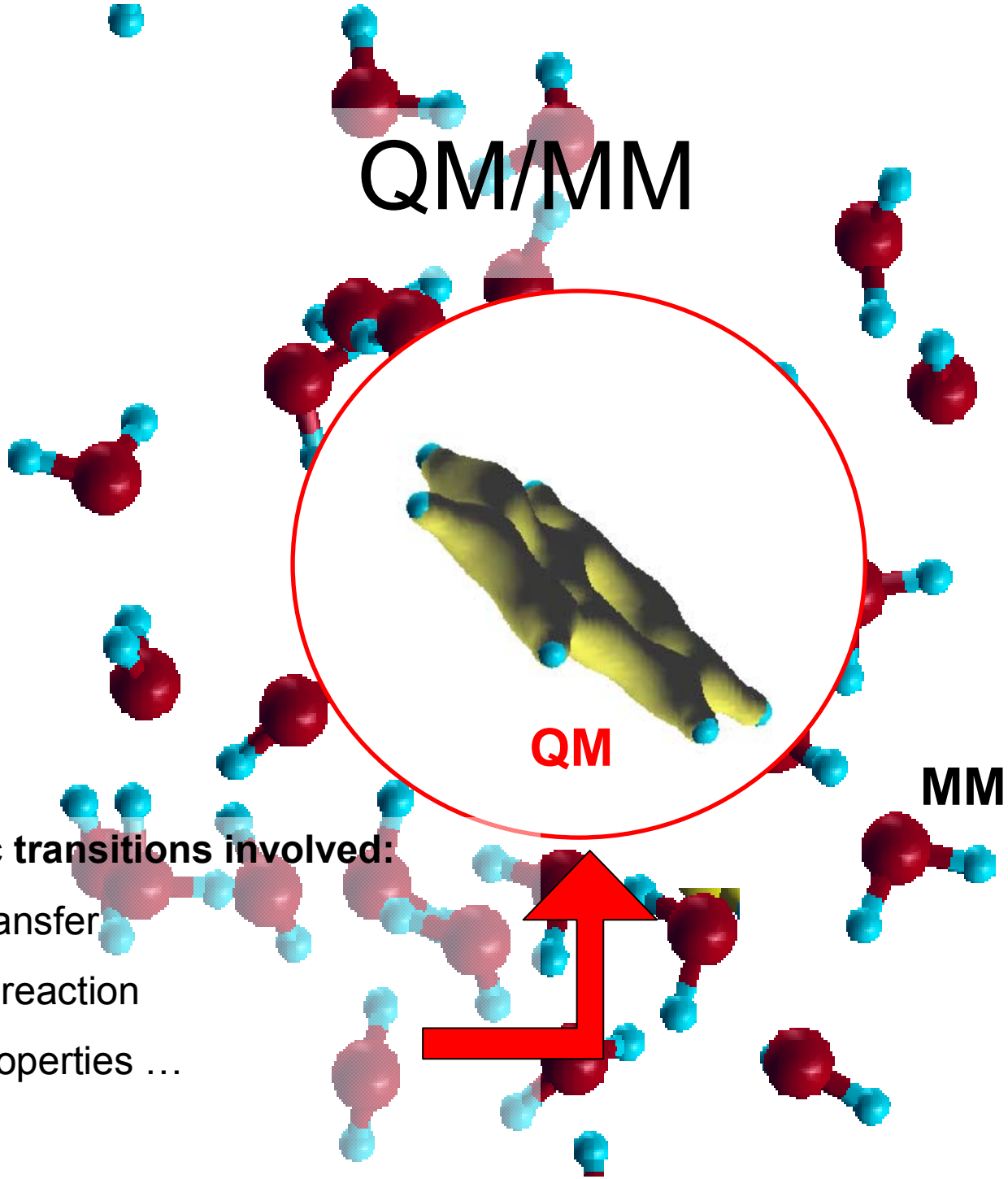
•MBPT

2 particle excitations (absorption)



Neutral excitations

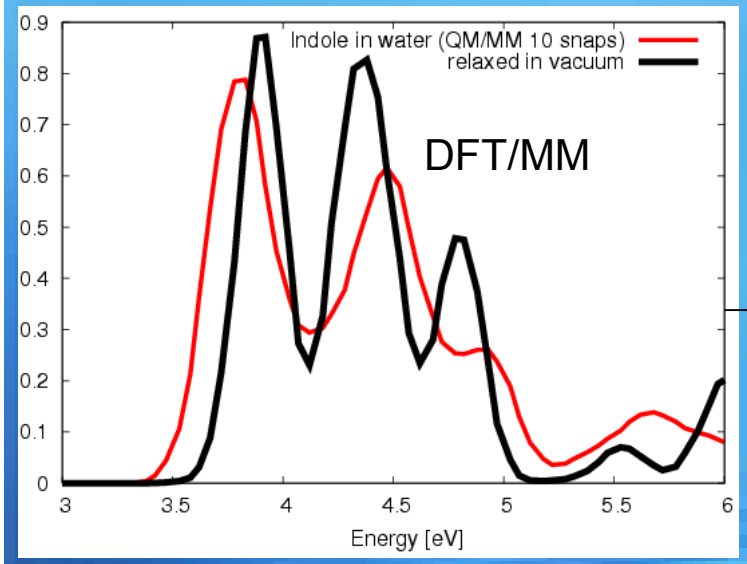
QM/MM



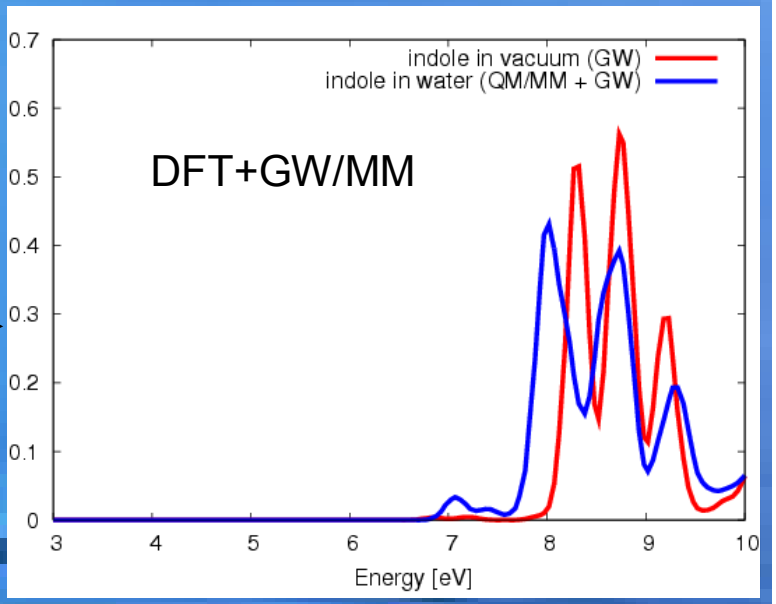
Electronic transitions involved:

- Charge transfer
- Chemical reaction
- Optical properties …

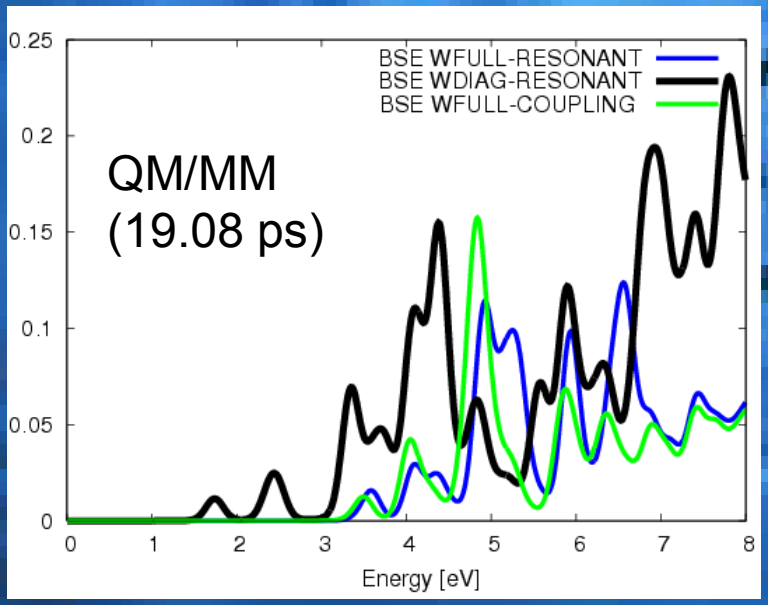
GW:

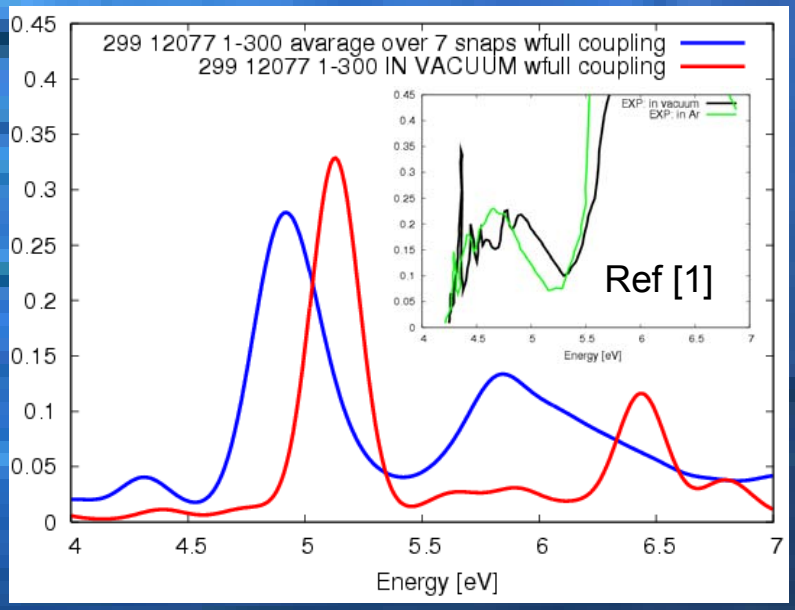


GW opens the GAP (+4eV)



Optical properties (BSE):



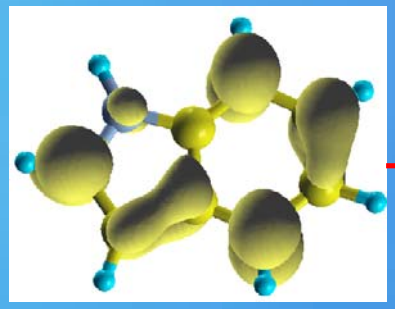


[1] J. Chem. Phys., **67**, n 7, 3277 (1977)

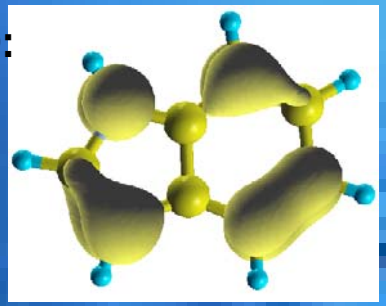
Indole in water solution: RPA

HOMO:

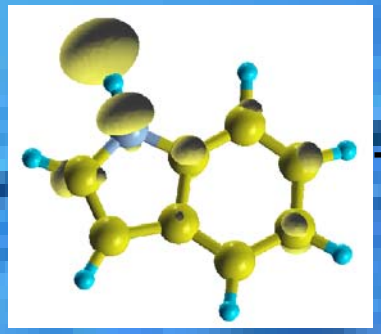
LUMO:

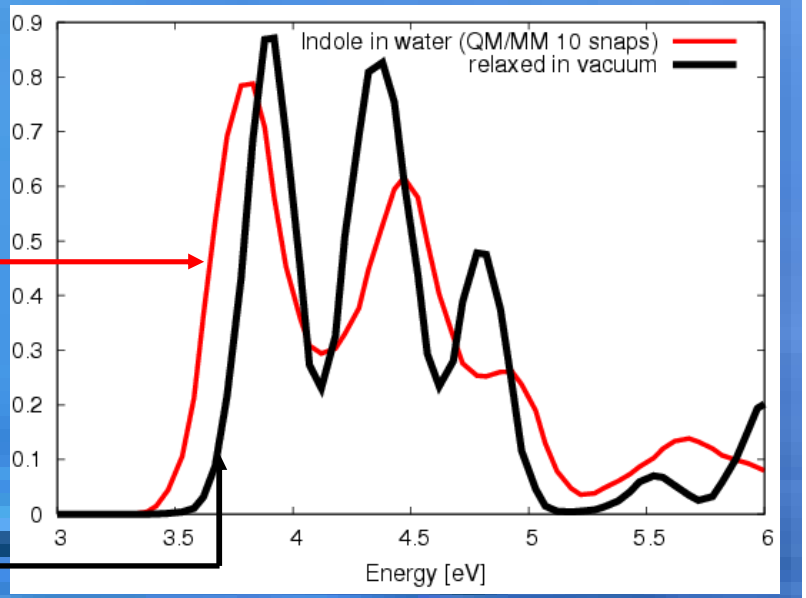


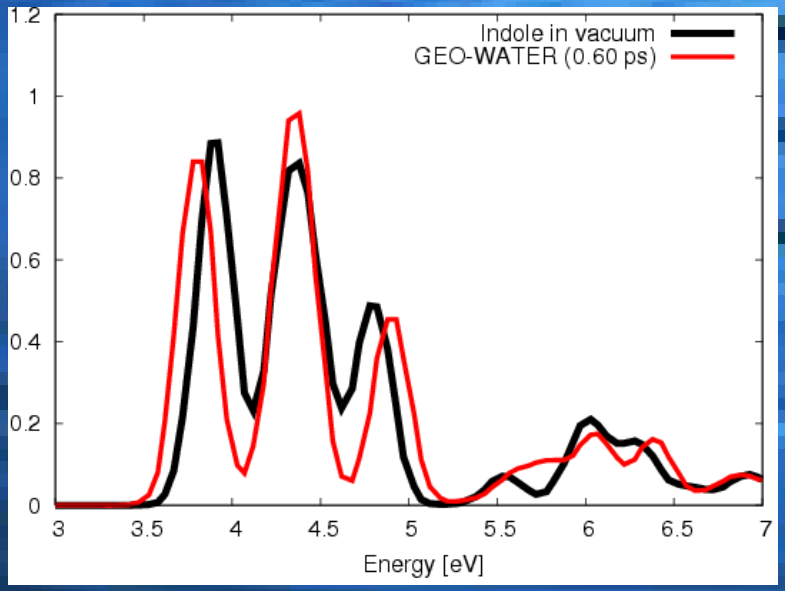
HOMO:

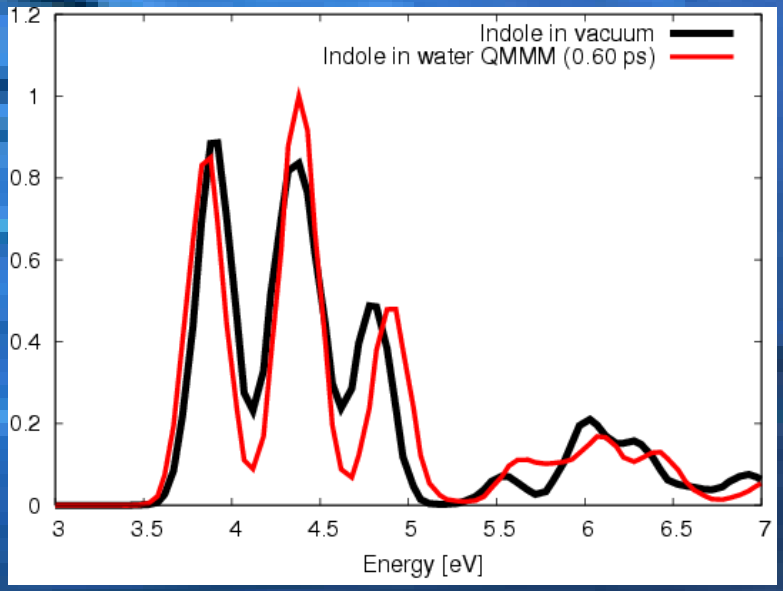


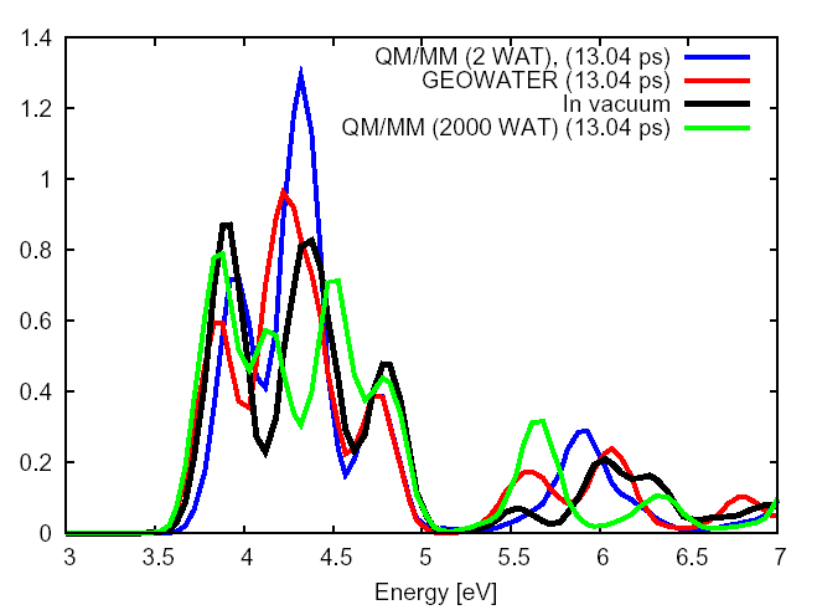
LUMO+1:

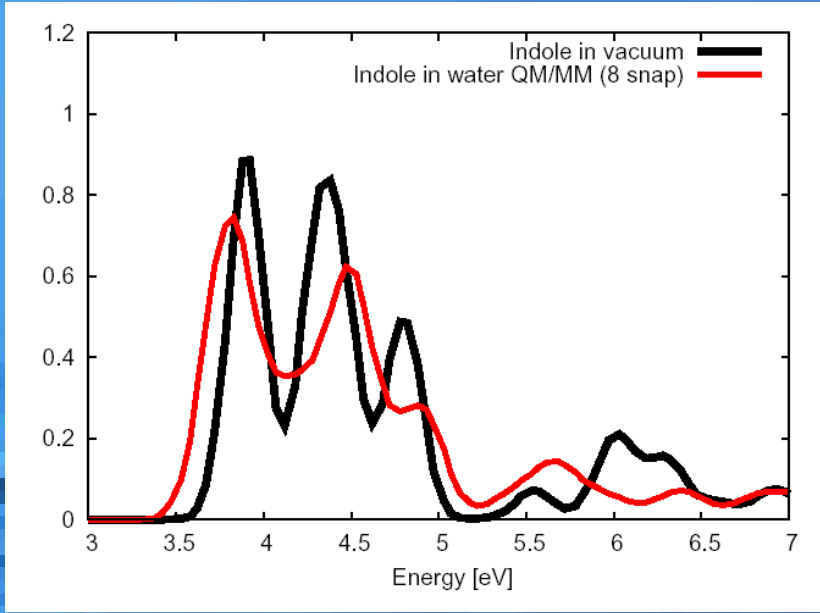


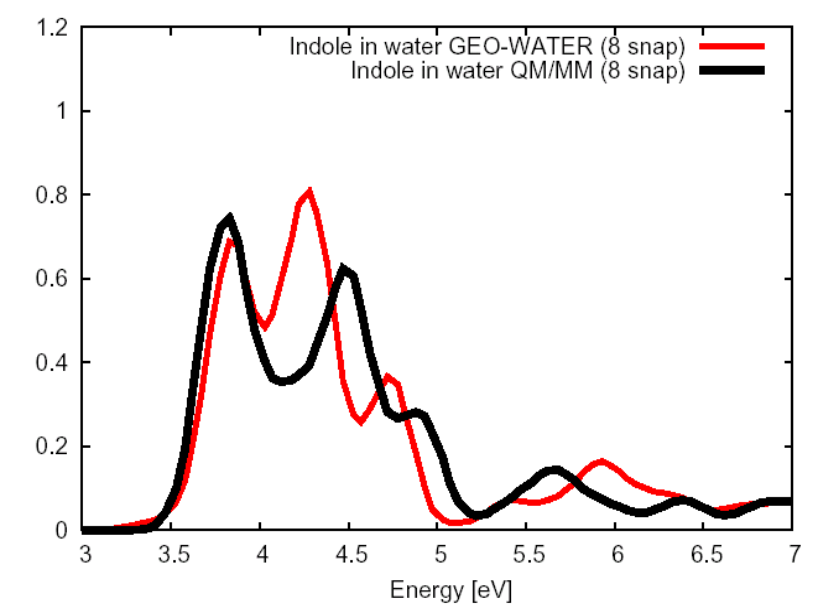


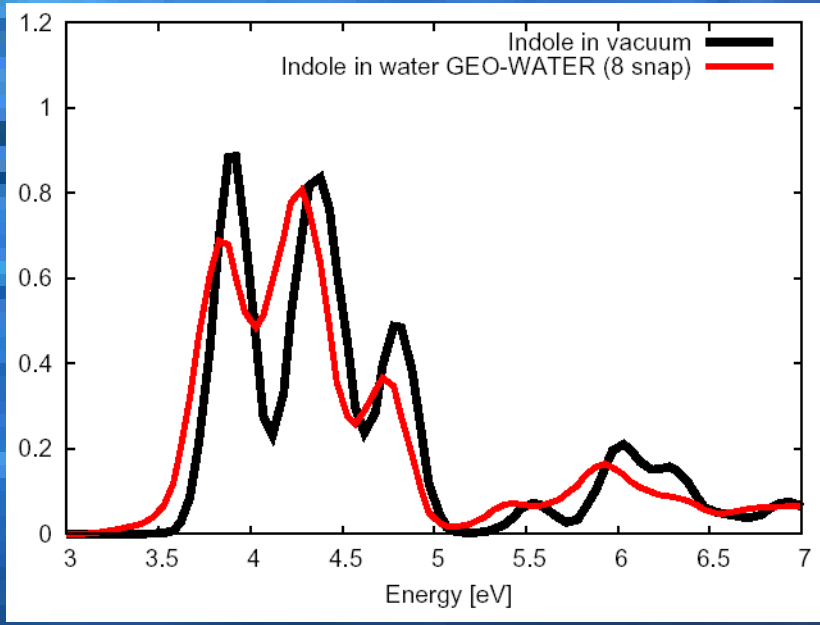




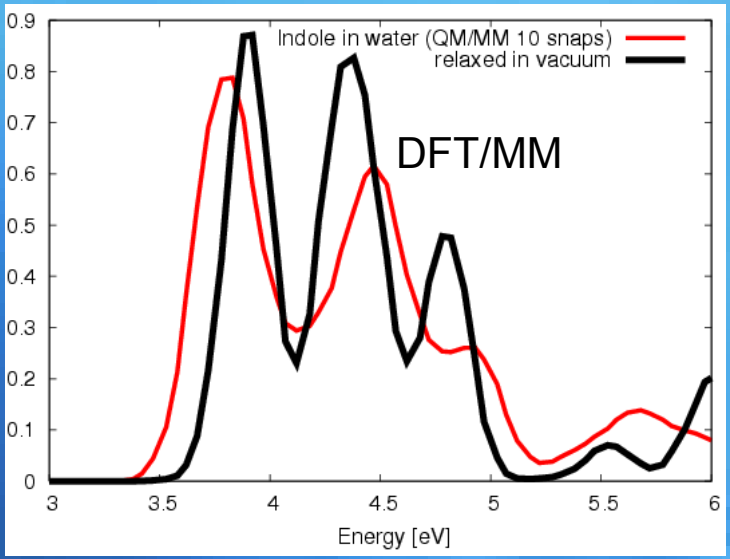

QM/MM (2 WAT), (13.04 ps)
GEOWATER (13.04 ps)
In vacuum
QM/MM (2000 WAT) (13.04 ps)
Energy [eV]


Indole in vacuum
Indole in water QM/MM (8 snap)
Energy [eV]

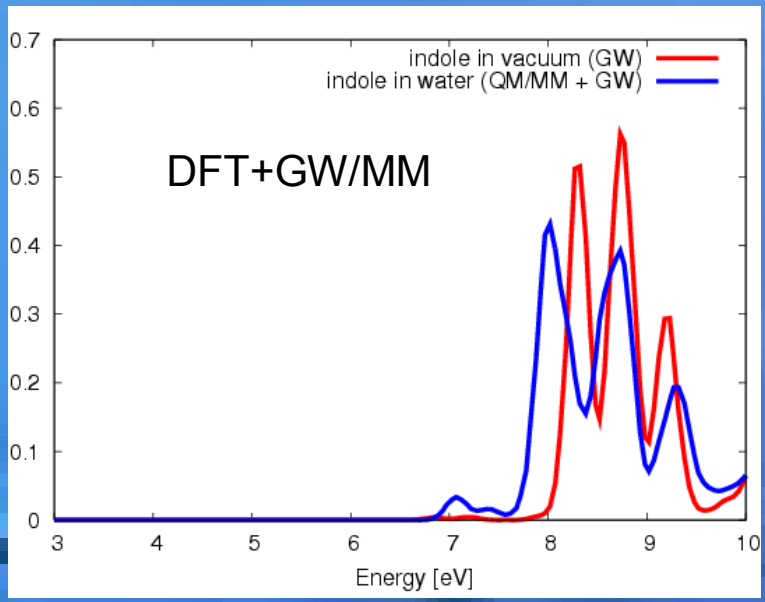

Indole in water GEO-WATER (8 snap)
Indole in water QM/MM (8 snap)
Energy [eV]


Indole in vacuum
Indole in water GEO-WATER (8 snap)
Energy [eV]

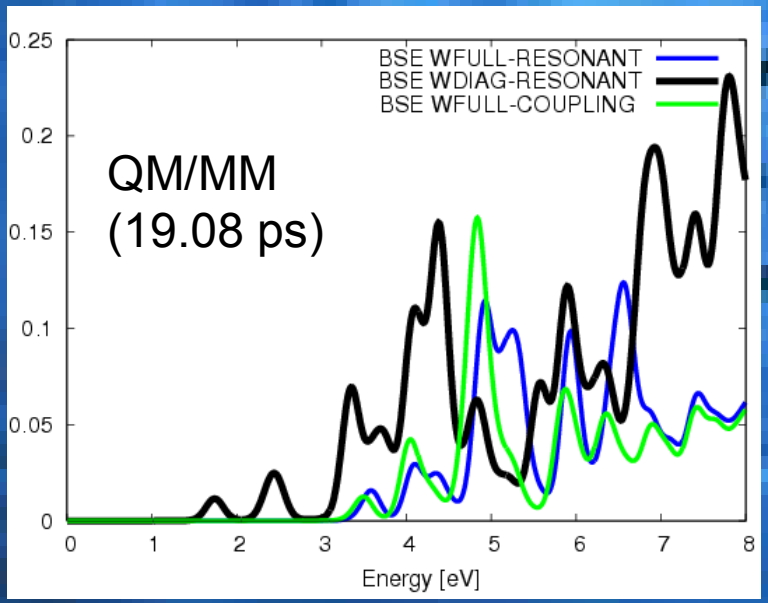
GW:

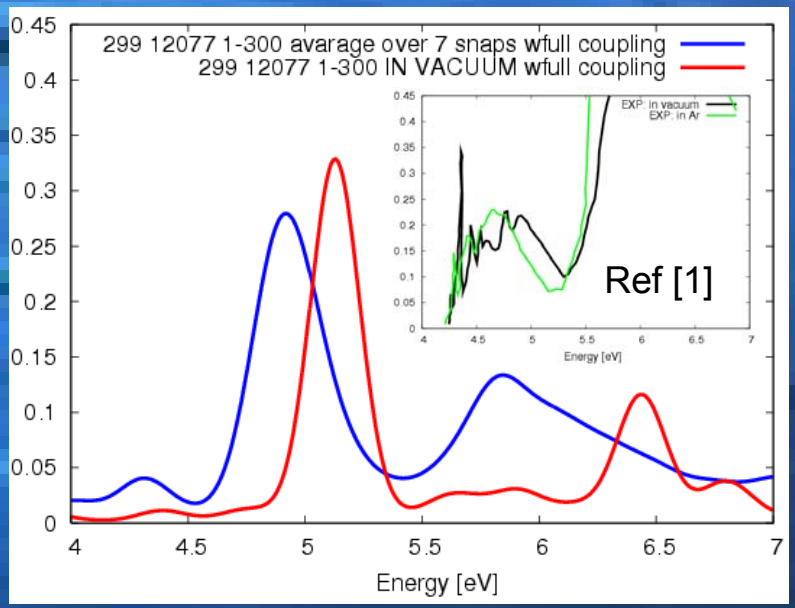


GW opens the GAP (+4eV)



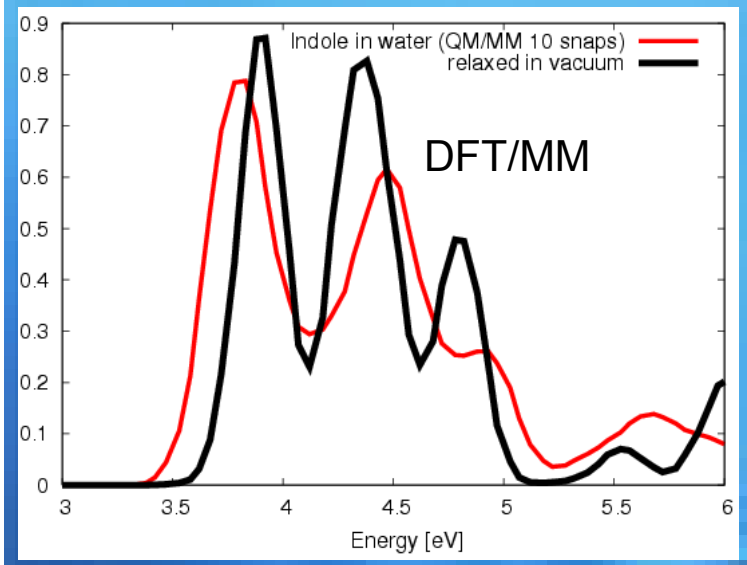
Optical properties (BSE):



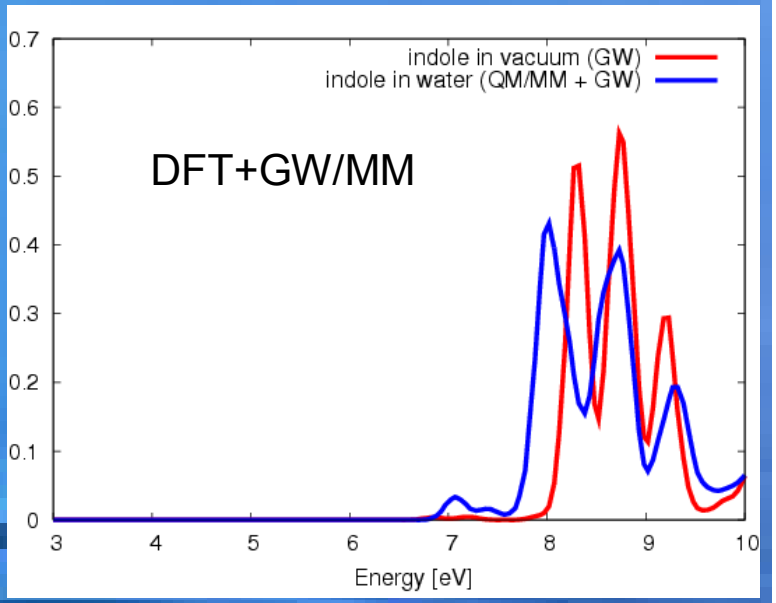


[1] J. Chem. Phys., **67**, n 7, 3277 (1977)

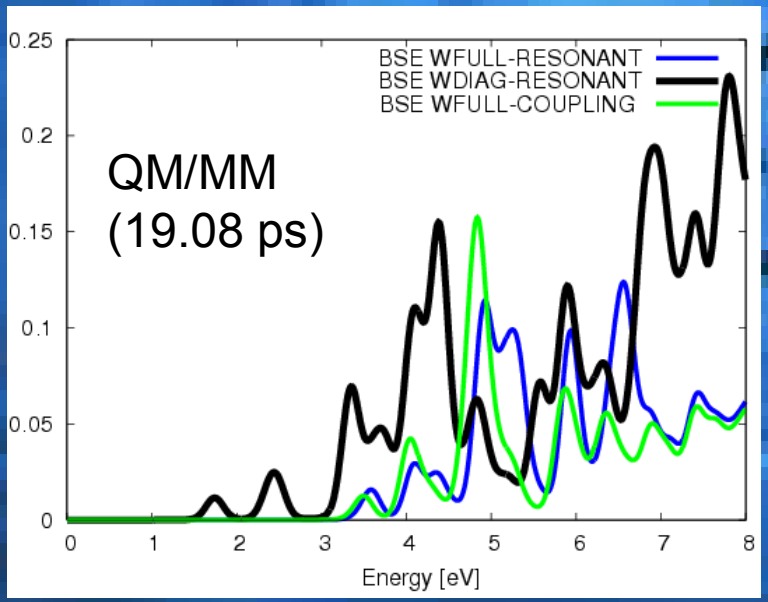
GW:

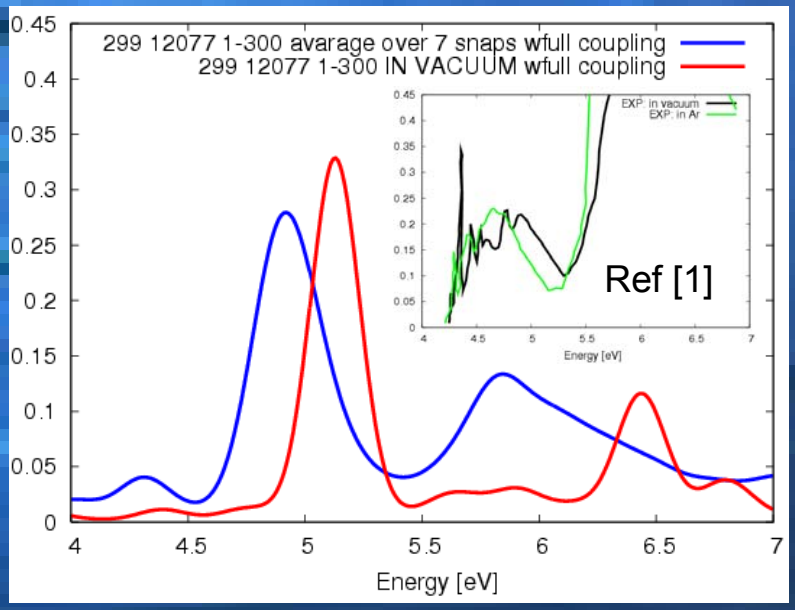


GW opens the GAP (+4eV)



Optical properties (BSE):

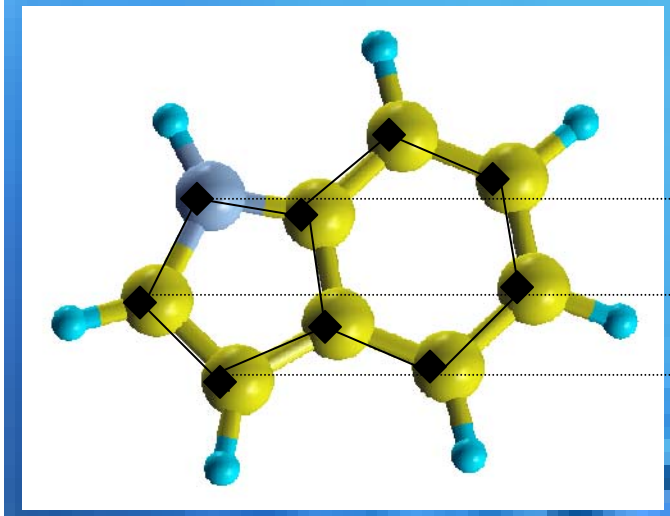


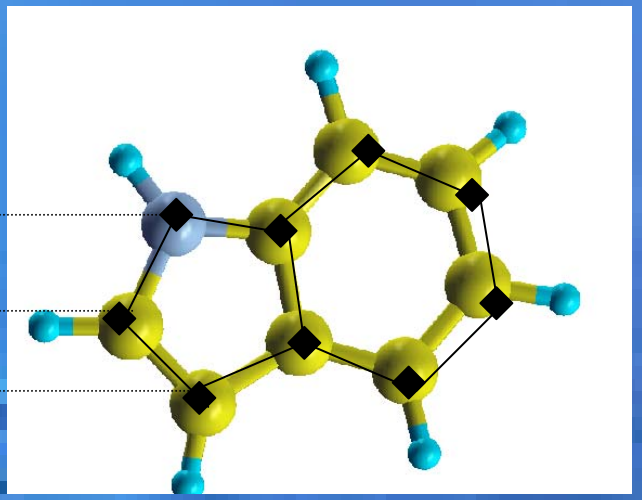


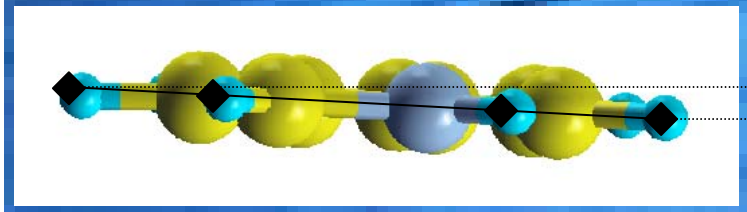
[1] J. Chem. Phys., **67**, n 7, 3277 (1977)

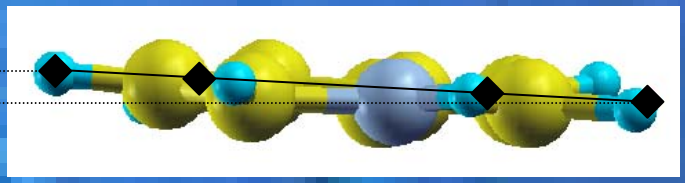
IN VACUUM

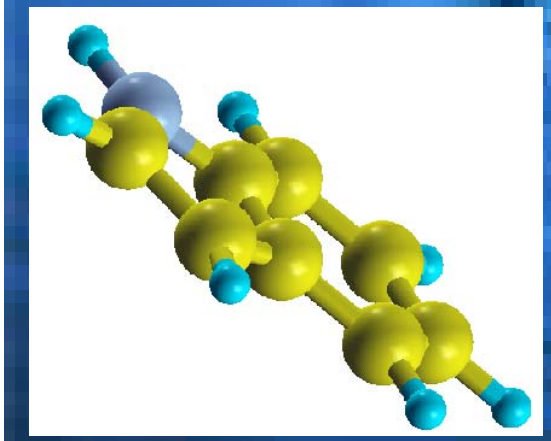
GEOWATER (13.08 ps)

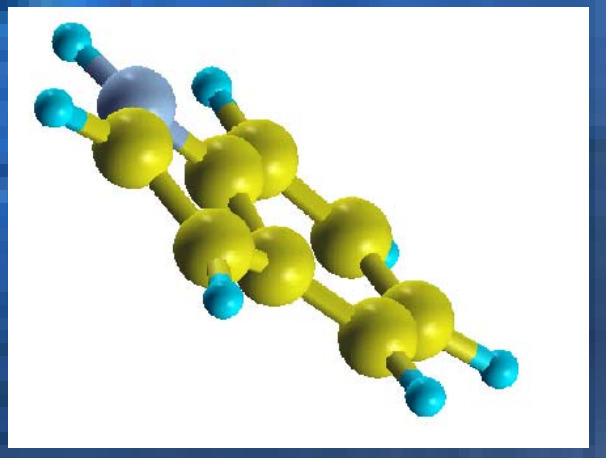


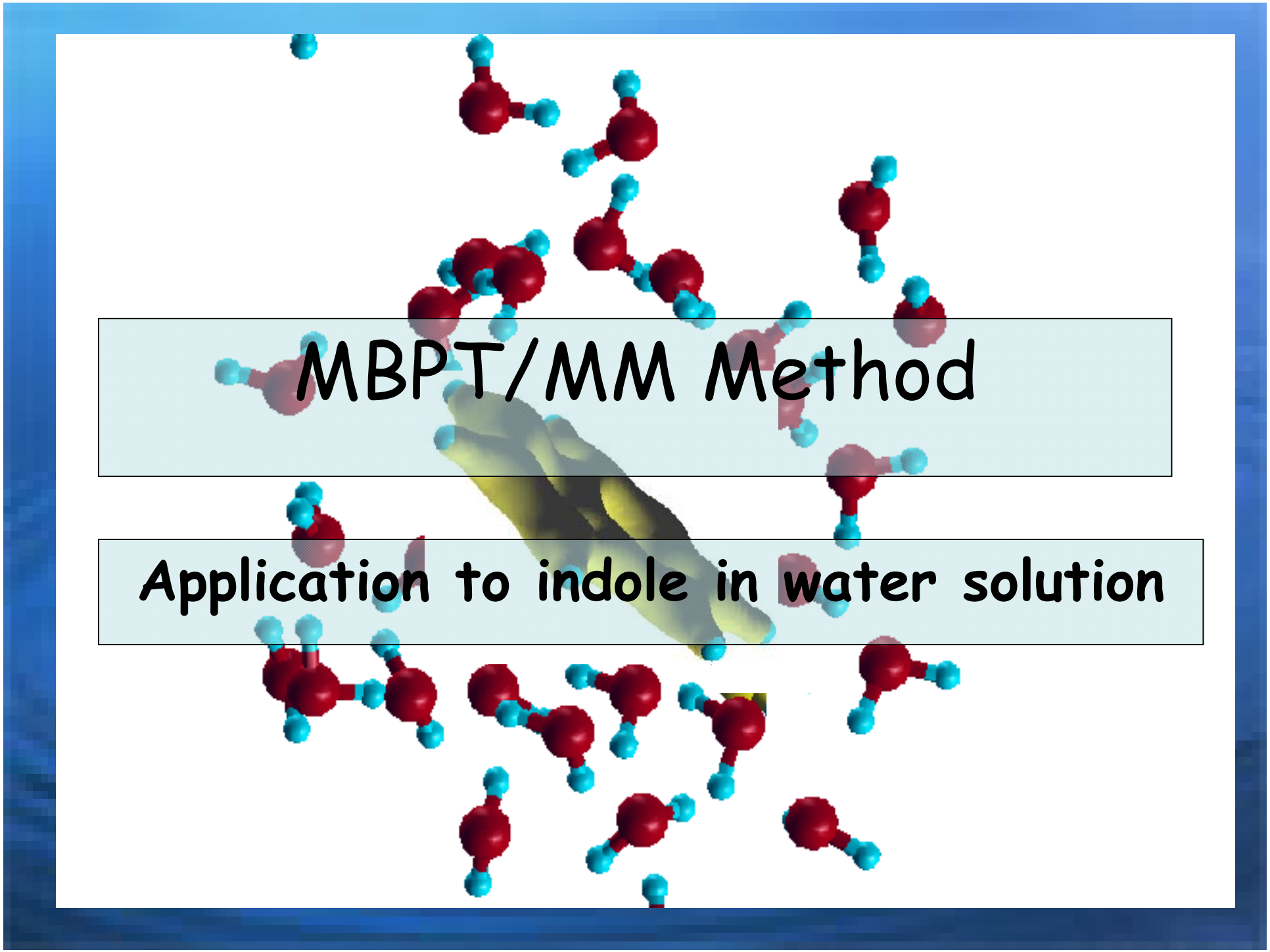










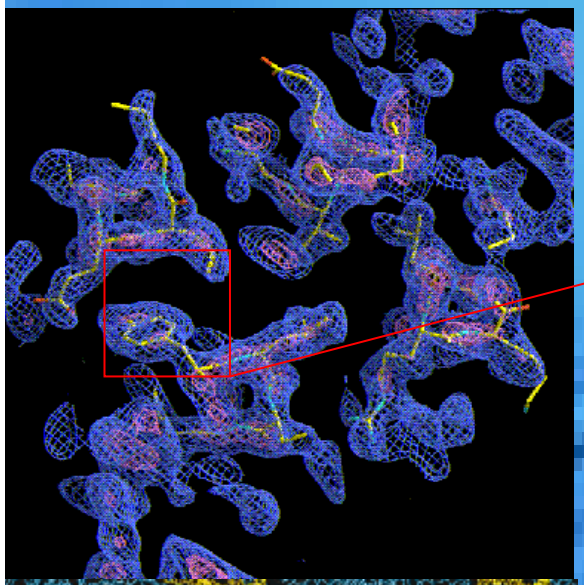

MBPT/MM Method
Application to indole in water solution

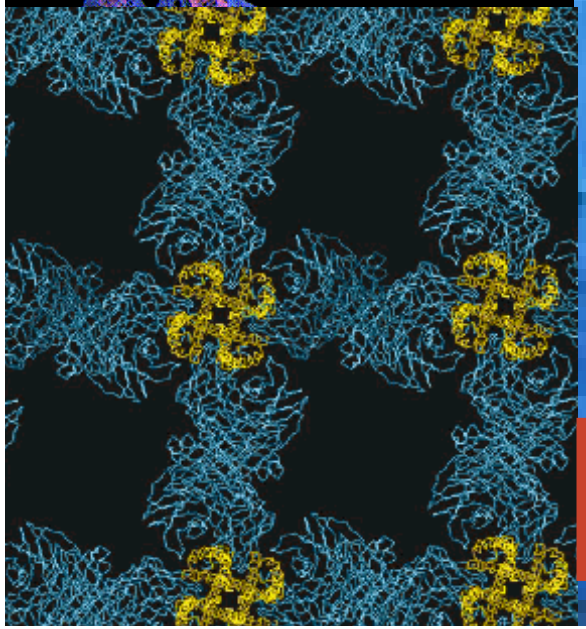
Bridging Structural Biology to Biomolecular properties

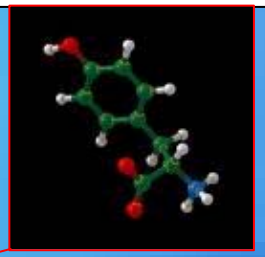
X-rays, NMR, Electron Microscopy

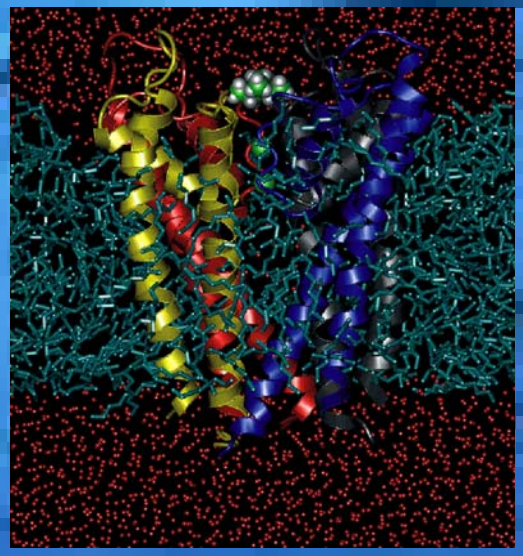
Computational Molecular Biophysics

Other techniques in Biophysics, Biochemistry and Molecular Biology





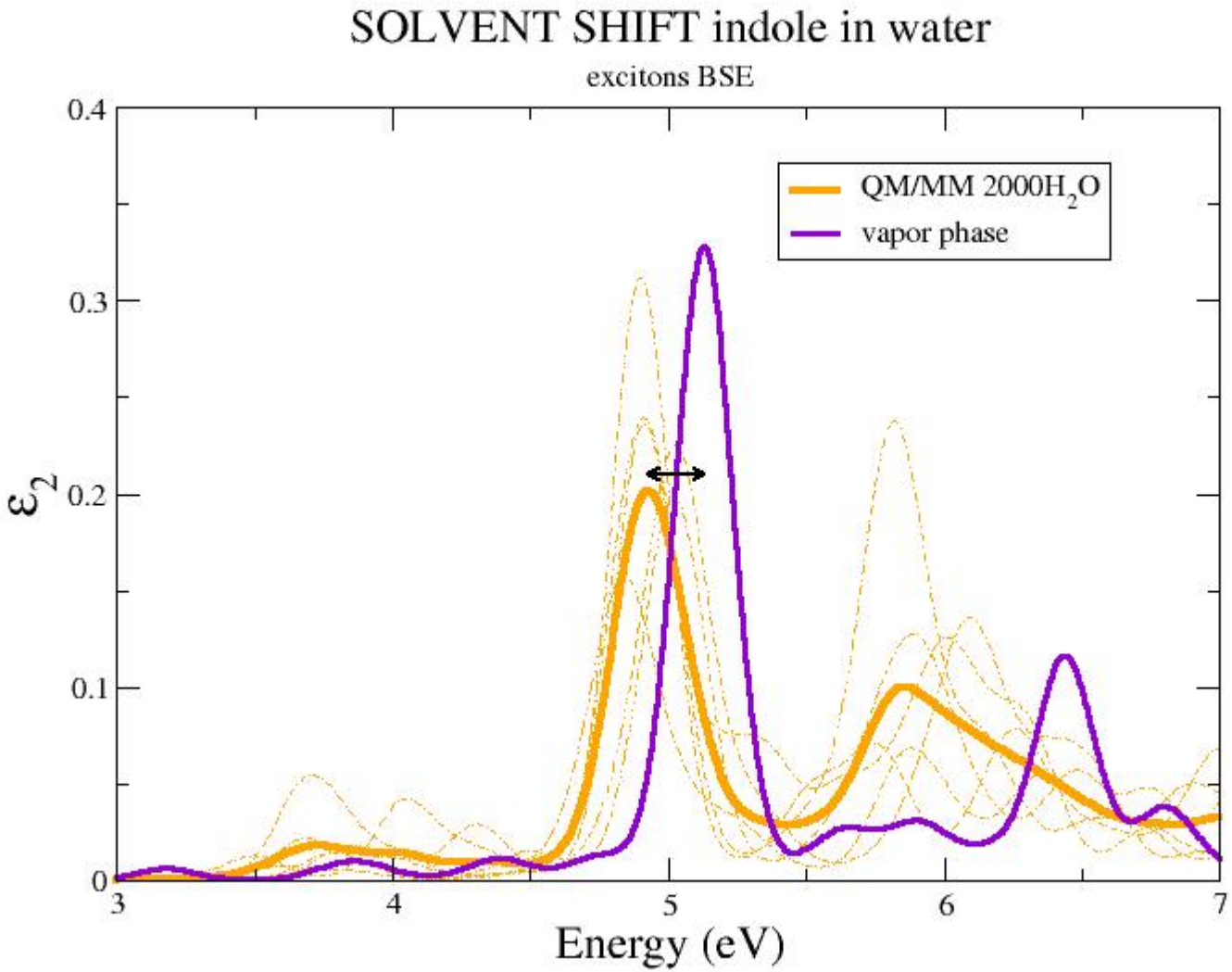




- Protein dynamics and folding
- Enzyme Kinetics
- Infra Red Spectroscopy
- Raman Spectroscopy
- Electron Paramagnetic Resonance (EPR)
- Light/Protein interactions: absorption and emission spectra, photoreactions, etc…
- Electron Transfer properties
- Other…

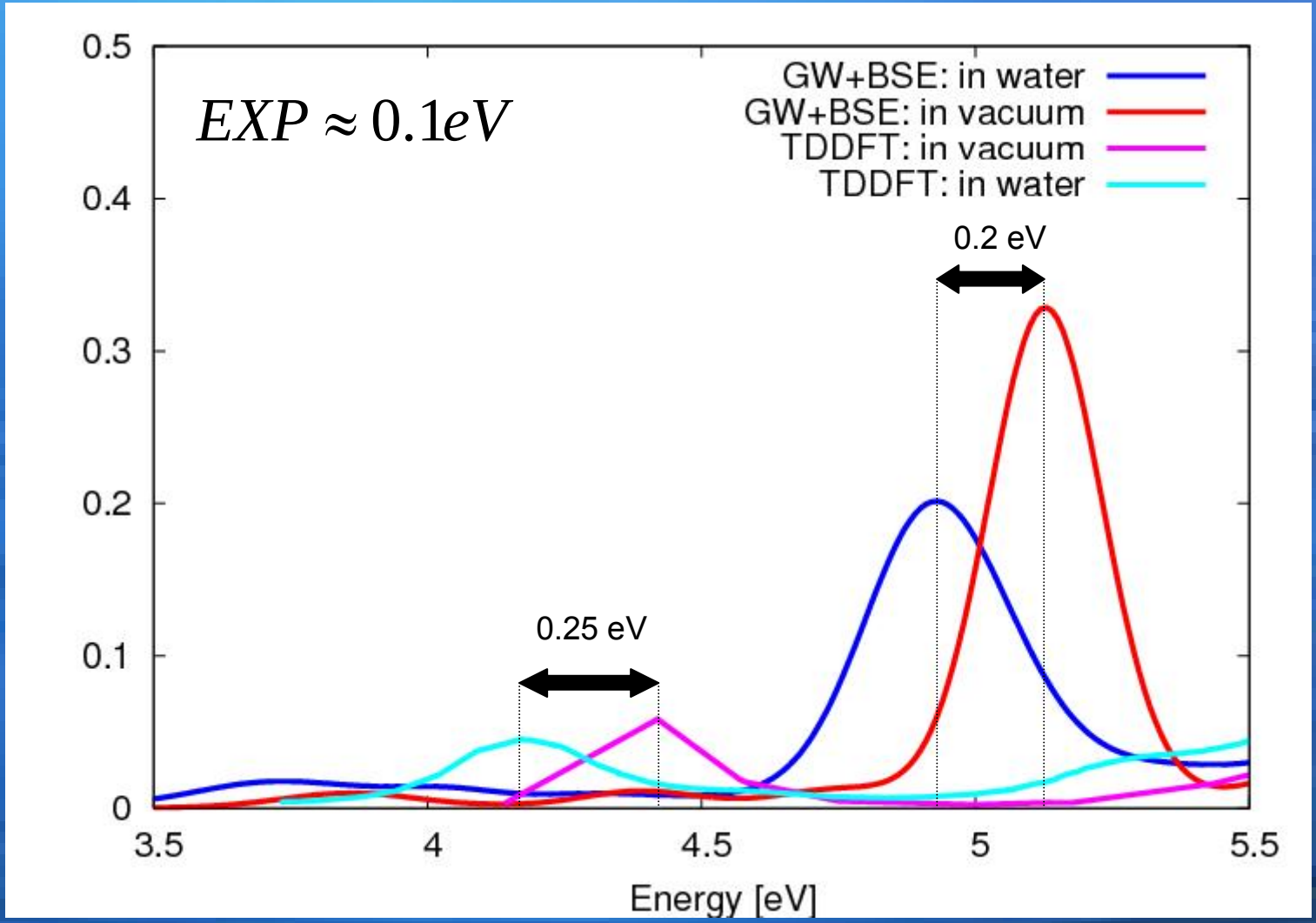
Compute Molecular properties

We need Calculations
- Accurate (Quantum Mechanics)
- Large systems (10^5 atoms)

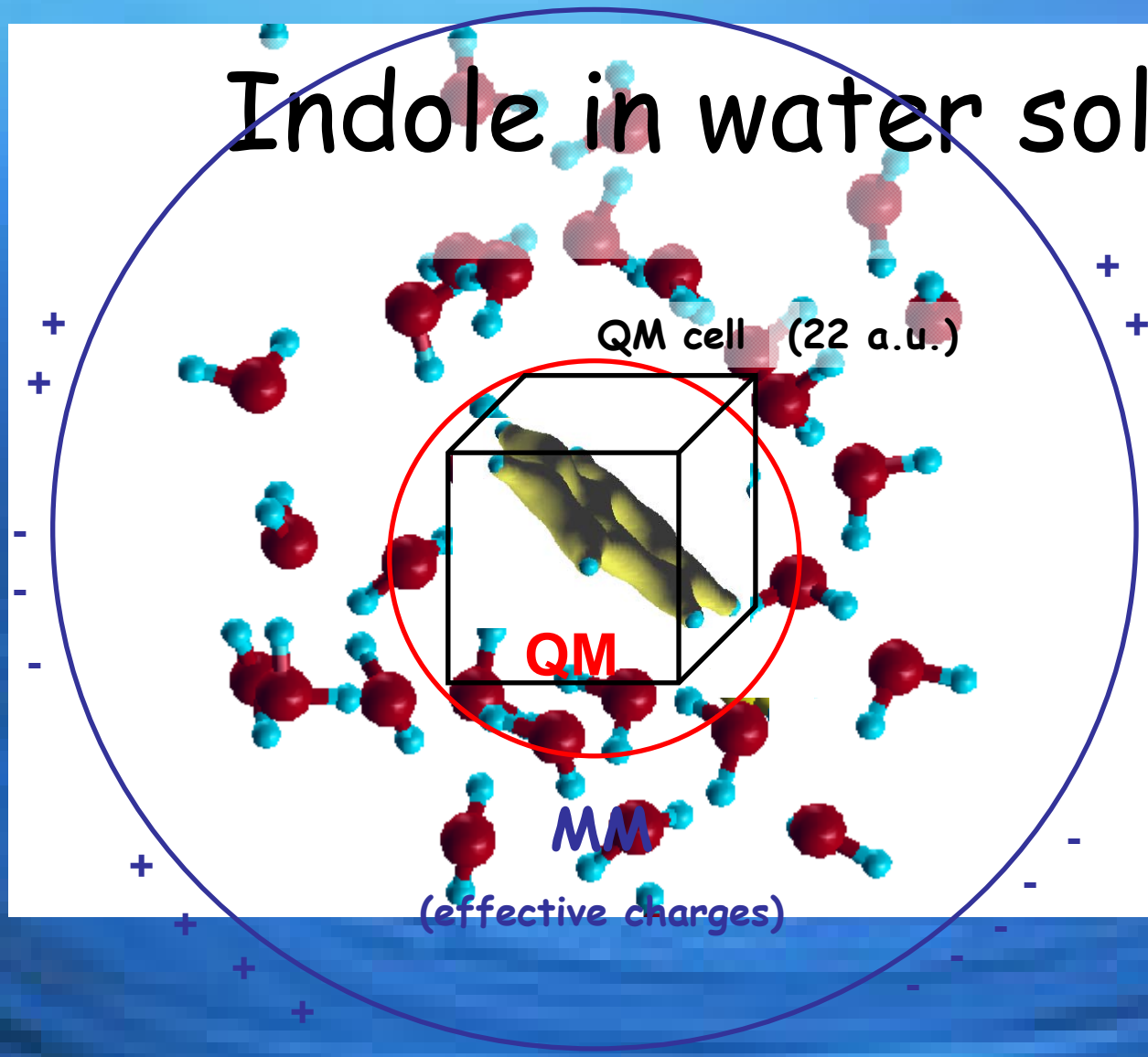


Average over 6 QM/MM snapshots

MBPT/MM compared to TDDFT/MM

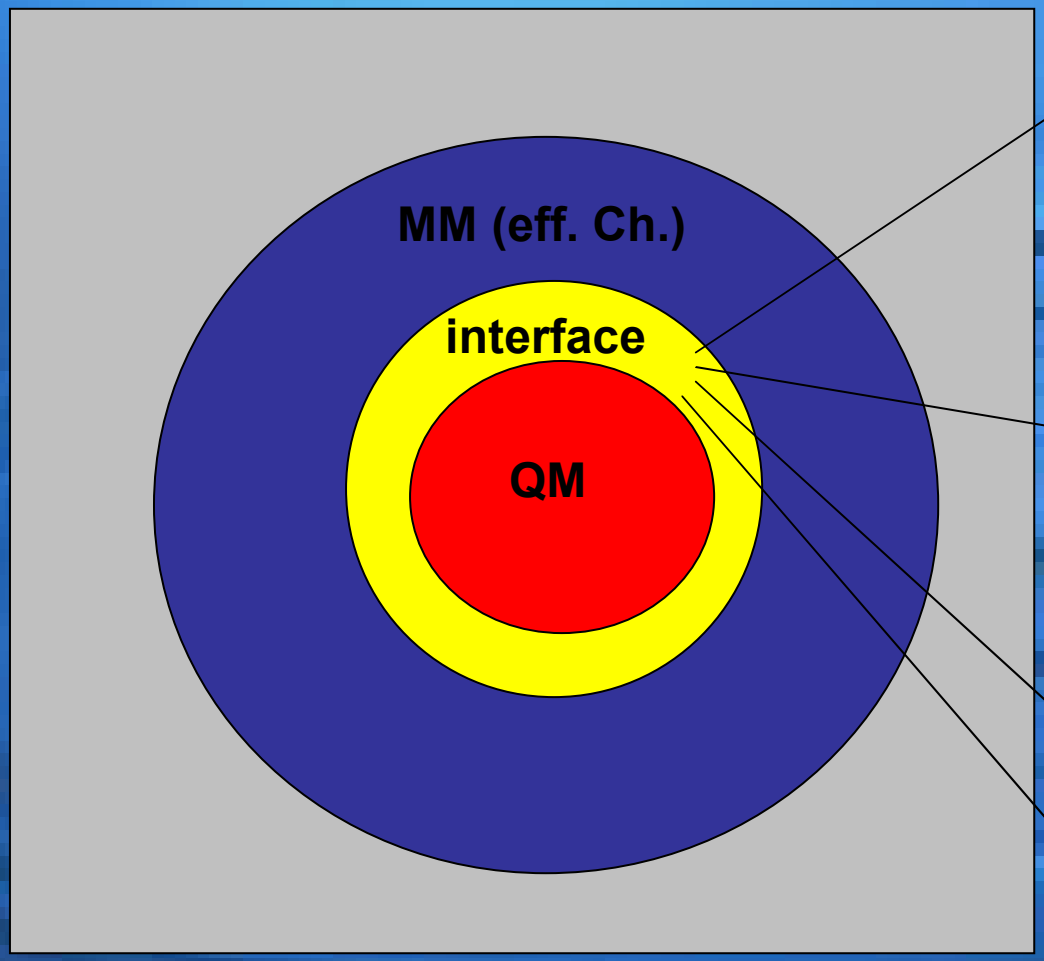


Indole in water solution



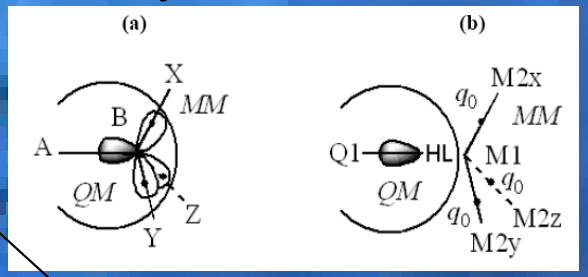
- 2000 H_2O molecules
- Car-Parrinello dynamics (20 ps)
- Environment conditions: 300 K, 1 atm
- $E_{GAP}(H_2O)$=7.0 eV
- E_{GAP}(ind)=4.3 eV

QM/MM



Link-atoms method:

Hybrid-orbital techn.:



Pseudo bond approach

Other

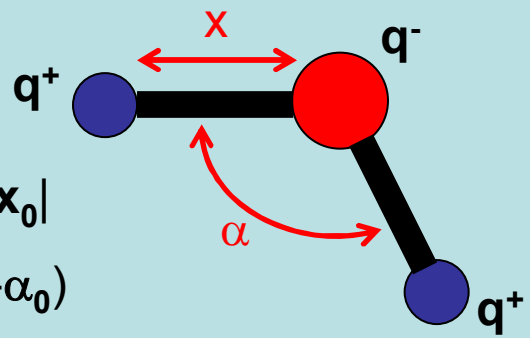
QM simulations:

- Electronic properties
- Magnetic properties
- Optical properties
- …

MM simulations:

- Dynamics
- Atomic coord. relaxation
- Protein folding
- …

Parametrization of forces and charges:

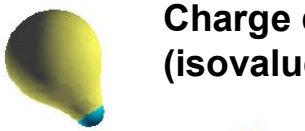


$F_x = \eta|x - x_0|$

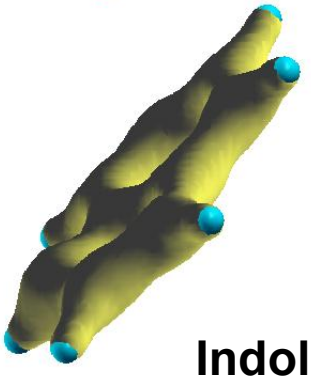
$F_\alpha = \beta(\alpha - \alpha_0)$

Advantage:

Computationally less expensive

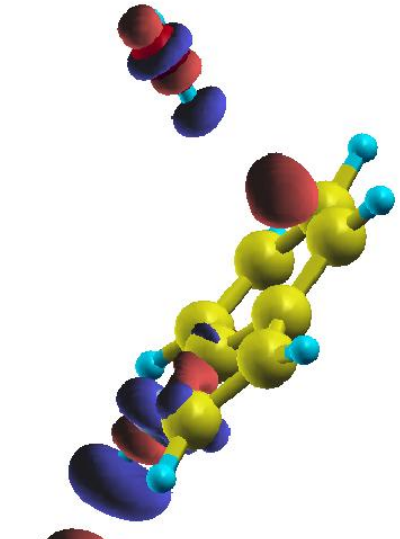


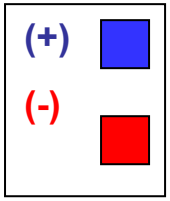
Charge distribution
(isovalue=0.1)



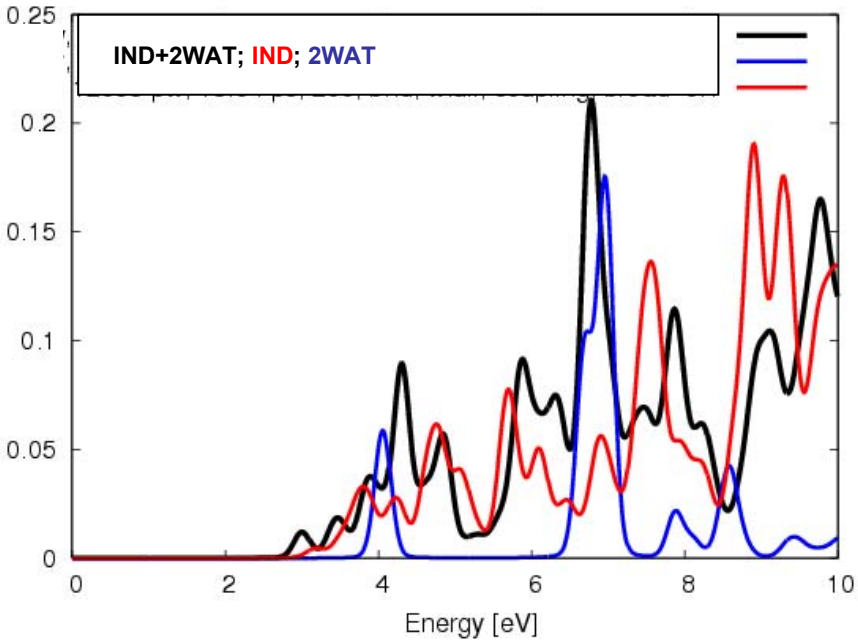
Indole + 2 water molecules

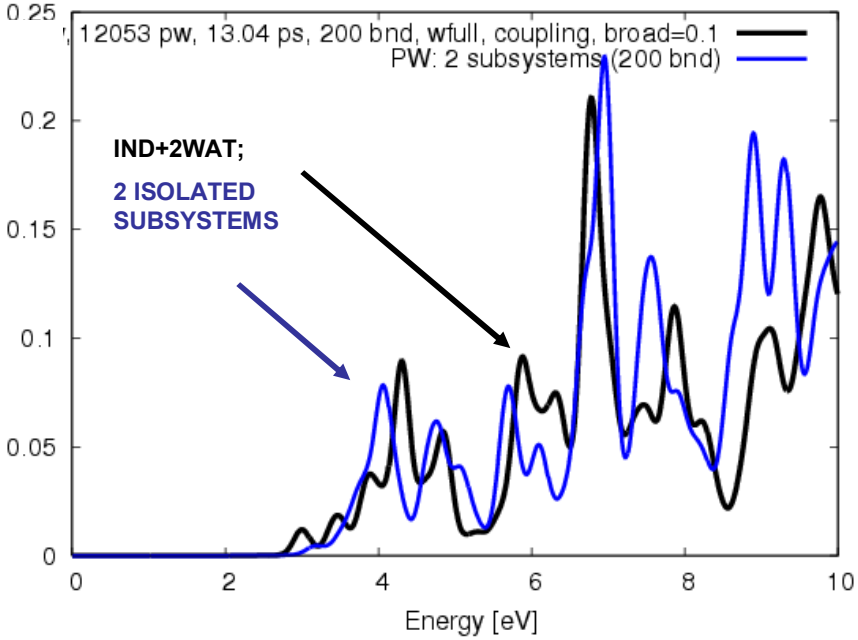
ALL-QUANTUM CALCULATION





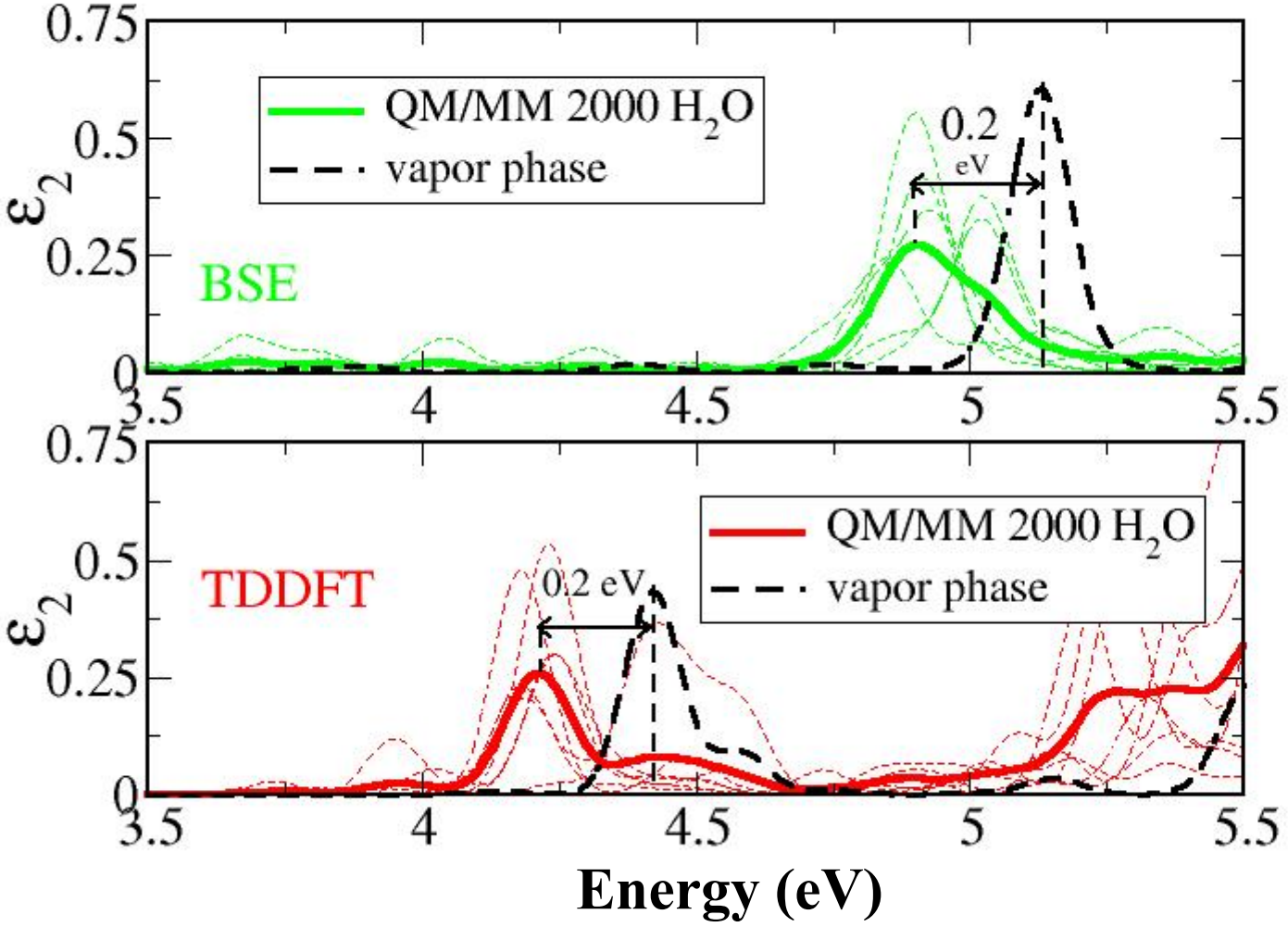
Charge difference
(isovalue=0.001)



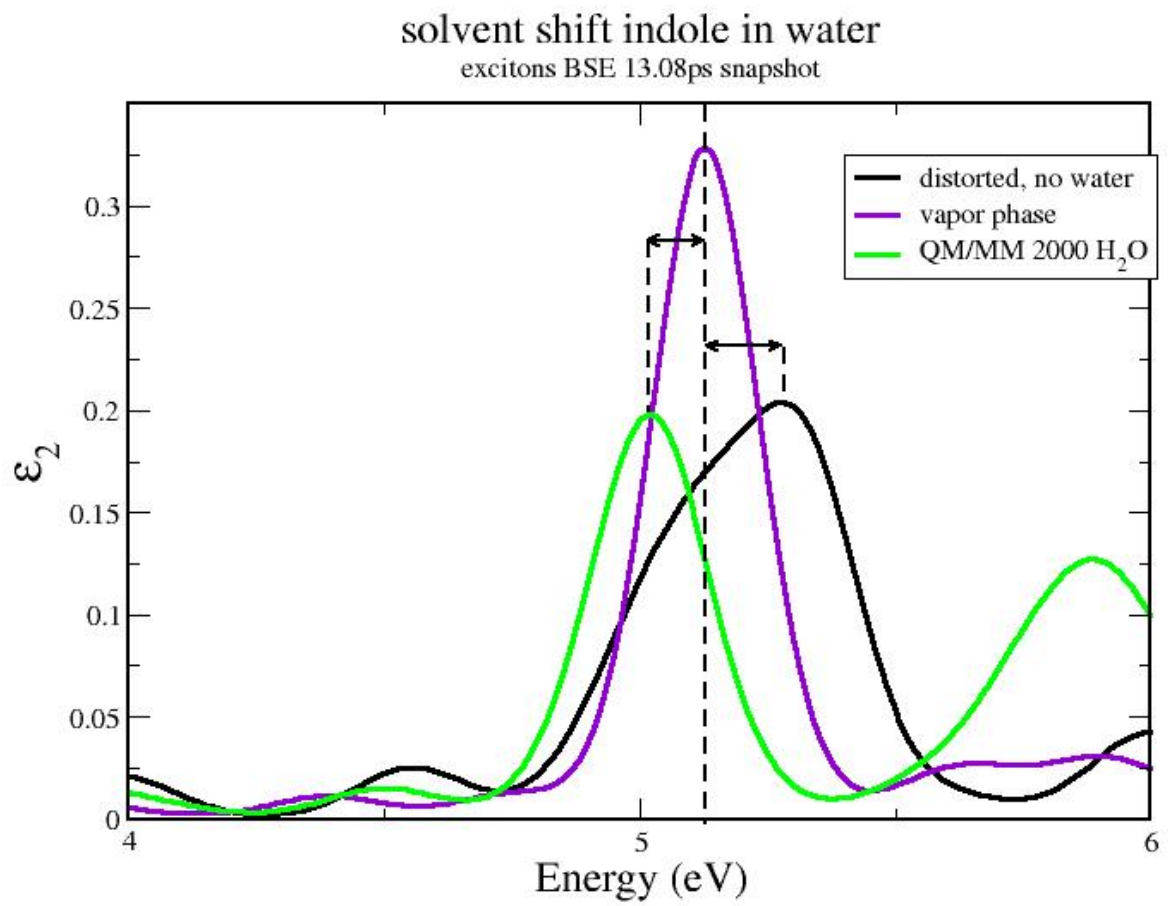


CONCLUSIONS

1. We include MBPT in a QM/MM scheme.
2. We apply this new scheme to indole in water solution.
3. Red shift calculated is in agreement with experiments.
4. We show that this shift is a consequence of the combination of the geometrical distortion and of electrostatic interaction with water molecules.
5. We show that H_2O quantum states do not modify the electron-hole interaction.
6. This scheme opens the way to many applications (especially for biological systems).


0.75
0.5
0.25
0
ε_2
QM/MM 2000 H_2O
vapor phase
BSE
0.2
eV
3.5
4
4.5
5
5.5
TDDFT
0.2 eV
Energy (eV)

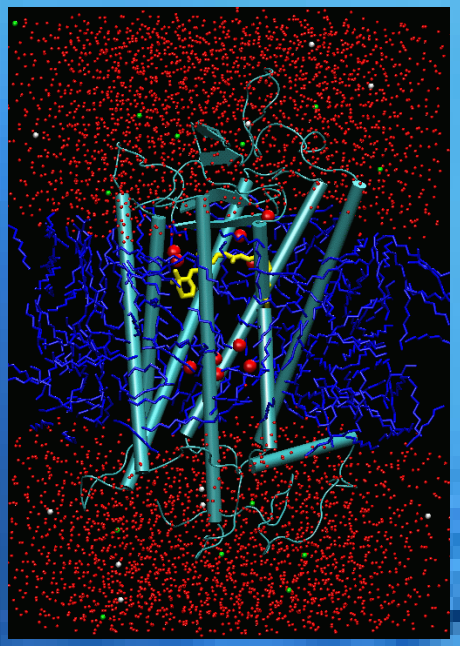
BSE, single snapshot



Inclusion of water important to get the right sign in the solvent shift!!!

A. Mosca Conte, E. Ippoliti, R. Del Sole, P. Carloni, and O. P., submitted

MOTIVATION



Optical spectra of Biological systems *in vivo*

Spectral properties of chromophores are used to probe complex biological processes in *vitro* and in *vivo*

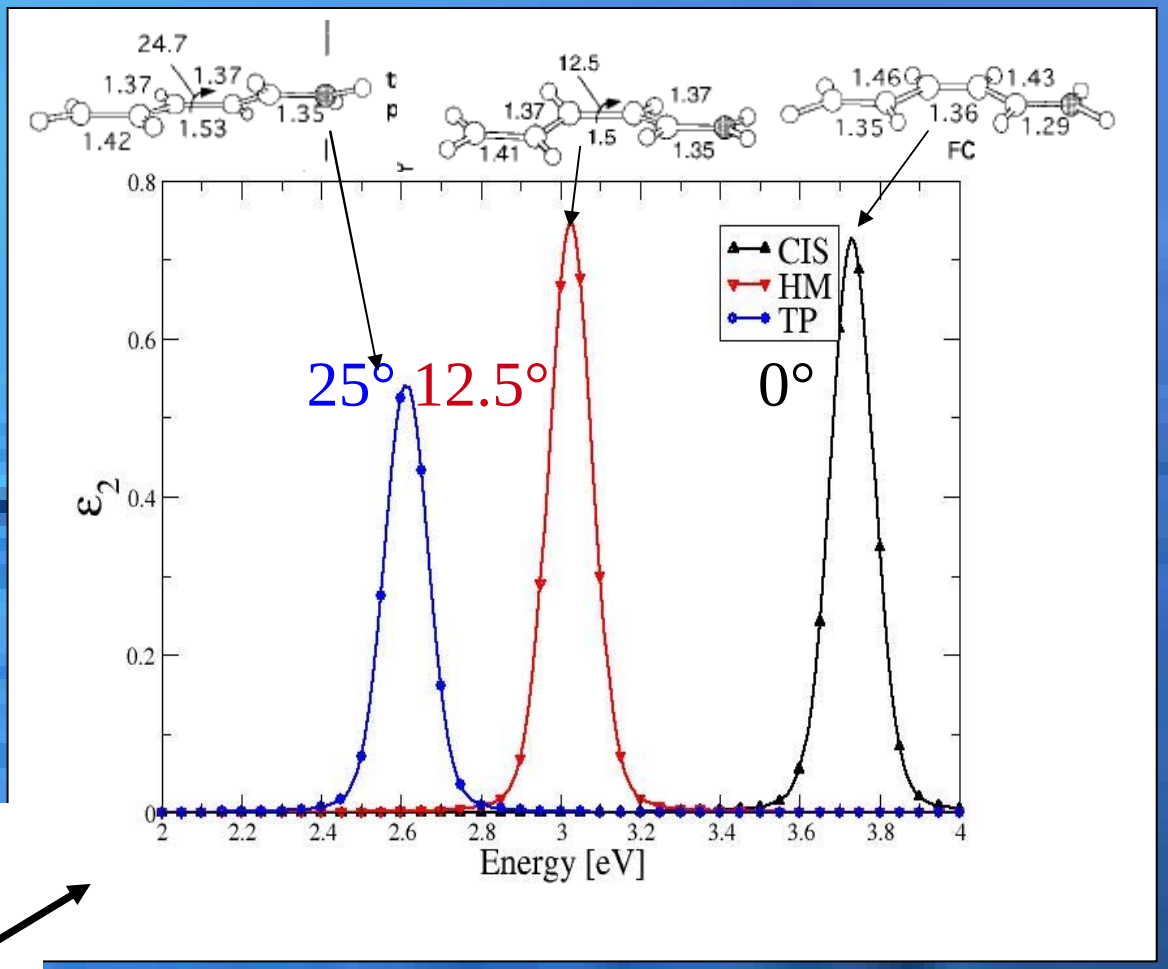
Methods:

Post-Hartree Fock, TDDFT
?! Many-Body Perturbation techniques (GW+BSE)

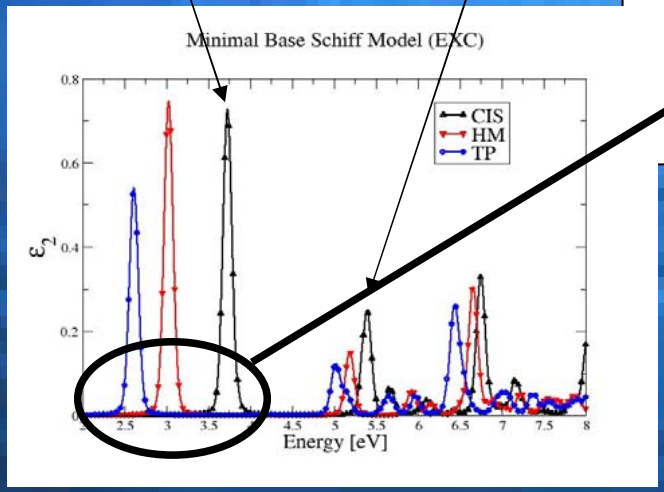
Assess the accuracy/ability of MBPT
versus the more conventional (and efficient) TDDFT

Optical spectra along the MEP

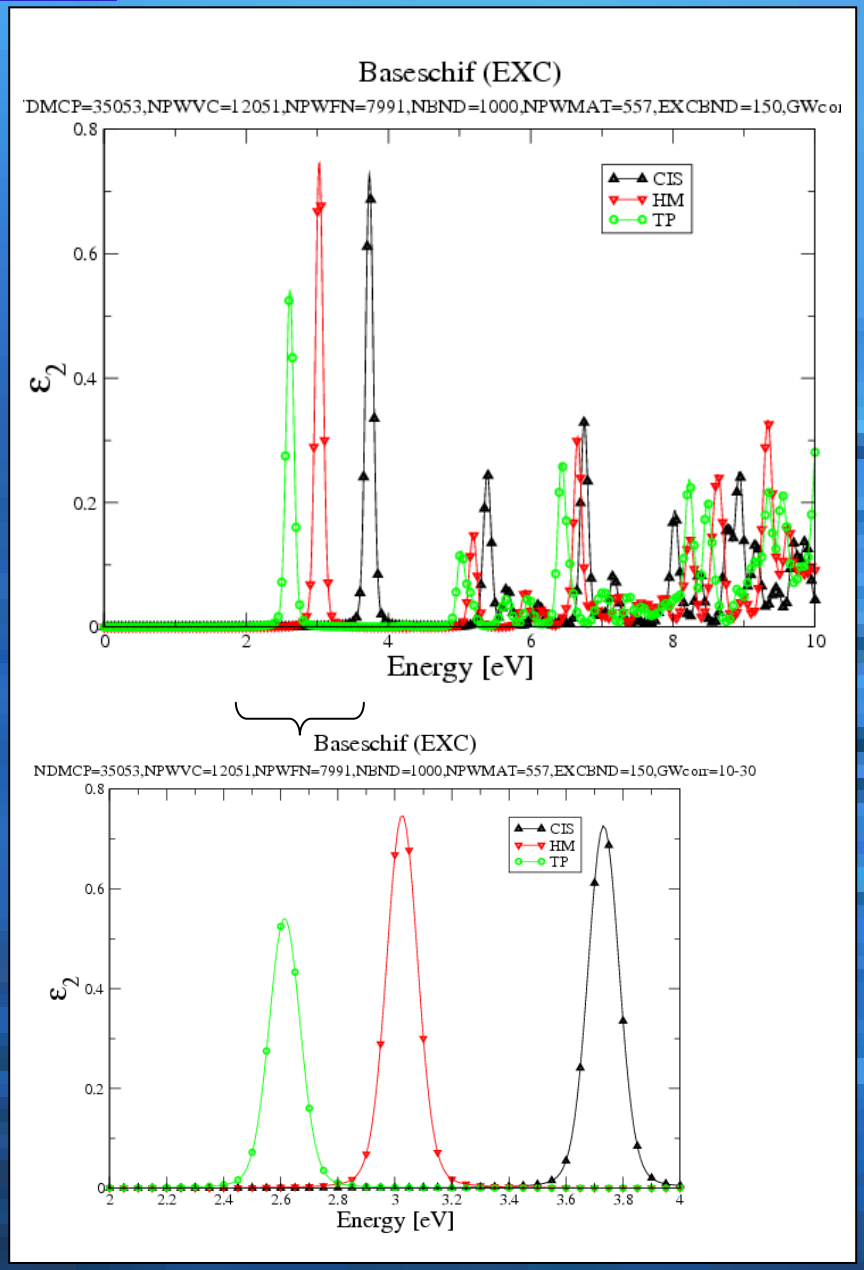
The optical gap decreases by rotating the molecule along the MEP (CIS→HM→TP→CI).

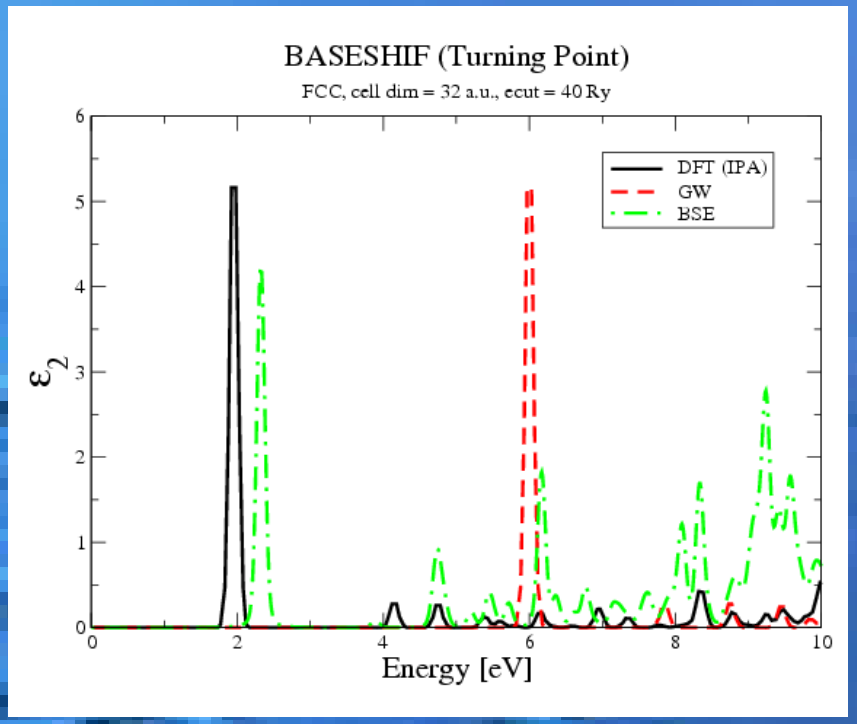


S_0-S_1 S_0-S_2



Optical spectra along the MEP

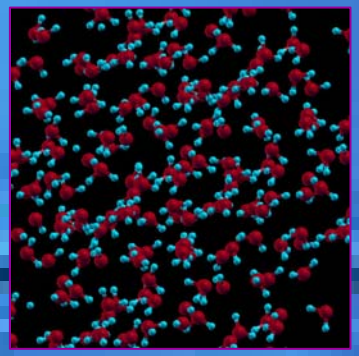




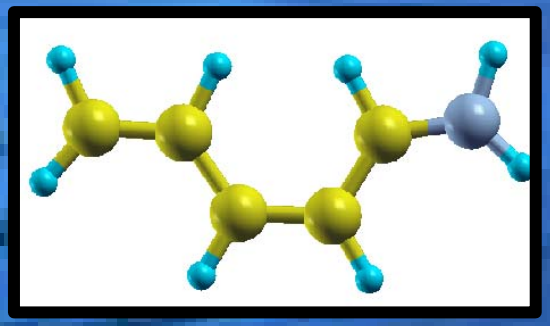
The optical gap decreases by rotating the molecule along the MEP (CIS→HM→TP→CI).

Examples:

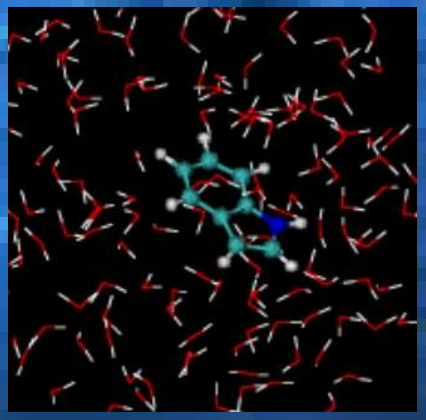
- Optical spectra of water



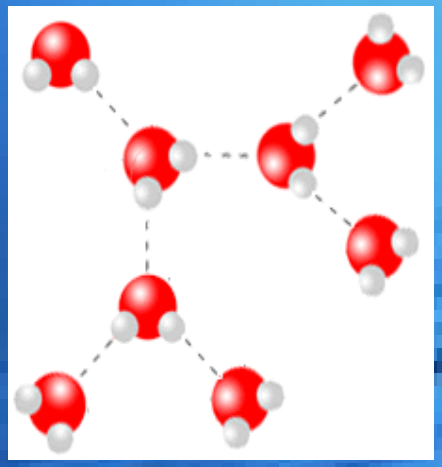
- Minimal Base Schiff Model



- indole in water solution: a QM/MM approach

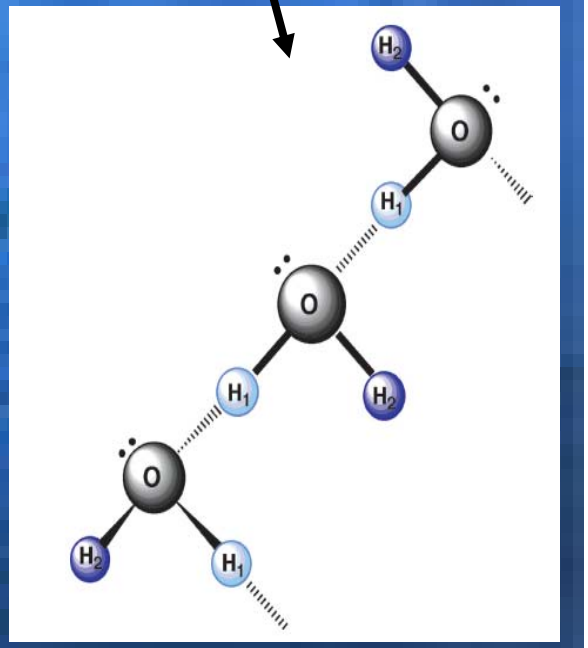


Liquid water "structure"



Random network of hydrogen bonds

Tetrahedral coordination or chains and rings?



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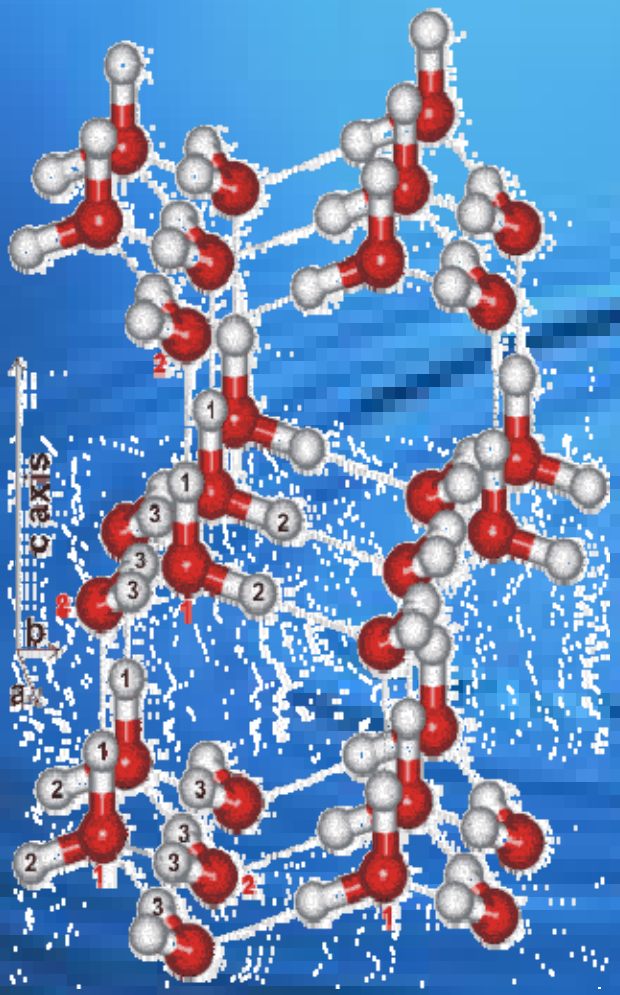
...

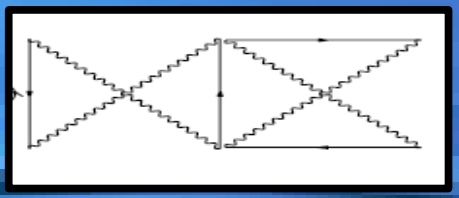
Ice XI



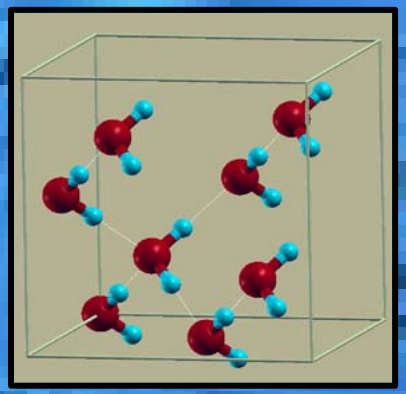
- It is the low temperature equilibrium structure of hexagonal ice (phase pairs: Ih-XI, V-XIII)
- It is proton ordered
- Oriented bonds parallel to the c-axis give ferroelectric character (net dipole)
- Ice XI breaks the “ice rules”

OUTLINE:

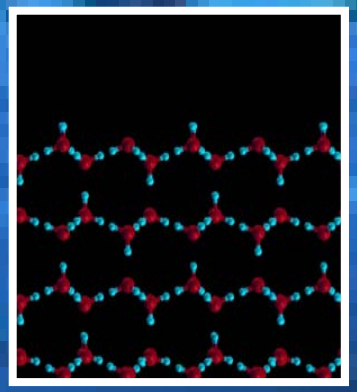
- Theoretical approach



- Ic Ice (bulk)

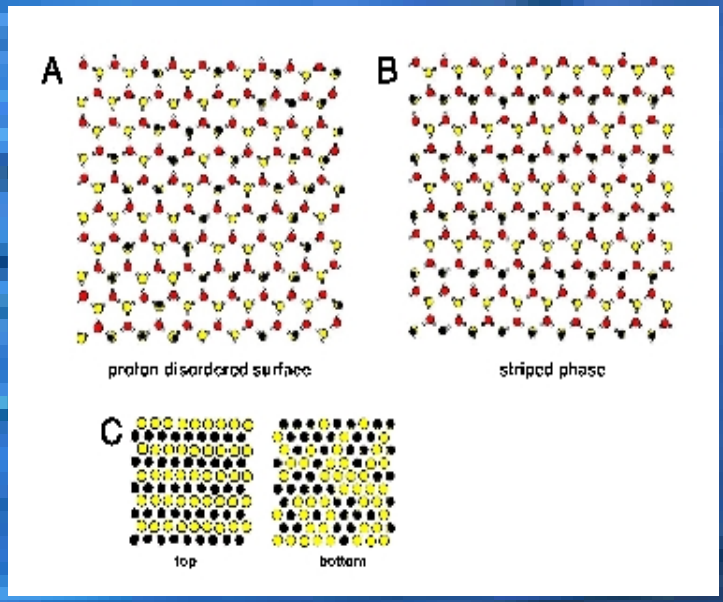


- Ice Ih surface



Proton disorder blabla

- Can influence several properties:
- Growth parameters
- Thermal properties
- (Anti)ferroelectricity
- Surface structure



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Ice structure

Oxygen atoms

several crystalline structures or amorphous

- Hexagonal ice (Ih) – wurtzite lattice
  "Natural ice" - 273 K down to 153 K
- Cubic ice (Ic) – diamond lattice
  153 K down to 113 K
- Ice XI – proton ordered ferroelectric phase
  At about 72 K
- Amorphous – below 113 K