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Applications of GW. GW quasi-particle spectra from occupied states only: latest developments.

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GW quasi-particle spectra from occupied states only: latest developments

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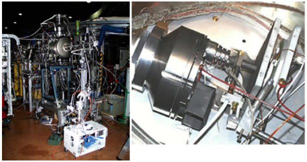
May 24, 2010

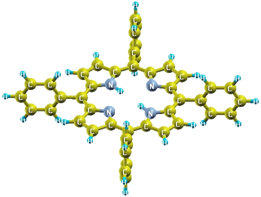
Theory@ELETTRA group

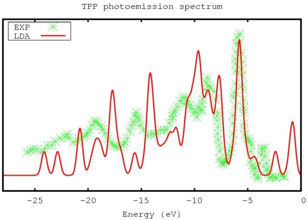
Outline

- Introduction
- Optimal polarizability basis
- GW without empty states
- Examples
- Polarizability basis: optimal vs plane waves

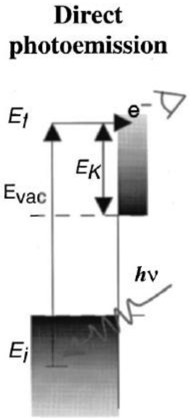
Photoemission spectroscopy







Many-Body Perturbation Theory



G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. **74**, 601 (2002)

- Quasi-particle energies
- $N \rightarrow N \pm 1$
- $E^*_{N\pm1} - E_N$
- Many-Body Perturbation Theory (MBPT)

GWA

M.S. Hybertsen and S.G. Louie, Phys. Rev. Lett 55, 1418 (1985)

$$E_n \simeq \epsilon_n + \langle \Sigma_{G^\circ W^\circ}(E_n) \rangle_n - \langle V_{xc} \rangle_n$$

$$\Sigma_{G^\circ W^\circ}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' G^\circ(\mathbf{r}, \mathbf{r}'; \omega - \omega') W^\circ(\mathbf{r}, \mathbf{r}'; \omega')$$

$$\mathrm{W}^\circ \quad = \quad v + v \cdot \Pi^\circ \cdot v \quad \text{where} \quad \Pi^\circ = P^\circ \cdot (1 - v \cdot P^\circ)^{-1}$$

$$P^\circ(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{2\pi} \int d\omega' G^\circ(\mathbf{r}, \mathbf{r}'; \omega - \omega') G^\circ(\mathbf{r}, \mathbf{r}'; \omega')$$

$$G^\circ(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i \frac{\psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}')}{\omega - \epsilon_i \pm i\delta}$$

For accurate(?) calculations: analytic continuation method

M.M. Rieger, L. Steinbeck, I.D. White, H.N. Rojas and R.W. Godby, Comp. Phys. Comm. **117** 211 (1999)

Two big challenges:

- Computational cost:
  - We must represent operators $\hat{O}(\mathbf{r},\mathbf{r}')$
  - prohibitive for large systems
- Sums over empty states
  - In principle sums over all empty-states
  - prohibitive for large systems
  - analogous to DFPT

Polarization basis

If an optimal representation of P° can be found:

$$P^\circ(\mathbf{r},\mathbf{r}';\omega) \simeq \sum_{\alpha\beta} \Phi_\alpha(\mathbf{r}) P^\circ{}_{\alpha\beta}(\omega) \Phi_\beta(\mathbf{r}')$$

$$\Pi^\circ(\mathbf{r},\mathbf{r}';\omega) \simeq \sum_{\alpha\beta} \Phi_\alpha(\mathbf{r}) \Pi^\circ{}_{\alpha\beta}(\omega) \Phi_\beta(\mathbf{r}')$$

$$W^\circ(\mathbf{r},\mathbf{r}';\omega) \simeq \int d\mathbf{r}'' d\mathbf{r}''' \sum_{\alpha\beta} v(\mathbf{r},\mathbf{r}'') \Phi_\alpha(\mathbf{r}'') \Pi^\circ{}_{\alpha\beta}(\omega) \Phi_\beta(\mathbf{r}''') v(\mathbf{r}''',\mathbf{r}')$$

then a **huge** speed-up can be achieved

The same optimal basis for $\Pi^\circ(\mathbf{r},\mathbf{r}';\omega)$ and $P^\circ(\mathbf{r},\mathbf{r}';\omega)$ with:

$$P^\circ(\mathbf{r},\mathbf{r}';\omega)=\sum_{v,c}\frac{\psi_v(\mathbf{r})\psi_c(\mathbf{r})\psi_v(\mathbf{r}')\psi_c(\mathbf{r}')}{\epsilon_c-\epsilon_v+\omega}$$

we want to build a basis for the products in real space of valence and conduction states

1. Wannier transformation:

$$\psi_v \rightarrow w_v$$
$$\psi_c \rightarrow w_c$$

2. Reject the small overlaps:

$$w_v(\mathbf{r})w_c(\mathbf{r}) \rightarrow \bar{\Phi}_{vc}(\mathbf{r})$$

3. Orthonormalization

$$\bar{\Phi}_{vc} \rightarrow \Phi_\mu$$

we use a treshold s_2 for rejecting almost linear dependent terms

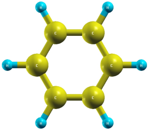
- Analytic continuation approach

  M.M. Rieger, L. Steinbeck, I.D. White, H.N. Rojas and R.W. Godby, Comp. Phys. Comm. **117** (1999) 211

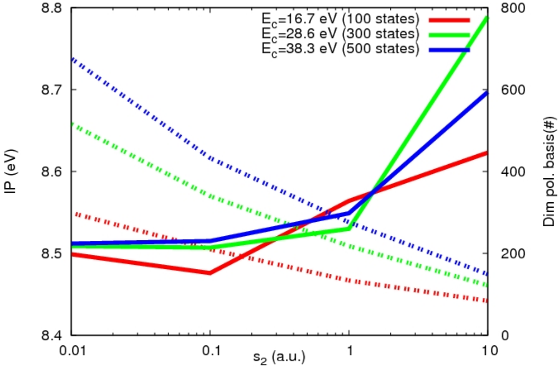
- Γ-sampling only, real wavefunctions
- Implemented in the **Quantum-ESPRESSO** code; a community project for high-quality quantum simulation software, coordinated by P. Giannozzi. See http:/www.quantum-espresso.org

See: PU, G.Stenuit, S.Baroni, Phys. Rev. B **79**, 201104(R) (2009)

Isolated benzene molecule



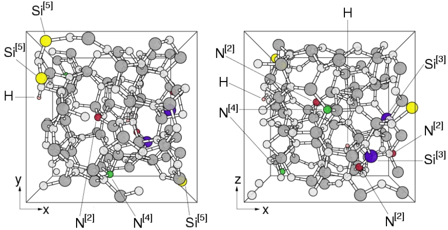
C_6H_6

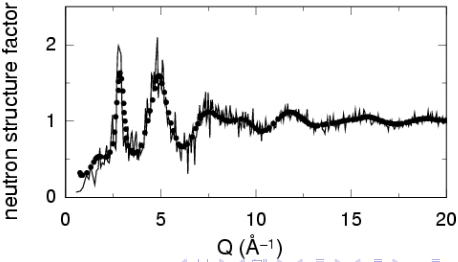


Convergence within 10 meV is achieved with $E_c^2 \geq$ 30 eV (300 states) and a polarizability basis set of only 340 elements ($s_2 \leq 0.1$).

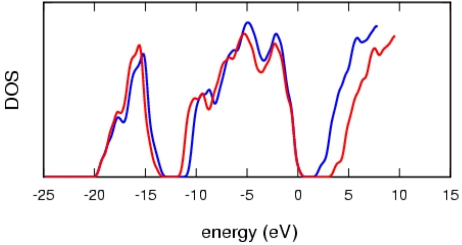
amorphous Si_3N_4

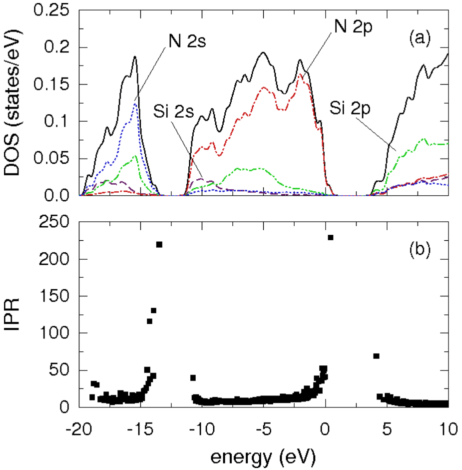
- model obtained by Car-Parrinello MD
- 152 atoms at exp. density
- 344 valence states
- US pseudopotentials
- Neutron, IR, Raman





amorphous Si_3N_4





- E_G(DOS)=2.9 eV
- E_G(GW)=4.4 eV
- E_G(exp)=∼5 eV

See: L.Giacomazzi and P.U. PRB 80, 144201 (2009)

An optimal polarizability basis can be found solving:

$$\int d\mathbf{r}' P(\mathbf{r},\mathbf{r}';t=0)\Phi_\mu = q_\mu \Phi_\mu(\mathbf{r}) \text{ with: } q_\mu > q^*$$

where:

$$P(\mathbf{r},\mathbf{r}';t=0) = Q_v(\mathbf{r},\mathbf{r}')Q_c(\mathbf{r},\mathbf{r}') = Q_v(\mathbf{r},\mathbf{r}')(\delta(\mathbf{r}-\mathbf{r}') - Q_v(\mathbf{r},\mathbf{r}'))$$

we can approximate:

$$P(\mathbf{r},\mathbf{r}';t=0) \approx Q_v(\mathbf{r},\mathbf{r}')Q_e(\mathbf{r},\mathbf{r}')$$

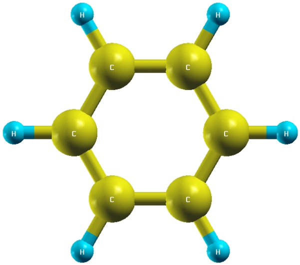
with

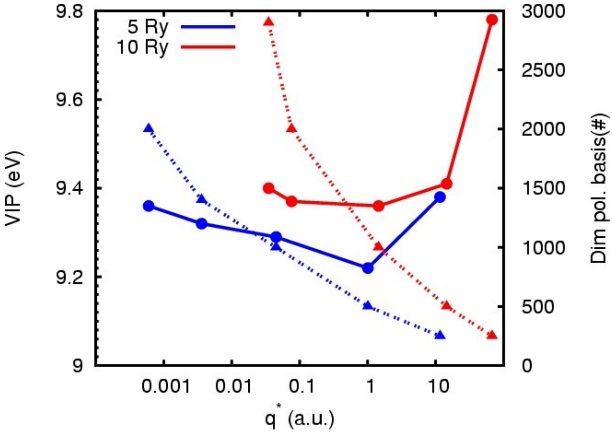
$$Q_e \approx \sum_{\mathbf{G},\mathbf{G}'} Q_c|\mathbf{G}\rangle R^{-1}_{\mathbf{G},\mathbf{G}'}\langle \mathbf{G}'|Q_c \Theta(G^2 - E)\Theta(G'^2 - E)$$

with:

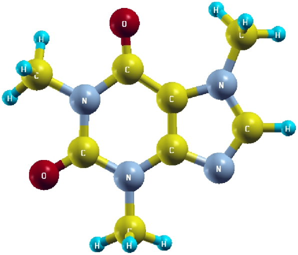
$$R_{\mathbf{G},\mathbf{G}'} = \int d\mathbf{r}\langle \mathbf{G}|Q_c|\mathbf{r}\rangle\langle \mathbf{r}|Q_c|\mathbf{G}'\rangle$$

IP of the benzene molecule

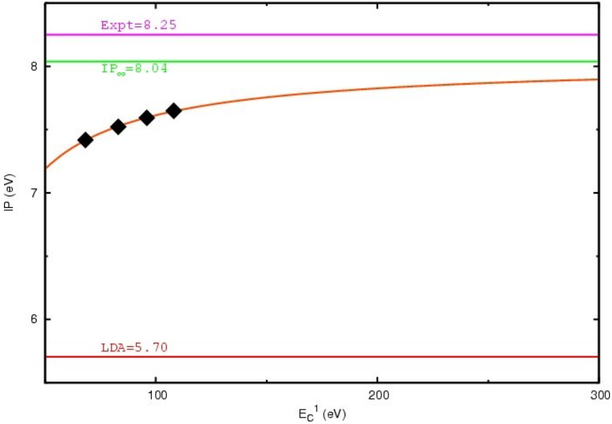




IP of the caffeine molecule



$$\text{IP}(E_c) = \text{IP}(\infty) - \frac{\alpha}{E_c}$$



The solution I

We work on the imaginary frequency axis

M.M. Rieger, L. Steinbeck, I.D. White, H.N. Rojas and R.W. Godby, Comp. Phys. Comm. **117** 211 (1999)

Polarizability basis

- we work with real wavefunctions (Γ-point)
- Let $\{\Phi_\mu\}$ be a basis for the irreducible polarizability P
- $\{\Phi_\mu\}$ is also a basis for the reducible polarizability Π

  - plane waves
  - localized basis sets
  - optimal basis sets

Sternheimer approach for P

The polarizability matrix $P^{\circ}_{\mu\nu}(i\omega)$:

$$P^{\circ}_{\mu\nu}(i\omega) = -4\Re\sum_{v,c}\frac{\int d\mathbf{r}d\mathbf{r}'\Phi_{\mu}(\mathbf{r})\psi_v(\mathbf{r})\psi_c(\mathbf{r})\psi_v(\mathbf{r}')\psi_c(\mathbf{r}')\Phi_{\nu}(\mathbf{r}')}{\epsilon_c-\epsilon_v+i\omega}.$$

the projector over the conduction manifold Q_c:

$$Q_c(\mathbf{r},\mathbf{r}') = \sum_c \psi_c(\mathbf{r})\psi_c(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') - \sum_v \psi_v(\mathbf{r})\psi_v(\mathbf{r}'),$$

with the notation:

$$\langle\mathbf{r}|\psi_i\Phi_{\nu}\rangle = \psi_i(\mathbf{r})\Phi_{\nu}(\mathbf{r}).$$

We can now eliminate the sum over c :

$$P^{\circ}_{\mu\nu}(i\omega) = -4\Re\sum_v\langle\Phi_{\mu}\psi_v|Q_c(H-\epsilon_v+i\omega)^{-1}Q_c|\psi_v\Phi_{\nu}\rangle,$$

The solution III

The computational load can be hugely reduced:

with an optimal basis:

$$\langle r|Q_c|\psi_v \Phi_\mu\rangle \approx \sum_\alpha t^0_\alpha(\mathbf{r}) T_{\alpha,v\mu},$$

We can easily solve:

$$\langle t^0_\alpha|(H-\epsilon_v+i\omega)^{-1}|t^0_\beta\rangle$$

for every ϵ_v and every ω
For each t^0_α: Lanczos-chain: $t^1_\alpha, t^2_\alpha, t^3_\alpha, ..$

$$\langle t^i_\alpha|H-\epsilon_v+i\omega|t^j_\alpha\rangle = \delta_{i,j}(d^i-\epsilon_v+i\omega)+\delta_{i,j+1}f^i+\delta_{i,j-1}f^j.$$

Equivalent Lanczos approach for the self-energy:

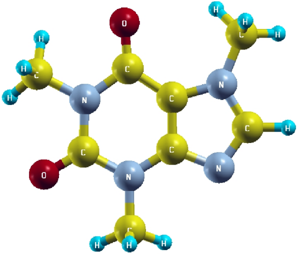
$$\langle \mathbf{r} | \psi_n (v\Phi_\mu) \rangle \approx \sum_\alpha s^0_\alpha(\mathbf{r}) S_{\alpha,n\mu},$$

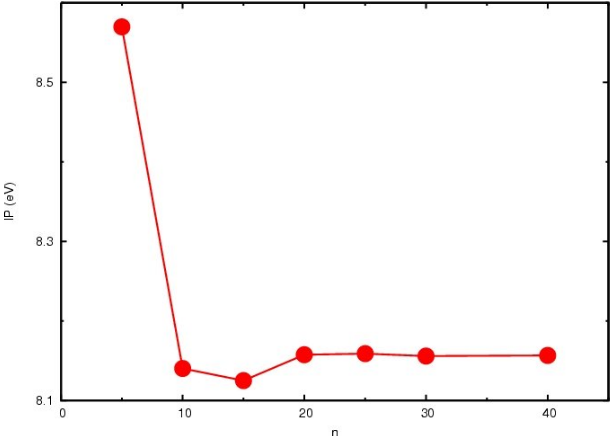
with:

$$\langle \mathbf{r} | (v\Phi_\mu) \rangle = \int d\mathbf{r}' v(\mathbf{r},\mathbf{r}') \Phi_\mu(\mathbf{r}')$$

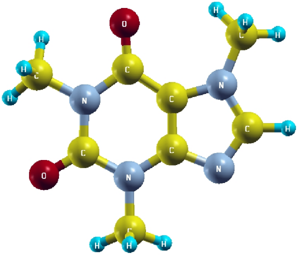
Implemented in the *quantum-Espresso* package
www.quantum-espresso.org
See: PU, G. Stenuit, and S. Baroni, Phys. Rev. B **81**, 115104 (2010)

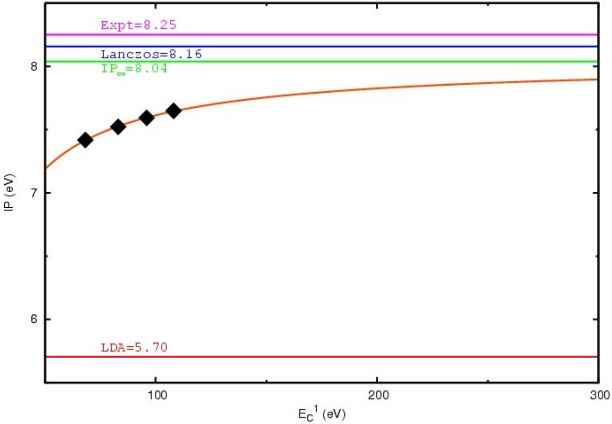
Convergence with respect to Lanczos steps



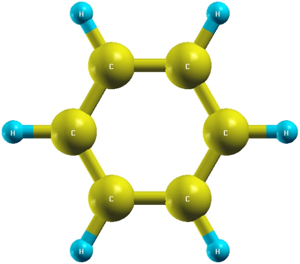


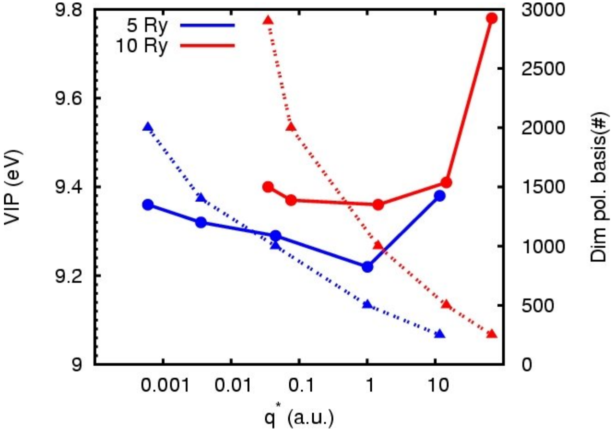
IP of the caffeine molecule



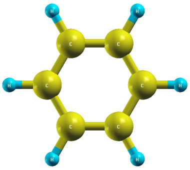


IP of the benzene molecule

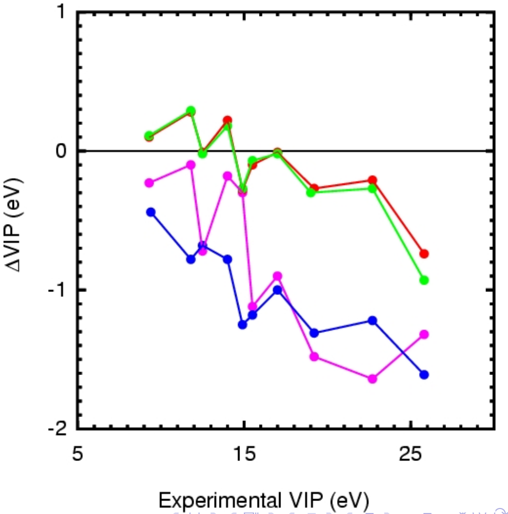




IPs of the benzene molecule



- $E = 10$ Ry $q^* = 0.035$ a.u. $N = 2900$
- $E = 10$ Ry $q^* = 14.5$ a.u. $N = 500$
- Extrapolations
- Plane waves $E = 5$ Ry $N = 1500$



Extension to extended systems

- Head$(\mathbf{G}=0,\mathbf{G}'=0)$ and wings $(\mathbf{G}=0,\mathbf{G}'\neq 0)$ of the symmetric dielectric matrix are calculated using Lanczos chains ($\mathbf{k}$-points sampling implemented)
- Wings are projected over the polarizability basis vectors
- Element $\mathbf{G}=0$ added to the polarizability basis
- $v(\mathbf{G})=\frac{1}{\Omega}\int d\mathbf{q}\frac{1}{|\mathbf{G}+\mathbf{q}|^2}$
- Grid on imaginary frequency can be denser around $\omega=0$

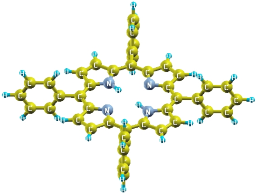
Extension to extended systems: test

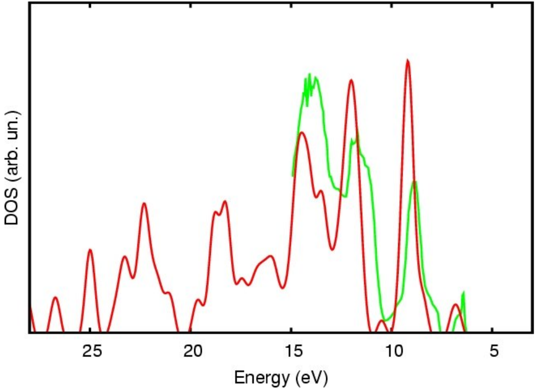
- Bulk Si: 64 atoms cubic cell
- Optimal polarizability basis: E^*=2Ry, q^*=2.7 a.u. (#2000)
- k-points sampling for: head and wings, DFT charge density

state	LDA	GW	Expt.
Γ_{1v}	-11.94	-11.63	-12.5
X_{1v}	-7.80	-8.77	
X_{4v}	-2.88	-2.90	-2.9,-3.3
Γ_{25v}	0.	0.	0.
X_{1c}	0.67	1.36	1.25

Tetraphenylporphyrin

$C_{44}H_{30}N_4$

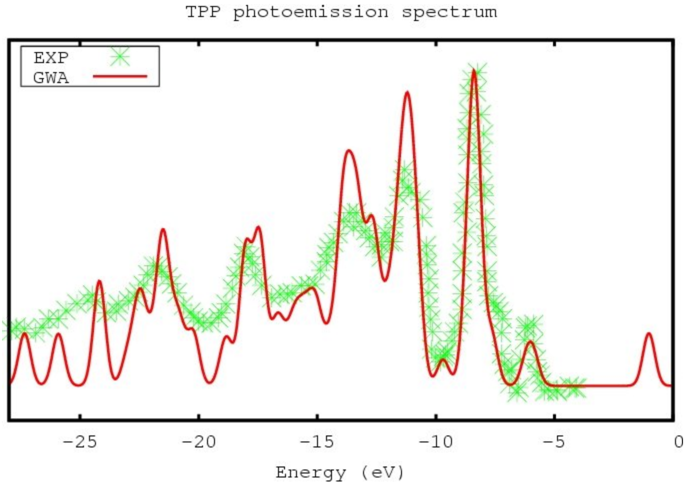




IP^{exp}=6.4 eV
IP^{LDA}=5.0 eV
IP^{GWA}=6.7 eV

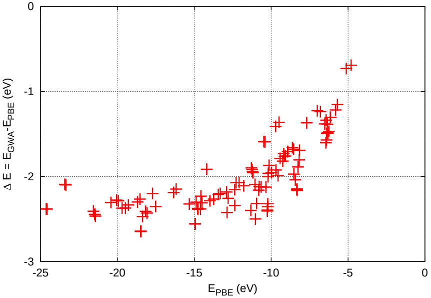
Experimental PS spectrum: N.E. Gruhn, et al. Inor Chem (1999)

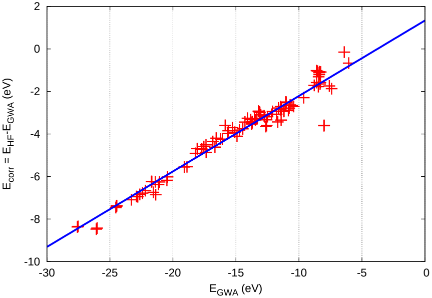
Tetraphenylporphyrin



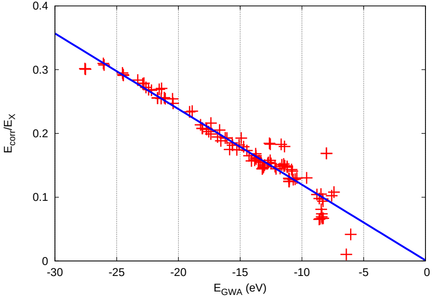
Experimental PS spectrum: C. Cudia Castellarin and A. Goldoni

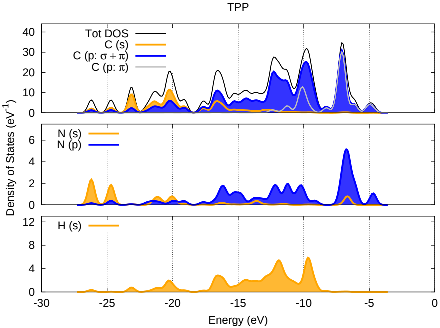
Tetraphenylporphyrin: analysis





Tetraphenylporphyrin: analysis

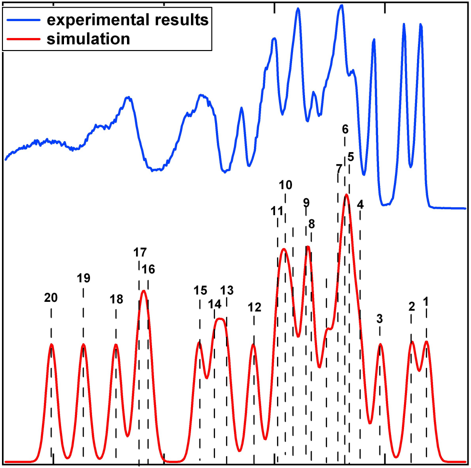




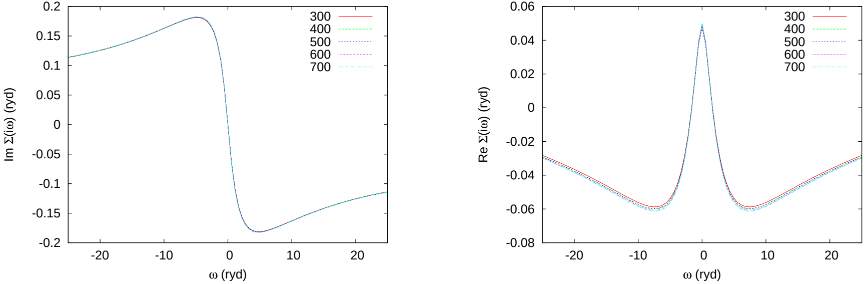
G. Stenuit, C. Castellarin-Cudia,O.Plekan, V. Feyer, K.C. Prince, A. Goldoni, and PU, PCCP (accepted) (2010).

Indene molecule

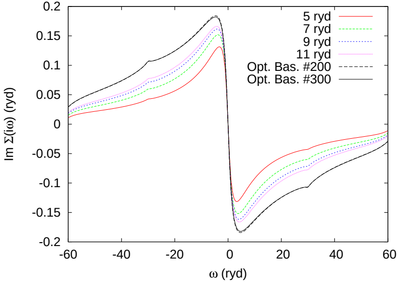
GWW is now a standard tool for PS analysis:

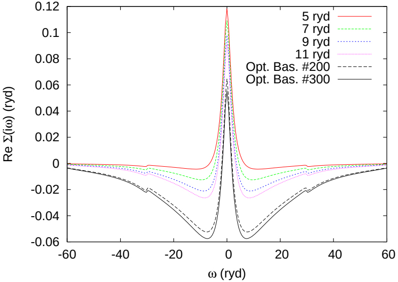


Polarizability basis for H_2O: optimal

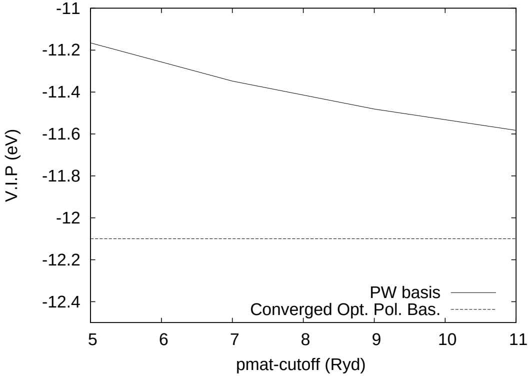


Polarizability basis for H_2O: plane-waves





VIP convergence: plane-waves



Conclusions

- Concept and importance of optimal polarizability basis
- Lanczos chain approach
- Large systems affordable without loss of accuracy

Acknowledgments

- G. Stenuit (CNR-INFM DEMOCRITOS)
- S. Baroni (CNR-INFM DEMOCRITOS & SISSA)
- L. Giacomazzi (CNR-INFM DEMOCRITOS & ICTP)
- X.-F. Qian (MIT)
- A. Goldoni (Elettra)
- C. Cudia Castellarin (Elettra)
- V Feyer Elettra
- K.C. Prince (Elettra)

Don't go to the beach!

- Dr. L. Martin Samos's lecture: today 14:00
- TDDFT&GWW hands on: tomorrow 15:30 (Adriatico)