GWL (GW + Wannier +Lanczos)

Introduction to GW in QE: the GWL code

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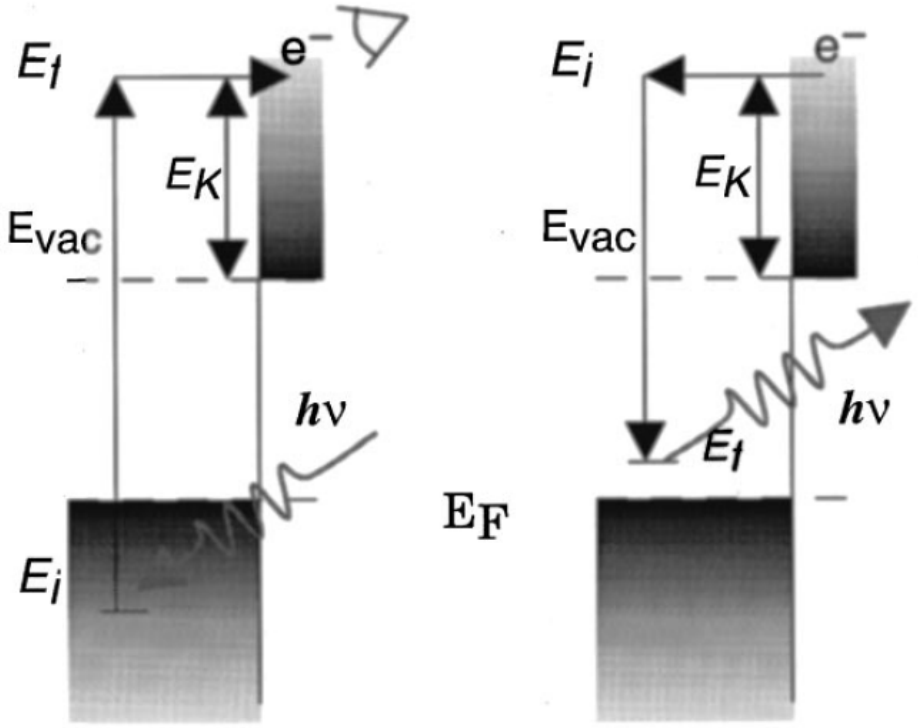
Summary

- General introduction

- Applications

- GWL
    - analytic continuation
    - no summation over empty states
    - optimal representation of large sets of vectors
    - use of Lanczos chain
    - optimal basis set for the polarizability

What quantities are we looking for?



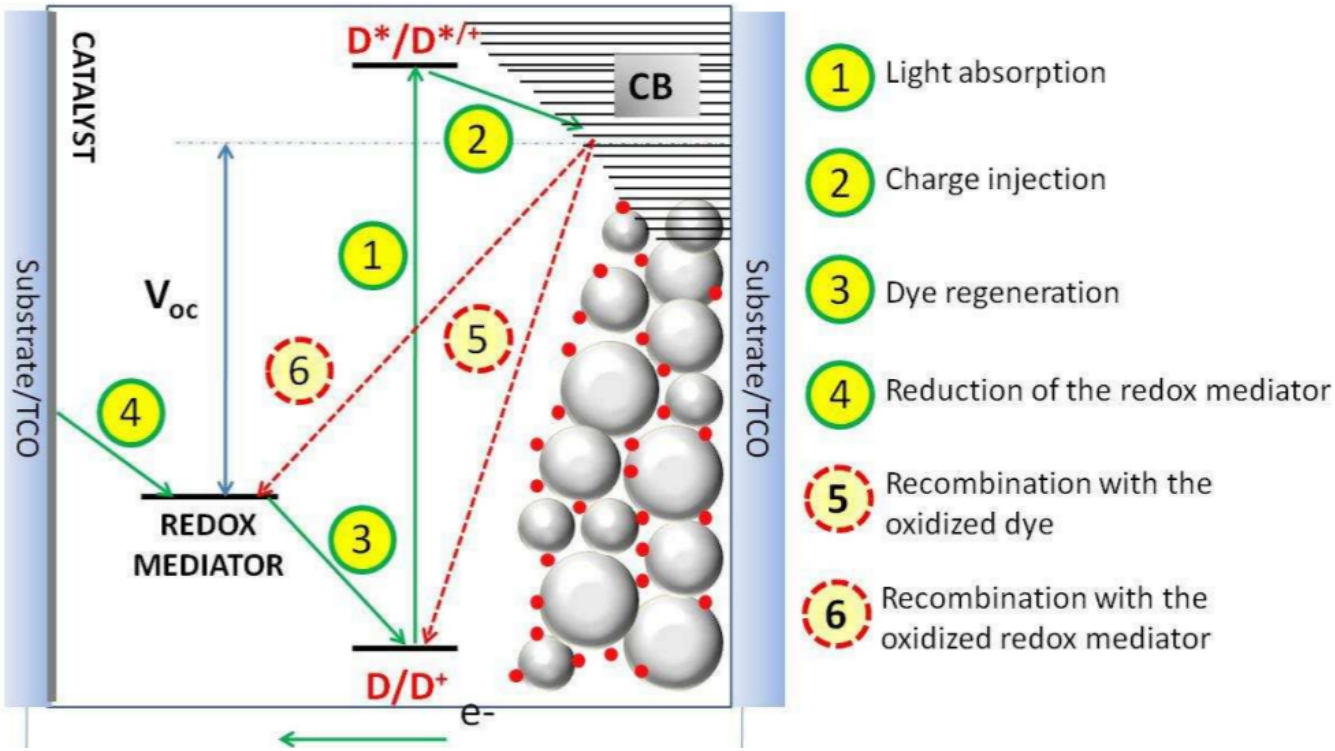
Photoemission:
Experimentally we access **difference of total energies between the neutral N-particle ground state and charged N+1 or N-1 particle excited states.**

$$h\nu = E_f - E_i = E_{kin} + (E^*(N-1) - E^0(N))$$

$$h\nu = E_i - E_f = E_{kin} + (E^0(N) - E^*(N-1))$$

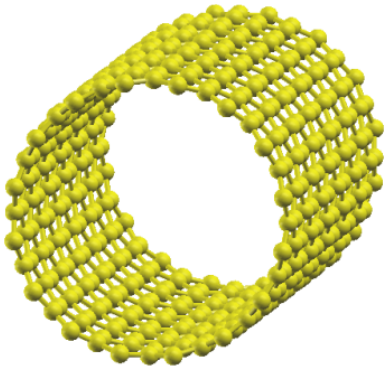
Why?

The knowledge of electronic-energy level alignments, of defect levels, etc.. is extremely important for device design in photovoltaics, electronics, opto-electronics, catalysis etc…



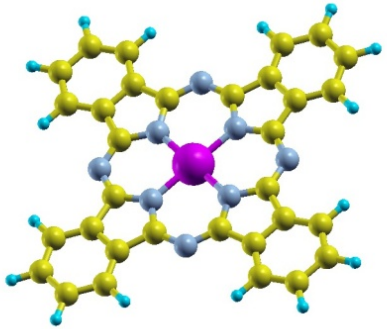
In dye-sensitized solar cells the alignment of the electronic levels of the different part of the device is crucial for cells' functioning and performance.

What kind of systems are we looking at? (1)



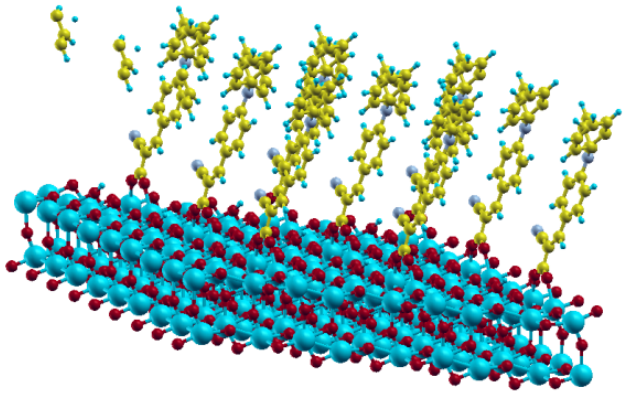
Carbon Nanotubes

P. Umari, O. Petrenko, S. Taioli, and M.M. de Souza, J. Chem. Phys.136, 181101 (2012).



Zn-Phthalocyanine

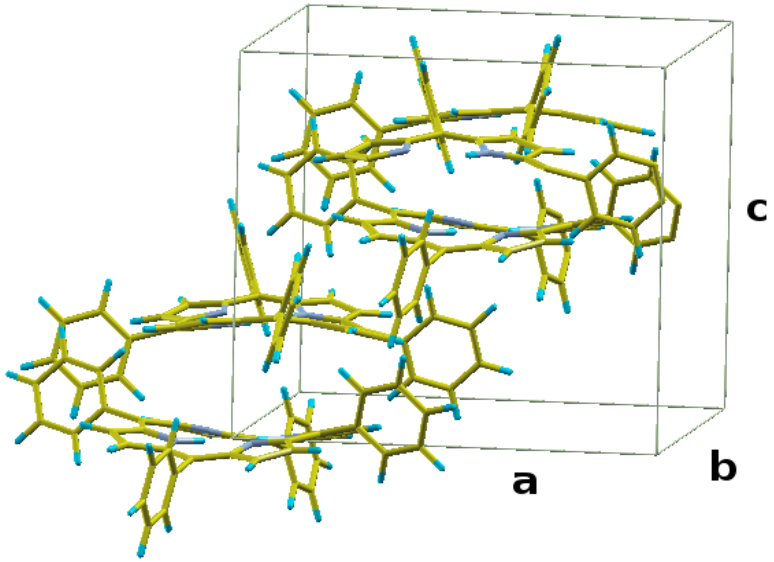
P.Umari and S.Fabris J. Chem. Phys, 136, 174310 (2012)



Organic dyes on TiO_2 surfaces

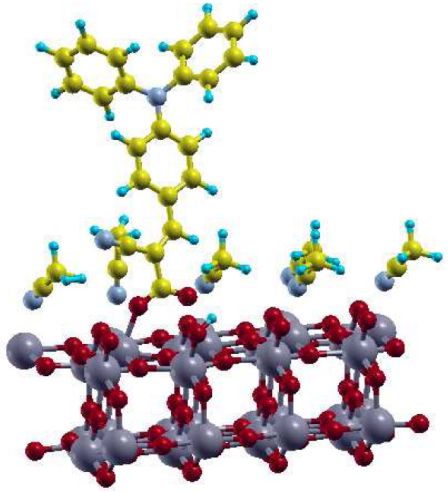
P.Umari, L.Giacomazzi,F. De Angelis, M. Pastore,S. Baroni, JCP 139, 014709 (2013)

What kind of systems are we looking at? (2)



H_2TPP thin films
(4 porphyrin molecules in the unit cell)

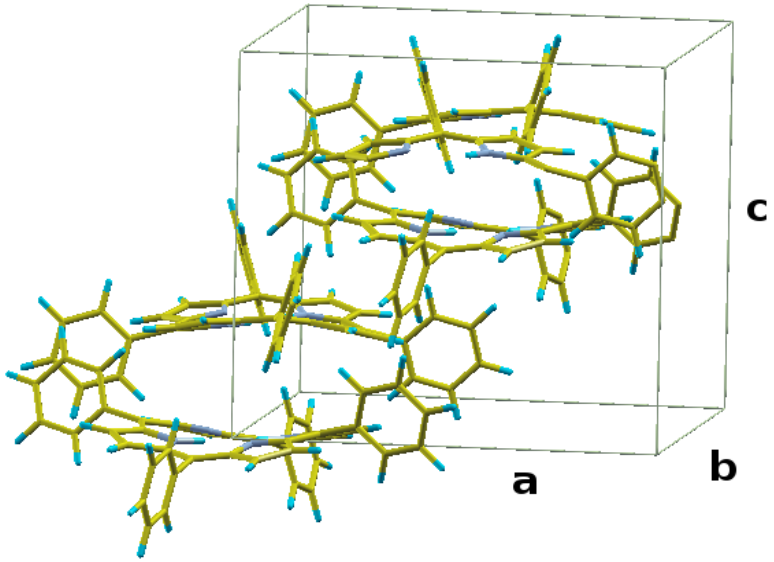
M. Marsili, P. Umari, M. Pedio,
in progress



Organic dyes + <u>solvent</u> on TiO_2 surfaces

C. Verdi, E. Mosconi, F. De Angelis, M. Marsili, P. Umari
Submitted to PRB (2014)

What kind of systems are we looking at? (3)



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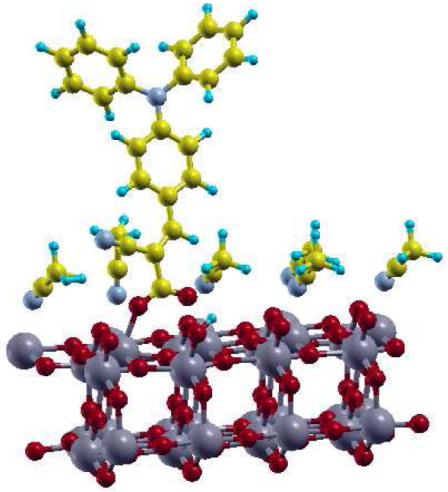

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SYSTEMS WITH MORE THAN 900 ELECTRONS!!

GW standard approach

One of the main bottleneck of GW calculations arise from the computation of the electronic dielectric function.

$$\epsilon(r, r'; \omega) = \delta(r - r') - \int dr'' v(r - r'') P(r'', r', \omega)$$

$$P^0(r, r'; \omega) = \sum_{ij} (f_i - f_j) \frac{\Psi_i(r)\Psi_j^*(r)\Psi_j(r')\Psi_i^*(r')}{\omega - (\epsilon_j - \epsilon_i) + i\eta}$$

Computationally demanding for:

- sum over empty states
- dimension and frequency dependence of dielectric matrix

GWL

GWL main features:

- Perturbative G_0W_0 approach for large and inhomogeneous systems
- No summation on empty states
- Optimal basis set for the polarizability
- Polarizability and self-energy operators are expressed through a set of linear-response equations solved using the Lanczos-chain algorithm
- Full frequency dependence of the screening (no plasmon-pole)
- Mixed openmp and mpi parallelization

GWL

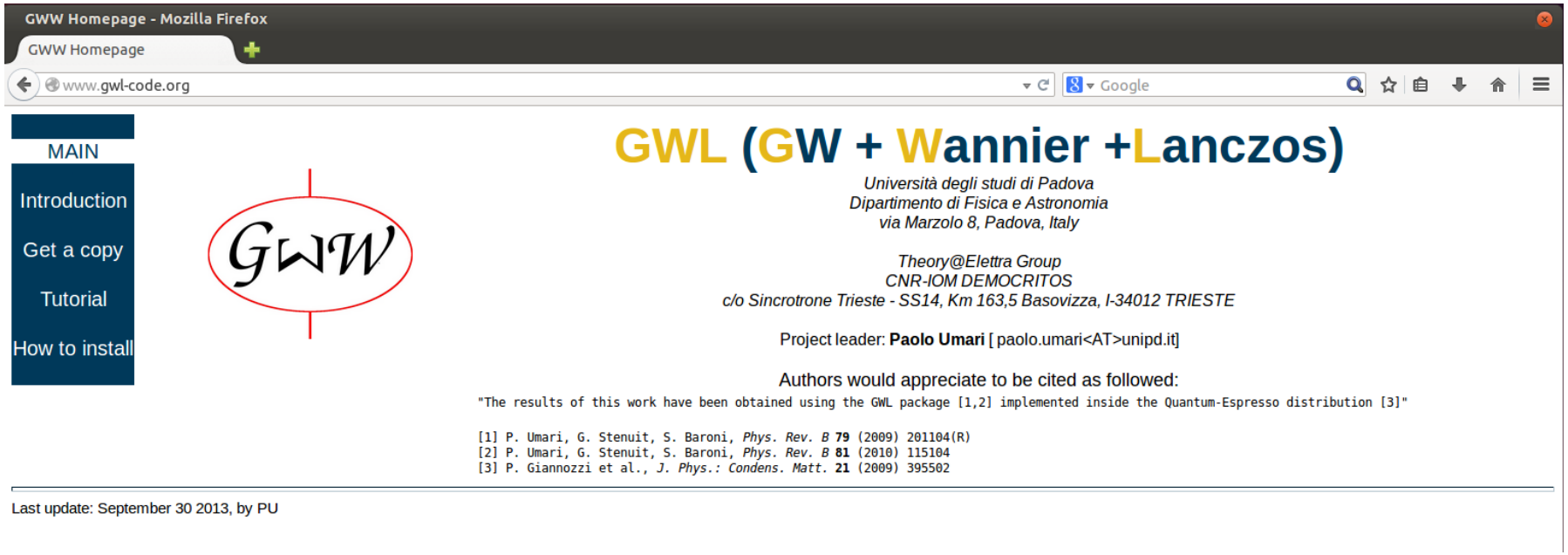
- GWL is downloaded directly within the QE distribution

- pw.x make.sys should work so GWL can be compiled simply by typing:

```
make gwl
```

in QE main directory.

- www.gwl-code.org is the code website where you can find tutorials and the user manual.



GW approximation, W_c

QP energies (that can be compared with direct and inverse PE) are computed in first order perturbation theory using $\Sigma - V_{xc}$ as perturbation to the KS Hamiltonian.

$$\Sigma(1,2) = iG(1,2)W(1^+,2) \qquad 1 = (\mathbf{r}_1, t_1)$$

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$$W(1,2) = v(1,2) + \int d(3,4)v(1,3)\Pi(3,4)v(4,2)$$

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$$\Sigma_c(\mathbf{r}_1, \mathbf{r}_2; \omega)$$

Frequency dependence, analytic continuation

$$\langle \Psi_n | \Sigma_c(\epsilon_n) | \Psi_n \rangle$$

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Analytic continuation.

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Expectation values computed on an imaginary frequency grid and then fitted to a multipole function.
(Some) input variables:

`n`
`grid_freq`
`n_multipoles`
`n_grid_fit`
`offset_fit`

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Analytic continuation.

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FFT

$$\langle \Psi_n | \Sigma_c(i\tau) | \Psi_n \rangle$$

From Wc to the irreducible polarizability

$$\langle \Psi_n | \Sigma_c(i\tau) | \Psi_n \rangle = i \int dr dr' \Psi_n(r) G(r, r'; i\tau) W_c(r, r'; i\tau) \Psi_n(r')$$

To compute W_c we must compute the reducible polarizability $\Pi(r, r'; i\tau)$

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$$\Pi(i\omega) = P(i\omega)[1 - vP(i\omega)]^{-1}$$

Irreducible polarizability

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Irreducible polarizability

$$P(i\omega) = -4Re \sum_{vc} \frac{\Psi_v(r)\Psi_c(r)\Psi_v(r')\Psi_c(r')}{\epsilon_c - \epsilon_v + i\omega}$$

$$\simeq \sum_{\alpha\beta} \phi_\alpha(r) P_{\alpha\beta}(i\omega) \phi_\beta(r')$$

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Optimal basis set. How do I get this?

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GWL approach at work: irreducible polarizability

$$P_{\alpha\beta}(i\omega) = -4Re\sum_{vc}\int dr dr' \phi_\alpha(r)\frac{\Psi_v(r)\Psi_c(r)\Psi_v(r')\Psi_c(r')}{\epsilon_c - \epsilon_v + i\omega}\phi_\beta(r')$$

1) Avoid summation on empty states $\hat{P}_c = 1 - \sum_v |v\rangle\langle v|$

2) $\hat{P}|\Psi_v\phi_\nu\rangle \simeq \sum_{\alpha=1}^{N_t} T_{\alpha,\mu v}|t_\alpha>$; $N_t << N_v * N_\phi$

3) Use lanczos-chain algorithm to compute: $\langle t_\alpha|(H - \epsilon_v + i\omega)^{-1}|t_\beta\rangle$

GWL approach at work:
(1) no summation on empty states

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$$= -4Re\sum_{cv}\int dr dr' \frac{\langle\Psi_v\phi_\alpha|r\rangle\langle r|\Psi_c\rangle\langle\Psi_c|r'\rangle\langle r'|\phi_\beta\Psi_v\rangle}{\epsilon_c - \epsilon_v + i\omega}$$

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$$= -4Re\sum_{cvc'}\langle\Psi_v\phi_\alpha|\Psi_c\rangle\langle\Psi_c|\frac{1}{\hat{H}_0-\epsilon_v+i\omega}|\Psi_{c'}\rangle\langle\Psi_{c'}|\phi_\beta\Psi_v\rangle$$

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$$= -4Re\sum_{v}\langle\Psi_v\phi_\alpha|\hat{P}_c\frac{1}{\hat{H}_0-\epsilon_v+i\omega}\hat{P}_c|\phi_\beta\Psi_v\rangle$$

$$\hat{P}_c = 1-\sum_v|v\rangle\langle v|$$

GWL approach at work: (2) optimal representations

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Whatever way we choose to compute this expression we have to do it $N_v \times N_\phi^2$ times!

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The effort is reduced if we find an optimal set of vectors, in terms of which we decompose the vectors belonging to the original set.

$$\hat{P}_c |\phi_\alpha \Psi_v\rangle \simeq \sum_{\nu=1}^{N_t} T_{\nu,\alpha v} |t_\nu\rangle \qquad N_t << N_v * N_\phi$$

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For every valence state v:

1) $\hat{P}_c|\phi_\alpha \Psi_v\rangle \longrightarrow \hat{P}_c|\phi_\alpha w_v\rangle = |\bar{\Psi}_{v\alpha}\rangle$

Rotate valence state into maximally localized Wannier function.

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3) $\sum_\beta O^v_{\alpha\beta}|o^\mu_\beta\rangle_v = o_\mu|o^\mu_\alpha\rangle_v$ Solve the eigenvalue problem and k**eep the Nt eigenvectors with the largest eigenvalues**.

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This procedure is called singular value decomposition (SVD). Important input variable: n_pola_lanczos it defines the number of eigenvectors to be kept.

GWL approach at work: (2) optimal representations

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We are still left with Nv blocks made of Nt “local” t states!

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We are still left with Nv blocks made of Nt "local" t states!

4) We perform an other SVD among the blocks keeping the eigenvectors with eigenvalue above a threshold value s.

Important input variable: `s_pola_lanczos`

GWL approach at work: (2) optimal representations

$$\hat{P}_c|\phi_\alpha \Psi_v\rangle \simeq \sum_{\nu=1}^{N_t} T_{\nu,\alpha v}|t_\nu\rangle \qquad N_t << N_v * N_\phi$$

We can now express P0 in terms of the new set of vectors:

$$P_{\alpha\beta}(i\omega) = -4Re \sum_{v\nu\mu} T^*_{\nu,\alpha v} T_{\mu,\beta v} \langle t_\nu | \frac{1}{\hat{H}_0 - \epsilon_v + i\omega} | t_\mu \rangle$$

The dimension of the |t> set is determined by:
n_pola_lanczos and s_pola_lanczos.

GWL tricks at work:
(2) optimal representations

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GWL approach at work: (3) lanczos chain algorithm

Efficient computation of $\langle t_\nu | \frac{1}{\hat{H}_0 - \epsilon_v + i\omega} | t_\mu \rangle$

GWL approach at work: (3) lanczos chain algorithm

Efficient computation of $\langle t_\nu | \frac{1}{\hat{H}_0 - \epsilon_v + i\omega} | t_\mu \rangle$

1) It is possible (see documentation) to recursively build a set of orthonormal vectors for which $(\hat{H}_0 - \epsilon_v + i\omega)$ is tridiagonal starting from an arbitrary vector.

$$|t_\mu^0\rangle = |t_\mu\rangle, |t_\mu^1\rangle, ..., |t_\mu^{N_l}\rangle$$

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GWL approach at work: (2) lanczos chain algorithm

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This procedure is part of the so called Lanczos-chain algorithm. Important input variable: n_steps_lanczos_pola, it determines the dimension of the vectors chain.

Optimal representation of the dynamical polarizability (1)

$$P(i\omega) \simeq \sum_{\alpha\beta} \phi_\alpha(r) P_{\alpha\beta}(i\omega) \phi_\beta(r') \qquad \{\phi_\alpha(r)\}$$

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We choose the eigenvectors with largest eigenvalues of the time 0-polarizability

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This requires a great number of conduction states to be computed!

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1) Consider “fake” conduction states, namely: planewaves below a certain threshold projected onto the conduction manifold.

$$|\tilde{G}\rangle = \hat{P}_c |G\rangle; \quad \tfrac{1}{2}|G|^2 \leq E^* \Rightarrow P_0(t=0) = \sum_{vG} |\Psi_v \tilde{G}\rangle\langle \tilde{G}\Psi_v|$$

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Relevant input variables: pmat_cutoff, cutoff for the plane waves; s_pmat threshold for the f-states; numw_prod dimension of the final basis set.

Summary of algorithms and relevant input variables

✓ Use of optimal representations when expensive operations on large sets of vectors are needed.

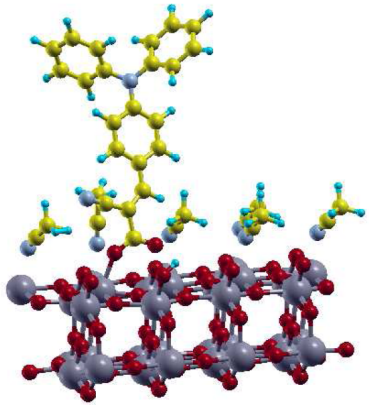
```
n_pola_lanczos
s_pola_lanczos
n_self_lanczos
s_self_lanczos
```

✓ Use of lanczos chain algorithm for the computation of response functions.

```
n_steps_lanczos_pola, n_steps_lanczos_self
```

✓ Optimal basis set for the polarizability

```
pmat_cutoff, s_pmat, numw_prod
```



Thank you, references, acknowledgments

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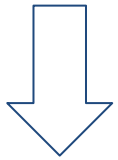
Dott. Paolo Umari,
Università di Padova
GWL main developer

GWW approach at work:
(1) no summation on empty states

$$P_{\alpha\beta}(i\omega) = -4Re\sum_{vc}\int dr dr' \phi_\alpha(r)\frac{\Psi_v(r)\Psi_c(r)\Psi_v(r')\Psi_c(r')}{\epsilon_c - \epsilon_v + i\omega}\phi_\beta(r')$$



$$P_{\alpha\beta}(i\omega) = -4Re\sum_{v}\langle\Psi_v\phi_\alpha|\hat{P}_c(H - \epsilon_v + i\omega)^{-1}\hat{P}_c|\Psi_v(r)\phi_\beta\rangle$$

$$\hat{P}_c = 1 - \sum_v |v\rangle\langle v|$$

GWL approach

GWL is used to compute GW corrections for systems with more than 900 electrons. What makes this possible?

- ✓ Use of optimal representations when expensive operations on large sets of vectors are needed.
- ✓ Use of lanczos chain algorithm for the computation of response functions.
- ✓ Use of maximally localized Wannier functions.
- ✓ Exact removal of summation over empty states. (In traditional approaches the number of empty states to be considered is ~4 times the number of valence bands!)