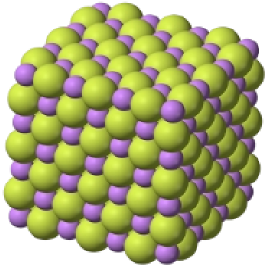
Solving TD-DFT/BSE equations with Lanczos- Haydock approch

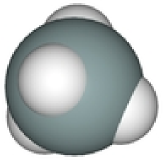
C. Attaccalite and M. Grüning

Linear response TD-DFT/BSE



Solid State approach: Dyson-like equation

Casida approach: Eq. rewritten in a basis of e-h pairs

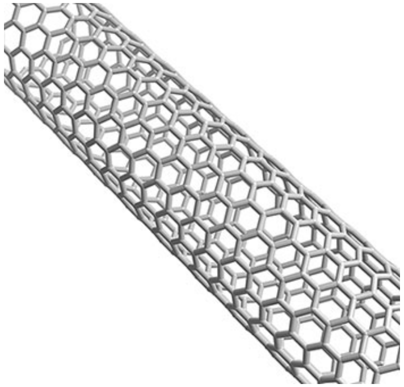


$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & C \\ \langle he| & -C^* & -R^* \end{array}\right)$$

Casida approach to TD-DFT/BSE

The matrix in term of e-h pairs:

$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & C \\ \langle he| & -C^* & -R^* \end{array}\right)$$



- Can be very large, e.g.10^6x10^6 (diagonalization: N^3)
- Is not Hermitian (less efficient/stable algorithms)

Tamm-Dancoff approximation

Only positive e-h pairs are considered and coupling between e-h pair at positive and negative energiesis neglected

$$H = \left(\begin{array}{c|cc} & |eh\rangle & |he\rangle \\ \hline \langle eh| & R & \cancel{C} \\ \langle he| & -\cancel{C}^* & -R^* \end{array}\right)$$

1) Successful to describe optics absorption of many systems

2) The non-Hermitian BSE reduces to a Hermitian one

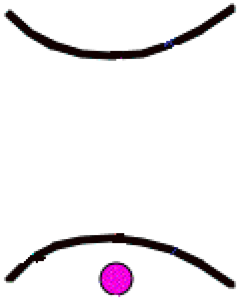
3) BSE can be solved using efficient iterative schemes

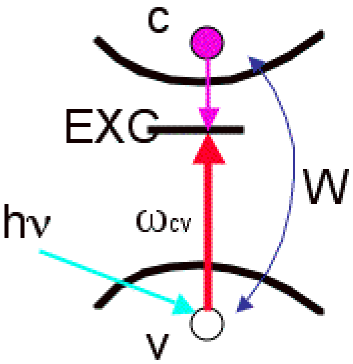
BSE and dielectric function

dielectric function can be expressed in terms of the ground state |0> and the eigenstates of the BSE

$$\epsilon_2(\omega,q)=4\pi\sum_f\left|\langle f|\frac{e^{iqr}}{q}|0\rangle\right|^2\delta(E_f-E_i-\omega)$$

where





$$|0\rangle=\left(\prod_v a^+_{v\uparrow}a^+_{v\downarrow}\rangle\right)|vacuum\rangle \qquad |f\rangle=\sum_{c,v}\psi(c,v)a^+_c a_v|0\rangle$$

BSE and dielectric function

We can eliminate the sum over |f>

$$\epsilon_2(\omega,q)=4\pi\sum_f\langle 0\left|\frac{e^{iqr}}{q}\right|f\rangle\,\delta(H_{BSE}-\omega)\langle f\left|\frac{e^{iqr}}{q}\right|0\rangle$$

Using the Dirac idensity: $\frac{1}{x+i\epsilon}=P\left(\frac{1}{x}\right)-i\pi\delta(x)$

$$\epsilon_2(\omega,q)=-4\pi\,\Im\left[\langle P|\frac{1}{\omega-H_{BSE}+i\eta}|P\rangle\right]$$

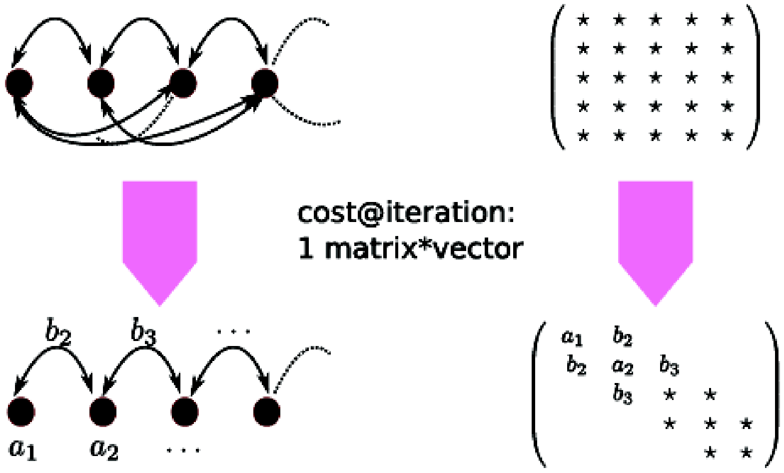
This formula involves only
The ground state

Where: $|P\rangle=\lim_{q\to 0}\frac{e^{iqr}}{q}|0\rangle$

L. X. Benedict and E. L. Shirley PRB, **59**, 5441 (1999)
M. Marsili, Ph.D. thesis, Universita di Roma "Tor Vergata", 2006

Lanczos-Haydock method

Main idea:



cost@iteration:
1 matrix*vector

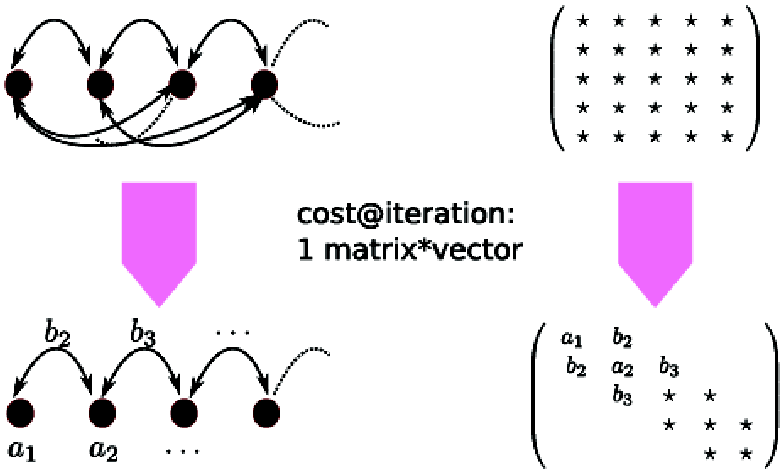
This allows to rewrite the dielectric function as:

$$\epsilon(\omega) \rightarrow \langle P|(\omega - H)^{-1}|P\rangle = \cfrac{1}{(\omega - a_1) - \cfrac{b_2^2}{(\omega - a_2) - \cfrac{b_3^2}{\cdots}}}$$

$$|P\rangle = \lim_{\mathbf{q}\rightarrow 0} \frac{1}{|\mathbf{q}|} |vc\mathbf{k}\rangle\langle v\mathbf{k} - \mathbf{q}| e^{-i\mathbf{q}\cdot\mathbf{r}} |c\mathbf{k}\rangle$$

R. Haydock, Comput. Phys. Commun. **20**, 11 (1980)

Lanczos-Haydock algorithm



cost@iteration:
1 matrix*vector

Matrix Elements: | **Basis:**

$$a_1 = \langle 1|H|1\rangle \longleftrightarrow |1\rangle = |P\rangle$$

$$a_2 = \langle 2|H|2\rangle$$

$$b_2 = \langle 1|H|2\rangle \qquad |2\rangle = \frac{H|1\rangle - a_1|1\rangle}{\langle 2|2\rangle}$$

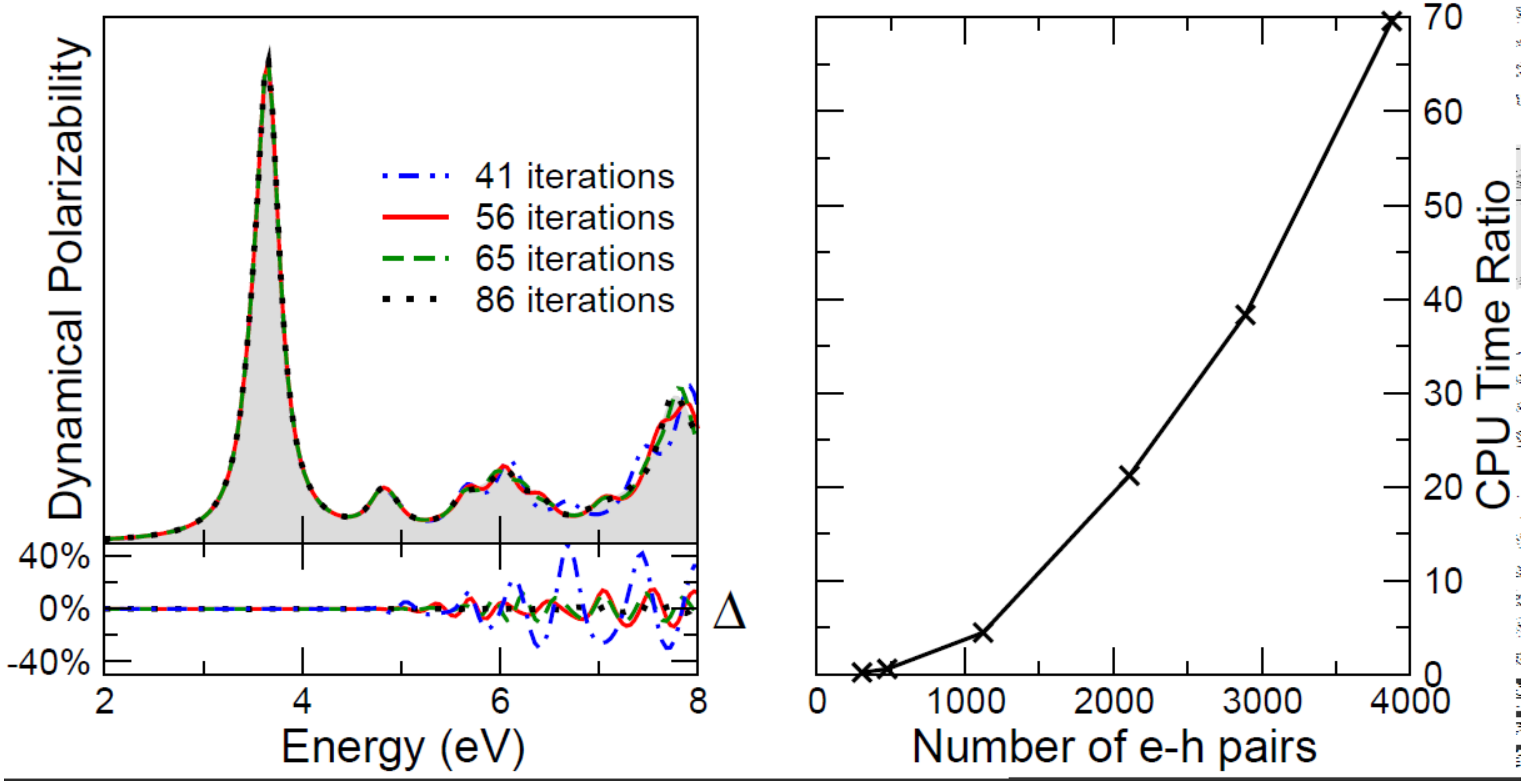
$$\langle 1|H|3\rangle = 0\,! \qquad |3\rangle = \frac{H|2\rangle - a_2|2\rangle - b_1|1\rangle}{|\langle 3|3\rangle|}$$

....

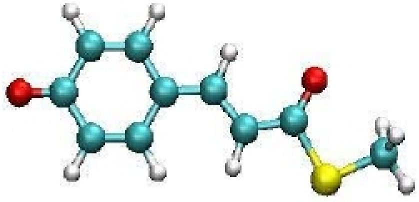
$$b_i = \langle i-1|H|i\rangle \qquad |i+1\rangle = \frac{H|i\rangle - a_i|i\rangle - b_{i-1}|i-1\rangle}{|\langle i+1|i+1\rangle|}$$

$$a_i = \langle i|H|i\rangle$$

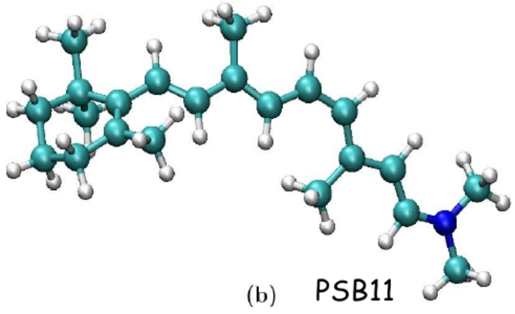
Lanczos-Haydock performance



Tamm-Dancoff breakdown 1



TMpCA⁻ (f)



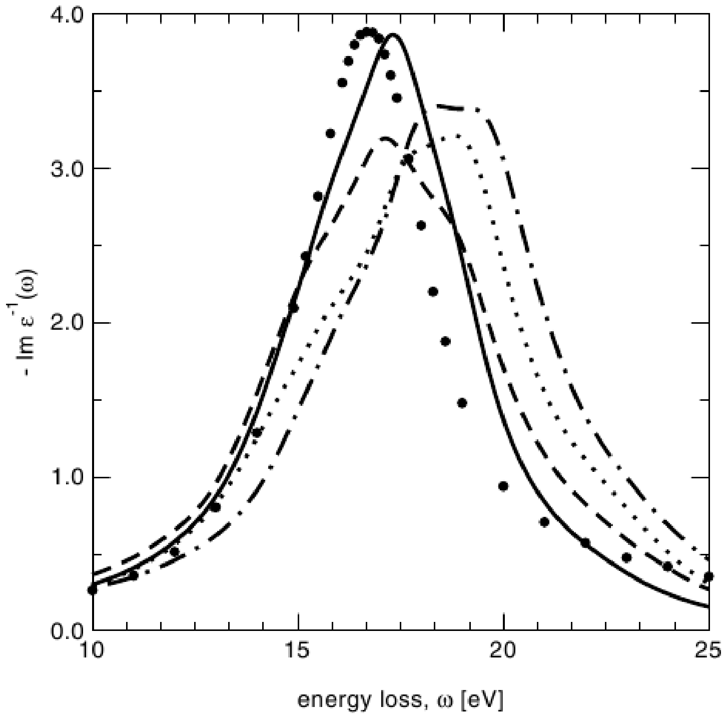
(b) PSB11

	v	c	R	C
TMpCA–	H-1 n	L π*	3.78	0.12
	H π	L π*	4.50	2.44
PSB11	H-1 π	L π*	3.98	1.60
	H π	L π*	3.30	1.93

Cromophores

Y. Ma, M. Rohfling and C. Molteni

J. Chem. Theory Comput. **6**, 257–265 (2010)

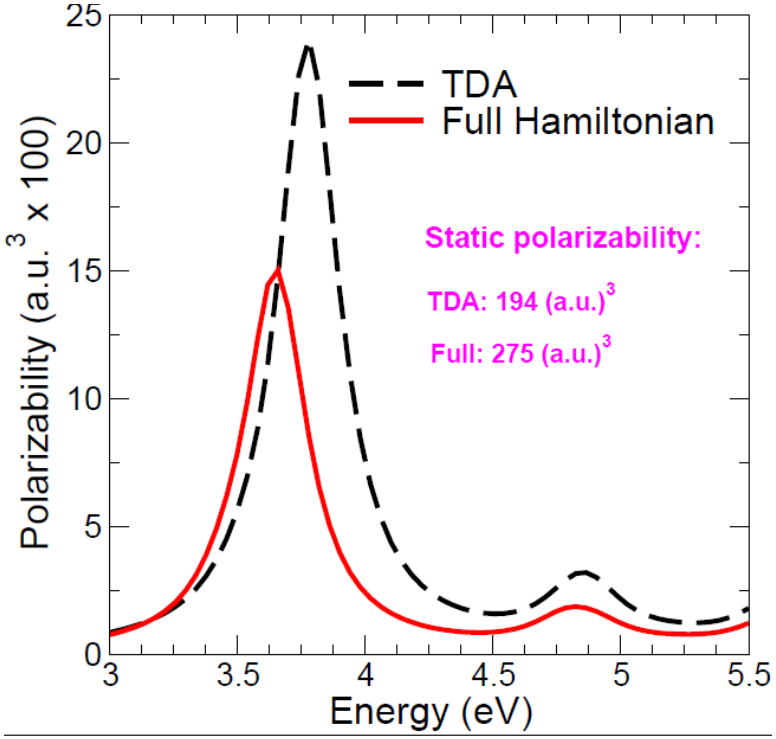


Plasmons in bulk materials

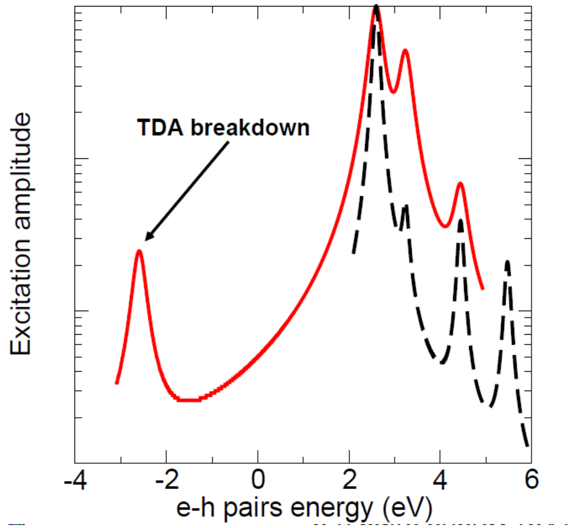
V. Olevano and L. Reining

PRL **86**, 5962 (2001)

Tamm-Dancoff breakdown 2

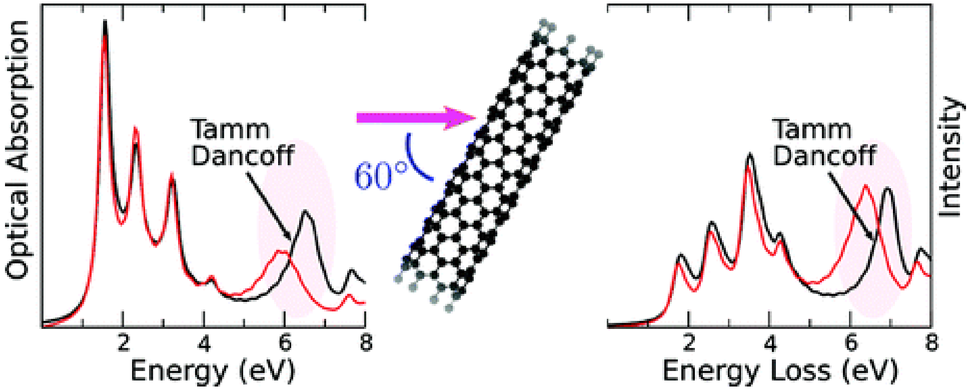


$$A^{\lambda}(\omega) = \sum_{\eta=\{eh\},\{\widetilde{eh}\}} |\langle \eta | \lambda \rangle|^2 \delta(\omega - E_{\eta})$$

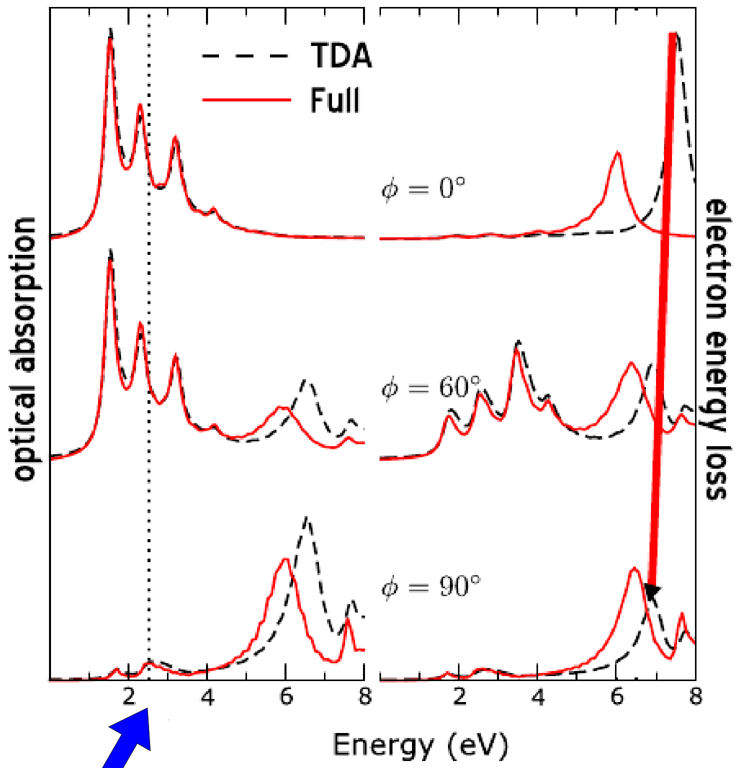


M. Gruning, A. Marini, X. Gonze
NanoLetters, **6**, 257–265 (2010)

Tamm-Dancoff breakdown 3



Mixed excitonic-plasmonic excitation



Quasiparticle band gap

Nanostructures

M. Gruning, A. Marini, X. Gonze
NanoLetters, **6**, 257–265 (2010)

Non-Hermitian algorithms

Standard
non-Hermitian case:

Arnoldi: $\mathbf{H} \longrightarrow \begin{pmatrix} \star & \star & \star & \star & \star \\ \star & \star & \star & \star & \star \\ & \star & \star & \star & \star \\ & & \star & \star & \star \\ & & & \star & \star \end{pmatrix}$

Bi-Lanczos: $\mathbf{H} \longrightarrow \begin{pmatrix} \star & \star & & & \\ \star & \star & \star & & \\ & \star & \star & \star & \\ & & \star & \star & \star \\ & & & \star & \star \end{pmatrix}$

Standard Lanczos is **unstable** for non-Herminitiam matrices
(see J. H. Wilkison, “The Algebrica Eigenvalue Problem”)

Definition pseudo-Hermicity

Hermitian:

$$\langle \nu | H | \nu' \rangle = \langle \nu' | H^{+} | \nu \rangle$$

Pseudo-Hermitian:

$$\langle \nu | H | \nu' \rangle_{\bar{H}} = \langle \nu' | H^{\dagger} \bar{H} | \nu \rangle^{*} = \langle \nu' | \bar{H} H | \nu \rangle^{*} =: \langle \nu' | H | \nu \rangle^{*}{}_{\bar{H}}$$

If H is Herminitian with respect $\langle \cdot || \cdot \rangle_{\bar{H}}$ inner product

we can reduce it in the form

$$\mathbf{H} \longrightarrow \begin{pmatrix} \star & \star & & & \\ \star & \star & \star & & \\ & \star & \star & \star & \\ & & \star & \star & \star \\ & & & \star & \star \end{pmatrix}$$

TD-DFT pseudo-Hermitian

In case of the TD-DFT or BSE Hamiltonian we have:

$$H = F\bar{H} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} R & C \\ C* & R* \end{pmatrix} \Longrightarrow \bar{H}H = H^{\dagger}\bar{H}$$

Using $\bar{H}$ we can define the inner product:

$$\langle \nu | H | \nu' \rangle_{\bar{H}} = \langle \nu' | H^{\dagger}\bar{H} | \nu \rangle^{*} = \langle \nu' | \bar{H}H | \nu \rangle^{*} =: \langle \nu' | H | \nu \rangle^{*}{}_{\bar{H}}$$

Then we rewrite our expectation value a complete basis set orthonormal respect to this inner product

$$\langle P | (\omega - H)^{-1} | P \rangle = \sum_{k} \langle P | q_k \rangle \langle q_k | (\omega - H)^{-1} | P \rangle_{\bar{H}}$$

For the Hermitian case

$$\mathbf{H} = \mathbf{H}^\dagger$$

$$\mathbf{H} \longrightarrow \begin{pmatrix} \star & \star & & & \\ \star & \star & \star & & \\ & \star & \star & \star & \\ & & \star & \star & \star \\ & & & \star & \star \end{pmatrix}, \qquad \begin{aligned} |s\rangle &= \mathbf{H}|q_j\rangle - a_j|q_j\rangle - b_j|q_{j-1}\rangle, \\ a_k &= \langle q_k|\ \mathbf{H}q_k\rangle\ , \\ b_k &= \|s\| \end{aligned}$$

For the pseudo-Hermitian case Lanczos-Haydock for full TD-DFT/BSE

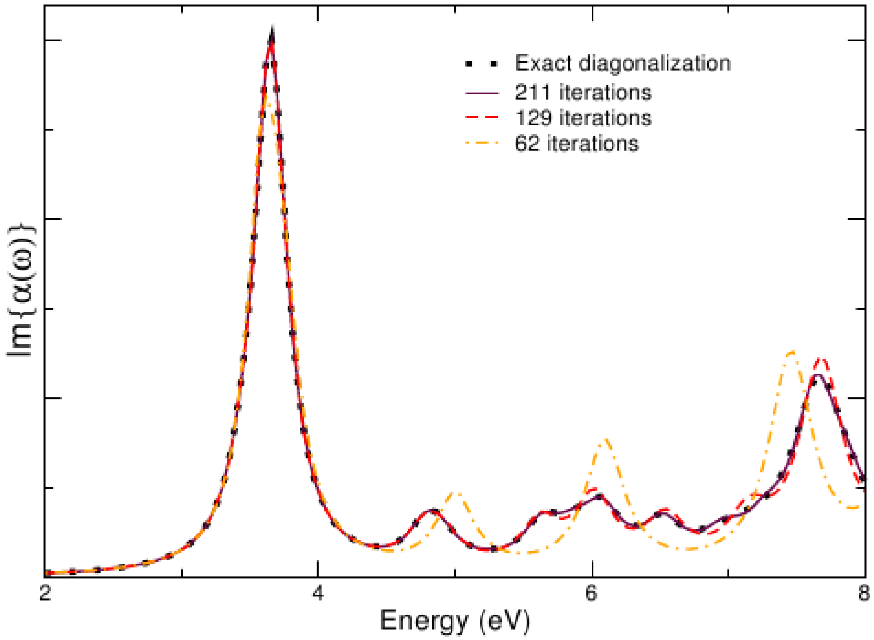
$$\mathbf{H} = \mathbf{H}^{\sharp}$$

$$\mathbf{H} \longrightarrow \begin{pmatrix} \star & \star & & & \\ \star & \star & \star & & \\ & \star & \star & \star & \\ & & \star & \star & \star \\ & & & \star & \star \end{pmatrix}, \qquad \begin{aligned} |s\rangle &= \mathbf{H}|q_j\rangle - a_j|q_j\rangle - b_j|q_{j-1}\rangle, \\ a_k &= \langle q_k || \mathbf{H} q_k\rangle_{\eta}, \\ b_k &= ||s||_{\eta} \end{aligned}$$

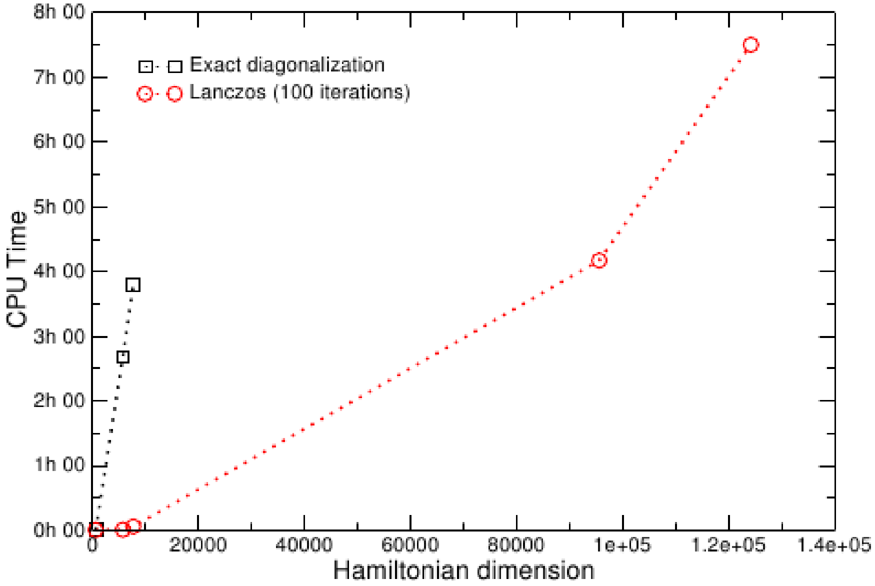
$$\mathbf{H}{=}\mathbf{P}\bar{\mathbf{H}}{=}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \mathbf{R} & \mathbf{C} \\ \mathbf{C}^{*} & \mathbf{R}^{*} \end{pmatrix}$$

1. $\mathbf{H}$ is $\bar{\mathbf{H}}$-pseudo-Hermitian, $\bar{\mathbf{H}}{>}0, \Rightarrow \eta{=}\bar{\mathbf{H}}$
2. $\langle q_k || q_k\rangle_{\eta}{=}\langle q_k|\mathbf{P}|\mathbf{H}q_k\rangle$

How does it work?



Number of iterations



Timing

Let's play with Yambo