"Faster G0W0 implementation for more accurate material design"

Laflamme Janssen, Jonathan ; Rousseau, Bruno ; Côté, Michel

Abstract

Density-functional theory (DFT) is currently the ab initio method most widely used to predict electronic energy levels of new materials. However, approxima- tions intrinsic to the theory limit the accuracy of calculated energy levels to about 0.5 eV. The G0W0 approach is an alternate ab initio method that provides an enhanced precision (about 0.05 eV). However, its computational cost is currently prohibitive for systems with more than a few tens of electrons, thus limiting its use in the simulation and design of technologically relevant materials. This limitation of current G0W0 implementations can be traced to two bottle- necks : the need to invert a large matrix (the dielectric matrix) and the need to carry out summations over a large number of electronic states (conduction states). The first bottleneck is caused by the choice of the basis in which the dielectric matrix is represented : traditional G0W0 implementations use a plane wave basis, which needs to be relatively large to p...

Document type : *Communication à un colloque (Conference Paper)*

Référence bibliographique

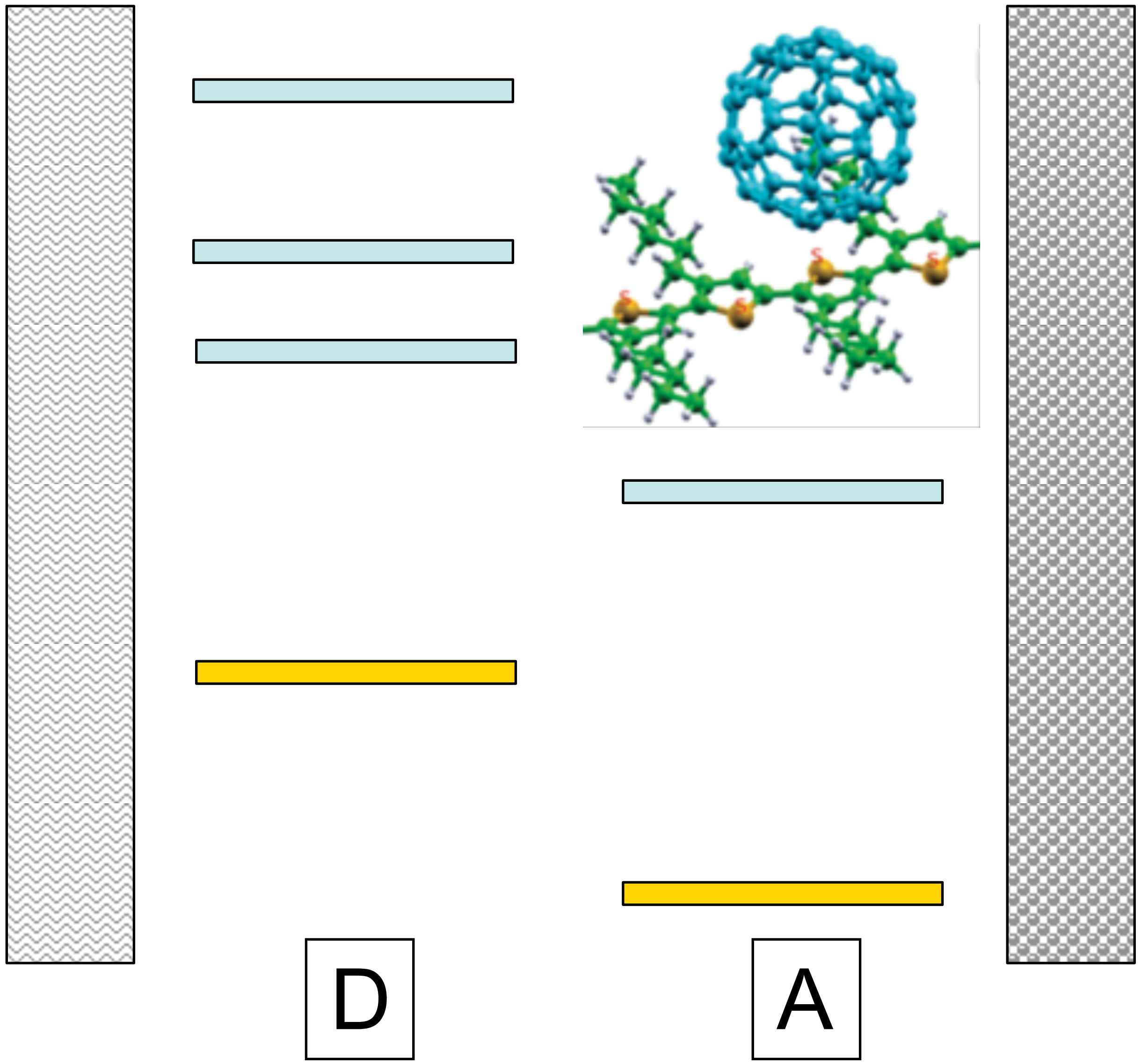
Laflamme Janssen, Jonathan ; Rousseau, Bruno ; Côté, Michel. *Faster G0W0 implementation for more accurate material design.*ABINIT Workshop 2013 (Dinard, France, du 15/04/2013 au 19/04/2013).

Faster G_0W_0 implementation for more accurate material design

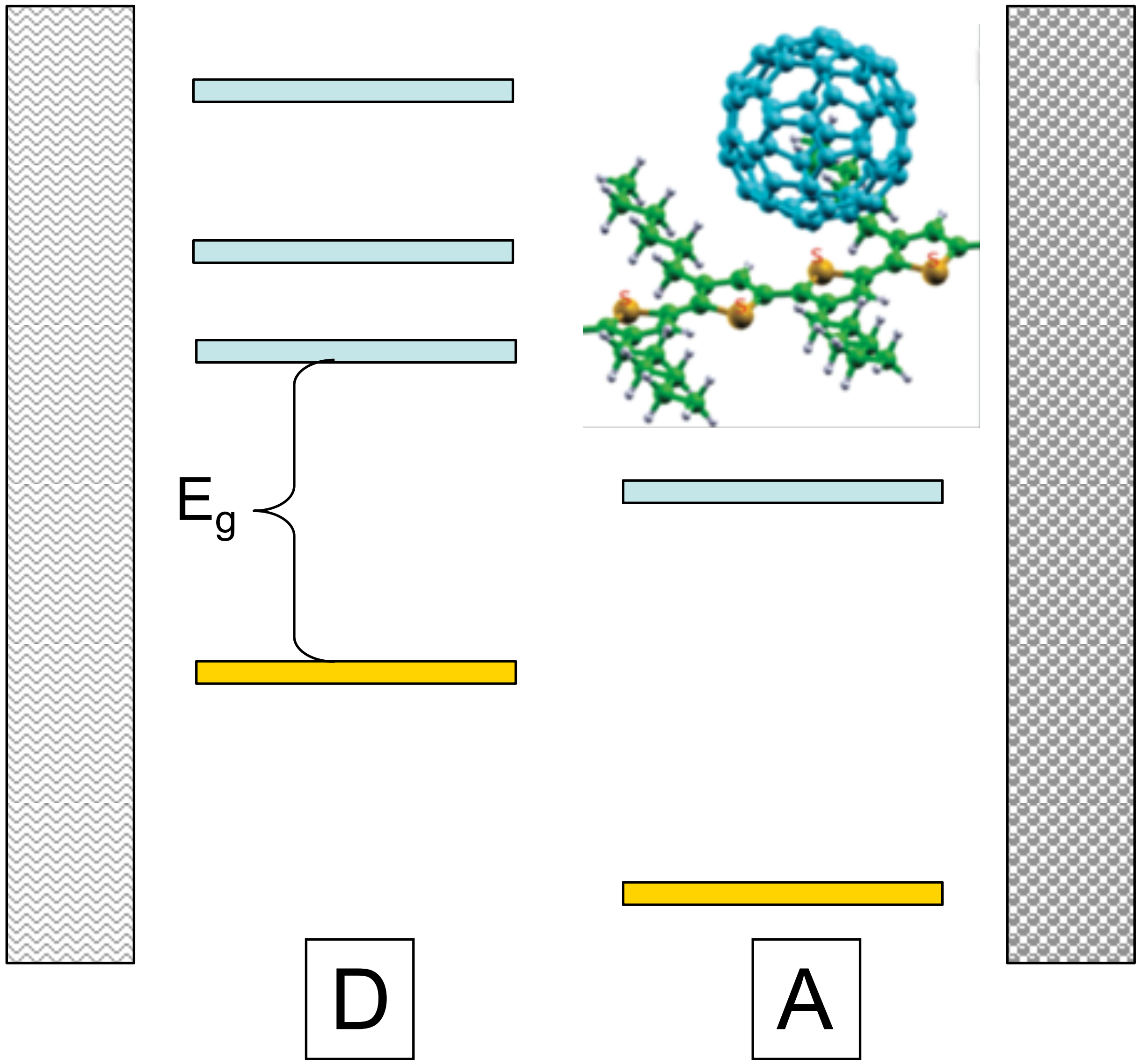
By Jonathan Laflamme Janssen
Département de physique, Université de Montréal

Université de Montréal

Design of polymers

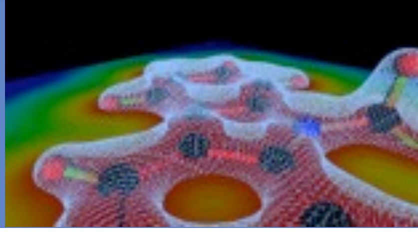


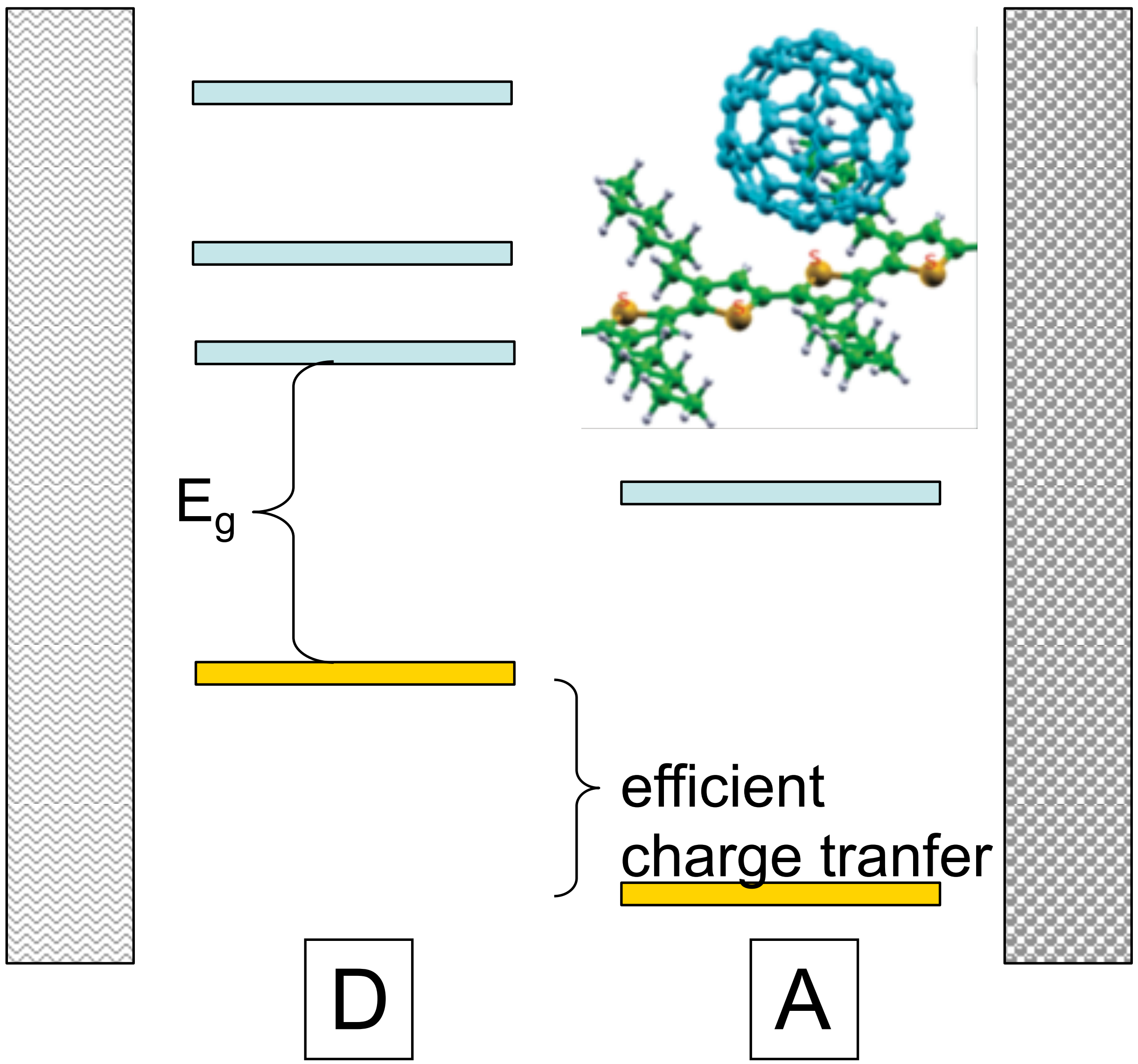
Design of polymers



- **Gap:** optimal for solar spectrum

Design of polymers

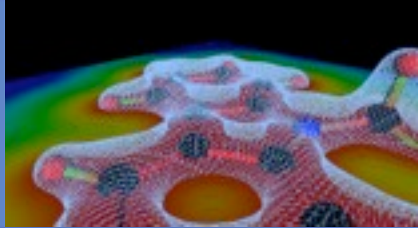


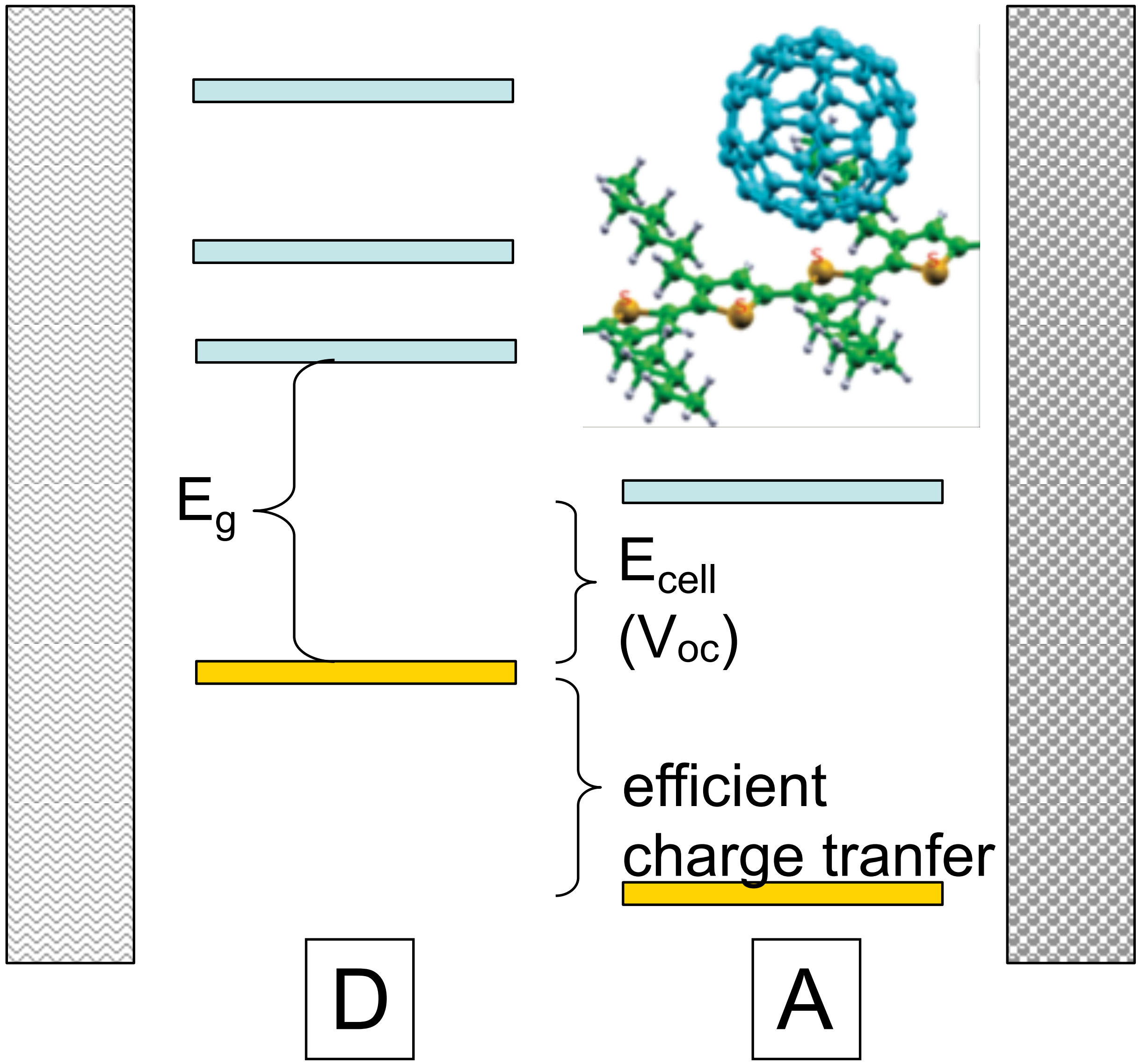


- Gap: optimal for solar spectrum
- HOMO :
  - higher than C_{60}

    (for good charge transfer)

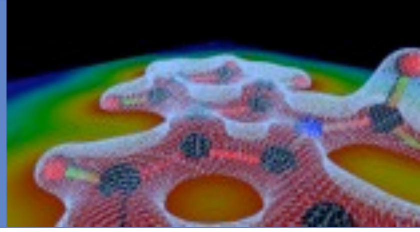
Design of polymers



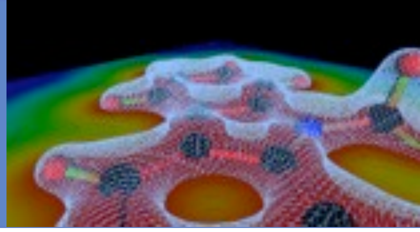


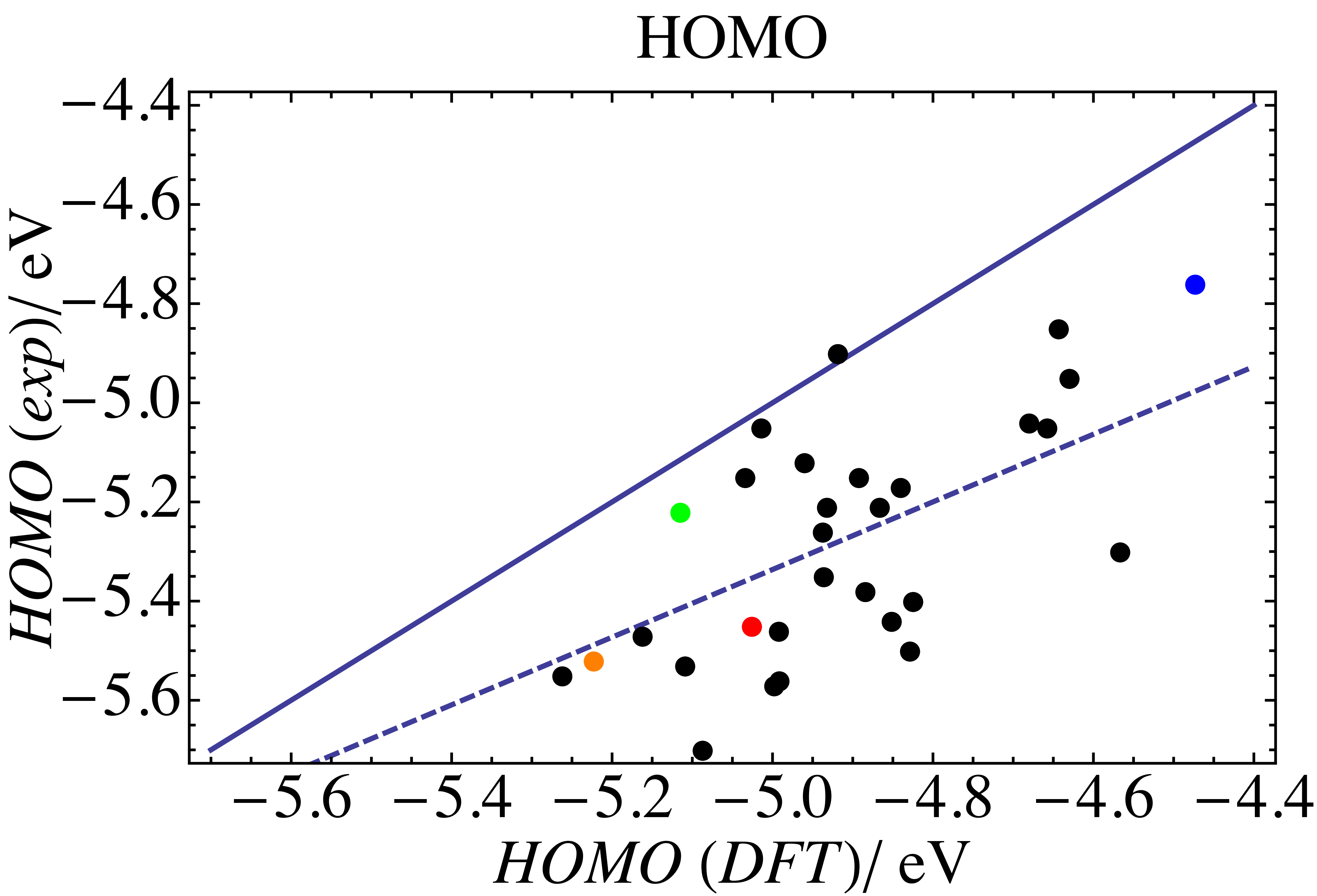
- Gap: optimal for solar spectrum
- HOMO :
  - higher than C_{60}
    (for good charge transfer)
  - low enough for good Voc
    and air stability

DFT to the rescue?

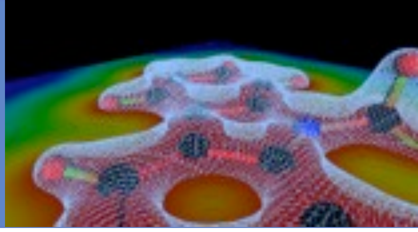


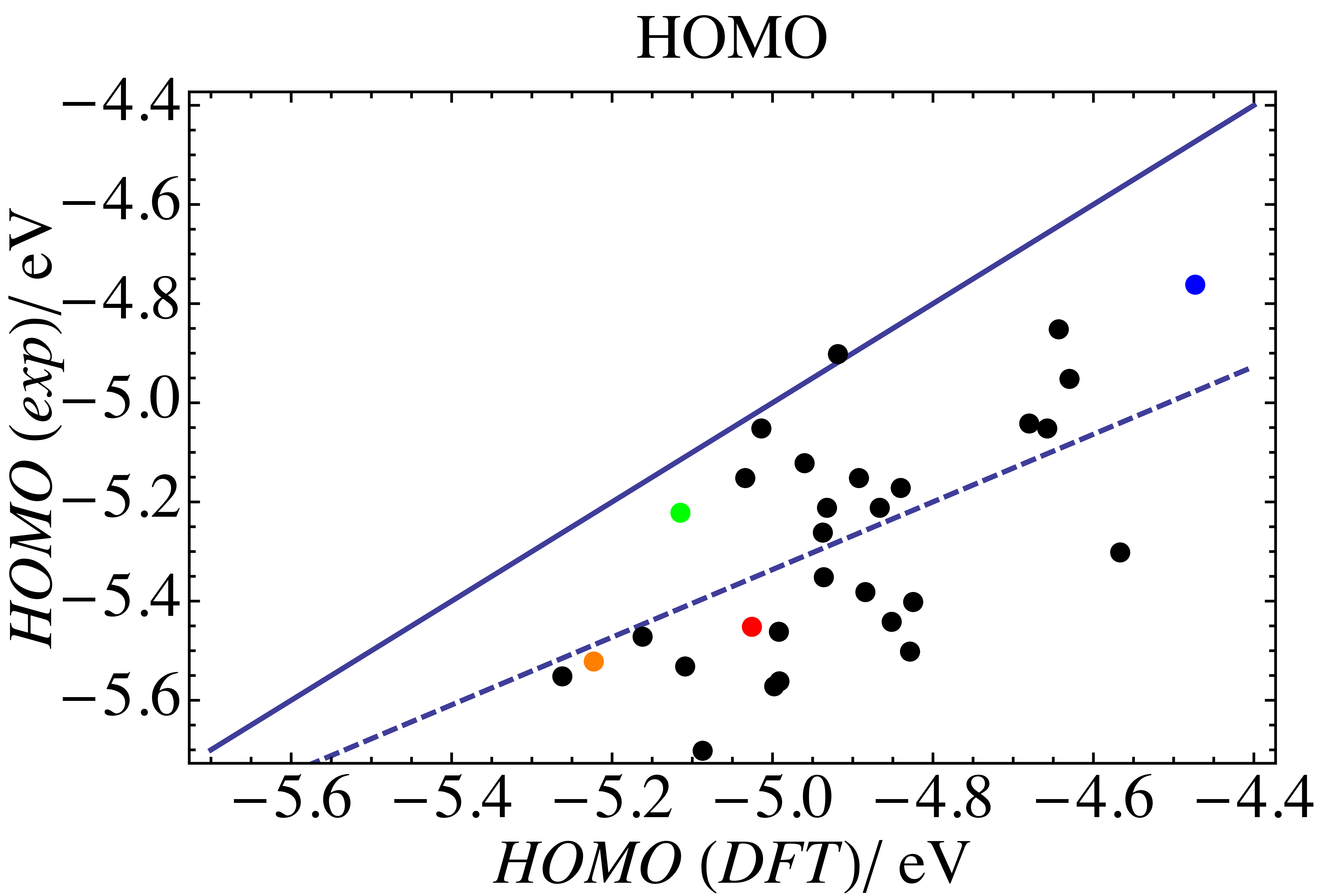
DFT to the rescue?





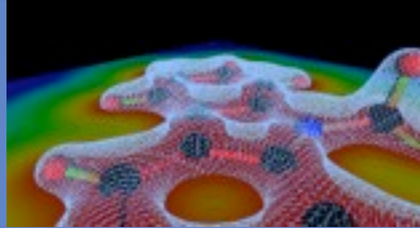
DFT to the rescue?





- Allows to select the top 10-20% candidates polymers

The G_0W_0 : performance



G_0W_0 :

$$\left(T + V_{ext} + V_H + V_{xc}\right)\left|\phi_n\right\rangle = \varepsilon_n \left|\phi_n\right\rangle$$

$$G = \sum_{n=1}^{\infty} \frac{\left|\phi_n\right\rangle\left\langle\phi_n\right|}{\omega - \varepsilon_n}$$

$$P = -iGG$$

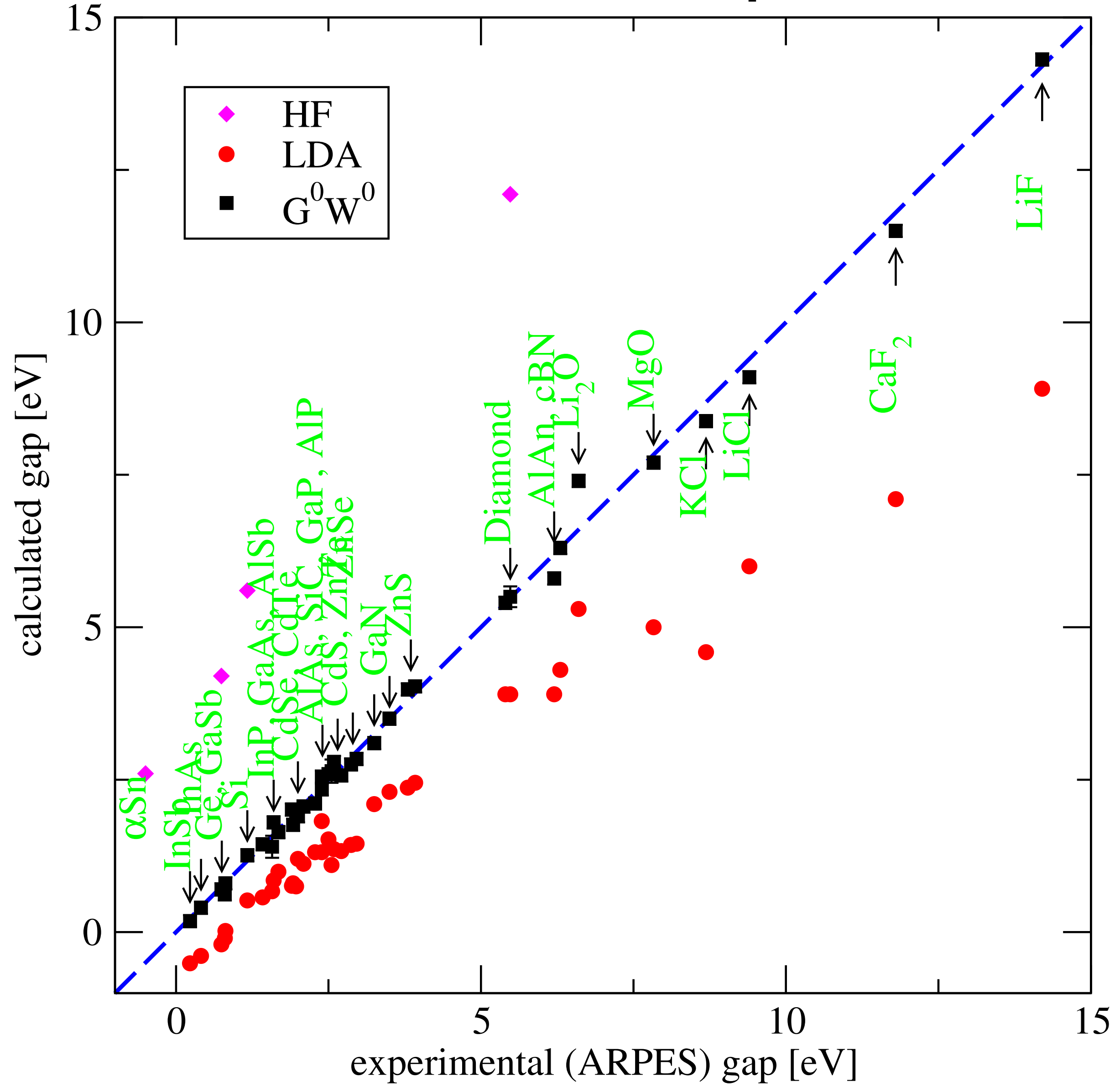
$$\epsilon = 1 - vP$$

$$W = \epsilon^{-1} v$$

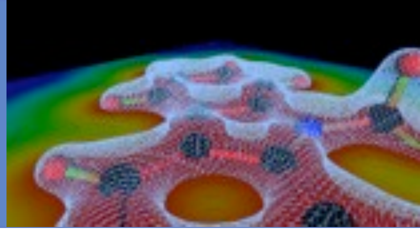
$$\Sigma = iGW$$

$$\epsilon_n \approx \varepsilon_n + \left\langle\phi_n\right|\Sigma - V_{xc}\left|\phi_n\right\rangle$$

LDA and G_0W_0 : precision



S. Faleev, PRL, 2004



G_0W_0 :

$$\left(T+V_{ext}+V_H+V_{xc}\right)\left|\phi_n\right\rangle=\varepsilon_n\left|\phi_n\right\rangle$$

$$G=\sum_{n=1}^{\infty}\frac{\left|\phi_n\right\rangle\left\langle\phi_n\right|}{\omega-\varepsilon_n}$$

$$P=-iGG$$

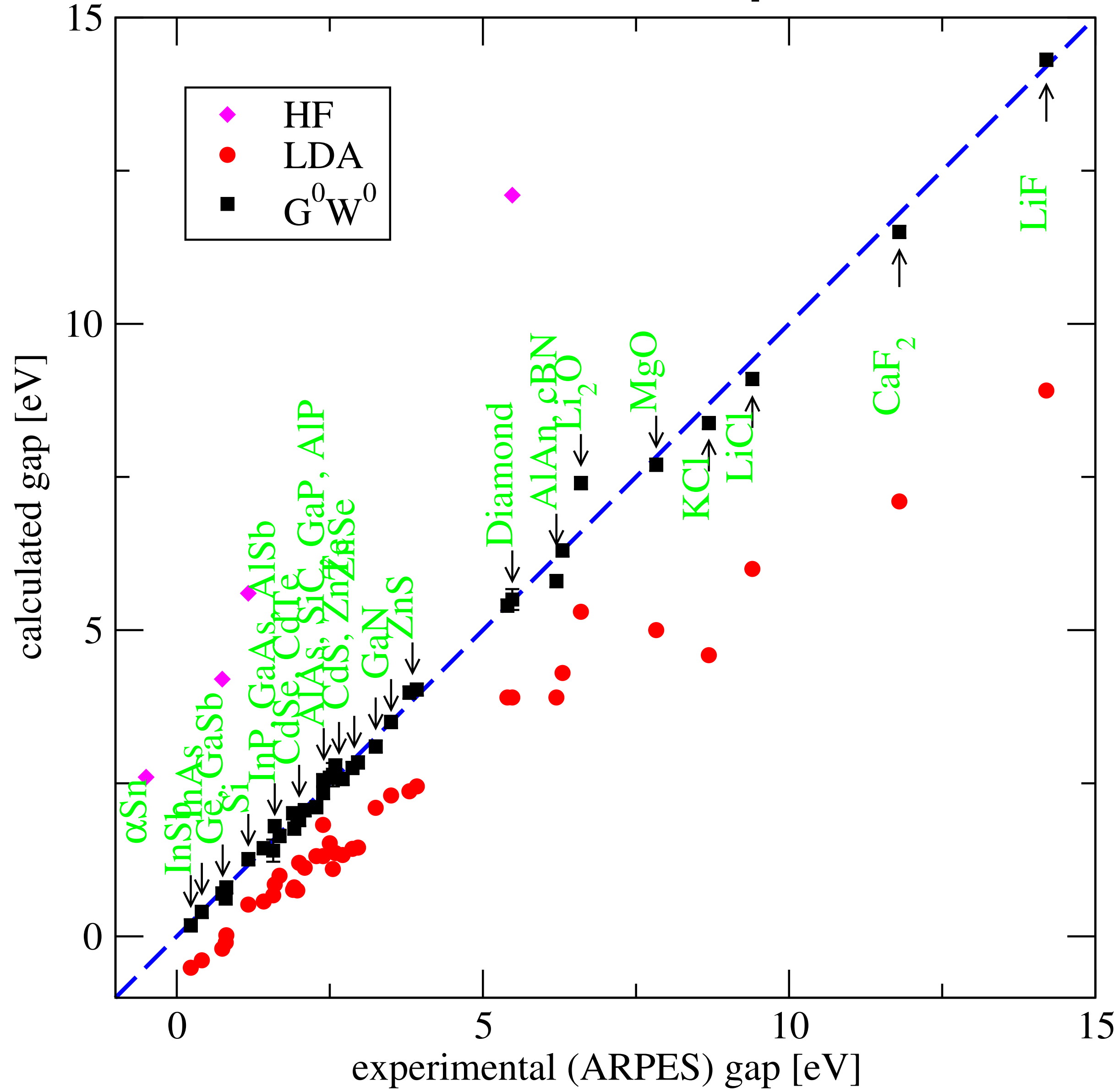
$$\epsilon=1-vP$$

$$W=\epsilon^{-1}v$$

$$\Sigma=iGW$$

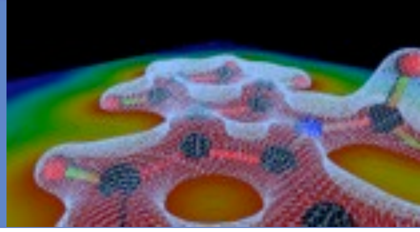
$$\epsilon_n\approx\varepsilon_n+\left\langle\phi_n\right|\Sigma-V_{xc}\left|\phi_n\right\rangle$$

LDA and G_0W_0 : precision



~ 10 atoms !

S. Faleev, PRL, 2004



G0W0 :

$$\left(T + V_{ext} + V_H + V_{xc}\right)\left|\phi_n\right\rangle = \varepsilon_n \left|\phi_n\right\rangle$$

$$G = \sum_{n=1}^{\infty} \frac{\left|\phi_n\right\rangle\left\langle\phi_n\right|}{\omega - \varepsilon_n}$$

$$P = -iGG$$

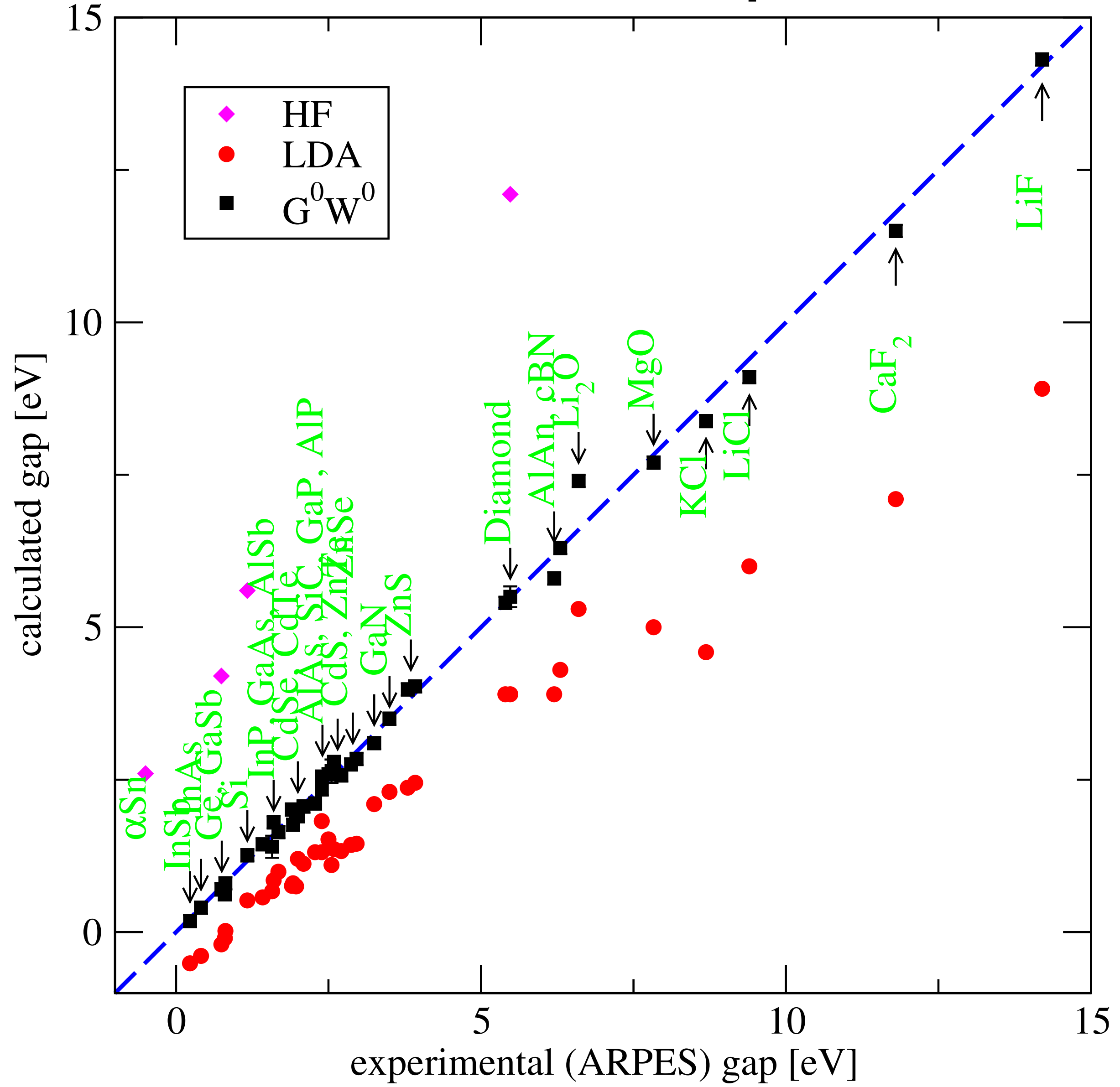
$$\epsilon = 1 - vP$$

$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

$$\epsilon_n \approx \varepsilon_n + \left\langle \phi_n \left| \Sigma - V_{xc} \right| \phi_n \right\rangle$$

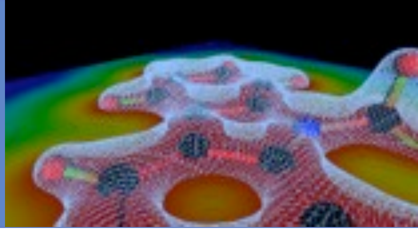
LDA and G0W0 : precision



~ 10 atoms !

S. Faleev, PRL, 2004

The G_0W_0 : bottlenecks



- Why G_0W_0 so expensive ?

$$P = -iGG$$

$$\epsilon = 1 - vP$$

$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

The G_0W_0 : bottlenecks

- Why G_0W_0 so expensive ?

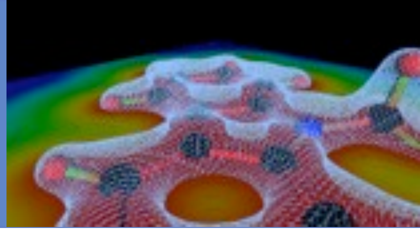
$$P = -iGG$$

$$\epsilon = 1 - vP$$

$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$



- Why G_0W_0 so expensive ?

$$P = -iGG$$

$$\epsilon = 1 - vP$$

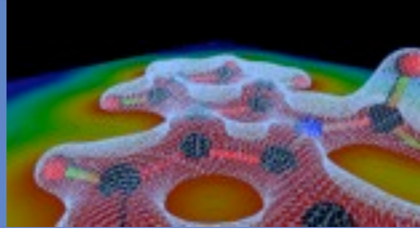
$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

The G_0W_0 : bottlenecks



- Why G_0W_0 so expensive ?

$$P = -iGG$$

$$\epsilon = 1 - vP$$

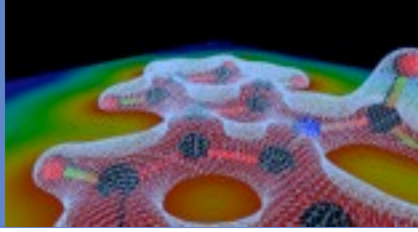
$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

- $N_c \sim 10\, N_v$ to $100\, N_v$ for ϵ_n at ± 0.05 eV



- Why G_0W_0 so expensive ?

$$P = -iGG$$

$$\epsilon = 1 - vP$$

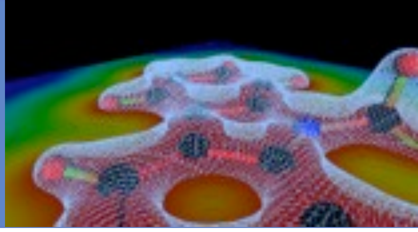
$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

- $N_c \sim 10\ N_v$ to $100\ N_v$ for ϵ_n at ± 0.05 eV



- Why G_0W_0 so expensive ?

$$P = -iGG$$

$$\epsilon = 1 - vP$$

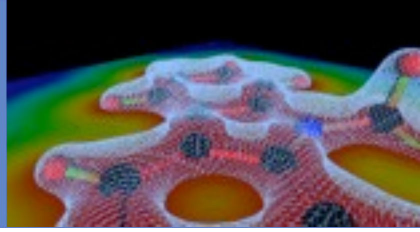
$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

- $N_c \sim 10\ N_v$ to $100\ N_v$ for ϵ_n at ± 0.05 eV



- Why G_0W_0 so expensive ?

$$P = -iGG$$

$$\epsilon = 1 - vP$$

$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

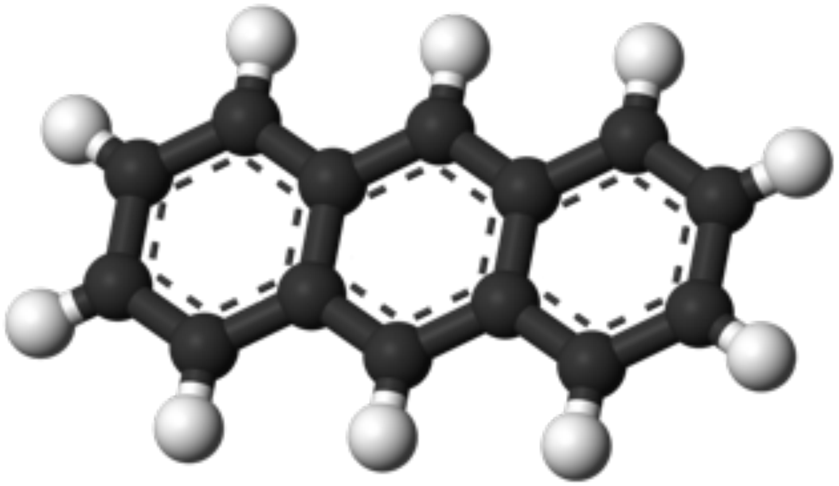
N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

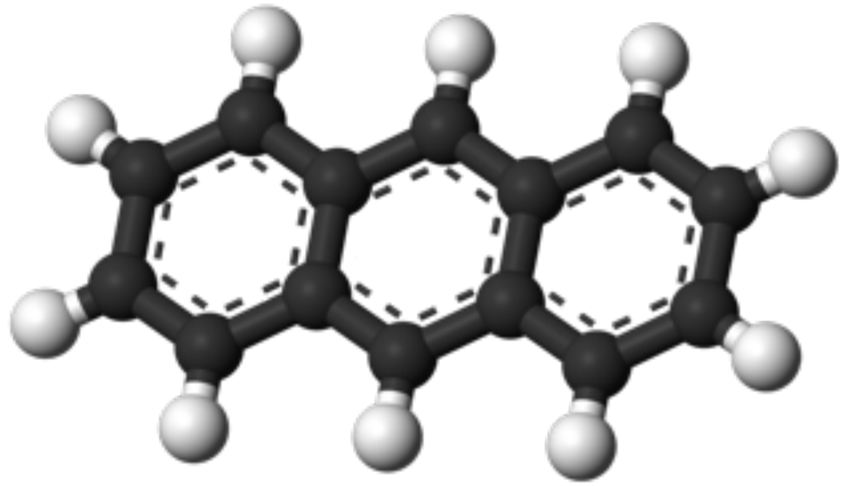
- $N_c \sim 10\ N_v$ to $100\ N_v$ for ϵ_n at ± 0.05 eV

- inversion of $\epsilon \Rightarrow N^3$ operation (N = basis size)

The case of antracene

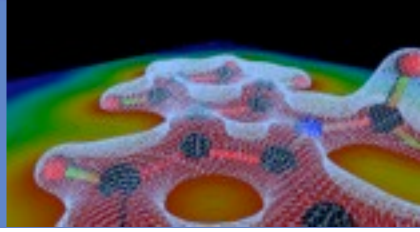


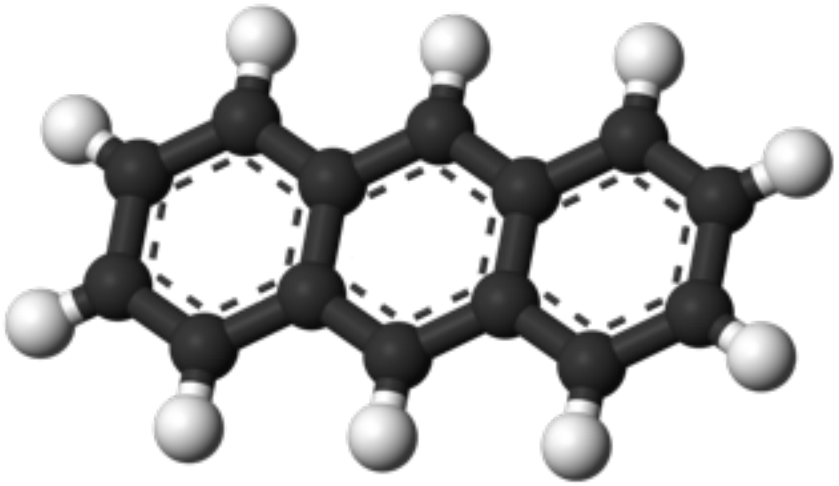
The case of antracene



$N_v = 33$

The case of antracene

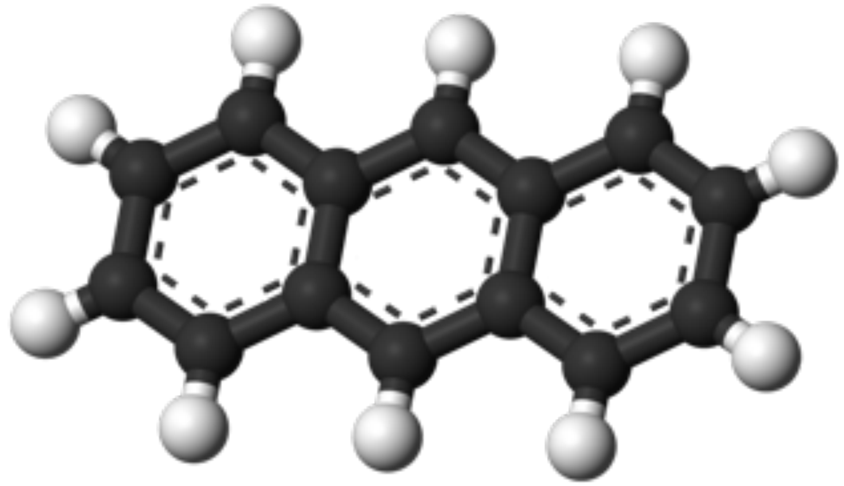




$N_v = 33$

- $N_c \sim 3000$ and $N_{basis} \sim 200\ 000$

The case of antracene

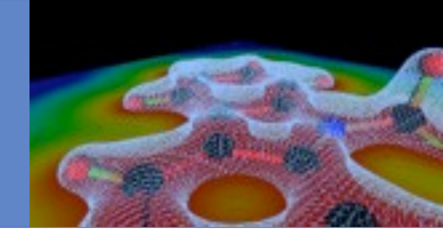


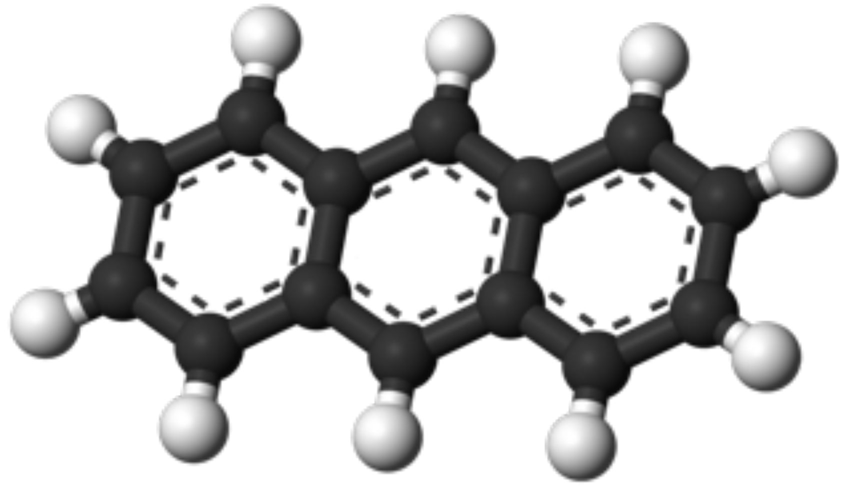
$N_v = 33$

- $N_c \sim 3000$ and $N_{basis} \sim 200\,000$

➡ 10 Gb of RAM usage to store $\{|c\rangle\}$

The case of antracene





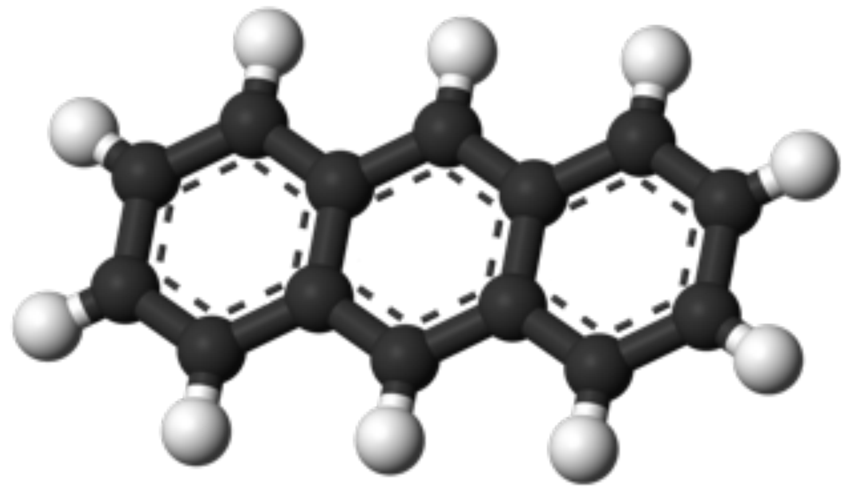
$N_v = 33$

- $N_c \sim 3000$ and $N_{basis} \sim 200\,000$

➡ 10 Gb of RAM usage to store $\{|c\rangle\}$

➡ 100's hours of CPU time to obtain $\{|c\rangle\}$

The case of antracene



$N_v = 33$

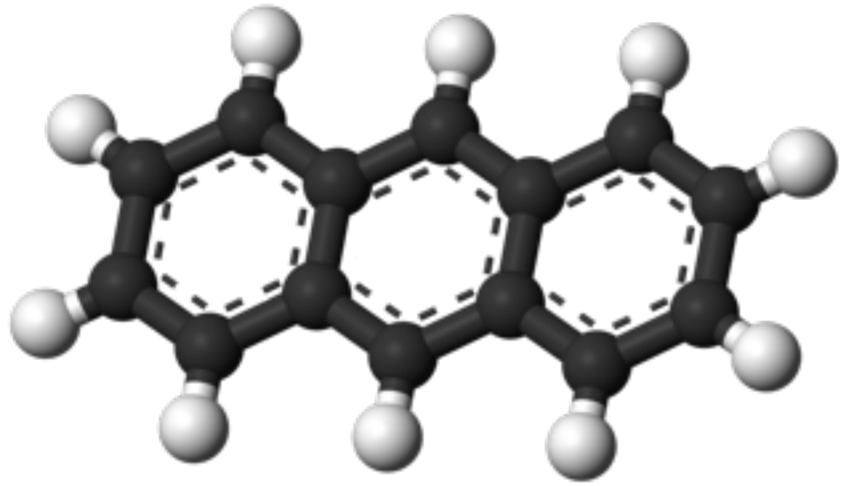
- N_c ~ 3000 and N_{basis} ~ 200 000

➡ 10 Gb of RAM usage to store $\{|c\rangle\}$

➡ 100's hours of CPU time to obtain $\{|c\rangle\}$

- ϵ matrix ~ 7000 x 7000 planewaves

The case of antracene



$N_v = 33$

- N_c ~ 3000 and N_{basis} ~ 200 000

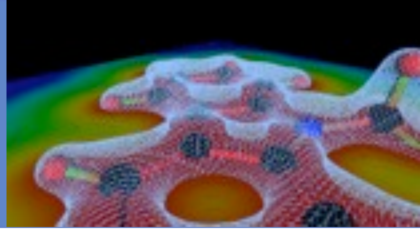
  ➡ 10 Gb of RAM usage to store $\{|c\rangle\}$

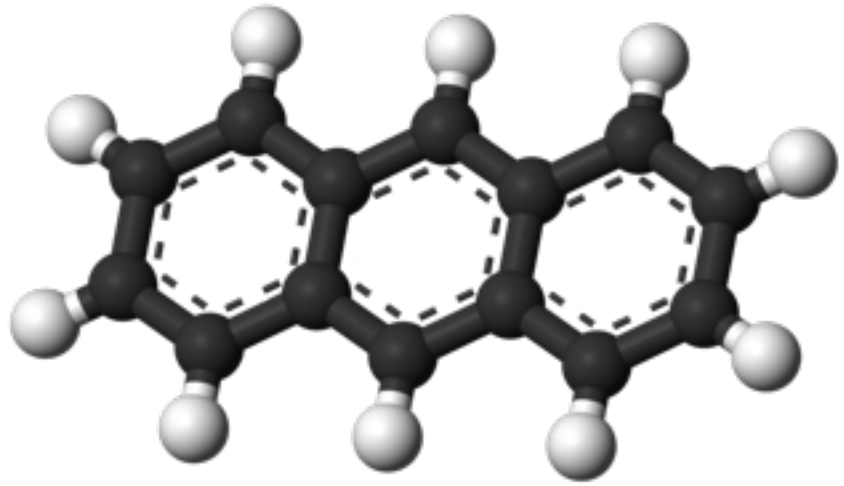
  ➡ 100's hours of CPU time to obtain $\{|c\rangle\}$

- ϵ matrix ~ 7000 x 7000 planewaves

  ➡ 1 Gb of RAM usage to store ϵ

The case of antracene

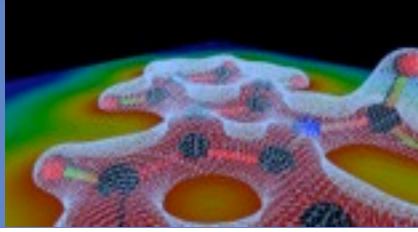




$N_v = 33$

- $N_c \sim 3000$ and $N_{basis} \sim 200\,000$
  - ➡ 10 Gb of RAM usage to store $\{|c\rangle\}$
  - ➡ 100's hours of CPU time to obtain $\{|c\rangle\}$

- ϵ matrix ~ 7000 x 7000 planewaves
  - ➡ 1 Gb of RAM usage to store ϵ
  - ➡ 10's hours of CPU time to ϵ^{-1}



$$P = -iGG$$

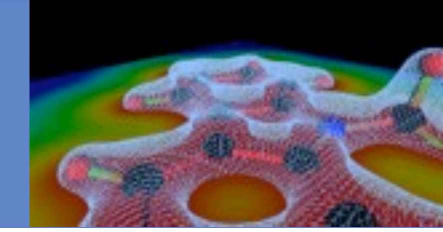
$$\epsilon = 1 - vP$$

$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$



The plan

$$P = -iGG$$

$$\epsilon = 1 - vP$$

$$W = \epsilon^{-1} v$$

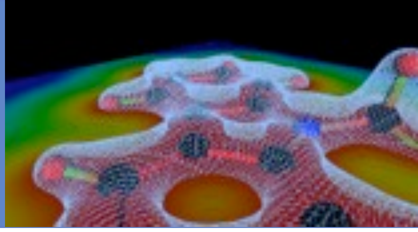
$$\Sigma = iGW$$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

- summations → Sternheimer's equations

The plan



$$1)\quad P = -iGG$$

$$\epsilon = 1 - vP$$

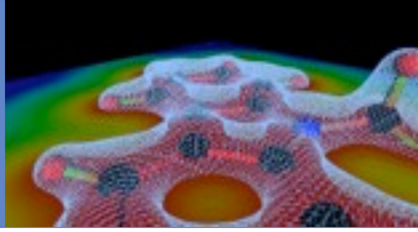
$$W = \epsilon^{-1} v$$

$$\Sigma = iGW$$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

- summations → Sternheimer's equations



The plan

1) $P = -iGG$

$\epsilon = 1 - vP$

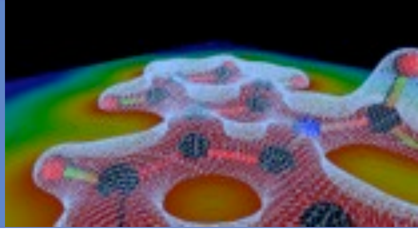
$W = \epsilon^{-1} v$

2) $\Sigma = iGW$

N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

- summations → Sternheimer's equations



$$1)\quad P = -iGG$$

$$\epsilon = 1 - vP$$

$$3)\quad W = \epsilon^{-1} v$$

$$2)\quad \Sigma = iGW$$

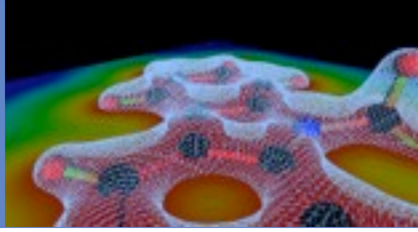
N_c : number of conduction states

$$G = \sum_{n=1}^{\infty \sim N_c} \frac{|n\rangle\langle n|}{\omega - \varepsilon_n}$$

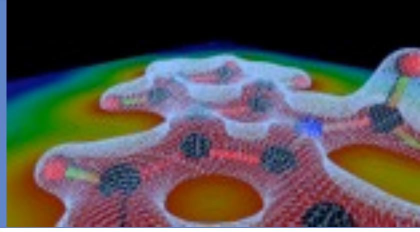
- summations → Sternheimer's equations

- planewaves basis → Lanczos basis

1) $P = -iGG$ Sternheimer's equation

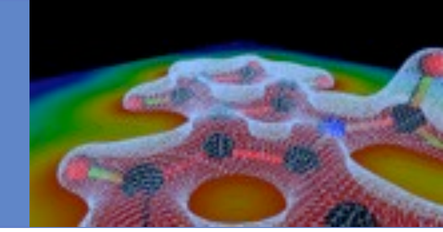


- $$P|\psi\rangle = \sum_v |v\rangle \left(\sum_c |c\rangle \frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)} \langle c| \langle v| \right) |\psi\rangle$$



- $P\left|\psi\right\rangle = \sum_{v}\left|v\right\rangle\left(\sum_{c}\left|c\right\rangle \frac{1}{\omega-(\varepsilon_c-\varepsilon_v)} - \frac{1}{\omega+(\varepsilon_c-\varepsilon_v)}\left\langle c\right|\left\langle v\right|\right)\left|\psi\right\rangle$

Sternheimer's equation



- $$P\left|\psi\right\rangle = \sum_v \left|v\right\rangle \left(\sum_c \left|c\right\rangle \frac{1}{\omega-(\varepsilon_c-\varepsilon_v)} - \frac{1}{\omega+(\varepsilon_c-\varepsilon_v)} \left\langle c\right| \left\langle v\right| \right) \left|\psi\right\rangle$$

- We define :

$$\left|\phi_v^-\right\rangle \equiv \sum_c \frac{\left|c\right\rangle\left\langle c\right|}{\omega-(\varepsilon_c-\varepsilon_v)} \left|v\right\rangle \left|\psi\right\rangle$$

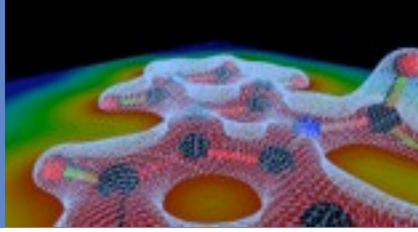
1) $P = -iGG$ Sternheimer's equation

- $$P\left|\psi\right\rangle = \sum_{v}\left|v\right\rangle\left(\sum_{c}\left|c\right\rangle\frac{1}{\omega-(\varepsilon_c-\varepsilon_v)}-\frac{1}{\omega+(\varepsilon_c-\varepsilon_v)}\left\langle c\right|\left\langle v\right|\right)\left|\psi\right\rangle$$

- We define :

$$\left|\phi_v^-\right\rangle \equiv \sum_{c}\frac{\left|c\right\rangle\left\langle c\right|}{\omega-(\varepsilon_c-\varepsilon_v)}\left|v\right\rangle\left|\psi\right\rangle$$

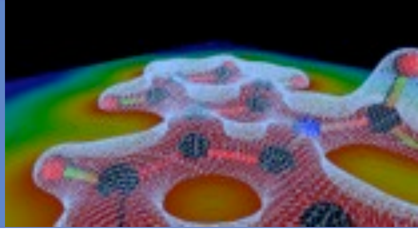
Sternheimer's equation



- $$P|\psi\rangle=\sum_v |v\rangle\left(\sum_c |c\rangle\frac{1}{\omega-(\varepsilon_c-\varepsilon_v)}-\frac{1}{\omega+(\varepsilon_c-\varepsilon_v)}\langle c|\langle v|\right)|\psi\rangle$$
- We define :

$$|\phi_v^-\rangle\equiv\sum_c \frac{|c\rangle\langle c|}{\omega-(\varepsilon_c-\varepsilon_v)}|v\rangle|\psi\rangle$$

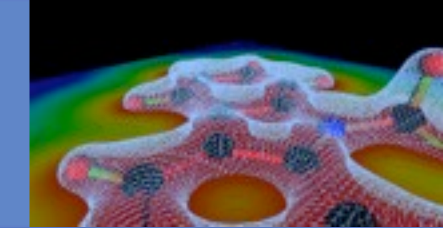
Sternheimer's equation



- $$P|\psi\rangle = \sum_v |v\rangle \left(\sum_c |c\rangle \frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)} \langle c| \langle v| \right) |\psi\rangle$$
- We define :

$$|\phi_v^-\rangle \equiv \sum_c \frac{|c\rangle\langle c|}{\omega - (\varepsilon_c - \varepsilon_v)} |v\rangle|\psi\rangle = \frac{1}{\omega - H + \varepsilon_v} \mathcal{P}_c |v\rangle|\psi\rangle$$

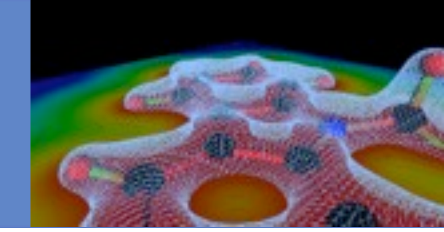
Sternheimer's equation



- $$P\left|\psi\right\rangle = \sum_v \left|v\right\rangle \left(\sum_c \left|c\right\rangle \frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)} \left\langle c\right| \left\langle v\right| \right) \left|\psi\right\rangle$$
- We define :

$$\left|\phi_v^-\right\rangle \equiv \sum_c \frac{\left|c\right\rangle\left\langle c\right|}{\omega - (\varepsilon_c - \varepsilon_v)} \left|v\right\rangle \left|\psi\right\rangle = \frac{1}{\omega - H + \varepsilon_v} \mathcal{P}_c \left|v\right\rangle \left|\psi\right\rangle$$

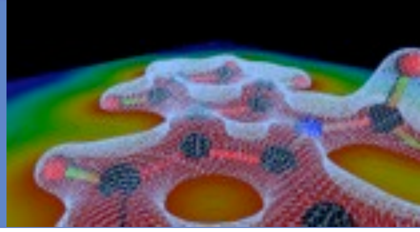
Sternheimer's equation



- $$P|\psi\rangle = \sum_v |v\rangle \left(\sum_c |c\rangle \frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)} \langle c| \langle v| \right) |\psi\rangle$$
- We define :

$$|\phi_v^-\rangle \equiv \sum_c \frac{|c\rangle\langle c|}{\omega - (\varepsilon_c - \varepsilon_v)} |v\rangle |\psi\rangle = \frac{1}{\omega - H + \varepsilon_v} \mathcal{P}_c |v\rangle |\psi\rangle$$

Sternheimer's equation

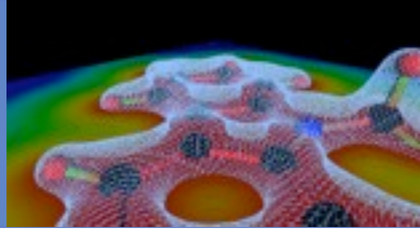


- $$P|\psi\rangle = \sum_v |v\rangle \left(\sum_c |c\rangle \frac{1}{\omega-(\varepsilon_c-\varepsilon_v)} - \frac{1}{\omega+(\varepsilon_c-\varepsilon_v)} \langle c|\langle v| \right) |\psi\rangle$$

- We define :

$$|\phi_v^-\rangle \equiv \sum_c \frac{|c\rangle\langle c|}{\omega-(\varepsilon_c-\varepsilon_v)} |v\rangle|\psi\rangle = \frac{1}{\boxed{\omega - H + \varepsilon_v}} \mathcal{P}_c |v\rangle|\psi\rangle$$

Sternheimer's equation



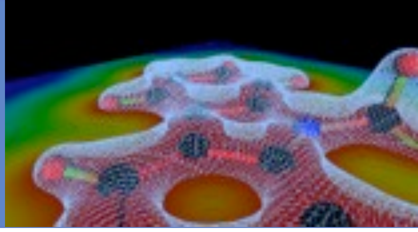
- $$P\left|\psi\right\rangle = \sum_v \left|v\right\rangle \left(\sum_c \left|c\right\rangle \frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)} \left\langle c\right| \left\langle v\right| \right) \left|\psi\right\rangle$$

- We define :

$$\left|\phi_v^-\right\rangle \equiv \sum_c \frac{\left|c\right\rangle\left\langle c\right|}{\omega - (\varepsilon_c - \varepsilon_v)} \left|v\right\rangle \left|\psi\right\rangle = \frac{1}{\boxed{\omega - H + \varepsilon_v}} \mathcal{P}_c \left|v\right\rangle \left|\psi\right\rangle$$

$$\left(H - \varepsilon_v - \omega\right)\left|\phi_v^-\right\rangle = -\mathcal{P}_c \left|v\right\rangle \left|\psi\right\rangle$$ Sternheimer equation

Sternheimer's equation



- $$P|\psi\rangle = \sum_v |v\rangle \left(\sum_c |c\rangle \frac{1}{\omega - (\varepsilon_c - \varepsilon_v)} - \frac{1}{\omega + (\varepsilon_c - \varepsilon_v)} \langle c| \langle v| \right) |\psi\rangle$$
- We define :

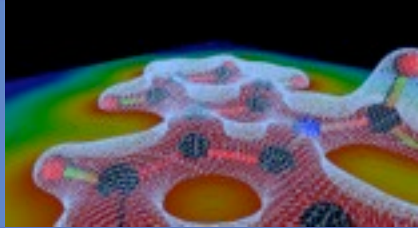
$$|\phi_v^-\rangle \equiv \sum_c \frac{|c\rangle\langle c|}{\omega - (\varepsilon_c - \varepsilon_v)} |v\rangle |\psi\rangle = \frac{1}{\boxed{\omega - H + \varepsilon_v}} \mathcal{P}_c |v\rangle |\psi\rangle$$

$$(H - \varepsilon_v - \omega)|\phi_v^-\rangle = -\mathcal{P}_c |v\rangle |\psi\rangle$$ Sternheimer equation

$\cancel{\sum_c}$ $\longrightarrow$ Solving $\boxed{A|x\rangle = |b\rangle}$

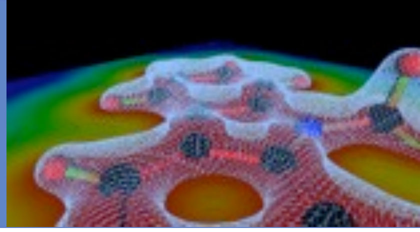
2) $\Sigma = iGW$ Sternheimer's equation

Sternheimer's equation



- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

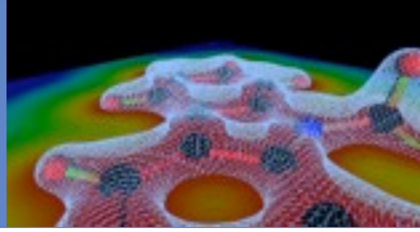
Sternheimer's equation



- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_n \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

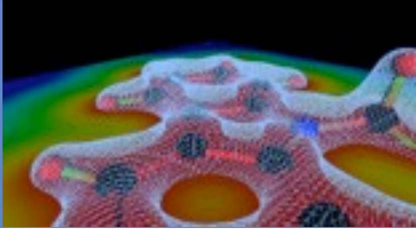
Sternheimer's equation



- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_n \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

Sternheimer's equation

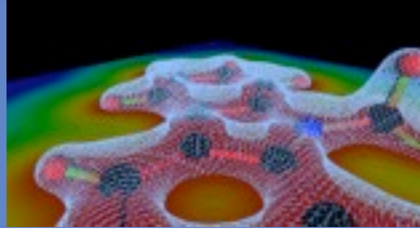


- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_{n} \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle n^* | \Phi_m^\dagger | q \rangle \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

Sternheimer's equation

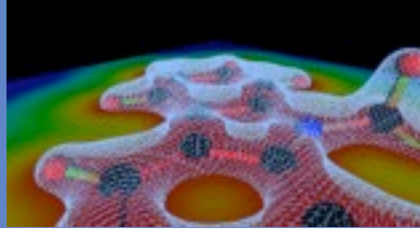


- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_{n} \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle n^* | \Phi_m^\dagger | q \rangle \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

Sternheimer's equation



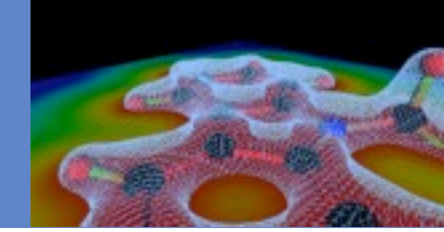
- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_n \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle n^* | \Phi_m^\dagger | q \rangle \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle q^* | \Phi_m^\dagger | n \rangle \langle n | \Phi_m v^T \left[\epsilon^{-T} - 1 \right] (\omega) | q^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

Sternheimer's equation



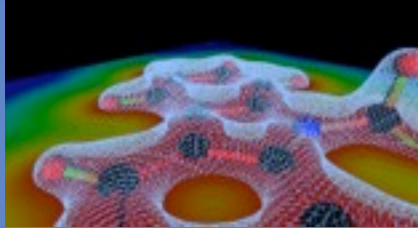
- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_{n} \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle n^* | \Phi_m^\dagger | q \rangle \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle q^* | \Phi_m^\dagger | n \rangle \langle n | \Phi_m v^T \left[\epsilon^{-T} - 1 \right] (\omega) | q^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

Sternheimer's equation



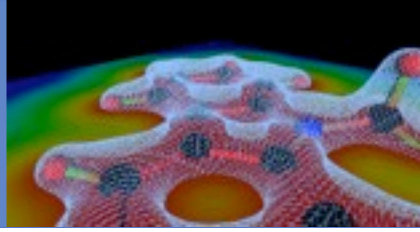
- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_n \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle n^* | \Phi_m^\dagger | q \rangle \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle q^* | \Phi_m^\dagger | n \rangle \langle n | \Phi_m v^T \left[\epsilon^{-T} - 1 \right] (\omega) | q^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

Sternheimer's equation



- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

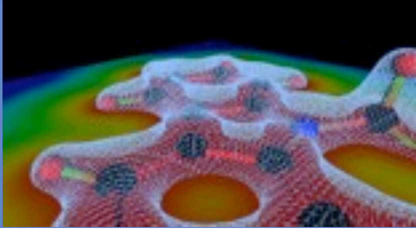
$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_{n} \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle n^* | \Phi_m^\dagger | q \rangle \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle q^* | \Phi_m^\dagger | n \rangle \langle n | \Phi_m v^T \left[\epsilon^{-T} - 1 \right](\omega) | q^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{q} \langle q^* | \Phi_m^\dagger \frac{1}{\omega - (H - \varepsilon_m)} \Phi_m v^T \left[\epsilon^{-T} - 1 \right](\omega) | q^* \rangle$$

Sternheimer's equation



- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

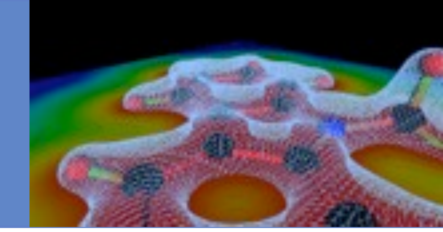
$$\langle m | \Sigma_c | m \rangle = \langle m | iGW_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_{n} \frac{\langle n^* | \Phi_m^\dagger \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle n^* | \Phi_m^\dagger | q \rangle \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m | n^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{nq} \frac{\langle q^* | \Phi_m^\dagger | n \rangle \langle n | \Phi_m v^T \left[\epsilon^{-T} - 1 \right](\omega) | q^* \rangle}{\omega - (\varepsilon_n - \varepsilon_m)}$$

$$= (\ldots) \sum_{q} \langle q^* | \Phi_m^\dagger \frac{1}{\omega - (H - \varepsilon_m)} \Phi_m v^T \left[\epsilon^{-T} - 1 \right](\omega) | q^* \rangle$$

Sternheimer's equation



- We want : $\epsilon_m \approx \varepsilon_m + \langle m | \Sigma_x + \Sigma_c - V_{xc} | m \rangle$

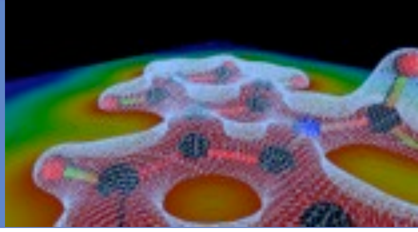
$$\langle m|\Sigma_c|m\rangle = \langle m|iGW_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_{n} \frac{\langle n^*|\Phi_m^\dagger\left[\epsilon^{-1}-1\right]v\Phi_m|n^*\rangle}{\omega-(\varepsilon_n-\varepsilon_m)}$$

$$= (\ldots)\sum_{nq}\frac{\langle n^*|\Phi_m^\dagger|q\rangle\langle q|\left[\epsilon^{-1}-1\right]v\Phi_m|n^*\rangle}{\omega-(\varepsilon_n-\varepsilon_m)}$$

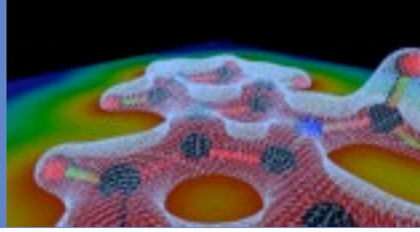
$$= (\ldots)\sum_{nq}\frac{\langle q^*|\Phi_m^\dagger|n\rangle\langle n|\Phi_m v^T\left[\epsilon^{-T}-1\right](\omega)|q^*\rangle}{\omega-(\varepsilon_n-\varepsilon_m)}$$

$$= (\ldots)\sum_{q}\langle q^*|\Phi_m^\dagger \frac{1}{\omega-(H-\varepsilon_m)}\Phi_m v^T\left[\epsilon^{-T}-1\right](\omega)|q^*\rangle$$

Sternheimer's equation

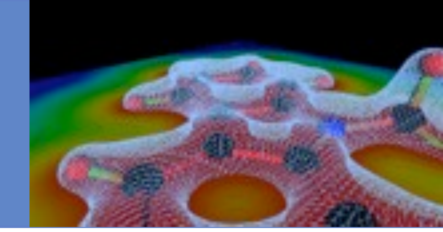


2) $\Sigma = iGW$ Sternheimer's equation



$$\langle m | \Sigma_c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_q \langle q | \left[\epsilon^{-1} - 1 \right] v \Phi_m^T \frac{1}{\omega - H^T + \varepsilon_m} \Phi_m^{\dagger T} | q \rangle$$

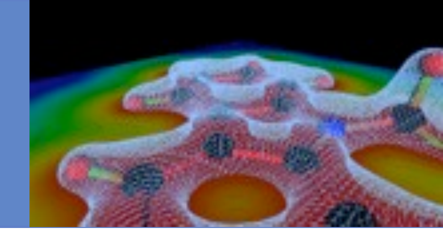
Sternheimer's equation



$$\langle m|\Sigma_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T \frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle$$

$$= \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T\Big|x_q\Big\rangle$$

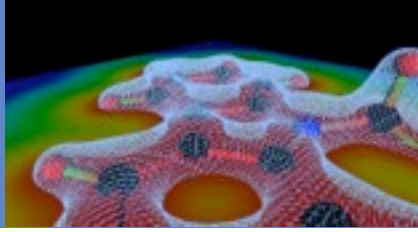
Sternheimer's equation



$$\langle m|\Sigma_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T \boxed{\frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle}$$

$$= \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T|x_q\rangle$$

Sternheimer's equation

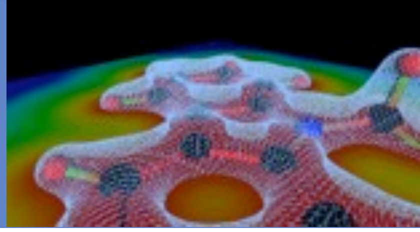


$$\langle m|\Sigma_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T \boxed{\frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle}$$

$$= \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T|x_q\rangle$$

$$|x_q\rangle \equiv \frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle$$

Sternheimer's equation

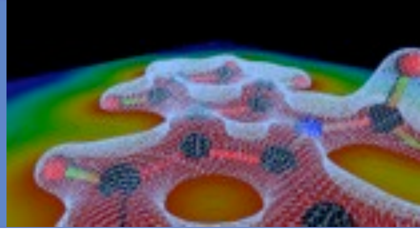


$$\langle m|\Sigma_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T \boxed{\frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle}$$

$$= \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T|x_q\rangle$$

$$|x_q\rangle \equiv \frac{1}{\boxed{\omega - H^T + \varepsilon_m}}\Phi_m^{\dagger T}|q\rangle$$

Sternheimer's equation



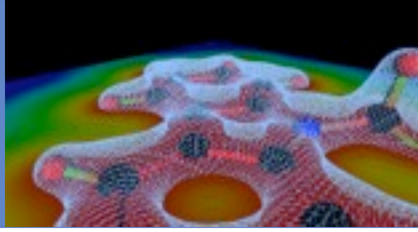
$$\langle m|\Sigma_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T \boxed{\frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle}$$

$$= \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right]v\Phi_m^T |x_q\rangle$$

$$|x_q\rangle \equiv \frac{1}{\boxed{\omega - H^T + \varepsilon_m}}\Phi_m^{\dagger T}|q\rangle$$

$$\left(\omega - H^T + \varepsilon_m\right)|x_q\rangle = \Phi_m^{\dagger T}|q\rangle$$ Sternheimer equation

Sternheimer's equation



$$\langle m|\Sigma_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right] v\Phi_m^T \boxed{\frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle}$$

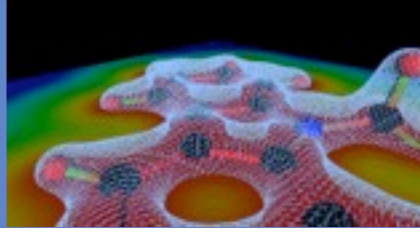
$$= \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right] v\Phi_m^T |x_q\rangle$$

$$|x_q\rangle \equiv \frac{1}{\boxed{\omega - H^T + \varepsilon_m}}\Phi_m^{\dagger T}|q\rangle$$

$$\left(\omega - H^T + \varepsilon_m\right)|x_q\rangle = \Phi_m^{\dagger T}|q\rangle$$ Sternheimer equation

$$\cancel{\sum_n}$$

Sternheimer's equation



$$\langle m|\Sigma_c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right] v\Phi_m^T \boxed{\frac{1}{\omega - H^T + \varepsilon_m}\Phi_m^{\dagger T}|q\rangle}$$

$$= \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right] v\Phi_m^T |x_q\rangle$$

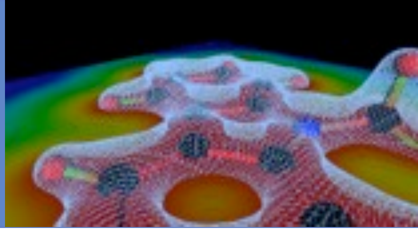
$$|x_q\rangle \equiv \frac{1}{\boxed{\omega - H^T + \varepsilon_m}}\Phi_m^{\dagger T}|q\rangle$$

$$\left(\omega - H^T + \varepsilon_m\right)|x_q\rangle = \Phi_m^{\dagger T}|q\rangle$$ Sternheimer equation

$$\cancel{\sum_n} \longrightarrow$$

Solving $\boxed{A|x\rangle = |b\rangle}$

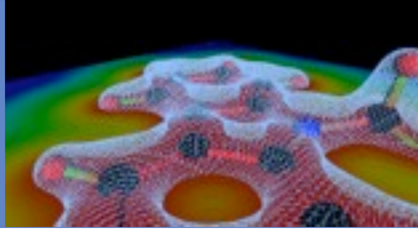
Lanczos algorithm



$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right](\ldots)|q\rangle$$

$2)\ \Sigma = iGW$

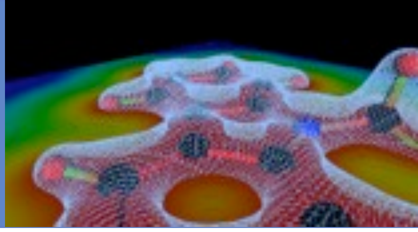
Lanczos algorithm



$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right](\ldots)|q\rangle$$

- Need a basis: $\{|q\rangle\}$

Lanczos algorithm

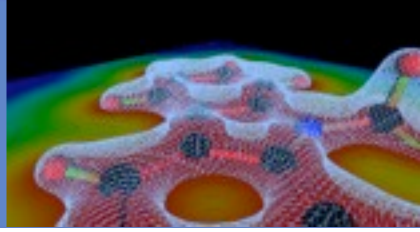


$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right](\ldots)|q\rangle$$

- Need a basis: $\{|q\rangle\}$

- The ideal basis:

Lanczos algorithm

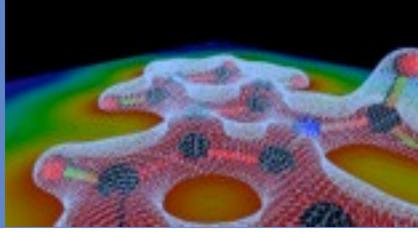


$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1}-1\right](\ldots)|q\rangle$$

- Need a basis: $\{|q\rangle\}$

- The ideal basis:
  - Is small, e.g.
    - $\Rightarrow$ NOT planewaves

2) $\Sigma = iGW$ Lanczos algorithm



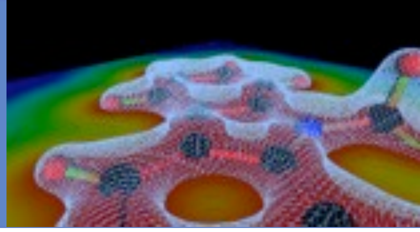
$$\langle m | \Sigma^{c} | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_{q} \langle q | \left[\epsilon^{-1} - 1 \right] (\ldots) | q \rangle$$

- Need a basis: $\{|q\rangle\}$

- The ideal basis:
  - Is small, e.g.
    $\Rightarrow$ NOT planewaves
  - Is easy to compute
    $\Rightarrow$ NOT $\{|n\rangle\}$

$2)\ \Sigma = iGW$

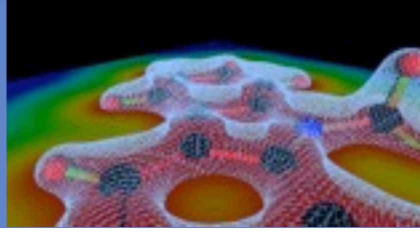
Lanczos algorithm



Lanczos algorithm

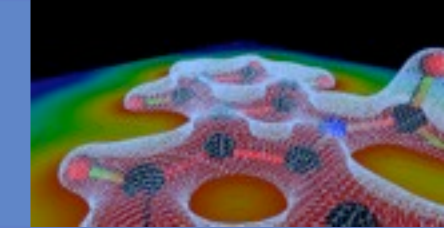
- Idea :

Lanczos algorithm



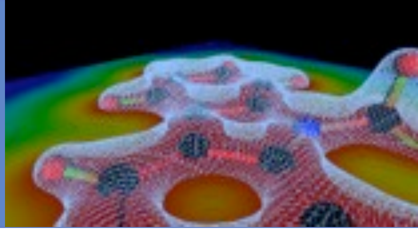
- Idea :
  - efficient sampling of big eigenvalues of : $\epsilon^{-1} - 1 \approx 1 - \epsilon = vP$

2) $\Sigma = iGW$ Lanczos algorithm



- Idea :
  - efficient sampling of big eigenvalues of : $\epsilon^{-1} - 1 \approx 1 - \epsilon = vP$
  - Take (any) vector : $|\psi\rangle$

Lanczos algorithm



- Idea :
  - efficient sampling of big eigenvalues of : $\epsilon^{-1} - 1 \approx 1 - \epsilon = vP$
  - Take (any) vector : $|\psi\rangle$
  - Build : $\left\{ |\psi\rangle, (vP)|\psi\rangle, (vP)^2|\psi\rangle, \ldots \right\}$

    $\rightarrow$ biggest eigenvalues pop out

Lanczos algorithm

- Idea :

  - efficient sampling of big eigenvalues of : $\epsilon^{-1} - 1 \approx 1 - \epsilon = vP$

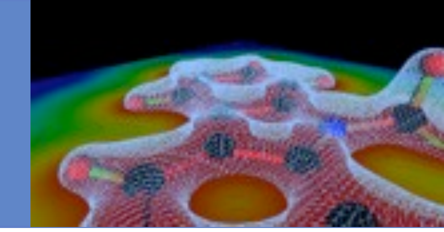
  - Take (any) vector : $|\psi\rangle$

  - Build : $\{|\psi\rangle, (vP)|\psi\rangle, (vP)^2|\psi\rangle, \ldots\}$

    $\rightarrow$ biggest eigenvalues pop out

  - Orthonormalize : $\{|q\rangle\}$

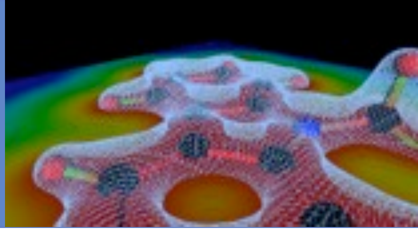
Lanczos algorithm



- Idea :
  - efficient sampling of big eigenvalues of : $\epsilon^{-1} - 1 \approx 1 - \epsilon = vP$
  - Take (any) vector : $|\psi\rangle$
  - Build : $\{|\psi\rangle, (vP)|\psi\rangle, (vP)^2|\psi\rangle, \ldots\}$

    $\rightarrow$ biggest eigenvalues pop out
  - Orthonormalize : $\{|q\rangle\}$
- Lanczos procedure: same $\{|q\rangle\}$

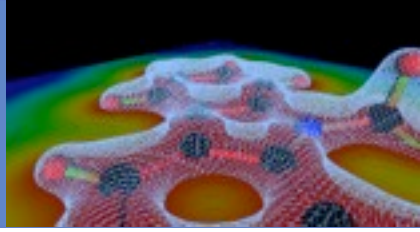
Lanczos algorithm



- Idea :
  - efficient sampling of big eigenvalues of : $\epsilon^{-1} - 1 \approx 1 - \epsilon = vP$
  - Take (any) vector : $|\psi\rangle$
  - Build : $\{|\psi\rangle, (vP)|\psi\rangle, (vP)^2|\psi\rangle, \ldots\}$

    $\rightarrow$ biggest eigenvalues pop out
  - Orthonormalize : $\{|q\rangle\}$
- Lanczos procedure: same $\{|q\rangle\}$
  - Don’t pay all orthogonalization

Lanczos algorithm

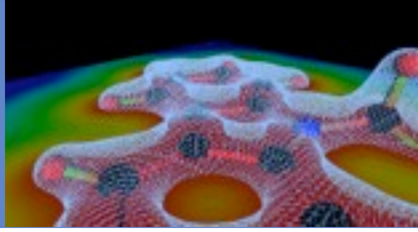


- Idea :
  - efficient sampling of big eigenvalues of : $\epsilon^{-1} - 1 \approx 1 - \epsilon = vP$
  - Take (any) vector : $|\psi\rangle$
  - Build : $\{|\psi\rangle, (vP)|\psi\rangle, (vP)^2|\psi\rangle, \ldots\}$

    $\rightarrow$ biggest eigenvalues pop out
  - Orthonormalize : $\{|q\rangle\}$
- Lanczos procedure: same $\{|q\rangle\}$
  - Don’t pay all orthogonalization
  - Obtain ϵ for free

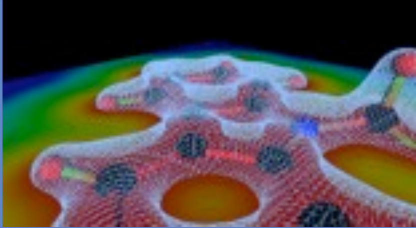
$3)\ W = \epsilon^{-1} v$

Lanczos algorithm



3) $W = \epsilon^{-1} v$

Lanczos algorithm



$$\langle m | \Sigma^c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_q \langle q | \left[\epsilon^{-1} - 1 \right] (\ldots) | q \rangle$$

3) $W = \epsilon^{-1} v$ Lanczos algorithm

$$\langle m | \Sigma^c | m \rangle = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega \sum_q \langle q | \left[\epsilon^{-1} - 1 \right] (\ldots) | q \rangle$$

3) $W = \epsilon^{-1} v$ Lanczos algorithm

$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1} - 1\right](\ldots)|q\rangle$$

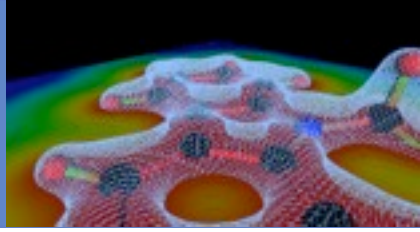
3) $W = \epsilon^{-1} v$ Lanczos algorithm

$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1} - 1\right](\ldots)|q\rangle$$

- We have a small $\{|q\rangle\}$

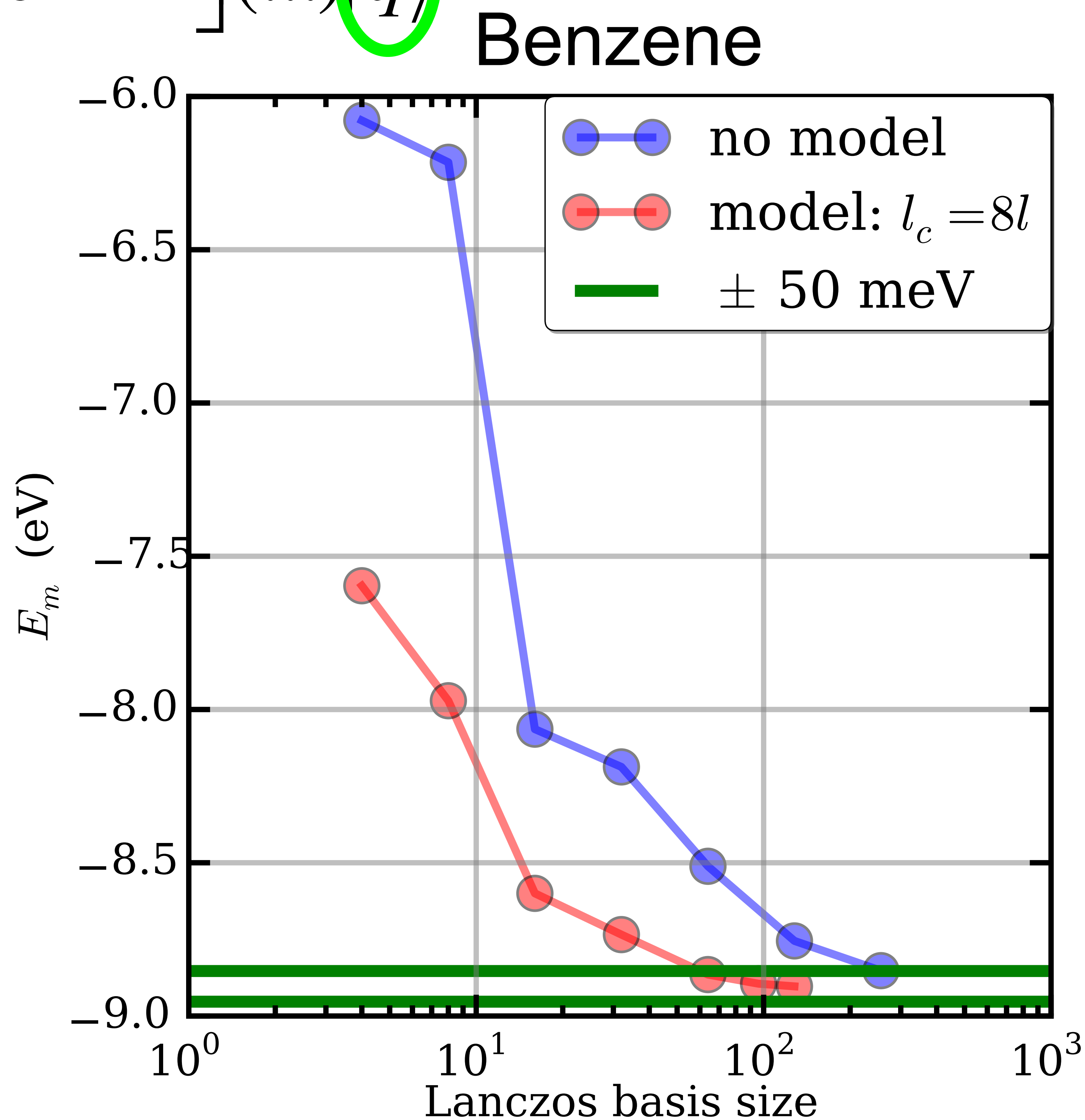
$3)\ W = \epsilon^{-1} v$

Lanczos algorithm

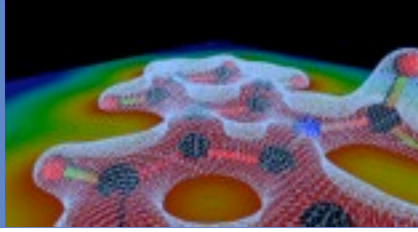


$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1} - 1\right](\ldots)|q\rangle$$

- We have a small $\{|q\rangle\}$



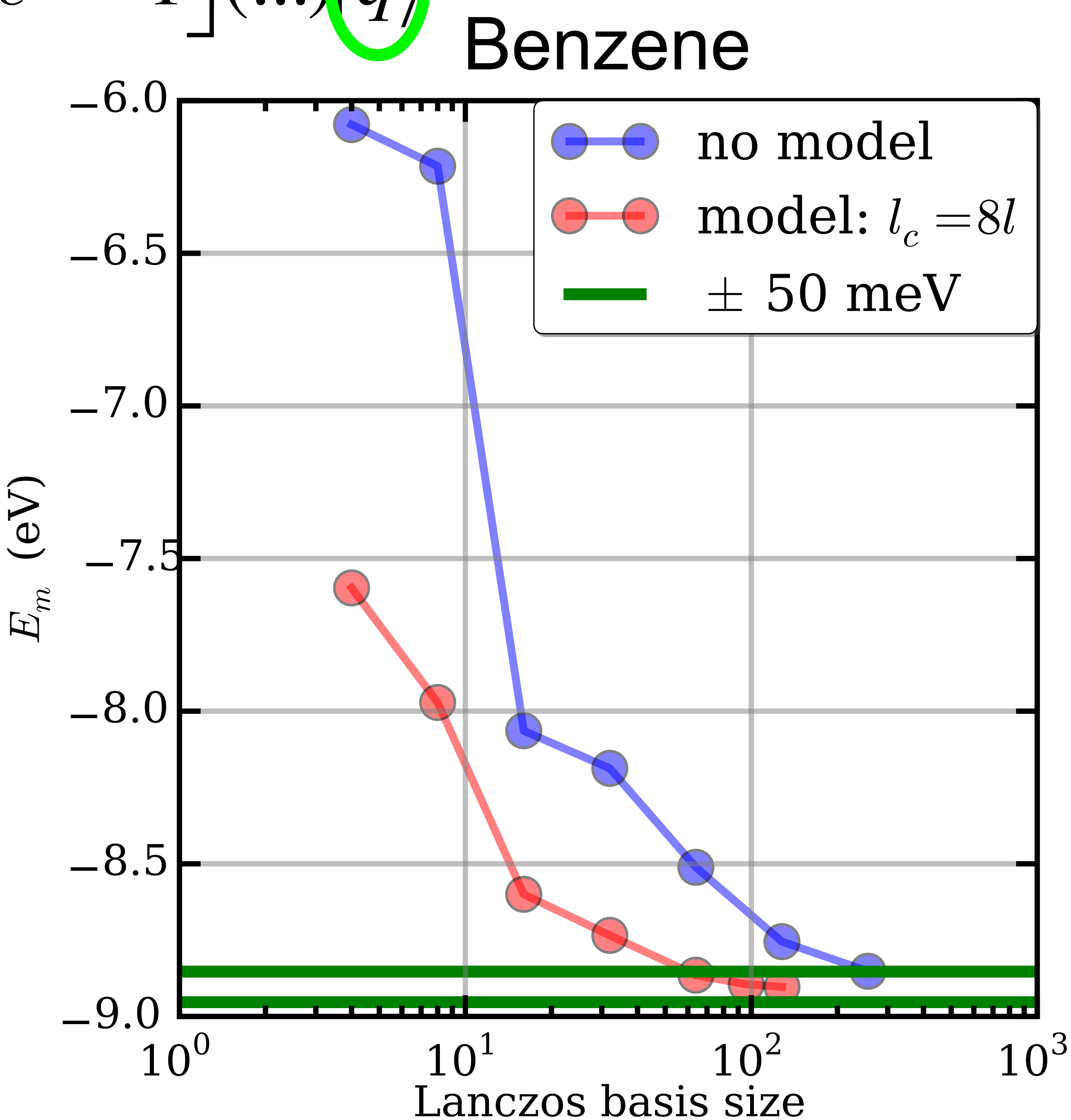
Lanczos algorithm



$$\langle m|\Sigma^c|m\rangle = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega \sum_q \langle q|\left[\epsilon^{-1} - 1\right](\dots)|q\rangle$$

- We have a small $\{|q\rangle\}$

  $\rightarrow \epsilon^{-1}$ ~ free



Performance

Performance

$$\cancel{\sum_{n}}$$

Performance

$$\cancel{\sum_n}$$

$$\cancel{\epsilon^{-1}}$$

(smaller)

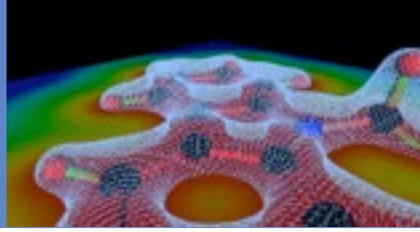
Performance

$$\cancel{\sum_n}$$

$$\cancel{\epsilon^{-1}}$$

(smaller)

$$\boxed{A|x\rangle = |b\rangle}$$



$$\cancel{\sum_n}$$

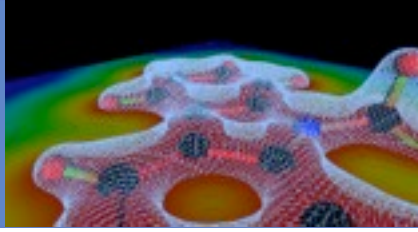
$$\cancel{\epsilon^{-1}}$$

(smaller)

$$\boxed{A|x\rangle = |b\rangle}$$

$$\boxed{\{|q\rangle\}}$$

Performance



$$\cancel{\sum_n}$$

$$\cancel{\epsilon^{-1}}$$

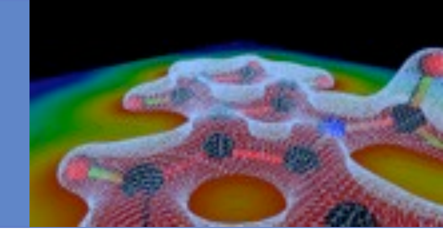
(smaller)

$$\boxed{A|x\rangle = |b\rangle}$$

$$\boxed{\{|q\rangle\}}$$

Faster ?

Performance



$\cancel{\sum_n}$

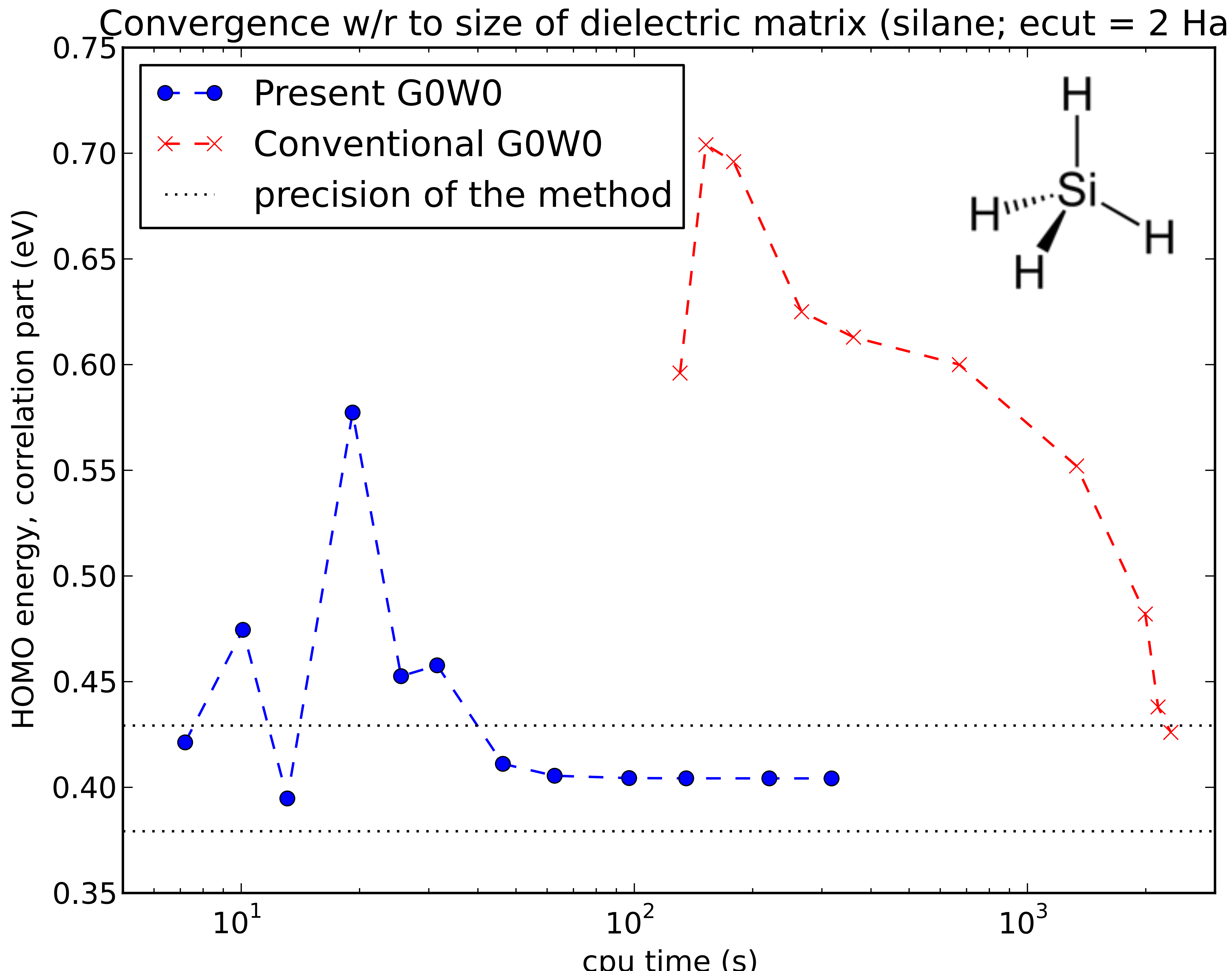
$\cancel{\epsilon^{-1}}$

(smaller)

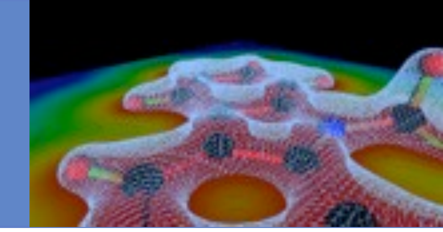
$\boxed{A|x\rangle = |b\rangle}$

$\boxed{\{|q\rangle\}}$

Faster ?



Performance



$\cancel{\sum_n}$

$\cancel{\epsilon^{-1}}$

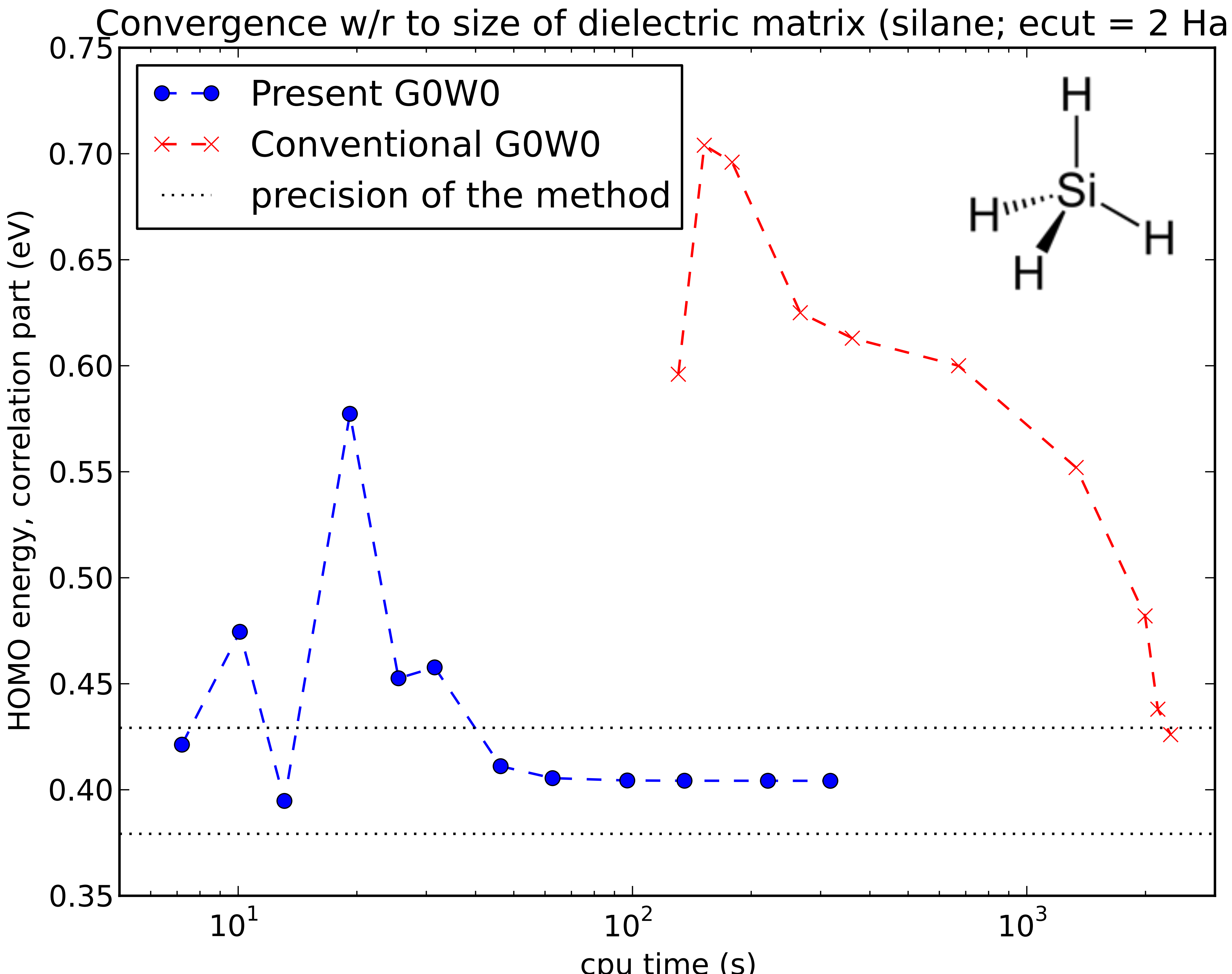
(smaller)

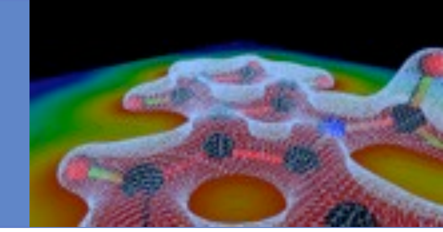
$\boxed{A|x\rangle = |b\rangle}$

$\boxed{\{|q\rangle\}}$

Faster ?

Yes!





Performance

$\cancel{\sum_n}$

$\cancel{\epsilon^{-1}}$

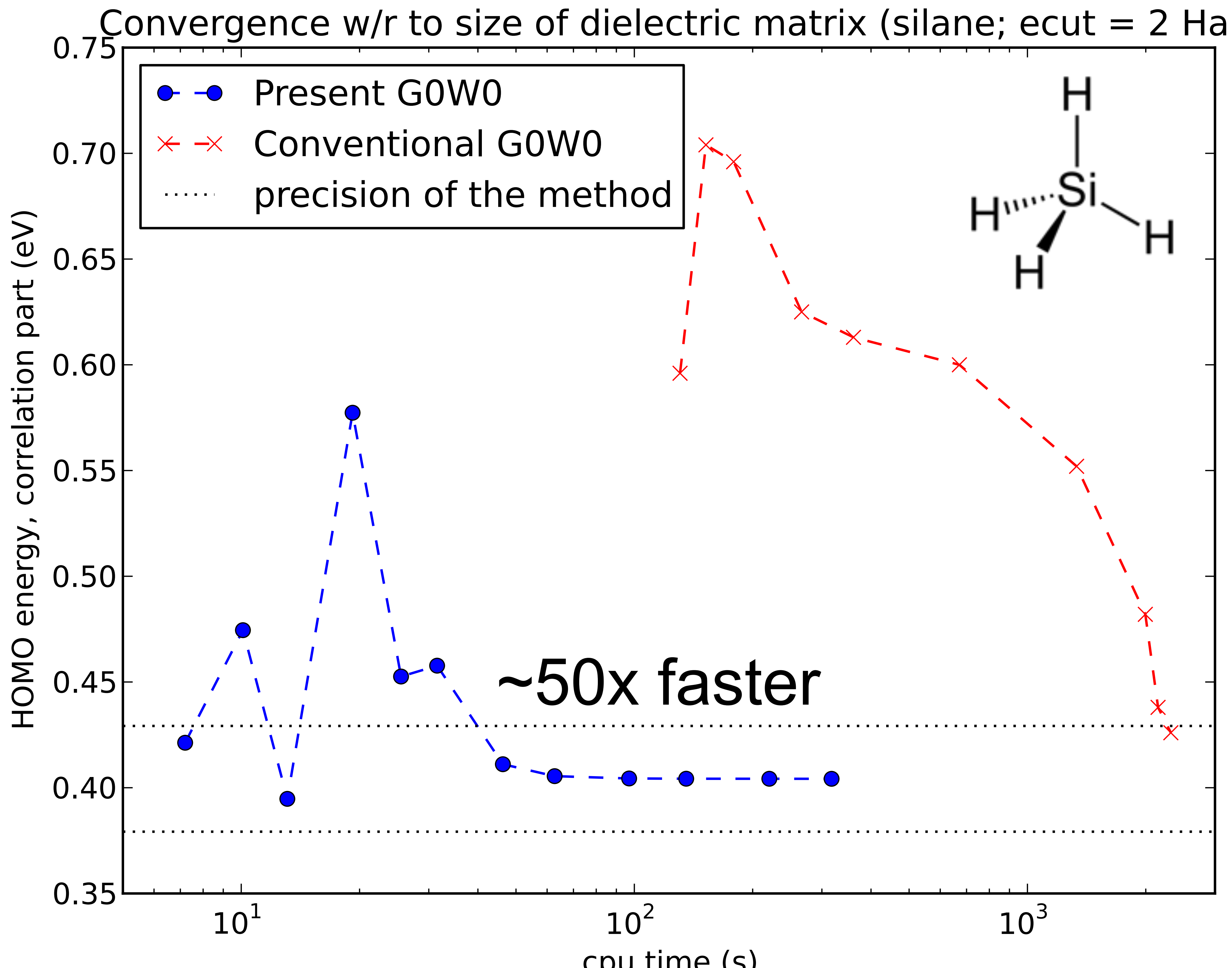
(smaller)

$\boxed{A|x\rangle = |b\rangle}$

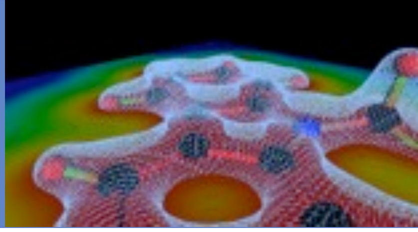
$\boxed{\{|q\rangle\}}$

Faster ?

Yes!



Preliminary results



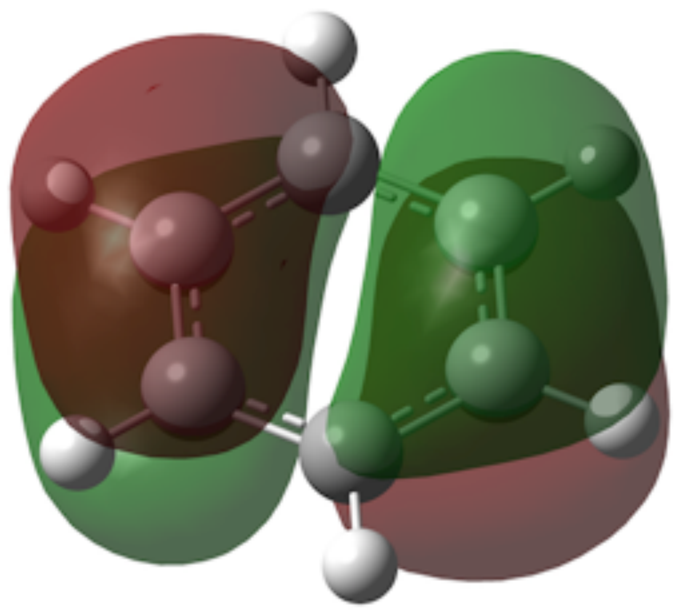
Preliminary results

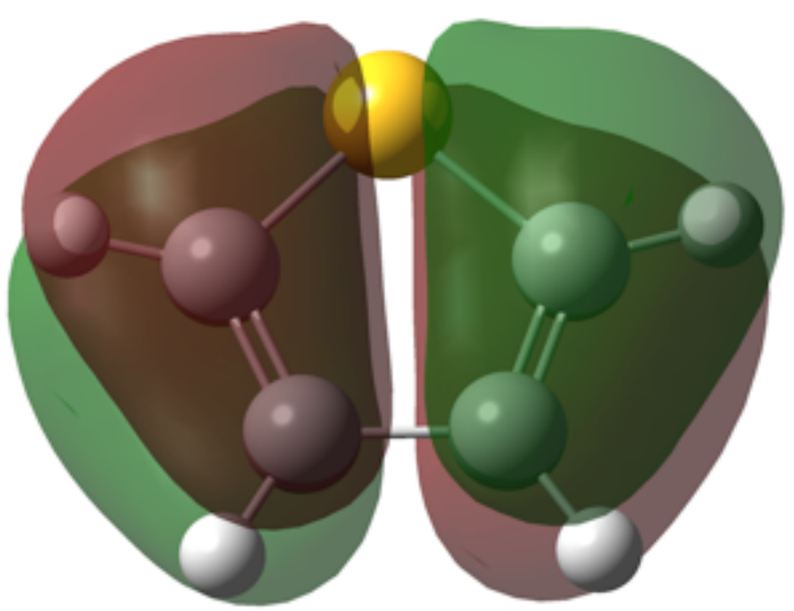
- Working in reals systems?

Preliminary results

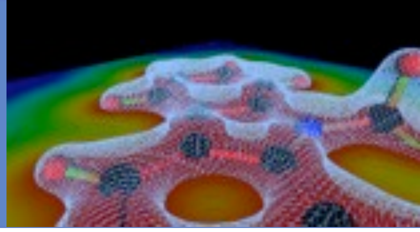
- Working in reals systems?

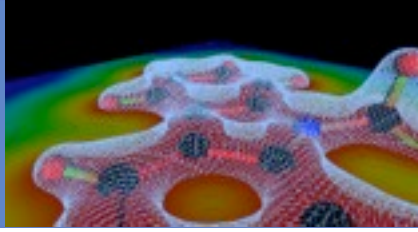
	HOMO (eV)		
	LDA	**G_0W_0**	**Exp.**
Benzene	-6.51	-9.22	-9.30
Thiophene	-6.05	-8.94	-8.85





Conclusion

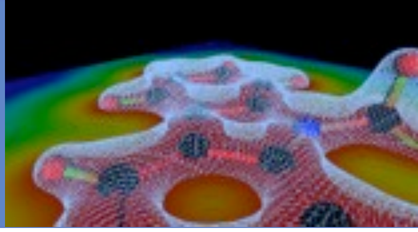




Conclusion

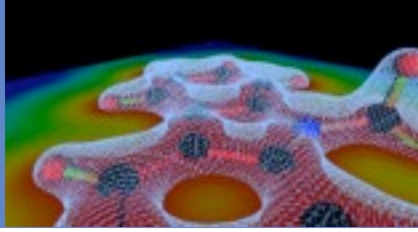
- Bottleneck assessed :

Conclusion



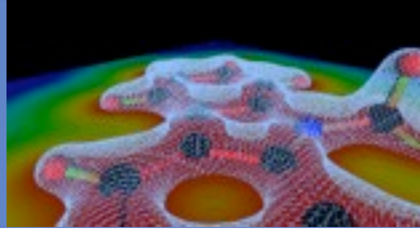
- Bottleneck assessed :
  - no knowledge of conduction states required

Conclusion



- Bottleneck assessed :
  - no knowledge of conduction states required
  - no inversion of ϵ in cumbersome basis

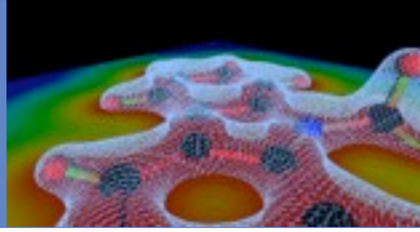
Conclusion



- Bottleneck assessed :
  - no knowledge of conduction states required
  - no inversion of ϵ in cumbersome basis

- Future work :

Conclusion



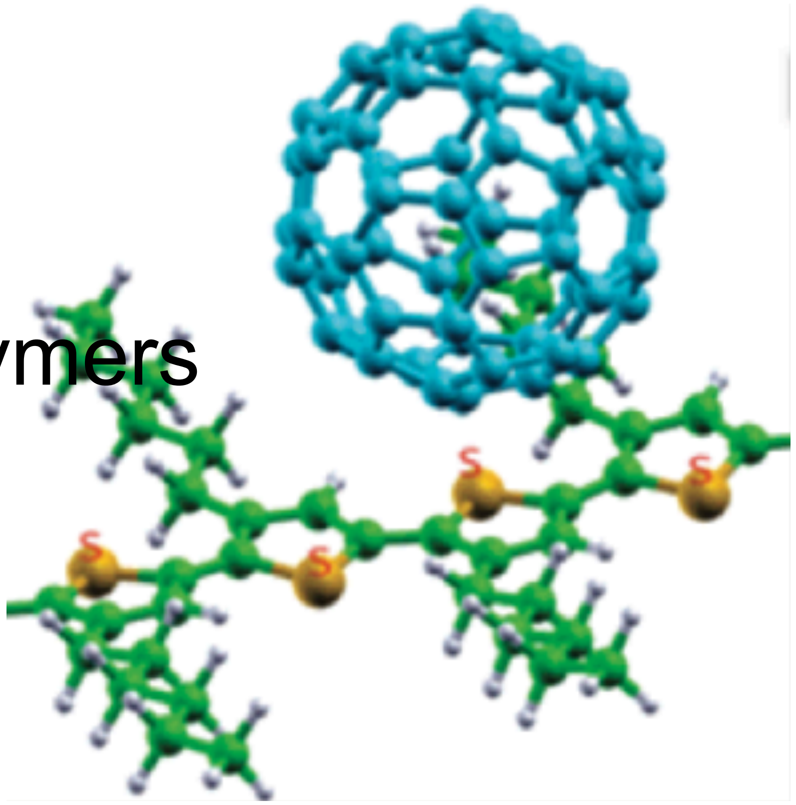
- Bottleneck assessed :
  - no knowledge of conduction states required
  - no inversion of ϵ in cumbersome basis

- Future work :
  - refine DFT calculations for candidate polymers

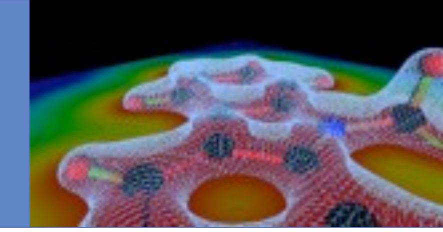
Conclusion

- Bottleneck assessed :
  - no knowledge of conduction states required
  - no inversion of ϵ in cumbersome basis

- Future work :
  - refine DFT calculations for candidate polymers
  - interface states : what do they look like?



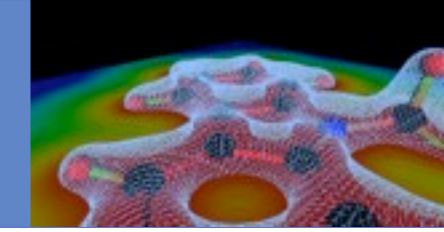
Acknowledgments



Thank you!

Université de Montréal

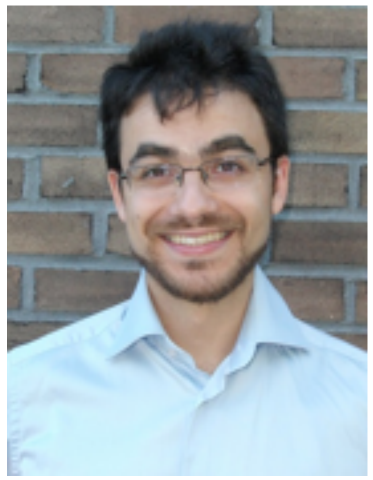
Acknowledgments



Michel Côté’s group

Thank you!

Bruno Rousseau



Nicolas Bérubé

Gabriel Antonius

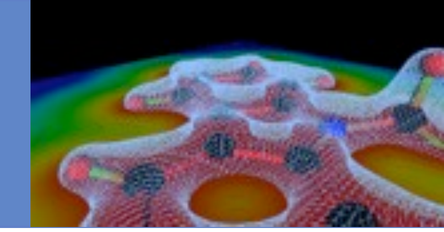
Simon Blackburn

Hélène Antaya

Vincent Gosselin

Université de Montréal

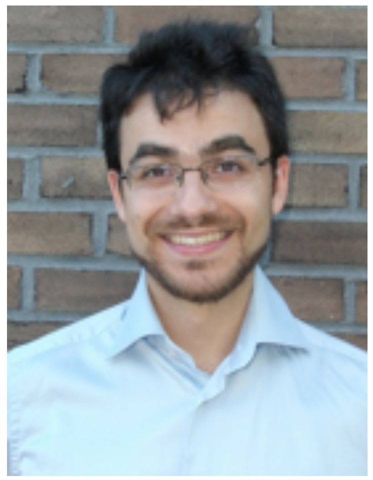
Acknowledgments



Michel Côté's group

Thank you!

Bruno Rousseau



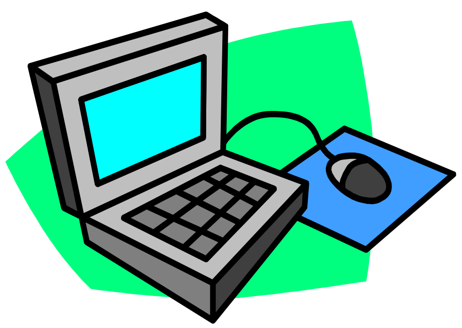
Nicolas Bérubé

Gabriel Antonius

Simon Blackburn

Hélène Antaya

Vincent Gosselin

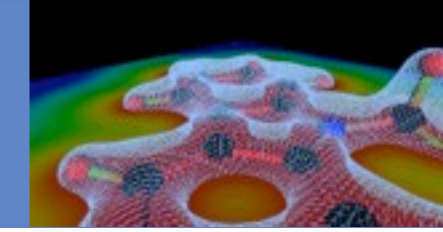


Calcul Québec

compute • calcul CANADA

Université de Montréal

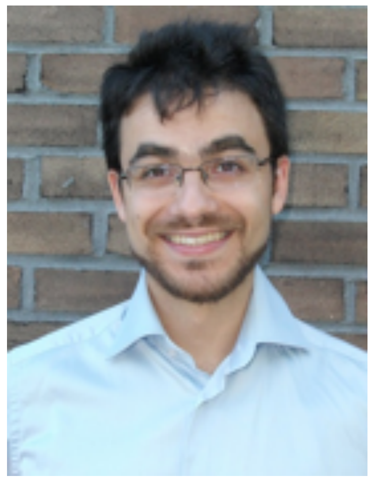
Acknowledgments



Michel Côté's group

Thank you!

Bruno Rousseau



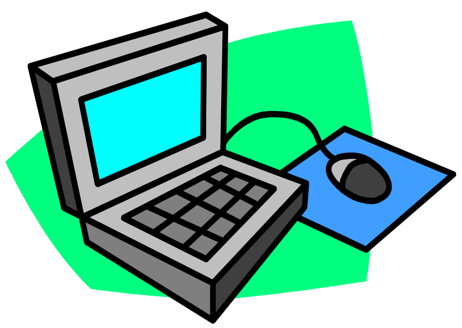
Nicolas Bérubé

Gabriel Antonius

Simon Blackburn

Hélène Antaya

Vincent Gosselin



RQMP

Calcul Québec

Fonds de recherche sur la nature et les technologies Québec

Photovoltaic Innovation Network We get the Sun

compute • calcul CANADA

NSERC CRSNG

Université de Montréal