Introduction to GW

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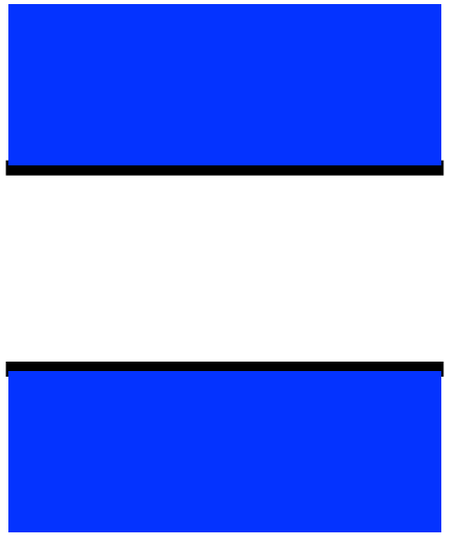
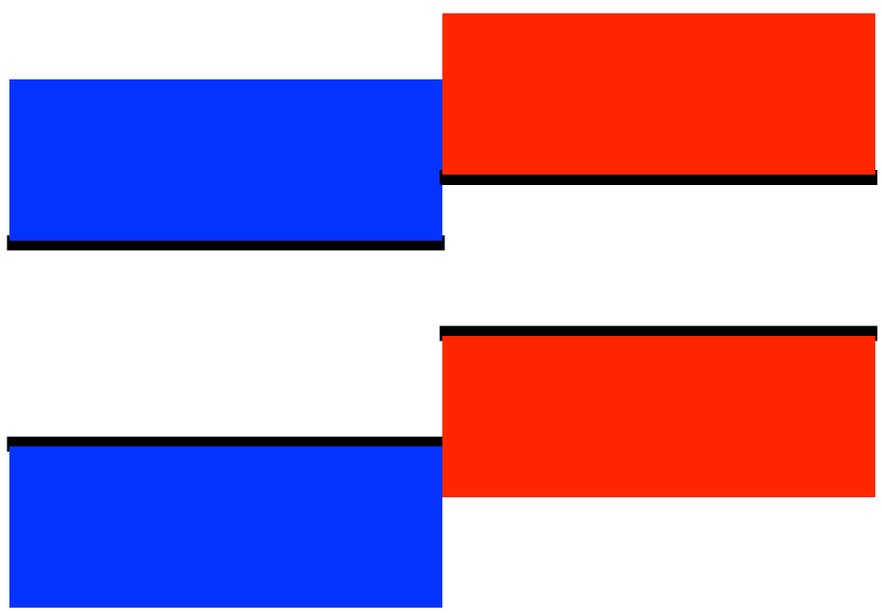
Motivations

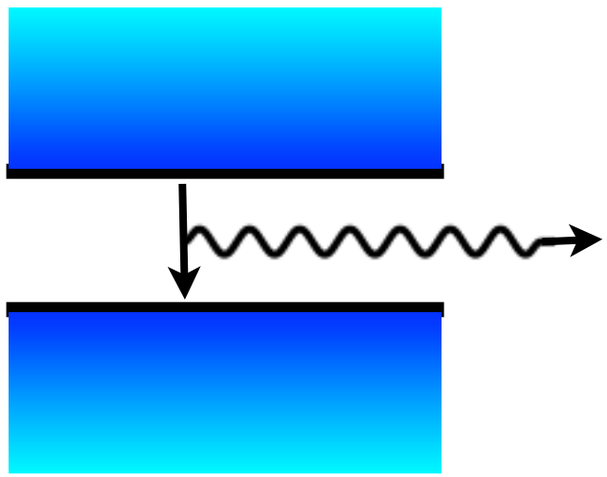
When we want to model a material for energy application, it is more than likely that we want to know with good accuracy one or more of the following properties:



Electronic band gap



Level alignment



Optical band gap

Motivations

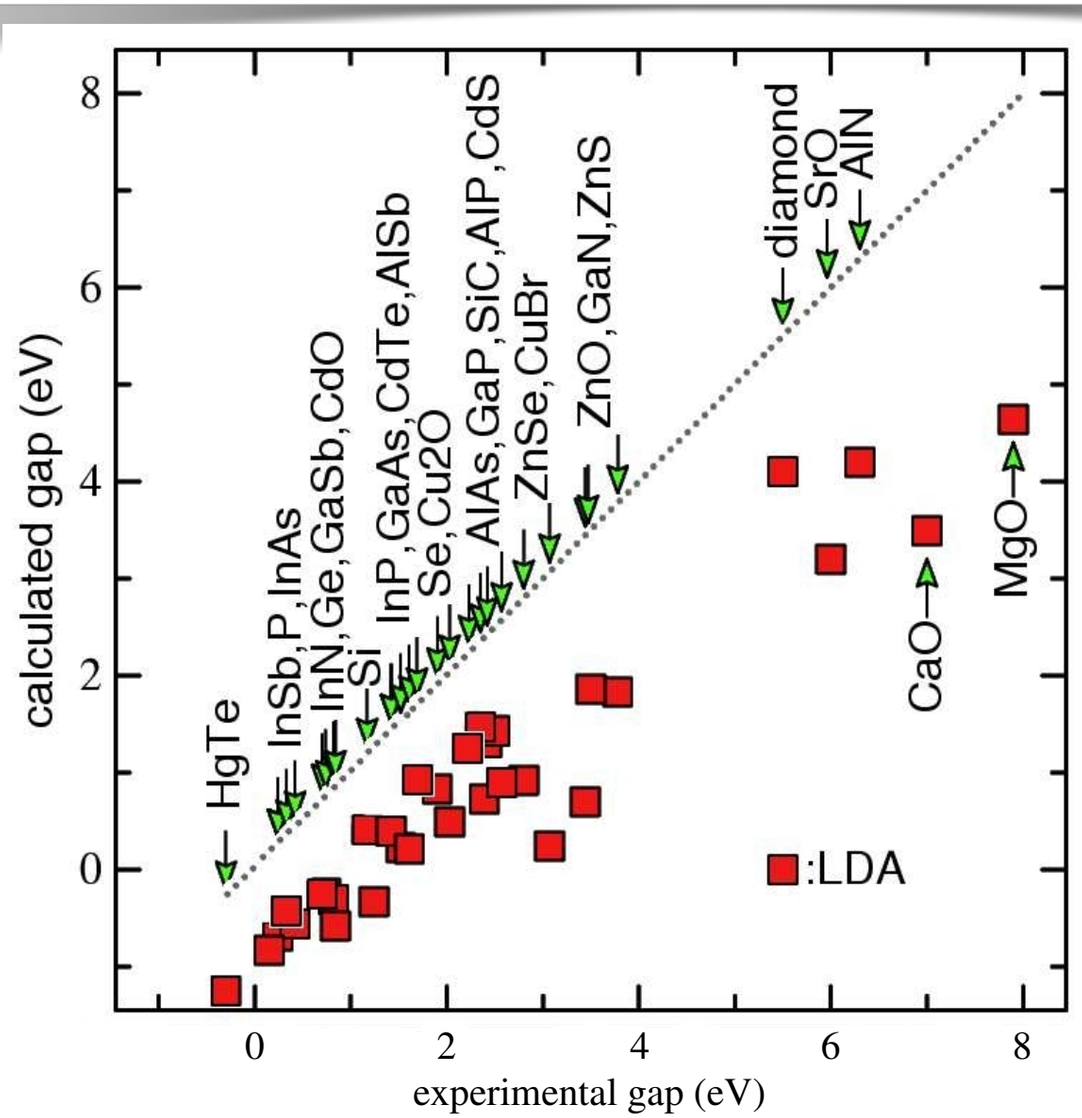
Idea: use Density Functional Theory:

$$\left(-\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_H[n](\mathbf{r}) + V_{xc}[n](\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

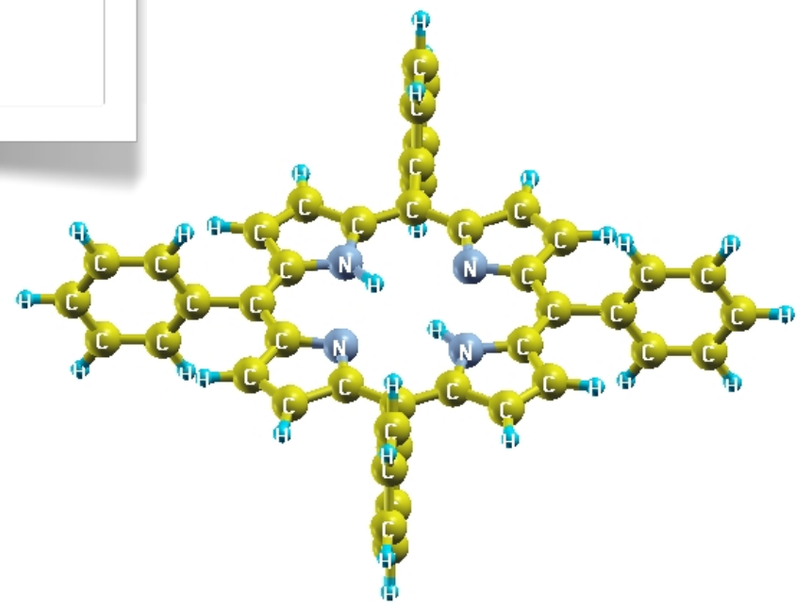
$$n(\mathbf{r}) = 2\sum_{i=1,N}\psi_i^*(\mathbf{r})\,\psi_i(\mathbf{r})$$

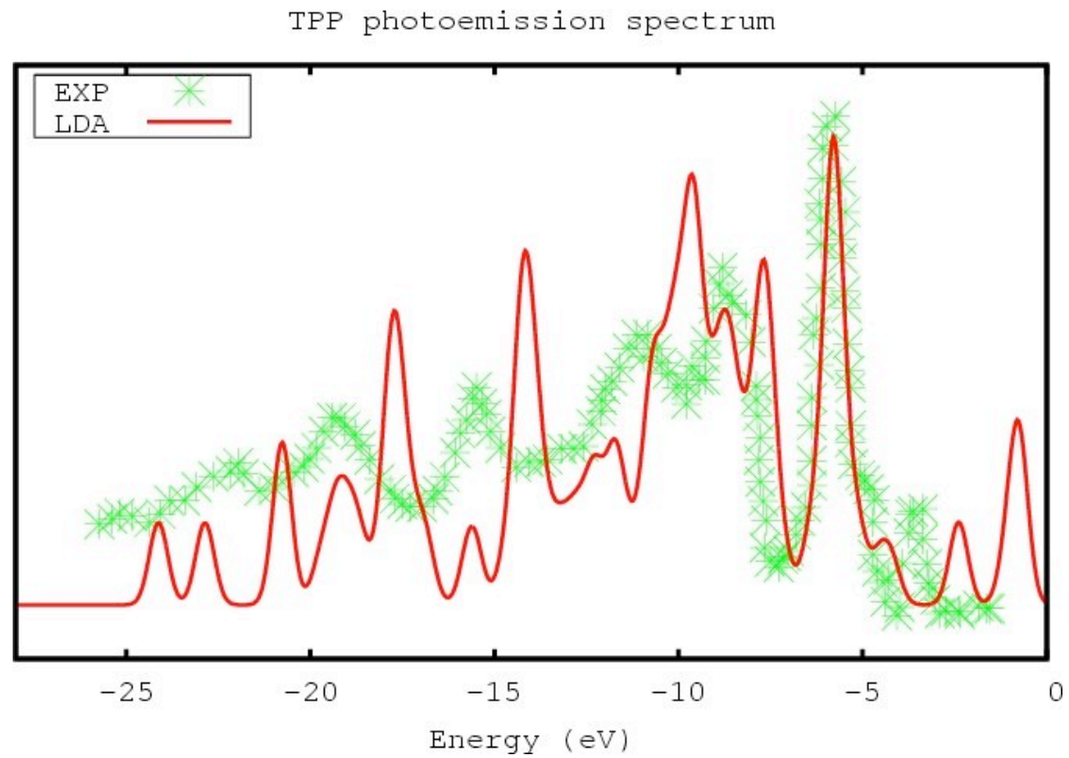
Motivations

Result: disaster



M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).

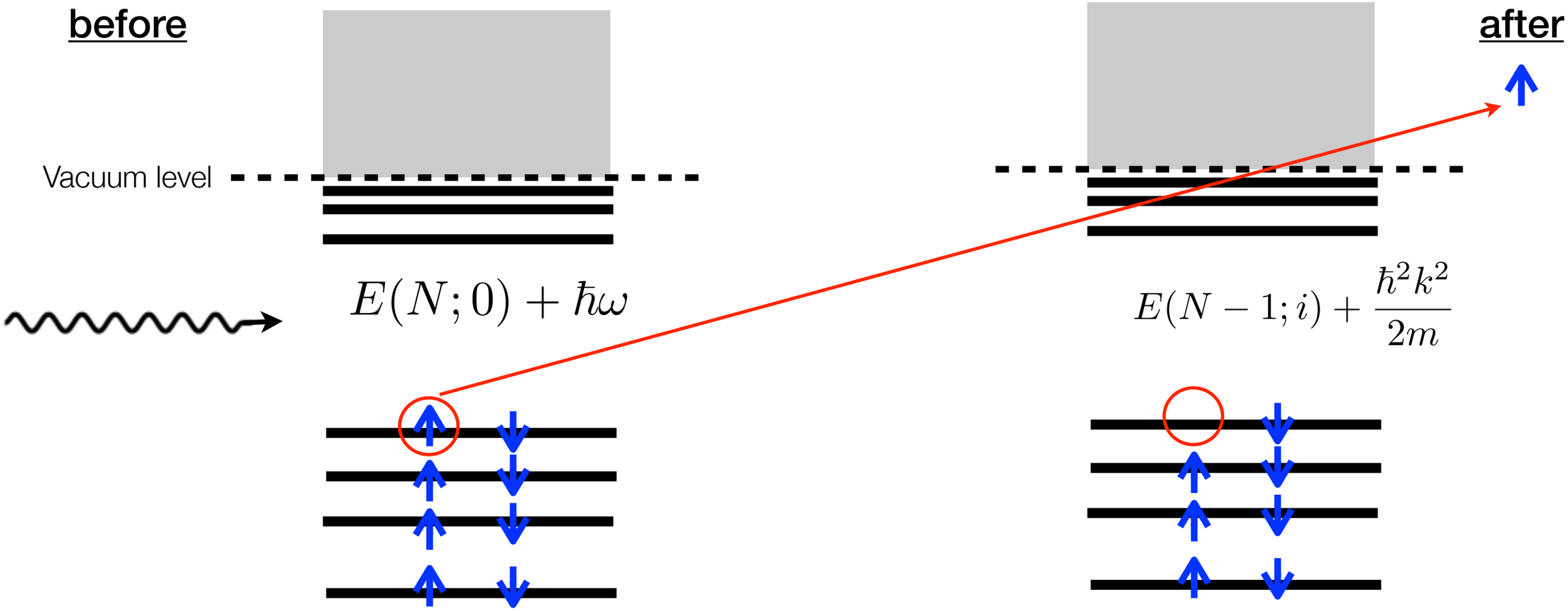




Our wish: model direct photoelectron spectroscopy

We want to calculate energies corresponding to particle addition and removal:

Electron removal

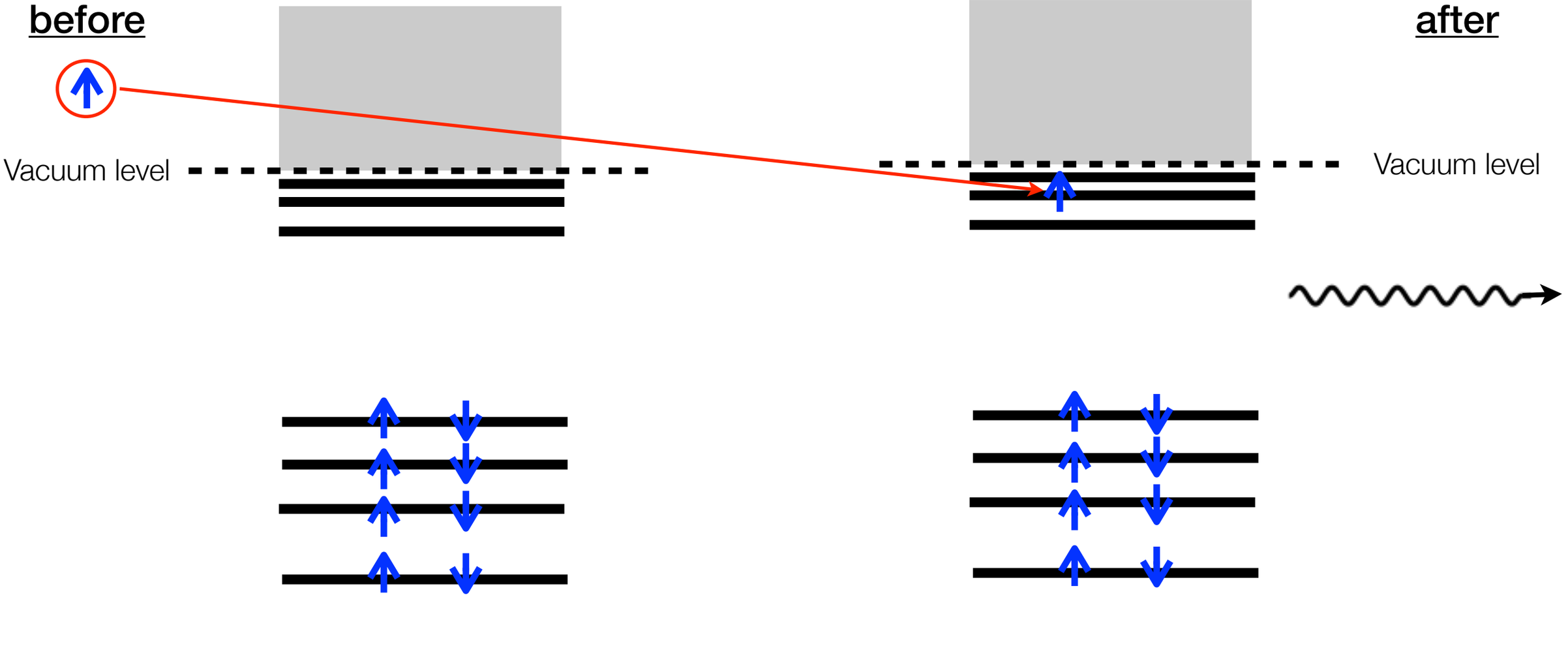


Our wish: model inverse photoelectron spectroscopy

Electron addition

$E(N;0) + \frac{\hbar^2 k^2}{2m}$

$E(N+1;i) + \hbar\omega$



Quasi-particle energies

electron removal:

$$E_{s'} = E(N;0) - E(N-1;i)$$

electron addiction:

$$E_s = E(N+1;i) - E(N;0)$$

quasi particles energies stay are given by the poles of the one-particle interacting Green's function:

$$G\left(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2\right) = i \left\langle N, 0 \right| T\left[\hat{\psi}_H\left(\mathbf{r}_1, t_1\right) \hat{\psi}_H^{\dagger}\left(\mathbf{r}_2, t_2\right)\right] \left| N, 0 \right\rangle$$

$$G\left(\mathbf{r}_1, \mathbf{r}_2; \omega\right) = \sum\nolimits_s \frac{f_s(\mathbf{r}_1) f_s^*(\mathbf{r}_2)}{\omega - E_s \pm i\eta}$$

Many Body Perturbation Theory

Gives a way for obtaining *G*

- rigorous framework
- in principles exact
- in practice improvable
- not only energy levels: neutral excitations, total energies
- good results for band-gaps

Many-Body Perturbation Theory

Idea: we start from a non-interacting Hamiltonian

$$\hat{H}_0 \left|\psi_i\right\rangle = \epsilon_i \left|\psi_i\right\rangle$$

then we switch on the e-e interaction:

$$\hat{H} = \hat{H}_0 + \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\hat{\psi}^\dagger\left(\mathbf{r}_1\right)\hat{\psi}^\dagger\left(\mathbf{r}_2\right)\hat{\psi}\left(\mathbf{r}_2\right)\hat{\psi}\left(\mathbf{r}_1\right)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|}$$

Many body perturbation theory

From the equation of motion for G:

$$\hat{H}_0(\mathbf{r}) f_s(\mathbf{r}) + V_H[n](\mathbf{r}) f_s(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_s) = E_s f_s(\mathbf{r})$$

unperturbed one-body Hamiltonian

The Self-energy gives access to the quasi-particle energies

How to get the self-energy:

Hedin's equations:

$$\Sigma(1,2) = \mathrm{i}\int \mathrm{d}(34)\, G(1,3^{+})W(1,4)\Lambda(3,2,4)$$

vertex

$$G(1,2) = G_0(1,2) + \int \mathrm{d}(34)\, G_0(1,3)\Sigma(3,4)G(4,2)$$

screened Coulomb's interaction

$$\Lambda(1,2,3) = \delta(1-2)\delta(2-3) + \int \mathrm{d}(4567)\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Lambda(6,7,3)$$

bare Coulomb's interaction

$$W(1,2) = v(1,2) + \int \mathrm{d}(34)\, v(1,3)P(3,4)W(4,2)$$

$$P(1,2) = -\mathrm{i}\int \mathrm{d}3\,\mathrm{d}4\, G(1,3)\Lambda(3,4,2)G(4,1^{+}).$$

irreducible polarizability

unperturbed Green's function

$$G_0(\mathbf{r}_1,\mathbf{r}_2;\omega) = \sum_i \frac{\psi_i(\mathbf{r}_1)\,\psi_i^*(\mathbf{r}_2)}{\omega - \epsilon_i \pm i\eta}$$

L. Hedin, Phys. Rev. 139, A769 (1965)

Approximations: Hartree

$$\Sigma(1,2) = \mathrm{i}\int \mathrm{d}(34)\, G(1,3^+) W(1,4) \Lambda(3,2,4)$$ =0

$$G(1,2) = G_0(1,2) + \int \mathrm{d}(34)\, G_0(1,3)\Sigma(3,4)G(4,2)$$

$$\Lambda(1,2,3) = \delta(1-2)\delta(2-3) + \int \mathrm{d}(4567)\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Lambda(6,7,3)$$

$$W(1,2) = v(1,2) + \int \mathrm{d}(34)\, v(1,3)P(3,4)W(4,2)$$

$$P(1,2) = -\mathrm{i}\int \mathrm{d}3\,\mathrm{d}4\, G(1,3)\Lambda(3,4,2)G(4,1^+).$$

Approximations: Hartree-Fock

$$\Sigma(1,2) = \mathrm{i}\int \mathrm{d}(34)\, G(1,3^+)W(1,4)\Lambda(3,2,4)$$ =iG(1,2)v(1,2)

$$G(1,2) = G_0(1,2) + \int \mathrm{d}(34)\, G_0(1,3)\Sigma(3,4)G(4,2)$$

$$\Lambda(1,2,3) = \delta(1-2)\delta(2-3) + \int \mathrm{d}(4567)\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Lambda(6,7,3)$$

$$W(1,2) = v(1,2) + \int \mathrm{d}(34)\, v(1,3)P(3,4)W(4,2)$$

$$P(1,2) = -\mathrm{i}\int \mathrm{d}3\,\mathrm{d}4\, G(1,3)\Lambda(3,4,2)G(4,1^+).$$

Approximations: DFT

$$\Sigma(1,2) = \mathrm{i}\int \mathrm{d}(34)\, G(1,3^{+})W(1,4)\Lambda(3,2,4)$$ $= V_{xc}(1)\delta(1,2)$

$$G(1,2) = G_0(1,2) + \int \mathrm{d}(34)\, G_0(1,3)\Sigma(3,4)G(4,2)$$

$$\Lambda(1,2,3) = \delta(1-2)\delta(2-3) + \int \mathrm{d}(4567)\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Lambda(6,7,3)$$

$$W(1,2) = v(1,2) + \int \mathrm{d}(34)\, v(1,3)P(3,4)W(4,2)$$

$$P(1,2) = -\mathrm{i}\int \mathrm{d}3\,\mathrm{d}4\, G(1,3)\Lambda(3,4,2)G(4,1^{+}).$$

Approximations: GW

Equations to be solved self-consistently

$$\Sigma(1,2) = \mathrm{i}\int \mathrm{d}(34)\, G(1,3^+) W(1,4) \Lambda(3,2,4)$$

screened Coulomb's interaction

$$G(1,2) = G_0(1,2) + \int \mathrm{d}(34)\, G_0(1,3)\Sigma(3,4)G(4,2)$$

$$\Lambda(1,2,3) = \delta(1-2)\delta(2-3) + \int \mathrm{d}(4567)\, \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Lambda(6,7,3)$$

$$W(1,2) = v(1,2) + \int \mathrm{d}(34)\, v(1,3) P(3,4) W(4,2)$$

$$P(1,2) = -\mathrm{i}\int \mathrm{d}3\,\mathrm{d}4\, G(1,3)\Lambda(3,4,2)G(4,1^+).$$

irreducible polarizability

Approximations: G_0W_0 aka one-shot GW

- **We start from a first guess for G_0 from DFT (or HF)**
- **perturbative, non self-consistent scheme**

$$
\begin{aligned}
\Sigma(1,2) &= iG_0\left(1,2^+\right)W(1,2) \\
G(1,2) &= G_0(1,2) + \int d(34) G_0(1,3)\,\Sigma(3,4)\,G(4,2) \\
W(1,2) &= v(1,2) + \int d(34)\, v(1,3)\, P(3,4)\, W(4,2) \\
P(1,2) &= -iG_0(1,2)\,G_0(2,1)
\end{aligned}
$$

Random phase approximation (RPA)

Approximations: diagonal G_0W_0

$$H_0(\mathbf{r}) f_i(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; E_i) f_i(\mathbf{r}') = E_i f_i(\mathbf{r})$$

we approximate: $f_i(\mathbf{r}) = \psi_i(\mathbf{r})$

$$\epsilon_i + \langle \psi_i | \Sigma(E_i) | \psi_i \rangle = E_i$$

G_0W_0 Approximation: the entire scheme

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

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

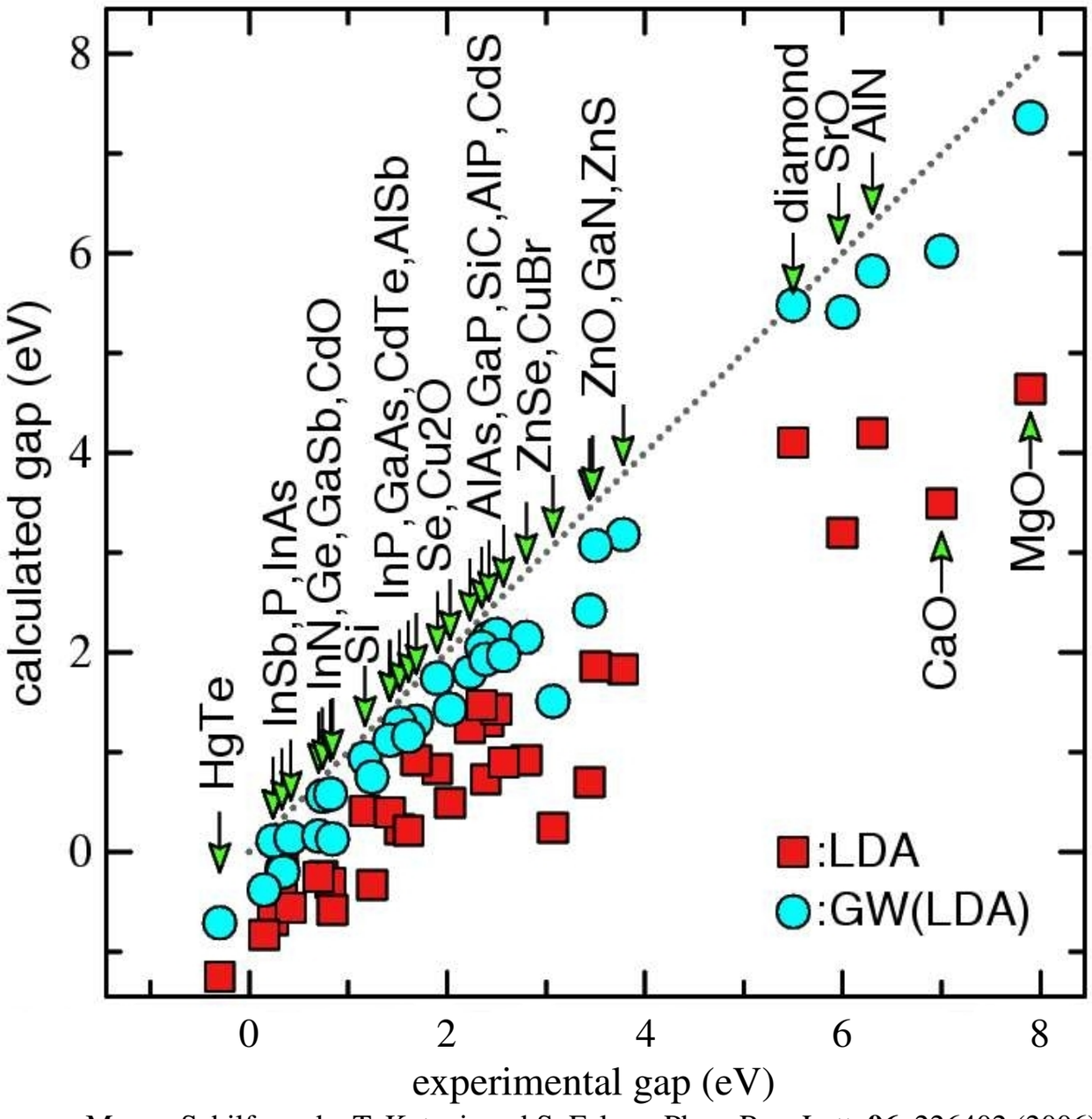
$$\Sigma_{G^\circ W^\circ}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' G^\circ(\mathbf{r}, \mathbf{r}'; \omega - \omega') W^\circ(\mathbf{r}, \mathbf{r}'; \omega')$$

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

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

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

It works!



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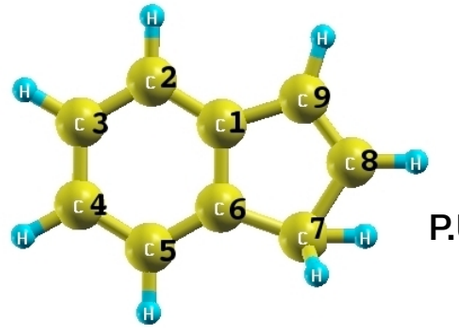
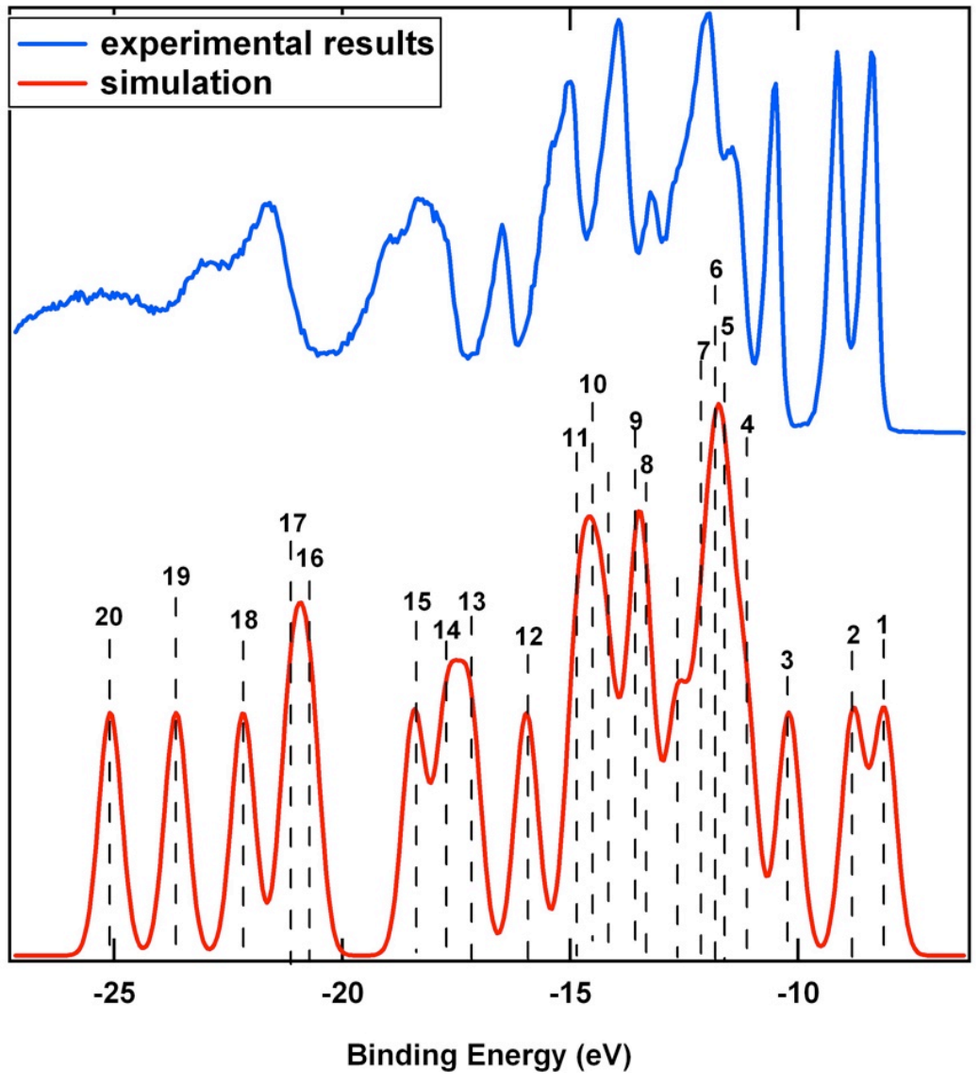


P.Umari et al. , Phys. Stat Sol. B 248 960 (2011)



Several codes Quantum-Espresso friendly

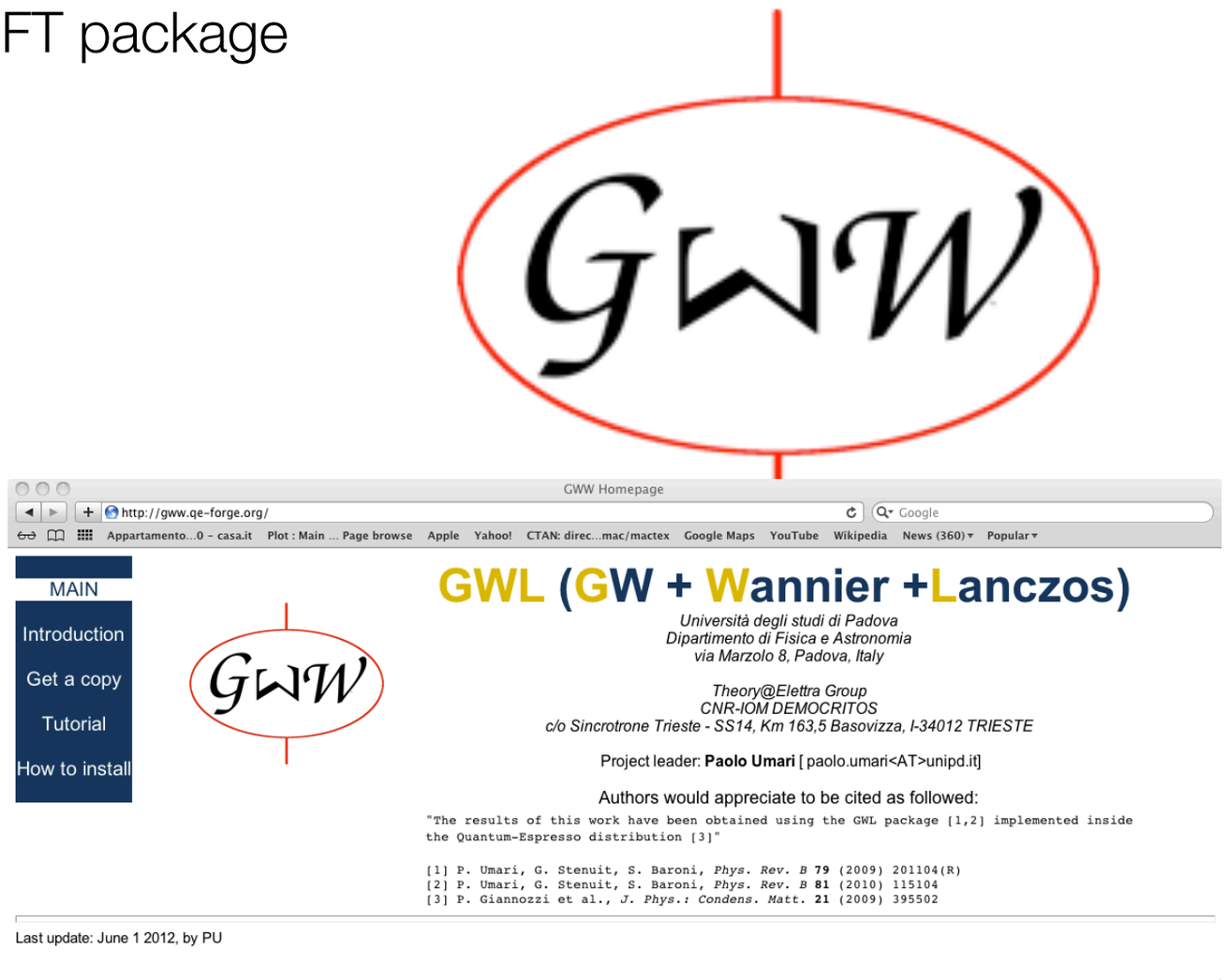
www.yambo-code.org

www.sax-project.org

The GWL code

Available on *gww.qe-forge.org* through the GNU-GPL license

- Implemented in the Quantum-Espresso DFT package
- pw4ggw.x and gww.x codes
- mixed OPENMP/MPI
- O(N3)-O(N4)
- large use of BLAS/LAPACK routine
- balance memory usage/communications
- tested up to 4096 computing cores



Integration schemes:

- Plasmon pole approximation: use a model for *W*

✓ Analytic continuation of self-energy: calculate *G,P,W* on imaginary frequency/time

Multipole expansion of the expectation values of the self-energy operator:

$$\langle\psi_i|\,\Sigma_{\mathrm{c}}\left(i\omega\right)|\psi_i\rangle = \sum_n \frac{a_n^i}{i\omega - b_n^i}$$

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

- Contour integration

$$\langle\psi_i|\,\Sigma_{\mathrm{c}}\left(\omega\right)|\psi_i\rangle = \int_{-\infty}^{\infty}\langle\psi_i|\,G_0\left(\omega - i\omega'\right)W_{\mathrm{c}}\left(i\omega'\right)|\psi_i\rangle$$
$$+\sum\int\psi_i^*\left(\mathbf{r}\right)\psi_j\left(\mathbf{r}\right)\psi_j^*\left(\mathbf{r}'\right)W_{\mathrm{c}}\left(\mathbf{r},\mathbf{r}';\epsilon_j - E\right)\psi_i\left(\mathbf{r}\right)d\mathbf{r}d\mathbf{r}'\left[\theta\left(\omega-\epsilon_j\right)-\theta\left(\epsilon_{\mathrm{F}}-\epsilon_j\right)\right]$$

A. Fleszar and W. Hanke, Phys. Rev. B 56, 10228 (1997).

✓ Contour integration, with analytic continuation of pole terms

- Real frequency integration

Large systems: two challenges

Two big challenges:

- Computational cost:

  We must represent operators

  prohibitive for large systems

- Sums over empty states

  In principles sums over all empty states

  prohibitive for large systems

  analogous to DFPT

How many empty states do I need?

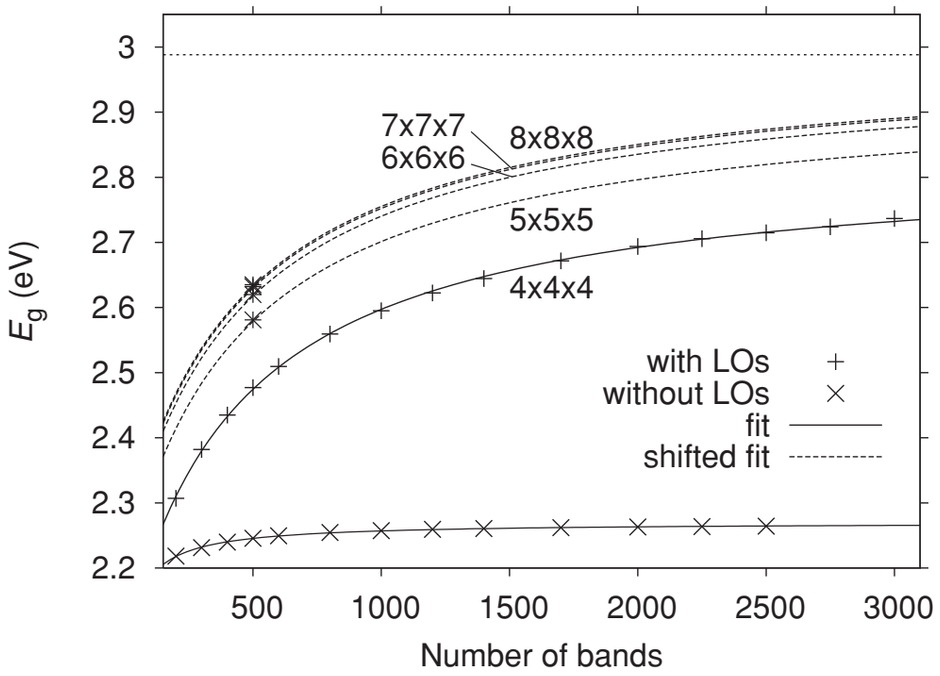
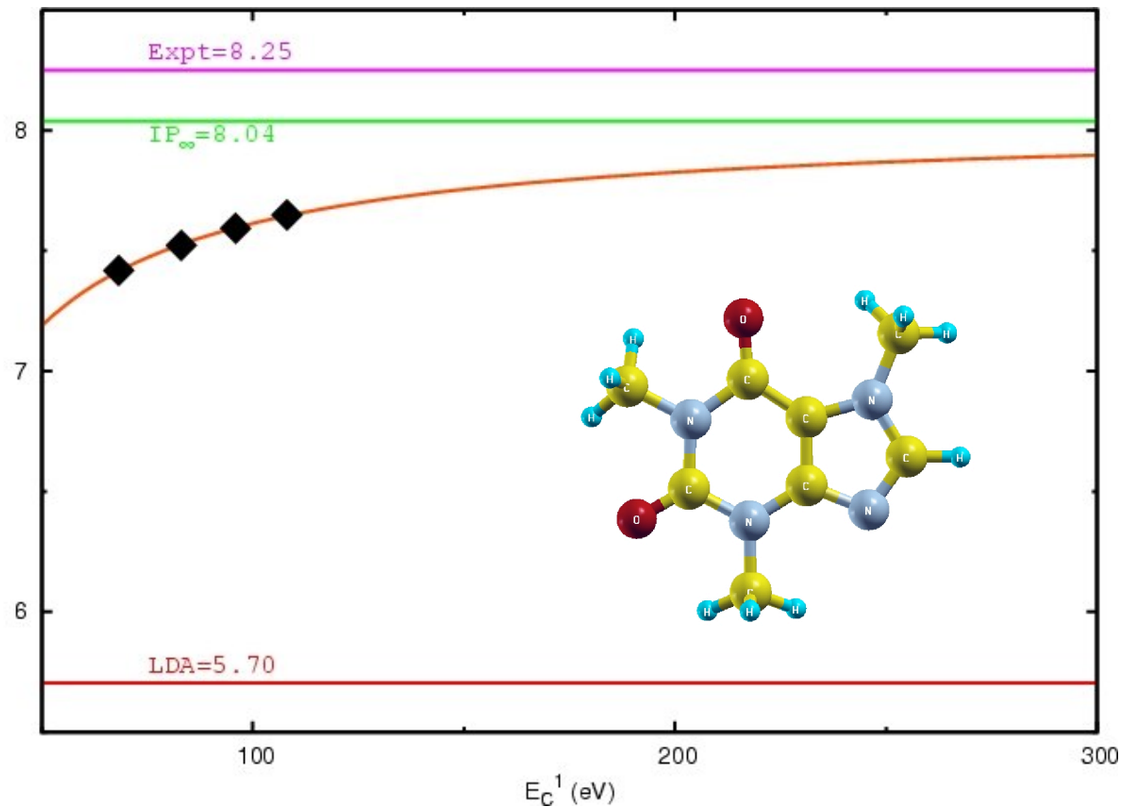


FIG. 1. Band convergence of the quasiparticle band gap of ZnO employing a 4×4×4 **k**-point set and calculated with (pluses) and without local orbitals (LOs) (crosses) for high-lying states. The solid lines show the hyperbolical fits. We also indicate results with finer **k**-point samplings (stars) calculated with LOs and 500 bands. The dashed lines show the hyperbolical fit shifted to align with these results. The fit asymptote for the 8×8×8 **k**-point set at 2.99 eV (dotted line) is considered the best estimate for the all-electron one-shot *GW* band gap.

C. Friedrich, M.Mueller, S. Blugel, Phys. Rev. B 081101R (11)

IP of the caffeine molecule



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

S. Baroni, et al.J. Phys.: Condens. Matter 22 074204

GW without empty states: Linear response

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 :

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

GW without empty states: Lanczos chains

We can <u>strongly reduce</u> the computational load in three steps:

1. Through a block algorithm, starting from Wannier's *valence* orbitals, we obtain a reduced basis for:

$$Q_c \left|\psi_v \Phi_\mu\right\rangle \cong \sum_\alpha T_{v\mu,\alpha} \left|t_\alpha\right\rangle$$

2. The problem is now that of solving:

$$\left\langle t_\alpha\right| \left(H_o - \epsilon_v + i\omega\right)^{-1} \left|t_\beta\right\rangle$$

3. This is achieved through a Lanczos chain algorithm

$$\sum_{nm} \left\langle t_\alpha\right| \left. l_n^\beta\right\rangle L_{nm}^{-1} \left(-\epsilon_v + i\omega\right) \left\langle l_m^\beta\right| \left. t_\beta\right\rangle \qquad \mathrm{L} = \begin{pmatrix} d_1 - \epsilon_v + i\omega & f_1 & 0 & 0 & 0 \\ f_1 & d_2 - \epsilon_v + i\omega & f_2 & 0 & 0 \\ 0 & f_2 & d_3 - \epsilon_v + i\omega & f_3 & 0 \\ 0 & & f_3 & d_3 - \epsilon_v + i\omega & f_4 \\ 0 & & & f_4 & d_3 - \epsilon_v + i\omega \end{pmatrix}$$

GW without empty states: self-energy

We want to calculate the expectation values:

$$\langle \psi_i | \, G\left(\omega - i\omega'\right) W_c\left(i\omega'\right) | \psi_i \rangle$$

- Starting from the reducible polarizability:

$$\sum_{\mu\nu} \langle \psi_i \left(v\Phi_\mu\right) | \left(\omega - i\omega' - H_0\right)^{-1} | \left(v\Phi_\nu\right) \psi_i \rangle \, \Pi_{\mu\nu}\left(i\omega'\right)$$

where:

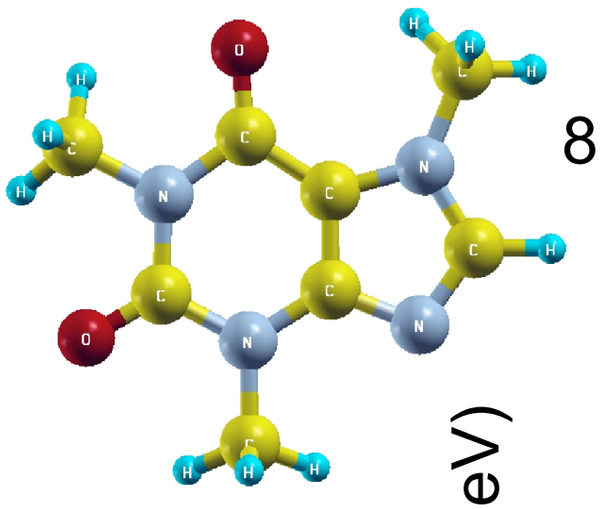
$$\langle \mathbf{r} | \, \left(v\Phi_\mu\right) \rangle = \int d\mathbf{r}' v\left(\mathbf{r}, \mathbf{r}'\right) \Phi_\mu\left(\mathbf{r}'\right)$$

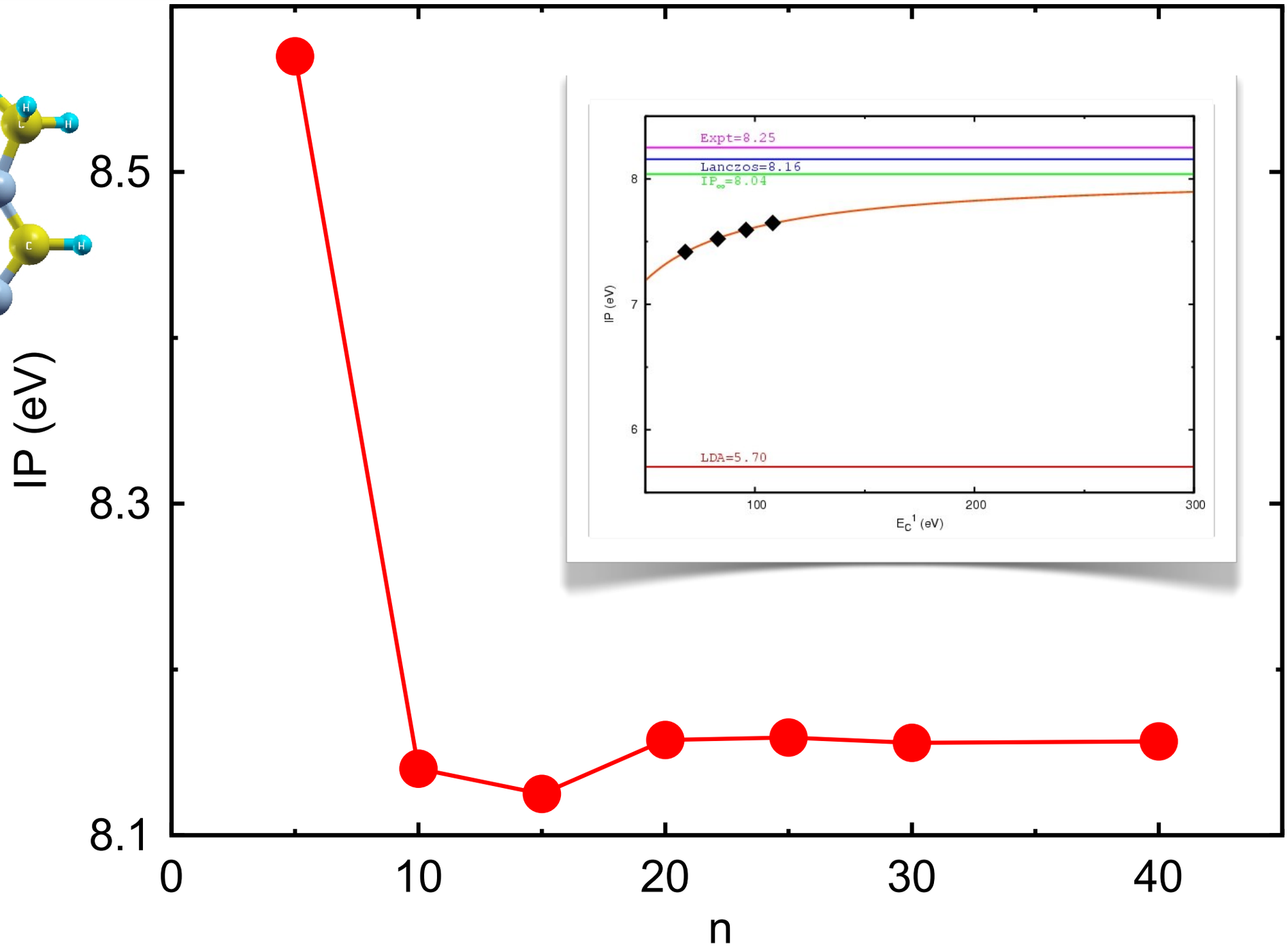
- The computational load is then <u>strongly reduced</u> with reduced basis sets and Lanczos chains:

$$|\psi_i\left(v\Phi_\mu\right)\rangle \cong \sum_\alpha S_{i\mu,\alpha} \, |s_\alpha\rangle \qquad\qquad \langle s_\alpha | \left(\omega - i\omega' - H_o\right)^{-1} | s_\beta \rangle$$

P.Umari, G. Stenuit, S.Baroni, Phys. Rev. B 81, 115104 (2010).

GW without empty states: Caffeine molecule





How to speed up GW: optimal polarizability basis

If an *optimal* representation of P° can be found:

$$P\left(\mathbf{r},\mathbf{r}';i\omega\right)\cong\sum_{\mu\nu}\Phi_{\mu}\left(\mathbf{r}\right)P_{\mu\nu}\left(i\omega\right)\Phi_{v}\left(\mathbf{r}'\right)$$

$$\Pi\left(\mathbf{r},\mathbf{r}';i\omega\right)\cong\sum_{\mu\nu}\Phi_{\mu}\left(\mathbf{r}\right)\Pi_{\mu\nu}\left(i\omega\right)\Phi_{v}\left(\mathbf{r}'\right)$$

$$W_{\mathrm{c}}\left(\mathbf{r},\mathbf{r}';i\omega\right)\cong\sum_{\mu\nu}\left(v\Phi_{\mu}\right)\left(\mathbf{r}\right)\Pi_{\mu\nu}\left(i\omega\right)\left(v\Phi_{v}\right)\left(\mathbf{r}'\right)$$

if the basis is small then a high speed-up can be achieved

Optimal polarizability basis

- We consider the average polarizability in frequency:

$$\tilde{P}\left(\mathbf{r},\mathbf{r}';t=0\right)=\sum_{vc}\psi_{v}\left(\mathbf{r}\right)\psi_{c}\left(\mathbf{r}\right)\psi_{v}\left(\mathbf{r}'\right)\psi_{c}\left(\mathbf{r}'\right)$$

- We take the basis formed by the most important eigenvectors:

$$\tilde{P}\left(t=0\right)\left|\Phi_{\mu}\right\rangle=p_{\mu}\left|\Phi_{\mu}\right\rangle\quad p_{\mu}>q^{*}$$

- We can avoid any calculation of empty states, however the basis sets are quite large
- It is better to consider the *modified* operator:

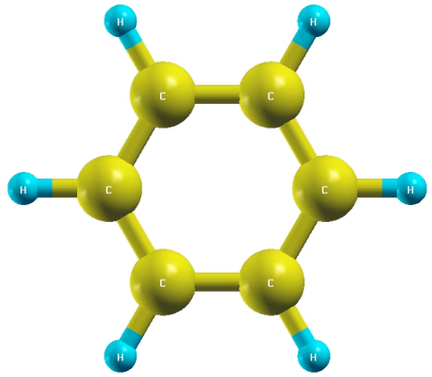
$$\tilde{P}'\left(\mathbf{r},\mathbf{r}';t=0\right)=\sum_{vc}\psi_{v}\left(\mathbf{r}\right)\psi_{c}\left(\mathbf{r}\right)\psi_{v}\left(\mathbf{r}'\right)\psi_{c}\left(\mathbf{r}'\right)\quad\epsilon_{c}<E^{*}$$

- For avoiding the calculation of empty states we consider:

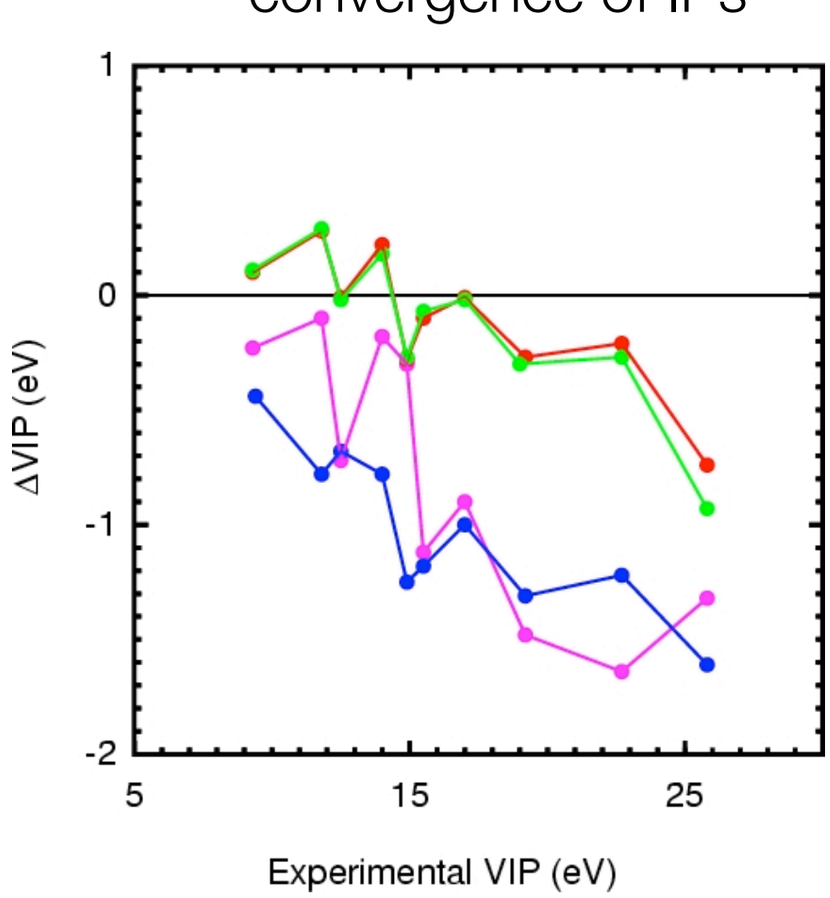
$$\tilde{P}''\left(\mathbf{r},\mathbf{r}';t=0\right)=\sum_{v\tilde{\mathbf{G}}}\psi_{v}\left(\mathbf{r}\right)\tilde{\mathbf{G}}\left(\mathbf{r}\right)\psi_{v}\left(\mathbf{r}'\right)\tilde{\mathbf{G}}\left(\mathbf{r}'\right)$$

- Where $\tilde{\mathbf{G}}$ are planewaves defined by *E** projected over the conduction manifold, and orthonormalized

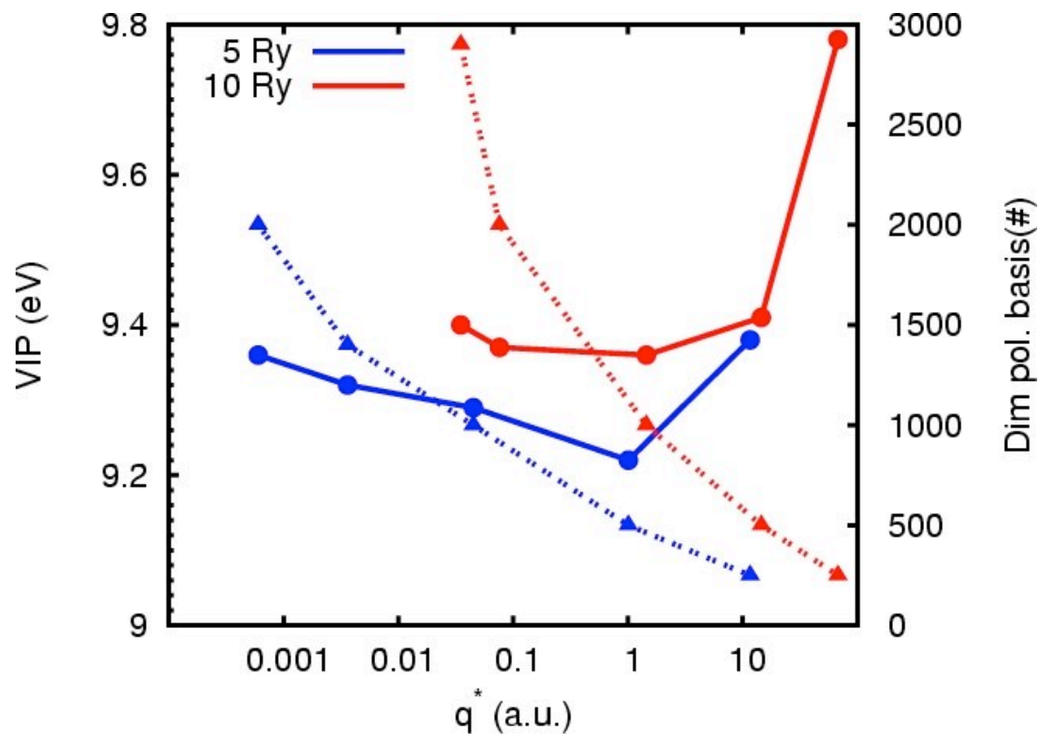
Optimal polarizability basis: Benzene



convergence of IPs



convergence of first IP



- E=10Ry q_* =0.035a.u. N = 2900
- E=10Ry q_* =14.5a.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 $\omega = 0$

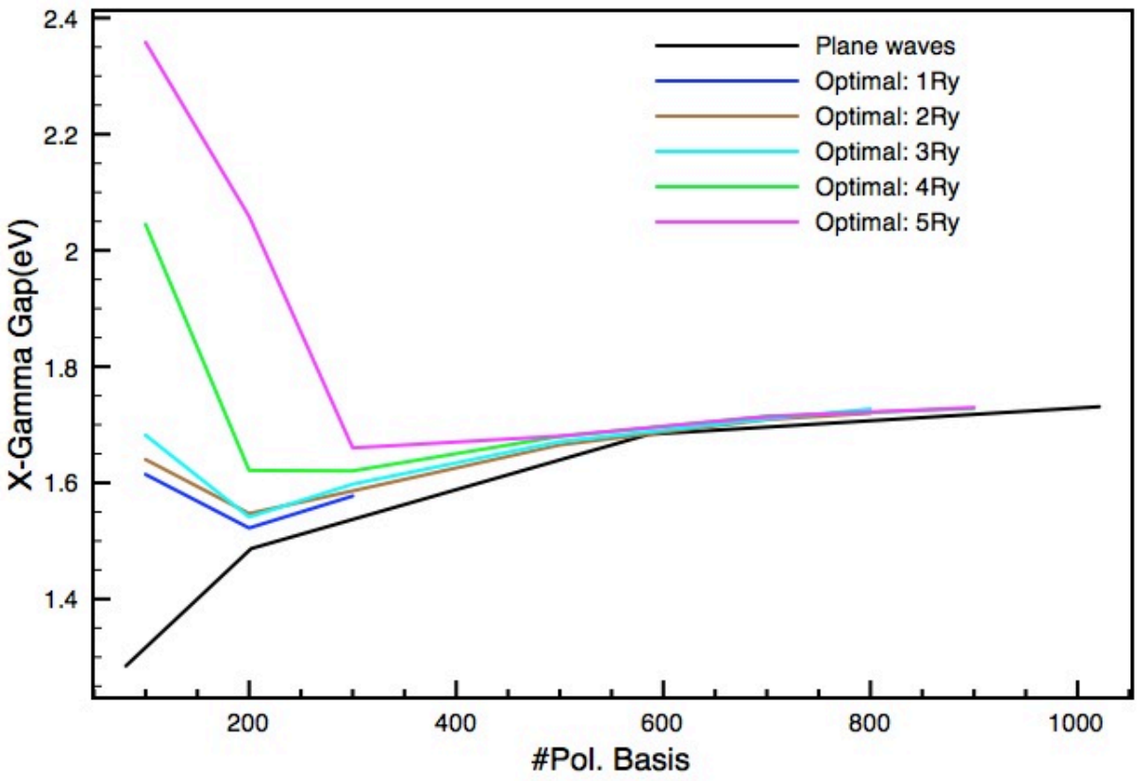
Test: bulk Si

- 64 atoms cell
- 4x4x4 k-points mesh for head and wings
- E^*=3Ry ; q^*=7.93 a.u.
- Polarizability basis: 2000 vectors

state	LDA	GW	Ref LDA	Ref GW	Expt
Γ_{1v}	-11.91 eV	-11.59 eV	-11.89 eV	-11.57 eV	-12.5 eV
X_{1v}	-7.77 eV	-7.68 eV	-7.78 eV	-7.67 eV	
X_{4v}	-2.82 eV	-2.85 eV	-2.82 eV	-2.80 eV	-2.9;-3.3 eV
Γ'_{25v}	0 eV	0 eV	0 eV	0 eV	0 eV
X_{1c}	0.67 eV	1.44 eV	0.61 eV	1.34 eV	1.25 eV

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

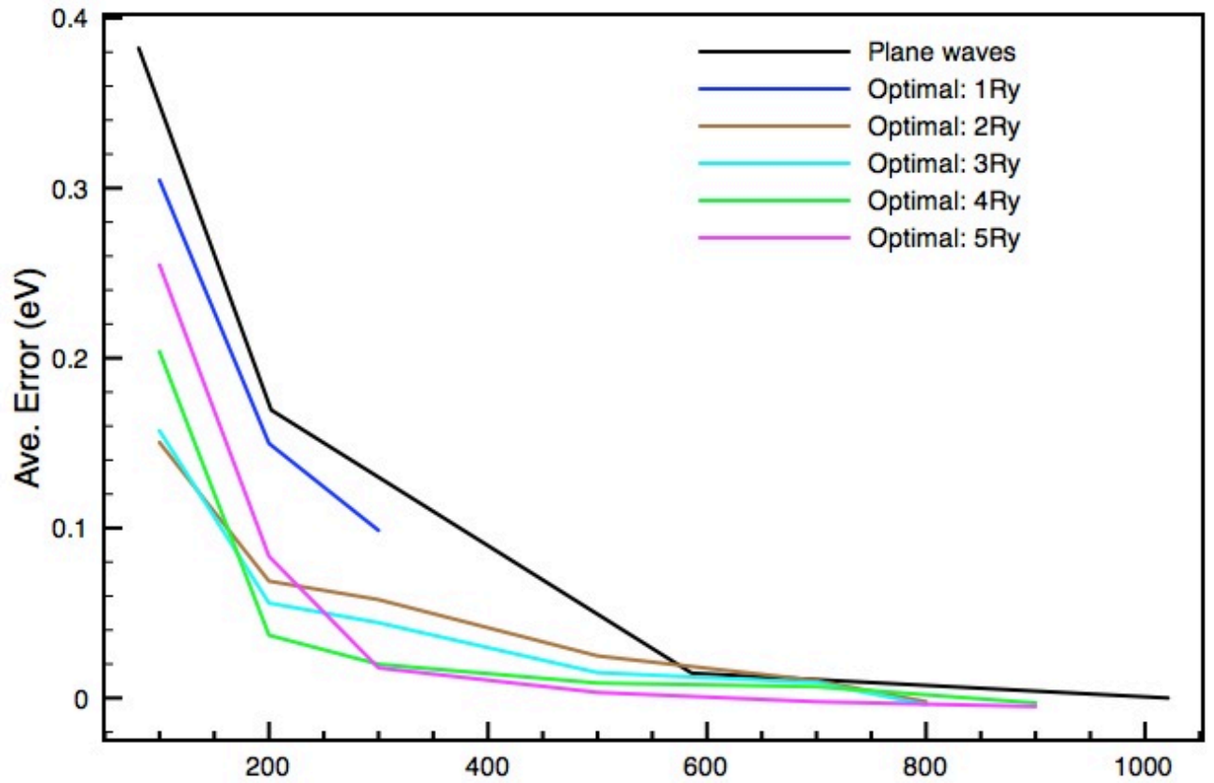
Optimal polarizability basis vs Plane-waves: bulk-Si



8 atoms Si cell: Gamma only calculation

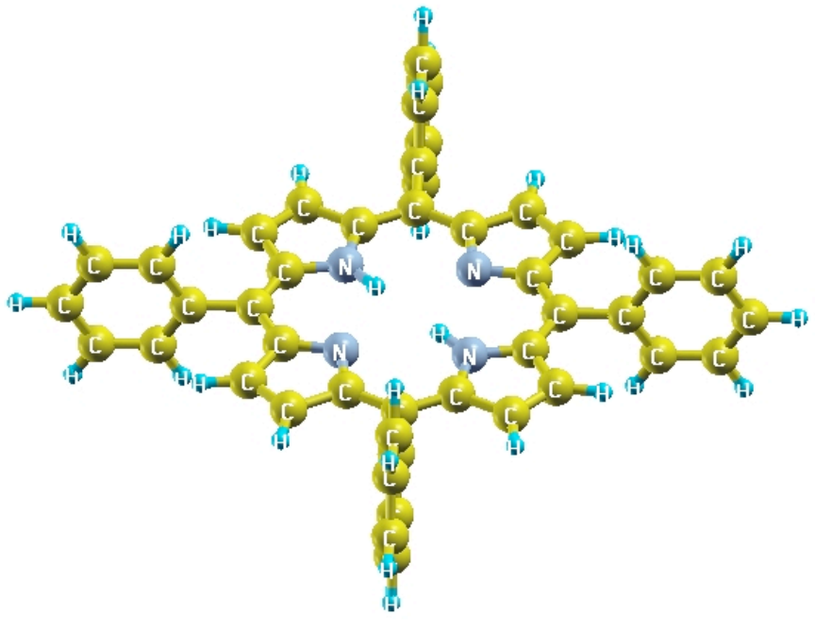
k-points integration only for long range terms

Optimal basis sets improve upon plane-waves



Applications: larger molecules

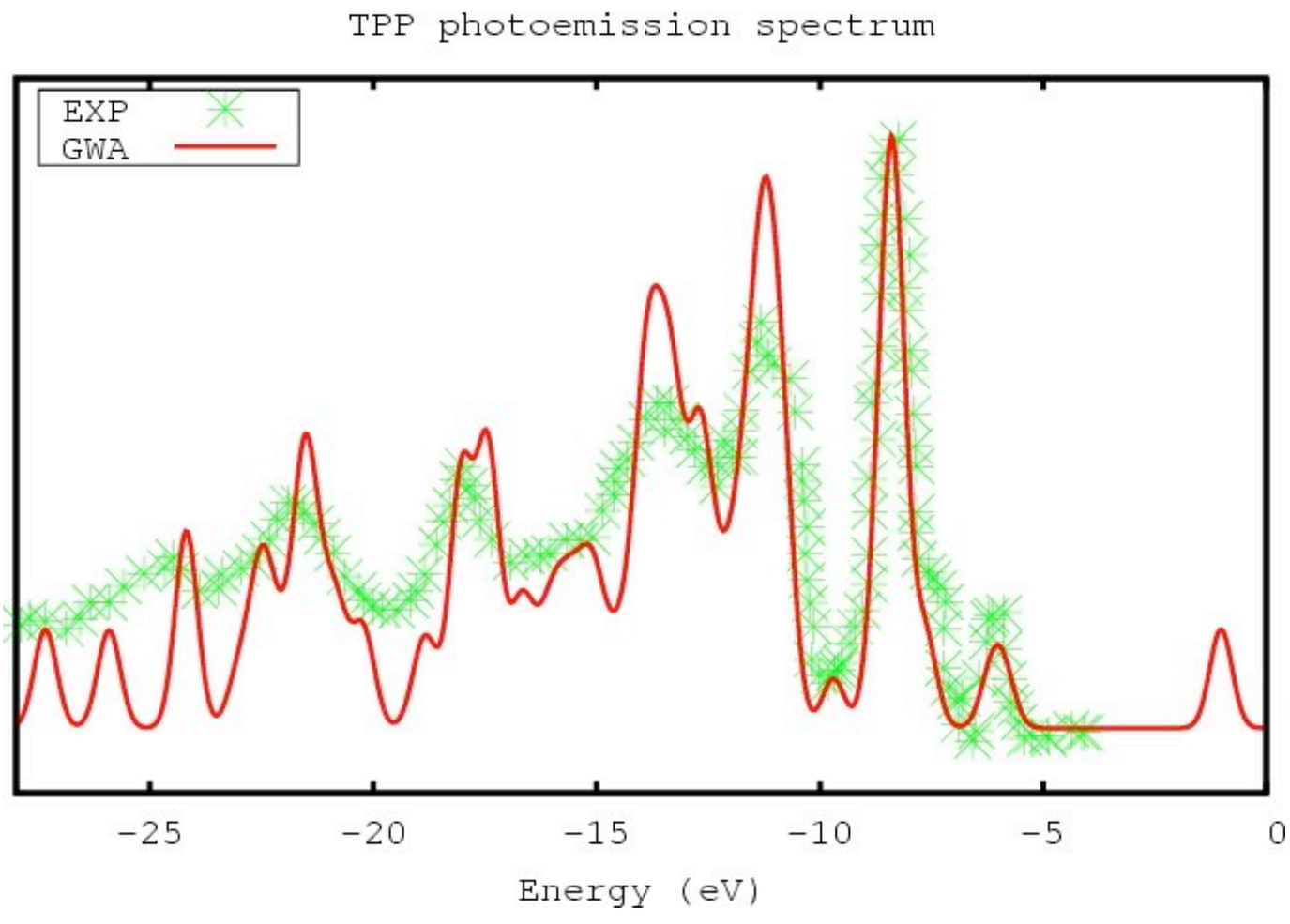
$C_{44}H_{30}N_4$



IP^{exp}=6.4 eV

IP^{LDA}=5.0 eV

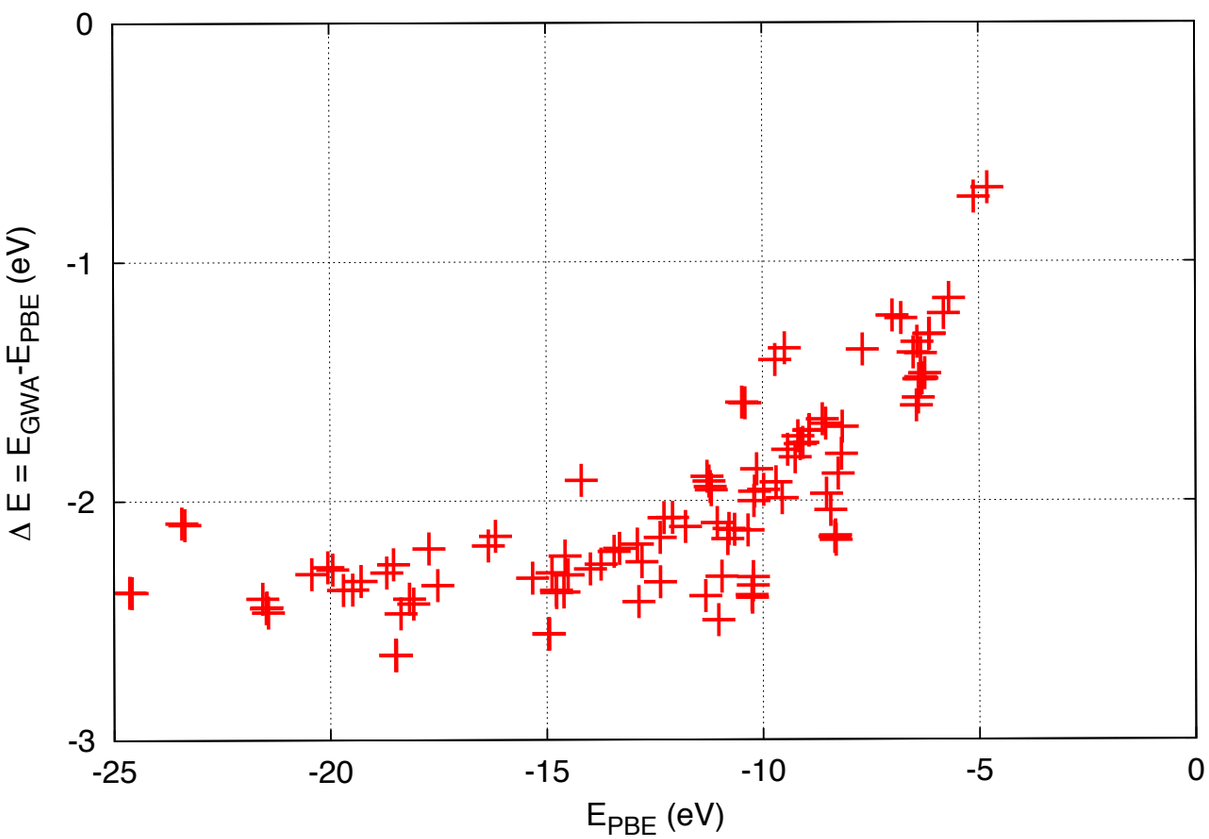
IP^{GWA}=6.7 eV

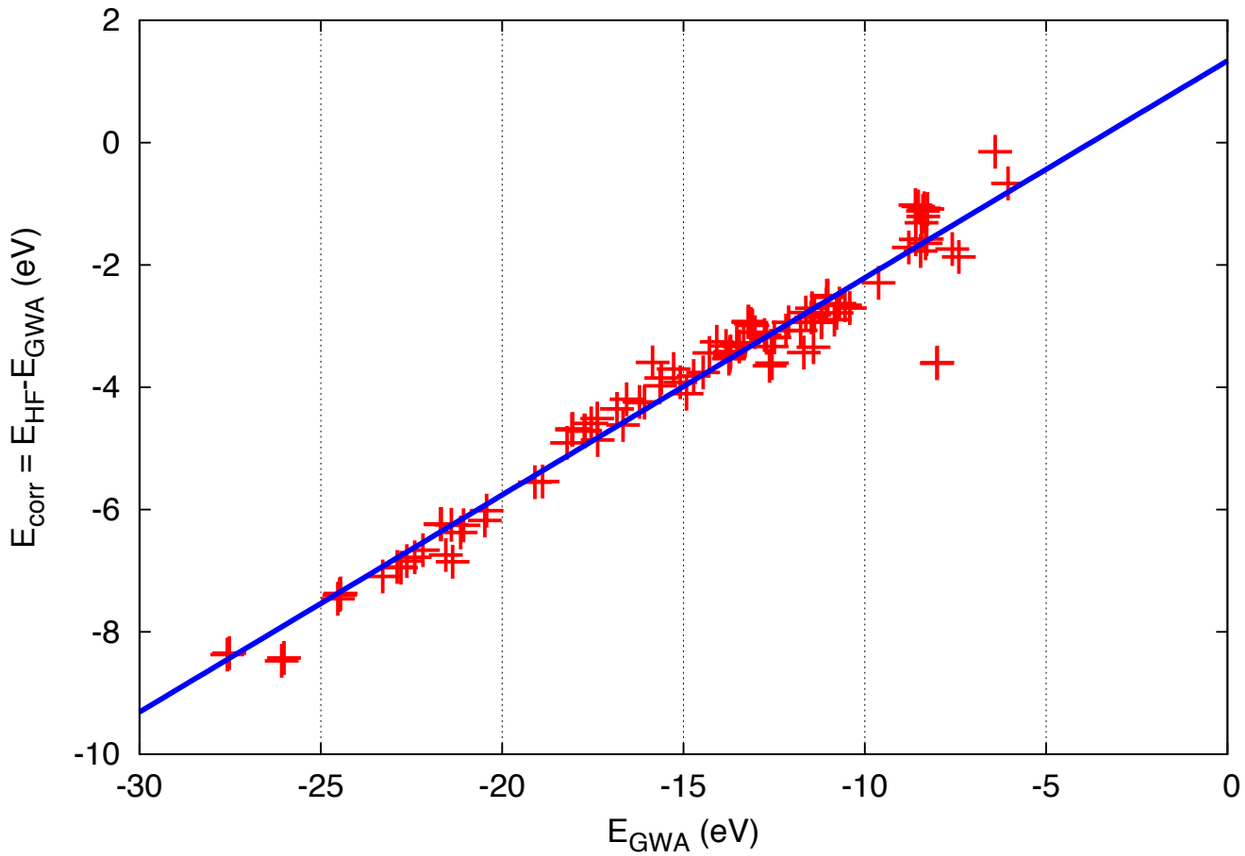


G.Stenuit, C. Castellarin-Cudia, O.Plekan, V. Feyer, K.C. Prince, A. Goldoni, and P. Umari, Phys. Chem. Chem. Phys., 12, 10812 (2010)

Tetraphenylporphyrin

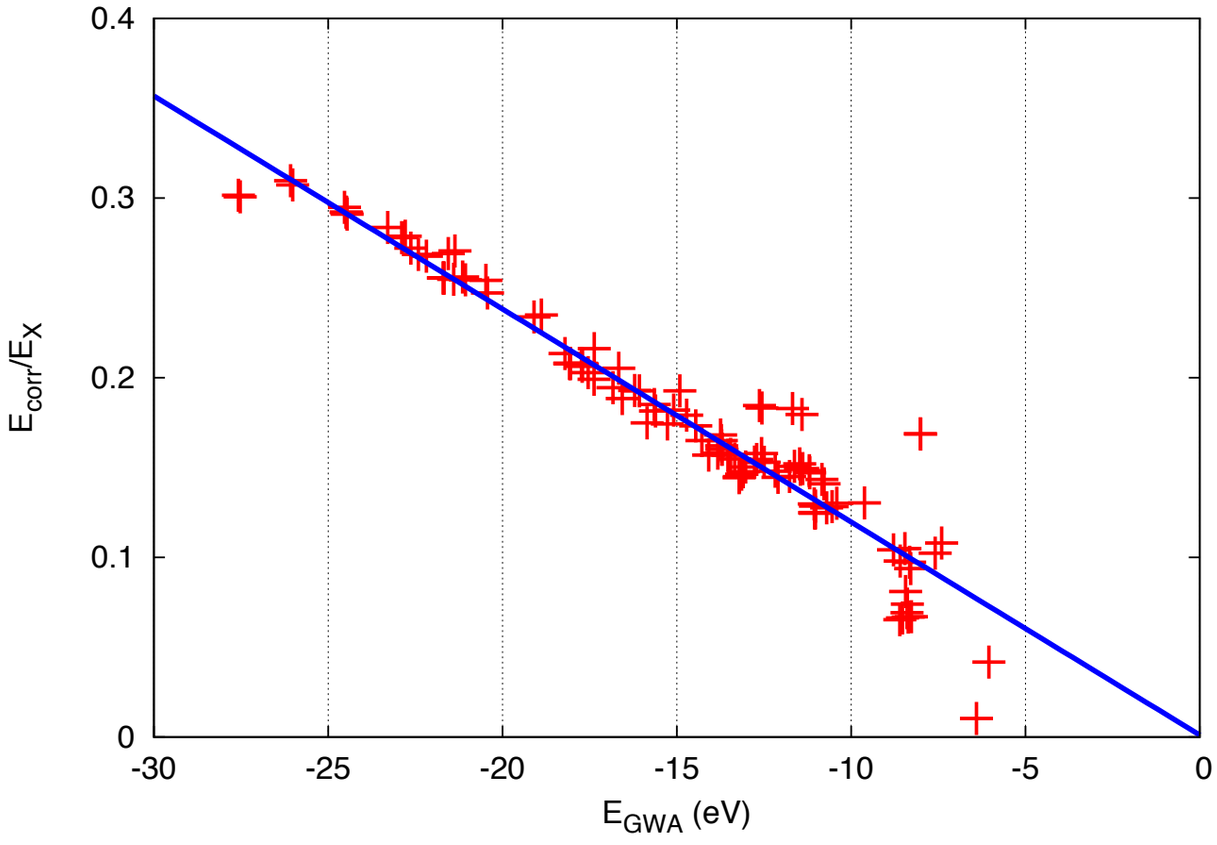
Analysis

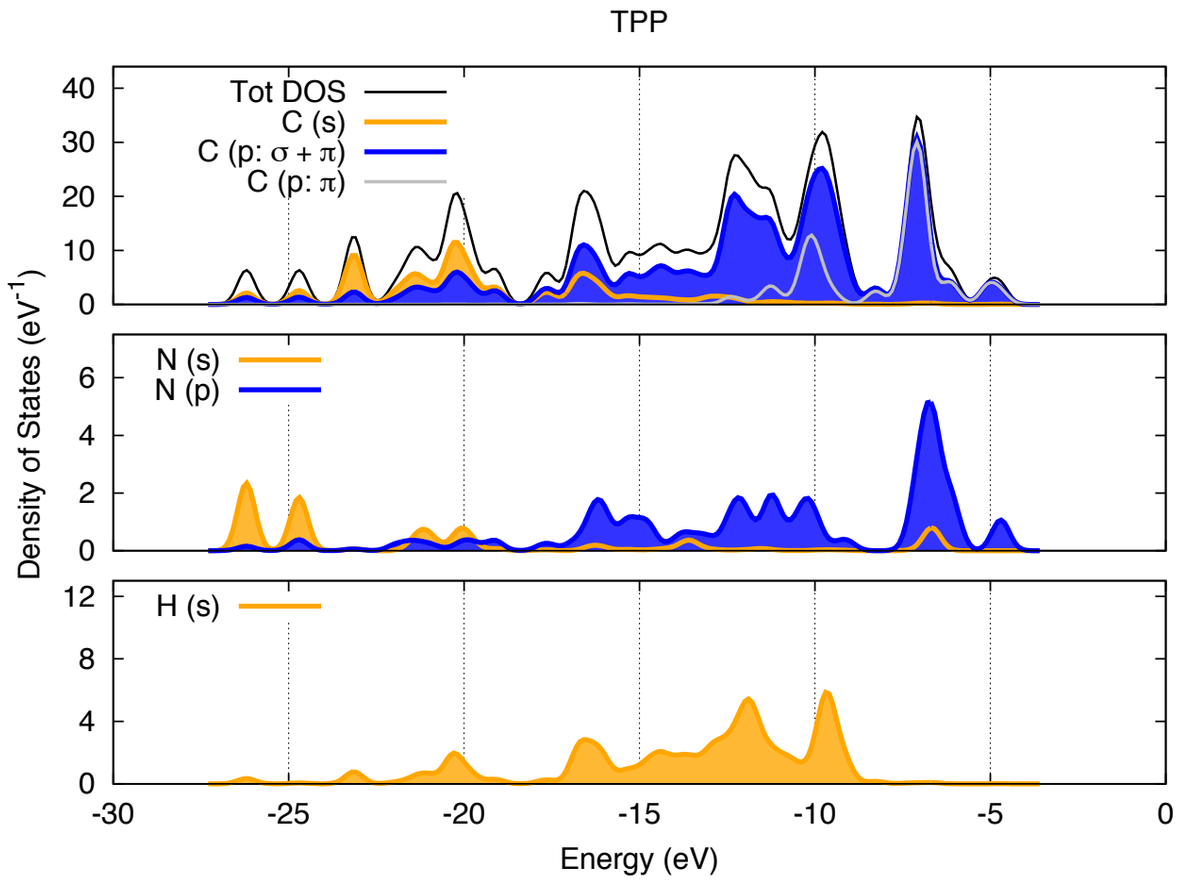




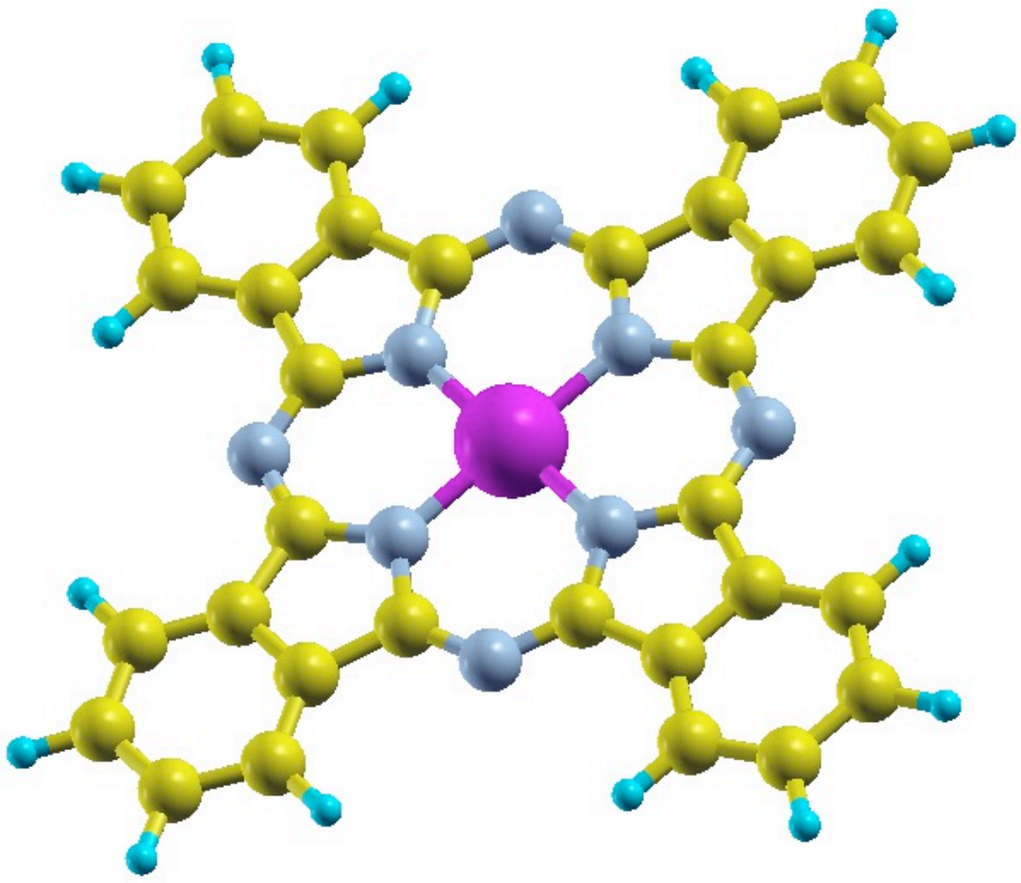
Tetraphenylporphyrin

Analysis





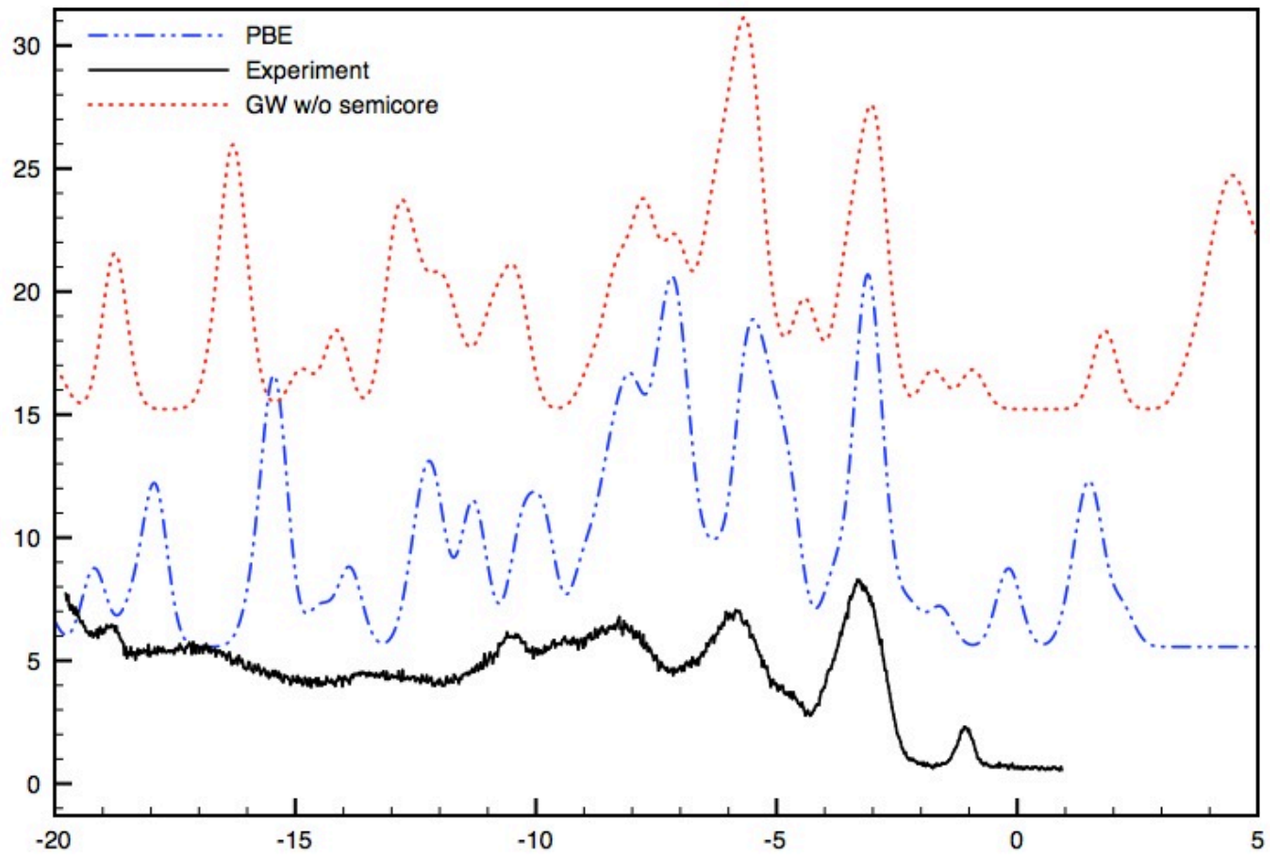
Zn-Phthalocyanine



GW calculation w/o Zn(3s,3p) semicore in valence:

IP_{exp}=6.35 eV

IP_{GW}=5.7eV



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

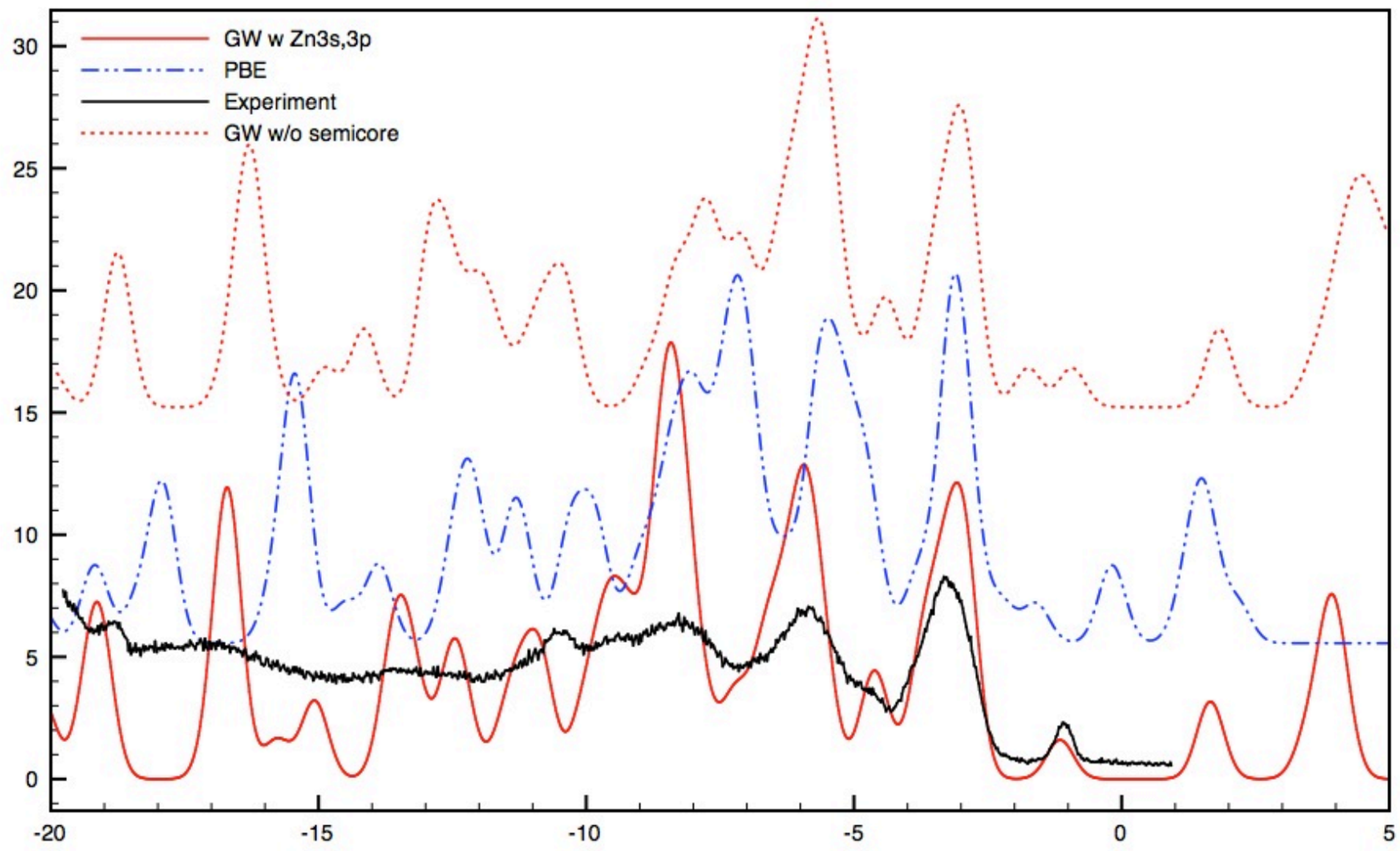
Importance of semicore states

We must include semicore Zn 3s and 3p states in valence:

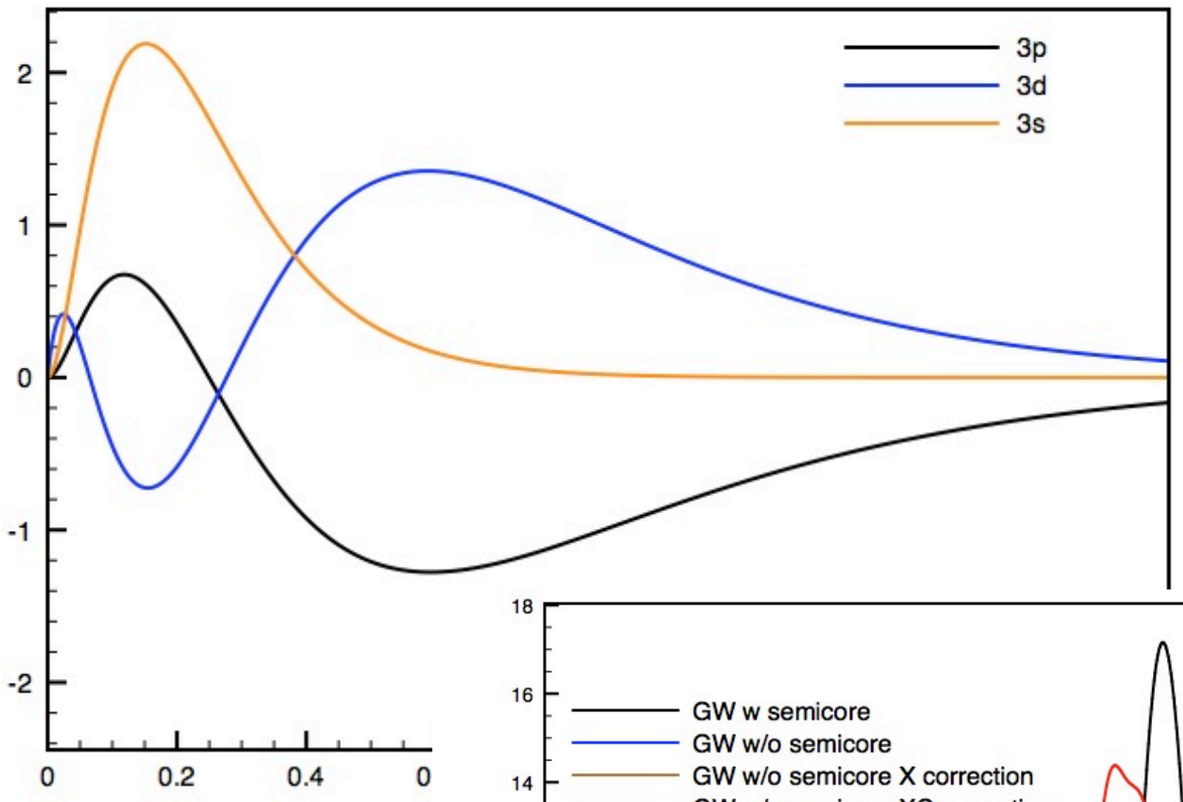
300Ry Plane-waves cutoff

IP_{exp}=6.35 eV

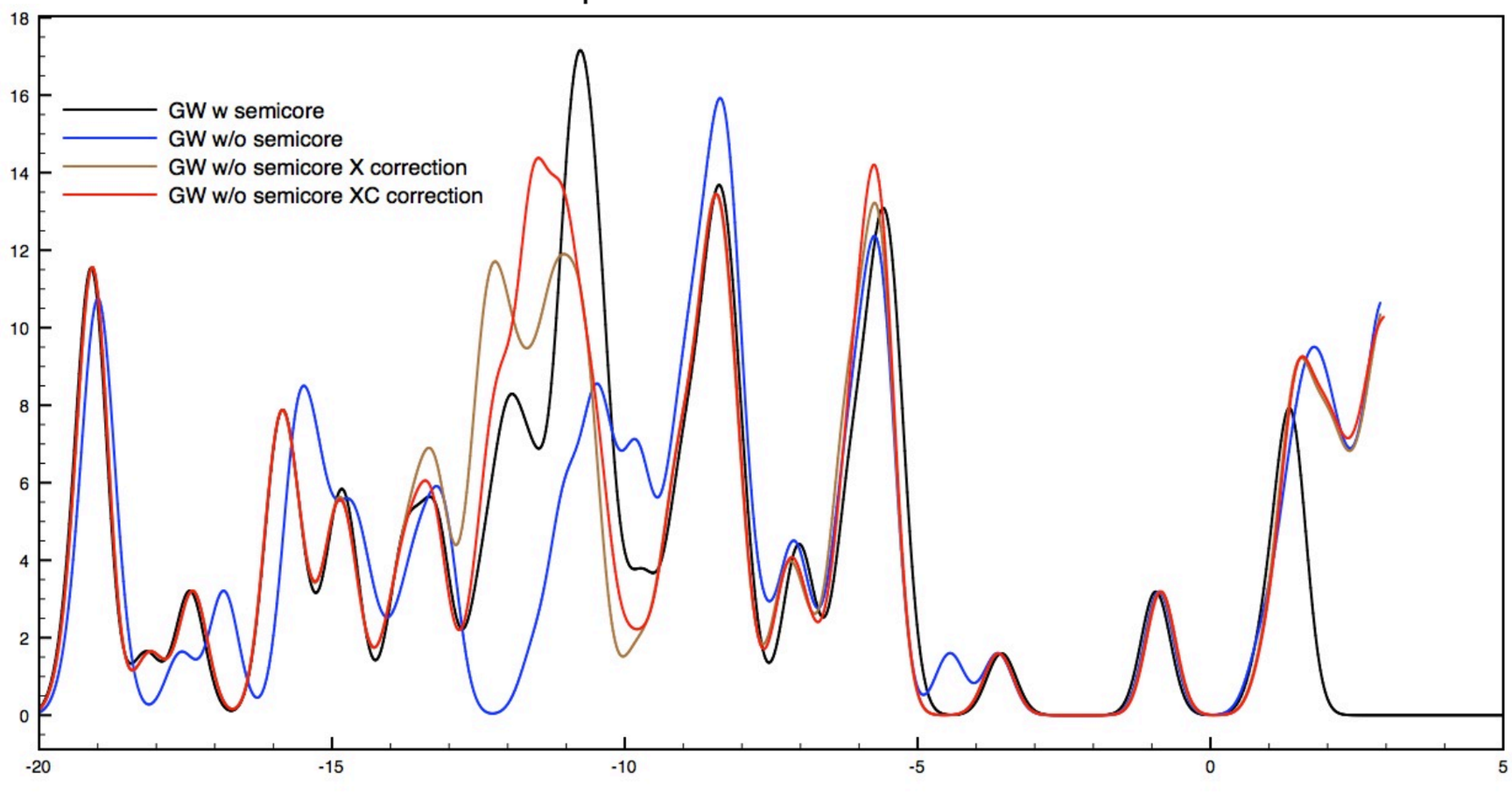
IP_{GW}=5.7eV



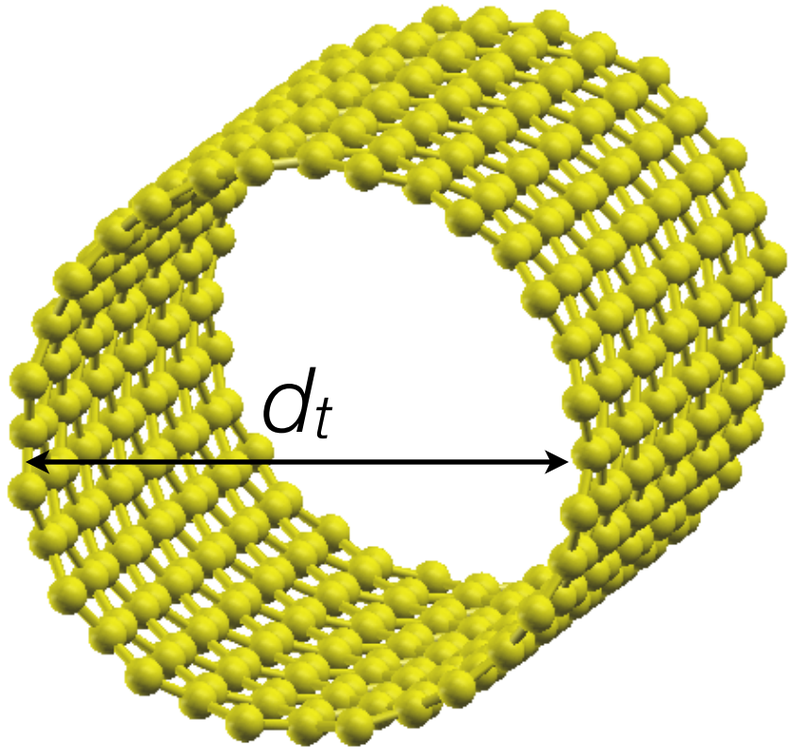
Explanation



1 0	1S 1(2.00)	-700.1289	-350.0644	-9525.7378
2 0	2S 1(2.00)	-85.1358	-42.5679	-1158.3319
2 1	2P 1(6.00)	-73.7947	-36.8974	-1004.0283
3 0	3S 1(2.00)	-9.4984	-4.7492	-129.2319
3 1	3P 1(6.00)	-6.1299	-3.0650	-83.4022
3 2	3D 1(10.00)	-0.7453	-0.3726	-10.1401
4 0	4S 1(2.00)	-0.4394	-0.2197	-5.9784
4 1	4P 1(0.00)	-0.0820	-0.0410	-1.1157

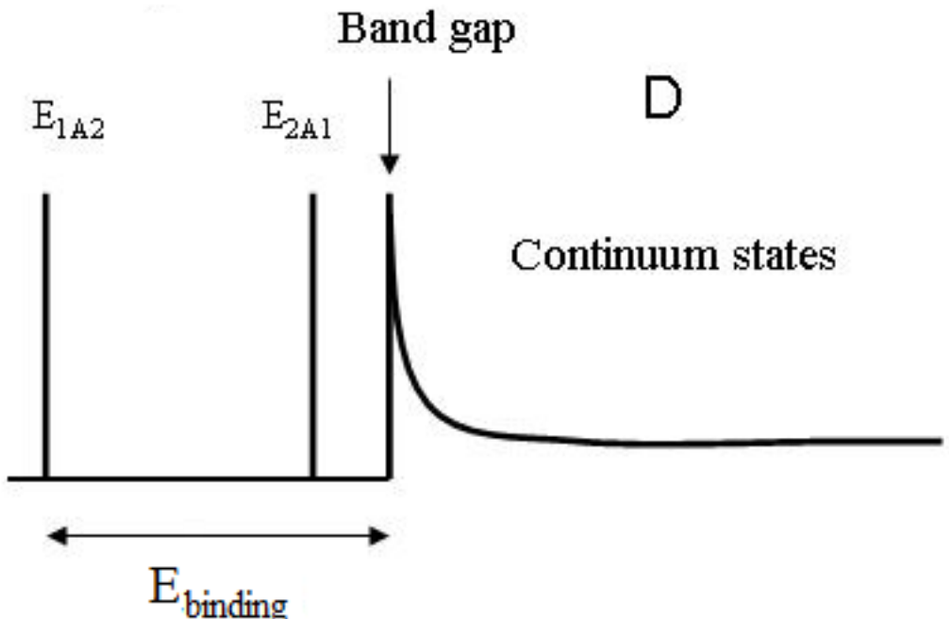


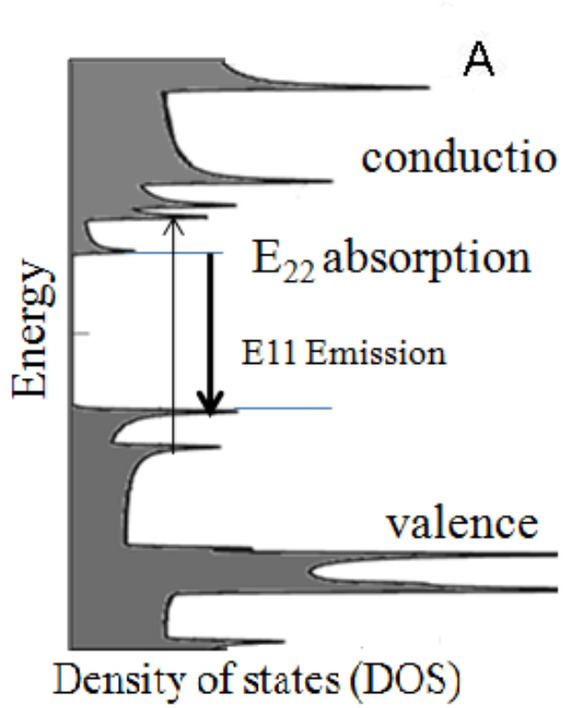
The *electronic band gap* of Carbon nanotubes



For semiconducting zig-zag CNTs we want to study the dependance of the *electronic band gap* wrt the diameter d_t

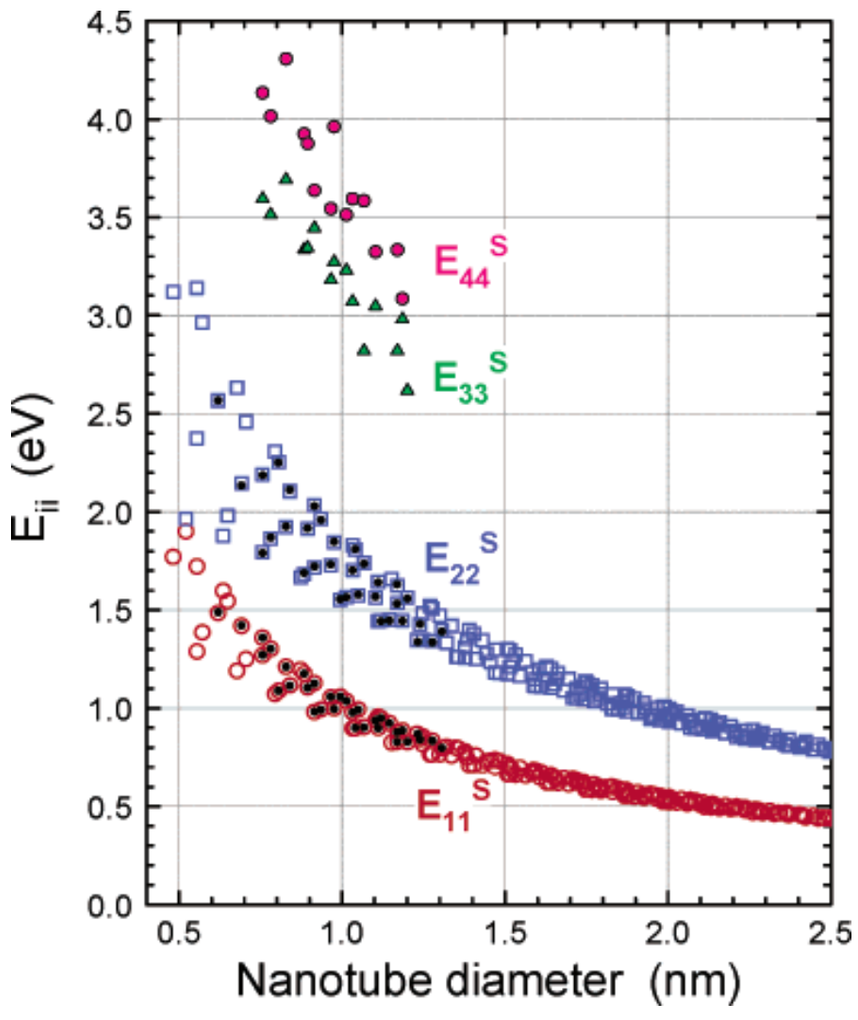
The electronic band gaps can be measured with great difficulties, *optical band gap* instead are measured with great accuracy:





cont'ed

Electronic gaps could be obtained combing theoretical results for exciton binding energies with optical measurements:



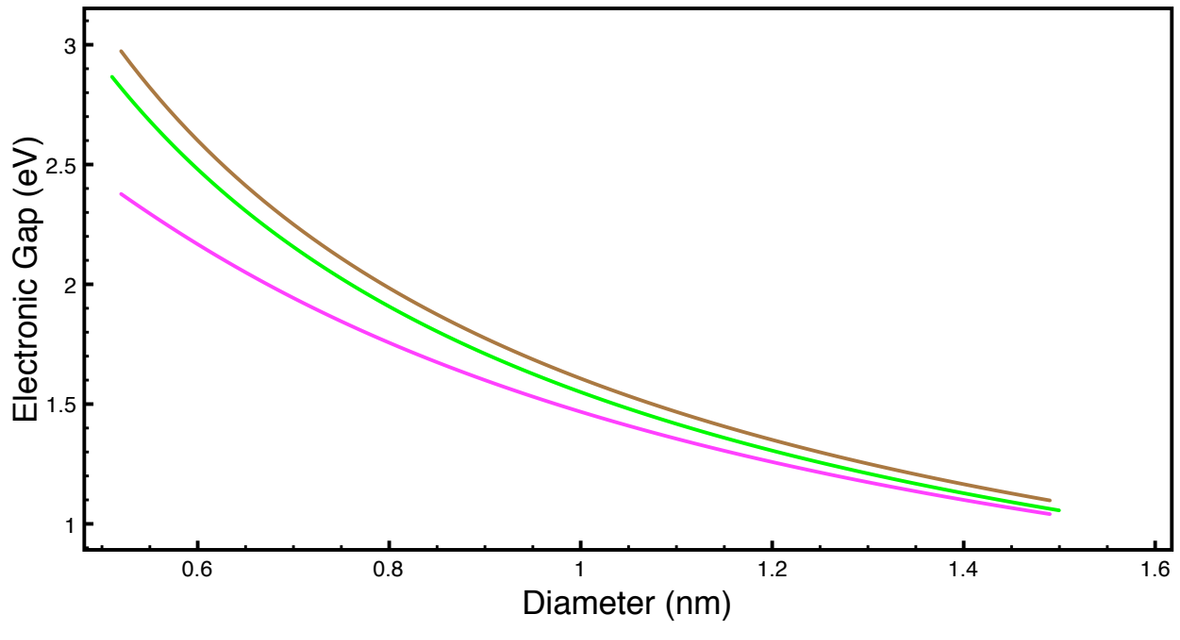
R.B. Weisman and S.M. Bachilo Nano Lett. 3, 1235 (2003)

$$E^{11} = E^{11}_{\mathrm{op}} + E^{\mathrm{bind}}_{1A2}$$

From theory:

$$E^{\mathrm{bind}}_{1A2} \approx 2.3\left(E^{22}_{\mathrm{op}} - E^{11}_{\mathrm{op}}\right)$$

J. Deslippe, M. Dipoppa, D. Prendergast, M.V.O. Moutinho, R.B. Capaz, and S.G. Louie, Nano Lett. **9**, 1330 (2009).



GW+L results

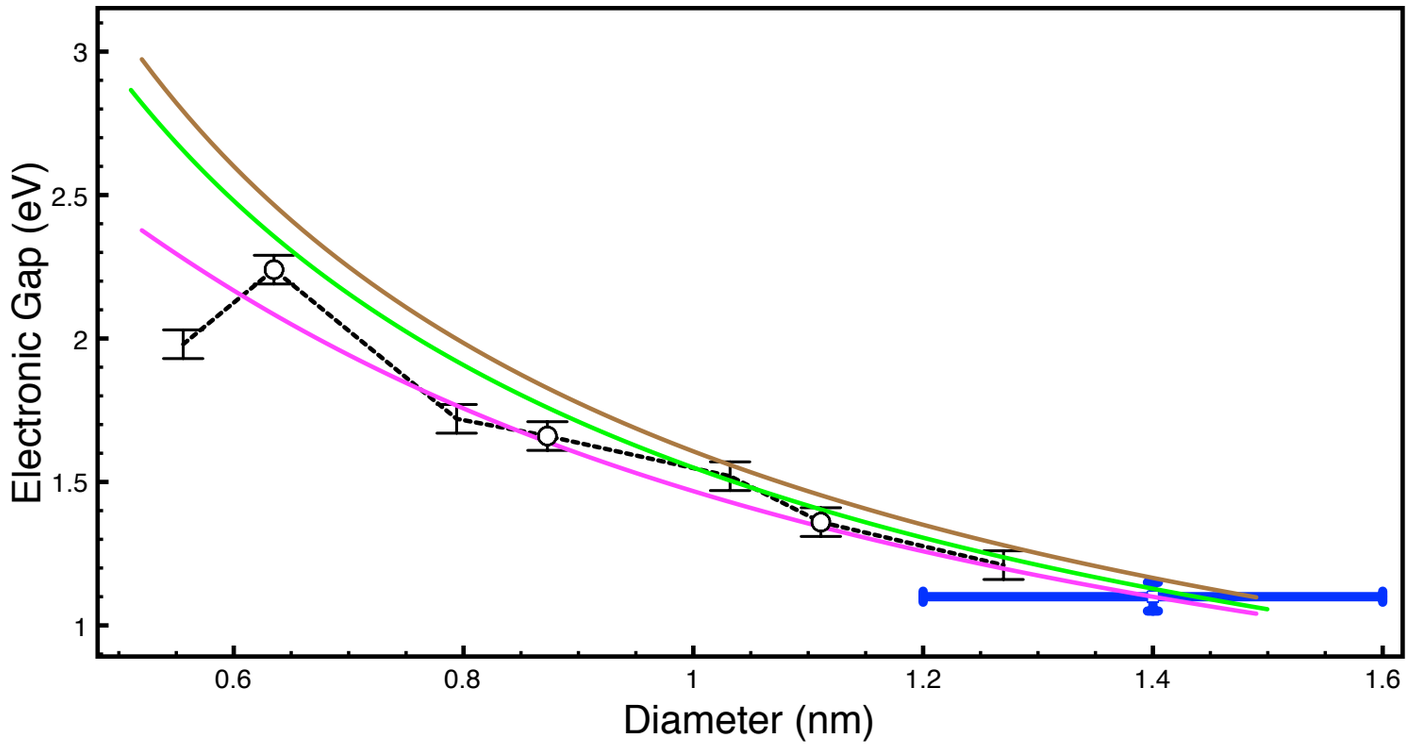
(m,n)	#cells	#atoms	#k-points	dimensions (Bohr)
(7,0)	4	112	4	30.0 × 32.0 × 30.0
(8,0)	3	96	4	30.0 × 24.3× 30.0
(10,0)	3	120	6	34.0× 24.0 × 34.0
(11,0)	3	132	6	36.0 × 24.0 ×36.0
(13,0)	2	104	9	39.0 × 16.0 × 39.0
(14,0)	2	112	9	40.0 × 16.0 × 40.0
(16,0)	2	128	9	40.0 × 16.0 × 40.0

(m,n)	LDA (eV)	GW(eV)	Ref. GW(eV)
(7,0)	0.16	1.98 (1.47)	(0.60[a]-1.12[b])
(8,0)	0.5	2.24 (1.80)	2.54[c] (2.12-1.75[c]-1.51[d])
(10,0)	0.80	1.72	
(11,0)	0.95	1.66	
(13,0)	0.65	1.52	
(14,0)	0.74	1.36	
(16,0)	0.56	1.21	

a) T. Miyake and S. Saito, Phys. Rev. B **68**, 155423 (2003).

c) C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402

d) W. Kang and M. S. Hybertsen, Phys. Rev. B **82**, 195108 (2010).



Experimental STM measure: H. Lin et al. Nat. Mat. 9, 235 (2010).

We can extrapolate the GW results:

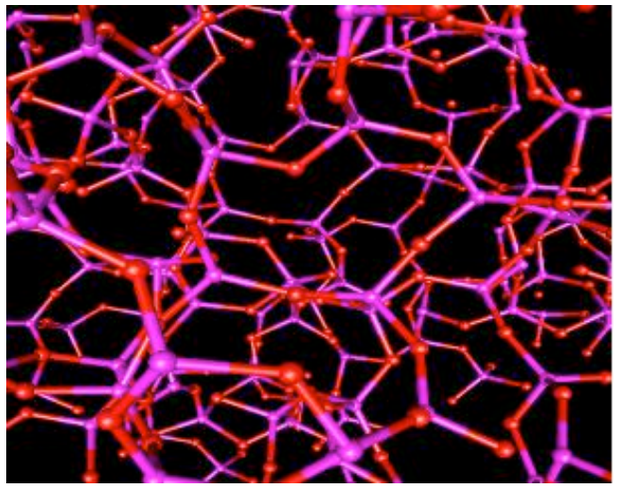
$$E^{11} = a/d_t$$

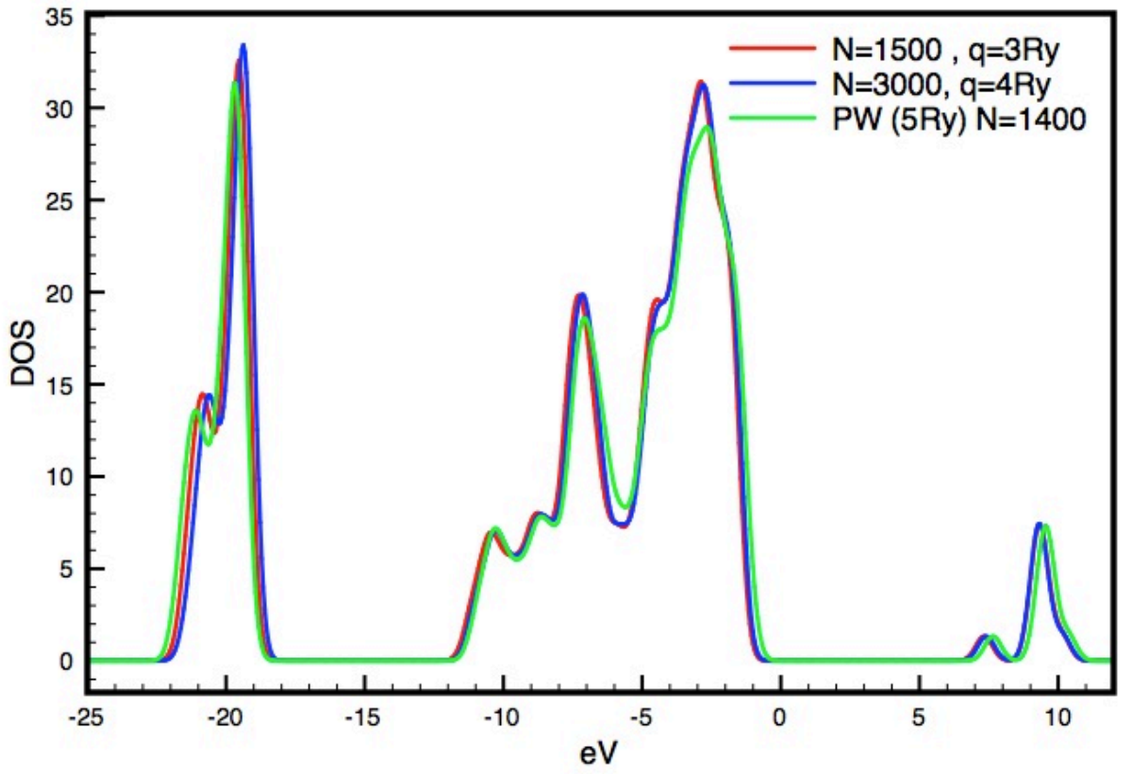
$$a = 1.54 \pm 0.14 \text{ eV} \times \text{nm}$$

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

Extension to extended systems

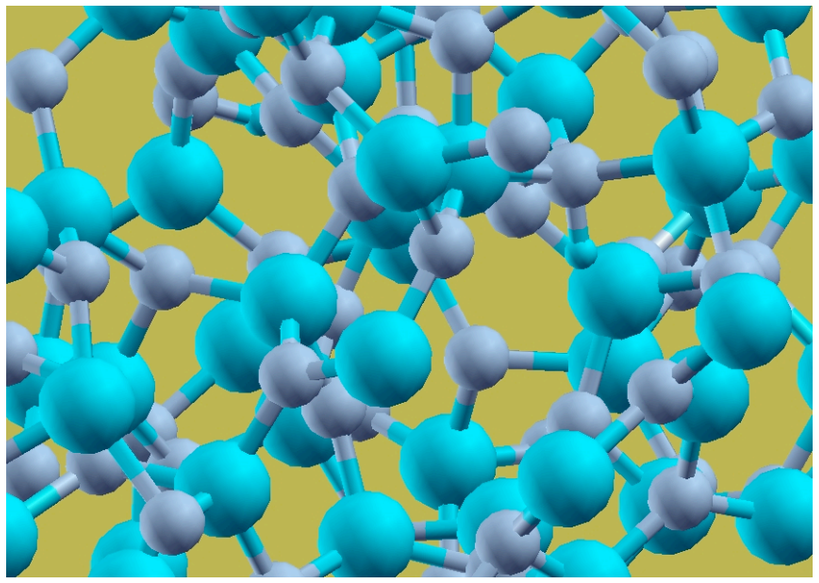
72 atoms -SiO_2

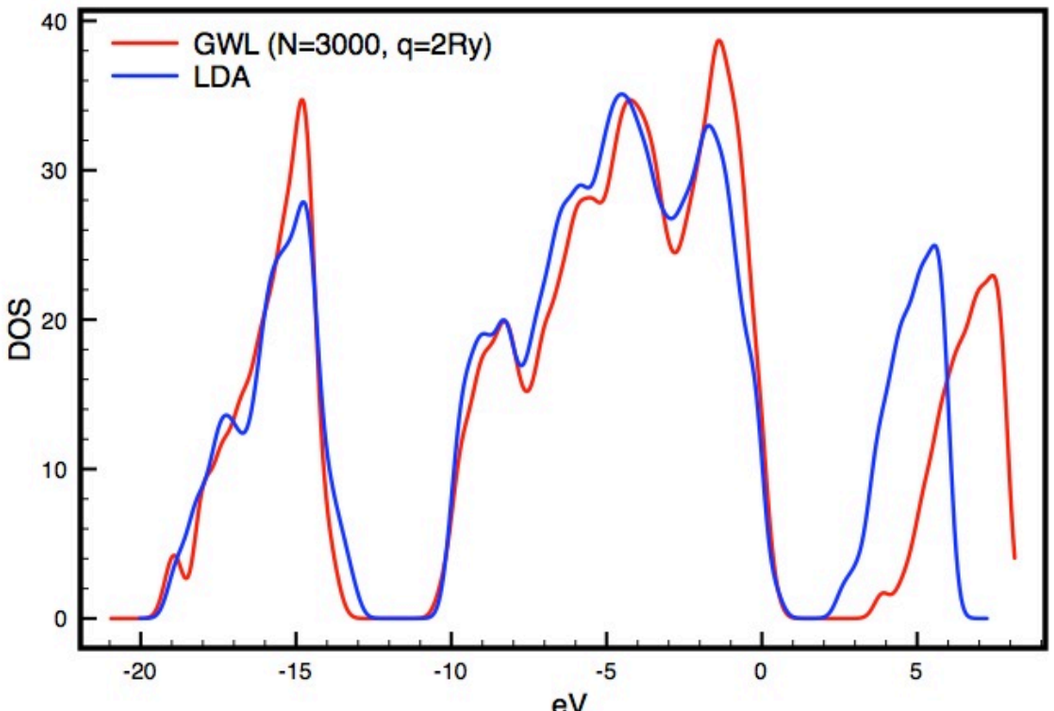




- E_{gap}(GW)=8.9eV
- E_{gap}(exp)=8.9-9.7eV

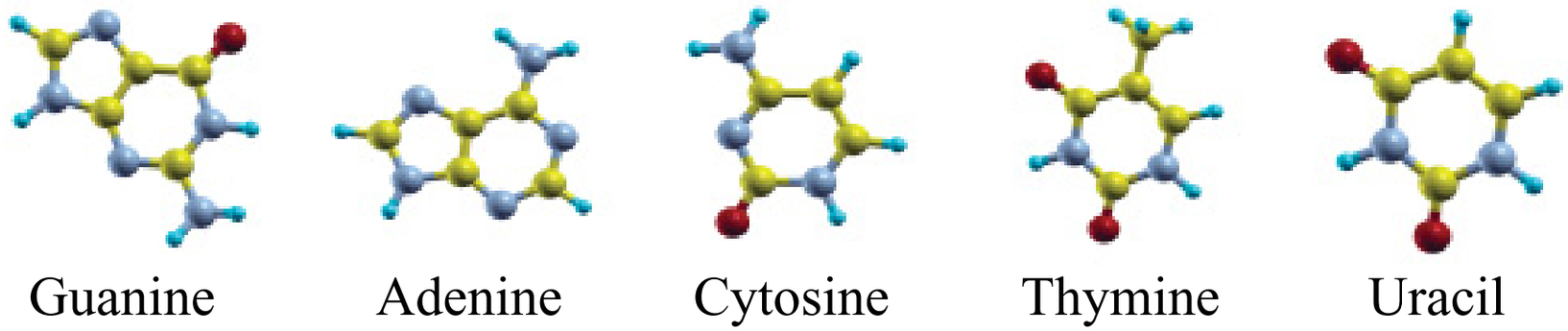
152 atoms -Si_3N_4

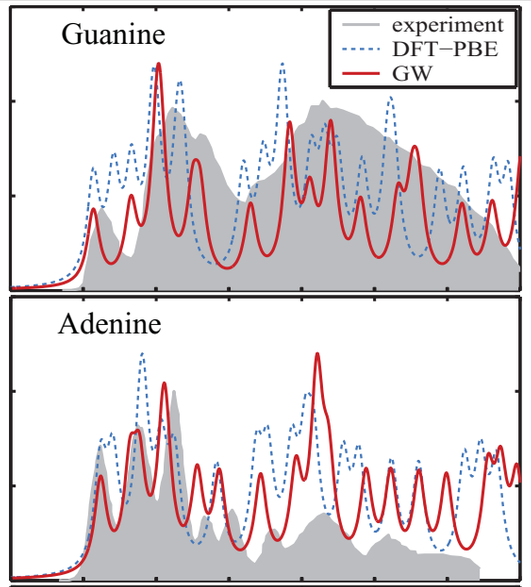


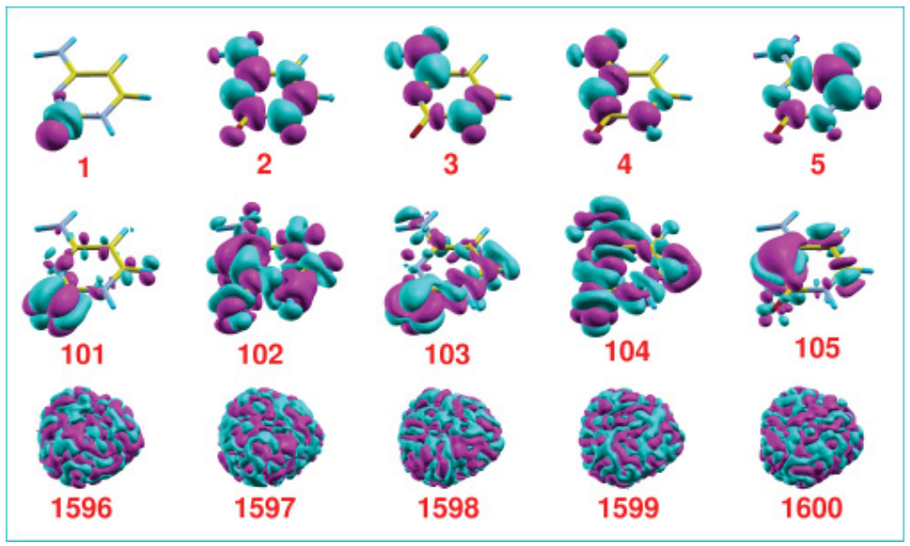


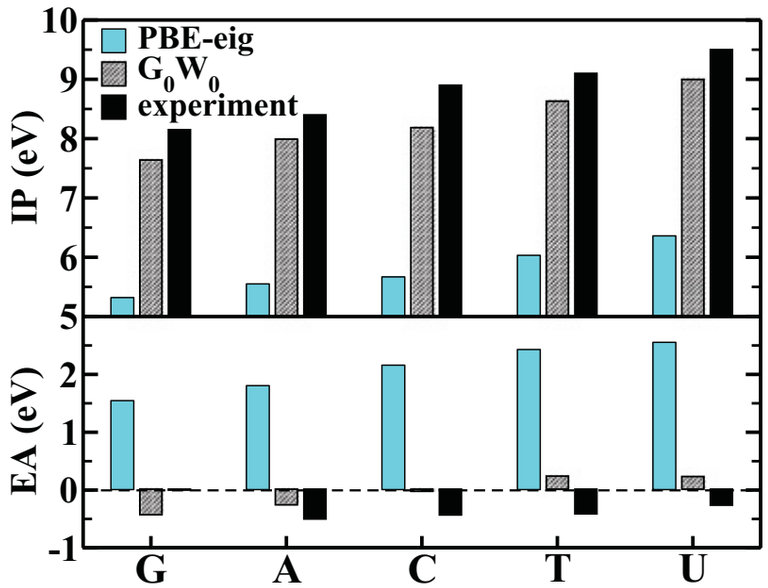
- E_{gap}(GW)=4.5eV
- E_{gap}(exp)=~5eV

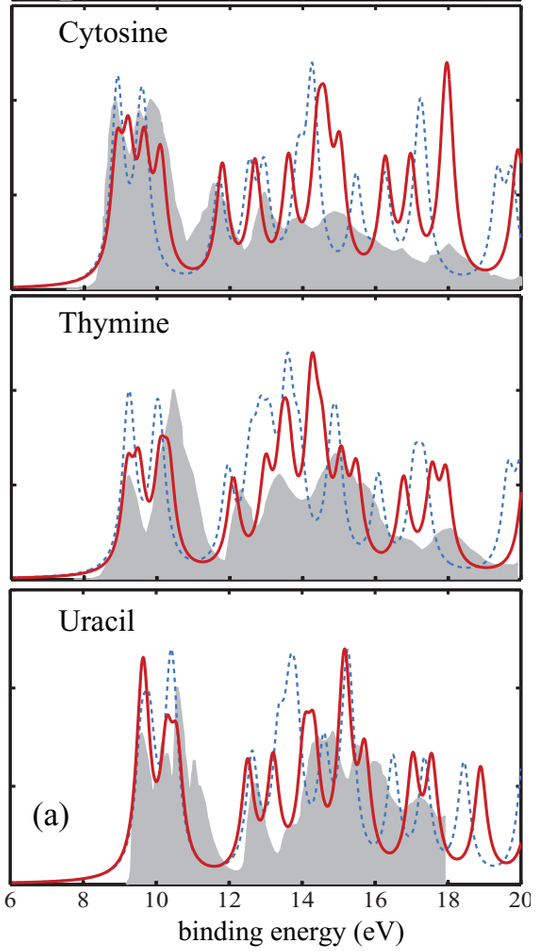
DNA from single bases to larger models





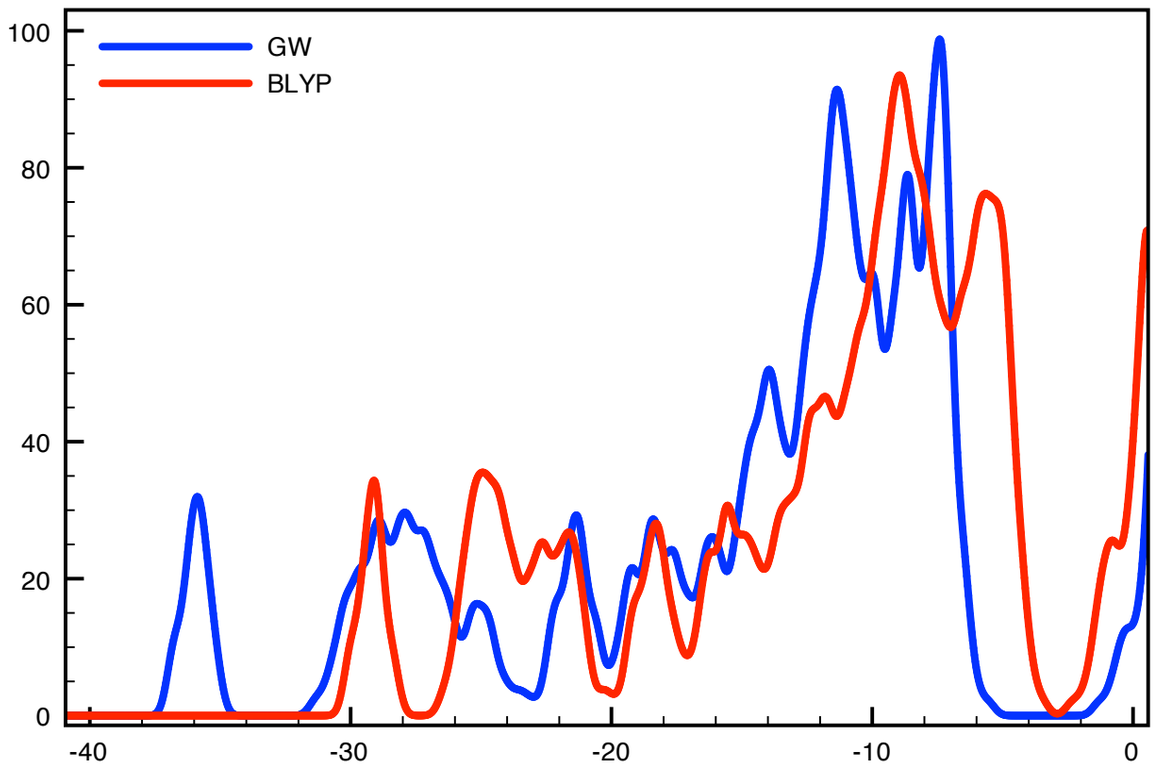




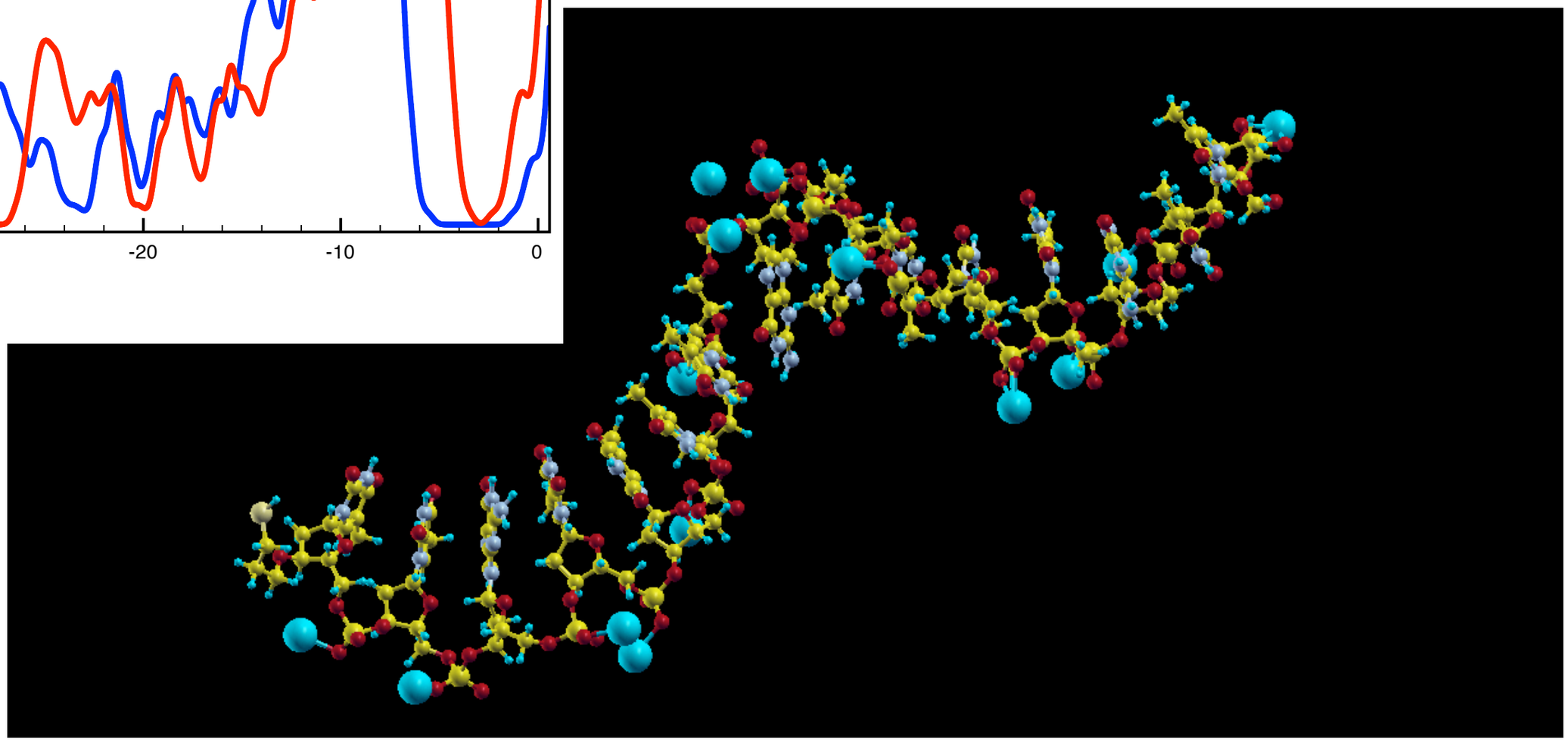


X. Qian, P. Umari, and N. Marzari, Phys. Rev. B 84 075103 (2011).

Single DNA strand



- 10 basis single strand model
- 509 atoms
- 1794 electrons



Conclusions

- GW calculation with no empty states now possible
- both plane-waves and optimal basis sets
- large systems are affordable
- GWL part of the Quantum-Espresso package
- GNU license
- new features implemented: spin polarized systems, partly occupied systems
- still working on: self-consistency, BSE

Acknowledgements

- G.Stenuit(Democritos)
- X. Qian(MIT)
- L.Giacomazzi(Sissa)
- J. Xian(Sissa)
- L. Martin-Samos(Democritos)
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- F. De Angelis
- A. Goldoni (Elettra)
- C. Castellarin-Cudia(Elettra)
- C. Cavazzoni(Cineca)
- M. Betti (Rome)
- S. Fabris(Demcoritos)