Applications of the $O(N^3)$ Hedin's GW

Peter Koval, Dietrich Foerster, Daniel Sanchéz-Portal

Bilbao 14/04/2011

Outline

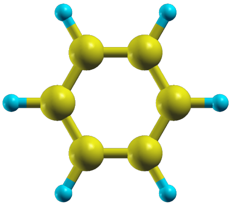
- Parameter calculations (+view on the methods)
- DOS, HOMO & LUMO
- HPC features
- Conclusion & Outlook

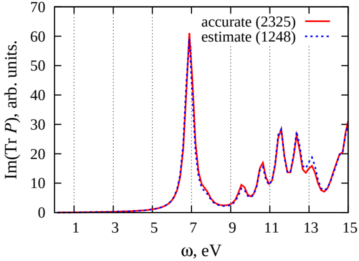
Size of dominant products basis

- Basis of dominant products is distinguishing feature[1]

$$f^a(\boldsymbol{r})f^b(\boldsymbol{r}) = V^{ab}_{\mu} F^{\mu}(\boldsymbol{r})$$

- Each pair of atoms has its own (sub)set of $F^{\mu}(\boldsymbol{r})$ and vertex V^{ab}_{μ}
- Within a given pair, $F^{\mu}(\boldsymbol{r})$ are optimal ($\perp$ with respect to Coulomb metric)
- How many $F^{\mu}(\boldsymbol{r})$ do we need in total ?





TDDFT: optical absorption

[1] D. Foerster, J. Chem. Phys. **128**, 34108 (2008).

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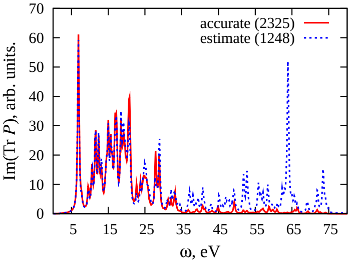
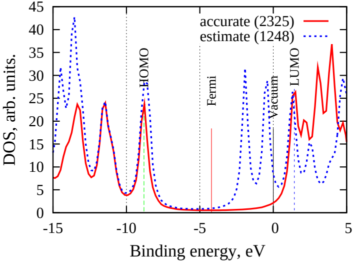
- We need more of them in GW.





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Non-local compression: method

- Response function reads in products basis

$$\chi^0_{\mu\nu} = \sum_{E<0,F>0} \frac{V^{EF}_{\mu} V^{EF}_{\nu}}{\omega \pm (E-F) + \mathrm{i}\varepsilon}, \text{ where } V^{EF}_{\mu} = X^E_a V^{ab}_{\mu} X^F_b$$

- Electron-hole pairs *EF* built a natural basis for χ^0, but redundand !

[2] D. Foerster, P. Koval, D. Sanchez-Portal, arXiv:1101.2065.

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- $\Rightarrow$ form linear combinations of V^{EF}_{μ} & choose important ones[2]
  - Build a (Coulomb) metric $g^{EF,E'F'} = V^{EF}_{\mu} v^{\mu\nu} V^{E'F'}_{\nu}$;
  - Diagonalize $g^{EF,E'F'} X^{\lambda}_{E'F'} = \lambda X^{\lambda}_{EF}$ & choose threshold for λ.
  - Build linear combinations of V^{EF}_{μ}: $Z^{\lambda}_{\mu} = V^{EF}_{\mu} X^{\lambda}_{EF}$

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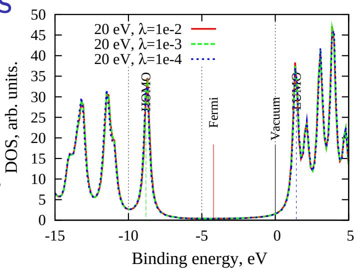
Non-local compression: parameters



- Only subset of EF's can be diagonalized otherwise $O(N^6)$ complexity
- We choose low-energy difference EF's pairs $\Rightarrow |E - F| < E_{\text{max}}$
- $\#EF$'s can be kept $O(N)$
- Threshold for eigenvalues λ.
  Can we get out with $\#\lambda$'s less $\#F^{\mu}(\boldsymbol{r})$?
- Typically $\#\lambda$'s can be $N_{\text{prod}}/10$ and more! (1000x acceleration in inversion for W)

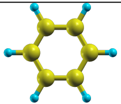
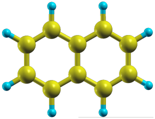
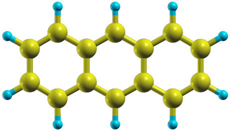
E_{max} eV	$\lambda = 10^{-2}$	$\lambda = 10^{-3}$	$\lambda = 10^{-4}$
10	2.50 (33)	2.48 (37)	2.48 (39)
20	1.39 (96)	1.41 (133)	1.42 (171)
40	1.43 (132)	1.43 (192)	1.43 (279)

The electron affinity of benzene, eV.

In brackets $\#\lambda$'s

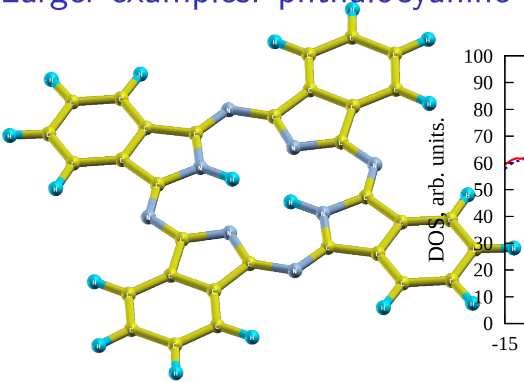
compare with $\#F^{\mu}(\boldsymbol{r})$=2325

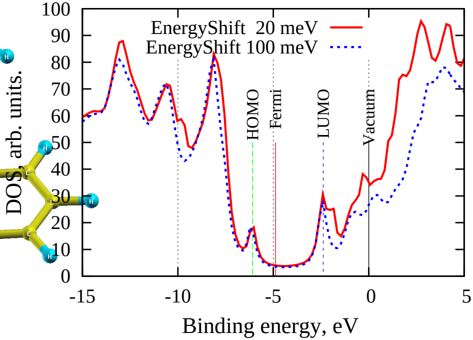
Examples: rings

Picture	IP, eV	EA, eV	N_ω	Runtime, s
	8.82 (9.25)	-1.43 (-1.12)	64	977
	7.58 (8.14)	-0.15 (-0.19)	64	2075
	6.88 (7.44)	0.79 (0.530)	64	8434

LDA G_0W_0 correctly predicts anthracene to be an aceptor while benzene and naphthalene to be donor. Dynamical part of $\Sigma(\omega)$ is responsible for this change $\Rightarrow$ correlation makes the difference.

Larger examples: phthalocyanine



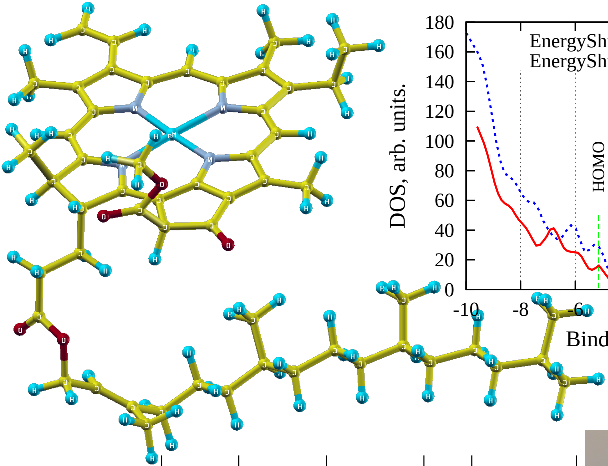


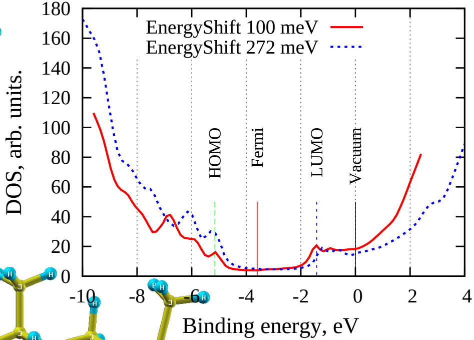
Program	IP, eV	EA, eV	Gap, eV	N_ω	Runtime
Our LDA G_0W_0	6.08	2.38	3.71	64	22 hours
Xavier Blase[3]	6.01	2.02	3.99		

One core of Intel®Core™2 Quad CPU Q9400 2.66GHz Cache 3MB/RAM 4GB

[3] X. Blase, C. Attaccalite, V. Olevano, Phys. Rev. B **83**, 115103 (2011).

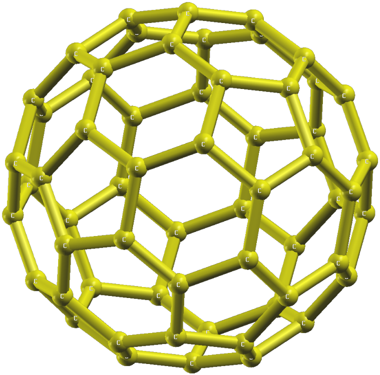
Larger examples: chlorophyll-a

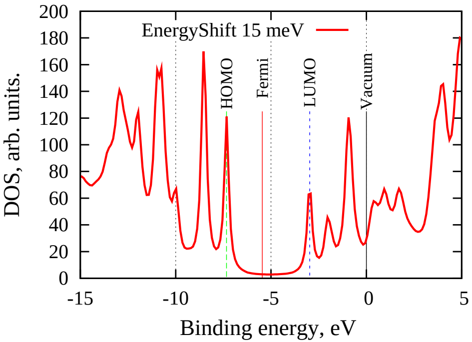




Program	IP, eV	EA, eV	Gap, eV	N_ω	Runtime
Our LDA G_0W_0	5.18	1.42	3.76	48	36 hours

Larger examples: fullerene C_{60}





Source	IP, eV	EA, eV	Gap, eV	N_ω	Runtime
Our LDA G_0W_0	7.33	2.97	4.36	128	26 hours
Experimental	7.58	2.65	4.93		

8 cores of Intel® E5520 2.27GHz, Cache 8M / DDR3 RAM 12 GB

Fast convolutions in time-by-time fashion

- Response and self-energy are computed via their spectral functions

$$\chi^0_{\mu\nu}(\omega) = \int \frac{a_{\mu\nu}(s)}{\omega - s + \mathrm{i}\varepsilon} ds$$

- Spectral functions are formulated as convolutions ⇒ FFT

$$a_{\mu\nu}(s) = \rho_{ab}(\omega) V_{\mu}^{bc} \otimes \rho_{ad}(\omega) V_{\nu}^{dc}$$

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  - Tensor calcul in time domain simplifies and speedups the program

Algorithm: Calculation of response in time-by-time fashion

$\rho_{ab}(t) = \mathrm{FFT} \rho_{ab}(\omega)$

for $t = 1 \ldots N_t$ **do**

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  - OpenMP parallelization of the time loop is straigthforward

Partially allocatable/deallocatable storage

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- ...?

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- Time-by-time fast, but needs storage of both $a_{\mu\nu}(s)$ and $\chi_{\mu\nu}(\omega)$
- . . . ?
- Structures with allocatable fields allow to circumvent the drawback

Algorithm: Usage of partially allocatable/deallocatable storage

Store $a_{\mu\nu}(t)$ into a structure $a(\nu,t)\%array(\mu)$

for $\nu = 1 \dots N_{prod}$ **do**

$\chi^{\text{auxiliary}}(\omega,\mu) = \text{Cauchy}(a(\nu,t)\%array(\mu))$

deallocate part of spectral function: $a(\nu,t)\%array$

allocate part of response function: $\chi^0(\nu,\omega)\%array(\mu)$

$\chi^0(\nu,\omega)\%array(\mu) = \chi^{\text{auxiliary}}(\omega,\mu)$

endfor

Conclusion & Outlook

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- Reducing the number of dominant products
- Developing alternatives to current basis of dominant products
- Extension to periodical systems (large unit cells)
- BSE with dominant products

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- Xavier Blase (Grenoble, France)
- Björn Lange (Düsseldorf, Germany)

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Thank you for your attention!

Second window technique: method

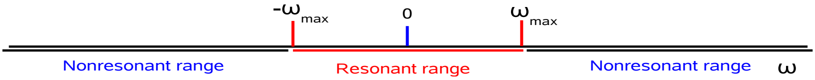
…allows for rough resolution in high energy.

- Response $\chi_0(\omega)$ via its spectral function $a(s)$

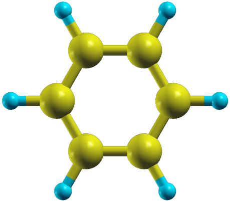
$$\chi_0(\omega) = \int_{-\infty}^{\infty} \frac{a(s)\, ds}{\omega - s + \mathrm{i}\varepsilon}$$

- We need $a(s)$ at high frequencies even low frequency response is computed

$$\int_{-\infty}^{-\omega_{\mathrm{max}}} d\lambda \frac{b(\lambda)}{\omega - \lambda + \mathrm{i}\varepsilon} + \int_{-\omega_{\mathrm{max}}}^{+\omega_{\mathrm{max}}} d\lambda \frac{a(\lambda)}{\omega - \lambda + \mathrm{i}\varepsilon} + \int_{\omega_{\mathrm{max}}}^{+\infty} d\lambda \frac{b(\lambda)}{\omega - \lambda + \mathrm{i}\varepsilon}$$



Second window technique: parameters



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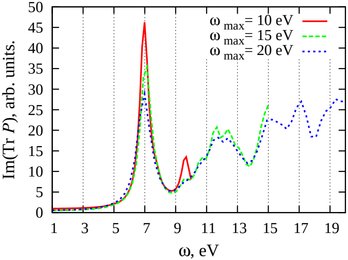

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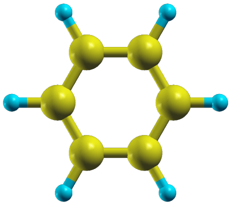

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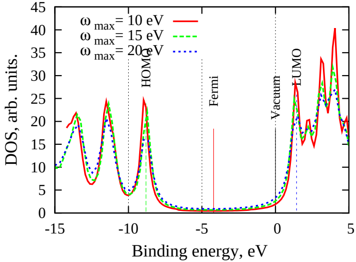
- ...Response was never a problem for second window technique...
- ...GW needed more attention: different ε



$$\int_{-\infty}^{-\omega_{\max}} d\lambda \frac{b(\lambda)}{\omega - \lambda + \mathrm{i}\varepsilon_2} + \int_{-\omega_{\max}}^{+\omega_{\max}} d\lambda \frac{a(\lambda)}{\omega - \lambda + \mathrm{i}\varepsilon_1} + \int_{\omega_{\max}}^{+\infty} d\lambda \frac{b(\lambda)}{\omega - \lambda + \mathrm{i}\varepsilon_2}$$

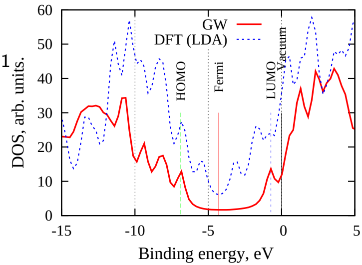
Calculation of partial densities

- Dyson equation

$$G_{ab}(\omega) = \left(S^{ab}\omega + H^{ab} + \Sigma^{ab}(\omega)\right)^{-1}$$

- Density of states

$$\rho(\omega) = S^{ab}\mathrm{Im}\, G_{ab}(\omega)$$



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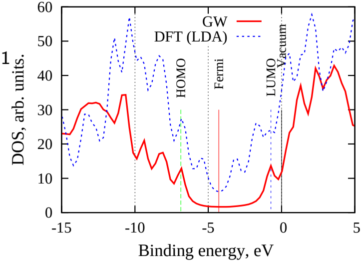

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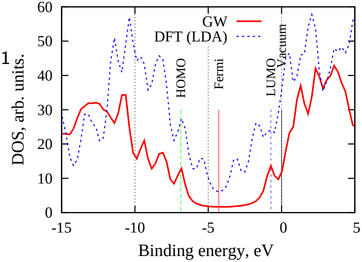

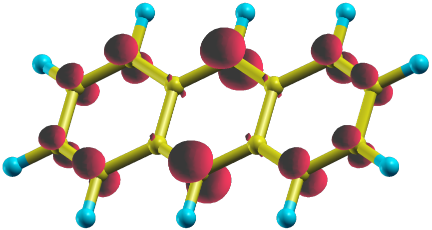

GWA HOMO

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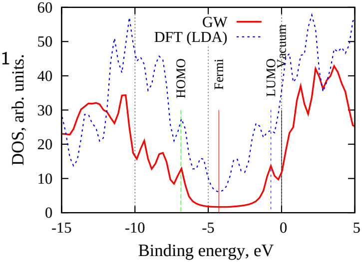

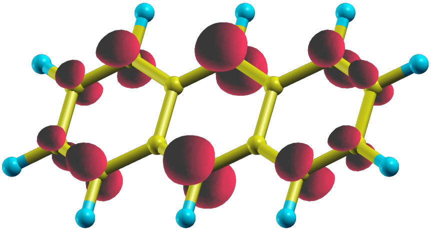

DFT HOMO

Optimization of atomic orbitals

- Radial shapes of localized orbitals can be optimized against a plane-wave (PW) calculation[4]
- Minimization of spillage gives better atomic orbitals

$$\mathrm{Spillage} = \frac{1}{N_{PW}} \sum_{E} n_E \langle \Psi_E^{PW} | 1 - P | \Psi_E^{PW} \rangle$$

P is a projector onto atomic orbitals $P = |f^a\rangle (S^{ab})^{-1} \langle f^b|$

Orbitals	IP, eV	EA, eV	gap, eV
SIESTA split 3 meV	8.82	-1.44	10.0
Björn Lange (Quamols)	8.96	-1.02	9.98
Experiment	9.25	-1.22	10.47

[4]B. Lange, Ch. Freysoldt, J. Neugebauer, Phys. Rev. B **submitted** (2010).