Implementing Hedin's GW scheme for molecules of N atoms in $O(N^3)$ operations

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Nanospain 14/4/2011 Bilbao

Experimental Motivation : Revolution in Organic Semiconductors

Must predict properties of constituent organic molecules before synthesis

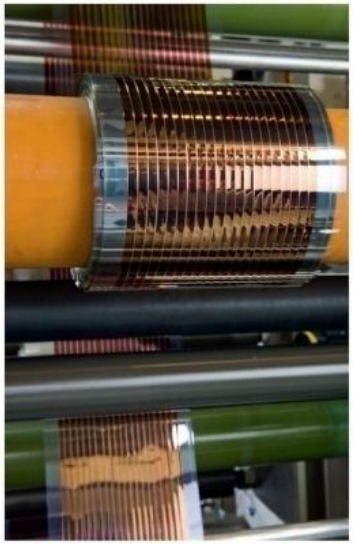
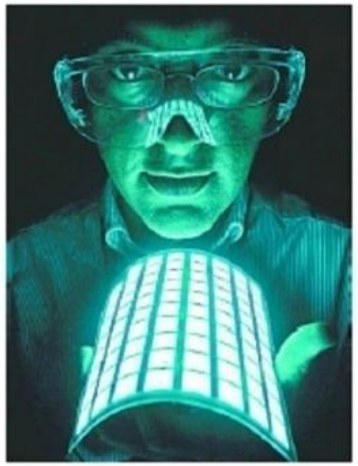
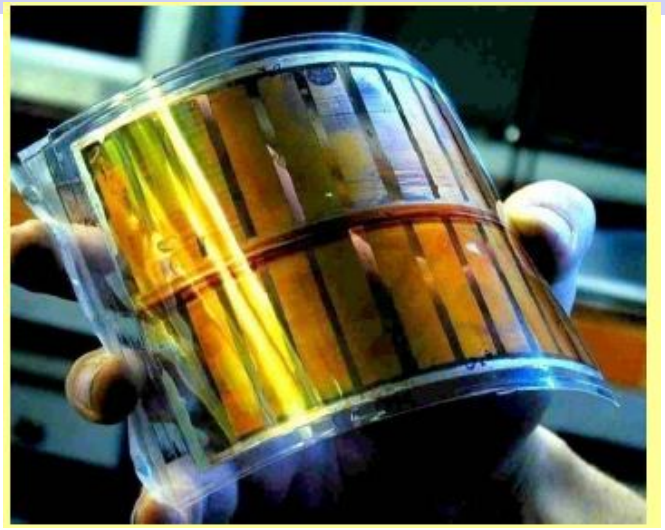
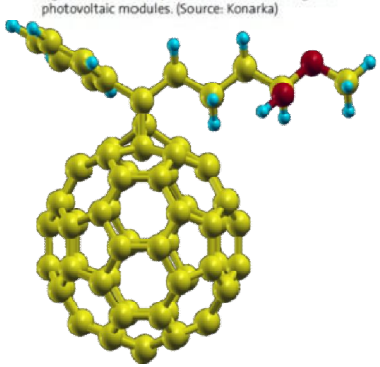


Figure 1: Roll-to-roll production of flexible organic photovoltaic modules. (Source: Konarka)

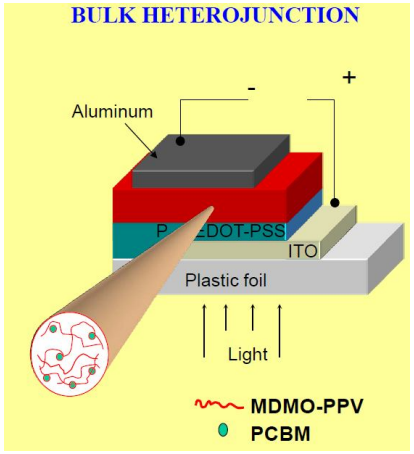


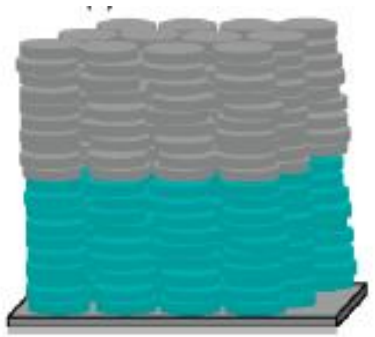
Anil Duggal, who heads up GE Global Research's Organic Electronics Project, says sheets of organic light-emitting diodes, such as the one above, might be the future of lighting.





Georges Hadziioannou, Bordeaux
Karl Leo, Dresden



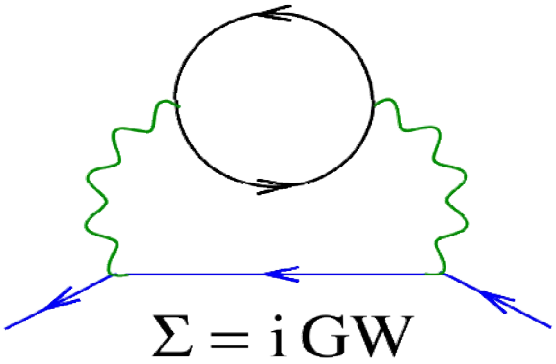


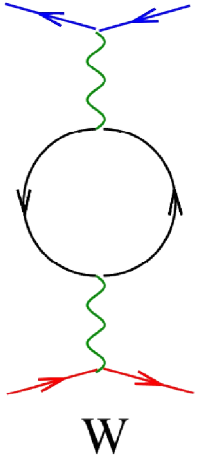
Thiebaut/Bock/Grelet Bordeaux 2010
columnar photo active cells

Theoretical Motivation: TDDFT does not work for excitons

GW+BSE work for excitons / organic molrcules

Existing implementations slow ~ N ^{4}





electron-hole interaction

Hedin's equations ~ 1965

Hedin's approximation applied to semi conductors ~1980

Hedin's approximation applied to molecules: ~1990's Louie + Rohlfing

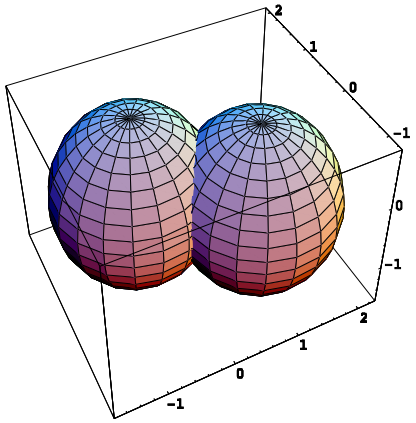
GW+BSE on biological chromophores ~ 2010 Rohlfing

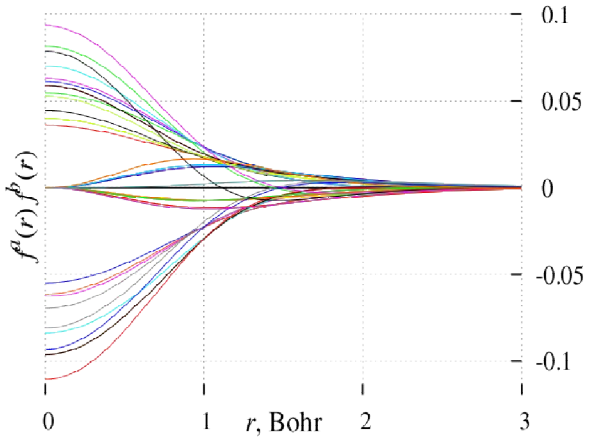
GW for typical small molecules of photovoltaics 2011 Blase et al.

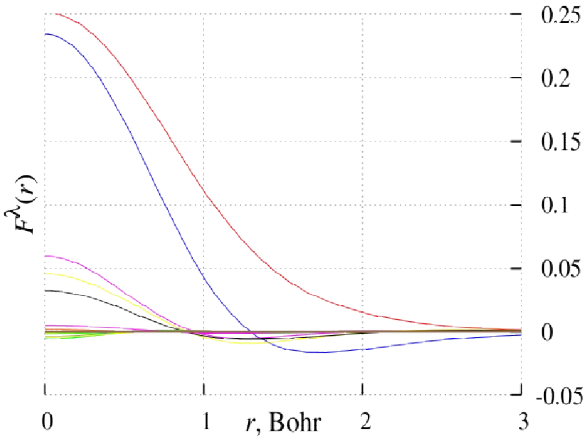
Construction of a local product basis

$$\psi(r,t) = \sum_a f^a(r) c_a(t)$$ LCAO 1927

$$n(r,t) = \psi^+(r,t)\psi(r,t) = \sum_{a,b} f^a(r) f^b(r) c_a^+(t) c_b(t)$$ « too many products » 1975







* no fitting functions
* O(N) operations
* locality

operations for one atom pair at a time

$$f^a(r) f^b(r) \sim \sum_\mu V_\mu^{ab} F^\mu(r)$$

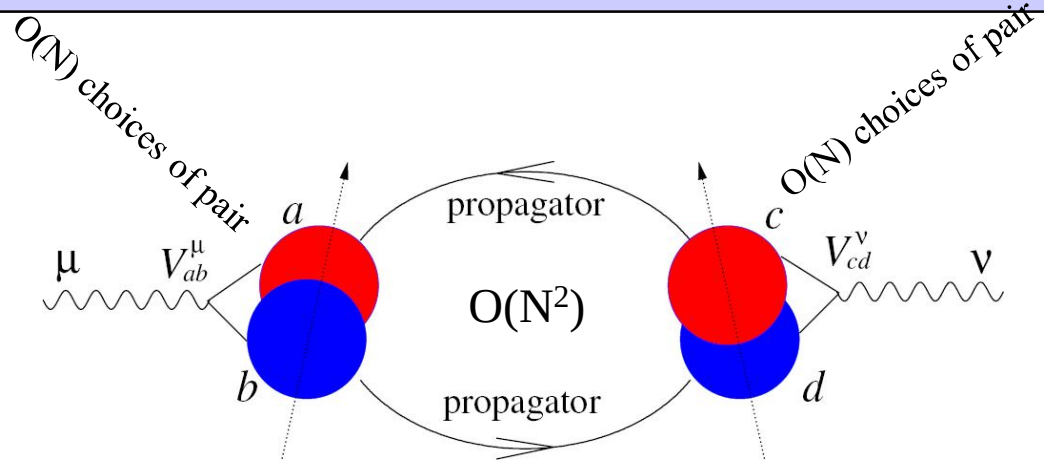
$$F^\lambda(r) = \sum_{a,b} X_{ab}^\lambda f^a(r) f^b(r)$$

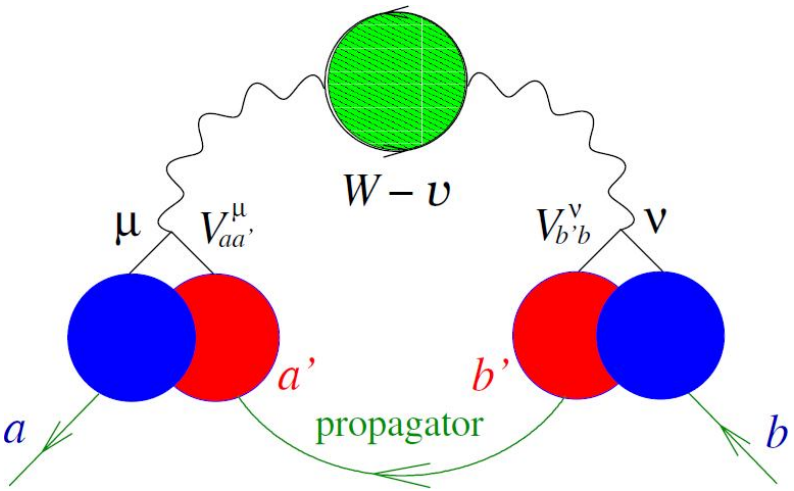
method of auxiliary functions
looses precision

Bebe-Lindenberg Cholesky deomposition
looses locality

basis from original space – thanks to Talman's algorithms

Locality in molecular interactions lowers complexity





$$\chi_{\mu\nu}(\omega) = -iTrV_\mu G(\omega)V_\nu G(-\omega)$$

$$\Sigma^{ab}(\omega) = iV_\mu^{aa'} G_{a'b'}(\omega)V_\mu^{b'b} W^{\mu\nu}(-\omega)$$

Given $G_{ab}(\omega)$ need $O(N^2)$ operations to find $\chi^0_{\mu\nu}$

Given $G_{ab}(\omega)$, $W^{\mu\nu}(\omega)$, need $O(N^2)$ operations to find $\Sigma_{ab}(\omega)$

→think locally, use $G_{ab}(\omega)$, $W^{\mu\nu}(\omega)$, $\Sigma_{ab}(\omega)$

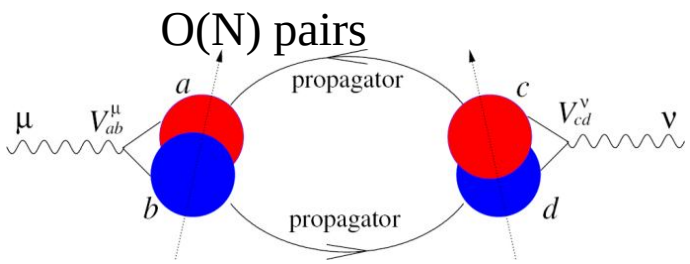
→avoid energy representation

→obtain $O(N^3)$ scaling

Reduction of dimension of products

too much memory in $\chi_{\mu\nu}(\omega)$

O(N)*O(N) frequency dependent matrix



« all products are equal, but some products are more equal than others »

George Orwell, 1945

$$\chi^0_{\mu\nu}(\omega) = \sum_{E,F} V^{EF}_{\mu} \frac{n_E - n_F}{\omega - (E - F)} V^{EF}_{\nu}$$

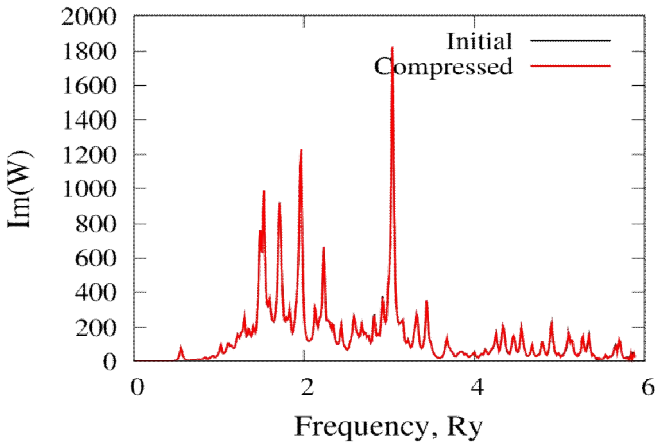
with

$$V^{EF}_{\mu} = \sum_{a,b} X^E_a V^{ab}_{\mu} X^F_b$$

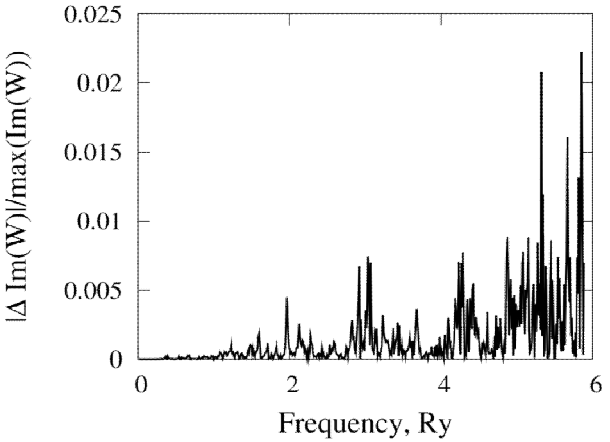
V_μ^{EF} are $O(N^2)$ vectors in O(N) dimensions

→ strong linear dependence of V_μ^{EF}

O(N) pairs {E,F} must suffice In practice, only ~ 1/10 of O(N) pairs important → 10^3 acceleration in screened Coulomb

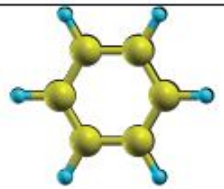
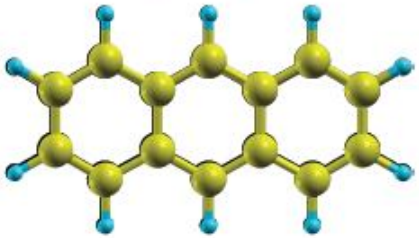


very small error in spectral function



Computational Results

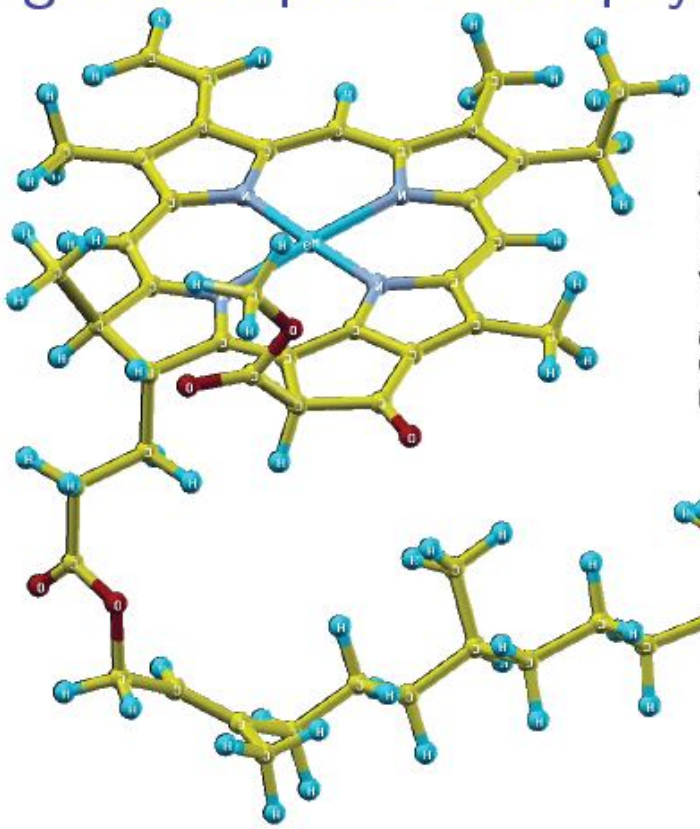
Examples: rings

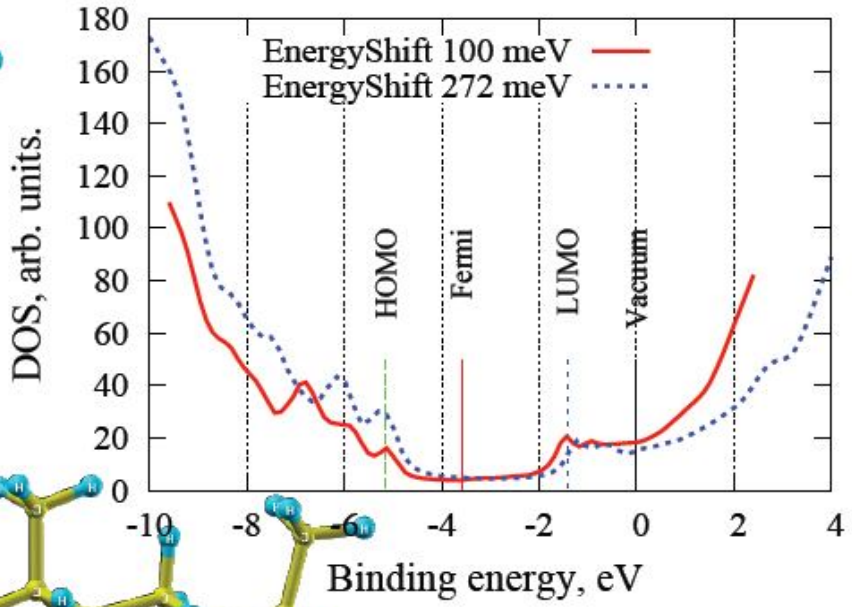
Picture	IP, eV	EA, eV	N_ω	Runtime, s
	8.82 (9.25)	-1.43 (-1.12)	64	977
	7.58 (8.14)	-0.15 (-0.19)	64	2075
	6.88 (7.44)	0.79 (0.530)	64	8434

GW 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.

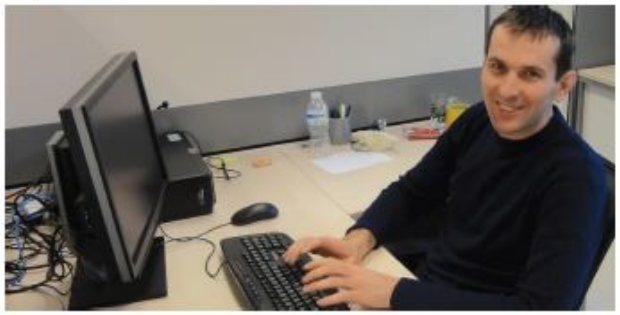
Computational results

Larger examples: chlorophyll-a





Program	IP, eV	EA, eV	Gap, eV	N_ω	Runtime, h
Our code	5.18	1.42	3.76	48	36

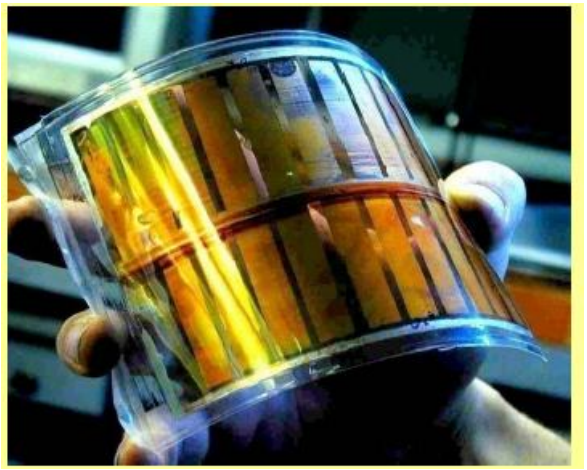


done on desktop computer

Conclusions

$O(N^3)$ implementation of Hedin's GW approach for organic molecules due to simple mathematical trick / GW+BS poised to replace TDDFT

Prediction of properties of organic molecules + their excitons before synthesis might help in organic photovolaics -



Apply same mathematical trick elsewhere in nano physics / nano chemistry

Thanks

James Talman, Western Ontario : algorithms + computer codes+correspondence

Arno Schindlmayr, Paderborn, **Xavier Blase,** Grenoble, **Michael Rohlfing,** Osnabrueck:
for correspondence

AND THANK YOU
FOR YOUR
ATTENTION!

more details by Peter Koval in HPC meeting