Efficient G_0W_0 using localized basis sets: a benchmark for molecules

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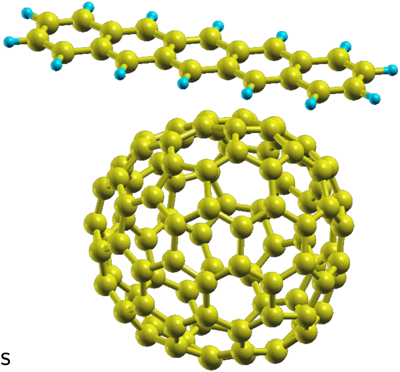
NanoSpain conference
San Sebastian, Spain, March 07–10 2017 (March 09)
`http://www.nanospainconf.org/2017`

Prerequisite for computer-aided nano structures design

! *LARGE* [number of atoms] usually implies MANY calculations, i.e. the calculations are better to be FAST.

- LCAO provides a basis for ab-initio, economical description of electronic structure; ANALYSIS is mostly straightforward.
- Locality is built-in into LCAO explicitly, allowing for *FAST* algorithms to be developed.
- This talk is about our efforts towards a fast, quantitave GWA

Outline of the talk



- Theory of GWA: simplistic
- Methods to realize GWA
- IPs for G2/97 test set
- IPs & EAs for acceptor molecules
- Analysis of core electron contributions to G_0W_0
- Conclusions

*GW*A as an extension of Hartree-Fock method

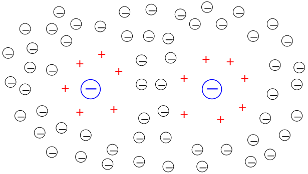
$$\text{Fock exchange: } \Sigma_x(\boldsymbol{r},\boldsymbol{r}') = -\sum_{n\in\text{occ}} \frac{\psi_n(\boldsymbol{r})\psi_n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

GW self-energy

$$\Sigma(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{\mathrm{i}}{2\pi}\int_{-\infty}^{\infty} d\omega'\, G(\boldsymbol{r},\boldsymbol{r}',\omega+\omega')W(\boldsymbol{r},\boldsymbol{r}',\omega')$$

$$W = v - v\,\chi_0\,W.$$

$$\chi_0(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{n,m} \frac{\psi_n(\boldsymbol{r})\psi_m(\boldsymbol{r})\psi_m(\boldsymbol{r}')\psi_n(\boldsymbol{r}')}{\omega-(E_m-E_n)}$$



Products of states appear $\psi_n(\boldsymbol{r})\psi_m(\boldsymbol{r})$.

Product of states in LCAO ansatz

LCAO ansatz for a molecule

$$\psi_n(\boldsymbol{r}) = \sum_a X_a^n \quad f^a(\boldsymbol{r} - \boldsymbol{R}_a) \quad ,$$

$$\text{Local} \qquad f^a(\boldsymbol{r}) \qquad = f^a_{l_a}(r) Y_{l_a,m_a}(\boldsymbol{r}).$$

⇒ Product of states $\psi_n(\boldsymbol{r})\psi_m(\boldsymbol{r}) = \sum_{a,b} X_a^n X_b^n \; f^a(\boldsymbol{r}) f^b(\boldsymbol{r})$

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$\Rightarrow$ Product of states $\psi_n(\boldsymbol{r})\psi_m(\boldsymbol{r}) = \sum_{a,b} X_a^n X_b^n \; f^a(\boldsymbol{r}) f^b(\boldsymbol{r})$

siesta $\longrightarrow$ MBPT_LCAO

$$H\psi_n(\boldsymbol{r}) = E\psi_n(\boldsymbol{r})$$

$$\chi_0(\boldsymbol{r}, \boldsymbol{r}', \omega) = \sum_{n,m} \frac{\psi_n(\boldsymbol{r})\psi_m(\boldsymbol{r})\psi_m(\boldsymbol{r}')\psi_n(\boldsymbol{r}')}{\omega - (E_m - E_n)}$$

Product of states in LCAO ansatz

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$\Rightarrow$ Product of states $\psi_n(\boldsymbol{r})\psi_m(\boldsymbol{r}) = \sum_{a,b} X_a^n X_b^n \; f^a(\boldsymbol{r}) f^b(\boldsymbol{r})$

LCAO is **too miser** for products of AOs $f^a(\boldsymbol{r})f^b(\boldsymbol{r})$: we cannot express the products within the same basis $\{f^i(\boldsymbol{r})\}$

$$f^a(\boldsymbol{r})f^b(\boldsymbol{r}) \neq \sum_i C_i^{ab} f^i(\boldsymbol{r})$$

Spatial degrees of freedom: product basis ansatz

…LCAO is parsimonious, but one constructs other basis set $\{F^{\mu}(\boldsymbol{r})\}$

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

All known procedures use localized product functions $F^{\mu}(\boldsymbol{r})$

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This is where LCAO can be cheaper than plane waves: $\mathrm{e}^a\mathrm{e}^b = \mathrm{e}^{a+b}$

$$\mathrm{e}^{\mathrm{i}\boldsymbol{G}\boldsymbol{r}}\mathrm{e}^{-\mathrm{i}\boldsymbol{G}'\boldsymbol{r}} = V_{\boldsymbol{G}''}^{\boldsymbol{G}\boldsymbol{G}'}\mathrm{e}^{\mathrm{i}\boldsymbol{G}''\boldsymbol{r}}$$

$O(N^2)$ elements in $V_{\boldsymbol{G}''}^{\boldsymbol{G}\boldsymbol{G}'} = \delta_{\boldsymbol{G}-\boldsymbol{G}',\boldsymbol{G}''}$

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

$O(N)$ elements in V_μ^{ab}

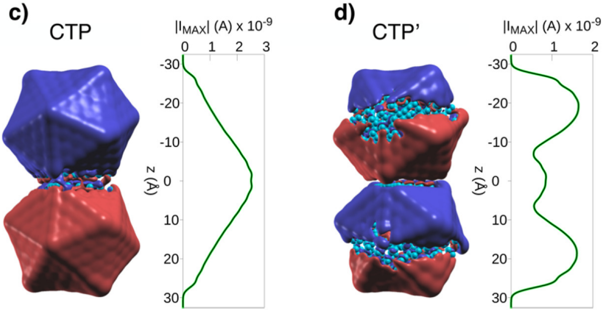
Compare with the revolutionary FFT: going from $O(N^2) \rightarrow O(N)$

Price to pay: implementation must use sparse matrices.

Product basis: (Marc Barbry yesterday)

We proposed a competitive solution for expanding density-like quantities for finite systems [1]

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



Imaginary part of the induced density and the corresponding modulus of the electron current flowing through the middle of the dimer 2 x Na_{380} [2]

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[1] PK, FM, DF, DSP, *J. Phys: Cond. Mat.* **28** (2016) 214001.

[2] FM, PK, MB, JA, DSP, *ACS Photonics* **3** (2016) 269.

Closed-shell molecules belonging to G2/97 test set

N	Molecule name	Hill sys.	Expt.	E_{PBE}	Δ_{PBE}	GW_{PBE}	GW_{HF}
001	Borane, Trifluoro-	BF_3	15.96	10.14	14.91	14.73	15.68
002	Borane, Trichloro-	BCl_3	11.64	7.69	11.00	10.65	11.56
003	Aluminum Trifluoride	AlF_3	15.45	9.81	14.00	14.14	15.03
004	Aluminum Trichloride	$AlCl_3$	12.01	8.06	11.13	11.03	11.90
005	Carbon Tetrafluoride	CF_4	14.70	10.41	14.73	14.87	16.04
006	Carbon Tetrachloride	CCl_4	11.69	7.65	10.62	10.48	11.50
007	Carbonyl Sulfide	COS	11.19	7.57	11.62	10.52	11.16
008	Carbon Disulfide	CS_2	10.09	6.85	10.32	9.37	9.95
009	Carbonic Difluoride	CF_2O	13.60	8.61	13.76	12.45	13.44
010	Silicon Tetrafluoride	F_4Si	16.40	10.81	14.74	15.16	16.24
011	Silane, Tetrachloro-	Cl_4Si	11.79	8.16	10.97	10.97	11.97
012	Nitrous Oxide	N_2O	12.89	8.41	13.29	11.88	12.57
	...	...	...	...	...	...	...
ME			0.00	-4.07	0.19	-0.65	0.06
MAE			0.00	4.07	0.44	0.74	0.27

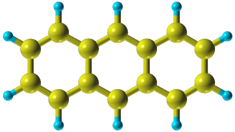
G2/97 test set contains 117 closed shell molecules

SIESTA basis set with extended AOs: Split DZP + two diffuse functions per angular momentum.

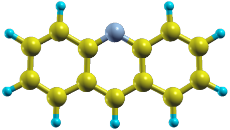
Acceptor molecules: reference

G_0W_0 done with FHI-aims package, all-electron starting point[3]

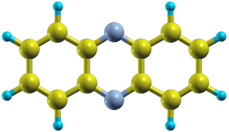
For 24 acceptor molecules. Examples



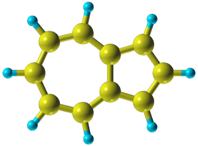
Anthracene



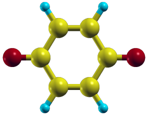
Acridine



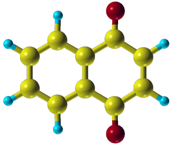
Phenazine



Azulene



Benzenoquinone



Naphtalenoquinone

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[3] JWK, XW, LG *etal* J. Chem. Theo. Comput. 12 (2016) 615-626

Acceptor molecules: basis sets for them (Federico's talk!)

- Very large basis sets were employed in FHI-aims,
  Tier4: [min]+4s4p4d3f2g
- We use correlation-consistent cc-pVXZ basis sets
  `https://bse.pnl.gov/bse/portal`
  core shells replaced by pseudo-potentials;
  occupied valence shells are replaced by solutions of radial Kohn-Sham equation ([min] in SIESTA)

Example of taken Gaussian exponents α_p for cc-pVTZ (X=3), carbon (Z=6)

$$f^o(\boldsymbol{r}) = \mathrm{e}^{-\alpha_p r^2} Y_{j_p m}(\boldsymbol{r})$$

Z	X	j_p	pAO	$-\alpha_p$
6	3	0	1	0.9059
6	3	0	2	0.1285
6	3	1	3	0.3827
6	3	1	4	0.1209
6	3	2	5	1.097
6	3	2	6	0.318
6	3	3	7	0.761

Acceptor molecules: Hartree-Fock, −HOMO

Molecule	AIMS	2ZP	3ZP	3ZP,f	4ZP	4ZP,f	5ZP	5ZP,f
anthracene	7.0643	7.4159	7.1648	7.1861	7.1064	7.1175	7.0792	7.0854
acridine	7.6708	8.0280	7.7730	7.7957	7.7168	7.7281	7.6887	7.6950
phenazine	8.1565	8.5275	8.2643	8.2869	8.2068	8.2181	8.1772	8.1836
azulene	7.1062	7.4293	7.1906	7.2149	7.1379	7.1497	7.1134	7.1196
BQ	11.224	11.559	11.305	11.329	11.244	11.257	11.215	11.223
NQ	9.8206	10.171	9.9095	9.9368	9.8530	9.8662	9.8241	9.8314
		...			...			
ME	0.0000	0.4031	0.0963	0.1147	0.0262	0.0350	0.0068	0.0020
MAE	0.0000	0.4031	0.0963	0.1147	0.0320	0.0400	0.0138	0.0135
Max	0.0000	0.6094	0.1766	0.1753	0.0530	0.0616	0.0740	0.0677

HF: a small discrepancy MAE = 0.0135 eV

Acceptor molecules: HF+G_0W_0, $-$HOMO

Molecule	AIMS	2ZP	3ZP	3ZP,f	4ZP	4ZP,f	5ZP	5ZP,f
anthracene	7.721	7.587	7.514	7.650	7.513	7.618	7.508	7.581
acridine	8.246	8.109	8.028	8.171	8.026	8.135	8.020	8.096
phenazine	8.682	8.559	8.479	8.624	8.474	8.585	8.467	8.543
azulene	7.672	7.538	7.488	7.628	7.493	7.598	7.490	7.562
BQ	11.27	11.58	11.56	11.58	11.49	11.54	11.37	11.51
NQ	10.23	10.13	9.993	10.14	10.01	10.10	9.987	10.06
		. . .			. . .			
ME	0.000	0.007	-0.150	-0.010	-0.172	-0.091	-0.186	-0.130
MAE	0.000	0.124	0.198	0.076	0.213	0.147	0.218	0.181
Max	0.000	0.474	0.296	0.434	0.288	0.416	0.324	0.494

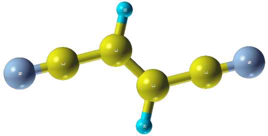
HF+G_0W_0: a small but sensible discrepancy MAE $=$ 0.181 eV.

Similar error in electron affinities MAE $=$ 0.241 eV.

Absence of core electrons cause such discrepancy ($\approx$ 0.18 eV) ?

Influence of core electrons

- All electron calculation with cc-pVDZ for Fumaronitrile



- Core electrons can influence Σ_c via G $\qquad \Sigma_c = \sum_n \frac{|\psi_n\rangle\langle\psi_n|}{\omega - \mathrm{i}\omega' - E_n} W_c(\mathrm{i}\omega')$

  Core electrons from G is negligible

- Core electrons can influence Σ_c via χ $\qquad \Sigma_c = G(1 - v\chi)^{-1} v\chi v$

		$\omega_{nm} = E_n - E_m$	
Contour def.	low + high	low	high
$\int$	-1.0504	-1.0035	-0.0470
Res	0.9818	0.9803	0.00153
$\int$ + Res	-0.0686	-0.0232	-0.04546

- Core electrons influence significantly the GW correction!

Conclusions & Problem to be solved

- $G_0 W_0$ can be computationally cheaper than Hartree-Fock
  (diagonal Σ_c, contour deformation, HOMO-LUMO only)
- Absence of core electrons causes a small, but *sensible* error.
- Small basis sets (3ZP,f) can be rather precise!

- Core-polarization potential (CPP) must be realized in our framework

Conclusions & Problem to be solved

- G_0W_0 can be computationally cheaper than Hartree-Fock (diagonal Σ_c, contour deformation, HOMO-LUMO only)
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- Small basis sets (3ZP,f) can be rather precise!
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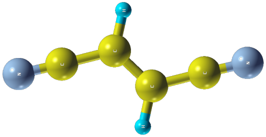
Thank you for your kind attention!

Calculations for Fumaronitrile

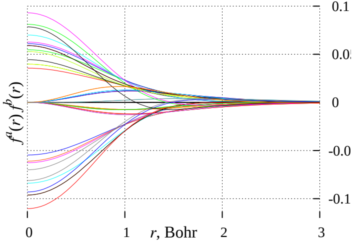
- All electron calculation with cc-pVDZ for Fumaronitrile



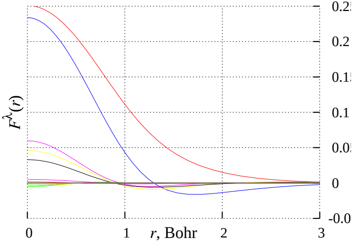
Molecule	AIMS	2ZP	3ZP	3ZP,f	4ZP	4ZP,f	5ZP	5ZP,f
Fumaronitrile	11.833	11.801	11.650	11.787	11.600	11.710	11.580	11.658

Implications of products of orbitals

- There are a lot of collinearity in products of orbitals $f^a(\boldsymbol{r})f^b(\boldsymbol{r})$



- However, there are linear combinations of products that would be mutually orthogonal

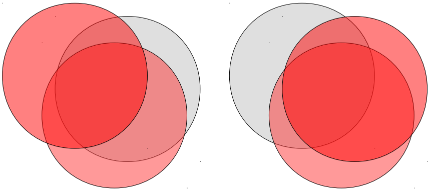


Dominant products

- Use the Coulomb metric

$$g^{ab,cd} \equiv \iint \frac{f^a(\boldsymbol{r})f^b(\boldsymbol{r})f^c(\boldsymbol{r}')f^d(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} d^3r d^3r'.$$

- A global metric $g^{ab,cd}$ of a big molecule is too big ⇒ lets diagonalize for each pair of atoms individually [4]



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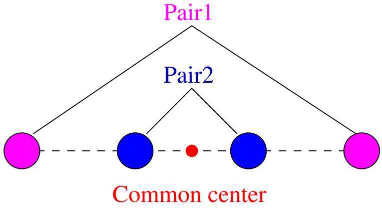
[4] D. Foerster, J. Chem. Phys. **128**, 034108 (2008).

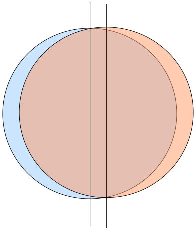
Dominant products: contra

- DP is too big comparing to PW…
- DP generates too overlapping functions
- DP can put extra functions where there are already functions

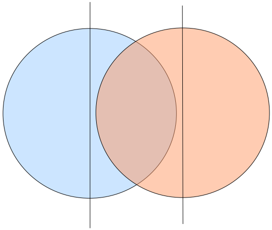


Atom-centered vertex: geometry problem

- Nuclei separations are normally smaller than orbital's spatial support

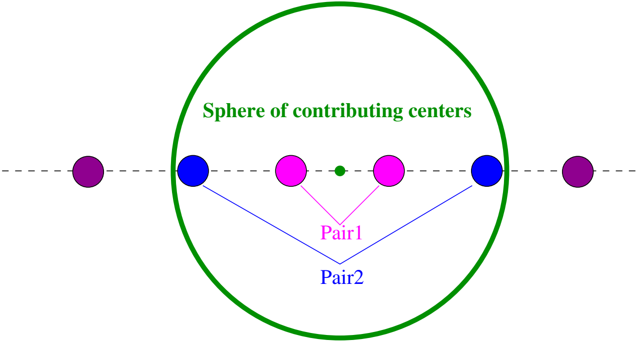


- If nuclei separations are comparable to the support then this product is small and not important…



Atom-centered vertex: geometry solution

- Metrod: put some basis functions exclusively at atom nuclei and define "contributing" atoms for a given orbital product.



- Corollary: functions get reused for Pair1 and Pair2.

Atom-centered vertex: contra and how to deal with it

- For atom-centered product basis we have $f^a(\boldsymbol{r})f^b(\boldsymbol{r}) = V^{ab}_{\mu}A^{\mu}(\boldsymbol{r})$
- For dominant products we have $f^a(\boldsymbol{r})f^b(\boldsymbol{r}) = V^{ab}_{\tilde{\mu}}F^{\tilde{\mu}}(\boldsymbol{r})$
- $N(A^{\mu}) \approx 1/4 \cdot N(F^{\tilde{\mu}})$ ☺
- but $N(V^{ab}_{\mu}) \approx 10 \cdot N(V^{ab}_{\tilde{\mu}})$ ☹ (Fock exchange 100x slower!)
- However, it is enormously more advantageous to factorize

$$V^{ab}_{\mu} = V^{ab}_{\tilde{\mu}}\, c^{\tilde{\mu}}_{\mu}$$

i.e.

Atom-centered = Dominant × Conversion

Atom-centered vertex: algebra

- We have dominant products $f^a(\boldsymbol{r}) f^b(\boldsymbol{r}) = V^{ab}_{\tilde{\mu}} F^{\tilde{\mu}}(\boldsymbol{r})$
- Let's express $F^{\tilde{\mu}}(\boldsymbol{r})$ in terms of atom-centered functions $A^{\mu}(\boldsymbol{r})$

$$F^{\tilde{\mu}}(\boldsymbol{r}) = c^{\tilde{\mu}}_{\mu} A^{\mu}(\boldsymbol{r})$$

Coulomb metric works best⇒

$$\int F^{\tilde{\mu}}(\boldsymbol{r}) \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} A^{\nu}(\boldsymbol{r}') dr\, dr' = c^{\tilde{\mu}}_{\mu} \int A^{\mu}(\boldsymbol{r}) \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} A^{\nu}(\boldsymbol{r}') dr\, dr'$$

- Invert square matrix $v^{\mu\nu}$: $c^{\tilde{\mu}}_{\mu} = R^{\tilde{\mu}\nu} v^{-1}_{\nu\mu}$.

$O(N^4)$ response function

```
$\chi^0_{\mu\nu}(\omega) = 0$
Loop over $\{mn\}$ chunks
    $A^{an}_{\tilde{\mu}} = V^{ab}_{\tilde{\mu}} X^n_b$
    $B^{mn}_{\tilde{\mu}} = X^m_a A^{an}_{\tilde{\mu}}$
    $B^{mn}_{\mu} = B^{mn}_{\tilde{\mu}} c^{\tilde{\mu}}_{\mu}$
    Loop over $\omega$
        $C^{mn}_{\mu} = B^{mn}_{\mu} \frac{f_n - f_m}{(\omega - (E_m - E_n))}$
        $\chi^0_{\mu\nu}(\omega) = \chi^0_{\mu\nu}(\omega) + \sum_{mn} B^{mn}_{\mu} C^{mn}_{\nu}.$
```

The algorithm to compute the response function for atom-centered product basis using sum-over-states expression. Critical part of the algorithm is the computation of the molecular-orbital product vertex B^{mn}_{μ}. It is computed utilizing the factorization of the atom-centered product vertex according to equation

$V = \tilde{V} \cdot c$

This is much faster than time-frequency domain techniques...