Compression of products of atomic orbitals – applied to TDDFT and GW for molecules

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Organic semiconductors / solar devices. Want properties of constituent organic molecules before synthesis \rightarrow Need better theoretical methods



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

Compression of products of atomic orbitals

$$\psi(r,t) = \sum_{a} f^{a}(r)c_{a}(t) \quad \text{LCAO 1927} \quad \text{method of auxiliary functions 1980} \\ \text{looses precision} \\ n(r,t) = \psi^{+}(r,t)\psi(r,t) = \sum_{a,b} f^{a}(r)f^{b}(r)c_{a}^{+}(t)c_{b}(t) \\ \text{Bebe-Lindenberg Cholesky} \\ \text{looses locality} \\ g^{ab,cd}_{Coulomb} = \int f^{a}(r)f^{b}(r)\frac{1}{|r-r'|}f^{c}(r')f^{d}(r')drdr' \\ g^{ab,cd}_{Coulomb} X^{\lambda}_{cd} = \lambda X^{\lambda}_{ab} \text{ many small functions} \\ F^{\lambda}(r) = \sum_{a,\delta} X^{\lambda}_{ab}f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) \sim \sum_{\lambda>\varepsilon} X^{\lambda}_{ab}F^{\lambda}(r) \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}(r)f^{b}(r) = \sum_{a,\delta} f^{a}(r)f^{b}(r) \text{ for each pair} \\ f^{a}($$

Application 1: Petersilka-Gossman-Gross equation for spectra

$$\chi(r,r',\omega) = \frac{1}{\chi_0^{-1} - f_{Hxc}}$$

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Figure 13. The relaxed geometry of the chlorophyll-a molecule obtained with the SIESTA package using a DZP basis set.



Figure 14. Low frequency absorption spectrum of chlorophyli-a.

code is O(N³) because of locality of V_{μ}^{ab}

competitive with other TDDFT codes

Application 2: Hedin's GW for molecules in $O(N^3)$ operations

- ~ 1965 Hedin's equations, GW = zeroth order approximation
- ~ 1980 used for gaps of semiconductors in 1980
- ~ 2000 application to molecules Louie+Rohlfing

GW + BS instead of DFT + TDFFT for organic molecules excitonic effects missed by TDDFT

step 1:
screened Coulomb
$$W^{\mu\nu}(\omega) = \frac{1}{\delta^{\mu}_{\alpha} - v^{\mu\beta}\chi^{(0)}_{\beta\alpha}(\omega)} v^{\alpha\nu}$$

$$W^{\mu\nu}(\omega) = \frac{1}{\delta^{\mu}_{\alpha} - v^{\mu\beta}\chi^{(0)}_{\beta\alpha}(\omega)} v^{\alpha\nu}$$

step 2: selfenergy

$$\begin{array}{lcl} \Sigma^{ab}(t) & = & i V^{aa'}_{\mu} G^{0}_{a'b'}(t) V^{b'b}_{\nu} W^{\mu\nu}(t) \\ G^{-1}_{ab}(\omega) & = & G^{-1}_{0ab}(\omega) - \Sigma_{ab}(\omega) \end{array}$$

many operations O(N²) from locality

But : requires too much memory



a propagator

Non local reduction of the dimension of the space of products

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

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

with

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

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



« all products are equal, but some products are more equal than others » George Orwell, 1945

 V_{μ}^{EF} are O(N²) vectors in O(N) dimensions

 \rightarrow strong linear dependence of V_µ^{EF}

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



Conclusions

local basis in the space of orbital products of LCAO method gives

- First efficient solution of Petersilka-Gossmann-Gross equation
- First O(N³) implementation of Hedin's GW approximation for molecules should help in organic photovoltaics



details \rightarrow Peter Koval's talk

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