

# Extension of LCAO to excited states: non interacting response and molecular spectra

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ANR



Evora 16/09/2009

## Petersilka–Gossmann–Gross equation: reminder

- ▶ Interacting response  $\chi$  satisfies<sup>1</sup>

$$\chi^{-1} = \chi_0^{-1} - \Sigma$$

$$\Sigma = \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta V_{xc}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \text{ still to be determined.}$$

- ▶ Interacting polarizability  $P^{ik}(\omega) = d^i \chi d^k$  is the goal.

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<sup>1</sup>Petersilka, Gossmann and Gross, Phys. Rev. Lett., **76** (1996) 1212

Construction of  $\chi_0$  from its spectral function

- ▶ Ansatz  $f_a(\mathbf{r})f_b(\mathbf{r}) = \sum_\mu V_{ab}^\mu F_\mu(\mathbf{r})$  leads to

$$\chi_{\mu\nu}^0(\omega) = \sum_{E < 0, F > 0} \sum_{pqrs} \chi_E^p \chi_F^q \chi_E^r \chi_F^s \frac{V_{pq}^\mu V_{rs}^\nu}{\omega - (E - F) + i\epsilon}$$

- ▶ Spectral function  $\rho_{\mu\nu} = \text{Im}\chi_{\mu\nu}^0$

$$\rho_{\mu\nu}(\lambda) = \sum_{E < 0, F > 0} \delta(\lambda - (E - F)) \sum_{pqrs} \chi_F^q \chi_F^s \chi_E^p \chi_E^r V_{pq}^\mu V_{rs}^\nu$$

- ▶  $\rho_{\mu\nu}(\lambda)$  via convolution

$$\rho_{\mu\nu}(\lambda) = \sum_{pqrs} \rho_{qs}^-(F) * \rho_{pr}^+(\lambda - F) V_{pq}^\mu V_{rs}^\nu$$

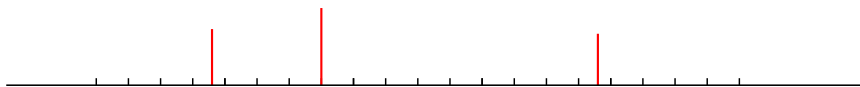
electronic spectral function  $\rho_{qs}^-(F < 0) = \sum_\nu \delta(\nu - F) \chi_F^q \chi_F^s$

- ▶ Discretise  $\lambda = E - F \Rightarrow \chi_{\mu\nu}^0(\omega)$  is again convolution

$$\chi_{\mu\nu}^0(\omega) = \sum_\lambda \rho_{\mu\nu}(\lambda) \cdot (\omega - \lambda + i\epsilon)^{-1}$$

## Spectral function: discretisation

- ▶ FFT needs equidistant grid, but energy differences do not fit any equidistant grid



- ▶ Solution: 'occupy' adjacent nodes



- ▶ Result:  $\chi_0$  exact up to discretisation

Coulomb self energy  $\Sigma_{\text{H}}$ : sketch of basis

- ▶ In the basis of dominant products  $\Sigma_{\text{H}}$  reads

$$\Sigma_{\text{H}}^{\mu\nu} = \int dr dr' F^{\mu}(r) |r - r'|^{-1} F^{\nu}(r').$$

Dominant functions  $F^{\mu}(r)$  are either local or bilocal.



- ▶ Generally  $F^{\mu}(r) = \sum_j F_j^{\mu}(r') S_{jm}(\mathbf{R}_{\mu} r')$ ,  $r' = r - \mathbf{C}_{\mu}$ .
- ▶ Radial functions  $F_j^{\mu}(r')$  are given on a logarithmic grid.

Coulomb self energy  $\Sigma_{\text{H}}$ : method

- ▶  $\Sigma_{\text{H}}^{\mu\nu}$  can be reduced to a sum over elementary Coulomb interactions

$$E_{jm,j'm'}(\mathbf{c}, \mathbf{c}') = \int d\mathbf{r} d\mathbf{r}' \frac{g_{jm}(\mathbf{r} - \mathbf{c}) g_{j'm'}(\mathbf{r}' - \mathbf{c}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$g_{jm}(\mathbf{r}) = g_j(r) S_{jm}(\mathbf{r})$$

- ▶  $E_{jm,j'm'}(\mathbf{c}, \mathbf{c}') = \langle g_{jm} | p^{-2} | g_{j'm'} \rangle$  in momentum space.
- ▶ Conversion to momentum space by Talman's transform<sup>2</sup>.
- ▶ No 4-center integrals involved :-)

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<sup>2</sup>Talman J. D., Comput. Phys. Commun. **180** 332 (2009)

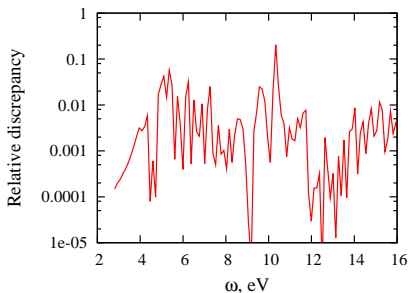
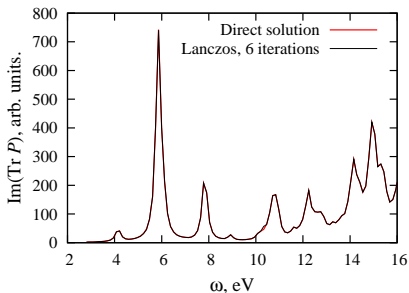
## Dynamical polarizability: CPU costs

- ▶ Non interacting response  $\chi_0$   $O(N^2 N_\omega)$
  - ▶ Self energies  $\Sigma_H, \Sigma_{xc}$   $O(N)$
  - ▶ Solving  $\chi^{-1} = \chi_0^{-1} - \Sigma$   $O(N^3 N_\omega)$
  - ☺ Fortunately  $P^{ik} = d^i \chi d^k$  can be calculated iteratively,  
thanks to a special Lanczos method  $O(N^2 N_\omega)$
- 
- ✓ Interacting polarizability  $P^{ik}$ , total CPU  $O(N^2 N_\omega)$



# Performance of iterative method: naphthalene $C_{10}H_8$

How well does the iterative method work?



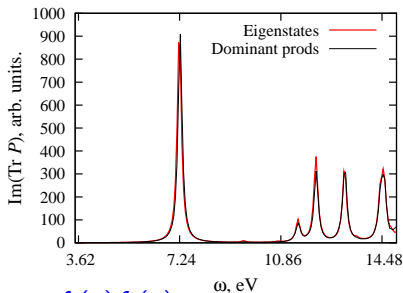
- ▶ 898 dominant products  $\rightarrow$  6 Krylov vectors.
- ▶ CPU cost is dramatically reduced.

# Performance of dominant products basis: benzene $C_6H_6$

How many dominant products  $F^\mu(\mathbf{r})$  needed?

- ▶ Compare with exact result in the conventional basis.
- ▶  $\chi_{EF,PQ}^0$  is diagonal ☺, but interaction kernel costs  $O(N^3)$  ☹

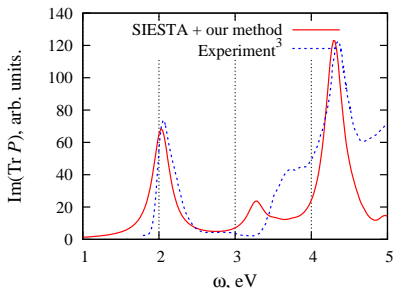
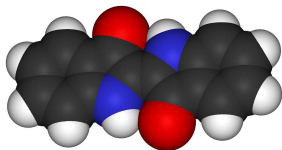
interaction kernel  $K$  via  
 self energy  $\Sigma$ , vertex  $V$   
 and density matrix  $D$   
 $K = (DV)\Sigma(V^T D)$



- ▶ Original basis 5832 products  $f_a(\mathbf{r})f_b(\mathbf{r})$   
 Dominant basis 1236 products  $F^\mu(\mathbf{r})$ .

# Comparison with experiment: indigo dye $C_{16}H_{10}N_2O_2$

How good can be comparison with experiment<sup>3</sup> ?

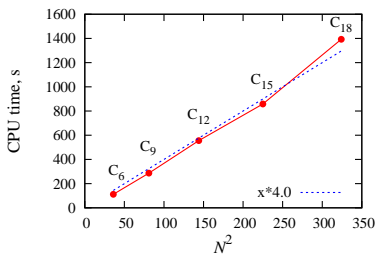
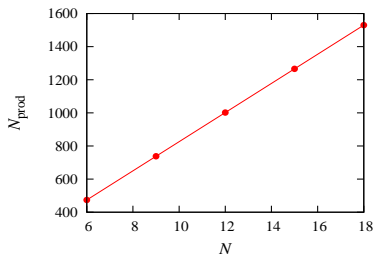


- ▶ Original basis 48050 products  $f_a(\mathbf{r})f_b(\mathbf{r})$   
Dominant basis 2831 products  $F^\mu(\mathbf{r})$ .
- ▶ One hour on 8 core machine; 11 GByte RAM.

<sup>3</sup>Ross Brown, IPREM unpublished (2008)

Scaling of CPU time: carbon chains  $C_n$ 

Does the approach really scale as  $N^2 N_\omega$  ?



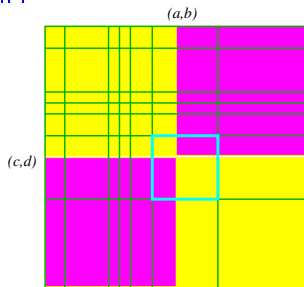
- ▶ Size of matrix is proportional to the number of atoms  $N$ ,  $O(N^2)$  non zero elements.
- ▶ Each element costs  $O(N_\omega)$  because of FFT.

# Parallelization approach versus runtime

Timing for benzene example, sequential version

Task	Time, s	Parallelization
Basis of dominant products	10	OMP
Self energies	160	OMP+MPI
Response function	1100	OMP+MPI
Excitation spectrum	120	OMP+MPI

- ▶ Easy to parallelize
- ▶ OMP mostly done
- ▶ MPI for response function  $\chi_0$  and polarizability  $P_{ik}(\omega)$  together



## Conclusions and Outlook

- ✓  $\chi^0$  is constructed in  $O(N^2 N_\omega)$  operations.
- ✓  $\Sigma$  is cheap in dominant products: no 4-center integrals
- ✓  $P^{ik}$  in  $O(N^2 N_\omega)$  operations due to Lanczos.
- ▶ The algorithm is easily parallelizable
  - ⊕ Memory bottleneck made less severe with MPI.
- ▶  $\chi^0$  in the basis of dominant products will be useful in applications to GW and Bethe–Salpeter.

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