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non interacting response and molecular spectra

Peter Koval, Olivier Coulaud, Dietrich Foerster

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Evora 16/09/2009

Petersilka–Gossmann–Gross equation: reminder

- ▶ Interacting response χ satisfies¹

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

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

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

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

Construction of χ_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: χ_0 exact up to discretisation

Coulomb self energy Σ_{H} : sketch of basis

- ▶ In the basis of dominant products Σ_{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 Σ_{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 transform².
- ▶ No 4-center integrals involved :-)

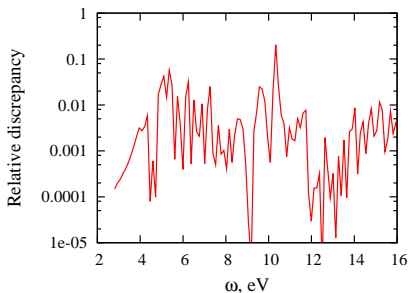
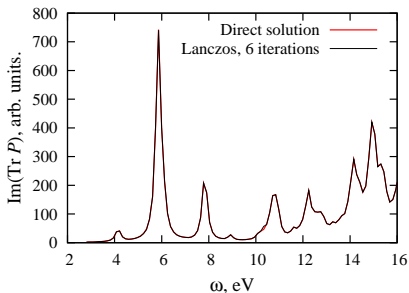
²Talman J. D., Comput. Phys. Commun. **180** 332 (2009)

Dynamical polarizability: CPU costs

- ▶ Non interacting response χ_0 $O(N^2 N_\omega)$
 - ▶ Self energies Σ_H, Σ_{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?



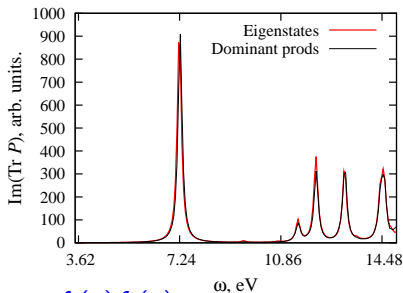
- ▶ 898 dominant products \rightarrow 6 Krylov vectors.
- ▶ CPU cost is dramatically reduced.

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 $O(N^3)$ ☹

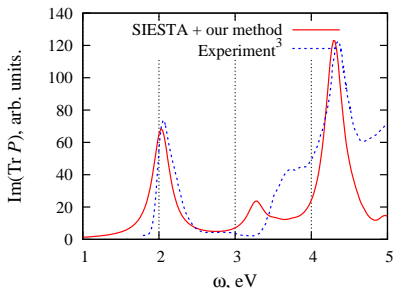
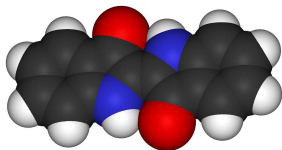
interaction kernel K via
 self energy Σ , vertex V
 and density matrix D
 $K = (DV)\Sigma(V^T D)$



- ▶ 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 experiment³ ?

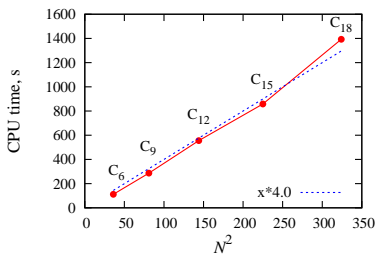
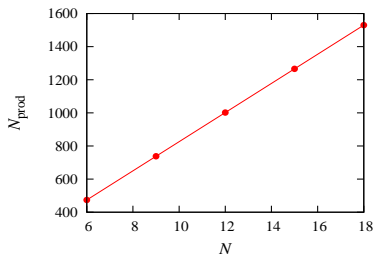


- ▶ Original basis 48050 products $f_a(\mathbf{r})f_b(\mathbf{r})$
Dominant basis 2831 products $F^\mu(\mathbf{r})$.
- ▶ One hour on 8 core machine; 11 GByte RAM.

³Ross Brown, IPREM unpublished (2008)

Scaling of CPU time: carbon chains C_n

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



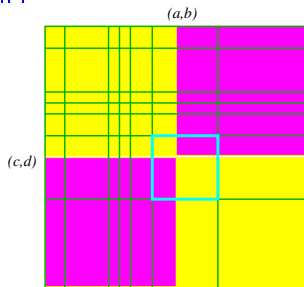
- ▶ Size of matrix is proportional to the number of atoms N , $O(N^2)$ non zero elements.
- ▶ Each element costs $O(N_\omega)$ because of FFT.

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 χ_0 and polarizability $P_{ik}(\omega)$ together



Conclusions and Outlook

- ✓ χ^0 is constructed in $O(N^2 N_\omega)$ operations.
- ✓ Σ 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.
- ▶ χ^0 in the basis of dominant products will be useful in applications to GW and Bethe–Salpeter.

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