1. Introduction

- Matrix product states (MPS) are the natural variational ansatz for 1D non-critical systems.
- They can capture all relevant entanglement, at a much lower cost than exact diagonalization (ED).
- Chemists are interested in the non-linear optical (NLO) properties of quasi-1D systems.
- MPS calculations of NLO properties allow to:
  - Assess approximate methods
  - Extrapolate highly accurate (quasi-ED accuracy) thermodynamic limit (TDL) data

2. Quantum chemistry vs. condensed matter

- The theory of quantum chemistry is known. In the non-relativistic regime & for quasi-instantaneous electron motion (Born-Oppenheimer approximation):
  $$\hat{H} = \sum_{i<j} Z_i \delta_{i-j} + \sum_{i} \left[ F_i + e \hat{a}_i^\dagger \hat{a}_i \right]$$
- To allow implementation on a computer, a finite basis set has to be chosen as orbital degrees of freedom.
- The Hamiltonian can then be written in discrete quantization as:
  $$\tilde{H} = \sum_{i,j} \left[ \hat{a}_i^\dagger \hat{a}_j + \frac{1}{2} \sum_{l} \hat{c}_l^\dagger \hat{c}_l \delta_{i-j-l} \right]$$
- Due to the general two-body interaction, it is hard to keep track of all matrix elements (in contrast to condensed matter systems). Several tricks exist though.

3. SU(2) ⊗ U(1) invariant MPS

- Spin and particle number are conserved for chemical systems under influence of an electric field.
- Global symmetry can be imposed on the MPS by requiring that each tensor operator of the imposed symmetry groups:
  $$M_{\alpha \beta} = \sum_{\nu} \left( \gamma \nu \right)_{\alpha \beta} \left( \nu \gamma \right)_{\alpha \beta}$$
- Finite field extrapolations

4. Convergence

- MV[1]ₙₜ corresponds to a virtual dimension of (1 + 1)MV[1]ₙₜ in a non-symmetry adapted MPS.
- The MPS ground state energy follows
  $$\ln(E_0 - E_{\text{exact}}) = -\sigma (\ln N)$$
  where N is the total virtual dimension.

5. Finite field extrapolations

- E.g. the longitudinal static 2nd hyperpolarizability γ₅₂₂₂

6. The raw data

- 3 H-chain configurations: $R_l = 2 \text{ a.u.}$ and $R$ varies
  $$H_{R_l} H_{R_l} H_{R_l} \rightarrow H_{R_l} H_{R_l} H_{R_l}$$
- Different chain lengths: $H_{2s}$ ($M$ $H_2$ molecules)
- 5 levels of theory: HF, MP2, CCSD, CCSD(T) & MPS
- 2 basis sets: STO-6G & 6-31G (Löwdin transformed for locality)

7. CCSD(T) accuracy

- Look at the relative deviation
  $$\delta_{\gamma_{\text{CCSD(T)}}}(M) = \left( \frac{\gamma_{\text{CCSD(T)}}(M) - \gamma_{\text{CCSD(T)}}(M + 1)}{\gamma_{\text{CCSD(T)}}(M) - \gamma_{\text{CCSD(T)}}(M + 1)} \right) \times 100\%$$
- Large R → well separated $H_2$ molecules
- Small R → delocalized electrons
- When going from large to small R (small to large electron delocalization), CCSD(T) begins to fail as it cannot describe the correlation of a large number of electrons correctly. CCSD(T), the current reference for NLO properties, can hence be inadequate.

8. TDL data extrapolation

- γ₅₂₂₂(M) is often proposed.
  $$\gamma_{\text{MPS}}(M) \rightarrow \gamma_{\text{MPS}}(\infty)$$
- a(M) depends on M. For small M, the possibility for optical excitations opens and a(M) is large. For large M, the chain can fully contain optical excitations and a(M) tends to 1.
- Estimate the exponent:
  $$\tilde{a}(M) = \left( \frac{\ln^2(\gamma_{\text{MPS}}(M)) - \ln^2(\gamma_{\text{MPS}}(M + 1))}{\ln(\gamma_{\text{MPS}}(M)) - \ln(\gamma_{\text{MPS}}(M + 1))} \right)$$
- If $a(M) \approx 1$, it’s reasonable to assume:
  $$\gamma_{\text{MPS}}(M) \approx a + \frac{a_1}{M} + \frac{a_2}{M^2} + \frac{a_3}{M^3}$$
- From this equation:
  $$\Delta \gamma_{\text{MPS}}(\infty) = \left( \frac{\gamma_{\text{MPS}}(M) - \gamma_{\text{MPS}}(M + 1)}{a_1 M^{-1} + a_2 M^{-2} + a_3 M^{-3}} \right)$$

9. Extrapolated MPS data

- Quantity | Basis set | $\gamma_{\text{MPS}}(M)/M \Delta \gamma_{\text{MPS}}(M)$
- $\alpha_{\text{CCSD(T)}}$ | [a.u.] | $\left[ \frac{\text{eV}}{\text{amu}} \right]$
- 3.0 STO-6G 3.0 9.46 9.46
- 3.0 6-31G 3.0 9.30 9.30
- 6-31G 3.0 10.4 10.4
- 3.0 6-31G 3.0 4.82 4.82
- 3.0 6-31G 3.0 8.25 8.26

Acknowledgements
- Research Foundation Flanders (S.W.)
- Swiss National Science Foundation (P.A.L.)
- NSERC (P.W.A.)
- Stevin Supercomputer Infrastructure at Ghent University
- Sharcnet ñ Compute Canada national HPC platform