The Present …

Second example: the Cr_2 puzzle resolved

H. R. Larsson, H. Zhai, C. J. Umrigar, G. K.-L. Chan, JACS, 144, 15932 (2022)

Cr_2 potential energy curse...

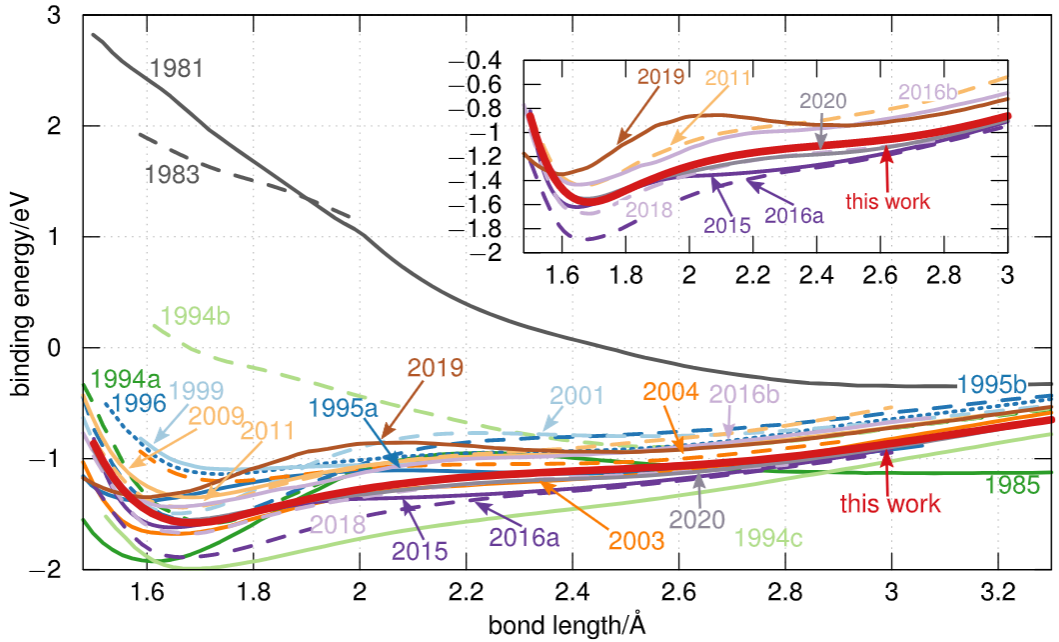


FIG. 1. Some of the simulated potential energy curves (PECs) of the chromium dimer that are available in the literature. The PECs are labeled by the study's year. The red curve marks the PEC from this work. The inset shows selected PECs from 2011 onwards. (List of references in SI).

Short and weak bond with a narrow minimum around 1.68 Å & extended shelf at around 2.5 Å.
→ Cr 4s and 3d AOs different in size, with the minimum corresponding mostly to 3d orbital interactions and the shelf to 4s orbital interactions.

A unique bonding and its consequences

- Complex electronic structure arises from interplay of two types of electron correlation
  - type I — “static correlation”: spin-coupling of the 12 valence electrons (3*d* + 4*s* shells)

energy-driven degeneracy

  - type II — "spatial correlation / dynamic correlation”: need for a large basis to capture excitations involving non-valence orbitals

overlap-driven degeneracy

—> formation of 3*d*-3*d* bonds requires the 3*p* electrons to move out of the same spatial region by exciting to higher lying orbitals

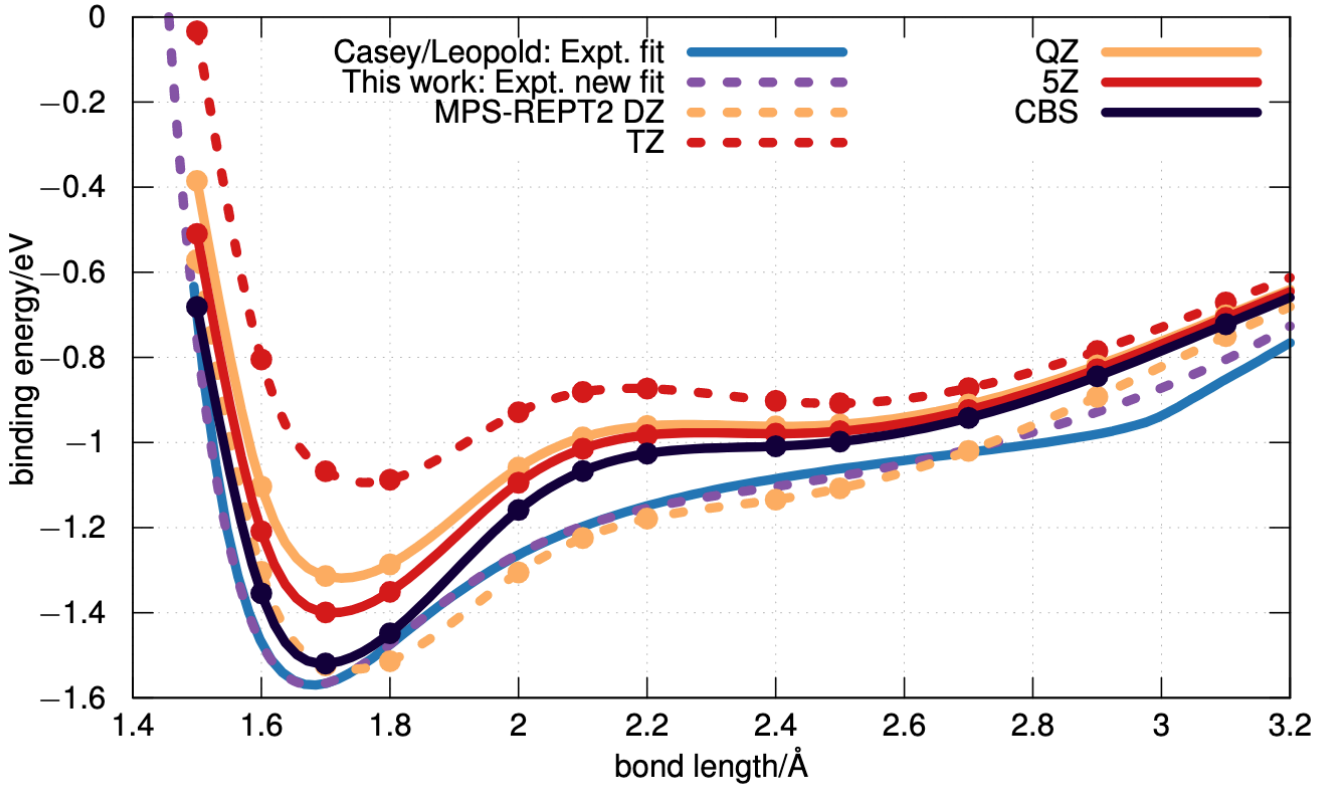
- **Challenge:**
  “The problem is computationally challenging because **both the static and dynamic correlation** must be computed sufficiently well even for a qualitatively reasonable description.”

Computational approach I

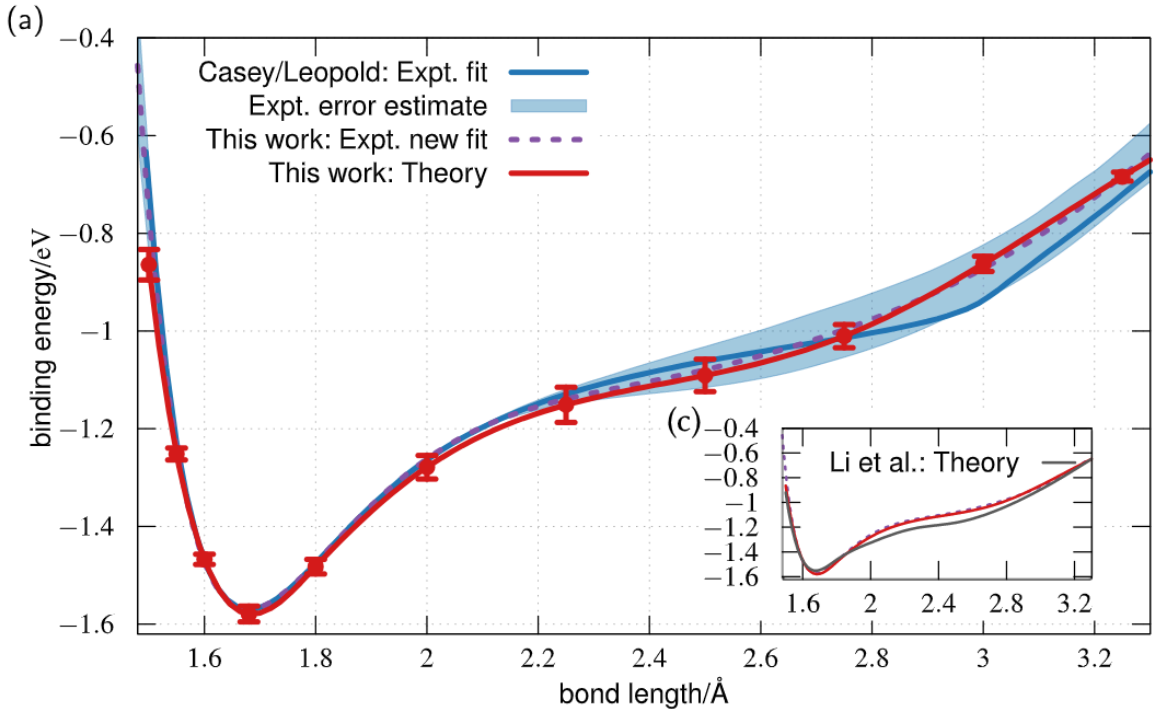
$$\Delta E = \Delta E_{\mathrm{PDZ}}(\text{“exact”}) + \Delta E_{\mathrm{CBS}}(\text{MPS-REPT2}) - \Delta E_{\mathrm{DZ}}(\text{MPS-REPT2})$$

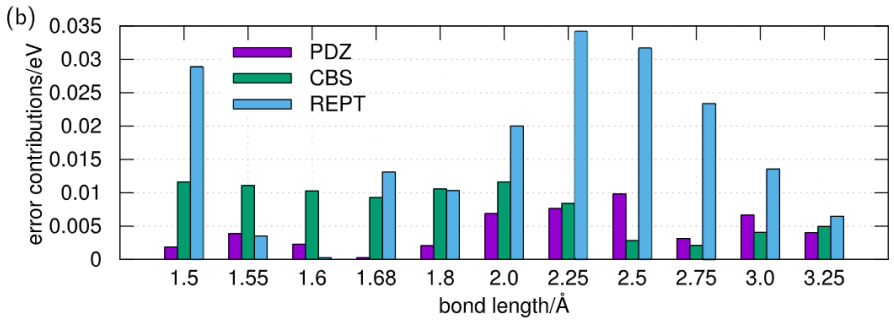
- Static electron correlation: CAS(28e,76o)/cc-pVDZ-DK
  - Heat-Bath CI (selective CI)
  - DMRG (with huge bond dimension!)
- Dynamic electron correlation: CAS(12,12)/MRPT2
  - PT2 correlation of 3*s* and 3*p* inner-valence shells
  - all secondary shells considered
- Basis set: MRPT2 with cc-pv*N*Z-DK (*N*=2,3,4,5) with extrapolation to CBS limit

Computational approach II



New state-of-the-art





$$\epsilon = \sqrt{\epsilon_{\text{PDZ}}^2 + \epsilon_{\text{CBS}}^2 + \epsilon_{\text{REPT}}^2},$$

with the individual error contributions as defined above,

$$\epsilon_{\text{PDZ}} = |\Delta E(\text{SHCI}) - \Delta E(\text{DMRG})|/2,$$
$$\epsilon_{\text{CBS}} = \sigma_{\text{CBS}},$$
$$\epsilon_{\text{REPT}} = |\Delta E(\text{MPS-REPT2}) - \Delta E[\text{UCCSD(T)}]|/2.$$

Thinking outside the box

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$\left|\Psi\right\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} \left|k_1\right\rangle \otimes \left|k_2\right\rangle \otimes \ldots \otimes \left|k_L\right\rangle$$

- Could we do better or, say, something else?

Thinking outside the box

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$|\Psi\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_L\rangle$$

- Could we do better or, say, something else?
  - select many-particle basis sets / configurations / etc. based on some energy/weighting criteria:
    → selected CI approaches
    → difference dedicated CI,
    → many-body expansion FCI
    → ...
  - find “best” many-particle basis set based on correlations among orbitals → **DMRG**

Thinking outside the box

Standard CI approach

- CI-type diagonalization for a **preselected** set of many-particle basis states

$$|\Psi\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_L\rangle$$

DMRG

- **Determine** CI coefficients from correlations among orbitals

$$|\Psi\rangle = \sum_{k_1,k_2,\ldots,k_L} c_{k_1,k_2,\ldots,k_L} |k_1\rangle \otimes |k_2\rangle \otimes \ldots \otimes |k_L\rangle$$

- Local space k_l of l-th spatial orbital is of dimension $d = 4$:

$$k_l = \{ |\uparrow\downarrow\rangle \; |\uparrow\rangle, |\downarrow\rangle, |0\rangle \}$$

From a CI wave function to Matrix Product States (MPS): Optimising an MPS with the DMRG algorithm

Optimising an MPS wave function with the DMRG algorithm

- Optimisation algorithm
- Parameters that determine DMRG accuracy

U. Schollwöck, The density-matrix renormalization group in the age of matrix product states, Annals of Physics, 326 (2011) 96–192.

Some reviews on about 20 years of DMRG in quantum chemistry

- Ö. Legeza *et al.*, Lect. Notes Phys., 739, 653 (2008)
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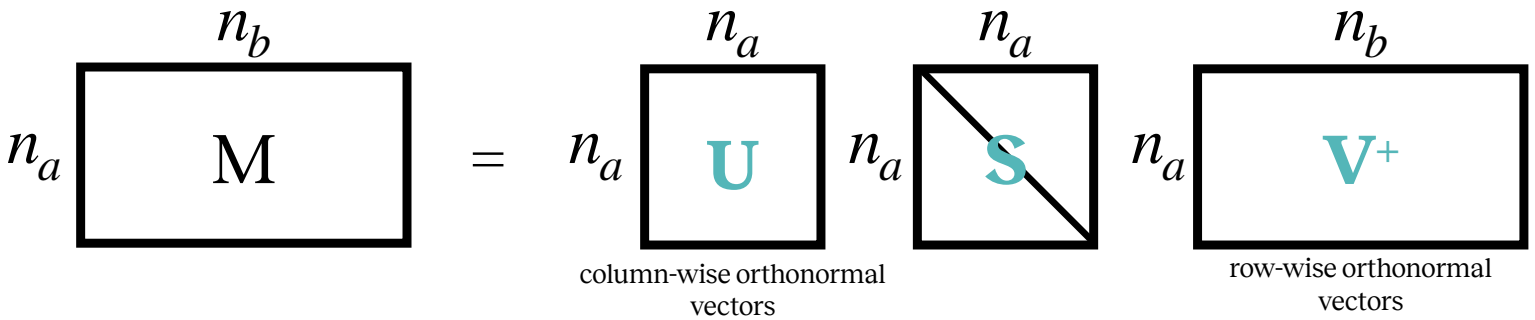
Intermission: singular value decomposition

- Singular value decomposition (SVD) of a matrix $\mathbf{M}$ $(n_a \times n_b)$

Remember?

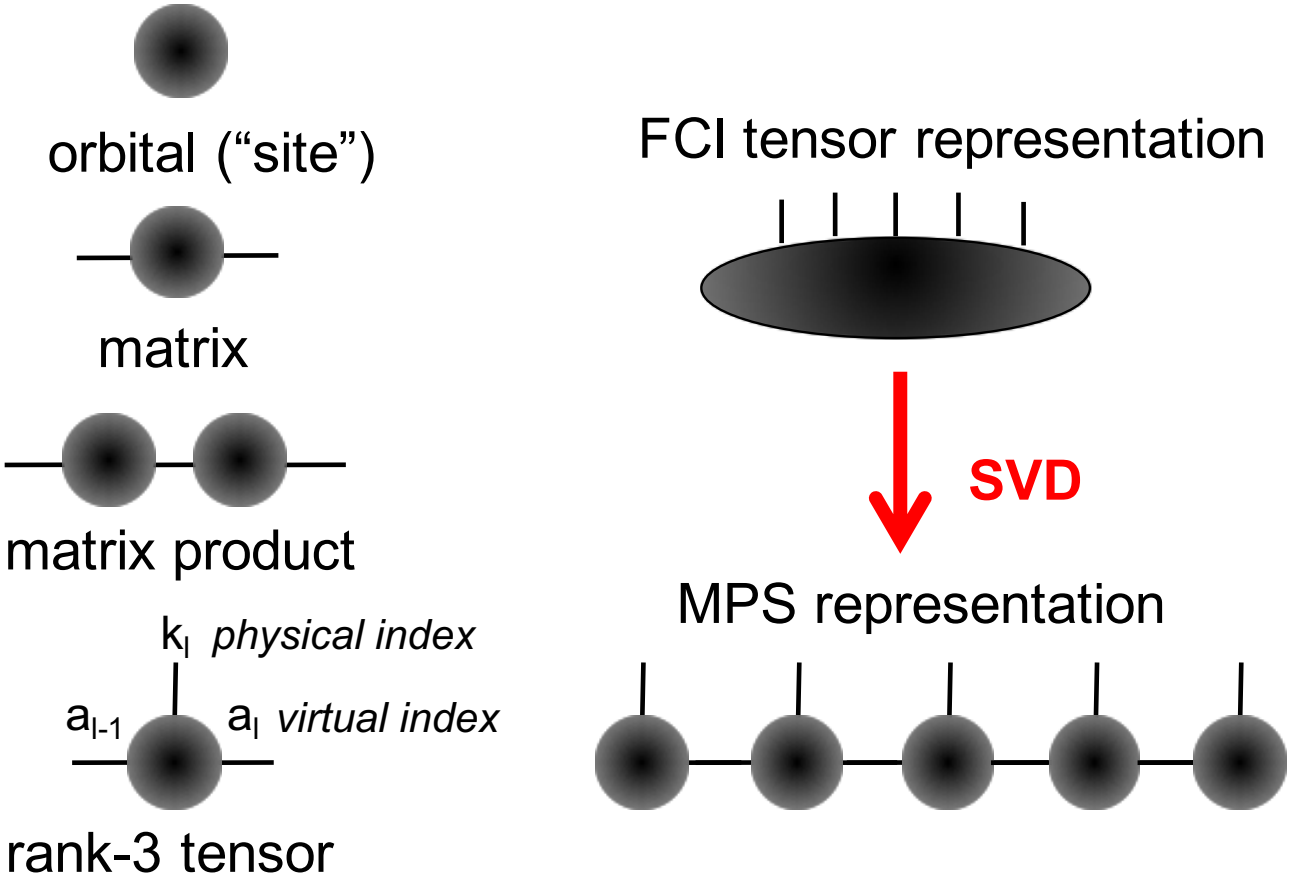
yields:

- Left-singular matrix **U** $(n_a \times \min(n_a, n_b))$ with $\mathbf{U}^\dagger\mathbf{U} = 1$
- Right-singular matrix **V** $(\min(n_a, n_b) \times n_b)$ with $\mathbf{V}^\dagger\mathbf{V} = 1$
- Diagonal singular value matrix **S** $(\min(n_a, n_b) \times \min(n_a, n_b))$ with r nonzero singular values $\rightarrow$ r is the (Schmidt) rank of $\mathbf{M}$



From a CI to an MPS parametrisation I

- Successive application of SVD to CI tensor → MPS wave function



From a CI to an MPS parametrisation II

- Reshape coefficient tensor $c_{k_1,k_2,\ldots,k_L}$ into a $d \times d^{L-1}$ matrix $\mathbf{\Gamma}$

$$\Gamma_{k_1,(k_2,\ldots,k_L)} = c_{k_1,k_2,\ldots,k_L}$$

- SVD of $\Gamma_{k_1,(k2,\ldots,k_L)}$ yields

$$\Gamma_{k_1,(k_2,\ldots,k_L)} = \sum_{a_1}^{r_1} U_{k_1,a_1} S_{a_1,a_1} (V^\dagger)_{a_1,(k_2,\ldots,k_L)}$$

$$\equiv \sum_{a_1}^{r_1} A^{k_1}_{1,a_1} c_{a_1,(k_2,\ldots,k_L)}$$

with

  - $\mathbf{S}$ and $\mathbf{V}^\dagger$ multiplied and reshaped into coefficient tensor $c_{a_1,(k_2,\ldots,k_L)}$
  - $r_1 \leq d$
  - collection of $d(=4)$ row vectors A^{k_1} with entries $A^{k_1}_{1,a_1} = U_{k_1,a_1}$

From a CI to an MPS parametrisation III

- Reshape coefficient tensor $c_{a_1,(k_2,\ldots,k_L)}$ into a $r_1 d \times d^{L-2}$ matrix $\mathbf{\Gamma}$

$$c_{k_1,k_2,\ldots,k_L} = \sum_{a_1}^{r_1} A^{k_1}_{1,a_1} \Gamma_{(a_1 k_2),(k_3,\ldots,k_L)}$$

$$\overset{\text{SVD}}{=} \sum_{a_1}^{r_1} \sum_{a_2}^{r_2} A^{k_1}_{1,a_1} U_{(a_1 k_2),a_2} S_{a_2,a_2} (V^\dagger)_{a_2,(k_3,\ldots,k_L)}$$

$$\overset{\text{reshape}}{\equiv} \sum_{a_1}^{r_1} \sum_{a_2}^{r_2} A^{k_1}_{1,a_1} A^{k_2}_{a_1,a_2} \Gamma_{(a_2 k_3),(k_4,\ldots,k_L)}$$

with

  - $\mathbf{S}$ and $\mathbf{V}^\dagger$ multiplied and reshaped into coefficient tensor $c_{a_1,(k_2,\ldots,k_L)}$
  - $r_2 \leq r_1 d \leq d^2$
  - collection of d matrices A^{k_2} with entries $A^{k_2}_{a_1,a_2} = U_{(a_1 k_2),a_2}$

From a CI to an MPS parametrisation IV

- Continue with SVDs until last site which then gives

$$
\begin{aligned}
c_{k_1,k_2,\ldots,k_L} &= \sum_{a_1,a_2,\ldots,a_L-1} A^{k_1}_{1,a_1} A^{k_2}_{a_1,a_2} \cdots A^{k_{L-1}}_{a_{L-2,L-1}} A^{k_L}_{a_{L-1},1} \\
&\equiv A^{k_1} A^{k_2} \cdots A^{k_{L-1}} A^{k_L}
\end{aligned}
$$

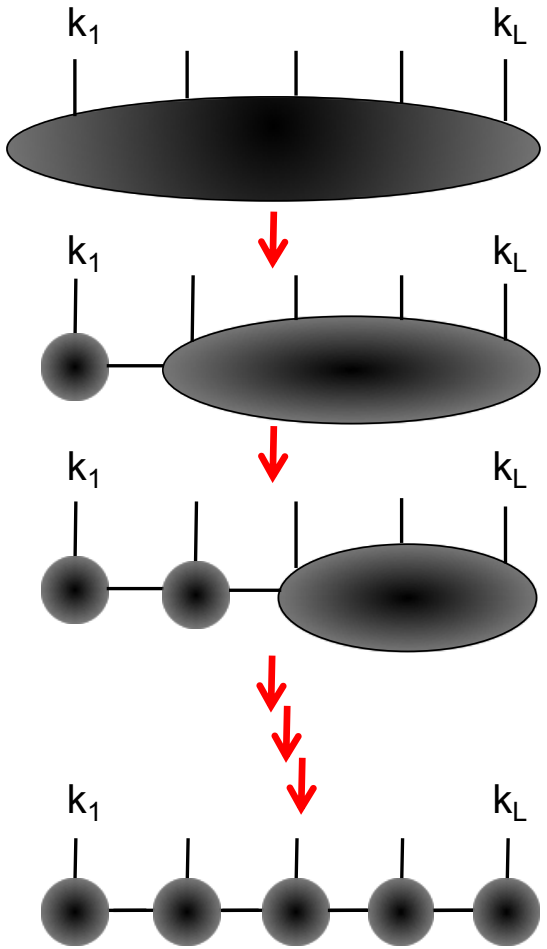
  with

  - interpretation of sums as matrix-matrix multiplications
  - first and last matrices are row- and column vectors!

- CI wave function rewritten as MPS wave function:

$$
\left|\Psi\right\rangle = \sum_{\boldsymbol{k}} c_{\boldsymbol{k}} \left|\boldsymbol{k}\right\rangle = \sum_{k_1,k_2,\ldots,k_L} A^{k_1} A^{k_2} \cdots A^{k_{L-1}} A^{k_L} \left|\boldsymbol{k}\right\rangle
$$

From a CI to an MPS parametrisation V

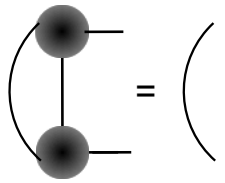


Properties of the MPS I

- Matrix dimensions grow exponentially up to $\dim(d^{L/2-1} \times d^{L/2})$ **if no truncation** occurs, i.e., all singular values are kept

- From $U^\dagger U = I$ follows that all matrices $\{A^{k_l}\}$ are **left-normalised**

$$\sum_{k_l} A^{k_l \dagger} A^{k_l} = I$$



- MPS built from left-normalised matrices is called **left-canonical**

- For any lattice bipartition at site l, the states on sites $1, \ldots, l$

$$|\, a_l \,\rangle_{\mathscr{L}} = \sum_{k_1, k_2, \ldots, k_l} \left(A^{k_1} \cdots A^{k_l}\right)_{1, a_l} |\, k_1, \ldots, k_l \,\rangle$$

span a left subsystem $\mathscr{L}$ and form an orthonormal basis

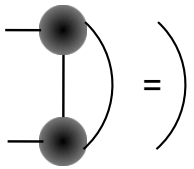
Properties of the MPS II

- Starting SVD on coefficient tensor from right-hand side

$$\Gamma_{(k_1,k_2,\ldots,k_{L-1}),k_L} = c_{k_1,k_2,\ldots,k_L}$$

yields **right-normalised** matrices $\{B^{k_l}\}$ (as $V^\dagger V = I$)

$$\sum_{k_l} B^{k_l} B^{k_l\dagger} = I$$



- MPS built from right-normalised matrices is called **right-canonical**

- For any lattice bipartition at site $l+1$, the states on sites $l+1\ldots,L$

$$|\, a_{l+1} \,\rangle_{\mathscr{R}} = \sum_{k_{l+1},k_{l+2},\ldots,k_L} \left(B^{k_{l+1}}\cdots B^{k_L}\right)_{a_l,1} |\, k_{l+1},\ldots,k_L \,\rangle$$

span a right subsystem $\mathscr{R}$ and form an orthonormal basis

Gauge freedom and mixed-canonical form

- MPS representations are not unique $\leftrightarrow$ existence of a gauge degree of freedom
- Consider two adjacent matrices M^{k_l} and $M^{k_{l+1}}$ of shared column/row dimension D and a square invertible matrix X ($D \times D$)
- Invariance of MPS immediately follows from

$$M^{k_l} \to M^{k_l} X; \quad M^{k_{l+1}} \to X^{-1} M^{k_{l+1}}$$

since

$$M^{k_l} \underbrace{X X^{-1}}_{=I} M^{k_{l+1}} = M^{k_l} \cdot M^{k_{l+1}}$$

Mixed-canonical MPS representation

- Gauge freedom allows to write an MPS in **mixed canonical** form at sites $\{l, l+1\}$

$$\left|\Psi\right\rangle = \sum_{\boldsymbol{k}} A^{k_1} \cdots A^{k_{l-1}} M^{k_l k_{l+1}} B^{k_{l+2}} \cdots B^{k_L} \left|\boldsymbol{k}\right\rangle$$

by starting from a general MPS wave function

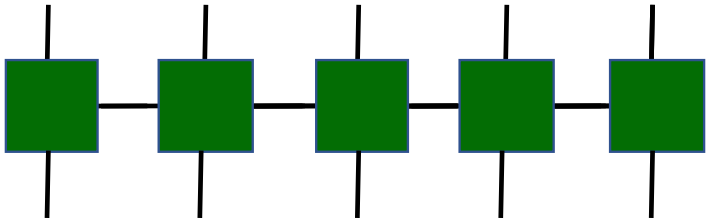
$$\left|\Psi\right\rangle = \sum_{\boldsymbol{k}} M^{k_1} M^{k_2} \cdots M^{k_L} \left|\boldsymbol{k}\right\rangle$$

and the **two-site MPS tensor** $M^{k_l k_{l+1}}$ reading as

$$M^{k_l k_{l+1}} \equiv M^{k_l k_{l+1}}_{a_{l-1}, a_{l+1}} = \sum_{a_l} M^{k_l}_{a_{l-1}, a_l} M^{k_{l+1}}_{a_l, a_{l+1}}$$

Matrix product operators I

- MPS concept applied to operators → matrix product operators (MPOs)



- N-electron operator $\hat{\mathscr{W}}$ in MPO form

$$\hat{\mathscr{W}} = \sum_{\boldsymbol{k}\boldsymbol{k}'} \sum_{b_1,\ldots,b_{L-1}} W^{k_1 k_1'}_{1,b_1} W^{k_2 k_2'}_{b_1,b_2} \ldots W^{k_L k_L'}_{b_{L-1},1} \left|\boldsymbol{k}\right\rangle \left\langle \boldsymbol{k}'\right|$$

$$= \sum_{\boldsymbol{k}\boldsymbol{k}'} W^{k_1 k_1'} W^{k_2 k_2'} \ldots W^{k_L k_L'} \left|\boldsymbol{k}\right\rangle \left\langle \boldsymbol{k}'\right|$$

$$\equiv \sum_{\boldsymbol{k}\boldsymbol{k}'} w_{\boldsymbol{k}\boldsymbol{k}'} \left|\boldsymbol{k}\right\rangle \left\langle \boldsymbol{k}'\right|$$

Matrix product operators II

- For efficiency, rearrange summations such that the contraction proceeds first over the local site indices $k_l k_l'$

$$\widehat{W^l_{b_{l-1},b_l}} = \sum_{k_l k_l'} W^{k_l k_l'}_{b_{l-1},b_l} \left| k_l \right\rangle \left\langle k_l' \right|$$

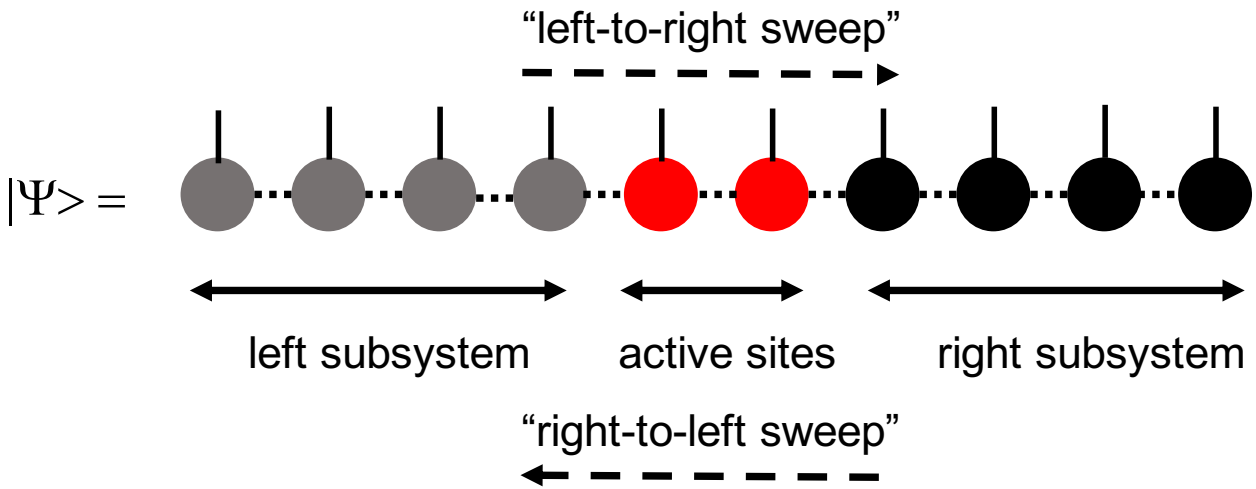
- This allows us to write the equation on previous slide as

$$\widehat{\mathscr{W}} = \sum_{b_1,\ldots,b_{L-1}} \widehat{W^1_{1,b_1}} \cdots \widehat{W^l_{b_{l-1},b_l}} \cdots \widehat{W^L_{b_{L-1},1}}$$

- **Note**: the entries of $\{\widehat{W^l_{b_{l-1},b_l}}\}$ matrices comprise the elementary, *local* operators acting on the l-th orbital, e.g.,

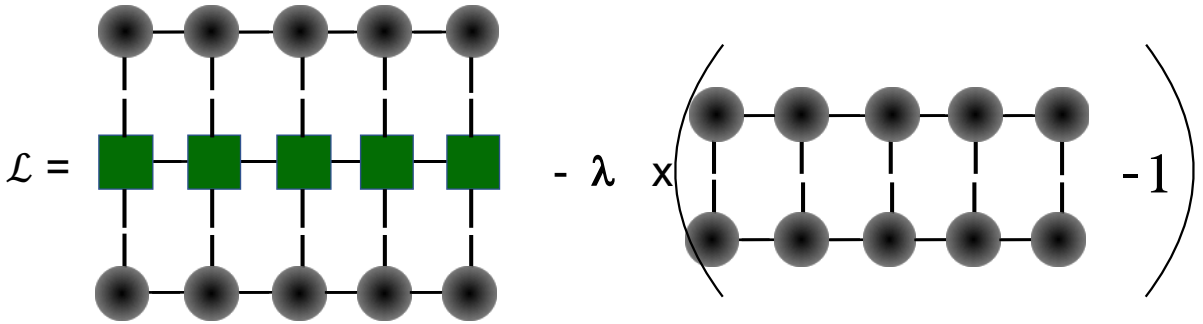
$$\tilde{a}^\dagger_{\uparrow_l} = \left| \uparrow\downarrow \right\rangle \left\langle \downarrow \right| + \left| \uparrow \right\rangle \left\langle 0 \right|$$

Variational MPS optimisation I



- **Goal**: find optimal approximation $|\tilde{\Psi}\rangle$ to $|\Psi\rangle$ (in a least-square sense)
- Prerequisite: initialise suitable (valid) trial MPS wave function $|\tilde{\Psi}\rangle$
  - choices: random guess, encode HF determinant, CI-DEAS, “old MPS” …
  - assume normalisation, i.e., $\langle\Psi|\Psi\rangle = 1$

Variational MPS optimisation II



- *Ansatz* for variational MPS optimization: extremize the Lagrangian

$$\mathscr{L} = \langle \Psi \left| \hat{H} \right| \Psi \rangle - \lambda \left(\langle \Psi \left| \Psi \right\rangle - 1 \right)$$

  with the two-site $\{M^{k_l k_{l+1}}\}$ matrices as optimization parameters

- Optimize at each step of a ”sweep” entries of site matrices of **two orbitals** (“two-site DMRG”) while keeping all the others fixed

- Sweep through all sites multiple times until energy converges

Variational MPS optimisation III

- At sites $\{l, l+1\}$, take derivative of $\mathscr{L}$ with respect to complex conjugate of $M^{k_l,k_{l+1}}$

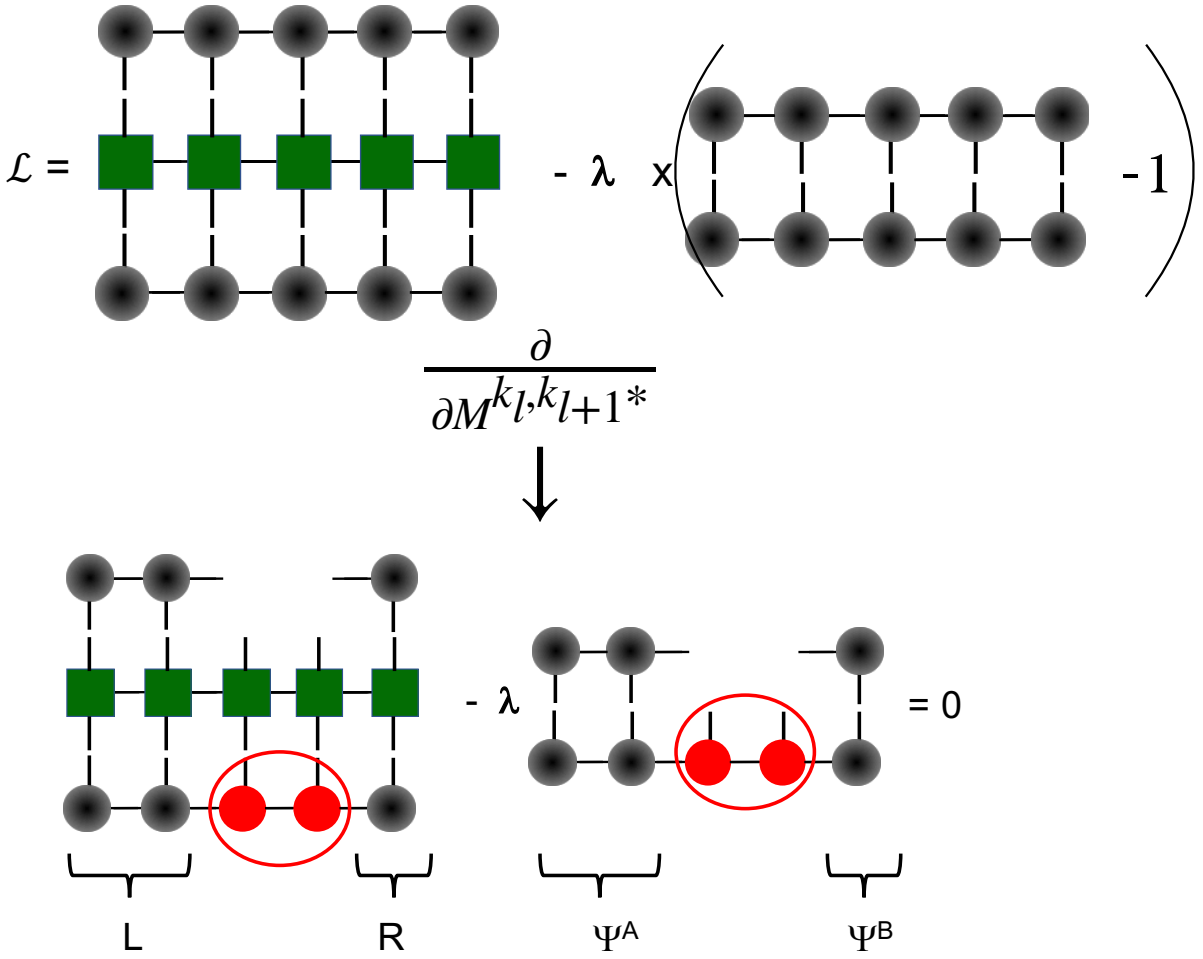
$$\frac{\partial}{\partial M^{k_l,k_{l+1}*}}\left(\langle\Psi|\,\hat{H}\,|\Psi\rangle - \lambda\left[\langle\Psi|\,\Psi\rangle - 1\right]\right) = 0$$

  which then yields

$$\sum_{\substack{a'_{l-1}a'_l\\ b_{l-1}b_{l+1}}}\sum_{k_l k'_{l+1}} L^{b_{l-1}}_{a_{l-1},a'_{l-1}} W^{k_l k_{l+1},k'_l k'_{l+1}}_{b_{l-1},b_{l+1}} R^{b_{l+1}}_{a'_{l+1},a_{l+1}} M^{k'_l k'_{l+1}}_{a'_{l-1},a'_{l+1}} = \lambda \sum_{a'_{l-1}a'_l} \Psi^A_{a'_{l-1},a_{l-1}} \times M^{k'_l k'_{l+1}}_{a'_{l-1},a'_{l+1}} \times \Psi^B_{a'_{l+1},a_{l+1}}$$

- L and R: *left* and *right* boundaries obtained by contracting the MPO with the bra and ket MPS starting from left (right) up to sites $l-1 (l+1)$

Variational MPS optimisation IV

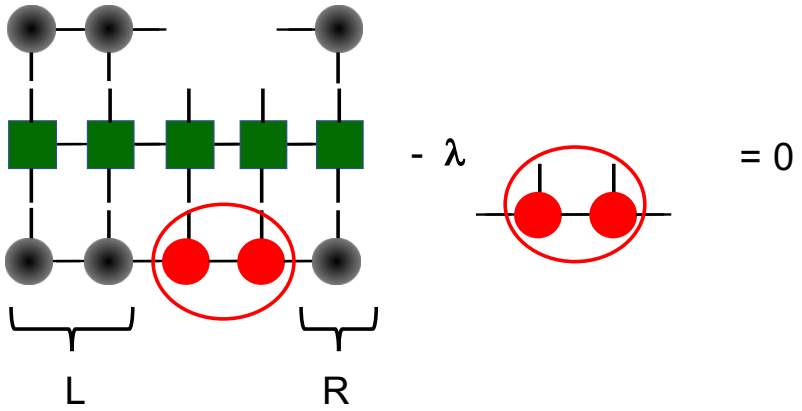


Variational MPS optimisation V

- **NB**: Simplify *generalized eigenvalue problem* to a *standard eigenvalue problem*

$$\sum_{\substack{a'_{l-1}a'_l \\ b_{l-1}b_{l+1}}} \sum_{k'_l k'_{l+1}} L^{b_{l-1}}_{a_{l-1},a'_{l-1}} W^{k_l k_{l+1},k'_l k'_{l+1}}_{b_{l-1},b_{l+1}} R^{b_{l+1}}_{a'_{l+1},a_{l+1}} M^{k'_l k'_{l+1}}_{a'_{l-1},a'_{l+1}} = \lambda M^{k'_l k'_{l+1}}_{a'_{l-1},a'_{l+1}}$$

if MPS is a canonical MPS!



- Requires the initial MPS to be right-normalized!

Variational MPS optimisation VI

- Recast last equation into a matrix eigenvalue equation

$$\mathscr{H} v - \lambda v = 0$$

  - by defining a local Hamiltonian matrix $\mathscr{H}$ at sites $\{l, l+1\}$

$$H_{(k_l k_{l+1} a_{l-1} a_{l+1}),(k'_l k'_{l+1} a'_{l-1} a'_{l+1})} = \sum_{b_{l-1}, b_{l+1}} L^{b_{l-1}}_{a_{l-1}, a'_{l-1}} W^{k_l k_{l+1}, k'_l k'_{l+1}}_{b_{l-1}, b_{l+1}} R^{b_{l+1}}_{a'_{l+1}, a_{l+1}}$$

  - and a vector v

$$v_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}} = M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}}$$

- Solving EV problem —> eigenvalue λ^0 and corresponding eigenvector $v^0_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}}$

Variational MPS optimisation VII

- Reshape $v^0_{k'_l k'_{l+1} a'_{l-1} a'_{l+1}}$ back to $M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}}$
- $M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}}$ is subsequently subject to a left- or right-normalisation (SVD!)

$$M^{k'_l k'_{l+1}}_{a'_{l-1}, a'_{l+1}} = M_{(k'_l, a'_{l-1})(k'_{l+1}, a'_{l+1})} = U_{(k'_l, a'_{l-1}) s'_l} S_{s'_l s'_l} V_{s'_l (a'_{l+1}, k'_{l+1})}$$

- By **discarding** the $3m$ smallest singular values in $S_{s'_l s'_l}$ to obtain $S_{a'_l a'_l}$ we achieve the **desired reduction in bond dimensionality**!
- The maximum (fixed) number m of retained singular values is usually called **number of renormalized block states**

Variational MPS optimisation VIII

- Discarding $3m$ smallest singular values corresponds to discarding the last $3m$ columns (rows) of U (V) such that

$$A^{k'_l}_{a'_{l-1},a'_l} \equiv U_{(k'_l,a'_{l-1})a'_l}$$

$$M^{k'_{l+1}}_{a'_l,a'_{l+1}} = \frac{1}{1 - \sum_{s_l=m+1}^{4m} S_{s_l s_l}} S_{a'_l a'_l} V_{a'_l(a'_{l+1},k'_{l+1})}$$

- Energy calculated as a function of the truncation error ϵ

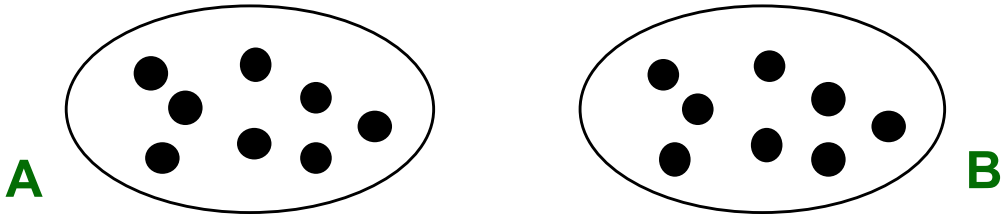
$$\epsilon = \sum_{s_l=m+1}^{4m} S_{s_l s_l} = ||\Psi_{16m^2} - \Psi_{4m^2}||$$

can be employed to obtain an error estimate through extrapolation

Variational MPS optimisation IX

- Moving from sites $\{l, l+1\}$ to sites $\{l+1, l+2\}$ completes local optimization step

Optimal bipartition in a least square sense I

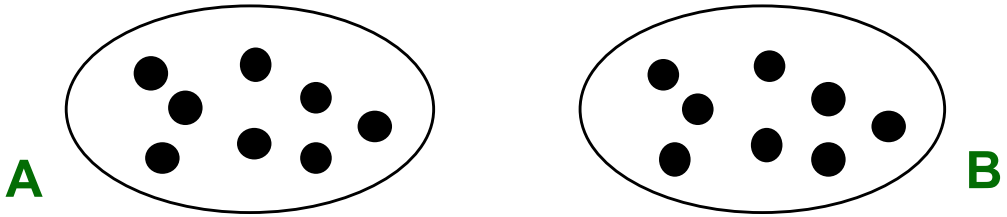


- **Given:** many-body state $|\Psi\rangle$ of composite system **AB**

$$|\Psi\rangle = \sum_{ij} C_{ij} |i\rangle_A \otimes |j\rangle_B$$

- $\{|i\rangle_A\}$ ($\{|j\rangle_B\}$) are orthonormal bases of **A** (**B**) with dimension N_A (N_B)

Optimal bipartition in a least square sense II



- SVD of $|\Psi\rangle = \sum_{ij} \sum_{a=1}^{\min(N_A,N_B)} U_{ia} S_{aa} V^*_{ja} |i\rangle_A |j\rangle_B$

$$= \sum_{a=1}^{\min(N_A,N_B)} \left(\sum_i U_{ia} |i\rangle_A \right) s_a \left(\sum_j V^*_{ja} |j\rangle_B \right)$$

$$= \sum_{a=1}^{\min(N_A,N_B)} s_a |a\rangle_A |a\rangle_B$$

Optimal bipartition in a least square sense III

- Restricting the sum in last equation to some value $m' \leq \min(N_A, N_B)$ yields the *Schmidt decomposition*

$$|\Psi\rangle = \sum_{a=1}^{m'} s_a |a\rangle_A |a\rangle_B$$

where $m' = 1$ corresponds to (classical) product states and $m' > 1$ to entangled (quantum) states

- For orthonormal states in **A** and **B**, the two-norm $||\Psi||_2^2$ is identical to the Frobenius norm of the matrix $\{C_{ij}\}$

$$\|\Psi\|_2^2 = \|\mathbf{C}\|_F^2 = \sum_{a=1}^{\min(N_A,N_B)} s_a^2$$

Optimal bipartition in a least square sense IV

- Hence, an optimal approximation $|\tilde{\Psi}\rangle$ to $|\Psi\rangle$ with respect to the 2-norm immediately follows from optimal approximation of **C** by $\tilde{\mathbf{C}}$ in the Frobenius norm, with $\tilde{\mathbf{C}}$ being a matrix of rank $m \leq m'$

$$|\tilde{\Psi}\rangle = \sum_{a=1}^{m} s_a |a\rangle_A |a\rangle_B$$

- c.f.: Eckart–Young theorem states that among all matrices of rank at most m, the best approximation to **C** in the Frobenius norm is obtained simply by keeping the **largest singular values** $\mathbf{s}_a$.

- **BUT:** how does this relate to the truncation (dimensionality reduction) in the variational MPS optimization?

Optimal bipartition in a least square sense V

- SVD of MPS in mixed-canonical form at site l

$$
\begin{aligned}
\left|\Psi\right\rangle &= \sum_{\substack{k_1,\ldots,k_L \\ a_1,\ldots,a_{L-1}}} A^{k_1}_{1,a_1}\cdots A^{k_l}_{a_{l-1},a_l} S_{a_l,a_l} B^{k_{l+1}}_{a_l,a_{l+1}}\cdots B^{k_L}_{a_{L-1},1} \left|k_1,\ldots,k_l,\ldots,k_L\right\rangle \\
&= \sum_{a_l}\left(\sum_{\substack{k_1,\ldots,k_l \\ a_1,\ldots,a_{l-1}}} A^{k_1}_{1,a_1}\cdots A^{k_l}_{a_{l-1},a_l}\left|k_1,\ldots,k_l\right\rangle\right)\cdot S_{a_l,a_l}\cdot \\
&\quad\left(\sum_{\substack{k_{l+1},\ldots,k_L \\ a_{l+1},\ldots,a_{L-1}}} B^{k_{l+1}}_{a_l,a_{l+1}}\cdots B^{k_L}_{a_{L-1},1}\left|k_{l+1},\ldots,k_L\right\rangle\right) \\
&= \sum_{a_l} S_{a_l,a_l}\left|a_l\right\rangle_{\mathscr{L}}\left|a_l\right\rangle_{\mathscr{R}}
\end{aligned}
$$

Optimal bipartition in a least square sense VI

- Comparison of last equation and the Schmidt decomposition immediately reveals that *an optimal bipartition in a least square sense* can be obtained for $|\tilde{\Psi}\rangle$ from an SVD retaining the lowest m values with $m < \dim(|\Psi\rangle)$

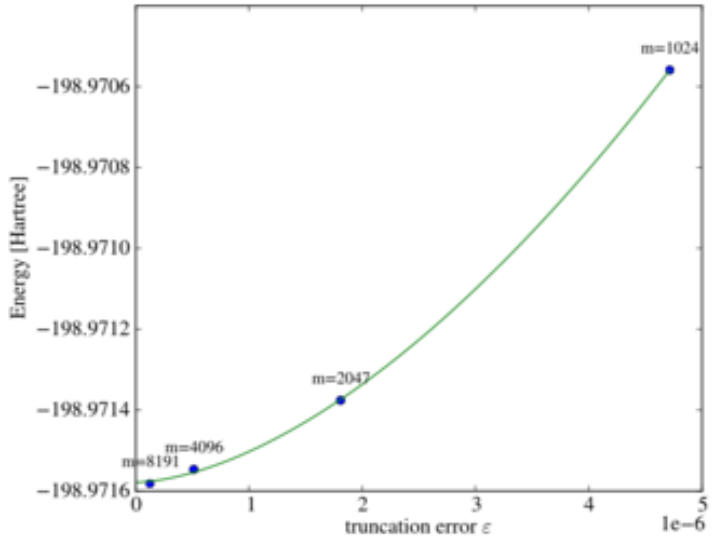
$$|\tilde{\Psi}\rangle = \sum_{a_l=1}^{r} S_{a_l a_l} |a_l\rangle_{\mathscr{L}} |a_l\rangle_{\mathscr{R}}$$

Extrapolation

- Extrapolate E based on truncation error ϵ for different values of m

$$\ln\left(\frac{E_{\mathrm{DMRG}} - E_{\mathrm{FCI}}}{E_{\mathrm{FCI}}}\right) = a \ln \epsilon + b$$

- Example: ground-state calculation of F_2



Scaling of variational MPS optimisation

- **Scaling is dominated** by cost of contracting the operator with the MPS on one site and is proportional to the number of non-zero elements in the MPO matrices $\{ \widehat{W} \}$
  - in a naïve MPO ansatz this step scales as $\mathcal{O}(L^5)$
  - in an optimized code scaling reduces to $\mathcal{O}(L^4)$
- Further reduction through symmetry: $U(1)$ and $SU(2)$
- SVD scales as $\mathcal{O}(m^3)$ (but there are L of them in a sweep)
- Taking into account all operations a sweep scales $\approx \mathcal{O}(L^4 m^3)$

Determining factors of DMRG convergence

- Size L of the CAS
- Type of molecular orbitals (HF, NO's, localized orbitals, …)
- MPS guess for the right subsystem (initial sweep)
- Ordering of orbitals (exploit quantum information / graph theory)
- Number of renormalized block states m

One should never calculate results for just a single m, but increase it in various runs until results converge!

Properties of DMRG

DMRG

- Variational
- Size-consistent
- (approximate) FCI for a CAS
- Polynomial scaling ($\approx L^4 m^3$)
- MPS wave function
- For large m invariant wrt orbital rotations

CASCI

- Variational
- Size-consistent
- FCI for a CAS
- Factorial scaling
- Linearly parametrised wave function
- Invariant wrt orbital rotations

(Incomplete) List of DMRG codes for QC

ID	Name	Language	OSS	Gen.	Sym. A	Sym. NA	HPC SM	HPC DM	HPC GPU
1	ALPS DMRG	C++, Python[i]	[102]	1st	✓	–	*	–	–
2	ALPS MPS	C++, Python[i]	[102]	2nd	✓	–	✓	–	–
3	BAGEL	C++	[106]	1st	✓	–	✓	✓	–
4	Block2	C++, Python[i]	[114]	2nd‡	✓	✓	✓	✓	–
5	CheMPS2	C++, Python[i]	[123]	1st	✓	✓	✓	✓	–
6	ChemTensor	C, Python[i]	[125]	2nd†	✓	✓	✓	–	–
7	Chen et al.	C++	–	1st	✓	–	✓	–	S
8	Cytnx	C++, Python[i]	[133]	2nd†	✓	–	✓	–	S
9	DMRG-Budapest	C++, MATLAB[i]	–	2nd‡	✓	✓	✓	✓	M
10	DMRG++	C++	[150]	1st	✓	–	✓	–	S
11	DMRGPy	Python	[153]	2nd	–	–	*	–	–
12	FOCUS	C++	–	1st	✓	✓	✓	✓	M
13	Hong et al.	C++	–	2nd	–	–	✓	–	S
14	ITensor	C++	[161]	2nd	✓	–	✓	–	–
15	ITensorMPS.jl	Julia	[162]	2nd	✓	–	✓	–	S
16	Kylin	C++	–	2nd	✓	✓	✓	–	–
17	MOLMPS	C++	–	1st	✓	–	✓	✓	S
18	MPSKit.jl	Julia	[172]	2nd	✓	✓	✓	–	–
19	MPToolkit	C++	[180]	2nd	✓	✓	✓	–	–
20	OSMPS	Fortran, Python[i]	[185]	2nd	✓	–	✓	✓	–
21	PyTeNet	Python	[188]	2nd	✓	–	*	–	–
22	pyTTN	C++, Python[i]	[190]	2nd†	–	–	✓	–	–
23	QCMaquis	C++, Python[i]	[195]	2nd	✓	✓	✓	–	–
24	QSpace	C++, MATLAB[i]	[209]	2nd‡	✓	✓	✓	–	–
25	Quantum TEA	Fortran, Python[i]	[212]	2nd†	✓	–	*	–	S
26	quimb	Python	[216]	2nd	–	–	✓	–	–
27	Renormalizer	Python	[224]	2nd†	✓	–	*	–	S
28	SeeMPS2	Python	[231]	2nd	–	–	*	–	–
29	SUNDMRG.jl	Julia	[234]	1st	–	✓	✓	✓	S
30	SymMPS	C++	[236]	2nd	✓	–	✓	–	–
31	SyTen	C++, Python[i]	–	2nd	✓	✓	✓	✓	S
32	TeNPy	Python	[244]	2nd	✓	–	✓	✓	–
33	tensor-tools	C++	[246]	2nd	✓	–	✓	✓	–
34	TensorTrack	MATLAB	[250]	2nd	✓	✓	*	–	–
35	UltraDMRG	C++	[251]	2nd	✓	–	✓	✓	S
36	xDMRG++	C++	[253]	2nd	–	–	*	–	–
37	YASTN	Python	[255]	2nd	✓	–	*	–	S

Other classical methods for large CAS

- FCI-**Q**uantum **M**onte **C**arlo aka FCIQMC
- Heat-Bath CI (aka SHCI)
- selective CI / CIPSI-like approaches
- v(ariational) 2RDM
- …

—> Approaches to recover dynamical electron correlation available
see discussion for post-CASSCF.