THE UNIVERSITY OF CHICAGO

Introduction to Computational Quantum Physics

Nan Sheng[1]

[1]The University of Chicago

nansheng@uchicago.edu

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Spin system as an example

- A classical spin: $\sigma \in \{+1, -1\}$
- N classical spins:
  $\sigma_1\sigma_2\cdots\sigma_N \in \{+1, -1\}$

- A quantum spin: $|\sigma\rangle \in \mathcal{H} = \mathbb{C}^2$
  - Inner product $\langle\sigma|\sigma\rangle = 1$.
  - $|\sigma\rangle = \alpha\,|\uparrow\rangle + \beta\,|\downarrow\rangle$, where
    $|\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ and $|\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}$
- N quantum spins:
  $|\sigma_1\sigma_2\cdots\sigma_N\rangle \in \mathbb{C}^{2^N}$
  - Inner product
    $\langle\sigma_1\sigma_2\cdots\sigma_N|\sigma_1\sigma_2\cdots\sigma_N\rangle = 1$.

Spin system as an example

Consider the energy of a 1D chain of N spins:

- Classical: $H(\sigma_1\sigma_2\cdots\sigma_N) = -J\sum_{<ij>}\sigma_i\sigma_j - g\sum_i \sigma_i$
  - $H(\sigma)$ is a function of $\sigma_1\sigma_2\cdots\sigma_N$
- Quantum: $\hat{H} = -J\sum_{<ij>}\hat{Z}_i\hat{Z}_j - g\sum_i \hat{X}_i$
  - $X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, $Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ are Pauli matrices
  - $\hat{H} : \mathbb{C}^{2^N} \to \mathbb{C}^{2^N}$ is a Hermitian operator
  - The energy $E = \langle\sigma_1\sigma_2\cdots\sigma_N|\hat{H}|\sigma_1\sigma_2\cdots\sigma_N\rangle$

Problem of Interest

- Zero-temperature
  - Time-dependent problem
    - $\hat{H}|\Psi\rangle = i\partial_t|\Psi\rangle$
    - $|\Psi(t)\rangle = e^{-i\hat{H}t}|\Psi(0)\rangle$
  - Time-independent problem
    - $\hat{H}|\Psi\rangle = E|\Psi\rangle$
    - $E_{\text{min}} = \min_{|\Psi\rangle}\langle\Psi|\hat{H}|\Psi\rangle$
- Finite-temperature
  - Partition function $\mathcal{Z} = \text{tr}(e^{-\beta\hat{H}})$
  - Expectation value $E = \frac{1}{\mathcal{Z}}\sum_{|\Psi\rangle}\langle\Psi|\hat{H}e^{-\beta\hat{H}}|\Psi\rangle$

Slater determinants as a basis set

Usually, Ψ need to be

- Symmetric (Bosonic):
  $|\Psi\rangle = \Psi(x_1 \cdots x_i \cdots x_j \cdots x_N) = \Psi(x_1 \cdots x_j \cdots x_i \cdots x_N)$
- Anti-symmetric (Fermionic):
  $|\Psi\rangle = \Psi(x_1 \cdots x_i \cdots x_j \cdots x_N) = -\Psi(x_1 \cdots x_j \cdots x_i \cdots x_N)$

An example of $\hat{H}$ is the electronic Hamiltonian
$\hat{H}_{\text{el}} = \sum_i (-\frac{1}{2}\nabla_i^2 + V_i) + \sum_{ij, i\neq j} \frac{1}{|x_i - x_j|}$

If we approximate $\hat{H}_{\text{el}} \approx \sum_i (-\frac{1}{2}\nabla_i^2 + V_i)$

- $\Phi(x_1 x_2 \cdots x_N) = \psi_1(x_1)\psi_2(x_2)\cdots\psi_N(x_N)$
- To satisfy the (anti-)symmetry,
  $\Phi(x_1 x_2 \cdots x_N) = \frac{1}{\sqrt{N}} \sum_P (\pm)^P \psi_1(x_{P(1)})\psi_2(x_{P(2)})\cdots\psi_N(x_{P(N)})$

We can use a group of Slater determinants to approximate true Ψ!

$$\Psi = c_0\Phi_0 + \sum_{ra} c_a^r \Phi_a^r + \cdots$$

Full and selected configuration interaction

- Full configuration interaction (exact diagonalization)

$$H_{\text{el}} = \begin{pmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & \langle \Phi_0 | \hat{H} | \Phi_a^r \rangle & \cdots \\ \langle \Phi_0 | \hat{H} | \Phi_a^r \rangle & \langle \Phi_a^r | \hat{H} | \Phi_a^r \rangle & \cdots \\ \cdots & \cdots & \cdots \end{pmatrix} \xrightarrow{\text{Diagonalization}} \Psi$$

- Selected configuration interaction
  Limit the space of Ψ to low order, such as

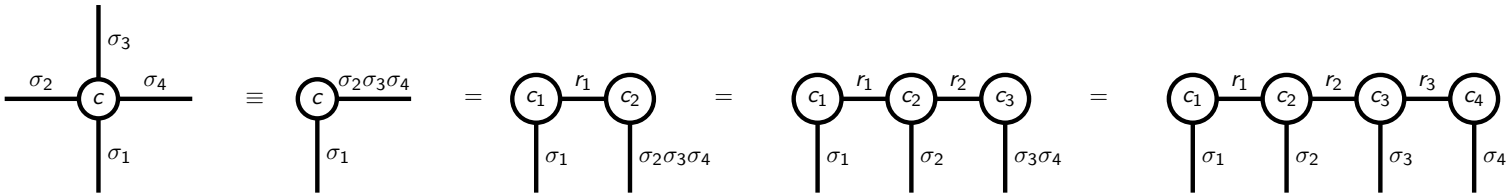
$$\Psi \approx c_0 \Phi_0 + \sum_{ra} c_a^r \Phi_a^r$$

$$H_{\text{el}} \approx \begin{pmatrix} \langle \Phi_0 | \hat{H} | \Phi_0 \rangle & \langle \Phi_0 | \hat{H} | \Phi_a^r \rangle \\ \langle \Phi_0 | \hat{H} | \Phi_a^r \rangle & \langle \Phi_a^r | \hat{H} | \Phi_a^r \rangle \end{pmatrix} \xrightarrow{\text{Diagonalization}} \Psi$$

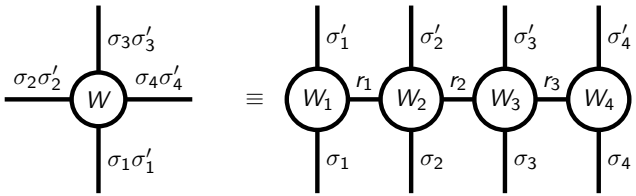
Tensor-train representation

Recall the 1D chain of N spins. Suppose $N = 4$

- $|\Psi\rangle = \sum_{\{\sigma\}} c^{\sigma_1\sigma_2\sigma_3\sigma_4} |\sigma_1\sigma_2\sigma_3\sigma_4\rangle$
  Tensor diagram:

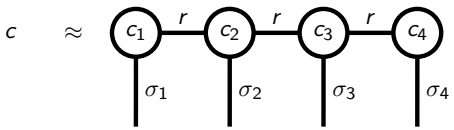


- $\hat{H} = \sum_{\{\sigma\sigma'\}} W^{\sigma_1\sigma_2\sigma_3\sigma_4}_{\sigma'_1\sigma'_2\sigma'_3\sigma'_4} |\sigma_1\sigma_2\sigma_3\sigma_4\rangle \langle\sigma'_1\sigma'_2\sigma'_3\sigma'_4|$
  Tensor diagram:

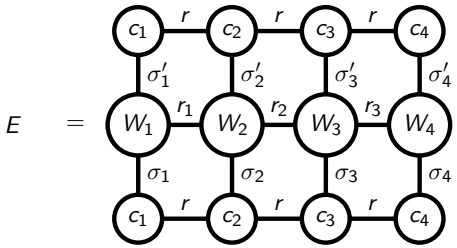


Density-matrix renormalization group

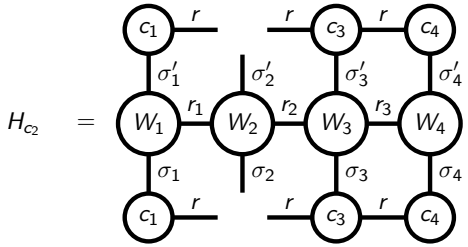
- Tensor-train ansatz



- Energy $E = \langle \Psi | \hat{H} | \Psi \rangle$



$$\frac{\partial E}{\partial c_i} = 0 \longrightarrow H_{c_i} c_i = E c_i$$



For example,

Quantum Monte Carlo

- Variational Monte Carlo

  $$E(\alpha) = \frac{\langle \Psi(\alpha)|\hat{H}|\Psi(\alpha)\rangle}{\langle \Psi(\alpha)|\Psi(\alpha)\rangle} = \int \left(\frac{|\Psi(\alpha)|^2}{\int |\Psi(\alpha)|^2} \right) \frac{\hat{H}|\Psi(\alpha)\rangle}{\Psi(\alpha)}$$

  $$E_{\text{min}} = \min_{\alpha} E(\alpha)$$

- Projector Monte Carlo

  $$|\Psi\rangle \propto \lim_{\beta\to\infty} e^{-\beta\hat{H}} |\Phi\rangle \longrightarrow |\Psi^{n+1}\rangle = e^{-\Delta\tau H} |\Psi^{n}\rangle$$

  $$E_{\text{min}} = \lim_{n\to\infty} \frac{\langle \Phi|\hat{H}|\Psi\rangle}{\langle \Phi|\Psi\rangle}$$

Variational quantum eigensolver

$$\Psi(c) \approx c_0\Phi_0 + \sum_{ra} c_a^r \Phi_a^r \overset{\text{mapping}}{\longrightarrow} \text{qubit space}$$

$$\hat{H} \overset{\text{mapping}}{\longrightarrow} \text{quantum gates}$$

$$E = \langle \Psi(c)|\hat{H}|\Psi(c)\rangle \longrightarrow \text{circuit measurements}$$

$$\frac{\partial E}{\partial c} \longrightarrow \text{computed from classical computers}$$

Density-matrix embedding

Generally, $\hat{H}$ is huge and typically structured. We only care about a specific part of $\hat{H}$.

- Build up a mapping $\hat{H} \longrightarrow \hat{H}_S$
- High level method such as exact diagonalization for $\hat{H}_S$

Density-matrix embedding:
Suppose $|\Psi\rangle \approx \text{Det}\{|\psi_1\psi_2\cdots\psi_N\rangle\}$. Choose an active space $\mathcal{A} \in \mathcal{H}$.
Tensor diagram:
From CS decomposition, we can get $|\Psi\rangle \in \mathcal{F}_A \otimes \mathcal{F}_B \otimes |\Psi_{\text{core}}\rangle$. Thus, $\hat{H}_S$ can be built up from $\mathcal{A} \cup \mathcal{B}$ and solved by exact diagonalization.

Green's function embedding

From a different perspective, consider $(\omega - H)G = I$

$$H = \begin{pmatrix} H_S & H_{SR} \\ H_{RS} & H_R \end{pmatrix}, \; G = \begin{pmatrix} G_S & G_{SR} \\ G_{RS} & G_R \end{pmatrix}, \; I = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}$$

$$\longrightarrow G_S = \left(\left[G_S^0(\omega) \right]^{-1} - H_{SR} G_R^0(\omega) H_{RS} \right)^{-1}$$

$$G_S^{-1} = \left[G_S^0(\omega) \right]^{-1} - \Sigma_S(\omega)$$

Here $G_S^0 = (\omega - H_S)^{-1}$ and $G_R^0 = (\omega - H_R)^{-1}$.

Green's function embedding

Σ_S is due to the interaction between the system and the environment. From many-body perturbation theory, we can do the following mapping

- $H[G_0, v] \longrightarrow H_S[G_R, W_R]$[1], where
  $$\left[G^R\right]^{-1} = G_0^{-1} - \Sigma^{\text{low}} + \Sigma_S^{\text{dc}}$$
  $$\left[W^R\right]^{-1} = v^{-1} - P^{\text{low}} + P_S^{\text{dc}}$$
- Σ^{low}, Σ_S^{dc}, P^{low}, P_S^{dc} can be obtained from a low level of theory

[1] Nan Sheng, Christian Vorwerk, Marco Govoni, and Giulia Galli. In: *Journal of Chemical Theory and Computation* 18.6 (2022), pp. 3512–3522.

Path integral

- Real-time path integral
  - Time evolution operator: $\hat{U} = e^{-i\hat{H}t} = \left[e^{-i\hat{H}\Delta t}\right]^N$
  - $\langle q_\mathrm{f}|\hat{U}|q_\mathrm{i}\rangle = \langle q_\mathrm{f}|e^{-i\hat{T}\Delta t}e^{-i\hat{V}\Delta t} \wedge e^{-i\hat{T}\Delta t}e^{-i\hat{V}\Delta t} \wedge \cdots \wedge e^{-i\hat{T}\Delta t}e^{-i\hat{V}\Delta t}|q_\mathrm{i}\rangle = \int_{q(0)=q_\mathrm{i}}^{q(t)=q_\mathrm{f}} Dq\; e^{i\int_0^t dt' L(q,\dot{q})}$, where $L = T - V$
- Imaginary-time path integral
  - Partition function $\mathcal{Z} = \mathrm{tr}(e^{-\beta\hat{H}}) = \int dq \int_{q(0)=q}^{q(\beta)=q} Dq\; e^{-\int_0^\beta d\tau H(q,\dot{q})}$, where $H = T + V$

Path integral Monte Carlo

Any expectation value

$$\begin{aligned}\langle \hat{O} \rangle &= \frac{1}{\mathcal{Z}} \mathrm{tr}(\hat{O} e^{-\beta H}) \\ &= \frac{1}{\mathcal{Z}} \int dq \int_{q(0)=q}^{q(\beta)=q} Dq\ \hat{O} e^{-\int_0^\beta d\tau H(q,\dot{q})}\end{aligned}$$

Sample over the path, and average over $\hat{O}$

Open quantum systems

- Full Hamiltonian $\hat{H} = \hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{B}} + \hat{H}_{\mathrm{SB}}$
  - $\hat{H}_{\mathrm{S}} = -\frac{1}{2}\nabla_i^2 + V_i(\hat{x})$
  - $\hat{H}_{\mathrm{B}} = \sum_i \frac{1}{2} m_i {\omega_i}^2 \hat{q}_i^2$
  - $\hat{H}_{\mathrm{SB}} = -\sum_{\hat{q}_i} F_{\hat{q}_i}(x)\hat{q}_i$
- $\hat{\rho}(t) = e^{-\beta\hat{H}}$
- $\hat{\rho}_{\mathrm{S}}(t) = \mathrm{tr}_{\mathrm{B}}(\hat{\rho}(t))$ can be analytically integrated from path integral $\longrightarrow$ quantum master equation for the system

Resources

- Dissertation and talk from Prof. Michael Lindsey at Berkeley[2]
- An introductory book by Prof. Lin Lin at Berkeley and Prof. Jianfeng Lu at Duke[3]
- A self-contained book of quantum many-body theory[4]

[2] https://quantumtative.github.io/.

[3] Lin Lin and Jianfeng Lu. *A mathematical introduction to electronic structure theory*. SIAM, 2019.

[4] Gianluca Stefanucci and Robert Van Leeuwen. *Nonequilibrium many-body theory of quantum systems: a modern introduction*. Cambridge University Press, 2013.