

Supporting Information for “Multi-state quantum simulations via model-space quantum imaginary time evolution”

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I. SUPPLEMENTARY NOTES

QITE

In QITE, the imaginary time evolution of the state $|\Phi\rangle$ is Trotterized and the following unitary approximation was applied¹,

$$|\Phi'\rangle = \frac{1}{\sqrt{c}} e^{-\Delta\beta\hat{H}}|\Phi\rangle \approx e^{-i\Delta\beta\hat{A}}|\Phi\rangle \quad (1)$$

where

$$c = \langle\Phi|e^{-2\Delta\beta\hat{H}}|\Phi\rangle \quad (2)$$

is the squared norm, and $\hat{A}$ is defined as

$$\hat{A} = \sum_{\mu} a_{\mu} \hat{\sigma}_{\mu} \quad (3)$$

with Pauli strings $\hat{\sigma}_{\mu}$.

The real coefficients a_{μ} are determined by minimizing the following quantity to the second order of $\Delta\beta$ ²,

$$F(\mathbf{a}) = \left\| \frac{1}{\sqrt{c}} e^{-\Delta\beta\hat{H}}|\Phi\rangle - e^{-i\Delta\beta\hat{A}}|\Phi\rangle \right\|^2 \quad (4)$$

yielding

$$M_{\mu\nu} = 2\text{Re}\langle\Phi|\hat{\sigma}_{\mu}\hat{\sigma}_{\nu}|\Phi\rangle \quad (5)$$

$$b_{\mu} = \text{Im}\langle\Phi|[\hat{H}, \hat{\sigma}_{\mu}]|\Phi\rangle \quad (6)$$

Fermionic-QITE

Fermionic-QITE uses anti-Hermitian fermionic operators to construct the chemistry-inspired $\hat{A}$,

$$\hat{A} = \hat{A}_1 + \hat{A}_2 + \dots \quad (7a)$$

$$\hat{A}_1 = \sum_{pq} t_{pq} (c_p^{\dagger} c_q - c_q^{\dagger} c_p) \quad (7b)$$

$$\hat{A}_2 = \frac{1}{4} \sum_{pqrs} t_{pqrs} (c_p^{\dagger} c_q^{\dagger} c_s c_r - c_r^{\dagger} c_s^{\dagger} c_q c_p) \quad (7c)$$

where $\mathbf{t}$ is purely imaginary. $\hat{A}_k$ comprises the k -rank excitation and de-excitation operators, and Eq. (7) is appropriately transformed to the qubit basis as Eq. (7). Truncated after $\hat{A}_3$, $\hat{A} = \hat{A}_1 + \hat{A}_2$ is known as unitary coupled-cluster with generalized singles and doubles (UCCGSD) and defines “UCCGSD-based QITE” after a certain transformation to the qubit representation.

Derivation of the working equations of MSQITE and MS-QLanczos

Our goal is to find the approximation

$$|\Phi_I^{(\ell+1)}\rangle = \sum_J d_{IJ} e^{-\Delta\beta(\hat{H}-E_J)} |\Phi_J^{(\ell)}\rangle \approx e^{-i\Delta\beta\hat{A}} |\Phi_I^{(\ell)}\rangle. \quad (8)$$

To obtain the equation for MSQITE, we minimize F^I , i.e., the distance between the left and right hand sides of Eq. (8), noting that it is also crucial to take into account the dependence of $\mathbf{d}$ on $\Delta\beta$. As described in the main text, $\mathbf{d}$ is determined by orthonormalizing $\tilde{S}_{IJ} = \langle \Phi_I | e^{-\Delta\beta(\hat{H}-E_I)} e^{-\Delta\beta(\hat{H}-E_J)} | \Phi_J \rangle$. Because $\tilde{S}_{IJ} \rightarrow \delta_{IJ}$ as $\Delta\beta \rightarrow 0$, we also have $d_{IJ} \rightarrow \delta_{IJ}$ (see the Methods section in the main text). Note that, for the state-specific problem, the state basis $\{|\Phi_I^{(\ell)}\rangle\}$ are not necessarily orthogonal to each other because they are evolved by different unitaries. Therefore we need to assume or impose the same limit for d_{IJ} , because otherwise Eq. (8) would become obviously contradictory at $\Delta\beta = 0$. The condition can be strictly imposed by defining $\mathbf{d}$ from $\tilde{\mathbf{S}}$ in the transformed model space so that $\mathbf{S} = \mathbf{1}$, which is then back-transformed to the current model space. Namely, one may have $\mathbf{d}$ by the Löwdin symmetric orthonormalization of the following overlap:

$$\tilde{S}'_{IJ} = \mathbf{d}' \tilde{\mathbf{S}} \mathbf{d}' \quad (9)$$

where $\mathbf{d}'$ itself is the Löwdin symmetric orthonormalization coefficients of $\mathbf{S}$, which is independent of $\Delta\beta$ (for the purpose of expanding F^I). However, our numerical tests revealed that this procedure does not affect the convergence behavior, and hence we simply use the $\mathbf{d}$ defined in the main text and assume that the limit $d_{IJ} \rightarrow \delta_{IJ}$ holds.

Then, it is convenient to write

$$d_{JI} = \delta_{JI} + \Delta\beta \Delta d_{JI} + O(\Delta\beta^2) \quad (10)$$

and let us consider the expansion of F^I up to the second-order in $\Delta\beta$ as follows:

$$\begin{aligned}
F^I(\mathbf{a}^I) &= \left\| \sum_J d_{JI} e^{-\Delta\beta(\hat{H}-E_J)} |\Phi_J^{(\ell)}\rangle - e^{-i\Delta\beta\hat{A}^I} |\Phi_I^{(\ell)}\rangle \right\|^2 \\
&= 2 - \sum_J d_{JI} \left(\langle \Phi_J^{(\ell)} | e^{-\Delta\beta(\hat{H}-E_J)} e^{-i\Delta\beta\hat{A}^I} |\Phi_I^{(\ell)}\rangle + \langle \Phi_I^{(\ell)} | e^{i\Delta\beta\hat{A}^I} e^{-\Delta\beta(\hat{H}-E_J)} |\Phi_J^{(\ell)}\rangle \right) \\
&= 2 - \sum_J (\delta_{JI} + \Delta\beta\Delta d_{JI} + O(\Delta\beta^2)) \left(\right. \\
&\quad \langle \Phi_J^{(\ell)} | (1 - \Delta\beta(\hat{H} - E_J) + \frac{1}{2}\Delta\beta^2(\hat{H} - E_J)^2)(1 - i\Delta\beta\hat{A}^I - \frac{1}{2}\Delta\beta^2(\hat{A}^I)^2) |\Phi_I^{(\ell)}\rangle \\
&\quad \left. + \langle \Phi_I^{(\ell)} | (1 + i\Delta\beta\hat{A}^{I\dagger} - \frac{1}{2}\Delta\beta^2(\hat{A}^I)^2)(1 - \Delta\beta(\hat{H} - E_J) + \frac{1}{2}\Delta\beta^2(\hat{H} - E_J)^2) |\Phi_J^{(\ell)}\rangle \right) + O(\Delta\beta^3) \\
&= \text{const.} + \Delta\beta \sum_J (\delta_{JI} + \Delta\beta\Delta d_{JI}) \left(i\langle \Phi_J^{(\ell)} | \hat{A}^I | \Phi_I^{(\ell)}\rangle - i\langle \Phi_I^{(\ell)} | \hat{A}^I | \Phi_J^{(\ell)}\rangle \right) \\
&\quad + \Delta\beta^2 \sum_J \delta_{JI} \left(\langle \Phi_J^{(\ell)} | \left(-i(\hat{H} - E_J)\hat{A}^I + \frac{1}{2}(\hat{A}^I)^2 \right) | \Phi_I^{(\ell)}\rangle \right. \\
&\quad \left. + \langle \Phi_I^{(\ell)} | \left(i\hat{A}^I(\hat{H} - E_J) + \frac{1}{2}(\hat{A}^I)^2 \right) | \Phi_J^{(\ell)}\rangle \right) + O(\Delta\beta^3) \tag{11} \\
&= \text{const.} + \Delta\beta^2 \left(\langle \Phi_I^{(\ell)} | (\hat{A}^I)^2 | \Phi_I^{(\ell)}\rangle - i\langle \Phi_I^{(\ell)} | [\hat{H}, \hat{A}^I] | \Phi_I^{(\ell)}\rangle \right. \\
&\quad \left. + i \sum_J \Delta d_{JI} \left(\langle \Phi_J^{(\ell)} | \hat{A}^I | \Phi_I^{(\ell)}\rangle - \langle \Phi_I^{(\ell)} | \hat{A}^I | \Phi_J^{(\ell)}\rangle \right) \right) + O(\Delta\beta^3) \tag{12}
\end{aligned}$$

Perhaps surprisingly, the terms in the parenthesis do not have an explicit energy dependence; however, the constant term does. Also, it is important to introduce E_I for Δd_{JI} to be small so that Eq. (10) is valid. The additional third term in the parenthesis maintains the orthogonality. We approximate Δd_{JI} by using Eq. (10),

$$\Delta d_{JI} \approx \frac{d_{JI} - \delta_{JI}}{\Delta\beta} \tag{13}$$

and arrive at

$$\begin{aligned}
f^I(\mathbf{a}^I) &= \langle \Phi_I^{(\ell)} | (\hat{A}^I)^2 | \Phi_I^{(\ell)}\rangle + \text{Im}\langle \Phi_I^{(\ell)} | [\hat{H}, \hat{A}^I] | \Phi_I^{(\ell)}\rangle \\
&\quad + \frac{2}{\Delta\beta} \sum_J d_{JI} \text{Im}\langle \Phi_I^{(\ell)} | \hat{A}^I | \Phi_J^{(\ell)}\rangle. \tag{14}
\end{aligned}$$

We also show the derivation of the matrix element required in MS-QLanczos for clarity. For the overlap matrix,

$$\begin{aligned}
\mathcal{S}_{I(\ell),J(\ell')} &\equiv \langle \Phi_I^{(\ell)} | \Phi_J^{(\ell')} \rangle \\
&= \sum_{KL} \left(\tilde{\mathbf{d}}^{(0)} \tilde{\mathbf{d}}^{(1)} \dots \tilde{\mathbf{d}}^{(\ell-1)} \right)_{KI} \left(\tilde{\mathbf{d}}^{(0)} \tilde{\mathbf{d}}^{(1)} \dots \tilde{\mathbf{d}}^{(\ell'-1)} \right)_{LJ} \underbrace{\langle \Phi_K^{(0)} | e^{-\ell \Delta \beta (\hat{H} - E_0)} e^{-\ell' \Delta \beta (\hat{H} - E_0)} | \Phi_L^{(0)} \rangle}_{\langle \Phi_K^{(0)} | e^{-(\ell+\ell')/2 \Delta \beta (\hat{H} - E_0)} e^{-(\ell+\ell')/2 \Delta \beta (\hat{H} - E_0)} | \Phi_L^{(0)} \rangle} \\
&= \sum_{KLMN} \left(\tilde{\mathbf{d}}^{(0)} \tilde{\mathbf{d}}^{(1)} \dots \tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2}-1)} \right)_{KM} \left(\tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2})} \dots \tilde{\mathbf{d}}^{(\ell-1)} \right)_{MI} \times \\
&\quad \left(\tilde{\mathbf{d}}^{(0)} \tilde{\mathbf{d}}^{(1)} \dots \tilde{\mathbf{d}}^{(\ell'-1)} \tilde{\mathbf{d}}^{(\ell')} \dots \tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2}-1)} \right)_{LN} \left((\tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2}-1)})^{-1} \dots (\tilde{\mathbf{d}}^{(\ell')})^{-1} \right)_{NJ} \times \\
&\quad \langle \Phi_K^{(0)} | e^{-\frac{\ell+\ell'}{2} \Delta \beta (\hat{H} - E_0)} e^{-\frac{\ell+\ell'}{2} \Delta \beta (\hat{H} - E_0)} | \Phi_L^{(0)} \rangle \\
&= \sum_{MN} \left(\tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2})} \dots \tilde{\mathbf{d}}^{(\ell-1)} \right)_{MI} \left((\tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2}-1)})^{-1} \dots (\tilde{\mathbf{d}}^{(\ell')})^{-1} \right)_{NJ} \underbrace{\langle \Phi_M^{(\frac{\ell+\ell'}{2})} | \Phi_N^{(\frac{\ell+\ell'}{2})} \rangle}_{S_{MN}^{(\frac{\ell+\ell'}{2})}} \\
&= \sum_{MN} \left(\tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2})} \dots \tilde{\mathbf{d}}^{(\ell-1)} \right)_{MI} \left(\tilde{\mathbf{d}}^{(\ell')} \dots \tilde{\mathbf{d}}^{(\frac{\ell+\ell'}{2}-1)} \right)_{NJ}^{-1} S_{MN}^{(\frac{\ell+\ell'}{2})} \\
&= \left[\left(\mathbf{D}^{(\frac{\ell+\ell'}{2} \rightarrow \ell-1)} \right)^\top \mathbf{S}^{(\frac{\ell+\ell'}{2})} \left(\mathbf{D}^{(\ell' \rightarrow \frac{\ell+\ell'}{2}-1)} \right)^{-1} \right]_{IJ}. \tag{15}
\end{aligned}$$

The matrix elements for the effective Hamiltonian and other operators (that commute with $\hat{H}$ such as $\hat{S}^2$) are derived similarly.

II. SUPPLEMENTARY TABLES

We provide the coefficients of eigenstates for BeH₂ obtained by the exact diagonalization in Table I.

SUPPLEMENTARY REFERENCES

¹Motta, M. *et al.* Determining eigenstates and thermal states on a quantum computer using quantum imaginary time evolution. *Nat. Phys.* **16**, 205–210 (2020).

²Tsuchimochi, T., Ryo, Y., Ten-no, S. L. & Sasasako, K. Improved algorithms of quantum imaginary time evolution for ground and excited states of molecular systems. *J. Chem. Theory Comput.* **19**, 503–513 (2023).

Supplementary Table I. Coefficients of exact eigenstates for BeH₂.

Configuration	$X\Sigma_g^+$	$2\Sigma_g^+$	$1\Delta_g$	$3\Sigma_g^+$
$ 000000001111\rangle^a$	0.9859	0.0678	0.0000	-0.0086
$ 000000011011\rangle$	0.0000	0.0000	0.0000	0.0000
$ 000000100111\rangle$	0.0000	0.0000	0.0000	0.0000
$ 000000110011\rangle^b$	0.0004	-0.3357	0.4987	0.4113
$ 000000111100\rangle$	-0.0558	0.3785	-0.4663	-0.2003
$ 000001001011\rangle$	0.0000	0.0000	0.0000	0.0000
$ 000010000111\rangle$	0.0000	0.0000	0.0000	0.0000
$ 000011000011\rangle^c$	0.0004	-0.3357	-0.4987	0.4113
$ 000011001100\rangle$	-0.0558	0.3785	0.4663	-0.2003
$ 000100001110\rangle$	-0.0115	0.4004	0.0000	0.5211
$ 000100101001\rangle$	0.0000	0.0000	0.0000	0.0000
$ 000100110010\rangle$	0.0068	-0.0977	0.1115	0.0533
$ 000111000010\rangle$	0.0068	-0.0977	-0.1115	0.0533
$ 001000001101\rangle$	0.0115	-0.4004	0.0000	-0.5211
$ 001000010110\rangle$	0.0000	0.0000	0.0000	0.0000
$ 001000110001\rangle$	-0.0068	0.0977	-0.1115	-0.0533
$ 001011000001\rangle$	-0.0068	0.0977	0.1115	-0.0533
$ 001100000011\rangle$	-0.0794	0.2671	0.0000	0.1143
$ 001100001100\rangle$	-0.0587	-0.1425	0.0000	-0.0236

^a Configuration (i) of Fig. 3(a) in the main text.

^b Configuration (ii) of Fig. 3(a) in the main text.

^c Configuration (iii) of Fig. 3(a) in the main text.