

# DelphiQ: *Mitre Quantum Chemistry*

Mathematical theory for DelphiQ in GIC Mitre Quantum Chemistry Challenge

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## 1 Five-Stage Quantum Simulation Protocol for Phenanthrene Oxidation

Phenanthrene ( $C_{14}H_{10}$ ) serves as a model polycyclic aromatic hydrocarbon for asphalt, capturing  $\pi$ -electron delocalisation and aromaticity relevant to oxidative aging. The oxidative formation of

carbonyl groups (quinone-type  $C = O$ ) in phenanthrene – a key pathway in asphalt degradation – involves complex electron redistribution and potential multi-reference character. To tackle this with quantum computing, we outline a five-stage Hamiltonian construction and simulation protocol. This approach avoids traditional CASSCF active-space truncation by leveraging Quantum Imaginary Time Evolution (QITE) and Sample-based Quantum Diagonalisation (SQD), while enforcing symmetries and using a fermionic pairing Hamiltonian as a benchmark.

## 2 Quantum Imaginary Time Evolution (QITE) with Pauli Decomposition

### 2.1 Imaginary-Time Propagation

QITE drives an initial state toward the ground state by simulating imaginary-time Schrodinger evolution, without deep ancilla-driven circuits required by phase estimation. Starting from some trial state  $|\Psi(0)\rangle$ , the imaginary time evolution is:

$$|\Psi(\tau)\rangle = \frac{e^{-\tau\hat{H}}|\Psi(0)\rangle}{\|e^{-\tau\hat{H}}|\Psi(0)\rangle\|},$$

where  $\hat{H}$  is the molecular Hamiltonian and  $\tau$  is the imaginary time parameter. In practice, we discretize  $\tau$  in small steps  $\Delta\tau$  and approximate the non-unitary propagator  $e^{-\Delta\tau\hat{H}}$  by a unitary operator. We first Trotter-decompose  $e^{-\Delta\tau\hat{H}}$  into local pieces and then map each to a unitary via Pauli string decomposition:

$$e^{-\Delta\tau\hat{H}} \approx \prod_i e^{-\Delta\tau h_i} \approx \prod_i e^{-i\theta_i \hat{A}_i},$$

where  $\hat{H} = \sum_i h_i$  (sum of local terms or Pauli strings  $h_i$ ) and each  $\hat{A}_i$  is a Hermitian Pauli operator (or Pauli string) chosen to approximate the action of  $h_i$ . The angles  $\theta_i$  are real parameters to be determined. This formula uses the first-order Trotter expansion and then treats each  $e^{-\Delta\tau h_i}$  as a small unitary rotation  $e^{-i\theta_i \hat{A}_i}$  on the quantum state.

### 2.2 Linearized Update Equations

For a sufficiently small time step  $\Delta\tau$ , we linearize the propagator. Acting on the current state  $|\Psi(\tau)\rangle$ , we require:

$$e^{-\Delta\tau\hat{H}}|\Psi(\tau)\rangle \approx \prod_i e^{-i\theta_i \hat{A}_i}|\Psi(\tau)\rangle,$$

Expanding both sides to first order gives the imaginary-time update condition:

$$(I - \Delta\tau\hat{H})|\Psi(\tau)\rangle \approx \left(I - i \sum_i \theta_i \hat{A}_i\right)|\Psi(\tau)\rangle,$$

Equating the first-order terms and dropping the identity on both sides yields a set of linear equations for the small angle parameters  $\theta_i$ :

$$-\Delta\tau\hat{H}|\Psi(\tau)\rangle \approx -i \sum_i \theta_i \hat{A}_i|\Psi(\tau)\rangle,$$

We determine  $\theta_i$  by projecting this equation onto the subspace spanned by  $\hat{A}_j|\Psi(\tau)\rangle$ . That is, for each  $j$  we impose

$$\langle\Psi(\tau)|\hat{A}_j^\dagger \left(e^{-\Delta\tau\hat{H}} - \prod_i e^{-i\theta_i \hat{A}_i}\right)|\Psi(\tau)\rangle = 0$$

which at first order yields  $\langle\Psi|\hat{A}_j(-\Delta\tau\hat{H} + i \sum_i \theta_i \hat{A}_i)|\Psi\rangle = 0$ . Taking Hermitian  $\hat{A}_j$  so that  $\hat{A}_j^\dagger = \hat{A}_j$ , this yields the normal equations for  $\theta_i$ :

$$\sum_i \langle\Psi(\tau)|\hat{A}_j \hat{A}_i|\Psi(\tau)\rangle \theta_i = \Delta\tau \langle\Psi(\tau)|\hat{A}_j \hat{H}|\Psi(\tau)\rangle, \quad \in j$$

This is a linear system  $G\vec{\theta} = \Delta\tau\vec{b}$ , where we define the Gram matrix  $G$  and vector  $b$  as:

- **Gram matrix elements:**  $G_{ji}; =; \langle \Psi(\tau) |, \hat{A}_j \hat{A}_i, | \Psi(\tau) \rangle$ . In practice we take  $G_{ji} = \text{Re} \langle \Psi | \hat{A}_j \hat{A}_i | \Psi \rangle$  to ensure  $G$  is real and symmetric (Any imaginary parts can be shown to cancel or are handled by a gauge choice in the ansatz).
- **Coefficient vector:**  $b_j; =; \langle \Psi(\tau) |, \hat{A}_j \hat{H}, | \Psi(\tau) \rangle$ . If  $\hat{A}_j$  and  $\hat{H}$  are Hermitian,  $b_j$  is real as well; otherwise we again take the real part relevant to the subspace. (Often  $b_j$  is purely imaginary and an extra factor of  $i$  is absorbed, but here we present the form yielding a real  $b_j$ .)

Solving this linear system gives the optimal angle updates  $\theta_i$  that minimize the norm of the difference in the above approximation. Because the solution comes from a linear least-squares (no variational search in a high-dimensional landscape), there are no issues of barren plateaus or local minima in each step. If  $G$  is singular (has a null space), one can choose the minimum-norm solution or regularize by restricting to the span where  $G$  is invertible. This step is repeated sequentially: update the state  $|\Psi(\tau + \Delta\tau)\rangle = \frac{\prod_i e^{-i\theta_i \hat{A}_i} |\Psi(\tau)\rangle}{|\cdot|}$ , then recompute  $G, b$  at the new state and continue until convergence (energy stops decreasing).

### 2.2.1 Operator Basis

The choice of Pauli operators  $\hat{A}_i$  is crucial. In practice, one uses a local operator pool that spans the effect of  $H$ . For our molecular Hamiltonian mapped to qubits (via Jordan-Wigner or Bravyi-Kitaev), a natural choice is to include all Pauli strings that appear in  $H$  (or that can be generated through commutators up to a certain range). This ensures  $e^{-i\theta_i \hat{A}_i}$  can approximate  $e^{-\Delta\tau h_i}$  for each term. The finite correlation length assumption guarantees that a unitary on a local domain can mimic the imaginary time step sufficiently well. Inexact QITE with truncated domains remains a valid heuristic that monotonically lowers energy until convergence.

### 2.2.2 Energy & Observables

At each QITE step or after convergence, one can measure the energy  $E(\tau) = \frac{\langle \Psi(\tau) | \hat{H} | \Psi(\tau) \rangle}{\langle \Psi(\tau) | \Psi(\tau) \rangle}$  as well as other observables of interest (e.g. spin densities, etc.). By gradually increasing  $\tau$ ,  $E(\tau)$  will approach the ground-state energy from above, since imaginary time projection guarantees convergence to the lowest-energy state in the initial subspace. This makes QITE especially suitable for phenanthrene’s carbonyl-forming reaction which may involve a multi-reference transition state or intermediate: unlike a fixed ansatz VQE, QITE will continue converging as long as the initial state had overlap with the true ground state.

### 2.2.3 Justification

In essence, QITE provides a systematic path to the ground state by a sequence of shallow circuits (each of depth determined by the locality of  $\hat{A}_i$  operators). It avoids the overhead of deep phase-estimation circuits and the classical parameter optimisation of VQE. In the context of phenanthrene oxidation, QITE can capture the strongly correlated electronic restructuring (e.g. forming an O–H bond then C=O double bond) by gradually evolving a reactant state into the product state, which is challenging for single-reference methods.

## 3 Sample-Based Quantum Diagonalization (SQD)

### 3.1 Molecular Orbital Theory Analysis

#### 3.1.1 Canonical Molecular Orbitals and Frontier Orbital Selection

We begin with a Hartree-Fock (HF) calculation on the phenanthrene fragment undergoing oxidation. The canonical molecular orbitals (MOs) are expressed via the LCAO ansatz:

$$\phi_i(\mathbf{r}) = \sum_{\mu} C_{\mu i} \chi_{\mu}(\mathbf{r}), \quad (1)$$

where  $\chi_{\mu}$  are atomic basis functions and  $C_{\mu i}$  are coefficients from HF diagonalization. The orbital energies  $\varepsilon_i$  provide a Koopmans spectrum. We define the active MOT space:

$$A_{\text{MOT}} = \{\phi_{h-1}, \phi_h, \phi_l, \phi_{l+1}\}, \quad (2)$$

where  $h$  and  $l$  denote HOMO and LUMO indices, respectively.

### 3.1.2 Spin–Orbital Basis and Occupancy Vectors

Each spatial orbital  $\phi_i$  generates two spin orbitals. A Slater determinant is encoded as bitstring  $x$ :

$$x = (x_{1\uparrow}, \dots, x_{N_{\text{orb}}\uparrow}; x_{1\downarrow}, \dots, x_{N_{\text{orb}}\downarrow}), \quad x_{p\sigma} \in \{0, 1\}, \quad (3)$$

with constraints:

$$\sum_p x_{p\uparrow} = N_\alpha, \quad \sum_p x_{p\downarrow} = N_\beta, \quad N = N_\alpha + N_\beta. \quad (4)$$

Singlet states satisfy  $N_\alpha = N_\beta$ , doublets satisfy  $N_\alpha = N_\beta \pm 1$ .

### 3.1.3 Sample-Based Subspace and Hamiltonian Projection

Define the sampled set of determinants:

$$S = \{|x_j\rangle\}_{j=1}^M. \quad (5)$$

The projected Hamiltonian is:

$$H_S = \Pi_S H \Pi_S = \sum_{i,j \in S} |x_i\rangle \langle x_i| H |x_j\rangle \langle x_j|. \quad (6)$$

The full molecular Hamiltonian is:

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_s a_r. \quad (7)$$

These are transformed from AO integrals using HF coefficients  $C$ :

$$h_{pq} = \sum_{\mu\nu} C_{\mu p} C_{\nu q} h_{\mu\nu}^{(AO)}, \quad (8)$$

$$g_{pqrs} = \sum_{\mu\nu\lambda\sigma} C_{\mu p} C_{\nu q} C_{\lambda r} C_{\sigma s} (\mu\nu || \lambda\sigma). \quad (9)$$

### 3.1.4 Qubit Mapping and Symmetry Constraints

Each spin-orbital maps to a qubit:  $|0\rangle$  for empty,  $|1\rangle$  for occupied. Jordan–Wigner transformation yields:

$$H_{\text{qubit}} = \sum_j c_j P_j, \quad P_j \in \{I, X, Y, Z\}^{\otimes n}. \quad (10)$$

Only basis states with valid  $N_\alpha, N_\beta$  are used. Optionally, enforce total spin  $S$  using penalty Hamiltonian:

$$\tilde{H}_S = H + \lambda(\hat{S}^2 - S(S+1)). \quad (11)$$

### 3.1.5 Subspace Diagonalisation and Amplitude Recovery

Diagonalize  $H_S$  classically:

$$H_S |\Psi_S^{(k)}\rangle = E_k |\Psi_S^{(k)}\rangle, \quad |\Psi_S\rangle = \sum_j c_j |x_j\rangle. \quad (12)$$

Use reconstructed  $|\Psi_S\rangle$  to compute orbital occupations:

$$n_{p\sigma} = \langle \Psi_S | a_{p\sigma}^\dagger a_{p\sigma} | \Psi_S \rangle, \quad (13)$$

and feed back into the sampling circuit. Iterative SQD with NISQ hardware refines  $|\Psi_S\rangle$ .

### 3.2 Subspace Construction via Sampling

Once QITE prepares an approximate ground state  $|\Psi_g\rangle$  of the phenanthrene fragment Hamiltonian, we can refine this result using Sample-Based Quantum Diagonalization (SQD). SQD is essentially a quantum-classical selected configuration interaction (CI) method. The quantum processor is used to sample important basis states (configurations) from  $|\Psi_g\rangle$ , and then a classical computation exactly diagonalizes  $\hat{H}$  in the subspace spanned by those basis states. This approach dramatically extends the feasible molecular size, as demonstrated by SQD simulations of up to 77 qubits (36 orbitals) on present-day devices.

Formally, let  $|x_j\rangle$  be a set of bitstring basis states (computational basis states) chosen from measuring  $|\Psi_g\rangle$  in the computational basis. Each bitstring  $|x_j\rangle$  encodes a Slater determinant (occupation of each spin-orbital). We define the sampled subspace  $S = \text{Span}, |x_1\rangle, |x_2\rangle, \dots, |x_M\rangle$  consisting of the top- $M$  configurations (for example, those with highest probabilities or chosen via some threshold). The projector onto this subspace is

$$\prod_S = \sum_{j=1}^M |x_j\rangle\langle x_j|$$

which acts as the identity on  $S$  and annihilates states orthogonal to  $S$ . We then construct the subspace Hamiltonian by projecting  $\hat{H}$  into  $S$ :

$$\hat{H}_S = \prod_S \hat{H} \prod_S$$

In the basis  $|x_j\rangle_{j=1}^M$ ,  $\hat{H}_S$  is an  $M \times M$  matrix with elements:

$$(H_S)_{ij} = \langle x_i | \hat{H} | x_j \rangle$$

These matrix elements can be computed efficiently using the known structure of  $\hat{H}$  in second quantization. For a molecular electronic Hamiltonian (in an orthonormal spin-orbital basis),  $\hat{H}$  has the form:

$$\hat{H} = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} g_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

where  $a_p^\dagger, a_p$  are fermionic creation/annihilation operators and  $h_{pq}, g_{pqrs}$  are one- and two-electron integrals. The nonzero values of  $\langle x_i | a_p^\dagger a_q | x_j \rangle$  and  $\langle x_i | a_p^\dagger a_q^\dagger a_r a_s | x_j \rangle$  occur only when  $|x_i\rangle$  and  $|x_j\rangle$  differ by the appropriate single or double substitutions (excitation/de-excitation). Thus,  $\langle x_i | \hat{H} | x_j \rangle$  can be evaluated by applying Slater–Condon rules, which yield the integral  $h_{pq}$  or  $g_{pqrs}$  (with a sign from fermion reordering) if  $|x_j\rangle$  can be reached from  $|x_i\rangle$  by the corresponding one- or two-body operator, and zero otherwise. The diagonal entries  $(H_S)_{ii} = \langle x_i | \hat{H} | x_i \rangle$  are just the sum of one-body energies of occupied orbitals in  $|x_i\rangle$  plus the sum of pairwise Coulomb repulsion energies for electrons in that configuration.

In practice, instead of calculating each matrix element from scratch, one can use the measured bitstrings to estimate them. For instance, the **diagonal energies**  $\langle x_i | \hat{H} | x_i \rangle$  can be obtained directly by measuring all Pauli terms of  $\hat{H}$  on the state  $|x_i\rangle$  (which is computational basis, so diagonal in  $Z$  basis) – essentially, summing the known integrals for occupied orbitals. **Off-diagonals** (couplings) between two different sampled configurations  $|x_i\rangle$  and  $|x_j\rangle$  can be obtained if  $|x_i\rangle$  and  $|x_j\rangle$  differ by, say, two spin-orbital occupancies (a double excitation); then  $\langle x_i | \hat{H} | x_j \rangle$  equals the corresponding two-electron integral  $g_{pqrs}$ , which is known from classical pre-computation. If they differ by one orbital (single excitation), only if spin-conserving, then  $\langle x_i | \hat{H} | x_j \rangle$  is the one-electron integral  $h_{pq}$ . If they differ by more than two orbitals,  $\langle x_i | \hat{H} | x_j \rangle = 0$ . Therefore,  $H_S$  is a sparse matrix in this basis, with structure mirroring excitations.

### 3.3 Classical Diagonalisation

Once  $H_S$  is assembled (dimension  $M \times M$  with  $M \ll$  dimension of full Hilbert space), we solve the eigenvalue problem:

$$H_S \vec{c} = E \vec{c}$$

yielding eigenpairs  $(E_k, \mathbf{c}^{(k)})$  for  $k = 1, \dots, M$ . Here  $E_k$  are approximate eigenvalues of the full problem and  $\mathbf{c}^{(k)} = (c_1, \dots, c_M)^T$  are the components of the  $k$ -th eigenvector expressed in the basis  $|x_j\rangle$ . Typically, the lowest eigenvalue  $E_0$  will be a variationally improved ground-state energy (upper bound to the true ground energy, since  $S$  is a subspace of the full Hilbert space). The corresponding eigenvector gives an improved ground-state wavefunction:

$$|\Psi_{\text{subspace}}\rangle = \sum_{j=1}^M c_j |x_j\rangle$$

This state generally has better accuracy than the original  $|\Psi_g\rangle$  from QITE/VQE, because the diagonalisation effectively reweights and linearly combines configurations beyond what a single circuit could easily produce. Importantly, the subspace diagonalisation recovers dynamic correlation that may be missing if  $|\Psi_g\rangle$  was constrained (e.g. a short-depth ansatz).

In the case of phenanthrene oxidation, this means subtle electron correlation effects (like long-range polarisation or multi-reference configurations) can be captured by including the relevant determinants in  $S$  even if they had small amplitudes in the initial state.

### 3.4 Configuration Recovery & Iteration

The SQD procedure can be iterated or enhanced by configuration recovery techniques. Because sampling on quantum hardware can be noisy, one must *mitigate errors* and enforce symmetries on the samples (see **Stage 4**). In practice, each measured bitstring is first validated: for example, we discard or correct those that do not have the correct number of electrons or spin (those likely arising from hardware errors). The remaining *clean* bitstrings are taken as the  $|x_j\rangle$  in  $S$ . One may choose  $M$  by a threshold on measured probability or by picking the top few bitstrings repeatedly observed. After diagonalising  $H_S$ , we obtain a new state  $|\Psi_{\text{subspace}}\rangle$  as above. We can then re-sample this state by preparing it on the QPU (for example, via amplitude loading or by running a circuit that approximately prepares the  $|x_j\rangle$  superposition with coefficients  $c_j$ ), to see if additional important configurations (with non-negligible amplitude) outside the current  $S$  should be added. This iterative enrichment of  $S$  (analogous to selected CI or iterative Krylov methods) allows approaching full-CI accuracy with far fewer basis states. In recent work, this SQD approach (also called Quantum Selected CI) has yielded chemical accuracy for challenging bond dissociations by progressively expanding the subspace using sampled ‘‘Cartesian product states’’ and other enhancements.

### 3.5 Context and Scalability

*Robledo-Moreno et al.* (Science Advances 2025) demonstrated that SQD in a quantum-centric workflow can handle much larger active spaces than conventional exact diagonalisation. The QPU serves as a co-processor that provides the important subspace through sampling, while a classical HPC backend handles the heavy eigenproblem in the reduced space. This distributed quantum-classical approach enabled, for example, a 77-qubit simulation (36 orbital active space) for a transition metal complex. In our phenanthrene case, after QITE prepares the ground state of the oxidized fragment, SQD would pick out determinant basis states corresponding to, say, the dominant resonance structures or multi-exciton configurations in the carbonyl formation. By diagonalising in that subspace, we can extract not only the ground-state energy more accurately, but also excited-state energies and wavefunctions (e.g. to estimate gap to an excited triplet state or a transition state). Indeed, extended SQD methods now allow computation of excited states by constructing multiple subspaces or using deflation techniques, which could be applied to study photochemical aspects of asphalt aging as well.

## 4 Fermionic Pairing Hamiltonian Benchmark

To validate the above methods, we consider the **fermionic pairing Hamiltonian** as a benchmark system. The pairing Hamiltonian (also known as the reduced BCS Hamiltonian or Richardson model in nuclear physics) describes a set of orbitals where electrons form paired singlet states. In second-quantized form, a general spin-singlet pairing Hamiltonian can be written as:

$$\hat{H}_{\text{pair}} = \sum_{i=1}^L \varepsilon_i (n_{i,\uparrow} + n_{i,\downarrow}) - g \sum_{i,j=1}^L P_i^\dagger P_j$$

where:

- $i, j$  index a set of  $L$  single-particle orbitals (energy levels).
- $\varepsilon_i$  is the single-particle energy of orbital  $i$ .
- $n_{i,\Sigma} = a_{i,\Sigma}^\dagger a_{i,\Sigma}$  is the number operator for orbital  $i$  and spin  $\Sigma \in \uparrow, \downarrow$ .
- $P_i^\dagger = a_{i,\uparrow}^\dagger a_{i,\downarrow}^\dagger$  is the pair creation operator on orbital  $i$ , creating a spin-up/spin-down pair in that orbital;  $P_i = a_{i,\downarrow} a_{i,\uparrow}$  is the corresponding pair annihilation operator.
- $g > 0$  is the pairing interaction strength, favoring the formation of pairs.

The first term is just the normal one-body energy (like a mean-field), and the second term  $-g \sum_{i,j} P_i^\dagger P_j$  is a correlated interaction that scatters pairs between orbitals. Physically, it means any pair of electrons (one up, one down) can hop between any two orbitals  $i$  and  $j$  with coupling  $g$ . All such scattering terms contribute equally (in the simplest form of the model), reflecting a constant pairing interaction. The Hamiltonian conserves the total number of electrons  $N = \sum_i (n_{i,\uparrow} + n_{i,\downarrow})$  (each  $P_i^\dagger P_j$  operator creates a pair in  $i$  and destroys a pair in  $j$ , leaving  $N$  unchanged). It also conserves total spin – in fact,  $\hat{H}_{\text{pair}}$  commutes with the total spin operator  $\mathbf{S}^2$  and  $S_z$  because it always creates or annihilates pairs of opposite-spin electrons. Thus, the pairing Hamiltonian acts within fixed- $(N, S)$  sectors, and in particular it has a bias toward  $S = 0$  (spin-singlet) states since the ground state puts electrons in singlet pairs.

## 4.1 Symmetry Sectors: Seniority and Spin

A crucial quantum number for the pairing Hamiltonian is seniority  $\nu$ , defined as the number of unpaired electrons in a state (electrons not forming a spin-up/down pair). In  $\hat{H}_{\text{pair}}$ , seniority is conserved:  $[\hat{H}_{\text{pair}}, \nu] = 0$ . In fact,  $\hat{H}_{\text{pair}}$  is one of the few non-trivial Hamiltonians for which seniority is a good quantum number. For example, a state with all electrons paired (seniority  $\nu = 0$ ) cannot transition under  $\hat{H}_{\text{pair}}$  to a state with an unpaired electron ( $\nu = 1$ ), because the terms  $P_i^\dagger P_j$  always move pairs as whole units. This block structure allows solving the pairing model for each seniority sector separately. The ground state at even  $N$  typically lies in the  $\nu = 0$  (fully paired) sector and is a global spin singlet ( $S = 0$ ). For odd  $N$ , one electron remains unpaired ( $\nu = 1$ ), giving a lowest doublet state ( $S = \frac{1}{2}$ ), etc. The conservation of spin  $S$  is related – in this simple pairing model, we assume a *spin-independent* interaction that is invariant under  $\text{SU}(2)$  rotations of all spins, so total spin is also a good quantum number (the interaction is constructed from singlet pair operators, which commute with  $\mathbf{S}^2$ ).

### 4.1.1 Qubit Mapping

We can map  $\hat{H}_{\text{pair}}$  to qubits in two ways:

- ◇ **Direct mapping (Jordan-Wigner):** Represent each spin-orbital as a qubit. Then  $n_{i,\Sigma} = \frac{1}{2}(1 - Z_{i,\Sigma})$  (if we choose  $|0\rangle$  as occupied and  $|1\rangle$  as empty or vice versa), and  $a_{i,\Sigma}$  maps to a Pauli string with an  $X \pm iY$  on that qubit and  $Z$  strings on preceding qubits (Jordan-Wigner). The pair operators  $P_i^\dagger = a_{i,\uparrow}^\dagger a_{i,\downarrow}^\dagger$  become products of Pauli operators on the two qubits corresponding to  $(i, \uparrow)$  and  $(i, \downarrow)$ . This mapping yields  $\hat{H}_{\text{pair}}$  as a sum of multi-qubit Pauli terms (including four-qubit terms for  $P_i^\dagger P_j$  across two orbitals). While straightforward, this doubles the qubit count relative to orbitals (since each orbital has two spin states).
- ◇ **Quasi-spin mapping:** Because each orbital can only be empty, singly occupied (two ways), or doubly occupied, one can encode the paired vs. unpaired occupancy in a more compact form. In the seniority-zero subspace (all electrons paired), each orbital  $i$  is either empty or occupied by a singlet pair. This is effectively a two-level system, which we can map to a single qubit: e.g. define  $|0\rangle_i = \text{“orbital } i \text{ empty”}$ , and  $|1\rangle_i = \text{“orbital } i \text{ doubly occupied by a pair”}$ . Then  $P_i^\dagger$  acts like  $\sum_i^+$  (raising the qubit from 0 to 1 by adding a pair), and  $P_i$  like  $\sum_i^-$ . The number operator for that orbital is  $N_i = 2, P_i^\dagger P_i$ , which corresponds to  $2|1\rangle_i \langle 1| = I - Z_i$  (up to a shift). Using this mapping,  $\hat{H}_{\text{pair}}$  for seniority-zero states can be written in spin-1/2 language as:

$$\hat{H}_{\text{pair}}^{(\nu=0)} = \sum_{i=1}^L \varepsilon_i (I - Z_i) - g \sum_{i,j=1}^L \frac{1}{2} (X_i X_j + Y_i Y_j)$$

where we used  $P_i^\dagger P_j + P_j^\dagger P_i$  mapping to  $\frac{1}{2}(X_i X_j + Y_i Y_j)$ , and dropped constant terms. This Hamiltonian acts on  $L$  qubits (one per orbital), and consists of local  $Z$  terms and all-to-all  $XX + YY$  coupling. It is equivalent to an  $XY$  model with global coupling, or the so-called uniform pairing Hamiltonian in the quasi-spin formalism. This model is exactly solvable via Richardson’s equations, but it is non-trivial enough to test quantum algorithms.

The use of the **pairing Hamiltonian as a benchmark** is motivated by its intermediate complexity: it has strong correlation (especially when  $g$  is large, leading to a superconducting-like ground state with large pairing gap), but it also has symmetries that allow analytic or high-precision solutions for validation. For instance, one can compare QITE’s convergence on this model against known exact ground-state energies, or use SQD to pick out the dominant pair configurations and see if it reproduces the known BCS-like ground state. Moreover, since seniority is good, one can intentionally break seniority in a trial state and test if adding symmetry enforcement (next section) improves the results. The pairing Hamiltonian is also relevant as a reduced model for superconductivity and nuclear structure, so demonstrating accurate quantum simulations for it builds confidence for more complex Hamiltonians. In our context, it serves as a **verification system** to ensure our QITE+SQD pipeline (with symmetry enforcement) works correctly before applying it to phenanthrene’s chemistry, which lacks such simplifying symmetries.

## 5 Symmetry Enforcement in Quantum Simulation

### 5.1 Need for Symmetry Enforcement

Enforcing known symmetries of the molecular Hamiltonian is crucial for both accuracy and efficiency. Phenanthrene’s electronic Hamiltonian conserves particle number  $N$  (electrons) and total spin  $S^2$  (assuming a non-spin-orbit approximation), among other symmetries (such as spatial symmetry if considered). However, quantum algorithms can inadvertently explore or collapse into states of the wrong symmetry – for example, hardware noise might produce an output state with the wrong number of electrons, or a variational ansatz might produce a superposition of different total spin sectors. We employ two complementary strategies: projection operators to constrain the subspace, and penalty terms added to the Hamiltonian or energy functional.

### 5.2 Projection Operators

If  $\hat{O}$  is a symmetry operator with eigenvalue  $o$  for the desired sector (e.g.  $\hat{N}|\Psi\rangle = N_{\text{target}}|\Psi\rangle$  or  $\hat{S}^2|\Psi\rangle = s(s+1)|\Psi\rangle$  for spin- $s$ ), the ideal projector onto the  $o$  subspace is

$$\prod_o = \prod_{\ell \neq o} \frac{\hat{O} - \ell}{o - \ell}$$

where  $\ell$  runs over all other eigenvalues of  $\hat{O}$ . In practice, one often uses an integral representation. For particle number,  $N$  has integer eigenvalues, so one convenient form is:

$$\prod_{N_0} = \frac{1}{2\pi} \int_0^{2\pi} e^{i\phi(\hat{N}-N_0)} d\phi$$

which projects onto the eigenspace of  $\hat{N}$  with eigenvalue  $N_0$  (this works because the exponential adds a phase  $e^{i\phi(N-N_0)}$  which integrates to 1 if  $N = N_0$  and to 0 if  $N \neq N_0$ ). Similarly, for total spin  $S^2$ , one can use the group theory of  $SU(2)$ :

$$\prod_{S=s} = \frac{2s+1}{8\pi} \int_0^\pi \sin\beta d\beta \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma D_{m,m'}^{(s)}(\alpha, \beta, \gamma) e^{-i\alpha S_z} e^{-i\beta S_y} e^{-i\gamma S_z}$$

where  $D_{m,m'}^{(s)}$  is the Wigner D-matrix and the integration over Euler angles projects onto total spin- $s$  subspace (with  $m = m' = s$  usually for singlet). This formula is more complicated, but for spin-0 (singlet) it simplifies significantly (essentially averaging over all spin rotations so that any triplet or higher component cancels out).

On current quantum hardware, implementing these projectors directly (which involve many controlled operations or non-unitary averaging) is challenging. Instead, we often enforce symmetries by restricting the ansatz and sampling, or by penalising deviations, as discussed next.



### 5.3 Penalty Terms in Hamiltonian

A simpler, variationally friendly method is to add a penalty term to the Hamiltonian or the cost function that energetically punishes wrong-symmetry states. For example:

- To enforce correct electron number  $N_0$ , we can use

$$\hat{H}' = \hat{H} + \lambda_N (\hat{N} - N_0)^2$$

where  $\lambda_N$  is a large positive constant. Any state with  $N \neq N_0$  will incur a large energy penalty  $\lambda_N(N - N_0)^2$ , raising its energy relative to the target subspace. In the limit  $\lambda_N \rightarrow \infty$  this strictly confines the ground state to the  $N = N_0$  sector. In practice, a finite  $\lambda_N$  is chosen large enough that the optimizer or QITE will avoid generating any amplitude on the wrong-number states.

- To enforce spin- $s$  (e.g. singlet  $s = 0$ ), we add

$$\lambda_S (\hat{S}^2 - s(s+1))^2$$

since  $\hat{S}^2$  has eigenvalues  $s(s+1)$  for spin- $s$ . Any contamination by  $S \neq s$  will increase the expectation of this term. For a spin-0 target,  $\langle (S^2 - 0)^2 \rangle = \langle S^4 \rangle$  is minimized (zero) iff the state is a pure singlet.

These penalty terms can be incorporated during QITE or VQE by simply augmenting the measured energy. For QITE, one could include these terms in  $\hat{H}$  with moderately large coefficients so that the imaginary-time evolution naturally suppresses components in the wrong symmetry sectors (they have higher effective energy). For VQE, one includes them in the cost function  $E'(\theta) = \langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle + \lambda_N \langle (\hat{N} - N_0)^2 \rangle + \lambda_S \langle (\hat{S}^2 - s(s+1))^2 \rangle$ , and optimizes  $E'(\theta)$ . If the ground state of  $\hat{H}$  already has the correct symmetries (which it should for physical reasons, e.g. minimum energy is at correct  $N$  and usually a singlet for even electrons), adding these terms does not change the true minimum but helps guide the algorithm to stay in the correct subspace.

### 5.4 Symmetry Enforcement in Sampling

In the SQD stage, we **filter the sampled bitstrings by symmetry**. For number symmetry, this is straightforward: each computational basis bitstring has a well-defined number of electrons (just count the 1s if 1 = occupied). We simply discard any samples not having the exact  $N_0$  electrons (or if an error-correction scheme is available, adjust bitstrings with minor errors to the nearest valid configuration). In experiments, this dramatically improves results: for instance, Robledo-Moreno et al. report an error mitigation strategy that postselects on the correct number of electrons for each sample, ensuring no leakage into other sectors.

For spin symmetry, a single bitstring does not carry a total  $S$  label (because computational basis is a  $S_z$  eigen-basis, not  $S^2$ ). However, one can enforce spin multiplicities indirectly: for example, in a singlet  $S = 0$  system with  $N$  even, the number of  $\uparrow$  and  $\downarrow$  electrons each should be  $N/2$ . So we can at least discard bitstrings where  $N_\uparrow \neq N_\downarrow$  if we expect a singlet (though this only enforces  $S_z = 0$ , not full  $S = 0$ ). More sophisticated approaches measure  $S^2$  for the state ensemble: for instance, after obtaining the subspace eigenvector  $\sum_j c_j |x_j\rangle$ , one can calculate  $\langle S^2 \rangle$  and if it is higher than  $s(s+1)$ , one might try expanding  $S$  by adding configurations that can cancel the spin contamination. In practice, it's often effective to use spin-adapted ansätze from the start (see next section) so that every sampled configuration already respects the desired spin symmetry.

### 5.5 Symmetry in Circuit Construction

Another proactive measure is to design the quantum circuit ansatz to preserve symmetries by construction. For number symmetry, this means every gate in the circuit should conserve the number of 1s (occupied orbitals) – e.g. using only fermionic excitation gates that replace two 0→1 and two 1→0 (for double excitations) or one 0→1 and one 1→0 (for single excitation) simultaneously, so that if you start in a state with  $N_0$  ones, you end with  $N_0$  ones. Many chemistry ansätze (like unitary coupled cluster with singles and doubles, UCCSD) have this property built-in. In QITE, one can restrict the operator pool  $\hat{A}_i$  to number-conserving Pauli strings (those with equal numbers of  $X$  on creation and annihilation operators).

This ensures the QITE evolution never leaves the  $N = N_0$  subspace. For total spin, one can use spin-adapted orbitals or gates: for instance, always excite pairs of electrons with opposite spin together (so as not to break singlet symmetry), or use Givens rotations and pair hopping gates that respect  $S = 0$ . In the pairing Hamiltonian benchmark, our mapping to qubits (one per orbital pair) inherently preserved spin-singlets. Similarly, in phenanthrene’s Hamiltonian, we can group spin-up/spin-down orbitals and apply symmetric operations to them.

In summary, symmetry enforcement is achieved by a mix of preventative measures (symmetry-respecting ansatz and operations) and corrective measures (post-selection and penalties). This not only improves accuracy (by avoiding symmetry-broken variational states) but also reduces the effective search space, focusing the algorithm on the physically relevant manifold. Indeed, IBM’s SQD implementation attributed much of its success at 77 qubit scale to error mitigation *at the level of individual samples, ensuring the conservation of molecular symmetries*. Effectively, filtering out any sampled determinant that violated  $N$  or spin symmetry before constructing the subspace Hamiltonian. By incorporating the projector  $\Pi_S$  and  $\Pi_N$  logic in our workflow, we maintain high fidelity to the true reaction mechanism of phenanthrene oxidation (which must obey these symmetries).

## 6 Circuit Ansatz & Execution Considerations

### 6.1 Ansatz and Circuit Structure

We employ an ansatz of layered Pauli rotations, chosen to balance expressiveness with hardware feasibility. Each layer consists of a sequence of unitary exponentials of Pauli strings (usually 1- and 2-qubit terms) acting on the  $n$  qubits of the system. For example, a generic layer may implement something like  $U(\theta) = \exp(-i\theta_1 X_1) \exp(-i\theta_2 Z_2 Z_3) \exp(-i\theta_3 X_2 Y_3) \cdots$  – i.e. parameterized rotations about Pauli operators. In practice, for chemistry, we choose these Pauli operators to correspond to fermionic excitation generators. For instance, a two-qubit unitary  $\exp(-i\theta, (X_i X_j + Y_i Y_j))$  is equivalent (up to Jordan-Wigner mapping) to a spin-conserving exchange between orbital  $i$  and  $j$  (a bit like a beamsplitter for fermions). By stacking such operations, we can build a highly flexible trial wavefunction. This **product of exponentials of local Pauli operators** ansatz aligns with the QITE decomposition operators. Indeed, each QITE step effectively yields one layer of this form with the  $\theta_i$  computed from the linear system. For VQE usage, one could treat all  $\theta$  in all layers as variational parameters to minimize energy.

### 6.2 Number of Parameters

The number of parameters is (no. Pauli terms per layer)  $\times$  (no. layers). In QITE, each imaginary time step introduces as many parameters as there are terms in the operator pool (though they are determined by solving linear equations rather than by gradient descent). For example, if we have 50 Pauli terms covering all unique single and double excitations in a 12-qubit system, and we perform 10 QITE steps, that’s effectively on the order of 500 parameters applied sequentially (though not all remain independent, since each step overwrites the previous state). In a fixed-depth VQE, one might choose e.g. 20-40 parameters for a 12-qubit phenanthrene fragment ansatz. The circuit is thus shallow enough to run on current hardware yet expressive enough for strongly correlated chemistry.

### 6.3 Circuit Depth per Step

Each Pauli rotation  $\exp(-i\theta P)$  can be compiled into a small number of primitive gates. A single-qubit rotation is one gate; a two-qubit Pauli like  $Z_i Z_j$  can be done with one CNOT and one RZ and another CNOT; a two-qubit  $X_i X_j$  or  $X_i Y_j$  needs a little more but on the order of 2 CNOTs around a single-qubit rotation. Thus, if we have  $K$  Pauli exponentials in a layer, the depth might be roughly  $2K$  (if done sequentially and assuming some parallelization when non-overlapping qubits). Our previous proposal specs targeted **depth  $\leq 40$  per QITE step**. In our phenanthrene example (12–18 qubits after active space reduction), this is achievable by trotterizing complex operations into 40 simple gates. Over, say, 5–10 QITE steps, the total depth  $\approx 200$ –400 might be required, which starts to challenge coherence on NISQ devices, but can be mitigated by executing steps one at a time (re-preparing state for each step) or using mid-circuit measurement and re-initialisation tricks.

## 6.4 Symmetry Adaptation in Ansatz

As noted, we pick ansatz gates that respect symmetries. For number conservation, we include only those two-qubit rotations that move an electron from one orbital to another (and its paired opposite-spin electron accordingly). An example gate on 4 qubits (2 spin-orbitals in one spatial orbital and 2 in another) is

$$\exp\left[-i\theta(a_{p,\uparrow}^\dagger a_{q,\uparrow} + a_{p,\downarrow}^\dagger a_{q,\downarrow} + \text{h.c.})\right]$$

which in qubit terms is  $\exp[-i\theta(X_{p\uparrow}X_{q\uparrow} + Y_{p\uparrow}Y_{q\uparrow} + X_{p\downarrow}X_{q\downarrow} + Y_{p\downarrow}Y_{q\downarrow})/2]$ . This entangles orbitals  $p$  and  $q$  while conserving  $N$  and  $S_z$ . Using such gates as building blocks ensures the circuit never leaves the intended symmetry sector by construction.

## 6.5 Shot Count and Measurement Overhead

Both QITE and SQD require extensive measurement of observables. In QITE, at each step one must measure all matrix elements  $G_{ij} = \langle \Psi | A_j A_i | \Psi \rangle$  and  $b_j = \langle \Psi | A_j H | \Psi \rangle$  needed for the linear system. The number of such terms can be on the order of tens to hundreds (scaling roughly as the square of number of operators in the pool). Each expectation is estimated via repeated circuit runs (shots). Similarly, SQD requires measuring terms of  $\hat{H}$  in the subspace states (though many can be calculated analytically if we know the integrals, as discussed). The number of shots per expectation should be high (to suppress statistical error in  $G$  and  $b$  which otherwise could lead to inaccurate  $\theta$  update). In our plan, we allocate  $10^4$ – $10^5$  shots per QITE step for stable estimates. For SQD, if using direct measurement of off-diagonals, similar shot budgets would apply; but typically one relies on known integrals for matrix elements, reducing quantum measurement needs mainly to state preparation probabilities (i.e. sampling the bitstrings themselves). Our previous proposal cited  $10^4$ – $10^5$  shots and 12–18 qubits as the working range, which is consistent with our phenanthrene case.

## 6.6 Hardware Constraints and Execution

Running this protocol on real hardware requires careful consideration of gate fidelity, qubit connectivity, and parallelization. The circuit uses a lot of two-qubit gates, which are error-prone; hence error mitigation and possibly error correction are vital. Techniques like **zero-noise extrapolation** and **dynamical decoupling** were considered – these can be applied to each QITE step’s circuit to reduce decoherence impact. Moreover, advanced error-suppressing compilers like Q-CTRL’s Fire Opal can be used. Indeed, Fire Opal provided 3–6 $\times$  improvements in effective error rates in benchmark tests, which would significantly help in this multi-step algorithm.

Another consideration is concurrent execution and distributed computation. IBM’s Heron qubit architectures and others allow parallel execution of multiple circuit instances. This is useful, for example, when one needs to collect measurements for many Pauli terms – one can distribute these measurements across parallel shots on separate qubit subsets or separate processors if available. The quantum-centric HPC integration means while the QPU handles state preparation and sampling, a classical supercomputer (like Japan’s Fugaku used in IBM’s work) handles constructing and diagonalising the  $H_S$  matrix. This distributed approach ensures that even if  $M$  (the number of sampled configurations) is large (hundreds to thousands), the classical part can diagonalize that matrix using parallel linear algebra.

Referencing *Robledo-Moreno et al.* (2025): In their Science Advances paper, Robledo-Moreno et al. effectively demonstrated subspace filtering (post-selecting symmetry-valid samples) and distributed diagonalisation (solving the subspace eigenproblem on HPC) as key enablers for reaching the largest chemistry simulations to date. We incorporate the same principles: after each sampling phase, we filter out any bitstrings violating conservation laws (as described in Stage 4), and we utilize a powerful classical solver (possibly distributed across nodes) to handle the diagonalisation of  $\hat{H}_S$  when  $S$  grows. Since diagonalisation is  $O(M^3)$  in time, having HPC resources means we can push  $M$  (and thus accuracy) higher. In the phenanthrene use-case, we expect  $M$  need not be extremely large (phenanthrene’s active space might be 12 orbitals if we freeze core and truncate virtuals, giving a full CI dimension of  $\sim \binom{24}{N}$  which is large, but chemical intuition suggests only tens of determinants might be significant for the carbonyl formation). Still, the ability to scale up  $M$  provides a safety net to systematically approach exact results.

## 7 Final Remarks

Our five-stage protocol;

1. build the molecular Hamiltonian,
2. apply QITE for ground state,
3. refine via SQD,
4. enforce symmetries throughout,
5. execute on optimised circuits with mitigation

offers an end-to-end quantum simulation workflow for complex chemistry like phenanthrene oxidation. By avoiding manual active-space selection (CASSCF) and instead using QITE to obtain a correlated ground state and SQD to diagonalize in its support, we let the quantum hardware handle the correlation within a manageable subspace identified on-the-fly. Phenanthrene’s carbonyl formation, being a paradigm of aromatics’ oxidative aging, stands as an ideal test: it is classically challenging due to potential multi-reference character, but small enough for near-term quantum devices (with a suitable basis and encoding giving on the order of 14–16 qubits after truncation). The outlined approach promises to capture the energetics of  $O-H$  addition and  $C=O$  formation accurately, shedding light on the reaction barriers and mechanisms that govern asphalt longevity. Each stage of the protocol has been defined with rigorous equations and justified by recent advancements, ensuring a mathematically complete and physically sound framework for quantum chemistry simulations in this domain.