ZenKO: Guided and Iterative Quantum-Classical Method for Molecular Electronic Structure using Sample-Based Quantum Diagonalization

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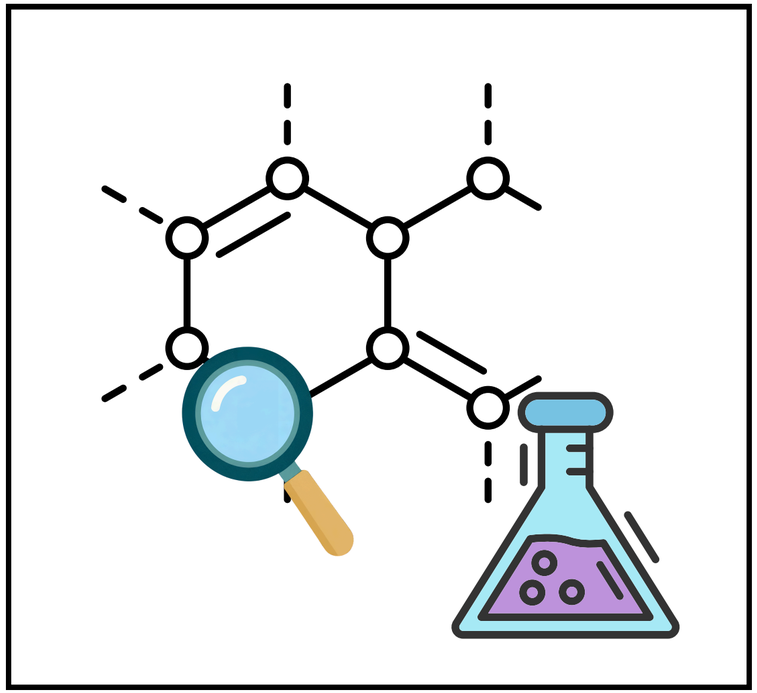
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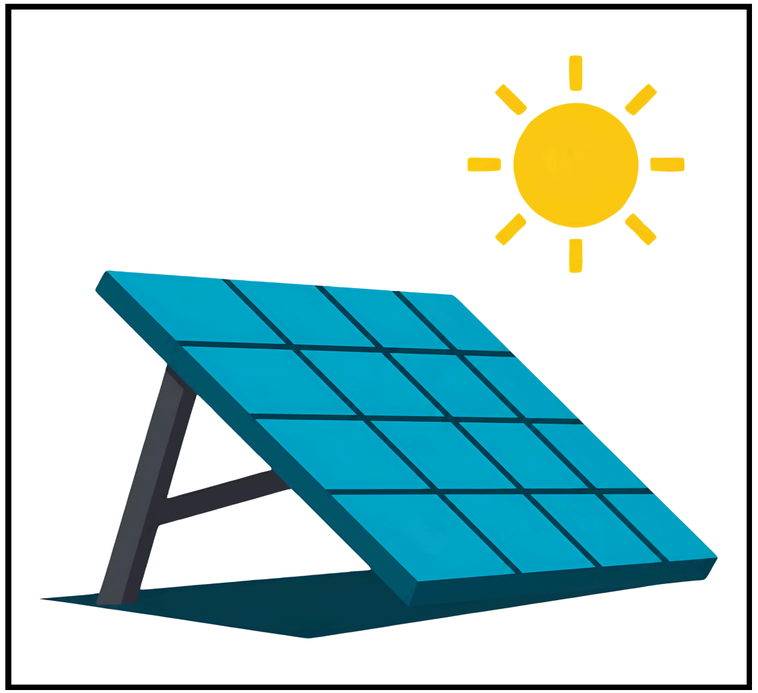
Why Molecular Electronic Structure?

Determines molecular stability, bonding, and chemical reactivity.

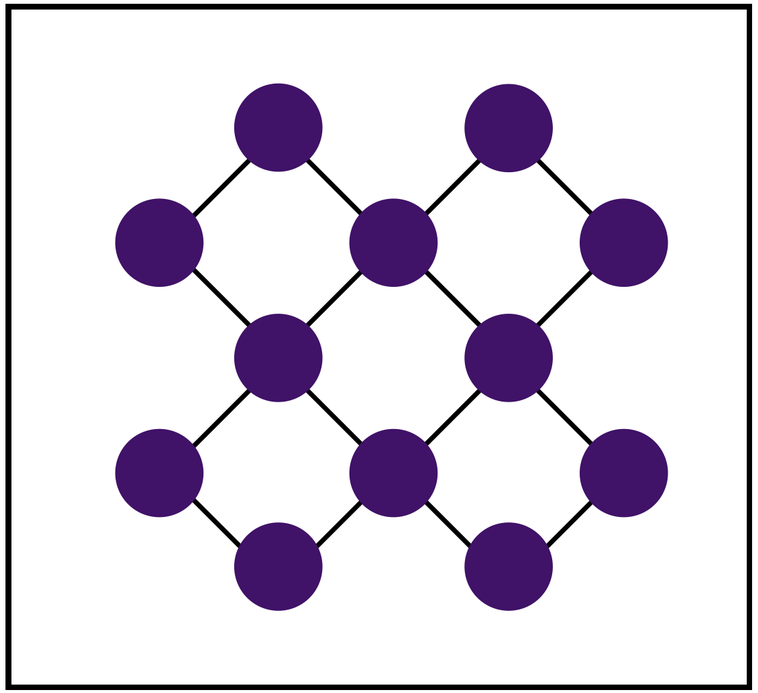
Drug Discovery



Energy Technology



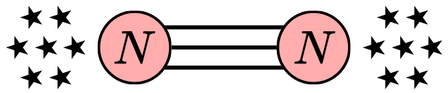
Material Design



Exact solution for real-world application remains computationally intractable!

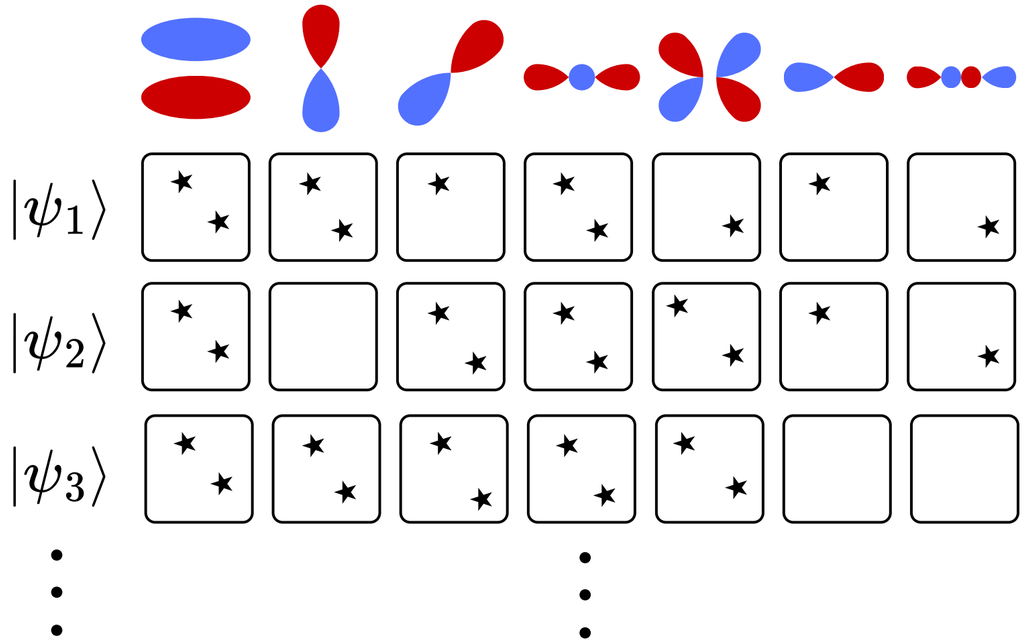
Molecular Electronic States

Nitrogen Molecule

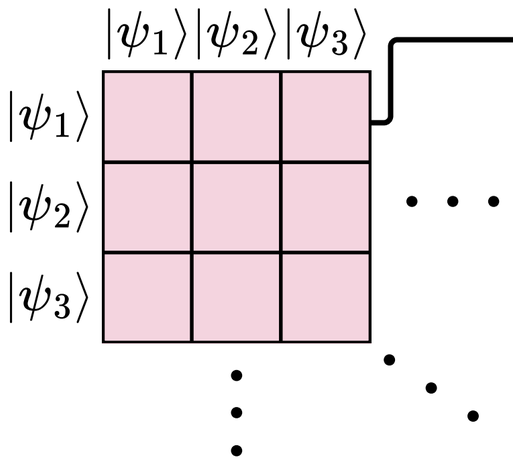


The molecular structure is described by how the electrons are distributed.

Molecular Orbitals



Ground State as an Eigenproblem



Hamiltonian Matrix (H_{FCI})

$$H_{ij} = \langle\psi_i|H|\psi_j\rangle$$

Diagonalize H_{FCI}

$$H_{FCI}|\psi_g\rangle = E_g|\psi_g\rangle$$

Ground State corresponds to the lowest eigenvector of the H_{FCI} Matrix.

General Quantum State: $|\psi_s\rangle = \sum_i \alpha_i|\psi_i\rangle$

with energy: $E_s = \langle\psi_s|H|\psi_s\rangle$

Ground State: $|\psi_g\rangle$ with energy: $E_g = \min_s E_s$

Finding the Ground State: Huge Space, Few Configurations

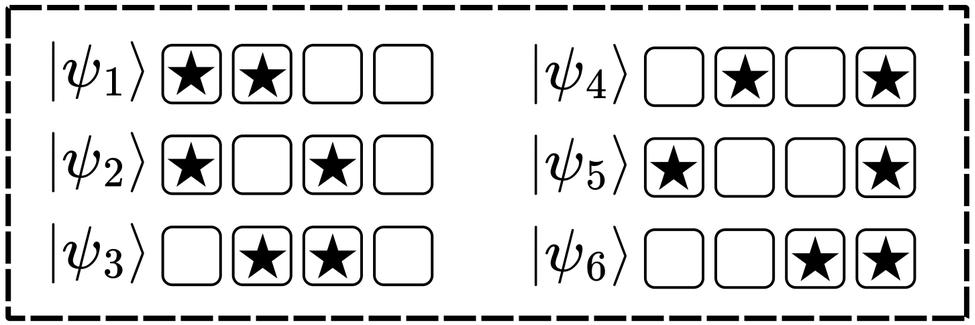
Toy Molecule

★ ★ Electrons in

□ □ □ □ Orbitals

4 orbitals, 2 electrons

$\Rightarrow {}^4C_2 = 6$ Configurations

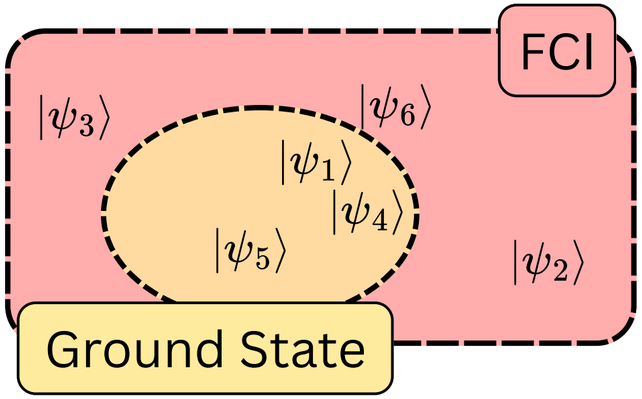


Full Configuration Interaction

Solved by diagonalizing a $H_{FCI}(6 \times 6)$ matrix

$$|\psi_g\rangle = v_1|\psi_1\rangle + v_2|\psi_4\rangle + v_3|\psi_5\rangle$$

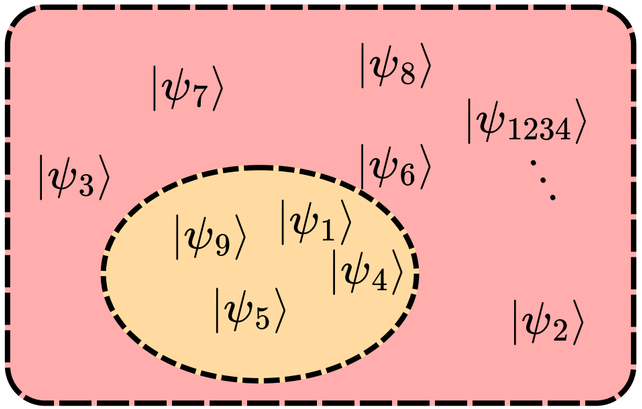
Toy Molecule



FCI size: 6, Easily Solvable

Ground state size ≈ FCI size

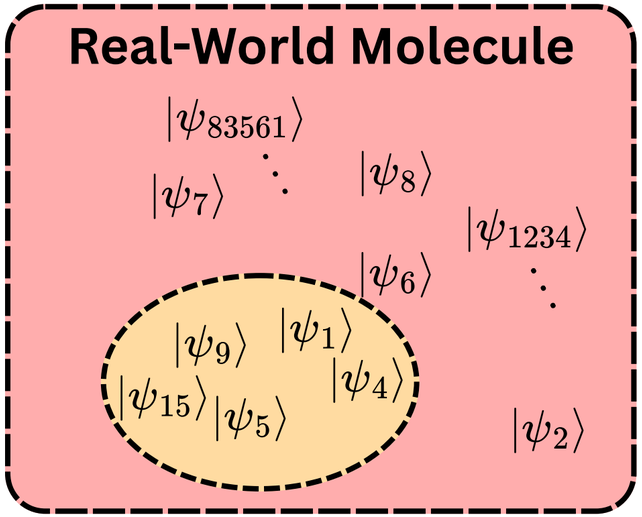
Nitrogen Molecule



FCI size: 19 Million, Solvable

Ground state size < FCI size

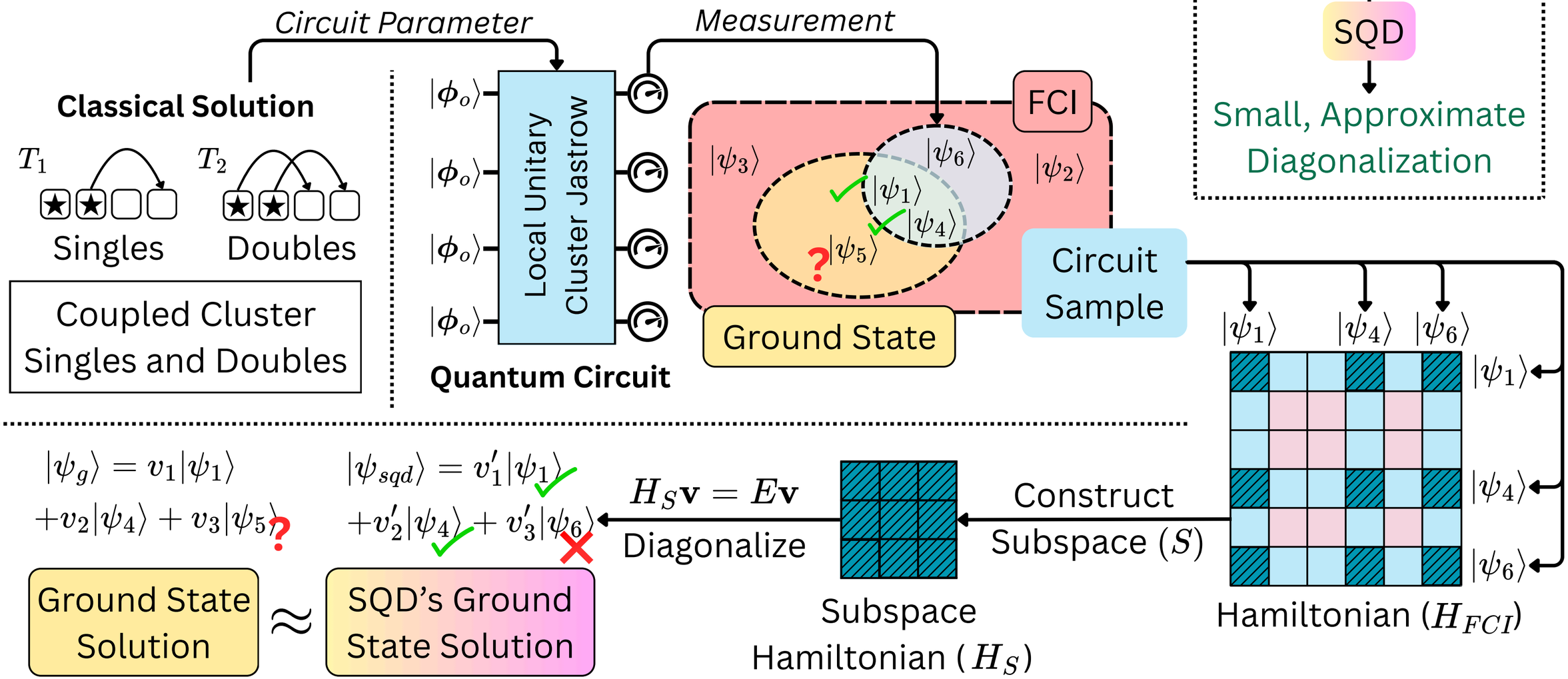
Real-World Molecule



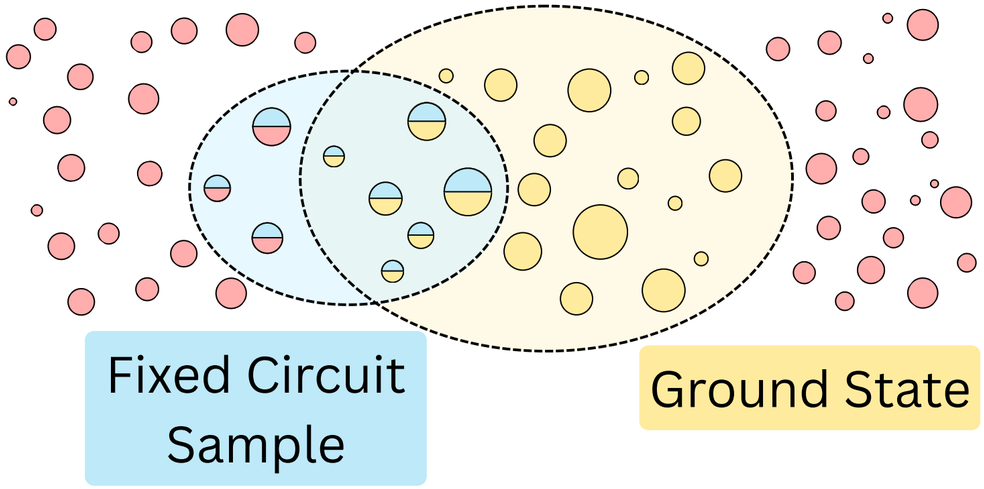
FCI size: ~Billions, Unsolvable

Ground state size << FCI size

From Classical Solution to Quantum Primer: Sample-Based Quantum Diagonalization



SQD: Limitations and Optimization



SQD

Static Circuit, Single Diagonalization

Samples Few Configurations

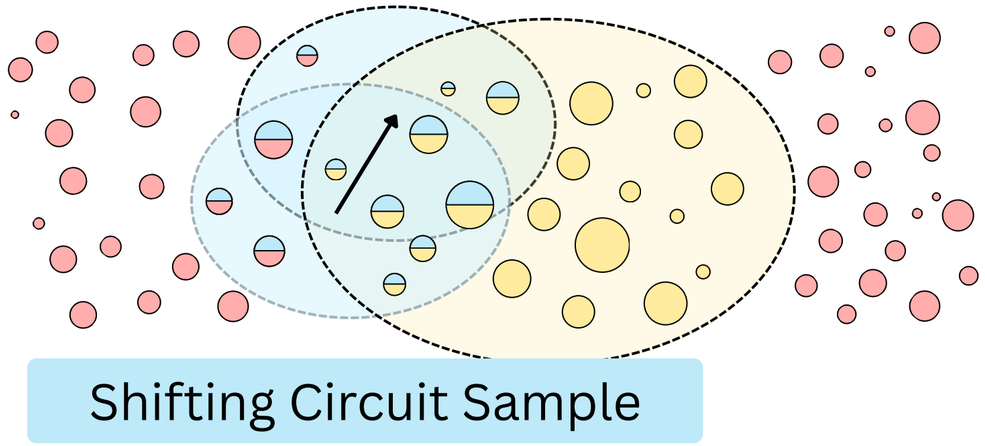
Stuck in One Region

Iterative SQD

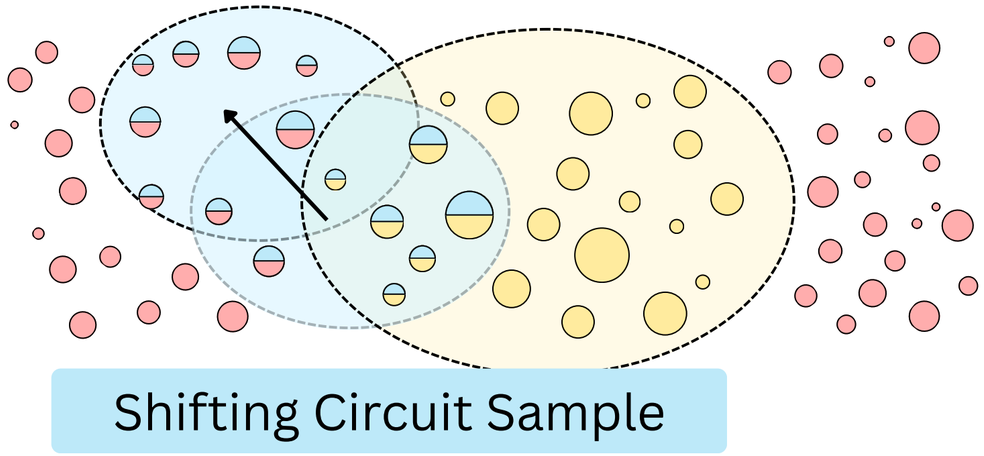
Indirect Exploration via Energy Minimization

High Cost, Repeated Diagonalizations

Optimization towards Ground State



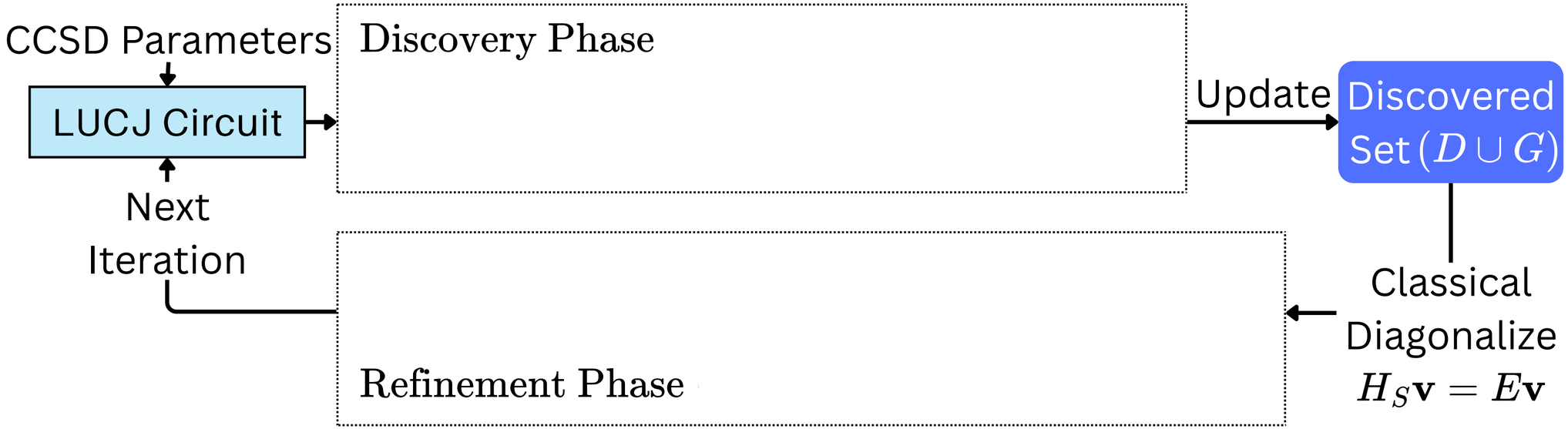
Optimization away from Ground State



Naive Iterative Optimization leads to unreliable, inefficient exploration!

ZenKO's Two Phase Direct Optimization

ZenKO changes the optimization objective; dividing exploration into two parts:
Discovery and Refinement



Discovery Phase

Find unseen configurations
relevant to the Ground State

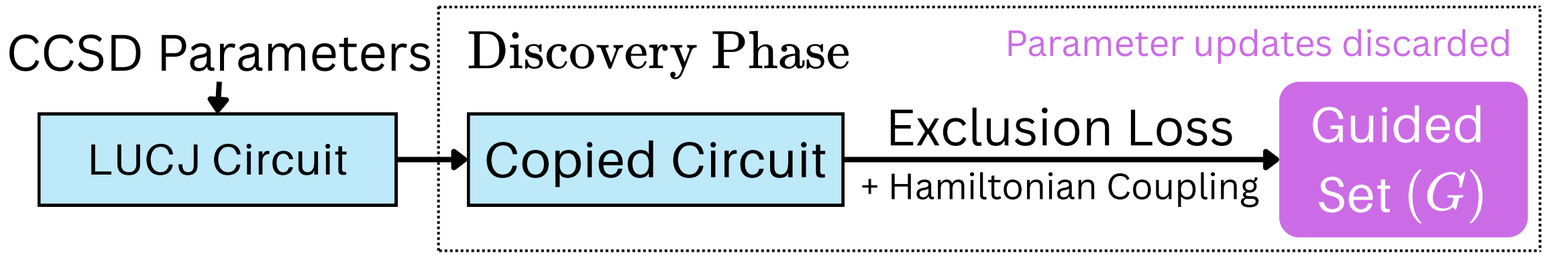
Refinement Phase

Optimize the circuit towards
the newly explored "useful" configurations

Discovering New Configurations

Goal: Find unseen configurations, relevant to the ground state

Train a copied quantum circuit towards new regions



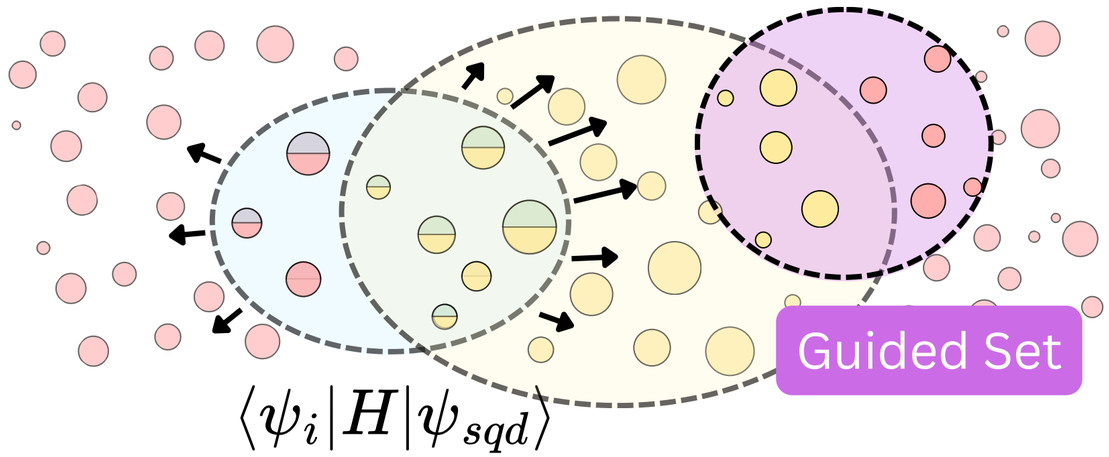
$$L_e(\theta) = \sum_{\psi_i \in D} p_\theta(\psi_i)$$

Penalize discovered configurations (D).

Favor new samples (S) strongly coupled to the SQD solution.

$$L_g(\theta) = \sum_{\psi_i \in S} \langle \psi_i | H | \psi_{SQD} \rangle p_\theta(\psi_i)$$

Result: Guided set (G) of unseen relevant configurations.



Discovery Proposes, Diagonalization Validates!

Goal: Identify the “useful configurations” from the guided set

Diagonalize the expanded set to test which new configurations matter.

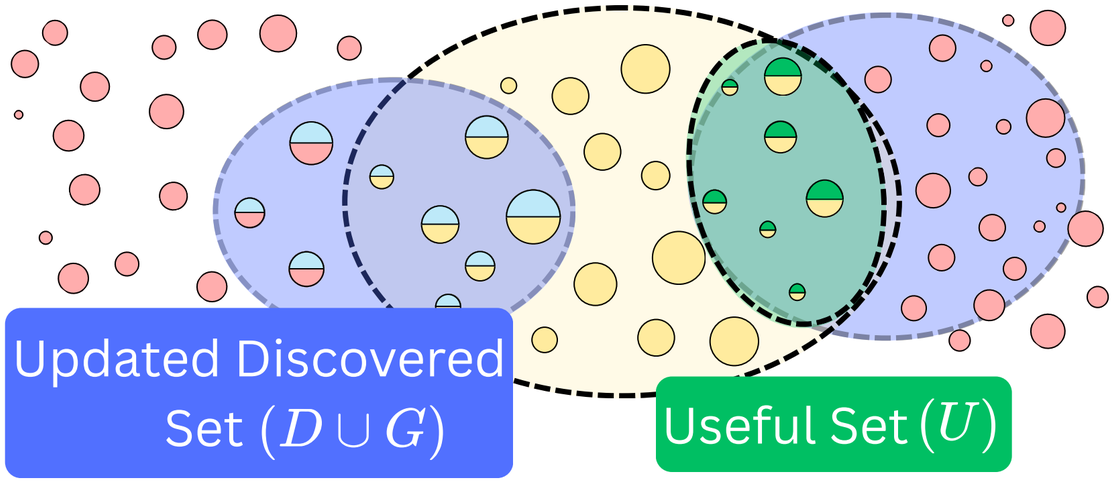
Guided Set (G) → Update → Discovered Set $(D \cup G)$ → Classical Diagonalize → Useful Set (U)

Diagonalize

$$D \cup G \implies |\psi_{SQD'}\rangle$$

$$U = \{\psi_i \in G : p_{SQD'}(\psi_i) > 10^{-12}\}$$

New configurations $U \subset G$ with non-negligible weight in the updated solution $(p_{SQD'})$.



Refinement Towards New Regions

Goal: Start the next exploration from another useful region

Train the circuit to sample more of the useful set

Useful Set (U) → Maximize $p(U)$ + Weighted Refinement → Updated Parameters

Refinement Phase

Parameter updates kept

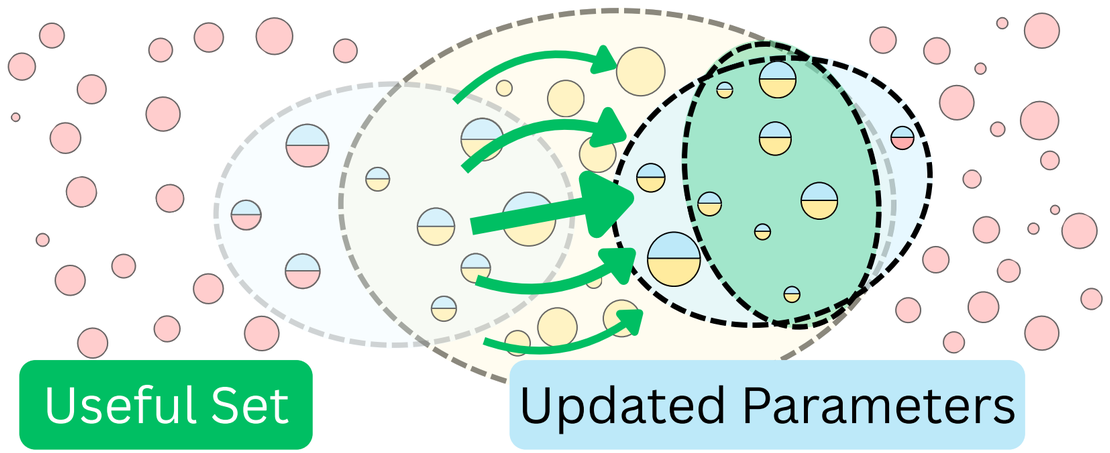
$$L_r(\theta) = -\sum_{\psi_i \in U} p_\theta(\psi_i)$$

Favor useful configurations (U).

Weight each configuration by its contribution to the SQD solution.

$$L_w(\theta) = -\sum_{\psi_i \in U} p_\theta(\psi_i) \cdot p_{SQD'}(\psi_i)$$

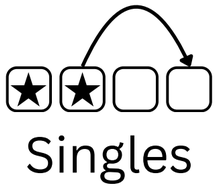
Result: Updated parameters that sample from the new useful region.



Different Parameters, Different Roles

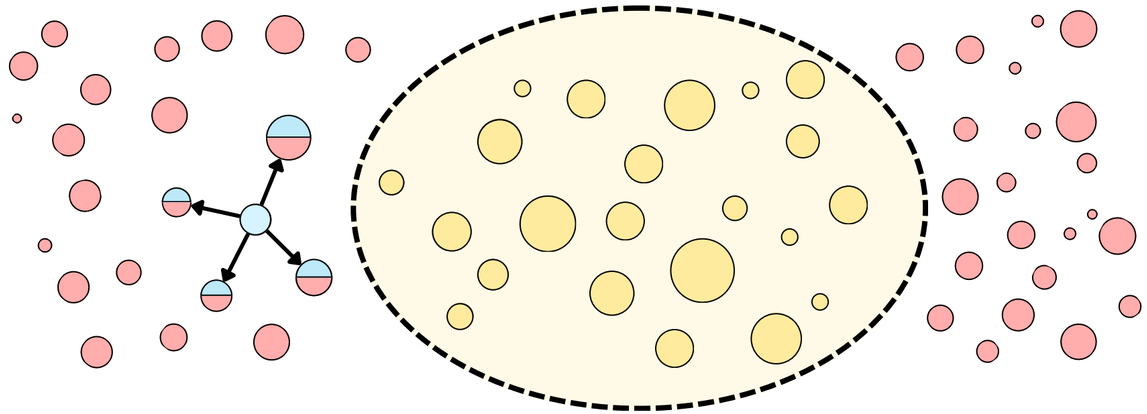
Single Excitation (T_1)

Small perturbations,
Few Configurations

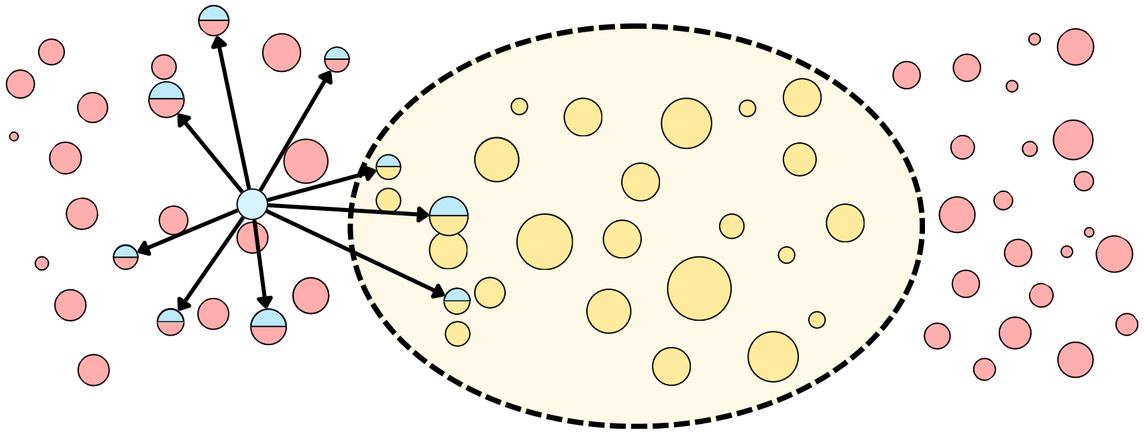


Ideal for Controlled Refinement towards Target Configurations

Refinement Phase

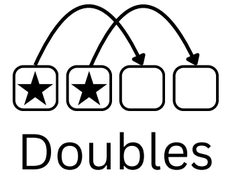


Discovery Phase



Double Excitations (T_2)

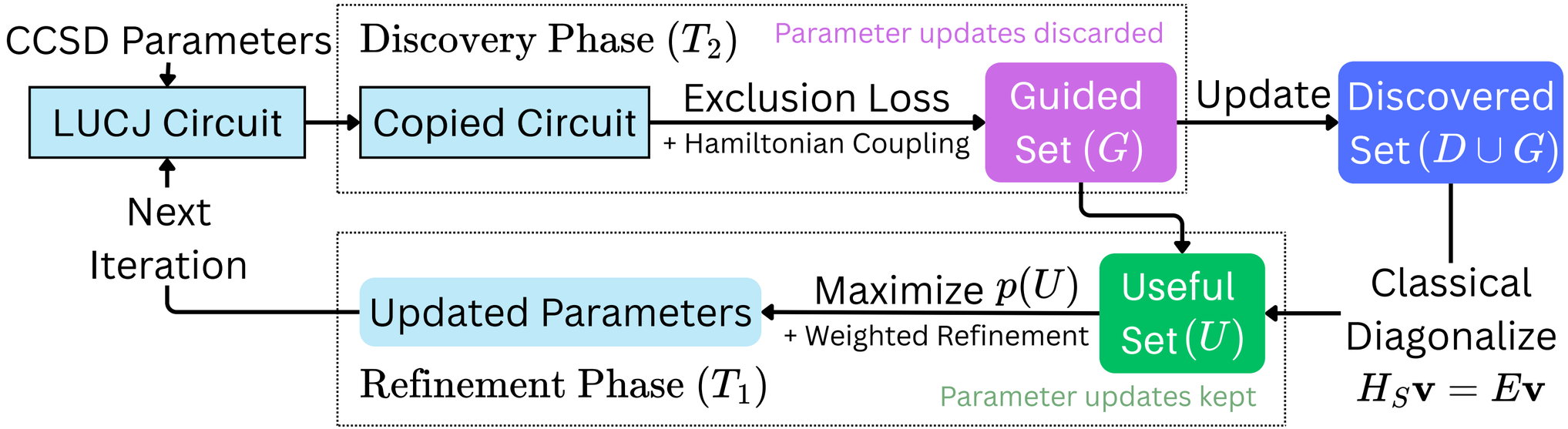
Large redistributions,
Many Configurations



Ideal for Discovering New Configurations Efficiently

ZenKO: Guided Discovery, Weighted Refinement

Guided Discovery (T_2) finds new configurations relevant to the ground state.



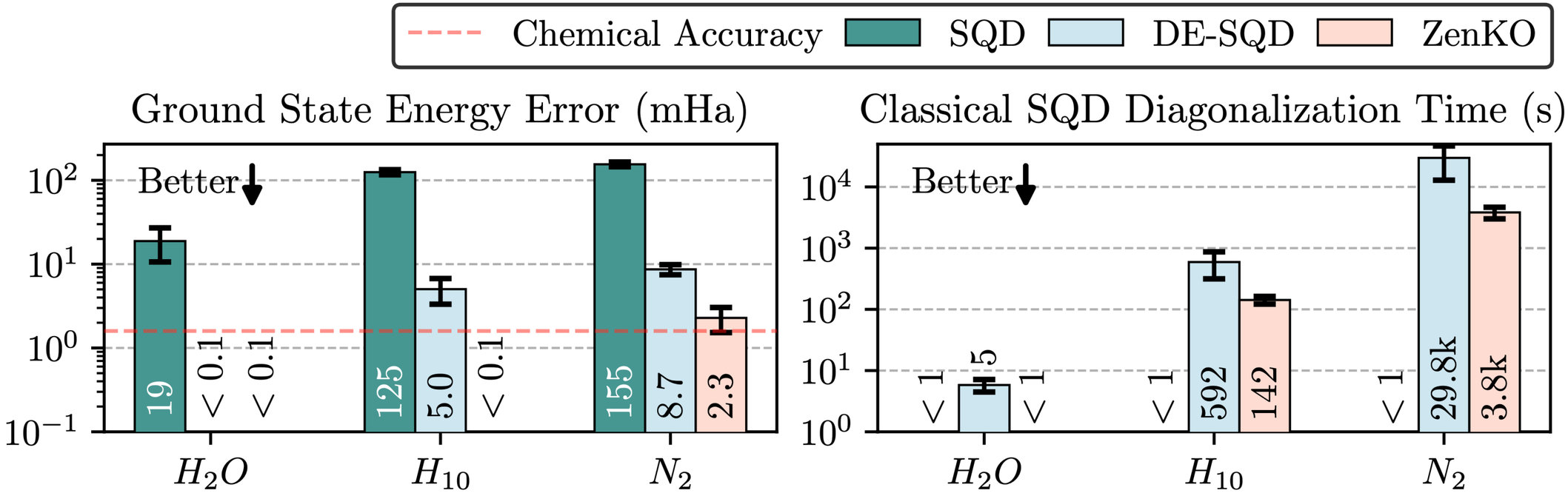
Diagonalization identifies which guided configurations are useful.

Weighted Refinement (T_1) updates the next exploration from a new useful region.

ZenKO vs. SQD and DE-SQD (Iterative SQD)

Three molecular problems of increasing size

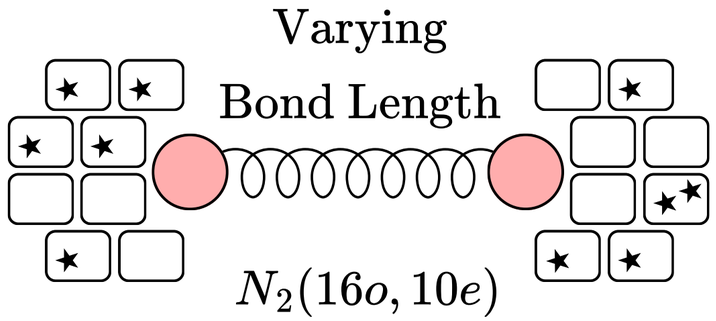
$H_2O(6o, 8e)$	$H_{10}(10o, 10e)$	$N_2(16o, 10e)$
12 qubits	20 qubits	32 qubits
225 Configs	63, 504 Configs	19 Million Configs

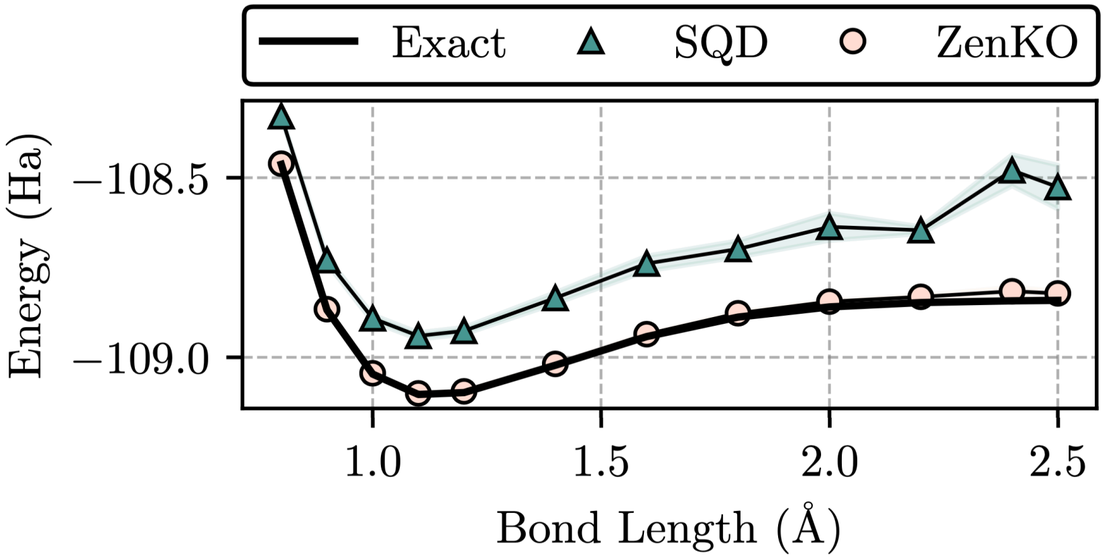


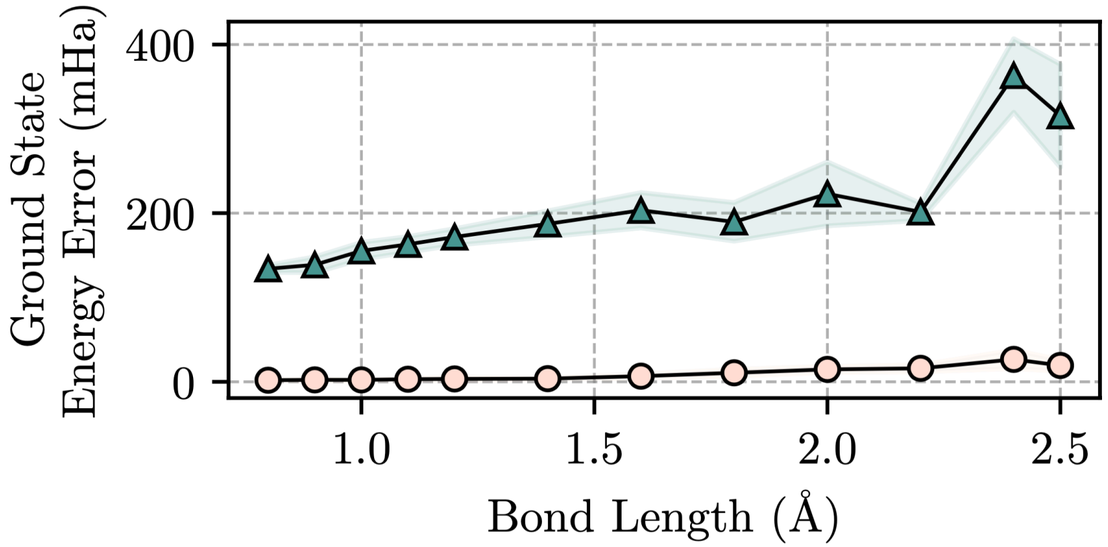
ZenKO beats SQD and iterative SQD in accuracy, and iterative SQD in classical cost.

Robustness Across Bond Lengths

Stretching the N_2 bond strengthens correlation, spreading the ground state over many configurations, increasing problem complexity.







ZenKO outperforms SQD across all bond lengths.

Summary

- Divided exploration into two phases, discovery to find new configurations and refinement to update the circuit, each with a direct objective.
- Introduced guided discovery via Hamiltonian coupling and weighted refinement via SQD contributions, at lower classical cost.
- Exploited excitation parameters, assigning T_2 to discovery and T_1 to refinement for more efficient exploration.
- Validated on H_2O, H_{10}, and N_2 and across N_2 bond lengths, with higher accuracy at lower classical cost than iterative SQD.



Our framework is open-source.

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