

University of Southern California

Coding Project Presentation

Quantum Chemistry Ground-State Estimation with VQE on Hydrogen Molecule (H_2)

EE520 – Quantum Information Processing

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Instructed by - Dr. Todd Brun

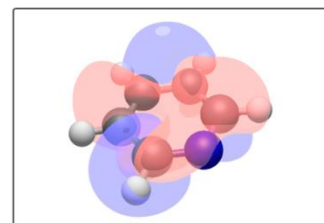


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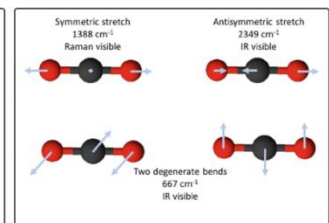
Goal: Solving Quantum Chemistry Electronic Structure Problem using Variational Quantum Classical algorithms

- Quantum Computing Applications
- Quantum Chemistry and Electronic Structure problems
- Molecular Hamiltonians, First & Second Quantizations
- Current/Existing Classical Methods (Exact & Hartree-Fock, ...)
- Quantum Speed-up and Basis Set Limitations
- H₂ Molecule
- Process Map of Electronic Structure Problem Solving for H_2 Molecule with VQE
- Variational Quantum Eigensolver
- Results
- Improvements & Further work

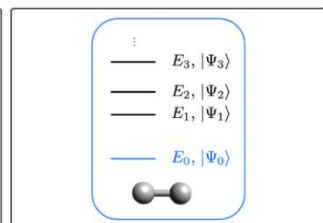
Applications of Quantum Computing



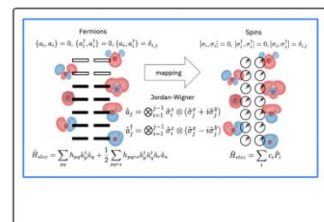
Electronic structure



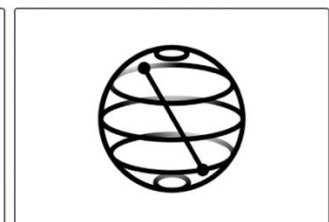
Vibrational structure



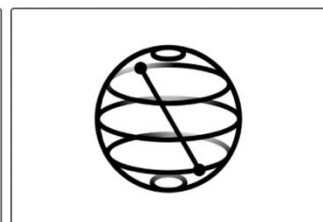
Ground state solvers



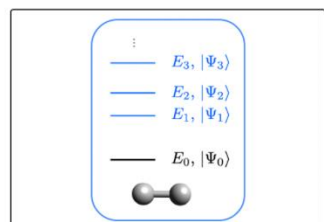
Mapping to the Qubit Space



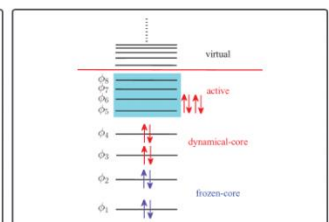
QCSchema



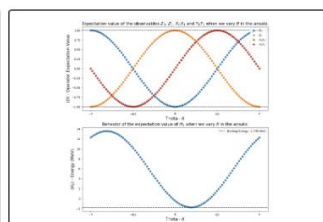
Properties - or - Operator Factories



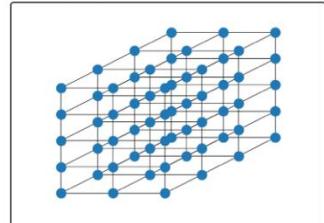
Excited states solvers



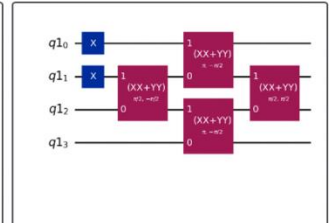
Transforming Problems



Binding Energy between proton and neutron in the Deuteron nucleus



Lattice models

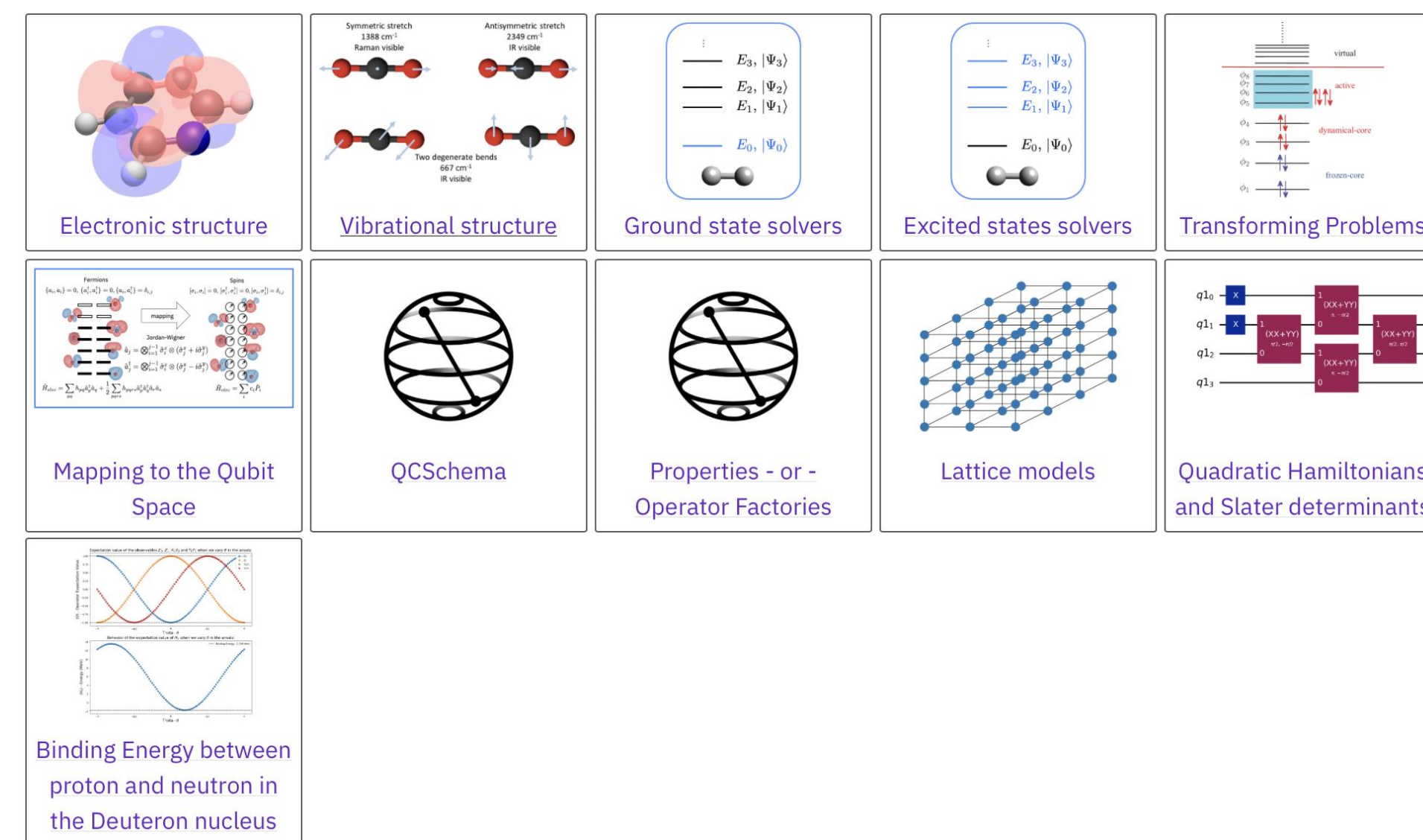


Quadratic Hamiltonians and Slater determinants

Applications	work
Computer Algorithms, processes, and methods	<ul style="list-style-type: none">Shor’s AlgorithmBB84QKDGrover’s AlgorithmQuantum Phase Estimation
Quantum Chemistry	<ul style="list-style-type: none">Electronic Structure problemGround State and Excited State energiesReaction Mechanisms
Quantum Machine Learning	<ul style="list-style-type: none">Quantum Neural NetworksQuantum-Classical ClassifiersQuantum Kernel Methods
Quantum Finance	<ul style="list-style-type: none">Portfolio OptimizationValue-at-Risk Calculations
Quantum computing in High Energy Physics <ul style="list-style-type: none">Uncover useful data from Clients to help them succeedUncover ideas for revenue generation and upselling	<ul style="list-style-type: none">Simulating Particle InteractionsLattice Gauge Theories
Quantum computing in Healthcare and Life Sciences <ul style="list-style-type: none">Client informed content creationOrganize internal collaboration on projects	<ul style="list-style-type: none">Drug DiscoveryProtein Folding
Quantum computing in Material Science <ul style="list-style-type: none">Propose strategies to other teamsGet buy-in from other teamscollaborate with other teams	<ul style="list-style-type: none">Defect characterization in semi conductorsMagnetic properties and band structure in Condensed Matter Physics
Quantum Simulations	<ul style="list-style-type: none">Spin Chains and Lattice ModelsMolecular dynamicsOpen Quantum SystemsMany-body Physics
Quantum Optimization	<ul style="list-style-type: none">Travelling Salesman Problem3-SAT problemLogistics Optimization(Flight route optimization, ...)Max-Cut

Quantum Chemistry & Electronic Structure Problems

- The electronic structure problem involves solving the Schrödinger equation to determine the behavior of electrons in a molecule
- Key Quantities that can be Derived are:
 - Ground-State Energy (GSE):** Determines molecular stability and chemical reactivity.
 - Excited-State Energies:** Critical for photochemistry and understanding light-matter interactions.
 - Bond Lengths and Angles:** Helps optimize molecular geometries for chemical and biological studies.
 - Electron Correlation:** Explains phenomena like magnetism and superconductivity.



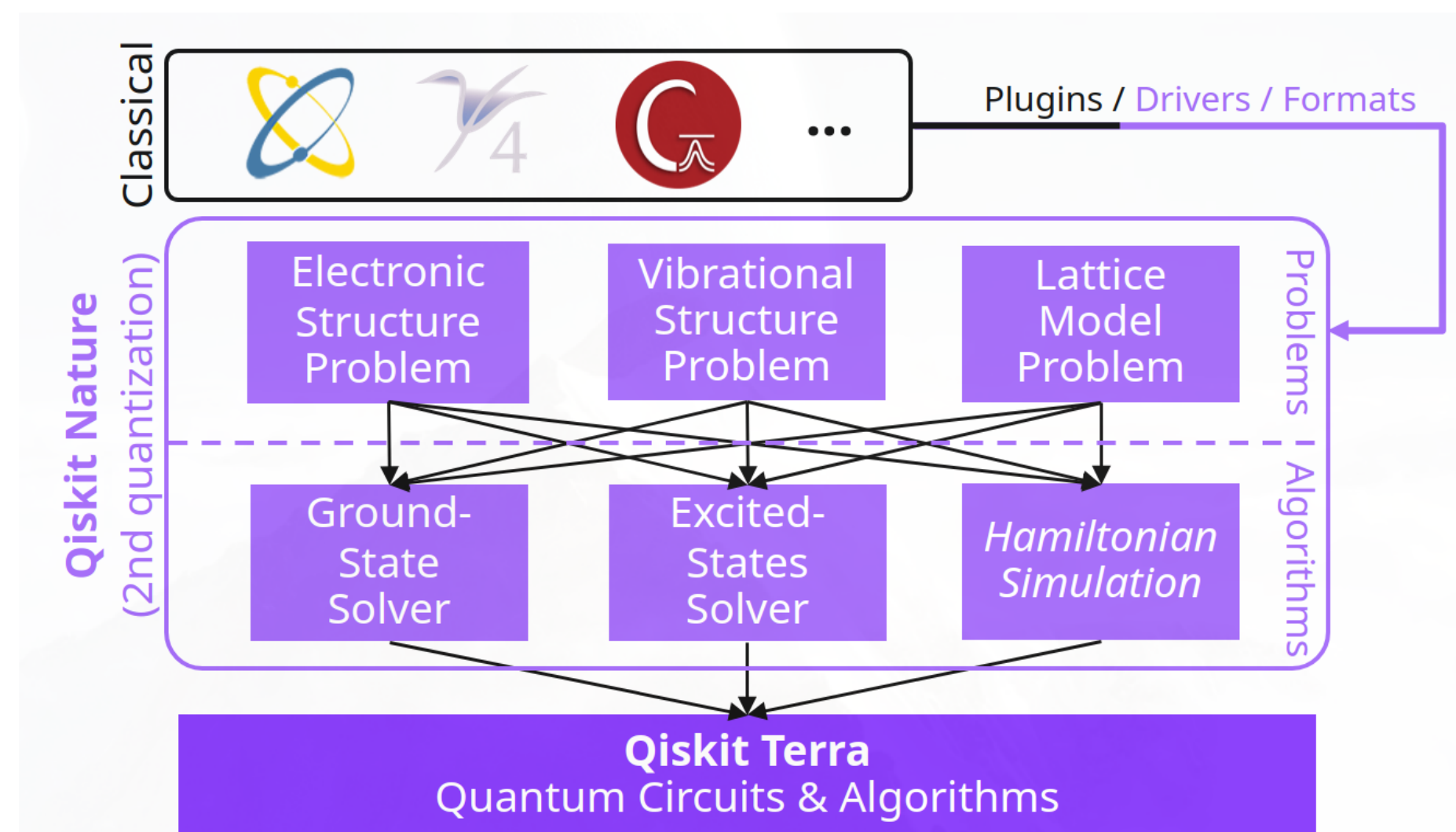
Current State-of-the-art Applications:

Electron Transfer in Biomolecules

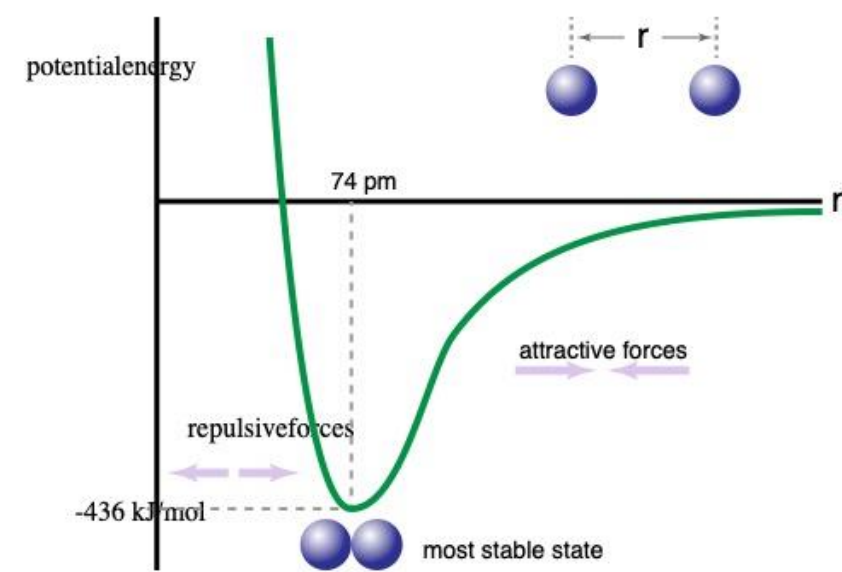
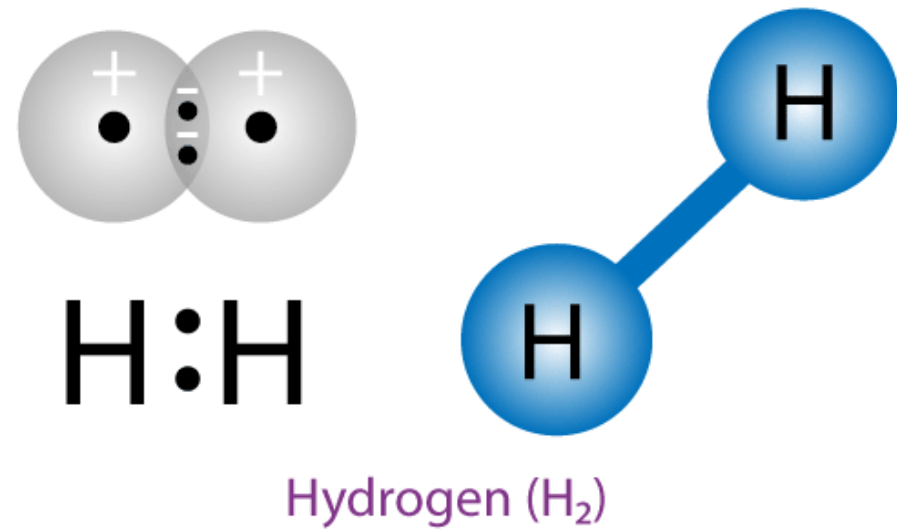
- Accurate modeling of electron movement in large biomolecules, such as DNA, helps in understanding mutations and their role in diseases.
- Insight into repair mechanisms for designing effective treatments.

Simulating Energy Storage Materials

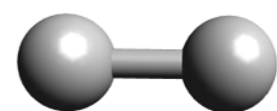
- Understanding GSE in new materials for developing efficient batteries and fuel cells.
- And more...



First Quantization



$$\begin{array}{l} \vdots \\ \text{---} E_3, |\Psi_3\rangle \\ \text{---} E_2, |\Psi_2\rangle \\ \text{---} E_1, |\Psi_1\rangle \\ \text{---} E_0, |\Psi_0\rangle \end{array}$$



Molecular Hamiltonian

RI: The position vector of the I-th nucleus in the molecule.

ri: The position vector of the i-th electron in the molecule.

$$\mathcal{H} = - \sum_I \frac{\nabla_{R_I}^2}{M_I} - \sum_i \frac{\nabla_{r_i}^2}{m_e} - \sum_I \sum_i \frac{Z_I e^2}{|R_I - r_i|} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|} + \sum_I \sum_{J>I} \frac{Z_I Z_J e^2}{|R_I - R_J|}$$

Kinetic energy of Nuclei
Kinetic energy of Electrons
Nucleus-Electron Coulomb attraction
Nucleus-Electron Coulomb repulsion
Nucleus-Nucleus Coulomb repulsion

First Approximation:

Because the **nuclei are** much **heavier than** the **electrons** they do not move on the same time scale and therefore, the behavior of nuclei and electrons can be decoupled. This is the **Born-Oppenheimer approximation**.

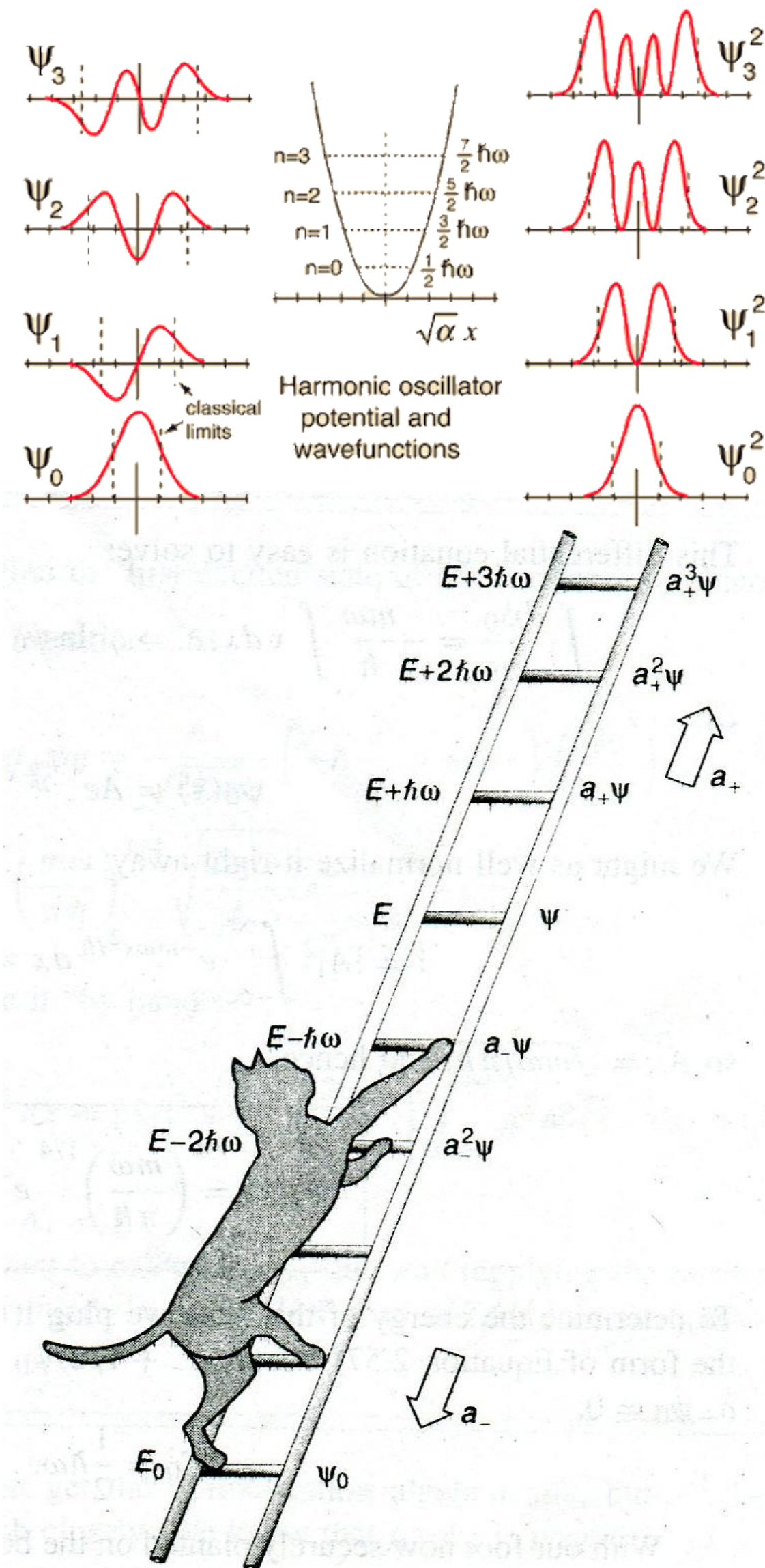
$$\mathcal{H}_{el} = - \sum_i \frac{\nabla_{r_i}^2}{m_e} - \sum_I \sum_i \frac{Z_I e^2}{|R_I - r_i|} + \sum_i \sum_{j>i} \frac{e^2}{|r_i - r_j|}.$$

Ground State Energy ($|\Psi_0\rangle$)

However, the dimensionality of this problem grows exponentially with the number of degrees of freedom. To tackle this issue we would like to prepare $|\Psi_0\rangle$ on a quantum computer and measure the Hamiltonian expectation value (or) directly.

$$E_0 = \frac{\langle \Psi_0 | H_{el} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle}$$

Second Quantization



$$\hat{H}_{elec} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s$$

A **good starting** point for solving this problem is the **Hartree-Fock (HF)** method. This method **approximates the N-body problem by N one-body problems** where each electron evolves in the mean-field of the others. Classically solving the HF equations is efficient and leads to the exact exchange energy but does not include any electron correlation. Therefore, it is usually a good starting point to which to add correlation.

One-Body Integrals

$$h_{pq} = \int \phi_p^*(r) \left(\underbrace{-\frac{1}{2} \nabla^2}_{\text{Kinetic energy}} - \sum_I \underbrace{\frac{Z_I}{R_I - r}}_{\text{Attraction to Nuclei}} \right) \phi_q(r) dr$$

- Together, $a_p^\dagger a_q$ represents a **transition operator** that moves an electron from orbital q to orbital p.
- The integral h_{pq} describes the contribution of a single electron's energy due to kinetic energy and attraction to nuclei.

Two-Body Integrals

$$h_{pqrs} = \int \frac{\phi_p^*(r_1) \phi_q^*(r_2) \phi_r(r_2) \phi_s(r_1)}{|r_1 - r_2|} dr_1 dr_2.$$

- The two-body integrals, h_{pqrs} , represent the **electron-electron interaction energy** in the second-quantized electronic Hamiltonian.
- These integrals arise from the Coulomb repulsion between two electrons located at positions r_1 and r_2 :

$\frac{1}{r_1 - r_2}$: The **Coulomb potential** between two electrons, ensuring that their interaction decreases as their separation increases. The four molecular orbitals ($\phi_p, \phi_q, \phi_r, \phi_s$) correspond to initial and final states of the interacting electrons.

The Hamiltonian can then be re-expressed in the basis of the solutions of the HF method, also called **Molecular Orbitals (MOs)**: The MOs (ϕ_u) can be occupied or virtual (unoccupied). One MO can contain 2 electrons. However, in what follows we actually work with Spin Orbitals which are associated with a spin up (α) or spin down (β) electron. Thus Spin Orbitals can contain one electron or be unoccupied.

Current / Existing Classical Methods

Exact Diagonalization

- Provides the exact solution to the electronic Schrödinger equation within a chosen basis set.
- Computational cost grows exponentially with the size of the system.
- Used for small molecules to benchmark other methods.

Hartree-Fock

- Approximates the N-electron wavefunction as a single Slater determinant.
- Captures mean-field interactions but neglects electron correlation.
- Often used as the starting point for more advanced methods.

Density Functional Theory

- Models the ground-state energy as a functional of the electron density.
- Includes electron correlation through exchange-correlation functionals.
- Widely used due to its balance between accuracy and computational efficiency.

Post Hartree-Fock Methods

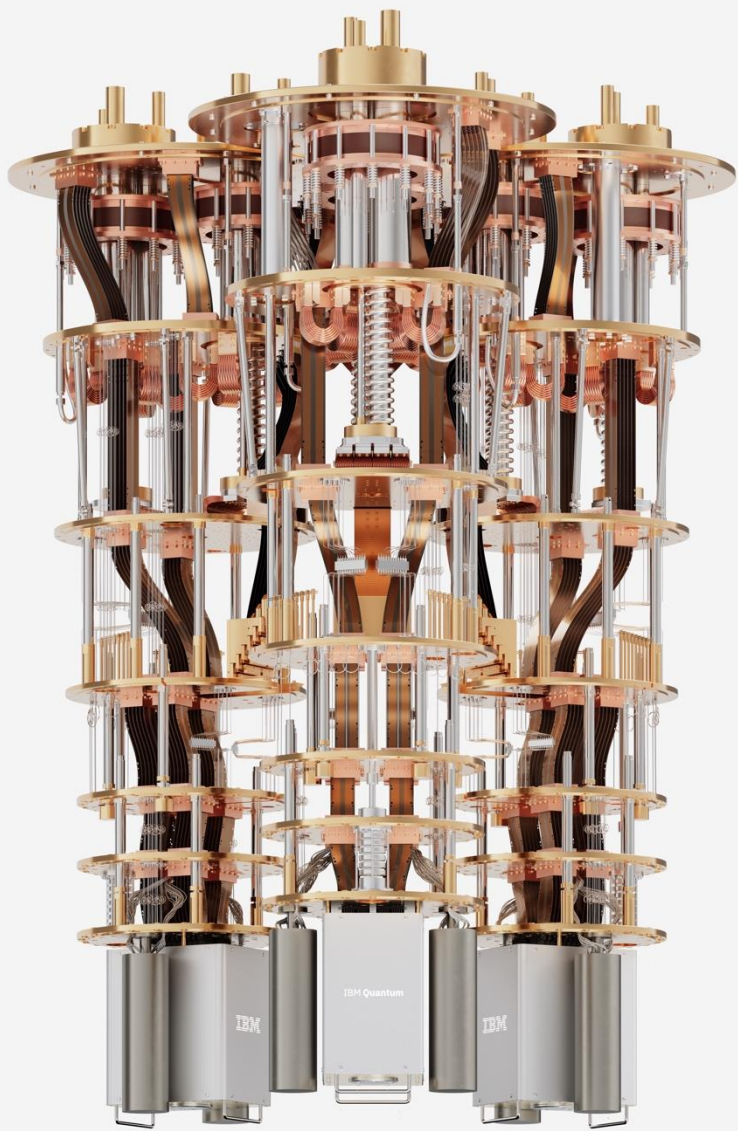
- Møller-Plesset Perturbation Theory
- Configuration Interaction (CI)
- Coupled Cluster (CC)
 - Expands the wavefunction using exponential operators.
 - Highly accurate; CC with singles, doubles, and perturbative triples (CCSD(T)) is the gold standard for many systems.

Limitations

Many methods fail to scale efficiently with system size.

Accuracy depends on the choice of basis set and approximations (e.g., DFT functional).

Classical methods, while effective for small or moderately sized systems, are fundamentally limited by computational scaling and approximation accuracy.



Quantum Speed-Up & Basis Set limitations

- Quantum Phase Estimation achieves an **exponential speedup** for finding eigenvalues of the Hamiltonian compared to classical FCI. For an MM-orbital system, the scaling is $O(\text{poly}(M))$ vs. $O(M_{c_N})$ classically.
- Requires deep quantum circuits, making it impractical for near-term devices.
- VQE uses a variational approach to minimize the expectation value of the Hamiltonian

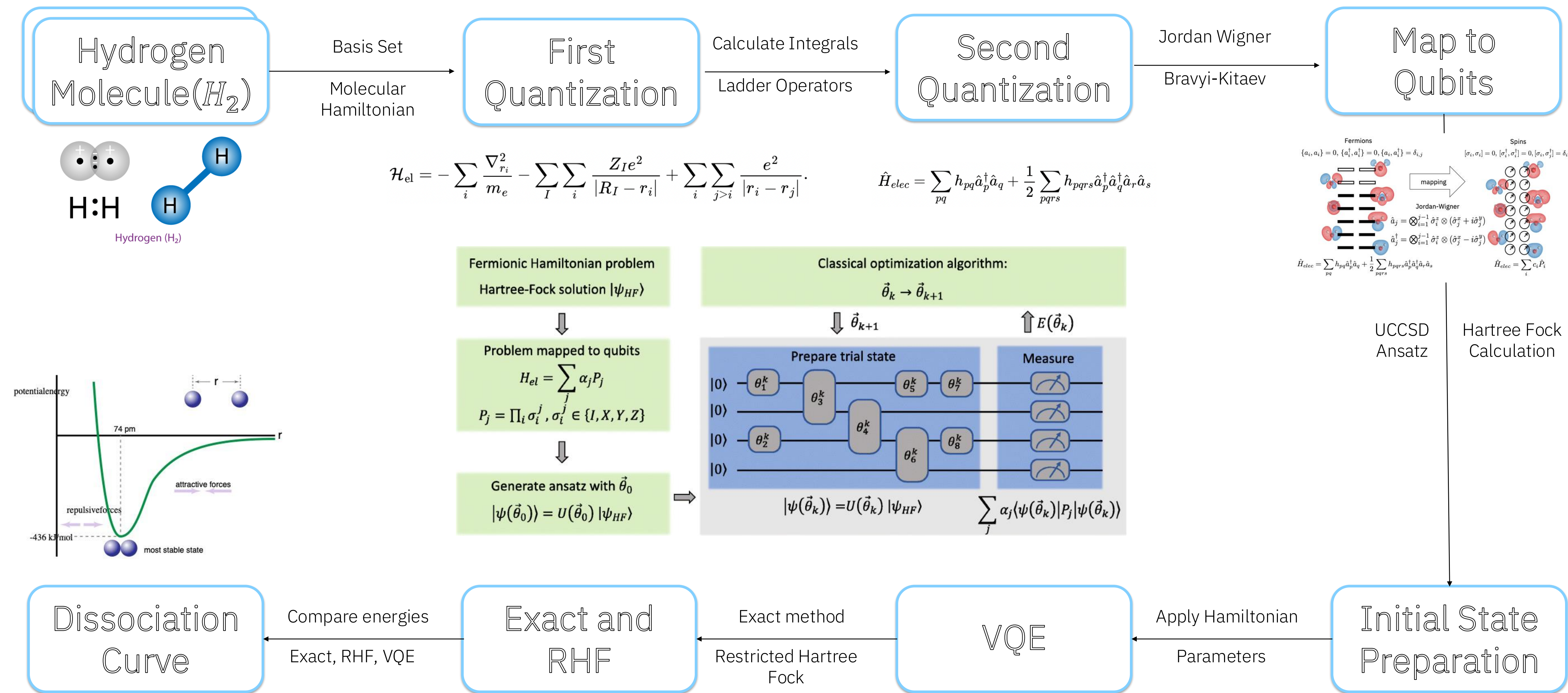
$$E_{\min} = \min_{\theta} \langle \psi(\theta) | \hat{H} | \psi(\theta) \rangle.$$

Basis Sets

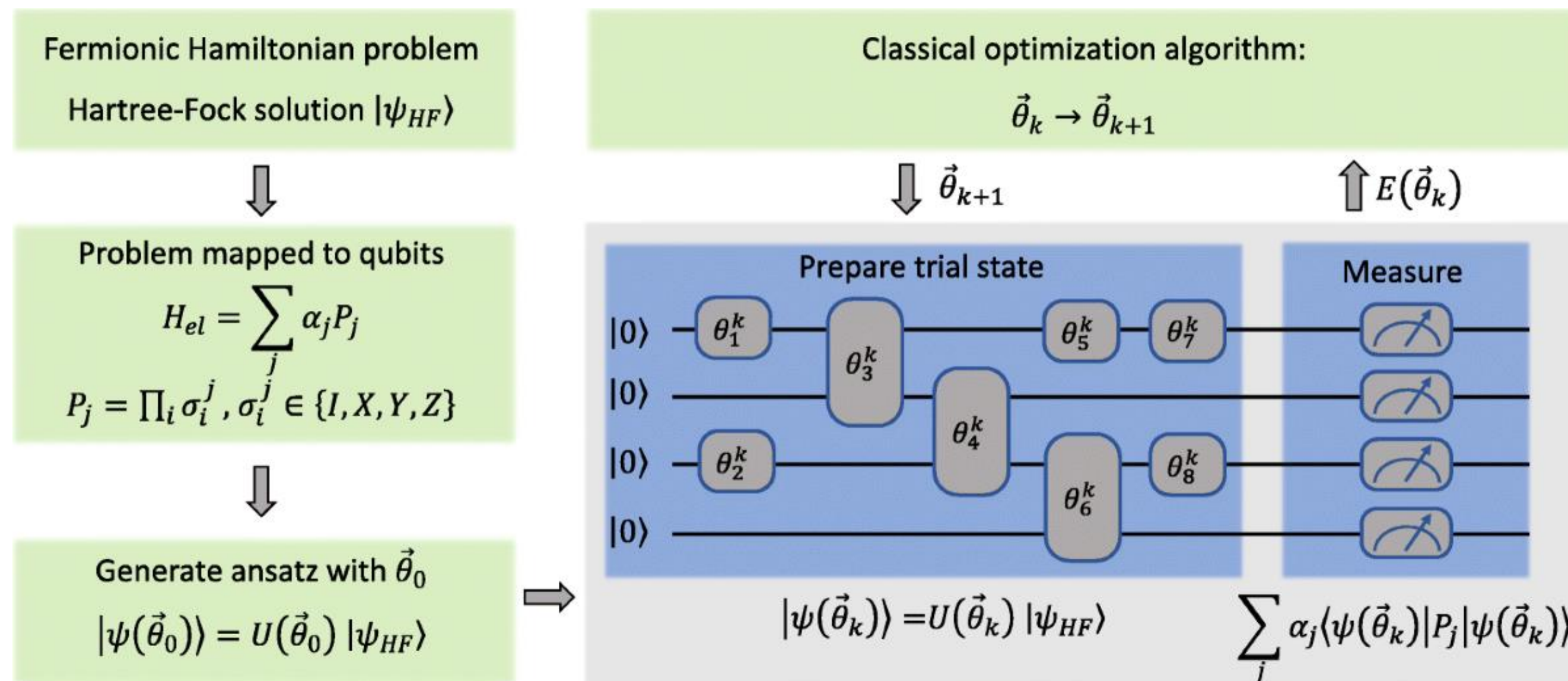
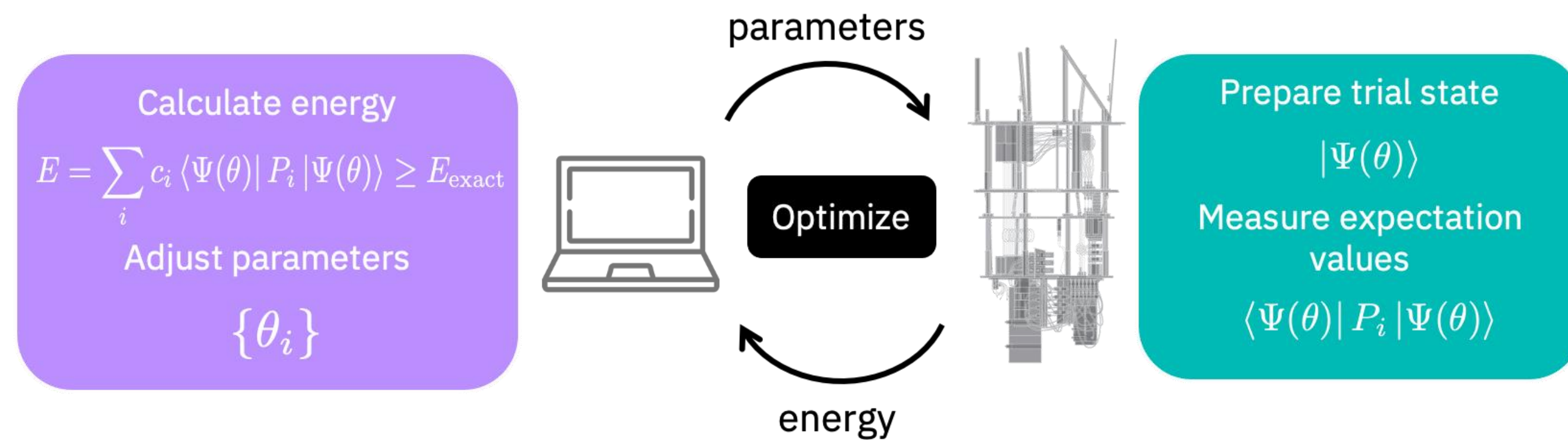
- Basis sets are a set of mathematical functions used to represent the wavefunctions of electrons** in quantum chemistry calculations.
- Wavefunctions are expressed as a linear combination of these basis functions.
- The original choice of **basis affects** the **number of qubits required** and the Hamiltonian complexity. A larger basis set leads to more qubits and more terms in Hamiltonian.
- Quantum computers do not rely on basis set approximations in the same way as classical methods.
- They can theoretically handle the full Hilbert space directly, bypassing the limitations and trade-offs of basis sets in classical computations.
- Current quantum hardware noise and qubit limitations restrict practical applications, making basis sets still relevant for hybrid quantum-classical algorithms like **VQE**.

Types of Basis Sets	
Gaussian-Type Orbitals (GTOs)	Most widely used because they allow for efficient computation of integrals.
Slater-Type Orbitals (STOs)	Better represent electron behavior near nuclei but are computationally more expensive.
Minimal Basis Sets (e.g., STO-3G)	Represent each atomic orbital with a single function. They are computationally efficient but less accurate.
Double-Zeta (e.g., 6-31G)	Use two functions per orbital for more flexibility.
Triple-Zeta and Beyond (e.g., 6-311G)	Add even more functions per orbital to capture finer details of electron behavior.

Process Map of ES Problem Solving for H_2 Molecule with VQE



Variational Quantum Eigensolver Process



Steps involved in Variational Quantum EigenSolver:

1. Define the Hamiltonian (with a specific bond length mapped from second quantization).
2. Choose an ansatz (e.g., UCCSD with Hartree Fock or hardware-efficient circuits).
3. Initialize parameters θ .
4. Use the quantum computer to prepare the trial state and measure energies.
5. Update θ using a classical optimizer.
6. Iterate until convergence to approximate the ground-state energy.
7. Then update the bond length and do the minimization process again
8. Find the bond length for which the final energy is the lowest, i.e, the Ground State Energy.

The VQE Code

1

```
# Loop over bond lengths
for bond_length in bond_lengths:
    # Define molecule for PySCFDriver
    driver = PySCFDriver(
        atom=f"H 0 0 0; H 0 0 {bond_length}",
        basis="sto3g",
        charge=0,
        spin=0,
        unit=DistanceUnit.ANGSTROM,
    )
```

Looping over the bond lengths and creating the Hydrogen molecule with PySCF

2

```
# Set up problem
es_problem = driver.run()

# Define VQE ansatz and solver
ansatz = UCCSD(
    es_problem.num_spatial_orbitals,
    es_problem.num_particles,
    mapper,
    initial_state=HartreeFock(
        es_problem.num_spatial_orbitals,
        es_problem.num_particles,
        mapper,
    ),
)
```

- Creating the Electronic Structure problem with the molecule driver
- Creating the initial state (ansatz)

3

```
Set up and solve with VQE
vqe_solver = VQE(Estimator(), ansatz, SLSQP())
vqe_solver.initial_point = [0.0] * ansatz.num_parameters

calc = GroundStateEigensolver(mapper, vqe_solver)
vqe_result = calc.solve(es_problem)
vqe_energies.append(vqe_result.total_energies[0])
```

- Solving for Ground state energy using Variational Quantum Eigensolver

4

```
Set up and solve with exact diagonalization
from qiskit_algorithms import NumPyMinimumEigensolver
exact_solver = NumPyMinimumEigensolver()
calc_exact = GroundStateEigensolver(mapper, exact_solver)
exact_result = calc_exact.solve(es_problem)
exact_diagonalization_energies.append(exact_result.total_energies[0])
```

- Solving using Exact Diagonalization

5

```
Solve using Restricted Hartree-Fock (RHF)
mol = gto.M(
    atom=f'H 0 0 0; H 0 0 {bond_length}',
    basis='sto-3g',
    unit='Angstrom',
    spin=0,
    charge=0
)
mf = scf.RHF(mol)
rhf_energy = mf.kernel()
rhf_energies.append(rhf_energy)
```

- Solving for Ground state energy using Restricted Hartree Fock Method

6

```
Find minimum energies and corresponding bond lengths for VQE and exact solver
min_vqe_energy = min(vqe_energies)
min_vqe_bond = bond_lengths[vqe_energies.index(min_vqe_energy)]

min_exact_energy = min(exact_diagonalization_energies)
min_exact_bond = bond_lengths[exact_diagonalization_energies.index(min_exact_energy)]

min_rhf_energy = min(rhf_energies)
min_rhf_bond = bond_lengths[rhf_energies.index(min_rhf_energy)]
```

- Calculating the minimum eigen value/ energy value throughout all the iterations over varied bond lengths

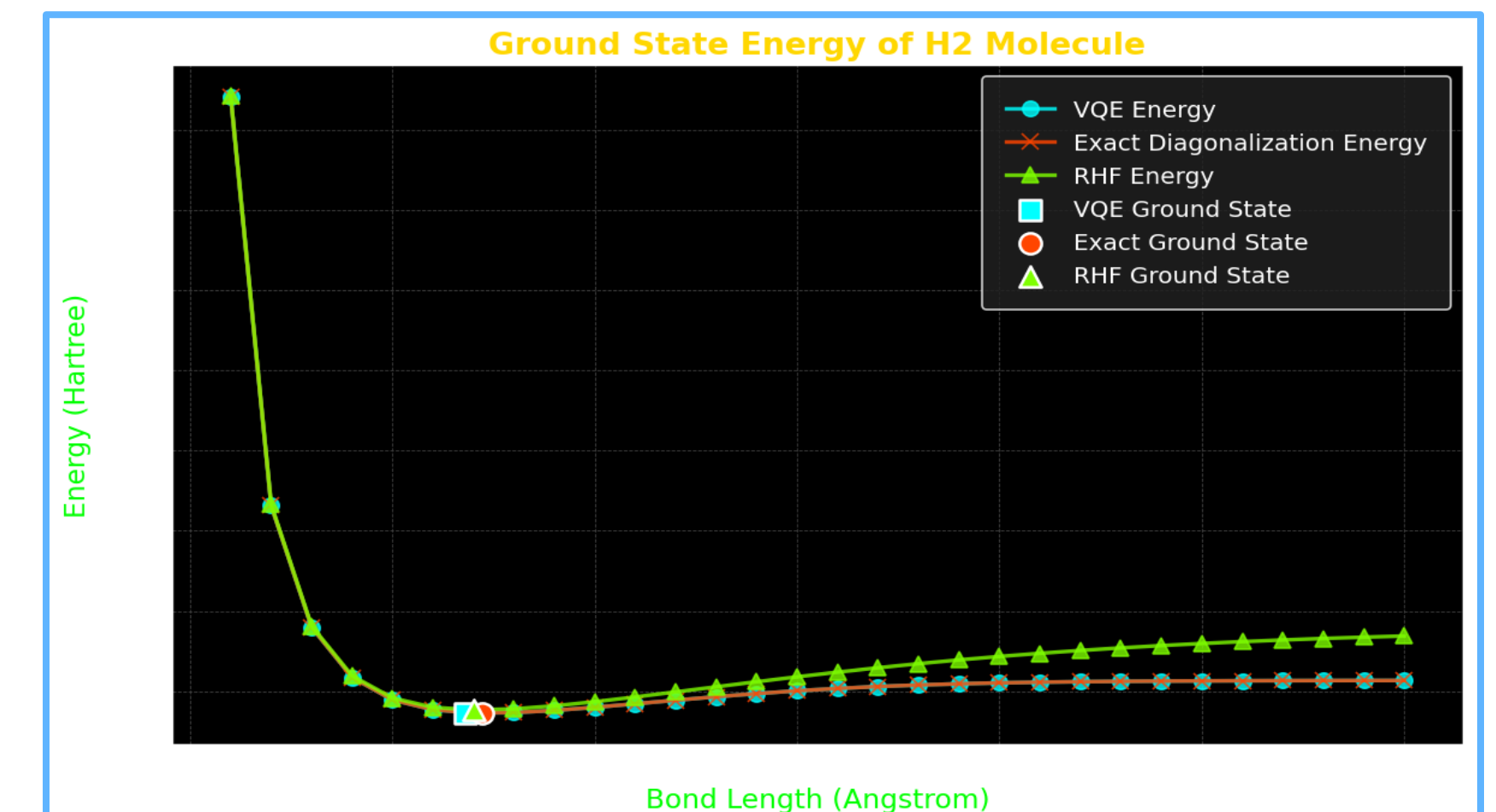
7

```
Plot results
plt.plot(bond_lengths, vqe_energies, label="VQE Energy", markers='o', color='blue')
plt.plot(bond_lengths, exact_diagonalization_energies, label="Exact Diagonalization Energy", markers='x', color='orange')
plt.plot(bond_lengths, rhf_energies, label="RHF Energy", markers='^', color='green')

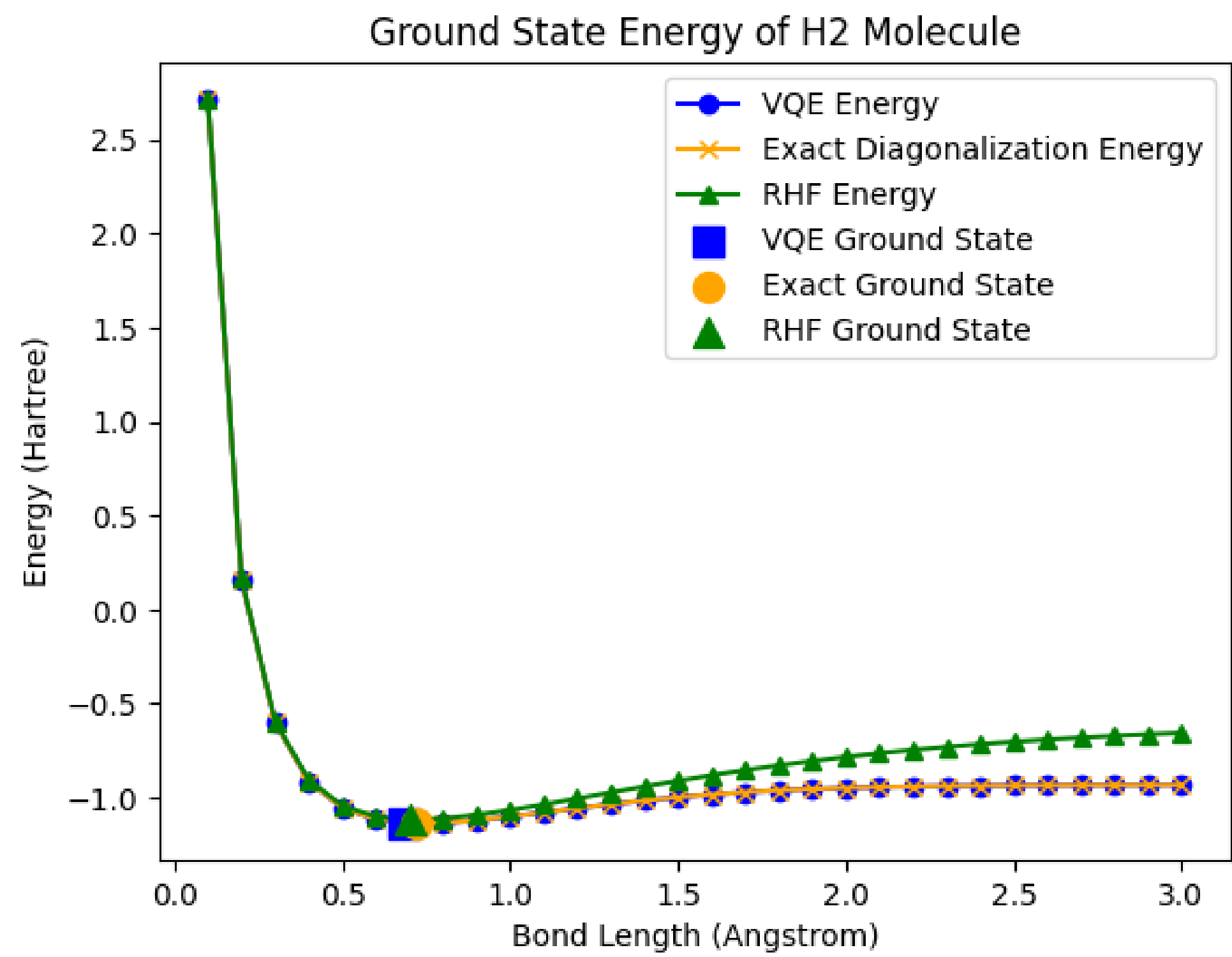
# Mark the ground state energy points with offset and different shapes
plt.scatter(min_vqe_bond - 0.02, min_vqe_energy, color='blue', label='VQE Ground State', s=100, zorder=5, marker='s') # Square for VQE, slightly offset
plt.scatter(min_exact_bond + 0.02, min_exact_energy, color='orange', label='Exact Ground State', s=100, zorder=5, marker='o') # Circle for Exact, slightly offset
plt.scatter(min_rhf_bond, min_rhf_energy, color='green', label='RHF Ground State', s=100, zorder=5, marker='^') # Triangle for RHF

# Labels and title
plt.xlabel("Bond Length (Angstrom)")
plt.ylabel("Energy (Hartree)")
plt.title("Ground State Energy of H2 Molecule")
plt.legend()
plt.show()
```

- Plotting the results



Results



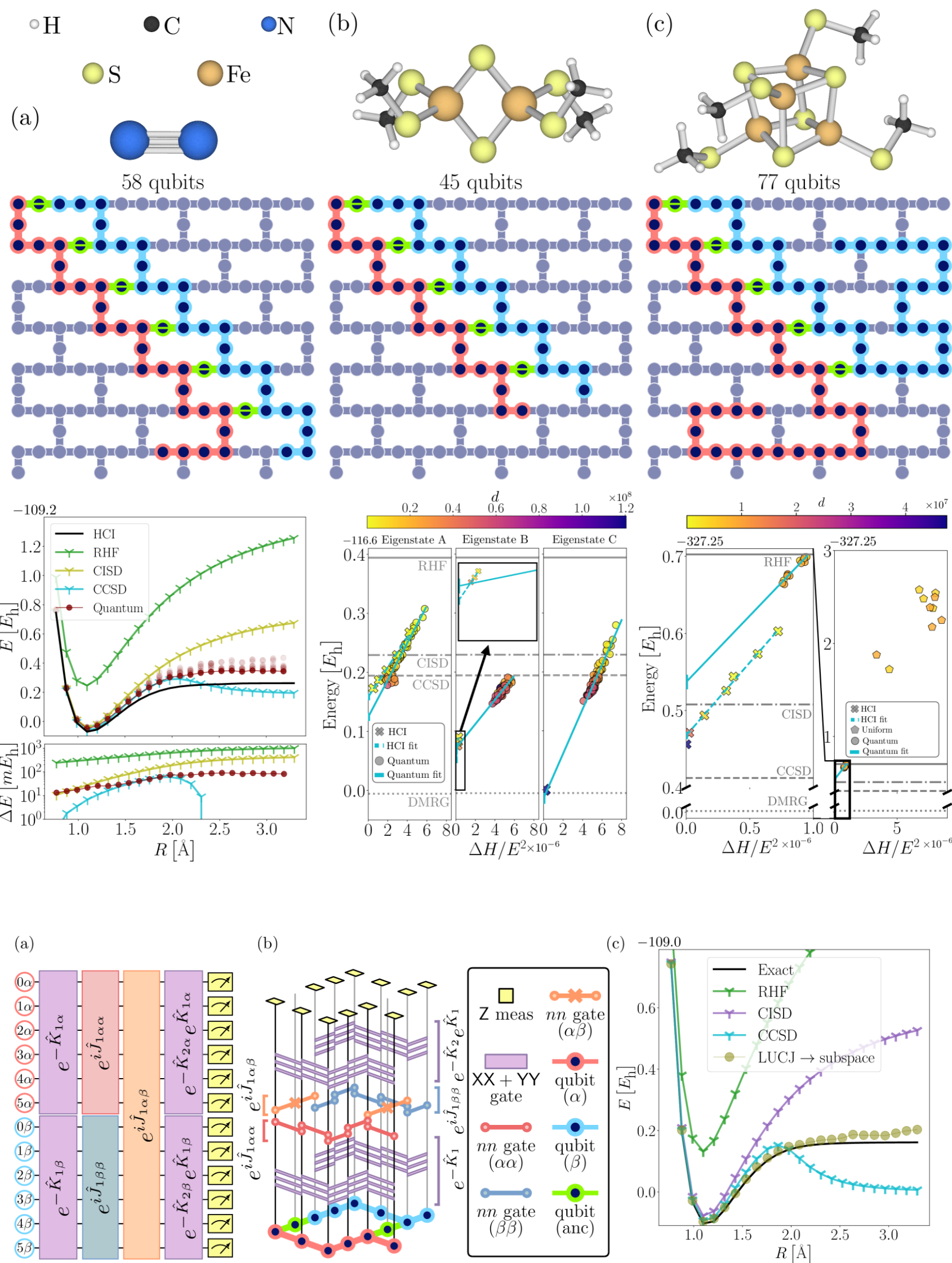
Fig(1): Energy of the Hydrogen molecule as a function of Bond length or Bond distance(dissociation curve).

Method	Ground State Energy	Bond Length
Variational Quantum Eigensolver	-1.1136189	0.70 Å
Exact Diagonalization	-1.136189	0.70 Å
Restricted Hartree Fock	-1.117349	0.70 Å

- The results compare VQE, Exact Diagonalization, and RHF for the ground-state energy of H_2 .
- VQE closely approximates the exact ground-state energy, outperforming RHF.
- RHF overestimates energy due to its neglect of electron correlation effects.
- RHF deviates significantly at larger bond lengths, while VQE aligns closely with exact results.
- VQE demonstrates the potential of quantum algorithms for accurate molecular energy calculations.

Further / Interested work

- **Incorporate Error Mitigation Techniques:** Apply methods like Zero Noise Extrapolation (ZNE), Probabilistic Error Cancellation (PEC), and Phase Estimation Algorithm (PEA) to improve VQE accuracy.
- **Adapt VQE for Scalability:** Exploring adaptive VQE variants to reduce circuit depth and optimize computational resources.
- **Krylov Subspace Methods:** As a better alternative for QPE, investigate their integration with quantum algorithms to enhance convergence and capture excited states.
- **State-of-the-Art Quantum Chemistry:** Leverage IBM's advancements in hardware-efficient ansatz and multi-reference methods for strongly correlated systems.
- Novel approaches like Quantum Monte Carlo, Variational Hamiltonian Ansatz, and Tensor Network integration for quantum chemistry.



arXiv - 2405.05068v1

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