

Calculating the H₂ bond energy

Chemistry using a quantum computer

Marijn Tiggelman & Ruben van Gulik





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- Converting the molecular Hamiltonian to qubit gates
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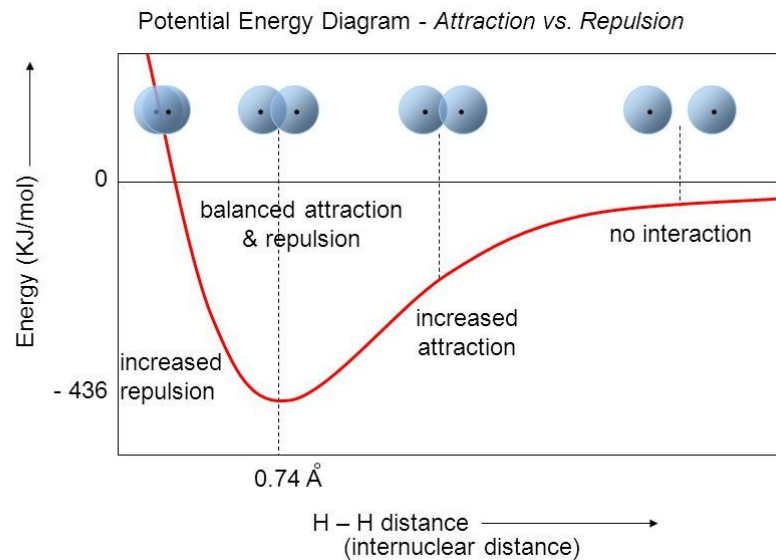
Computational chemistry

- Calculate structure/properties of molecules
- Applications
 - Efficient synthesis of compounds
 - Design of medicine or catalysts
- Doesn't require (difficult/dangerous/etc) experiments
- Requirement: 'chemical accuracy' (1 kcal/mol or $\sim 0.04\text{eV}$)
- Difficulties
 - Molecules are quantum (think superposition/entanglement of electron states)
- But wait, we can represent these states efficiently using a quantum computer!
- Interesting: simple molecules can already be simulated with a few qubits

Project:

Hydrogen molecule bond energy

- Simple(st) molecule
- Quantity of interest: bond energy



Molecular Hamiltonian

- Ab-initio (from first principles): Solve the Schrodinger equation
 - This is hard! So make assumptions: stationary nuclei (first quantization)

$$\begin{aligned}\hat{H} &= \hat{T}_n + \hat{T}_e + \hat{V}_{ne} + \hat{V}_{nn} + \hat{V}_{ee} \\ &= -\cancel{\sum_i \frac{\nabla_{R_i}^2}{2M_i}} - \sum_i \frac{\nabla_{r_i}^2}{2} - \sum_{ij} \frac{Z_i}{|R_i - r_j|} + \cancel{\sum_{i<j} \frac{Z_i Z_j}{|R_i - R_j|}} + \sum_{i<j} \frac{1}{|r_i - r_j|}\end{aligned}$$

- Second quantization (occupation of orbitals instead of coordinates/momenta)

$$H = H_1 + H_2 = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

- State is described by occupations, example: $|0011\rangle$ (4 orbits, 2 electrons in lowest orbit)
- How to write creation/annihilation operators as qubit gates?



Jordan-Wigner transformation

- Each qubit represents an electron being present ($|1\rangle$) or not ($|0\rangle$) in an orbital
- First guess for the creation/annihilation operators:

$$\hat{Q}^- = \frac{1}{2}(\hat{X} + i\hat{Y}) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \hat{Q}^+ = \frac{1}{2}(\hat{X} - i\hat{Y}) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}.$$

- Now we can put electrons in and out of orbitals!

$$\hat{Q}^- |0\rangle = 0 \quad \hat{Q}^- |1\rangle = |0\rangle \quad \hat{Q}^+ |0\rangle = |1\rangle \quad \hat{Q}^+ |1\rangle = 0.$$

- But we also have to account for the phase of the wavefunction (fermions), the final result is:

$$a_j^\dagger = \left(\prod_{k=1}^{j-1} \hat{Z}_k \right) \frac{1}{2}(\hat{X}_j + i\hat{Y}_j) \quad a_j = \left(\prod_{k=1}^{j-1} \hat{Z}_k \right) \frac{1}{2}(\hat{X}_j - i\hat{Y}_j).$$

Hydrogen molecule (H₂) Hamiltonian

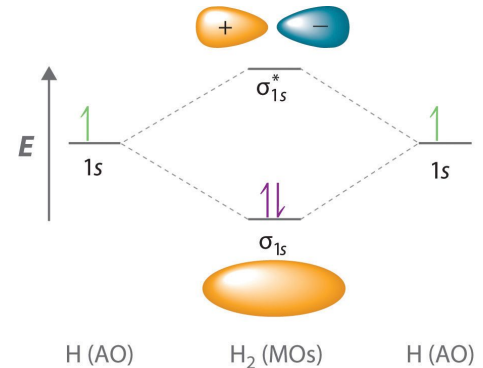
- Two spin-degenerate orbitals (so requires 4 qubits)
- Use symbolic math and quantum chemistry software to derive the Hamiltonian:

$$H = H_1 + H_2 = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$



$$\begin{aligned} & 1.0h_0 + 0.5h_0Z_0 + 0.5h_0Z_1 + 1.0h_1 + 0.5h_1Z_2 + 0.5h_1Z_3 + 0.25h_2 + 0.25h_2Z_0 + 0.25h_2Z_0Z_1 + 0.25h_2Z_1 \\ & + 0.25h_3 + 0.25h_3Z_2 + 0.25h_3Z_2Z_3 + 0.25h_3Z_3 + 1.0h_4 + 0.5h_4Z_0 + 0.25h_4Z_0Z_2 + 0.25h_4Z_0Z_3 + 0.5h_4Z_1 \\ & + 0.25h_4Z_1Z_2 + 0.25h_4Z_1Z_3 + 0.5h_4Z_2 + 0.5h_4Z_3 + 1.0h_5 - 0.25h_5X_0X_2X_1X_3 - 0.25h_5Y_0Y_2X_1X_3 \\ & - 0.25h_5Y_1Y_3X_0X_2 - 0.25h_5Y_1Y_3Y_0Y_2 + 0.5h_5Z_0 + 0.25h_5Z_0Z_2 + 0.25h_5Z_0Z_3 + 0.5h_5Z_1 + 0.25h_5Z_1Z_2 \\ & + 0.25h_5Z_1Z_3 + 0.5h_5Z_2 + 0.5h_5Z_3 \end{aligned}$$

- Run the variational eigensolver using this Hamiltonian in QISKit (IBM software) for different distances between H atoms





Quantum Variational Eigensolver (QVE)

- Variational principle

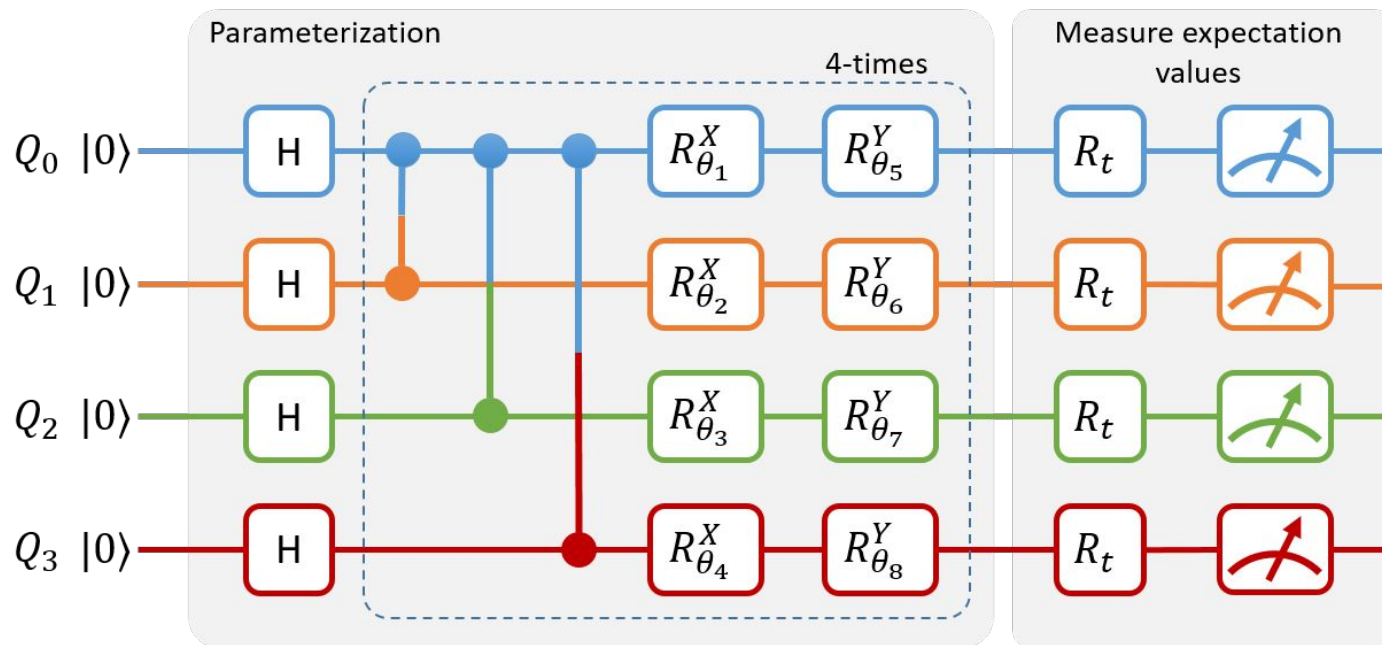
$$E_{\text{ground}} \leq \langle \psi | \hat{H} | \psi \rangle$$

- Generate a wavefunction (highly entangled) depending on parameters:

$$\psi(\theta_1, \theta_2, \dots, \theta_N)$$

- Tune the parameters by searching for a minimum in the energy expectation value

Quantum Variational Eigensolver (QVE)



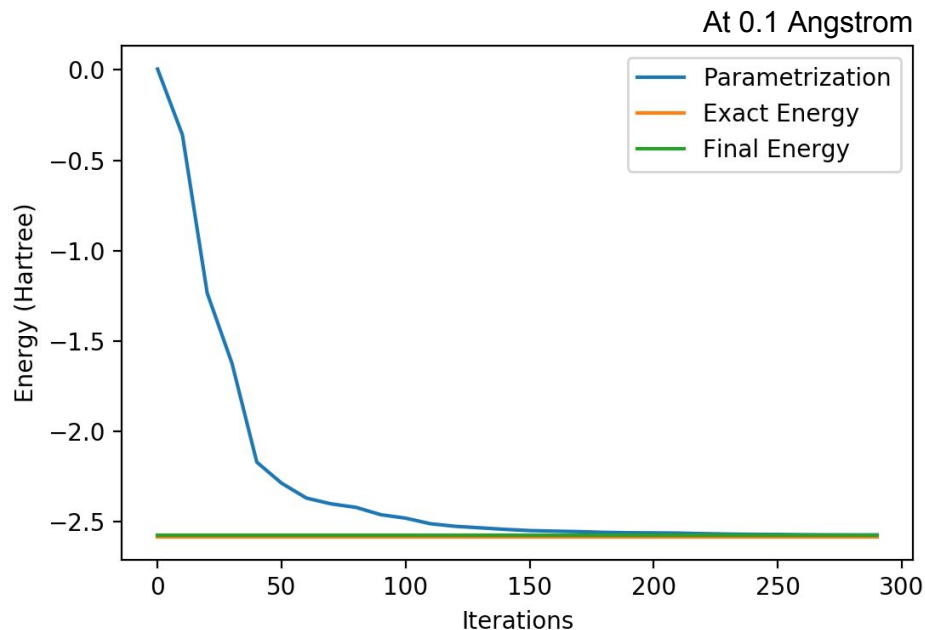
Hamiltonian terms:

IIII	ZIIZ
ZIII	IZZI
IZII	IZIZ
IIZI	IIZZ
IIIZ	XXXX
ZZII	XYXY
ZIZI	YXYX
	YYYY



Quantum Variational Eigensolver (QVE)

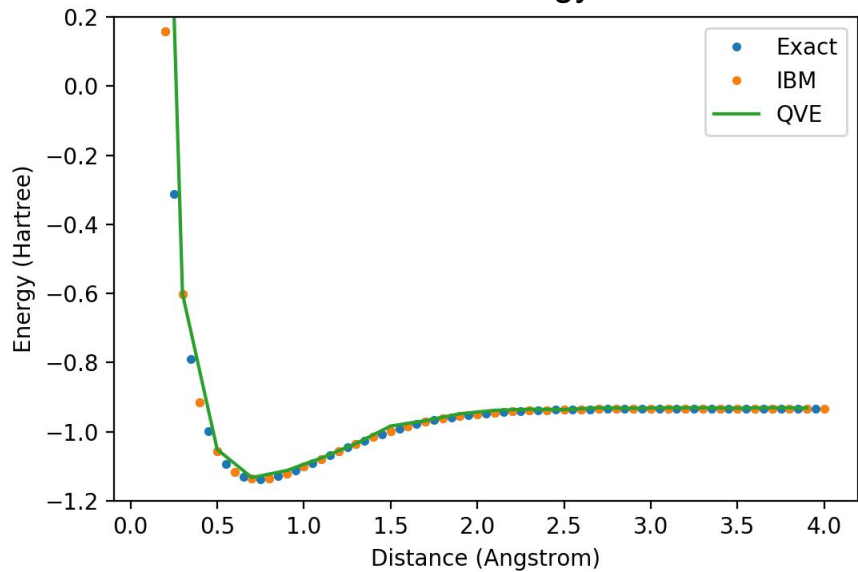
- Parameter optimization runs on a classical computer
- Simultaneous perturbation stochastic approximation (SPSA):
 - Generate random initial angles
 - Calculate/measure the energy
 - Optimize using gradient descent
- Final error: 0.00769 Hartree



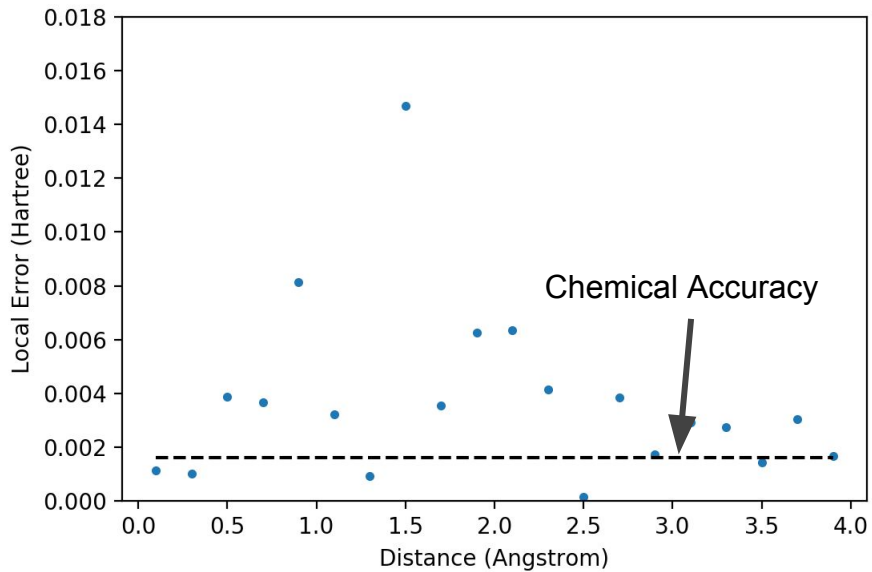


Results

Potential Energy



Error





Conclusion and outlook

- Can achieve ground state energy using QVE within chemical accuracy
- Apply different transformation (Bravyi-Kitaev) to minimize necessary qubits
- Use different parameterization (Coupled Cluster) to minimize parametrization gates



h-parameters

$$h_{pq} = \langle \phi_p | \hat{T}_e + \hat{V}_{ne} | \phi_q \rangle = \int \phi_p^*(\sigma) \left(-\frac{\nabla_r^2}{2} - \sum_i \frac{Z_i}{|R_i - r|} \right) \phi_q(\sigma) d\sigma$$

$$h_{pqrs} = \langle \phi_p \phi_q | \hat{V}_{ee} | \phi_r \phi_s \rangle = \int \phi_p^*(\sigma_1) \phi_q^*(\sigma_2) \left(\frac{1}{|r_1 - r_2|} \right) \phi_s(\sigma_1) \phi_r(\sigma_2) d\sigma_1 d\sigma_2.$$



QVE Steps

