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Master-class on quantum chemistry

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Outline

- Introduction to quantum chemistry
- Jordan-Wigner transformation
- Variational Quantum eigensolver
- H_2 molecule example

Molecular electronic structure problem

Time-independent Schrodinger equation: $\hat{H}|\psi_n >= E_n|\psi_n >$

Molecular Hamiltonian is a sum of terms (**R** is nuclear, **r** are electronic coordinates):

$$\hat{H} = \hat{T_N}(R) + \hat{T_e}(r) + \hat{V_{eN}}(r,R) + \hat{V_{NN}}(R) + \hat{V_{ee}}(r)$$

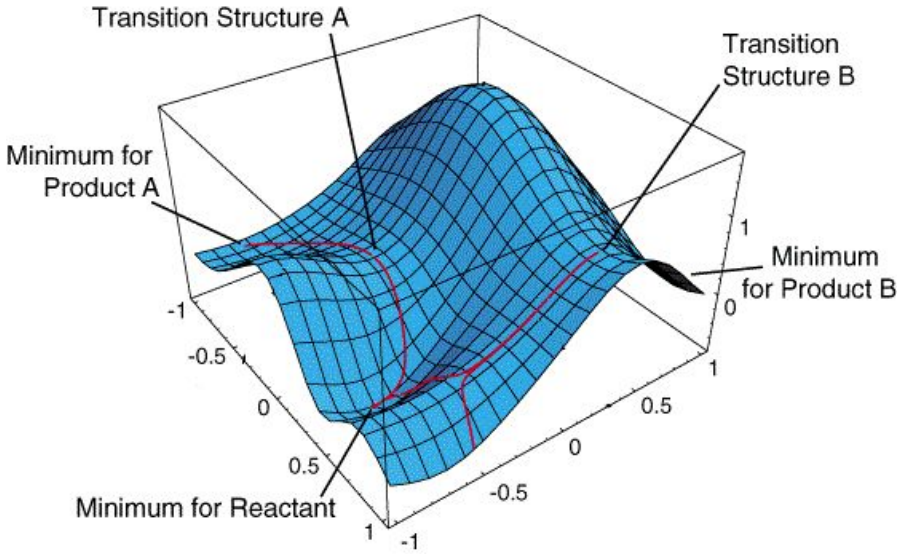
In atomic units: $$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_{i,A}\frac{Z_A}{r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B}{R_A B} + \sum_{i>j}\frac{1}{r_{ij}}$$

Born-Oppenheimer approximation (**R** is the parameter, not variable!):

$$\hat{H_{el}} = \hat{T_e}(r) + \hat{V_{eN}}(\mathbf{r;\ R}) + \hat{V_{NN}}(R) + \hat{V_{ee}}(r)$$

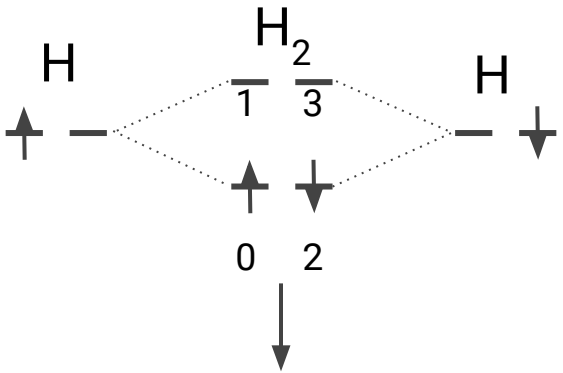
Quantum chemistry: Key problems

Forward problem: to predict the properties of a predefined molecular structure



- Investigation of the potential energy surfaces (barrier heights and reaction paths)
- Prediction of the geometrical structure of molecules
- Molecular properties (charges, dipole moments, polarizability)
- Molecular vibrations and thermodynamic properties

Qubit representation



$$\underbrace{|f_{n-1}\cdots f_1 f_0>}_{\text{occupation numbers of spin-orbitals}}, \quad f_i = \{0,1\}$$

$|0101>$

Statevector

Jordan-Wigner transformation

$|0> \otimes |1> \otimes |0> \otimes |1>$

Qubit state

Example: H_2 molecule (4 spin-orbitals and 2 electrons)

$$|\psi> = a_1|0101> + a_2|0110> + a_3|1001> + a_4|1010>$$

Qubit representation

Creation operator:

$$a_j^\dagger|...0... >= (-1)^p|...1... >$$

Annihilation operator:

$$a_j|...1... >= (-1)^p|...0... >$$

Anti-commutation relations:

$$[a_j, a_k]_+ = 0, \quad [a_j^\dagger, a_k^\dagger]_+ = 0, \quad [a_j, a_k^\dagger]_+ = \delta_{jk}\mathbf{1},$$

Electronic Hamiltonian in form of second quantization:

$$\hat{H} = \sum_{i,j} h_{ij}\, a_i^\dagger a_j + \frac{1}{2}\sum_{i,j,k,l} h_{ijkl}\, a_i^\dagger a_j^\dagger a_k a_l$$

Jordan-Wigner transformation:

$$a_j^\dagger = 1_{n-1} \otimes ...1_{j+1} \otimes \frac{1}{2}(\sigma_j^x - i\sigma_j^y) \otimes \sigma_{j-1}^z ... \sigma_0^z$$

$$a_j = 1_{n-1} \otimes ...1_{j+1} \otimes \frac{1}{2}(\sigma_j^x + i\sigma_j^y) \otimes \sigma_{j-1}^z ... \sigma_0^z$$

Quantum computing

Algorithms:

- Quantum Annealing
  - Map qubit Hamiltonian to Ising
  - Unreasonable number of qubits
- Quantum Phase Estimation
  - Too large circuit
  - Requires multiple Trotter steps
- **Variational Quantum Eigensolver**
  - Suitable for NISQ devices

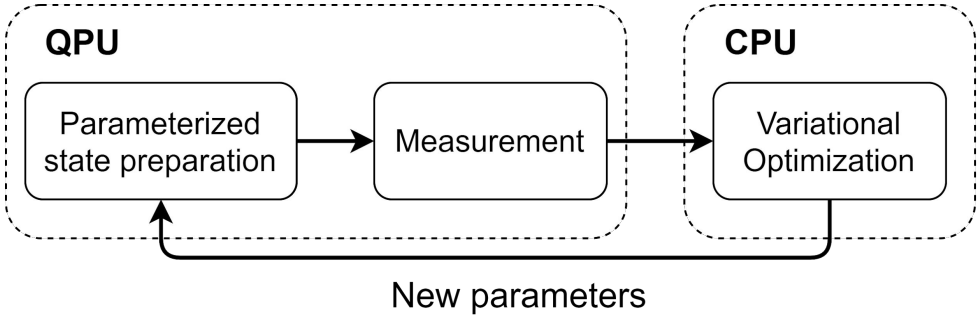
Platforms:

- **Qiskit (IBM)**
- Openfermion (Google)
- Pennylane (Xanadu)
- Forest (Rigetti)
- QDK (Microsoft)

Variational quantum eigensolver (VQE)

Variational principle:

$$\frac{<\psi(\vec{\theta})|H|\psi(\vec{\theta})>}{<\psi(\vec{\theta})|\psi(\vec{\theta})>} \geq E_0$$



1. Build parameterized quantum circuit
2. Select initial parameters
3. Run circuit (on QPU)
4. Measure energy
5. Update parameters (on CPU)
6. Repeat 2-5 until convergence

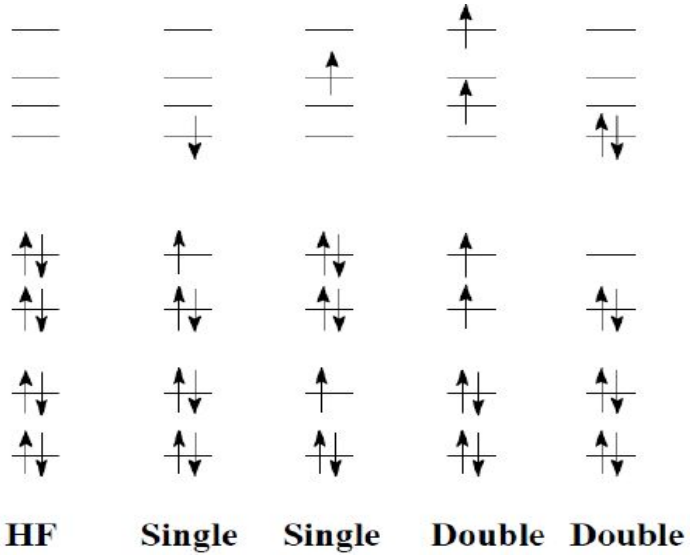
$$U(\vec{\theta}) = U_1(\theta_1)U_2(\theta_2)...U_n(\theta_n)$$

$$|\psi(\vec{\theta})>= U(\vec{\theta})|\phi>$$

$$H = \sum_{l=0}^{L-1} a_l H_l \qquad E(\vec{\theta}) = \sum_{l=0}^{L} a_l <\psi(\vec{\theta})|H_l|\psi(\vec{\theta})>$$

$$\vec{\theta} \longrightarrow \vec{\theta}_{new}$$

Variational quantum eigensolver (VQE)



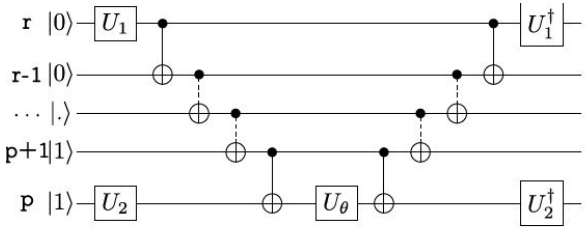
Unitary coupled cluster: $|\Psi(\vec{\theta})\rangle = e^{\hat{T}(\vec{\theta}) - \hat{T}^{\dagger}(\vec{\theta})} |\Phi_0\rangle$

Cluster operator: $\hat{T}(\vec{\theta}) = \hat{T}_1(\vec{\theta}) + \hat{T}_2(\vec{\theta})$

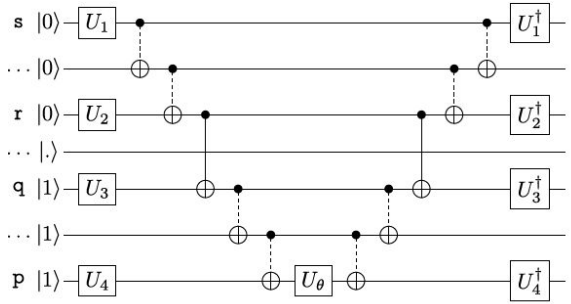
Single excitations: $\hat{T}_1(\vec{\theta}) = \sum_{i;m} \theta_i^m \, \hat{a}_m^{\dagger} \hat{a}_i$

Double excitations: $\hat{T}_2(\vec{\theta}) = \frac{1}{2} \sum_{i,j;m,n} \theta_{i,j}^{m,n} \, \hat{a}_n^{\dagger} \hat{a}_m^{\dagger} \hat{a}_j \hat{a}_i$

Single excitation:



Double excitation:



References

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https://arxiv.org/pdf/1208.5986.pdf

Variational quantum eigensolver:
https://arxiv.org/pdf/1701.02691.pdf
https://arxiv.org/pdf/1805.04340.pdf

Quantum annealing:
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Quantum phase estimation:
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