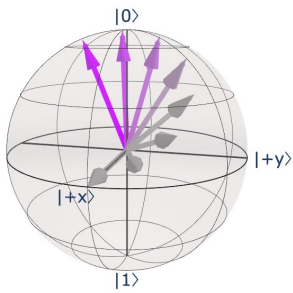


# Quantum Static Simulation

Dr. Ieva Liepuoniute  
IBM Quantum, IBM Research-Almaden



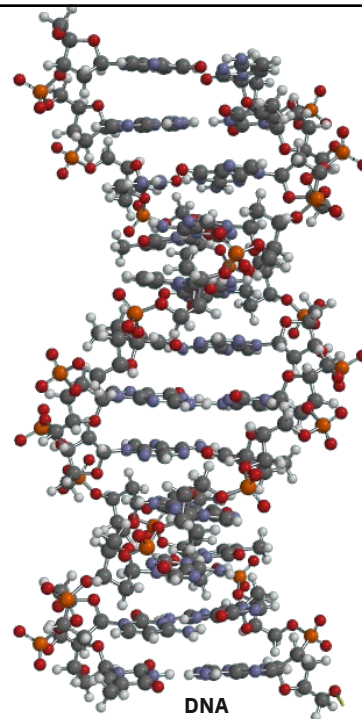
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## Quantum Chemistry

Molecules and materials are systems of many  
**electrons** and **nuclei** interacting with each other  
and obeying the laws of quantum mechanics



DNA

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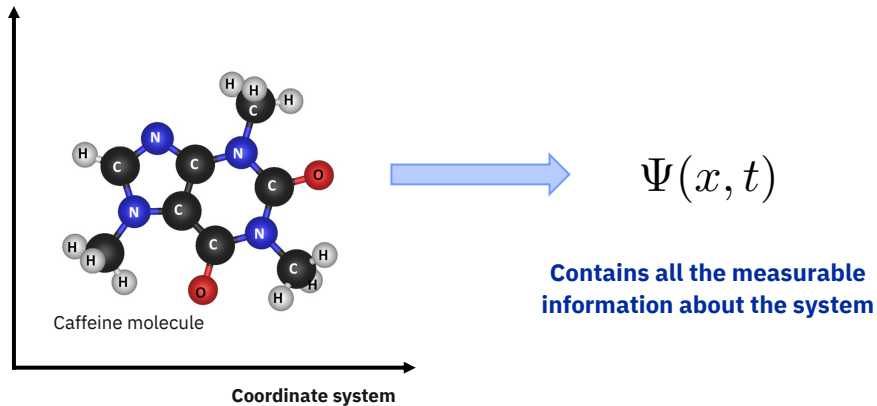
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## Wavefunction Formalism

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Properties of a molecule are determined by a **wavefunction**



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## Separation of Variables

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We use **separation of variables** to express our wavefunction as a product of two functions, each of which is a function of one variable only:

$$\Psi(x, t) = \underbrace{\psi(x)}_{\text{position}} \underbrace{\phi(t)}_{\text{time}}$$

Further separation of the total wavefunction into an **electronic** and **nuclear** degrees of freedom is possible!

**Born-Oppenheimer approximation** – nuclei are stationary and wavefunction describes the motion of electrons

$$\psi(x) = \psi(R, r) = \Phi(R)\varphi(r)$$

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## Schrödinger Equation

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Time-independent Schrödinger equation for the **Born-Oppenheimer Hamiltonian**:

$$\hat{H}\Psi = E\Psi$$

$$\hat{H}_{mol} = \underbrace{-\frac{1}{2} \sum_i^n \nabla_i^2}_{\text{electronic kinetic energy}} \underbrace{- \sum_i^n \sum_I^N \frac{Z_I}{r_{Ii}}}_{\text{electron-nuclei attraction}} \underbrace{+ \sum_{i<j}^n \frac{1}{r_{ij}}}_{\text{electronic repulsion}} \underbrace{+ V_{nuc}}_{\text{constant!}}$$

kinetic energy
potential energy

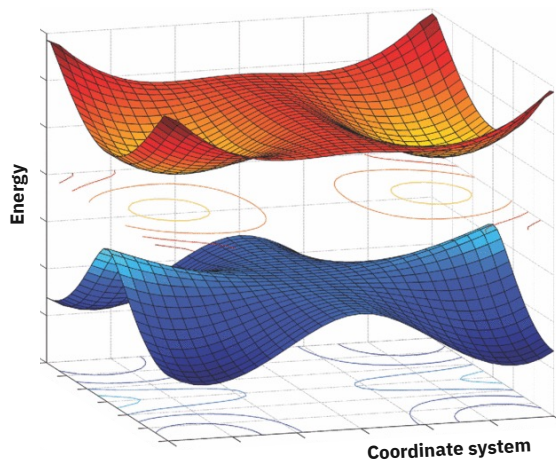
$$\hat{H}_{mol} = \hat{T} + \hat{V}$$

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## Potential Energy Surface (PES)

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PES relies upon the validity of the Born-Oppenheimer approximation

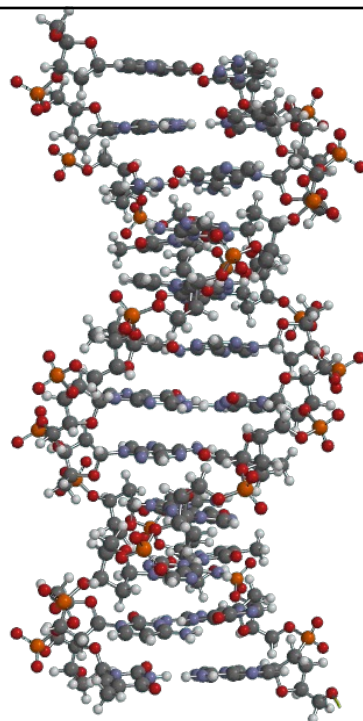
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## Quantum Chemistry

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*Ab initio* quantum chemistry attempts to solve the **Schrödinger equation** to yield information about a molecular system such as potential energy surfaces, electron densities, vibrational frequencies, etc.



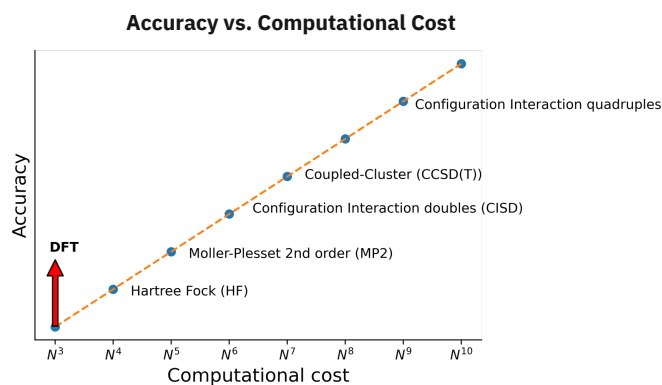
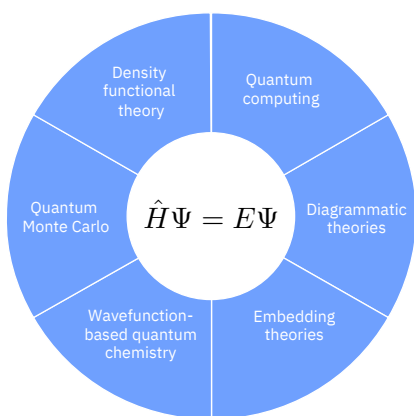
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## Approximations to Schrödinger Equation

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Computational resources increase **exponentially** with the number of atoms!



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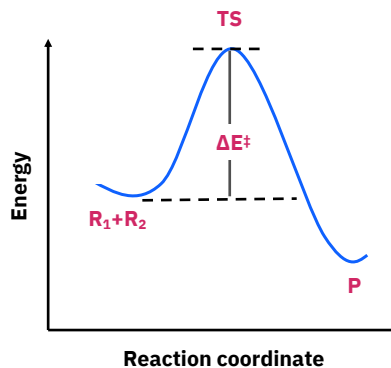
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## Desired Accuracy for Chemistry Calculations

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In chemistry, it is important to calculate the energy of molecules within **chemical accuracy**, which is required to predict reaction rates:

$$k_B T \approx 1 \text{ kcal/mol}$$



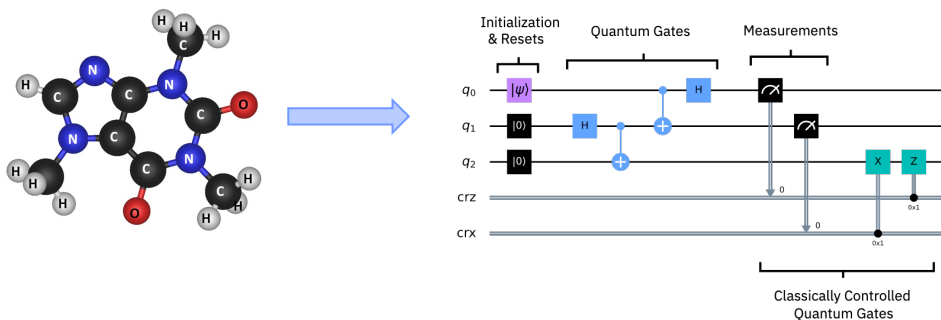
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## Quantum Computers for Chemistry

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In 1982, Richard Feynman suggested that an avenue for the tractable simulation of quantum systems would be to build quantum mechanical simulators.



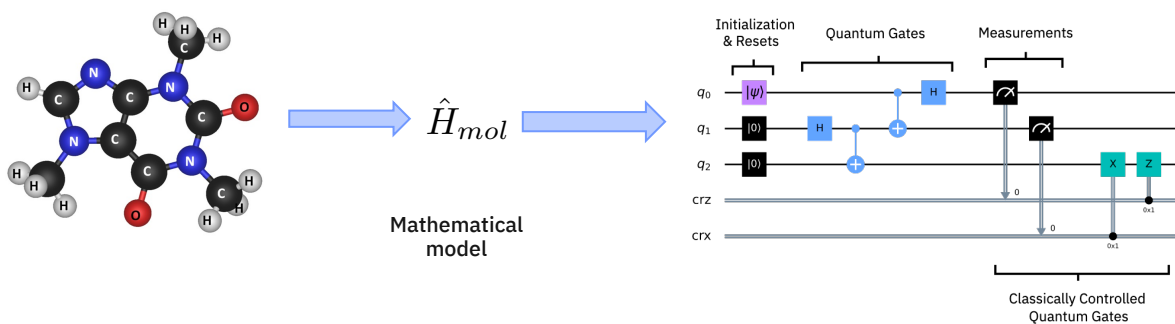
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## Quantum Computers for Chemistry

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In 1982, Richard Feynman suggested that an avenue for the tractable simulation of quantum systems would be to build quantum mechanical simulators.

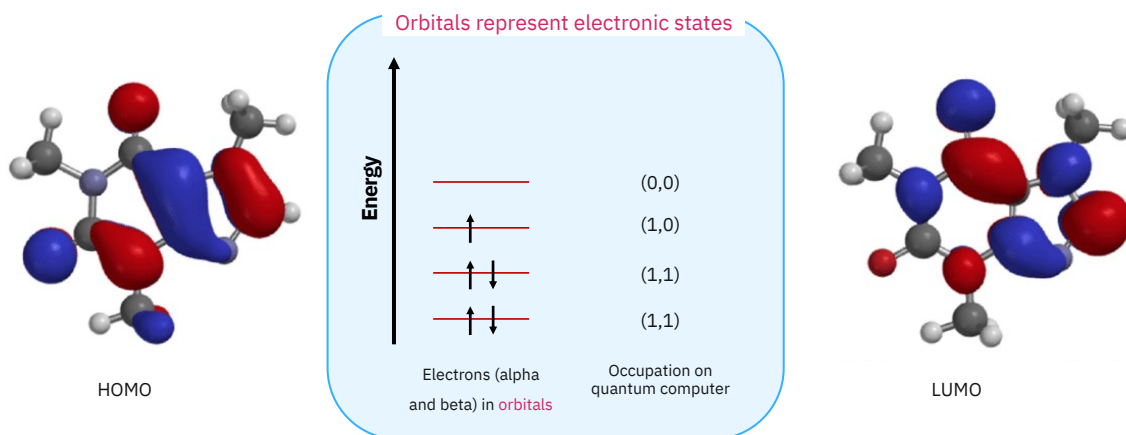


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## Electrons Occupy Orbitals

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Orbitals are mathematical functions that are approximate solutions to the Born-Oppenheimer Schrödinger equation

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## Mathematical Model: Second Quantization

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**Second quantization** is an **occupation number** formalism used to describe quantum many-body systems of identical particles

- In **second-quantization**, we ask: How many particles are there in every state?
- Any generic second-quantized many-body state is a linear combination of **Fock states**

$$|\Psi\rangle = \sum_{[n]} \Psi[n] |[n]\rangle \quad |[n]\rangle = [n_1, n_2, \dots, n_\alpha, \dots, n_D]$$

Fock states

- **Pauli exclusion principle**: identical fermions can not occupy the same state simultaneously.

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## Mathematical Model: Second Quantization

IBM Quantum

Fermion **creation** and **annihilation**:

- Fermionic **creation** operator adds a fermion to the single-particle state, **increasing** the occupation number by one:

$$a_\alpha^\dagger [n_1, n_2, \dots, n_\alpha, \dots, n_D] = (-1)^{\sum_{i=0}^{\alpha-1} n_i} (1 - n_\alpha) [n_1, n_2, \dots, n_{\alpha+1}, \dots, n_D]$$

- Fermionic **annihilation** operator removes a fermion from the single-particle state **reducing** the occupation number by one:

$$a_\alpha [n_1, n_2, \dots, n_\alpha, \dots, n_D] = (-1)^{\sum_{i=0}^{\alpha-1} n_i} (n_\alpha) [n_1, n_2, \dots, n_{\alpha-1}, \dots, n_D]$$

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## Hamiltonian in Second Quantization

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Molecular Hamiltonian

$$\hat{H}_{mol} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_i^n \sum_I^N \frac{Z_I}{r_{Ii}} + \sum_{i<j}^n \frac{1}{r_{ij}} + V_{nuc}$$

Second quantization

Fermionic Hamiltonian

$$\hat{H}_{mol} = \underbrace{\sum_{p,q} h_{pq} a_p^\dagger a_q}_{\text{1-particle operator}} + \frac{1}{2} \underbrace{\sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s}_{\text{2-particle operator}}$$

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## Hamiltonian Mapping onto Quantum Computers

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Fermionic Hamiltonian

$$\hat{H}_{mol} = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

$$X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad Y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad Z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Pauli matrices

 $I, X, Y, Z$ Parity;  
Jordan-Wigner;  
Bravyi Kitaev

$$\hat{H}_{k-local} = \sum_i c_i \sigma_{i,1} \sigma_{i,2} \dots \sigma_{i,k}$$

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## Mapping: Jordan–Wigner Transformation

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$$\hat{H}_{mol} = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

Definition of rising and lowering operators for **Jordan-Wigner mapping**:

$$Q_i^+ = \frac{1}{2}(X_i - iY_i) \otimes_{j<i} Z_j$$

$$Q_i^- = \frac{1}{2}(X_i + iY_i) \otimes_{j<i} Z_j$$

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## Variational Quantum Eigensolver (VQE)

IBM Quantum

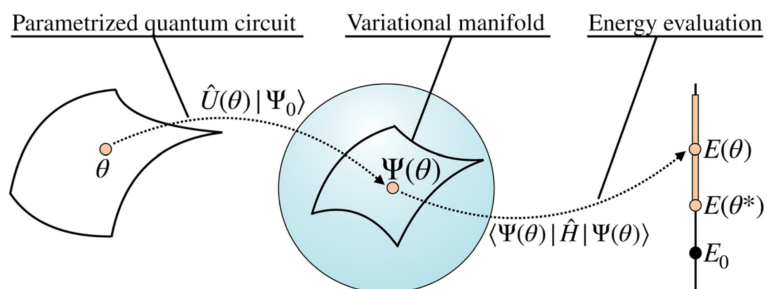


Image source: Motta, M., & Rice, J. E. (2021). Emerging quantum computing algorithms for quantum chemistry. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, e1580.

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## Variational Quantum Eigensolver (VQE)

IBM Quantum

**Ground state** is fundamental in quantum chemistry!

We use ground states to calculate many other properties such as reaction rates and reaction pathways.

VQE allows us to find an upper bound of the lowest eigenvalue of a given Hamiltonian.

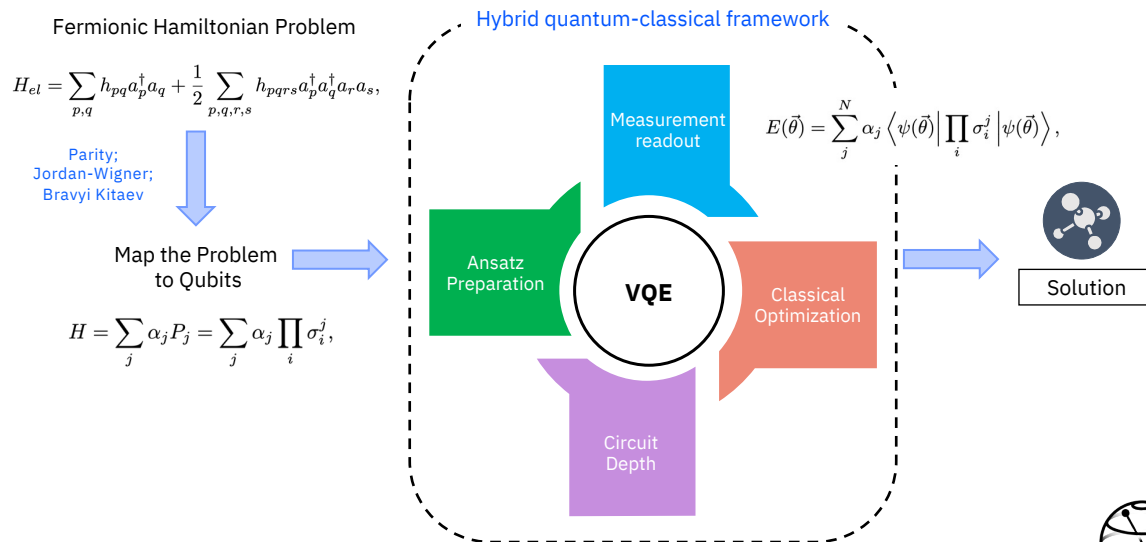
- Our goal is to estimate:  $\hat{H}|\Psi_\lambda\rangle = \lambda|\Psi_\lambda\rangle \longrightarrow \langle\Psi_0|\hat{H}|\Psi_0\rangle = E_0$
- For an arbitrary state, its eigenvalue will be an upper bound to for the ground state energy:  $E_\Psi \geq E_0$
- But we do not know the eigenstates!  $\langle\Psi|\hat{H}|\Psi\rangle = E(\Psi)$
- We start with a parametrized trial state aka **Ansatz** (approximation to the ground state).

The goal is to get the upper bound as close to the real ground state energy as possible

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## Variational Quantum Eigensolver Implementation

IBM Quantum



Kandala, A.; Mezzacapo, A.; Temme, K.; Takita, M.; Brink, M.; Chow, J. M.; Gambetta, J. M. Nature, 2017, 549, 242–246  
Lanyon, Benjamin P., et al. "Towards quantum chemistry on a quantum computer." Nature chemistry 2.2 (2010): 106–111.

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## Chemistry on Near-term Quantum Devices

- Small number of qubits
- Relatively short coherence times
- Noise from environment



IBM Quantum

How can we simulate Chemistry accurately?

How can we cut down on computational cost?

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## VQE State of Research

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Ansatz selection

Hamiltonian construction

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## VQE State of Research

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**Ansatz selection**

Hamiltonian construction

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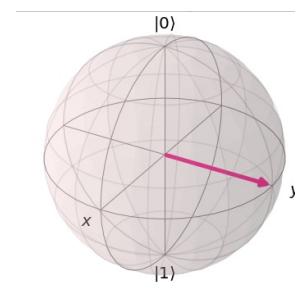
## VQE Ansatz

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**Ansatz:** quantum circuit that have parametrized gates

## Desired Ansätze

- ❑ Expressible - span sufficient Hilbert space
- ❑ Have small number of qubits
- ❑ Are short-depth (N operations per circuit)
- ❑ Hardware-efficient



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## Measuring the Cost of Ansatz

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**Ansatz:** quantum circuit that have parametrized gates

Circuit depth

Circuit connectivity

Number of parameters

Number of 2-qubit gates

Gate type

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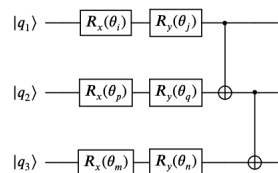
## Fixed Structure Ansätze

IBM Quantum

### Hardware Efficient

- Quantum gates directly tailored to the quantum device
- Spans a very large portion of Hilbert space (inefficient)
- Large number of parameters must be optimized

$$|\Psi(\theta)\rangle = \left[ \prod_{i=1}^d U_{\text{rota}}(\theta_i) U_{\text{ent}} \right] U_{\text{rota}}(\theta_{d+1}) |\psi_{\text{init}}\rangle$$



### Quantum Unitary Coupled Cluster

- Chemistry inspired exponential Ansatz – FCI level results can be achieved
- Operator generates single and double particle-hole excitations
- Not hardware efficient, agnostic to device connectivity
- Deep circuits needed

$$|\Psi\rangle = e^{\hat{T}-\hat{T}^\dagger} |\Psi_{HF}\rangle$$

$$e^{\hat{T}-\hat{T}^\dagger} \approx \prod_{ia} e^{\theta_i^a (\hat{a}_a^\dagger \hat{a}_i - \hat{a}_i^\dagger \hat{a}_a)} \prod_{ijab} e^{\theta_{ij}^{ab} (\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i - \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_b \hat{a}_a)}$$

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## VQE State of Research

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Ansatz selection

Hamiltonian construction

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## Hamiltonian Strategies

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Single and double particle excitations in the molecular orbital space

$$\hat{H}_{mol} = \sum_{p,q} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_r a_s$$

$$h_{pq} = \int d\sigma \varphi_p^*(\sigma) \left( \frac{-\nabla_r^2}{2} - \sum_i \frac{Z_i}{|R_i - r|} \right) \varphi_q(\sigma), \quad h_{pqrs} = \int d\sigma_1 d\sigma_2 \frac{\varphi_p^*(\sigma_1) \varphi_q^*(\sigma_2) \varphi_r(\sigma_1) \varphi_s(\sigma_2)}{|r_1 - r_2|},$$

↑  
spin orbitals

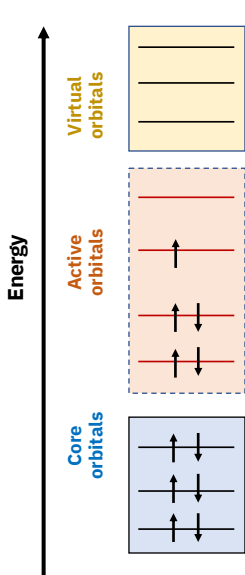
The number of qubits is also reduced by using an **active space approximation** – dividing a set of active and inactive orbitals

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## Active Space Selection

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Orbitals and electrons that are presumed to be the most important for an adequate description of the wave function

- The external (virtual) orbitals are empty.
- Active orbitals can be occupied by none, one, or two electrons.
- Core orbitals are always occupied by two electrons.

Goal: reducing number of qubits. Each active qubit will represent a state on QC

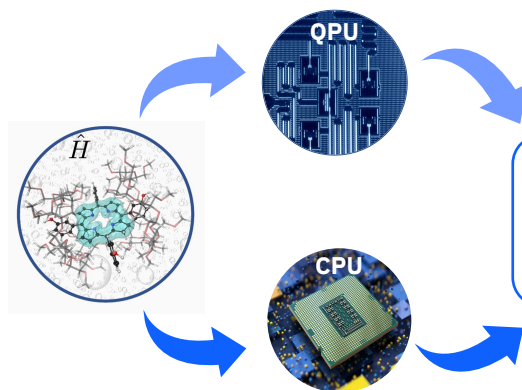
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## The Idea of Embedding

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**Embedding** which will allow us to compute energies of certain electrons and molecular orbitals in a quantum computer, leaving the rest of the MO's to be calculated classically.



### Importance of embedding

- Solving memory and convergence issues
- Studying larger systems
- Getting more accurate results quickly.

Ma, He, et al. "Quantum embedding theory for strongly correlated states in materials." *Journal of Chemical Theory and Computation* 17.4 (2021): 2116-2125.

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## Parameter Optimization Strategies

IBM Quantum

Optimizers account for the statistical nature of quantum measurement and update parameters

### Local Optimizers

Searches within the **neighboring set of a candidate solution**

- Constrained Optimization by Linear Approximation (COBYLA)
- Conjugate gradient (CG)
- Limited-memory BFGS Bound optimizer
- Simultaneous Perturbation Stochastic Approximation (SPSA)
- Gradient Descent (GD)
- Sequential Least Squares Programming optimizer (SLSQP)

### Global Optimizers

Searches among **all possible solutions**

- Controlled Random Search with local mutation optimizer (CRS)
- Improved Stochastic Ranking Evolution Strategy Optimizer (ISRES)

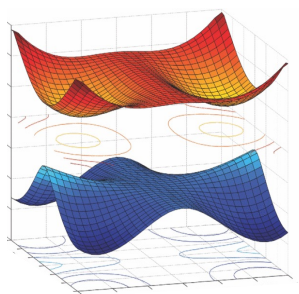
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## Extension of VQE to Excited State Energies

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The computation of molecular **excitation energies** is essential for predicting photo-induced reactions of chemical and technological interest.



**Excited states – higher energy configuration**



**Ground states – electrons in a system are in the lowest possible energy**

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## Extension of VQE to Excited State Energies

IBM Quantum

### Quantum Subspace Expansion (QSE)

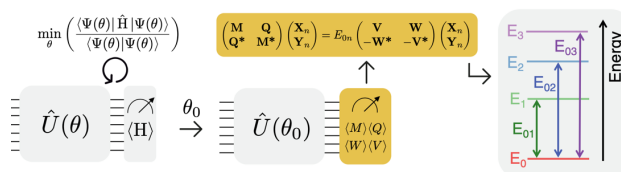
- No modifications to the quantum circuit needed
- Analogous to classical CISD
- Describes low-lying excitations and improve accuracy of VQE ground state
- Measurement of additional matrix elements of the GS wavefunction

$$Hc = ScE$$

$$H_{ij} = \langle \psi_0 | \sigma_i^\dagger H \sigma_j | \psi_0 \rangle \quad S_{ij} = \langle \psi_0 | \sigma_i^\dagger \sigma_j | \psi_0 \rangle$$

### Quantum Equations of Motion (qEOM)

- Pseudo-eigenvalue problem
- Uses the VQE ground state to compute the EOM matrix elements excitations
- Each matrix element is measured on the quantum computer with the corresponding ground state



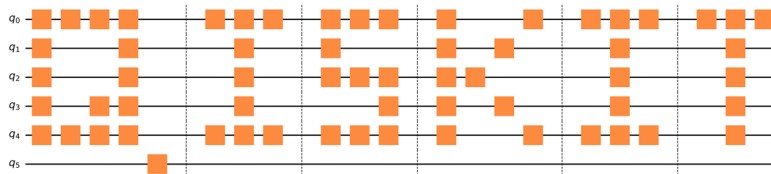
Ollitrault, Pauline J., et al. "Quantum equation of motion for computing molecular excitation energies on a noisy quantum processor." *Physical Review Research* 2.4 (2020): 043140.  
 McClean, Jarrod R., et al. "Hybrid quantum-classical hierarchy for mitigation of decoherence and determination of excited states." *Physical Review A* 95.4 (2017): 042308.

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## Qiskit Nature

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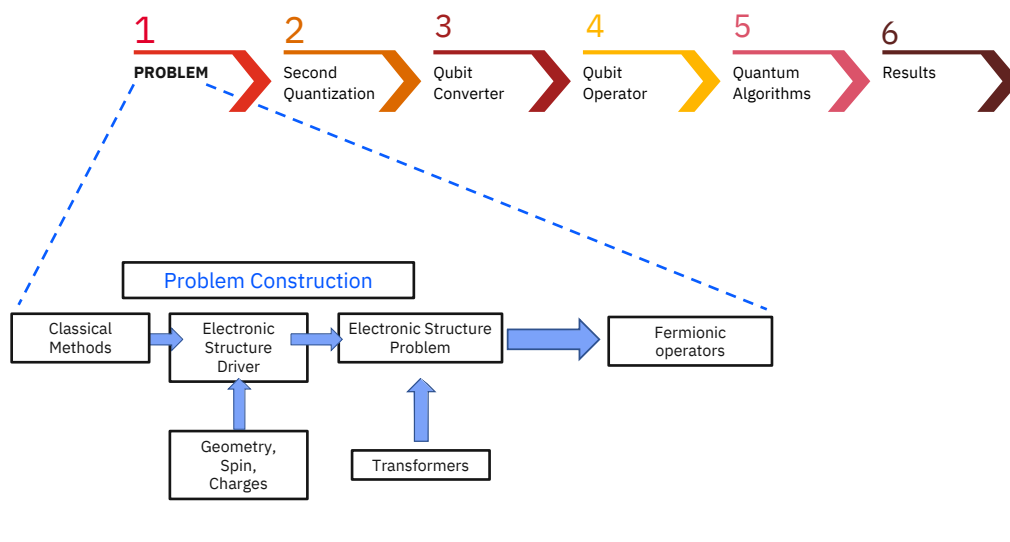


- ✓ Electronic Structure
- ✓ Vibrational Structure
- ✓ Excited State Solvers
- ✓ Ground State Solvers
- ✓ Property Folding
- ✓ Lattice models
- ✓ Calculating Thermodynamics Observables with a Quantum Computer
- ✓ Sampling the Potential Energy Surface

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## Qiskit Research Code Setup

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