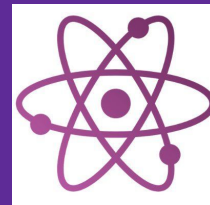


# QKRISHI PROJECT

Dinesh Kumar

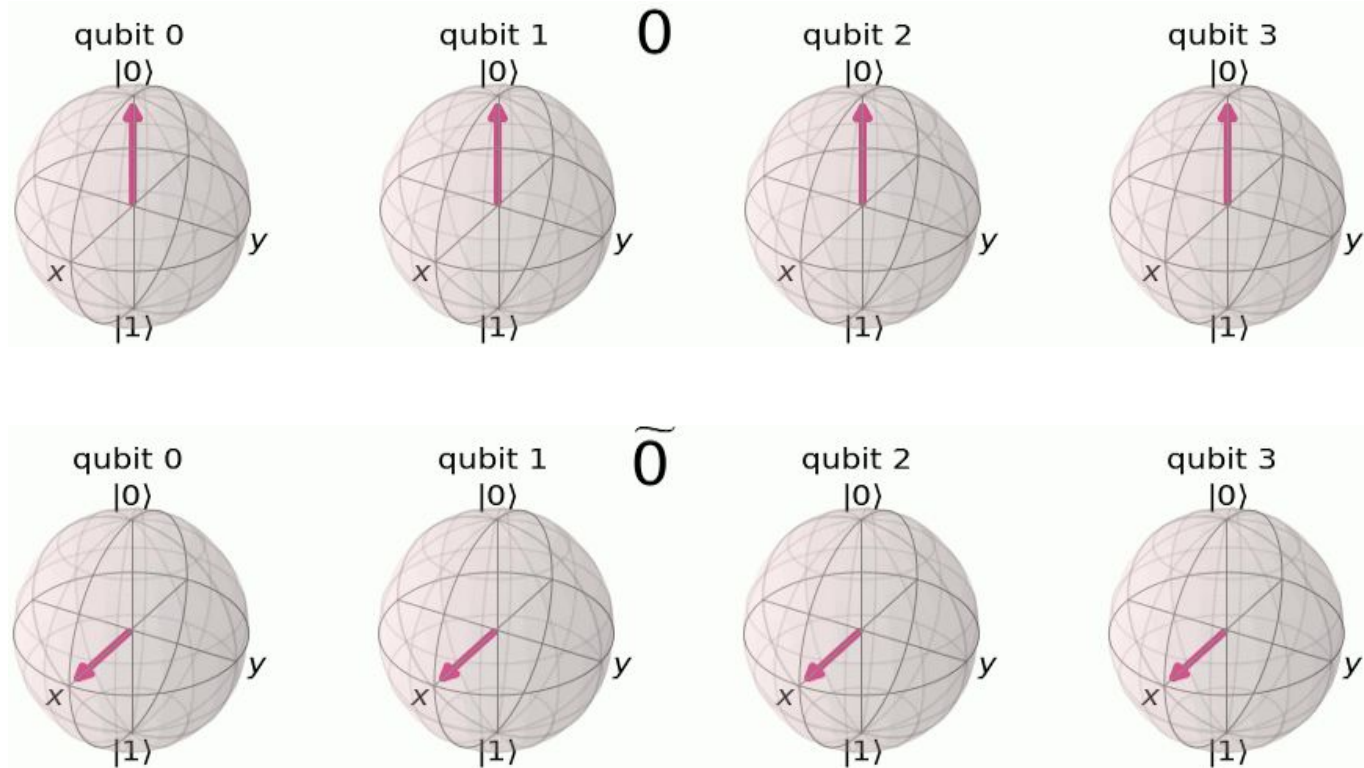


# Quantum Fourier Transform

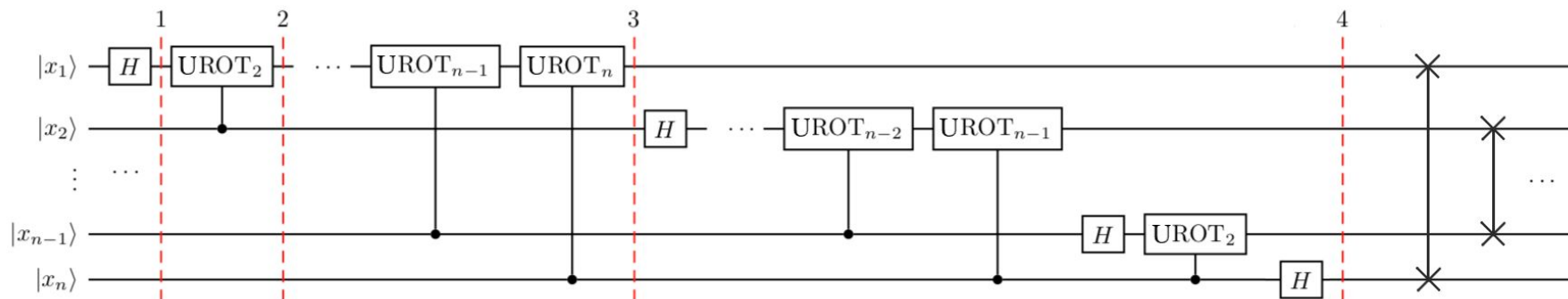
- The Quantum Fourier transform (QFT) is the quantum implementation of the discrete Fourier transform over the amplitudes of a wavefunction.
- QFT changes basis from computational/z basis  $\{ |0\rangle, |1\rangle \}$  to fourier basis  $\{ |+\rangle, |-\rangle \}$
- Doing QFT reduces the computational complexity from  $O(\exp(n^{1/3}(\log n)^{2/3}))$  [complexity of z basis] to  $O(n^2 \log(n) \log(\log n))$  [complexity of fourier basis].
- This is an exponential speed up!

$$y_k = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} x_j \omega_N^{jk} \quad \text{where } \omega_N^{jk} = e^{2\pi i \frac{jk}{N}}$$

# Quantum Fourier Transform



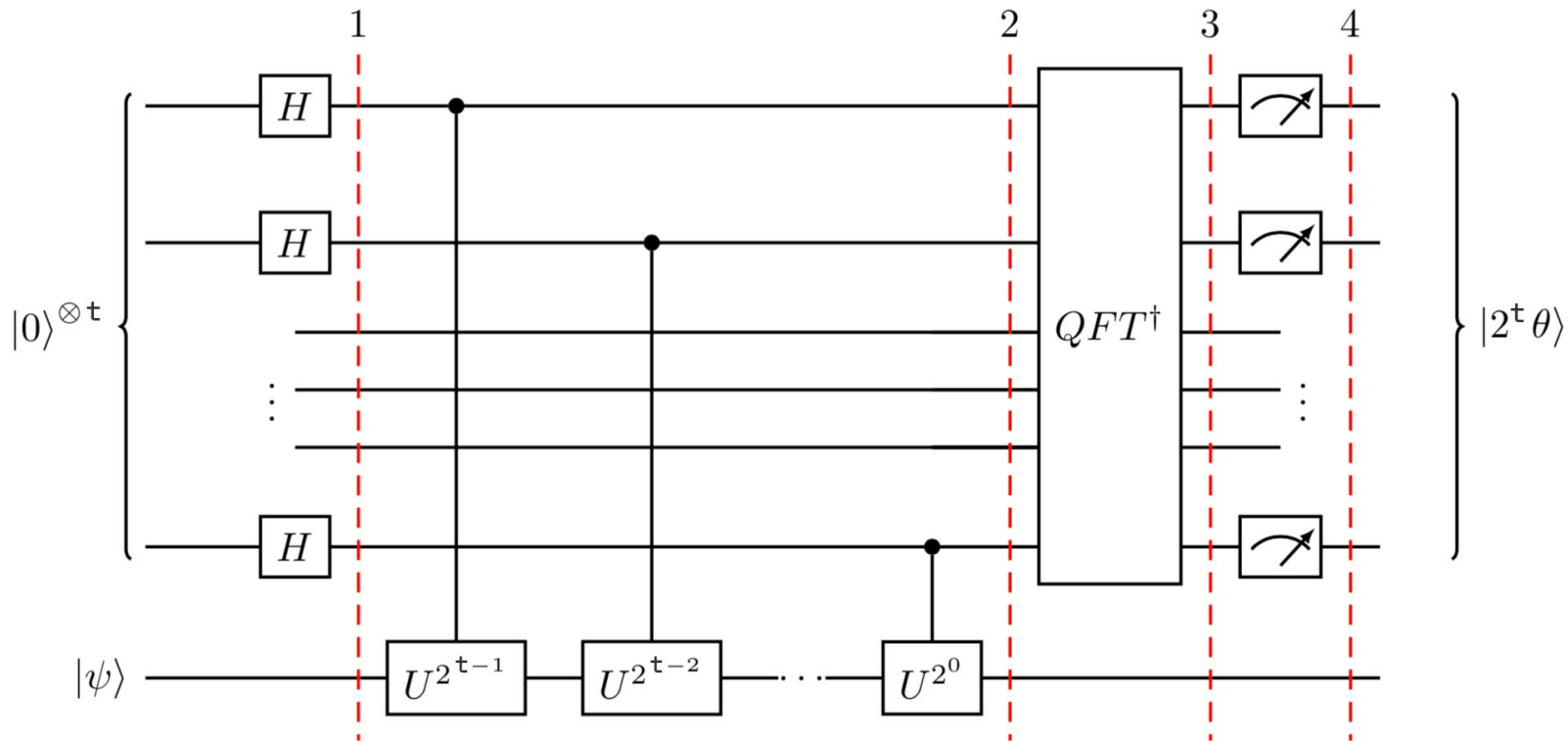
# Implementing QFT



# Quantum Phase Estimation

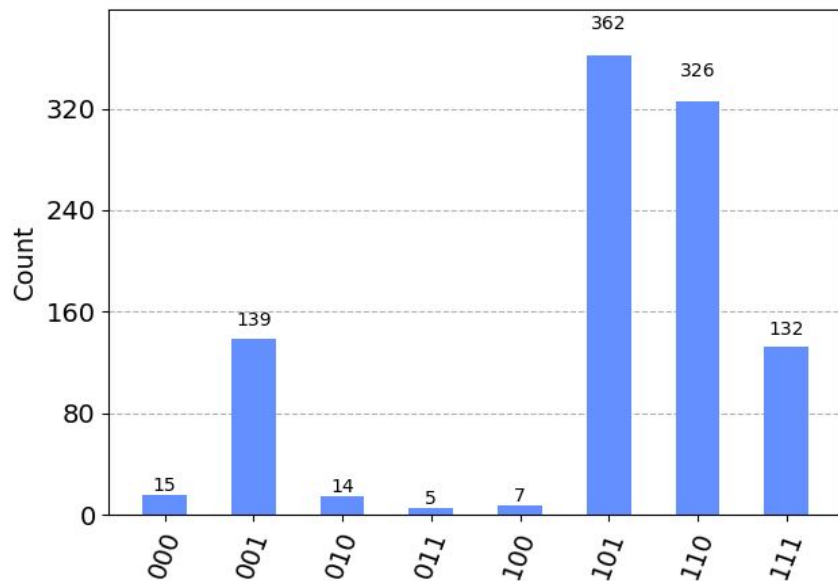
- Given a unitary operator  $U$ , the algorithm estimates  $\theta$   $U|\psi\rangle = e(2\pi i\theta)|\psi\rangle$ .
- Here  $|\psi\rangle$  is an eigenvector and  $e2\pi i\theta$  is the corresponding eigenvalue.
- Quantum phase estimation is one of the most important subroutines in quantum computation and is the idea for many quantum algorithms and one such algorithm is Shor's algorithm.
- Using more qubits in QPE results in better precision. Let's say we use 1 qubit and get the probabilities for 0 & 1 as 0.9924 & 0.0075. If we use 10 qubits we would get roughly 1000x ( $2^{10}$ ) more precision. So we have something like 992.4... & 7.5...
- QPE also helps in signal to noise limitation.

# Implementing QPE

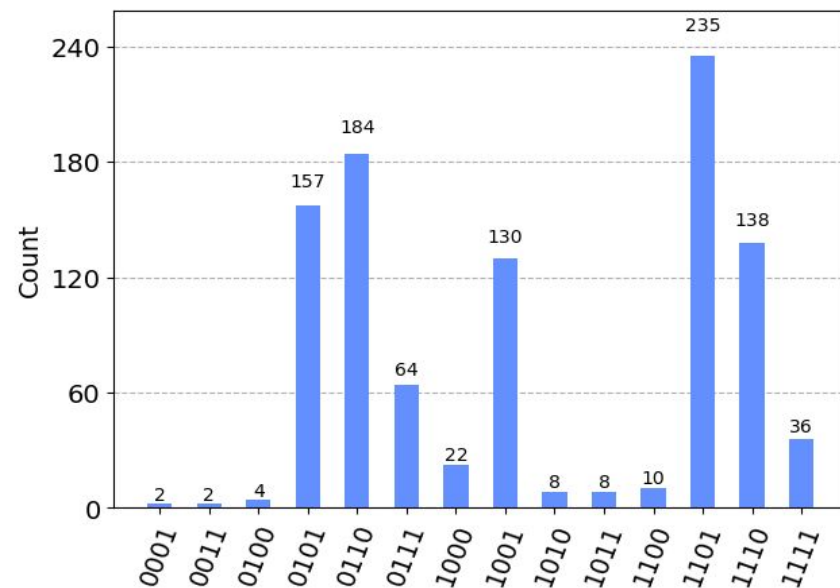


# Determining phase using QPE

We measure theta using QPE with different n (# measurement qubits).



Using 3 qubits with  $\theta = 0.70$ ,  $\text{measured\_theta} = 0.62$ .



Using 4 qubits with  $\theta = 0.70$ ,  $\text{measured\_theta} = 0.69$ .

# Electronic Structure

- Discussion is with time independent, non-relativistic Schrodinger equation. The molecular Hamiltonian is

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

- We do Born-Oppenheimer approximation since electrons and nuclei are at different mass scale so time moves differently or doesn't change much for nuclei w.r.t. Electron. So we decouple electron and nuclei and

$$\mathcal{H}_{\text{el}}|\Psi_n\rangle = E_n|\Psi_n\rangle$$

- The dimensionality of solving this problem grows exponentially with the number of degrees of freedom. To tackle this issue we prepare ground state on quantum computer and measure the Hamiltonian expectation value directly.



# Electronic Structure

- Running BeH<sub>2</sub> molecule with PySCF Driver with STO-3G.

Interface for selecting basis sets from the Basis Set Exchange website.

**Left Panel: Filter and List**

Filter: All roles (dropdown) | All (dropdown)

search basis sets...

- STO-2G
- STO-3G**
- STO-4G
- STO-5G
- STO-6G
- SV (Dunning-Hay)
- SVP (Dunning-Hay)
- SVP + Diffuse (Dunning-Hay)
- TZ (Dunning-Hay)
- TZP-ZORA
- UGBS
- un-ccemnd-ref
- un-pcemd-ref
- x2c-JFIT
- x2c-JFIT-universal
- x2c-QZVPall
- x2c-QZVPall-2c
- x2c-QZVPall-2c-s
- x2c-QZVPall-s
- x2c-QZVPPall
- x2c-QZVPPall-2c
- x2c-QZVPPall-2c-s
- x2c-QZVPPall-s
- x2c-SV(P)all

**Right Panel: Periodic Table**

Total found: 315 basis sets

Select All | Reset Selection

Periodic table showing elements with their corresponding basis set counts (e.g., H: 1, He: 2, Li: 3, Be: 4, ..., Fr: 87, Ra: 88, ..., Lr: 103).

<https://www.basissetexchange.org/>

# Exploring electronic structure

- The coefficients for electronic integrals turn out to be:

"+-":

```
[[[-8.65723399e+00  2.26410847e-01 -1.95047567e-15 -4.32348849e-17  
-6.78302338e-17  1.92822204e-01  6.75402566e-16]
```

```
 [ 2.26410847e-01 -2.47287700e+00  6.21613707e-16 -2.75152981e-16  
3.23510362e-16 -1.68545220e-01 -2.53627721e-15]
```

```
 [-1.94223133e-15  5.85990990e-16 -2.43578895e+00 -3.11889156e-16  
3.41475791e-16  3.05454834e-15 -2.78086282e-01]
```

```
 [-4.32348849e-17 -2.75152981e-16 -3.11889156e-16 -2.30175759e+00  
4.55827322e-16  5.70778845e-16  2.23950788e-16]
```

```
 [-6.78302338e-17  3.23510362e-16  3.41475791e-16  3.83080996e-16  
-2.30175759e+00  2.42147410e-16  1.14424257e-16]
```

```
 [ 1.92822204e-01 -1.68545220e-01  2.73268054e-15  5.70778845e-16  
2.42147410e-16 -1.91605433e+00  4.91374876e-16]
```

```
 [ 7.16765354e-16 -2.98856896e-15 -2.78086282e-01  2.23950788e-16  
1.14424257e-16  3.60165327e-16 -1.79494816e+00]]
```

"++--":

```
[[[[[ 2.27148263e+00 -1.99577764e-01  2.29010818e-15 ...  
8.09108131e-19 -1.80336852e-01 -2.57319408e-16]
```

```
 [-1.99577764e-01  2.69049560e-02 -2.28304569e-16 ...  
3.22282302e-19  2.49843632e-02  1.97746251e-16]
```

```
 [ 2.29666750e-15 -2.28704939e-16  6.08236710e-03 ...  
-1.38457182e-18 -3.21368337e-16  1.13182331e-02]
```

...

```
 [ 8.09108131e-19  3.22282302e-19 -1.38457182e-18 ...  
1.57674385e-02...
```

```
 [ 1.64364292e-02 -5.61531240e-02  1.32293654e-16 ...  
3.51937931e-17  1.40932405e-01  1.20760500e-15]
```

```
 [ 2.22023480e-18 -5.84481546e-16 -1.19251845e-02 ...  
-1.39212510e-17  9.46464627e-16  4.90603402e-01]]]]
```

# Exploring electronic structure

- The second quantization operator turns out to be

Fermionic Operator

number spin orbitals=14, number terms=1938

```
- 8.657233989401442 * ( +_0 -_0 )
+ 0.22641084730126987 * ( +_0 -_1 )
+ 0.1928222041459474 * ( +_0 -_5 )
+ 0.22641084730126973 * ( +_1 -_0 )
+ -2.4728769961639414 * ( +_1 -_1 )
+ -0.16854522048678797 * ( +_1 -_5 )
+ -2.4357889483357633 * ( +_2 -_2 )
+ -0.27808628202592334 * ( +_2 -_6 )
+ -2.3017575929316743 * ( +_3 -_3 )
+ -2.301757592931674 * ( +_4 -_4 )
+ 0.19282220414594742 * ( +_5 -_0 )
+ -0.16854522048678855 * ( +_5 -_1 )
+ -1.9160543326994175 * ( +_5 -_5 )
+ -0.2780862820259231 * ( +_6 -_2 )
+ -1.7949481593439092 * ( +_6 -_6 )
```

```
+ -8.657233989401442 * ( +_7 -_7 )
+ 0.22641084730126987 * ( +_7 -_8 )
+ 0.1928222041459474 * ( +_7 -_12 )
+ 0.22641084730126973 * ( +_8 -_7 )
+ -2.4728769961639414 * ( +_8 -_8 )
+ -0.16854522048678797 * ( +_8 -_12 )
+ -2.4357889483357633 * ( +_9 -_9 )
+ -0.27808628202592334 * ( +_9 -_13 )
...
+ -0.02807656202109904 * ( +_13 +_13 -_12 -_8 )
+ 0.07046620266936564 * ( +_13 +_13 -_12 -_12 )
+ -0.005962592231203295 * ( +_13 +_13 -_13 -_9 )
+ 0.24530170117779518 * ( +_13 +_13 -_13 -_13 )
```

# Solving electronic structure

=== GROUND STATE ENERGY ===

\* Electronic ground state energy (Hartree):  
-19.002818399935

- computed part: -19.002818399935

~ Nuclear repulsion energy (Hartree):  
3.407580524864

> Total ground state energy (Hartree):  
-15.595237875071

=== MEASURED OBSERVABLES ===

0: # Particles: 6.000  
S: 0.000 S^2: 0.000 M: 0.000

=== DIPOLE MOMENTS ===

~ Nuclear dipole moment (a.u.): [0.0 0.0  
14.96663091]

0:

\* Electronic dipole moment (a.u.): [0.0 0.0  
14.96663091]

- computed part: [0.0 0.0  
14.96663091]

> Dipole moment (a.u.): [0.0 0.0 0.0]  
Total: 0.0

(debye): [0.0 0.0  
0.00000001] Total: 0.0000

0001

# Vibrational Structure

- Within the Born-Oppenheimer approximation, a molecular wave function is factorized as a product of an electronic part, which is the solution of the electronic Schrodinger equation, and a vibro-rotational one, which is the solution of the nuclear Schrodinger equation in the potential energy surface (PES).
- $\mathcal{H}_{\text{vib}}|\Psi_n\rangle = E_n|\Psi_n\rangle$
- $\mathcal{H}_{\text{vib}}(Q_1, \dots, Q_L) = -\frac{1}{2} \sum_{l=1}^L \frac{\partial^2}{\partial Q_l^2} + V(Q_1, \dots, Q_L)$

# Vibrational Structure

- A single-particle basis obtained either by the harmonic approximation applied to the PES or from a vibrational self-consistent field (VSCF) calculation.
- Vibrational anharmonic correlations are added a-posteriori with variational approaches like Vibrational Configuration Interaction (VCI) and Vibrational Coupled Cluster (VCC) for highly-accurate anharmonic energies.
- The main advantage of VCI and VCC over alternative approaches (such as perturbation theories) is that their accuracy can be systematically improved towards the complete basis set limit for a given PES. However, their applicability is limited to small molecules with up to about 10 atoms due to their unfavorable scaling with system size.

# Vibrational Structure

- Hvib must be mapped to an operator that acts on the states of a given set of qubits in order to calculate its eigenfunctions in quantum hardware.
- In electronic structure calculations, the mapping is achieved by expressing the non-relativistic electronic Hamiltonian in second quantization.
- The second quantisation obtained from Watson Hamiltonian is expressed as:

$$\begin{aligned}\mathcal{H}_{\text{vib}}^{SQ} = & \sum_{l=1}^L \sum_{k_l, h_l}^{N_l} \langle \phi_{k_l} | T(Q_l) + V^{[l]}(Q_l) | \phi_{h_l} \rangle a_{k_l}^+ a_{h_l} \\ & + \sum_{l < m}^L \sum_{k_l, h_l}^{N_l} \sum_{k_m, h_m}^{N_m} \langle \phi_{k_l} \phi_{k_m} | V^{[l,m]}(Q_l, Q_m) | \phi_{h_l} \phi_{h_m} \rangle a_{k_l}^+ a_{k_m}^+ a_{h_l} a_{h_m} + \dots\end{aligned}$$

# Coding Vibrational Structure

- Can't run vibrational structure since my system is missing G16 (Gaussian) library.



# Transformer Problems

## **BasisTransformer**

- BasisTransformer allows you to transform an ElectronicStructureProblem from one basis into another AO→MO or MO→AO.

## **FreezeCoreTransformer**

- It freezes the core orbitals and remove virtual orbitals which helps reduce number of qubits used.

## **ActiveSpaceTransformer**

- It allows us to specify an active space by selecting the number of active electrons and the number of active spatial orbitals after performing FreezeCore transformation.

# FreezeCoreTransformer

Again working with BeH<sub>2</sub> molecule.

Molecule:

Multiplicity: 1  
Charge: 0  
Unit: Bohr  
Geometry:

Be	(0.0, 0.0, 0.0)
H	(0.0, 0.0, -2.494438484425882)
H	(0.0, 0.0, 2.494438484425882)

Masses:

Be	9
H	1
H	1

(3, 3)

7

# FreezeCoreTransformer

If we apply the FreezeCoreTransformer it will remove the single lowest energy orbital (reducing the total number of spatial orbitals from 7 to 6) and also removing the two electrons from within that orbital (as reflected by the changed number of particles).

```
from qiskit_nature.second_q.transformers import FreezeCoreTransformer

fc_transformer = FreezeCoreTransformer()

fc_problem = fc_transformer.transform(full_problem)
print(fc_problem.num_particles)
print(fc_problem.num_spatial_orbitals)
```

(2, 2)

6

This transformation will result in a constant energy offset resulting from the removal of the core electrons. This offset is registered inside of the Hamiltonian's constants.

# ActiveSpaceTransformer

We apply the ActiveSpaceTransformer with 4 active electrons and 4 active orbitals.

```
from qiskit_nature.second_q.transformers import ActiveSpaceTransformer

as_transformer = ActiveSpaceTransformer(4, 4)

as_problem = as_transformer.transform(full_problem)
print(as_problem.num_particles)
print(as_problem.num_spatial_orbitals)
print(as_problem.hamiltonian.electronic_integrals.alpha)
```

```
(2, 2)
4
Polynomial Tensor
"+-":
[[-1.52068450e+00 -7.32789503e-17  5.73169590e-17 -3.68000995e-18]
 [-1.86921158e-16 -1.52143297e+00  1.82664332e-16  1.58672331e-16]
 [ 5.73169590e-17  1.82664332e-16 -1.17917888e+00  2.68820171e-17]
 [-3.68000995e-18  1.58672331e-16  1.84281666e-17 -1.17917888e+00]]
"++--":
[[[ 3.99710434e-01  1.26362602e-15 -3.63183824e-17  1.66370508e-18]
```

...

```
[[[-3.63183824e-17 -2.20216559e-17  4.95573429e-02 -1.14961977e-18]
 [-4.63891053e-17 -1.55722545e-17 -1.42987481e-16  2.17982890e-21]
 [ 3.69994408e-01 -5.47475268e-17  9.10888668e-18  7.62279167e-19]
 [-9.18818127e-18  4.59818691e-33 -3.58420282e-19  1.08949739e-17]]
...
[[ 4.95573429e-02 -1.42154296e-16  1.08949739e-17  4.54386029e-20]
 [-1.43655656e-16  1.47653982e-02 -1.68729109e-18 -4.98560632e-17]
 [ 1.08949739e-17 -1.68729109e-18  2.42493792e-02 -1.35805319e-17]
 [ 4.54386029e-20 -4.98560632e-17 -1.50232331e-17  4.49859041e-01]]]]
```