

Note on Quantum Chemistry

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1 Introduction

2 Molecular orbital models

2.1 PEA

2.2 Hamiltonian reduction methods

To address molecular problems on our quantum processor, we rely on a compact encoding of the second- quantized fermionic Hamiltonians on to qubits.

2.3 Hydrogen molecule

The H_2 molecular Hamiltonian has 4 spin-orbitals, representing the spin-degenerate $1s$ orbitals of the two Hydrogen atoms. By using a binary tree encoding [12], the map to a 4 qubit system can be reduced to 2 qubit system due to the spin-parities of the system [9].

2.4 Beryllium hydride molecule

In STO-3G basis set, BeH_2 has 7 spatial orbitals and a Hilbert space of dimension $2^{14} = 16384$. By starting with the HF state with two α (spin-up) and two β (spin-down) electrons and using only number conserving operators, the relevant subspace to explore has a dimension of $\binom{7}{3} \cdot \binom{7}{3} = 1225$.

The equilibrium bond length: 1.342 Å [arXiv: 1812.11173].

The BeH_2 Hamiltonian is defined upon the $1s$, $2s$, $2p_x$ orbitals associated to Be, assuming zero filling for the $2p_y$ and $2p_z$ orbitals since they do not interact strongly with the subset of orbitals considered, and $1s$ orbital associated to each H atom, for a total of 10 spin orbitals. We then assume perfect filling of the two innermost $1s$ spin-orbitals of Be, after dressing them via the diagonalization of the non-interacting part of the fermionic Hamiltonian. We map the 8 spin-orbital Hamiltonian of BeH_2 spin-orbital Hamiltonian using the parity mapping, and remove, as in the case of H_2 , two qubits associated to the spin-parity symmetries, reducing this to a 6 qubit problem that encodes 8 spin-orbitals.

2.5 Lithium hydride molecule

In STO-3G basis set, LiH has 6 spatial orbitals and a Hilbert space of dimension $2^{12} = 4096$. By starting with the HF state with two α (spin-up) and two β (spin-down) electrons and using only number conserving operators, the relevant subspace to explore has a dimension of $\binom{6}{2} \cdot \binom{6}{2} = 225$. In this basis, the occupied orbitals are $\{1,2\}$, and the virtual orbitals are $\{3,4,5,6\}$.

The equilibrium bond length: 2.39 Å [arXiv: 1812.11173]

A similar approach described in [arXiv: 1704.05018] is also used to map LiH onto 4 qubits.

The Hamiltonians for H_2 , LiH and BeH_2 at their equilibrium distance are explicitly given in the Supplementary Information (TABLE S2) of [arXiv: 1704.05018] and the derivation of them are given at Appendix III.

2.6 BK-tree

2.7 VQE

2.7.1 Ground state

2.7.2 Excited state

2.7.3 Ansatz

2.7.4 UCC

Calculation check on Appendix B of [arXiv: 1805.04340]

$$T_1 = \sum_{ij} \theta_{ij} (a_i^\dagger a_j - a_j^\dagger a_i) \quad (1)$$

$$T_2 = \sum_{ijkl} \theta_{ijkl} (a_i^\dagger a_j^\dagger a_k a_l - a_l^\dagger a_k^\dagger a_j a_i) \quad (2)$$

After the Jordan-Wigner transformation for N qubits, which is given by:

$$a_j = 1^{\otimes j} \otimes \frac{1}{2}(X + iY) \otimes Z^{\otimes N-j-1} \quad (3)$$

$$a_j^\dagger = 1^{\otimes j} \otimes \frac{1}{2}(X - iY) \otimes Z^{\otimes N-j-1} \quad (4)$$

then for $i > j$

$$a_i^\dagger = 1^{\otimes j} \otimes 1^{\otimes i-j} \otimes \frac{1}{2}(X + iY) \otimes Z^{\otimes N-i-1} \quad (5)$$

$$a_j = 1^{\otimes j} \otimes \frac{1}{2}(X - iY) \otimes Z^{\otimes i-j} \otimes Z^{\otimes N-i-1} \quad (6)$$

$$a_i^\dagger a_j = 1^{\otimes j} \otimes \frac{1}{2}(X - iY) \otimes Z^{\otimes i-j-1} \otimes \frac{1}{2}(X + iY)Z \otimes 1^{\otimes N-i-1} \quad (7)$$

$$= 1^{\otimes j} \otimes \frac{1}{2}(X - iY) \otimes Z^{\otimes i-j-1} \otimes \frac{1}{2}(-Y + iX) \otimes 1^{\otimes N-i-1} \quad (8)$$

$$a_j^\dagger a_i = 1^{\otimes j} \otimes \frac{1}{2}(X + iY) \otimes Z^{\otimes i-j-1} \otimes \frac{1}{2}Z(X - iY) \otimes 1^{\otimes N-i-1} \quad (9)$$

$$= 1^{\otimes j} \otimes \frac{1}{2}(X + iY) \otimes Z^{\otimes i-j-1} \otimes \frac{1}{2}(Y + iX) \otimes 1^{\otimes N-i-1} \quad (10)$$

Then

$$a_i^\dagger a_j - a_j^\dagger a_i = 1^{\otimes j} \otimes \frac{1}{2} [X \otimes Z^{\otimes i-j-1} \otimes Y - Y \otimes Z^{\otimes i-j-1} \otimes X] \otimes 1^{\otimes N-i-1} \quad (11)$$

$$= \frac{i}{2} \bigotimes_{a=j+1}^{i-1} Z_a [Y_j X_i - X_j Y_i] \quad (12)$$

Since

$$[Y_j X_i, X_j Y_i] = Y_j X_i X_j Y_i - X_j Y_i Y_j X_i = -Z_j Z_i + Z_j Z_i = 0, \quad (13)$$

Therefore

$$\prod_{ij} \exp [\theta_{ij} (a_i^\dagger a_j - a_j^\dagger a_i)] = \prod_{i>j} \exp \left[\frac{i}{2} \theta_{ij} \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i - X_j Y_i) \right] \quad (14)$$

$$= \prod_{i>j} \exp \left[\frac{i}{2} \theta_{ij} \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i) \right] \exp \left[-\frac{i}{2} \theta_{ij} \bigotimes_{a=j+1}^{i-1} Z_a (X_j Y_i) \right] \quad (15)$$

Suppose we choose a set of $(a_i^\dagger a_j - a_j^\dagger a_i)$ so each of them conserves s_z , and the total number of electrons.

$$\exp \left[\frac{i}{2} \theta \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i) \right] = \cos \left(\frac{\theta}{2} \right) 1 + i \sin \left(\frac{\theta}{2} \right) \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i) \quad (16)$$

$$\exp \left[-\frac{i}{2} \theta \bigotimes_{a=j+1}^{i-1} Z_a (X_j Y_i) \right] = \cos \left(\frac{\theta}{2} \right) 1 - i \sin \left(\frac{\theta}{2} \right) \bigotimes_{a=j+1}^{i-1} Z_a (X_j Y_i) \quad (17)$$

$$\exp \left[\frac{i}{2} \theta \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i - X_j Y_i) \right] = \cos^2 \left(\frac{\theta}{2} \right) 1 + \sin^2 \left(\frac{\theta}{2} \right) (Z_j Z_i) \quad (18)$$

$$+ i \cos \left(\frac{\theta}{2} \right) \sin \left(\frac{\theta}{2} \right) \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i - X_j Y_i) \quad (19)$$

Now since i is the index of a virtual orbital and j the index of an occupied orbital, $(Z_j \otimes Z_i)$ on HF state yields -1 . And also,

$$\bigotimes_{a=j+1}^{i-1} Z_a Y_j X_i |00 \cdots 01 \cdots 11\rangle = \bigotimes_{a=j+1}^{i-1} Z_a (i Z_j X_j) X_i |00 \cdots 01 \cdots 11\rangle \quad (20)$$

$$= i(-)^n |0 \cdots 1 \cdots 01 \cdots 1 \cdots 1\rangle \quad (21)$$

and

$$\bigotimes_{a=j+1}^{i-1} Z_a X_j Y_i |00 \cdots 01 \cdots 11\rangle = \bigotimes_{a=j+1}^{i-1} Z_a X_j (i Z_i X_i) |00 \cdots 01 \cdots 11\rangle \quad (22)$$

$$= -i(-)^n |0 \cdots 1 \cdots 01 \cdots 1 \cdots 1\rangle \quad (23)$$

Thus we can simplify Eq. 18 to obtain

$$\exp \left[\frac{i}{2} \theta \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i - X_j Y_i) \right] = \cos^2 \left(\frac{\theta}{2} \right) 1 - \sin^2 \left(\frac{\theta}{2} \right) 1 \quad (24)$$

$$+ 2i \cos \left(\frac{\theta}{2} \right) \sin \left(\frac{\theta}{2} \right) \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i) \quad (25)$$

$$= \cos(\theta) 1 + i \sin(\theta) \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i) \quad (26)$$

On the contrary, if we were to choose (i, j) are both the indices of occupied or virtual orbitals, we obtain $(Z_j \otimes Z_i) = 1$ and

$$\bigotimes_{a=j+1}^{i-1} Z_a X_j Y_i |\text{HF}\rangle = \bigotimes_{a=j+1}^{i-1} Z_a Y_j X_i |\text{HF}\rangle. \quad (27)$$

Therefore Eq. 18 becomes

$$\exp \left[\frac{i}{2} \theta \bigotimes_{a=j+1}^{i-1} Z_a (Y_j X_i - X_j Y_i) \right] = \cos^2 \left(\frac{\theta}{2} \right) 1 + \sin^2 \left(\frac{\theta}{2} \right) 1 = 1 \quad (28)$$

For UCCD, from the relation $Y|0\rangle = -i|1\rangle$ and $Y|1\rangle = i|0\rangle$, we obtain

$$X_0 X_1 Y_2 X_3 |0011\rangle = -i |1100\rangle \quad (29)$$

$$Y_0 X_1 Y_2 Y_3 |0011\rangle = (-i)^2 i |1100\rangle \quad (30)$$

$$X_0 Y_1 Y_2 Y_3 |0011\rangle = (-i)^2 i |1100\rangle \quad (31)$$

$$X_0 X_1 X_2 Y_3 |0011\rangle = -i |1100\rangle \quad (32)$$

and

$$Y_0 X_1 X_2 X_3 |0011\rangle = i |1100\rangle \quad (33)$$

$$X_0 Y_1 X_2 X_3 |0011\rangle = i |1100\rangle \quad (34)$$

$$Y_0 Y_1 Y_2 X_3 |0011\rangle = (-i) i^2 |1100\rangle \quad (35)$$

$$Y_0 Y_1 X_2 Y_3 |0011\rangle = (-i) i^2 |1100\rangle \quad (36)$$

In the same token, if we choose (k, l) are both the indices of occupied orbitals and (i, j) the indices of virtual orbitals,

$$\left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) X_l X_k Y_j X_i |\text{HF}\rangle = \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) Y_l X_k Y_j Y_i |\text{HF}\rangle \quad (37)$$

$$= \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) X_l Y_k Y_j Y_i |\text{HF}\rangle \quad (38)$$

$$= \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) X_l X_k X_j Y_i |\text{HF}\rangle \quad (39)$$

$$= - \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) Y_l X_k X_j X_i |\text{HF}\rangle \quad (40)$$

$$= - \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) X_l Y_k X_j X_i |\text{HF}\rangle \quad (41)$$

$$= - \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) Y_l Y_k Y_j X_i |\text{HF}\rangle \quad (42)$$

$$= - \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) Y_l Y_k X_j Y_i |\text{HF}\rangle \quad (43)$$

and

$$\exp \left[i \frac{\theta}{8} \bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a (X_l X_k Y_j X_i + \dots - Y_l X_k X_j X_i - \dots) \right] \quad (44)$$

$$= \exp \left[i \frac{\theta}{2} \bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a (X_l X_k Y_j X_i - Y_l X_k X_j X_i) \right] \quad (45)$$

$$= \cos^2 \left(\frac{\theta}{2} \right) 1 + \sin^2 \left(\frac{\theta}{2} \right) (Z_l Z_j) \quad (46)$$

$$+ i \cos \left(\frac{\theta}{2} \right) \sin \left(\frac{\theta}{2} \right) \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) (X_l X_k Y_j X_i - Y_l X_k X_j X_i) \quad (47)$$

$$= \cos(\theta) 1 + i \sin(\theta) \left(\bigotimes_{b=l+1}^{k-1} Z_b \bigotimes_{a=j+1}^{i-1} Z_a \right) X_l X_k Y_j X_i \quad (48)$$

2.7.5 Heuristic Ansatz

2.7.6 Circuit building

$$SXS^\dagger = Y \quad (49)$$

$$HXY = Z \quad (50)$$

$$HYH = -Y \quad (51)$$

$$\text{CNOT}_{12}(1 \otimes Z_2)\text{CNOT}_{12} = Z_1 \otimes Z_2 \quad (52)$$

Applying the last relation recursively, we obtain

$$Z_1 \otimes Z_2 \otimes \dots \otimes Z_n = \text{CNOT}_{12}(1 \otimes Z_2 \otimes \dots \otimes Z_n)\text{CNOT}_{12} \quad (53)$$

$$= \text{CNOT}_{12} \dots \text{CNOT}_{(n-1),n}(1 \otimes \dots \otimes Z_n)\text{CNOT}_{(n-1),n} \dots \text{CNOT}_{12} \quad (54)$$

And using this relation and the fact that $\text{CNOT}_{ij}^2 = 1$, we see for instance

$$\exp \left[i \frac{\theta}{2} Z_1 \otimes Z_2 \otimes Z_3 \right] = \text{CNOT}_{12} \text{CNOT}_{23} \exp \left(i \frac{\theta}{2} Z_3 \right) \text{CNOT}_{23} \text{CNOT}_{12} \quad (55)$$

3 non-MO