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 useing 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 hydroride molecule

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 hydroride molecule

A similar approach 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]

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

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

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

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

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

then for $i > j$

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

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

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

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

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

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

Then

$$a_i^\dagger a_j - a_j^\dagger a_i = 1^{\otimes j} \otimes \frac{1}{2}\left[X \otimes Z^{\otimes i-j-1} \otimes Y - Y \otimes Z^{\otimes i-j-1} \otimes X\right] \otimes 1^{\otimes N-i-1} \tag{11}$$

$$= \frac{i}{2} \bigotimes_{a=j+1}^{i-1} Z_a \left[Y_j X_i - X_j Y_i\right] \tag{12}$$

Since

$$[Y_j X_i, X_j Y_i] = Y_j X_i X_j Y_i - X_j Y_i Y_j X_i = -Z_j Z_i + Z_j Z_i = 0, \tag{13}$$

Therefore

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

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

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.

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

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

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

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

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 yiels -1. And also,

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

$$= i(-)^n \left|0\cdots 1\cdots 01\cdots 1\cdots 1\right\rangle \tag{21}$$

and

$$\bigotimes_{a=j+1}^{i-1} Z_a X_j Y_i |00\cdots01\cdots11\rangle = \bigotimes_{a=j+1}^{i-1} Z_a X_j (iZ_i X_i) |00\cdots01\cdots11\rangle \tag{22}$$

$$= -i(-)^n |0\cdots1\cdots01\cdots1\cdots1\rangle \tag{23}$$

Thus we can simplify Eq. 18 to obtain

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

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

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

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

$$\bigotimes_{a=j+1}^{i-1} Z_a X_j Y_i |\mathrm{HF}\rangle = \bigotimes_{a=j+1}^{i-1} Z_a Y_j X_i |\mathrm{HF}\rangle . \tag{27}$$

Therefore Eq. 18 becomes

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

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

$$X_0X_1Y_2X_3|0011\rangle = -i|1100\rangle \tag{29}$$

$$Y_0X_1Y_2Y_3|0011\rangle = (-i)^2 i|1100\rangle \tag{30}$$

$$X_0Y_1Y_2Y_3|0011\rangle = (-i)^2 i|1100\rangle \tag{31}$$

$$X_0X_1X_2Y_3|0011\rangle = -i|1100\rangle \tag{32}$$

and

$$Y_0X_1X_2X_3|0011\rangle = i|1100\rangle \tag{33}$$

$$X_0Y_1X_2X_3|0011\rangle = i|1100\rangle \tag{34}$$

$$Y_0Y_1Y_2X_3|0011\rangle = (-i)i^2|1100\rangle \tag{35}$$

$$Y_0Y_1X_2Y_3|0011\rangle = (-i)i^2|1100\rangle \tag{36}$$

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

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

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

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

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

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

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

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

and

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

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

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

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

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

2.7.5 Heuristic Ansatz

2.7.6 Circuit building

$$SXS^\dagger = Y \tag{49}$$

$$HXY = Z \tag{50}$$

$$HYH = -Y \tag{51}$$

$$\mathrm{CNOT}_{12}(1 \otimes Z_2)\mathrm{CNOT}_{12} = Z_1 \otimes Z_2 \tag{52}$$

Applying the last relation recursively, we obtain

$$Z_1 \otimes Z_2 \otimes \cdots \otimes Z_n = \mathrm{CNOT}_{12}(1 \otimes Z_2 \otimes \cdots \otimes Z_n)\mathrm{CNOT}_{12} \tag{53}$$

$$= \mathrm{CNOT}_{12} \cdots \mathrm{CNOT}_{(n-1),n}(1 \otimes \cdots \otimes Z_n)\mathrm{CNOT}_{(n-1),n} \cdots \mathrm{CNOT}_{12} \tag{54}$$

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

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

3 non-MO