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Quantum Computing for Quantum Chemistry

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Schrödinger equation solutions for multi-electron atoms

Let us compute each term :

$$\begin{aligned}
\langle \Phi_n | \sum_i h(i) | \Phi_n \rangle &= \sum_i \langle \Phi_n | h(i) | \Phi_n \rangle = \sum_i \langle \varphi_1 \dots \varphi_i \dots \varphi_M | h(i) | \varphi_1 \dots \varphi_i \dots \varphi_M \rangle \\
&= \frac{1}{M!} \sum_i \langle det(\varphi_1 \dots \varphi_M) | h(i) | det(\varphi_1 \dots \varphi_M) \rangle = \{ \frac{1}{M!} \mathcal{A}^2 = \mathcal{A} \} \\
&= \sum_i \langle \varphi_1 \dots \varphi_M | h(i) | det(\varphi_1 \dots \varphi_M) \rangle = \sum_i \langle \varphi_1 \dots \varphi_M | h(i) | \varphi_1 \dots \varphi_M \rangle \\
&= \sum_i \langle \varphi_1 \dots \varphi_{i-1} \varphi_{i+1} \dots \varphi_M | \, | \varphi_1 \dots \varphi_{i-1} \varphi_{i+1} \dots \varphi_M \rangle \, \langle \varphi_i | h(i) | \varphi_i \rangle \\
&= \sum_i \langle \varphi_i | h(i) | \varphi_i \rangle \equiv \sum_i h_{ii}
\end{aligned}$$

Schrödinger equation solutions for multi-electron atoms

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Let us compute each term :

$$\begin{aligned}
\langle \Phi_n | \sum_{i<j} r_{ij}^{-1} | \Phi_n \rangle &= \sum_{i<j} \langle \Phi_n | \, r_{ij}^{-1} \, | \Phi_n \rangle = \sum_{i<j} \langle \varphi_1 \dots \varphi_M | \, r_{ij}^{-1} \, | \varphi_1 \dots \varphi_M \rangle \\
&= \frac{1}{M!} \sum_{i<j} \langle det(\varphi_1 \dots \varphi_M) | \, r_{ij}^{-1} \, | det(\varphi_1 \dots \varphi_M) \rangle = \{ \frac{1}{M!} \mathcal{A}^2 = \mathcal{A} \} \\
&= \sum_{i<j} \langle \varphi_1 \dots \varphi_M | \, r_{ij}^{-1} \, | det(\varphi_1 \dots \varphi_M) \rangle \\
&= \sum_{i<j} \langle \varphi_1 \dots \varphi_i \dots \varphi_j \dots \varphi_M | \, r_{ij}^{-1} \, | \varphi_1 \dots \varphi_i \dots \varphi_j \dots \varphi_M \rangle \\
&- \sum_{i<j} \langle \varphi_1 \dots \varphi_i \dots \varphi_j \dots \varphi_M | \, r_{ij}^{-1} \, | \varphi_1 \dots \varphi_j \dots \varphi_i \dots \varphi_M \rangle \\
&= \{ \dots \} = \sum_{i<j} \Big(\langle \varphi_i \varphi_j | \, r_{ij}^{-1} \, | \varphi_i \varphi_j \rangle - \langle \varphi_i \varphi_j | \, r_{ij}^{-1} \, | \varphi_j \varphi_i \rangle \Big)
\end{aligned}$$

Self-consistant field equations (Hartree-Fock)

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Two terms above are very simple to vary :

- one-electron Hamiltonian variation

$$\delta \sum_i h_{ii} = \int \frac{\partial}{\partial \varphi_k^*} \left[\sum_i \varphi_i^* h \varphi_i \right] \delta \varphi_k^* d\vec{r}$$
$$= \int d\vec{r} h(\vec{r}) \varphi_k(\vec{r}) \delta \varphi_k^*(\vec{r})$$

- Lagrangian multiplier variation

$$\delta \sum_i \epsilon_i \int d\vec{r} |\varphi_i|^2 = \sum_i \epsilon_i \int d\vec{r} \frac{\partial}{\partial \varphi_k^*} \varphi_i^* \varphi_i \delta \varphi_k^*$$
$$= \int d\vec{r} \epsilon_k \varphi_k(\vec{r}) \delta \varphi_k^*(\vec{r})$$

Self-consistant field equations (Hartree-Fock)

For the term $\langle ij|\, r_{12}^{-1}\, |ij\rangle$:

$$\delta \sum_{i,j} \langle ij|\, r_{12}^{-1}\, |ij\rangle = \int d\vec{r}_1 d\vec{r}_2 \frac{\partial}{\partial \varphi_k^*} \left[\sum_{i,j} \varphi_i^*(\vec{r}_1)\varphi_j^*(\vec{r}_2) r_{12}^{-1} \varphi_i(\vec{r}_1)\varphi_j(\vec{r}_2) \right]$$

$$= \int d\vec{r}_1 d\vec{r}_2 \left[\sum_{i,j} \varphi_j^*(\vec{r}_2) r_{12}^{-1} \varphi_k(\vec{r}_1)\varphi_j(\vec{r}_2) \right] \delta\varphi_k^*(\vec{r}_1)\delta_{ik}$$

$$+ \int d\vec{r}_1 d\vec{r}_2 \left[\sum_{i,j} \varphi_i^*(\vec{r}_1) r_{12}^{-1} \varphi_i(\vec{r}_1)\varphi_k(\vec{r}_2) \right]]\delta\varphi_k^*(\vec{r}_2)\delta_{jk}$$

$$= 2 \int d\vec{r}_1 d\vec{r}_2 \left[\sum_{j} \varphi_j^*(\vec{r}_2) r_{12}^{-1} \varphi_j(\vec{r}_2) \right] \varphi_k(\vec{r}_1)\delta\varphi_k^*(\vec{r}_1)$$

Self-consistant field equations (Hartree-Fock)

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$$= \int d\vec{r}_1 d\vec{r}_2 \left[\sum_{i,j} \varphi_j^*(\vec{r}_2) r_{12}^{-1} \varphi_j(\vec{r}_1)\varphi_k(\vec{r}_2) \right] \delta\varphi_k^*(\vec{r}_1)\delta_{ik}$$

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$$= 2 \int d\vec{r}_1 d\vec{r}_2 \left[\sum_{j} \varphi_j^*(\vec{r}_2) r_{12}^{-1} \varphi_j(\vec{r}_1) \right] \varphi_k(\vec{r}_2)\delta\varphi_k^*(\vec{r}_1)$$

Hartree-Fock in Second Quantization

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We recall that the general form of the Hartree-Fock energy is (**??**). Let us express each term in the Second Quantization formalism :

$$E^{HF} = \langle HF| \mathbf{H} |HF\rangle = \langle HF| \left[\sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} V_{pq,rs} a_p^\dagger a_p^\dagger a_r a_s \right] |HF\rangle + V_{nuc-nuc}$$

For the first term :

$$\begin{aligned} E_1^{HF} &= \langle HF| \left[\sum_{pq} h_{pq} a_p^\dagger a_q \right] |HF\rangle = \sum_{pq} h_{pq} \langle HF| a_p^\dagger a_q |HF\rangle \\ &= \sum_{pq} h_{pq} \langle \underbrace{1 \dots 1}_{p-1} 0 \underbrace{1 \dots 1}_{m-p+1} \underbrace{0 \dots 0}_{M-m} | \underbrace{1 \dots 1}_{q-1} 0 \underbrace{1 \dots 1}_{m-q+1} \underbrace{0 \dots 0}_{M-m} \rangle \\ &= \left[\sum_{pq} h_{pq} \delta_{pq} \right]_{\text{occupied}} = \sum_i h_{ii} \end{aligned}$$

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For the second term :

$$\begin{aligned} E_2^{HF} &= \frac{1}{2} \langle HF| \left[\sum_{pqrs} V_{pq,rs} a_p^\dagger a_q^\dagger a_r a_s \right] |HF\rangle = \frac{1}{2} \sum_{pqrs} V_{pq,rs} \langle HF| a_p^\dagger a_q^\dagger a_r a_s |HF\rangle \\ &= \{\dots\} = \frac{1}{2} \left[\sum_{pqrs} V_{pq,rs} \left(\delta_{pr}\delta_{qs} - \delta_{ps}\delta_{qr} \right) \right]_{\text{occupied}} \\ &= \frac{1}{2} \sum_{i \neq j} \left(V_{ij,ij} - V_{ij,ji} \right) = \frac{1}{2} \sum_{ij} \left(\langle ij| \, |ij\rangle - \langle ij| \, |ji\rangle \right) \end{aligned}$$

Fermionic to Qubit mappings : Bravyi-Kitaev

While the Jordan-Wigner is an efficient and simple mapping, it is :

1. only scaling linearly in terms of orbitals $\mathcal{O}(M)$
2. storing locally the occupancy of the orbitals but non-locally the associated parity information

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The Bravyi-Kitaev mapping is constructed such that both the occupancy and parity information of the orbitals is stored locally. Doing so, the construction, especially for the operators is more difficult.
For the Slater determinant :

$$|f_0, \ldots, f_{M-1}\rangle \rightarrow |q_0, \ldots, q_{M-1}\rangle\,, \;\; q_p = \sum_{q=0}^{p} \beta_{pq} f_q \tag{1}$$

where β_{pq} is the so-called *BK matrix*.

Fermionic to Qubit mappings : Bravyi-Kitaev

The BK matrix β_{pq} is constructed recursively as :

$$\beta_1 = [1]$$

$$\beta_{2^{x+1}} = \begin{pmatrix} \beta_{2^x} & \mathbf{0} \\ \mathbf{A} & \beta_{2^x} \end{pmatrix}$$

here, $\mathbf{0}$ is $(2^x, 2^x)$ matrix of zeros while $\mathbf{A}$ is a $(2^x, 2^x)$ matrix of zeros with the bottom row filled with ones.

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As an example, for the case of $M = 4 (x = 1)$ orbitals, the BK matrix is given by

$$\beta_4 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

Fermionic to Qubit mappings : Bravyi-Kitaev

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Constructing qubit operators in the Bravyi-Kitaev mapping is much more challenging than in the Jordan-Wigner mapping, thus we are going to explicit them (complete details can be found here https://arxiv.org/pdf/1208.5986.pdf).

However we can detail the properties of this mapping :

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1. by storing locally both occupancy and parity information, it reduces the weight of all Pauli string to $\mathcal{O}(\log_2 M)$
2. always at least efficient as JW mapping, with increased efficiency for systems with increased number of orbitals

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1. by storing locally both occupancy and parity information, it reduces the weight of all Pauli string to $\mathcal{O}(\log_2 M)$
2. always at least efficient as JW mapping, with increased efficiency for systems with increased number of orbitals
3. can be modified to be more adapted to near-term or long-term quantum computers
4. can be modified to be encoded in a graph approach