"Simulating Molecules using VQE"

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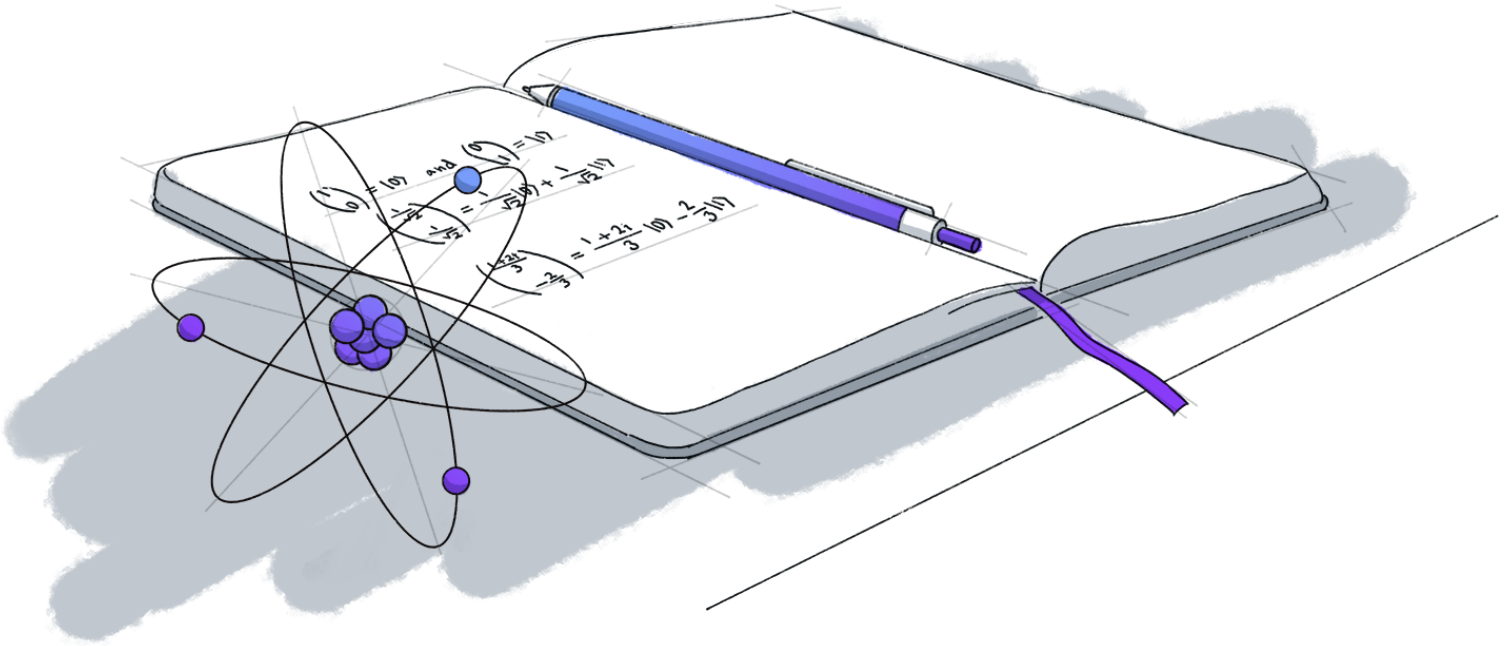
About project

The project is devoted to molecular modeling, a widely used and rapidly developing field of science.
This field requires a high level of knowledge in quantum physics and quantum chemistry, the understanding of which is certainly not without mathematics, and the successful implementation of the methods requires computation on quantum computers.



About project

By modeling molecules, we can greatly increase productivity of programs related to computing characteristics for molecules, take into account all their peculiarities. Many problems of quantum mechanics are reduced to solving SLAEs or searching for eigennumbers, as in the problem I am considering.
The main task of my project is to get acquainted with such a tool as quantum computing and how it helps to solve a certain applied problem, which undoubtedly also needs to be dealt with.

Subject field analysis

Definition

The molecular orbital φ is a wave function describing the behavior of an electron in a molecule. The atomic orbital χ is similarly defined. MO will be indexed in Latin letters, AO in Greek letters.

The model considered and taken as the basis for the reasoning that follows is that the molecular orbital is represented as a linear combination of the atomic ones:

$$\varphi_i^\sigma = \sum_\mu C_{i\mu}^\sigma \cdot \chi_\mu$$

The coefficients $C_{i\mu}^\sigma$ are independent variables, where σ stands for either α - spin-up MO, or β - spin-down MO, and these are what we must find. They are written in matrices C^α, C^β.

Subject field analysis

Since χ acts as a basis function, we can write the corresponding Gram matrix S, where

$$S_{\mu\nu} = \int d\vec{r}\, \chi_\nu(\vec{r}),\ \chi_\mu(\vec{r}) \neq \delta_{\nu\mu}$$

The molecular orbitals corresponding in spin are orthogonal, this can be written using an integral or through the S matrix:

$$\int d\vec{r}\, \varphi_i^\sigma(\vec{r})\ \varphi_j^\sigma(\vec{r}) = \delta_{ij},\ (C^\sigma)^T S C^\sigma = \mathbf{1}$$

The last two equations are the conditions determining the state of the system in question. We will return to them later.

About electron density

Definition

$\rho(\vec{r}) = \rho_\alpha(\vec{r}) + \rho_\beta(\vec{r})$ - electron density. By N_σ we denote the number of electrons σ-spin. The terms can be found, for example, as follows:

$$\rho_\sigma(\vec{r}) = \sum_{i=1}^{N_\sigma} |\varphi_i^\sigma(\vec{r})|^2 = \sum_{i=1}^{N_\sigma} \sum_{\mu\nu} C_{\mu i}^\sigma C_{\nu i}^\sigma \chi_\mu(\vec{r})\chi_\nu(\vec{r}) = \sum_{\mu\nu} P_{\mu\nu}^\sigma \chi_\mu(\vec{r})\chi_\nu(\vec{r}).$$

Here we defined $P_{\mu\nu}^\sigma = \sum_{i=1}^{N_\sigma} C_{\mu i}^\sigma C_{\nu i}^\sigma$. Then it is easy to see that the corresponding matrix $P^\sigma = C^\sigma (C^\sigma)^T$ and then we define $P = P^\alpha + P^\beta$ - total density matrix.

Formula of Total Energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu \mid \lambda\sigma)$$

$$-\frac{a}{2} \sum_{\mu\nu\lambda\sigma} \left(P^{\alpha}_{\mu\lambda} P^{\alpha}_{\nu\sigma} + P^{\beta}_{\mu\lambda} P^{\beta}_{\nu\sigma} \right) (\mu\nu \mid \lambda\sigma) + b \int f(\vec{r}) \mathrm{d}\vec{r},$$

where the electron repulsion integral

$$(\mu v \mid \lambda\sigma) = \int d\vec{r_1} \int d\vec{r_2} \chi_\mu(\vec{r}) \chi_\nu(\vec{r}) \frac{1}{r_{12}} \chi_\lambda(\vec{r}) \chi_\sigma(\vec{r})$$

It is precisely its minimization that we deal with in the conditions of the problem. To do this we use the Lagrange multiplier method.

$$L = E - \sum_{ij,\sigma \in \alpha,\beta} \varepsilon^{\sigma}_{ij} \left(\int d\vec{r}\, \varphi^{\sigma}_{i}(\vec{r})\, \varphi^{\sigma}_{j}(\vec{r}) - \delta_{ij} \right)$$

Partial derivatives of components with Lagrange multipliers $\varepsilon_{ij}^{\sigma}$

$$\frac{\partial}{\partial C_{\theta k}^{\sigma}} \sum_{ij} \varepsilon_{ij}^{\sigma} \left[\int \mathrm{d}\vec{r} \varphi_i^{\sigma}(\vec{r}) \varphi_j^{\sigma}(\vec{r}) - \delta_{ij} \right] = \sum_{ij} \varepsilon_{ij}^{\sigma} \frac{\partial}{\partial C_{\theta k}^{\sigma}} \sum_{\eta\zeta} \left[C_{\eta i}^{\sigma} S_{\eta\zeta} C_{\zeta j}^{\sigma} - \delta_{ij} \right] =$$

$$\sum_{ij} \varepsilon_{ij}^{\sigma} \sum_{\eta\zeta} \left[\delta_{\eta\theta} \delta_{ki} C_{\zeta j}^{\sigma} + C_{\eta j}^{\sigma} \delta_{\zeta\theta} \delta_{kj} \right] S_{\eta\zeta} = \sum_{\eta} \sum_{i} \varepsilon_{ki}^{\sigma} C_{\eta i}^{\sigma} S_{\theta\eta} + \sum_{\eta} \sum_{i} \varepsilon_{ik}^{\sigma} C_{\eta i}^{\sigma} S_{\eta\theta}$$

Remark

It is clear that when differentiated by C^{α}, the components with ε^{β} will be zero.

Partial derivatives of total energy

Note that total energy depends only on the electron density and is written through it, not through the coefficients C. Therefore let us calculate

$$\frac{\partial}{\partial C^{\sigma}_{\theta k}} = \sum_{\eta\zeta} \frac{\partial P^{\sigma}_{\eta\zeta}}{\partial C^{\sigma}_{\theta k}} \frac{\partial}{\partial P^{\sigma}_{\eta\zeta}}$$

$$\frac{\partial P^{\sigma}_{\eta\zeta}}{\partial C^{\sigma}_{\theta k}} = \frac{\partial \sum_{i=1}^{N_\sigma} C^{\sigma}_{\eta i} C_{\zeta i}}{\partial C^{\sigma}_{\theta k}{}^{\sigma}} = \sum_{i=1}^{N_\sigma} \delta_{\theta\eta}\delta_{ki} C^{\sigma}_{\zeta i} + \sum_{i=1}^{N_\sigma} \delta_{\theta\zeta}\delta_{ki} C^{\sigma}_{\eta i} = \delta_{\theta\eta} C^{\sigma}_{\zeta k} + \delta_{\theta\zeta} C^{\sigma}_{\eta k}$$

Let us introduce the notation $F^{\sigma}_{\eta\zeta} = \frac{\partial E}{\partial P^{\sigma}_{\eta\zeta}}$ - elements of the Kohn–Sham–Fock matrix. Then the energy derivatives can be written as:

$$\frac{\partial E}{\partial C^{\sigma}_{\theta k}} = \sum_{\eta\zeta} \frac{\partial P^{\sigma}_{\eta\zeta}}{\partial C^{\sigma}_{\theta k}} \frac{\partial E}{\partial P^{\sigma}_{\eta\zeta}} = \sum_{\eta\zeta} \left[\delta_{\theta\eta} C^{\sigma}_{\zeta k} + \delta_{\theta\zeta} C^{\sigma}_{\eta k}\right] F^{\sigma}_{\eta\zeta}$$

Kohn–Sham–Fock matrix, E^H

Let us consider each summand in the total energy formula separately and differentiate. $E^H = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}$ - interaction energy of electrons with all nuclei + free energy. $H_{\mu\nu} = \int dr \chi_\mu(\vec{r}) \left(-\frac{1}{2}\nabla^2 + \sum_N \frac{Z_N}{r_N} \right) \chi_\nu(\vec{r})$
Consider the expression in parentheses - it is known as the Hamiltonian. $-\frac{1}{2}\nabla^2$, where ∇^2 is the Laplace operator, is responsible for the free particle. Z_N is the charge of the nucleus, r_N is the distance between the electron and the nucleus.

$$\frac{\partial E^H}{\partial P^\sigma_{\eta\zeta}} = \frac{\partial \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}}{\partial P^\sigma_{\eta\zeta}} = H_{\eta\zeta}$$

Remark

Recall that $P_{\mu\nu} = P^\alpha_{\mu\nu} + P^\beta_{\mu\nu}$, so the only summand with a nonzero derivative after the brackets are opened is $P^\sigma_{\eta\zeta} H_{\eta\zeta}$

Kohn-Sham-Fock matrix, E^J

$E^J = \frac{1}{2}\sum_{\mu\nu\lambda\sigma} P_{\mu\nu}P_{\lambda\sigma}(\mu\nu \mid \lambda\sigma)$ - is responsible for the interaction of electrons with each other. This time and next time, for convenience, we take $\sigma = \alpha$ and describe in advance
$P_{\mu\nu}P_{\lambda\sigma} = P^{\alpha}_{\mu\nu}P^{\alpha}_{\lambda\sigma} + P^{\alpha}_{\mu\nu}P^{\beta}_{\lambda\sigma} + P^{\beta}_{\mu\nu}P^{\alpha}_{\lambda\sigma} + P^{\beta}_{\mu\nu}P^{\beta}_{\lambda\sigma}$

$$\frac{\partial E^J}{\partial P^{\alpha}_{\eta\zeta}} = \frac{1}{2}(\sum_{\mu\nu}(\mu\nu \mid \eta\zeta)(P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu}) + \sum_{\lambda\delta}(\eta\zeta \mid \lambda\sigma)(P^{\alpha}_{\lambda\sigma} + P^{\beta}_{\lambda\sigma}))$$

Note that $\mu\nu$, like $\lambda\delta$, runs through all indices. Moreover, $(\mu\nu \mid \eta\zeta) = (\eta\zeta \mid \mu\nu)$ -we can swap integrals. So the sums are absolutely identical, so the final expression is transformed to:

$$\frac{\partial E^J}{\partial P^{\alpha}_{\eta\zeta}} = \sum_{\mu\nu} P_{\mu\nu}(\mu\nu \mid \eta\zeta) = J_{\eta\zeta}$$

J is known as Coulomb matrix.

Kohn-Sham-Fock matrix, E^K

$E^K = -\frac{a}{2}\sum_{\mu\nu\lambda\sigma}\left(P^{\alpha}_{\mu\lambda}P^{\alpha}_{\nu\sigma} + P^{\beta}_{\mu\lambda}P^{\beta}_{\nu\sigma}\right)(\mu\nu \mid \lambda\sigma)$ - is responsible for the spin interaction and is a model term, that in other words, it sets the parameters of the model, some laws by which it exists

$$\frac{\partial E^K}{\partial P^{\sigma}_{\eta\zeta}} = -\frac{a}{2}(\sum_{\nu\sigma}(\eta\nu \mid \zeta\sigma)P^{\sigma}_{\nu\sigma} + \sum_{\lambda\mu}(\mu\eta \mid \lambda\zeta)P^{\sigma}_{\mu\lambda})$$

Note that again nothing depends on renaming, so let us make one sum with indices $\mu\nu$. Moreover, it is obvious that within one half of the repulsion integral the indices can be swapped. So the sums are absolutely identical, so the final expression is transformed to:

$$\frac{\partial E^K}{\partial P^{\sigma}_{\eta\zeta}} = \sum_{\mu\nu} P^{\sigma}_{\mu\nu}(\mu\eta \mid \nu\zeta) = -K^{\sigma}_{\eta\zeta}$$

K as known as exchange matrix with the spin σ.

$E^X C$ and the Kohn-Sham-Fock matrix summary

$E^{XC} = b \int f(\vec{r}) \mathrm{d}\vec{r}$, responsible for the correlation interaction, is also a parameter of the model under consideration. We will write its derivative as $bK_{\eta\zeta}^{XC;\sigma}$ and we will not go into the details of its calculation.
In total we get that $F_{\eta\zeta}^{\sigma} = H_{\eta\zeta} + J_{\eta\zeta} - K_{\eta\zeta}^{\sigma} + bK_{\eta\zeta}^{XC;\sigma}$ - note that it is symmetric. Then let us return to our partial derivative of the Lagrangian:

$$\frac{\partial L}{\partial C_{\theta k}^{\sigma}} = \sum_{\eta\zeta} \left[\delta_{\theta\eta} C_{\zeta k}^{\sigma} + \delta_{\theta\zeta} C_{\eta k}^{\sigma}\right] F_{\eta\zeta}^{\sigma} - \sum_{\eta} \sum_{i} \varepsilon_{ki}^{\sigma} C_{\eta i}^{\sigma} S_{\theta\eta} - \sum_{\eta} \sum_{i} \varepsilon_{ik}^{\sigma} C_{\eta i}^{\sigma} S_{\eta\theta} =$$

$= 2\sum_{\mu} F_{\theta\mu}^{\sigma} C_{\mu k}^{\sigma} - 2\sum_{\mu}\sum_{i} \varepsilon_{ik}^{\sigma} S_{\mu\theta} C_{\mu i}^{\sigma}$, so by the Lagrange method it must equal zero, i.e. $\sum_{\mu} F_{\theta\mu}^{\sigma} C_{\mu k}^{\sigma} = \sum_{\mu}\sum_{i} \varepsilon_{ik}^{\sigma} S_{\mu\theta} C_{\mu i}^{\sigma}$, which is written in matrix form as

$$\boxed{\mathrm{F}^{\sigma} C^{\sigma} = S C^{\sigma} E^{\sigma}}$$

Unitary Invariance of density

Orbitals can be free and occupied. It is stated that all free ones are not included in the density matrix, but all occupied ones are, so if we prove that by turning occupied ones the density does not change, then the same fact will be true for free ones. Consider some orthogonal transformation U

$$\varphi_i^{\alpha'} = \sum_k^{N_\sigma} \varphi_k^\alpha U_{ki} \Longleftrightarrow C_{\mu i}^{\alpha'} = \sum_k^{N_\sigma} C_{\mu k}^\alpha U_{ki} \Longleftrightarrow C^{\alpha'} = C^\alpha U$$

Therefore for density matrix it's clear that

$$P^{\alpha'} = C^{\alpha'}(C^{\alpha'})^T = C^\alpha U U^T (C^\alpha)^T = C^\alpha (C^\alpha)^T = P^\alpha$$

Preparing formula

To begin with, the matrix E is symmetric, so it can be diagonalized, and its eigennumbers will be real.

$$E_{ij}^{\alpha} \to E_{ij}^{\alpha'} = \sum_{kl} U_{ki}^{\alpha} E_{kl}^{\alpha} U_{lj}^{\alpha} = \delta_{ij} \varepsilon_i^k,$$

where ε^{α} - eigennumbers.
Consider then how an orthogonal transformation acts on C^{α}:
$\mathrm{C}^{\alpha} = \mathrm{C}^{\alpha'} \left(\mathbf{U}^{\alpha}\right)^{\mathrm{T}}$, and then the equality is converted as:

$$\mathbf{F}^{\alpha} \mathbf{C}^{\alpha'} \left(\mathbf{U}^{\alpha}\right)^{\mathrm{T}} = \mathbf{S} \mathbf{C}^{\alpha'} \left(\mathbf{U}^{\alpha}\right)^{\mathrm{T}} \mathbf{E}^{\alpha}$$

Multiply on U^{α} the right side of equation:

$$\mathbf{F}^{\alpha} \mathbf{C}^{\alpha'} = \mathbf{S} \mathbf{C}^{\alpha'} \mathbf{E}^{\alpha'}$$

And matrix $\mathbf{E}^{\alpha'}$ is already diagonalized. Choose a form of U so that *occupied* $-$ *virtual* and *virtual* $-$ *occupied* blocks are zeros.

$$\mathbf{U} = \begin{pmatrix} \mathbf{U}_{\mathrm{oo}} & \mathbf{U}_{\mathrm{ov}} \\ \mathbf{U}_{\mathrm{vo}} & \mathbf{U}_{\mathrm{vV}} \end{pmatrix} = \begin{pmatrix} \mathbf{U}_{\mathrm{oo}} & 0 \\ 0 & \mathbf{U}_{\mathrm{vv}} \end{pmatrix}$$

Final formula

$$\begin{cases} \mathbf{F}^u\mathbf{C}^u = \mathbf{S}\mathbf{C}^\alpha\mathbf{E}^u \\ \mathbf{F}^\beta\mathbf{C}^\beta = \mathbf{S}\mathbf{C}^\beta\mathbf{E}^\beta \end{cases}$$

Then we can choose such conditions of the system that the spin-up and spin-down density matrices are equal, so by adding the two conditions we obtain the central equation:

$$\mathrm{FC} = \mathrm{SCE}$$

Let us learn how to solve it. Choose a transition matrix X such that $X^T SX = 1$. Then the basis X will write everything as $F^* C^* = C^* E^*$, where $C^* = CX$ and $F^* = X^T FX$, and $E^* = X^T EX$ is still diagonal. Such an equation is solved so that the columns of the matrix C^* are the eigenvectors of F, and E is a matrix with corresponding eigenvalues.
It remains to learn how to find the minimal eigenvalue and the corresponding vectors of the Kohn-Sham-Fock matrix. We will do this with the help of VQE.

VQE - Causes and mathematical reasoning

We use the VQE method because by entering the parameters of the molecular model, we can immediately obtain the Hamiltonian and the remaining terms of the Kohn-Sham-Fock matrix, and then find the minimal eigenvalue thanks to the following observation:

$$A\left|\psi_i\right\rangle = \lambda_i \left|\psi_i\right\rangle$$

The H matrix is hermitian, which means the following:

$$H = H^\dagger$$

In addition, we know remarkable properties about it - the eigennumbers are real, and there exists an orthonormalized basis of eigenvectors. From the latter follows an equally nice statement below - just on each basis vector we get an upper identity:

$$H = \sum_{i=1}^{N} \lambda_i \left|\psi_i\right\rangle \left\langle\psi_i\right|$$

where λ_i - eigennumber of the eigenvector $\left|\psi_i\right\rangle$.

Mathematical reasoning of the VQE method

Moreover, the quantum computer count of the H matrix on the vector looks like

$$\langle H\rangle_\psi \equiv \langle\psi|H|\psi\rangle = \left\langle \psi \middle| \left(\sum_{i=1}^{N} \lambda_i \left|\psi_i\right\rangle \left\langle\psi_i\right|\right) \middle| \psi \right\rangle = \sum_{i=1}^{N} \lambda_i \left\langle \psi \mid \psi_i \right\rangle \left\langle \psi_i \mid \psi \right\rangle$$

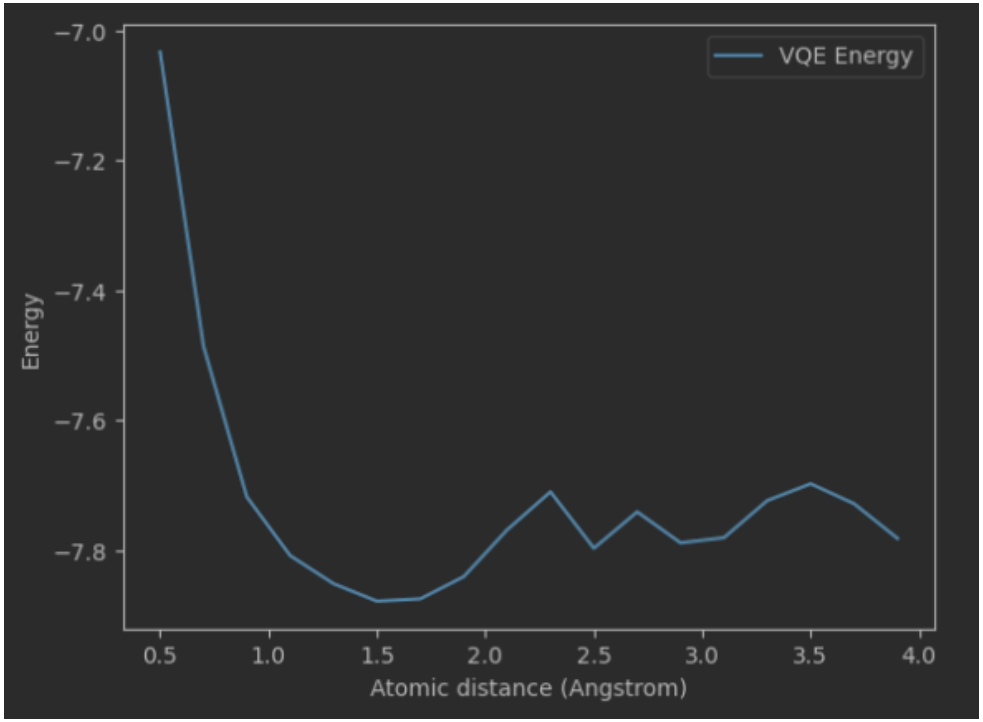
$$= \sum_{i=1}^{N} \lambda_i \left|\left\langle \psi_i \mid \psi \right\rangle\right|^2$$

Note that $\left|\langle\psi_i \mid \psi\rangle\right|^2 \geq 0$ are exactly weights with sum one, because all quantum vectors have norm 1, and this is its square in the orthonormalized basis of eigenvectors. Then the following estimation is true

$$\lambda_{\text{min}} \leq \langle H\rangle_\psi = \langle\psi|H|\psi\rangle = \sum_{i=1}^{N} \lambda_i \left|\left\langle \psi_i \mid \psi \right\rangle\right|^2$$

Energy search for the molecule *LiH*: Program output and plot

```
Interatomic Distance: 1.1 VQE Result: -7.80874
Interatomic Distance: 1.3 VQE Result: -7.85195
Interatomic Distance: 1.5 VQE Result: -7.87880
Interatomic Distance: 1.7 VQE Result: -7.87523
Interatomic Distance: 1.9 VQE Result: -7.84111
Interatomic Distance: 2.1 VQE Result: -7.76904
Interatomic Distance: 2.3 VQE Result: -7.71043
Interatomic Distance: 2.5 VQE Result: -7.79737
Interatomic Distance: 2.7 VQE Result: -7.74129
Interatomic Distance: 2.9 VQE Result: -7.78899
Interatomic Distance: 3.1 VQE Result: -7.78103
Interatomic Distance: 3.3 VQE Result: -7.72385
Interatomic Distance: 3.5 VQE Result: -7.69804
Interatomic Distance: 3.7 VQE Result: -7.72876
Interatomic Distance: 3.9 VQE Result: -7.78211
All energies have been calculated
```



Program output for the molecule H_2

```
Interatomic Distance: 0.27 VQE Result: -1.13604
Interatomic Distance: 0.28 VQE Result: -1.13600
Interatomic Distance: 0.28 VQE Result: -1.13595
Interatomic Distance: 0.28 VQE Result: -1.13591
Interatomic Distance: 0.28 VQE Result: -1.13586
Interatomic Distance: 0.28 VQE Result: -1.13582
Interatomic Distance: 0.29 VQE Result: -1.13577
Interatomic Distance: 0.29 VQE Result: -1.13572
Interatomic Distance: 0.29 VQE Result: -1.13567
Interatomic Distance: 0.29 VQE Result: -1.13562
Interatomic Distance: 0.29 VQE Result: -1.13557
Interatomic Distance: 0.3 VQE Result: -1.13551
Interatomic Distance: 0.3 VQE Result: -1.13546
All energies have been calculated
```

Performance issues

- Deprecated documentation - many references to documentation have been removed, the same class is defined differently in the new and old version.
- Lots of quantum physics, quantum chemistry, and complex mathematics.

Conclusion

I learned how:

- Efficiently dealt with documentation in the English language
- Familiarized with quantum circuits and calculations, optimization algorithms
- Visualized quantum circuits using matplotlib and wrote code on the Jupyter platform

Project perspectives:

- Using more advanced solvers for more accurate energy calculations
- Calculation of energy of methane molecule taking into consideration hybridization - allows to estimate the reaction rate of carbon production by catalysis, a particular practical process.

Sources

An Overview of Self-Consistent Field Calculations Within Finite Basis Sets
Qiskit