

Calculating Ground-State-Energy of LiCoO_2 by using Fragment molecular orbital-based Variational Quantum Eigensolver

Abstract

Variational Quantum Eigensolver (VQE) is a quantum computer algorithm that calculates the energy of the ground state and is highly anticipated to be effective in the development of new materials, such as in the field of drug and battery development. However, the application of VQE to molecules used in industry is limited due to the limited number of qubits available in current quantum computers. To solve this problem, this study proposes the use of FMO/VQE. The Fragment Molecular Orbital (FMO) method divides the whole system into small fragments for processing. FMO/VQE is a method that applies the FMO method to VQE.[1] In this study, to show the effectiveness of FMO/VQE, we calculate the ground state energy of the anode material of a secondary battery using FMO/VQE. LiCoO_2 used as anode material of secondary battery was calculated using FMO/VQE. This allows us to reduce the number of qubits required by the classical VQE algorithm from 24 to a maximum of 14. Nevertheless, we obtained almost the same accuracy (99.989%) as the results obtained by the classical method. This study shows that the proposed VQE algorithm can be successfully applied in the field of battery and drug discovery.

1.Introduction.

The ground state of a molecule and its energy is the most stable state and lowest energy that a molecule can have. Knowing this information can be used to understand the bonds between molecules and the structure of molecules, which can be used in various fields of chemical research, such as the development of new drugs or new anode materials for secondary batteries. Currently, the ground state energy of a molecule is mostly calculated on classical computers. However, as the number of atoms in a molecule increases or the atomic number of the atoms in a molecule increases, the number of particles to be considered increases and the interactions of each particle to be considered increases exponentially. The

interactions of each particle are considered in the Hamiltonian of the molecule, and representing this molecular Hamiltonian on a computer requires a lot of memory and computation. Therefore, calculating the ground state energy of a molecule using current classical computers is difficult to apply to large molecules.

Quantum computers are an emerging field that is currently undergoing a lot of research. Quantum computers use different qubits than classical computers, namely quantum bits, which are qubits with overlapping 0 and 1 states, as opposed to bits that represent only 0s and 1s in classical computers. This is why, in calculating the ground state energy of a molecule, when the number of particles increases and the memory required doubles, a quantum computer can do the calculation with one more qubit. Where a classical computer would require an exponential increase in memory, a quantum computer can solve with a polynomial increase in qubits.

Therefore, even large molecules that are currently incomputable can be computed by quantum computers. The quantum computer algorithm Quantum Phase Estimation (QPE) is an algorithm that calculates the eigenvalues and eigenstates of a unitary matrix on a quantum computer, which can be used to find the ground state energy of a molecule. However, QPE is known to be very accurate and requires a large number of qubits to implement. Current quantum computers are said to be at the level of noisy intermediate-scale quantum devices (NISQs). NISQ means that the quantum computer is noisy and has intermediate-scale qubits. Current quantum computers are still noisy and lack accuracy, and the number of qubits is still low, in the tens or hundreds, making it difficult to implement a QPE.

Variational Quantum Eigensolver (VQE) is an algorithm for solving eigenvalue problems using these NISQ-level quantum computers that uses both quantum and classical computers. VQE uses variational principles to construct a parameterized trial wavefunction to obtain the basis of the molecular Hamiltonian. The algorithm iterates by adjusting the parameters until this basis value converges to a constant value to obtain an upper bound on the ground state energy of the molecule. In this process, the molecular Hamiltonian and the test wavefunction are replaced by quantum circuits, and the process of obtaining the expectation value is performed by a quantum computer, and the optimization process of adjusting the parameters of the test wavefunction is performed by a classical computer. Unlike QPE, VQE does not require a large number of qubits, and the optimization that is difficult for current quantum computers is calculated by a classical computer, so there are many

expectations that quantum computers can be commercialized in the NISQ era. However, current quantum computers have too many errors, their accuracy decreases significantly as the circuit depth increases, and the number of qubits available is limited, which is not enough to compute very large molecules.

Therefore, among the various methods to solve this problem is the Fragment Molecular Orbital method based Variational Quantum Eigensolver (FMO/VQE) method. FMO/VQE was first devised by Hocheol Lim, et al. as an algorithm that applies the FMO method, a quantum chemistry method, to VQE to improve the limitations of VQE due to the limitations of current quantum computers. The FMO method approximates the ground-state energy of the whole molecule by dividing the whole system into small pieces, and then finds the ground-state energy of the small pieces (monomer) and the pair of small pieces (dimer) and uses them to approximate the ground-state energy of the whole molecule. By breaking the molecule into smaller pieces, the maximum size of the system that needs to be considered in the overall calculation can be reduced, and this can be applied to VQE to reduce the number of qubits required and the depth of the quantum circuit. Therefore, FMO/VQE is expected to be a way to realize quantum computers in the near future.

In this paper, we utilize FMO/VQE to calculate the ground state energy of LiCoO_2 , a representative material used as an anode material in secondary batteries, and compare it with classical computer calculations. We also compare the accuracy of FMO/VQE with classical VQE to confirm the feasibility of FMO/VQE in the NISQ era.

2.Method.

2.1 Lithium-ion battery

Lithium-ion batteries are one of the secondary batteries used in various industries. A lithium-ion battery consists of an anode material, a cathode material, and an electrolyte, where the anode material is lithium oxide. The anode material is an oxide with lithium ions in a layered structure. The degree to which the lithium ions are oxidized in the oxide creates an energy charge. Lithium is known to have a limited amount of deposits in the world. Many methods have been proposed as a solution to this problem, one of which is an approach that seeks to maximize the energy charged per lithium ion. This is a critical situation, both in terms of lithium reserves

and in terms of battery miniaturization. In order to calculate the amount of energy stored per lithium, it is essential to calculate the ground state of the molecule. However, this calculation is classically performed, and the ability to calculate larger molecules or more diverse combinations is limited. In this study, we show the results of applying the VQE algorithm to LiCoO_2 molecules and demonstrate the applicability of quantum computers in the field of battery development.

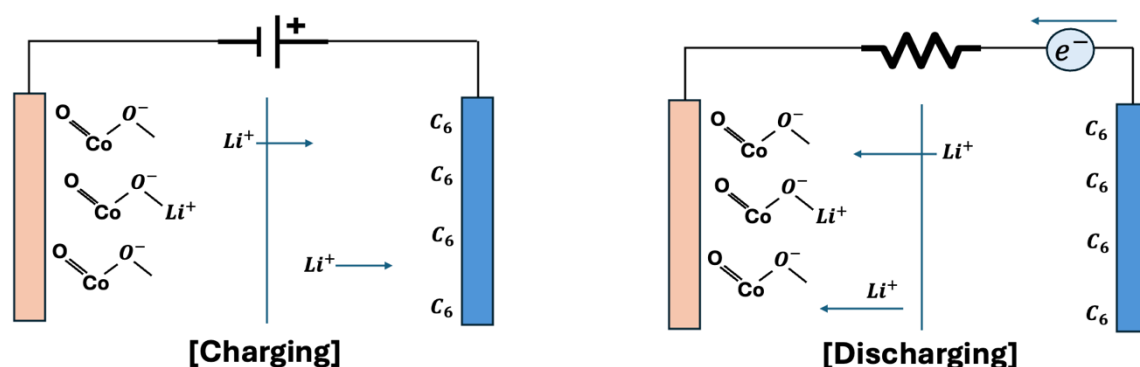


Table 1 How the battery works

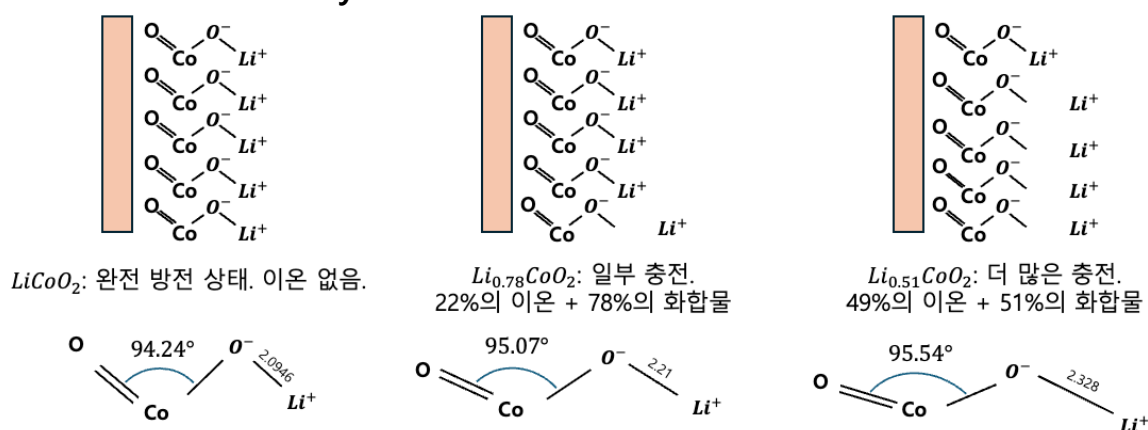


Figure 1

When you apply a voltage to a molecule and supply it with electrons (i.e., charge it), Li^+ ions will move toward the cathode material. When you discharge this charged state, the ions that were on the cathode rejoin the anode as shown in the figure below. Li^+ ions from the cathode material are bound to the anode material again, and current flows through the resistor. At this time, depending on the oxidation state of lithium, the average geometry of the molecular structure changes as shown in Figure (), so the energy in the bulk can be estimated using the geometry. The energy of the molecule is calculated by assuming the gas-phase model, which considers the average oxide structure as a single molecule.

2.2 Variational Quantum Eigensolver (VQE)

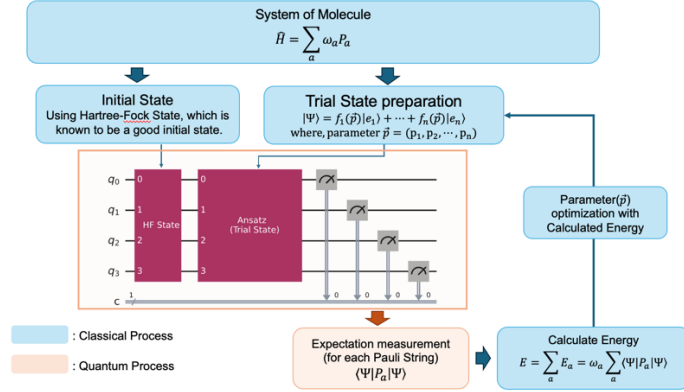


Figure 2 VQE Pipeline

The VQE algorithm is an eigenvalue problem solving algorithm first proposed by Peruzzo et al. in [2] that works by computing the energy in Hilbert space that provides an upper bound on the ground state preparation energy according to the Variational Principle. VQE computes the ground state energy of a system by measuring the energy on a quantum computer and performing optimization on a classical computer. To measure the energy of a system on a quantum computer, we need to map the Hamiltonian to a foliate, represent an arbitrary quantum state, and encode it in a quantum circuit.

(1) Hamiltonian

The Hamiltonian corresponding to the energy of the molecule is represented by the Electronic Structure Hamiltonian as shown below.

$$\hat{H}_{el} = -\sum_i \frac{\nabla_{\mathbf{r}_i}^2}{m_e} - \sum_I \sum_i \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_i \sum_{j>i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

(where \mathbf{r}_i denotes the position vector of the i -th electron and \mathbf{R}_I denotes the position of the i -th nucleus, and Z_I is the atomic number of the i th nucleon). To map this Hamiltonian to the Fourier gate, we write it in second quantized form, which is expressed through the fermionic creation/annihilation operator as follows

$$\begin{aligned} \hat{H}_{el} &= \sum_{p,q} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{p,q,r,s} h_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s, \quad (\text{second quantized hamiotnian}) \\ h_{pq} &= \langle \phi_p | \hat{H} | \phi_q \rangle = \int_{-\infty}^{\infty} \phi_p^*(r) \left(-\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}|} \right) \phi_q(r) dr \\ h_{pqrs} &= \langle \phi_p \phi_q | \hat{H} | \phi_r \phi_s \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\phi_p^*(r_1) \phi_q^*(r_2) \phi_r(r_2) \phi_s(r_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} dr_1 dr_2 \end{aligned}$$

Fermionic operators can be mapped to Pauli gates using Jordan-Wigner mapping, Parity mapping, bravyi kitaev mapping, etc. In this experiment, we will use the Parity mapping method. Parity mapping expresses the creation/annihilation operator through a Pauli gate by corresponding the parity of the i -th qubit to the parity of the electron occupancy of the i -th orbital. The α -spin β The parity of the β -spin of the numerator can be utilized to reduce the number of qubits required by two. The resulting Hamiltonian of the mapping is a Pauli string (\mathcal{P}_a) and its weights or linear coefficients (ω_a) and its weights or linear coefficients (

$$\hat{H} = \sum_a \omega_a \mathcal{P}_a$$

(2) Ansatz

To represent arbitrary quantum states, we construct a parameterized quantum circuit (PQC) with linear coefficients corresponding to each basis as parameters. The performance of the ansatz is difficult to evaluate, and it is in the a priori domain that it is not known which ansatz is better for different systems. Therefore, in this experiment, we use two different ansatzes.

a) Two-Local (Efficient SU2) Ansatz

The quantum state of a single qubit is represented by a rotation gate for two arbitrary angles on a Bloch sphere. If the angle of the rotation gate is the parameter and the entanglement, which is the property of a qubit in a multi-qubit system, is expressed using the CNOT gate, the quantum state of an arbitrary multi-qubit system can be expressed using the parameter.

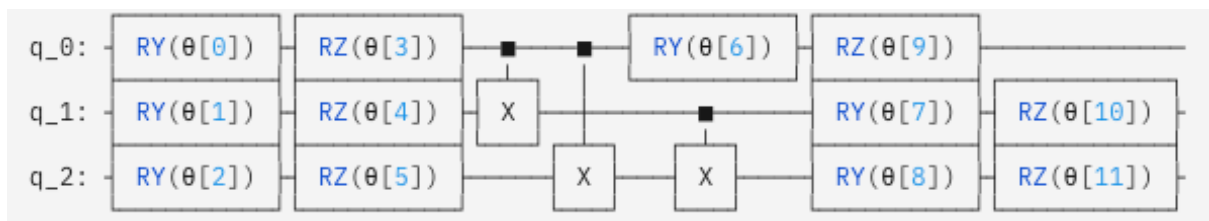


Illustration 3 Example of an Efficient SU2 Ansatz in three qubits.

The construction of the Two_Local Ansatz does not involve a Hamiltonian interpretation. It is a representation of an arbitrary quantum state expressed in hardware and is hardware efficient.

b) UCCSD Ansatz

2nd quantize to represent the Hamiltonian operator as the basis of the molecular

orbitals of the system. Since the state we are looking for is described in the same Hilbert space as the Hamiltonian, we can use the same spin-orbitals as the basis to describe any quantum state in that Hilbert space. These quantum states are expressed through Coupled-Cluster Theory, and only up to 2nd -order excitations are considered, and the unitary expression is UCCSD (Unitary Coupled Cluster Singles and Doubles), and the form is as follows.

$$\hat{T} = \hat{T}_1 + \hat{T}_2, \quad (\text{Cluster operator})$$

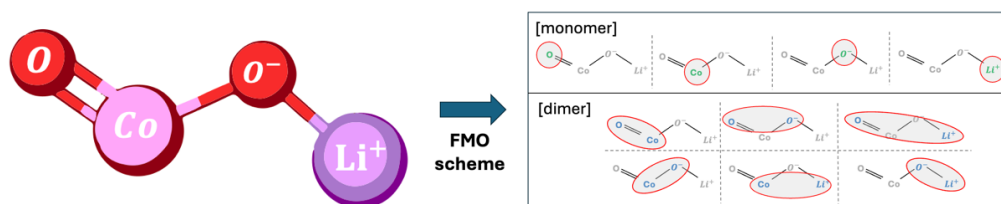
$$\text{where,} \quad T_1 = \sum_{i,a} c_i^a \hat{a}_a^\dagger \hat{a}_i, \quad T_2 = \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$$

$$|\Psi\rangle_{UCCSD} = e^{\hat{T}-\hat{T}^\dagger} |\psi_{ref}\rangle$$

The state is represented via creation/destruction operators, which can be encoded in a quantum circuit via Jordan-Wigner mapping or parity mapping.

For this constructed quantum circuit, calculate the energy of the system by measuring the expectation value for each Pauli string in the Hamiltonian. Find the minimum of the upper bound on the ground state energy by optimizing the parameters of the ansatz so that the energy is minimized. The resulting minimum corresponds to the ground state energy calculated by the VQE algorithm for the system.

2.2 Fragmental Molecular orbital (FMO)



In the calculation of the ground state energy of a molecule, the computational complexity has an exponential scale with the size of the system, so it is usually very difficult to deal with large systems. Therefore, a method of dividing a large system into several repeating structures, called fragments, has been proposed [kitaura]. The basic idea of the FMO method is to divide the whole molecular system into small fragments and obtain the energy of the whole system by using the energy of all fragments and the energy of all pairs of fragments. One fragment is called a

monomer and a pair of fragments is called a dimer. Usually, a specific stable structure, such as a benzene ring, NH_3 and other stable structures, such as benzene rings, are used as fragments to perform the calculations. However, in this study, we will use a single atom as a fragment. The energies of monomer and dimer are calculated using the Electronic Structure Hamiltonian defined earlier.

$$\hat{H}_{el} = -\sum_i \frac{\nabla_{\mathbf{r}_i}^2}{m_e} - \sum_I \sum_i \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_i \sum_{j>i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Using the calculated energies of the monomer and dimer, we can calculate the energy of the molecule, taking into account the overlapping interactions, as shown below.

$$E = \sum_{I>J}^N E_{IJ} - (N - 2) \sum_I^N E_I$$

2.3 FMO/VQE (Fragment molecular orbital-based Variational Quantum Eigensolver)

FMO/VQE is an algorithm first introduced by Hochel Lim et al. that combines the VQE algorithm with the FMO method. In the VQE algorithm, the system is represented based on the molecular spinorbitals, so it requires as many qubits as the number of molecular spinorbitals. However, the number of qubits is currently limited, so the number of molecules that can be simulated in the existing VQE algorithm is limited. However, if the FMO Method is applied to the existing VQE algorithm, the number of qubits required for a single calculation can be reduced by dividing the total system into pieces and simulating them in parallel. The number of qubits is equal to the number of spinorbitals that need to be considered in the system (which is reduced by two when using the parity mapper). If the core orbitals, which are less likely to be involved in bonding, are calculated separately as constants, and the Freeze_core method, which considers only the valence orbitals of each atom, is used, the number of qubits required in the conventional VQE calculation is as follows.

atom	Orbital representation	Number of Valence orbital	Number of Valence electron
Li	$(1s)^2(2s)^1$	2	1
O	$(1s)^2(2s)^2(2p)^4$	6	8
Co	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^7$	10	7

Therefore, the number of spinorbitals required for the VQE calculation is 24, considering that oxygen has 2. If we use the parity mapper here, we can reduce the number of qubits needed for the calculation by 2, so 22 qubits are needed to solve this system via conventional VQE.

Let's apply the FMO method, where each atom is a fragment, which means that 4 monomers are created and 6 dimer systems need to be calculated. The number of spin-orbitals required for each calculation is shown below (only one is shown for configurations with the same composition).

	Configuration	Number of Valence orbital	Number of Valence electron
Monomer	Li	2	1
	O	6	4
	Co	10	7
Dimer	<i>Li – O</i>	6	5
	<i>Li – Co</i>	12	8
	<i>O – O</i>	12	8
	<i>Co – O</i>	16	11

Therefore, the maximum number of qubits required in the calculation is 14 (using Parity mapper). By applying the FMO method, we can reduce the number of qubits required for the calculation by 8. Furthermore, the potential of this method is in larger systems. Recently used LiCoO_2 . When simulating larger molecules with Ni, Mn, etc. added to the molecule, conventional VQE requires more qubits than the number of outermost spin orbitals of the corresponding atoms. However, in FMO/VQE, the increase in the size of the system leads to an increase in the number of fragments, so it is possible to calculate the energy of larger molecules using the same number of qubits.

Result

LiCoO_2 A molecule is a system with a total of 50 molecular spinorbitals, and in the process of computing it on a quantum computer, the spinorbitals of the molecule are usually corresponded to qubits, so a total of 50 qubits are

required. A 50-qubit system is a computational amount that cannot be solved within a meaningful computation with a simulator, and the circuitry is too deep to be solved with current noisy hardware. Therefore, there have been many efforts to reduce the number of qubits needed to solve the problem, among which the well-known "ActiveCoreTransformer" and "Parity mapper" can be used to obtain values of similar precision using only 22 qubits. However, the number of qubits required increases with the number of spin-orbitals of the valence orbitals of each atom as the system grows larger, i.e., more atoms need to be considered. Therefore, we applied the FMO method here to achieve the same precision calculation using up to 14 qubits, which does not require more qubits when more atoms of similar size are added.

4.1 Fragment Energy Calc.

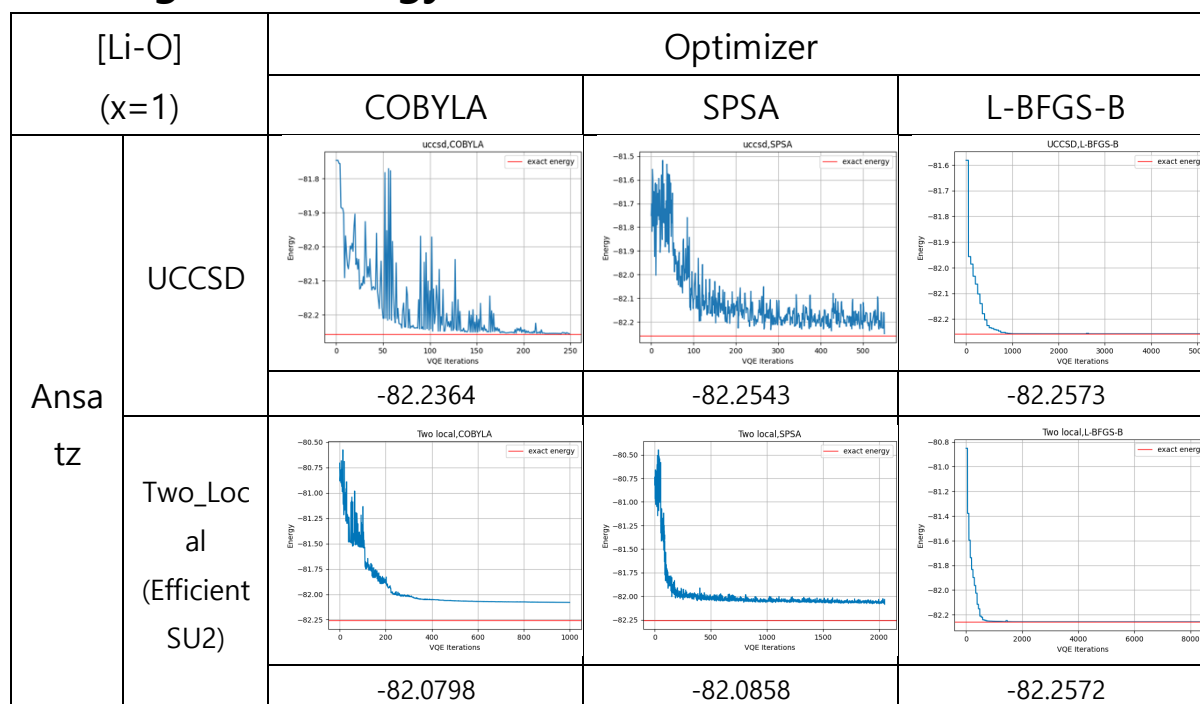


Figure 4 Calculating Energy in a Fragment (Energy over Iteration)

$[x = 1]$	configuration	계산값 (<i>a. u.</i>)	Numpy Minimum Eigensolver (<i>a. u.</i>)	오차 (<i>a. u.</i>)
monomer	<i>O</i>	-74.7875	-74.7875	$< 10^{-4}$
	<i>Li</i>	-7.4324	-7.4324	$< 10^{-4}$
	<i>Co</i>	-1381.3542	-1381.3587	0.0035
dimer	<i>O – Li (close)</i>	-82.2573	-82.2573	$< 10^{-4}$
	<i>O – Li (far)</i>	-82.2203	-82.2203	$< 10^{-4}$
	<i>Co – Li</i>	-1388.7298	-1388.7296	0.0002
	<i>O – O</i>	-149.5510	-149.5510	$< 10^{-4}$
	<i>Co = O</i>	-1456.0502	-1456.0511	0.0009
	<i>Co – O</i>	-1456.1472	-1456.1719	0.0248

Table 2 Energy of a Fragment in One Oxidation State

Among the factors that affect the performance of VQE, the performance of Ansatz and Optimizer is unpredictable. Depending on the nature of the system, it is not possible to specify which Ansatz and Optimizer performs better. Therefore, for the calculation of a fragment, we use two of the most common ansatzes (UCCSD, Two-Local (Efficient-SU2)) and three optimizers (COBYLA, SPSA, L-BFGS-B), which are known to perform well in the VQE field, to perform a total of six calculations, and use the lowest convergence value as the ground state energy of the fragment. Figure 2 shows the calculation results of the O-Li dimer. Out of the six calculations, the result using UCCSD Ansatz and L-BFGS-B Optimizer showed the lowest convergence value and will be used as the energy of the O-Li fragment in subsequent calculations. The results of similar calculations for the remaining fragments are shown in Table 1.

4.1 Molecular Energy Calc.

$$E_{Li_{0.94}CoO_2} = \sum_{I>J}^N E_{dimer,IJ} - (N - 2) \sum_I^N E_{monomer,I}$$

In the FMO method, the energy of a molecule can be calculated by using the energy of a fragment to calculate the energy of the molecule.

Oxidation number	FMO/VQE (<i>a. u.</i>)	Numpy Minimum Eigensolver (<i>a. u.</i>)	Accuracy (%)
1	-1538.16043	-1538.33411	99.989
0.94	-1538.10099	-1538.26750	99.989
0.78	-1538.04882	-1538.22281	99.989

Conclusions

With the quantum algorithm FMO/VQE proposed in this work, LiCoO_2 we were able to calculate the ground state energy of a molecule with 99.989% accuracy compared to a classical simulator. This result shows the applicability of the FMO/VQE method to the future synthesis of new drugs and development of new materials. Classical computing methods are not capable of calculating the complex molecules required for drug synthesis and new material development.

The FMO/VQE algorithm proposed in this study reduces the number of qubits required for computation by using the FMO method, which makes it possible to solve molecules that are difficult to compute using quantum computers using VQE. These results show that the FMO/VQE algorithm can be a new paradigm in the field of drug synthesis and new material development that requires the computation of complex molecules.

Reference

- [1] Hocheol Lim, et al., Fragment molecular orbital-based variational quantum eigensolver for quantum chemistry in the age of quantum computing, *Scientific Reports* 14, 2422 (2024)
- [2] Peruzzo A., et al, A variational eigenvalue solver on a photonic quantum processor, *Nature Communications* 5, 4213 (2014).

- [3] Jules Tilly, et al. The Variational Quantum Eigensolver: A review of methods and best practices, *Physic Reports* 986, 1-12 (2022)
- [4] J.T.Hertz et al. Magnetism and structure of Li_xCoO_2 and comparison to Na_xCoO_2 , Department of Chemistry, Princeton University, DOI: 10.1103/PhysRevB.77.075119
- [5] Kazuo Kitaura, et al, Fragment molecular orbital method: an approximate computational method for large molecules, *Chemical Physics Letters* 313, 701-706 (1999)
- [6] Dmitri G. Fedorov, Kazuo Kitaura, Coupled-cluster theory based upon the fragment molecular-orbital method, *The Journal of Chemical Physics* 123, 134103 (2005)
- [7] Stewart, Robert F. (1 January 1970). "Small Gaussian Expansions of Slater-Type Orbitals". *The Journal of Chemical Physics*. **52** (1). pp: 431–438. [doi:10.1063/1.1672702](https://doi.org/10.1063/1.1672702).

Acknowledgment

This work is supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF2022R1F1A1064459) and Creation of the Quantum Information Science R&D Ecosystem (Grant No. 2022M3H3A106307411) through the National Research Foundation of Korea (NRF) funded by the Korean government (Ministry of Science and ICT).