

Reduction of orbital space for molecular orbital calculations with quantum computation simulator for educations

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Abstract

Recently, the molecular orbital (MO) calculations with quantum computations (QCs) have attracted considerable interest. The cost of QCs highly depends on the number of qubits even on quantum simulators. The reduction of MO space can thus be a crucial issue for the practical applicability of MO-QC. Besides the frozen-core restriction for the occupied MO space, we have used the pseudo-natural orbital derived from the second-order Møller-Plesset perturbation (MP2) theory for the virtual MO space. A preliminary test on the LiH molecule (STO-3G basis) showed acceleration by a factor larger than 500 for MO-QC with the Blueqat simulator, where the required time was 72 s per solution. Simulations of MO-QC may be used as practical teaching materials in classes.

Keywords

Molecular Orbital (MO); Quantum Computation (QC); Frozen Core (FC); Pseudo Natural Orbital (PNO); Blueqat; Teaching Material

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1. Introduction

Aspuru-Guzik et al. [1] proposed an epoch-making approach to evaluate molecular energies with the molecular orbital (MO) framework by using quantum computation (QC) in the phase estimation algorithm (PEA) in 2005. After this work, methodological developments of MO-QC have been extensively made, as compiled in a couple of recent reviews by Aspuru-Guzik’s group [2,3]. In 2017, Kandala et al. [4] reported a pioneering MO-QC study with a real quantum computer device made by IBM, where H_2 , LiH , and BeH_2 molecules were treated with the minimal basis set of STO-3G [5]. Recently, the future potential of MO-QC has been attracting considerable interest in the molecular design of functional materials and new catalysts.

A typical MO-QC workflow for the ground state of a given molecular geometry may be summarized as below. As the first step, conventional MO calculations are performed to obtain the set of one-electron integrals (OEIs) and two-electron integrals (TEIs) with atomic orbital (AO) basis functions as well as the Hartree-Fock (HF) reference wavefunction as an AO-MO coefficient matrix, and then the second quantized molecular Hamiltonian are prepared with the list of transformed integrals [5]. For this first step, PySCF [6] or Psi4 [7] programs may be utilized, since the interface to OpenFermion [8] for the Bravyi-Kitaev (BK) transformation for the second quantized Hamiltonian [9,10] as the second step has been supported. As the third step, the wavefunction ansatz of unitary coupled cluster (UCC) type [11] is optimized by the variational quantum eigensolver (VQE) [12,13]. Several platforms for VQE-UCC processing have been available; Qiskit [14], Q-Sharp [15], and Blueqat [16]. The electronic energy is determined when the VQE iteration converges, providing the total energy with the nuclear repulsion energy.

The cost of the above-mentioned third step steeply depends on the number of required qubits associated with the numbers of electrons and orbitals [2,3]. For this reason, both

size of molecules and quality of basis sets are limited in actual MO-QC studies, regardless of using QC simulators and real QC devices. The minimal STO-3G basis set [5] has thus been typically used. Although the low flexibility of STO-3G has been recognized, especially in describing the dynamic electron correlation, chemical pictures involving the static electron correlation or near-degeneracy may be obtainable in qualitatively correct fashion.

From a viewpoint of physical chemistry education, the MO-QC practices with minimal basis set can be good examples not only to teach the fundamentals of MO theory but also to introduce the framework of QC in classes for students. Note that even the smallest H₂ molecule with STO-3G is an educational example to illustrate both static and dynamic correlations as documented in Ref. [5]. Classes with practical exercises may induce student's interest in the potential of MO-QC for molecular science and material research. Along this line, we have been developing an education-oriented environment of MO-QC, based on the Blueqat simulator [16]; the first version (unpublished) was interfaced with PySCF [6] and OpenFermion [8]. However, the actual costs should still be of concern for such educational applications, if the target molecule contains atom(s) after the second row in the periodic table or consists of more than three atoms. A couple of countermeasures to reduce the active MO space can be considered as follows.

The first countermeasure is the reduction of occupied MO space. It is well known that inner core electrons (e.g., the 1s electrons in the second row atoms) do not directly contribute to chemical properties which are essentially described by valence electrons (e.g., the 2s and 2p electrons). The frozen-core (FC) restriction [17] was introduced for configuration interaction (CI) calculations in 1975, where the core electrons (or shells) were kept frozen at the HF level. This approximation has been widely used as a default option in correlated calculations. McCaskey et al. [18] recently applied the FC restriction

to the MO-QC study of VQE-UCC with the STO-3G basis for several alkali hydride molecules such as NaH. The error due to FC was found to be small as expected. The number of active occupied MOs is decreased by FC (from 6 to 1 for NaH), reducing qubit demands. Namely, molecules containing heavier atoms is made accessible; Qiskit [14] has already supported the FC option.

The second countermeasure involves the virtual MO space. At the end of HF calculations, the virtual MOs with ascending order in orbital energies relate with the electron affinity by the Koopmans theorem [5]. The simple energy-judged omission should thus cause a sizable loss of correlation energy. Löwdin [19] showed that the use of natural orbitals (NOs) leads to the fast convergence in CI expansions, where the NOs are the eigenfunctions of one-body density matrix and the associated occupation numbers corresponds to the eigenvalues. Note that the cut-off of NOs having small occupation numbers does not affect the total accuracy. There is a difficulty that the set of NO is obtained as the result of (costly) CI calculations [5], however. Various schemes to generate NO-like virtual MOs without CI calculations have thus been proposed. Very recently, Kühn et al. [20] has addressed enormous possibilities of frozen NOs [21] for MO-QC with extended basis sets. The reduction of active virtual MO space based on the NO concept [19] is attractive certainly.

In this work, we investigate the reduction of active space in MO-QC via the FC restriction [17] and also the pseudo NO (PNO) set generated by the second-order Møller-Plesset perturbation (MP2) theory [22]. H_2 , LiH, and NaH are calculated by the VQE-UCC [12,13] with Blueqat [16], and then the calculated energies are compared with the full-CI reference data. In Section 2, the computations schemes are described. The results of test calculations on H_2 , LiH, and NaH are shown in Section 3.

2. Computational scheme

Hereafter, it is assumed that the HF ground state as the reference of UCC [11] is of closed-shell restricted type [5]. The FC restriction [17] is briefed as follows. The FC-modified OEs with general MO labels pq is defined as

$$h_{pq}^{\text{Core}} = h_{pq} + \sum_u^{\text{Core}} (2g_{pq,uu} - g_{pu,qu}), \quad (1)$$

where matrices \mathbf{h} and \mathbf{g} correspond to usual transformed OEs and TEs with the converged AO-MO coefficients, respectively. The form of Eq. (1) is similar to the regular Fock matrix, except for the summation range [5],

$$f_{pq} = h_{pq} + \sum_u^{\text{Core}} (2g_{pq,uu} - g_{pu,qu}) + \sum_i^{\text{Valence}} (2g_{pq,ii} - g_{pi,qi}). \quad (2)$$

The FC energy is then evaluated as

$$E^{\text{Core}} = \sum_u^{\text{Core}} (h_{uu} + h_{uu}^{\text{Core}}). \quad (3)$$

E^{Core} should be added to the energy of valence electrons to be calculated by VQE-UCC [12,13].

The MP2 PNO [22] is obtained by diagonalizing the virtual space density matrix (specified with labels ab)

$$\rho_{ab} = 2 \sum_{ij}^{\text{Valence}} \sum_c^{\text{Virtual}} \frac{T_{ij}^{ac} g_{ib,jc}}{\epsilon_i + \epsilon_j - \epsilon_b - \epsilon_c}, \quad (4)$$

$$T_{ij}^{ab} = \frac{2g_{ia,jb} - g_{ib,ja}}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (5)$$

where ϵ_i and ϵ_a mean the orbital energies of occupied MO and virtual MO, respectively.

Note that the MP2 correlation energy is given as

$$E^{\text{MP2}} = \sum_{ij}^{\text{Valence}} \sum_{ab}^{\text{Virtual}} T_{ij}^{ab} g_{ia,jb}. \quad (6)$$

As in the case of CI NO [19], the MP2 PNO with small occupation number may be omitted without significant loss of correlation energy. For the selected set of MP2 PNOs with a

given threshold, the virtual space Fock matrix using Eq. (2) should be re-diagonalized to make the pseudo-canonical virtual MO set. After this care, the lists of OEIs and TEIs with MO labels are generated again for the second quantized Hamiltonian. Care should be taken for the fact that the MP2 description degrades at a molecular geometry far from the minimum.

The data flow of our present MO-QC system for a given molecular system at a single geometry is illustrated in Figure 1. The GAMESS program (2003 version) [23] is used to prepare the list of AO integrals and to solve the HF reference wavefunction [5]. As the reference, the full-CI calculations are performed also by GAMESS, with and without the FC restriction [17]; no virtual MO is omitted. Both FC-modified OEIs preparation and PNO MP2 treatment are performed by a prototype code named Int-Gen (written in Fortran). Int-Gen outputs the transformed TEIs in the Mulliken notation [5], and thus the sorting adjusted to the Dirac notation used in the regular second quantized Hamiltonian is done by a Python script, Data-Conv. The sorted list of integrals are passed to OpenFermion [8] for the BK transformation [9,10]; tiny modification was needed in the interface part of OpenFermion. The BK-transformed Hamiltonian is subjected to the VQE-UCC solving [12,13] by the Blueqat simulator [16]. The above-listed processing (see again Figure 1) can be looped to scan the potential energy curve/surface.

3. Test calculations

All test calculations were carried out on several personal computers (equipped with, e.g., Intel Core i7-6700 for Blueqat), mimicking the typical computer environment of a class room. Appropriate servers (with such as Intel Xeon) could be used when necessary in acceleration of processing, of course.

The first test molecule was H_2 with the 6-31G basis set of valence double zeta (DZ) type [5]. The AO coefficients of virtual space MOs are listed in Table 1. As expected,

there is a resemblance between full-CI NO and MP2 NO; in contrast, the HF MOs differ significantly. The third NO had a small occupation number and hence was omitted. The MO-QC problem thus turned from "2 electrons in 4 orbitals" to "2 electrons in 3 orbitals", corresponding to the decrease in the number of needed qubits in Blueqat from 8 to 6. The VQE-UCC results around the minimum are plotted in Figure 2. The mean absolute error (MAE) was as small as 4.7×10^{-4} au and the curve shape was kept almost parallel relative to the full-CI reference. The time required for VQE-UCC (average in sample points) with and without the PNO omission were 17.7 s and 348.9 s, respectively, achieving 20-fold acceleration.

Both the FC restriction and the MP2 PNO omission were applied to the LiH molecule with STO-3G. Table 2 compiles the AO coefficients of virtual space MOs for LiH. The two σ type MO of HF were mixed in Full CI NO (under FC) and MP2 PNO, and the second σ NO was omitted due to its small occupation number. Note that the two π type 2p orbitals are essentially unchanged within rotations. The size of "4 electrons in 6 orbitals" problem (12 qubits) was thus reduced to "2 electrons in 4 orbitals" (8 qubits). Figure 3 plots the three potential energy curves, where the results of full-CI without FC (labeled as "nf") are included as well. The difference of VQE-UCC curve from full-CI curves is reasonably small, and the MAE values to full-CI with and without the FC restriction were 4.8×10^{-4} au and 7.1×10^{-4} au, respectively. The experimental length of Li-H is 1.60 Å [24], but the present calculations showed a shorter minimum point. A sizable basis set superposition error (BSSE) [25] of STO-3G is responsible for this discrepancy. The average time for VQE-UCC of the original problem size was about 40000 s, and it dramatically decreased to 72.1 s for the reduced problem. Namely, an acceleration of 555 times was obtained.

The STO-3G basis set preset in GAMESS for the third row atoms [26] is different from the standard STO-3G set [27] in the orbital exponents of 3s3p-L shells. We used

the former set for NaH as the third test molecule, since the artificial contraction of Na-H length (in comparison with the experimental value of 1.89 Å [24]) due to BSSE [25] was rather moderate relative to the latter. The valence orbital features of NaH were similar to those of LiH, and thus the AO coefficients of virtual space MO are not listed. The reduction of problem size was "12 electrons in 10 orbitals" (20 qubits) to "2 electrons in 4 orbitals" (8 qubits). The MAE values to full-CI with and without the FC restriction were 2.1×10^{-3} au and 2.1×10^{-2} au, respectively. The negative influence of the reduction of virtual MO space should be acceptable, because the shape of VQE-UCC curve plotted in Figure 4 was still almost parallel to that of full-CI with FC. The average time for VQE-UCC was only 32.8 s; the non-reduced problem was hard to solve on personal computers.

Practical exercises in classes would be possible if the required MO-QC time per geometry is manageable within at most a couple of minutes, as seen in the present examples of H₂, LiH, and NaH. The interface modification to real QC devices is straightforward in Blueqat. Ideally, students can experience "real MO-QC processing" if such a device is available through internet.

4. Summary

In this work, the reduction of active MO space by FC [17] and also MP2 PNO [22] was investigated for the VQE-UCC calculations [12,13] on the Blueqat QC simulator [16]. The H₂ molecule was calculated with the 6-31G basis set of DZ type [5], where the number of virtual MOs was reduced by MP2 PNO from 4 to 3 at a negligible loss of energy. The factor of acceleration was 20. For the case of LiH with the minimal STO-3G basis [5], both the FC restriction [18] and the PNO omission provided 555-fold acceleration relative to the case without the reduction ("2 electrons in 4 orbitals" versus "4 electrons in 6 orbitals"), while the numerical differences from the full-CI reference energies were reasonably small. The same recipe was applied to NaH; the problem of

demanding "12 electrons in 10 orbitals" was reduced to that of only "2 electrons in 4 orbitals". Our MO-QC implementation at the present level may be usable for practical exercises in classes of the computational chemistry course. Works for other molecules as more educational examples (e.g., Li_2) have been in progress in conjunction with the improvement of quantum circuit logic in Blueqat. If a wide range scan of potential energy curve/surface including bond breaking process is required, other approaches to prepare "good starting MOs" (e.g., proposed by Ref. [28]) will be necessary to implement. Works along this line is a future subject.

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Table 1. Lists of virtual orbital AO coefficients of H₂ with 6-31G basis (at 0.75 Å).

HF MO			
Vir. No.	1	2	3
Orb. Ener.	0.2358	0.7796	1.3914
1 H 1 S1	0.124609	0.770742	-1.114530
2 H 1 S2	1.689904	-0.686876	1.341808
3 H 2 S1	-0.124609	0.770742	1.114530
4 H 2 S2	-1.689904	-0.686876	-1.341808
Full-CI NO			
Vir. No.	1	2	3
Occ. Num.	0.0241	0.0050	0.0003
1 H 1 S1	0.732382	0.768874	-0.849306
2 H 1 S2	0.636546	-0.688429	2.061803
3 H 2 S1	-0.732382	0.768874	0.849306
4 H 2 S2	-0.636546	-0.688429	-2.061803
MP2 PNO			
Vir. No.	1	2	3
Occ. Num.	0.0100	0.0031	0.0003
1 H 1 S1	-0.781751	-0.770742	-0.804096
2 H 1 S2	-0.512395	0.686876	2.096110
3 H 2 S1	0.781751	-0.770742	0.804096
4 H 2 S2	0.512395	0.686876	-2.096110

Table 2. Lists of virtual orbital AO coefficients of LiH with STO-3G basis (at 1.6 Å).

HF MO				
Vir. No.	1	2	3	4
Orb. Ener.	0.0782	0.1639	0.1639	0.5477
1 Li 1 S1	-0.210041	0.000000	0.000000	0.093458
2 Li 1 S2	0.799540	0.000000	0.000000	-0.702683
3 Li 1 PX	0.000000	-0.441197	0.897410	0.000000
4 Li 1 PY	0.000000	0.897410	0.441197	0.000000
5 Li 1 PZ	-0.612072	0.000000	0.000000	-0.979457
6 H 2 S	-0.140173	0.000000	0.000000	1.184722
Full-CI NO				
Vir. No.	1	2	3	4
Occ. Num.	0.0426	0.0015	0.0015	0.0000
1 Li 1 S1	0.179707	0.000000	0.000000	0.134399
2 Li 1 S2	-0.991817	0.000000	0.000000	-0.353419
3 Li 1 PX	0.000000	0.767350	0.641229	0.000000
4 Li 1 PY	0.000000	-0.641229	0.767350	0.000000
5 Li 1 PZ	-0.567156	0.000000	0.000000	1.015516
6 H 2 S	1.116532	0.000000	0.000000	-0.419343
MP2 PNO				
Vir. No.	1	2	3	4
Occ. Num.	0.0150	0.0014	0.0014	0.0001
1 Li 1 S1	0.167707	0.000000	0.000000	-0.157245
2 Li 1 S2	-0.958076	0.000000	0.000000	0.463809
3 Li 1 PX	0.000000	-0.441197	0.897410	0.000000
4 Li 1 PY	0.000000	0.897410	0.441197	0.000000
5 Li 1 PZ	-0.664795	0.000000	0.000000	-0.944466
6 H 2 S	1.146141	0.000000	0.000000	0.331023

Figure captions

Figure 1. Data flow of MO-QC processing (see text).

Figure 2. Potential energy curves of H_2 with 6-31G basis (see text).

Figure 3. Potential energy curves of LiH with STO-3G basis (see text).

Figure 4. Potential energy curves of NaH with STO-3G basis (see text).

Figure 1

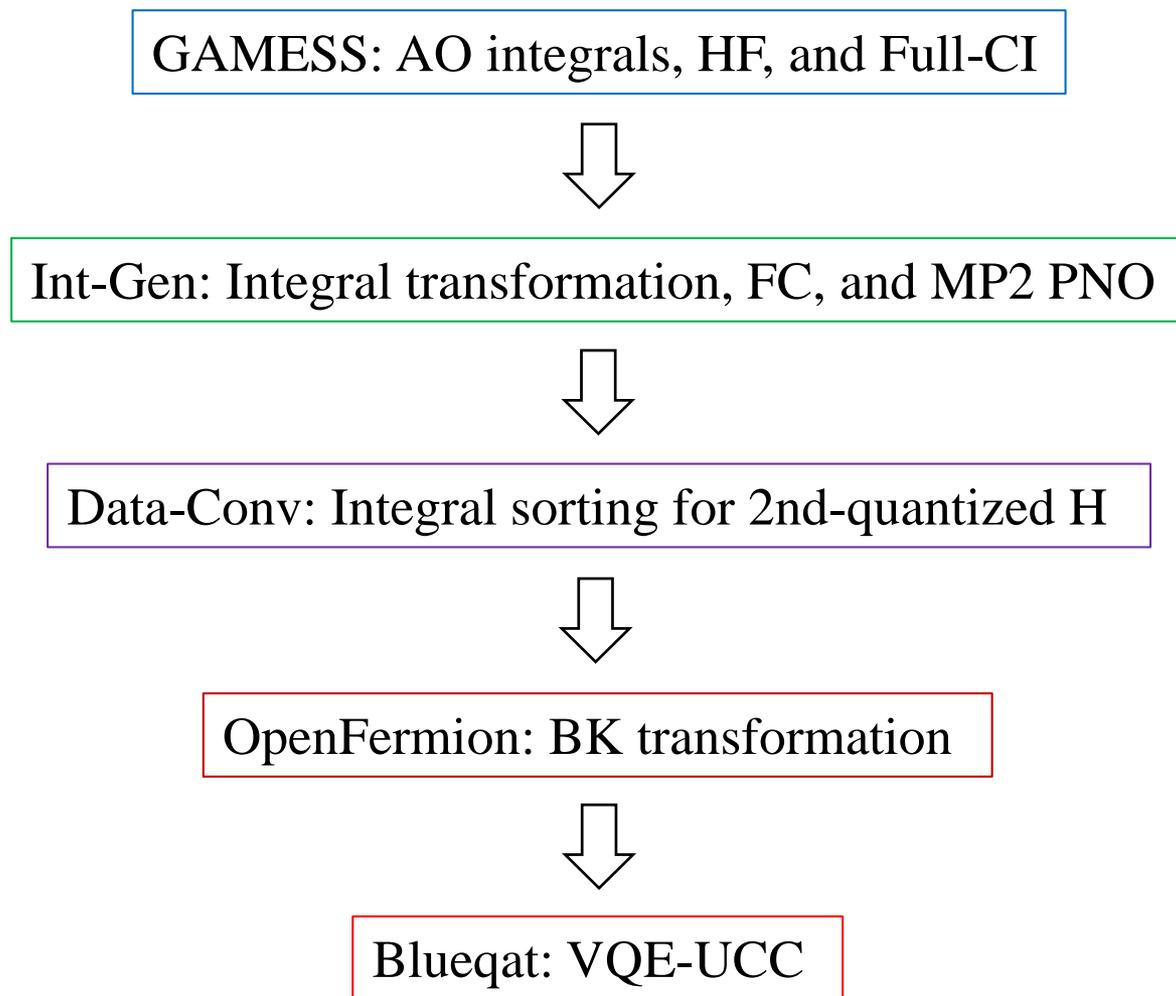


Figure 2

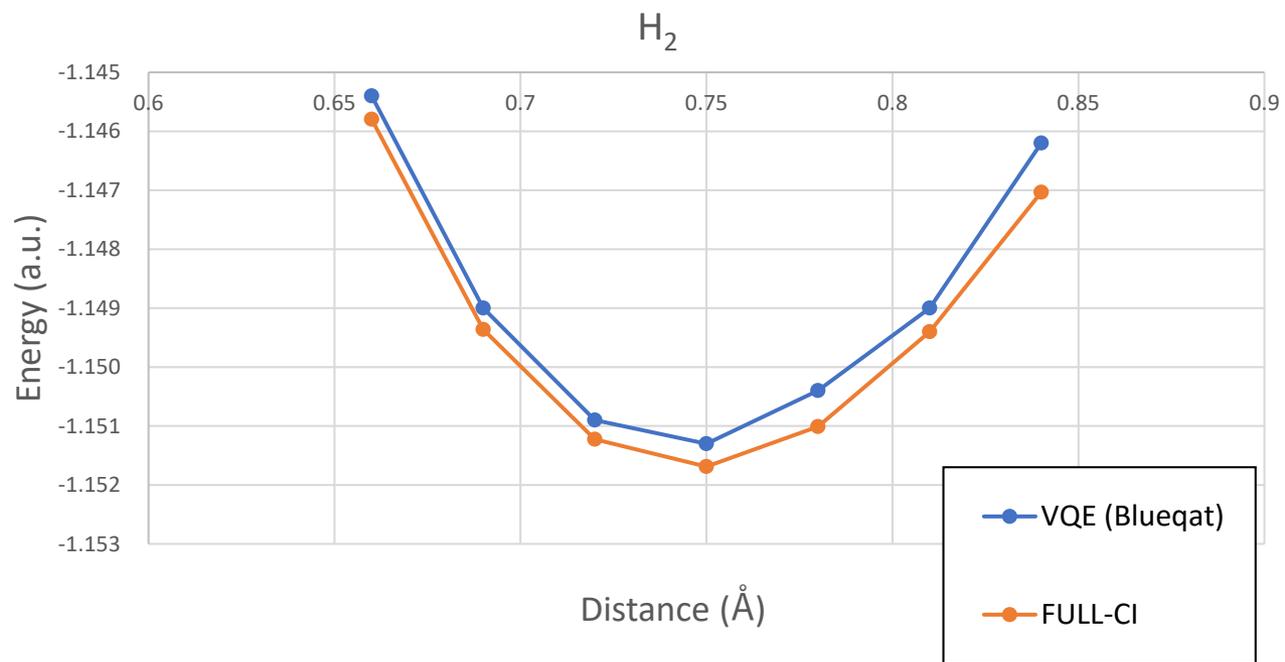


Figure 3

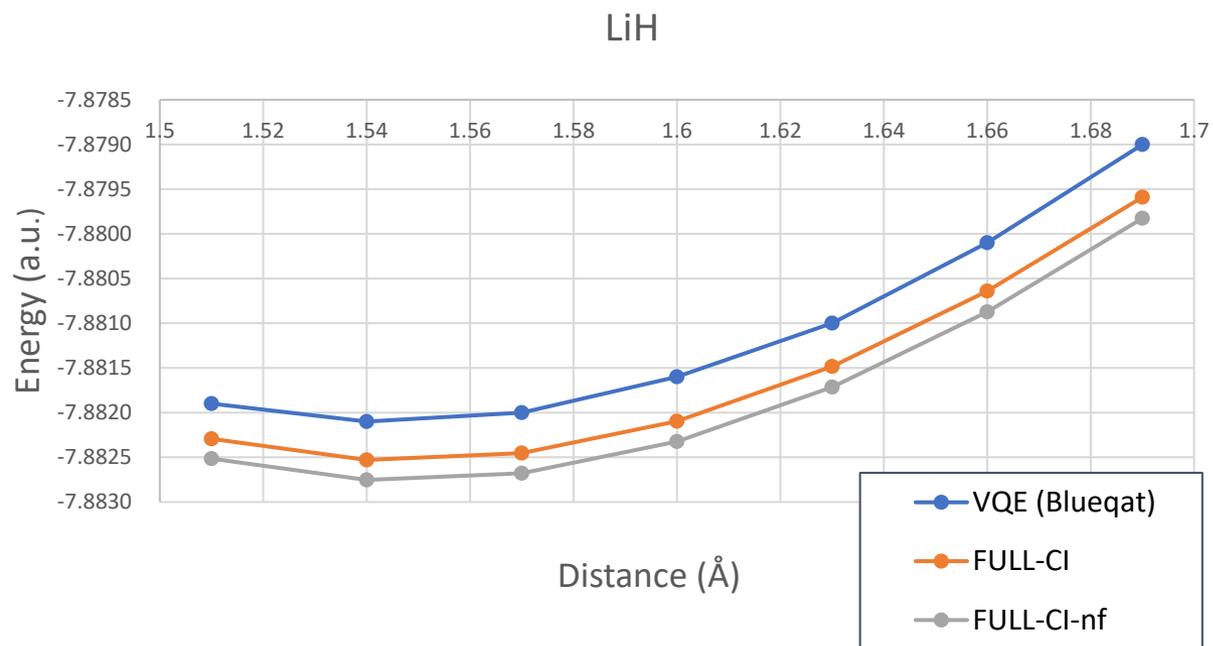
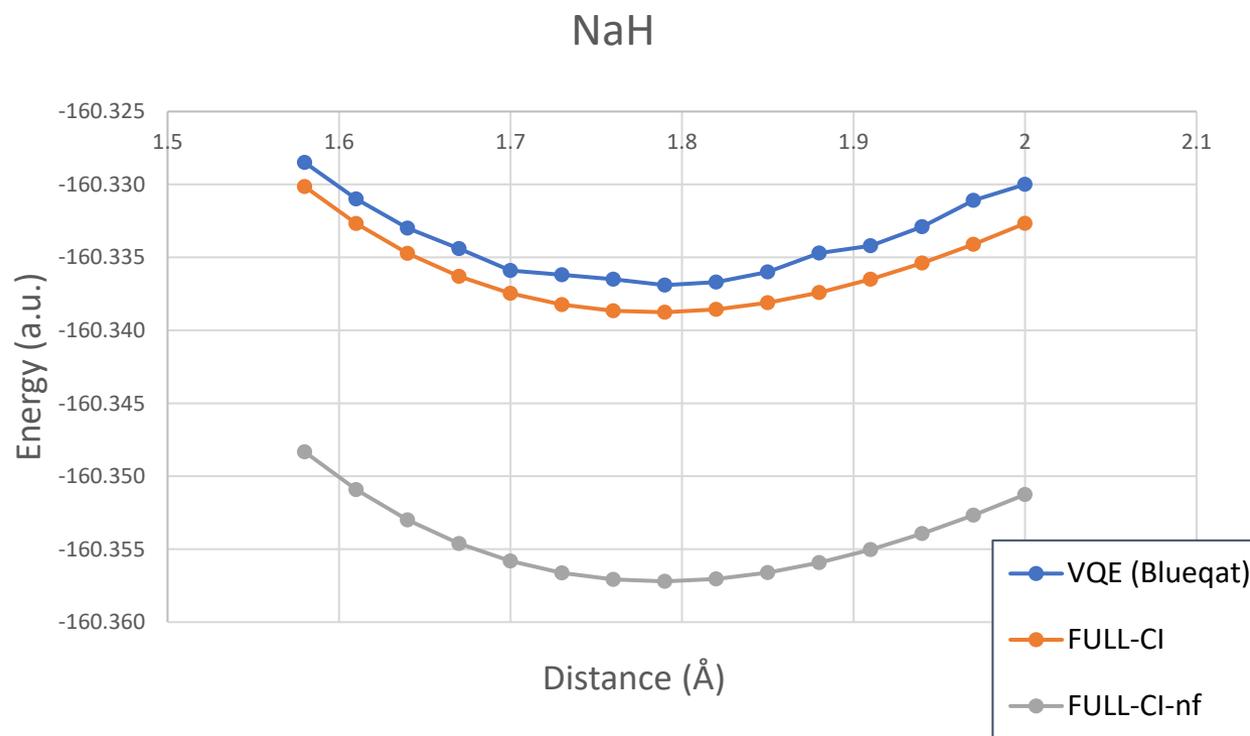


Figure 4

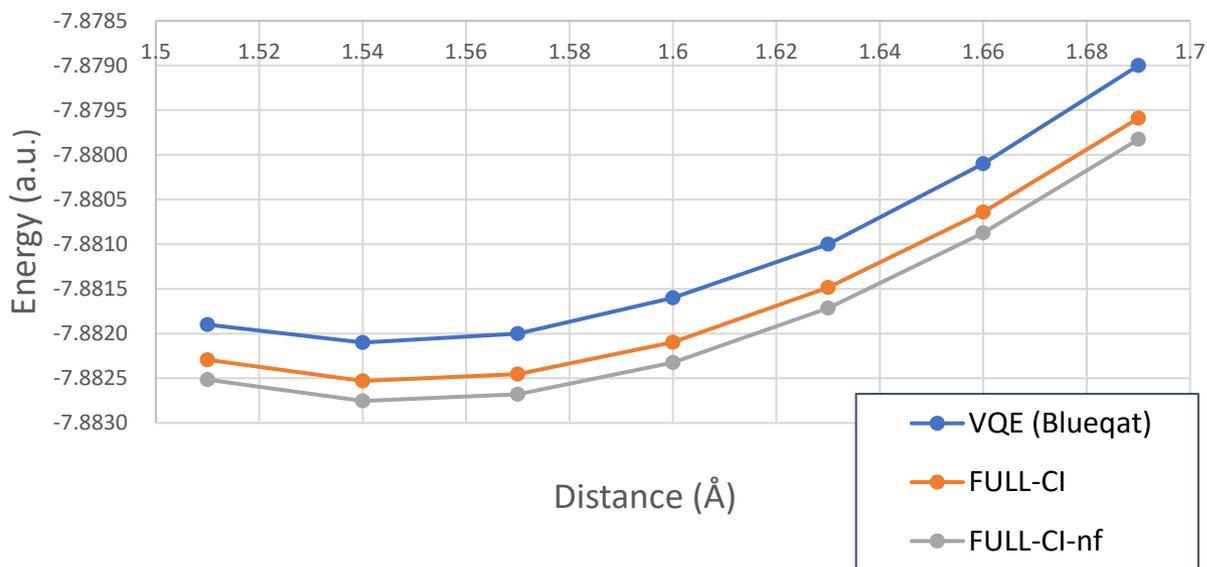


Graphical Abstract

Problem size reduction for VQE-UCC by FC & MP2 PNO

“4 electrons in 6 orbitals” → “2 electrons in 4 orbitals”

LiH



MAE (VQE - FULL-CI) : 4.8×10^{-4} a.u.

(VQE - FULL-CI-nf): 7.1×10^{-4} a.u.