**Grid-Based and Qubit-Scarce Quantum Computation of Chemical Reaction Energies**

*Alejandro Becerra,1 Siddhant Gupta,2 Eric A. Walker\*,2*

*1Tufts University- Medford, MA*

*2University at Buffalo, The State University of New York- Buffalo, NY*

**Abstract**

A single-particle electronic structure method using a spatial discretization approach is presented and executed on a quatum computer simulator. The systems demonstrated in this work are CO2 over a Ru layer and CO and O adsorbed on the Ru layer. A Hamiltonian matrix is constructed from electron-electron potential energy, electron kinetic energy, electron-nucleus potential energy and nucleus-nucleus potential energy. Quantum phase estimation (QPE) is applied to estimate the minimum ground-state energy for each system. Ultimately, this grid-based framework is more qubit-scarce than existing alternative methods. Futhermore, this paper opens up investigations of our novel framework with other catalytic systems as well as other quantum eigensolvers.

**Keywords**

Heterogeneous Catalysis, Computational Catalysis, CO oxidation, Quantum Computing, Electronic Structure, Density Functional Theory

\*ericwalk@buffalo.edu *Furnas Hall, Mary Putnam Way*, *Buffalo NY, 14260*

1. **Introduction**

In the current Noisy Intermediate Scale Quantum (NISQ) era, the goal is to find immediately useful applications of existing or near-term quantum computers.1 Since the inception of quantum computers, a known application for them is computing the energy profiles of given chemical reactions. Thus far, progress has been made in computing ground state energies of molecules with less than ~10 atoms and with elements under a certain atomic number. Quantum phase estimation (QPE)2 is used to obtain the ground-state energy.3 Existing approaches are largely based upon molecular orbital bases.4 In the case of BeH2,5 which used molecular orbitals as the basis, its 6 electrons were mapped to 6 qubits.5 However, Ru, an element modeled in this work, has 44 electrons. That would require 44 qubits to simulate a Ru atom. In analogous existing DFT, on the order of ~40 Ru atoms are simulated for a heterogeneous Ru catalyst (not an exact number, but on the order of 10’s of atoms).6 Then, 1000’s of qubits are needed, which are too many in the NISQ era.

The proposed method here is in the direction of DFT, where a single field is modeled rather than individual electrons. Instead of the electron density, the field in DFT,7 an electronic wavefunction is the field in this work. Here, the wavefunction is discretized over planes.4 Should the energies approximated by QPE prove as reliable as density functional theory (DFT), they could provide a much less resource-demanding alternative to DFT. Currently, DFT is limited in the size of reaction networks that may be practically studied.8-9

In the first part of this article, the components of the Hamiltonian matrix are defined. Two diatomic molecules, H2 and O2, are modeled using a single plane perpendicular to the bond coordinate. The matrices for the C, O and Ru- containing systems are written out. The spatial discretization is 16 planes along the x-coordinate. In the second part, the results from QPE are reported and analyzed. All code and data to reproduce the results of this work are publicly available at:

https://github.com/ericwalkwalke299/quantum\_computing\_materials\_thermodynamics

**Hamiltonian matrix development**

The Hamiltonian matrix is based off of the Schrödinger equation, which is,

(1)

is the kinetic energy operator acting on the electron wavefunction . The other operators are , the external potential energy due to the nuclei-electron attraction; , the nucleus-nucleus potential energy; and , the electron-electron potential energy.

In the following subsections, these four contributions are discussed one at a time. An effective approximation that is used in Equation (1) is the Born-Oppenheimer approximation.10 In the Born-Oppenheimer approximation, the positions of the nuclei are held constant and the electronic structure is converged to a self-consistent field. Therefore, in Equation (1), there is no kinetic energy of the nuclei.

*Kinetic energy of the electron wavefunction*

, is defined,

(2)

The atomic units of energy are Hartree (). , is the Laplacian operator. In the diatomic molecule examples, there is one plane and kinetic energy is neglected because no finite difference may be constructed. When moving up from diatomic molecules, a finite difference is used for the planes along the x-axis (Figure 1). The finite difference formula for the second derivative, , is what is expressed in Equation (3), for the x-direction only. For the CO2 dissociative adsorption over Ru, the matrix becomes,

(3)

16 planes along the x-coordinate are the discretization. The space between planes, , is atomic units of length.

*Three potential energies*

The electron-nucleus potential, also known as external potential, in the plane wave case, is

(4)

is any vector denoting spatial position. is the nuclear charge. The nuclear index is . A vector that points to nucleus from position is . The vector is from plane to nucleus . is the total number of valence electrons. Figure 2 illustrates various vectors in Equation 1. Atomic units are employed. has an amplitude at each spatial point , and they are influenced by the nuclei positions .

is a diagonal matrix with a different value at each . For the diatomic molecule case, there is only one , and so the summation becomes over two nuclei, only. Also, the plane in the diatomic model is exactly in the middle of the bond of two identical atoms, and is exactly half the bond length. In the Ru system, the summation is taken over the planes and and the nuclei . is capped at a maximum of 10. Otherwise, Ru atoms exhibit an outsized contribution than adsorbates, masking the changes in due to the C-O bond breaking. A pseudopotential is used rather than a Coulombic potential.11-12 This measure is to prevent outsized contributions from nuclei that are close to planes.

Another potential is the nucleus-nucleus potential energy:

(5)

Pseudopotentials are of the same form as the electron-nucleus potential. is a vector between two nuclei and . However, the potentials in could be left in their Coulombic form, and there exists an analytical solution to their total potential energy. The electron-nucleus potential and the nucleus-nucleus potential are the two terms in the diatomic molecules. The energy versus bond length is plotted in Figure 3. The equation for is,

(5)

The distance between and for any is . In principle, potential energy is from every spatial point to every other. The discretization is 16 plane waves over 24 Å. Any more than one plane away has a diminishing influence. The Hamiltonians for both CO2 over Ru and CO and O over Ru are diagonally dominant. The associated eigenvector to the minimum eigenvalue was a vector close to one in the third index (beginning counting at zero). Therefore, this minimum eigenvalue is prepared with gates in the circuit. For CO2 over Ru, the eigenvector being close to , 4 gates are placed on the bottom 4 qubits. For CO and O over Ru, the minimum eigenvector associated with the minimum eigenvalue is an approximate one in the second index. Therefore, the eigenvector is , and gates are placed in that pattern on the bottom register.

**QPE Algorithm and Results**

A Hermitian Hamiltonian matrix offers the benefit being transformed into a unitary matrix without doubling the dimension.13 A standard, Trotterized QPE is constructed on a quantum simulator by exploiting a known Pauli decomposition and standard Qiskit operations.14

(6)

Another line of questioning is whether the approximation used in Equation (6) is accurate enough matrix exponential without slowing down to the time scale of DFT on a classical computer. In our code, we evolve to by stepping through sizes of .

Figure 4 shows a QPE circuit with three qubits in the top register. For simulations, eight qubits are used in the top register. More qubits in the top register also increases the gate depth in the inverse quantum fourier transform. Figure 5 displays the result of 5,000 shots of the quantum circuit for the CO2 over Ru structure. Figure 6 shows the results for the CO and O over Ru structure, also with 5,000 shots.

**Discussion**

Computed with DFT, CO plus O over Ru is 23.11 kJ/mol higher in energy than CO2 over Ru.6 Computed with QPE, the change in energy from CO2 over Ru to CO and O over Ru is 12 on an 8-bit scale (i.e.: with a maximum value of ). A conversion factor is therefore necessary when reading QPE results. An expanded number of tests could reveal an appropriate scaling factor.

It may be advantageous to work with nuclei-centered potentials. Brockherde, et al.12 developed was a machine learned map from electron density to potential energy and the reverse, potential energy to electron density. They conducted a molecular dynamics simulation, solving energy at various time points using the machine-learned functionals to approximate the energy of the system. Their basis was spatial grid points. Each grid point was associated with one electron density. The machine learning algorithm received potential and returned electron density. Such a method could be transferrable to a quantum computer, and the QPE algorithm in particular.

Furthermore, the quantum method proposed could also be useful in transition state searches. The growing string15-17 transition state search method also works with any computational chemistry model that inputs nuclear positions and returns the energy and gradients in energy with respect to space for each of the nuclei. The transition state search locates a saddle point which is a maximum along the reaction coordinate and a minimum along all other coordinates. The transition state is the saddle point. Knowledge of the reaction coordinate could be useful in preparing the eigenvector in QPE. The results exhibit an uncertainty distribution. The inclusion of uncertainty is also a charcteristic DFT.18-19

**Conclusions**

Ultimately, QPE has the potential to quickly approximate the minimum eigenvalue of large Hamiltonian matrices. In this application, very large Hamiltonians are associated with a very fine spatial mesh. Future work may also explore the Variational Quantum Eigensolver (VQE) as opposed to QPE.20 VQE minimizes the Rayleigh quotient and does not require prior knowledge of the eigenvector or ground-state wavefunction like QPE.

A unique advantage of using a real-space plane wave basis is that the number of qubits required scales with the choice of the number of real-space planes, rather than the number of electrons. One remaining challenge is converting the result from QPE to units of energy, but a suitable scaling factor might be found with benchmark data.

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**Figures**

Chart

Description automatically generated

Figure 1. The plane wave discretization along the x-direction for the CO2 over Ru and CO and O over Ru systems.

Diagram

Description automatically generated

Figure 2. Examples in real space of vectors encountered in the Schrödinger equation. The purpose of this cartoon is for clarifying how vectors are named and what they represent.

**Chart, line chart

Description automatically generated**

Figure 3. Diatomic molecule simulation. There is a minimum energy at a bond length of and , for and , respectively. The actual bond lengths are and . (a) A single plane midway between the nuclei is utilized. (b) Result for H2 and O2.

Chart

Description automatically generated with medium confidence

Figure 4. Quantum phase estimation (QPE) circuit for three qubits in the top register.

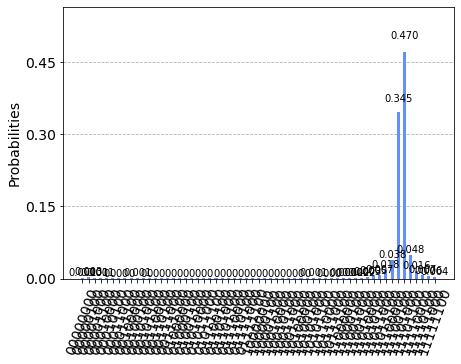


Figure 5. CO2 over Ru QPE result. The peak is at 11101000, or 232.

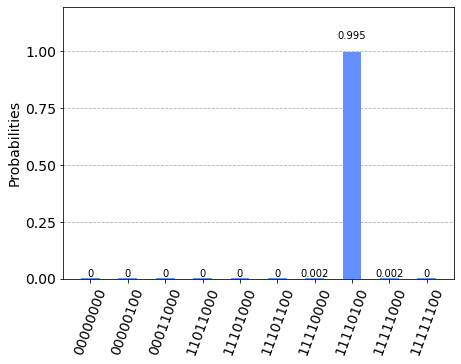


Figure 6. CO and O over Ru QPE result. The peak is at 11110100, or 244.

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