

Quantum Chemistry

Eesh Gupta

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1 Aims

Purpose: Given an intuitive outlook on quantum computation of molecular energies.

This paper is not rigorous. There is too much material. Nonetheless, I will present equations and wierd constants to aid intuition of certain methods.

2 Introduction

This paper concerns with understanding the recent advancements made in simulation of electronic structure through quantum computers. A good question to ask is why simulate molecules? Why bother about calculating the ground state energies of molecules?

Suppose you are the manager of a fertilizer making company. You look at the bills and see a huge chunk of your money being invested in carrying out the born haber process. To save some money, you look more into this issue and find out that expense is largely coming from the maintaining high pressures and temperatures to carry out the reaction. So the obvious solution is to tell your scientists to somehow make this reaction happen without the high pressures and temperatures. But the scientists complain that we need those conditions to allow the action of a really important enzyme called nitrogenase. Well you ask them to use their science to study the enzyme and somehow make it work to reduce costs. But the scientists say their science isn't advanced enough because the analysis of electronic structure requires exponential costs. And you are left with the high costs and you can't get your next promotion.

Accurately calculating the ground state energies of small molecules such as hydrogen gas or lithium hydride might seem insignificant in comparison to simulations of large drug molecules that are of interest to practical applications. However, not all aspects of simulations of such drug molecules are important. If we decompose such problem in a way that the most important aspect of the system is accurately simulated and other aspects are simulated potentially in a less accurate manner, we can see why our work on small molecules may be of importance to solve the much larger simulation problems.

3 Chemistry Context

What exactly is the electronic structure problem? What we need to find is the minimum energy configuration of an atom or the ground state energy of a molecule. To study the energy profile of a molecule, we need to be familiar with the term potential energy surface. Abbreviated as PES, this term refers to a graph of energy based on a set of parameters like bond angle, bond length, etc. Making this plot requires you to calculate energy for every possible configuration of those parameters. It's easy to see that the more the parameters, the harder (in terms of computational cost) it becomes to make these plots.

But how do we even compute the energy? Well we gotta use something called the Hamiltonian H . When the hamiltonian acts on the exact ground state wavefunction Ψ_0 , the eigenvalue gives us the exact ground state E_0 according to the equation:

$$H\Psi_0 = E_0\Psi_0$$

3.1 Brief Review of Quantum Mechanics

3.1.1 State

The state of the system is completely specified by $\Psi(r, z)$ where r denotes the position of system and z denotes spin. Think system here as an electron.

Wavefunction: Reports the “status” of a particle in terms of position and time. If we know the wavefunction $\Psi(r, t)$, we can find all the measurable properties of a particle

Now wavefunction is a complex number but if you square it, you’ll get the real part only and this real part can be interpreted physically.

Born Interpretation: $\Psi^*(x)\Psi(x)dx =$ Probability of a particle being in the space between x and dx , AS SHOWN IN FIGURE ! This is why we also call the square of the norm of the wavefunction probability density function...because it tells us the probability that the particle is in some space.

Bonus Intuition: What do we mean when we say that the wavefunction of a particle is normalized? Well, if it is , you get

$$\int_{-\infty}^{\infty} \Psi^*(x)\Psi(x)dx = 1$$

which makes sense since the probability of a particle being in all of universe is 1.

3.1.2 Operators

In quantum physics, to measure a physical observable like position, momentum or energy of a particle, you need a hermitian, linear operator or what John Wheeler called machines. They take an input vector and give you an output vector.

Operator: Does something to a state to output a new state (a matrix transformation in the Hilbert Space!?)

Now what the heck does hermitian mean? Well it means that the operator/matrix must have real eigenvalues. In the next postulate you will learn that the eigenvalues correspond to measurement. And you do want a real number measurement, don’t you?!?

3.1.3 Eigenvalue

Measuring an observable on some state is equivalent to computing the eigenvalue of the eigenfunctions of the observable?!?

3.1.4 Expectation Value

Expectation values is the weighted sum of eigenvalues of an operator. For example, the expectation value of the pauli matrices is 0 because all their eigenvalues consist of +1 and -1.

3.2 Second Quantization

Suppose a hypothetical atom has the orbitals or discrete energy levels indexed as following A, B, C, D, \dots . Also suppose the system only contains one electron in the state

$$|\Psi\rangle_1 = |A\rangle_1 + |B\rangle_1$$

where electron 1 is simultaneously occupying orbitals A and B. So far, our notation looks elegant and easy to interpret. But when we account for the second electron, let's say in the state $|\Psi\rangle_2 = |C\rangle_2$ occupying orbital C, our notation for the state of whole system $|\Phi\rangle$ gets messy. You might assume it will look like this:

$$|\Phi\rangle = (|A\rangle_1 + |B\rangle_1) \otimes |C\rangle_2$$

But, this is wrong since we have failed to account for exchange symmetry. What is exchange symmetry? In a quantum mechanical systems, particles are indistinguishable. For example, in the equation $1 + 1 = 2$ the two 1's are same. (Cite stack exchange answer) If we were to swap the 1 on the right side of + with the 1 on the left side of +, no one would notice any difference. (Start citing quora answer) Similarly if an observer is looking at a quantum system and observes some probability density $P(1, 2)$, if we swap the electrons 1 and 2, the probability density should stay the same.

$$P(1, 2) = P(2, 1)$$

Equivalently,

$$||\Psi(1, 2)\rangle|^2 = ||Psi(2, 1)\rangle|^2$$

But when we unsquare both sides, we have to attach a phase as shown below

$$|\Psi(1, 2)\rangle = e^{i\Phi} |Psi(2, 1)\rangle$$

where $0 \leq \Phi \leq 2\pi$. 'It turns out that all the fundamental particles correspond to either $\Phi = 0$, called bosons, or $\Phi = \pi$, called fermions.' Hence we obtain the antisymmetry principle for fermions which is

$$|Psi(1, 2)\rangle = -|Psi(2, 1)\rangle$$

Coming back to our case, the combined state of the system will then be

$$|\Phi\rangle = (|A\rangle_1 + |B\rangle_1) \otimes |C\rangle_2 - |C\rangle_1 \otimes (|A\rangle_2 + |B\rangle_2)$$

which can be represented as a determinant of a matrix as shown below:

$$\det \begin{pmatrix} |A\rangle_1 + |B\rangle_1 & |C\rangle_1 \\ |A\rangle_2 + |B\rangle_2 & |C\rangle_2 \end{pmatrix}$$

As you can tell, the more orbitals we have and the more electrons we have, the worse-looking such notation becomes. Here we introduce second quantization through an analogy to violin strings.

Suppose the state of the some system is a violin string, doing some crazy oscillations. To represent that wave, using the fourier series formulas, we deconstruct the complicated wave into sum of simpler waves called vibrational modes. Now each vibrational mode does not contribute equally to the complicated wave. Some modes contribute more than others, represented by the weight or amplitude of the mode a_n . So, we have

$$\text{complicated wave} = \sum_{\text{mode } n}^{\infty} a_n * \text{mode}_n$$

Insert GRAPHIC of wave decomposition.

In this analogy, each mode represents a particular orbital or state and the amplitude refers to the number of particles occupying that state. Notice how in this formulation, we are summing all the modes and not the amplitudes. Each mode mode_n or orbital is assigned an amplitude a_n or number of electrons. The notation is clean and makes sense.

But if we were to sum over the particles or unit amplitudes, suddenly we lose intuition. For example, suppose a k th mode mode_k has the amplitude $a_k = 3$. Since $3 = 1 + 1 + 1$, each 1 or unit amplitude corresponds to a particle. Each of these particles is assigned the same orbital or mode mode_k . So far so good. If we have lets say the mode $(k+1)$ with $a_{k+1} = 1$, what makes the electron or unit amplitude in mode_{k+1} different from the first electron or the first unit amplitude in mode_k ? Nothing. So now we have to account for exchange symmetry and antisymmetry. More specifically, we would have to account for the state where the first electron of mode_k is swapped with the electron in $\text{mode}_{(k+1)}$. And now representing the combined state of the system by summing over all particles will be a nightmare.

And moreover, this method doesn't even make sense. By summing over all the particles, we are summing over all unit amplitudes. But amplitude is just a number not some entity. More appropriate way is to consider the mode as an entity and amplitudes or the number of particles is that mode's weight/contribution to the complicated wave or the combined state.

So the analogy illustrates that it is more intuitive to emphasize how excited each state or orbital is instead of showing what electron occupies what orbital. In fact, assigning numbers to electrons doesn't make sense because they are indistinguishable. And because we did so, we ended up with the horrible notation as a result of the antisymmetry principle. To curb this mess, we can try to avoid assigning numbers or names to electrons and just focus on showing how excited each orbital configuration is.

To show the underlying simplicity of the approach shown in the analogy, we turn back to our example from before. Note that each state will now be

represented as

$$|n_a\rangle_A |n_b\rangle_B |n_c\rangle_C |n_d\rangle_D$$

where each n_i denotes the number of particles in the corresponding orbital. So from previous discussion, Ψ_1 becomes

$$|\Psi_1\rangle = |1\rangle_A |0\rangle_B |0\rangle_C |0\rangle_D + |0\rangle_A |1\rangle_B |0\rangle_C |0\rangle_D$$

or for sake of simplicity

$$|\Psi_1\rangle = |1000\rangle + |0100\rangle$$

and Ψ_2 becomes

$$|\Psi_2\rangle = |0\rangle_A |0\rangle_B |1\rangle_C |0\rangle_D$$

or

$$|\Psi_2\rangle = |0010\rangle$$

Hence the combined state is

$$|\Phi\rangle = (|1\rangle_A |0\rangle_B |0\rangle_C |0\rangle_D + |0\rangle_A |1\rangle_B |0\rangle_C |0\rangle_D) \otimes (|0\rangle_A |0\rangle_B |1\rangle_C |0\rangle_D)$$

which is equivalent to

$$|\Phi\rangle = (|1000\rangle + |0100\rangle) \otimes (|0010\rangle)$$

$$|\Phi\rangle = |1010\rangle + |0110\rangle$$

Notice that $|1010\rangle$ says that 2 electrons occupy orbital A and orbital C. It doesn't matter which electron occupies which because we haven't labeled or assigned an id to each electron. If you were to id each electron as we did previously, then you would have to account for antisymmetry. In other words, in first quantization, we had to explicitly account for indistinguishable particles which made our notation cumbersome. But in second quantization, that notion of exchange symmetry is already embedded into our notation so there is no need to add further details

If particles are reduced to units of excitation under second quantization, what are they excitations of? To explain this, let's turn back to our violin example. Recall that the violin string made some complicated wave and we used fourier analysis to deconstruct that wave into simpler plane waves. In this analogy, the violin string represents a field and those simpler plane waves/modes represent quantum states. Each particle is a unit excitation of some mode in that field. For example, in an ideal hydrogen atom, ignoring the nucleus, the whole atom is a field and the only mode or quantum state contributing to that field/complicated wave is the 1s orbital. Moreover, that 1s orbital would have an amplitude of 1 since that represents a unit excitation in 1s orbital which is the sole electron in 1s orbital. In an ideal lithium atom, we see more quantum states with addition of the 2s orbital. The 1s orbital will now have 2 units of excitation and the 2s orbital will have a single unit, giving us a total of 3 electrons.

At this point we will introduce creation and annihilation operators. Suppose you notice that the k th orbital of some atom/molecule is unoccupied and you want to add an electron to that orbital. Right now, the state is $|0\rangle$ (vacuum state). So what you do is open your second quantization toolkit and pull out the creation operator a_k^\dagger and apply to the vacuum state as shown:

$$|k\rangle = a_k^\dagger |0\rangle$$

By applying that creation operator, you have changed the status of the k th orbital from being unoccupied (being vacuum state) to occupied. To undo this change, we use the annihilation operator as following:

$$|0\rangle = a_k |k\rangle$$

We will use these tools to construct the hamiltonian for the system. Before we dive into the hamiltonian jungle, its important to clarify the nature of orbitals. In the conventional sense, we refer to orbitals as a region within a subshell occupied by 2 electrons with opposite spins. From now on, these orbitals will be referred to as spatial orbitals. These spatial orbitals will each contain 2 spin orbitals which will only occupy 1 electron. This will make representing spin orbitals in terms of quantum states easier as

$$|0\rangle \implies \text{unoccupied}$$

$$|1\rangle \implies \text{occupied}$$

This allows us to use binary representation where each digit corresponds to an orbital. This is utilized in quantum fourier transform and quantum phase estimation algorithms.

3.3 Hartree Fock Theory

To find the total energy of the system, we have to consider 4 factors:

1. Electron-Nucleus attraction (Potential Energy)
2. Electron-Electron repulsion (Potential Energy)
3. Nucleon-Nucleon repulsion (Potential Energy)
4. Kinetic energy of electrons

Since the first and the fourth factors involve only one electron, we group them to construct the following one-electron integral h_{pq}

$$h_{pq} =$$

The second factor involves 2 electrons and hence the corresponding two electron integral is

$$h_{pqrs} =$$

The third factor requires no electrons so we denote it as h_{nuc}

$$h_{nuc} =$$

Note that when we talk about simulating molecules, we use the term “electronic structure” more often as opposed to “molecular structure”. This is because when we zoom down to level of atoms, nucleons are bigger than electrons by 4 orders of magnitude. Hence, we utilize the Born-Oppenheimer approximation, according to which electrons are treated as quantum particles but nuclei are treated as classical particles, fixed in their positions with no kinetic energies. This simplifies the hamiltonian as h_{nuc} is treated as a constant. With all these

To demonstrate the Hartree fock method, we will use an example of the helium atom. Note that helium atom has 2 electrons. The hamiltonian of this system looks something like this:

$$H = \text{Kinetic Energies of electrons} + \text{Electron-Nucleon Repulsions} + \text{Electron-Electron Repulsions}$$

In the first 2 terms, we only work with 1 electron at a time. Computationally, this translates to single-electron integrals with 3 degrees of freedom (because the electrons live in a 3 dimensional space). However, the last term involves 2 electrons. Computationally, this translates to 2-electron integrals with 6 degrees of freedom (3 for each electron). Since each additional degree of freedom is computationally expensive, the last term becomes significantly harder to compute. To avert this mess, Hartree-fock suggested we assign an effective hamiltonian to each electron and introduce mean field operator. The resulting hamiltonians look like this:

$$H_1 = \text{Kinetic Energies of electron 1} + \text{Electron 1-Nucleon Repulsion} + V(r_1)$$

$$H_2 = \text{Kinetic Energies of electron 2} + \text{Electron 2-Nucleon Repulsion} + V(r_2)$$

What is this mean field operator $V(r)$? In Hartree Fock method, we only want to evaluate the single electron integral and not the 2 electron integral.

///Brief Explanation of Hartree Fock Theory

To explain Hartree Fock, we will rely on a high level description analogy by Chemical Physicist Jay Whitfield.

Here is a brief sketch of problem

Problem: Need to compute orbitals of electrons in some atom/molecule.

To do so, you need to evaluate Problem Rephrased:

Solution:

Context of Analogy: Orchestra Players need to tune to a reference note say F. Some players are too sharp. Some players instruments are too flat. No-body has any clue what the real note is.

3.3.1 Initial Guess

The orchestra players start playing their own variation of F.

We pick a certain set of atomic orbitals which may or may not be the true orbitals of the atom.

3.3.2 Calculation of Mean Field

Once everyone starts playing, the players hear the combined note.

We use these orbitals to calculate mean field for each electron in our atomic system. When we have done so, we can start calculating the effective hamiltonians for each of our electrons.

3.3.3 Obtaining New Orbitals

If the player's individual note is sharper than the combined note, then he/she will make the necessary adjustments to make their note flatter. In this sense, all players are trying to converge their sounds to the combined note they heard before.

We use a set of equations to calculate the new orbitals using the hamiltonians obtained from the previous step. Note that ideally orbitals should be eigenstates of their respective hamiltonians. So we should not obtain new orbitals. But if we do obtain new orbitals, then there must be something wrong with our initial orbitals (the ones we guessed and used to calculate the mean field operators). This implies that our mean field operator is also wrong.

OBVIOUS HOLE: If the mean field operator is wrong, how do we know that the new orbitals we obtained are any better than the new orbitals? How do we know that the resultant orbitals are improvement upon the original orbitals? How do we know that SCF converges?

3.3.4 Repeat Process

The players play the modified note and hear the new combined note. The above steps are repeated until every player is in tune with the final combined note.

We keep generating mean operators until the orbitals don't change when acted upon by their hamiltonians. At that point those orbitals won't generate a new mean field. They will keep generating the same mean field..ie the mean field becomes self consistent.

3.4 Post Hartree Fock Methods

3.4.1 Basis Sets

A basis set is comprised of a set of known functions whose linear combo produces an approximation for a molecular orbital (unknown function) Basis Functions = Atomic Orbitals Think of an MO as a vector in a coord space with infinitely many directions. The same coord space is spanned by basis functions. So when you choose a finite basis set, you restrict yourself to calculate MO along those finite directions...and hence obtaining an approximation. Size If basis set is complete (ie there are infinite basis functions), then their combo exactly describes an MO Type The better a single basis function is able to produce an unknown function, the less basis functions we need to approach some re accuracy. Why

Quantum (Maybe) Classical computers cannot work with infinite basis functions...we can't get good accuracy on them Other factors such as integrating over basis function is computationally expensive. 2 types of Basis Functions Slater Type Orbitals Gaussian Type Orbitals - improvement over STOs Difference GTOs have zero slope near nucleus; thus problems in describing electron behaviour near nucleus. STOs just have a cusp near nucleus GTOs fall too rapidly away from nucleus Thus, need more GTOs than STOs to achieve a given level of accuracy (ie to represent each STO, need a lin combo of GTOs) Construction of Basis Sets Terminology A basis function (contracted function) is made of a linear combination of GTOs (primitive function) It contains parameters such as the number of GTOs, the exponents on those GTOs and the coefficients of GTOs Parameters Exponents of GTOs Determine the radial distance (large= tight functions near nucleus; small = better approx tail behavior of wavefunction) Can be determined by variational principle (parameters that give lowest energy are the best) The more the GTOs, the more the exponents that need to be optimized, the more the computational cost.

3.4.2 Need for Post Hartree Fock Methods

Molecular Orbitals (MOs) are made from basis functions which are atomic orbitals. Now Hartree Fock only cares about the ground state MOs which are occupied. The unoccupied virtual MOs are ignored. Thus, HF Slater determinant is formed out of the occupied MOs only. But if we replace the occupied MOs in HF determinant with unoccupied virtual MOs (to represent some form of excitations), we can obtain excited determinants. The number of virtual MOs is dictated by number of basis functions: the larger the basis set, the more the virtual MOs, the more excitations accounted for, the better the approximation for energy Hence, for infinite basis, we recover all the correlation (previously ignored by HF) and therefore Schrodinger equation is solved exactly (we obtain the exact energy eigenvalues)

The single slater determinant means HF ignores correlation

3.5 Unitary Coupled Cluster

Once you have the determinants for the many electron wavefunction, its time to determine the coefficients a 's as shown in the equation below:

Coupled Cluster Exponential operator What do they mean by connected and disconnected types? What is the physical interpretation of product of excitations? Why does CI include that and CC doesn't? Calculation of amplitudes Variational Principle: Choosing a reference wavefunction, by either variational principle or some other method, and then using variational principle again to obtain all the amplitudes (computationally expensive as we are accounting for near infinite excited states) Projecting the SE: Why are we using e^T and Ecc to calculate amplitudes when we use amplitudes to calculate those quantities? WHY is H made from single and doubly occupied shells? 2 confusing assumption in CC Hamiltonian only contains interaction for 2 particles so we can ignore triply

and quadruply excited states That's because triply and higher excited states require more than 2 electrons which is not relevant because Hamiltonian only deals with 2 body systems?!? Brillouin's Theorem Approximation Coefficient on quadruply excited states as product of coefficients on doubly excited states KEY: double excited states...is accounting for any pair of electrons out of N electrons and accounting for all the excited-orbital-configuration KEY: quadruply excited states is taking 4 electrons out of N electrons....which is 2 pairs....so the permutations of exciting 4 electrons is approximately equal to product of permutations of doubly excited states (remember 2 pairs)

Unitary Coupled cluster is just adding Tdagger on top of the exponential operator. This makes operator unitarizes which makes it workable using the variational principle(referenced later)

The UCCSD method, we only look at first and second excitations. If system is strongly correlated or the higher excited states are equivalent in energy to ground states, this method fails massively. BUT for smaller molecules, this serves as a good approximation.

4 Quantum Computing

What do QUantum computers have to offer here? Well calculation of mol. ground state energies requires us to repeatedly create a state and calculate expectation value of that parameterized state w.r.t hamiltonian. these tasks can be efficiently performed on a quantum device.

To further see the correspondence between these methods, we examine quantum encoding methods, which is telling us how to represent the system using qubits.

4.1 Quantum Encoding Methods

Jordan Wigner: Every orbital can be described by a qubit. We already discussed how 0 corresponds to unoccupied and 1 corresponds to occupied. Remember those creation and annihilation operators. Turns out if 0 is $[1 \ 0]$ and 1 is $[0 \ 1]$, then we can write as :- formulas for creat/annhi

We can talk about the anticommuting problem as well

Parity Basis: 1 is occupied and 0 is empty ...qubit i stores sum modulo 2 of occupation of all qubits less than or equal to iso only a single qubit ops is applied to each qubit. But if you change qubit j, now you gotta change all qubits of index less than j . so still linear time

Comparison between Parity and JORDAN: occupation is local but parity is nonlocal. for parity tho, occupation number is nonlocal and parity is local.

Now a faster encoding paradigm exists called bravyi kitaev where every electronic operation only requires $O(\log n)$ time...we achieve that by combining occupation number and parity. How? Even qubits store only their occupation, odd qubits store their occupation + other qubits occupation number mod 2 (parity)

WHAT DO THESE METHODS TELL US: We can encode orbitals into qubits and express creation and annihilation operators as combo of pauli gates. Since creat and annhi ops make us hamiltonian, we see that we can simulate hamiltonian processes using quantum circuits.

4.2 Variational Method

If Ψ_0 denotes the exact ground state wavefunction and E_0 denotes the exact ground state energy, then we get this nice eigenvalue equation.

Now the unknowns in this equations are the exact ground state wavefunction and the exact ground state energy. While we could just find the eigenvalues of the hamiltonian, we don't know the relative wight of those eigenvalues to give us the expectation of energy.

So what we do is we guess the wavefunction and calculate ground state energies accordingly to this equation.

Now this approximate ground state energy will always be an upper bound to the total ground state energy. Variational principle relies on make sure to choose parameters in a way that reach the min energy possible. Then the guess state is really close to exact ground state energy.

Problems with this description: What if we find the smallest eigenvalue and say that the state is exactly that associated eigenstate...no need for this iterative procedure.

4.3 Quantum Computing Tools

Universal feature of quantum algorithms:

1. Initial state must be close to ground state
2. Coherently (without loss of info) implement time evolution under Hamiltonian

Why not QPE: too many gates and large fault tolerance?!? impossible for NISQ.

Empowered with these tools, we can now describe the general approach behind the variational quantum algorithms

1. Initialize state
2. Apply a series of parameterized gates to get ansatz
3. obtain trial wavefunction
4. measure expectation value of molecular hamiltonian ?!?
5. Classical optimization routine —> output new param and prepare new trial state which is ideally lower in energy

***Discussion on hardware efficient and chemically efficient ansatz looks unnecessary.

5 Variational Quantum Eigensolver

5.1 State Preparation

The closer the initial state is to exact ground state, the more likely it is that there will be convergence and variational method is successful. That's why for our ansatz, we use the hartree fock which is a good starting point for uncorrelated systems.

there are other types of ansatz if you are concerned with strongly correlated systems. bc hf then does not have a lot of overlap with exact ground state wavefunction.

5.2 Energy Measurement

After state has been prepared, we move on to energy measurement which boils down to measuring expectation value of each term and combining according to the equation: Now we first have to explain how cluster operators can be represented by simple pauli matrices. Then show how exponentiation of pauli happens and then we can arrive at measuring expectation value of bunch of paulis.

5.3 Parameter Optimization

We can use direct search algos or gradient based methods Eg: Nelder meade Objective Function: Something we have to optimize. Better tackles noise but too many function evaluations to achieve convergence.

What about COYBLA?

Gradient based methods more useful as quantum computers improve. analytically calculating grad..using hammy averaging and quantum circuits to calculate gradient of energy...ultimate cost is of iterations to achieve convergence

5.4 Qiskit Implementation

To tie everything together, we show how to implement VQE algorithm on LIH molecule using IBM's qiskit package and using their quantum computers.