

Numerical Methods for Solving Fermion System Ground State

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Abstract

¹ This article presents numerical methods in solving the ground state of Fermion system, including self-consistent field (SCF) theory and variational monte carlo (VMC). As a demonstration of the algorithms, Helium and Beryllium atoms are solved independently by each algorithm in succession. Then a combination of the two methods is used to produce better ground state for Beryllium atom. It shows that each method alone produces results within 3% of the exact value, while the combination of the two methods reduces the error to 0.1% at least for the systems chosen in the article. (He and Be atoms)

1 Introduction

Hamiltonians for a Fermion system has a general expression as follows:

$$\hat{H} = \frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}, \quad (1)$$

- first two terms are called single body term, representing electron-nucleus interaction;
- last term called many body term, representing electron-electron interaction, which can be then break down into direct term J and exchange term K ;

Without the last term, system eigen states would be simply produced by Slater determinants. Otherwise, the system is not solvable analytically.

Common numerical methods for solving many body quantum systems include Variational Monte Carlo (VMC) [6] methods, density functional theory (DFT) [8], and Self-consistent field (SCF) [1] thoery. These methods use various computational techniques to approximate the solutions to many body quantum systems. This article, in particular, uses self-consistent field (SCF) theory and Variational Monte Carlo (VMC) to solve the ground state of Helium and Beryllium. There are several mature libraries and software packages for quantum Monte Carlo and density functional theory simulation. For example, Quantum ESPRESSO, QMCPACK, CASINO for VMC; NWChem and DFTB+ for DFT.

¹Source code available on Github

But for the purpose of illumination only, in this article I opt to implement them ground up. For the next two chapters I am going to review the principles of the two algorithms and lay out the procedure to solve the specific problems in concern, which is ground state of Helium and Beryllium.

2 Principle

In this chapter, derivation of the whole theory is not the main focus. One can refer to [2] [7] for detailed derivations. Instead, we review important conclusions about and stipulate notations for SCF and VMC.

2.1 Hartree-Fock equations

The Hartree-Fock self-consistent field (SCF) theory is a method used in quantum chemistry to approximate the wave function and energy of a many-electron system. The theory is based on the Hartree-Fock approximation, which assumes that the many-electron wave function can be represented as a determinant, known as Slater determinant, of single-electron wave functions (often not orthogonal), or orbitals. The SCF method involves iteratively solving the Hartree-Fock equations to determine the orbitals and the energy of the system, and then using these solutions as the starting point for the next iteration. This process is repeated until the solutions converge to a self-consistent set of orbitals and energy, which represents the best approximation of the true wave function and energy of the system.

Closed and open shell systems are usually treated differently. In a closed shell system, every electron got paired with another with the same spatial orbit but opposite spin so number of basis functions equal to one half of total number of electrons. The SCF procedure typically converges quickly and accurately, since the electrons are paired and the total spin is zero. In an open shell system, on the other hand, the SCF procedure may take longer to converge and may not be as accurate, due to the presence of unpaired electrons and non-zero total spin. [4] Considering the examples used in this article are inert gases, it makes more sense to use closed shell SCF.

Adapted from original Hamiltonian 1(How?). Hartree-Fock equation for a closed-shell atomic system reads as follows: [5]

$$\hat{f}(r_i) = \hat{h}(r_i) + \sum_{a=1}^{N/2} (2\hat{J}_a(r_i) - \hat{K}_a(r_i)) \quad (2)$$

where

- $\hat{f}(r_i)$: Fock operator;
- $\hat{h}(r_i)$: single body operator;
- $\hat{J}_a(r_i)$: direct operator attributed to electron-electron coulomb repulsion;

- $\hat{K}_a(r_i)$: exchange operator attributed to same-spin electron exchange effect. The factor is half of that of the direct operator.

One strong assumption of SCF is that the composite wavefunction can be written as the determinant of basis functions evaluated at each electron position.

$$\Psi(r_1, r_2, \dots, r_N) = \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_N(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_N) & \psi_2(r_N) & \cdots & \psi_N(r_N) \end{vmatrix}$$

Remember set of basis $\{\psi_1, \dots, \psi_N\}$ is not necessarily orthogonal. The Fock operator under the representation becomes:

$$F_{\mu\nu} = H_{\mu\nu}^{core} + G_{\mu\nu} \quad (3)$$

where

- $H_{\mu\nu}^{core} = \int dv_1 \phi_\mu^*(r_1) \hat{h}_1(r_1) \phi_\nu(r_1)$; $\hat{h}_1(r_1) = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}$; single body term.
- $G_{\mu\nu} = \sum_{a=1}^{N/2} (2(\mu\nu|aa) - (\mu a|a\nu))$
- $(\mu\nu|aa) = \int dv_1 dv_2 \psi_\mu^*(r_1) \psi_\nu(r_1) \frac{1}{r_{12}} \psi_a^*(r_2) \psi_a(r_2)$; direct term.
- $(\mu a|a\nu) = \int dv_1 dv_2 \psi_\mu^*(r_1) \psi_a(r_1) \frac{1}{r_{12}} \psi_a^*(r_2) \psi_\nu(r_2)$; exchange term.

The relation between energy and Fock operator is:

$$E(\Psi(r_1, r_2, \dots, r_N)) = \sum_{\mu, \nu} (H_{\mu\nu} + \frac{1}{2} G_{\mu\nu}) = \frac{1}{2} \sum_{\mu, \nu} (H_{\mu\nu}^{core} + F_{\mu\nu}) \quad (4)$$

However, it is more convenient to choose another set of basis $\{\phi_1, \phi_2, \dots, \phi_N\}$ with relation $\psi_j = \sum_i \phi_i \cdot C_{ij}$, where C_{ij} is called the coefficient matrix. After the transformation fock matrix of the system becomes:

$$\begin{aligned} F_{\mu\nu} &= H_{\mu\nu} + \sum_a \sum_{\lambda, \sigma}^{N/2} C_{\lambda a} C_{\sigma a} (2(\mu\nu|\lambda\sigma) - (\mu\sigma|\lambda\nu)) \\ &= H_{\mu\nu} + \sum_{\lambda, \sigma} P_{\lambda\sigma} ((\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu)) \end{aligned}$$

where

$$P_{\lambda\sigma} = 2 \sum_a^{N/2} C_{\lambda a} C_{\sigma a} \quad (5a)$$

is called density matrix.

The advantage of this approach is that we can calculate and tabulate the matrix elements such as $(\mu\nu|\lambda\sigma)$ once and for all, which is very expensive to calculate. The disadvantage is that the basis set is not orthogonal, which makes the calculation of the energy more complicated.

By minimizing the energy functional $\langle \Psi | \hat{H} | \Psi \rangle$ coefficients can be produced by solving eigen equations over and over again. Each time plug in the old coefficients from the last loop and solve the eigen equations again. This is called SCF procedure. The eigen equation to be solved is called Roothaan-Hall Equations [10]:

$$FC = SC\epsilon \quad (6)$$

where S is the overlap matrix. $S_{ij} := \int dv \phi_i^*(r) \phi_j(r)$ The eigenvalues ϵ are the energies of the basis functions. The eigenvectors $C_{\mu i}$ are the coefficients of the basis functions. I will talk about the precise procedure of implementing solving Roothaan-Hall equation by recursion in chapter 3.2.

2.2 Variational Monte Carlo

3 Procedure

3.1 Model

For simplicity's sake, the system we only consider is a closed shell system where there are $N/2$ different spatial orbits given N electrons. We assume form of the atomic wavefunction is

$$\Psi = \text{Det}(\phi_1(r_1), \phi_2(r_2), \dots, \phi_N(r_N)) \cdot \prod_{i < j} \exp\left(\frac{r_{ij}}{2(1 + \beta_{ij} r_{ij})}\right) \quad (7)$$

where the determinant part encapsulates electron exchange effect while the second part includes electron correlation which is not taken care of by Hartree-Fock approximation.

Slater type orbitals are used for basis functions: [3]

- $\phi_{1s}(r_i) = N_{1s} \exp(-\alpha_1 r_i)$
- $\phi_{2s}(r_i) = N_{2s} (1 - \alpha_2 r_i/2) \exp(-\alpha_2 r_i/2)$
- $\phi_{2p}(r_i) = N_{2p} \alpha_3 \mathbf{r} \exp(-\alpha_3 r_i/2)$
- \vdots

where α and β reflects shielding effect and correlation effect physically. Those parameters are optimized by minimizing the energy of the system. Since SCF is usually faster than VMC, which will be proved in later implementations. All α will be optimized by SCF by finding the minimum of the convergent energy before all β are optimized by VMC by using the very combination of α .

3.2 SCF

Let's observe the roothaan-hall equation 6 again. S is Hermitian and thus can be Diagonalized using $S = T^\dagger \Lambda T$ where T is orthonormal. Define another Hermitian matrix $\chi = T^\dagger \Lambda^{-1/2} T$ and . One can find that $\chi^\dagger \chi = \chi^2 = S^{-1}$. Let define $F' = \chi^\dagger F \chi$ and $C' = X^{-1} C$. Insert $\chi^{-1} \chi$ between F and C , S and C . We can have the eigen equation as follows:

$$F' C' = C' \epsilon \quad (8)$$

However, it is not a trivial eigen system problem because F' is implicitly dependent on its eigen vectors C' . To solve this, we need to first assume a plausible assumption about C matrix use it as first guess to solve the eigen equation. Then we can use the eigen vectors C' to calculate the new F' and use it to solve the eigen equation again. This process is called recursion. The recursion is terminated when the difference between the new F' and the old F' is small enough. Summarizing the procedure of SCF:

1. Specify system and basis set $\{\phi_1, \dots, \phi_{N/2}\}$
2. Calculate one and two-electron integrals
3. Diagonalise the overlap matrix, to obtain a transformation matrix, $\chi = S^{-1/2}$
4. Provide initial guess as to the density matrix.
5. Caculate G matrix ($2J - K$) using P and the two-electron integrals
6. Obtain Fock matrix from sum of the core Hamiltonian matrix and G matrix, $F = H^{core} + G$
7. Caculate transformed Fock matrix $F' = \chi^\dagger F \chi$
8. Diagonalize F' to get C'
9. Caculate the real coefficient matrix $C = \chi C'$
10. These coefficients form the new matrix P
11. Determine convergence of the density matrix, by comparing the new density matrix with the old density matrix within a specified criterion. If the convergence has not been met then return to step (5) with the new density matrix P to form a new Fock matrix and repeat
12. If convergence has been met then end the SCF cycle and return desired quantities, e.g. Energy, coefficient matrix.

If convergence has been met then end the SCF cycle and return desired quantities, e.g. Energy, coefficient matrix. The process can be sumarized as following figure:

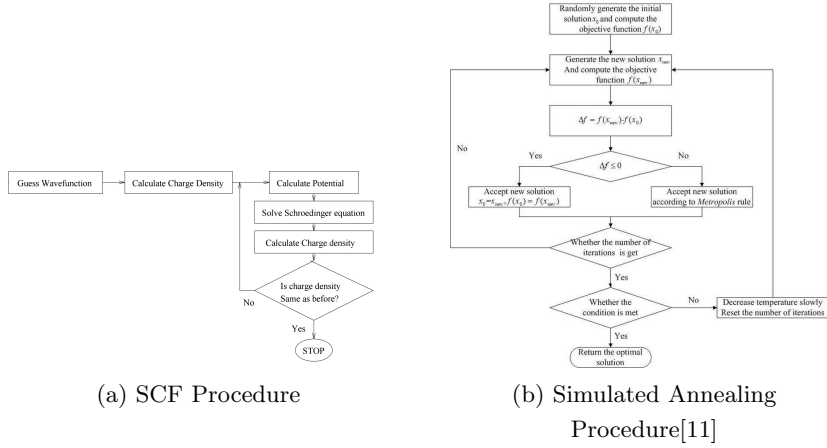


Figure 1: Flowchart of SCF algorithms

Now we think SCF as a black box. It takes into parameters like α and β of the basis functions and produces energy and convergent coefficient matrix. The next goal is to find the optimal parameters that makes energy as low as possible. This would mean we need to search over the parameter space to find the best configuration of α and β . Brute force iteration can always acheive the goal, namely, iterate all possible combination of α and β and record the lowest energy. Also we can vectorize and parallelize the code since results are independent for different set of parameters. However, as the number of parameters grows, time complexity grows exponentially. In that case we have to resort to simulated annealing to probe the optimal parameters. [9]

The process of simulated annealing involves iteratively perturbing the current state of a system and then accepting or rejecting the new state based on its energy. If the new state has a lower energy, it is always accepted. If the new state has a higher energy, it is sometimes accepted, with the probability of acceptance determined by a "temperature" parameter. This temperature is gradually reduced over time, which helps the algorithm escape local minima and converge on the global minimum. Diagrammatically, the process looks like figure 1

3.3 VMC

The process of VMC involves two main steps:

1. Finding a trial wave function that is a good approximation of the true ground state wave function
2. Using Monte Carlo sampling to compute expectation values of the Hamiltonian with respect to the trial wave function.

In the first step, the trial wave function is parameterized using a set of adjustable parameters. These parameters are chosen to minimize the so-called "variational energy", which is the expectation

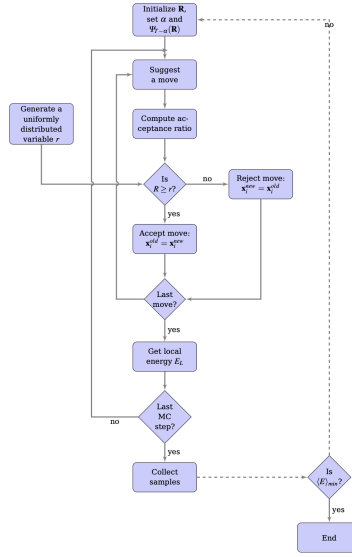


Figure 2: Flowchart of VMC algorithms

value of the Hamiltonian with respect to the trial wave function. This step is usually performed using some form of optimization algorithm, such as gradient descent or simulated annealing.

In the second step, the trial wave function is used to generate a set of random samples from the many-body system. These samples are then used to compute the expectation values of the Hamiltonian and other physical observables. Because the trial wave function is a good approximation of the true ground state wave function, the expectation values computed using VMC are also good approximations of the true values. As is shown by figure 2.

4 Initialization

4.1 SCF

4.2 VMC

5 Results

5.1 SCF–Beryllium

5.2 VMC–Helium

5.3 Combination

6 Conclusion

References

- [1] J.P. Desclaux. “Hartree Fock Slater self consistent field calculations”. In: *Computer Physics Communications* 1.3 (1970), pp. 216–222. ISSN: 0010-4655. DOI: [https://doi.org/10.1016/0010-4655\(70\)90008-1](https://doi.org/10.1016/0010-4655(70)90008-1). URL: <https://www.sciencedirect.com/science/article/pii/0010465570900081>.
- [2] Pablo Echenique and José Luis Alonso. “A mathematical and computational review of Hartree–Fock SCF methods in quantum chemistry”. In: *Molecular Physics* 105.23-24 (2007), pp. 3057–3098.
- [3] Morten Hjorth-Jensen. “COMPUTATIONAL PHYSICS Morten Hjorth-Jensen”. In: ().
- [4] Van Alsenoy C Lehtola S Blockhuys F. “An Overview of Self-Consistent Field Calculations Within Finite Basis Sets”. In: *Molecules* 1218.25 (2020). DOI: 10.3390/molecules25051218.
- [5] I.N Levine. *Quantum Chemistry*. 4th. Prentice-Hall, 1991, pp. 407–408.
- [6] W. L. McMillan. “Ground State of Liquid He⁴”. In: *Phys. Rev.* 138 (2A Apr. 1965), A442–A451. DOI: 10.1103/PhysRev.138.A442. URL: <https://link.aps.org/doi/10.1103/PhysRev.138.A442>.
- [7] R J Needs et al. “Continuum variational and diffusion quantum Monte Carlo calculations”. In: *Journal of Physics Condensed Matter* 22.2 (2009). <http://arxiv.org/pdf/1002.2127>, p. 023201. DOI: 10.1088/0953-8984/22/2/023201. URL: <https://arxiv.org/abs/1002.2127>.
- [8] Robert G Parr. “Density functional theory”. In: *Annual Review of Physical Chemistry* 34.1 (1983), pp. 631–656.

- [9] Martin Pincus. “Letter to the Editor—A Monte Carlo Method for the Approximate Solution of Certain Types of Constrained Optimization Problems”. In: *Operations Research* 18.6 (1970), pp. 1225–1228. DOI: 10.1287/opre.18.6.1225. eprint: <https://doi.org/10.1287/opre.18.6.1225>. URL: <https://doi.org/10.1287/opre.18.6.1225>.
- [10] C. C. J. Roothaan. “New Developments in Molecular Orbital Theory”. In: *Rev. Mod. Phys.* 23 (2 Apr. 1951), pp. 69–89. DOI: 10.1103/RevModPhys.23.69. URL: <https://link.aps.org/doi/10.1103/RevModPhys.23.69>.
- [11] Ai-Hua Zhou et al. “Traveling-Salesman-Problem Algorithm Based on Simulated Annealing and Gene-Expression Programming”. In: *Information* 10 (Dec. 2018), p. 7. DOI: 10.3390/info10010007.