

Numerical Methods for Solving Fermion System Ground State

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Abstract

⁰ 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) [4] methods, density functional theory (DFT) [6], 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.

⁰Source 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] [5] 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.

Adapted from original Hamiltonian 1(How?). Hartree-Fock equation for a closed-shell atomic system reads as follows: [3]

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

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 $\{\psi_1, \dots, \psi_m\}$ 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:

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

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.

2.2 Variational Monte Carlo

3 Procedure

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

$$\Psi = \text{Det}(\phi_1(r_1), \phi_2(r_2), \dots, \phi_N(r_N)) \cdot \prod_{i < j} \exp\left(\frac{r_{ij}}{2(1 + \beta_{ij} r_{ij})}\right) \quad (5)$$

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.

For the basis function set, Slater type orbitals are used.

3.1 SCF

3.2 VMC

3.3 Combintation

4 Initialization

4.1 SCF

4.2 VMC

5 Results

6 Conclusion

References

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