

Iterative Techniques for the N-electron Hamiltonian: The Hartree-Fock method

Tony Hyun Kim

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I wish to give an introduction to iterative techniques for solving the interacting N -electron Hamiltonian. My intent is to take the reader to a point where he or she is able to implement a computer program for the N -electron problem. Such numerical methods are extremely relevant in fields such as computational chemistry, where it is utilized to calculate *ab initio* (i.e. without relying on empirical parameters) various quantities of great modern interest, such as reactivities of molecules and mechanisms of chemical reactions. The general outline follows:

1 Introduction

I will introduce the notion of iteration for a multi-particle Hamiltonian by a discussion of the Hartree method. The initial argument is meant to be intuitive and appealing, but will fall short on three points:

1. The Hartree method ignores the antisymmetry requirement for the many-electron wavefunction.
2. It is not clear how the intuitive arguments of the method connect explicitly to the principles of QM. We will show that the technique is an advanced application of the variational principle.
3. Coordinate-space integration of the Hamiltonian is difficult. Since we seek bound states, there will be some R such that when $|\vec{x}| > R$, the electron is in a classically forbidden region, e.g. $E - V(\vec{x}) < 0$. This means that we are attempting to integrate an ODE over a region where one of the modes is a growing exponential $Ae^{x/L}$. Since we seek bounded solutions, our conditions must be such that the coefficient A is precisely zero. My previous experience in integrating the Schroedinger equation by “stepping” methods (of varying complexity) has shown me that this feat is remarkably tricky, involving a careful choice of integration bounds and other “fudge” factors. I wish to introduce a mathematical technique that can convert the spatial iteration equations into a matrix equation, which are much more tractable, and are actually how Hamiltonian solvers are implemented in practice.

2 Slater determinant wavefunctions

The main technique I will be describing is called the Hartree-Fock (HF) method. With HF, we make the fundamental assumption that the many particle wavefunction Ψ can be written as a single Slater determinant.

Hence, we are assuming that the coordinates of the N -electrons are *separable* into some set of single-particle wavefunctions $\chi_i(\vec{x}_j)$ which have yet to be determined.

Because HF is a determinant-wavefunction theory, we will need ability in calculating with Slater determinants. For the purposes of this paper, it will be sufficient to discuss:

1. How to evaluate matrix elements of the form $\langle \Psi | H | \Psi \rangle$: Here I will discuss the organization of this matrix element into its “one-electron” and “two-electron” parts.
2. How Ψ responds to a unitary transformation $\chi_i \rightarrow \chi'_i$ of the single-particle wavefunctions. The main point here is that matrix elements of the form $\langle \Psi | H | \Psi \rangle$ are invariant to a unitary transform of the single particle states that comprise Ψ .

3 Derivation of Hartree-Fock from the Variational Principle

The iterative equation will be derived by applying the calculus of variations on the functional $E_0 = \langle \Psi | H | \Psi \rangle$. We will find that the equation is identical to that of the intuitive Hartree method, save for an additional term called the “exchange term” which follows from the determinantal wavefunction. The theoretical derivation of the HF equation ends here.

Next, I will begin to simplify the equation, by integrating out the spin variable. In addition, for the implementation that follows, we will assume that N is even, so that the $N/2$ spatial wavefunctions of lowest energy are each occupied by a pair of electrons with opposite spin. Although not essential to the theory, this “closed-shell” restriction makes the subsequent implementation simpler.

4 Roothaan’s equations

In this section, I will demonstrate how to convert the iterative equations (integro-differential in space) to a set of matrix equations.

We will get a chance to define a bewildering number of matrices: $S_{\mu\nu}$, $H_{\mu\nu}^{core}$, $T_{\mu\nu}$, $V_{\mu\nu}^{nucl}$, $P_{\mu\nu}$, $G_{\mu\nu}$, $F_{\mu\nu}$, $C_{\mu\nu}$. There are no new physical concepts associated with these new quantities, but they are simply objects that arise when we convert the iterative equations into matrix form. In addition, many of these have simple physical meaning, and will make the HF iterative procedure easier to understand and describe.

At this point, it will be possible to algorithmically describe the implementation of HF on a computer.

5 Calculations on HeH+

Following the very heavy discussion of theory and linear algebra, I wish to reinforce to the reader why we are interested in this entire business in the first place. To that effect, I will report the result of my calculation on two physically meaningful quantities:

- The equilibrium bond length of HeH+;

- The electrostatic potential surface of HeH⁺ (something like this: <http://content.answers.com/main/content/wp/en-commons/thumb/7/7f/200px-Nitrate-ion-elpot.png>. These are familiar pictures from my chemistry courses and I've always wanted to know how to compute them "by hand.")

6 Appendix A: Further mathematical details

Here are a few items that I wish to take for granted in the main paper without derivation. They are actually quite simple, I only relegate them here for the sake of continuity in the main text.

- The Lagrange multiplier matrix $\epsilon_{\mu\nu}$ is Hermitian. (Section 3)
- The overlap matrix $S_{\mu\nu}$ is positive-definite. (Section 4)
- Results used for the integration of Gaussian basis sets. (Appendix B)

7 Appendix B: Matlab code for Hartree-Fock implementation

I will include my implementation of Hartree-Fock used for the HeH⁺ calculations.

References:

- [1] Szabo and Ostlund. *Modern Quantum Chemistry*. (New York: McGraw-Hill, Inc., 1989)
 - [2] Bethe and Jackiw. *Intermediate Quantum Mechanics*. (California: Benjamin/Cummings Publishing Company, 1986)
- and, of course:
- [3] Griffiths. *Introduction to Quantum Mechanics*. (New York: Prentice Hall, 2005)

Peer Editor

Connor McEntee

Contact

Tony Kim
kimt@mit.edu