

Lab Course of Scientific Computing

Quantum Many-Body Simulations in Haskell using the Hartree-Fock Method

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1. Simple Quantum Systems

In this chapter simple quantum systems will be studied. Consider a particle in a three-dimensional potential $V(\vec{x})$. The corresponding wave function $\psi(\vec{x}, t)$ is the solution of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x}, t) = H\psi(\vec{x}, t) = -\frac{\hbar^2}{2m} \Delta \psi(\vec{x}, t) + V(\vec{x})\psi(\vec{x}, t), \quad (1)$$

where Δ is the Laplacian differential operator: $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. For a time-independent potential $V(\vec{x})$ the Schrödinger equation can be formally solved by

$$\psi(\vec{x}, t) = U(t, t_0)\psi(\vec{x}, t_0) = \exp \left\{ -\frac{i(t-t_0)}{\hbar} H \right\} \psi(\vec{x}, t_0). \quad (2)$$

For a time-dependent potential like an oscillating laserfield, the time evolution of the wave function becomes

$$\begin{aligned} \psi(\vec{x}, t) &= U(t, t_0)\psi(\vec{x}, t_0) = \hat{T}_t \exp \left\{ \frac{i}{\hbar} \int_{t_0}^t H(\tau) d\tau \right\} \psi(\vec{x}, t_0) \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n \hat{T}_t \{ H(t_1)H(t_2)\dots H(t_n) \}, \end{aligned} \quad (3)$$

where \hat{T}_t is the time ordering operator. A simple approach is to divide the interval $[0 \dots t]$ into a sequence of N steps so that

$$U(t, t_0) = U(t, t_{N-1}) \dots U(t_2, t_1)U(t_1, t_0) \quad (4)$$

and to neglect small deviations of the Hamiltonian in the small interval $\Delta t = t_n - t_{n-1}$.

1.1. Discretization of the kinetic Energy

Dividing the Hamiltonian H into $H = T + V$, the non-local kinetic energy operator can be written as

$$T\psi(\vec{x}, t) = -\frac{\hbar^2}{2m} \Delta \psi(\vec{x}, t). \quad (5)$$

1.1.1. Method of Finite Differences

Taking a grid (k, l, m) in three dimensions, the kinetic energy operator can be approximated by finite differences

$$T\psi(\vec{x}, t) = -\frac{\hbar^2}{2m} \left(\frac{\psi_{(k+1,l,m)}^n - 2\psi_{(k,l,m)}^n + \psi_{(k-1,l,m)}^n}{\Delta x^2} + \frac{\psi_{(k,l+1,m)}^n - 2\psi_{(k,l,m)}^n + \psi_{(k,l-1,m)}^n}{\Delta y^2} + \frac{\psi_{(k,l,m+1)}^n - 2\psi_{(k,l,m)}^n + \psi_{(k,l,m-1)}^n}{\Delta z^2} \right) \quad (6)$$

with higher order terms $\mathcal{O}(\Delta x^2, \Delta y^2, \Delta z^2)$ where n represents the discrete time index of the wave function. Considering the time independent Schrödinger equation we can write the operator in one dimension as a matrix satisfying the eigenvalue equation

$$\begin{bmatrix} 2 & -1 & & \dots & 0 \\ -1 & 2 & -1 & & \vdots \\ \vdots & \ddots & \ddots & \ddots & \\ & & -1 & 2 & -1 \\ 0 & \dots & -1 & 2 \end{bmatrix} + V_{kk} \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_k \\ \vdots \\ \psi_N \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_k \\ \vdots \\ \psi_N \end{pmatrix} \quad (7)$$

where $\vec{\psi}$ are the values of the wave function on the evaluation points x_k . V_{kk} represents the potential for each x_k , thus it is a diagonal matrix.

For the example of a particle in a box the potential is

$$V_{kk} = \begin{cases} \infty & \text{for } k = 0, k = N \\ 0 & \text{else} \end{cases} . \quad (8)$$

Solving the above eigenvalue equation yields the eigenfunctions ψ_n with eigenenergies E_n . The boundary conditions $V = \infty$ at $k = 0$ and $k = N$ are satisfied even when the boundary conditions are left out. An example of the first four eigenstates is shown in figure 1. To reduce the problem of a particle in three dimensions to a simple matrix equation, the spatial wave function $\vec{\psi}$ can be stacked, to obtain an

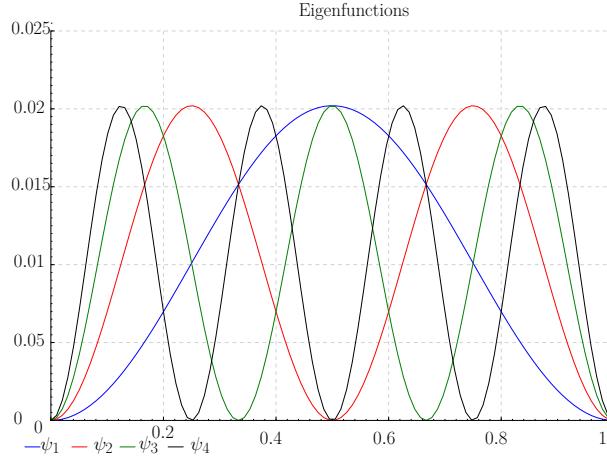


Figure 1: Probability densities for the calculated eigenfunctions ψ_n , with the method of finite differences and a grid of $N = 100$ for $n = 1, 2, 3$ and 4 in one dimension. For simplicity the pre-factor $\frac{\hbar^2}{2m}$ was set to one, obtaining non-normalized eigenfunctions.

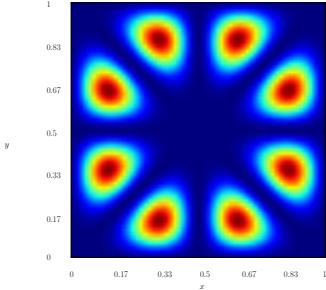
N^3 dimensional vector

$$\vec{\psi}_{k,l,m} = \begin{pmatrix} \vec{\psi}_{1,1,m} \\ \vdots \\ \vec{\psi}_{1,N,m} \\ \vdots \\ \vec{\psi}_{N,1,m} \\ \vdots \\ \vec{\psi}_{N,N,m} \end{pmatrix}, \text{ through nested vectors.} \quad (9)$$

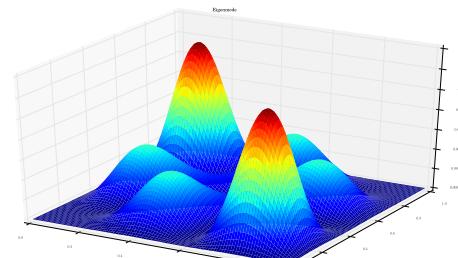
For two dimensions the approximated kinetic energy operator T thus becomes the tridiagonal block matrix

$$T \approx \begin{pmatrix} 4 & -1 & & & & & & 0 \\ & \ddots & & & & & & \\ & -1 & 4 & & & & -1 & \\ -1 & & & 4 & -1 & & & \ddots \\ & \ddots & & & \ddots & & & \\ 0 & & -1 & & & -1 & 4 & \end{pmatrix}. \quad (10)$$

In figure 2(a) an example of an eigenstate for a particle in a two dimensional box is shown.



(a) Color map, ψ_{12} , $N = 60$.



(b) Surface graphic, ψ_{34} , $N = 100$.

Figure 2: Probability densities for the calculated eigenfunctions with the method of finite differences and a grid of $N = 100$ and $N = 60$ in two dimensions. For simplicity the pre-factor $\hbar^2/2m$ was set to one, obtaining non-normalized eigenfunctions.

In three dimensions, we obtain a N^3 -dimensional Matrix, for example for $N = 2$:

$$T \approx \begin{pmatrix} & & & & & 0 \\ & 6 & -1 & -1 & -1 & \\ & -1 & 6 & -1 & -1 & -1 \\ & -1 & -1 & 6 & -1 & -1 & -1 \\ & -1 & -1 & -1 & 6 & -1 & -1 \\ & -1 & & -1 & -1 & 6 & -1 & -1 \\ & & -1 & & -1 & -1 & 6 & -1 \\ 0 & & & -1 & & -1 & -1 & 6 \end{pmatrix}$$

Still Missing: Comparison with exact results

Referring back to the time expansion in chapter 1, the time evolution of an eigenfunction of the hamiltonian is trivial, since ψ_t only differs in phase from the initial state ψ_0 , so $|\psi_t|^2$ is time-independent, although linear combinations of eigenfunctions depend on time, which will not be calculated here.

If we take the computing time into account, it is obvious that even with a small grid size $N < 100$ and parallelized computing the simulation of a particle in a square well potential lead to unexecutable applications. The increase of dimensions with

constant gridsize results in a growing computing time higher than $\mathcal{O}(t_0^n)$.

To proceed to coupled quantum mechanical systems it seems to be mandatory to use efficient approximations.

2. Many-Body Simulations

Consider a real physical system, where particles are not independent like in atoms, ions, molecules, etc. . Assuming the system consists only of K nuclei and N electrons the hamiltonian consists of the terms

$$H = T_i + T_n + V_{ii} + V_{in} + V_{nn} ,$$

where T_i and T_n are the kinetic energies of the electrons and nuclei, respectively. V_{ii} represents the Coulomb repulsion between electrons, V_{nn} between the nuclei and V_{in} the attraction between electrons and nuclei. So the hamiltonian reads

$$\begin{aligned} H = & \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{n=1}^K \frac{P_n^2}{2M_n} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i,j=1, i \neq j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^K \sum_{n=1}^N \frac{Z_n e^2}{|\mathbf{r}_j - \mathbf{R}_n|} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n,n'=1; n \neq n'}^K \frac{Z_n Z_{n'} e^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|}, \end{aligned}$$

where m is the electron mass and M_n the nuclei mass. The index i refers to the electrons, the index n to the nuclei. This hamiltonian describing the system looks quite complicated and in fact, computing the dynamics of this system seems to be unsolvable even for a few particles and an efficient super computer. Therefore, approximations must be made, still comprising the important information about the system. One approach is the Born-Oppenheimer approximation. It uses the fact that the nuclei are much heavier than the electrons, so the motions of the nuclei are much slower compared to the electrons, justifying to neglect the coulomb repulsion between the nuclei and the kinetic energy of the nuclei, so the approximated hamiltonian becomes

$$H_{\text{BO}} = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i,j=1, i \neq j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^K \sum_{n=1}^N \frac{Z_n e^2}{|\mathbf{r}_j - \mathbf{R}_n|}. \quad (11)$$

The positions of the nuclei can be varied to find the minimum of the total energy.

2.1. The Hartree-Fock Method and Equations

In equation (11) the antisymmetry of the fermion wave functions was not taken into account. Fock extended the so called *Hartree equation* by taking antisymmetry into account. The derivation of the *Hartree* and *Hartree-Fock equations* will not be given here, since the main aim here is the implementation of the method. Therefore see e.g. [3, p. 56-60] and [2, chapter 3]. The *Fock operator* is in natural units given by

$$\begin{aligned} \mathcal{F}\psi_k = & \left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \right] \psi_k(\mathbf{x}) + \sum_{l=1}^N \int d\mathbf{x}' |\psi_l(\mathbf{x}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_k(\mathbf{x}) \\ & - \sum_{l=1}^N \int d\mathbf{x}' \psi_l^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_k(\mathbf{x}') \psi_l(\mathbf{x}), \end{aligned} \quad (12)$$

satisfying the *Hartree-Fock equation*

$$\mathcal{F}\psi_k = \epsilon_k \psi_k.$$

The fourth term in equation (12) is called the exchange term [3, p. 55] and is nonlocal since the operator is acting on ψ_k , but the value at the position \mathbf{r} is determined by the value assumed by ψ_k at all possible positions \mathbf{r}' . The eigenvalues ϵ_k of the Fock operator are related to the total energy by

$$\begin{aligned} E = & \frac{1}{2} \sum_k [\epsilon_k + \langle \psi_k | h | \psi_k \rangle], \text{ with} \\ \langle \psi_k | h | \psi_k \rangle = & \int d^3\mathbf{x} \psi_k^*(\mathbf{x}) \left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \right] \psi_k(\mathbf{x}). \end{aligned}$$

It is obvious that the Fock operator in equation (12) which acts on ψ_k also depends on ψ_k itself.

2.2. The Roothaan Equation

For molecules numerical basis sets are not efficient, so we use atom centered basis sets to describe the molecular orbital

$$\psi_k(\vec{x}) = \sum_{p=1}^M C_{pk} \chi_p(\vec{x}), \quad (13)$$

with $k = 1, \dots, M$, where M is the number of basis states. So the Hartree-Fock equation reads

$$\mathcal{F}(\vec{x})\psi_k(\vec{x}) = \epsilon_k\psi_k(\vec{x}). \quad \text{Using Eq. (13) yields}$$

$$\mathcal{F}(\vec{x}) \sum_{p=1}^M C_{pk}\chi_p(\vec{x}) = \epsilon_k \sum_{p=1}^M C_{pk}\chi_p(\vec{x}).$$

We can now multiply from the left by a specific basis function χ_ν . Integrating over the space yields

$$\sum_{p=1}^M C_{pk} \int \chi_\nu^*(\vec{x}) \mathcal{F}(\vec{x}) \chi_p(\vec{x}) d^3\vec{x} = \epsilon_k \sum_{p=1}^M C_{pk} \int \chi_\nu^*(\vec{x}) \chi_p(\vec{x}) d^3\vec{x}.$$

This can be written in matrix notation of the Hartree-Fock equations, expressed in the atomic orbital basis:

$$\sum_{p=1}^M C_{pk} F_{\nu p} = \epsilon_k \sum_{p=1}^M C_{pk} S_{\nu p}$$

$$\mathbf{FC}_k = \epsilon_k \mathbf{SC}_k, \quad (14)$$

which is called the *Roothaan equation*. Since the Fock operator itself depends on \mathbf{C}_k we have the problem of self consistency, because \mathcal{F} has the solution already inside. The Self Consistent Field Method (SCF) uses the approach to solve the above equation iteratively, until the solution deviates only small from the next iteration.

Equation (14) looks similar to the Hartree-Fock equation, but here \mathbf{S} is the overlap matrix for the given orbital basis $\chi_p(\mathbf{r})$. In comparison with eq. (12) we can write the Fock matrix as [3]

$$F_{pq} = h_{pq} + \sum_k \sum_{rs} C_{rk}^* C_{sk} (2 \langle pr|g|qs \rangle - \langle pr|g|sq \rangle),$$

where h_{pq} is identified with the first term of the Fock operator

$$h_{pq} = \langle p|h|q \rangle = \int d^3r \chi_p^*(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|\mathbf{R}_n - \mathbf{r}|} \right] \chi_q(\mathbf{r}).$$

The terms $\langle pr|g|qs \rangle$ and $\langle pr|g|sq \rangle$ are the two-electron integrals given by

$$\langle pr|g|qs \rangle = \int d^3r_1 d^3r_2 \chi_p^*(\mathbf{r}_1) \chi_r^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_q(\mathbf{r}_1) \chi_s(\mathbf{r}_2).$$

Here p, q, r and s label the basis functions and k labels the orbitals ϕ_k . For simplicity and implementation it is convenient to define the density matrix as

$$P_{pq} = 2 \sum_k C_{pk}^* C_{qk},$$

where the factor 2 is conventionally due to the spin [3]. Now the Fock matrix reads

$$F_{pq} = h_{pq} + \sum_{rs} P_{sr} (2 \langle pr|g|qs \rangle - \langle pr|g|sq \rangle).$$

In this orbital representation the energy is given by

$$E = \sum_{pq} P_{pq} h_{pq} + \frac{1}{2} \sum_{pqrs} P_{pq} P_{sr} \left[\langle pr|g|qs \rangle - \frac{1}{2} \langle pr|g|sq \rangle \right].$$

2.3. Program Structure

Here a general overview of the general program structure will be given. As outlined before it is important to consider a suitable set of basis functions describing the electrons electrons of the atoms. The accuracy and efficiency of the basis largely depend on the choice of the basis functions, so they need to be chosen carefully. For suitable calculations we use gaussian basis functions, so the important integrals can be calculated analytically. For a more detailed view on basis functions, see appendix A. Below the program procedure is sketched.

1. Input data:

Here the basis sets as well as the geometry of the atoms in the molecule will be provided and parsed to the program. Furthermore the numbers of electrons N and the atomic charge numbers Z_n are needed as input.

2. Calculate independent matrices

All matrices that are independent of the eigenvectors \mathbf{C}_k can be calculated:

- The overlap matrix S_{pq} ,
- The two-electron integrals $\langle pr|g|qs \rangle$,

- The uncoupled one-electron Hamiltonian h_{pq} .
- 3. Make an initial guess for the density matrix \mathbf{P} .**

A possibility is to use $\mathbf{P} = 0$ as an initial guess, which means that the electrons only feel the nuclei but not each other.

4. Self-consistency procedure

This program section is the most important, since it solves the Roothaan equation recursively. It consists of the following steps.

- Calculate the Coulomb and exchange contributions to the Fock matrix,
- Construct the Fock matrix,
- Solve the Roothaan equation by diagonalization of the Fock matrix for the given density matrix \mathbf{P} ,
- With the obtained eigenvectors a new density matrix \mathbf{P} is constructed.

5. Output data

The output is the converged eigenstates \mathbf{C}_k and its corresponding Fock levels.

In figure 3 a schematic representation of the general program scheme is shown.

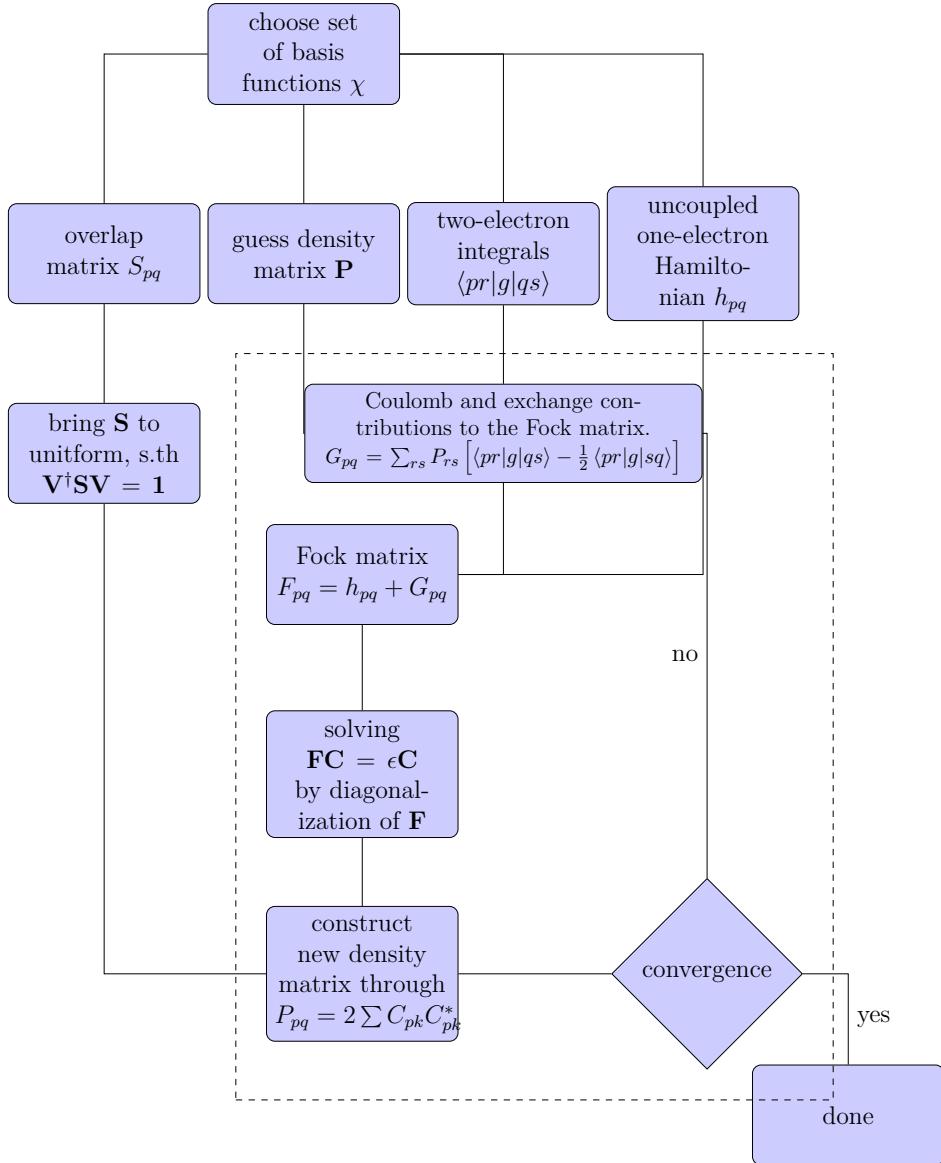


Figure 3: General scheme of the program structure.

Appendices

A. Basis Functions

References

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