Hartree-Fock

It is probably the simplest method to treat the many-particle system. The dynamic many particle problem is replaced by an effective one-electron problem: electron is moving in an effective static potential field.

It can be viewed as a variational method where the full many-body wave function is replaced by a single Slater determinant. The elements of the determinant are one electron orbitals with orbital and spin part.

It can also be viewed as the lowest order term in perturbative expansion (linear in U) with respect to interaction between electrons.

These two views will be substantiated below by equations. But first we will use decoupling method to derive the Hartree-Fock equations.

In the second quantization, the many electron problem takes the form

$$H = \int d\mathbf{r}\Psi^\dagger(\mathbf{r})[-\frac{1}{2}\nabla^2+V_{ext}(\mathbf{r})]\Psi(\mathbf{r})+\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\Psi^\dagger(\mathbf{r})\Psi^\dagger(\mathbf{r}')v_c(\mathbf{r}-\mathbf{r}')\Psi(\mathbf{r}')\Psi(\mathbf{r})$$

(1)

where $\Psi(\mathbf{r})$ is the field operator of electron, $V_{ext}(\mathbf{r})$ is the potential of nucleous and $v_c(\mathbf{r}-\mathbf{r}')$ is the Coulomb interaction $1/|\mathbf{r}-\mathbf{r}'|$. We assumed Born-Oppenheimer approximation for nuclei motion (freezing them since their kinetic energy is of the order of M_{nuclei}/m_e).

The Hartree-Fock approximation replaces the two-body interaction term by an effective one body term

$$\Psi^\dagger(\mathbf{r})\Psi^\dagger(\mathbf{r}')\Psi(\mathbf{r}')\Psi(\mathbf{r}) \rightarrow \langle\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})\rangle\Psi^\dagger(\mathbf{r}')\Psi(\mathbf{r}') + \langle\Psi^\dagger(\mathbf{r}')\Psi(\mathbf{r}')\rangle\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}) \quad (2)$$

$$-\langle\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}')\rangle\Psi^\dagger(\mathbf{r}')\Psi(\mathbf{r}) - \langle\Psi^\dagger(\mathbf{r}')\Psi(\mathbf{r})\rangle\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}') \quad (3)$$

With the generalized density $\rho(\mathbf{r},\mathbf{r}') = \langle\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r}')\rangle$ the effective Hartree-Fock Hamiltonian takes the form

$$H^{eff} = \int d\mathbf{r}d\mathbf{r}'\Psi^\dagger(\mathbf{r})\left\{\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + \int d\mathbf{r}''\rho(\mathbf{r}'',\mathbf{r}'')v_c(\mathbf{r}''-\mathbf{r})\right]\delta(\mathbf{r}-\mathbf{r}')\right.$$

$$\left.-\rho(\mathbf{r}',\mathbf{r})v_c(\mathbf{r}'-\mathbf{r})\right\}\Psi(\mathbf{r}')$$

- H_{eff} is a one-particle Hamiltonian

- The effective potential is non-local (very different from the LDA approximation)

- Higher order terms in perturbative expansion are completely neglected (so-called correlation part in Density Functional Theory)

If we write the field operator Ψ in one electron basis

$$\Psi(\mathbf{r}) = \sum_\alpha \psi_\alpha(\mathbf{r}) c_\alpha \tag{5}$$

where c_α creates an electron in one electron state $\psi_\alpha(\mathbf{r})$ we get

$$H^{eff} = \sum_{\alpha\beta} H^{eff}_{\alpha\beta} c^\dagger_\alpha c_\beta \tag{6}$$

where

$$H^{eff}_{\alpha\beta} = H^0_{\alpha\beta} + \sum_{ab} (U_{a\alpha b\beta} - U_{a\alpha\beta b}) n_{ab} \tag{7}$$

with $n_{ab} = \langle c^\dagger_a c_b \rangle$ and matrix elements

$$H^0_{\alpha\beta} = \langle \psi_\alpha | -\frac{1}{2}\nabla^2 + V_{ext} | \psi_\beta \rangle \tag{8}$$

$$U_{\alpha\beta\gamma\delta} = \langle \psi_\alpha(\mathbf{r})\psi_\beta(\mathbf{r}') | v_c(\mathbf{r} - \mathbf{r}') | \psi_\gamma(\mathbf{r})\psi_\delta(\mathbf{r}') \rangle \tag{9}$$

If the one electron orbitals ψ_α are othogonal, we are done.

First, we need to calculate matrix elements of H^0 and U. Then we can proceed to construct $H^{eff}_{\alpha\beta}$ according to Eq. (7) and finally we can diagonalize the matrix $H^{eff}_{\alpha\beta}$. In Eq. (7) the sum over a and b runs over all occupied states only (since $n_{ab} = \delta_{ab}n_a$ is 0 for unoccupied and 1 for occupied eigenstates). Weather the orbital is occupied or not, we know only after we calculate the one-electron levels, i.e., diagonalize $H^{eff}_{\alpha\beta}$ by $\langle \psi_\alpha | H^{eff} - \varepsilon | \psi_\beta \rangle = 0$. Hence, the system of equations needs to be solved self-consistently by iteration.

# Interpretation in terms of electron self-energy

In many-body problems, one usually defines the so-called self-energy. It is the quantity that needs to be added to non-interacting Hamiltonian to get the interacting effective Hamiltonian

$$H^{eff} = \int d\mathbf{r} d\mathbf{r}' \Psi^\dagger(\mathbf{r}) \left\{ H^0(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + \Sigma(\mathbf{r}, \mathbf{r}') \right\} \Psi(\mathbf{r}') \tag{10}$$

From Eq. (4) we can see that

$$\Sigma(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \int d\mathbf{r}'' \rho(\mathbf{r}'', \mathbf{r}'') v_c(\mathbf{r}'' - \mathbf{r}) - \rho(\mathbf{r}', \mathbf{r}) v_c(\mathbf{r}' - \mathbf{r}) \tag{11}$$

This term is just the lowest order term in perturbation expansion of self-energy in powers of Coulomb repulsion and its diagrammatic representation in terms of Feyman diagrams is
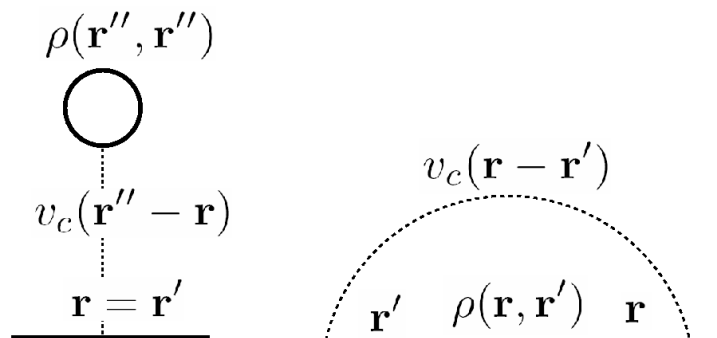
Derivation for beginners

We mentioned in the previous chapter (second quantization) that Hartree Fock approximation corresponds to the approximation where one finds single "properly symmetrized" Slater determinant that minimizes the total energy for the interacting Hamiltonian

$$E = \langle \Phi_{n_1 n_2, \cdots n_N} | H | \Phi_{n_1 n_2, \cdots n_N} \rangle \tag{12}$$

We can vary one-electron basis functions with constraint that they are normalized.

In previous chapter we called one-electron basis functions $u_k(x)$. Here, we called them $\psi(x)$ therefore we will stick to later definition. We remember from previous lecture

$$E = \sum_{\alpha} \psi_{\alpha}^*(x) H^0(x) \psi_{\alpha}(x) dx + \frac{1}{2} \sum_{\alpha\beta} \int dx dx' \psi_{\alpha}^*(x) \psi_{\beta}^*(x') v_C(x - x') \psi_{\alpha}(x) \psi_{\beta}(x')$$

$$- \frac{1}{2} \sum_{\alpha\beta} \int dx dx' \psi_{\alpha}^*(x) \psi_{\beta}^*(x') v_C(x - x') \psi_{\beta}(x) \psi_{\alpha}(x')$$

We would like to minimize

$$E - \sum_\alpha \epsilon_\alpha \int dx \psi_\alpha^*(x) \psi_\alpha(x) = min \tag{15}$$

We look for the best ψ_β, so we will vary the functional with respect to ψ_β^*

$$0 = \frac{\delta E}{\delta \psi_\beta^*} = H^0(x)\psi_\beta(x) + \left[\sum_\gamma \int dx' \psi_\gamma^*(x') v_C(x-x') \psi_\gamma(x') \right] \psi_\beta(x) \tag{16}$$

$$- \sum_\gamma \int dx' \psi_\gamma^*(x') v_C(x-x') \psi_\beta(x') \psi_\gamma(x) - \epsilon_\beta \psi_\beta(x) \tag{17}$$

We can multiply the equation by $\psi_\alpha(x)$ and integrate over x to get

$$\int \psi_\alpha^*(x) H^0(x) \psi_\beta(x) dx + \sum_\gamma \int dx dx' \psi_\alpha^*(x) \psi_\gamma^*(x') v_C(x-x') \psi_\gamma(x') \psi_\beta(x) \tag{18}$$

$$- \sum_\gamma \int dx dx' \psi_\alpha^*(x) \psi_\gamma^*(x') v_C(x-x') \psi_\beta(x') \psi_\gamma(x) - \epsilon_\beta \int \psi_\alpha^*(x) \psi_\beta(x) dx \tag{19}$$

or

$$H^0_{\alpha\beta} + \sum_{\gamma \in occupied} (U_{\gamma\alpha\gamma\beta} - U_{\gamma\alpha\beta\gamma}) = \epsilon_\alpha \delta_{\alpha\beta} \tag{20}$$

This is equivalent to Eq.(7). One needs to be carefull and sum only over occupied states γ. This is because in this derivation we worked with fixed number of particles N and all states of the Slater determinant must be occupied. This is hardly a surprise since the minimization gives ground state only, thus, this is zero temperature analog of the above more general perturbation formalism.

Nonorthogonal base

In actual calculation, the one electron orbitals are choosen very carefully because we would like to get (at least) the ground state with only few orbitals (The computation time increases as N^3, where N is the number of orbitals - solving eigenvalue problem). Those optimally chosen orbitals are almost never orthogonal!

One way around would be to orthogonalize basis functions first. This is a time consuming task and also leads to basis functions which are less localized. It is more convenient to generalize the equations to non-orthogonal basis functions than to orthogonalize basis functions.

Let us call the non-orthogonal basis functions $\Phi_p(\mathbf{r})$. Further, let us write the transformation from non-orthogonal base to eigenbase-base as

$$\psi_\alpha(\mathbf{r}) = \sum_p A_{p\alpha}\Phi_p(\mathbf{r}) \tag{21}$$

We want to solve

$$\langle\psi_\alpha|H^{eff} - \varepsilon|\psi_\beta\rangle = 0 \tag{22}$$

and using Eq. (21) we get

$$A^*_{p\alpha}(H^{eff}_{pq} - \varepsilon O_{pq})A_{q\beta} = 0 \qquad (23)$$

where O_{pq} is the overlap matrix $O_{pq} = \langle \Phi_p | \Phi_q \rangle$. This is the generalized eigenvalue problem $H^{eff} A = \varepsilon O A$, where H is Hermitian and O is positive definite matrix. The eigenvectors A are not orthogonal, but rather satisfy the relation $A^\dagger O A = 1$ which can be deduced from the relation $\langle \psi_\alpha | \psi_\beta \rangle = \delta_{\alpha\beta}$.

We also need the density matrix in the non-orthogonal base. It follows from

$$\rho(\mathbf{r}, \mathbf{r'}) = \langle \Psi^\dagger(\mathbf{r})\Psi(\mathbf{r'}) \rangle = \sum_{\alpha\beta} \psi^*_\alpha(\mathbf{r}) n_{\alpha\beta} \psi_\beta(\mathbf{r'}) = \sum_{pq,\alpha\beta} \Phi^*_p(\mathbf{r}) A^*_{p\alpha} n_{\alpha\beta} A_{q\beta} \Phi_q(\mathbf{r'}),$$

$$(24)$$

and since $n_{\alpha\beta} = \delta_{\alpha\beta} f(\varepsilon_\alpha - \mu)$ we conclude $\rho_{qp} = A^*_{p\alpha} A_{q\alpha} f(\varepsilon_\alpha - \mu)$.

The total energy of the system is not $\sum_\alpha \varepsilon_\alpha$! The right total energy in the eigen-base is

$$E = \sum_\alpha H^0_{\alpha\alpha} n_\alpha + \frac{1}{2} \sum_{\alpha a} (U_{a\alpha a\alpha} - U_{a\alpha\alpha a}) n_a n_\alpha = \frac{1}{2}\text{Tr}[(H^{eff} + H^0)n] \quad (25)$$

In the non-orthogonal basis, the total energy takes the form

$$E = \frac{1}{2}\sum_\alpha \varepsilon_\alpha n_\alpha + \frac{1}{2}\sum_\alpha (A^\dagger H^0 A)_{\alpha\alpha} n_\alpha = \frac{1}{2}\sum_\alpha \varepsilon_\alpha n_\alpha + \frac{1}{2}\sum_{pq} H^0_{pq}\rho_{qp} \quad (26)$$

Now we sketch algorithm to solve the general Hartree-Fock problem

1 Pick a set of one electron orbitals $\phi_p(\mathbf{r})$ and add them the spin part of the wave function to get $\Phi_p(\mathbf{r}) = \phi_p(\mathbf{r})|s\rangle$.

2 Calculate H^0 and U matrix elements from

$$H^0_{pq} = \langle\Phi_p| - \frac{1}{2}\nabla^2 + V_{ext}|\Phi_q\rangle \quad (27)$$

$$U_{pqrs} = \langle\Phi_p(\mathbf{r})\Phi_q(\mathbf{r'})|v_c(\mathbf{r} - \mathbf{r'})|\Phi_r(\mathbf{r})\Phi_s(\mathbf{r'})\rangle \quad (28)$$

3 Calculate H^{eff} by

$$H_{pq}^{eff} = H_{pq}^0 + \sum_{rs}(U_{rpsq} - U_{rpqs})\rho_{rs} \tag{29}$$

$$\tag{30}$$

4 Solve the generalized eigenvalue problem

$$\sum_{q}(H_{pq}^{eff} - \varepsilon_\alpha O_{pq})A_{q\alpha} = 0$$

with normalization $A^\dagger O A = 1$

5 Determin the chemical potential μ by requiring $N = \sum_\alpha f(\varepsilon_\alpha - \mu)$.

6 Calculate the new density matrix and new total energy by

$$\rho_{pq} = \sum_\alpha A_{p\alpha}f(\varepsilon_\alpha - \mu)A_{q\alpha}^* \tag{31}$$

$$E = \frac{1}{2}\sum_\alpha \varepsilon_\alpha f(\varepsilon_\alpha - \mu) + \frac{1}{2}\sum_{qq}H_{pq}^0\rho_{qp} \tag{32}$$

7 Return to 3 with updated ρ_{pq} as long as total energy is changing

Every index p corresponds to spin and orbital index. Treating spin index explicitly results in more tractable equations for computation. We have

$$H^{0\,\sigma\sigma'}_{pq} = H^{0\,\sigma\sigma}_{pq}\delta_{\sigma\sigma'} = H^0_{pq}\delta_{\sigma\sigma'} \tag{33}$$

$$U^{\sigma_1,\sigma_2,\sigma_3,\sigma_4}_{pqrs} = U^{\sigma_1,\sigma_2,\sigma_1,\sigma_2}_{pqrs}\delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4} = U_{pqrs}\delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4} \tag{34}$$

$$H^{eff\,\sigma\sigma}_{pq} = H^0_{pq} + \sum_{rs}\left[U_{rpsq}(\rho^\sigma_{rs} + \rho^{\bar\sigma}_{rs}) - U_{rpqs}\rho^\sigma_{rs}\right] \tag{35}$$

Two methods can be used

- Restricted Hartree-Fock : $\rho^\sigma = \rho^{\bar\sigma}$

- Non-Restricted Hartree-Fock: $\rho^\sigma \neq \rho^{\bar\sigma}$

Restricted HF is better if the number of electrons is even $\rightarrow$ the symmetry between $\uparrow$ and $\downarrow$ is preserved. For Restricted HF we simply have

$$H^{eff}_{pq} = H^0_{pq} + \sum_{rs}\left[2U_{rpsq} - U_{rpqs}\right]\rho_{rs} \tag{36}$$

where p and q run over orbital index only and not over spin.

The algorithm for restricted HF is simplified to

1 Pick a set of one electron orbitals $\phi_p(\mathbf{r})$

2 Calculate H^0 and U matrix elements from

$$H^0_{pq} = \langle \phi_p| - \frac{1}{2}\nabla^2 + V_{ext}|\phi_q\rangle \tag{37}$$

$$U_{pqrs} = \langle \phi_p(\mathbf{r})\phi_q(\mathbf{r}')|v_c(\mathbf{r} - \mathbf{r}')|\phi_r(\mathbf{r})\phi_s(\mathbf{r}')\rangle \tag{38}$$

3 Calculate H^{eff} by

$$H^{eff}_{pq} = H^0_{pq} + \sum_{rs}(2U_{rpsq} - U_{rpqs})\rho_{rs} \tag{39}$$

$$\tag{40}$$

4 Solve the generalized eigenvalue problem

$$\sum_q (H^{eff}_{pq} - \varepsilon_\alpha O_{pq})A_{q\alpha} = 0$$

with normalization $A^\dagger O A = 1$

5 Determin the chemical potential μ by requiring $N = \sum_\alpha 2f(\varepsilon_\alpha - \mu)$ where N is the number of all electrons.

6 Calculate the new density matrix and total energy by

$$\rho_{pq} = \sum_\alpha A_{p\alpha} f(\varepsilon_\alpha - \mu) A_{q\alpha}^* \tag{41}$$

$$E = \sum_\alpha \varepsilon_\alpha f(\varepsilon_\alpha - \mu) + \sum_{qq} H_{pq}^0 \rho_{qp} \tag{42}$$

7 Return to 3 with updated ρ_{pq} until the total energy is changing

Example: He atom and H_2 molecule

For practical computation, we need to specify basis functions. One possible choice are the Hydrogen-like orbitals (Slater Type Orbitals - STO) of the form

$$\phi(\mathbf{r}) = r^m P_l(x, y, z) e^{-\xi|\mathbf{r}|}. \tag{43}$$

They are less practical for molecule calculations. A better choice are Gaussian Type Orbitals (GTO)

$$\phi(\mathbf{r}) = P_l(x, y, z) e^{-\alpha \mathbf{r}^2}. \tag{44}$$

since the product of Gaussian functions is Gaussian. The polinomials P_l are the same as for hydorgen atom, i.e.

- s : 1

- p : x,y,z

- d: $xy,yz,xz,x^2 - y^2,3z^2 - r^2$

. The exponents α need to be determined by minimization of the total energy.

For the moment, we will take coefficients α from literature. For Hydrogen and He we need only few (four) 1s-like orbitals with coefficients

- H : 13.00773,1.962079,0.444529,0.1219492

- He: 0.298073,1.242567,5.782948,38.47497

With the basis functions of the form

$$\phi_p(\mathbf{r}) = e^{-\alpha_p \mathbf{r}^2} \tag{45}$$

or in Dirac notation

$$|\alpha_p \mathbf{R}\rangle \equiv \phi_p(\mathbf{r} - \mathbf{R}) = e^{-\alpha_p(\mathbf{r}-\mathbf{R})^2} \tag{46}$$

the matrix elements become

$$O_{p1,q2} \equiv \langle \alpha_p \mathbf{R}_1 | \alpha_q \mathbf{R}_2 \rangle = \left(\frac{\pi}{\alpha_p + \alpha_q} \right)^{3/2} e^{-\alpha_{pq}(\mathbf{R}_1 - \mathbf{R}_2)^2}$$

$$\langle \alpha_p \mathbf{R}_1 | - \frac{1}{2} \nabla^2 | \alpha_q \mathbf{R}_2 \rangle = O_{p1,q2} \, \alpha_{pq} [3 - 2\alpha_{pq}(\mathbf{R}_1 - \mathbf{R}_2)^2]$$

$$\langle \alpha_p \mathbf{R}_1 | \frac{1}{|\mathbf{r} - \mathbf{R}_N|} | \alpha_q \mathbf{R}_2 \rangle = 2 \, O_{p1,q2} \sqrt{\frac{\alpha_p + \alpha_q}{\pi}} F_0[(\alpha_p + \alpha_q)(\mathbf{R}_N - \mathbf{R}_{pq,12})^2]$$

$$\langle \alpha_p \mathbf{R}_1 \alpha_q \mathbf{R}_2 | \frac{1}{\mathbf{r} - \mathbf{r}'} | \alpha_r \mathbf{R}_3 \alpha_s \mathbf{R}_4 \rangle = 2 \, O_{p1,r3} O_{q2,s4} \sqrt{\frac{\alpha_{pr,qs}}{\pi}} F_0[\alpha_{pr,qs}(\mathbf{R}_{pr,13} - \mathbf{R}_{qs,24})$$

where $\alpha_{pq} = \frac{\alpha_p \alpha_q}{\alpha_p + \alpha_q}$, $\mathbf{R}_{pq,12} = \frac{\alpha_p \mathbf{R}_1 + \alpha_q \mathbf{R}_2}{\alpha_p + \alpha_q}$ and $\alpha_{pr,qs} = \frac{(\alpha_p + \alpha_r)(\alpha_q + \alpha_s)}{\alpha_p + \alpha_q + \alpha_r + \alpha_s}$

$$F_0[x] = \frac{1}{\sqrt{x}} \int_0^{\sqrt{x}} dy \, e^{-y^2} = \frac{\sqrt{\pi} \mathrm{erf}(\sqrt{x})}{2\sqrt{x}} \tag{47}$$

With the above described Hartee-Fock method we get for the ground state energy of He atom -2.85516 Hartree while the exact ground state energy is -2.86166 Hartree.

The equlibrium distance for the Hydrogen molecule H_2 in the Hartee-Fock calculation is $R_0 = 1.388$, while the exact one is 1.401.
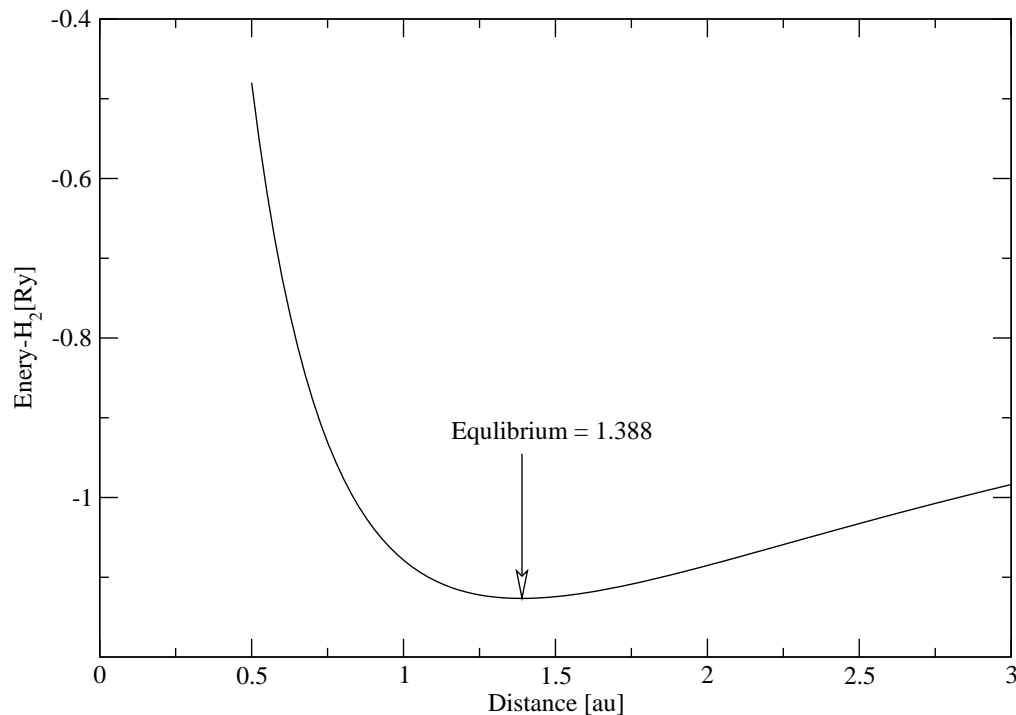

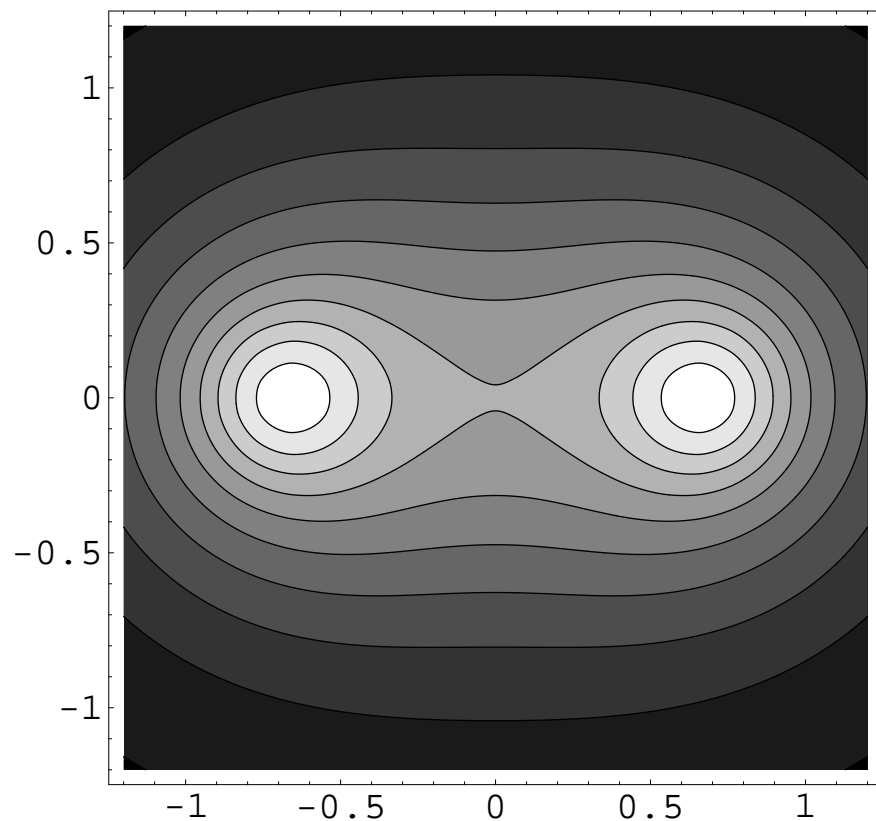Figure 1: The energy versus distance for H_2 molecule

Figure 2: The electron density of H_2 molecule at equilibrium distance

Homework:

The Python implementation of Hartree-Fock Eq. for He and H2 were started in our lecture.

Finish one of the two projects.