

Advanced Computational Physics - Exercise 3

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Mean Field methods/Hartree-Fock

In class we have discussed the mean field approximation to the solution of the many-body problem. We are interested in computing some ground state properties of a system of N particles described by the generic Hamiltonian:

$$\hat{H} = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V_{ext}(\vec{r}_i) \right] + \frac{1}{2} \sum_{i \neq j}^N v(\vec{r}_i, \vec{r}_j),$$

where $\vec{r}_1 \dots \vec{r}_N$ are the coordinates of our N particles, V_{ext} is some external field and v is the interaction potential. We have seen that the mean field approximation consists of assuming that the wave function (in coordinate space) can be written as a product of *single particle* functions:

$$\Psi(\vec{r}_1 \dots \vec{r}_N) = \hat{\mathcal{P}}_{s,a} \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) \dots \phi_N(\vec{r}_N),$$

where

$$\hat{\mathcal{P}}_s = \frac{1}{\sqrt{N!}} \sum_{\hat{P}} \hat{P} \quad \text{for Bosons}$$

$$\hat{\mathcal{P}}_a = \frac{1}{\sqrt{N!}} \sum_{\hat{P}} (-1)^P \hat{P} \quad \text{for Fermions}$$

with \hat{P} all the elements in the permutation group for the N particles, and P the corresponding parity (even-odd). The problem is solved using once again the variational principle. One needs to minimize the expectation:

$$E_T = \langle \Psi | \hat{H} | \Psi \rangle$$

with respect to the set of single particle function used, with the constraint that the normalization of each of the ϕ_i is normalized, and that they constitute an orthonormal set.

In this exercise you will deal with simple atoms, described (in natural units) as:

$$\sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i<j}^N \frac{1}{r_{ij}}.$$

Questions

1. Draw a flowchart for the self-consistent solution of the HF equations, assuming that the solution is expanded over some basis. Explicitly consider the *mixing procedure*, i.e. the fact that at each step the new effective potential (depending on the wave function which is a solution of the equation) is given in terms of $v_{\text{new}} = \alpha v_{\text{new}} + (1 - \alpha) v_{\text{old}}$, with $\alpha \ll 1$.
2. Consider the STO-4G basis for the Hydrogen atom ($Z=N=1$), where the 4 Gaussians on which the 1s orbital is expanded are defined as:

$$\chi_p(r) = e^{-\alpha_p r^2},$$

and the α coefficients are:

$$\alpha_1 = 13.00773, \alpha_2 = 1.962079, \alpha_3 = 0.444529, \alpha_4 = 0.1219492.$$

Find by means of the variational procedure the coefficients of the linear combination of the 4 Gaussians minimizing the expectation value of the Hamiltonian.

3. Consider now the He atom ($Z=N=2$). Use again an STO-4G basis, as defined in the previous question, where the exponents are¹:

$$\alpha_1 = 14.899983, \alpha_2 = 2.726485, \alpha_3 = 0.757447, \alpha_4 = 0.251390.$$

Considering the para-He state (the ground state) write and solve the HF equations.

4. Repeat the same procedure for the Be atom ($Z=4, N=4$), assuming a $1s^2 2s^2$ configuration. In this case there are 8 Gaussians of s type to be considered, the first 4 for the 1s orbital and the second 4 for the 2s orbitals. This time use contracted orbitals. The following table gives

¹More accurate basis expansion data can be found on the web site *basissetexchange.org*

you in the first column the α parameters at the exponent, and in the second column the coefficients of the expansion:

| | | |
|----|------------------|-------------------|
| 1s | 0.7064859542E+02 | 0.5675242080E-01 |
| | 0.1292782254E+02 | 0.2601413550E+00 |
| | 0.3591490662E+01 | 0.5328461143E+00 |
| | 0.1191983464E+01 | 0.2916254405E+00 |
| 2s | 0.3072833610E+01 | -0.6220714565E-01 |
| | 0.6652025433E+00 | 0.2976804596E-04 |
| | 0.2162825386E+00 | 0.5588549221E+00 |
| | 0.8306680972E-01 | 0.4977673218E+00 |

Try now to solve the problem *without contractions*, and compare your findings with those reported in the table, together with the estimated energies.

In all cases report clearly the results for the energy, and plot the resulting orbitals and electronic densities.

Here some useful integrals:

$$\int d^3r \exp(-\alpha_p r^2) \exp(-\alpha_q r^2) = \left(\frac{\pi}{\alpha_p + \alpha_q} \right)^{3/2}$$

$$-\frac{1}{2} \int d^3r \exp(-\alpha_p r^2) \nabla^2 \exp(-\alpha_q r^2) = 3 \frac{\alpha_p \alpha_q \pi^{3/2}}{(\alpha_p + \alpha_q)^{5/2}}$$

$$\int d^3r \exp(-\alpha_p r^2) \frac{1}{r} \exp(-\alpha_q r^2) = \frac{2\pi}{\alpha_p + \alpha_q}$$