Computational Nanoscience: Solution to Exercise Sheet No. 3

Exercise 3.1: Derivation of the Rothaan-Hall equations

Multiply from the left with $\phi_\mu(\mathbf{r})$ and integrate.

Exercise 3.2: Hartree-Fock energy from eigenvalues

We have

$$\begin{aligned}\mathbf{S}^{-1/2}\mathbf{F}\mathbf{C} &= \mathbf{S}^{1/2}\mathbf{C}\boldsymbol{\varepsilon}\\ \mathbf{C}^{\mathrm{T}}\mathbf{F}\mathbf{C} &= \mathbf{C}^{\mathrm{T}}\mathbf{S}\mathbf{C}\boldsymbol{\varepsilon}\\ \mathbf{C}^{\mathrm{T}}\mathbf{F}\mathbf{C} &= \boldsymbol{\varepsilon}\,.\end{aligned}$$

Then,

$$\sum_{n=1}^{N/2}\varepsilon_n = \sum_{n=1}^{N/2} C_{n\nu}F_{\nu\mu}C_{n\mu} = \frac{T}{2} + \frac{E_{\mathrm{Ne}}}{2} + E_{\mathrm{H}} + E_{\mathrm{x}}\,.$$

The result from the exercise sheet follows with $E_{\mathrm{HF}} = T + E_{\mathrm{Ne}} + E_{\mathrm{H}} + E_{\mathrm{x}} + E_{\mathrm{NN}}$.

(a) In closed-shell Hartree-Fock, every molecular orbital is occupied by two electrons.

(b) Consider the Hartree-Fock equation

$$\int F(\mathbf{r},\mathbf{r}')\,\psi_n(\mathbf{r}')\,d\mathbf{r}' = \varepsilon_n\,\psi_n(\mathbf{r})\,, \tag{1}$$

$$F(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')\left(-\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}} - \sum_A \frac{Z_A e^2}{|\mathbf{r}-\mathbf{R}_A|} + V_{\mathrm{H}}(\mathbf{r})\right) + V_{\mathrm{x}}(\mathbf{r},\mathbf{r}')\,, \tag{2}$$

$$V_{\mathrm{H}}(\mathbf{r}) = 2e^2\sum_{m=1}^{N/2}\int d^3\mathbf{r}'\,\frac{|\psi_m(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\,,\qquad V_{\mathrm{x}}(\mathbf{r},\mathbf{r}') = -e^2\sum_{m=1}^{N/2}\frac{\psi_m(\mathbf{r})\,\psi_m(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,. \tag{3}$$

You can obtain the eigenvalue from Eq. (1) by multiplying with $\psi_n(\mathbf{r})$ from the left and integrating over the whole space. In this way, you see from Eq. (1) - (3) that

$$\varepsilon_n = -\frac{\hbar^2}{2m}\langle\psi_n|\nabla^2_{\mathbf{r}}|\psi_n\rangle - \langle\psi_n|\sum_A\frac{Z_A e^2}{|\mathbf{r}-\mathbf{R}_A|}|\psi_n\rangle + \langle\psi_n|V_{\mathrm{H}}|\psi_n\rangle + \langle\psi_n|V_{\mathrm{x}}|\psi_n\rangle \tag{4}$$

with

$$\langle\psi_n|V_{\mathrm{H}}|\psi_n\rangle = \int d^3\mathbf{r}\;\psi_n(\mathbf{r})V_{\mathrm{H}}(\mathbf{r})\psi_n(\mathbf{r}) = 2e^2\sum_{m=1}^{N/2}\iint d^3\mathbf{r}\,d^3\mathbf{r}'\;\frac{|\psi_n(\mathbf{r})|^2\,|\psi_m(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \tag{5}$$

and

$$\langle\psi_n|V_{\mathrm{x}}|\psi_n\rangle = \int d^3\mathbf{r}\, d^3\mathbf{r}'\ \psi_n(\mathbf{r}) V_{\mathrm{x}}(\mathbf{r},\mathbf{r}')\psi_n(\mathbf{r}') = -e^2 \sum_{m=1}^{N/2} \iint d^3\mathbf{r}\, d^3\mathbf{r}'\ \frac{\psi_n(\mathbf{r})\,\psi_n(\mathbf{r}')\,\psi_m(\mathbf{r})\,\psi_m(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,. \tag{6}$$

For the Hartree interaction, it is apparent that the orbital $\psi_n(\mathbf{r})$ interacts with all other orbitals $\psi_m(\mathbf{r})$. When summing up all eigenvalues, there is a double counting, since in another eigenvalue ε_m ($m \neq n$), there is also a Hartree interaction with orbital $\psi_n(\mathbf{r})$. This double counting of Hartree interactions is cancelled by subtracting the Hartree energy from the eigenvalue sum to obtain the Hartree-Fock energy. For the exchange interaction, the double counting is also present and has to be cancelled by subtracting the exchange energy.

(c) In MO theory, there is no electron-electron interaction and hence, also the double counting problem is absent. So, we don't need to subtract anything from the eigenvalue sum to obtain the total energy.

(d) In a Hartree-Fock calculation, we compute N_{b} eigenvalues, where N_{b} is the number of basis functions. The reason is that we obtain N_{b} eigenvalues from diagonalizing the Fock matrix $F_{\mu\nu}$ that is of size $N_{\mathrm{b}} \times N_{\mathrm{b}}$. It is reasonable that we only use the lowest $N/2$ eigenvalues for the sum to obtain the total energy since orbitals with higher eigenvalue are not occupied with electrons and therefore, are not expected to contribute to the Hartree-Fock energy.

Exercise 3.3: Reaction energy of the H_2O forming reaction

Geometry	Basis set	E_{HF} of H_2 (H)	E_{HF} of O_2 (H)	E_{HF} of H_2O (H)	Δ (H)	Δ (kJ/mol)
Force field	def2-QZVPP	-1.12600957119	-149.6696676332	-76.0667464078	-0.10590	-278.0
Hartree-Fock	def2-QZVPP	-1.1335965686	-149.6941678081	-76.0672794984	-0.08661	-227.4,
Hartree-Fock	def2-TZVPP	-1.1330038892	-149.6872420705	-76.0628939946	-0.08627	-226.5

(d) First line (geometry: force field, basis set for Hartree-Fock energy difference: def2-QZVPP): method is inaccurate since a geometry obtained with a force field is less accurate than a geometry obtained with a quantum mechanical method. Moreover, the method is inconsistent since the total energy method for computing energy differences should be identical to the method of the geometry optimization. (Only exception: method for computing energy difference is extremely expensive such that a geometry optimization with this method would be prohibitive). The calculation is numerically fully converged (very big basis set for Hartree-Fock; probably numerically very well-converged optimization of the geometry in Avogadro).

Second line (geometry: Hartree-Fock def2-QZVPP geometry, basis set for Hartree-Fock energy difference: def2-QZVPP): Among the three calculations, the method (Hartree-Fock for geometry optimization and for total energy difference) is the most accurate. Also, numerical convergence is best since the largest basis set has been used.

Third line (geometry: Hartree-Fock def2-QZVPP geometry, basis set for Hartree-Fock energy difference: def2-TZVPP): As for the second line, the method is most accurate among the methods that have been used in the table. However, a numerical parameter (basis set for total energy difference) is not as well converged as for the second line.

(e) The reference value from the NIST WebBook is – 241.83 kJ/mol. There are two main sources of the discrepancies:

1. In Hartree-Fock, we miss the correlation energy. This can have a large effect on total energy differences (effect on a chemical reaction energy is typically on the order of 10 kJ/mol).
2. The reaction enthalpy from the WebBook is a measurement at a standard temperature, probably at 293.15 K. At this temperature, rotations and vibrations of molecules are excited. When measuring the energy difference between the reactants and the products, the energy difference of the vibrational and rotational energy between reactants and products is included. These contributions are absent in our zero-temperature Hartree-Fock calculations. Note that at 293.15 K, we have $k_B T = 2.4$ kJ/mol and we expect a discrepancy of this order of magnitude between our Hartree-Fock result and the measurement at 293.15 K due to missing rotations and vibrations.