ABC of DFT: Hands-on session 3
Molecules: computation of ionization energies & electron affinities

Tutor: Alexej Bagrets

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Wo? KIT Campus Nord, Flachbau Physik, Geb. 30.22, Computerpool, Raum FE-6
Overview

- Reminder: formulation of the Kohn-Sham DFT and the Hartree-Fock method

- Performance of HF and approximate DFT exchange-correlation (XC) functionals:
  - ionization energies (IE)
  - electron affinities (EA)
  - bond lengths
  - examples: $\text{O}_2$, $\text{N}_2$, $\text{F}_2$, $\text{Cl}_2$, $\text{Br}_2$
Preparing for the hands-on session 3 …

- Log into **intact** cluster (have a look at a separate sheet of paper with instructions)
- Switch to a working directory:
  
  ```
  cd ~/ABC_of_DFT/hands-on-sessions/
  ```
- Copy a script `session3` from **dft20** account:
  
  ```
  cp ~/../dft20/ABC_of_DFT/session3 .
  ```
- Type from a command line:
  
  ```
  ./session3
  ```
- Examples (with this tutorial) will be imported to a directory
  
  ```
  ~/ABC_of_DFT/hands-on-sessions/session3
  ```
Reminder: Hartree-Fock approximation

Assume that ground state wave function can be written as single Slater determinant

\[
\langle r_1 \sigma_1, \ldots, r_N \sigma_N \left| \tilde{\Psi}^0_{\nu_1 \ldots \nu_N} \right. \rangle = \frac{1}{\sqrt{N!}} \begin{pmatrix}
\phi_{\nu_1}(r_1 \sigma_1) & \cdots & \phi_{\nu_1}(r_N \sigma_N) \\
\phi_{\nu_2}(r_1 \sigma_1) & \cdots & \phi_{\nu_2}(r_N \sigma_N) \\
\vdots & \cdots & \vdots \\
\phi_{\nu_N}(r_1 \sigma_1) & \cdots & \phi_{\nu_N}(r_N \sigma_N)
\end{pmatrix}
\]

where \( \phi_{\nu}(r \sigma) \) are spin orbitals (with \( s = \uparrow, \downarrow \)):

\[
\phi_{\nu}(r \sigma) = \phi_l(r) \chi_s(\sigma)
\]
Reminder: Hartree-Fock approximation

- Using variational principle, minimize the energy of the trial state $|\tilde{\Psi}_0\rangle$ ...

$$E(\tilde{\Psi}_0) = \frac{\langle \tilde{\Psi}_0 | H | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi}_0 | \tilde{\Psi}_0 \rangle}$$

- ... we come to HF equations:

$$\begin{bmatrix}
-\frac{\hbar^2}{2m} \nabla^2 + \sum_I v(x - X_I) \\
\end{bmatrix} \phi_{l_i}(x) +$$

Hartee term

$$\int dx' \ v(x-x') \sum_{j=1}^{\text{occ.}} \phi^*_j(x') \left[ \phi_{l_j}(x') \phi_{l_i}(x) - \phi_{l_j}(x) \phi_{l_i}(x') \delta_{s_is_j} \right]$$

exchange term

$$= \epsilon_{l_i} \ \phi_{l_i}(x)$$
Reminder: Kohn-Sham formulation of DFT

- Ansatz for the electron density:

\[ \rho(r) = \rho_s(r) = \sum_{i=1}^{N_{el.}} \left| \varphi_i(r) \right|^2 \]

- Energy of the system is a functional of density:

\[ E[\rho] = T_s[\rho] + \int dr \ v_{\text{ext}}(r) \rho(r) + V_H[\rho] + E_{xc}[\rho] \]

\[ T_s[\rho] = \sum_{i=1}^{N_{el.}} \int dr \ \varphi_i^*(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_i(r) \]

\[ V_H[\rho] = \frac{e^2}{2} \int dr \int dr' \ \frac{\rho(r)\rho(r')}{|r - r'|} \]
Reminder: Kohn-Sham formulation of DFT

- Minimization of the energy functional vs $\varphi_i$ under constrain $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ $\Rightarrow$ KS equations:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_s(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r)$$

$$V_s(r) = v_{\text{ext}}(r) + \int \frac{e^2 \rho_s(r')}{|r - r'|} d^3r' + V_{\text{XC}}[\rho_s(r)]$$

- External potential
- Hartree potential
- "exchange & correlation" potential

$$V_{\text{XC}}[\rho_s(r)] = \frac{\delta E_{\text{XC}}[\rho_s]}{\delta \rho_s(r)}$$
Confronting DFT with Hartree-Fock

- Make a directory, where calculations are going to run
  
  ```
  cd ~/ABC_of_DFT/hands-on-sessions/session.3/
  mkdir my.xc
  cd my.xc
  ```

- A script `xc` is designed to confront the Hartree-Fock (HF) approximation with commonly used DFT xc-functionals (BP86, PBE, and B3LYP) by computing bond lengths, ionization energies (IE) and electron affinities (EA) of a few diatomic molecules

- Type from a command line: `xc`, and read a short description
Confronting DFT with Hartree-Fock

- As input, \( xc \) script takes a molecule’s symbol (accepted ones are \( o_2, n_2, f_2, cl_2, br_2 \)), and abbreviation of the TURBOMOLE basis set (e.g., \( \text{def-SVP} \))

- A script set-ups calculations for the charge neutral molecule \( X \) (TURBOMOLE module \( \text{define} \)), its positive \( (X^+) \) & negative \( (X^-) \) ions, computes their ground state energies and optimizes interatomic distances (TURBOMOLE \( \text{jobex} \) script)

- Based on computed energies, ionization energies (IE) and electron affinities (EA) are evaluated
Confronting DFT with Hartree-Fock

- Ionization energy $IE$ is the minimum (positive) energy required to remove an electron from a molecule $X$ (with $N$ electrons) to form an ion $X^+$

$$X + (IE) \rightarrow X^+ + \bar{e}$$

$$IE = E_0(N-1) - E_0(N)$$

If the ion $X^+$ retains the geometry of the initial $X$, the value of $IE$ is referred to as the **vertical ionization energy**. If the ion $X^+$ is relaxed to its ground state, $IE$ is referred to as the **adiabatic ionization energy**.

- Electron affinity $EA$ is the energy released upon attachment of an electron to a molecule $X$ resulting in the formation of the negative ion $X^-:

$$X + \bar{e} \rightarrow X^- + (EA)$$

$$EA = E_0(N) - E_0(N+1)$$

The adiabatic $EA$ is equal to the difference between the total energies of a neutral system ($X$) and the corresponding anion ($X^-$) in its equilibrium geometry.
Confronting DFT with Hartree-Fock

- Type, e.g., from a command line: `xc f2 def-TZVP`
  
  ... output will follow on

- Results of your calculations can be found in a directory with a self-explanatory name, e.g., type

  `cd ./results.f2.def-TZVP`

- You will see a subdirectory structure which contains set of HF calculations (directory `HF`), and set of DFT calculations with BP86, PBE and hybrid B3LYP functional (directories `b-p`, `pbe`, `b3-lyp`) performed for a charge neutral molecule (subdirectory `q0`) and its ionized states (subdirectories `q-1` and `q+1`)
Confronting DFT with Hartree-Fock

- To get summary of your results, type, e.g.:
  ```
  cat data.f2.def-SVP.dat
  ```

- A table will show up, where theory is compared with experimental data taken from NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/)

<table>
<thead>
<tr>
<th>molecule: f2</th>
<th>basis: def-TZVP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(vertical)</td>
<td>(adiabatic)</td>
</tr>
<tr>
<td>----------------</td>
<td>---------</td>
</tr>
<tr>
<td>bp86</td>
<td>15.53</td>
</tr>
<tr>
<td>pbe</td>
<td>15.42</td>
</tr>
<tr>
<td>b3-lyp</td>
<td>15.85</td>
</tr>
<tr>
<td>Hartree-Fock</td>
<td>15.79</td>
</tr>
<tr>
<td>experiment*</td>
<td>15.60</td>
</tr>
</tbody>
</table>
Confronting DFT with Hartree-Fock

- Perform calculations for a few molecules (electron affinities are computed only for \( \text{F}_2, \text{Cl}_2, \) and \( \text{Br}_2 \)) and analyze your results.
- Check bond lengths: which results, HF or DFT, are superior to experiment?
- A bond length is changed, when electron is added or removed from a molecule. Information on the bond length can be obtained with help of \texttt{dist} script, e.g. type \texttt{cd ./b-p/q-1}

\texttt{dist 1 2} (a message will come out …)
\texttt{dist 1 \textbackslash f -- 2 \textbackslash f = 3.9148 au = 207.16 pm}

- Is there any “rule of thumb” for the bond length, when going from a negative ion, over a neutral molecule, to a positive ion?
Confronting DFT with Hartree-Fock

- Koopman’s theorem states that ionization energy (IE) is the negative of the HOMO’s orbital energy: \( \text{IE} = -\varepsilon_{\text{HOMO}} \) (in case of HF, a statement is approximately valid as a result of the frozen core approximation, while in case of DFT the exact xc-functional is required)

- Orbital energies can be obtained, by viewing files, e.g.:

  ```
  cat ./b-p/q0/molecular.levels.f2.q0.def-SVP.dat
  cat ./HF/q0/molecular.levels.f2.q0.def-SVP.dat
  ```

- Compare HF and DFT (but with approx. xc-functional !). When \( -\varepsilon_{\text{HOMO}} \) is a good approximation for IE?

- When you switch from a semi-local functional (BP86 or PBE) to the hybrid functional B3-LYP, does result improve?