ABC of DFT: Hands-on session 3

Molecules: computation of ionization energies & electron affinities

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Wann? 23.11.2012, 11:30-13:00
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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: **O_2, N_2, F_2, Cl_2, 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

$$\langle \mathbf{r_1}\sigma_1, \ldots, \mathbf{r}_N\sigma_N | \tilde{\Psi}^0_{\nu_1\ldots\nu_N} \rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\nu_1}(\mathbf{r_1}\sigma_1) & \cdots & \phi_{\nu_1}(\mathbf{r}_N\sigma_N) \\ \phi_{\nu_2}(\mathbf{r_1}\sigma_1) & \cdots & \phi_{\nu_2}(\mathbf{r}_N\sigma_N) \\ \vdots & \cdots & \vdots \\ \phi_{\nu_N}(\mathbf{r_1}\sigma_1) & \cdots & \phi_{\nu_N}(\mathbf{r}_N\sigma_N) \end{vmatrix}$$

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

$$\phi_\nu(\mathbf{r}\sigma) = \phi_l(\mathbf{r})\chi_s(\sigma)$$

Reminder: Hartree-Fock approximation

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

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

- … we come to **HF equations:**

external potential

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \sum_{\mathbf{I}} v(\mathbf{x} - \mathbf{X_I}) \right] \phi_{l_i}(\mathbf{x}) +$$

Hartee term   exchange term

$$\int d\mathbf{x}' \ v(\mathbf{x} - \mathbf{x}') \sum_{j=1}^{\text{occ.}} \phi_{l_j}^*(\mathbf{x}') \left[\phi_{l_j}(\mathbf{x}') \phi_{l_i}(\mathbf{x}) - \phi_{l_j}(\mathbf{x}) \phi_{l_i}(\mathbf{x}') \delta_{s_i s_j} \right]$$

$$= \ \epsilon_{l_i} \ \phi_{l_i}(\mathbf{x})$$

Reminder: Kohn-Sham formulation of DFT

- Ansatz for the electron density:

$$\rho(\mathbf{r}) \stackrel{\text{def.}}{=} \rho_s(\mathbf{r}) = \sum_{i=1}^{N_{\text{el.}}} |\varphi_i(\mathbf{r})|^2$$

- Energy of the system is a functional of density:

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

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

$$V_H[\rho] = \frac{e^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \, \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Reminder: Kohn-Sham formulation of DFT

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

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

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

external potential   Hartree potential   "exchange & correlation" potential

$$V_{\text{XC}}[\rho_s(\mathbf{r})] = \frac{\delta E_{\text{XC}}[\rho_s]}{\delta \rho_s(\mathbf{r})}$$

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 `o2, n2, f2, cl2, br2`), and abbreviation of the TURBOMOLE basis set (e.g., `def-SVP`)

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

$$X + (IE) \rightarrow X^+ + \bar{e}$$
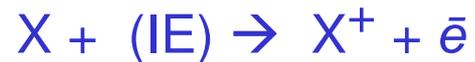
$$IE = E_0(N-1) - E_0(N)$$

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/)

```
================================================================
molecule: f2    basis: def-TZVP


                   (vertical) (adiabatic) (adiabatic)
functional/method   IE [eV]     IE [eV]     EA [eV]    bond length [a.u.]
----------------------------------------------------------------
bp86                 15.53      15.36        n/a          2.6886
pbe                  15.42      15.25        n/a          2.6862
b3-lyp               15.85      15.63        3.35         2.6532
Hartree-Fock         15.79      15.34        2.67         2.5179


experiment*                    15.60        3.12         2.6834
================================================================
```

Confronting DFT with Hartree-Fock

- Perform calculations for a few molecules (electron affinities are computed only for F_2, Cl_2, and 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 `dist` script, e.g. type

  `cd ./b-p/q-1`

  `dist 1 2` (a message will come out ...)

  `dist  1  f --  2  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: **$IE = -\varepsilon_{HOMO}$** (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 **$-\varepsilon_{HOMO}$** 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?