Lecture 7

The self-consistent field procedure for Kohn-Sham DFT calculations

C.-K. Skylaris
Kohn-Sham energy expression

- The explicit form of the Kohn-Sham energy functional is written using the molecular orbitals to express the (non-interacting) kinetic energy and the density for the other energy components

\[
E_{KS}[n] = 2 \sum_{j=1}^{N_{e1}/2} \int \psi_j^*(r) \left(-\frac{1}{2} \nabla^2 \right) \psi_j(r) \, d\mathbf{r} + E_{ext}[n] + E_{Coul}[n] + E_{xc}[n]
\]

Write down explicit expressions for the terms that depend on the density
Kohn-Sham energy minimisation

• The energy is a functional of the density

• In the Kohn-Sham approach the exact, interacting electrons density is made up from the molecular orbitals (MOs) of the non-interacting electrons

\[ n(r) = 2 \sum_{i=1}^{N_{el}/2} |\phi_i(r)|^2 \]

• So ultimately the energy is a functional of the Kohn-Sham MOs

\[ E_{KS}[n] = 2 \sum_{i=1}^{N_{el}/2} \int \phi_i^*(r) \left( -\frac{1}{2} \nabla^2 \right) \phi_i(r) dr + E_{Coul}[n] + E_{ext}[n] + E_{xc}[n] \]

• How do we calculate the Kohn-Sham MOs?

• Following the variational principle, we need to minimise the energy with respect to the density, in order to find the ground state energy
• In the Kohn-Sham case we need to minimise in with respect to the orbitals on which the density depends.

• We need to retain the orthonormality of the orbitals, and for this we will use a set of Lagrange multipliers, so we actually need to minimise the following Lagrangian expression:

\[ \Omega_{\text{KS}}[n] = E_{\text{KS}}[n] - 2 \sum_{i=1}^{N_{\text{el}}/2} \sum_{j=1}^{N_{\text{el}}/2} \epsilon_{ij} \left( \int \phi_i^*(r) \phi_j(r) \, dr - \delta_{ij} \right) \]

• To calculate the functional derivative with respect to the orbitals we can use the following “chain rule”:

\[ \frac{\delta \Omega_{\text{KS}}[n]}{\delta \phi_j^*(r)} = \frac{\delta \Omega_{\text{KS}}[n]}{\delta n(r)} \frac{\partial n(r)}{\partial \phi_j^*(r)} \]

• With the following result:

\[ \frac{\partial n(r)}{\partial \phi_j^*(r)} = 2\phi_j(r) \]
• So, the functional derivative with respect to the MOs is

\[
\frac{\delta \Omega_{\text{KS}}[n]}{\delta \phi_j^*(\mathbf{r})} = \frac{\delta \Omega_{\text{KS}}[n]}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \phi_j^*(\mathbf{r})} = \frac{\delta \Omega_{\text{KS}}[n]}{\delta n(\mathbf{r})} 2\phi_j(\mathbf{r})
\]

• The orbitals that minimise the energy must satisfy the condition

\[
\frac{\delta \Omega_{\text{KS}}[n]}{\delta \phi_j^*(\mathbf{r})} = 0
\]

Which, using the expression for the energy, can be expanded as

\[
\frac{\delta \Omega_{\text{KS}}[n]}{\delta \phi_j^*(\mathbf{r})} = 2 \left( -\frac{1}{2} \nabla^2 \phi_j(\mathbf{r}) \right) + 2 \left( \frac{\delta E_{\text{Coul}}}{\delta n} \frac{\partial n}{\partial \phi_j^*(\mathbf{r})} + \frac{\delta E_{\text{ext}}}{\delta n} \frac{\partial n}{\partial \phi_j^*(\mathbf{r})} + \frac{\delta E_{\text{xc}}}{\delta n} \right) \phi_j(\mathbf{r}) - 2 \sum_{i=1}^{N_{\text{el}}/2} \epsilon_{ij} \phi_j(\mathbf{r}) = 0
\]
\[
\frac{\delta \Omega_{KS}[n]}{\delta \phi^*_{j}(r)} = 2 \left(-\frac{1}{2} \nabla^2 \phi_j(r)\right) + 2 \left(\frac{\delta E_{\text{Coul}}}{\delta n} + \frac{\delta E_{\text{ext}}}{\delta n} + \frac{\delta E_{\text{xc}}}{\delta n}\right) \phi_j(r) - 2 \sum_{i=1}^{N_{\text{el}}/2} \epsilon_{ij} \phi_j(r) = 0
\]

- It is possible to transform the set of \(\{\phi\}\) orbitals to a new set of orbitals \(\{\psi\}\) with the same electronic density but a diagonal matrix of Lagrange multipliers

\[
\left( -\frac{1}{2} \nabla^2 \psi_j(r) \right) + \left( \frac{\delta E_{\text{Coul}}}{\delta n} + \frac{\delta E_{\text{ext}}}{\delta n} + \frac{\delta E_{\text{xc}}}{\delta n} \right) \psi_j(r) - \epsilon_j \psi_j(r) = 0
\]

\[
\left\{ -\frac{1}{2} \nabla^2 + \left( \frac{\delta E_{\text{Coul}}}{\delta n} + \frac{\delta E_{\text{ext}}}{\delta n} + \frac{\delta E_{\text{xc}}}{\delta n} \right) \right\} \psi_j(r) = \epsilon_j \psi_j(r)
\]

\[
\left( -\frac{1}{2} \nabla^2 + V_{KS}(r) \right) \psi_j(r) = \epsilon_j \psi_j(r)
\]

- The result is a one-electron Schrödinger equation that can be solved for the Kohn-Sham molecular orbitals
The Kohn-Sham potential

- We therefore have an expression for a Schrödinger equation for the MOs

\[
\left( -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \right) \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r})
\]

\[
\hat{h}_{KS} \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r})
\]

- It contains an expression for the “effective” potential

\[
V_{KS}(\mathbf{r}) = \frac{\delta E_{\text{Coul}}}{\delta n} + \frac{\delta E_{\text{ext}}}{\delta n} + \frac{\delta E_{\text{xc}}}{\delta n}
\]

\[
= \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{ext}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})
\]

which generates the fictitious system of non-interacting electrons with density equal to the density of the interacting electrons.

- Kohn-Sham non-interacting electrons
- Approximate Hamiltonian for fictitious molecule
• Let us examine the Kohn-Sham potential in more detail

\[ V_{KS}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{Coul}}(\mathbf{r}) + V_{xc}(\mathbf{r}) \]

\[ = V_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'} + \frac{\delta E_{xc}}{\delta n} \]

• The last two terms (the Coulomb and the exchange-correlation potentials) depend on the density and hence on the MOs that we seek when we are trying to solve the Kohn-Sham Schrödinger equations:

\[ \left( -\frac{1}{2} \nabla^2 + V_{KS}(\mathbf{r}) \right) \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}) \]

• In order to find these MOs we need to construct the Kohn-Sham potential from them, but these MOs are unknown as they are the very MOs we seek!

• How do we go about solving these equations?
The Self-Consistent Field (SCF) procedure

- The Kohn-Sham operator depends on the molecular orbitals which we seek
- Therefore an iterative procedure needs to be used to find these orbitals
- This procedure is often called a Self-Consistent Field (SCF) calculation

Select initial \( \{ \psi_i^{(n)} \}, n = 0 \)

Construct Kohn-Sham operator \( \hat{h}_{KS}^{(n)} = \hat{h}_{KS}[\{ \psi_i^{(n)} \}] \)

Solve \( \hat{h}_{KS}^{(n)} \psi_i^{(n+1)} = \epsilon_i^{(n+1)} \psi_i^{(n+1)} \) to obtain \( \{ \psi_i^{(n+1)} \} \)

Are \( \{ \psi_i^{(n+1)} \} \) same as \( \{ \psi_i^{(n)} \} \) to within expected tolerance?

Set \( \{ \psi_i^{(n)} \} \rightarrow \{ \psi_i^{(n+1)} \} \)

\( n \rightarrow n + 1 \)

DFT calculation converged
Example: DFT calculation on a water molecule

### SCF procedure

<table>
<thead>
<tr>
<th>convergence</th>
<th>iter</th>
<th>energy</th>
<th>DeltaE</th>
<th>RMS-Dens</th>
<th>Diis-err</th>
<th>time</th>
</tr>
</thead>
<tbody>
<tr>
<td>d= 0,ls=0.0,diis</td>
<td>1</td>
<td>-76.4209831586</td>
<td>-8.56D+01</td>
<td>1.02D-02</td>
<td>4.57D-01</td>
<td>0.7</td>
</tr>
<tr>
<td>d= 0,ls=0.0,diis</td>
<td>2</td>
<td>-76.4096395117</td>
<td>1.13D-02</td>
<td>5.04D-03</td>
<td>6.06D-01</td>
<td>0.9</td>
</tr>
<tr>
<td>d= 0,ls=0.0,diis</td>
<td>3</td>
<td>-76.4595101335</td>
<td>-4.99D-02</td>
<td>7.10D-04</td>
<td>2.33D-02</td>
<td>1.1</td>
</tr>
<tr>
<td>d= 0,ls=0.0,diis</td>
<td>4</td>
<td>-76.4612059383</td>
<td>-1.70D-03</td>
<td>1.22D-04</td>
<td>2.85D-04</td>
<td>1.3</td>
</tr>
<tr>
<td>d= 0,ls=0.0,diis</td>
<td>5</td>
<td>-76.4612295784</td>
<td>-2.36D-05</td>
<td>9.96D-06</td>
<td>2.92D-06</td>
<td>1.5</td>
</tr>
<tr>
<td>d= 0,ls=0.0,diis</td>
<td>6</td>
<td>-76.4612298436</td>
<td>-2.65D-07</td>
<td>9.13D-07</td>
<td>1.20D-08</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Total DFT energy = -76.461229843644
One electron energy = -123.152783376272
Coulomb energy = 46.845330497950
Exchange-Corr. energy = -9.348757895598
Nuclear repulsion energy = 9.194980930276

Numeric. integr. density = 9.99999849828

Total iterative time = 1.4s
Some properties from the DFT calculation on water

Dipole moment 1.9215463499 Debye(s)

DMX 0.0000000000 DMXEFC 0.0000000000
DMY 0.0000000000 DMYEFC 0.0000000000
DMZ -1.9215463499 DMZEFC 0.0000000000

-EFC- dipole 0.0000000000 DEBYE(S)
Total dipole 1.9215463499 DEBYE(S)

Experimentally determined value: 1.85D

Energy of Highest Occupied Molecular Orbital -0.23440Ha -6.378eV
HOMO is orbital number 5
LUMO is orbital number 6

<table>
<thead>
<tr>
<th>state</th>
<th>eigenvalue (au)</th>
<th>occupation (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 + 1</td>
<td>a1.1 -18.757723</td>
<td>2.000</td>
</tr>
<tr>
<td>2 + 2</td>
<td>a1.1 -0.863579</td>
<td>2.000</td>
</tr>
<tr>
<td>3 + 1</td>
<td>a1.1 -0.436548</td>
<td>2.000</td>
</tr>
<tr>
<td>4 + 3</td>
<td>a1.1 -0.310631</td>
<td>2.000</td>
</tr>
<tr>
<td>5 + 1</td>
<td>a1.1 -0.234403</td>
<td>2.000</td>
</tr>
<tr>
<td>6 + 4</td>
<td>a1.1 -0.007900</td>
<td>0.000</td>
</tr>
<tr>
<td>7 + 2</td>
<td>a1.1 0.057462</td>
<td>0.000</td>
</tr>
<tr>
<td>9 + 5</td>
<td>a1.1 0.596166</td>
<td>0.000</td>
</tr>
<tr>
<td>10 + 2</td>
<td>b2.1 0.618430</td>
<td>0.000</td>
</tr>
<tr>
<td>14 + 1</td>
<td>a2.1 1.467383</td>
<td>0.000</td>
</tr>
</tbody>
</table>
DFT calculation on water (continued)

Some isovalue surface plots

Density

HOMO

LUMO

Optimised geometry

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stretch</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>0.96107</td>
</tr>
<tr>
<td>2</td>
<td>Stretch</td>
<td>1</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>0.96107</td>
</tr>
<tr>
<td>3</td>
<td>Bend</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td></td>
<td></td>
<td>104.56336</td>
</tr>
</tbody>
</table>
Energy of the non-interacting electrons

- The energy of the non-interacting electrons is equal to the sum of the energies of the occupied MOs

\[ \hat{h}_{KS} \psi_j(r) = \varepsilon_j \psi_j(r) \quad \Rightarrow \quad \int \psi_j^*(r) \hat{h}_{KS} \psi_j(r) dr = \varepsilon_j \int \psi_j^*(r) \psi_j(r) dr = \varepsilon_j 1 = \varepsilon_j \]

\[ \varepsilon_j = \int \psi_j^*(r) \left( -\frac{1}{2} \nabla^2 + V_{\text{ext}}(r) + V_{\text{Coul}}(r) + V_{\text{xc}}(r) \right) \psi_j(r) dr \]

\[ E_{BS} = 2 \sum_{j=1}^{N_{e1}/2} \varepsilon_j = 2 \sum_{j=1}^{N_{e1}/2} \int \psi_j^*(r) \left( -\frac{1}{2} \nabla^2 \right) \psi_j(r) dr + 2 \sum_{j=1}^{N_{e1}/2} \int \psi_j^*(r) \left( V_{\text{ext}}(r) + V_{\text{Coul}}(r) + V_{\text{xc}}(r) \right) \psi_j(r) dr \]

\[ = 2 \sum_{j=1}^{N_{e1}/2} \int \psi_j^*(r) \left( -\frac{1}{2} \nabla^2 \right) \psi_j(r) dr + \int V_{\text{ext}}(r) n(r) dr + \int V_{\text{Coul}}(r) n(r) dr + \int V_{\text{xc}}(r) n(r) dr \]

- This also called “band structure energy”. Notice that it is different from the energy of the interacting electrons
Energy of the interacting electrons

• By comparing the energy of the interacting and non-interacting electrons

Interacting:
\[ E_{KS}[n] = 2 \sum_{j=1}^{N_{el}/2} \int \psi_j^*(r) \left( -\frac{1}{2} \nabla^2 \right) \psi_j(r) \, dr + E_{ext}[n] + E_{Coul}[n] + E_{xc}[n] \]

Non-interacting:
\[ E_{BS} = 2 \sum_{j=1}^{N_{el}/2} \varepsilon_j = 2 \sum_{j=1}^{N_{el}/2} \int \psi_j^*(r) \left( -\frac{1}{2} \nabla^2 \right) \psi_j(r) \, dr + \int V_{ext}(r)n(r) \, dr + \int V_{Coul}(r)n(r) \, dr + \int V_{xc}(r)n(r) \, dr \]
\[ \cdot \int \frac{n(r')}{|r - r'|} \, dr' \]
\[ \frac{\delta E_{xc}}{\delta n} \]

• We obtain the following expression, which clearly shows that the energy of the interacting electrons is not equal to just a sum of orbital energies

\[ E_{KS}[n] = 2 \sum_{j=1}^{N_{el}/2} \varepsilon_j - E_{Coul}[n] - \int V_{xc}(r)n(r) \, dr + E_{xc}[n] \]
The energy of the interacting electrons is not equal to the sum of their MO energies

The energy of MO $\psi_j$:

$$\varepsilon_j = \int \psi_j^* (\mathbf{r}) \left( -\frac{1}{2} \nabla^2 + V_{\text{ext}} (\mathbf{r}) + V_{\text{Coul}} (\mathbf{r}) + V_{xe} (\mathbf{r}) \right) \psi_j (\mathbf{r}) d\mathbf{r}$$

includes Coulomb interaction with all other electrons

Example: For two electrons,

$$E_{BS} = \varepsilon_1 + \varepsilon_2$$

is over-estimating the Coulomb energy (counting it twice)
1) What types of energy each electron “feels” according to the expression for an orbital energy

\[ \varepsilon_j = \int \psi_j^* (r) \left( -\frac{1}{2} \nabla^2 + V_{\text{ext}} (r) + V_{\text{Coul}} (r) + V_{\text{xc}} (r) \right) \psi_j (r) \, dr \]

Discuss why it would be wrong to consider the energy of many interacting electrons simply as a sum of these energies.

2) Write down explicit expressions in terms of molecular orbitals only (so no density) for the Kohn-Sham energy of interacting electrons and for the Kohn-Sham potential. Assume \( E_{\text{xc}} [n] = C \int n^{\frac{5}{3}} (r) \, dr \) where \( C \) is a constant.

3) Using functional differentiation derive the expression for the Coulomb potential as the functional derivative of the Coulomb energy.
5-minute quiz

Name:
Surname:

1) What parts of the Kohn-Sham potential depend on the density?

2) Why do we need to use the SCF approach to do DFT calculations?

3) If you were to neglect completely from the Kohn-Sham Hamiltonian all the parts that depend on the density, what kind of electronic system would the resulting Hamiltonian describe? Would this be useful for any practical application?