CHEM6085: Density Functional Theory

Lecture 7

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

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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

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

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

$$n(\mathbf{r}) = 2 \sum_{i=1}^{N_{\mathrm{el}}/2} |\phi_i(\mathbf{r})|^2$$

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

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

- 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:

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

- To calculate the functional derivative with respect to the orbitals we can use the following "chain rule"

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

- With the following result

$$\frac{\partial n(\mathbf{r})}{\partial\phi_j^*(\mathbf{r})} = 2\phi_j(\mathbf{r})$$

- So, the functional derivative with respect to the MOs is

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

- The orbitals that minimise the energy must satisfy the condition

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

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

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

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

- It is possible to transform the set of {φ} orbitals to a new set of orbitals {ψ} with the same electronic density but a diagonal matrix of Lagrange multipliers

$$\left(-\frac{1}{2}\nabla^2\psi_j(\mathbf{r})\right) + \left(\frac{\delta E_{\mathrm{Coul}}}{\delta n} + \frac{\delta E_{\mathrm{ext}}}{\delta n} + \frac{\delta E_{\mathrm{xc}}}{\delta n}\right)\psi_j(\mathbf{r}) - \varepsilon_j\psi_j(\mathbf{r}) = 0$$

$$\left\{-\frac{1}{2}\nabla^2 + \left(\frac{\delta E_{\mathrm{Coul}}}{\delta n} + \frac{\delta E_{\mathrm{ext}}}{\delta n} + \frac{\delta E_{\mathrm{xc}}}{\delta n}\right)\right\}\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r})$$

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

- 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

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

$$\hat{h}_{KS}\,\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r})$$

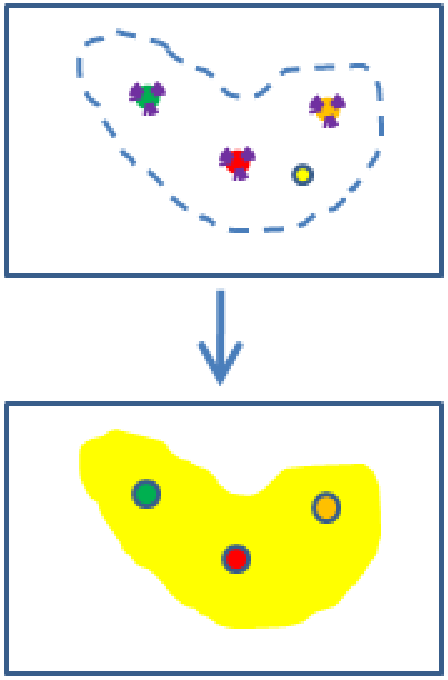
- It contains an expression for the "effective" potential

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

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

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



Density of fictitious system of non-interacting electrons (= exact density of interacting electrons)

- Let us examine the Kohn-Sham potential in more detail

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

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

- 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:

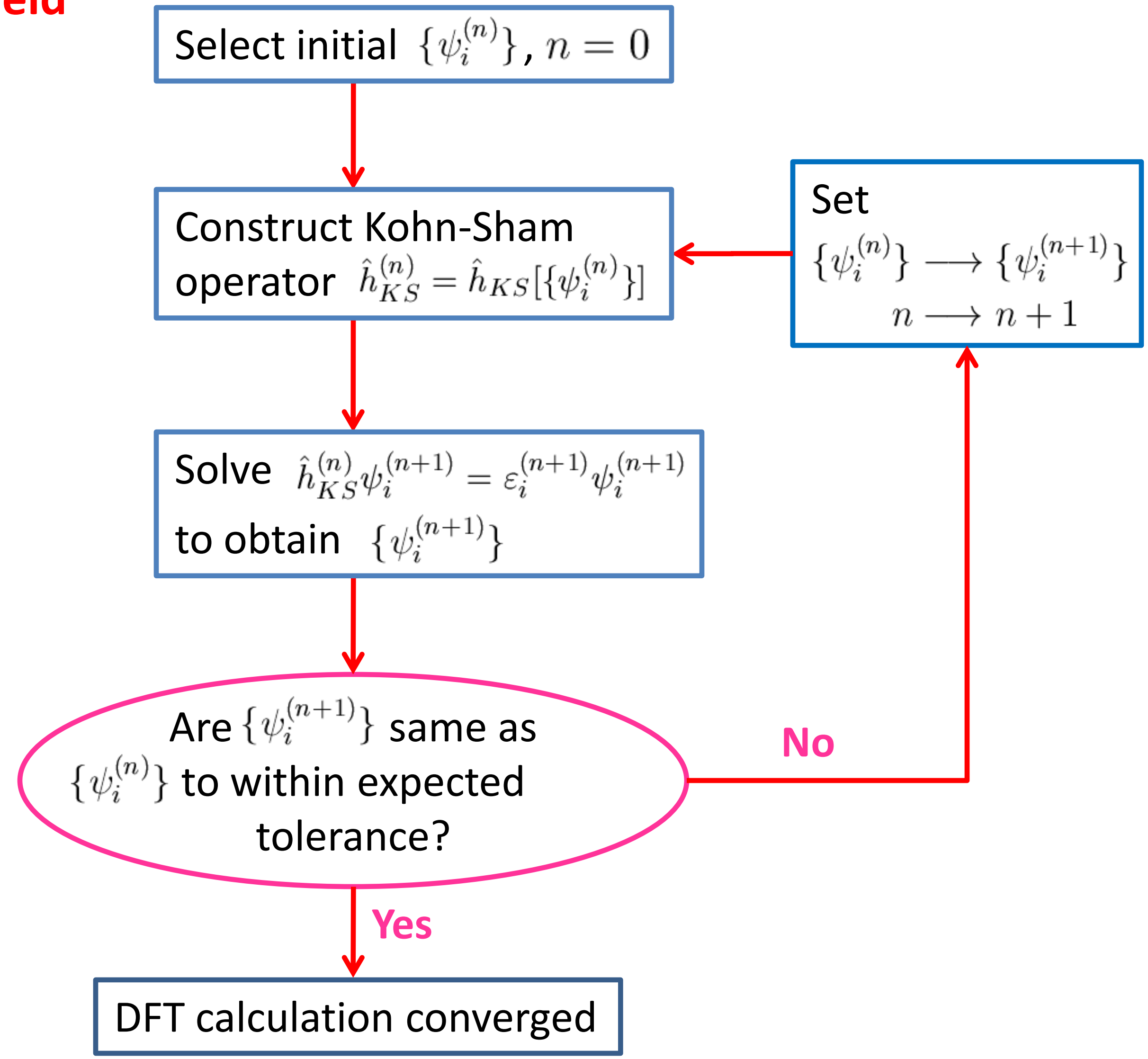
$$\left(-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right)\psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r})$$

- 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 $\hat{h}_{KS}^{(n)}\psi_i^{(n+1)} = \varepsilon_i^{(n+1)}\psi_i^{(n+1)}$ to obtain $\{\psi_i^{(n+1)}\}$

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

No

Set $\{\psi_i^{(n)}\} \longrightarrow \{\psi_i^{(n+1)}\}$ $n \longrightarrow n+1$

Yes

DFT calculation converged

Example: DFT calculation on a water molecule

SCF procedure

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


        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 =        9.999999849828

     Total iterative time =      1.4s
```

Some properties from the DFT calculation on water

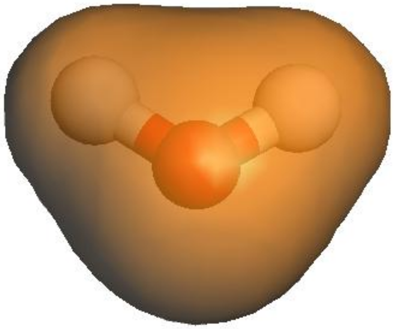
```
Dipole moment          1.9215463499 Debye(s)
          DMX          0.0000000000 DMXEFC        0.0000000000
          DMY          0.0000000000 DMYEFC        0.0000000000
          DMZ         -1.9215463499 DMZEFC        0.0000000000
-EFC- dipole           0.0000000000 DEBYE(S)
Total dipole           1.9215463499 DEBYE(S)
```

Experimentally determined value: 1.85D

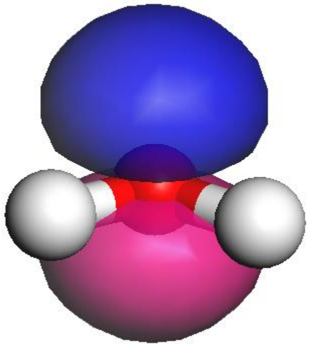
```
Energy of Highest Occupied Molecular Orbital  -0.23440Ha    -6.378eV
  HOMO is orbital number     5
  LUMO is orbital number     6

    state                         eigenvalue        occupation
                              (au)            (ev)

    1    +    1    a1.1    -18.757723      -510.424      2.000
    2    +    2    a1.1     -0.863579       -23.499      2.000
    3    +    1    b1.1     -0.436548       -11.879      2.000
    4    +    3    a1.1     -0.310631        -8.453      2.000
    5    +    1    b2.1     -0.234403        -6.378      2.000
    6    +    4    a1.1     -0.007900        -0.215      0.000
    7    +    2    b1.1      0.057462         1.564      0.000
    9    +    5    a1.1      0.596166        16.222      0.000
   10    +    2    b2.1      0.618430        16.828      0.000
   14    +    1    a2.1      1.467383        39.930      0.000
```

DFT calculation on water (continued)

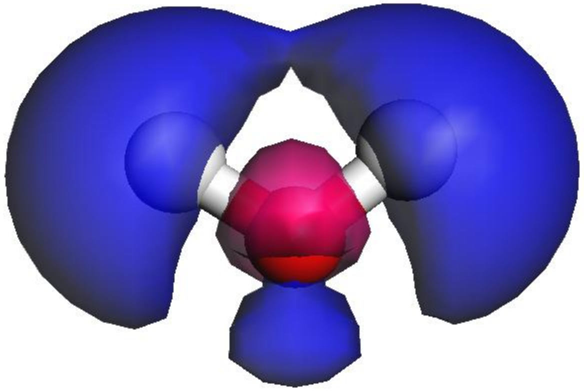
Some isovalue surface plots



Density



HOMO



LUMO

Optimised geometry

```
   Type          Name      I     J     K     L     M       Value
   ----------- --------  ----- ----- ----- ----- ----- ----------
 1 Stretch                 1     2                        0.96107
 2 Stretch                 1     3                        0.96107
 3 Bend                    2     1     3                104.56336
```

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

$$\hat{h}_{KS}\,\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r}) \Longrightarrow \int \psi_j^*(\mathbf{r})\hat{h}_{\mathrm{KS}}\psi_j(\mathbf{r})d\mathbf{r} = \varepsilon_j \int \psi_j^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} = \varepsilon_j\, 1 = \varepsilon_j$$

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

$$E_{\mathrm{BS}} = 2\sum_{j=1}^{N_{\mathrm{el}}/2}\varepsilon_j = 2\sum_{j=1}^{N_{\mathrm{el}}/2}\int\psi_j^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_j(\mathbf{r})d\mathbf{r} + 2\sum_{j=1}^{N_{\mathrm{el}}/2}\int\psi_j^*(\mathbf{r})\left(V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{Coul}}(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\psi_j(\mathbf{r})d\mathbf{r}$$

$$= 2\sum_{j=1}^{N_{\mathrm{el}}/2}\int\psi_j^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_j(\mathbf{r})d\mathbf{r} + \int V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int V_{\mathrm{Coul}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int V_{\mathrm{xc}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

- 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:

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

Non-interacting:

$$E_{\text{BS}} = 2\sum_{j=1}^{N_{\text{el}}/2} \varepsilon_j = 2\sum_{j=1}^{N_{\text{el}}/2} \int \psi_j^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_j(\mathbf{r}) d\mathbf{r} + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \int \underset{\underset{\displaystyle \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'}{\big\downarrow}}{V_{\text{Coul}}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \int \underset{\underset{\displaystyle \frac{\delta E_{\text{xc}}}{\delta n}}{\big\downarrow}}{V_{\text{xc}}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

- 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**

$$E_{\text{KS}}[n] = 2\sum_{j=1}^{N_{\text{el}}/2} \varepsilon_j - E_{\text{Coul}}[n] - \int V_{xc}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{\text{xc}}[n]$$

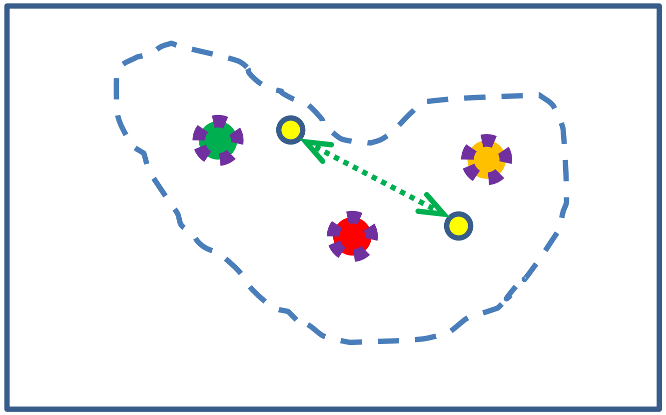
The energy of the interacting electrons is not equal to the sum of their MO energies

The energy of MO ψ_j :

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

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)

Homework

1) What types of energy each electron "feels" according to the expression for an orbital energy $\varepsilon_j = \int \psi_j^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{Coul}}(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \psi_j(\mathbf{r}) d\mathbf{r}$ 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 $E_{\text{xc}}[n] = C \int n^{\frac{4}{3}}(\mathbf{r}) d\mathbf{r}$ 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:

Date :

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?