This assignement is divided in two parts: **i)** in the first part you have to derive the KS equations (see instructions below); **ii)** in the second part you have to write the total energy as a function of the KS eigenvalues.

i) <u>Derive the KS equations</u> We have the following minimization problem :

$$\frac{\delta\big[E[n] - \lambda_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})\big]}{\delta\psi_i^*} = 0. \tag{1}$$

Let's replace the functional $E[n]$ by its full expression :

$$\frac{\delta\big[T_s[n] + \int \mathrm{d}\mathbf{r}n(\mathbf{r})V_{\text{ext}}(\mathbf{r}) + \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r'}\frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|} + E_{\text{xc}}[n] - \lambda_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})\big]}{\delta\psi_i^*} = 0. \tag{2}$$

We expand it (by additivity of the operator) and pass the last term of the left hand side to the right hand side :

$$\frac{\delta T_s[n]}{\delta\psi_i^*} + \frac{\delta\big[\int \mathrm{d}\mathbf{r}n(\mathbf{r})V_{\text{ext}}(\mathbf{r})\big]}{\delta\psi_i^*} + \frac{\delta\big[\frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r'}\frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|}\big]}{\delta\psi_i^*} + \frac{\delta E_{\text{xc}}[n]}{\delta\psi_i^*} = \frac{\delta\big[\lambda_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})\big]}{\delta\psi_i^*}. \tag{3}$$

We compute the i-th part of $\dfrac{\delta T_s[n]}{\delta\psi_i^*}$:

$$\frac{\delta}{\delta\psi_i^*}\left[\int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\frac{-\nabla^2}{2}\psi_i(\mathbf{r})\right] = -\frac{\nabla^2}{2}\psi_i(\mathbf{r}). \tag{4}$$

Now, the problem is that the ψ_i^* does not explicitly appear in the expression of the other terms of the left hand side. Let's multiply ingenuously by a quantity equal to one each term :

$$\frac{\delta\big[\int \mathrm{d}\mathbf{r}n(\mathbf{r})V_{\text{ext}}(\mathbf{r})\big]}{\delta\psi_i^*} = \frac{\delta\big[\int \mathrm{d}\mathbf{r}n(\mathbf{r})V_{\text{ext}}(\mathbf{r})\big]}{\delta n(\mathbf{r})}\frac{\delta n(\mathbf{r})}{\delta\psi_i^*} \tag{5}$$

In a previous lecture we found that $\dfrac{\delta n(\mathbf{r})}{\delta\psi_i^*} = \psi_i(\mathbf{r})$. And, by definition the first fraction of the right hand side is equal to $V_{\text{ext}}(\mathbf{r})$. We repeat the exact same process to compute $\dfrac{\delta\big[\frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r'}\frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|}\big]}{\delta\psi_i^*}$ and find : $\displaystyle\int \mathrm{d}\mathbf{r'}\frac{n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|} \times \psi_i(\mathbf{r})$.

The right hand side is equal to $\lambda_i\psi_i(\mathbf{r})$.

So, if we conclude, we found the following expression :

$$\left[-\frac{\nabla^2}{2}+V_{\text{ext}}(\mathbf{r})+\int \mathrm{d}\mathbf{r'}\frac{n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|}+\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}\right]\psi_i(\mathbf{r})=\lambda_i\psi_i(\mathbf{r}) \tag{6}$$

2) Total energy as function of KS eigenvalues

We want to make the formula $\sum_i \lambda_i$ appears, i.e. the sum of the eigenvalues. We think about the sum because we want to have the total energy.

A fondamental postulate of quantum mechanics is that, for orthonormalized wave-functions ψ, $\int_{\text{whole space}} \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) = 1$. So, a good move would be to multiply by the complex conjugate, integrate over the whole space and then sum for all i. Let's do that for the right hand side first :

$$\sum_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\lambda_i\psi_i(\mathbf{r}) = \sum_i \lambda_i. \tag{7}$$

Now, repeat the same process on the left hand side of the Kohn-Sham equations:

$$\sum_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\left[-\frac{\nabla^2}{2}+V_{\text{ext}}(\mathbf{r})+\int \mathrm{d}\mathbf{r'}\frac{n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|}+\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}\right]\psi_i(\mathbf{r}). \tag{8}$$

The first part is equal to :

$$\sum_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\frac{-\nabla^2}{2}\psi_i(\mathbf{r}) = T_s[n]. \tag{9}$$

The second part is equal to :

$$\sum_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})V_{\text{ext}}(\mathbf{r})\psi_i(\mathbf{r}) = \int \mathrm{d}\mathbf{r}n(\mathbf{r})V_{\text{ext, total}}(\mathbf{r}). \tag{10}$$

The third part is equal to :

$$\sum_i \int \mathrm{d}\mathbf{r}\psi_i^*(\mathbf{r})\int \mathrm{d}\mathbf{r'}\frac{n(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|}\psi_i(\mathbf{r}) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r'}\frac{n(\mathbf{r})n(\mathbf{r'})}{|r-r'|}. \tag{11}$$

And the last part is equal to :

$$\sum_i \int d\mathbf{r}\psi_i^*(\mathbf{r})\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}\psi_i(\mathbf{r}) = \int d\mathbf{r}n(\mathbf{r})\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \tag{12}$$

At last, the following expression was derived :

$$\sum_i \lambda_i = T_s[n] + \int d\mathbf{r}n(\mathbf{r})V_{\text{ext, total}}(\mathbf{r}) + \int d\mathbf{r}d\mathbf{r'}\frac{n(\mathbf{r})n(\mathbf{r'})}{|r-r'|} + \int d\mathbf{r}n(\mathbf{r})\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \tag{13}$$

We, finally, recall the definition of the total energy :

$$E[n] = T_s[n] + \int d\mathbf{r}n(\mathbf{r})V_{\text{ext, total}}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r'}\frac{n(\mathbf{r})n(\mathbf{r'})}{|r-r'|} + E_{\text{xc}}[n]. \tag{14}$$

Then, substituting $T_s[n]$ from equation (13) to equation (14) :

$$E[n] = \sum_i \lambda_i - \frac{1}{2}\int d\mathbf{r}d\mathbf{r'}\frac{n(\mathbf{r})n(\mathbf{r'})}{|r-r'|} + E_{\text{xc}}[n] - \int d\mathbf{r}n(\mathbf{r})\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \tag{15}$$