Derivation of Kohn-Sham Equation using variational calculus

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[Pardon me for any mistakes if any. I have used the same symbols as in lectures and assumed the constant value of m, h, etc. as 1 for all the document]

1 Kohn-Sham Idea

From the lecture, we understand that the Kohn-Sham idea was to visualize many-particle system as one-body problem as we do not have the idea of the Kinetic Energy and the Interactive internal Potential Energy term in the normal expression.
While performing this transition, we will be assured about the Kinetic Energy term for a single-particle system, and we can modify our (effective) potential energy term to include some variations along with a new: exchange-correlation functional.
The details of the equations can be seen from the lectures, and we start from the modification part. Our final equation of Kohn-Sham resembling the one-body system looks like:

$$\Big[\frac{-\nabla^2}{2} + V^{eff}(\mathbf{r})\Big]\psi_i(\mathbf{r}) = \lambda_i \psi_i(\mathbf{r}) \tag{1}$$

In the above equation, $V^{eff}(\mathbf{r})$, represents the effective potential, and the first term is a representation of the single-particle energy functional.
If clearly checked, one can write the expression of total energy in our case as:

$$E[n] = E^H[n] + E_{xc}[n] \tag{2}$$

where, $E^H[n]$, represents similarly the total energy of single particle system, and and the latter is called the Exchange-Correlation Energy, which is basically a correction term but it cannot be avoided.

$$E^H[n] = T_s[n] + \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{3}$$

where, the first term of RHS is the Kinetic Energy of the single-body term, second is the External potential functional including electron interaction with ion, and the last is the Hartree-Potential term for electron interaction. Also, representing the Exchange-Correlation energy:

$$E_{xc}[n] = T[n] - T_s[n] + E_{ee}[n] - \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{4}$$

where, $T[n]$ is the actual kinetic energy term, and the $E_{ee}[n]$ represents the actual electronic interaction potential.

Now, if we need to determine the $V^{eff}(\mathbf{r})$ term, and solve our DFT equation, we will need variational principles to dignify that the suitable wave function is the one, which gives us the minimum energy based on the constraints.

2 Assignment: Part I, Derivation:

For the minimization we take the variation of actual Energy term of many-body problem along with wave-function normalization constraint, and will try to resemble it to the Equation [1].

$$\frac{\delta[E[n] - \lambda_i(\int d\mathbf{r}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) - 1)]}{\delta\psi_i^*} = 0 \Rightarrow \frac{\delta[E[n] - \lambda_i(\int d\mathbf{r}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}))]}{\delta\psi_i^*} = 0 \tag{5}$$

Let us break the energy term using the relations shown in the Equation [2] and Equation [3]:

$$\frac{\delta\Big[T_s[n] + \int d\mathbf{r}n(\mathbf{r})V_{ext}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc} - \lambda_i(\int d\mathbf{r}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}))\Big]}{\delta\psi_i^*} = 0 \tag{6}$$

We are unknown to only the E_{xc} term, on which the approximations would be made at the later stages. Thus, we can proceed with our variation on all the rest functional present in the above equation.
Let us consider the first term, that is the Single-Body Kinetic Energy term:

$$T_s[n] = \sum_j \Big\langle \psi_j \Big| \frac{-\nabla^2}{2} \Big| \psi_j \Big\rangle = \sum_j \psi_j^* \Big(\frac{-\nabla^2}{2}\Big)\psi_j$$

Thus, for the above case variation can be simply written as:

$$\frac{\delta T_s[n]}{\delta\psi_i^*} = \delta_{ij}\Big(\frac{-\nabla^2}{2}\psi_j\Big) = \frac{-\nabla^2}{2}\psi_i \tag{7}$$

Let us move onto the second term of the Equation [6]. We will use the functional derivative explained in the lectures, where we derive the variations using Taylor's series expansion. I am just using expression and the derivations can be looked upon the lectures. For simple local functional like them, we can extract the variation as:

$$\frac{dF[f(x) + \epsilon\eta(x)]}{d\epsilon}\Big|_{\epsilon=0} = \int dx\frac{\delta F[f]}{\delta f(x)}\eta(x) \tag{8}$$

In our case, we have to apply the product rule as:

$$\frac{\delta \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r})}{\delta \psi_i^*} = \frac{\delta \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r})}{\delta n(\mathbf{r})} \frac{\delta n(\mathbf{r})}{\delta \psi_i^*}$$

Also, $n(\mathbf{r}) = \sum_j \psi_j^*(\mathbf{r})\psi_j(\mathbf{r})$, thus, $\frac{\delta n(r)}{\delta \psi_i^*} = \frac{\delta \sum_j \psi_j^*(\mathbf{r})\psi_j(\mathbf{r})}{\delta \psi_i^*} = \delta_{ij}\psi_j(\mathbf{r}) = \psi_i(\mathbf{r})$. Therefore following Equation [8], we get:

$$\frac{d \int d\mathbf{r}(n(\mathbf{r}) + \epsilon\eta(\mathbf{r}) V_{ext}(\mathbf{r})}{d\epsilon}\Big|_{\epsilon=0} = \int d\mathbf{r} V_{ext}(\mathbf{r})\eta(\mathbf{r})$$

Therefore, we get the result as:

$$\frac{\delta \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r})}{\delta \psi_i^*} = V_{ext}(\mathbf{r})\psi_i \tag{9}$$

Let us jump to our third term now in the Equation [6].
Again I am showing a functional derivative formula for similar case:

$$F[f] = \int dx \int dy f(x) W(x,y) f(y)$$

Here, if we apply the variation we get:

$$\frac{dF[f+\epsilon\eta]}{d\epsilon}\Big|_{\epsilon=0} = \frac{d}{d\epsilon}\int dx \int dy [f(x) + \epsilon\eta(x)] W(x,y) [f(y) + \epsilon\eta(y)]\Big|_{\epsilon=0}$$

$$\Rightarrow \int dx \int dy f(y) W(x,y)\eta(x) + \int dx \int dy f(x) W(x,y)\eta(y)$$

$$\Rightarrow \int dx \int dy f(y) W(x,y)\eta(x) + \int dx \int dy f(y) W(y,x)\eta(x)$$

Therefore:

$$\frac{\delta F[f]}{\delta f(x)} = \int dy f(y)(W(x,y) + W(y,x)) \tag{10}$$

Thus, in our third term, we apply Equation [10] as well as the product rule for $n(\mathbf{r})$ similar to the previous term:

$$\frac{\delta \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}{\delta \psi_i^*} = \frac{\delta \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}{\delta n(\mathbf{r})}\psi_i = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\psi_i \tag{11}$$

We are unknown to Exchange correlation term, thus we now focus to the last term of Equation [6], which by following the Equation [8], we obtain:

$$\frac{\delta \int d\mathbf{r} \psi_i^*(\mathbf{r})\psi_i(\mathbf{r})}{\delta \psi_i^*} = \psi_i(\mathbf{r}) \tag{12}$$

Therefore, our final equation out of Equation [6] using Equations [7], [9], [11] and [12] as well as product rule on Exchange-Correlation term we get:

$$\Big[\frac{-\nabla^2}{2} + V_{ext}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\Big]\psi_i(\mathbf{r}) = \lambda\psi_i(\mathbf{r}) \tag{13}$$

Thus, we can also clearly derive from Equation [13] and Equation [1] that,

$$V^{eff}[n] = V_{ext}[n] + V_H[n] + V_{xc}[n] \tag{14}$$

, where $V_H[n]$ represents the Hartree Potential Term in the Equation [13], and $V_{xc} = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$ is called the Exchange-Correlation Potential Term.

[This brings an end to this section. I am really sorry, for this has gone so long, but I wanted to clear my concept too, thus, explained every detail in my knowledge for this :)]

3 Assignment: Part II, Total Energy term:

Let us begin from the Equation [1], and recognize that the term in bracket in LHS is the Hamiltonian of the system considered as one-body particle. Let us exploit it:

$$E_s[n] = \sum_i \psi_i^* \hat{H}\psi_i = \sum_i \psi_i^* [\frac{-\nabla^2}{2} + V^{eff}(\mathbf{r})\Big]\psi_i = \sum_i \psi_i^* \lambda_i \psi_i = \sum_i \lambda_i \tag{15}$$

Therefore:

$$T_s[n] = \sum_i \lambda_i - \int d\mathbf{r} n(\mathbf{r}) V^{eff}(\mathbf{r}) \tag{16}$$

Now, let us look for V^{eff} term using Equation [14]:

$$\int d\mathbf{r} V^{eff}(\mathbf{r}) n(\mathbf{r}) = \int d\mathbf{r}(V_{ext}[n] + V_H[n] + V_{xc}[n]) n(\mathbf{r})$$

$$\int d\mathbf{r} V^{eff}(\mathbf{r}) n(\mathbf{r}) = \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) + 2 \times \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r}) V_{xc}[n] \tag{17}$$

Now, let us compile with Equations [2], [3], [16] and [17]:

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

$$\Rightarrow E[n] = \sum_i \lambda_i - \int d\mathbf{r} n(\mathbf{r}) V^{eff}(\mathbf{r}) + \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n]$$

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$$\Rightarrow E[n] = \sum_i \lambda_i - \Big(\int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) + 2 \times \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r}) V_{xc}[n] \Big)$$

$$+ \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]$$

Therefore, we get:

$$E[n] = \sum_i \lambda_i - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d\mathbf{r} n(\mathbf{r}) V_{xc}[n] + E_{xc}[n] \tag{18}$$

where, $V_{xc} = \frac{\delta E_{xc}[n]}{\delta n(r)}$ as defined above.
This marks the completion of the expression of Total Energy in term of eigen values, and the Equation [18] is our desired answer. Thanks!