Kohn-Sham Equation

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Part I: Derivation of Kohn-Sham Equations

The total energy functional of the electron density $E[n]$ is given by:

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

where:

- $T_s[n]$ is the kinetic energy functional of non-interacting electrons.
- $\int dr\, n(r) V_{\text{ext}}(r)$ is the external potential energy.
- $\frac{1}{2} \int dr\, dr' \, \frac{n(r)n(r')}{|\mathbf{r}-\mathbf{r}'|}$ is the Hartree energy.
- $E_{xc}[n]$ is the exchange-correlation energy.

Using Lagrange multipliers to impose the orthonormality of the single-particle wavefunctions $\psi_i(r)$:

$$\delta \left[E[n] - \sum_i \lambda_i \left(\int dr\, \psi_i^*(r) \psi_i(r) - 1 \right) \right] = 0 \tag{2}$$

The density is given by:

$$n(r) = \sum_i |\psi_i(r)|^2 \tag{3}$$

The energy functional becomes:

$$E[n] = -\frac{1}{2} \sum_i \int dr\, \psi_i^*(r) \nabla^2 \psi_i(r) + \int dr\, n(r) V_{\text{ext}}(r) + \frac{1}{2} \int dr\, dr' \, \frac{n(r)n(r')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \tag{4}$$

The functional derivative with respect to $\psi_i^*(r)$ gives:

$$\frac{\delta E[n]}{\delta \psi_i^*(r)} = -\frac{1}{2} \nabla^2 \psi_i(r) + V_{\text{ext}}(r) \psi_i(r) + \int dr' \, \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|} \psi_i(r) + \frac{\delta E_{xc}[n]}{\delta n(r)} \psi_i(r) \tag{5}$$

Setting the derivative to zero, we obtain the Kohn-Sham equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r)\right]\psi_i(r) = \lambda_i \psi_i(r) \tag{6}$$

where:

$$V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int dr' \, \frac{n(r')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(r)} \tag{7}$$

Part II: Total Energy as a Function of Kohn-Sham Eigenvalues

The Kohn-Sham energy functional is:

$$E_s[n] = T_s[n] + \int dr \, n(r) V_{\text{eff}}(r) \tag{8}$$

Using the Kohn-Sham eigenvalues, the total energy can be written as:

$$E = \sum_i \lambda_i - \frac{1}{2}\int dr \, dr' \, \frac{n(r)n(r')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] - \int dr \, n(r) \frac{\delta E_{xc}[n]}{\delta n(r)} \tag{9}$$

Summary

1. The Kohn-Sham equations were derived by minimizing the total energy functional with respect to the single-particle wavefunctions, subject to orthonormality constraints.
2. The total energy was expressed as a function of the Kohn-Sham eigenvalues, highlighting the relationship between the non-interacting system and the real interacting system.