Inverse Kohn-Sham method

Kadantsev and Stott, PRA 69, 012502 (2004).

Astala and Stott, PRB 73, 115127 (2006).

Since we consider an independent-particle system, the eigenstates are given by a single determinant which satisfies the Schrödinger eq.:

$$(\hat{T} + V_{ext})\,\Phi_I = E_I\,\Phi_I \quad \cdots\cdots (1)$$

where

$$\Phi_I = \frac{1}{\sqrt{N!}} \left| \varphi_{I1}\,\varphi_{I2} \cdots \varphi_{IN-1}\,\varphi_{IN} \right| \quad \cdots\cdots (2)$$

Inserting (2) to (1), we have

$$\left(-\frac{1}{2}\nabla^2 + V_{ext}\right)\varphi_{I\mu}(r) = \varepsilon_{I\mu}\,\varphi_{I\mu}(r) \quad \cdots\cdots (3)$$

Noting $\{\varphi_{I\mu}\}$ satisfies

$$\sum_{\mu}^{occ.} |\varphi_{I\mu}(r)|^2 = \underbrace{\rho(r)}_{\text{density}} \quad \cdots\cdots (5)$$

multiplying (3) by $\varphi_{I\mu}^*$, and summing over μ, we have

$$V_{ext}(r) = \frac{1}{\rho(r)} \sum_{\mu}^{occ.} \left[\frac{1}{2}\varphi_{I\mu}^*\nabla^2\varphi_{I\mu} + \varepsilon_{I\mu}|\varphi_{I\mu}|^2 \right] \quad \cdots\cdots (6)$$

If V_{ext} is replaced by V_{eff} in the KS method, ②

We need to find V_{eff} which gives a given ρ_0.

So, we consider the case.

KS eq.

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\varphi_\mu = \varepsilon_\mu \varphi_\mu \quad \cdots\cdots (6)$$

$$\rho_0(r) = \sum_\mu^{occ.} |\varphi_\mu(r)|^2 \quad \cdots\cdots (7)$$

From (6), we have

$$T_s[V_{eff}, \rho_0] = \sum_\mu^{occ.} \varepsilon_\mu[V_{eff}] - \int dr^3\, V_{eff}(r)\rho_0(r) \quad \cdots\cdots (8)$$

T_s can be rewritten as

$$T_s[V_{eff}, \rho_0] = \min_{\{|\Phi\rangle \to \rho_0\}} \left[\langle\Phi|(\hat{T} + V_{eff})|\Phi\rangle\right] - \int dr^3\, V_{eff}\, \rho_0 \quad \cdots (9)$$

It is important to notice that (9) is valid for any V_{eff}. So one can write as

$$T_s[V, \rho_0] = \min_{\{|\Phi\rangle \to \rho_0\}} \left[\langle\Phi|(\hat{T} + V)|\Phi\rangle\right] - \int dr^3\, V \rho_0 \quad \cdots (10)$$

any external potential

However, we know that

$$\left.\begin{array}{l}\hat{T} + V \to \rho \\ \hat{T} + V_{eff} \to \rho_0\end{array}\right\} \Longrightarrow \rho \neq \rho_0 \quad \text{unless } V = V_{eff} + \text{const}$$

So, we have

$$\min_{\{|\Phi\rangle \to \rho_0\}} \left[\langle \Phi | (\hat{T} + V) | \Phi \rangle \right] \geq \min_{\{|\Phi\rangle \to \rho\}} \left[\langle \Phi | (\hat{T} + V) | \Phi \rangle \right]$$

$$= \sum_{\mu}^{occ.} \varepsilon_\mu [V] \quad \cdots\cdots (11)$$

From (10), we see

$$\min_{\{|\Phi\rangle \to \rho_0\}} \left[\langle \Phi | (\hat{T} + V) | \Phi \rangle \right] = T_s [V, \rho_0] + \int d\vec{r}^3 V \rho_0 \quad \cdots\cdots (12)$$

Putting (12) into the left-hand side of Eq. (11), we have

$$T_s [V, \rho_0] \geq \sum_{\mu}^{occ.} \varepsilon_\mu [V] - \int d\vec{r}^3 V \rho_0 \quad \cdots (13)$$

$$- T_s [V, \rho_0] \leq - \sum_{\mu}^{occ.} \varepsilon_\mu [V] + \int d\vec{r}^3 V \rho_0 \quad \cdots\cdots (13')$$

Then, we define Y as

$$Y [V] \equiv - \sum_{\mu}^{occ.} \varepsilon_\mu [V] + \int d\vec{r}^3 V(r) \rho_0(r) \quad \cdots\cdots (14)$$

Thus, from (13') and (14), we see the following variational property.

$$Y [V] \geq - T_s [V, \rho_0] \quad \cdots\cdots (15)$$

The equality in Eq. (15) holds in case of

There fore $V = V_{eff} + \text{const.}$

$$\left[\frac{\delta Y[V]}{\delta V} \right]_{V = V_{eff} + \text{Const}} = 0 \quad \cdots\cdots (16)$$

From (14), we obtain

$$\frac{\delta Y[V]}{\delta V} = - \frac{\delta}{\delta V} \left[\min_{\{\Phi\} \to \rho} \langle \Phi | (\hat{T} + V) | \Phi \rangle \right] + \rho_0 (r)$$

↳ Hellman - Feynman theorem

$$= - \rho(r) + \rho_0(r) \quad \cdots\cdots (17)$$

So, using (17) one can update V step by step.

$$V_{eff}^{new} = V_{eff}^{old} - \alpha (\rho_0 - \rho) \quad \cdots\cdots (18)$$

The converged V_{eff} gives ρ_0.

This procedure is an inverse Kohn - Sham method.