Hohenberg-Kohn

Fact

For any Hermitian operator $\hat{Q}$, $\exists$ function $E(Q)$ that is minimized (with $E = E_{\rm gs}$) when $Q = \langle\hat{Q}\rangle_{\rm gs}$.

Universality: Adding $\alpha\hat{Q}$ to the Hamiltonian just adds αQ to the function. The function is just

$$E(Q) = \min_{\psi\to Q}\langle\psi|H|\psi\rangle$$

Generalized HK theorem

For any continuous set of Hermitian operators $\hat{Q}(\mathbf{r})$, $\exists$ functional $E[Q(\mathbf{r})]$ that is minimized (with $E = E_{\rm gs}$) when $Q(\mathbf{r}) = \langle\hat{Q}(\mathbf{r})\rangle_{\rm gs}$.

Universality: Adding $\int V(\mathbf{r})\hat{Q}(\mathbf{r})$ to the Hamiltonian just adds $\int V(\mathbf{r})Q(\mathbf{r})$ to the function. The functional is just

$$E[Q(\mathbf{r})] = \min_{\psi\to Q}\langle\psi|H|\psi\rangle$$

Just apply this to $\rho_I(\mathbf{r}) \equiv \rho(\mathbf{r} + \hat{\mathbf{R}}_{\rm CM})$ $\quad \int V(\mathbf{r})\hat{\rho}_I(\mathbf{r}) \longrightarrow \sum_i V(\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_{\rm CM})$

Legendre Transform Interpretation

$$\mathcal{E}[J] \equiv \langle \hat{H} + \int J(\mathbf{r})\hat{\rho}_I(\mathbf{r})d\mathbf{r}\rangle_{\rm gs}^J ,$$

$$E[\rho_I] = \mathcal{E}[J_{\rho_I}] - \int J_{\rho_I}(\mathbf{r})\rho_I(\mathbf{r})d\mathbf{r} \qquad \frac{\delta E[\rho_I]}{\delta \rho_I} = -J_{\rho_I} \longrightarrow 0 \quad \text{at } \rho_I\text{(gs)}$$

Inversion Procedure

$$\mathcal{E}[J] \quad = \quad \mathcal{E}_0[J] + \mathcal{E}_c[J] \quad = \quad \mathcal{E}_0[J_0 + J_c] + \mathcal{E}_c[J_0 + J_c]$$

$$E[\rho_I] = E_0[\rho_I] + E_c[\rho_I]$$

$$E_0[\rho_I] = \mathcal{E}_0[J_0] - \int J_0(\mathbf{r})\rho_I(\mathbf{r})d\mathbf{r} \qquad E_c[\rho_I] = \mathcal{E}_c[J_0] + \cdots$$

$$\frac{\delta E_c}{\delta \rho_I} = \frac{\delta E}{\delta \rho_I} - \frac{\delta E_0}{\delta \rho_I} = -(J - J_0) \longrightarrow J_0 \quad \text{(ground state)}$$

Kohn-Sham Orbitals

For normal density, choose $\mathcal{E}_0$ to be noninteracting.

Here, choose $\mathcal{E}_0$ to be mean-field approximation.

For 1-d system with spin degeneracy N and contact interaction:

$$H = -\frac{1}{2m}\sum_{i=1}^{N}\frac{d^2}{dx_i^2} - g\sum_{i<j}\delta(x_i - x_j)$$

$$\mathcal{E}_0[J_0] = \int dx\left[\frac{N}{2m}|\phi'(x)|^2 - \frac{N(N-1)g}{2}|\phi(x)|^4 + J_0(x)\langle\hat{\rho}_I(x)\rangle_{\mathrm{mf}}\right]$$

$$E_0[\rho_I] = \int dx\left[\frac{N}{2m}|\phi'(x)|^2 - \frac{N(N-1)g}{2}|\phi(x)|^4\right]$$

$$\langle\hat{\rho}_I(x)\rangle_{\mathrm{mf}} = N\left[|\phi(x+\bar{x})|^2 + \frac{1}{N}\left(|\phi(x+\bar{x})|^2 + x\frac{d}{dx}|\phi(x+\bar{x})|^2 + \frac{\mu}{2}\frac{d^2}{dx^2}|\phi(x+\bar{x})|^2\right) + .$$

$$\mu = \langle(x-\bar{x})^2\rangle$$

Next Order: Ring Diagrams

Mean-field Equations:

$$-\frac{\phi''(x)}{2m}-\left[(N-1)g|\phi(x)|^2-J_0^{\bar{x}}(x)+(x-\bar{x})\int J_0^{\bar{x}\prime}(y)|\phi(y)|^2dy\right]\phi(x)$$

$$+\frac{\mu}{2N}\left[J_0^{\bar{x}\prime\prime}(x)-(x-\bar{x})\int J_0^{\bar{x}\prime\prime\prime}(y)|\phi(y)|^2dy+\frac{(x-\bar{x})^2}{\mu}\int J_0^{\bar{x}\prime\prime}(y)|\phi(y)|^2dy\right]\phi(x)=\epsilon\phi(x)$$

Effective interaction:

$$V(x_1,x_2)=-g\delta(x_1-x_2)-\frac{1}{N}\left[(x_1-\bar{x})\,J_0'(x_2-\bar{x})+(x_2-\bar{x})\,J_0'(x_1-\bar{x})\right]$$
$$-\frac{1}{N}\left[(x_1-\bar{x})(x_2-\bar{x})\left(\int J_0''(y-\bar{x})|\phi^2(y)|dy\right)\right]+\ldots$$

Correction to functional:

$$E_c[\rho_I]=\frac{1}{2\pi}\int_0^\infty \mathrm{Re}\left(\mathrm{Tr}\left[\ln(1-\hat{R}(i\omega)\hat{V})+\hat{R}(i\omega)\hat{V}\right]\right)d\omega+\ldots$$

$$R(x,x';\omega)=\phi(x)\phi(x')\left[\langle x|\frac{1}{\omega+\epsilon+i\eta-\hat{h}[J_0]}|x'\rangle+\langle x'|\frac{1}{-\omega+\epsilon+i\eta-\hat{h}[J_0]}|x\rangle\right]$$

Phenomenological functional

$$E[\rho_I] = E_0^*[\rho_I] + E_c[\rho_I]\,, \quad E_c[\rho_I] = -\int dx \left(\frac{\beta g}{2N}\rho_I^2 + \frac{\gamma}{6m^* N^3}\rho_I^3 \right) + \ldots$$

Kohn-Sham equation:

$$-\frac{\phi''}{2m^*} - (N-1+\beta)g|\phi|^2\phi - \frac{\gamma}{2m^* N}|\phi|^4\phi = \epsilon\phi$$

β,γ, m^* can be determined so that KS equation gets E and ρ_I right to $\mathcal{O}(1/N)$. Not correct away from minimum.