# Basic Existence Theorems in DFT and DMFT

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## Definition of Density:

$$\rho(r_1) = N \int \cdots \int \Psi^*(x_1, x_2 \cdots x_N)\, \Psi(x_1, x_2 \cdots x_N)\, ds_1\, dx_2 \cdots dx_N$$

## An Infinite Number of Wavefunctions Yields Any Density: Example I

$$\left\{ \begin{array}{l} \Psi(r) = e^{-r} \\ \Psi(r) = e^{-r} e^{i f(r)} \end{array} \right.$$

$$\downarrow$$

$\rho(r) = e^{-2r}$ in both cases.

# Example II

$$\Psi(x_1, x_2) = \left[ c_A \varphi_A(r_1) \varphi_A(r_2) + c_B \varphi_B(r_1) \varphi_B(r_2) \right] \Theta_{spin}$$

$$\Psi(x_1, x_2) = \left[ c_A \varphi_A(r_1) \varphi_A(r_2) - c_B \varphi_B(r_1) \varphi_B(r_2) \right] \Theta_{spin}$$

where $\langle \varphi_A | \varphi_A \rangle = \langle \varphi_B | \varphi_B \rangle = 1$,

$$\langle \varphi_A | \varphi_B \rangle = 0.$$

Then, for both cases,

$$\rho(r_1) = 2 \left[ c_A^2 \varphi_A(r_1)^2 + c_B^2 \varphi_B(r_1)^2 \right],$$

where $\varphi_A$ and $\varphi_B$ are real,

and $c_A$ and $c_B$ are real.

## Integral of Density and External Potential: Two-Electron Example:

$$\langle \Psi(x_1\, x_2) \,|\, v(r_2) \,|\, \Psi(x_1\, x_2) \rangle$$

$$= \langle -\Psi(x_2\, x_1) \,|\, v(r_2) \,|\, -\Psi(x_2\, x_1) \rangle$$

$$= \langle \Psi(x_2\, x_1) \,|\, v(r_2) \,|\, \Psi(x_2\, x_1) \rangle$$

$$= \langle \Psi(x_1, x_2) \,|\, v(r_1) \,|\, \Psi(x_1\, x_2) \rangle .$$

So,

$$\langle \Psi(x_1\, x_2) \,|\, v(r_1) + v(r_2) \,|\, \Psi(x_1\, x_2) \rangle$$

$$= 2 \langle \Psi(x_1\, x_2) \,|\, v(r_1) \,|\, \Psi(x_1\, x_2) \rangle .$$

$$= 2 \int d^3r_1\, v(r_1) \iint \Psi^*(x_1 x_2)\, \Psi(x_1 x_2)\, ds_1\, dx_2$$

$$= \int d^3r_1\, v(r_1)\, \rho(r_1) .$$

# Euler Equation and the Functional Derivative

$$E_{GS} = \min_{\rho} \left\{ \int v(r)\rho(r)\, d^3r + F[\rho] \right\}$$

$$E_{GS} = \int v(r)\, \rho_{GS}(r)\, d^3r + F[\rho_{GS}].$$

Therefore,

$$\frac{\partial}{\partial \epsilon} \left\{ \int v(r) [\rho_{GS}(r) + \epsilon \underbrace{\Delta\rho(r)}_{\text{arbitrary}}]\, d^3r + F[\rho_{GS}(r) + \epsilon \Delta\rho(r)] \right\}_{\epsilon=0} = 0$$

Obtain

$$\int v(r)\, \Delta\rho(r)\, d^3r + \left( \frac{\partial F}{\partial \epsilon}[\rho_{GS} + \epsilon\Delta\rho] \right)_{\epsilon=0} = 0.$$

or,

$$\int v(r)\,\Delta\rho(r)\,d^3r + \int \left(\frac{\delta F}{\delta \rho}\right)_{\rho=\rho_{GS}} \Delta\rho(r)\,d^3r$$

$$= 0,$$

so that

$$\int \left[ v(r) + \left(\frac{\delta F}{\delta \rho}\right)_{\rho=\rho_{GS}} \right] \Delta\rho(r)\,d^3r = 0.$$

Moreover, since $\Delta\rho$ is arbitrary and since $\int \Delta\rho(r)\,d^3r = 0$, it follows that

$$v(r) + \left(\frac{\delta F}{\delta \rho}\right)_{\rho=\rho_{GS}} = \text{constant},$$

which is the Euler Equation.

Examples of Obtaining $\frac{\delta F[\rho]}{\delta \rho}$, the functional derivative.

Say $F[\rho] = \int \rho^M(r)\, d^3r$.

Then,

$$F[\rho + \epsilon \Delta\rho] = \int [\rho(r) + \epsilon \Delta\rho(r)]^M d^3r$$

$$\left.\frac{\partial F[\rho + \epsilon\Delta\rho]}{\partial \epsilon}\right|_{\epsilon=0} = \int M\rho(r)^{M-1} \Delta\rho(r)\, d^3r.$$

Therefore,

$$\frac{\delta F[\rho]}{\delta \rho} = M\rho^{M-1}(r).$$

(M was $\frac{4}{3}$ in John Perdew's Example)

Say $F[\rho] = \int \rho(r) \nabla^2 \rho(r) \, d^3r$.

Then,

$$F[\rho + \epsilon \Delta\rho] = \int [\rho + \epsilon \Delta\rho] \nabla^2 [\rho + \epsilon \Delta\rho] \, d^3r,$$

so that

$$\frac{\partial F[\rho + \epsilon \Delta\rho]}{\partial \epsilon}$$

$$= \int \frac{\partial}{\partial \epsilon} [\rho + \epsilon \Delta\rho] \nabla^2 [\rho + \epsilon \Delta\rho] \, d^3r$$

$$+ \int [\rho + \epsilon \Delta\rho] \nabla^2 \frac{\partial}{\partial \epsilon} [\rho + \epsilon \Delta\rho] \, d^3r.$$

Or, because $\nabla^2$ is Hermitian, it follows that

$$\left(\frac{\partial F[\rho+\epsilon\Delta\rho]}{\partial\epsilon}\right)_{\epsilon=0}$$

derivative not taken here

$$= 2\left(\int \frac{\partial}{\partial\epsilon}\,[\rho+\epsilon\Delta\rho]\,\nabla^2[\rho+\epsilon\Delta\rho]\,d^3r\right)_{\epsilon=0}$$

$$= 2\int \Delta\rho(r)\,\nabla^2\rho(r)\,d^3r.$$

Thus, if we pretend that

$$F[\rho] = \int \rho(r)\,\nabla^2\rho(r)\,d^3r,$$

then

$$\frac{\delta F[\rho]}{\delta\rho} = 2\nabla^2\rho(r).$$

$\Psi_{GS}$ is an eigenfunction of only one Hamiltonian with a multiplicative potential.

Say $[\hat{T} + \hat{W}]\Psi_{GS} = E\Psi_{GS}$

multiplicative

$$[\hat{T} + \hat{W}']\Psi_{GS} = E'\Psi_{GS}$$

Subtract. Obtain

$$(\hat{W}' - \hat{W})\Psi_{GS} = (E' - E)\Psi_{GS},$$

so that

$$\hat{W}' = \hat{W} + (E' - E).$$

Thus,

$\hat{W}' = \hat{W}$ within an additive constant.

# Constrained-Search Proof of Generalized Hohenberg-Kohn Variational Theorem

$$E_{GS} = \underset{\Psi}{\mathrm{Min}} \langle \Psi | \sum_{i=1}^{N} v(r_i) + \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$E_{GS} = \underset{\rho}{\mathrm{Min}} \underset{\Psi \to \rho}{\mathrm{Min}} \langle \Psi | \sum_{i=1}^{N} v(r_i) + \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$E_{GS} = \underset{\rho}{\mathrm{Min}} \left\{ \int v(r) \rho(r) d^3r + \underset{\Psi \to \rho}{\mathrm{Min}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \right\}$$

(for degeneracies and non-degeneracies)

$$E_{GS} = \min_{\rho} \left\{ \int v(r)\rho(r)\,d^3r + F[\rho] \right\},$$

where

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle .$$

Applies for degenerate as well as non-degenerate situations.

Given $\rho_{GS}$, $\Psi_{GS}$ is clearly identified as the wavefunction that yields $\rho_{GS}$ and simultaneously minimizes the expectation value of $\hat{T} + \hat{V}_{ee}$. Thus,

$$\left[ \rho_{GS} \rightarrow \Psi_{GS} \rightarrow \hat{H} \rightarrow \text{all properties of the system.} \right]$$

The step $\Psi_{GS} \rightarrow \hat{H}$ follows from the fact that a wavefunction can only be an eigenfunction of only one Hamiltonian with a local-multiplicative attractive potential.

(applies for degeneracies and non-degeneracies)

$$E_{GS} = \underset{\rho}{\mathrm{Min}} \left\{ \int v(r)\rho(r)\, d^3r + F[\rho] \right\}$$

$$v(r) = -\left.\frac{\delta F[\rho]}{\delta \rho}\right|_{\rho=\rho_{GS}}$$

So, $\rho_{GS}(r) \rightarrow v(r)$

Also,

$$\int \rho_{GS}(r)\, d^3r = N \begin{array}{l} \nearrow \hat{T} \\ \searrow \hat{V}_{ee} \end{array}$$

Thus,

$\rho_{GS} \rightarrow \hat{H} \rightarrow$ all properties of the system.

(applies for degeneracies and non-degeneracies)

# Coordinate Scaling Properties of Functionals And Other Thoughts

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# Partition of $F[\rho]$

$$F[\rho] = T_s[\rho] + J[\rho] + E_x[\rho] + E_c[\rho]$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} d^3r_1 \, d^3r_2$$

$$T_s[\rho] = \underset{\Psi \to \rho}{\mathrm{Min}} \langle \Psi | \hat{T} | \Psi \rangle$$

$$T_s[\rho] = \langle \Phi | \hat{T} | \Phi \rangle$$

$$E_x[\rho] = \langle \Phi | \hat{V}_{ee} | \Phi \rangle - J[\rho]$$

$$E_c[\rho] = F[\rho] - \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle$$

$\Phi$ = KS Determinant.

# Coordinate Scaling of the Density

start with $\rho(r) = \rho(x, y, z)$

and form

$$\rho_\lambda(r) = \lambda^3 \rho(\lambda x, \lambda y, \lambda z),$$

or

$$\rho_\lambda(r) = \lambda^3 \rho(\lambda r).$$

The $\lambda^3$ is to keep the density normalized to N electrons.

$$\int \rho_\lambda(r)\, d^3r = \int \lambda^3 \rho(\lambda x, \lambda y, \lambda z)\, dx\, dy\, dz$$

$$= \int \rho(\lambda x, \lambda y, \lambda z)\, d(\lambda x)\, d(\lambda y)\, d(\lambda z)$$

$$= \int \rho(x', y', z')\, dx'\, dy'\, dz'$$

$$= \int \rho(x, y, z)\, dx\, dy\, dz = N$$

$$J[\rho] = \frac{1}{2}\int \frac{\rho(r_1)\,\rho(r_2)}{|r_1 - r_2|}\,d^3r_1\,d^3r_2$$

$$J[\rho_\lambda] = \frac{1}{2}\int \frac{\lambda^3\rho(\lambda r_1)\,\lambda^3\rho(\lambda r_2)}{|r_1 - r_2|}\,d^3r_1\,d^3r_2$$

$$J[\rho_\lambda] = \frac{1}{2}\int \frac{\rho(\lambda r_1)\,\rho(\lambda r_2)}{|r_1 - r_2|}\,d^3(\lambda r_1)\,d^3(\lambda r_2)$$

$$J[\rho_\lambda] = \frac{1}{2}\lambda\int \frac{\rho(\lambda r_1)\,\rho(\lambda r_2)}{|\lambda r_1 - \lambda r_2|}\,d^3(\lambda r_1)\,d^3(\lambda r_2)$$

$$J[\rho_\lambda] = \frac{1}{2}\lambda \int \frac{\rho(\lambda r_1)\,\rho(\lambda r_2)}{|\lambda r_1 - \lambda r_2|}\, d^3(\lambda r_1)\, d^3(\lambda r_2)$$

$$J[\rho_\lambda] = \frac{1}{2}\lambda \int \frac{\rho(r_1')\,\rho(r_2')}{|r_1' - r_2'|}\, d^3(r_1')\, d^3(r_2')$$

$$J[\rho_\lambda] = \frac{1}{2}\lambda \int \frac{\rho(r_1)\,\rho(r_2)}{|r_1 - r_2|}\, d^3(r_1)\, d^3(r_2)$$

$$J[\rho_\lambda] = \lambda J[\rho].$$

$$\Phi(r_1 \cdots r_N) \to \rho(r)$$

$$\Phi_\lambda(r_1 \cdots r_N) = \lambda^{3N/2} \Phi(\lambda r_1 \cdots \lambda r_N) \to \lambda^3 \rho(\lambda r) \to \rho_\lambda(r).$$

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$$\int \Phi_\lambda^*(r_1 \cdots r_N) \frac{1}{|r_i - r_j|} \Phi_\lambda(r_1 \cdots r_N)\, d^3r_1 \cdots d^3r_N$$

$$= \int \Phi^*(\lambda r_1 \cdots \lambda r_N) \frac{1}{|r_i - r_j|} \Phi(\lambda r_1 \cdots \lambda r_N)\, d^3(\lambda r_1) \cdots d^3(\lambda r_N)$$

$$= \lambda \int \Phi^*(\lambda r_1 \cdots \lambda r_N) \frac{1}{|\lambda r_i - \lambda r_j|} \Phi(\lambda r_1 \cdots \lambda r_N)\, d^3(\lambda r_1) \cdots d^3(\lambda r_N)$$

$$= \lambda \int \Phi^*(r_1 \cdots r_N) \frac{1}{|r_i - r_j|} \Phi(r_1 \cdots r_N)\, d^3r_1 \cdots d^3r_N$$

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so,

$$\int \Phi_\lambda^* \hat{V}_{ee} \Phi_\lambda = \lambda \int \Phi^* \hat{V}_{ee} \Phi .$$

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# Coordinate Scaling of Exchange Energy

$$E_x[\rho] = \langle \Phi | \hat{V}_{ee} | \Phi \rangle - J[\rho]$$

$$E_x[\rho_\lambda] = \langle \Phi_\lambda | \hat{V}_{ee} | \Phi_\lambda \rangle - J[\rho_\lambda]$$

$$E_x[\rho_\lambda] = \lambda \langle \Phi | \hat{V}_{ee} | \Phi \rangle - \lambda J[\rho]$$

$$E_x[\rho_\lambda] = \lambda E_x[\rho].$$

$\Phi$ = KS Determinant.

## Form of $E_x[\rho]$ from Coordinate Scaling (Dimensional) Requirement.

$$E_x[\rho] = -c \int \rho^m(r) + \cdots$$

$E_x[\rho_\lambda] = \lambda E_x[\rho]$ is satisfied with $M = \frac{4}{3}$.

So,

$$E_x[\rho] = -c \int \rho^{4/3}(r)\, d^3r + \cdots$$

## Proof

$$\int \rho_\lambda(r)^{4/3} d^3r = \int [\lambda^3 \rho(\lambda r)]^{4/3} d^3r$$

$$= \lambda^4 \int \rho(\lambda r)^{4/3} d^3r$$

$$= \lambda \int \rho(\lambda r)^{4/3} d^3(\lambda r)$$

$$= \lambda \int \rho(r)^{4/3} d^3r. \Leftarrow \text{Great}$$

## Coordinate Scaling Requirements for $E_c$.

$$E_c[\rho] = F[\rho] - \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle$$

$$E_c[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$- \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle,$$

where $\Phi \to \rho$ and minimizes $\langle \hat{T} \rangle$.

It can be shown that $E_c$ exhibits more complicated scaling than $E_x$ because $E_c$ involves 2 constrained searches, interacting and non-interacting.

Complicated scaling of $E_c$ results from the fact that if $\Psi_{min}(x_1 \cdots x_N)$ yields $\rho$ and minimizes $\langle \hat{T} + \hat{V}_{ee} \rangle$, then $\lambda^{3N/2} \Psi_{min}(\lambda x_1 \cdots \lambda x_N)$ yields $\rho_\lambda$ and minimizes $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$.

## Results are

with $\rho_\lambda(r) = \lambda^3 \rho(\lambda x, \lambda y, \lambda z)$,

$$E_c[\rho_\lambda] > \lambda E_c[\rho]; \quad \lambda > 1$$

$$\lim_{\lambda \to \infty} E_c[\rho_\lambda] = \text{constant}$$

$$\lim_{\lambda \to 0} \frac{E_c[\rho_\lambda]}{\lambda} = \text{constant}.$$

The complicated coordinate scaling requirements dictate that $E_c$ has a more complicated form than $E_x$.

# H. W.

(1) H-atom.

(a) Form as a DFT problem.

(b) Find the Euler Equation by taking the functional derivative.

(2). Given $J[\rho] = \frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}$

Determine $\frac{\delta J[\rho]}{\delta \rho}$

(3). Given $T_s[\rho] = -c\int \rho^M(r)\,d^3r + \cdots$,

use coordinate scaling to get M.

# H-atom as a DFT problem

$$E_{GS} = \min_{\rho} \left\{ \int v(r)\rho(r)\,d^3r + F[\rho] \right\}$$

(where $v(r) = -\frac{1}{r}$).

$$\boxed{\int \rho(r)\,d^3r = 1}$$

From yesterday,

$$v(r) + \left.\frac{\delta F[\rho]}{\delta \rho}\right|_{\rho=\rho_{GS}} = \text{constant}$$

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Here $F[\rho] = \int \rho^{1/2}(r)\left[-\frac{1}{2}\nabla^2\right]\rho^{1/2}(r)\,d^3r$

because $\rho(r) = \varphi(r)^2$ for one electron.

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$$v(r) - \frac{\frac{1}{2}\nabla^2 \rho_{GS}^{1/2}}{\rho_{GS}^{1/2}} = \text{Constant}$$

Functional Derivative of F

(Euler Equation)

(see page 31)

Multiply by $\rho_{GS}^{1/2}$. Obtain

$$-\frac{1}{2}\nabla^2 \rho_{GS}^{1/2} + v(r)\,\rho_{GS}^{1/2} = \text{constant}\ \rho_{GS}^{1/2}.$$

<u>Evaluation of constant</u>

Multiply by $\rho_{GS}^{1/2}$, integrate, and use $\varphi_{GS}(r) = \rho_{GS}^{1/2}(r)$, to obtain

$$\langle \varphi_{GS}(r) | -\tfrac{1}{2}\nabla^2 + v(r) | \varphi_{GS}(r)\rangle = \text{constant}\ \langle \varphi_{GS}(r) | \varphi_{GS}(r)\rangle,$$

constant $= E_{GS}$ because $\langle \varphi_{GS} | \varphi_{GS}\rangle = 1$.

Pretend $F[\rho] = \int \rho^{1/2}(-\frac{1}{2}\nabla^2)\rho^{1/2}$ and find $\frac{\delta F}{\delta \rho}$:

$$\frac{\partial F(\rho+\epsilon\Delta\rho)}{\partial \epsilon} = \frac{\partial}{\partial \epsilon}\int (\rho+\epsilon\Delta\rho)^{1/2}(-\tfrac{1}{2}\nabla^2)(\rho+\epsilon\Delta\rho)^{1/2}$$

$$= \int \frac{\partial}{\partial \epsilon}(\rho+\epsilon\Delta\rho)^{1/2}(-\tfrac{1}{2}\nabla^2)(\rho+\epsilon\Delta\rho)^{1/2}$$

$$+ \int (\rho+\epsilon\Delta\rho)^{1/2}(-\tfrac{1}{2}\nabla^2)\frac{\partial}{\partial \epsilon}(\rho+\epsilon\Delta\rho)^{1/2}$$

$$= \int 2\frac{\partial}{\partial \epsilon}(\rho+\epsilon\Delta\rho)^{1/2}(-\tfrac{1}{2}\nabla^2)(\rho+\epsilon\Delta\rho)^{1/2}$$

because $-\frac{1}{2}\nabla^2$ is an Hermitian operator.

Now consider $\epsilon \to 0$ and obtain

$$\left(\frac{\partial F[\rho+\epsilon\Delta\rho]}{\partial \epsilon}\right)_{\epsilon\to 0} = \int \left(\frac{-\frac{1}{2}\nabla^2\rho^{1/2}}{\rho^{1/2}}\right)\Delta\rho(r).$$

Thus,

$$\frac{\delta F}{\delta \rho} = \frac{-\frac{1}{2}\nabla^2\rho^{1/2}}{\rho^{1/2}}$$

$$J[\rho] = \frac{1}{2}\iint \frac{\rho(r_1)\,\rho(r_2)}{|r_1 - r_2|}\, d^3r_1\, d^3r_2$$

Find $\dfrac{\delta J[\rho]}{\delta \rho}$.

Let $g = \dfrac{1}{2}\,\dfrac{1}{|r_1 - r_2|} = g(12) = g(21)$

$$J[\rho] = \iint \rho(r_1)\; g\; \rho(r_2)\, d^3r_1\, d^3r_2$$

$J[\rho + \epsilon\Delta\rho] =$

$$\iint [\rho(1) + \epsilon\Delta\rho(1)]\; g\; [\rho(2) + \epsilon\Delta\rho(2)]\, d^3r_1\, d^3r_2$$

$$\left.\frac{\partial J[\rho + \epsilon\Delta\rho]}{\partial \epsilon}\right|_{\epsilon=0}$$

$$= \iint \Delta\rho(1)\, g\, \rho(2)\, d^3r_1\, d^3r_2 + \iint \Delta\rho(2)\, g\, \rho(1)\, d^3r_1\, d^3r_2$$

$$\left.\frac{\partial J[\rho+\epsilon\Delta\rho]}{\partial\epsilon}\right|_{\epsilon=0}$$

$$=\iint \Delta\rho(1)\, g(12)\, \rho(2) + \iint \Delta\rho(2)\, g(21)\, \rho(1)$$

$$= 2\iint \Delta\rho(1)\, g(12)\, \rho(2)\, d^3r_1\, d^3r_2$$

(by symmetry)

$$=\int d^3r_1\, \Delta\rho(r_1)\left[\int \rho(r_2)\, 2g(12)\, d^3r_2\right]$$

$$=\int d^3r_1\, \Delta\rho(r_1)\int \frac{\rho(r_2)}{|r_1-r_2|}\, d^3r_2 .$$

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$$\frac{\delta J[\rho]}{\delta\rho(r)} = \int \frac{\rho(r_2)\, d^3r_2}{|r-r_2|}$$

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$$T_s[\rho] = c\int \rho^m(r)\, d^3r + \dots$$

$T_s[\rho_\lambda] = \lambda^2 T_s[\rho]$, because operator is $-\frac{1}{2}\nabla^2$.

solution, $m = \frac{5}{3}$

So,

$$T_s[\rho] = c\int \rho(r)^{5/3}\, d^3r + \dots$$