BETTER SINGLE - PARTICLE HAMITONIAN THAN HF

$\Downarrow$

WE HAVE TO USE A "FAKE" HAMILTONIAN

SYSTEM WITH INTERACTING ELECTRONS IN A POTENTIAL $V(\vec{r})$ $\left[\text{E.G. } V(\vec{r}) = -\sum_{I}^{\text{ATOMS}} \frac{e^2 Z_I}{|\vec{r} - R_I|}\right]$

$\Downarrow$ WE MAP

SYSTEM WITH NON-INTERACTING ELECTRONS (SAME NUMBER) IN A FICTITIOUS POTENTIAL $V'(\vec{r}) \neq V(\vec{r})$ WITH THE SAME TOTAL ENERGY AND THE SAME ELECTRONIC DENSITY

DENSITY FUNCTIONAL THEORY

[HOHENBERG AND KOHN PRB 136, 864 (1964)]

THE DENSTY AS THE BASIC VARABLE

HOHENBERG AND KOHN THEOREM

N-INTERACTING ELECTRONS IN AN EXTERNAL $\overbrace{\text{SPIN-INDEP}}^{\text{NO-SO}}$ POTENTIAL $V_{EXT}(\vec{r})$ WITH A NON DEGENERATE G.S. (NO MAGNETIC SYSTEM - BUT GENERALISATION IS POSSIBLE BY SPIN-DENSITY FUNCTIONAL THEORY)

$$\Downarrow$$

$\exists^1$ (JUST ONE SINCE THE G.S. NON DEGENERATE) GROUND STATE DENSITY

$$\rho(\vec{r}) = \langle \underbrace{\psi_{GS}}_{GS} | \sum_s \sum_i^N |\vec{r}, s\rangle_i \langle \vec{r}, s|_i \, |\psi_{GS}\rangle \qquad \langle \psi_{GS} | \psi_{GS} \rangle = 1$$

$$\Downarrow$$

THEOREM: IF $V'_{EXT}(\vec{r})$ HAS THE SAME GS $\rho(\vec{r})$

THEN $V'_{EXT}(\vec{r}) = V(\vec{r}) + \text{CONST.}$

PROOF:

$$\langle B | \underbrace{\underbrace{T_e}_{\sum_i^N \frac{p_i^2}{2m}} + \underbrace{V_{ee}}_{\sum_{i\neq j}^N H^{2e}_{ij}} + \overset{\sum_{\cancel{i\neq j}}^N V_{EXT}(\vec{r}_i)}{V_{EXT}}}_{H} | B \rangle = \langle B | T_e + V_{ee} | B \rangle + \int d^3r \, \rho_{|B\rangle}(\vec{r}) V_{EXT}(\vec{r})$$

$|\psi_{GS}\rangle \rightarrow$ GS OF $V(\vec{r})$ AND GS ENERGY E_{GS}

$|\psi'_{GS}\rangle \rightarrow$ GS OF $V'(\vec{r})$ AND GS ENERGY E'_{GS}

WITH $\rho_{|\psi_{GS}\rangle}(\vec{r}) = \rho_{|\psi'_{GS}\rangle}(\vec{r})$

CASE 1 $$|\psi_{GS}\rangle = \overset{\varphi\in\mathbb{R}}{e^{i\varphi}}|\psi_{GS}\rangle \xrightarrow{\text{CHANGE PHASE}} |\psi_{GS}\rangle = |\psi'_{GS}\rangle$$

$$\Delta V(\vec{r}) = V(\vec{r}) - V(\vec{r}') - \left(\frac{E_{GS}}{N} - \frac{E'_{GS}}{N}\right)$$

$$H|\psi_{GS}\rangle = E_{GS}|\psi_{GS}\rangle$$
$$H'|\psi_{GS}\rangle = E'_{GS}|\psi_{GS}\rangle$$

$$(H-H')|\psi_{GS}\rangle = \Delta V|\psi_{GS}\rangle = 0$$

IN SCHRÖDINGER $$\left[\Delta V(\vec{r}_1) + \Delta V(\vec{r}_2) + \dots \Delta V(\vec{r}_N)\right]\psi_{GS}(\vec{r}_1 s_1, \dots \vec{r}_N, s_N) = 0$$

$$\forall\, \vec{r}_1, \vec{r}_N : \psi_{GS}(\vec{r}_1 s_i, \dots) \neq 0$$

$$\left[\Delta V(\vec{r}_1) + \Delta V(\vec{r}_2) + \dots \Delta V(\vec{r}_N)\right] = 0$$

$$\Downarrow$$

$$\Delta V(\vec{r}) = 0$$

$$\Downarrow$$

$$\boxed{V(\vec{r}) = V(\vec{r}') + \text{CONST.}}$$

CASE 2 $$|\psi_{GS}\rangle \neq e^{i\varphi}|\psi'_{GS}\rangle$$

SINCE GS. NON DEG

$$\langle\psi_{GS}|H'|\psi_{GS}\rangle > \langle\psi'_{GS}|H'|\psi'_{GS}\rangle$$

$$\langle\psi_{GS}|H|\psi_{GS}\rangle + \langle\psi_{GS}|V'-V|\psi_{GS}\rangle > E'_{GS}$$

$$E_{GS} + \int d^3r\, \rho(r)\left(V'(\vec{r}) - V(\vec{r})\right) > E'_{GS}$$

EXCHANGING ' WITH NO '

$$E'_{GS} + \int d^3r\, \rho'(\vec{r})\left(V(\vec{r}) - V'(\vec{r})\right) > E_{GS}$$

SUMMING THE TWO INEQUALITIES

$$E_{GS} + E'_{GS} > E'_{GS} + E_{GS}$$ IMPOSSIBLE

LEMMA OF HK THEOREM

- WE CAN USE THE DENSITY AS BASIC VARIABLE

FOR $\forall \rho(\vec{r})$

$$\Downarrow$$

$\exists^1$ $V_{EXT}(\vec{r}) + C$ (C ARBITRARY CONSTANT) :

$\rho(\vec{r})$ IS THE GROUND STATE ENERGY

FROM SUCH V_{EXT}

$$\Downarrow$$

$\exists^1$ $e^{i\varphi}|\psi_{GS}\rangle$ GROUND STATE WAVEFUNCTION OF $T_e + V_{ee} + V_{EXT}$

$$\Downarrow$$

FROM $|\psi_{GS}\rangle$ ALL PROPERTIES CAN BE COMPUTED

$|\Psi_{GS}\rangle \equiv$ FUNCTIONAL OF ρ

$$|\Psi^{[\rho]}\rangle \overset{def}{\equiv} |\Psi_{GS}\rangle$$

DENSITY FUNCTIONAL THEORY

"THE FUNCTIONAL"

$$F[\rho] \overset{def}{\equiv} \langle \psi^{[\rho]} | T_e + V_{ee} | \psi^{[\rho]} \rangle \quad \text{WITH} \int d^3r\, \rho(\vec{r}) = N$$

$\downarrow$

IS A UNIVERSAL FUNCTION OF THE DENSITY
I.E. IT DOES NOT REFER TO A SPECIFIC $V_{EXT}(\vec{r})$

TOTAL ENERGY

$$E[\rho] \overset{def}{\equiv} F[\rho] + \int d^3r\, \rho(\vec{r})\, V_{EXT}(\vec{r})$$

PROPERTIES OF $E[\rho]$

1) $E[\rho] = \langle \psi^{[\rho]} | \overbrace{T_e + V_{ee} + V_{EXT}}^{H} | \psi^{[\rho]} \rangle \geq \overset{\text{OF } H}{\overset{\nearrow}{E}}_{GS}$

2) $\min\limits_{\substack{\rho \\ \int d^3r \rho(\vec{r}) = N}} E[\rho] = E_{GS}^{V_{EXT}}$

3) AT THIS MINIMUM $\rho = \rho_{GS}$

DFT IS AN EXACT BUT USELESS THEORY

?

SOME USEFUL APPROXIMATIONS

1) THOMAS-FERMI (1927 DEVELOPED BY THE TWO IN)

$$F[\rho] = \langle \psi^{[\rho]} | T_e + V_{ee} | \psi^{[\rho]} \rangle \overset{\substack{\text{APPROXIMATED BY} \\ \downarrow}}{\simeq} F_{TF}[\rho]$$

$$F_{TF}[\rho] = \int d^3r'\, t(\rho(\vec{r}')) + \frac{1}{2} \int d^3r'' \int d^3r'\, \frac{e^2 \rho(\vec{r}'')\rho(\vec{r}')}{|\vec{r}'' - \vec{r}'|}$$

WHERE $t(\rho(\vec{r}))$ = KINETIC ENERGY DENSITY FOR THE GROUND STATE OF A NON-INTERACTING JELLIUM WITH DENSITY $\rho_I = \rho(\vec{r}')$

$$= A \rho^{5/3} \qquad A = \frac{\hbar^2}{m} \frac{3}{10} (3\pi^2)^{4/3}$$

$$\min_{\substack{\rho \\ \int d^3r \rho = N}} \left[E[\rho] = F_{TF}[\rho] + \int d^3r'\, \rho(\vec{r}') V_{EXT}(\vec{r}') \right]$$

$$\Updownarrow$$

$$\frac{d}{d\rho(\vec{r})} \left[E[\rho] + \underset{\substack{\nearrow \\ \text{LAGRANGIAN MULTIPLIER}}}{\mu} \left[N - \int d^3r\, \rho(\vec{r}) \right] \right] = 0$$

$$\begin{cases} \frac{5}{3} A \rho^{2/3}(\vec{r}) + V_H^{[\rho]}(\vec{r}) + V_{EXT}(\vec{r}) = \mu & V_H(\vec{r}) = e^2 \int d^3r'\, \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \\ \int d^3r\, \rho(\vec{r}) = N & \leftarrow \text{FIX } \mu \text{ IN ORDER TO SATISFY THIS} \end{cases}$$

TF GOOD FOR EXTIMATIONS BUT:

- LOW PRECISION
- LACKS OF SHELL STRUCTURE
- LACKS OF CHEMICAL BONDING

AN OTHER EXACT (USEFUL?) DFT:

KOHN-SHAM MAPPING INTO A NON-INTERACTING N-ELECTRON SYSTEM

[KOHN-SHAM PRA 140, 1133 (1965)]

OBSERVATION: THE HK THEOREM IS VALID ALSO FOR A NON-INTERACTING SYSTEM $(V_{ee}=0)$

GIVEN A G.S. CHARGE DENSITY $\rho_{GS}(\vec{r})$ OF A N-ELECTRON <u>INTERACTING</u> SYSTEM (WITH A GIVEN POTENTIAL $V_{EXT}(\vec{r})$)

$\exists^1$ (JUST ONE) EXTERNAL POTENTIAL $V_{KS}(\vec{r}) + C$

A PART A CONSTANT

FOR A NON-INTERACTING N-ELECTRON SYSTEM THAT HAS $\rho_{GS}(\vec{r})$ AS GROUND STATE CHARGE

$$\boxed{H_{KS} \overset{def}{=} \frac{p^2}{2m_e} + V_{KS}(\vec{r})}$$

SINGLE PARTICLE (KOHN-AND SHAM) HAMILTONIAN

$$\underbrace{\{|\psi^i_{KS}\rangle\}_{i=1,\dots,\frac{N}{2}}}_{\text{KS SINGLE PARTICLE ORBITALS}}$$

$|\psi^i_{KS}\rangle$: $\frac{N}{2}$ LOWEST EIGENVECTORS OF H_{KS} $\quad H_{KS}|\psi^i_{KS}\rangle = \varepsilon^i_{KS}|\psi^i_{KS}$

$$\rho_{GS}(\vec{r}) \overset{\text{BY CONSTRUCTION}}{=} \sum_{i=1}^{N/2} \overset{\text{FOR SPIN}}{2} \langle\psi^i_{KS}|\vec{r}\rangle\langle\vec{r}|\psi^i_{KS}\rangle$$

$$\boxed{|\psi^i_{KS}\rangle\text{: FUNCTIONAL OF } \rho = |\psi^{i\,[\rho]}_{KS}\rangle}$$

THE KS EXACT FUNCTIONAL

ORDINARY DFT FUNCTIONAL

$$E[\rho]=F[\rho]+\int d^3r\,\rho(\vec{r})V_{EXT}(\vec{r})$$

NEW DEFINITIONS

$$T_0[\rho]\overset{def}{\equiv}\sum_{i=1}^{N/2}2\langle\psi_{KS}^{i[\rho]}|\frac{p^2}{2m_e}|\psi_{KS}^{i[\rho]}\rangle$$

↙ KINETIC ENERGY OF THE KS SYSTEM (UNIVERSAL FUNCTONA OF ρ)

$$E_H[\rho]\overset{def}{\equiv}\int d^3r\,d^3r'\,\frac{1}{2}\,\frac{e^2\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

$$E_{XC}[\rho]\overset{def}{\equiv}F[\rho]-T_0[\rho]-E_H[\rho]$$

DEFINED AS EXCHANGE AND CORRELATION ENERGY FUNCTIONAL

$$\Downarrow$$

$$E[\rho]=T_0[\rho]+E_H[\rho]+E_{XC}[\rho]+\int d^3r\,\rho(\vec{r})V_{Ext}(\vec{r})$$
$$=T_0[\rho]+E_{KS}[\rho]$$

- IT IS JUST A NEW WAY TO SPLIT THE DFT FUNCTIONAL
- ALL THE DIFFICULT PART ARE HIDDEN IN E_{XC}
- $T_0[\rho]$ IS <u>NOT</u> THE KINETIC ENERGY OF THE REAL INTERACTING SYSTEM BUT THAT OF THE FICTITIOUS NON INTERACTING ONE

KS ORBITALS AS BASIC VARIABLES

FOR A GIVEN $V_{EXT}(\vec{r})$

$$\min_{\substack{\rho \\ \int \rho d^3r = N}} E[\rho] = \min_{\substack{\{\psi_i\}_{i=1,\frac{N}{2}} \\ \langle\psi_i|\psi_j\rangle = \delta_{ij}}} T_0[\{\psi_i\}] + E_H[\rho] + E_{xc}[\rho] + \int d^3r \rho(\vec{r}) V_{EXT}(\vec{r})$$

SINGLE PARTICLE WAVE FUNCTION

$$\rho(\vec{r}) = 2\sum_{i=1}^{N} \langle\psi_i|\vec{r}\rangle\langle\vec{r}|\psi_i\rangle$$

SPIN

$$E_{DFT} = \min_{\{\psi_i\}} E[\{\psi_i\}]$$

RELATION BETWEEN KS POTENTIAL AND KS FUNCTIONAL

WE CAN OBTAIN THE GROUND STATE ENERGY BY IMPOSING THAT:

$$\frac{d}{d\rho(\vec{r})}\left[E[\rho]+\mu\left(N-\int d^3r\,\rho(\vec{r})\right)\right]=0$$

BUT SINCE $\rho(\vec{r})$ IS A FUNCTION OF $|\psi^i\rangle$ WE CAN ARTERNATIVELY ASK THAT

$$\frac{d}{d\langle\psi^k|}\left[E[\{\psi^i\}]-\sum_{ij=1}^{N/2}2\lambda_{ij}\left[\langle\psi^j|\psi^i\rangle-\delta_{ij}\right]\right]=0$$

WHERE $\{|\psi^i\rangle\}_{i=1,\frac{N}{2}}$ SINGLE PARTICLE ORBITALS

AND $\rho(\vec{r})=\sum_{i=1}^{N/2}2\langle\psi^i|\vec{r}\rangle\langle\vec{r}|\psi^i\rangle$

$$\frac{dT_0}{d\langle\psi^k|}=4\,\frac{p^2}{2m_e}|\psi^k\rangle$$

$$\frac{d\rho(\vec{r})}{d\langle\psi^k|}=4|\vec{r}\rangle\langle\vec{r}|\psi_k\rangle$$ (SINCE $\rho(\vec{r})=\sum_{i=1}^{N/2}\langle\psi^i|\vec{r}\rangle\langle\vec{r}|\psi^i\rangle$)

$$\frac{dE_H[\rho]}{d\langle\psi^k|}=\int d^3r\,\frac{dE_H}{d\rho(\vec{r})}\,\frac{d\rho(\vec{r})}{d\langle\psi^k|}=$$

$$=\int d^3r\,\int d^3r'\,\frac{e^2\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\;4|\vec{r}\rangle\langle\vec{r}|\psi_k\rangle$$

$$=4\,V_H^{[\rho]}(\vec{r})|\psi^k\rangle$$ $\left(V_H(\vec{r})=\int d^3r'\,\frac{e^2\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\right)$

$$\frac{dE_{xc}}{d\langle\psi^{k}|} = \int d^3r \, \frac{dE_{xc}[\rho]}{d\rho(\vec{r})} \frac{d\rho(\vec{r})}{d\langle\psi^{k}|}$$

EXCHANGE AND CORRELAT
POTENTIAL

$$= V_{xc}^{[\rho]}(\vec{r})|\psi^{k}\rangle \qquad \text{WHERE} \qquad V_{xc}^{[\rho]}(\vec{r}) \overset{def}{=} \frac{dE_{xc}[\rho]}{d\rho(\vec{r})}$$

AT THE GROUND STATE:

$$\left[\frac{p^2}{2m_e} + V_H^{[\rho]}(\vec{r}) + V_{xc}^{[\rho]}(\vec{r}) + V_{EXT}(\vec{r})\right]|\psi^{k}_{min}\rangle = \sum_i |\psi^{i}_{min}\rangle\lambda_{ik}$$

BY THE ROTATION THAT DIAGONALIZED λ_{ij}

$$\left[\frac{p^2}{2m_e} + V_H^{[\rho]}(\vec{r}) + V_{xc}^{[\rho]}(\vec{r}) + V_{EXT}(\vec{r})\right]|\tilde{\psi}^{k}_{min}\rangle = \varepsilon^{k}_{min}|\tilde{\psi}^{k}_{min}\rangle$$

$$\Downarrow$$

$$\boxed{\begin{aligned} &V_{KS}^{[\rho]}(\vec{r}) = V_H^{[\rho]} + V_{xc}^{[\rho]} + V_{EXT}(\vec{r}) = \frac{dE_{KS}[\rho]}{d\rho(\vec{r})} \\ &|\psi^{k[\rho]}_{KS}\rangle = |\tilde{\psi}^{k[\rho]}_{min}\rangle \end{aligned}}$$

- HK DFT THEORY IS A MEAN FIELD THEORY

  $H_{KS} = \frac{p^2}{2m_e} + V_{KS}^{[\rho]}(\vec{r})$ IS A SINGLE PARTICLE HAMILTONIAN THAT DEPENDS ON THE CHARGE DENSITY

- IT IS AN EXACT THEORY

THE KS THEORY IS AN EXACT BUT USELESS THEORY

WE DEFINE NOW AN APPROXIMATE VERY USEFUL THEORY

LOCAL DENSITY APPROXIMATION (LDA)

IN LDA

$$E_{xc}[\rho] \simeq E_{xc}^{LDA}[\rho]$$

WHERE

$$E_{xc}^{LDA}[\rho] \overset{def}{=} \int d^3\vec{r}\, \rho(\vec{r})\, \mathcal{E}_{xc}(\rho(\vec{r}))$$

WHERE $\mathcal{E}_{xc}(\rho)$ IS THE EXCHANGE CORRELATION ENERGY PER ELECTRON OF THE HOMOGENEUS INTERACTING ELECTRON GAS (KNOWN NUMERICALLY BY MC. CALCULATIONS)

$$\Downarrow$$

THE THEORY IS EXACT IN THE JELLIUM

$$V_{xc}^{LDA[\rho]}(\vec{r}) = \overset{\text{FUNCTION OF THE DENSITY AT } \vec{r}}{f(\rho(\vec{r}))} = \varepsilon_{xc}(\rho(\vec{r})) + \rho(\vec{r}) \frac{d\varepsilon_{xc}(\rho(\vec{r}))}{d\rho(\vec{r})}$$

DFT-LDA :
- CONTAINS THE SHELL STRUCTURE } AS HF
- DESCRIBES THE CHEMICAL BONDING } AS HF
- BONDS LENGHTS (OF STRONG BONDS COVALENT AND METALLIC) 1-2% ERROR COMPARED TO EXP } MUCH BETTER THAN HF
- VIBRATIONAL FREQUENCIES 1-4% ERROR } MUCH BETTER THAN HF
- COMPUTATIONALLY FASTER THAN HF (IT CAN BE APPLIED TO SYSTEM WITH ~1000 ATOMS IN THE UNIT CELL)

ε^{i}_{KS} → AUSILIARY VARIABLE ≠ QUASIPARTICLES (MEASURED BY ARPES) EVEN WITH THE EXACT DFT FUNCTIONAL

DFT DESIGNED FOR TOTAL ENERGY NOT FOR QUASIPARTICLE SPECTRUM

HOWEVER EVEN ε^{i}_{KS+LDA} GOOD APPROXIMATION OF QUASIPARTICLE SPECTRUM

BAND WIDTH UNDERESTIMATED BY LDA BY 10-20%

BAND GAP OF SEMICONDUCTOR / INSULATOR UNDERESTIMATED BY 50%

GENERALIZED GRADIENT APPROXIMATION (GGA)

$$E_{xc}[\rho] \simeq E_{xc}^{GGA}[\rho]$$

$$E_{xc}^{GGA}[\rho] = \int d^3r \, \underset{\nearrow}{f}\left(\rho(\vec{r}), |\vec{\nabla}\rho(\vec{r})|\right)$$

JUST A LOCAL FUNCTION OF THE DENSITY AND OF ITS GRADIENT

f CAN BE DETERMINED BY A GRADIENT EXPANSION OF THE XC HOLE SURROUNDING THE ELECTRON IN A SYSTEM OF SLOWLY VARING DENSITY + SOME EXACT CONDITIONS (E.G. SUM RULE FOR THE HOLE)

[SEE E.G. PERDEW, BURKE, ERNZERHOF, PRL 77, 3865 (1996)]

FROM LDA TO GGA

- BETTER TOTAL ENERGIES (ATOMISATION ENERGIES, ENERGY BARRIERS, STRUCTURAL ENERGY DIFFERENCES)
- BETTER GEOMETRY FOR WEAK BONDS (E.G. H-BONDS), WHICH ARE TOO SHORT IN LDA
- BAND STRUCTURE OF GGA VERY SIMILAR OF THAT OF LDA

WHAT IS $E_{xc}[\rho]$ AND WHY DOES DFT-LDA (OR GGA) WORK?

• ADIABATIC CONNECTION IN DFT [HARRIS, PRA 29, 1648 (1984)]

WE CONSIDER A SYSTEM WITH N-ELECTRON H:

$$H^{\lambda} = T_e + \lambda V_{ee} + V_{EXT}^{\lambda}$$

WHERE V_{EXT}^{λ} IS FIXED IN ORDER TO KEEP THE GS DENSITY INTEPENDENT OF λ

$$\boxed{H^{\lambda=1} = T_e + V_{ee} + V_{EXT} \qquad H^{\lambda=0} = T_e + V_{KS}}$$

$|\Psi_{GS}^{\lambda}\rangle$: $|\Psi_{GS}^{\lambda=1}\rangle$ = N-ELECTRON GS OF THE TRUE SYSTEM

$$|\Psi_{GS}^{\lambda=0}\rangle = |SD\{\text{KS ORBITALS}\}\rangle$$

$g^{\lambda}(\vec{r},\vec{r}\,')$ = PAIR CORRELATION FUNCTION OF $|\Psi_{GS}^{\lambda}\rangle$ $= \dfrac{\rho^{(2)}_{|\Psi_{GS}^{\lambda}\rangle}(\vec{r},\vec{r}\,')}{\rho(\vec{r})\,\rho(\vec{r}\,')}$

INDEP OF λ

$$E^{\lambda} = \langle\Psi_{GS}^{\lambda}|H^{\lambda}|\Psi_{GS}^{\lambda}\rangle$$

$$E^{1} - E^{0} = \int_0^1 d\lambda \frac{dE^{\lambda}}{d\lambda} \overset{\text{HELLMANN-FEYNMAN}}{=} \int_0^1 d\lambda \langle\Psi_{GS}^{\lambda}|\frac{dH^{\lambda}}{d\lambda}|\Psi_{GS}^{\lambda}\rangle =$$

$$= \int_0^1 d\lambda \left[\langle\Psi_{GS}^{\lambda}|V_{ee}|\Psi_{GS}^{\lambda}\rangle + \int d^3r\, \underset{\substack{\uparrow \\ \text{INDEP. OF } \lambda}}{\rho(\vec{r})} \frac{dV_{EXT}^{\lambda}(\vec{r})}{d\lambda}\right] =$$

$$= \int_0^1 d\lambda \left[\langle \psi_{GS}^{\lambda} | V_{ee} | \psi_{GS}^{\lambda} \rangle - \underset{\substack{\uparrow \\ \text{INDEP OF } \lambda}}{E_H[\rho]} \right] + \langle \psi_{GS}^{\lambda=1} | V_{EXT} | \psi_{GS}^{\lambda=1} \rangle$$

$$- \langle \psi_{GS}^{\lambda=0} | V_{KS} | \psi_{GS}^{\lambda=0} \rangle + E_H[\rho]$$

$$\Downarrow$$

$$\overset{\substack{F[\rho] \\ \uparrow}}{\langle \psi_{GS}^{\lambda=1} | T_e + V_{ee} | \psi_{GS}^{\lambda=1} \rangle} - \overset{\substack{T_0[\rho] \\ \uparrow}}{\langle \psi_{GS}^{\lambda=0} | T_e | \psi_{GS}^{\lambda=0} \rangle} - E_H[\rho]$$

$$= E_{xc}[\rho] = \int_0^1 d\lambda \left[\langle \psi_{GS}^{\lambda} | V_{ee} | \psi_{GS}^{\lambda} \rangle - E_H[\rho] \right]$$

$$\boxed{\begin{aligned} E_{xc}[\rho] &= \int d^3r\, \rho(\vec{r}) \int d^3R\, \frac{e^2}{2R}\, \rho_{xc}(\vec{r}, \vec{R}) \\ \rho_{xc}(\vec{r}, \vec{R}) &\overset{\text{def}}{=} \rho(\vec{r} + \vec{R}) \int_0^1 d\lambda \left[g^{\lambda}(\vec{r}, \vec{r} + \vec{R}) - 1 \right] \end{aligned}}$$

LDA APPROXIMATION: WE REPLACE $\rho_{xc}(\vec{r}, \vec{R})$ BY $\rho_{xc}^{\text{JELLIUM}}(\vec{r}, \vec{R})$ OF DENSITY $\rho(\vec{r})$

WHY IS IT GOOD (PROPERTIES OF g^{λ})

1) $\lim_{R \to \infty} (g^{\lambda} - 1) \to 0$ LONG RANGE PART EXACT IN E_H

2) COULOMB INTERACTION ISOTROPIC

$$E_{xc} = \int d^3r\, \rho(\vec{r}) \int_0^{\infty} dR\, R^2 \frac{e}{2R}\, 4\pi \overbrace{\left(\frac{1}{4\pi} \int d^2\Omega\, \rho_{xc}(\vec{r}, \vec{R}_{\Omega}) \right)}^{\text{SPHERICAL AVERAGE}}$$

$\rho_{xc}(\vec{r}, \vec{R}) \neq \rho_{xc}^{\text{JELLIUM}}(\vec{r}, \vec{R})$ BUT $\langle \rho_{xc}(\vec{r}, \vec{R}) \rangle_{\text{SPHERICAL}} \simeq \langle \rho_{xc}^{\text{JELLIUM}}(\vec{r},$

3) SUM RULE $\int d^3R\, \rho_{xc}(\vec{r}, \vec{r}+\vec{R}) = -1$ (THE HOLE CONTAIN 1e)

SATISFIED BY CONSTRUCTION BY LDA SINCE

$$\int d^3R\, \rho_{xc}^{JELLIUM}(\vec{r}, \vec{r}+\vec{R}) = -1$$

PROOF OF THE SUM RULE

(1) $\rho^{(2)}_{|A\rangle}(\vec{r}, \vec{r}\,') = N(N-1)\langle A|\vec{r}\rangle_1\, {}_1\langle\vec{r}|\, |\vec{r}\,'_2\rangle\langle\vec{r}\,'_2|A\rangle$

(2) $\rho_{|A\rangle}(\vec{r}) = N\langle A||\vec{r}\rangle_1\, {}_1\langle\vec{r}|A\rangle$

(3) $\int d^3r'\, \rho^{(2)}_{A}(\vec{r}, \vec{r}\,') \overset{\overset{(1)}{\downarrow}}{=} N(N-1)\langle A||\vec{r}\rangle_1\, {}_1\langle\vec{r}|A\rangle \overset{\overset{(2)}{\downarrow}}{=} (N-1)\rho(\vec{r})$

(4) $\int d^3r\, \rho(\vec{r}) \overset{\overset{(2)}{\downarrow}}{=} N$

$$\int d^3R\, \rho_{xc}(\vec{r}, \vec{r}+\vec{R}) = \int d^3R \left[\frac{\rho^{(2)}(\vec{r}, \vec{r}+\vec{R})}{\rho(\vec{r})} - \rho(\vec{r}+\vec{R})\right]$$

$$= (N-1)\frac{\rho(\vec{r})}{\rho(\vec{r})} - N = -1$$