GROUND STATE OF N-INDEPENDENT ELECTRON SYSTEM

$$H = \sum_i H_i^{1e}$$

$$H^{1e} |\vec{a}\rangle = E_a |\vec{a}\rangle$$

$\mathcal{B} = \{|\vec{a}\rangle\}_a$ NORMALIZED COMPLETE BASIS FOR 1 ELECTRON SPACE

$$\{ |\vec{a_1}\rangle_1 \otimes |\vec{a_2}\rangle_2 \otimes |\vec{a_3}\rangle \cdots \otimes |\vec{a_N}\rangle_N \}_{a_1, a_2 \ldots a_N}$$

↑ INDEX OF HILBERT SPACE

↑ COMPLETE BASIS FOR N DISTINGUISHIBLE PARTICLES

COMPLETE BASIS FOR N INDISTINGUISHIBLE FERMIONS

$$\{ |SD(a_1, a_2, \ldots, a_N)\rangle \}_{a_1, a_2, \ldots}$$

$$|SD(\vec{a_1}, \ldots a_N)\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\vec{a_1}\rangle_1 & |\vec{a_1}\rangle_2 & |\vec{a_1}\rangle_3 & \cdots & |\vec{a_1}\rangle_N \\ |\vec{a_2}\rangle_1 & |\vec{a_2}\rangle_2 & & & |\vec{a_2}\rangle_N \\ \cdots & & & & \\ |\vec{a_N}\rangle_1 & & & & |\vec{a_N}\rangle_N \end{vmatrix}$$

EXAMPLE $N=2$

$$|SD(a_1,a_2)\rangle = \frac{1}{\sqrt{2}}\left(|\overline{a_1}\rangle_1 |\overline{a_2}\rangle_2 - |\overline{a_2}\rangle_1 |\overline{a_1}\rangle_2\right)$$

PROPERTIES

$|SD(a_1, \dots a_N)\rangle = 0$ IF $a_i = a_j$ WITH $i \neq j$

OTHERWISE $\langle SD(a_1,..,a_N) | SD(a_1,..,a_N)\rangle = 1$

$$H|SD(a_1,..a_N)\rangle = E|SD(a_1,..,a_N)\rangle$$

$$E = \sum_i E_{a_i}$$

$$A = \sum_{i=1}^{N} O_i^{1e}$$

$$\langle SD(a_2..,a_N)| A |SD(a_2..,a_N)\rangle = \sum_{i=1}^{N} \langle a_i | O^{1e} | a_i \rangle$$

$$B = \sum_{\substack{j \\ i \neq j}}^{N} \sum_{i=1}^{N} O_{ij}^{2e}$$

$$\langle SD(a_2..a_N)| B |SD(a_2..a_N)\rangle =$$

$$= \sum_{i=1}^{N}\sum_{j=1}^{N}\Big[\langle a_i|_1 \langle a_j|_2 O_{12}^{2e} |a_i\rangle_1 |a_j\rangle_2 - \langle a_i|_1 \langle a_j|_2 O_{12}^{2e} |a_j\rangle_1 |a_i\rangle_2\Big]$$

GROUND STATE OF INTERACTING N-ELECTRON SYSTEM

$$H = \sum_i H_i^{1e} + \sum_{\substack{i,j \\ i \neq j}} H_{ij}^{2e}$$

GROUND STATE $H|GS\rangle = E_{GS}|GS\rangle$

$|GS\rangle$ LINEAR COMBINATION OF $\{|SD(a_1 \ldots a_N)\}_{a_1 \ldots a_N}$

BUT NOT A SINGLE ONE

$$E_{GS} = \min_{|A\rangle \in N\text{-ELEC SPACE}} \langle A|H|A\rangle$$

$\langle A|A\rangle = 1$

IN ABSENCE OF SPIN ORBIT

$$H_i^{1e} = \frac{1}{2m} p_i^2 + V(\vec{r}_i) \qquad H_{ij}^{2e} = \frac{1}{2} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$\langle A| \sum_i H_i^{1e} |A\rangle = \langle A| \sum_i \frac{1}{2m} p_i^2 |A\rangle + \int d^3r \, V(\vec{r}) \rho_{|A\rangle}(\vec{r})$$

WHERE $\rho_{|A\rangle}(\vec{r})$ = PROBABILITY TO FIND AN ELECTRON IN $\vec{r}$

$$= \langle A| \sum_i |\vec{r}\rangle\langle\vec{r}| A\rangle = N \langle A|\vec{r}\rangle_{1\,1}\langle\vec{r}|A\rangle$$

$$\int d^3r \, \rho_{|A\rangle}(\vec{r}) = N$$

$$\langle A| \sum_{\substack{i,j \\ i \neq j}} \frac{1}{2} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} |A\rangle = \int d^3r \, d^3r' \, \rho^{(2)}_{|A\rangle}(\vec{r}, \vec{r}') \frac{e^2}{2|\vec{r} - \vec{r}'|}$$

WHERE $\rho^{(2)}_{|A\rangle}(\vec{r},\vec{r}')$ = TWO-BODY PROBABILITY DENSITY TO FIND AN ELECTRON IN $\vec{r}$ AND AN OTHER IN $\vec{r}'$

$$\rho^{(2)}_{|A\rangle}(\vec{r},\vec{r}') = \langle A| \sum_{\substack{ij \\ i\neq j}} |\vec{r}\rangle_i \langle \vec{r}| \cdot |\vec{r}'\rangle_j \langle \vec{r}'| A\rangle$$

$$= N(N-1) \langle A| |\vec{r}\rangle_1 \langle \vec{r}| \; |\vec{r}\rangle_2 \langle \vec{r}'| A\rangle$$

EXPERIMENTAL OBSERVATION: SINGLE PARTICLE DESCRIPTION GOOD!!

HARTREE FOCK APPROXIMATION

$|SD(b_1,\dots,b_N)\rangle$ $\quad |b_i\rangle$ arbitrary 1e WAVE-FUNC.

$\langle b_i|b_j\rangle = \delta_{ij}$

$$E^{HF}_{GS} = \min_{\substack{\{|b_i\rangle\}_i \\ \langle b_i|b_j\rangle=\delta_{ij}}} E^{HF}_{\{b_i\}} \qquad E^{HF}_{\{b_i\}} = \langle SD(b_1..b_N)| H |SD(b_1..b_N)\rangle$$

$$E^{HF}_{GS} \geq E_{GS}$$

$$E^{HF}_{\{b_i\}} = \underbrace{\langle SD| \sum_i H^{1e}_i |SD\rangle}_{E^{HF1e}_{\{b_i\}}} + \underbrace{\langle SD| \sum_{\substack{ij \\ i<j}} H^{2e}_{ij} |SD\rangle}_{E^{HF2e}_{\{b_i\}}}$$

$$E^{HF_{1e}}_{\{b_i\}} = \sum_i \langle \overline{b_i} | H^{1e} | \overline{b_i} \rangle$$

$$H^{2e}_{ij} = \frac{1}{2} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \qquad \text{(FOR SYMPLICTY NO SO)}$$

$$E^{HF_{2e}}_{\{b_i\}} = \int d^3r\, d^3r' \sum_{s,s'}^{\uparrow,\downarrow} \frac{1}{2} \frac{e^2}{|\vec{r} - \vec{r}'|} \sum_{i,j}^{1\ldots N}$$

spin — includes $j = i$ term

$$\Big[\langle \overline{b_i} | \vec{r}, s \rangle \langle \vec{r}, s | \overline{b_i} \rangle \langle \overline{b_j} | \vec{r}', s' \rangle \langle \vec{r}', s' | \overline{b_j} \rangle +$$

$$- \langle \overline{b_i} | \vec{r}, s \rangle \langle \vec{r}, s | \overline{b_j} \rangle \langle \overline{b_j} | \vec{r}', s' \rangle \langle \vec{r}', s' | \overline{b_i} \rangle \Big]$$

HF ENERGY INVARIANT UPON ROTATIONS IN THE OCCUPIED SPACE (GAUGE FREEDOM)

$$E^{HF}_{\{b_i\}} = E^{HF}_{\{b'_i\}} \qquad |\overline{b'_i}\rangle = \sum_j U_{ij} |\overline{b_i}\rangle$$

U_{ij} = UNITARY MATRIX $\left(\sum_k U^*_{ik} U_{jk} = \delta_{ij} \right)$

ONE BODY DENSITY MATRIX EXPLICIT INVARIANT

$$\equiv P \overset{def}{\equiv} \sum_{i=1}^{N} |\overline{b_i}\rangle \langle \overline{b_i}|$$

P IS A PROJECTOR: $P^2 = P$ (IN THE OCCUPIED SUBSPACE)

$$\underset{\uparrow}{\mathrm{Tr}_2}[P] = N = \#\text{ OF ELECTRONS}$$

1e HILBERT

$$E^{HF\,1e}_{\{b_i\}} = \mathrm{tr}\left[P H^{1e} \right]$$

$\rho(\vec{r},s) = \langle \vec{r},s | \hat{\rho} | \vec{r},s \rangle =$ ELECTRON DENSITY

$$\rho(\vec{r},s;\vec{r}',s') = \langle \vec{r},s | P | \vec{r}',s' \rangle =$$ ONE BODY DENSITY MATRIX IN SCHRÖDINGER REPRESENTATION

$$\rho(\vec{r}) = \sum_s \rho(\vec{r},s,\vec{r},s) = \text{ELECTRON DENSITY} \quad \left(\int d^3r\, \rho(\vec{r}) = N \right)$$

$$E^{HF\,2e}_{\{b_i\}} = \overbrace{\int d^3r\, d^3r' \, \frac{1}{2} e^2 \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}}^{\text{HARTREE ENERGY} = E^H_{\{b_i\}}} +$$

$$\underbrace{- \int d^3r\, d^3r' \, \frac{1}{2} \frac{e^2}{|\vec{r}-\vec{r}'|} \sum_{s s'} \rho(\vec{r},s,\vec{r}',s')\, \rho(\vec{r}',s',\vec{r},s)}_{\text{EXCHANGE ENERGY } E^X_{\{b_i\}}}$$

INTERPRETATION

PROBABILITY TO FIND ONE ELECTRON IN $\vec{r}$ AND AN OTHER IN $\vec{r}' = 2$ BODY - PROBABILITY DENSITY

$$\rho^{(2)}_{|A\rangle}(\vec{r},\vec{r}') = \langle A | \sum_{\substack{i,j \\ i \neq i}} \sum_{s s'} |\vec{r},s\rangle_i \langle \vec{r},s|_i \; |\vec{r}',s'\rangle_j \langle \vec{r}',s'| \; |A\rangle$$

i HILBERT-SPACE

$$\langle A | \sum_{\substack{i,j \\ i \neq j}} H^{2e}_{i,j} | A \rangle = \int d^3r \, d^3r' \, \frac{1}{2} \frac{e^2}{|\vec{r} - \vec{r}'|} \rho^{(2)}_{|A\rangle}(\vec{r}, \vec{r}')$$

IF $|A\rangle$ IS A SINGLE SLATER DETERMINANT (ONLY IN THIS CASE!)

$\rho^{(2)}(\vec{r}, \vec{r}')$ CAN BE WRITTEN IN TERMS OF THE ONE-BODY DENSITY MATRIX

$$\rho(\vec{r}) \quad \rho(\vec{r}')$$

$$\rho^{(2)}_{|SD(b_1, \ldots b_N)\rangle}(\vec{r}, \vec{r}') = \sum_{\sigma\sigma'} \rho(\vec{r}, \sigma, \vec{r}, \sigma) \rho(\vec{r}', \sigma', \vec{r}', \sigma') - \sum_{\sigma\sigma'} \rho(\vec{r}, \sigma, \vec{r}', \sigma') \rho(\vec{r}', \sigma', \vec{r}, \sigma)$$

PAULI OR EXCHANGE HOL

HF IN THE COLINEAR CASE (NO SPIN-ORBIT NO NON-COLINEAR MAGNETISM)

ONE-ELECTRON WAVE-FUNCTIONS IN THE SD OF TYPE

UP SPIN DOWN SPIN

$$|\vec{\alpha_i}\rangle = \begin{pmatrix} |\alpha_i\rangle \\ 0 \end{pmatrix} \quad |\overline{\beta_i}\rangle = \begin{pmatrix} 0 \\ |\beta_i\rangle \end{pmatrix}$$

$i = 1, \dots, N_\uparrow$ $\quad i = 1, N_\downarrow$ $\quad N_\uparrow + N_\downarrow = N$

P IS FACTORIZED $\quad P = P^\uparrow \otimes |\uparrow\rangle\langle\uparrow| + P^\downarrow \otimes |\downarrow\rangle\langle\downarrow|$

$$P^\uparrow = \sum_{i=1}^{N^\uparrow} |\alpha_i\rangle\langle\alpha_i|$$

$$P^\downarrow = \sum_{i=1}^{N_\downarrow} |\beta_i\rangle\langle\beta_i|$$

$$\rho^\uparrow(\vec{r}, \vec{r}') = \langle \vec{r} | P^\uparrow | \vec{r}' \rangle$$

$$\rho^\downarrow(\vec{r}, \vec{r}') = \langle \vec{r} | P^\downarrow | \vec{r}' \rangle$$

$$\rho^{(2)}_{|SD(\alpha_i \dots \beta_i)\rangle}(\vec{r}, \vec{r}') = \rho(\vec{r})\rho(\vec{r}') - \rho^\uparrow(\vec{r}, \vec{r}')\rho^\uparrow(\vec{r}', \vec{r}) - \rho^\downarrow(\vec{r}, \vec{r}')\rho^\downarrow(\vec{r}', \vec{r})$$

PROBABILITY TO FIND 2e IN SAME PLACE

$$\rho^{(2)}_{--}(\vec{r}, \vec{r}) = 2\rho^\uparrow(\vec{r}, \vec{r})\rho^\downarrow(\vec{r}, \vec{r})$$

HATREE FOCK IN THE COLINEAN SPIN-UNPOLORIZED CASE

$N^{\uparrow} = N^{\downarrow}$

$|\alpha_i\rangle = |\beta_i\rangle = |a_i\rangle$ $\quad \rho^{\uparrow} = \rho^{\downarrow}$

$$\rho^{(2)}_{SD}(\vec{z}, \vec{z}') = \rho(\vec{z})\rho(\vec{z}) - 2\rho^{\uparrow}(z, z')\rho^{\uparrow}(\vec{z}', z)$$

$$\rho^{(2)}_{SD}(\vec{z}, \vec{z}) = \frac{1}{2}\rho(\vec{z})\rho(z)$$

HARTREE FOCK GROUND STATE

$$E_{GS}^{HF} = \min_{\{|\bar{b}_i\rangle\}} E^{HF}_{\{\bar{b}_i\}}$$
$$\langle \bar{b}_i | \bar{b}_j \rangle = \delta_{ij}$$

$\Updownarrow$

CONSTRAINED MINIMIZATION

functional derivative WITH RESPECT TO WAVEFUNCTION

WAVEFUNCTION : 4 COMPONENTS IN SCHRÖDINGER REPRESENTATION

$$|\bar{b}_i\rangle \Leftrightarrow \begin{pmatrix} b_i(\vec{r},\uparrow) \\ b_i(\vec{r},\downarrow) \end{pmatrix} = \begin{pmatrix} \mathrm{Re}(b_i(\vec{r},\uparrow)) + i\,\mathrm{Im}(b_i(\vec{r},\uparrow)) \\ \mathrm{Re}(b_i(\vec{r},\downarrow)) + i\,\mathrm{Im}(b_i(\vec{r},\downarrow)) \end{pmatrix}$$

4 independent real component FOR EACH ELECTRON

ENERGY STATIONARY IF THE FUNCTIONAL DERIVATIVE EQUAL TO ZERO WITH RESPECT TO ALL ($4N$ COMPONENT)

$E^{HF}_{\{\bar{b}_i\}}$ = REAL $\quad \frac{\partial E^{HF}}{\partial \mathrm{Re}(b_i(\vec{r},\uparrow))}, \frac{\partial E^{HF}}{\partial \mathrm{Im}(b_i(\vec{r},\uparrow))}, \ldots, \ldots$

$$= \text{Real}$$

IN SCHÖDINGER REPRESENTATION

$$\frac{\partial}{\partial \langle \bar{b}_i|} \overset{def}{=} \begin{pmatrix} \frac{\partial}{\partial \mathrm{Re}(b_i(\vec{r},\uparrow))} + i\frac{\partial}{\partial \mathrm{Im}(b_i(\vec{r},\uparrow))} \\ \frac{\partial}{\partial \mathrm{Re}(b_i(\vec{r},\downarrow))} + i\frac{\partial}{\partial \mathrm{Im}(b_i(\vec{r},\downarrow))} \end{pmatrix}$$

$\forall O$: HERMITIAN $\quad \frac{\partial}{\partial \langle \bar{b}_k|} \sum_i \langle \bar{b}_i | O | \bar{b}_i \rangle = 2O|\bar{b}_k\rangle$

STATIONARY CONDITION

$\forall k$

$$\frac{\partial}{\partial \langle \bar{b}_k |} \left[E^{HF}_{\{b_i\}} - \sum_{ij} \lambda_{ji} \left(\langle \bar{b}_i | \bar{b}_j \rangle - \delta_{ij} \right) \right] = 0$$

λ_{ji}: COMPLEX LAGRANGHIAN MULTIPLYERS

$\lambda^*_{ij} = \lambda_{ji}$ (IN PRINCIPLE WE CAN IMPOSE FOR $i \geq j$)

$$\frac{\partial}{\partial \langle \bar{b}_k |} \left[\sum_{ij} \lambda_{ji} \left(\langle \bar{b}_i | \bar{b}_j \rangle - \delta_{ij} \right) \right] = 2 \sum_j \lambda_{jk} | \bar{b}_j \rangle$$

$$\frac{\partial}{\partial \langle \bar{b}_k |} \left[E^{HF\,1e}_{\{b_i\}} \right] = 2 H^{1e} | \bar{b}_k \rangle$$

$$\frac{\partial}{\partial \langle \bar{b}_k |} \left[H^{H}_{\{b_i\}} \right] = 2 V^{H}(\vec{r}) | \bar{b}_k \rangle$$

$$V^{H}_{\{b_i\}}(\vec{r}) = \int d^3 r' \frac{e^2}{|\vec{r} - \vec{r}'|} \rho(\vec{r}')$$

$$\frac{\partial}{\partial \langle \bar{b}_k |} \left[H^{X}_{\{b_i\}} \right] = +2 H^{X} | b_k \rangle$$

$$H^{X}_{\{b_i\}} = -\int d^3 r \, d^3 r' \sum_{ss'} \frac{e^2}{|\vec{r} - \vec{r}'|} | \vec{r}, s \rangle \rho(\vec{r}, s; \vec{r}', s') \langle \vec{r}', s' |$$

1e HAMILTONIAN

$$H^{HF} \overset{def}{=} H^{1e} + V^{H}_{\{b_i\}}(\vec{r}) + H^{X}_{\{b_i\}}$$

H^{1e}: NON SELF-CONSISTENT PART

$V^{H}_{\{b_i\}}(\vec{r}) + H^{X}_{\{b_i\}}$: DEPEND ON WAVE FUNCTION (SELF-CONSISTENT PART)

STATIONARY CONDITION

$$H^{HF}_{\{b_i\}} |\bar{b}_K\rangle = \sum_J \lambda_{JK} |\bar{b}_J\rangle$$

BY MULTIPLYING BOTH SIDE BY $\langle \bar{b}_J |$

$$\lambda_{KJ} = \langle \bar{b}_J | H^{HF}_{\{b_i\}} | \bar{b}_K \rangle$$

ROTATION TO BASIS THAT DIAG $\lambda_{JK} \to \varepsilon_i$

STATIONARY CONDITION

$$\boxed{H^{HF}_{\{a_i\}} |\bar{a}_i\rangle = \varepsilon_i^{HF} |\bar{a}_i\rangle}$$

SELF-CONSISTENT SINGLE-PARTICLE HAMILTONIAN

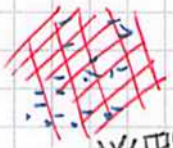
$$\begin{cases} E^{HF}_{GS} = \sum_i \langle \bar{a}_i | H^{1e} | \bar{a}_i \rangle + E^H_{\{a_i\}} + E^X_{\{a_i\}} \\ H^{HF}_{\{a_i\}} |\bar{a}_i\rangle = \varepsilon_i |\bar{a}_i\rangle \end{cases}$$

$\Updownarrow$

DOUBLE COUNTING

$$\begin{cases} E^{HF}_{GS} = \sum_i^N \varepsilon_i^{HF} - E^H_{\{a_i\}} - E^X_{\{a_i\}} \\ H^{HF}_{\{a_i\}} |\bar{a}_i\rangle = \varepsilon_i |\bar{a}_i\rangle \end{cases}$$

INTERACTING 3D JELLIUM (3D ELECTRON GAS)



POSITIVE UNIFORM IONIC DENSITY

WITH CHARGE $+|e|\rho_I(\vec{r}) = \text{constant} = \rho_I|e|$

NEGATIVE ELECTRONIC CHARGE WITH $-\frac{|e|N}{V} = -\rho_I|e|$

(N → ELECTRON PER VOLUME, V → VOLUME)

TOTAL ENERGY FOR A WAVE FUNCTION $|A\rangle$

$$E = E_{II} + E_{IE}^{1e} + \overbrace{T^{1e}}^{\text{KINETIC}} + \overbrace{E^{2e}}^{e\text{-}e\ \text{INTERACTION}}$$

$$E_{II} = \int_V d^3r\, d^3r'\, \rho_I(\vec{r})\,\rho_I(\vec{r}')\,\frac{e^2}{2|\vec{r}-\vec{r}'|}$$

$$E_{IE}^{1e} = -\int d^3r\, d^3r'\, \rho_{|A\rangle}(\vec{r})\,\rho_I(r')\,\frac{e^2}{|\vec{r}-\vec{r}'|}$$

HARTREE FOCK SOLUTION

- NO SYMMETRY BREAKING SOLUTION

  ⇓

  H^{HF} INVARIAN UPON TRASLATION

  SINGLE PARTICLES EIGENFUNCTION PLANE WAVES

- NON MAGNETIC SOLUTION $N_\uparrow = N_\downarrow$

$$\{a_i\} = \begin{cases} \{|\vec{K}\rangle|\uparrow\rangle\}_{|\vec{K}|<k_F} \\ \{|\vec{K}\rangle|\downarrow\rangle\}_{|\vec{K}|<k_F} \end{cases} \qquad \langle\vec{r}|\vec{k}\rangle = \frac{1}{\sqrt{V}}e^{i\vec{K}\cdot\vec{r}}$$

$$\rho_{SD}(\vec{r}) = \rho_I \Rightarrow \boxed{E_{II} + E_{IE}^{1e} + E_{SD}^{H} = 0}$$

$K_F = ?$ DENSITY OF ELECTRON EQUAL TO ρ_I

ELECTRON DENSITY

$$\rho_{\{a_i\}}(\vec{r}) = \sum_i \langle \vec{a}_i | \vec{r} \rangle \langle \vec{r} | a_i \rangle = \overset{\text{SPIN}}{2} \sum_{|\vec{k}| < k_F} \frac{1}{V}$$

$$\frac{1}{V} \sum_{\vec{k}} \xrightarrow{V \to \infty} \int \frac{d^3k}{(2\pi)^3}$$

$$\rho = 2 \int_{|\vec{k}| < k_F} \frac{d^3k}{(2\pi)^3} = 2 \frac{1}{(2\pi)^3} \frac{4\pi k_F^3}{3} = \frac{k_F^3}{3\pi^2}$$

$$k_F = (3\pi^2)^{1/3} \rho_I^{1/3}$$

$$E^{HF} = T^{HF}_{\{a_i\}} + E^{x}_{\{a_i\}}$$

$$\frac{1}{V} T^{HF}_{\{a_i\}} = \frac{1}{V} \sum_i \langle \vec{a}_i | \frac{p^2}{2m} | \vec{a}_i \rangle \overset{\text{SPIN}}{=} 2 \frac{1}{V} \sum_k \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{m} \frac{1}{(2\pi)^3} \int_{k<k_F} d^3k \, k^2$$

$$= \frac{\hbar^2}{m} \frac{4\pi}{(2\pi)^3} \int_0^{k_F} k^2 dk \, k^2 = \frac{\hbar^2}{m} \frac{4\pi}{(2\pi)^3} \frac{k_F^5}{5} = \frac{\hbar^2}{m} \frac{4\pi}{(2\pi)^3} \frac{(3\pi^2)^{5/3}}{5} \times \rho_I^{5/3}$$

$$= \frac{\hbar^2}{m} \frac{3}{10} (3\pi^2)^{2/3} \rho_I^{5/3}$$

$$\frac{1}{V} E^{x}_{\{a_i\}} = -\frac{(2)}{V}\int d^3r\, d^3r'\ \frac{1}{2}\frac{e^2}{|\vec{r}-\vec{r}'|}\,|\rho(\vec{r},\uparrow,\vec{r}',\uparrow)|^2$$

(2) ← SPIN

$$\rho(\vec{r},\uparrow,\vec{r}',\uparrow) = \sum_{|\vec{k}|<k_F} \langle \vec{r}|\vec{k}\rangle\langle\vec{k}|\vec{r}'\rangle$$

$$= \frac{1}{V}\sum_{|\vec{k}|<k_F} e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} = \int_{|\vec{k}|<k_F} \frac{d^3k}{(2\pi)^3}\, e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}$$

$$= -\frac{2}{V}\int d^3r\, d^3r' \frac{1}{2}\frac{e^2}{|\vec{r}-\vec{r}'|}\int_{k<k_F}\frac{d^3k}{(2\pi)^3}\, e^{i\vec{k}(\vec{r}-\vec{r}')}\int_{k'<k_F}\frac{d^3k'}{(2\pi)^3}\, e^{-i\vec{k}'(\vec{r}-\vec{r}')}$$

CHANGE OF VARIABLE: $\vec{r}-\vec{r}'=\vec{r}''$

$$= -e^2\int d^3r''\ \frac{1}{r''}\int_{|k|<k_F}\frac{d^3k}{(2\pi)^3}\, e^{i\vec{k}\cdot\vec{r}''}\int_{|k'|<k_F}\frac{d^3k'}{(2\pi)^3}\, e^{-i\vec{k}'\cdot\vec{r}''}$$

$$= -\frac{e^2}{(2\pi)^6}\int_{k<k_F} d^3k \int_{k'<k_F} d^3k' \int d^3r''\, \frac{e^{+i(\vec{k}-\vec{k}')\cdot\vec{r}''}}{r''}$$

FOURIER TRANSFORM (FT)

$$\tilde{f}(\vec{k}) = FT(f(\vec{r})) = \int d^3r\, f(\vec{r})\, e^{-i\vec{k}\cdot\vec{r}}$$

INVERSE FT

$$f(\vec{r}) = IFT(\tilde{f}(\vec{k})) = \int \frac{d^3k}{(2\pi)^3}\, \tilde{f}(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}$$

$$\boxed{FT\left(\frac{1}{r}\right) = \frac{4\pi}{k^2}}$$

$$\frac{1}{V}E^x = -e^2 \int_{k<k_F} \frac{d^3k}{(2\pi)^3} \int_{k<k_F} \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|\vec{k}-\vec{k}'|^2}$$

$$\int_{k<k_F} \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|\vec{k}-\vec{k}'|} = \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right)$$

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right|$$

$$\frac{1}{V}E^x = -e^2 \int_{k<k_F} \frac{d^3k}{(2\pi)^3} \frac{2k_F}{\pi} F\left(\frac{k}{k_F}\right) =$$

$$= -\frac{3}{4} e^2 \left(\frac{3}{\pi}\right)^{1/3} \rho_I^{4/3}$$

$$E^{HF} = \frac{\hbar^2}{m} \frac{3}{10} (3\pi^2)^{4/3} \rho_I^{5/3} - \frac{3}{4} e^2 \left(\frac{3}{\pi}\right)^{1/3} \rho_I^{4/3}$$

$$= A\rho_I^{5/3} - B\rho_I^{4/3} \rightarrow \text{DOMINATES AT LOW } \rho_I$$

DOMINATE AT LARGE ρ_I

IN THE PRESENT CASE $\rho_I = \rho_\uparrow + \rho_\downarrow$ WITH $\rho_\uparrow = \rho_\downarrow$

JELLIUM REDUCED UNITS

RELEVANT LENGTHS:

1) WITH $e, \hbar, m_e$

$\Downarrow$

BOHR RADIUS

$$a_0 = \frac{\hbar^2}{m_e e^2} = 0.592177\ \text{Å}$$

2) WITH ρ_I AVERAGE DISTANCE BETWEEN ELECTRONS: r_e

$$r_e^3 \sim \frac{1}{\rho_I} \Rightarrow \text{CONVENTIONALLY } \frac{4}{3}\pi r_e^3 = \frac{1}{\rho_I}$$

$\Downarrow$

ADIMENSIONAL PARAMETER r_s

$$r_s = \frac{r_e}{a_0} = \left(\frac{3}{4\pi\rho_I}\right)^{1/3} \frac{1}{a_0} = \left(\frac{3e^6 m_e^3}{4\pi\hbar^6 \rho_I}\right)^{1/3}$$

$r_s \to 0$ $\rho_I \to +\infty$; $r_s \to +\infty$ $\rho_I \to 0$ (IN REAL METALS $r_s \sim 1-3$)

ADIMENSIONAL LENGTH REDUCED UNITS

$$\vec{\tilde{r}} = \frac{\vec{r}}{r_e} = \frac{\vec{r}}{a_0 r_s}$$

ENERGY $Ry = \frac{e^2}{2a_0} = \frac{e^4 m_e}{2\hbar^2} = 13.605\ \text{eV}$

HAMILTONIAN IN REDUCED UNITS

KINETIC ENERGY (T^{1e})

$$-\frac{1}{2}\frac{\hbar^2}{m_e}\nabla_i^2 \overset{\text{REDUCED UNITS}}{=} -\frac{1}{2}\frac{\hbar^2}{m_e}\frac{1}{(a_0 r_s)^2}\tilde{\nabla}_i = \frac{Ry}{r_s^2}\left(-\tilde{\nabla}_i^2\right) =$$

POTENTIAL ENERGY (E_{II}, E_{Ie}, E_{ee})

$$\frac{e^2}{2|\vec{r}_i - \vec{r}_j|} = \frac{e^2}{2(a_0 r_s)}\frac{1}{|\vec{\tilde{r}}_i - \vec{\tilde{r}}_j|} = \frac{Ry}{r_s^2}\left[r_s \frac{1}{|\vec{\tilde{r}}_i - \vec{\tilde{r}}_j|}\right]$$

DENSITY OF ELECTRONS IN REDUCED UNITS

$$\tilde{\rho}_I = \rho_I \cdot (a_0 r_s)^3 = \frac{3}{4\pi} = \text{CONSTANT}$$

HAMILTONIAN

$$\frac{Ry}{r_s^2}\left\{-\sum_i \tilde{\nabla}_i^2 + r_s\left[\sum_{\substack{i,j=2 \\ i\neq j}}^{N}\frac{1}{|\vec{\tilde{r}}_i - \vec{\tilde{r}}_j|}\right] - r_s \tilde{E}_I^H\right\}$$

$r_s = 0$ (HIGH DENSTY) KINETIC ENERGY DOMINATES

$r_s \to \infty$ (LOW DENSITY $|\vec{\tilde{r}}_i - \vec{\tilde{r}}_j| > \sim 1$) e-e ENERGY DOMINATES (EXCHANGE AND CORRELATION ENERGY)

- IN REDUCED UNITS GROUD STATE WAVEFUNCTION (SCHRÖDINGER REPRESENTATION) JUST DEPENDS ON r_s & $\frac{e^{*2} m^*}{\rho_I^{1/3}}$

HF ENERGY IN REDUCED UNITS

ENERGY PER ELECTRON

$$\epsilon^{HF} = E^{HF} \times \frac{V}{N} = \frac{E^{HF}}{\rho_I} = \left(\underbrace{\frac{2.21}{r_s^2}}_{\epsilon_{KIN}} - \underbrace{\frac{0.916}{r_s}}_{\epsilon_X} \right) Ry$$

CORRELATION ENERGY

CORRELATION ENERGY

$$\epsilon_c \equiv \frac{E^{EXACT}}{\rho_I} - E^{HF}$$

PARAMETRISATION ON MONTECARLO RESULTS
PERDEW-WANG PRB 45, 13244 (1992)

AT $r_s = 1$ $\epsilon_c \sim -0.18\ Ry$ $\left(\frac{\epsilon_x}{\epsilon_c} = 5.1\right)$

$r_s = 4$ $\epsilon_c \sim -0.065\ Ry$ $\left(\frac{\epsilon_x}{\epsilon_c} = 3.5\right)$

FOR $r_s \to \infty$ ϵ_c BECOMES MORE IMPORTANT!

SYMMETRY BREAKING SOLUTION IN HF FERROMAGNETIC STATE

COLINEAR BUT $\rho_\uparrow \neq \rho_\downarrow$ $\quad \rho_\uparrow = \frac{\rho_I}{2}(1+x)$

$$\rho_\downarrow = \frac{\rho_I}{2}(1-x)$$

$$E^{HF}(x) = E^{HF}_\uparrow + E^{HF}_\downarrow = \frac{1}{2}\left\{A(2\rho_\uparrow)^{5/3} - B(2\rho_\downarrow)^{4/3} + A(2\rho_\uparrow)^{5/3} - B(2\rho_\downarrow)^{4/3}\right\}$$

$$E^{HF}(1) - E^{HF}(0) = \frac{2}{2}A\rho_I^{5/3} - \frac{2}{2}B\rho_I^{4/3} - A\rho_I^{5/3} + B\rho_I^{4/3}$$

$$= \Delta E = \left(2^{2/3}-1\right)A\rho^{5/3} - \left(2^{1/3}-1\right)B\rho^{4/3}$$

$\Delta E < 0$ FERROMAG GROUND STATE

FOR $\rho \to 0$ THIS DOMINATES

$$\rho_I^{1/3} < \frac{B\left(2^{1/3}-1\right)}{A\left(2^{2/3}-1\right)} \quad \to r_s = 5.45$$

MONTE CARLO CALCULATION $r_s \sim 73$!

CALCULATION OF EXACT ENERGY

$$E^{GS}_{EXACT} = \underbrace{\langle A | \sum_{i=1}^{N} \frac{p_i^2}{2m} | A \rangle}_{\text{KINETIC ENERGY}} + E_{II} + E_{IE} + E^{HARTREE} + E^{HARTREE} + \underbrace{\langle A | \sum_{ij} H^{2e}_{ij} | A \rangle - E^{HARTREE}}_{E^{2e}_{|A\rangle}}$$

$E^{2e}_{|A\rangle}$ → POTENTIAL ENERGY

$E_{II} + E_{IE} + E^{HARTREE} + E^{HARTREE}$ → UNIFORM SOLUTION $= 0$

$$\frac{E^{2e}_{|A\rangle}}{N} = \frac{V}{N} \int d^3r' \left[\rho^{(2)}(\vec{r}, \vec{r}') - \rho_I \rho_I \right] \frac{e^2}{2|\vec{r} - \vec{r}'|}$$

$1/\rho_I$

$E_{POTENTIAL}$

$\rho^{(2)}$ IN JELLIUM $= \rho^{(2)}(|\vec{r} - \vec{r}'|)$

$g(\vec{r}, \vec{r}')$ = PAIR CORRELATION FUNCTION =

$$= \frac{\rho^{(2)}(\vec{r}, \vec{r}')}{\rho(\vec{r}) \rho(\vec{r}')}$$

→ IN JELLIUM $= g(|\vec{r} - \vec{r}'|)$, $\rho(\vec{r}) = \rho_I$

$$\frac{E^{2e}_{|A\rangle}}{N} = \rho_I \int d^3r \left[g(|\vec{r}|) - 1 \right] \frac{e^2}{2r}$$

$$\frac{1}{N} \langle A | \sum_{i=1}^{N} \frac{p_i^2}{2m} | A \rangle = ?$$

HELLMANN - FEYNMAN THEOREM

$\hat{H}^\lambda$ $\qquad$ λ = PARAMETER

$$\hat{H}^\lambda |A_i^\lambda\rangle = \varepsilon_i^\lambda |A_i^\lambda\rangle \qquad \langle A_i^\lambda | A_j^\lambda \rangle = \delta_{ij}$$

$$\varepsilon_i^\lambda = \langle A_i^\lambda | \hat{H}^\lambda | A_i^\lambda \rangle$$

$$\frac{d\varepsilon_i^\lambda}{d\lambda} = \left(\frac{d}{d\lambda}\langle A_i^\lambda|\right) \hat{H}^\lambda |A_i^\lambda\rangle + \langle A_i^\lambda | \hat{H}^\lambda \left(\frac{d}{d\lambda}|A_i^\lambda\rangle\right)$$

$$+ \langle A_i^\lambda | \frac{d\hat{H}^\lambda}{d\lambda} | A_i^\lambda \rangle = \varepsilon_i^\lambda \frac{d}{d\lambda}\left(\underbrace{\langle A_i^\lambda | A_i^\lambda \rangle}_{=0}\right)$$

$$+ \langle A_i^\lambda | \frac{d\hat{H}^\lambda}{d\lambda} | A_i^\lambda \rangle$$

$$\boxed{\frac{d\varepsilon_i^\lambda}{d\lambda} = \langle A_i^\lambda | \frac{d\hat{H}^\lambda}{d\lambda} | A_i^\lambda \rangle}$$

JELLIUM INTERACTING KINETIC ENERGY

IN THE JELLIUM HAMILTONIAN WE REPLACE $e^2 \to \lambda e^2$

$$E^{GS}_{EXACT} \to E^{GS\lambda}_{EXACT} \begin{cases} \lambda=0 & \text{NON INTERACTING JELLIUM} \\ \lambda=1 & \text{FULLY INTERACTING JELLIUM} \end{cases}$$

$$\frac{E^{GS}_{EXACT}}{N} = \frac{E^{GS\,\lambda=0}_{EXACT}}{N} + \int_0^1 d\lambda \frac{dE^{GS\lambda}_{EXACT}}{d\lambda}\frac{1}{N}$$

T^{HF} = NON-INTERACTING FREE ELECTRON KINETIC ENERGY

HELLMAN FEYNMAN

$$\frac{1}{N}\frac{dE^{GS\lambda}}{d\lambda} = \frac{E^{2e}_{|A^\lambda\rangle}}{N} = \rho_I \int d^3r \left[g^\lambda(|\vec{r}|)-1\right]\frac{e^2}{2r}$$

$$\frac{1}{N}\langle A|\sum_{i=1}^{N}\frac{p_i^2}{2m}|A\rangle = \frac{T^{HF}}{N} + \rho_I\int d^3r \int_1^\lambda d\lambda \left[g^\lambda(r)-g(r)\right]\frac{e^2}{2r}$$

NON-INTE KIN

$$g^\lambda(r,\rho_I) = \tilde{g}\left(\frac{\vec{r}}{a_0^\lambda r_s^\lambda}, r_s^\lambda\right) =$$

WHERE $a_0^\lambda = \frac{\hbar}{m_e \lambda e^2} = \frac{a_0}{\lambda}$

$$r_s^\lambda = \left(\frac{3\lambda e^6 m_e^3}{4\pi\hbar^6\rho_I}\right)^{1/3} = \lambda r_s$$

$\tilde{g}(\tilde{r}, r_s)$ IN REDUCED UNITS JUST DEPENDS ON r_s SINCE THE G.S. WAVE FUNC. JUST DEPENDS ON r_s

$$= \tilde{g}\left(\frac{\lambda r}{a_0(\lambda r_s)}, \lambda r_s\right) = g\left(\lambda r, \frac{\rho_I}{\lambda^3}\right)$$

HARTREE FOCK : BAND STRUCTURE

$$\varepsilon^{HF}_{\vec{k}} = \underbrace{\frac{\hbar^2 k^2}{2m}}_{\varepsilon^{kin}_{\vec{k}}} + \underbrace{\langle \vec{k} | H^x | \vec{k} \rangle}_{\varepsilon^x_{\vec{k}}}$$

$\rho(\vec{r},\uparrow;\vec{r}',\uparrow)$

$$\varepsilon^x_{\vec{k}} = -\int d^3r\, d^3r' \, \frac{e^{-i\vec{k}(\vec{r}-\vec{r}')}}{V} \, \frac{e^2}{|\vec{r}-\vec{r}'|} \int_{k'<k_F} \frac{d^3k'}{(2\pi)^3} e^{i\vec{k}'(\vec{r}-\vec{r}')}$$

$\vec{r}-\vec{r}' = \vec{r}''$

$\int d^3r = V$

$$= -\int_{k'<k_F} \frac{d^3k'}{(2\pi)^3} \int d^3r'' \; e^{-i\vec{r}''\cdot(\vec{k}-\vec{k}')} \frac{e^2}{r''} = -e^2 \int_{k'<k_F} \frac{d^3k'}{(2\pi)^3} \frac{4\pi}{|\vec{k}-\vec{k}'|^2}$$

$$\varepsilon^x_{\vec{k}} = -e^2 \, 2\frac{k_F}{\pi} F\left(\frac{k}{k_F}\right) \qquad F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right|$$

$F(0)=1 \quad F(1)=\frac{1}{2}$

$$k_F = (3\pi^2)^{1/3} \rho_I^{1/3} \qquad \rho_I^{1/3} = \left(\frac{3}{4\pi}\right)^{1/3} \frac{1}{r_s a_B}$$

$$k_F = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{a_B} \frac{1}{r_s} \qquad \frac{e^2}{2a_B} = 1\,Ry$$

in Ry

$$\varepsilon^x_{\vec{k}} = -\frac{4}{\pi}\left(\frac{9\pi}{4}\right)^{1/3} Ry \, \frac{1}{r_s} F(x) = -\frac{2.44}{r_s} F(x)$$

$$\varepsilon^{kin}_{\vec{k}} = \frac{\hbar^2}{2m} k_F^2 x^2 = \frac{\hbar}{2m}\left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2 a_B^2} x^2 = \left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2} Ry \, x^2$$

$$= \frac{3.68}{r_s^2} x^2$$

HARTREE-FOCK ERROR

- IN 3DEG INDEP. ELECTRON BAND STRUCTURE BETTER THAN HF
- HF METHOD FOR TOTAL ENERGY (TOTAL ENERGY OF HF BETTER THAN INDEP ELECTRON
- THE ELECTRON-ELECTRON INTERACTION SCREENED BY OTHER ELECTRON.
  WE SHOULD USE DYNAMICALLY SCREENED INTERACTION

REPLACE

$$\frac{4\pi e^2}{q^2} \longrightarrow \frac{1}{\varepsilon(q,\omega)} \frac{4\pi e^2}{q^2} = W(q,\omega)$$

AS IN GW OR RPA CALCULATIONS

IN METALS THE SCREENING IS VERY EFFICIENT

$\left(\lim_{\substack{q\to 0 \\ \omega\to 0}} \varepsilon(q,\omega) \to \infty \right)$ WORST CASE FOR HF

IN INSULATOR $\lim_{\substack{q\to 0 \\ \omega\to 0}} \varepsilon(q,\omega) =$ FINITE

BETTER CASE FOR HF

BETTER SINGLE-PARTICLE HAMILTONIAN THAN HF

⇓

WE HAVE TO USE A "FAKE" HAMILTONIAN

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

⇓ WE MAP

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