Select/Special Topics from 'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 16

Electron Gas in Hartree Fock and Random Phase Approximations

First,
a short *revisit* to Hartree Fock Formalism,
but from a different route….

Recapitulate,
with a *rather brief re-visit*, but ***from a different route:***

Hartree Fock Self Consistent Field Method:
Special/Select Topic in Atomic Physics
STiAP Unit 4

Reference→
http://www.nptel.ac.in/downloads/115106057/

We shall **supplement** and **complement** that discussion to equip ourselves to build the machinery to see **how the methods of 2nd quantization developed in Unit 2 can be extended to address the electron <u>'COULOMB' correlations</u>** that are left ***<u>out</u>*** of the HF method….

HF SCF Method: STiAP Unit 4 L21
Reference→http://www.nptel.ac.in/downloads/115106057/

$$H = H_1 + H_2$$

$$= \sum_{i=1}^{N} f(q_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ \boxed{i \neq j}}}^{N} \mathrm{v}(q_i, q_j)$$

$$f(q_i) = \left(-\frac{1}{2} \nabla_i^{\,2} - \frac{Z}{r_i} \right)$$

Many-Electron Hamiltonian *in the notation of* **FIRST QUANTIZATION**

$$H = \sum_i \sum_j c_i^{\dagger} \langle i | f | j \rangle c_j + \frac{1}{2} \sum_i \sum_j \sum_k \sum_l c_i^{\dagger} c_j^{\dagger} \langle ij | \mathrm{v} | kl \rangle c_l c_k$$

Many-Electron Hamiltonian *in the notation of* **SECOND QUANTIZATION**

$$\langle ij | \mathrm{v} | kl \rangle = \int dq_1 \int dq_2 \phi_i^{*}(q_1) \phi_j^{*}(q_2) \mathrm{v}(q_1, q_2) \phi_k(q_1) \phi_l(q_2)$$

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle =$$

$$=\left[\sum_i\sum_j c_i^\dagger\langle i|f|j\rangle c_j+\frac{1}{2}\sum_i\sum_j\sum_k\sum_l c_i^\dagger c_j^\dagger\langle ij|\mathrm{v}|kl\rangle c_l c_k\right]|\Psi(t)\rangle$$

$$H=\sum_i\sum_j c_i^\dagger\langle i|f|j\rangle c_j+\frac{1}{2}\sum_i\sum_j\sum_k\sum_l c_i^\dagger c_j^\dagger\langle ij|\mathrm{v}|kl\rangle c_l c_k$$

Fetter & Walecka (p.18); Raimes (p.31; 42)

Note: ↑Order↑

$$\langle ij|\mathrm{v}|kl\rangle=\int dq_1\int dq_2\,\psi_i^*(q_1)\,\psi_j^*(q_2)\,\mathrm{v}(q_1,q_2)\,\psi_k(q_1)\,\psi_l(q_2)$$

The $\boxed{\text{order}}$ does not matter for Bosons; *for Fermions, it does matter*.

For electrons,

$$\psi_i(q)=\psi_i(\vec{r})\chi_i(\zeta)$$

$$spin-orbital$$

$\chi_i(\zeta)$ is either $\alpha=\begin{bmatrix}1\\0\end{bmatrix}$ *for* $m_{s_i}=+\frac{1}{2}$ ↑

or $\beta=\begin{bmatrix}0\\1\end{bmatrix}$ *for* $m_{s_i}=-\frac{1}{2}$ ↓

Linear combination of creation & destruction operators

Field operators

definition → II Quantization

$$\begin{cases} \hat{\psi}(q) = \sum_i \psi_i(q) c_i \\ \hat{\psi}^\dagger(q) = \sum_i \psi_i^*(q) c_i^\dagger \end{cases}$$

$\psi_i(q)$: single particle wavefunctions *i.e.* spin-orbitals

$c_i, c_i^\dagger$: 2nd quantization destruction & creation operators

$i \equiv \{\vec{k}_i, m_{s_i}\}$ or $i \equiv \{n_i, l_i, j_i, m_{j_i}\}$ with $m_{s_i} = +\frac{1}{2}$ *or* $-\frac{1}{2}$

Free electron — *Hydrogenic Potential*

Spin-orbitals→ $\psi_i(q) = \psi_i(\vec{r})\chi_i(\zeta)$

where $\chi_i(\zeta) = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ or $\chi_i(\zeta) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

for $m_{s_i} = +\frac{1}{2}$ or $m_{s_i} = -\frac{1}{2}$

<u>adjoint *spin–orbitals*</u>

$\psi_i^*(q) = \psi_i^*(\vec{r})\chi_i^\dagger(\zeta)$

$\chi_i^\dagger(\zeta) = [1 \quad 0]$ or $\chi_i^\dagger(\zeta) = [0 \quad 1]$

for $m_{s_i} = +\frac{1}{2}$ or $m_{s_i} = -\frac{1}{2}$

$$H^{(N)}\Phi^{(N)} = E^{(N)}\Phi^{(N)}$$ ← N-electron Schrodinger equation

$$\Phi^{(N)}{}_{n_1,n_2,..,n_i,..,n_\infty}(q_1,q_2,..,q_N) \equiv \Phi^{(N)}{}_{a_1,a_2,..,a_N}(q_1,q_2,..,q_N)$$

Ordered set: $a_1 < a_2 < .. < a_i < .. < a_j < .. < a_N$

Slater determinantal wavefunction

$$\Phi^{(N)}{}_{n_1,n_2,..,n_i,..,n_\infty}(q_1,q_2,..,q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{a_1}(q_1) & .. & .. & \psi_{a_1}(q_N) \\ .. & & & .. \\ .. & \psi_{a_i}(q_j) & & .. \\ \psi_{a_N}(q_1) & .. & .. & \psi_{a_N}(q_N) \end{vmatrix}$$

$$\int \psi^*_i(q)\psi_j(q)\,dx = \delta_{ij}$$ *Orthonormal complete set of one-electron spin-orbitals*

$$\sum_i \psi^*_i(q')\psi_i(q) = \delta(q-q') = \delta(\vec{r}-\vec{r}\,')\delta_{\zeta\zeta'}$$

Field Operators

$$\hat{\psi}(q)=\sum_i \psi_i(q)c_i$$

$$\hat{\psi}^\dagger(q)=\sum_i \psi_i^*(q)c_i^\dagger$$

Inclusion of spin: multi-component spin-orbitals

In general, for spin = j : $\alpha = 1, 2, ...(2j+1)$

j : integer for Bosons, half-integer for Fermions

Multi-component spin-orbital wavefunction ***(2j+1) number of components***

$$\psi_i(q) \equiv \begin{bmatrix} \psi_{i,\alpha=1}(q) \\ \psi_{i,\alpha=2}(q) \\ \psi_{i,\alpha=3}(q) \\ \psi_{i,\alpha=....}(q) \\ \psi_{i,\alpha=2j+1}(q) \end{bmatrix}$$

Field Operator

$$\hat{\psi}_\alpha(q)=\sum_i \psi_{i\alpha}(q)c_i$$

$$\hat{\psi}_\alpha^\dagger(q)=\sum_i \psi_{i\alpha}^*(q)c_i^\dagger$$

$$\alpha = 1, 2, 3, ..., (2j+1)$$

$$\left[\hat{\psi}_\alpha(q), \hat{\psi}_\beta^\dagger(q')\right]_\pm = \delta_{\alpha\beta}\delta(q-q')$$

Fermi→ + Bose→ -

Field operators

$$\left[\hat{\psi}_\alpha(q), \hat{\psi}_\beta(q')\right]_\pm = 0$$

$$\left[\hat{\psi}_\alpha^\dagger(q), \hat{\psi}_\beta^\dagger(q')\right]_\pm = 0$$

Field Operator

$$\alpha = 1,2,3,.....,(2j+1)$$

$$\hat{\psi}_\alpha(q) = \sum_i \psi_{i\alpha}(q)c_i$$

$$\hat{\psi}_\alpha^\dagger(q) = \sum_i \psi_{i\alpha}^*(q)c_i^\dagger$$

$$\left[c_{r_1\sigma_1}, c_{r_2\sigma_2}^\dagger\right]_\pm = \delta_{r_1r_2}\delta_{\sigma_1\sigma_2}$$

$$\left[c_{r_1\sigma_1}^\dagger, c_{r_2\sigma_2}^\dagger\right]_\pm = 0$$

$$\left[c_{r_1\sigma_1}, c_{r_2\sigma_2}\right]_\pm = 0$$

F→ +
B→ -

$$\text{spin } \frac{1}{2}: \quad \psi_i(q) \equiv \begin{bmatrix} \psi_{i,\alpha=1}(q) \\ \psi_{i,\alpha=2}(q) \end{bmatrix}$$

$$\alpha = 1 \rightarrow m_s = +\frac{1}{2}$$

$$\alpha = 2 \rightarrow m_s = -\frac{1}{2}$$

Hamiltonian in terms of single particle creation and destruction operators

$$H = \sum_i \sum_j c_i^\dagger \langle i|f|j\rangle c_j + \frac{1}{2}\sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij|\mathrm{v}|kl\rangle c_l c_k$$

$$\left[\hat{\psi}_\alpha(q), \hat{\psi}_\beta^\dagger(q')\right]_\pm = \delta_{\alpha\beta}\delta(q-q')$$

$$\left[\hat{\psi}_\alpha(q), \hat{\psi}_\beta(q')\right]_\pm = 0$$

$$\left[\hat{\psi}_\alpha^\dagger(q), \hat{\psi}_\beta^\dagger(q')\right]_\pm = 0$$

↓ Hamiltonian in terms of field operators

$$H = \int \hat{\psi}^\dagger(q) f(q)\hat{\psi}(q)dq + \frac{1}{2}\int\int \hat{\psi}^\dagger(q)\hat{\psi}^\dagger(q')\mathrm{v}(q,q')\hat{\psi}(q')\hat{\psi}(q)dqdq'$$

Note: ↑Order↑

That ↑this↑ form is correct can be seen easily as shown on next slide→

$$H = \int \hat{\psi}^\dagger(q) f(q)\hat{\psi}(q)dq + \frac{1}{2}\int\int \hat{\psi}^\dagger(q)\hat{\psi}^\dagger(q')\mathrm{v}(q,q')\hat{\psi}(q')\hat{\psi}(q)dqdq'$$

$$\hat{\psi}(q) = \sum_i \psi_i(q)c_i \qquad \hat{\psi}^\dagger(q) = \sum_i \psi_i^*(q)c_i^\dagger$$

equivalent

$$H = \sum_i \sum_j c_i^\dagger \int \psi_i^*(q) f(q)\psi_j(q)dq c_j + \frac{1}{2}\sum_i \sum_j c_i^\dagger c_j^\dagger \sum_k \sum_l \int\int \psi_i^*(q)\psi_j^*(q)\mathrm{v}(q,q')\psi_l(q)\psi_k dqdq' \, c_k c_l$$

$$H = \sum_i \sum_j c_i^\dagger \langle i | f | j \rangle c_j + \frac{1}{2}\sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij | \mathrm{v} | lk \rangle c_k c_l$$

Raimes, Many Electron Theory / Eq.2.117 / p.42

Complete expressions for the Hamiltonian, inclusive of spin labels

$$\left[c_{a_1\sigma_1}, c_{a_2\sigma_2}{}^{\dagger}\right]_{\pm} = \delta_{a_1 a_2}\delta_{\sigma_1\sigma_2} \qquad \left[c_{a_1\sigma_1}{}^{\dagger}, c_{a_2\sigma_2}{}^{\dagger}\right]_{\pm} = 0 \qquad \left[c_{a_1\sigma_1}, c_{a_2\sigma_2}\right]_{\pm} = 0$$

$$H = \int \hat{\psi}^{\dagger}_{\alpha}(q) f(q) \hat{\psi}_{\beta}(q) dq + \frac{1}{2}\int\int \hat{\psi}^{\dagger}_{\alpha}(q)\hat{\psi}^{\dagger}_{\beta}(q) \mathrm{v}(q,q')\hat{\psi}_{\delta}(q')\hat{\psi}_{\gamma}(q) dq dq'$$

$$\hat{\psi}_{\alpha}(q) = \sum_{\alpha}\sum_{i} \psi_{i\alpha}(q) c_{i\alpha} \qquad \hat{\psi}^{\dagger}_{\beta}(q) = \sum_{\beta}\sum_{j} \psi_{j\beta}{}^{*}(q) c^{\dagger}_{j\beta}$$

$$H = \sum_{\substack{i\\ \sum_{\alpha}}}\sum_{\substack{j\\ \sum_{\beta}}} c^{\dagger}_{i\alpha}\int \psi_{i\alpha}{}^{*}(q) f(q) \psi_{j\beta}(q) dq\, c_{j\beta} +$$
$$+\frac{1}{2}\sum_{\substack{i\\ \sum_{\alpha}}}\sum_{\substack{j\\ \sum_{\beta}}}\sum_{\substack{k\\ \sum_{\delta}}}\sum_{\substack{l\\ \sum_{\gamma}}} c^{\dagger}_{i\alpha} c^{\dagger}_{j\beta}\int\int \psi_{i\alpha}{}^{*}(q)\psi_{j\beta}{}^{*}(q)\mathrm{v}(q,q')\psi_{l\delta}(q)\psi_{k\gamma} dq dq'\, c_{k\gamma} c_{l\delta}$$

$$H = \sum_{\substack{i\\ \sum_{\alpha}}}\sum_{\substack{j\\ \sum_{\beta}}} c^{\dagger}_{i\alpha}\langle i\alpha | f | j\beta\rangle c_{j\beta} + \frac{1}{2}\sum_{\substack{i\\ \sum_{\alpha}}}\sum_{\substack{j\\ \sum_{\beta}}}\sum_{\substack{k\\ \sum_{\delta}}}\sum_{\substack{l\\ \sum_{\gamma}}} c^{\dagger}_{i\alpha} c^{\dagger}_{j\beta}\langle i\alpha, j\beta | \mathrm{v} | l\delta, k\gamma\rangle c_{k\gamma} c_{l\delta}$$

Raimes / p.42 / Eq.2.117 → inclusive of spin labels

We recognize that c_i and $c_i^\dagger$ are Hermitian conjugates.

These operators were introduced as destruction & creation operators.

Proof : $$\left.\begin{aligned} Let\ \Phi_a &= \Phi^{N+1}(,,,,,1_i,......) \\ \Phi_b &= \Phi^{N}(,,,,,0_i,......) \end{aligned}\right\}$$

all other occupation numbers in $\Phi_a = \Phi^{N+1}$ & $\Phi_b = \Phi^N$ being same

$c_i\Phi_a = \Phi_b$ and $\int \Phi_b^* c_i \Phi_a d\tau = 1$ ←Number of occupied states preceding the i[th] state: even

destruction operator

$$let\ c_i^H = \underbrace{Hermitian\ conjugate}\ \text{of } c_i$$

$$we\ must\ show\ that:\ c_i^H = c_i^\dagger$$

creation operator

c_i :destruction operator

$$\underbrace{1 = \int \Phi_b^* c_i \Phi_a d\tau}_{\text{normalization integral}} \overset{\substack{by\\definition\\of}}{\underset{\substack{Hermitian\\conjugate}}{=}} \int \left(c_i^H \Phi_b\right)^* \Phi_a d\tau = \underbrace{\left(\int \Phi_a{}^* c_i^H \Phi_b d\tau\right)^*}_{\text{normalization integral}} = 1$$

$$\therefore\ c_i^H \Phi_b = \Phi_a$$

$c_i^H = c_i^\dagger$

i.e. c_i and $c_i^\dagger$ are Hermitian conjugates

Hartree-Fock method & the free electron gas

Raimes/Ch.3

N-electron Hamiltonian

$$H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^{\,2}-\frac{Z}{r_i}\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$=\sum_{i=1}^{N}f(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}$$

$$\boxed{H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)}$$

add and subtract

$$H^{(N)}(q_1,q_2,..,q_N)=\underbrace{\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified one-electron operator}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)}_{\text{Modified interaction}}$$

$$F=?$$

$$H^{(N)}(q_1,q_2,..,q_N)=\underbrace{\sum_{i=1}^{N} f(\vec{r}_i)+\sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified one-electron operator would contain much/most of the effect of the two-electron terms.}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified, residual, interaction between pairs of electrons.}}$$

$$-\frac{1}{2}\nabla_i^{\,2}-\frac{Z}{r_i}=f(\vec{r}_i)$$

$$\mathrm{H}_1=\sum_{i=1}^{N} f(\vec{r}_i)\;=f$$

Modified one-electron operator would contain much/most of the effect of the two-electron terms.

Modified, residual, interaction between pairs of electrons.

This term would be weak, and would be treated perturbatively.

$$H^{(N)}(q_1,q_2,..,q_N)=f\;+F+H_2-F$$

Choice of the operator F is to be so made that the total energy is minimised.

$$H^{(N)}(q_1,q_2,..,q_N)=\underbrace{\sum_{i=1}^{N} f(\vec{r}_i)+\sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified one-electron operator}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified interaction}}$$

$$\boxed{-\frac{1}{2}\nabla_i^{2}-\frac{Z}{r_i}=f(\vec{r}_i)}$$

When the $\boxed{2^{nd}}$ term is neglected, $\boxed{\text{this}}$ determinant is the unperturbed ground state wavefunction.

$$\Phi^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{1\uparrow}(1) & .. & .. & .. & \psi_{1\uparrow}(N) \\ \psi_{1\downarrow}(1) & .. & .. & .. & \psi_{1\downarrow}(N) \\ .. & .. & .. & \langle j\,|\,i\rangle=\psi_i(q_j) & .. \\ \psi_{\frac{N}{2}\uparrow}(1) & .. & .. & .. & \psi_{\frac{N}{2}\uparrow}(N) \\ \psi_{\frac{N}{2}\downarrow}(1) & .. & .. & .. & \psi_{\frac{N}{2}\downarrow}(N) \end{vmatrix}$$

$$\left[f(\vec{r})+F(\vec{r})\right]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})$$

<u>with</u> $\psi_{i\sigma}(\vec{r})=\psi_{i\downarrow}(\vec{r})$ *or* $\psi_{i\uparrow}(\vec{r})$

ε_i : doubly degenerate, with one eigenfunction each for spin $\uparrow$ & $\downarrow$

$$H^{(N)}(q_1,q_2,..,q_N) = \underbrace{\sum_{i=1}^{N} f(\vec{r}_i) + \sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified one-electron operator}} + \underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) - \sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified interaction}}$$

$$\boxed{-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} = f(\vec{r}_i)}$$

$$\Phi^{(N)} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{1\uparrow}(1) & .. & .. & .. & \psi_{1\uparrow}(N) \\ \psi_{1\downarrow}(1) & .. & .. & .. & \psi_{1\downarrow}(N) \\ .. & .. & .. & \langle j|i\rangle = \psi_i(q_j) & .. \\ \psi_{\frac{N}{2}\uparrow}(1) & .. & .. & .. & \psi_{\frac{N}{2}\uparrow}(N) \\ \psi_{\frac{N}{2}\downarrow}(1) & .. & .. & .. & \psi_{\frac{N}{2}\downarrow}(N) \end{vmatrix}$$

$$\boxed{\begin{array}{l} [f(\vec{r}) + F(\vec{r})]\psi_{i\sigma}(\vec{r}) = \varepsilon_i \psi_{i\sigma}(\vec{r}) \\ \text{with } \psi_{i\sigma}(\vec{r}) = \psi_{i\downarrow}(\vec{r}) \text{ or } \psi_{i\uparrow}(\vec{r}) \\ \varepsilon_i: \text{ doubly degenerate, with one} \\ \text{eigenfunction each for spin } \uparrow \& \downarrow \end{array}}$$

Redesignation of the one-particle wavefunctions

as $\psi_1, \psi_2, \psi_3, ..., \psi_{N-1}, \psi_N$

which constitute the elements of the Slater determinant

$$\Phi^{(N)} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(1) & .. & .. & .. & \psi_1(N) \\ \psi_2(1) & .. & .. & .. & \psi_2(N) \\ .. & .. & .. & \langle j|i\rangle = \psi_i(q_j) & .. \\ \psi_{N-1}(1) & .. & .. & .. & \psi_{N-1}(N) \\ \psi_N(1) & .. & .. & .. & \psi_N(N) \end{vmatrix}$$

$$\Phi^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & .. & .. & .. & \psi_1(N) \\ \psi_2(1) & .. & .. & .. & \psi_2(N) \\ .. & .. & .. & \langle j|i\rangle = \psi_i(q_j) & .. \\ \psi_{N-1}(1) & .. & .. & .. & \psi_{N-1}(N) \\ \psi_N(1) & .. & .. & .. & \psi_N(N) \end{vmatrix}$$

$$\boxed{\begin{aligned} &H^{(N)}(q_1,..,q_N) = \\ &= \sum_{i=1}^{N} f(\vec{r}_i) + \sum_{i=1}^{N} F(\vec{r}_i) \\ &+ \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) - \sum_{i=1}^{N} F(\vec{r}_i) \end{aligned}}$$

$$\boxed{[f(\vec{r}) + F(\vec{r})]\psi_{i\sigma}(\vec{r}) = \varepsilon_i \psi_{i\sigma}(\vec{r})}$$

i=1,2,3,……, N

ε_i: Lowest N/2 eigenvalues

ε_i : doubly degenerate, with one eigenfunction each for spin $\uparrow$ & $\downarrow$

Wave functions of the EXCITED unperturbed states are also Nth order determinants, made up eigenfunctions of

$$[f(\vec{r}) + F(\vec{r})]\psi_{i\sigma}(\vec{r}) = \varepsilon_i \psi_{i\sigma}(\vec{r})$$

but with

one or more $\varepsilon_i > \varepsilon_{N/2}$

$$H^{(N)}(q_1,q_2,..,q_N)=\underbrace{\sum_{i=1}^{N} f(\vec{r}_i)+\sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified one-electron operator would contain much/most of the effect of the two-electron terms.}}+\underbrace{\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N} F(\vec{r}_i)}_{\text{Modified, residual, interaction between pairs of electrons.}}$$

$$\boxed{-\frac{1}{2}\nabla_i^{\,2}-\frac{Z}{r_i}=f(\vec{r}_i)}$$

$$\mathrm{H}_1=\sum_{i=1}^{N} f(\vec{r}_i)\ =f$$

$$F=\sum_{i=1}^{N} F(\vec{r}_i)$$

This term would be weak, and would be treated perturbatively.

Choice of the operator F is to be made such that the total energy is minimised.

It turns out,

as will be shown presently,

that this happens when: $\langle q|F|p\rangle=\sum_{i=1}^{N}\left[\langle iq|\mathrm{v}|ip\rangle-\langle qi|\mathrm{v}|ip\rangle\right]$

$$H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N}f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)$$

$$\boxed{-\frac{1}{2}\nabla_i^2-\frac{Z}{r_i}=f(\vec{r}_i)}$$

Choice of the operator F is to be so made that the total energy is minimised.

It turns out that this happens when:

$$\langle q|F|p\rangle=\sum_{i=1}^{N}\Big[\overbrace{\langle iq|\mathrm{v}|ip\rangle}^{\text{coulomb}}-\overbrace{\langle qi|\mathrm{v}|ip\rangle}^{\text{exchange}}\Big]$$

Remember the two centre COULOMB & EXCHANGE integrals:

$$\langle ij|\mathrm{v}|kl\rangle=\int dq_1\int dq_2\psi_i^*(q_1)\psi_j^*(q_2)\mathrm{v}(q_1,q_2)\psi_k(q_1)\psi_l(q_2)$$

$$\langle iq|\mathrm{v}|ip\rangle=\int dq_1\int dq_2\psi_i^*(q_1)\psi_q^*(q_2)\mathrm{v}(q_1,q_2)\underbrace{\psi_i(q_1)\psi_p(q_2)}_{\text{same}}$$

$$\langle qi|\mathrm{v}|ip\rangle=\int dq_1\int dq_2\psi_q^*(q_1)\psi_i^*(q_2)\mathrm{v}(q_1,q_2)\overbrace{\psi_i(q_1)\psi_p(q_2)}^{\text{same}}$$

Let the ground state unperturbed wave function described above be:

$$\Phi_0^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & .. & .. & .. & \psi_1(N) \\ .. & .. & .. & .. & .. \\ \psi_p(1) & .. & .. & .. & \psi_p(1) \\ .. & .. & .. & .. & .. \\ \psi_N(1) & .. & .. & .. & \psi_N(N) \end{vmatrix}$$

All other single-electron orbitals are the same in

Let an excited state wave function, in which only a single electron from the above state is excited, be:

$$\Phi_q^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & .. & .. & .. & \psi_1(N) \\ .. & .. & .. & .. & .. \\ \psi_q(1) & .. & .. & .. & \psi_q(1) \\ .. & .. & .. & .. & .. \\ \psi_N(1) & .. & .. & .. & \psi_N(N) \end{vmatrix}$$

In the ordered set of the

single *particle states* : $p \le N$ & $q > N$

$$H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^{\,2}-\frac{Z}{r_i}\right)+\sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$=\sum_{i=1}^{N}h_0(q_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} \qquad =H_1+H_2$$

Same Slater determinant

$$\langle\Phi^{(N)}\,|\,H_1|\,\Phi^{(N)}\rangle=\sum_{i=1}^{N}\langle\alpha_i\,|\,f\,|\,\alpha_i\rangle=\sum_{i=1}^{N}\langle i\,|\,f\,|\,i\rangle$$

$$\langle\Phi^{(N)}\,|\,H_2|\,\Phi^{(N)}\rangle=\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij\,|\,\mathrm{v}\,|\,ij\rangle-\langle ij\,|\,\mathrm{v}\,|\,ji\rangle\right]$$

$$\langle\Phi^{(N)}\,|\,H\,|\,\Phi^{(N)}\rangle=\sum_{i=1}^{N}\langle i\,|\,f\,|\,i\rangle+$$

$$+\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij\,|\,\mathrm{v}\,|\,ij\rangle-\langle ij\,|\,\mathrm{v}\,|\,ji\rangle\right]$$

$$H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N} f(\vec{r}_i)+\sum_{i=1}^{N} F(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N} F(\vec{r}_i)$$

$$H^{(N)}_{approx}(q_1,q_2,..,q_N)=\boxed{\sum_{i=1}^{N} f(\vec{r}_i)+\sum_{i=1}^{N} F(\vec{r}_i)=f+F}$$

Note the NOTATION!

$$\Phi_0^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_p(1) & .. & .. & .. & \psi_p(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}=\Phi_p^{(N)}$$

$$\Phi_q^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_q(1) & .. & .. & .. & \psi_q(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

Using same techniques discussed in STiAP Unit 4 L21

Reference→ http://www.nptel.ac.in/downloads/115106057/

we can find

$$\boxed{\left\langle\Phi_q^{(N)}\left|H^{(N)}_{approx}(q_1,q_2,..,q_N)\right|\Phi_p^{(N)}\right\rangle=\left\langle\Phi_q^{(N)}\left|f+F\right|\Phi_p^{(N)}\right\rangle=?}$$

slide 14: $\left[f(\vec{r})+F(\vec{r})\right]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})$ $\Rightarrow$

i.e. $\left[f(\vec{r})+F(\vec{r})\right]$ is diagonal in $\{\psi_{i\sigma}(\vec{r})\}$

$$\left\langle\Phi_q^{(N)}\left|f+F\right|\Phi_p^{(N)}\right\rangle=0$$

$$H^{(N)}_{approx}(q_1,q_2,..,q_N)=\sum_{i=1}^{N} f(\vec{r}_i)\ +\sum_{i=1}^{N} F(\vec{r}_i)= f+F$$ $\leftarrow$ operators in

SINGLE COORDINATES

$$\Phi_p^{(N)}=\Phi_0^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_p(1) & .. & .. & .. & \psi_p(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

$$\Phi_q^{(N)}=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(1) & .. & .. & .. & \psi_1(N)\\ .. & .. & .. & .. & ..\\ \psi_q(1) & .. & .. & .. & \psi_q(1)\\ .. & .. & .. & .. & ..\\ \psi_N(1) & .. & .. & .. & \psi_N(N)\end{vmatrix}$$

$$\boxed{\left\langle \Phi_q^{(N)} \middle| H^{(N)}_{approx}(q_1,q_2,..,q_N) \middle| \Phi_p^{(N)} \right\rangle = \left\langle \Phi_q^{(N)} \middle| f+F \middle| \Phi_p^{(N)} \right\rangle = 0}$$

$f+F:$ diagonal with respect to one-electron functions and $q\neq p$

But, $$H^{(N)}(q_1,q_2,..,q_N)=H^{(N)}_{approx}(q_1,q_2,..,q_N)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)$$

of which the first term gives $\left\langle \Phi_q^{(N)} \middle| H^{(N)}_{approx} \middle| \Phi_p^{(N)} \right\rangle = \left\langle \Phi_q^{(N)} \middle| f+F \middle| \Phi_p^{(N)} \right\rangle = 0$

$$H^{(N)}(q_1,q_2,..,q_N) = H^{(N)}_{approx}(q_1,q_2,..,q_N) + \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) - \sum_{i=1}^{N} F(\vec{r}_i)$$

of which the first term gives $\left\langle \Phi_q^{(N)} \middle| H^{(N)}_{approx} \middle| \Phi_p^{(N)} \right\rangle = 0$

Matrix elements of the above two terms would cancel; equal & opposite signs…

Hence, if we choose F such that

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \left\langle \Phi_q^{(N)} \middle| \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) \middle| \Phi_p^{(N)} \right\rangle$$

then we shall get $\left\langle \Phi_q^{(N)} \middle| H^{N} \middle| \Phi_p^{(N)} \right\rangle = 0$

THUS, choose F such that

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \left\langle \Phi_q^{(N)} \middle| \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) \middle| \Phi_p^{(N)} \right\rangle$$

$$= \sum_{i=1}^{N}\Big[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle\Big]$$

in order *to* get

$$\left\langle \Phi_q^{(N)} \middle| H^{N} \middle| \Phi_p^{(N)} \right\rangle = 0$$

Having shown now that the choice F which gives

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \left\langle \Phi_q^{(N)} \middle| \frac{1}{2} \sum_{i=1;i\neq j}^{N} \sum_{j=1}^{N} \mathrm{v}(\vec{r}_i, \vec{r}_j) \middle| \Phi_p^{(N)} \right\rangle$$

$$= \sum_{i=1}^{N} \left[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle \right]$$

gives us :

$$\left\langle \Phi_q^{(N)} \middle| H^N \middle| \Phi_p^{(N)} \right\rangle = 0 \,,$$

we now show that the above choice of F concurrently gives the best single determinantal ground state wave function according to the variation principle (Hartree-Fock SCF approximation)

$$NOTE: \left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \int d^3\vec{r}\, \psi_q^*(\vec{r}) F(\vec{r}) \psi_p^*(\vec{r})$$

Let us ask: If $\Phi_0^{(N)} = \Phi_p^{(N)}$ were not the correct ground state wavefunction ,

could any other wave function be the ground state?

The most general form in which just one of the constituent spin orbital is different would be

$$\psi = \left[\Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \right],$$

apart from an overall normalization.....

For this wavefunction, the energy functional is:

$$E(\varepsilon) = \frac{\left\langle \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \middle| H \middle| \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \right\rangle}{\left\langle \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \middle| \Phi_0^{(N)} + \varepsilon \Phi_q^{(N)} \right\rangle}$$

$$E(\varepsilon)=\frac{\left\langle \Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\right\rangle}{\left\langle \Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\middle|\Phi_0^{(N)}+\varepsilon\Phi_q^{(N)}\right\rangle}$$

$$=\frac{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\varepsilon\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle}{\left\langle \Phi_0^{(N)}\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\langle \Phi_q^{(N)}\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\langle \Phi_0^{(N)}\middle|\Phi_q^{(N)}\right\rangle+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|\Phi_q^{(N)}\right\rangle}$$

orthogonal

$$=\frac{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle}{\left\langle \Phi_0^{(N)}\middle|\Phi_0^{(N)}\right\rangle+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|\Phi_q^{(N)}\right\rangle}$$

$$=\frac{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle+\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle}{1+\varepsilon^2}$$

$$E(\varepsilon) =$$

$$= \frac{\left\langle \Phi_0^{(N)} \middle| H \middle| \Phi_0^{(N)} \right\rangle + \varepsilon \left\{ \left\langle \Phi_0^{(N)} \middle| H \middle| \Phi_q^{(N)} \right\rangle + \left\langle \Phi_q^{(N)} \middle| H \middle| \Phi_0^{(N)} \right\rangle \right\} + \varepsilon^2 \left\langle \Phi_q^{(N)} \middle| H \middle| \Phi_q^{(N)} \right\rangle}{1+\varepsilon^2}$$

differentiating with respect to ε

$$\frac{d}{d\varepsilon} E(\varepsilon) =$$

$$= \frac{\frac{d}{d\varepsilon}\left[\left\langle \Phi_0^{(N)} \middle| H \middle| \Phi_0^{(N)} \right\rangle + \varepsilon \left\{ \left\langle \Phi_0^{(N)} \middle| H \middle| \Phi_q^{(N)} \right\rangle + \left\langle \Phi_q^{(N)} \middle| H \middle| \Phi_0^{(N)} \right\rangle \right\} + \varepsilon^2 \left\langle \Phi_q^{(N)} \middle| H \middle| \Phi_q^{(N)} \right\rangle \right]}{1+\varepsilon^2}$$

$$+ \left[\left\langle \Phi_0^{(N)} \middle| H \middle| \Phi_0^{(N)} \right\rangle + \varepsilon \left\{ \left\langle \Phi_0^{(N)} \middle| H \middle| \Phi_q^{(N)} \right\rangle + \left\langle \Phi_q^{(N)} \middle| H \middle| \Phi_0^{(N)} \right\rangle \right\} + \varepsilon^2 \left\langle \Phi_q^{(N)} \middle| H \middle| \Phi_q^{(N)} \right\rangle \right] \frac{d}{d\varepsilon}\left(1+\varepsilon^2\right)^{-1}$$

$$\frac{d}{d\varepsilon}E(\varepsilon)=$$

$$=\frac{\left[\left\{\left\langle\Phi_0^{(N)}\left|H\right|\Phi_q^{(N)}\right\rangle+\left\langle\Phi_q^{(N)}\left|H\right|\Phi_0^{(N)}\right\rangle\right\}+2\varepsilon\left\langle\Phi_q^{(N)}\left|H\right|\Phi_q^{(N)}\right\rangle\right]}{1+\varepsilon^2}$$

$$+\left[\left\langle\Phi_0^{(N)}\left|H\right|\Phi_0^{(N)}\right\rangle+\varepsilon\left\{\left\langle\Phi_0^{(N)}\left|H\right|\Phi_q^{(N)}\right\rangle+\left\langle\Phi_q^{(N)}\left|H\right|\Phi_0^{(N)}\right\rangle\right\}+\varepsilon^2\left\langle\Phi_q^{(N)}\left|H\right|\Phi_q^{(N)}\right\rangle\right]\frac{d}{d\varepsilon}\left(1+\varepsilon^2\right)^{-1}$$

$$\frac{d}{d\varepsilon}\left(1+\varepsilon^2\right)^{-1}=-1\left(1+\varepsilon^2\right)^{-2}\times 2\varepsilon=-\frac{2\varepsilon}{\left(1+\varepsilon^2\right)^2}=-\frac{2\varepsilon}{\left(1+2\varepsilon^2+\varepsilon^4\right)},$$

which goes to zero as $\varepsilon\rightarrow 0$

$$\left[\frac{d}{d\varepsilon}E(\varepsilon)\right]_{\varepsilon\rightarrow 0}=\frac{\left[\left\{\left\langle\Phi_0^{(N)}\left|H\right|\Phi_q^{(N)}\right\rangle+\left\langle\Phi_q^{(N)}\left|H\right|\Phi_0^{(N)}\right\rangle\right\}\right]}{1}$$

$$\left[\frac{d}{d\varepsilon}E(\varepsilon)\right]_{\varepsilon\to 0} = \frac{\left[\left\{\left\langle \Phi_0^{(N)}\middle|H\middle|\Phi_q^{(N)}\right\rangle + \left\langle \Phi_q^{(N)}\middle|H\middle|\Phi_0^{(N)}\right\rangle\right\}\right]}{1}$$

But we had seen that the choice F which gives

$$\Phi_0^{(N)} = \frac{1}{\sqrt{N!}}|\ |_{SD} = \Phi_p^{(N)}$$

$$\left\langle \Phi_q^{(N)}\middle|F\middle|\Phi_p^{(N)}\right\rangle = \left\langle \Phi_q^{(N)}\middle|\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)\middle|\Phi_p^{(N)}\right\rangle$$

$$= \sum_{i=1}^{N}\left[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle\right]$$

gave us :

$$\left\langle \Phi_q^{(N)}\middle|H^N\middle|\Phi_p^{(N)}\right\rangle = 0$$

$$\Rightarrow \quad \left[\frac{d}{d\varepsilon}E(\varepsilon)\right]_{\varepsilon\to 0} = 0$$

we get the best single determinantal ground state wave function according to the variation principle

$E(\varepsilon)$: extremum ... minimum

Thus, the choice F which gives

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_0^{(N)} \right\rangle = \left\langle \Phi_q^{(N)} \middle| \frac{1}{2} \sum_{i=1;i\neq j}^{N} \sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) \middle| \Phi_0^{(N)} \right\rangle$$

$$= \sum_{i=1}^{N} \left[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle \right]$$

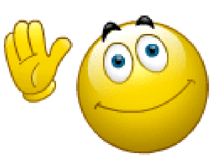
gives us:

$$\left\langle \Phi_q^{(N)} \middle| H^N \middle| \Phi_0^{(N)} \right\rangle = 0$$

and it gives the best single determinantal ground state wave function according to the variation principle

since $\varepsilon \to 0$ MINIMISES the variational energy functional:

$$E(\varepsilon) = \frac{\left\langle \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \middle| H \middle| \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \right\rangle}{\left\langle \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \middle| \Phi_0^{(N)} + \varepsilon\Phi_q^{(N)} \right\rangle}$$



Hartree-Fock approximation.

Questions: pcd@physics.iitm.ac.ic

Select/Special Topics from 'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 17

Electron Gas in Hartree Fock and Random Phase Approximations

HF SCF for Free Electron Gas

$$H^{(N)}(q_1,q_2,..,q_N) = \sum_{i=1}^{N} f(\vec{r}_i) + \sum_{i=1}^{N} F(\vec{r}_i) + \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N} \mathrm{v}(\vec{r}_i,\vec{r}_j) - \sum_{i=1}^{N} F(\vec{r}_i)$$

$$H_{approx}^{(N)}(q_1,q_2,..,q_N) = \sum_{i=1}^{N} f(\vec{r}_i) + \sum_{i=1}^{N} F(\vec{r}_i) = f + F$$

$$\Phi_0^{(N)} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(1) & .. & .. & .. & \psi_1(N) \\ .. & .. & .. & .. & .. \\ \psi_p(1) & .. & .. & .. & \psi_p(1) \\ .. & .. & .. & .. & .. \\ \psi_N(1) & .. & .. & .. & \psi_N(N) \end{vmatrix} = \Phi_p^{(N)}$$

$$\Phi_q^{(N)} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(1) & .. & .. & .. & \psi_1(N) \\ .. & .. & .. & .. & .. \\ \psi_q(1) & .. & .. & .. & \psi_q(1) \\ .. & .. & .. & .. & .. \\ \psi_N(1) & .. & .. & .. & \psi_N(N) \end{vmatrix}$$

NOTE

The variational function we considered is: $\psi = \left[\Phi_0^{(N)} + \varepsilon\Phi_q^{(N)}\right]$

… Variation considered is in just one orbital

All other orbitals FROZEN

Hartree Fock: **FROZEN ORBITAL APPROXIMATION**

Spin / statistical / Fermi correlations included

Coulomb correlations ignored

STiAP Unit 4 L21 Reference→ http://www.nptel.ac.in/downloads/115106057/

SCF: self consistent field

Recall!

Hartree Fock Self Consistent Field Equation:

Special/Select Topic in Atomic Physics

STiAP Unit 4

Reference→

http://www.nptel.ac.in/downloads/115106057

Specifically, the HF SCF equation as it appears on slide number 104

$$f(\vec{r}_1)u_i(\vec{r}_1)+$$

$$\sum_j\left[\int dV_2\,\frac{u^*{}_j(\vec{r}_2)}{r_{12}}\Big(u_i(\vec{r}_1)u_j(\vec{r}_2)-\delta(m_{s_i},m_{s_j})u_i(\vec{r}_2)u_j(\vec{r}_1)\Big)\right]$$

$$=\varepsilon_i\,u_i\left(\vec{r}_1\right)$$

$$f(\vec{r}_1)u_i(\vec{r}_1)+$$

$$\sum_j\left[\int dV_2\,\frac{u^*_j(\vec{r}_2)}{r_{12}}\left(u_i(\vec{r}_1)u_j(\vec{r}_2)-\delta(m_{s_i},m_{s_j})u_i(\vec{r}_2)u_j(\vec{r}_1)\right)\right]$$

$$=\varepsilon_i\;u_i\left(\vec{r}_1\right)$$

Change of notation slightly:

$$H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2-\frac{Ze^2}{r_i}\right)+\sum_{i<j=1}^{N}\frac{e^2}{r_{ij}}$$

$$=\sum_{i=1}^{N}f(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{e^2}{r_{ij}}\quad=H_1+H_2$$

$$i\rightarrow p;\; j\rightarrow i;\; u(\vec{r})\rightarrow\psi(\vec{r})$$

$$\vec{r}_1\rightarrow\vec{r};\;\;\vec{r}_2\rightarrow\vec{r}\,'$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right)\psi_p(\vec{r})+$$

Notation changed only to bring it closer to that in Raimes: 'Many Electron Theory' (1972; North Holland)

$$\sum_{i=1}^{N}\left[\int dV'\,\frac{\psi_i^*(\vec{r}\,')e^2}{|\vec{r}-\vec{r}\,'|}\left(\psi_p(\vec{r})\psi_i(\vec{r}\,')-\delta(m_{s_p},m_{s_i})\psi_p(\vec{r}\,')\psi_i(\vec{r})\right)\right]$$

$$=\varepsilon_p\;\psi_p\left(\vec{r}\right)$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right)\psi_p(\vec{r})+\sum_{i=1}^{N}\left[\int dV'\frac{\psi_i^*(\vec{r}')e^2}{|\vec{r}-\vec{r}'|}\Big(\psi_p(\vec{r})\psi_i(\vec{r}')-\delta(m_{s_p},m_{s_i})\psi_p(\vec{r}')\psi_i(\vec{r})\Big)\right]$$

$$=\varepsilon_p\ \psi_p\left(\vec{r}\right)$$

Writing the terms in the bracket separately:

coulomb

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right)\psi_p(\xi)+\sum_{i=1}^{N}\left[\int d^4V'\frac{\psi_i^*(\xi')\psi_i(\xi')\psi_p(\xi)e^2}{|\vec{r}-\vec{r}'|}\right]$$

Includes sum over discrete spin variable

$$-\sum_{i=1}^{N}\delta(m_{s_p},m_{s_i})\left[\int d^4V'\frac{\psi_i^*(\xi')\Big(\psi_p(\xi')\psi_i(\xi)\Big)e^2}{|\vec{r}-\vec{r}'|}\right]=\varepsilon_p\ \psi_p\left(\xi\right)$$

exchange

Non-ferromagnetic systems: equal number of $\uparrow$ & $\downarrow$

ε_i : doubly degenerate; one eigenfunction each for spin $\uparrow$ & $\downarrow$

Ground state Slater determinant contains the set of one-electron orbitals:

$$\psi_1, \psi_2, \psi_3, \ldots\ldots, \psi_{N-1}, \psi_N \equiv \psi_{1\uparrow}, \psi_{1\downarrow}, \psi_{2\uparrow}, \psi_{2\downarrow}, \ldots\ldots, \psi_{\frac{N}{2}\uparrow}, \psi_{\frac{N}{2}\downarrow}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right)\psi_p(\xi)+\sum_{i=1}^{N}\left[\int d^4V'\frac{\psi_i^*(\xi')\psi_i(\xi')\boxed{\psi_p(\xi)}e^2}{|\vec{r}-\vec{r}'|}\right]$$

$$-\sum_{i=1}^{N}\delta(m_{s_p},m_{s_i})\left[\int d^4V'\frac{\psi_i^*(\xi')\left(\psi_p(\xi\boxed{')\psi_i(\xi)}\right)e^2}{|\vec{r}-\vec{r}'|}\right] = \varepsilon_p\ \psi_p(\xi)$$

Carrying out the discrete sum over the spin variables:

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right)\psi_p(\vec{r})+2\sum_{i=1}^{N/2}\left[\int dV'\frac{\psi_i^*(\vec{r}')\psi_i(\vec{r}')e^2}{|\vec{r}-\vec{r}'|}\right]\boxed{\psi_p(\vec{r})}$$

$$-\sum_{i=1}^{N/2}\left[\int dV'\frac{\psi_i^*(\vec{r}')\psi_p(\vec{r}')e^2}{|\vec{r}-\vec{r}'|}\right]\boxed{\psi_i(\vec{r})} = \varepsilon_p\ \psi_p\left(\vec{r}\right)$$

Hartree-Fock one electron Self consistent field equation.

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right)\psi_p(\vec{r})+2\sum_{i=1}^{N/2}\left[\int dV'\frac{\psi_i^*(\vec{r}\,')\psi_i(\vec{r}\,')e^2}{|\vec{r}-\vec{r}\,'|}\right]\psi_p(\vec{r})$$

$$-\sum_{i=1}^{N/2}\left[\int dV'\frac{\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')e^2}{|\vec{r}-\vec{r}\,'|}\right]\psi_i(\vec{r}) = \varepsilon_p\ \psi_p\left(\vec{r}\right)$$

$$\frac{e^2}{|\vec{r}-\vec{r}\,'|}=\mathrm{v}(\vec{r},\vec{r}\,')\rightarrow Coulomb\ \text{interaction}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2-\frac{Ze^2}{r}\right)\psi_p(\vec{r})+2\sum_{i=1}^{N/2}\left[\int dV'\left|\psi_i(\vec{r}\,')\right|^2\mathrm{v}(\vec{r},\vec{r}\,')\right]\psi_p(\vec{r})$$

coulomb

$$-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')\mathrm{v}(\vec{r},\vec{r}\,')\right] = \varepsilon_p\ \psi_p\left(\vec{r}\right)$$

exchange

Raimes / Many Electron Theory
/ Eq.3.23; page 53

Recall that IF $H = H_0 + H'$

$$= \sum_{i=1}^{N} f(q_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ \boxed{i \neq j}}}^{N} \mathrm{v}(q_i, q_j)$$

$$f(q_i) = \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right)$$

Many-Electron Hamiltonian *in the notation of* **FIRST QUANTIZATION**

THEN

$$H = \sum_i \sum_j c_i^\dagger \langle i | f | j \rangle c_j + \frac{1}{2} \sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij | \mathrm{v} | kl \rangle c_l c_k$$

Many-Electron Hamiltonian *in the notation of* **SECOND QUANTIZATION**

$$\langle ij | \mathrm{v} | kl \rangle = \int dq_1 \int dq_2 \psi_i^*(q_1) \psi_j^*(q_2) \mathrm{v}(q_1, q_2) \psi_k(q_1) \psi_l(q_2)$$

IF $H=\sum_{i=1}^{N} f(q_i)+\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ \boxed{i\neq j}}}^{N} \mathrm{v}(q_i,q_j)$ I Q

THEN

$$H=\sum_i\sum_j c_i^\dagger \langle i|f|j\rangle c_j+\frac{1}{2}\sum_i\sum_j\sum_k\sum_l c_i^\dagger c_j^\dagger \langle ij|\mathrm{v}|kl\rangle c_l c_k$$ II Q

Hence, IF

$$H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N} f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)$$ I Q

THEN

$$H=\sum_i\sum_j c_i^\dagger \langle i|f+F|j\rangle c_j$$

$$+\frac{1}{2}\sum_i\sum_j\sum_k\sum_l c_i^\dagger c_j^\dagger \langle ij|\mathrm{v}|kl\rangle c_l c_k-\sum_i\sum_j c_i^\dagger \langle i|F|j\rangle c_j$$ II Q

Raimes / Many Electron Theory / Eq.3.27; page 55

$$\Phi_q^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & .. & .. & .. & \psi_1(N) \\ .. & .. & .. & .. & .. \\ \psi_q(1) & .. & .. & .. & \psi_q(1) \\ .. & .. & .. & .. & .. \\ \psi_N(1) & .. & .. & .. & \psi_N(N) \end{vmatrix}$$

$$\left(f+F\right)\phi_j(q)=\varepsilon_j\phi_j(q)$$

Eigenfunctions of the single particle operator

$$\langle i|\left(f+F\right)|j\rangle=\varepsilon_j\langle i|j\rangle=\varepsilon_j\delta_{ij}$$

$$H=\sum_{i=1}^{N} f(q_i)+\frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ \boxed{i\neq j}}}^{N} \mathrm{v}(q_i,q_j)$$

$$H^{(N)}(q_1,q_2,..,q_N)=\sum_{i=1}^{N} f(\vec{r}_i)+\sum_{i=1}^{N}F(\vec{r}_i)+\frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\mathrm{v}(\vec{r}_i,\vec{r}_j)-\sum_{i=1}^{N}F(\vec{r}_i)$$

From slide # 24, U3L17:

$$\left\langle\Phi_q^{(N)}\left|F\right|\Phi_0^{(N)}\right\rangle=\left\langle\Phi_q^{(N)}\left|F\right|\Phi_p^{(N)}\right\rangle=\sum_{i=1}^{N}\left[\langle iq|\mathrm{v}|ip\rangle-\langle qi|\mathrm{v}|ip\rangle\right]$$

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \sum_{i=1}^{N} \left[\langle iq|\mathrm{v}|ip\rangle - \langle qi|\mathrm{v}|ip\rangle \right]$$

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \sum_{i=1}^{N} \iint d^4\xi_1\, d^4\xi_2\;\; \psi_i^*(\xi_1)\psi_q^*(\xi_2)\,\mathrm{v}(\vec{r}_1,\vec{r}_2)\,\psi_i(\xi_1)\psi_p(\xi_2)$$

$$-\sum_{i=1}^{N} \iint d^4\xi_1\, d^4\xi_2\;\; \psi_q^*(\xi_1)\psi_i^*(\xi_2)\,\mathrm{v}(\vec{r}_1,\vec{r}_2)\,\psi_i(\xi_1)\psi_p(\xi_2)$$

$$\boxed{\begin{aligned} \left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = & \sum_{i=1}^{N} \int d^4\xi_2 \psi_q^*(\xi_2) \left[\int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1,\vec{r}_2) \right] \psi_p(\xi_2) \\ & - \sum_{i=1}^{N} \int d^4\xi_1 \psi_q^*(\xi_1) \left[\int d^4\xi_2 \psi_i^*(\xi_2)\, \mathrm{v}(\vec{r}_1,\vec{r}_2)\; \psi_p(\xi_2) \right] \psi_i(\xi_1) \end{aligned}}$$

interchanging $\xi_1 \rightleftharpoons \xi_2$ in the second (exchange) term:

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \sum_{i=1}^{N} \int d^4\xi_2 \psi_q^*(\xi_2) \left[\int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1,\vec{r}_2) \right] \psi_p(\xi_2)$$

$$-\sum_{i=1}^{N} \int d^4\xi_2 \psi_q^*(\xi_2) \left[\int d^4\xi_1 \psi_i^*(\xi_1)\,\mathrm{v}(\vec{r}_1,\vec{r}_2)\,\psi_p(\xi_1) \right] \psi_i(\xi_2)$$

$$\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \sum_{i=1}^{N} \int d^4\xi_2 \psi_q^*(\xi_2) \left[\int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1, \vec{r}_2) \right] \psi_p(\xi_2)$$

$$- \sum_{i=1}^{N} \int d^4\xi_2 \psi_q^*(\xi_2) \left[\int d^4\xi_1 \psi_i^*(\xi_1) \mathrm{v}(\vec{r}_1, \vec{r}_2) \psi_p(\xi_1) \right] \psi_i(\xi_2)$$

$$\boxed{\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \sum_{i=1}^{N} \int d^4\xi_2 \psi_q^*(\xi_2) \left\{ \begin{array}{l} \left[\int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1, \vec{r}_2) \psi_p(\xi_2) \right] \\ - \left[\int d^4\xi_1 \psi_i^*(\xi_1) \mathrm{v}(\vec{r}_1, \vec{r}_2) \psi_p(\xi_1) \psi_i(\xi_2) \right] \end{array} \right\}}$$

$$\boxed{\left\langle \Phi_q^{(N)} \middle| F \middle| \Phi_p^{(N)} \right\rangle = \int d^4\xi_2 \psi_q^*(\xi_2) \sum_{i=1}^{N} \left\{ \begin{array}{l} \left[\int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1, \vec{r}_2) \psi_p(\xi_2) \right] \\ - \left[\int d^4\xi_1 \psi_i^*(\xi_1) \mathrm{v}(\vec{r}_1, \vec{r}_2) \psi_p(\xi_1) \psi_i(\xi_2) \right] \end{array} \right\}}$$

$$\boxed{\Rightarrow \quad F\psi_p(\xi_2) = \sum_{i=1}^{N} \left\{ \begin{array}{l} \left[\int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1, \vec{r}_2) \psi_p(\xi_2) \right] \\ - \left[\int d^4\xi_1 \psi_i^*(\xi_1) \mathrm{v}(\vec{r}_1, \vec{r}_2) \psi_p(\xi_1) \psi_i(\xi_2) \right] \end{array} \right\}}$$

Raimes / Many Electron Theory / Eq.3.19; page 52

$$\Rightarrow \quad F\psi_p(\xi_2) = \sum_{i=1}^{N} \left\{ \begin{array}{l} \left[\int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\xi_2) \right] \\ -\left[\int d^4\xi_1 \psi_i^*(\xi_1)\mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\xi_1)\psi_i(\xi_2) \right] \end{array} \right\}$$

$$\Rightarrow$$

$$F\psi_p(\xi_2) = \sum_{i=1}^{N} \int d^4\xi_1 \left|\psi_i(\xi_1)\right|^2 \mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\xi_2) - \sum_{i=1}^{N} \int d^4\xi_1 \psi_i^*(\xi_1)\mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\xi_1)\psi_i(\xi_2)$$

carrying out the summation over the discrete spin variable:

$$F\psi_p(\vec{r}_2) = 2\sum_{i=1}^{N/2} \int d^3\vec{r}_1 \left|\psi_i(\vec{r}_1)\right|^2 \mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\vec{r}_2) - \sum_{i=1}^{N/2} \int d^3\vec{r}_1 \psi_i^*(\vec{r}_1)\mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\vec{r}_1)\psi_i(\vec{r}_2)$$

carrying out the summation over the discrete spin variable:

$$\boxed{F\psi_p(\vec{r}_2)} = 2\sum_{i=1}^{N/2} \int d^3\vec{r}_1 \left|\psi_i(\vec{r}_1)\right|^2 \mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\vec{r}_2)$$

$$-\sum_{i=1}^{N/2} \int d^3\vec{r}_1 \psi_i^*(\vec{r}_1)\mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_p(\vec{r}_1)\psi_i(\vec{r}_2)$$

$$\vec{r}_1 \rightarrow \vec{r}\,'$$

$$\vec{r}_2 \rightarrow \vec{r}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\psi_p(\vec{r}) + 2\sum_{i=1}^{N/2}\left[\int dV'\frac{\psi_i^*(\vec{r}\,')\psi_i(\vec{r}\,')e^2}{|\vec{r}-\vec{r}\,'|}\right]\psi_p(\vec{r})$$

$$-\sum_{i=1}^{N/2}\left[\int dV'\frac{\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')e^2}{|\vec{r}-\vec{r}\,'|}\right]\psi_i(\vec{r}) = \varepsilon_p\ \psi_p(\vec{r})$$

HF-SCF Eq.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\psi_p(\vec{r}) + \boxed{F\psi_p(\vec{r})} = [f+F]\psi_p(\vec{r}) = \varepsilon_p\ \psi_p(\vec{r})$$

Raimes / Many Electron Theory / Eq.3.23; page 53

Recall, from Special/Select Topics in Atomic Physics,

STiAP: Unit 4, Lecture 23, Slide 111

Hartree-Fock Self-Consistent Field formalism

Reference→ http://www.nptel.ac.in/downloads/115106057

$$E(N)=\langle\psi^{(N)}\,|\,H\,|\,\psi^{(N)}\rangle$$

$$=\sum_{i=1}^{N}\varepsilon_i-\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij\,|\,\mathrm{v}\,|\,ij\rangle-\langle ij\,|\,\mathrm{v}\,|\,ji\rangle\right]$$

Raimes, Eq.3.35

slide 14: $\left[f(\vec{r})+F(\vec{r})\right]\psi_{i\sigma}(\vec{r})=\varepsilon_i\psi_{i\sigma}(\vec{r})$

i.e. $\left[f(\vec{r})+F(\vec{r})\right]$ is diagonal in $\left\{\psi_{i\sigma}(\vec{r})\right\}$

$\Rightarrow\langle i|f+F|i\rangle=\varepsilon_i=\langle i|f|i\rangle+\langle i|F|i\rangle$

$$E(N)=\sum_{i=1}^{N}\left[\langle i|f|i\rangle+\langle i|F|i\rangle\right]-\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij\,|\,\mathrm{v}\,|\,ij\rangle-\langle ij\,|\,\mathrm{v}\,|\,ji\rangle\right]$$

Raimes, Eq.3.36

$$E(N) = \sum_{i=1}^{N} \left[\langle i|f|i\rangle + \langle i|F|i\rangle \right] - \boxed{\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij\,|\,\mathrm{v}\,|\,ij\rangle - \langle ij\,|\,\mathrm{v}\,|\,ji\rangle\right]}$$

$$\boxed{\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij\,|\,\mathrm{v}\,|\,ij\rangle - \langle ij\,|\,\mathrm{v}\,|\,ji\rangle\right]} = \boxed{-E(N) + \sum_{i=1}^{N} \left[\langle i|f|i\rangle + \langle i|F|i\rangle \right]}$$

Also,

$$\langle \Phi^{(N)}\,|\,H\,|\,\Phi^{(N)}\rangle = E(N) = \sum_{i=1}^{N}\langle i\,|\,f\,|\,i\rangle + \boxed{\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\left[\langle ij\,|\,\mathrm{v}\,|\,ij\rangle - \langle ij\,|\,\mathrm{v}\,|\,ji\rangle\right]}$$

$\Rightarrow$

$$E(N) = \sum_{i=1}^{N}\langle i\,|\,f\,|\,i\rangle \boxed{- E(N) + \sum_{i=1}^{N} \left[\langle i|f|i\rangle + \langle i|F|i\rangle \right]}$$

$\Rightarrow$

$$E(N) = \frac{1}{2}\left\{\sum_{i=1}^{N}\langle i\,|\,f\,|\,i\rangle + \sum_{i=1}^{N} \left[\langle i|f|i\rangle + \langle i|F|i\rangle \right]\right\} = \frac{1}{2}\left\{\sum_{i=1}^{N}\langle i\,|\,f\,|\,i\rangle + \sum_{i=1}^{N} \varepsilon_i\right\}$$

Raimes, Many Electron Theory Eq.3.38 / page 56

Hartree Fock Self Consistent Field for the Free Electron Gas

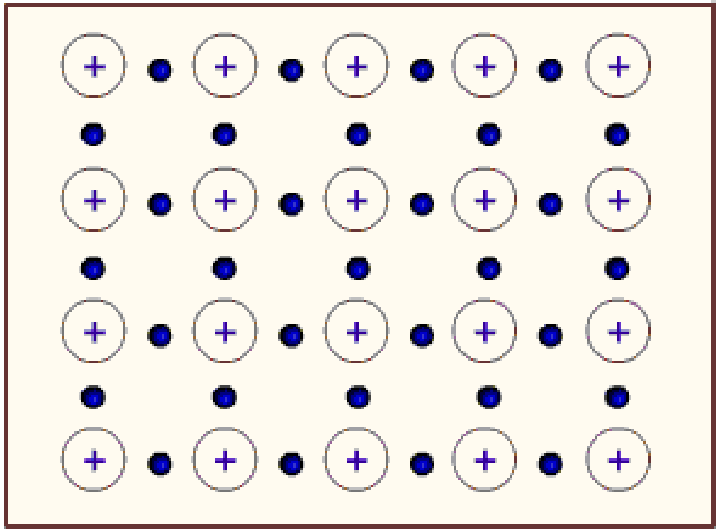
For FEG, the HF-SCF can be obtained ANALYTICALLY

- FEG → only many-electron system for which HF-SCF can be obtained ANALYTICALLY

'free'

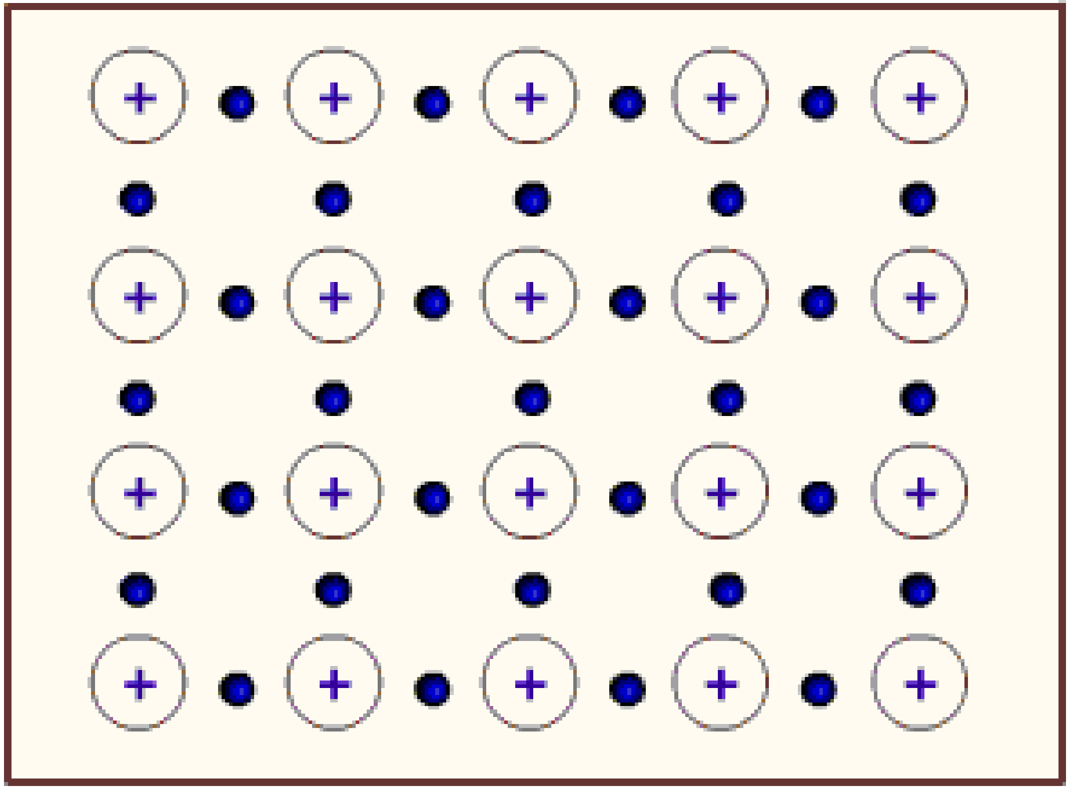
in V=0

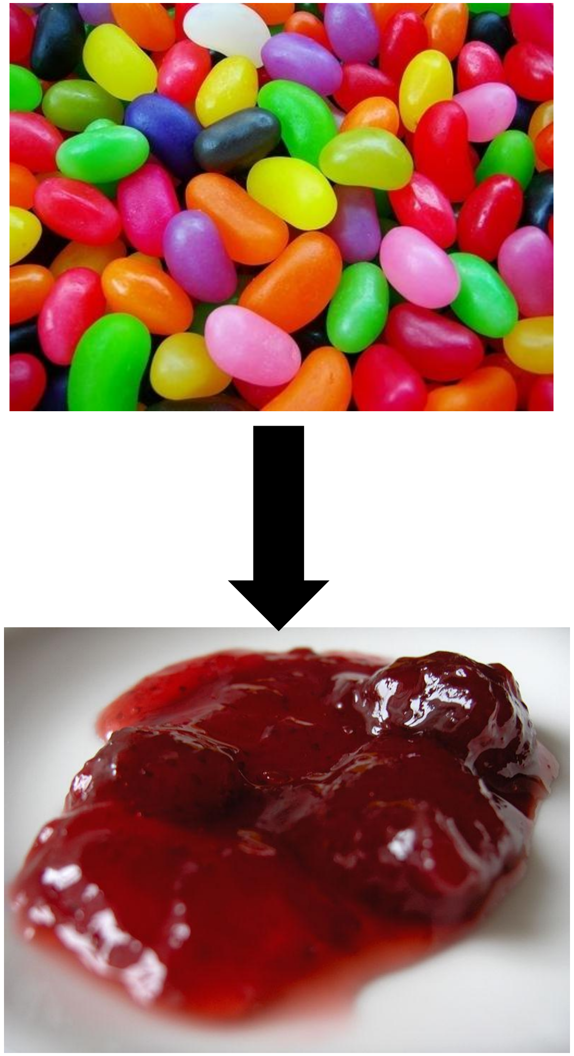
No interaction with any external field



What about the effect of the positive nuclei?

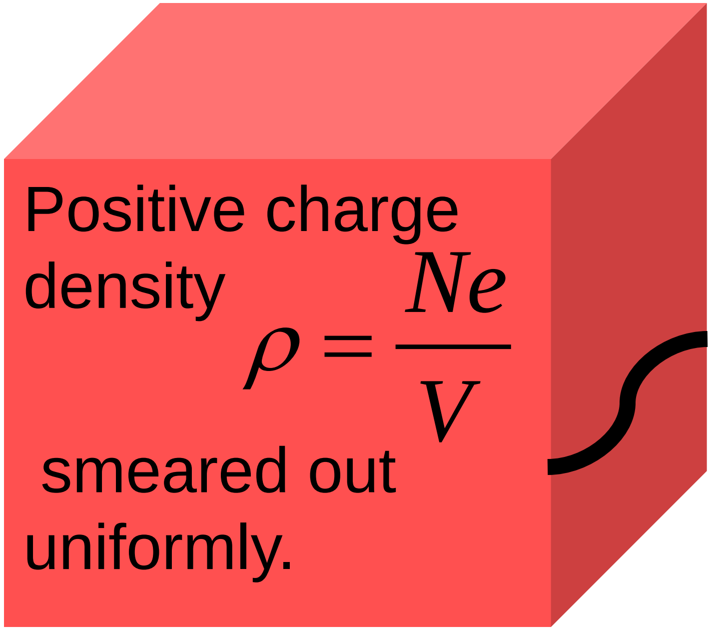
Fermi gas of electrons which interact only with each other.





discrete positive charges in the nuclei considered smeared out, like jelly beans into a jellium.

Whole system: electrically neutral.



N electrons in a cubical box.

Each side has length = L

Volume of the box = $V = L^3$

Box normalization with Born von Karmann boundary conditions

How many wavelengths fit in the box?

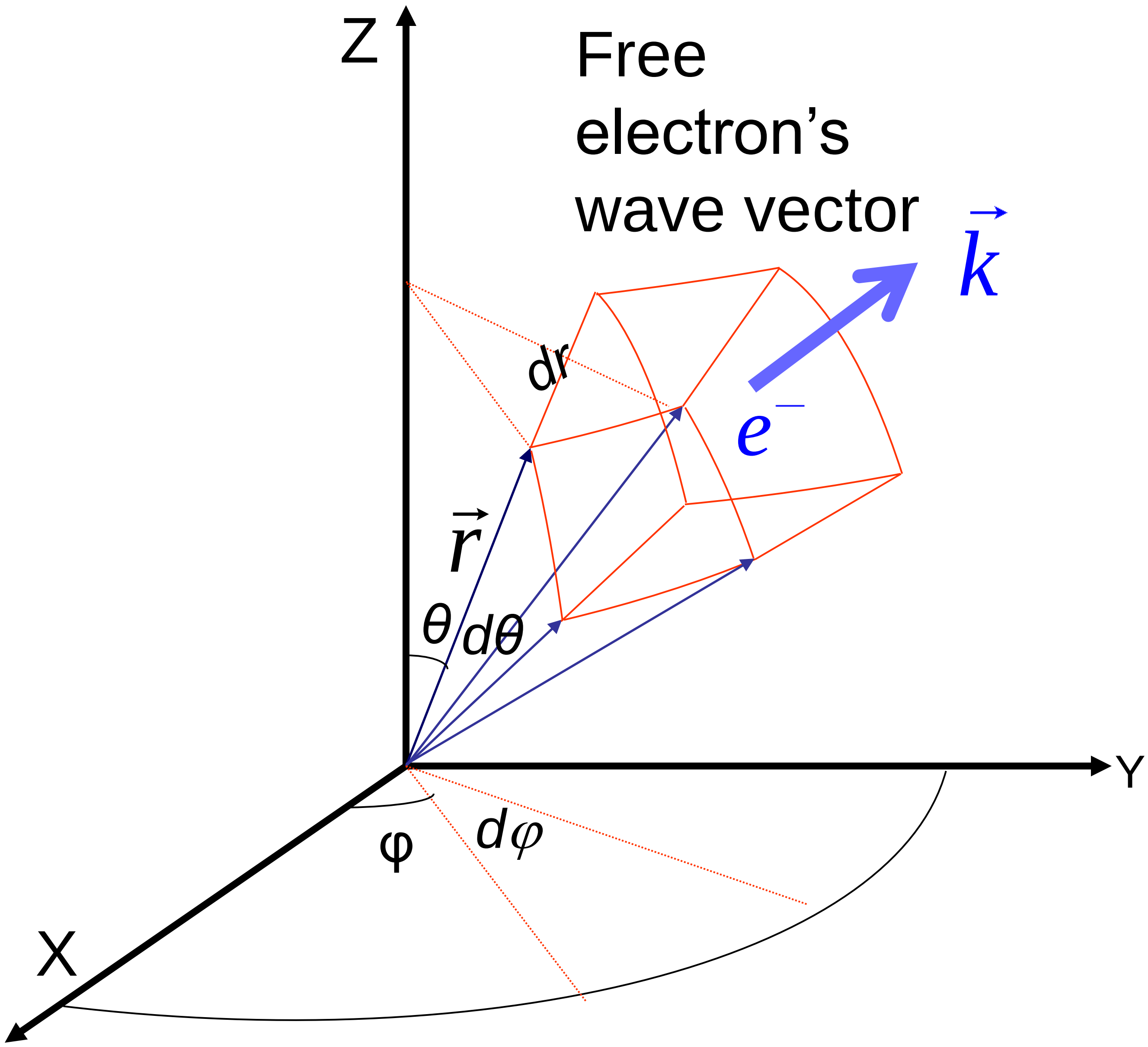
$$n_x \lambda_x = L$$

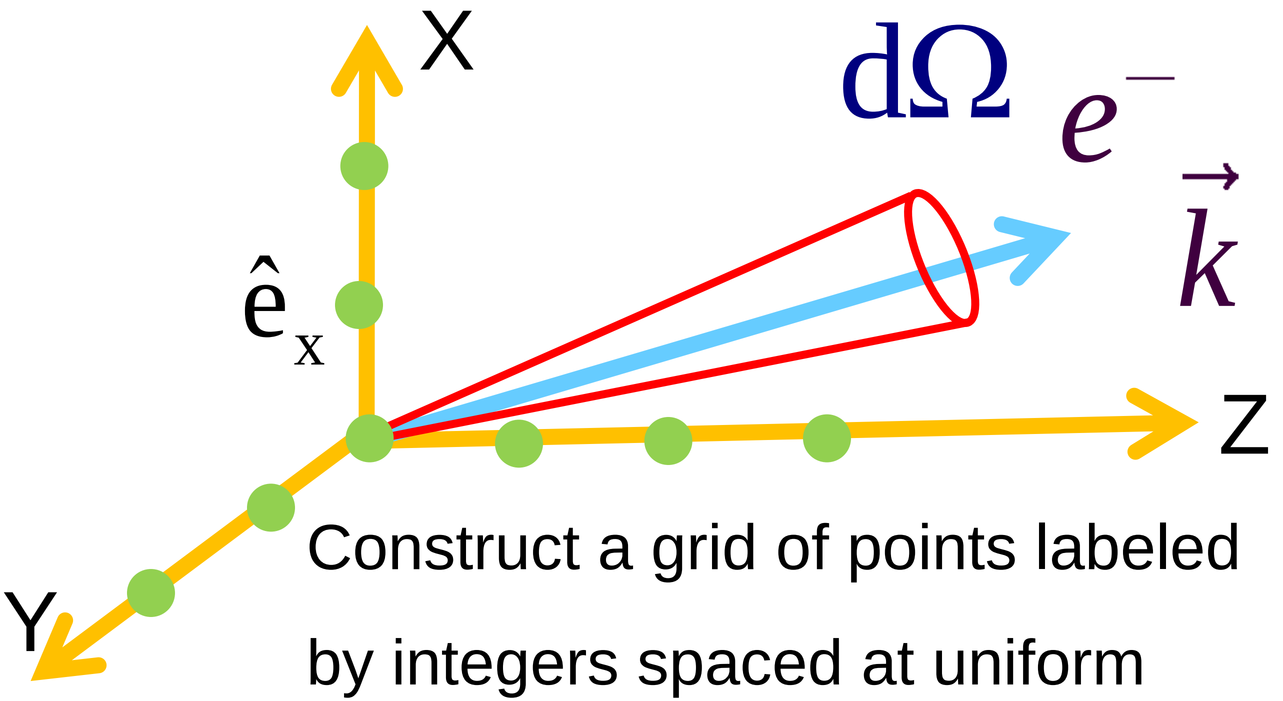
$$n_x \frac{2\pi}{k_x} = L; \qquad k_x = \frac{2\pi n_x}{L}$$

$$\vec{k} = \frac{2\pi}{L}\left(n_x \hat{e}_x + n_y \hat{e}_y + n_z \hat{e}_z\right)$$

$$\psi_{\vec{k}\sigma}(\vec{r}) = \left(\frac{1}{\sqrt{L^3}} e^{i\vec{k}\bullet\vec{r}}\right)\chi_\sigma(\zeta)$$

orbital part spin part


Z
Free
electron's
wave vector
$\vec{k}$
dr
e^-
$\vec{r}$
θ
$d\theta$
Y
$d\varphi$
φ
X



Construct a grid of points labeled by integers spaced at uniform distances along the X, Y, Z axes.

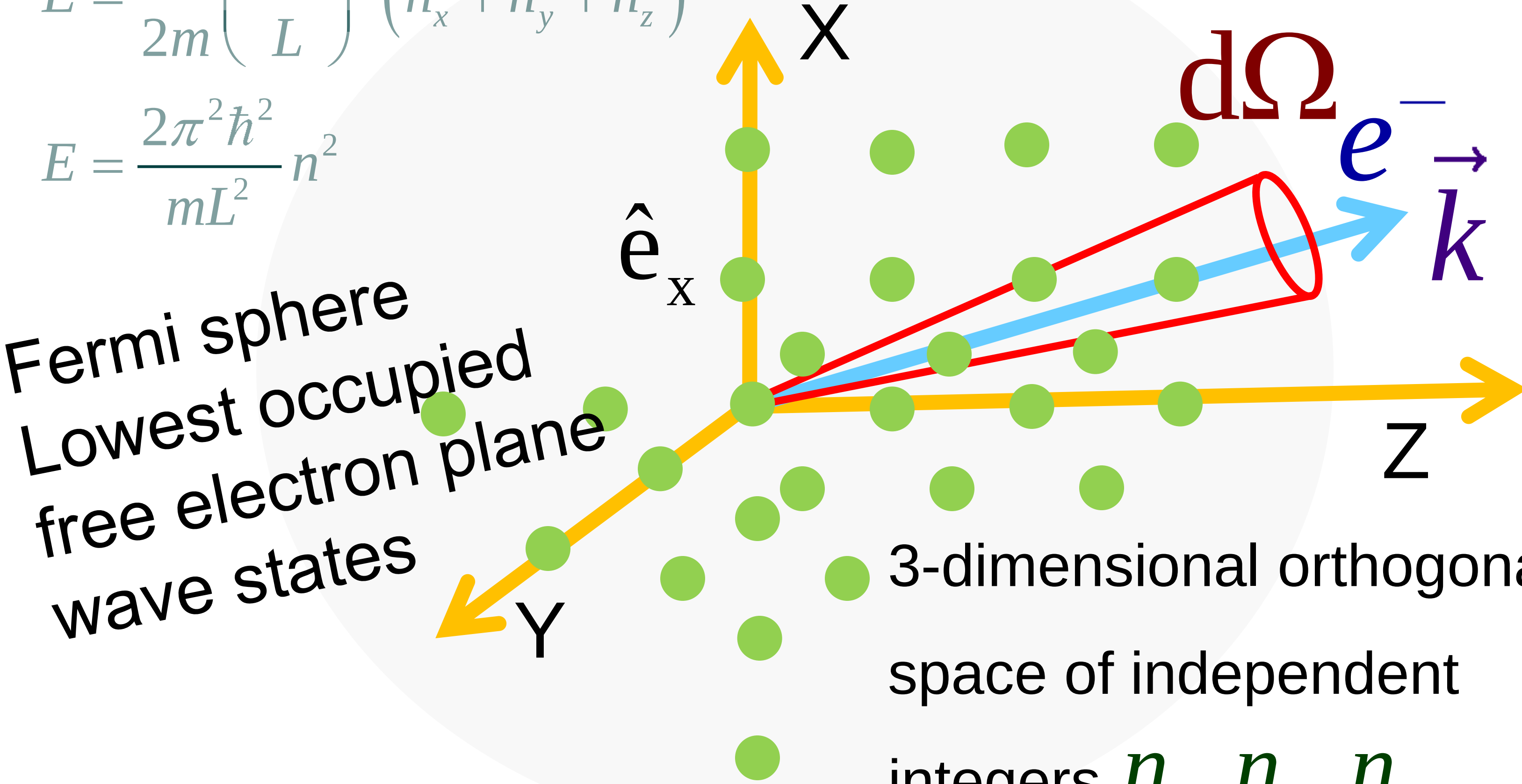
$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$E = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$E = \frac{2\pi^2\hbar^2}{mL^2} n^2$$

states with different n_x, n_y, n_z

$\left(n_x^2 + n_y^2 + n_z^2\right) = n^2$ are degenerate



3-dimensional orthogonal space of independent integers n_x, n_y, n_z.

HF equation

attractive $-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})$

jellium potential $\boxed{\cancel{+V(\vec{r})\psi_p(\vec{r})}}$

electron-electron Coulomb repulsion $\boxed{\cancel{+2\sum_{i=1}^{N/2}\left[\int dV'\left|\psi_i(\vec{r}\,')\right|^2 \mathrm{v}(\vec{r},\vec{r}\,')\right]\psi_p(\vec{r})}}$

electron-electron exchange interaction $-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')\mathrm{v}(\vec{r},\vec{r}\,')\right]$

$$= \varepsilon_p\ \psi_p(\vec{r})$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')\mathrm{v}(\vec{r},\vec{r}\,')\right]=\varepsilon_p\ \psi_p(\vec{r})$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})-\boxed{\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}')\psi_p(\vec{r}')\mathrm{v}(\vec{r},\vec{r}')\right]}=\varepsilon_p\,\psi_p\left(\vec{r}\right)$$

Recall, from Special/Select Topics in Atomic Physics,
STiAP Unit 4, Lecture 23, Slide 118 HF SCF formalism

Reference→ http://www.nptel.ac.in/downloads/115106057

$$V_i^{exchange}(q)\;\psi_p(q)=\psi_i(q)\left[\int dq'\frac{\psi_i^*(q')\psi_p(q')}{|\vec{r}-\vec{r}'|}\right]$$

Sum over i

$$\boxed{\sum_{i=1}^{N} V_i^{exchange}(q)}\;\psi_p(q)=\sum_{i=1}^{N}\psi_i(q)\left[\int dq'\frac{\psi_i^*(q')\psi_p(q')}{|\vec{r}-\vec{r}'|}\right]$$

$$\sum_{\zeta'}\langle m_{s_i}|\zeta'\rangle\langle\zeta'|m_{s_p}\rangle=\delta_{m_{s_i},m_{s_p}}$$

$$\boxed{V^{exchange}(q)}\psi_p(q)=\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int d^3\vec{r}'\psi_i^*(\vec{r}')\psi_p(\vec{r}')\mathrm{v}\left(\vec{r},\vec{r}'\right)\right]$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}')\psi_p(\vec{r}')\mathrm{v}(\vec{r},\vec{r}')\right]=\varepsilon_p\ \psi_p\left(\vec{r}\right)$$

$$V^{exchange}(q)\psi_p(q)=\sum_{i=1}^{N/2}\ \psi_i(\vec{r})\left[\int d^3\vec{r}\,'\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')\mathrm{v}\left(\vec{r},\vec{r}\,'\right)\right]$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})-V^{exchange}(q)\psi_p(q)=\ \varepsilon_p\ \psi_p\left(\vec{r}\right)$$

$$i.e.\quad\left[-\frac{\hbar^2}{2m}\nabla^2-V^{exchange}(q)\right]\psi_p(q)=\ \varepsilon_p\ \psi_p\left(\vec{r}\right)$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2+F_{exchange}(q)\right]\psi_p(q)=\ \varepsilon_p\ \psi_p\left(\vec{r}\right)$$

$$F_{exchange}(q)=\ -V^{exchange}(q)$$

Raimes, Many Electron Theory Eq.3.44 / page 58

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}')\psi_p(\vec{r}')\mathrm{v}(\vec{r},\vec{r}')\right]=\varepsilon_p\ \psi_p\left(\vec{r}\right)$$

Note sign

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}_1)\boxed{-\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\psi_{\vec{k}'}^*(\vec{r}_2)\psi_{\vec{k}}(\vec{r}_2)\mathrm{v}(\vec{r}_1,\vec{r}_2)\left\{\psi_{\vec{k}'}(\vec{r}_1)\right\}\right]}=\varepsilon\left(\vec{k}\right)\ \psi_{\vec{k}}\left(\vec{r}_1\right)$$

Exchange Term
Slide 57

$$\Psi_{\vec{k}\sigma}(\vec{\mathrm{r}})=\left(\frac{1}{\sqrt{\mathrm{L}^3}}\mathrm{e}^{\mathrm{i}\vec{\mathrm{k}}\bullet\vec{\mathrm{r}}}\right)\chi_\sigma\left(\zeta\right)$$

orbital part spin part

Note sign

$$\boxed{-\frac{e^2}{L^3}\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\frac{e^{i\left(\vec{k}-\vec{k}'\right)\bullet\vec{r}_2}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}'\bullet\vec{r}_1}\right\}}{r_{12}}\right]}=ET,S57$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}_1)\boxed{-\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\psi^*_{\vec{k}'}(\vec{r}_2)\psi_{\vec{k}}(\vec{r}_2)\mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_{\vec{k}'}(\vec{r}_1)\right]}= \varepsilon\left(\vec{k}\right)\psi_{\vec{k}}\left(\vec{r}_1\right)$$

$$\boxed{-\frac{e^2}{L^3}\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\frac{e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_2}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}'\bullet\vec{r}_1}\right\}}{r_{12}}\right]}=ET,S57$$

$$\boxed{-\frac{e^2}{L^3}\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\frac{e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_2}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}'\bullet\vec{r}_1}\right\}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}\bullet\vec{r}_1}\right\}}{r_{12}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}\bullet\vec{r}_1}\right\}}\right]}$$

$$-\frac{e^2}{L^3}\sum_{\vec{k}'}\left[\int d^3\vec{r}_2 \frac{e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_2}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}'\bullet\vec{r}_1}\right\}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}\bullet\vec{r}_1}\right\}}{r_{12}\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}\bullet\vec{r}_1}\right\}}\right]$$

$$-\frac{e^2}{L^3}\sum_{\vec{k}'}\left[\int d^3\vec{r}_2 \frac{e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_2}\left\{e^{-i(\vec{k}-\vec{k}')\bullet\vec{r}_1}\right\}}{r_{12}}\right]\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}\bullet\vec{r}_1}\right\}$$

$$ET, S57 =$$

$$-\frac{e^2}{L^3}\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\,\frac{e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_2}\left\{e^{-i(\vec{k}-\vec{k}')\bullet\vec{r}_1}\right\}}{r_{12}}\right]\left\{\frac{1}{\sqrt{L^3}}e^{i\vec{k}\bullet\vec{r}_1}\right\}$$

$$\boxed{-\frac{e^2}{L^3}\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\,\frac{e^{i(\vec{k}-\vec{k}')\bullet(\vec{r}_2-\vec{r}_1)}}{r_{12}}\right]\psi_{\vec{k}}(\vec{r}_1)}$$

$$\boxed{-\frac{e^2}{L^3}\sum_{\vec{k}'}e^{-i(\vec{k}-\vec{k}')\bullet\vec{r}_1}\underbrace{\left[\int d^3\vec{r}_2\,\frac{e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_2}}{r_{12}}\right]}\psi_{\vec{k}}(\vec{r}_1)}$$

$$-\frac{e^2}{L^3}\sum_{\vec{k}'}e^{-i(\vec{k}-\vec{k}')\bullet\vec{r}_1}\,\phi(\vec{r}_1)\,\psi_{\vec{k}}(\vec{r}_1)$$

$$ET, S57 = -\frac{e^2}{L^3}\sum_{\vec{k}'} e^{-i(\vec{k}-\vec{k}')\bullet\vec{r}_1} \boxed{\phi(\vec{r}_1)} \psi_{\vec{k}}(\vec{r}_1)$$

Exchange Term

$$\phi(\vec{r}_1) = \int d^3\vec{r}_2 \frac{e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_2}}{r_{12}} = \boxed{\frac{4\pi e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_1}}{|\vec{k}-\vec{k}'|^2}}$$

The Wave Mechanics of Electrons in Metals – by Stanley Raimes, page 170, Eq.7.40

$$ET, S57 =$$

$$= -\frac{e^2}{L^3}\sum_{\vec{k}'} e^{-i(\vec{k}-\vec{k}')\bullet\vec{r}_1} \boxed{\frac{4\pi e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_1}}{|\vec{k}-\vec{k}'|^2}} \psi_{\vec{k}}(\vec{r}_1)$$

Subscript, not argument

$$= \boxed{-\frac{4\pi e^2}{L^3}\sum_{\vec{k}'} \frac{1}{|\vec{k}-\vec{k}'|^2}} \psi_{\vec{k}}(\vec{r}_1) = \boxed{\varepsilon_{\vec{k}}} \psi_{\vec{k}}(\vec{r}_1)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}_1)\boxed{-\sum_{\vec{k}'}\left[\int d^3\vec{r}_2\psi^*_{\vec{k}'}(\vec{r}_2)\psi_{\vec{k}}(\vec{r}_2)\mathrm{v}(\vec{r}_1,\vec{r}_2)\psi_{\vec{k}'}(\vec{r}_1)\right]} = \varepsilon\left(\vec{k}\right)\ \psi_{\vec{k}}\left(\vec{r}_1\right)$$

$$= \varepsilon_{\vec{k}}\ \ \psi_{\vec{k}}\left(\vec{r}_1\right)$$

Hartree-Fock Eq for Free Electron Gas

Note sign

←Exchange Term

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}_1)}_{\text{K.E.}}+\varepsilon_{\vec{k}}\ \ \psi_{\vec{k}}\left(\vec{r}_1\right)= \varepsilon\left(\vec{k}\right)\ \psi_{\vec{k}}\left(\vec{r}_1\right)$$

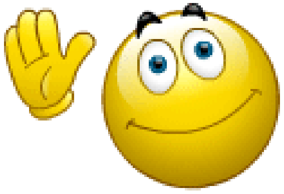
Note sign

$$\frac{\hbar^2 k^2}{2m}+\varepsilon_{\vec{k}} = \varepsilon\left(\vec{k}\right) \qquad \text{where} \qquad \varepsilon_{\vec{k}} = -\frac{4\pi e^2}{L^3}\sum_{\vec{k}'}\frac{1}{\left|\vec{k}-\vec{k}'\right|^2}$$

Raimes / Wave Mechanics of Electrons in Metals / Eq.7.41, page 171

Next: calculation of $\varepsilon_{\vec{k}}$

Questions: pcd@physics.iitm.ac.ic



Select/Special Topics from 'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 18

Electron Gas in Hartree Fock and Random Phase Approximations

Electron-Electron Exchange Energy

Hartree-Fock Eq for Free Electron Gas

K.E.

←Exchange Term

$$\overbrace{-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}(\vec{r}_1)}^{\text{K.E.}}+\varepsilon_{\vec{k}}\;\psi_{\vec{k}}\left(\vec{r}_1\right)=\;\varepsilon\left(\vec{k}\right)\;\psi_{\vec{k}}\left(\vec{r}_1\right)$$

Subscript

←Exchange Term

←Argument

origin: Lagrange variational multiplier in the HFSCF method

$$\frac{\hbar^2 k^2}{2m}+\varepsilon_{\vec{k}}=\;\varepsilon\left(\vec{k}\right)$$

where $\varepsilon_{\vec{k}}=-\frac{4\pi e^2}{L^3}\sum_{\vec{k}'}\frac{1}{\left|\vec{k}-\vec{k}'\right|^2}$

Raimes / Wave Mechanics of Electrons in Metals / Eq.7.41, page 171

Determination of $\varepsilon_{\vec{k}}$

←Exchange Term →

$$E_K+E_{\substack{exchange\\correlation}}=E_{HF}^{\substack{\text{electron gas in}\\\text{jellium potential}}}$$

N electrons in a cubical box.

Each side has length = L

Volume of the box = $V = L^3$

Positive charge density $\rho = \dfrac{Ne}{V}$ smeared out uniformly.

Box normalization with Born von Karmann boundary conditions

How many wavelengths fit in the box?

$$n_x \lambda_x = L$$

$$n_x \frac{2\pi}{k_x} = L; \quad k_x = \frac{2\pi n_x}{L}$$

$$\vec{k} = \frac{2\pi}{L}\left(n_x \hat{e}_x + n_y \hat{e}_y + n_z \hat{e}_z\right)$$

In the k-space

$$\text{'volume' of each state} = \left(\frac{2\pi}{L}\right)^3$$

$$\varepsilon_{\vec{k}} = -\frac{4\pi e^2}{L^3}\sum_{\vec{k}'}\frac{1}{\left|\vec{k}-\vec{k}'\right|^2}$$ ←Exchange Term

In the k-space

'volume' of each state = $\left(\frac{2\pi}{L}\right)^3$

Sum over all states

$$\sum_{\vec{k}'} \rightarrow \frac{1}{\left(\frac{2\pi}{L}\right)^3}\iiint d^3\vec{k}' \text{ : integration in } \vec{k} \text{ space}$$

$$\varepsilon_{\vec{k}} = -\frac{4\pi e^2}{L^3}\frac{1}{\left(\frac{2\pi}{L}\right)^3}\iiint d^3\vec{k}'\frac{1}{\left|\vec{k}-\vec{k}'\right|^2}$$

Integration up to the Fermi level

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\pi^2}\int_{k'=0}^{k'=k_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{k'^2\,dk'\sin\theta\,d\theta\,d\varphi}{(\vec{k}-\vec{k}')\bullet(\vec{k}-\vec{k}')}$$

Raimes / Wave Mechanics of Electrons in Metals / Eq.7.42next, page 171

←Exchange Term

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\pi^2}\int_{k'=0}^{k'=k_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} \frac{k'^2\, dk' \sin\theta\, d\theta\, d\varphi}{\left(\vec{k}-\vec{k}'\right)\bullet\left(\vec{k}-\vec{k}'\right)}$$

Raimes / Wave Mechanics of Electrons in Metals / Eq.7.42next, page 171

$$\vec{p} = \hbar\vec{k} \Rightarrow p^2 = \hbar^2 k^2$$

$$2pdp = \hbar^2 2kdk \Rightarrow pdp = \hbar^2 kdk$$

$$dk = \frac{dp}{\hbar}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\pi^2}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} \frac{\left(\frac{p'^2}{\hbar^2}\right)\frac{dp'}{\hbar}\sin\theta\, d\theta\, d\varphi}{\left(\frac{1}{\hbar}\right)\left(\vec{p}-\vec{p}'\right)\bullet\left(\frac{1}{\hbar}\right)\left(\vec{p}-\vec{p}'\right)}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\hbar\pi^2}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi} \frac{p'^2\, dp' \sin\theta\, d\theta\, d\varphi}{\left(\vec{p}-\vec{p}'\right)\bullet\left(\vec{p}-\vec{p}'\right)}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\hbar\pi^2}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\frac{p'^2\,dp'\sin\theta\,d\theta\,d\varphi}{(\vec{p}-\vec{p}\,')\bullet(\vec{p}-\vec{p}\,')}$$

←Exchange Term

integrating over φ

$$\varepsilon_{\vec{k}} = -\frac{e^2}{2\hbar\pi^2}(2\pi)\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\frac{p'^2\,dp'\sin\theta\,d\theta}{(\vec{p}-\vec{p}\,')\bullet(\vec{p}-\vec{p}\,')}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}\int_{\theta=0}^{\pi}\frac{p'^2\,dp'\sin\theta\,d\theta}{p^2+p'^2-2pp'\cos\theta}$$

$\boxed{\cos\theta=\mu\ ;\ \text{i.e.}\quad -\sin\theta\,d\theta=d\mu}$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}\int_{\mu=-1}^{\mu=+1}\frac{p'^2\,dp'\,d\mu}{p^2+p'^2-2pp'\mu}$$

←Exchange Term

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F}\int_{\mu=-1}^{\mu=+1}\frac{p'^2\,dp'\,d\mu}{p^2+p'^2-2pp'\mu}$$

$$\varepsilon_{\vec{k}} = -\frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F} p'^2\,dp'\int_{\mu=-1}^{\mu=+1}\frac{d\mu}{p^2+p'^2-2pp'\mu}$$

$$\varepsilon_{\vec{k}} = \frac{-e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F} p'^2\,dp'\frac{1}{(-2pp')}\ln\left[p^2+p'^2-2pp'\mu\right]_{\mu=-1}^{\mu=+1}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F} p'^2\,dp'\frac{1}{2pp'}\ln\left[p^2+p'^2-2pp'\mu\right]_{-1}^{+1}$$

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F} p'^2\, dp' \frac{1}{2pp'} \ln\left[p^2 + p'^2 - 2pp'\mu\right]_{\mu=-1}^{\mu=+1}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi}\int_{p'=0}^{p'=p_F} p'^2\, dp' \left[\frac{\ln\left(p^2 + p'^2 - 2pp'\right)}{2pp'} - \frac{\ln\left(p^2 + p'^2 + 2pp'\right)}{2pp'}\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{2\hbar\pi}\int_{p'=0}^{p'=p_F} \frac{p'}{p}\, dp' \left[\ln\left(p^2 + p'^2 - 2pp'\right) - \ln\left(p^2 + p'^2 + 2pp'\right)\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{2\hbar\pi}\int_{p'=0}^{p'=p_F} \frac{p'}{p}\, dp' \left[\ln\left(p - p'\right)^2 - \ln\left(p + p'\right)^2\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{2\hbar\pi}\int_{p'=0}^{p'=p_F}\frac{p'}{p}dp'\left[\ln\left(p-p'\right)^2-\ln\left(p+p'\right)^2\right]$$

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{2\hbar\pi}\int_{p'=0}^{p'=p_F}\frac{p'}{p}dp'\ \ln\left|\frac{p-p'}{p+p'}\right|^2$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\cancel{2}\hbar\pi}\int_{p'=0}^{p'=p_F}\frac{p'}{p}dp'\ \cancel{2}\ln\frac{|p-p'|}{|p+p'|}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi p}\int_{p'=0}^{p'=p_F}p'dp'\ \ln\frac{|p-p'|}{|p+p'|}$$

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar \pi p} \int_{p'=0}^{p'=p_F} p' \ \ln\left(\frac{|p-p'|}{|p+p'|}\right) dp' \qquad p \le p_f$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar \pi p} \left\{ \int_{p'=0}^{p'=p_F} p' \ \ln|p-p'| dp' - \int_{p'=0}^{p'=p_F} p' \ \ln|p+p'| dp' \right\}$$

$$\boxed{\int x \ln(x+a) dx = \frac{x^2 - a^2}{2} \ln(x+a) - \frac{(x-a)^2}{4}}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar \pi p} \left[\frac{p'^2 - p^2}{2} \ln|p-p'| - \frac{(p'+p)^2}{4} - \frac{p'^2 - p^2}{2} \ln|p+p'| + \frac{(p'-p)^2}{4} \right]_0^{p_f}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar \pi p} \left[\frac{p'^2 - p^2}{2} \ln\frac{|p-p'|}{|p+p'|} - \frac{(p'+p)^2}{4} + \frac{(p'-p)^2}{4} \right]_{p'=0}^{p'=p_f}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar \pi p}\left[\frac{p'^2 - p^2}{2}\ln\frac{|p-p'|}{|p+p'|} - \frac{(p'+p)^2}{4} + \frac{(p'-p)^2}{4}\right]_{p'=0}^{p'=p_f}$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar \pi p}\left[\frac{p_f^{\,2} - p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|} - \frac{(p_f+p)^2}{4} + \frac{(p_f-p)^2}{4} \cancel{+\frac{p^2}{2}\ln\frac{|p|}{|p|} + \frac{p^2}{4} - \frac{p^2}{4}}\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar \pi p}\left[\frac{p_f^{\,2} - p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|} - \frac{(p_f+p)^2}{4} + \frac{(p_f-p)^2}{4}\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi p}\left[\frac{p_f{}^2 - p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|} - \frac{(p_f+p)^2}{4} + \frac{(p_f-p)^2}{4}\right]$$

←Exchange Term

$$\varepsilon_{\vec{k}} = \frac{e^2}{\hbar\pi p}\left[\frac{p_f{}^2 - p^2}{2}\ln\frac{|p-p_f|}{|p+p_f|} - p_f p\right]$$

$$\varepsilon_{\vec{k}} = \frac{e^2(-p_f p)}{\hbar\pi p}\left[-\frac{p_f{}^2 - p^2}{2p_f p}\ln\frac{|p-p_f|}{|p+p_f|} + 1\right]$$

Exchange Term

$$\varepsilon_{\vec{k}} = \frac{-e^2 p_f}{\hbar\pi}\left[1 + \frac{p_f{}^2 - p^2}{2p_f p}\ln\frac{|p+p_f|}{|p-p_f|}\right] = \varepsilon_{exchange}(\vec{p})$$

$$\varepsilon(\vec{p}) = \frac{p^2}{2m} + \varepsilon_{exchange}(\vec{p})$$

$$\& \quad \varepsilon_{exchange}(\vec{p}) = \frac{-e^2 p_f}{\hbar\pi}\left[1 + \frac{p_f^{\,2} - p^2}{2 p_f p} \ln \frac{|p + p_f|}{|p - p_f|}\right]$$

$$\varepsilon(\vec{p}) = \frac{p^2}{2m} - \frac{e^2 p_f}{\hbar\pi}\left[1 + \frac{p_f^{\,2} - p^2}{2 p_f p} \ln \frac{|p + p_f|}{|p - p_f|}\right]$$

$$let \quad \rho = \frac{p_f}{p} \qquad \Rightarrow \quad \varepsilon(\vec{p}) = \frac{p^2}{2m} - \frac{e^2 p_f}{\hbar\pi}\left[1 + \frac{\rho^2 - 1}{2\rho} \ln \frac{|1 + \rho|}{|1 - \rho|}\right]$$

$$\varepsilon(\vec{p}) = \frac{p^2}{2m} - \frac{e^2 k_f}{\pi}\boxed{\left[1 + \frac{\rho^2 - 1}{2\rho} \ln \frac{|1 + \rho|}{|1 - \rho|}\right]}$$

define:

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

$$\varepsilon(\vec{k}) = \frac{p^2}{2m} + \varepsilon_{\vec{k}}$$

←Exchange Term

$$\varepsilon(\vec{k}) = \frac{p^2}{2m} - \frac{e^2 k_f}{\pi}\left[1 + \frac{\rho^2 - 1}{2\rho}\ln\frac{|1+\rho|}{|1-\rho|}\right]$$

$$\rho = \frac{p_f}{p} \qquad p \le p_f \Rightarrow \rho \ge 1 \qquad |1-\rho| \le |1+\rho|$$

$\varepsilon_{\vec{k}}$: EXCHANGE TERM IS NEGATIVE

Singlet State $\nearrow\swarrow$

Triplet State $\nearrow\nearrow$

Select/Special Topics in Atomic Physics
http://nptel.ac.in/courses/115106057/ Unit 4

"Triplet State is less punished by the coulomb interaction"
- Landau & Lifshitz

$$Singlet: \quad \chi(\zeta_2,\zeta_1) = -\chi(\zeta_1,\zeta_2)$$ anti-symmetric spin part

$$\phi(\vec{r}_2,\vec{r}_1) = +\phi(\vec{r}_1,\vec{r}_2) = N\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$$

$$\text{singlet}: orbital\ \ part \rightarrow double\ as\ \vec{r}_1 \rightarrow \vec{r}_2$$

Fermi correlation →

* electrons with **antiparallel spins** to lump together,

* as if in a **heap** of electrical charge

Fermi "heap"

* This causes INCREASED repulsion → less stable

$Triplet: \quad \chi(\zeta_2,\zeta_1) = +\chi(\zeta_1,\zeta_2)$ anti-symmetric space part

$$\phi(\vec{r}_2,\vec{r}_1) = -\phi(\vec{r}_1,\vec{r}_2) = N\left[\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right]$$

triplet: $orbital\ part \to 0\ as\ \vec{r}_1 \to \vec{r}_2$

Fermi correlation →

* electrons with **parallel spins** have an EXCLUSION region of space

*** as if a spherical cavity is generated around it in which another electron with a parallel spin cannot enter**

Fermi "hole"

Exchange hole

* DECREASED repulsion → more stable

Slide No. 54, Previous lecture

HF equation

attractive

jellium

potential

electron-electron

Coulomb repulsion

electron-electron

exchange

interaction

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})$$

$$\boxed{\cancel{+V(\vec{r})\psi_p(\vec{r})}}$$

$$\boxed{\cancel{+2\sum_{i=1}^{N/2}\left[\int dV'\left|\psi_i(\vec{r}\,')\right|^2 \mathrm{v}(\vec{r},\vec{r}\,')\right]\psi_p(\vec{r})}}$$

$$-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')\mathrm{v}(\vec{r},\vec{r}\,')\right]$$

$$=\varepsilon_p\ \psi_p\left(\vec{r}\right)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')\mathrm{v}(\vec{r},\vec{r}\,')\right]=\varepsilon_p\ \psi_p\left(\vec{r}\right)$$

in the $\vec{k}$ space

$$\text{'volume' of each state} = \left(\frac{2\pi}{L}\right)^3$$

$$\sum_{\vec{k}'} \rightarrow \frac{1}{\left(\frac{2\pi}{L}\right)^3} \iiint d^3\vec{k}' : \text{integration in } \vec{k} \text{ space}$$

in the $\vec{p}$ space

$$\text{'volume' of each state} = \left(\frac{2\pi\hbar}{L}\right)^3$$

$$\sum_{\vec{p}'} \rightarrow \frac{1}{\left(\frac{2\pi\hbar}{L}\right)^3} \iiint d^3\vec{p}' : \text{integration in } \vec{p} \text{ space}$$

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electron-electron Coulomb repulsion

electron-electron Exchange interaction

$$E_{HF}^{atom} = \langle \psi^{(N)} | H | \psi^{(N)} \rangle$$

$$= \sum_{i=1}^{N} \langle i | f | i \rangle + \frac{1}{2} \sum_{j=1}^{N} \sum_{i=1}^{N} \left[\langle ij | g | ij \rangle - \langle ij | g | ji \rangle \right]$$

The operator *f* contains the K.E. operators and the nuclear attraction operators

Electron gas in jellium potential

attractive jellium potential cancels the electron-electron direct Coulomb repulsion terms

* integration instead of the above discrete sum

$$E_{HF}^{\text{electron gas in jellium potential}} =$$

$$= 2\frac{L^3}{(2\pi\hbar)^3} \int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p}\bullet\vec{p}}{2m} + \frac{1}{2} \varepsilon_{exchange}(\vec{p}) \right]$$

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} =$$

$$= 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p}\bullet\vec{p}}{2m} + \frac{1}{2}\,\varepsilon_{exchange}(\vec{p}) \right]$$

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_K + E_{\substack{exchange\\ correlation}}$$

E_K : "Kinetic"

E_X : "Exchange Correlation"

where

$$E_K = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p}\bullet\vec{p}}{2m} \right]$$

and

$$E_{\substack{exchange\\ correlation}} = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{1}{2}\,\varepsilon_{exchange}(\vec{p}) \right]$$

$$E_{HF}^{\substack{\text{electron gas in} \\ \text{jellium potential}}} = E_K + E_{\substack{exchange \\ correlation}}$$

E_K : "Kinetic"
E_x : "Exchange Correlation"

where

$$E_K = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \underbrace{\int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi}\left[\frac{\vec{p}\bullet\vec{p}}{2m}\right]$$

$$E_K = 2\frac{L^3}{(2\pi\hbar)^3}\frac{4\pi}{2m}\int_{p=0}^{p=p_f} p^4 dp$$

$$\boxed{E_K = \frac{L^3}{(2\pi\hbar)^3}\frac{4\pi}{m}\frac{p_f^{\,5}}{5}}$$

$$E_K = \frac{\hbar^2 L^3}{10\pi^2 m} k_f^{\,5}$$

f : Fermi level

K: K.E. part of the HF energy of the degenerate free electron gas

$$E_K = \frac{\hbar^2 V}{10\pi^2 m} k_f^{\,5}$$

Raimes / Many Electron Theory / Eq.3.64, page 63

Estimation of E_K

$$\textit{in the } \vec{k} \textit{ space}$$

$$\text{'volume' of each state} = \left(\frac{2\pi}{L}\right)^3$$

$$Number\ \ of\ \ electrons = N$$

$N = \underline{Twice}$ the $Number\ \ of$ single-electron states $in\ the\ \ 'volume'$

$(in\ k\text{-}space)\ spanned\ \ by\ the\ Fermi\ sphere$

$whose\ volume\ is\ \ \frac{4}{3}\pi k_f^{\ 3}$

$$= 2\times\frac{\frac{4}{3}\pi k_f^{\ 3}}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{3\pi^2}k_f^{\ 3} = \frac{L^3}{\pi^2}\times\left(\frac{1}{4\pi}\right)\frac{4}{3}\pi k_f^{\ 3}$$

$$N = \frac{L^3}{4\pi^3}\times\frac{4}{3}\pi k_f^{\ 3}$$

$$= \frac{V}{4\pi^3}\times\frac{4}{3}\pi k_f^{\ 3}$$

$$k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

$$E_K = \frac{\hbar^2 V}{10\pi^2 m} k_f^{\,5} \qquad k_f = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

$$N \times \left(\frac{4}{3} \pi r_s^{\,3} \right) = V = \frac{3\pi^2 N}{k_f^{\,3}}$$

r_s : radius of a sphere whose volume is equal to the average volume per electron.

$$r_s^{\,3} = \frac{9\pi/4}{k_f^{\,3}} \Rightarrow r_s = \frac{\left(9\pi/4\right)^{1/3}}{k_f} = \frac{\hbar\left(9\pi/4\right)^{1/3}}{m\mathrm{v}_f}$$

$$E_K = \frac{\hbar^2 \left\{ N \times \left(\frac{4}{3} \pi r_s^{\,3} \right) \right\}}{10\pi^2 m} \left(\frac{3\pi^2 N}{N \times \left(\frac{4}{3} \pi r_s^{\,3} \right)} \right)^{5/3} = \frac{3\hbar^2}{10m} \left(\frac{9\pi}{4} \right)^{2/3} \frac{N}{r_s^{\,2}}$$

K.E. contribution to the *average* HF ground state energy *per electron* in a free-electron-gas

$$\frac{E_K}{N} = \frac{3\hbar^2}{10m} \left(\frac{9\pi}{4} \right)^{2/3} \frac{1}{r_s^{\,2}} = \frac{2.21}{r_s^{\,2}} Ryd$$

Raimes / Many Electron Theory / Eq.3.68, page 63

$$1\ Ryd = me^4/2\hbar^2 = 13.60569...\ eV; \qquad 1\ Bohr\ unit = \hbar^2/me^2 = 0.5292\ \mathring{A}$$

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_K + E_{\substack{exchange\\ correlation}}$$

K.E.

$$\boxed{\frac{E_K}{N} = \frac{2.21}{{r_s}^2} Ryd}$$

$$E_{\substack{exchange\\ correlation}} = 2\frac{V}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{1}{2}\ \varepsilon_{exchange}(\vec{p})\right]$$

$$\varepsilon_{exchange}(\vec{p}) = \frac{-e^2 p_f}{\hbar\pi}\left[1 + \frac{{p_f}^2 - p^2}{2 p_f p} \ln\frac{|p + p_f|}{|p - p_f|}\right]$$

Next: Estimation of $E_{\text{exchange-correlation}}$

and how to account for many-electron COULOMB CORRELATIONS (Bohm Pines: RPA)

Questions: pcd@physics.iitm.ac.ic

Select/Special Topics from 'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 19

Electron Gas in Hartree Fock and Random Phase Approximations

Free Electron Gas in Jellium Background Potential

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_{\substack{Kinetic\\ Energy}} + E_{\substack{Exchange\\ Correlation}}$$

where

$$E_{\substack{Kinetic\\ Energy}} = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \underbrace{\int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi}_{4\pi} \left[\frac{\vec{p}\bullet\vec{p}}{2m}\right]$$

$$E_K = 2\frac{L^3}{(2\pi\hbar)^3}\frac{4\pi}{2m}\int_{p=0}^{p=p_f} p^4 dp$$

$$\boxed{E_K = \frac{L^3}{(2\pi\hbar)^3}\frac{4\pi}{m}\frac{p_f{}^5}{5}}$$

$$E_K = \frac{\hbar^2 L^3}{10\pi^2 m} k_f{}^5 = \frac{\hbar^2 V}{10\pi^2 m} k_f{}^5$$

K: K.E. part of the HF energy of the degenerate free electron gas

f : Fermi level

Raimes / Many Electron Theory / Eq.3.64, page 63

$$E_K = \frac{\hbar^2 V}{10\pi^2 m} k_f^{\ 5}$$

$$N \times \left(\frac{4}{3}\pi r_s^{\ 3}\right) = V = \frac{3\pi^2 N}{k_f^{\ 3}}$$

r_s : radius of a sphere whose volume is equal to the average volume per electron.

$$r_s = \frac{\left(9\pi/4\right)^{1/3}}{k_f} = \frac{\hbar\left(9\pi/4\right)^{1/3}}{m\mathrm{v}_f}$$

$\boxed{r_s \text{ : Bohr units}}$

$$E_K = \frac{3\hbar^2}{10m}\left(\frac{9\pi}{4}\right)^{2/3}\frac{N}{r_s^{\ 2}}$$

r_s : Seitz parameter

K.E. contribution to the *average* HF ground state energy *per electron* in a free-electron-gas

$$\frac{E_K}{N} = \frac{3\hbar^2}{10m}\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{r_s^{\ 2}} = \frac{2.21}{r_s^{\ 2}} Ryd$$

Raimes / Many Electron Theory /
Eq.3.68, page 63

$1\ Ryd = me^4/2\hbar^2 = 13.60569...\ eV; \quad 1\ Bohr\ unit = \hbar^2/me^2 = 0.5292\ \overset{0}{\mathrm{A}}$

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_K + E_{\substack{exchange\\ correlation}}$$

K.E.

$$\frac{E_K}{N} = \frac{2.21}{r_s^{\,2}} Ryd$$

$$E_{\substack{exchange\\ correlation}} \overset{?}{=} \cancel{2} \frac{V}{(2\pi\hbar)^3} \int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\cancel{\frac{1}{2}} \varepsilon_{exchange}(\vec{p}) \right]$$

From last class
Slide No.86 →

$$\varepsilon_{exchange}(\vec{p}) = \frac{-e^2 p_f}{\hbar\pi} \left[1 + \frac{p_f^{\,2} - p^2}{2 p_f p} \ln\left(\frac{p_f + p}{p_f - p} \right) \right]$$

$$E_{\substack{exchange\\ correlation}} =$$

$$= \frac{V}{(2\pi\hbar)^3} \int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{-e^2 p_f}{\hbar\pi} \left\{ 1 + \frac{p_f^{\,2} - p^2}{2 p_f p} \ln\left(\frac{p_f + p}{p_f - p} \right) \right\} \right]$$

$$E_{\substack{exchange\\correlation}} =$$

$$= \frac{V}{(2\pi\hbar)^3} \int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{-e^2 p_f}{\hbar\pi} \left\{ 1 + \frac{p_f{}^2 - p^2}{2 p_f p} \ln\left(\frac{p_f + p}{p_f - p} \right) \right\} \right]$$

$$\boxed{p = \hbar k} \qquad \boxed{p^2 dp = \hbar^3 k^2 dk}$$

$$E_{\substack{exchange\\correlation}} =$$

$$-\frac{Ve^2}{8\pi^3} 4\pi \left(\frac{1}{2\pi} \right) \int_{k=0}^{k=k_f} dk \left[2k_f k^2 + k\left(k_f{}^2 - k^2 \right) \ln\left(\frac{k_f + k}{k_f - k} \right) \right]$$

$$E_{\substack{exchange\\correlation}} =$$

$$= -\frac{Ve^2}{4\pi^3} \int_{k=0}^{k=k_f} dk \left[2k_f k^2 + k\left(k_f{}^2 - k^2 \right) \ln\left(\frac{k_f + k}{k_f - k} \right) \right]$$

$$E_{\substack{exchange\\correlation}} =$$

$$= -\frac{Ve^2}{4\pi^3}\int_{k=0}^{k=k_f} dk\left[2k_f k^2 + k\left(k_f^{\,2} - k^2\right)\ln\left(\frac{k_f + k}{k_f - k}\right)\right]$$

$$\int \ln ax\, dx = x\ln ax - x$$

Standard Integrals

$$\int x\ln x\, dx = \frac{1}{2}x^2\ln x - \frac{x^2}{4}$$

with logarithm

$$\int x^2\ln x\, dx = \frac{1}{3}x^3\ln x - \frac{x^3}{9}$$

functions

$$\int x^n\ln x\, dx = x^{n+1}\left(\frac{\ln x}{n+1} - \frac{1}{(n+1)^2}\right), \quad n \neq -1$$

$$\boxed{E_{\substack{exchange\\correlation}} = V\left(-\frac{e^2 k_f^{\,4}}{4\pi^3}\right)}$$

$$E_{\substack{exchange\\correlation}} = V\left\{-\frac{e^2 k_f^{\ 4}}{4\pi^3}\right\}$$

$$k_f = \left(\frac{3\pi^2 N}{V}\right)^{1/3};\ \&\ N \times \left(\frac{4}{3}\pi r_s^{\ 3}\right) = V$$

from : slide 85, last class

$$-\frac{e^2 k_f^{\ 4}}{4\pi^3} = -\frac{e^2}{4\pi^3}\left(\frac{9\pi}{4}\right)^{4/3}\frac{1}{r_s^{\ 4}}$$

$$E_{\substack{exchange\\correlation}} = N\left(\frac{4}{3}\pi \boxed{r_s^{\ 3}}\right) \times \left\{-\frac{e^2}{4\pi^3}\left(\frac{9\pi}{4}\right)^{4/3}\boxed{\frac{1}{r_s^{\ 4}}}\right\}$$

$$= N \times \left\{-\frac{e^2}{3\pi^2}\left(\frac{9\pi}{4}\right)^{4/3}\frac{1}{\boxed{r_s}}\right\}$$

$$\boxed{\frac{E_{\substack{exchange\\correlation}}}{N} = \frac{-0.916}{r_s}\,Ryd}$$

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_{KE} + E_{\substack{exchange\\ correlation}}$$

← Adding both the terms

$$where \quad E_{KE} = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{\vec{p}\bullet\vec{p}}{2m}\right]$$

$$and \qquad E_{\substack{exchange\\ correlation}} = 2\frac{L^3}{(2\pi\hbar)^3}\int_{p=0}^{p=p_f} p^2 dp \int_{\theta=0}^{\theta=\pi} \sin\theta d\theta \int_{\varphi=0}^{\varphi=2\pi} d\varphi \left[\frac{1}{2}\ \varepsilon_{exchange}(\vec{p})\right]$$

For free electron gas in SCF *jellium potential :*

$$\left[\frac{E_{HF}}{N}\right] = \left(\frac{2.21}{r_s^{\ 2}} - \frac{0.916}{r_s}\right) Ryd$$

r_s : Bohr units

Average HF energy per electron

$$H = $$

$$= \sum_{i=1}^{N} f(q_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ \boxed{i\neq j}}}^{N} \mathrm{v}(q_i, q_j)$$

$$E_{HF}^{\substack{\text{electron gas in}\\ \text{jellium potential}}} = E_K + E_{\substack{exchange\\ correlation}}$$

$$\boxed{\frac{E_{HF}}{N} = \left(\frac{2.21}{r_s^{\;2}} - \frac{0.916}{r_s}\right) Ryd}$$

Average HF energy per electron

electron-electron interaction, reduces the energy <u>BELOW</u> that of the Sommerfeld gas **(of course in the positive jellium potential)**

HF equation

Origin of the 'reduction'

$$-\frac{\hbar^2}{2m}\nabla^2\psi_p(\vec{r})$$

attractive jellium potential

$$\cancel{\boxed{+V(\vec{r})\psi_p(\vec{r})}}$$

electron-electron Coulomb repulsion

$$\cancel{\boxed{+2\sum_{i=1}^{N/2}\left[\int dV'\left|\psi_i(\vec{r}\,')\right|^2 \mathrm{v}(\vec{r},\vec{r}\,')\right]\psi_p(\vec{r})}}$$

exchange interaction

$$-\sum_{i=1}^{N/2}\psi_i(\vec{r})\left[\int dV'\psi_i^*(\vec{r}\,')\psi_p(\vec{r}\,')\mathrm{v}(\vec{r},\vec{r}\,')\right]$$

$$= \varepsilon_p\ \psi_p\left(\vec{r}\right)$$

Average HF energy per electron

electron-electron interaction, reduces the energy BELOW that of the Sommerfeld gas (of course in the positive jellium potential)

$$FEG \; in \; \text{HF-SCF} \; jellium \; potential:$$

$$\left[\frac{E_{HF}}{N}\right] = \left(\frac{2.21}{r_s^{\,2}} - \frac{0.916}{r_s}\right) Ryd$$

$$1\; Ryd = {me^4}\big/{2\hbar^2} = 13.60569...\; eV$$

$$1\; Bohr\; unit = {\hbar^2}\big/{me^2} = 0.5292...\; \overset{0}{\mathrm{A}}$$

r_s : Bohr units

First Order Perturbative treatment of the exchange term → SAME RESULT (next class)

Second (and higher) Order Perturbative treatment of the electron-electron Coulomb interaction however diverges.

For free electron gas in jellium potential :

$$\left[\frac{E_{HF}}{N}\right] = \left(\frac{2.21}{r_s^{\,2}} - \frac{0.916}{r_s}\right) Ryd$$

COULOMB correlations ignored

Need! Many-body theory – *beyond perturbation methods*

Bohm & Pines: mid-fiftees

D.Pines (1963) Elementary excitations in solids (Benjamin, NY)

Random Phase Approximation

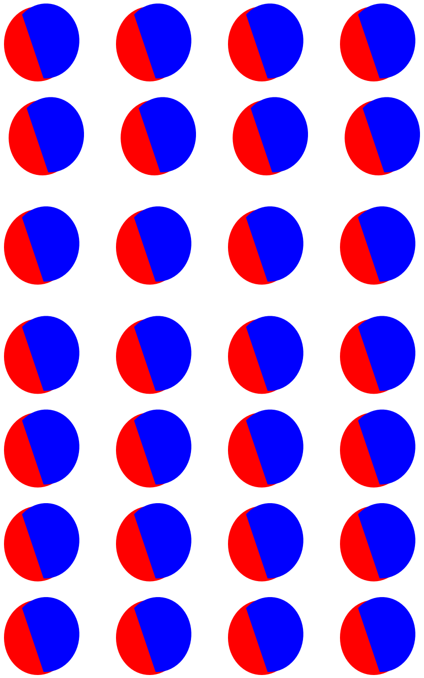
$$E_{BP} = \frac{2.21}{r_s^{\,2}} - \frac{0.916}{r_s} + \frac{\sqrt{3}}{2 r_s^{3/2}}\beta^2 - \frac{0.916}{r_s}\left(\frac{\beta^2}{2} - \frac{\beta^4}{48}\right)$$

$$\beta = \frac{k_c}{k_f}$$

k_c : Upper bound to wave number of plasma oscillations

→ Lower bound to wave length; since oscillations get damped by the random thermal motion of the electrons.

First, the 'classical model'

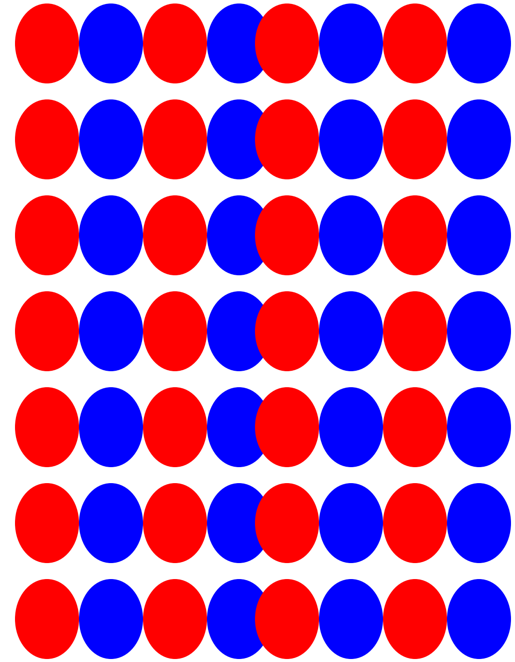


ρ : average volume charge density

$\rightarrow$

ξ

Displacement of all the electrons to the right



Positive and Negative charge in balance

First, the 'classical model'

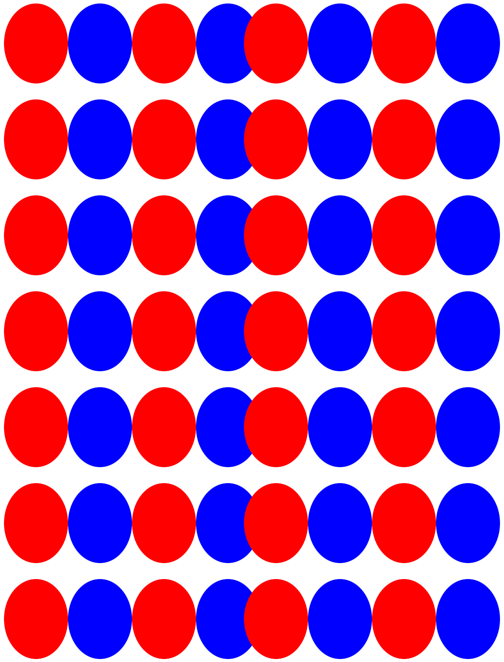
ρ : average volume charge density

$\vec{\xi}$

Displacement of all the electrons to the right

net positive surface charge per unit area

$= +e\rho_p\xi$



net negative surface charge per unit area

$= -e\rho_e\xi$

surface charge density : $\sigma = e\rho\xi$

<u>net field in-between</u>

$$\vec{E} = \frac{1}{\varepsilon_0} e\rho\xi\hat{u}$$

Eq. of motion

net field in-between

$$\vec{E} = \frac{1}{\varepsilon_0} e\rho\xi\hat{u}$$

$$m\frac{d^2\xi}{dt^2} = \left(\frac{1}{\varepsilon_0} e\rho\xi\right)(-e)$$

$$\frac{d^2\xi}{dt^2} = -\frac{\rho e^2}{m\varepsilon_0}\xi$$

S.H.O.

CGS units

$$\frac{1}{4\pi\varepsilon_0} \to 1 \quad ; \quad \frac{1}{\varepsilon_0} \to 4\pi$$

$$\omega_p = \sqrt{\frac{4\pi\rho e^2}{m}}$$

$$\omega_p = \sqrt{\frac{\rho e^2}{m\varepsilon_0}}$$

SI units

Frequency of plasma oscillations

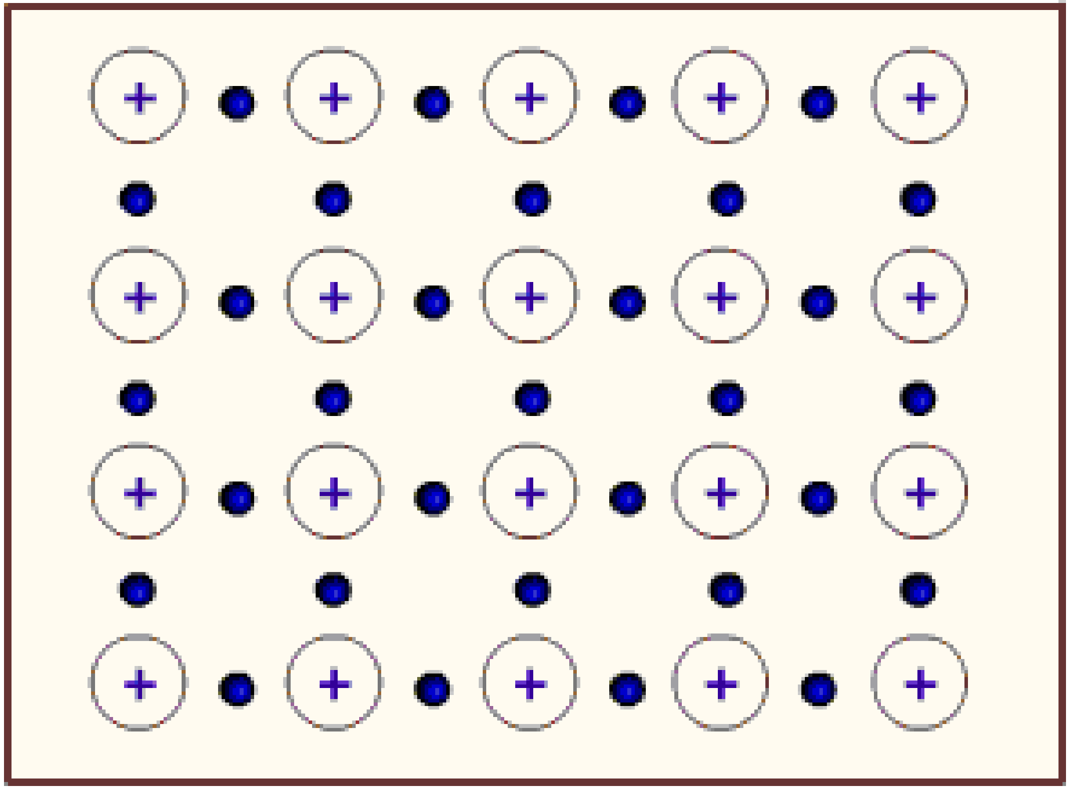
Thermal motion of electrons: ignored

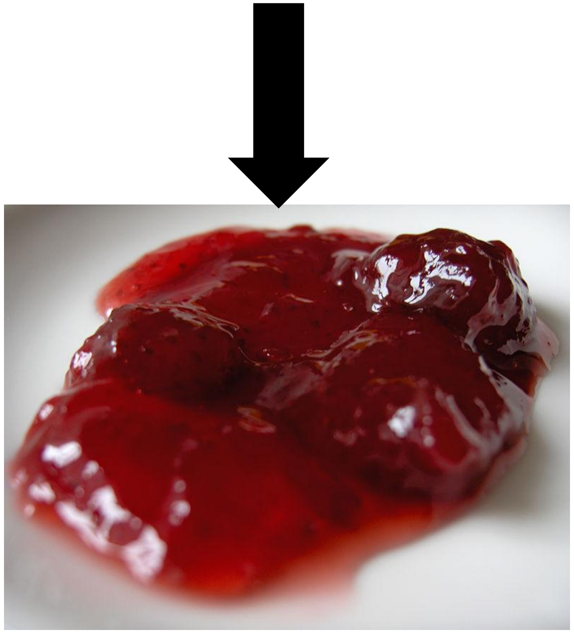
→except that thermal fluctuations would have ‘caused’ the onset of plasma oscillations

Thermal motion → dispersion

when dispersion is present:

$$\boxed{\omega^2 = \omega_p^{\ 2} - \frac{2E_F}{m}k^2}$$





discrete positive charges in the nuclei considered smeared out, like jelly beans into a jellium.

Uniform charge density

Whole system: electrically neutral.

Positive charge density

$$\rho = \frac{Ne}{V}$$

N electrons in volume V together with a uniform positive charge background jellium distribution.

Jellium **b**ackground

$$H = H_{el} + H_b + H_{el-b}$$

1st term in the Hamiltonian

$$H_{el} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} e^2 \sum_{\substack{j=1 \\ j \neq i}}^{N} \sum_{i=1}^{N} \frac{e^{-\mu|\vec{r}_i - \vec{r}_j|}}{|\vec{r}_i - \vec{r}_j|}$$

Mathematical device to avoid divergences. Later, we take the limit:

$$\mu \to 0$$

2nd term

$$H_b = \frac{1}{2} e^2 \iiint d^3\vec{x} \iiint d^3\vec{x}\,' \frac{\rho^+_{\vec{x}} \rho^+_{\vec{x}'} e^{-\mu|\vec{x} - \vec{x}'|}}{|\vec{x} - \vec{x}'|}$$

3rd term in the Hamiltonian

$$H_{el-b} = -e^2 \sum_{i=1}^{N} \iiint d^3\vec{x} \frac{\rho^+_{\vec{x}} e^{-\mu|\vec{x} - \vec{r}_i|}}{|\vec{x} - \vec{r}_i|}$$

N electrons and the background: NEUTRAL system

$\boxed{\text{2nd term}}$

$$H_b = \frac{1}{2} e^2 \iiint d^3\vec{x} \iiint d^3\vec{x}\,' \frac{\rho^+_{\vec{x}}\rho^+_{\vec{x}'} e^{-\mu|\vec{x}-\vec{x}'|}}{|\vec{x}-\vec{x}'|}$$

$$\rho^+_{\vec{x}} = \rho^+_{\vec{x}'} = \frac{N}{V} \text{ (uniform density)} \qquad H_b = \frac{1}{2} e^2 \left(\frac{N}{V}\right)^2 \iiint d^3\vec{x} \iiint d^3\vec{x}\,' \frac{e^{-\mu|\vec{x}-\vec{x}'|}}{|\vec{x}-\vec{x}'|}$$

$$\vec{x}\,' - \vec{x} = \vec{z}$$

$$d\vec{x}\,' = d\vec{z} \ldots \underline{at\ \text{constant}\ \vec{x}} \qquad H_b = \frac{1}{2} e^2 \left(\frac{N}{V}\right)^2 \left(\boxed{\iiint d^3\vec{x}}\right) \underbrace{\iiint d^3\vec{z}\, \frac{e^{-\mu z}}{z}}$$

$$\iiint d^3\vec{z}\, \frac{e^{-\mu z}}{z} = 4\pi \int_0^\infty z^2 dz \frac{e^{-\mu z}}{z} = 4\pi \int_0^\infty z e^{-\mu z} dz = \frac{4\pi}{\mu^2}$$

$$H_b = \frac{1}{2} e^2 \left(\frac{N}{V}\right)^2 \boxed{(V)} \frac{4\pi}{\mu^2} = \frac{1}{2} e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$

Contribution of this term (per electron) diverges as μ→0

μ^2 divergence

$$\frac{H_b}{N} \xrightarrow[\mu \to 0]{} diverges$$

Reference: Fetter & Walecka - Eq.3.7
in Quantum Theory of Many-Particle Systems; page 22

$$\boxed{3^{rd} \text{ term}}$$

$$H_{el-b} = -e^2 \sum_{i=1}^{N} \iiint d^3\vec{x} \, \frac{\rho_{\vec{x}}^{+} e^{-\mu|\vec{x}-\vec{r}_i|}}{|\vec{x}-\vec{r}_i|}$$

$$\rho = \left(\frac{N}{V}\right)$$

$$H_{el-b} = -e^2 \sum_{i=1}^{N} \left(\frac{N}{V}\right) \iiint d^3\vec{x} \, \frac{e^{-\mu|\vec{x}-\vec{r}_i|}}{|\vec{x}-\vec{r}_i|}$$

$$H_{el-b} = -e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$

Contribution of this term (per electron) diverges as μ→0

μ^2 divergence

$$H_b = \frac{1}{2} e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$

$$\frac{H_b}{N} \xrightarrow[\mu \to 0]{} \mu^2 \ divergence$$

Reference: Fetter & Walecka - Eq.3.8 in Quantum Theory of Many-Particle Systems; page 22

$$H = H_{el} + H_b + H_{el-b}$$

$$H = H_{el} + \frac{1}{2} e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2} - e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$

$$H = H_{el} - \frac{1}{2} e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$

Contribution of this term (per electron) diverges as μ→0

μ^2 divergence

Does the diverging term cancel with any part of H_{el}?

Procede to take limits:

FIRST: L→∞ (i.e. V→∞) and ***then*** μ→0

After due cancellation of appropriate parts, if any?

Reference: Eq.3.9 in
Fetter & Walecka - Quantum Theory of Many-Particle Systems; page 23

Recall, when

$$H_{el}^{I\,Q} = H_1 + H_2 = \sum_{i=1}^{N} f(q_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ \boxed{i\neq j}}}^{N} \mathrm{v}^C(q_i, q_j)$$

Coulomb

then

$$H^{II\,Q} = \sum_i \sum_j c_i^\dagger \langle i|f|j\rangle c_j + \frac{1}{2}\sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij|\mathrm{v}^C|kl\rangle c_l c_k$$

$$\langle ij|\mathrm{v}^C|kl\rangle = \int dq_1 \int dq_2 \phi_i^*(q_1)\phi_j^*(q_2)\mathrm{v}^C(q_1,q_2)\phi_k(q_1)\phi_l(q_2)$$

1st term

$$H_{el}^{I\,Q} = \sum_{i=1}^{N}\frac{p_i^2}{2m} + \frac{1}{2}e^2 \sum_{\substack{j=1\\ j\neq i}}^{N}\sum_{i=1}^{N} \boxed{\frac{e^{-\mu|\vec{r}_i-\vec{r}_j|}}{|\vec{r}_i-\vec{r}_j|}} \xrightarrow[\text{Coulomb}]{\text{Screened}} \boxed{\mathrm{v}^{sc}}$$

Hence

$$H_{el}^{II\,Q} = \sum_i \sum_j c_i^\dagger \langle i\left|\frac{p^2}{2m}\right|j\rangle c_j + \frac{1}{2}\sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij|\mathrm{v}^{sc}|kl\rangle c_l c_k$$

$$\langle ij|\mathrm{v}^{sc}|kl\rangle = \int dq_1 \int dq_2 \phi_i^*(q_1)\phi_j^*(q_2)\frac{e^{-\mu|\vec{r}_1-\vec{r}_2|}}{|\vec{r}_1-\vec{r}_2|}\phi_k(q_1)\phi_l(q_2)$$

$$H_{el}^{II\ Q} = \sum_i \sum_j c_i^\dagger \langle i \left| \frac{p^2}{2m} \right| j \rangle c_j + \frac{1}{2} \sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij \left| \mathrm{v}^{sc} \right| kl \rangle c_l c_k$$

$$\langle ij \left| \mathrm{v}^{sc} \right| kl \rangle = \int dq_1 \int dq_2 \phi_i^*(q_1) \phi_j^*(q_2) \frac{e^{-\mu|\vec{r}_1 - \vec{r}_2|}}{|\vec{r}_1 - \vec{r}_2|} \phi_k(q_1) \phi_l(q_2)$$

Showing the summation over spin variables explicitly:

$$H_{el}^{II\ Q} = \left[\begin{array}{l} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} c_{\vec{k}_1\sigma_1}^\dagger \left\langle \vec{k}_1 \sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2 \sigma_2 \right\rangle c_{\vec{k}_2\sigma_2} \\ + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\sigma_3} \sum_{\vec{k}_4} \sum_{\sigma_4} c_{\vec{k}_1\sigma_1}^\dagger c_{\vec{k}_2\sigma_2}^\dagger \left\langle \vec{k}_1 \sigma_1 \vec{k}_1 \sigma_1 \left| \mathrm{v}^{sc} \right| \vec{k}_3 \sigma_3 \vec{k}_4 \sigma_4 \right\rangle c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \end{array} \right]$$

$$H_{el}^{II\,Q} = \left[\sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} c^{\dagger}_{\vec{k}_1\sigma_1} \left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle c_{\vec{k}_2\sigma_2} \right.$$

←First, examine the K.E. term.

$$\left. + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\sigma_3} \sum_{\vec{k}_4} \sum_{\sigma_4} c^{\dagger}_{\vec{k}_1\sigma_1} c^{\dagger}_{\vec{k}_2\sigma_2} \left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2 \left| \mathrm{v}^{sc} \right| \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \right\rangle c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \right]$$

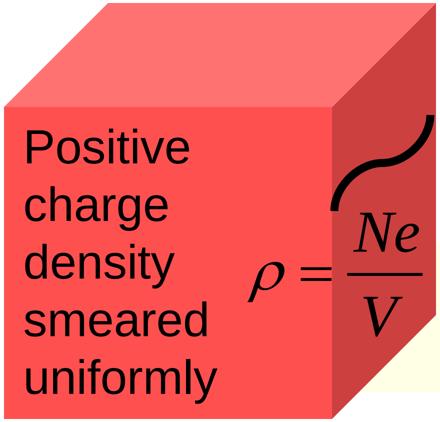
$$\left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle = \delta_{\sigma_1,\sigma_2} \iiint d^3\vec{x} \left(\frac{1}{\sqrt{V}} e^{-i\vec{k}_1\bullet\vec{x}} \right) \left(\frac{-\hbar^2\vec{\nabla}^2}{2m} \right) \left(\frac{1}{\sqrt{V}} e^{i\vec{k}_2\bullet\vec{x}} \right)$$

$$\left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle = \frac{-\hbar^2\delta_{\sigma_1,\sigma_2}}{2mV} \iiint d^3\vec{x}\; e^{-i\vec{k}_1\bullet\vec{x}} \vec{\nabla}^2 e^{i\vec{k}_2\bullet\vec{x}}$$

$$= \frac{\hbar^2 k_2{}^2}{2m} \delta_{\sigma_1,\sigma_2} \boxed{\frac{1}{V} \iiint d^3\vec{x}\; e^{i\left(\vec{k}_2-\vec{k}_1\right)\bullet\vec{x}}}$$

$$\boxed{\frac{1}{(2\pi)^3} \iiint d^3\vec{x}\; e^{i\left(\vec{k}_2-\vec{k}_1\right)\bullet\vec{x}} = \delta\left(\vec{k}_1 - \vec{k}_2\right)}$$

Dirac δelta function



N electrons in a cubical box.
Each side has length = L
Volume of the box = $V = L^3$

$$\langle \vec{x} | \vec{k} \rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\bullet\vec{x}}$$

Box normalization with Born von Karmann boundary conditions

$$n_x \lambda_x = L; \qquad n_x \frac{2\pi}{k_x} = L; \qquad k_x = \frac{2\pi n_x}{L}$$

$$\vec{k} = \frac{2\pi}{L}\left(n_x \hat{e}_x + n_y \hat{e}_y + n_z \hat{e}_z\right)$$

In the k-space
'volume' of each state $= \left(\frac{2\pi}{L}\right)^3$

$$\frac{1}{2\pi}\int dx\ e^{i(K-k)x} = \delta(K-k)$$

$$\frac{1}{(2\pi)^3}\iiint d^3\vec{x}\ e^{i\left(\vec{k}_2-\vec{k}_1\right)\bullet\vec{x}} = \delta\left(\vec{k}_1-\vec{k}_2\right)$$

$$\frac{1}{L^3}\iiint d^3\vec{x}\ e^{i\left(\vec{k}_2-\vec{k}_1\right)\bullet\vec{x}} = \delta_{\vec{k}_1,\vec{k}_2}$$

Eq.3.11; page 23; F&W

$$\left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle = \frac{\hbar^2 k_2^{\ 2}}{2mV}\delta_{\sigma_1,\sigma_2} \iiint d^3\vec{x}\ e^{i\left(\vec{k}_2-\vec{k}_1\right)\bullet\vec{x}} = \frac{\hbar^2 k_2^{\ 2}}{2m\cancel{V}}\delta_{\sigma_1,\sigma_2}\ \cancel{V}\delta_{\vec{k}_1,\vec{k}_2}$$

Eq.3.10; page 23; F&W

$$H_{el}^{II\ Q} = \left[\sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} c^{\dagger}_{\vec{k}_1\sigma_1} \left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle c_{\vec{k}_2\sigma_2} + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\sigma_3} \sum_{\vec{k}_4} \sum_{\sigma_4} c^{\dagger}_{\vec{k}_1\sigma_1} c^{\dagger}_{\vec{k}_2\sigma_2} \left\langle \vec{k}_1\sigma_1\, \vec{k}_2\sigma_2 \left| \mathrm{v}^{sc} \right| \vec{k}_3\sigma_3 \vec{k}_4\sigma_4 \right\rangle c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \right]$$

←First, examine the K.E. term.

$$\boxed{\left\langle \vec{k}_1\sigma_1 \left| \frac{p^2}{2m} \right| \vec{k}_2\sigma_2 \right\rangle = \frac{\hbar^2 k_2^{\ 2}}{2m} \delta_{\sigma_1,\sigma_2} \delta_{\vec{k}_1,\vec{k}_2}}$$

$$H_{el}^{II\ Q} = \left[\sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} c^{\dagger}_{\vec{k}_1\sigma_1} c_{\vec{k}_2\sigma_2} \frac{\hbar^2 k_2^{\ 2}}{2m} \delta_{\sigma_1,\sigma_2} \delta_{\vec{k}_1,\vec{k}_2} + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\sigma_3} \sum_{\vec{k}_4} \sum_{\sigma_4} c^{\dagger}_{\vec{k}_1\sigma_1} c^{\dagger}_{\vec{k}_2\sigma_2} \left\langle \vec{k}_1\sigma_1\, \vec{k}_2\sigma_2 \left| \mathrm{v}^{sc} \right| \vec{k}_3\sigma_3 \vec{k}_4\sigma_4 \right\rangle c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \right]$$

$$H_{el}^{II\ Q} = \left[\sum_{\vec{k}_1} \sum_{\sigma_1} c^{\dagger}_{\vec{k}_1\sigma_1} c_{\vec{k}_1\sigma_1} \frac{\hbar^2 k_1^{\ 2}}{2m} + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\sigma_3} \sum_{\vec{k}_4} \sum_{\sigma_4} c^{\dagger}_{\vec{k}_1\sigma_1} c^{\dagger}_{\vec{k}_2\sigma_2} \left\langle \vec{k}_1\sigma_1\, \vec{k}_2\sigma_2 \left| \mathrm{v}^{sc} \right| \vec{k}_3\sigma_3 \vec{k}_4\sigma_4 \right\rangle c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \right]$$

$$H_{el}^{II\ Q} = \left[\begin{array}{l} \sum_{\vec{k}_1} \sum_{\sigma_1} \frac{\hbar^2 k_1^{\ 2}}{2m} c^{\dagger}_{\vec{k}_1 \sigma_1} c_{\vec{k}_1 \sigma_1} \\ + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\sigma_3} \sum_{\vec{k}_4} \sum_{\sigma_4} c^{\dagger}_{\vec{k}_1 \sigma_1} c^{\dagger}_{\vec{k}_2 \sigma_2} \left\langle \vec{k}_1 \sigma_1\, \vec{k}_2 \sigma_2 \left| \mathrm{v}^{sc} \right| \vec{k}_3 \sigma_3 \vec{k}_4 \sigma_4 \right\rangle c_{\vec{k}_4 \sigma_4} c_{\vec{k}_3 \sigma_3} \end{array} \right]$$

$$2^{nd} \text{ term} \rightarrow \delta_{\sigma_1, \sigma_3} \delta_{\sigma_2, \sigma_4}$$

$$\left\langle \vec{k}_1 \sigma_1\, \vec{k}_2 \sigma_2 \left| \mathrm{v}^{sc} \right| \vec{k}_3 \sigma_1 \vec{k}_4 \sigma_2 \right\rangle =$$

$$= \delta_{\sigma_1, \sigma_3} \delta_{\sigma_2, \sigma_4} \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \phi^*_{\vec{k}_1 \sigma_1}(\vec{r}_1) \phi^*_{\vec{k}_2 \sigma_2}(\vec{r}_2) \frac{e^2 e^{-\mu |\vec{r}_1 - \vec{r}_2|}}{|\vec{r}_1 - \vec{r}_2|} \phi_{\vec{k}_3 \sigma_1}(\vec{r}_1) \phi_{\vec{k}_4 \sigma_2}(\vec{r}_2)$$

$$\left\langle \vec{x} \middle| \vec{k} \right\rangle = \frac{1}{\sqrt{V}} e^{i \vec{k} \bullet \vec{x}}$$

$$\left\langle \vec{k}_1 \sigma_1\, \vec{k}_2 \sigma_2 \left| \mathrm{v}^{sc} \right| \vec{k}_3 \sigma_3 \vec{k}_4 \sigma_4 \right\rangle = \delta_{\sigma_1, \sigma_3} \delta_{\sigma_2, \sigma_4} \frac{e^2}{V^2} \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \frac{e^{-\mu |\vec{r}_1 - \vec{r}_2|}}{|\vec{r}_1 - \vec{r}_2|} e^{+i(\vec{k}_3 - \vec{k}_1) \bullet \vec{r}_1} e^{+i(\vec{k}_4 - \vec{k}_2) \bullet \vec{r}_2}$$

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{r}_1\int d^3\vec{r}_2\,\frac{e^{-\mu|\vec{r}_1-\vec{r}_2|}}{|\vec{r}_1-\vec{r}_2|}\,e^{+i(\vec{k}_3-\vec{k}_1)\bullet\vec{r}_1}e^{+i(\vec{k}_4-\vec{k}_2)\bullet\vec{r}_2}$$

$$\vec{r}_2\rightarrow\vec{x}$$

$$\vec{r}_1-\vec{r}_2\rightarrow\vec{y}$$

$$\vec{r}_1=\vec{y}+\vec{r}_2=\vec{y}+\vec{x}$$

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\,\frac{e^{-\mu y}}{y}\,e^{+i(\vec{k}_3-\vec{k}_1)\bullet(\vec{y}+\vec{x})}e^{+i(\vec{k}_4-\vec{k}_2)\bullet\vec{x}}$$

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\,\frac{e^{-\mu y}}{y}\,e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\bullet(\vec{y}+\vec{x})}e^{-i(\vec{k}_4-\vec{k}_2)\bullet\vec{y}}$$

$$e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\bullet(\vec{y}+\vec{x})}e^{-i(\vec{k}_4-\vec{k}_2)\bullet\vec{y}} = e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\bullet\vec{x}}e^{+i(\vec{k}_3-\vec{k}_1)\bullet\vec{y}}$$

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\,\frac{e^{-\mu y}}{y}\,e^{+i(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2)\bullet\vec{x}}e^{+i(\vec{k}_3-\vec{k}_1)\bullet\vec{y}}$$

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\int d^3\vec{y}\int d^3\vec{x}\,\frac{e^{-\mu y}}{y}\,e^{+i\left(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2\right)\bullet\vec{x}}\,e^{+i\left(\vec{k}_3-\vec{k}_1\right)\bullet\vec{y}}$$

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}\underbrace{\int d^3\vec{x}\,e^{+i\left(\vec{k}_3-\vec{k}_1+\vec{k}_4-\vec{k}_2\right)\bullet\vec{x}}}\int d^3\vec{y}\,\frac{e^{-\mu y}}{y}\,e^{+i\left(\vec{k}_3-\vec{k}_1\right)\bullet\vec{y}}$$

Conservation of linear momentum in homogeneous space

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V^2}V\delta\left(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4\right)\int d^3\vec{y}\,\frac{e^{-\mu y}}{y}\,e^{+i\left(\vec{k}_3-\vec{k}_1\right)\bullet\vec{y}}$$

$$\left\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2\left|\mathrm{v}^{sc}\right|\vec{k}_3\sigma_3\vec{k}_4\sigma_4\right\rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\frac{e^2}{V}\delta\left(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4\right)\underbrace{\int d^3\vec{y}\,\frac{e^{-\mu y}}{y}\,e^{+i\left(\vec{k}_3-\vec{k}_1\right)\bullet\vec{y}}}$$

Fourier transform of the Screened Coulomb Potential

Small digression: Fourier transform of the Coulomb Potential

Fourier transform $g(\vec{k})$ *of* $f(\vec{r})$:

$$g(\vec{k}) = \iiint e^{-i\vec{k}\bullet\vec{r}} f(\vec{r}) d^3\vec{r}$$

When the integral does not converge:

$$g(\vec{k}) = \boxed{\lim_{\mu\to 0^+}} \iiint e^{-i\vec{k}\bullet\vec{r}} \boxed{e^{-\mu r}} f(\vec{r}) d^3\vec{r}$$

$\text{Given } g(\vec{k}), \textit{ how} \text{ do we recover } f(\vec{r})?$

$$f(\vec{r}) = \left(\frac{1}{2\pi}\right)^3 \iiint e^{+i\vec{k}\bullet\vec{r}} g(\vec{k}) d^3\vec{k}$$

When the integral does not converge:

$$f(\vec{r}) = \lim_{\mu\to 0^+} \iiint e^{+i\vec{k}\bullet\vec{r}} e^{-\mu k} g(\vec{k}) d^3\vec{k}$$

rotational symmetry:

When $f(\vec{r}) = f(|\vec{r}|)$, *then* $g(\vec{k}) = g(|\vec{k}|)$; & vice versa

$$\boxed{\begin{gathered}\textit{In the case of rotational symmetry, } f(\vec{r}) = f(|\vec{r}|) = f(r): \\ g(\vec{k}) = g(|\vec{k}|) = g(k) = \frac{4\pi}{k}\int_0^\infty dr\ r\ f(r)\sin(kr)\end{gathered}}$$

FT of Coulomb potential, $V(\vec{r}) = V(|\vec{r}|) = V(r) = \dfrac{1}{r}$

$$g(\vec{k}) = g(|\vec{k}|) = g(k) = \frac{4\pi}{k}\int_0^\infty dr\ \cancel{r}\ \frac{1}{\cancel{r}}\sin(kr) \quad = \frac{4\pi}{k}\int_0^\infty dr\ \sin(kr)$$

FT of Coulomb potential, $V(\vec{r}) = V(|\vec{r}|) = V(r) = \frac{1}{r}$

$$g(\vec{k}) = g(|\vec{k}|) = g(k) = \frac{4\pi}{k}\int_0^\infty dr\ r\ \frac{1}{r}\sin(kr) = \frac{4\pi}{k}\int_0^\infty dr\ \sin(kr)$$

The above integral does not converge

FT of Screened Coulomb potential, $V^{SC}(\vec{r}) = V^{SC}(|\vec{r}|) = V^{SC}(r) = \lim_{\mu\to 0^+}\frac{e^{-\mu r}}{r}$

$$g(\vec{k}) = g(|\vec{k}|) = g(k) = \lim_{\mu\to 0^+}\frac{4\pi}{k}\int_0^\infty dr\ r\ \frac{e^{-\mu r}}{r}\sin(kr) = \lim_{\mu\to 0^+}\frac{4\pi}{k}\int_0^\infty dr\ e^{-\mu r}\sin(kr)$$

$$g(\vec{k}) = \lim_{\mu\to 0^+}\frac{4\pi}{k}\int_0^\infty dr\ e^{-\mu r}\sin(kr) = \lim_{\mu\to 0^+}\frac{4\pi}{k}\int_0^\infty dr\ e^{-\mu r}\,\mathrm{Im}\left(e^{ikr}\right)$$

$$\boxed{g(\vec{k}) = \lim_{\mu\to 0^+}\frac{4\pi}{k}\mathrm{Im}\int_0^\infty dr\ \left(e^{ikr-\mu r}\right) = \lim_{\mu\to 0^+}\frac{4\pi}{k}\mathrm{Im}\left[\frac{e^{ikr-\mu r}}{ik-\mu}\right]_0^\infty}$$

$$g(\vec{k}) = \lim_{\mu \to 0^+} \frac{4\pi}{k} \mathrm{Im}\left[\frac{e^{ikr-\mu r}}{ik-\mu}\right]_0^\infty = \lim_{\mu \to 0^+} \frac{4\pi}{k} \mathrm{Im} \frac{1}{ik-\mu}\left[e^{ikr-\mu r}\right]_0^\infty$$

$$= \lim_{\mu \to 0^+} \frac{4\pi}{k} \mathrm{Im} \frac{1}{ik-\mu}[0-1]$$

$$g(\vec{k}) = \lim_{\mu \to 0^+} \frac{4\pi}{k} \mathrm{Im} \frac{-1}{ik-\mu} = \lim_{\mu \to 0^+} \frac{4\pi}{k} \mathrm{Im} \frac{1}{\mu-ik}$$

$$= \lim_{\mu \to 0^+} \frac{4\pi}{k} \mathrm{Im} \frac{\mu+ik}{\mu^2+k^2} = \lim_{\mu \to 0^+} \frac{4\pi}{\mu^2+k^2} = \frac{4\pi}{k^2}$$

$$FT \text{ of } \left(\frac{e^{-\mu r}}{r}\right)^{SC} = \frac{4\pi}{\mu^2+k^2}$$

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

$$FT \text{ of } \frac{4\pi}{\mu^2+k^2} = \left(\frac{e^{-\mu r}}{r}\right)^{SC}$$

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

$$\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2 \,|\mathrm{v}^{sc}|\, \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\,\frac{e^2}{V}\,\delta\left(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4\right)\int d^3\vec{y}\,\frac{e^{-\mu y}}{y}\,e^{+i\left(\vec{k}_3-\vec{k}_1\right)\bullet\vec{y}}$$

$$FT \quad \text{of} \left(\frac{e^{-\mu r}}{r}\right)^{SC} = \frac{4\pi}{\mu^2+k^2}$$

Reference: Fetter & Walecka
Quantum Theory of Many-Particle Systems
page 24 / Eq.3.14

Fourier transform
of Screened
Coulomb Potential

$$\langle \vec{k}_1\sigma_1\,\vec{k}_2\sigma_2 \,|\mathrm{v}^{sc}|\, \vec{k}_3\sigma_3\vec{k}_4\sigma_4 \rangle = \delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\,\frac{e^2}{V}\,\delta\left(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4\right)\frac{4\pi}{\left|\vec{k}_1-\vec{k}_3\right|^2+\mu^2}$$

$$H_{el}^{II\ Q} = \left[\sum_{\vec{k}_1}\sum_{\sigma_1}\frac{\hbar^2 k_1^{\ 2}}{2m}c^\dagger_{\vec{k}_1\sigma_1}c_{\vec{k}_1\sigma_1} + \frac{1}{2}\sum_{\vec{k}_1,\sigma_1}\sum_{\vec{k}_2,\sigma_2}\sum_{\vec{k}_3,\sigma_3}\sum_{\vec{k}_4,\sigma_4}\delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\left(\frac{e^2}{V}\delta\left(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4\right)\frac{4\pi}{\left|\vec{k}_1-\vec{k}_3\right|^2+\mu^2}c^\dagger_{\vec{k}_1\sigma_1}c^\dagger_{\vec{k}_2\sigma_2}c_{\vec{k}_4\sigma_4}c_{\vec{k}_3\sigma_3}\right)\right]$$

Reference:
Fetter & Walecka - Quantum Theory of Many-Particle Systems; page 24 / Eq.3.15

Rearrange the terms → Cancellations with terms from the background….

$$H = H_{el} + H_b + H_{el-b}$$

Contribution of this term (per electron) diverges as μ→0
μ² divergence

$$H = H_{el} \quad -\frac{1}{2} e^2 \frac{N^2}{V} \frac{4\pi}{\mu^2}$$

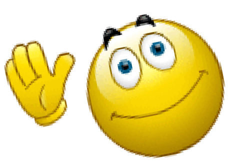
$$H_{el}^{II\ Q} = \left[\sum_{\vec{k}_1} \sum_{\sigma_1} \frac{\hbar^2 k_1^2}{2m} c_{\vec{k}_1\sigma_1}^{\dagger} c_{\vec{k}_1\sigma_1} + \frac{1}{2} \sum_{\vec{k}_1,\sigma_1} \sum_{\vec{k}_2,\sigma_2} \sum_{\vec{k}_3,\sigma_3} \sum_{\vec{k}_4,\sigma_4} \delta_{\sigma_1,\sigma_3} \delta_{\sigma_2,\sigma_4} \left(\frac{e^2}{V} \delta\left(\vec{k}_1 + \vec{k}_2, \vec{k}_3 + \vec{k}_4\right) \frac{4\pi}{\left|\vec{k}_1 - \vec{k}_3\right|^2 + \mu^2} c_{\vec{k}_1\sigma_1}^{\dagger} c_{\vec{k}_2\sigma_2}^{\dagger} c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \right) \right]$$

$$'\delta' \Rightarrow \vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4 \Rightarrow \vec{k}_4 - \vec{k}_2 = \vec{k}_1 - \vec{k}_3 = \vec{q}$$

Momentum transfer

$$\textit{For free electron gas in jellium}$$

$$\textit{potential}: \ \langle \mathrm{H} \rangle = \left[\frac{E_{\mathrm{I\ order\ PT}}}{N} \right] = ?$$



Next class:

Rearrange the terms → Cancellations with the ‘divergence’ terms from the background ….

Questions: pcd@physics.iitm.ac.ic

Select/Special Topics from 'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 20

Electron Gas in Hartree Fock and Random Phase Approximations

Plasma Oscillations in Free Electron Gas

Reference: Fetter & Walecka
Quantum Theory of Many-Particle Systems

References: 'The theory of plasma oscillations in metals'
- by S Raimes 1957 *Rep. Prog. Phys.* **20** 1
& 'Many Electron Theory' by Stanley Raimes

$$H = H_{el} + H_b + H_{el-b}$$

Free Electron Gas in Positive Jellium Background Potential

$$H = H_{el} - \frac{1}{2}e^2\frac{N^2}{V}\frac{4\pi}{\mu^2}$$

μ^2 divergence

Does the diverging term cancel with any part of H_{el}?

$$H_{el}^{II\ Q} = \left[\sum_{\vec{k}_1}\sum_{\sigma_1}\frac{\hbar^2 k_1^2}{2m}c^\dagger_{\vec{k}_1\sigma_1}c_{\vec{k}_1\sigma_1} + \frac{1}{2}\sum_{\vec{k}_1,\sigma_1}\sum_{\vec{k}_2,\sigma_2}\sum_{\vec{k}_3,\sigma_3}\sum_{\vec{k}_4,\sigma_4}\delta_{\sigma_1,\sigma_3}\delta_{\sigma_2,\sigma_4}\left(\begin{array}{l}\frac{e^2}{V}\delta\left(\vec{k}_1+\vec{k}_2,\vec{k}_3+\vec{k}_4\right)\\ \frac{4\pi}{\left|\vec{k}_1-\vec{k}_3\right|^2+\mu^2}c^\dagger_{\vec{k}_1\sigma_1}c^\dagger_{\vec{k}_2\sigma_2}c_{\vec{k}_4\sigma_4}c_{\vec{k}_3\sigma_3}\end{array}\right)\right]$$

$$'\delta' \Rightarrow \vec{k}_1+\vec{k}_2=\vec{k}_3+\vec{k}_4 \Rightarrow \vec{k}_4-\vec{k}_2=\vec{k}_1-\vec{k}_3=\vec{q}$$

Momentum transfer

Rearrange the terms → Cancellations with terms from the background….

Reference: Fetter & Walecka - Quantum Theory of Many-Particle Systems; page 24 / Eq.3.15

$$H_{el}^{II\ Q} = \left[\sum_{\vec{k}_1} \sum_{\sigma_1} \frac{\hbar^2 k_1^{\ 2}}{2m} c^\dagger_{\vec{k}_1\sigma_1} c_{\vec{k}_1\sigma_1} + \frac{1}{2} \sum_{\vec{k}_1,\sigma_1} \sum_{\vec{k}_2,\sigma_2} \sum_{\vec{k}_3,\sigma_3} \sum_{\vec{k}_4,\sigma_4} \delta_{\sigma_1,\sigma_3} \delta_{\sigma_2,\sigma_4} \left(\begin{array}{c} \frac{e^2}{V} \delta\left(\vec{k}_1 + \vec{k}_2, \vec{k}_3 + \vec{k}_4\right) \\ \frac{4\pi}{\left|\vec{k}_1 - \vec{k}_3\right|^2 + \mu^2} c^\dagger_{\vec{k}_1\sigma_1} c^\dagger_{\vec{k}_2\sigma_2} c_{\vec{k}_4\sigma_4} c_{\vec{k}_3\sigma_3} \end{array} \right) \right]$$

$$'\left[\delta\left(\vec{k}_1 + \vec{k}_2, \vec{k}_3 + \vec{k}_4\right)\right]' \Rightarrow \vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4$$

$$\vec{k}_4 - \vec{k}_2 = \vec{k}_1 - \vec{k}_3 = \vec{q} : \text{ momentum transfer}$$

constraint

$$\vec{k}_3 = \vec{k}$$

$$\vec{k}_1 = \vec{k}_3 + \vec{q} = \vec{k} + \vec{q}$$

$$\vec{k}_4 = \vec{p}$$

$$\vec{k}_2 = \vec{k}_4 - \vec{q} = \vec{p} - \vec{q}$$

i.e.

$$\vec{k}_1 = \vec{k} + \vec{q}$$

$$\vec{k}_2 = \vec{p} - \vec{q}$$

$$\vec{k}_3 = \vec{k}$$

$$\vec{k}_4 = \vec{p}$$

only 3 variables

$$H_{el}^{II\ Q} = \left[\begin{array}{l} \sum_{\vec{k}_1} \sum_{\sigma_1} \frac{\hbar^2 k_1^2}{2m} c^{\dagger}_{\vec{k}_1\sigma_1} c_{\vec{k}_1\sigma_1} \qquad \boxed{\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4} \\ + \frac{1}{2} \sum_{\vec{k}_1} \sum_{\sigma_1} \sum_{\vec{k}_2} \sum_{\sigma_2} \sum_{\vec{k}_3} \sum_{\vec{k}_4} \left(\begin{array}{l} \frac{e^2}{V} \delta\left(\vec{k}_1 + \vec{k}_2, \vec{k}_3 + \vec{k}_4\right) \times \\ \frac{4\pi}{\left|\vec{k}_1 - \vec{k}_3\right|^2 + \mu^2} c^{\dagger}_{\vec{k}_1\sigma_1} c^{\dagger}_{\vec{k}_2\sigma_2} c_{\vec{k}_4\sigma_2} c_{\vec{k}_3\sigma_1} \end{array} \right) \end{array} \right]$$

$$\vec{k}_1 = \vec{k} + \vec{q}; \quad \vec{k}_2 = \vec{p} - \vec{q}; \quad \vec{k}_3 = \vec{k}; \quad \vec{k}_4 = \vec{p}$$

$$H_{el}^{II\ Q} = \left[\begin{array}{l} \sum_{\vec{k}+\vec{q}} \sum_{\sigma} \frac{\hbar^2 \left(\vec{k} + \vec{q}\right)^2}{2m} c^{\dagger}_{\vec{k}+\vec{q}\sigma} c_{c^{\dagger}_{\vec{k}+\vec{q}}\sigma} \\ + \frac{1}{2} \frac{e^2}{V} \sum_{\vec{k}} \sum_{\vec{p}} \sum_{\vec{q}} \sum_{\sigma_1} \sum_{\sigma_2} \left(\frac{4\pi}{q^2 + \mu^2} c^{\dagger}_{\vec{k}+\vec{q}\sigma_1} c^{\dagger}_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right) \end{array} \right]$$

← K.E. term $\sum_{\vec{k}_1} \equiv \sum_{\vec{k}+\vec{q}}$

separate the $\vec{q} = \vec{0}$ term in the $\boxed{e-e}$ interaction

e-e term

$$H_{e-e}^{II\ Q} = \left[\begin{array}{l} \frac{1}{2} \frac{e^2}{V} \sum_{\vec{k}} \sum_{\vec{p}} \sum_{\vec{q} \neq \vec{0}} \sum_{\sigma_1} \sum_{\sigma_2} \left(\frac{4\pi}{q^2 + \mu^2} c^{\dagger}_{\vec{k}+\vec{q}\sigma_1} c^{\dagger}_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right) \\ + \frac{1}{2} \frac{e^2}{V} \sum_{\vec{k}} \sum_{\vec{p}} \sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}} \sum_{\sigma_2} \left(\frac{4\pi}{\mu^2} c^{\dagger}_{\vec{k}\sigma_1} c^{\dagger}_{\vec{p}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right) \\ \qquad \mu^2 = q^2 + \mu^2 \ \text{for} \ q = 0 \end{array} \right]$$

$$H_{e-e}^{II\ Q} = \left[\begin{array}{l} \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) \\ +\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}}\sum_{\sigma_2}\underbrace{\left(c^\dagger_{\vec{k}\sigma_1}c^\dagger_{\vec{p}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right)} \end{array}\right]$$

$\vec{q}=\vec{0}$ term separated

$$\boxed{\left[c_{r_1\sigma_1}, c_{r_2\sigma_2}{}^\dagger\right]_\pm = \delta_{r_1r_2}\delta_{\sigma_1\sigma_2} \qquad \left[c_{r_1\sigma_1}{}^\dagger, c_{r_2\sigma_2}{}^\dagger\right]_\pm = 0 \qquad \left[c_{r_1\sigma_1}, c_{r_2\sigma_2}\right]_\pm = 0}$$

$$\underbrace{c^\dagger_{\vec{k}\sigma_1}c^\dagger_{\vec{p}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}} = -c^\dagger_{\vec{k}\sigma_1}c^\dagger_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}c_{\vec{p}\sigma_2}$$

$$= \underbrace{c^\dagger_{\vec{k}\sigma_1}c_{\vec{k}\sigma_1}c^\dagger_{\vec{p}\sigma_2}c_{\vec{p}\sigma_2} - c^\dagger_{\vec{k}\sigma_1}c_{\vec{p}\sigma_2}\delta_{\sigma_1,\sigma_2}\delta_{\vec{k},\vec{p}}}$$

$$H_{e-e}^{II\ Q} = \left[\begin{array}{l} \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) \\ +\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}}\sum_{\sigma_2}\underbrace{\left(c^\dagger_{\vec{k}\sigma_1}c_{\vec{k}\sigma_1}c^\dagger_{\vec{p}\sigma_2}c_{\vec{p}\sigma_2} - c^\dagger_{\vec{k}\sigma_1}c_{\vec{p}\sigma_2}\delta_{\sigma_1,\sigma_2}\delta_{\vec{k},\vec{p}}\right)} \end{array}\right]$$

$$H = -\frac{1}{2}\frac{e^2 N^2}{V}\frac{4\pi}{\mu^2} + H_{el}^{II\ Q}$$

$$= -\frac{1}{2}\frac{e^2 N^2}{V}\frac{4\pi}{\mu^2} + \left[\sum_{\vec{k}_1}\sum_{\sigma_1}\frac{\hbar^2 k_1^2}{2m} c^\dagger_{\vec{k}_1\sigma_1} c_{\vec{k}_1\sigma_1} + \boxed{H_{e-e}^{II\ Q}}\right]$$

Reference: Fetter & Walecka - Quantum Theory of Many-Particle Systems; page 24 / Eq.3.15

$$\boxed{H_{e-e}^{II\ Q}} =$$

$$\boxed{\downarrow \vec{q} \neq \vec{0} \text{ terms}}$$

$$= \left[\begin{array}{l} \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2} c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1}\right) \\ +\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}}\sum_{\sigma_2}\left(c^\dagger_{\vec{k}\sigma_1} c_{\vec{k}\sigma_1} c^\dagger_{\vec{p}\sigma_2} c_{\vec{p}\sigma_2} - c^\dagger_{\vec{k}\sigma_1} c_{\vec{p}\sigma_2}\delta_{\sigma_1,\sigma_2}\delta_{\vec{k},\vec{p}}\right) \end{array}\right]$$

$$\boxed{\uparrow \vec{q} = \vec{0} \text{ terms}}$$

$$H_{e-e}^{II\ Q} = \left[\begin{array}{l} \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^{\dagger}_{\vec{k}+\vec{q}\sigma_1}c^{\dagger}_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) \\ +\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\substack{\vec{p}\\ \vec{q}=\vec{0}}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\underbrace{c^{\dagger}_{\vec{k}\sigma_1}c_{\vec{k}\sigma_1}c^{\dagger}_{\vec{p}\sigma_2}c_{\vec{p}\sigma_2}}_{\bigstar}-\underbrace{c^{\dagger}_{\vec{k}\sigma_1}c_{\vec{p}\sigma_2}\delta_{\sigma_1,\sigma_2}\delta_{\vec{k},\vec{p}}}_{\bigstar}\right) \end{array} \right]$$

We now write these two terms separately

$$H_{e-e}^{II\ Q} = \left[\begin{array}{l} \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^{\dagger}_{\vec{k}+\vec{q}\sigma_1}c^{\dagger}_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) \\ +\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\substack{\vec{p}\\ \vec{q}=\vec{0}}}\sum_{\sigma_1}\sum_{\sigma_2}c^{\dagger}_{\vec{k}\sigma_1}c_{\vec{k}\sigma_1}c^{\dagger}_{\vec{p}\sigma_2}c_{\vec{p}\sigma_2} \qquad \bigstar \\ -\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\substack{\vec{p}\\ \vec{q}=\vec{0}}}\sum_{\sigma_1}\sum_{\sigma_2}c^{\dagger}_{\vec{k}\sigma_1}c_{\vec{p}\sigma_2}\delta_{\sigma_1,\sigma_2}\delta_{\vec{k},\vec{p}} \qquad \bigstar \end{array} \right]$$

$$H_{e-e}^{II\ Q} = \left[\begin{array}{l} \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) \\ +\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}}\sum_{\sigma_2} \underbrace{c^\dagger_{\vec{k}\sigma_1}c_{\vec{k}\sigma_1}}\underbrace{c^\dagger_{\vec{p}\sigma_2}c_{\vec{p}\sigma_2}} \\ -\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}}\sum_{\sigma_2} \underbrace{c^\dagger_{\vec{k}\sigma_1}c_{\vec{p}\sigma_2}}\underbrace{\delta_{\sigma_1,\sigma_2}\delta_{\vec{k},\vec{p}}} \end{array} \right]$$

Number operator

$$H_{e-e}^{II\ Q} = \left[\begin{array}{l} \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) \\ +\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}}\sum_{\sigma_2} n_{\vec{k}\sigma_1}n_{\vec{p}\sigma_2} \\ -\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}} n_{\vec{k}\sigma_1} \end{array} \right]$$

$$H_{el}^{II\ Q}, ST = \left[\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) + \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}}\sum_{\sigma_2} n_{\vec{k}\sigma_1}n_{\vec{p}\sigma_2} - \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\sum_{\vec{k}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}} n_{\vec{k}\sigma_1} \right]$$

$\downarrow \vec{q} \neq \vec{0}$ terms

$$H_{el}^{II\ Q}, ST = \left[\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\boxed{\sum_{\vec{q}\neq\vec{0}}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) + \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\left(\sum_{\vec{k}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}} n_{\vec{k}\sigma_1}\right)\left(\sum_{\vec{p}}\sum_{\sigma_2} n_{\vec{p}\sigma_2}\right) - \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\left(\sum_{\vec{k}}\sum_{\substack{\sigma_1 \\ \vec{q}=\vec{0}}} n_{\vec{k}\sigma_1}\right) \right]$$

The above summations give the total number operator

$$H_{el}^{II\ Q}, ST = \left[\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) + \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\hat{N}^2 - \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\hat{N} \right]$$

$\vec{q} = \vec{0}$ terms

$$H_{e-e}^{II\ Q} = \left[\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) + \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\hat{N}^2 - \frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}\hat{N} \right]$$

We now replace the number operators by their eigenvalues

$$H_{e-e}^{II\ Q} = \left[\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) + \frac{1}{2}\frac{e^2}{V}\frac{4\pi N^2}{\mu^2} - \frac{1}{2}\frac{e^2}{V}\frac{4\pi N}{\mu^2} \right]$$

$\boxed{\vec{q}=\vec{0}\ \text{terms}}$

C-number contributions having μ^{-2} divergence

$$\vec{q} = \vec{0} \text{ terms } \rightarrow \cancel{+\frac{1}{2}\frac{e^2}{V}\frac{4\pi N^2}{\mu^2}} \boxed{-\frac{1}{2}\frac{e^2}{V}\frac{4\pi N}{\mu^2}}$$

C-number contributions to H_{e-e} *and* hence to

$$H = H_{el} + \underbrace{H_b + H_{el-b}}$$

contribution to $\frac{E_{HF}}{N}$: *per* particle

$$\boxed{-\frac{1}{2}\frac{e^2}{V}\frac{4\pi}{\mu^2}}$$

From slide 100:

$$H = H_{el} \underbrace{\cancel{-\frac{1}{2}e^2\frac{N^2}{V}\frac{4\pi}{\mu^2}}}$$

$First : V \rightarrow \infty, \quad next : \mu \rightarrow 0$

$L^3 = V : \quad \frac{1}{\mu} \ll L; \quad \frac{1}{L} \ll \mu$

Reference: Fetter & Walecka
Quantum Theory of Many-Particle Systems;
page 25

$$H_{e-e} = \left[\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2+\mu^2}c^{\dagger}_{\vec{k}+\vec{q}\,\sigma_1}c^{\dagger}_{\vec{p}-\vec{q}\,\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) + \cancel{\frac{1}{2}\frac{e^2}{V}\frac{4\pi N^2}{\mu^2}} - \cancel{\frac{1}{2}\frac{e^2}{V}\frac{4\pi N}{\mu^2}} \right]$$

$$\boxed{\vec{q}=\vec{0}\ \text{terms}}$$

cancel

$$H = H_{el} + \cancel{H_b + H_{el-b}}$$

$$1]\quad \lim_{V\to\infty}\frac{E_{HF}}{N}$$

Hamiltonian for a bulk electron gas in a uniform positive background jellium potential

$$H = \left[\sum_{\vec{k}}\sum_{\sigma}\frac{\hbar^2\vec{k}^2}{2m}c^{\dagger}_{\vec{k}\sigma}c_{\vec{k}\sigma} + \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{q}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{q^2}c^{\dagger}_{\vec{k}+\vec{q}\,\sigma_1}c^{\dagger}_{\vec{p}-\vec{q}\,\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right) \right]$$

$$2]\quad \mu \to 0$$

Reference: Fetter & Walecka
Quantum Theory of Many-Particle Systems; page 25 /
Eq.3.19

Hamiltonian for a bulk electron gas in a uniform positive background jellium potential

Ref: F & W; page 25 / Eq.3.19

$$H=\sum_{\vec{k}}\sum_{\sigma}\frac{\hbar^2\vec{k}^2}{2m}c^{\dagger}_{\vec{k}\sigma}c_{\vec{k}\sigma}+\frac{1}{2}\frac{e^2}{V}\sum_{\vec{k},\sigma_1}\sum_{\vec{p},\sigma_2}\sum_{\vec{q}\neq\vec{0}}\left(\frac{4\pi}{q^2}c^{\dagger}_{\vec{k}+\vec{q}\sigma_1}c^{\dagger}_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right)$$

$N\times\left(\frac{4}{3}\pi r_s^{\,3}\right)=V\leftrightarrow r_s$: radius of a sphere whose volume is equal to the average volume per electron.

$length\ scale:$

$$Bohr\ radius=a_0=\frac{\hbar^2}{me^2}$$

$$\text{dimensionless}:\ r_0=\frac{r_s}{a_0}$$

$$\text{scaling:}\quad \tilde{\vec{k}}=r_s\vec{k};\quad \tilde{V}=\frac{V}{r_s^{\,3}};\quad \tilde{\vec{p}}=r_s\vec{p};\quad \tilde{q}=r_s q$$

$$\frac{\hbar^2\vec{k}^2}{2m}=?\qquad\qquad \frac{1}{2}\frac{e^2}{V}\frac{1}{q^2}=?$$

$$\textit{length scale}:$$

$$\textit{Bohr radius} = a_0 = \frac{\hbar^2}{me^2}$$

$$\text{dimensionless}: \; r_0 = \frac{r_s}{a_0}$$

$$\text{scaling:} \quad \vec{\tilde{k}} = r_s \vec{k}; \quad \tilde{V} = \frac{V}{r_s^3}; \quad \vec{\tilde{p}} = r_s \vec{p}; \quad \tilde{q} = r_s q$$

$$\frac{\hbar^2 \vec{k}^2}{2m} = \frac{\hbar^2 \left(\frac{\vec{\tilde{k}}}{r_s} \right)^2}{2m} = \left(\frac{1}{r_s} \right)^2 \frac{\hbar^2 \vec{\tilde{k}}^2}{2m}$$

$$= \left(\frac{1}{a_0 r_0} \right)^2 \frac{\hbar^2 \vec{\tilde{k}}^2}{2m} = \left(\frac{me^2}{\hbar^2 r_0} \right) \left(\frac{me^2}{\hbar^2 r_0} \right) \frac{\hbar^2 \vec{\tilde{k}}^2}{2m}$$

$$= \boxed{\left(\frac{e^2}{a_0 r_0^{\;2}} \right) \frac{\vec{\tilde{k}}^2}{2}}$$

$$\frac{e^2}{2V} \frac{1}{q^2} = \frac{e^2}{2 r_s^{\;3} \tilde{V}} \frac{r_s^{\;2}}{\tilde{q}^2}$$

$$= \frac{e^2}{2 a_0 r_0 \tilde{V}} \frac{1}{\tilde{q}^2}$$

$$= \boxed{\frac{e^2}{a_0 r_0^{\;2}} \frac{r_0}{2\tilde{V}} \frac{1}{\tilde{q}^2}}$$

Hamiltonian for a bulk electron gas in a uniform positive background jellium potential

$$H = \sum_{\vec{k}} \sum_{\sigma} \frac{\hbar^2 \vec{k}^2}{2m} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} + \frac{1}{2}\frac{e^2}{V} \sum_{\vec{k},\sigma_1} \sum_{\vec{p},\sigma_2} \sum_{\vec{q}\neq\vec{0}} \left(\frac{4\pi}{q^2} c^{\dagger}_{\vec{k}+\vec{q}\sigma_1} c^{\dagger}_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right)$$

$$\frac{\hbar^2 \vec{k}^2}{2m} = \left(\frac{e^2}{a_0 r_0{}^2} \right) \frac{\vec{\tilde{k}}^2}{2} \qquad \frac{e^2}{2V}\frac{1}{q^2} = \left(\frac{e^2}{a_0 r_0{}^2} \right) \frac{r_0}{2\tilde{V}} \frac{1}{\tilde{q}^2}$$

$$H = \left(\frac{e^2}{a_0 r_0{}^2} \right) \left[\sum_{\vec{\tilde{k}}} \sum_{\sigma} \frac{\vec{\tilde{k}}^2}{2} c^{\dagger}_{\vec{\tilde{k}}\sigma} c_{\vec{\tilde{k}}\sigma} + \frac{1}{2}\frac{r_0}{\tilde{V}} \sum_{\vec{\tilde{k}}} \sum_{\vec{\tilde{p}}} \sum_{\vec{\tilde{q}}\neq\vec{0}} \sum_{\sigma_1} \sum_{\sigma_2} \left(\frac{4\pi}{\tilde{q}^2} c^{\dagger}_{\vec{\tilde{k}}+\vec{\tilde{q}}\sigma_1} c^{\dagger}_{\vec{\tilde{p}}-\vec{\tilde{q}}\sigma_2} c_{\vec{\tilde{p}}\sigma_2} c_{\vec{\tilde{k}}\sigma_1} \right) \right]$$

Reference: Fetter & Walecka
Quantum Theory of Many-Particle Systems; page 25 / Eq.3.24

$$H = \left(\frac{e^2}{a_0 r_0^{\ 2}}\right)\left[\sum_{\tilde{\vec{k}}}\sum_{\sigma}\frac{\tilde{\vec{k}}^2}{2}c^\dagger_{\tilde{\vec{k}}\sigma}c_{\tilde{\vec{k}}\sigma} + \frac{1}{2}\frac{r_0}{\tilde{V}}\sum_{\tilde{\vec{k}}}\sum_{\tilde{\vec{p}}}\sum_{\tilde{\vec{q}}\neq\vec{0}}\sum_{\sigma_1}\sum_{\sigma_2}\left(\frac{4\pi}{\tilde{q}^2}c^\dagger_{\tilde{\vec{k}}+\tilde{\vec{q}}\sigma_1}c^\dagger_{\tilde{\vec{p}}-\tilde{\vec{q}}\sigma_2}c_{\tilde{\vec{p}}\sigma_2}c_{\tilde{\vec{k}}\sigma_1}\right)\right]$$

Reference: Fetter & Walecka
Quantum Theory of Many-Particle Systems; page 25 / Eq.3.24

$r_0 \to 0$: "high density" 1st order perturbative treatment possible even if the perturbation is not weak.

$$H = \sum_{\vec{k}}\sum_{\sigma}\frac{\hbar^2\vec{k}^2}{2m}c^\dagger_{\vec{k}\sigma}c_{\vec{k}\sigma} + \frac{1}{2}\frac{e^2}{V}\sum_{\vec{k},\sigma_1}\sum_{\vec{p},\sigma_2}\sum_{\vec{q}\neq\vec{0}}\left(\frac{4\pi}{q^2}c^\dagger_{\vec{k}+\vec{q}\sigma_1}c^\dagger_{\vec{p}-\vec{q}\sigma_2}c_{\vec{p}\sigma_2}c_{\vec{k}\sigma_1}\right)$$

$$= H_0 \ (\text{unperturbed part}) + H_1 (\text{perturbation})$$

Reference: Fetter & Walecka
Quantum Theory of Many-Particle Systems; page 25 / Eq.3.24

$$\langle \Phi_0 | H | \Phi_0 \rangle = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$\langle \Phi_0 | H_0 | \Phi_0 \rangle = \left\langle \Phi_0 \left| \sum_{\vec{k}} \sum_{\sigma} \frac{\hbar^2 \vec{k}^2}{2m} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} \right| \Phi_0 \right\rangle$$

$$= \sum_{\vec{k}} \sum_{\sigma} \frac{\hbar^2 \vec{k}^2}{2m} = 2 \sum_{|\vec{k}| \leq |\vec{k}_F|} \frac{\hbar^2 \vec{k}^2}{2m}$$

$$\boxed{\sum_{\vec{k}'} \rightarrow \frac{1}{\left(\frac{2\pi}{L}\right)^3} \iiint d^3\vec{k}' : \text{integration in } \vec{k} \text{ space}}$$

STiTACS Unit 3 ← Lecture 18 Slide No. 80

$$\langle \Phi_0 | H_0 | \Phi_0 \rangle = 2 \times \frac{V}{8\pi^3} \times 4\pi \int_{k=0}^{k=k_f} k^2 dk \frac{\hbar^2 \vec{k}^2}{2m}$$

$$H = \sum_{\vec{k}} \sum_{\sigma} \frac{\hbar^2 \vec{k}^2}{2m} c^\dagger_{\vec{k}\sigma} c_{\vec{k}\sigma} + \frac{1}{2}\frac{e^2}{V} \sum_{\vec{k},\sigma_1} \sum_{\vec{p},\sigma_2} \sum_{\vec{q}\neq\vec{0}} \left(\frac{4\pi}{q^2} c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right)$$

Ref: F & W

$$= H_0 \,(\text{unperturbed part}) + H_1 \,(\text{perturbation})$$

QToMPS; p 25 Eq.3.19

$$\langle \Phi_0 | H | \Phi_0 \rangle = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | H_1 | \Phi_0 \rangle$$

$$\langle \Phi_0 | H_0 | \Phi_0 \rangle = \left\langle \Phi_0 \left| \sum_{\vec{k}} \sum_{\sigma} \frac{\hbar^2 \vec{k}^2}{2m} c^\dagger_{\vec{k}\sigma} c_{\vec{k}\sigma} \right| \Phi_0 \right\rangle$$

$$= \sum_{\vec{k}} \sum_{\sigma} \frac{\hbar^2 \vec{k}^2}{2m} = 2 \sum_{|\vec{k}| \le |\vec{k}_F|} \frac{\hbar^2 \vec{k}^2}{2m}$$

$$\langle \Phi_0 | H_0 | \Phi_0 \rangle = 2 \times \frac{V}{8\pi^3} \times 4\pi \int_{k=0}^{k=k_f} k^2 dk \frac{\hbar^2 \vec{k}^2}{2m}$$

$$= \frac{\hbar^2}{m} \times \frac{V}{8\pi^3} \times 4\pi \int_{k=0}^{k=k_f} k^4 dk$$

$$= \frac{\hbar^2}{m} \times \frac{V}{8\pi^3} \times 4\pi \frac{k_F^5}{5} = \frac{\hbar^2 V}{10 m \pi^2} k_F^5$$

K.E. contribution to the *average* HF ground state energy *per electron* in a free-electron-gas .

$$\left[\frac{E_{HF}^{(0)}}{N} \right] = \left(\frac{2.21}{r_s^2} \right) Ryd$$

Ref: F & W

QToMPS; p 27 Eq.3.30

Same: Slide 85↑

$$H = \sum_{\vec{k}} \sum_{\sigma} \frac{\hbar^2 \vec{k}^2}{2m} c^\dagger_{\vec{k}\sigma} c_{\vec{k}\sigma} + \frac{1}{2}\frac{e^2}{V} \sum_{\vec{k},\sigma_1} \sum_{\vec{p},\sigma_2} \sum_{\vec{q}\neq\vec{0}} \left(\frac{4\pi}{q^2} c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right)$$

$$= H_0 \text{ (unperturbed part)} + H_1 \text{ (perturbation)}$$

$$\langle \Phi_0 | H | \Phi_0 \rangle = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \boxed{\langle \Phi_0 | H_1 | \Phi_0 \rangle}$$

First order ←Perturbation Theory

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle = \left\langle \Phi_0 \left| \frac{1}{2}\frac{e^2}{V} \sum_{\vec{k},\sigma_1} \sum_{\vec{p},\sigma_2} \sum_{\vec{q}\neq\vec{0}} \left(\frac{4\pi}{q^2} c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right) \right| \Phi_0 \right\rangle$$

$$= \sum_{\vec{k},\sigma_1} \sum_{\vec{p},\sigma_2} \sum_{\vec{q}\neq\vec{0}} \frac{1}{2}\frac{4\pi}{q^2}\frac{e^2}{V} \langle \Phi_0 | c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} | \Phi_0 \rangle$$

Ref: F & W

QToMPS; p 27 Eq.3.31

$$\langle \Phi_0 | c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} | \Phi_0 \rangle \underset{\substack{would\\be}}{=} 0$$

unless $p, k \le k_f$ so that $c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1}$ annihilate electrons in those states

and $c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2}$ create particles in the same/corresponding empty states.

$$\left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle \underset{\substack{would\\be}}{=} 0$$

unless $p, k \le k_f$ so that $c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1}$ annihilate electrons in those states

and $c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2}$ create particles in the same/corresponding empty states.

$$\Rightarrow \ (1)\ \vec{k}+\vec{q}, \sigma_1 = \vec{k}, \sigma_1 \quad \& \quad \vec{p}-\vec{q}, \sigma_2 = \vec{p}, \sigma_2$$

$$\text{or} \quad (2)\ \vec{k}+\vec{q}, \sigma_1 = \vec{p}, \sigma_2 \quad \& \quad \vec{p}-\vec{q}, \sigma_2 = \vec{k}, \sigma_1$$

$\vec{q} \ne \vec{0} \Rightarrow$ second possibility must be correct, not first.

$$\Rightarrow \left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle = \delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_1,\sigma_2} \left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} \underbrace{c^\dagger_{\vec{k}\sigma_1} c_{\vec{k}+\vec{q}\sigma_1}} c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle$$

$$\left[a_r, a_s^\dagger \right]_+ = \delta_{rs} \underset{q \ne 0}{\Rightarrow} c^\dagger_{\vec{k}\sigma_1} c_{\vec{k}+\vec{q}\sigma_1} = -c_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{k}\sigma_1}$$

$$\Rightarrow \left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle = \delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_1,\sigma_2} \left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} \left(-c_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{k}\sigma_1} \right) c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle$$

$$\left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_2} c_{\vec{p}\sigma_2} c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle = \delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_1,\sigma_2} \left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} \left(-c_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{k}\sigma_1} \right) c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle$$

$$we\ had:\ \left\langle \Phi_0 \left| H_1 \right| \Phi_0 \right\rangle = \sum_{\vec{k},\sigma_1} \sum_{\vec{p},\sigma_2} \sum_{\vec{q}\neq\vec{0}} \frac{1}{2}\left(\frac{4\pi}{q^2}\right)\frac{e^2}{V} \left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{p}-\vec{q}\sigma_1} c_{\vec{p}\sigma_1} c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle$$

$$\left\langle \Phi_0 \left| H_1 \right| \Phi_0 \right\rangle =$$

$$= \sum_{\vec{k}} \sum_{\vec{p}} \sum_{\vec{q}\neq\vec{0}} \sum_{\sigma_1} \sum_{\sigma_2} \frac{1}{2}\left(\frac{4\pi}{q^2}\right)\frac{e^2}{V} \left\{ -\delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_1,\sigma_2} \left\langle \Phi_0 \left| c^\dagger_{\vec{k}+\vec{q}\sigma_1} c_{\vec{k}+\vec{q}\sigma_1} c^\dagger_{\vec{k}\sigma_1} c_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle \right\}$$

$$\left\langle \Phi_0 \left| H_1 \right| \Phi_0 \right\rangle =$$

number operators

$$= -\sum_{\vec{k}} \sum_{\vec{p}} \sum_{\vec{q}\neq\vec{0}} \sum_{\sigma_1} \sum_{\sigma_2} \frac{1}{2}\left(\frac{4\pi}{q^2}\right)\frac{e^2}{V} \delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_1,\sigma_2} \left\langle \Phi_0 \left| n_{\vec{k}+\vec{q}\sigma_1} n_{\vec{k}\sigma_1} \right| \Phi_0 \right\rangle$$

$$\left\langle \Phi_0 \left| n_{\vec{k}+\vec{q},\sigma_1} n_{\vec{k},\sigma_1} \right| \Phi_0 \right\rangle = 1 \text{ for } \left|\vec{k}+\vec{q}\right| \leq k_F \ \underline{and}\ k \leq k_F$$

$$= 0 \text{ for } \left|\vec{k}+\vec{q}\right| > k_F \ \underline{or}\ k > k_F \ (\text{or both } > k_f)$$

$$\left\langle \Phi_0 \middle| H_1 \middle| \Phi_0 \right\rangle =$$

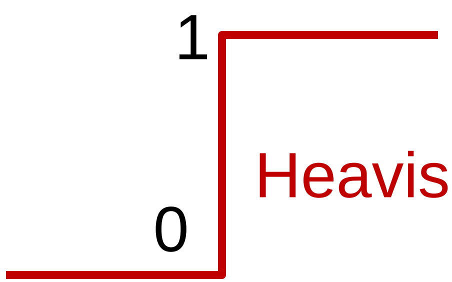
$$= -\sum_{\vec{k}} \sum_{\vec{p}} \sum_{\vec{q} \neq \vec{0}} \sum_{\sigma_1} \sum_{\sigma_2} \frac{1}{2} \frac{4\pi}{q^2} \frac{e^2}{V} \delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_2,\sigma_1} \left\langle \Phi_0 \middle| n_{\vec{k}+\vec{q},\sigma_1} n_{\vec{k},\sigma_1} \middle| \Phi_0 \right\rangle$$

$$\left\langle \Phi_0 \middle| n_{\vec{k}+\vec{q},\sigma_1} n_{\vec{k},\sigma_1} \middle| \Phi_0 \right\rangle = 1 \text{ for } \left|\vec{k}+\vec{q}\right| \leq k_F \ \underline{and} \ k \leq k_F$$

$$= 0 \text{ for } \left|\vec{k}+\vec{q}\right| > k_F \ \underline{or} \ k > k_F \ \underline{or} \ both > k_F$$

$$\left\langle \Phi_0 \middle| n_{\vec{k}+\vec{q}\sigma_1} n_{\vec{k}\sigma_1} \middle| \Phi_0 \right\rangle = 1 \text{ for } \left(\left|\vec{k}+\vec{q}\right| - k_F\right) \leq 0 \ \underline{and} \ \left(k - k_F\right) \leq 0$$

$$= 0 \text{ for } \left(\left|\vec{k}+\vec{q}\right| - k_F\right) > 0 \ \underline{or} \ \left(k - k_F\right) > 0$$



Heaviside step function

i.e. $$\left\langle \Phi_0 \middle| n_{\vec{k}+\vec{q}\sigma_1} n_{\vec{k}\sigma_1} \middle| \Phi_0 \right\rangle = \theta\left(k_F - \left|\vec{k}+\vec{q}\right|\right) \times \theta\left(k_F - k\right)$$

$$\left\langle \Phi_0 \left| H_1 \right| \Phi_0 \right\rangle =$$

$$= -\sum_{\vec{k}} \sum_{\vec{p}} \sum_{\vec{q}\neq\vec{0}} \sum_{\sigma_1} \sum_{\sigma_2} \frac{1}{2} \frac{4\pi}{q^2} \frac{e^2}{V} \delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_2,\sigma_1} \left\langle \Phi_0 \left| n_{\vec{k}+\vec{q},\sigma_1} n_{\vec{k},\sigma_1} \right| \Phi_0 \right\rangle$$

$$\left\langle \Phi_0 \left| n_{\vec{k}+\vec{q},\sigma_1} n_{\vec{k},\sigma_1} \right| \Phi_0 \right\rangle = \theta\left(k_F - \left|\vec{k}+\vec{q}\right|\right) \times \theta\left(k_F - k\right)$$

$$\left\langle \Phi_0 \left| H_1 \right| \Phi_0 \right\rangle =$$

$$= -\sum_{\vec{k}} \sum_{\vec{p}} \sum_{\vec{q}\neq\vec{0}} \sum_{\sigma_1} \sum_{\sigma_2} \frac{1}{2} \frac{4\pi}{q^2} \frac{e^2}{V} \delta_{\vec{k}+\vec{q},\vec{p}} \delta_{\sigma_2\sigma_1} \theta\left(k_F - \left|\vec{k}+\vec{q}\right|\right) \theta\left(k_F - k\right)$$

Ref: F & W

QToMPS; p 28 Eq.3.33

$$= -\sum_{\vec{k}} \sum_{\vec{q}\neq\vec{0}} \frac{4\pi}{q^2} \frac{e^2}{V} \theta\left(k_F - \left|\vec{k}+\vec{q}\right|\right) \theta\left(k_F - k\right)$$

$$\left\langle \Phi_0 \left| H_1 \right| \Phi_0 \right\rangle = -\sum_{\vec{k}} \sum_{\vec{q}\neq\vec{0}} \frac{4\pi}{q^2} \frac{e^2}{V} \theta\left(k_F - \left|\vec{k}+\vec{q}\right|\right) \theta\left(k_F - k\right)$$

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle = -\underbrace{\sum_{\vec{k}}}\ \underbrace{\sum_{\vec{q}\neq\vec{0}}} \frac{4\pi}{q^2}\frac{e^2}{V}\theta\left(k_F - |\vec{k}+\vec{q}|\right)\theta\left(k_F - k\right)$$

From Unit 3, Lecture 18, Slide Number 80:

$$\sum_{\vec{k}'} \rightarrow \left(\frac{L}{2\pi}\right)^3 \iiint d^3\vec{k}'$$

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle = -\underbrace{\left(\frac{L}{2\pi}\right)^3 \iiint d^3\vec{k}}\ \underbrace{\left(\frac{L}{2\pi}\right)^3 \iiint d^3\vec{q}}\left[\frac{4\pi}{q^2}\frac{e^2}{V}\theta\left(k_F - |\vec{k}+\vec{q}|\right)\theta\left(k_F - k\right)\right]$$

$q = 0$ <u>now</u> included: $d^3\vec{q} = q^2 dq \sin\theta d\theta d\phi$

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle = -\frac{4\pi e^2 V}{(2\pi)^6}\iiint d^3\vec{k} \iiint d^3\vec{q}\left[\frac{1}{q^2}\theta\left(k_F - |\vec{k}+\vec{q}|\right)\theta\left(k_F - k\right)\right]$$

Ref: F & W

QToMPS; p 28 Eq.3.34

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle = -\frac{4\pi e^2 V}{(2\pi)^6} \iiint d^3\vec{k} \iiint d^3\vec{q} \left[\frac{1}{q^2} \theta\left(k_F - |\vec{k}+\vec{q}|\right) \theta\left(k_F - k\right) \right]$$

Ref: F & W

QToMPS; p 28 Eq.3.34

change variable, $\vec{k} \rightarrow \left(\vec{k} + \frac{1}{2}\vec{q}\right) = \vec{P}$

$$\boxed{\iiint d^3\vec{k} \rightarrow \iiint d^3\vec{P}}$$

i.e. $\vec{k} = \vec{P} - \frac{1}{2}\vec{q}$ consequently: $\left(\vec{k} + \vec{q}\right) = \left(\vec{P} + \frac{1}{2}\vec{q}\right)$

Note the symmetry

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle = $$

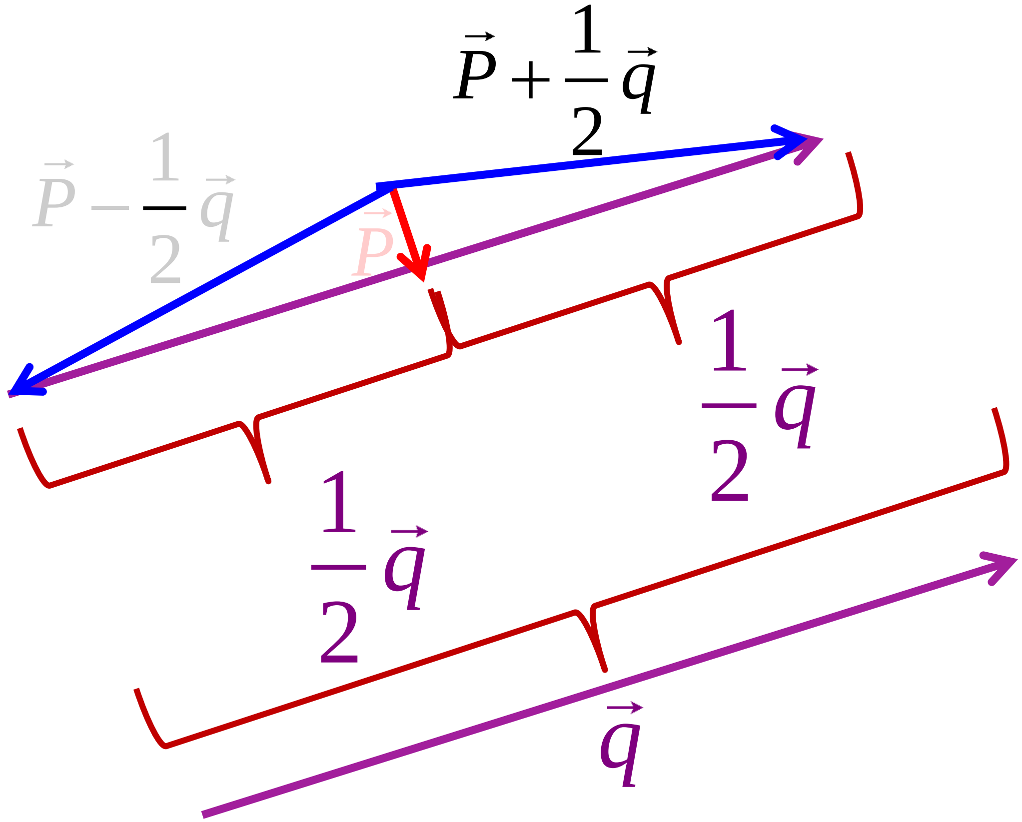
$$= -\frac{4\pi e^2 V}{(2\pi)^6} \iiint d^3\vec{q} \frac{1}{q^2} \underbrace{\left\{ \iiint d^3\vec{P} \left[\theta\left(k_F - \overbrace{\left|\vec{P} + \frac{1}{2}\vec{q}\right|} \right) \theta\left(k_F - \overbrace{\left|\vec{P} - \frac{1}{2}\vec{q}\right|} \right) \right] \right\}}$$

We have to evaluate this volume in the k-space.

$$\langle \Phi_0 | H_1 | \Phi_0 \rangle =$$

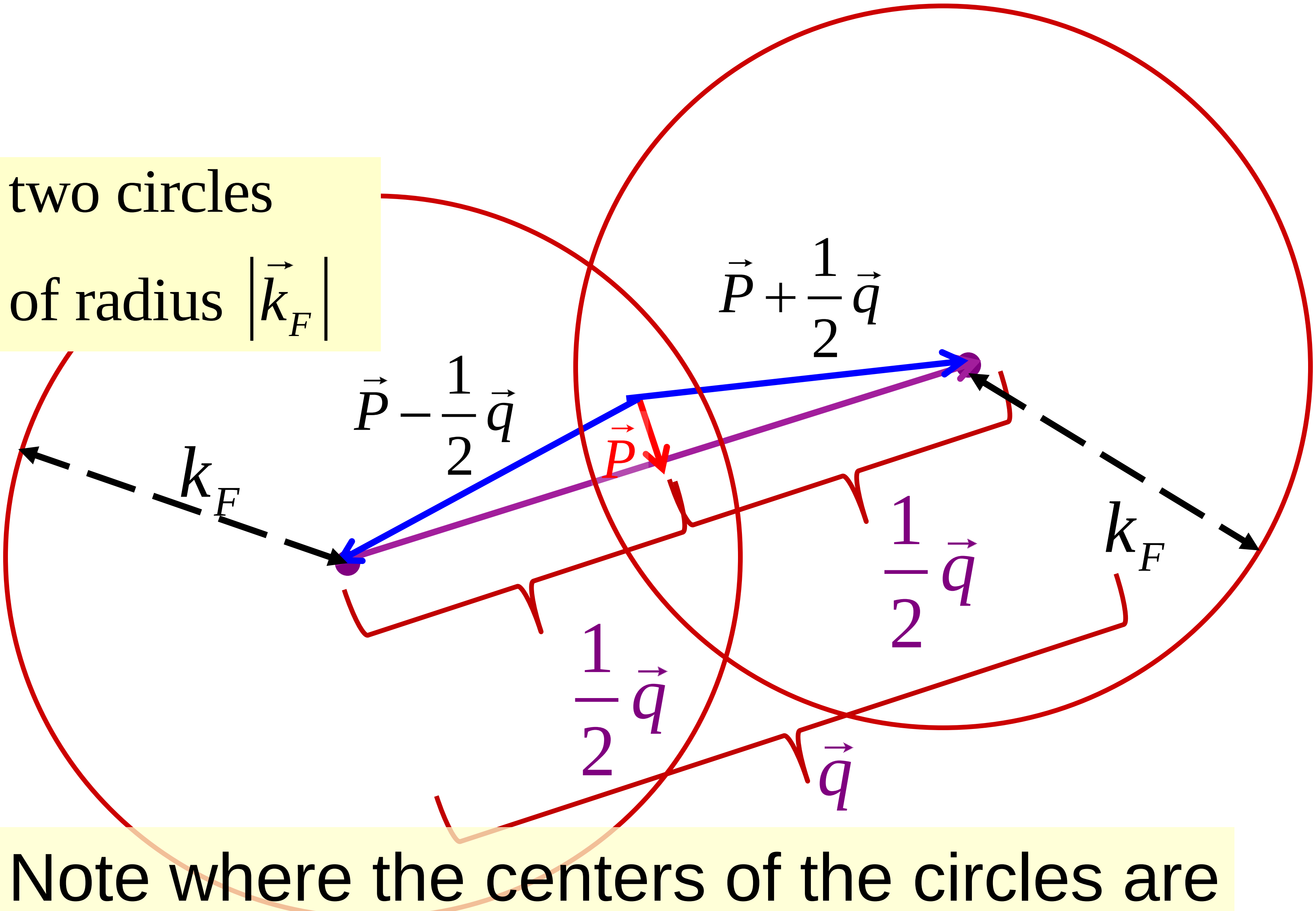
We have to evaluate this volume in the k-space.

$$= -\frac{4\pi e^2 V}{(2\pi)^6} \iiint d^3\vec{q}\, \frac{1}{q^2} \boxed{\left\{ \iiint d^3\vec{P} \left[\theta\left(k_F - \left| \vec{P} + \frac{1}{2}\vec{q} \right| \right) \theta\left(k_F - \left| \vec{P} - \frac{1}{2}\vec{q} \right| \right) \right] \right\}}$$



two circles

of radius $\left|\vec{k}_F\right|$

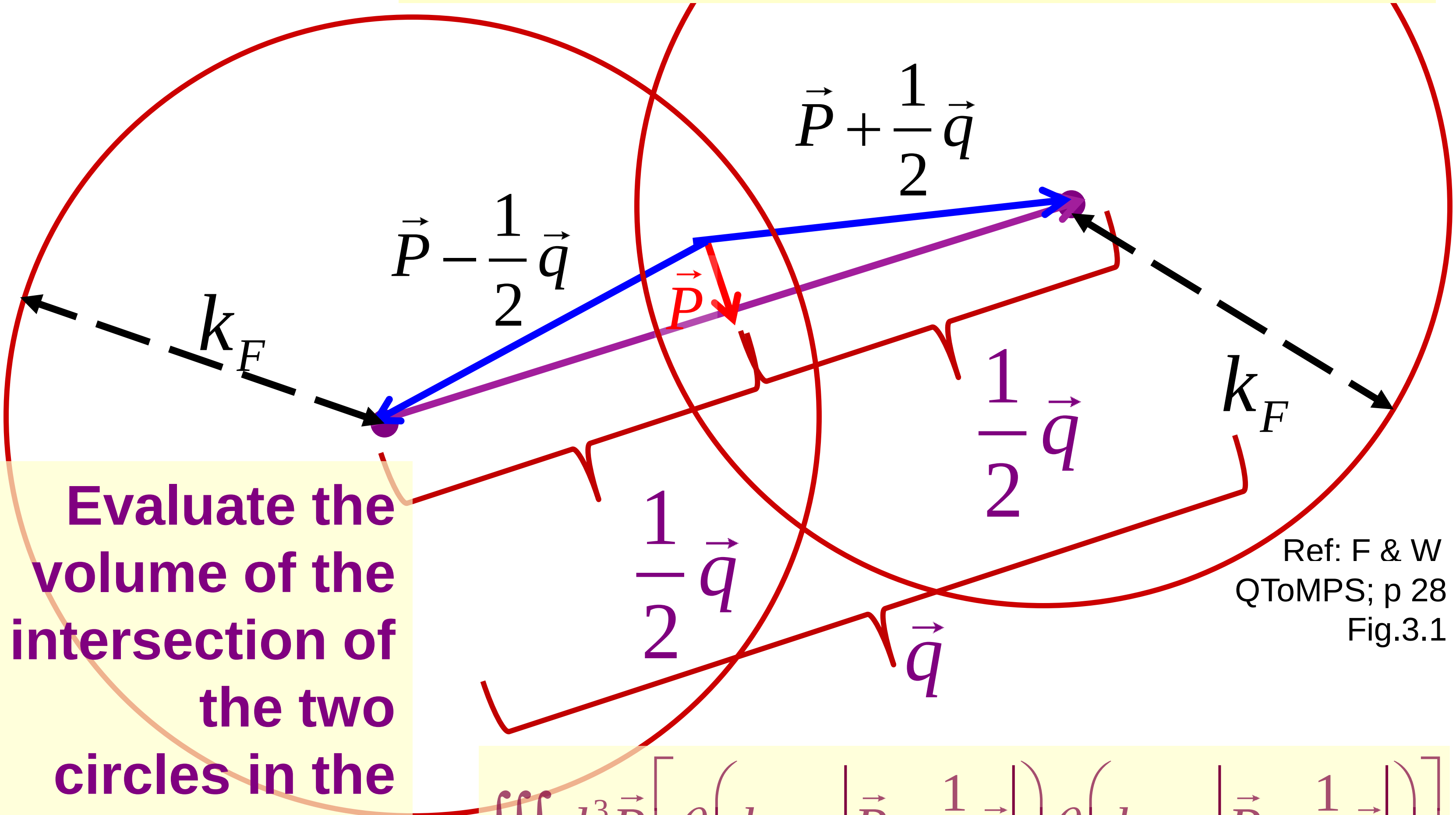


Note where the centers of the circles are chosen

k_F : radius of the circles

in the region of intersection of the two circles,

we have $\left|\vec{P}+\frac{1}{2}\vec{q}\right|<k_F$ $\boxed{and\ \ also}$ $\left|\vec{P}-\frac{1}{2}\vec{q}\right|<k_F$



Ref: F & W QToMPS; p 28 Fig.3.1

Evaluate the volume of the intersection of the two circles in the k-space.

$$\iiint d^3\vec{P}\left[\theta\left(k_F-\left|\vec{P}+\frac{1}{2}\vec{q}\right|\right)\theta\left(k_F-\left|\vec{P}-\frac{1}{2}\vec{q}\right|\right)\right]$$

$$\left\langle \Phi_0 \middle| H_1 \middle| \Phi_0 \right\rangle =$$

$$= -\frac{4\pi e^2 V}{(2\pi)^6} \iiint d^3\vec{q}\, \frac{1}{q^2} \boxed{\left\{ \iiint d^3\vec{P} \left[\theta\left(k_F - \left| \vec{P} + \frac{1}{2}\vec{q} \right| \right) \theta\left(k_F - \left| \vec{P} - \frac{1}{2}\vec{q} \right| \right) \right] \right\}}$$

$$\iiint d^3\vec{P} \left[\theta\left(k_F - \left| \vec{P} + \frac{1}{2}\vec{q} \right| \right) \theta\left(k_F - \left| \vec{P} - \frac{1}{2}\vec{q} \right| \right) \right] = \frac{4\pi}{3} k_F{}^3 \left(1 - \frac{3}{2}x + \frac{1}{2}x^3 \right) \theta(1-x),$$

F&W: QToMPS; p 28 Eq.3.35

$$with \quad x = \frac{q}{2k_F}$$

$$\left\langle \Phi_0 \middle| H_1 \middle| \Phi_0 \right\rangle =$$

$$= -\frac{4\pi e^2 V}{(2\pi)^6} \int_{\substack{whole\\ space}} \left(4\pi \cancel{q^2}\, dq \right) \frac{1}{\cancel{q^2}} \left\{ \frac{4\pi}{3} k_F{}^3 \left(1 - \frac{3}{2}x + \frac{1}{2}x^3 \right) \theta(1-x) \right\}$$

$$= -\frac{4\pi e^2 V}{(2\pi)^6} \int_{\substack{whole\\ space}} \left(4\pi 2k_F dx \right) \left\{ \frac{4\pi}{3} k_F{}^3 \left(1 - \frac{3}{2}x + \frac{1}{2}x^3 \right) \theta(1-x) \right\}$$

$$with \quad 2k_F dx = dq$$

$$\left\langle \Phi_0 \middle| H_1 \middle| \Phi_0 \right\rangle =$$

$$= -\frac{4\pi e^2 V}{(2\pi)^6} \iiint d^3\vec{q}\, \frac{1}{q^2} \left\{ \iiint d^3\vec{P} \left[\theta\left(k_F - \left| \vec{P} + \frac{1}{2}\vec{q} \right| \right) \theta\left(k_F - \left| \vec{P} - \frac{1}{2}\vec{q} \right| \right) \right] \right\}$$

$$= -\frac{4\pi e^2 V}{(2\pi)^6} \int_{\substack{whole\\ space}} (4\pi 2k_F dx) \left\{ \frac{4\pi}{3} k_F^{\ 3} \left(1 - \frac{3}{2}x + \frac{1}{2}x^3 \right) \theta(1-x) \right\}$$

$$= -\frac{4\pi e^2 V}{(2\pi)^6} \frac{4\pi}{3} k_F^{\ 3} \ (4\pi \times 2k_F) \int_{x=0}^{x=1} dx \left\{ \left(1 - \frac{3}{2}x + \frac{1}{2}x^3 \right) \right\} \qquad with \quad x = \frac{q}{2k_F}$$

$$r_s = \frac{\left(9\pi/4 \right)^{1/3}}{k_f} \ldots$$

....from slide 89, STiTACS, Unit3, Lecture 19

$$\underset{atomic\ units}{energy} \rightarrow \frac{me^4}{(4\pi\varepsilon_0 \hbar)^2} = 1$$

$$\underset{atomic\ units}{\text{distance}} \rightarrow a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2}$$

$$\underset{atomic\ units}{permittivity\ of\ vacuum} \rightarrow 4\pi\varepsilon_0 = 1$$

$$\underset{atomic\ units}{energy} \rightarrow \frac{e^2}{(4\pi\varepsilon_0)a_0} = \frac{e^2}{a_0} = 1$$

$$2Rydbergs = 1 \underset{of\ energy}{au} = 1 \text{ Hartree}$$

$$\boxed{\left[\frac{E_{\text{I order PT}}}{N} \right] \underset{r_s \to 0}{=} -\frac{0.916}{r_s} \text{ Rydbers}}$$

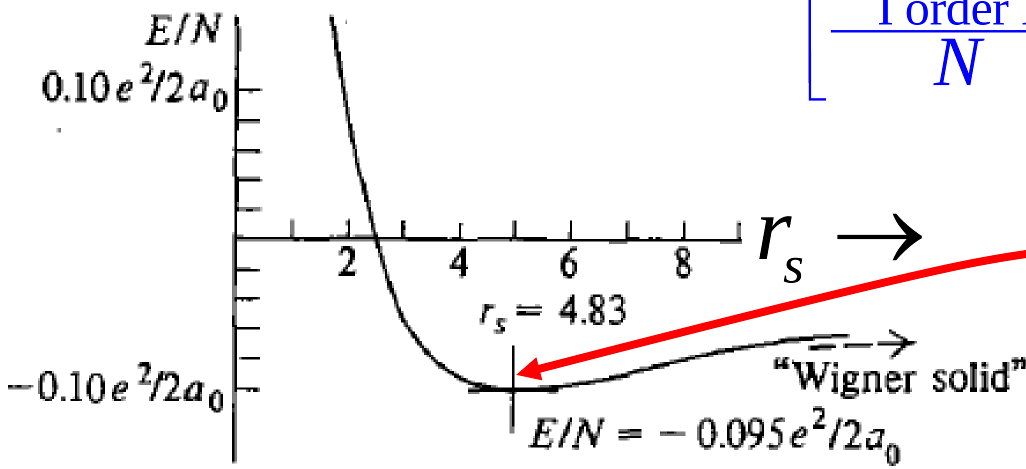
For HF-SCF *free electron gas in jellium potential :*

$$\left[\frac{E_{HF}}{N}\right]=\left(\frac{2.21}{r_s^{\ 2}}-\frac{0.916}{r_s}\right)Ryd$$

For free electron gas in jellium potential :

Perturbation theory gives the same result

$$\left[\frac{E_{\text{I order PT}}}{N}\right]=\left(\frac{2.21}{r_s^{\ 2}}-\frac{0.916}{r_s}\right)Ryd$$



Minimum
At negative energy
System: bound

Fig. 3.2 Approximate ground-state energy [first two terms in Eq. (3.37)] of an electron gas in a uniform positive background.

Reference: Fetter & Walecka Quantum Theory of Many-Particle Systems; Fig.3.2/page 29

NEXT CLASS: RPA

As $r_s \to \infty$ (low density)

$$\left[\frac{E_{\substack{\text{Wigner}\\ \text{solid}}}}{N}\right]=\frac{e^2}{2a_0}\left(-\frac{1.79}{r_s}+\frac{2.66}{r_s^{\ 2}}+..\right)$$

E.P.Wigner Phys Rev **46**:1002 (1934)

Questions: pcd@physics.iitm.ac.ic

Select/Special Topics from 'Theory of Atomic Collisions and Spectroscopy'

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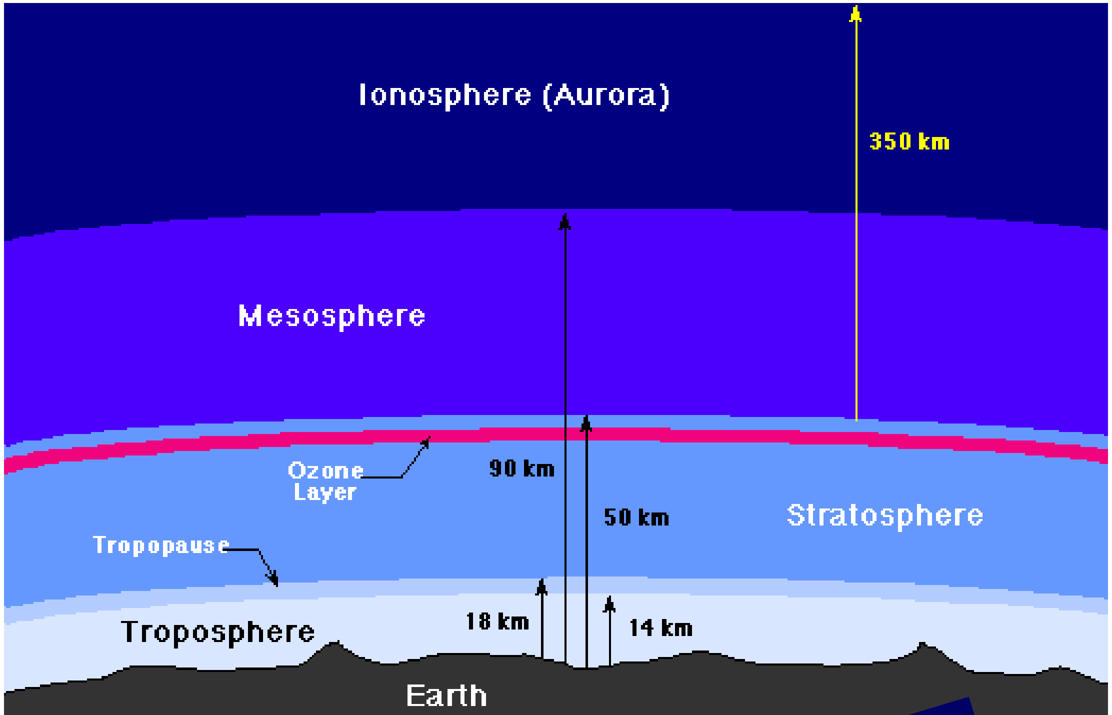
Unit 3 Lecture Number 21

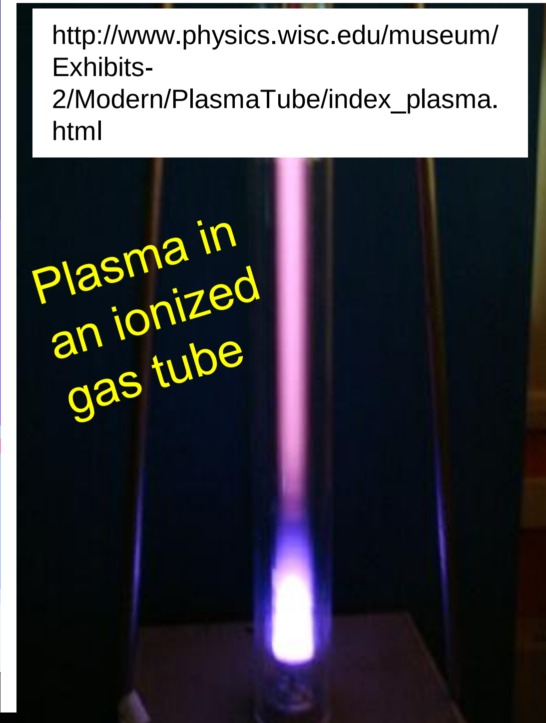
Electron Gas in the Random Phase Approximations

Plasma Oscillations in Free Electron Gas

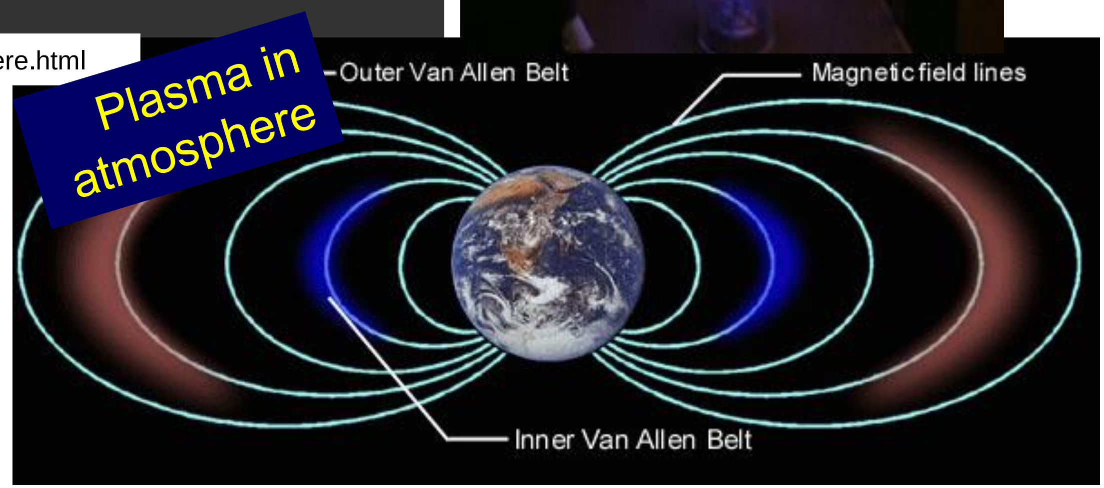
References: 'The theory of plasma oscillations in metals'
- by S Raimes 1957 *Rep. Prog. Phys.* **20** 1
Also: Chapter 4 in 'Many Electron Theory' by Stanley Raimes



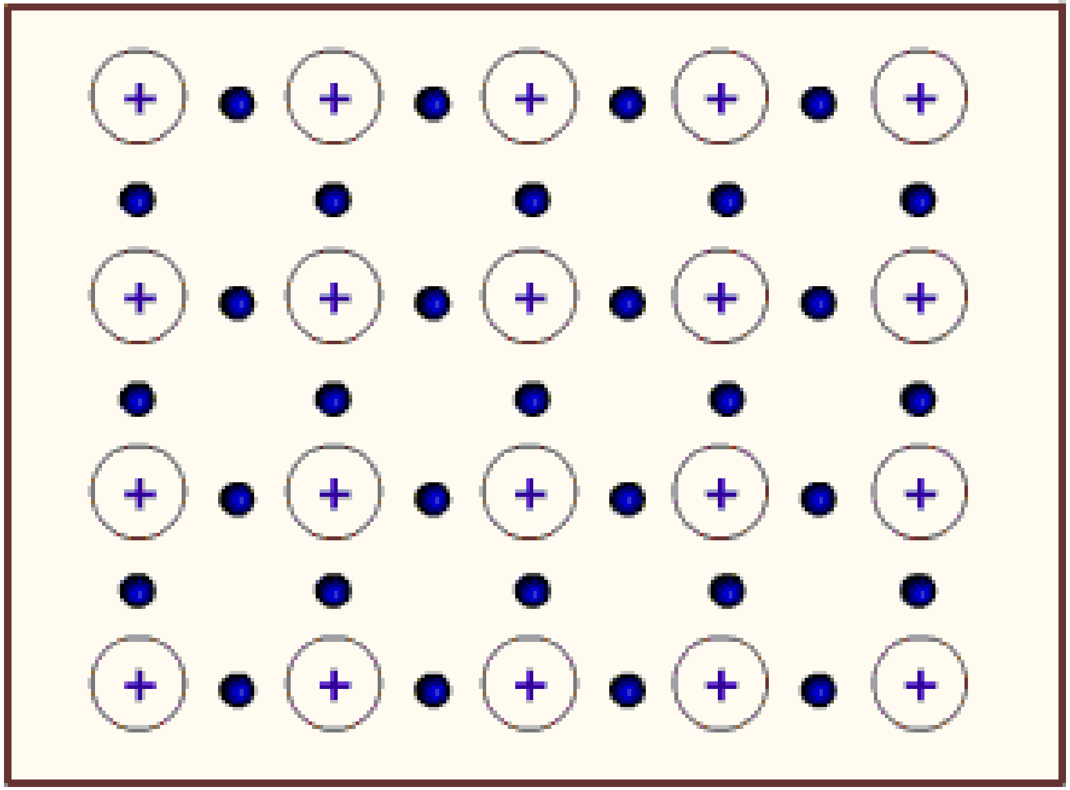
http://csep10.phys.utk.edu/astr161/lect/earth/atmosphere.html



PLASMA: 4th state of matter.. highly ionized region.. positive charged ions and virtually free electrons…



http://www.redorbit.com/education/reference_library/space_1/solar_system/2574610/van_allen_radiation_belt/

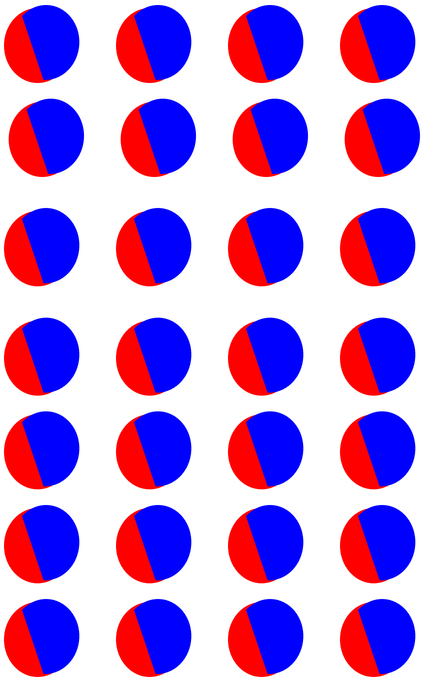


Ignore motion of the ions…. as if they are frozen….

Ions: relatively far more massive and have large inertia….

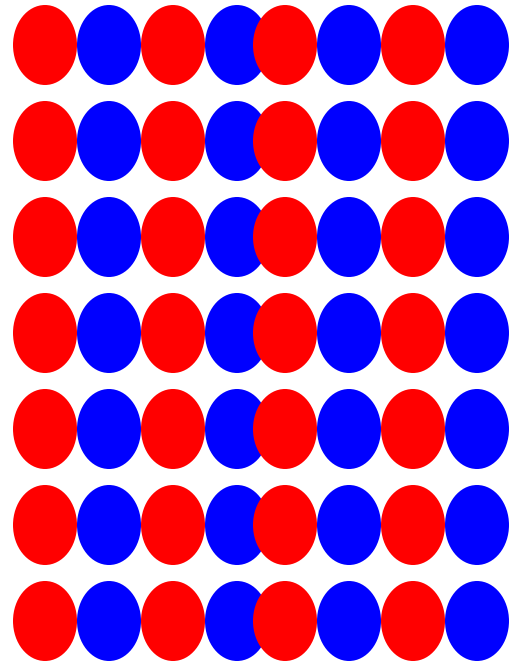
Metal → plasma

Whole system: electrically neutral.



$\vec{\xi}$

Displacement of all the electrons to the right



net negative charge per unit area = $-e\bar{\rho}_e\xi$

surface charge density : $\sigma = e\bar{\rho}\xi$

net positive charge per unit area = $+e\bar{\rho}_p\xi$

Positive and Negative charge in balance

<u>net field in-between</u>

$$\vec{E} = \frac{1}{\varepsilon_0} e\bar{\rho}\xi\hat{u}$$

<u>net field in-between</u>

Eq. of motion

$$\vec{E} = \frac{1}{\varepsilon_0} e\bar{\rho}\xi\hat{u}$$

$$m\frac{d^2\xi}{dt^2} = \left(\frac{1}{\varepsilon_0} e\bar{\rho}\xi\right)(-e)$$

$$\omega_p = \sqrt{\frac{\bar{\rho}e^2}{m\varepsilon_0}}$$

SI units

CGS units

$$\frac{1}{4\pi\varepsilon_0} \rightarrow 1 \quad ; \quad \frac{1}{\varepsilon_0} \rightarrow 4\pi$$

$$\frac{d^2\xi}{dt^2} = -\frac{\bar{\rho}e^2}{m\varepsilon_0}\xi$$

S.H.O.

CGS units

$$\omega_p = \sqrt{\frac{4\pi\bar{\rho}e^2}{m}}$$

Frequency of plasma oscillations

Thermal motion of electrons: ignored

<u>except</u> *that implicitly we assumed that thermal fluctuations would have caused departure from equilibrium in plasma density and thereby cause an onset of plasma oscillations.*

net field in-between

$$\vec{E} = \frac{1}{\varepsilon_0} e\bar{\rho}\xi\hat{u}$$

Eq. of motion

$$m\frac{d^2\xi}{dt^2} = \left(\frac{1}{\varepsilon_0} e\bar{\rho}\xi\right)(-e)$$

$$\frac{d^2\xi}{dt^2} = -\frac{\bar{\rho}e^2}{m\varepsilon_0}\xi$$

S.H.O.

CGS units

$$\omega_p = \sqrt{\frac{4\pi\bar{\rho}e^2}{m}}$$

$$\bar{\rho} = \frac{N}{N\frac{4}{3}\pi r_s^3} = \frac{3}{4\pi r_s^3}$$

Frequency of plasma oscillations

$$\omega_p = \sqrt{\frac{\cancel{4\pi}\left(\frac{3}{\cancel{4\pi}\, r_s^3}\right)e^2}{m}}$$

$$\omega_p = \sqrt{3e^2 / mr_s^3}$$

Thermal motion → dispersion

when dispersion is present:

$$\boxed{\omega^2 = \omega_p{}^2 - \frac{2E_F}{m}k^2}$$

$$For\ free\ electron\ gas\ in\ jellium\ potential:$$

Bohm & Pines: mid-fiftees

$$\left[\frac{E_{PT}^{HF}}{N}\right]=\left(\frac{2.21}{r_s^{\ 2}}-\frac{0.916}{r_s}\right)Ryd$$

D.Pines (1963)
Elementary excitations in solids (Benjamin, NY)

$$E_{BP}=\frac{2.21}{r_s^{\ 2}}+\frac{\sqrt{3}}{2r_s^{\ 3/2}}\beta^2-\frac{0.916}{r_s}\left(1+\frac{\beta^2}{2}-\frac{\beta^4}{48}\right)$$

Random Phase Approximation

$$\beta=\frac{k_c}{k_f};\quad k_c:\ \text{upper bound to the wave number}$$

oscillations get damped by random thermal motion of the electrons

$$\omega_p=\left(\sqrt{3/m}\right)\left(e/r_s^{3/2}\right)$$

zero point energy of the plasma oscillations

$$\frac{1}{2}\hbar\omega_p\ \text{ where }\hbar\omega_p=\frac{2\sqrt{3}}{r_s^{\ 3/2}}Ryd$$

Field Operators

$$\hat{\psi}(q) = \sum_i \psi_i(q) c_i$$

$$\hat{\psi}^\dagger(q) = \sum_i \psi_i^*(q) c_i^\dagger$$

Reference:

STiTACS / Unit 3 / lecture 19 /

$$\boxed{H = \int \hat{\psi}^\dagger(q) f(q) \hat{\psi}(q) dq + \frac{1}{2} \int \int \hat{\psi}^\dagger(q) \hat{\psi}^\dagger(q') \mathrm{v}(q,q') \hat{\psi}(q') \hat{\psi}(q) dq dq'}$$

equivalent

$$\boxed{H = \sum_i \sum_j c_i^\dagger \langle i | f | j \rangle c_j + \frac{1}{2} \sum_i \sum_j \sum_k \sum_l c_i^\dagger c_j^\dagger \langle ij | \mathrm{v} | lk \rangle c_k c_l}$$

Complete expressions for the operators,
inclusive of spin labels →

Complete expressions for the operators, inclusive of spin labels

$$\left[c_{a_1\sigma_1}, c_{a_2\sigma_2}{}^{\dagger}\right]_{\pm} = \delta_{a_1 a_2}\delta_{\sigma_1\sigma_2} \qquad \left[c_{a_1\sigma_1}{}^{\dagger}, c_{a_2\sigma_2}{}^{\dagger}\right]_{\pm} = 0 \qquad \left[c_{a_1\sigma_1}, c_{a_2\sigma_2}\right]_{\pm} = 0$$

$$\hat{\psi}_{\alpha}(q) = \sum_{\alpha}\sum_{i} \psi_{i\alpha}(q) c_{i\alpha} \qquad \hat{\psi}_{\beta}^{\dagger}(q) = \sum_{\beta}\sum_{j} \psi_{j\beta}{}^{*}(q) c_{j\beta}^{\dagger}$$

$$H = \int \hat{\psi}_{\alpha}^{\dagger}(q) f(q) \hat{\psi}_{\beta}(q) dq + \frac{1}{2}\int\int \hat{\psi}_{\alpha}^{\dagger}(q)\hat{\psi}_{\beta}^{\dagger}(q) \mathrm{v}(q,q')\hat{\psi}_{\delta}(q')\hat{\psi}_{\gamma}(q) dq dq'$$

becomes, inclusive of the explicit spin labels:

$$H = \sum_{i}\sum_{j}\sum_{\alpha}\sum_{\beta} c_{i\alpha}^{\dagger} \int \psi_{i\alpha}{}^{*}(q) f(q) \psi_{j\beta}(q) dq\, c_{j\beta} +$$
$$+\frac{1}{2}\sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{\alpha}\sum_{\beta}\sum_{\delta}\sum_{\gamma} c_{i\alpha}^{\dagger} c_{j\beta}^{\dagger} \int\int \psi_{i\alpha}{}^{*}(q)\psi_{j\beta}{}^{*}(q) \mathrm{v}(q,q')\psi_{l\delta}(q)\psi_{k\gamma} dq dq'\, c_{k\gamma} c_{l\delta}$$

$$H = \sum_{i}\sum_{j}\sum_{\alpha}\sum_{\beta} c_{i\alpha}^{\dagger} \langle i\alpha | f | j\beta \rangle c_{j\beta} + \frac{1}{2}\sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{\alpha}\sum_{\beta}\sum_{\delta}\sum_{\gamma} c_{i\alpha}^{\dagger} c_{j\beta}^{\dagger} \langle i\alpha, j\beta | \mathrm{v} | l\delta, k\gamma \rangle c_{k\gamma} c_{l\delta}$$

Raimes / p.42 / Eq.2.117 → inclusive of spin labels

$$\boxed{q \equiv \vec{r}, \zeta \rightarrow \text{space + spin coordinate}}$$

$$\psi^\dagger(q)\psi(q) = \rho(q) \leftarrow \text{ particle density operator}$$

$$\sum_\zeta \iiint d^3\vec{r}\rho(q) = \sum_\zeta \iiint d^3\vec{r}\psi^\dagger(q)\psi(q) = N$$

N : number of electrons in the region

$$\int \psi^\dagger(q')\underbrace{\delta(q-q')}\psi(q)dq' =$$

$$= \sum_{\zeta'} \int \psi^\dagger(\vec{r}')\chi^\dagger(\zeta')\underbrace{\delta(\vec{r}-\vec{r}')\delta_{\zeta,\zeta'}}\psi(\vec{r})\chi(\zeta)d^3\vec{r}'$$

$$= \sum_{\zeta'} \chi^\dagger(\zeta')\delta_{\zeta,\zeta'}\chi(\zeta)\int \psi^\dagger(\vec{r}')\delta(\vec{r}-\vec{r}')\psi(\vec{r})d^3\vec{r}'$$

$$= \chi^\dagger(\zeta)\chi(\zeta)\psi^\dagger(\vec{r})\psi(\vec{r}) = \psi^\dagger(q)\psi(q) = \rho(q)$$

$$\psi^\dagger(q)\psi(q) = \rho(q) \leftarrow \text{ particle density operator}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)$$

$$\iiint d^3\vec{r}\rho(\vec{r}) = \iiint d^3\vec{r} \boxed{\sum_{i=1}^{N}} \delta(\vec{r} - \vec{r}_i)$$

$$= \sum_{i=1}^{N} \iiint d^3\vec{r}\delta(\vec{r} - \vec{r}_i) = N$$

Raimes, Many Electron Theory Eq. 4.4; page 71 →

Fourier expansion:

$$\rho(\vec{r}) = \frac{1}{V} \sum_{\vec{k}=1}^{N} \rho_{\vec{k}} \; e^{i\vec{k}\bullet\vec{r}}$$

$$\left[\rho_{\vec{k}}\right] : \text{dimensionless}$$

N electrons per unit volume: $\rho = N/V$

Fourier expansion of the electron-electron Coulomb interaction

$$\frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\vec{k}} c_k e^{i\vec{k}\bullet\left(\vec{r}_i - \vec{r}_j\right)}$$

$$\left[c_k\right] = \left[\text{charge}\right]^2 L^2$$

The above sum is a triple sum, over the three components of $\vec{k}$.

$$\frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\vec{k}} c_{\vec{k}} e^{i\vec{k}\bullet(\vec{r}_i - \vec{r}_j)}$$

multiplying both sides by $\underbrace{e^{i\vec{k}'\bullet(\vec{r}_j - \vec{r}_i)}}$

consider first $\vec{k} \neq \vec{0}$

$$\underbrace{e^{i\vec{k}'\bullet(\vec{r}_j - \vec{r}_i)}}\frac{e^2}{r_{ij}} = \underbrace{e^{i\vec{k}'\bullet(\vec{r}_j - \vec{r}_i)}}\frac{1}{V}\sum_{\vec{k}} c_k e^{i\vec{k}\bullet(\vec{r}_i - \vec{r}_j)}$$

Note the sign

$$e^{i\vec{k}'\bullet(\vec{r}_j - \vec{r}_i)}\frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\vec{k}} c_k e^{i(\vec{k} - \vec{k}')\bullet(\vec{r}_i - \vec{r}_j)}$$

Integrating:

$$\iiint d^3\vec{r}_j \left[e^{i\vec{k}'\bullet(\vec{r}_j - \vec{r}_i)}\right]\frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\vec{k}} c_k \iiint d^3\vec{r}_j \left[e^{i(\vec{k} - \vec{k}')\bullet(\vec{r}_i - \vec{r}_j)}\right]$$

The Wave Mechanics of Electrons in Metals – by Stanley Raimes, page 285

$$\iiint d^3\vec{r}_j \; e^{i\vec{k}'\bullet(\vec{r}_j-\vec{r}_i)} \frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\vec{k}} c_k \iiint d^3\vec{r}_j \;\; e^{i(\vec{k}-\vec{k}')\bullet(\vec{r}_i-\vec{r}_j)}$$

$$\underbrace{e^2 \iiint d^3\vec{r}_j \frac{e^{i\vec{k}'\bullet(\vec{r}_j-\vec{r}_i)}}{r_{ij}}} = \frac{1}{V}\sum_{\vec{k}} c_k \iiint d^3\vec{r}_j \;\; e^{i(\vec{k}-\vec{k}')\bullet(\vec{r}_i-\vec{r}_j)}$$

from slide 117, *L*19 :

$$FT \text{ of } \left(\frac{1}{r}\right)^C = \frac{4\pi}{k'^2}$$

$$\frac{4\pi e^2}{\left|\vec{k}'\right|^2} = \sum_{\vec{k}} c_k \left(\frac{1}{V}\iiint d^3\vec{r}_j \left[e^{i(\vec{k}-\vec{k}')\bullet(\vec{r}_i-\vec{r}_j)}\right]\right)$$

Dirac δ

$$= \sum_{\vec{k}} c_k \; e^{i(\vec{k}-\vec{k}')\bullet\vec{r}_i}\delta\left(\vec{k}-\vec{k}'\right)$$

$$\frac{4\pi e^2}{\left|\vec{k}'\right|^2} = c_{\vec{k}'}$$

i.e. $c_{\vec{k}} = \dfrac{4\pi e^2}{\left|\vec{k}\right|^2} \rightarrow$ *except* when $\vec{k} = \vec{0}$

$$\left[c_k\right] = \left[\text{charge}\right]^2 L^2$$

$$\frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\vec{k}} c_{\vec{k}} e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}$$

$$c_{\vec{k}} = \frac{4\pi e^2}{|\vec{k}|^2} \rightarrow \textit{except} \text{ when } \vec{k}=\vec{0}$$

Integrating ↓

$$\textit{What is } c_{\vec{k}} \textit{ when } \vec{k}=\vec{0} \text{ ?}$$

$$e^2 \iiint d^3\vec{r}_j \frac{1}{r_{ij}} = \sum_{\vec{k}} c_{\vec{k}} \left\{ \frac{1}{V} \iiint d^3\vec{r}_j e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)} \right\}$$

$$\textit{now,} \quad \frac{1}{V}\iiint d^3\vec{r}_j \left[e^{i(\vec{k}-\vec{k}')\bullet(\vec{r}_i-\vec{r}_j)} \right] = \delta(\vec{k}-\vec{k}')$$

Eq.3.11; page 23; F&W

$$\textit{i.e.} \quad \text{for } \vec{k}'=\vec{0}: \quad \frac{1}{V}\iiint d^3\vec{r}_j e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)} = \delta(\vec{k}-\vec{0}) = \delta(\vec{k})$$

$$\boxed{e^2\iiint d^3\vec{r}_j\,\frac{1}{r_{ij}}}=\sum_{\vec{k}}c_{\vec{k}}\,\underbrace{\left\{\frac{1}{V}\iiint d^3\vec{r}_j\,e^{i\vec{k}\bullet\left(\vec{r}_i-\vec{r}_j\right)}\right\}}_{\frac{1}{V}\iiint d^3\vec{r}_j\,e^{i\vec{k}\bullet\left(\vec{r}_i-\vec{r}_j\right)}=\delta\left(\vec{k}\right)}$$

The Wave Mechanics of Electrons in Metals by Stanley Raimes, page 285

$$\vec{r}_j-\vec{r}_i=\vec{r}$$

$$e^2\iiint d^3\vec{r}\,\frac{1}{r}=\sum_{\vec{k}}c_{\vec{k}}\,\delta\left(\vec{k}\right)=c_{\vec{0}}$$

$$\therefore\quad c_{\vec{0}}=e^2\iiint d^3\vec{r}\,\frac{1}{r}$$

Potential energy of the i^{th} electron due to ***one*** electron charge uniformly smeared throughout the box.

Potential energy of the i^th^ electron due to the j^th^:

$$\frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\vec{k}} c_k e^{i\vec{k}\bullet(\vec{r}_i - \vec{r}_j)}$$

Potential energy of the i^th^ electron due to all the electrons:

$$P(\vec{r}_i) = \sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{\vec{k}} c_k e^{i\vec{k}\bullet(\vec{r}_i - \vec{r}_j)}$$

$$c_{\vec{k}} = \frac{4\pi e^2}{\left|\vec{k}\right|^2} \rightarrow except \text{ when } \vec{k} = \vec{0}$$

$$c_{\vec{0}} = e^2 \iiint d^3\vec{r}\,\frac{1}{r}$$

Potential energy of the ith electron due to ***all the electrons***:

$$P(\vec{r}_i) = \sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{e^2}{r_{ij}} = \frac{1}{V}\sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{\vec{k}} c_k e^{i\vec{k}\bullet(\vec{r}_i - \vec{r}_j)}$$

$$c_{\vec{k}} = \frac{4\pi e^2}{|\vec{k}|^2} \rightarrow \textit{except} \text{ when } \vec{k} = \vec{0}$$

$$c_{\vec{0}} = e^2 \iiint d^3\vec{r}\,\frac{1}{r}$$

Slide 130 (previous class)

$\vec{k} = \vec{0}$ term $\rightarrow$ *cancels the positive jellium*

Potential energy of the ith electron due to ***all the electrons*** ***and*** the positive background:

$$U(\vec{r}_i) = \frac{1}{V}\sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{4\pi e^2}{k^2} e^{i\vec{k}\bullet(\vec{r}_i - \vec{r}_j)}$$

Potential energy of the i^{th} electron due to **all the electrons** ***and*** the positive background:

$$U(\vec{r}_i) = \frac{1}{V}\sum_{\substack{j=1\\ j\neq i}}^{N}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{4\pi e^2}{k^2}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}$$

Force exerted on the i^{th} electron:

$$m\ddot{\vec{r}}_i = m\dot{\vec{v}}_i = -\vec{\nabla}_i U(\vec{r}_i)$$

weaker magnetic forces ignored

$$\ddot{\vec{r}}_i = \dot{\vec{v}}_i = -\frac{1}{m}\vec{\nabla}_i U(\vec{r}_i) = -\frac{1}{V}\sum_{\substack{j=1\\ j\neq i}}^{N}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{4\pi e^2}{mk^2}\left(\vec{\nabla}_i e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}\right)$$

acceleration of the i^{th} electron

$$= -\frac{1}{V}\sum_{\substack{j=1\\ j\neq i}}^{N}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{4\pi e^2}{mk^2}\left(i\vec{k}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}\right)$$

$\uparrow i = \sqrt{-1}$

$$\ddot{\vec{r}}_i = \dot{\vec{\mathrm{v}}}_i = -\frac{1}{m}\vec{\nabla}_i U(\vec{r}_i) = -\frac{1}{V}\sum_{\substack{j=1 \\ j\neq i}}^{N} \boxed{\sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{4\pi e^2}{mk^2}\left(i\vec{k}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}\right)}$$

$$\uparrow i = \sqrt{-1}$$

Due to the symmetrical distribution of the $\vec{k}$ vectors

the summand on the

RHS for $(j=i)$ is $\sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{4\pi e^2}{mk^2}(i\vec{k}) = \vec{0}$

Hence no need to exclude *j=i* term …..

$$\ddot{\vec{r}}_i = \dot{\vec{\mathrm{v}}}_i = -\frac{1}{m}\vec{\nabla}_i U(\vec{r}_i) = -\frac{1}{V}\sum_{j=1}^{N} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{4\pi e^2}{mk^2}\left(i\vec{k}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}\right)$$

$$\ddot{\vec{r}}_i = \dot{\vec{\mathrm{v}}}_i = -\frac{1}{m}\vec{\nabla}_i U(\vec{r}_i) = -\frac{4\pi e^2 i}{Vm}\sum_{j=1}^{N}\sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}}\frac{\vec{k}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}}{k^2}$$

acceleration of the i^th electron

electron charge density

$$\rho(\vec{r}) = \sum_{i=1}^{N}\delta\left(\vec{r}-\vec{r}_i\right)$$

$$\iiint d^3\vec{r}\rho(\vec{r}) = \sum_{i=1}^{N}\iiint d^3\vec{r}\delta\left(\vec{r}-\vec{r}_i\right) = N$$

Fourier expansion of charge density

$$\rho(\vec{r}) = \frac{1}{V}\sum_{\vec{k}=1}^{N}\rho_{\vec{k}}\ e^{i\vec{k}\bullet\vec{r}}$$

$$\left[\rho_{\vec{k}}\right]: \text{dimensionless}$$

Fourier expansion of charge density

$$\rho(\vec{r}) = \frac{1}{V}\sum_{\vec{k}=1}^{N}\rho_{\vec{k}}\; e^{i\vec{k}\bullet\vec{r}}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N}\delta\left(\vec{r}-\vec{r}_i\right)$$

$\left[\rho_{\vec{k}}\right]$: dimensionless

$$\rho_{\vec{k}} = \iiint d^3\vec{r}\,\rho(\vec{r})e^{-i\vec{k}\bullet\vec{r}} = \iiint d^3\vec{r} \boxed{\sum_{i=1}^{N}}\delta\left(\vec{r}-\vec{r}_i\right)\; e^{-i\vec{k}\bullet\vec{r}}$$

$$\rho_{\vec{k}} = \boxed{\sum_{i=1}^{N}}\iiint d^3\vec{r}\;\delta\left(\vec{r}-\vec{r}_i\right)\; e^{-i\vec{k}\bullet\vec{r}}$$

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}}$$

$$\boxed{\rho_{\vec{k}=\vec{0}} = N}$$

←total number of electrons

$\vec{k} \neq \vec{0}$ ←components: density fluctuations over the average

$$\ddot{\vec{r}}_i = \dot{\vec{\mathrm{v}}}_i = -\frac{1}{m}\vec{\nabla}_i U(\vec{r}_i) = -\frac{4\pi e^2 i}{Vm}\sum_{j=1}^{N}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{\vec{k}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}}{k^2}$$

acceleration of the i[th] electron

$$\ddot{\vec{r}}_i = \dot{\vec{\mathrm{v}}}_i = -\frac{4\pi e^2 i}{mV}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{\vec{k}e^{i\vec{k}\bullet\vec{r}_i}}{k^2}\sum_{j=1}^{N}e^{-i\vec{k}\bullet\vec{r}_j}$$

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N}e^{-i\vec{k}\bullet\vec{r}_i}}$$

$$\ddot{\vec{r}}_i = \dot{\vec{\mathrm{v}}}_i = -\frac{4\pi e^2 i}{mV}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{\vec{k}}{k^2}\rho_{\vec{k}}e^{i\vec{k}\bullet\vec{r}_i}$$

$$\Downarrow \quad \boxed{\dot{\rho}_{\vec{k}} = \frac{d}{dt}\rho_{\vec{k}}}$$

$$\dot{\rho}_{\vec{k}} = \sum_{i=1}^{N}e^{-i\vec{k}\bullet\vec{r}_i}\frac{d}{dt}\left(-i\vec{k}\bullet\vec{r}_i\right)$$

$$\dot{\rho}_{\vec{k}} = -i\sum_{i=1}^{N}e^{-i\vec{k}\bullet\vec{r}_i}\left(\vec{k}\bullet\dot{\vec{r}}_i\right)$$

$$\dot{\rho}_{\vec{k}} = -i\sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}\left(\vec{k}\bullet\dot{\vec{r}}_i\right)$$

$$\ddot{\rho}_k = \frac{d}{dt}\dot{\rho}_{\vec{k}} = -i\sum_{i=1}^{N} \frac{d}{dt}\left[e^{-i\vec{k}\bullet\vec{r}_i}\left(\vec{k}\bullet\dot{\vec{r}}_i\right)\right]$$

$$\boxed{\ddot{\rho}_{\vec{k}} = -i\sum_{i=1}^{N}\left[e^{-i\vec{k}\bullet\vec{r}_i}\left(-i\vec{k}\bullet\dot{\vec{r}}_i\right)\left(\vec{k}\bullet\dot{\vec{r}}_i\right) + e^{-i\vec{k}\bullet\vec{r}_i}\left(\vec{k}\bullet\ddot{\vec{r}}_i\right)\right]}$$

$$\ddot{\rho}_{\vec{k}} = \sum_{i=1}^{N}\left[-\left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 - i\left(\vec{k}\bullet\ddot{\vec{r}}_i\right)\right]e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = \sum_{i=1}^{N} \left[-\left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 - i\left(\vec{k}\bullet\ddot{\vec{r}}_i\right)\right] e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - i\sum_{i=1}^{N} \left(\vec{k}\bullet\ddot{\vec{r}}_i\right) e^{-i\vec{k}\bullet\vec{r}_i}$$

<u>from Slide 170</u>: $\ddot{\vec{r}}_i = \dot{\vec{\mathrm{v}}}_i = -\dfrac{4\pi e^2 i}{mV} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \dfrac{\vec{k}}{k^2} \rho_{\vec{k}} e^{i\vec{k}\bullet\vec{r}_i}$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - i\sum_{i=1}^{N} \left(\vec{k}\bullet\left\{-\frac{4\pi e^2 i}{mV} \sum_{\substack{\vec{k}' \\ \vec{k}'\neq\vec{0}}} \frac{\vec{k}'}{k'^2} \rho_{\vec{k}'} e^{i\vec{k}'\bullet\vec{r}_i}\right\}\right) e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{4\pi e^2}{m} \frac{1}{V} \sum_{i=1}^{N} \sum_{\substack{\vec{k}' \\ \vec{k}'\neq\vec{0}}} \frac{\vec{k}\bullet\vec{k}'}{k'^2} \rho_{\vec{k}'} e^{i\left(\vec{k}'-\vec{k}\right)\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi e^2}{m}\sum_{i=1}^{N}\sum_{\substack{\vec{k}' \\ \vec{k}'\neq\vec{0}}} \frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'} e^{i(\vec{k}'-\vec{k})\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = \left[\begin{array}{l} -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} \\ -\frac{1}{V}\frac{4\pi e^2}{m} \boxed{\frac{\vec{k}\bullet\vec{k}}{k^2}} \rho_{\vec{k}} \boxed{\sum_{i=1}^{N} e^0} \\ -\frac{1}{V}\frac{4\pi e^2}{m}\sum_{i=1}^{N}\sum_{\substack{\vec{k}'\neq\vec{k} \\ \vec{k}'\neq\vec{0}}} \frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'} e^{i(\vec{k}'-\vec{k})\bullet\vec{r}_i} \end{array} \right.$$

unity

$\vec{k}' = \vec{k}$ term

$\vec{k}' \neq \vec{k}$ terms

$$\sum_{i=1}^{N} e^0 = N$$

$$\ddot{\rho}_{\vec{k}} = $$

$$= -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi Ne^2}{m}\rho_{\vec{k}}$$

$$-\frac{1}{V}\frac{4\pi e^2}{m}\sum_{i=1}^{N}\sum_{\substack{\vec{k}'\neq\vec{k} \\ \vec{k}'\neq\vec{0}}} \frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'} e^{i(\vec{k}'-\vec{k})\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi N e^2}{m}\rho_{\vec{k}}$$

Eq. of motion for density fluctuations

$$-\frac{1}{V}\frac{4\pi e^2}{m}\boxed{\sum_{i=1}^{N}}\sum_{\substack{\vec{k}'\neq\vec{k}\\ \vec{k}'\neq\vec{0}}}\frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'}e^{i(\vec{k}'-\vec{k})\bullet\vec{r}_i}$$

Now, remember that ↓

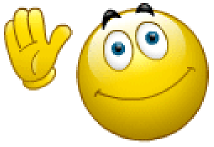
$$\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi N e^2}{m}\rho_{\vec{k}}$$

$$-\frac{1}{V}\frac{4\pi e^2}{m}\sum_{\substack{\vec{k}'\neq\vec{k}\\ \vec{k}'\neq\vec{0}}}\frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'}\underbrace{\left\{\boxed{\sum_{i=1}^{N}} e^{i(\vec{k}'-\vec{k})\bullet\vec{r}_i}\right\}}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi N e^2}{m}\rho_{\vec{k}}$$

$$-\frac{1}{V}\frac{4\pi e^2}{m}\sum_{\substack{\vec{k}'\neq\vec{k}\\ \vec{k}'\neq\vec{0}}}\frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'}\underbrace{\left(\rho_{\vec{k}-\vec{k}'}\right)}$$



Questions: pcd@physics.iitm.ac.ic

Select/Special Topics from 'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 22

Electron Gas in the Random Phase Approximations

QUANTUM THEORETICAL TREATMENT

Plasma Oscillations in Free Electron Gas

References: 'The theory of plasma oscillations in metals'
- by S Raimes 1957 *Rep. Prog. Phys.* **20** 1
Also: Chapter 4 in 'Many Electron Theory' by Stanley Raimes

Fourier expansion of charge density

$$\rho(\vec{r}) = \frac{1}{V}\sum_{\vec{k}=1}^{N}\rho_{\vec{k}}\ e^{i\vec{k}\bullet\vec{r}}$$

$$\left[\rho_{\vec{k}}\right]: \text{dimensionless}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N}\delta\left(\vec{r}-\vec{r}_i\right)$$

$$\rho_{\vec{k}} = \iiint d^3\vec{r}\,\rho(\vec{r})e^{-i\vec{k}\bullet\vec{r}}$$

$$\rho_{\vec{k}} = \sum_{i=1}^{N}\iiint d^3\vec{r}\ \delta\left(\vec{r}-\vec{r}_i\right)\ e^{-i\vec{k}\bullet\vec{r}}$$

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}}$$

$$\boxed{\rho_{\vec{k}=\vec{0}} = N}$$

←total number of electrons

$\vec{k} \neq \vec{0}$ ←components: density fluctuations over the average

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi N e^2}{m}\rho_{\vec{k}}$$

Eq. of motion for density fluctuations

$$-\frac{1}{V}\frac{4\pi e^2}{m}\boxed{\sum_{i=1}^{N}}\sum_{\substack{\vec{k}'\neq\vec{k}\\ \vec{k}'\neq\vec{0}}}\frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'}e^{i(\vec{k}'-\vec{k})\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi N e^2}{m}\rho_{\vec{k}}$$

Similar to ↓

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}}$$

$$-\frac{1}{V}\frac{4\pi e^2}{m}\sum_{\substack{\vec{k}'\neq\vec{k}\\ \vec{k}'\neq\vec{0}}}\frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'}\underbrace{\left\{\boxed{\sum_{i=1}^{N}} e^{i(\vec{k}'-\vec{k})\bullet\vec{r}_i}\right\}}_{\boxed{\rho_{\vec{k}-\vec{k}'}}}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi N e^2}{m}\rho_{\vec{k}}$$

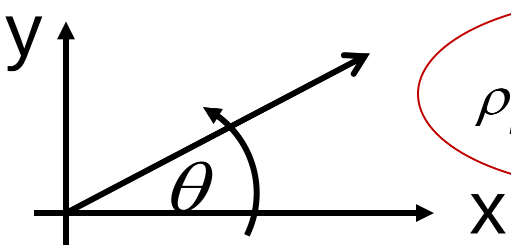
$$-\frac{1}{V}\frac{4\pi e^2}{m}\sum_{\substack{\vec{k}'\neq\vec{k}\\ \vec{k}'\neq\vec{0}}}\frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'}\underbrace{\left(\rho_{\vec{k}-\vec{k}'}\right)}$$

$$\ddot{\rho}_{\vec k} = -\frac{1}{V}\sum_{i=1}^{N} \left(\vec k \bullet \dot{\vec r}_i\right)^2 e^{-i\vec k \bullet \vec r_i} - \frac{1}{V}\frac{4\pi N e^2}{m}\rho_{\vec k}$$

Eq. of motion for density fluctuations

$$-\frac{4\pi e^2}{mV}\sum_{\substack{\vec k' \neq \vec k \\ \vec k' \neq \vec 0}} \frac{\vec k \bullet \vec k'}{k'^2}\rho_{\vec k'}\,\rho_{\vec k - \vec k'}$$

Quadratic terms in density fluctuations



$$\rho_{\vec k} = \sum_{i=1}^{N} e^{-i\vec k \bullet \vec r_i}$$

$$\rho_{\vec k - \vec k'} = \sum_{i=1}^{N} e^{i(\vec k' - \vec k)\bullet \vec r_i}$$

Phase factors of modulus unity

Sum of vectors, in random directions, in the complex plane $z=x+iy$ **Bohm & Pines** **(1952,53)**

Random Phase Approximation: Neglect quadratic terms in density fluctuations compared to the linear terms.

NOTE: **"LINEARIZATION"**

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi Ne^2}{m}\rho_{\vec{k}}$$

Random Phase Approximation

Eq. of motion for density fluctuations

$$\cancel{-\frac{4\pi e^2}{m}\sum_{\substack{\vec{k}'\neq\vec{k}\\ \vec{k}'\neq 0}}\frac{\vec{k}\bullet\vec{k}'}{k'^2}\rho_{\vec{k}'}\rho_{\vec{k}-\vec{k}'}}$$

"LINEARIZATION"

↓RPA

$$\ddot{\rho}_{\vec{k}} \simeq -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{1}{V}\frac{4\pi Ne^2}{m}\rho_{\vec{k}}$$

from Slide No.5; L22 : $\bar{\rho} = \frac{N}{V}$ $\qquad \rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}$

$$\ddot{\rho}_{\vec{k}} \underset{RPA}{=} \cancel{-\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i}} - \frac{4\pi\bar{\rho}e^2}{m}\rho_{\vec{k}}$$

?

$$\ddot{\rho}_{\vec{k}} \underset{RPA}{=} \underbrace{-\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i}} - \frac{4\pi\bar{\rho}e^2}{m}\rho_{\vec{k}}$$

This term does not have any 'acceleration' term.

It has only velocities: due to thermal motion;

*it is **not** due time-independent to e-e interaction*

$$1^{st}\ term:\ \mathrm{O}(k^2) \rightarrow ignorable \rightarrow\ for\ \underline{small\ values\ of\ k}$$

$$\rightarrow \underline{not\ ignorable}\ \text{if } k \text{ would get large beyond some limit.}$$

k must have an upper limit

RPA + $k \le k_c$

$$\ddot{\rho}_{\vec{k}} = -\frac{4\pi\bar{\rho}e^2}{m}\rho_{\vec{k}} = -\omega_p{}^2\rho_k$$

S.H.O.

$$\ddot{\rho}_{\vec{k}} \underset{RPA}{=} \underbrace{-\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i}} - \frac{4\pi\bar{\rho}e^2}{m}\rho_{\vec{k}}$$

RPA + $k \leq k_c$

$$\ddot{\rho}_{\vec{k}} = -\frac{4\pi\bar{\rho}e^2}{m}\rho_{\vec{k}} = -\omega_p{}^2\rho_k$$

S.H.O.

$$\boxed{\ddot{\rho}_{\vec{k}} + \omega_p{}^2\rho_k = 0}$$

← The Fourier components of the electron density oscillate at the plasma frequency.

$$\ddot{\rho}_{\vec{k}} \underset{RPA}{=} \underbrace{-\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i}} - \frac{4\pi\bar{\rho}e^2}{m}\rho_{\vec{k}}$$

S.H.O.

RPA + $k \le k_c$

$$\ddot{\rho}_{\vec{k}} + \omega_p^{\ 2}\rho_k = 0$$

← The Fourier components of the electron density oscillate at the plasma frequency.

Collective oscillations of the electron gas

"PLASMONS"

Quantized

'collective excitations'

"elementary excitations"

We shall now examine the 'upper limit' on k

$$\ddot{\rho}_{\vec{k}} = -\frac{1}{V}\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \frac{4\pi\bar{\rho}e^2}{m} \rho_{\vec{k}}$$

$$\ddot{\rho}_{\vec{k}} = -\frac{1}{V}\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \omega_p{}^2 \rho_{\vec{k}}$$

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 e^{-i\vec{k}\bullet\vec{r}_i} - \omega_p{}^2 \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left[\left(\vec{k}\bullet\dot{\vec{r}}_i\right)^2 + \omega_p{}^2 \right] e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\ddot{\rho}_{\vec{k}} = -\sum_{i=1}^{N} \left[\left(\vec{k} \bullet \dot{\vec{r}}_i \right)^2 + \omega_p{}^2 \right] e^{-i\vec{k} \bullet \vec{r}_i}$$

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k} \bullet \vec{r}_i}}$$

Neglect of 1st term requires: $\left\langle \left(\vec{k} \bullet \dot{\vec{r}}_i \right)^2 \right\rangle_{average} \ll \omega_p{}^2$

$k^2 v_i{}^2 \ll \omega_p{}^2$ .... *for* all i,

k must have an upper limit

including for electrons at the Fermi surface

$$v_i(\max) = v_{Fermi} = v_f$$

$$k v_f \ll \omega_p$$

$$k_{\max} \approx \frac{\omega_p}{v_f} \rightarrow \textit{denoted by } k_c$$

Upper bound to wave number of plasma oscillations

→ Lower bound to wave length

Quantum treatment → $H_0\psi = E\psi$

Hamiltonian for a bulk electron gas in a uniform positive background jellium potential

$$H_0 = H_{el} + H_b + H_{el-b}$$

$$H_0 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{1}{2}\frac{e^2}{V}\sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{i=1}^{N} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{4\pi}{k^2} e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}$$

$$H_0 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{2\pi e^2}{V}\sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{i=1}^{N} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{1}{k^2} e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}$$

$$H_0 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{i=1}^{N} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{1}{k^2} e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}$$

Quantum treatment

$$\boxed{H_0\psi = E\psi}$$

D. Bohm and D. Pines Phys. Rev. **82** 625 (1951)

D. Pines and D. Bohm Phys. Rev. **85** 338 (1952)

D. Bohm and D. Pines Phys. Rev. **92** 609 (1953)

D. Pines Reviews of Modern Physics **28** 184 (1956)

S Raimes 1957 *Rep. Prog. Phys.* 20 1

The theory of plasma oscillations in metals

Method: transform the above Hamiltonian such that plasma oscillations appear explicitly as solutions of a set of *Hamiltonians for simple harmonic oscillators* for various values of $\vec{k}$ with $k \le k_{\max} \approx \frac{\omega_p}{\mathrm{v}_f} \leftrightarrow k_c$

$$H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{i=1}^{N} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{1}{k^2} e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}$$

Method: transform the above Hamiltonian such that plasma oscillations appear explicitly as a set of *Hamiltonians for simple harmonic oscillators* for various $\vec{k}$ values,

with $k \leq k_{\max} \approx \dfrac{\omega_p}{\mathrm{v}_f}$

$$h'_{SHO} = \frac{p^2}{2m} + \frac{1}{2}kq^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

$$\omega^2 = \frac{k}{m}; \quad k = m\omega^2 \qquad m \times h' \rightarrow h_{SHO} = \underbrace{\frac{p^2}{2} + \frac{1}{2}\omega^2 q^2}$$

$\uparrow q, p : Hermitian$

$$H_k = \frac{P_k^{\dagger} P_k}{2} + \frac{1}{2}\omega^2 Q_k^{\dagger} Q_k \quad \longleftarrow \quad Q, P: \ Hermitian?$$

$\uparrow$ *Hermitian*

canonically conjugate operators

$$H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{j=1 \\ j\neq i}}^{N} \sum_{i=1}^{N} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{1}{k^2} \boxed{e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}}$$

$$H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{1}{k^2} \boxed{\sum_{i=1}^{N} e^{i\vec{k}\bullet\vec{r}_i}} \boxed{\sum_{\substack{j=1 \\ j\neq i}}^{N} e^{-i\vec{k}\bullet\vec{r}_j} \; ?}$$

$$\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\boxed{\rho_{\vec{k}}^{\,*} = \sum_{j=1}^{N} e^{+i\vec{k}\bullet\vec{r}_j}}$$

Include the j=i

term, and then

subtract its effect!

j=i terms would

give :

1+1+1+….+1 = N

$$H_0 = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{1}{k^2} \left(\rho_{\vec{k}}^{\,*}\rho_{\vec{k}} - N\right)$$

$$H_0 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{1}{k^2} \left(\rho_{\vec{k}}^{\,*} \rho_{\vec{k}} - N \right)$$

Transformation

$$H_{\vec{k}} = \frac{P_{\vec{k}}^{\,\dagger} P_{\vec{k}}}{2} + \frac{1}{2}\omega^2 Q_{\vec{k}}^{\,\dagger} Q_{\vec{k}}$$

Method: start with a 'model' Hamiltonian

$$H_1 = \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2} P_{\vec{k}}^{\,\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger} \rho_{\vec{k}} \qquad \text{with } M_k = \sqrt{\frac{4\pi e^2}{Vk^2}}$$

$Q, P:\ \underline{\text{NOT}}\ Hermitian \rightarrow$ $\qquad P_{\vec{k}}^{\,\dagger} = P_{-\vec{k}} \quad ; \quad Q_{\vec{k}}^{\,\dagger} = Q_{-\vec{k}}$

$$\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i} \qquad \rho_{\vec{k}}^{\,\dagger} = \rho_{\vec{k}}^{\,*} = \sum_{i=1}^{N} e^{+i\vec{k}\bullet\vec{r}_i} = \rho_{-\vec{k}}$$

$H_1 \rightarrow Hermitian$

$$H_1 = \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2} P_{\vec{k}}^{\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger} \rho_{\vec{k}} \; ; M_k = \sqrt{\frac{4\pi e^2}{Vk^2}}$$

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}}$$

$$\boxed{H_1^{\dagger} = \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2} \left(P_{\vec{k}}^{\dagger} P_{\vec{k}}\right)^{\dagger} - M_k \left(P_{\vec{k}}^{\dagger} \rho_{\vec{k}}\right)^{\dagger}}$$

$$\boxed{\rho_{\vec{k}}^{\dagger} = \rho_{\vec{k}}^{*} = \sum_{i=1}^{N} e^{+i\vec{k}\bullet\vec{r}_i} = \rho_{-\vec{k}}}$$

$$H_1^{\dagger} = \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2} P_{\vec{k}}^{\dagger} P_{\vec{k}} - M_k P_{\vec{k}} \rho_{\vec{k}}^{*}$$

$$P_{\vec{k}}^{\dagger} = P_{-\vec{k}} \quad ; \quad P_{\vec{k}} = P_{-\vec{k}}^{\dagger}$$

$$\boxed{H_1^{\dagger} = \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2} P_{\vec{k}}^{\dagger} P_{\vec{k}} - M_k P_{-\vec{k}}^{\dagger} \rho_{-\vec{k}}}$$

$\vec{k}$ space symmetry

$$\sum_{\substack{\vec{k} \\ k\langle k_c}} M_k P_{-\vec{k}}^{\dagger} \rho_{-\vec{k}} = \sum_{\substack{\vec{k} \\ k\langle k_c}} M_k P_{\vec{k}}^{\dagger} \rho_{\vec{k}}$$

$$H_1^{\dagger} = \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2} P_{\vec{k}}^{\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger} \rho_{\vec{k}} = H_1$$

$H_1 \rightarrow Hermitian$

$Q, P:$ $\underline{\text{NOT}}$ $Hermitian$

$$H_1 = \sum_{\substack{\vec{k} \\ k \langle k_c}} \frac{1}{2} P_{\vec{k}}^{\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger} \rho_{\vec{k}} \; ; M_k = \sqrt{\frac{4\pi e^2}{V k^2}}$$

$$k \le k_{\max} \approx \frac{\omega_p}{\mathrm{v}_f}$$

$$k \le k_{\max} \approx \frac{\omega_p}{\mathrm{v}_f} \leftrightarrow k_c$$

← The upper limit on k limits the total degrees of freedom so that the total number of degrees remains fixed at 3N

$$H_0 \psi = E \psi$$

← The wavefunction must be a function only of the electron coordinates.

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$$H_0\psi = E\psi$$

← The wavefunction must be a function only of the electron coordinates.

$$\psi \not\to function\left(Q_{\vec{k}};\ if\ k\langle k_c\right)$$

$$\psi \to function\left(q : electron\ coordinates\right)$$

We must not introduce any additional degrees of freedom

$$\frac{\partial \psi}{\partial Q_k} = 0 \ \text{ for } k < k_c$$

Subsidiary condition

$$P_k = -i\hbar \frac{\partial}{\partial Q_k}$$

Raimes: Many Electron Theory; Eq.4.20, page 76

$$P_k \psi = 0 \quad \text{for } k < k_c$$

$$\left[Q_k, P_{k'}\right]_- = i\hbar \delta_{k,k'}$$

canonical conjugation

$$H_0\psi = E\psi$$

$$H_1 = \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2} P_{\vec{k}}^{\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger} \rho_{\vec{k}} \; ; \; M_k = \sqrt{\frac{4\pi e^2}{Vk^2}}$$

$$\frac{\partial \psi}{\partial Q_k} = 0 \;\; \text{for } k < k_c ; \quad \text{i.e.} \quad P_k \psi = 0 \Rightarrow H_1 \psi = 0$$

$$\therefore \quad \left(H_0 + H_1\right)\psi = E\psi$$

Now, we effect a UNITARY TRANSFORMATION of the Hamiltonian $\left(H_0 + H_1\right)$ $U = e^{\frac{i}{\hbar}S}$

$$S = \sum_{\vec{k};\, k\langle k_c} M_k Q_{\vec{k}} \rho_{\vec{k}}$$

$$U^{\dagger} = e^{\frac{-i}{\hbar}S^{\dagger}}$$

$$\boxed{\begin{aligned} S^{\dagger} &= \sum_{\vec{k};\, k\langle k_c} M_k Q_{\vec{k}}^{\dagger} \rho_{\vec{k}}^{*} \\ &= \sum_{\vec{k};\, k\langle k_c} M_k Q_{-\vec{k}} \rho_{-\vec{k}} = S \end{aligned}}$$

UNITARITY

$$U^{\dagger} = e^{\frac{-i}{\hbar}S} = U^{-1}$$

Raimes: Many Electron Theory; page 76,77

$$U = e^{\frac{i}{\hbar}S}$$

$$S = \sum_{\vec{k};\, k\langle k_c} M_k Q_{\vec{k}} \rho_{\vec{k}}$$

$$\boxed{\begin{aligned} S^\dagger &= \sum_{\vec{k};\, k\langle k_c} M_k Q_{\vec{k}}^{\dagger} \rho_{\vec{k}}^{*} \\ &= \sum_{\vec{k};\, k\langle k_c} M_k Q_{-\vec{k}} \rho_{-\vec{k}} = S \end{aligned}}$$

$$U^\dagger = e^{\frac{-i}{\hbar}S^\dagger}$$

$$U^\dagger = e^{\frac{-i}{\hbar}S} = U^{-1}$$

Transformation of all operators and the wavefunction under the unitary transformation

$$\Omega_{new} = U^{-1}\Omega U = U^\dagger \Omega U$$

$$\psi_{new} = U^{-1}\psi = e^{\frac{-i}{\hbar}S}\psi$$

$$\boxed{\begin{aligned} \left(\vec{r}_i\right)_{new} &= U^{-1}\left(\vec{r}_i\right)U = \vec{r}_i \\ \left(Q_{\vec{k}}\right)_{new} &= U^{-1}\left(Q_{\vec{k}}\right)U = Q_{\vec{k}} \end{aligned}}$$

$$\left(\rho_{\vec{k}}\right)_{new} = U^{-1}\left(\rho_{\vec{k}}\right)U = \rho_{\vec{k}}$$

$$\text{since } \rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}$$

$$\boxed{\vec{r}_i,\ Q_{\vec{k}},\ \rho_{\vec{k}}\ :\ \text{invariant}}$$

$\underline{HOWEVER}$:

$$\vec{p}_i,\ P_{\vec{k}}\ :\ \text{change under the transformation}$$

$$P_k = -i\hbar \frac{\partial}{\partial Q_k} \qquad (P_k)_{new} = U^{-1}(P_k)U \; ?$$

$$U = e^{\frac{i}{\hbar}S}$$

$$S = \sum_{\vec{k};\, k \langle k_c} M_k Q_{\vec{k}} \rho_{\vec{k}}$$

$$[p_k, q_{k'}]_- = -i\hbar\delta_{k,k'} \Rightarrow [p_k, F(\vec{r})]_- = -i\hbar \frac{\partial F(\vec{r})}{\partial q_k}$$

$$[P_k, Q_{k'}]_- = -i\hbar\delta_{k,k'} \Rightarrow [P_k, F(Q)]_- = -i\hbar \frac{\partial F(Q)}{\partial Q_k}$$

$$[P_k, U]_- = -i\hbar \frac{\partial U}{\partial Q_k} \qquad P_k U = -i\hbar \frac{\partial U}{\partial Q_k} + U P_k$$

$$(P_k)_{new} = U^{-1}\left(-i\hbar \frac{\partial U}{\partial Q_k} + U P_k\right)$$

$$= P_k - i\hbar U^{-1} \frac{\partial U}{\partial Q_k}$$

$$\boxed{(P_k)_{new} = P_k + U^{-1}[P_k, U]_-}$$

$$\boxed{\left(P_k\right)_{new} = P_k + U^{-1}\left[P_k, U\right]_-}$$

$$\left[P_k, U\right]_- = -i\hbar\frac{\partial U}{\partial Q_k}$$

$$\boxed{\left(P_k\right)_{new} = P_k + U^{-1}\left(-i\hbar\frac{\partial U}{\partial Q_k}\right)}$$

$$U = e^{\frac{i}{\hbar}S} \quad \text{with} \quad S = \sum_{\vec{k};\, k\langle k_c} M_k Q_{\vec{k}}\rho_{\vec{k}}$$

$$\frac{\partial U}{\partial Q_k} = \frac{\partial e^{\frac{i}{\hbar}S}}{\partial Q_k} = e^{\frac{i}{\hbar}S}\frac{i}{\hbar}\frac{\partial S}{\partial Q_k} = U\frac{i}{\hbar}\frac{\partial S}{\partial Q_k}$$

$$\frac{\partial U}{\partial Q_k} = U\frac{i}{\hbar}M_k\rho_{\vec{k}}$$

$$\left(P_k\right)_{new} = P_k + U^{-1}\left(-i\hbar\right)\left(U\frac{i}{\hbar}M_k\rho_{\vec{k}}\right) = P_k + U^{-1}UM_k\rho_{\vec{k}}$$

$$\boxed{\left(P_k\right)_{new} = P_k + M_k\rho_{\vec{k}}}$$

Raimes: Many Electron Theory; Eq.4.35, page 77

Transformation of the x component of the momentum operator for the i^th electron:

$$(p_{ix})_{new} = U^{-1}(p_{ix})U$$

$$[p_k, q_{k'}]_- = -i\hbar\delta_{k,k'} \Rightarrow [p_k, F(\vec{r})]_- = -i\hbar\frac{\partial F(\vec{r})}{\partial q_k}$$

$$[p_k, U]_- = p_k U - U p_k = -i\hbar\frac{\partial U}{\partial q_k}$$

$$(p_{ix})_{new} = U^{-1}\left(Up_{ix} - i\hbar\frac{\partial U}{\partial q_{ix}}\right) = p_{ix} - i\hbar U^{-1}\frac{\partial U}{\partial q_{ix}}$$

$$\left(p_{ix}\right)_{new} = U^{-1}\left(Up_{ix} - i\hbar\frac{\partial U}{\partial q_{ix}}\right) = p_{ix} - i\hbar U^{-1}\frac{\partial U}{\partial q_{ix}}$$

$$\left[p_k, U\right]_- = p_k U - Up_k = -i\hbar\frac{\partial U}{\partial q_k}$$

$$\left(p_{ix}\right)_{new} = p_{ix} - i\hbar U^{-1}\left\{\frac{\left[p_{ix}, U\right]_-}{-i\hbar}\right\}$$

$$\left(p_{ix}\right)_{new} = p_{ix} + U^{-1}\left[p_{ix}, U\right]$$

$$(p_{ix})_{new} = p_{ix} + U^{-1}[p_{ix}, U]$$

$$(p_{ix})_{new} = p_{ix} - i\hbar\, U^{-1}\underbrace{\left(\frac{\partial U}{\partial q_{ix}}\right)}$$

since

$$[p_{ix}, U]_- = -i\hbar \frac{\partial U}{\partial q_{ix}}$$

$$Now\ :\ U = e^{\frac{i}{\hbar}S} \quad with \quad S = \sum_{\vec{k};\, k\langle k_c} M_{\vec{k}} Q_{\vec{k}} \rho_{\vec{k}}$$

$$\therefore\ \underbrace{\frac{\partial U}{\partial q_{ix}}} = U \frac{i}{\hbar} \frac{\partial S}{\partial q_{ix}} = U \frac{i}{\hbar} \sum_{\vec{k};\, k\langle k_c} M_{\vec{k}} Q_{\vec{k}} \frac{\partial \rho_{\vec{k}}}{\partial q_{ix}}$$

$$(p_{ix})_{new} = p_{ix} - i\hbar\, U^{-1}\left(U \frac{i}{\hbar} \sum_{\vec{k};\, k\langle k_c} M_{\vec{k}} Q_{\vec{k}} \frac{\partial \rho_{\vec{k}}}{\partial q_{ix}}\right)$$

$$(p_{ix})_{new} = p_{ix} + \sum_{\vec{k};\, k\langle k_c} \left(M_{\vec{k}} Q_{\vec{k}} \frac{\partial \rho_{\vec{k}}}{\partial q_{ix}}\right)$$

$$\left(p_{ix}\right)_{new} = p_{ix} + \sum_{\vec{k};\, k\langle k_c} \left(M_{\vec{k}} Q_{\vec{k}} \frac{\partial \rho_{\vec{k}}}{\partial q_{ix}} \right)$$

$$\boxed{\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}}$$

$$\frac{\partial \rho_{\vec{k}}}{\partial q_{ix}} = \frac{\partial}{\partial q_{ix}} \sum_{j=1}^{N} e^{-i\vec{k}\bullet\vec{r}_j}$$

$$= \frac{\partial}{\partial q_{ix}} e^{-i\vec{k}\bullet\vec{r}_i}$$

$$= e^{-i\vec{k}\bullet\vec{r}_i}\left(-ik_{ix}\right)$$

$$\left(p_{ix}\right)_{new} = p_{ix} + \sum_{\vec{k};\, k\langle k_c} M_{\vec{k}} Q_{\vec{k}} \left\{ e^{-i\vec{k}\bullet\vec{r}_i}\left(-ik_{ix}\right) \right\}$$

$$\left(p_{ix}\right)_{new} = p_{ix} - i \sum_{\vec{k};\, k\langle k_c} M_{\vec{k}} Q_{\vec{k}} k_{ix} e^{-i\vec{k}\bullet\vec{r}_i}$$

Similar relations for y and z components

$$\left(\vec{p}_i\right)_{new} = \vec{p}_i - i \sum_{\vec{k};\, k \langle k_c} M_{\vec{k}} Q_{\vec{k}} \; \vec{k} \; e^{-i\vec{k}\bullet\vec{r}_i}$$

← Raimes: Many Electron Theory; Eq.4.38, page 78

Similar relations for y and z components

$\vec{r}_i,\ Q_{\vec{k}},\ \rho_{\vec{k}}$: invariant under the transformation

HOWEVER, $\vec{p}_i,\ P_{\vec{k}}$: change under the transformation

Recall the consideration from SLIDE No.195

$$H_0\psi = E\psi$$

← The wavefunction must be a function only of the electron coordinates.

We must not introduce any additional degrees of freedom

$$\psi \not\to function\left(Q_{\vec{k}};\ \text{if } k < k_c\right)$$

$$\psi \to function\left(q : electron\ coordinates\right)$$

$$\frac{\partial \psi}{\partial Q_k} = 0 \quad \text{for } k < k_c$$

$$P_k = -i\hbar\frac{\partial}{\partial Q_k}$$

$$P_k\psi = 0 \quad \text{for } k < k_c$$

$$\left[Q_k, P_{k'}\right]_- = i\hbar\delta_{k,k'}$$

Subsidiary condition

canonical conjugation

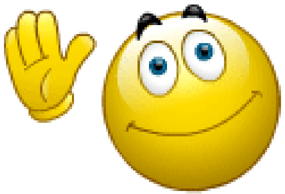
$$\frac{\partial \psi}{\partial Q_k} = 0 \quad \text{for } k < k_c$$

$$P_k = -i\hbar \frac{\partial}{\partial Q_k}$$

$$P_k \psi = 0 \quad \text{for } k < k_c$$

Subsidiary condition

$$\left(P_k\right)_{new} \psi_{new} = 0 \quad \text{for } k < k_c$$



$$\left(U^{-1} P_k U\right)\left(U^{-1} \psi\right) = 0 \quad \text{for } k < k_c$$

from slide 195: $\left(P_k\right)_{new} = P_k + M_k \rho_{\vec{k}}$

$$\left(P_k + M_k \rho_{\vec{k}} \right) \psi_{new} = 0 \quad \text{for } k < k_c$$

Questions:
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Select/Special Topics from
'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 23

Electron Gas in the Random Phase Approximations

Plasma Oscillations in Free Electron Gas

References: 'The theory of plasma oscillations in metals'
- by S Raimes 1957 *Rep. Prog. Phys.* **20** 1
Also: Chapter 4 in 'Many Electron Theory' by Stanley Raimes

$$H_0 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{2\pi e^2}{V} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} \frac{1}{k^2} \left(\rho_{\vec{k}}^{\,*} \rho_{\vec{k}} - N \right)$$

Hamiltonian for a bulk electron gas in a uniform positive background jellium potential

$$H_1 = \sum_{\substack{\vec{k} \\ k \langle k_c}} \frac{1}{2} P_{\vec{k}}^{\,\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger} \rho_{\vec{k}}$$

$$\text{with } M_k = \sqrt{\frac{4\pi e^2}{Vk^2}}$$

$$\Omega_{new} = U^{-1} \Omega U = U^{\dagger} \Omega U$$

$$U = e^{\frac{i}{\hbar} S}$$

$$S = \sum_{\vec{k};\, k \langle k_c} M_k Q_{\vec{k}} \rho_{\vec{k}}$$

$\vec{r}_i,\ Q_{\vec{k}},\ \rho_{\vec{k}}$: invariant under the transformation

$$\left(\vec{p}_i \right)_{new} = \vec{p}_i - i \sum_{\vec{k};\, k \langle k_c} M_{\vec{k}} Q_{\vec{k}}\, \vec{k}\, e^{-i\vec{k} \bullet \vec{r}_i}$$

$$\left(P_k \right)_{new} = P_k + M_k \rho_{\vec{k}}$$

We now ask: $\mathfrak{H} = H_{new} = U^{-1} \left(H_0 + H_1 \right) U = ?$

Transformation of all operators and the wavefunction under the unitary transformation

$$\Omega_{new} = U^{-1}\Omega U = U^{\dagger}\Omega U$$

$$\psi_{new} = U^{-1}\psi = e^{\frac{-i}{\hbar}S}\psi$$

$$U = e^{\frac{i}{\hbar}S}$$

$$S = \sum_{\vec{k};\, k\langle k_c} M_k Q_{\vec{k}} \rho_{\vec{k}}$$

Subsidiary conditions

$$\frac{\partial \psi}{\partial Q_k} = 0 \;\; \text{for } k < k_c$$

$$P_k \psi = 0 \;\; \text{for } k < k_c$$

$$\left(P_k\right)_{new} \psi_{new} = 0 \;\; \text{for } k < k_c$$

$$H_0 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{1}{2} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k^{\,2} \left(\rho_{\vec{k}}^{\,*} \rho_{\vec{k}} - N \right)$$

$$H_0 = H_{el} + H_b + H_{el-b}$$

N Electrons + Positive Background

$$H_1 = \sum_{\substack{\vec{k} \\ k \langle k_c}} \frac{1}{2} P_{\vec{k}}^{\,\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger} \rho_{\vec{k}}$$

$$\boxed{\frac{1}{2} M_k^{\,2} = \frac{2\pi e^2}{Vk^2}}$$

Auxiliery Hamiltonian

$$\boxed{\left(H_0 + H_1 \right) \psi = E \psi}$$

$$\boxed{\begin{gathered} H_0 + H_1 = \\ \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{1}{2} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k^{\,2} \left(\rho_{\vec{k}}^{\,*} \rho_{\vec{k}} - N \right) + \sum_{\substack{\vec{k} \\ k \langle k_c}} \left(\frac{1}{2} P_{\vec{k}}^{\,\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger} \rho_{\vec{k}} \right) \end{gathered}}$$

Our question: $\mathfrak{H} = H_{new} = U^{-1} \left(H_0 + H_1 \right) U = ?$

$$\underbrace{H_0 + H_1 = \sum_{i=1}^{N} \frac{p_i^2}{2m}}_{T_1} + \underbrace{\frac{1}{2}\sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} M_k^2\left(\rho_{\vec{k}}^* \rho_{\vec{k}} - N\right)}_{T_2} + \underbrace{\sum_{\substack{\vec{k} \\ k\langle k_c}} \left(\frac{1}{2} P_{\vec{k}}^\dagger P_{\vec{k}} - M_k P_{\vec{k}}^\dagger \rho_{\vec{k}}\right)}_{T_3}$$

Our question: $H_{new} = U^{-1}\left(H_0 + H_1\right)U = ?$

$$\left(p_{ix}\right)_{new} = p_{ix} + \sum_{\vec{k};\, k\langle k_c} \left(M_{\vec{k}} Q_{\vec{k}} \frac{\partial \rho_{\vec{k}}}{\partial q_{ix}} \right)$$

$(T_1)_{new}$

$$\left\{\sum_{i=1}^{N} \frac{p_i^2}{2m}\right\}_{new} = \left[\begin{array}{l} \displaystyle\sum_{i=1}^{N} \frac{p_i^2}{2m} - \frac{i}{2m}\sum_j \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\, \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right) e^{-i\vec{k}\bullet\vec{r}_j} \\ \displaystyle -\frac{1}{2m}\sum_j \sum_{\substack{\vec{k} \\ k\langle k_c}} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{\vec{k}} M_{\vec{\ell}}\, Q_{\vec{k}} Q_{\vec{\ell}}\, \vec{k}\bullet\vec{\ell}\; e^{-i(\vec{k}+\vec{\ell})\bullet\vec{r}_j} \end{array}\right]$$

Raimes: Many Electron Theory; Eq.4.48, page 79

$$(T_2)_{new} = \frac{1}{2}\sum_{\vec{k};\, \vec{k}\neq\vec{0}} M_k^2\left(\rho_{\vec{k}}^* \rho_{\vec{k}} - N\right) \quad \leftarrow \text{since } \rho_{\vec{k}} : \text{invariant}$$

$$H_0 + H_1 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \underbrace{\frac{1}{2}\sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} M_k^{\,2}\left(\rho_{\vec{k}}^{\,*}\rho_{\vec{k}} - N\right)}_{T_2} + \sum_{\substack{\vec{k} \\ k\langle k_c}} \left(\frac{1}{2}P_{\vec{k}}^{\,\dagger}P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger}\rho_{\vec{k}}\right)$$

$$(T_2)_{new} = \frac{1}{2}\sum_{\vec{k};\,\vec{k}\neq\vec{0}} M_k^{\,2}\left(\rho_{\vec{k}}^{\,*}\rho_{\vec{k}} - N\right) \qquad \leftarrow \text{since } \rho_{\vec{k}} : \text{invariant}$$

separate the summation $\sum_{\vec{k};\,\vec{k}\neq\vec{0}}$ in two parts:

for (1) $k > k_c$ and (2) $k < k_c$

$$k_c = k_{\max} \approx \frac{\omega_p}{v_f}$$

$$(T_2)_{new} = \boxed{\frac{1}{2}\sum_{\substack{\vec{k};\,\vec{k}\neq\vec{0} \\ k>k_c}} M_k^{\,2}\left(\rho_{\vec{k}}^{\,*}\rho_{\vec{k}} - N\right)} + \frac{1}{2}\sum_{\substack{\vec{k};\,\vec{k}\neq\vec{0} \\ k<k_c}} M_k^{\,2}\left(\rho_{\vec{k}}^{\,*}\rho_{\vec{k}} - N\right)$$

$H_{s.r.} \leftarrow$ Short range

long range

$$H_0 + H_1 = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \frac{1}{2} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k^{\,2} \left(\rho_{\vec{k}}^{\,*} \rho_{\vec{k}} - N \right) + \underbrace{\sum_{\substack{\vec{k} \\ k \langle k_c}} \left(\frac{1}{2} P_{\vec{k}}^{\,\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger} \rho_{\vec{k}} \right)}_{T_3}$$

$$(T_3)_{new} \quad = U^{-1} \left[\sum_{\substack{\vec{k} \\ k \langle k_c}} \left(\frac{1}{2} P_{\vec{k}}^{\,\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger} \rho_{\vec{k}} \right) \right] U$$

$$\left(P_{\vec{k}} \right)_{new} = P_{\vec{k}} + M_{\vec{k}} \rho_{\vec{k}}$$

$$\left(P_{\vec{k}}^{\,\dagger} \right)_{new} = P_{\vec{k}}^{\,\dagger} + M_{\vec{k}} \rho_{\vec{k}}^{\,\dagger} \quad \text{i.e.} \quad \left(P_{\vec{k}}^{\,\dagger} \right)_{new} = P_{-\vec{k}} + M_{\vec{k}} \rho_{-\vec{k}}$$

$$\left(P_{\vec{k}}^{\,\dagger} P_{\vec{k}} \right)_{new} = \left(P_{-\vec{k}} + M_{\vec{k}} \rho_{-\vec{k}} \right) \left(P_{\vec{k}} + M_{\vec{k}} \rho_{\vec{k}} \right)$$

$$\left(P_{\vec{k}}^{\,\dagger} P_{\vec{k}} \right)_{new} = P_{-\vec{k}} P_{\vec{k}} + M_{\vec{k}} \left(P_{-\vec{k}} \rho_{\vec{k}} + \rho_{-\vec{k}} P_{\vec{k}} \right) + M_{\vec{k}}^{\,2} \rho_{-\vec{k}} \rho_{\vec{k}}$$

$$\left(P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)_{new} = P_{-\vec{k}}P_{\vec{k}} + M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right) + M_{\vec{k}}^{\;2}\rho_{-\vec{k}}\rho_{\vec{k}}$$

$$\boxed{\rho_{\vec{k}}^{\;\dagger} = \rho_{\vec{k}}^{\;*} = \sum_{i=1}^{N} e^{+i\vec{k}\bullet\vec{r}_i} = \rho_{-\vec{k}} \quad \& \quad P_{\vec{k}}^{\;\dagger} = P_{-\vec{k}}}$$

$$\sum_{k<k_c} M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right) = \sum_{k<k_c} M_{\vec{k}}\left(P_{\vec{k}}^{\;\dagger}\rho_{\vec{k}}\right) + \sum_{k<k_c} M_{\vec{k}}\left(\rho_{\vec{k}}^{\;*}P_{-\vec{k}}^{\;\dagger}\right)$$

spherical symmetry of $\vec{k}$ *vectors*

$$\sum_{k<k_c} M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right) = \sum_{k<k_c} M_{\vec{k}}\left(P_{\vec{k}}^{\;\dagger}\rho_{\vec{k}}\right) + \sum_{k<k_c} M_{\vec{k}}\left(\rho_{-\vec{k}}^{\;*}P_{\vec{k}}^{\;\dagger}\right)$$

$$= \sum_{k<k_c} M_{\vec{k}}\left(P_{\vec{k}}^{\;\dagger}\rho_{\vec{k}}\right) + \sum_{k<k_c} M_{\vec{k}}\left(\rho_{\vec{k}}P_{\vec{k}}^{\;\dagger}\right)$$

Hence:

$$\sum_{k<k_c} M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right) = 2\sum_{k<k_c} M_{\vec{k}}\left(P_{\vec{k}}^{\;\dagger}\rho_{\vec{k}}\right)$$

$$(\mathrm{T}_3)_{\mathrm{new}} = U^{-1}\left[\sum_{\substack{\vec{k} \\ k\langle k_c}} \left(\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]U$$

$$\left[\sum_{\substack{\vec{k} \\ k\langle k_c}} \left(\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)\right]_{new} = U^{-1}\left[\sum_{\substack{\vec{k} \\ k\langle k_c}} \left(\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)\right]U$$

$$\left(P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)_{new} = P_{-\vec{k}}P_{\vec{k}} + M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right) + M_{\vec{k}}^{\ 2}\rho_{-\vec{k}}\rho_{\vec{k}}$$

$$\sum_{k<k_c} \frac{1}{2}\left(P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)_{new} = \sum_{k<k_c} \frac{1}{2}P_{-\vec{k}}P_{\vec{k}} + \sum_{k<k_c} \frac{1}{2}M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right)$$

$$+\sum_{k<k_c} \frac{1}{2}M_{\vec{k}}^{\ 2}\rho_{-\vec{k}}\rho_{\vec{k}}$$

$$\sum_{k<k_c} M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right) = 2\sum_{k<k_c} M_{\vec{k}}\left(P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)$$

$$(T_3)_{new} = U^{-1}\left[\sum_{\substack{\vec{k}\\ k\langle k_c}} \left(\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]U$$

$$\sum_{k<k_c} \frac{1}{2}\left(P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)_{new} = \sum_{k<k_c} \frac{1}{2}P_{-\vec{k}}P_{\vec{k}} + \sum_{k<k_c} \boxed{\frac{1}{2}} M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right)$$

$$+\sum_{k<k_c} \frac{1}{2}M_{\vec{k}}^{\;2}\rho_{-\vec{k}}\rho_{\vec{k}}$$

we have seen that: $\sum_{k<k_c} M_{\vec{k}}\left(P_{-\vec{k}}\rho_{\vec{k}} + \rho_{-\vec{k}}P_{\vec{k}}\right) = \boxed{2}\sum_{k<k_c} M_{\vec{k}}\left(P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)$

$$\sum_{k<k_c} \frac{1}{2}\left(P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)_{new} = \sum_{k<k_c} \frac{1}{2}P_{-\vec{k}}P_{\vec{k}} + \sum_{k<k_c} M_{\vec{k}}P_{\vec{k}}^{\dagger}\rho_{\vec{k}}$$

$$+\sum_{k<k_c} \frac{1}{2}M_{\vec{k}}^{\;2}\rho_{\vec{k}}^{\;*}\rho_{\vec{k}}$$

$$\left[\sum_{\substack{\vec{k}\\ k\langle k_c}} \left(-M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]_{new} = U^{-1}\left[\sum_{\substack{\vec{k}\\ k\langle k_c}} \left(-M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]U = ?$$

$$(T_3)_{new} = U^{-1}\left[\sum_{\substack{\vec{k}\\ k<k_c}} \left(\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]U$$

Remember the minus sign!

$$\left[\sum_{\substack{\vec{k}\\ k<k_c}} \left(-M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]_{new} = U^{-1}\left[\sum_{\substack{\vec{k}\\ k<k_c}} \left(-M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]U = ?$$

$$\boxed{\rho_{\vec{k}}^{\dagger} = \rho_{\vec{k}}^{*} = \sum_{i=1}^{N} e^{+i\vec{k}\bullet\vec{r}_i} = \rho_{-\vec{k}} \quad \& \quad P_{\vec{k}}^{\dagger} = P_{-\vec{k}}}$$

$$\left(P_{\vec{k}}\right)_{new} = P_{\vec{k}} + M_{\vec{k}}\rho_{\vec{k}}$$

$$\left(P_{\vec{k}}^{\dagger}\right)_{new} = P_{\vec{k}}^{\dagger} + M_{\vec{k}}\rho_{\vec{k}}^{\dagger} \quad \text{i.e.} \quad \left(P_{\vec{k}}^{\dagger}\right)_{new} = P_{-\vec{k}} + M_{\vec{k}}\rho_{-\vec{k}}$$

$$\left(M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)_{new} = M_k\left(P_{\vec{k}}^{\dagger}\right)_{new}\rho_{\vec{k}}$$

$$= M_k\left(P_{-k} + M_k\rho_{-\vec{k}}\right)\rho_{\vec{k}}$$

$$\boxed{\left(M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)_{new} = M_k P_{-k}\rho_{\vec{k}} + M_k^{2}\rho_{-\vec{k}}\rho_{\vec{k}}}$$

$(T_3)_{new}$ $$= U^{-1}\left[\sum_{\substack{\vec{k}\\ k\langle k_c}} \left(\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}} - M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)\right]U$$

Remember the minus sign!

$$\left(M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)_{new} = M_k P_{-k}\rho_{\vec{k}} + M_k^{\ 2}\rho_{-\vec{k}}\rho_{\vec{k}}$$

$$\boxed{\rho_{\vec{k}}^{\ \dagger} = \rho_{\vec{k}}^{\ *} = \sum_{i=1}^{N} e^{+i\vec{k}\bullet\vec{r}_i} = \rho_{-\vec{k}} \quad \& \quad P_{\vec{k}}^{\ \dagger} = P_{-\vec{k}}}$$

$$\left(M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)_{new} = M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}} + M_k^{\ 2}\rho_{\vec{k}}^{\ *}\rho_{\vec{k}}$$

$$-\left(M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}}\right)_{new} = -M_k P_{\vec{k}}^{\dagger}\rho_{\vec{k}} - M_k^{\ 2}\rho_{\vec{k}}^{\ *}\rho_{\vec{k}}$$

$(T_3)_{new}$ has $\sum_{\substack{\vec{k}\\ k\langle k_c}}$

Earlier, we showed that:

$$\sum_{k<k_c}\frac{1}{2}\left(P_{\vec{k}}^{\dagger}P_{\vec{k}}\right)_{new} = \sum_{k<k_c}\frac{1}{2}P_{-\vec{k}}P_{\vec{k}} + \sum_{k<k_c} M_{\vec{k}}P_{\vec{k}}^{\dagger}\rho_{\vec{k}} + \sum_{k<k_c}\frac{1}{2}M_{\vec{k}}^{\ 2}\rho_{\vec{k}}^{\ *}\rho_{\vec{k}}$$

$$H_0 + H_1 =$$

$$= \underbrace{\sum_{i=1}^{N} \frac{p_i^{\,2}}{2m}}_{T_1} + \underbrace{\frac{1}{2} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k^{\,2} \left(\rho_{\vec{k}}^{\,*} \rho_{\vec{k}} - N \right)}_{T_2} + \underbrace{\sum_{\substack{\vec{k} \\ k \langle k_c}} \left(\frac{1}{2} P_{\vec{k}}^{\,\dagger} P_{\vec{k}} - M_k P_{\vec{k}}^{\,\dagger} \rho_{\vec{k}} \right)}_{T_3}$$

We had asked:

$$\mathfrak{H} = H_{new} = U^{-1} \left(H_0 + H_1 \right) U = ?$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N}\frac{p_i^{\,2}}{2m} - \frac{i}{2m}\sum_j \sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\; \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right)e^{-i\vec{k}\bullet\vec{r}_j}$$

$(T_1)_{new}$ →

$$-\frac{1}{2m}\sum_j \sum_{\substack{\vec{k}\\ k\langle k_c}} \sum_{\substack{\vec{\ell}\\ \ell\langle k_c}} M_{\vec{k}}\; M_{\vec{\ell}}\; Q_{\vec{k}}\; Q_{\vec{\ell}}\; \vec{k}\bullet\vec{\ell}\; e^{-i(\vec{k}+\vec{\ell})\bullet\vec{r}_j}$$

$(T_2)_{new}$ →

$$+\frac{1}{2}\sum_{\vec{k};\,\vec{k}\neq\vec{0}} M_k^{\,2}\left(\rho_{\vec{k}}^{\,*}\rho_{\vec{k}} - N\right) + \frac{1}{2}\sum_{\vec{k};\,\vec{k}\neq\vec{0}} M_k^{\,2}\left(\rho_{\vec{k}}^{\,*}\rho_{\vec{k}} - N\right)$$

$k > k_c$ $k < k_c$

Short range long range

$(T_3)_{new}$ →

$$+\sum_{k<k_c}\frac{1}{2}P_{-\vec{k}}P_{\vec{k}} + \sum_{k<k_c} M_{\vec{k}}P_{\vec{k}}^{\,\dagger}\rho_{\vec{k}} + \sum_{k<k_c}\frac{1}{2}M_{\vec{k}}^{\,2}\rho_{\vec{k}}^{\,*}\rho_{\vec{k}}$$

$$-\sum_{\vec{k}} M_k P_{\vec{k}}^{\,\dagger}\rho_{\vec{k}} - \sum_{\vec{k}} M_k^{\,2}\rho_{\vec{k}}^{\,*}\rho_{\vec{k}}$$

$(T_3)_{new}$ has $\displaystyle\sum_{\substack{\vec{k}\\ k\langle k_c}}$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N}\frac{p_i^{\,2}}{2m} - \frac{i}{2m}\sum_{j}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\;\vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right)e^{-i\vec{k}\bullet\vec{r}_j}$$

$$-\frac{1}{2m}\sum_{j}\sum_{\substack{\vec{k}\\ k\langle k_c}}\sum_{\substack{\vec{\ell}\\ \ell\langle k_c}} M_{\vec{k}}\;M_{\vec{\ell}}\;Q_{\vec{k}}\;Q_{\vec{\ell}}\;\vec{k}\bullet\vec{\ell}\;e^{-i\left(\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}$$

$H_{s.r.}$

$$\boxed{+\frac{1}{2}\sum_{\vec{k};\,\vec{k}\neq\vec{0}} M_k^{\;2}\left(\rho_{\vec{k}}^{\;*}\rho_{\vec{k}} - N\right) \qquad k>k_c} + \frac{1}{2}\sum_{\vec{k};\,\vec{k}\neq\vec{0}} M_k^{\;2}\left(\rho_{\vec{k}}^{\;*}\rho_{\vec{k}} - N\right) \qquad k<k_c$$

Short range

long range

$$+\sum_{k<k_c}\frac{1}{2}P_{-\vec{k}}P_{\vec{k}} + \cancel{\sum_{k<k_c} M_{\vec{k}}P_{\vec{k}}^{\;\dagger}\rho_{\vec{k}}} + \sum_{k<k_c}\frac{1}{2}M_{\vec{k}}^{\;2}\rho_{\vec{k}}^{\;*}\rho_{\vec{k}}$$

$$\boxed{H_{s.r.} = \frac{1}{2}\sum_{\vec{k};\,\vec{k}\neq\vec{0}}^{k>k_c} M_k^{\;2}\left(\rho_{\vec{k}}^{\;*}\rho_{\vec{k}} - N\right)} \qquad -\cancel{\sum_{\vec{k}} M_k P_{\vec{k}}^{\;\dagger}\rho_{\vec{k}}} - \sum_{\vec{k}} M_k^{\;2}\rho_{\vec{k}}^{\;*}\rho_{\vec{k}}$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N} \frac{p_i^2}{2m} - \frac{i}{2m} \sum_j \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\, \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right) e^{-i\vec{k}\bullet\vec{r}_j}$$

The three terms shown by the arrows together cancel each other.

$$-\frac{1}{2m} \sum_j \sum_{\substack{\vec{k} \\ k\langle k_c}} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{\vec{k}}\, M_{\vec{\ell}}\, Q_{\vec{k}}\, Q_{\vec{\ell}}\, \vec{k}\bullet\vec{\ell}\, e^{-i(\vec{k}+\vec{\ell})\bullet\vec{r}_j}$$

$$+\ H_{s.r.}\ +\ \frac{1}{2} \sum_{\vec{k};\,\vec{k}\neq\vec{0}} M_k^{\,2}\left(\rho_{\vec{k}}^{\;*}\rho_{\vec{k}} - N\right)$$

$k > k_c$ $\qquad$ $k < k_c$

$$+\sum_{k<k_c} \frac{1}{2} P_{-\vec{k}} P_{\vec{k}} + \sum_{k<k_c} \frac{1}{2} M_{\vec{k}}^{\,2} \rho_{\vec{k}}^{\;*} \rho_{\vec{k}}$$

$(T_3)_{new}$ has $\displaystyle\sum_{\substack{\vec{k} \\ k\langle k_c}}$ $\displaystyle -\sum_{\vec{k}} M_k^{\,2} \rho_{\vec{k}}^{\;*} \rho_{\vec{k}}$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} - \frac{i}{2m} \sum_j \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k Q_{\vec{k}}\ \vec{k} \bullet \left(2\vec{p}_j + \hbar \vec{k} \right) e^{-i\vec{k} \bullet \vec{r}_j}$$

$$- \frac{1}{2m} \sum_j \sum_{\substack{\vec{k} \\ k \langle k_c}} \sum_{\substack{\vec{\ell} \\ \ell \langle k_c}} M_{\vec{k}}\ M_{\vec{\ell}}\ Q_{\vec{k}}\ Q_{\vec{\ell}}\ \vec{k} \bullet \vec{\ell}\ e^{-i(\vec{k}+\vec{\ell}) \bullet \vec{r}_j}$$

$$+ \ H_{s.r.} \qquad - \frac{1}{2} \sum_{\vec{k};\ \vec{k} \neq \vec{0}} M_k^{\,2} N$$

$$\boxed{+ \sum_{k<k_c} \frac{1}{2} P_{-\vec{k}} P_{\vec{k}}}$$

in the next step, we use:

$$\sum_{k<k_c} \frac{1}{2} P_{-\vec{k}} P_{\vec{k}} = \sum_{k<k_c} \frac{1}{2} P_{\vec{k}}^{\dagger} P_{\vec{k}}$$

$$M_k = \sqrt{\frac{4\pi e^2}{Vk^2}} \ \text{ i.e. } \ M_k^{\,2} = \frac{4\pi e^2}{Vk^2}$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} - \frac{i}{2m} \sum_{j} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k Q_{\vec{k}}\ \vec{k} \bullet \left(2\vec{p}_j + \hbar \vec{k} \right) e^{-i\vec{k} \bullet \vec{r}_j}$$

$$- \frac{1}{2m} \sum_{j} \sum_{\substack{\vec{k} \\ k \langle k_c}} \sum_{\substack{\vec{\ell} \\ \ell \langle k_c}} M_{\vec{k}}\ M_{\vec{\ell}}\ Q_{\vec{k}}\ Q_{\vec{\ell}}\ \vec{k} \bullet \vec{\ell}\ e^{-i(\vec{k}+\vec{\ell}) \bullet \vec{r}_j}$$

$$+\ H_{s.r.} - \sum_{\vec{k};\ \vec{k} \neq \vec{0}} \frac{2\pi e^2}{Vk^2} N\ +\ \sum_{k < k_c} \frac{1}{2} P_{\vec{k}}^{\ \dagger} P_{\vec{k}}$$

Separate in k=ℓ and k≠ℓ terms

$$-\frac{1}{2m} \sum_{j} \sum_{\substack{\vec{k} \\ k \langle k_c}}^{k=\ell} \sum_{\substack{\vec{\ell} \\ \ell \langle k_c}} M_{\vec{k}}\ M_{\vec{\ell}}\ Q_{\vec{k}}\ Q_{\vec{\ell}}\ \vec{k} \bullet \vec{\ell}\ e^{-i(\vec{k}+\vec{\ell}) \bullet \vec{r}_j}$$

$$-\frac{1}{2m} \sum_{j} \sum_{\substack{\vec{k} \\ k \langle k_c}}^{k \neq \ell} \sum_{\substack{\vec{\ell} \\ \ell \langle k_c}} M_{\vec{k}}\ M_{\vec{\ell}}\ Q_{\vec{k}}\ Q_{\vec{\ell}}\ \vec{k} \bullet \vec{\ell}\ e^{-i(\vec{k}+\vec{\ell}) \bullet \vec{r}_j}$$

$$-\frac{1}{2m}\sum_j \sum_{\substack{\vec{k} \\ k\langle k_C}}^{k=\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_C}} M_{\vec{k}}\, M_{\vec{\ell}}\, Q_{\vec{k}}\, Q_{\vec{\ell}}\, \vec{k}\bullet\vec{\ell}\, e^{-i(\vec{k}+\vec{\ell})\bullet\vec{r}_j}$$

$$-\frac{1}{2m}\sum_j \sum_{\substack{\vec{k} \\ k\langle k_C}}^{k\neq\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_C}} M_{\vec{k}}\, M_{\vec{\ell}}\, Q_{\vec{k}}\, Q_{\vec{\ell}}\, \vec{k}\bullet\vec{\ell}\, e^{-i(\vec{k}+\vec{\ell})\bullet\vec{r}_j}$$

$$\textit{spherical symmetry of } \vec{k} \textit{ vectors} \Rightarrow \sum_{\vec{k}} \equiv \sum_{-\vec{k}}$$

$$\boxed{\begin{aligned}&-\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_C}}^{k=\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_C}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(-\vec{k}\bullet\vec{\ell}\right) e^{-i(-\vec{k}+\vec{\ell})\bullet\vec{r}_j} \\ &-\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_C}}^{k\neq\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_C}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(-\vec{k}\bullet\vec{\ell}\right) e^{-i(-\vec{k}+\vec{\ell})\bullet\vec{r}_j}\end{aligned}}$$

$$-\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k=\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(-\vec{k}\bullet\vec{\ell}\right) e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}$$

$\uparrow \ell = k$ $\uparrow \ell = k$

$$M_{\vec{k}} = \sqrt{\frac{4\pi e^2}{Vk^2}} = M_{-\vec{k}}$$

$$-\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(-\vec{k}\bullet\vec{\ell}\right) e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}$$

$$\frac{N}{2m}\sum_{\substack{\vec{k} \\ k\langle k_c}} M_{\vec{k}}^{\,2}\; Q_{\vec{k}}^{\dagger}\; Q_{\vec{k}}\; k^2$$

$$+\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(\vec{k}\bullet\vec{\ell}\right) e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}$$

$$-\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k=\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(-\vec{k}\bullet\vec{\ell}\right) e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}$$

$$M_{\vec{k}} = \sqrt{\frac{4\pi e^2}{Vk^2}} = M_{-\vec{k}}$$

$$-\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(-\vec{k}\bullet\vec{\ell}\right) e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}$$

spherical symmetry of $\vec{k}$ *vectors*

$$\Rightarrow \sum_{\vec{k}} \equiv \sum_{-\vec{k}}$$

$$\boxed{\begin{aligned} &\frac{N}{2m}\sum_{\substack{\vec{k} \\ k\langle k_c}} M_{\vec{k}}^{\,2}\, Q_{\vec{k}}^{\dagger}\, Q_{\vec{k}}\, k^2 \\ &+\frac{1}{2m}\sum_j \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}}\, Q_{-\vec{k}}\, Q_{\vec{\ell}}\, \left(\vec{k}\bullet\vec{\ell}\right) e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j} \end{aligned}}$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N}\frac{p_i^{2}}{2m} - \frac{i}{2m}\sum_{j}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\ \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right)e^{-i\vec{k}\bullet\vec{r}_j}$$

$$-\frac{1}{2m}\sum_{j}\sum_{\substack{\vec{k}\\ k\langle k_c}}\sum_{\substack{\vec{\ell}\\ \ell\langle k_c}} M_{\vec{k}}\ M_{\vec{\ell}}\ Q_{\vec{k}}\ Q_{\vec{\ell}}\ \vec{k}\bullet\vec{\ell}\ e^{-i(\vec{k}+\vec{\ell})\bullet\vec{r}_j}$$

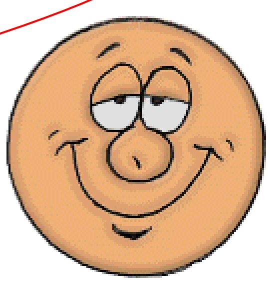
$$+\ H_{s.r.} - \sum_{\vec{k};\ \vec{k}\neq\vec{0}}\frac{2\pi e^{2}}{Vk^{2}}N + \sum_{k<k_c}\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}}$$

Separate in k=ℓ and k≠ℓ terms

$$\mathfrak{H} = H_{new} =$$

$$\sum_{i=1}^{N}\frac{p_i^{2}}{2m} - \frac{i}{2m}\sum_{j}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\ \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right)e^{-i\vec{k}\bullet\vec{r}_j} + \frac{N}{2m}\sum_{\substack{\vec{k}\\ k\langle k_c}} M_{\vec{k}}^{\,2}\ Q_{\vec{k}}^{\dagger}\ Q_{\vec{k}}\ k^{2}$$

$$+\frac{1}{2m}\sum_{j}\ \sum_{\substack{-\vec{k}\\ k\langle k_c}}^{k\neq\ell}\ \sum_{\substack{\vec{\ell}\\ \ell\langle k_c}} M_{-\vec{k}}\ M_{\vec{\ell}}\ Q_{-\vec{k}}\ Q_{\vec{\ell}}\ \left(-\vec{k}\bullet\vec{\ell}\right)\ e^{-i(-\vec{k}+\vec{\ell})\bullet\vec{r}_j}$$



$$+\ H_{s.r.} - \sum_{\vec{k};\ \vec{k}\neq\vec{0}}\frac{2\pi e^{2}}{Vk^{2}}N + \sum_{k<k_c}\frac{1}{2}P_{\vec{k}}^{\dagger}P_{\vec{k}}$$

Questions?
Write to: pcd@physics.iitm.ac.in

Select/Special Topics from
'Theory of Atomic Collisions and Spectroscopy'

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Unit 3 Lecture Number 24

Electron Gas in the Random Phase Approximations

Plasma Oscillations in Free Electron Gas

References: 'The theory of plasma oscillations in metals'
- by S Raimes 1957 *Rep. Prog. Phys.* **20** 1
Also: Chapter 4 in 'Many Electron Theory' by Stanley Raimes

$$\mathfrak{H} = H_{new} =$$

$$\sum_{i=1}^{N}\frac{p_i^{\,2}}{2m} \overbrace{- \frac{i}{2m}\sum_{j} \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\; \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right) e^{-i\vec{k}\bullet\vec{r}_j}}^{H_{\text{int}}} + \frac{N}{2m}\sum_{\substack{\vec{k} \\ k\langle k_c}} M_{\vec{k}}^{\;2}\; Q_{\vec{k}}^{\;\dagger}\; Q_{\vec{k}}\; k^2$$

$$\underbrace{+\frac{1}{2m}\sum_{j}\; \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell}\; \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\; M_{\vec{\ell}}\; Q_{-\vec{k}}\; Q_{\vec{\ell}}\; \left(\vec{k}\bullet\vec{\ell}\right)\; e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}}_{K}$$

$$+\; H_{s.r.} \;-\sum_{\vec{k};\;\vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2}N \;+\; \sum_{k<k_c}\frac{1}{2}P_{\vec{k}}^{\;\dagger}P_{\vec{k}}$$

$$H_{\text{int}} = -\frac{i}{2m}\sum_{j}\sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\; \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right) e^{-i\vec{k}\bullet\vec{r}_j}$$

$$K = \frac{1}{2m}\sum_{j}\; \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell}\; \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\; M_{\vec{\ell}}\; Q_{-\vec{k}}\; Q_{\vec{\ell}}\; \left(-\vec{k}\bullet\vec{\ell}\right)\; e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + H_{\text{int}} + \frac{N}{2m} \sum_{\substack{\vec{k} \\ k \langle k_c}} M_{\vec{k}}^{\ 2} \ Q_{\vec{k}}^{\ \dagger} \ Q_{\vec{k}} \ k^2$$

$$+ K + \ H_{s.r.} \ - \sum_{\vec{k};\ \vec{k} \neq \vec{0}} \frac{2\pi e^2}{V k^2} N \ + \ \sum_{k<k_c} \frac{1}{2} P_{\vec{k}}^{\ \dagger} P_{\vec{k}}$$

$$\boxed{\begin{aligned} M_{\vec{k}}^{\ 2} &= \frac{4\pi e^2}{V k^2} \\ M_{\vec{k}}^{\ 2} k^2 &= \frac{4\pi e^2}{V} \end{aligned}}$$

$$H_{\text{int}} = -\frac{i}{2m} \sum_{j} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k Q_{\vec{k}} \ \vec{k} \bullet \left(2\vec{p}_j + \hbar \vec{k} \right) e^{-i\vec{k} \bullet \vec{r}_j}$$

$$K = \frac{1}{2m} \sum_{j} \ \sum_{\substack{-\vec{k} \\ k \langle k_c}}^{k \neq \ell} \ \sum_{\substack{\vec{\ell} \\ \ell \langle k_c}} M_{-\vec{k}} \ M_{\vec{\ell}} \ Q_{-\vec{k}} \ Q_{\vec{\ell}} \ \left(\vec{k} \bullet \vec{\ell} \right) \ e^{-i\left(-\vec{k}+\vec{\ell}\right) \bullet \vec{r}_j}$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + H_{\text{int}} + \boxed{\frac{N}{2m} \sum_{\substack{\vec{k} \\ k\langle k_c}} M_{\vec{k}}^{\;2} \; Q_{\vec{k}}^{\;\dagger} \; Q_{\vec{k}} \; k^2}$$

$$+ K + \; H_{s.r.} \; - \sum_{\vec{k};\,\vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2} N \; + \sum_{k<k_c} \frac{1}{2} P_{\vec{k}}^{\;\dagger} P_{\vec{k}}$$

$$M_{\vec{k}}^{\;2} = \frac{4\pi e^2}{Vk^2}$$

$$M_{\vec{k}}^{\;2} k^2 = \frac{4\pi e^2}{V}$$

$$\boxed{\omega_p^{\;2} = \frac{4\pi\bar{\rho} e^2}{m} \quad ; \quad \bar{\rho} = \frac{N}{V}}$$

$$M_{\vec{k}}^{\;2} k^2 = \frac{4\pi e^2}{V}$$

$$M_{\vec{k}}^{\;2} k^2 = \frac{m\omega_P^2}{\bar{\rho}} \frac{1}{V}$$

$$NM_{\vec{k}}^{\;2} k^2 = \frac{m\omega_P^2}{\cancel{\bar{\rho}}} \frac{\cancel{N}}{\cancel{V}}$$

$$\frac{N}{2m} M_{\vec{k}}^{\;2} k^2 = \frac{1}{2} \omega_P^2$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N}\frac{p_i^{\,2}}{2m} + H_{\text{int}} + \frac{1}{2}\sum_{\substack{\vec{k}\\ k\langle k_c}} Q_{\vec{k}}^{\;\dagger}\; Q_{\vec{k}}\;\; \omega_P^2$$

$$+ K + \; H_{s.r.} \; - \sum_{\vec{k};\; \vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2} N \; + \sum_{k<k_c} \frac{1}{2} P_{\vec{k}}^{\;\dagger} P_{\vec{k}}$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N}\frac{p_i^{\,2}}{2m} + \boxed{\sum_{\substack{\vec{k}\\ k\langle k_c}}^{k=\ell} \frac{1}{2}\left(P_{\vec{k}}^{\;\dagger} P_{\vec{k}} + \omega_p^{\;2} Q_{\vec{k}}^{\;\dagger}\; Q_{\vec{k}}\right)} - \sum_{\vec{k};\; \vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2} N$$

$$+ \;\; H_{s.r.} + H_{\text{int}} + K$$

$$\mathfrak{H} = H_{new} = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \sum_{\substack{\vec{k} \\ k \langle k_C}} \frac{1}{2}\left(P_{\vec{k}}^{\dagger} P_{\vec{k}} + \omega_p^{\,2} Q_{\vec{k}}^{\dagger}\ Q_{\vec{k}} \right) - \sum_{\vec{k};\ \vec{k} \neq \vec{0}} \frac{2\pi e^2}{V k^2} N$$

$$+ \quad H_{s.r.} + H_{\text{int}} + K$$

"EXACT"

Raimes: Many Electron Theory
Eq.4.58, page 58

$$\boxed{H_{s.r.} = \frac{1}{2} \sum_{\vec{k};\ \vec{k} \neq \vec{0}}^{k > k_C} M_k^{\,2} \left(\rho_{\vec{k}}^{\,*} \rho_{\vec{k}} - N \right)}$$

$$H_{\text{int}} = -\frac{i}{2m} \sum_{j} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k Q_{\vec{k}}\ \vec{k} \bullet \left(2\vec{p}_j + \hbar\vec{k} \right) e^{-i\vec{k} \bullet \vec{r}_j}$$

"Random Phase Approximation"
"LINEARIZATION"

$$\cancel{K = \frac{1}{2m} \sum_{\substack{-\vec{k} \\ k \langle k_C}}^{k \neq \ell} \sum_{\substack{\vec{\ell} \\ \ell \langle k_C}} M_{-\vec{k}}\ M_{\vec{\ell}} \left(\vec{k} \bullet \vec{\ell} \right) \left\{ \sum_{j} \left(Q_{-\vec{k}} e^{+i\vec{k} \bullet \vec{r}_j} \times Q_{\vec{\ell}} e^{-i\vec{\ell} \bullet \vec{r}_j} \right) \right\}}$$

$$\mathfrak{H} = H_{new} = \sum_{\vec{k};\, k\langle k_C} \frac{1}{2}\left(P_{\vec{k}}^{\dagger} P_{\vec{k}} + \omega_p^{\;2} Q_{\vec{k}}^{\dagger}\; Q_{\vec{k}}\right) + \sum_{i=1}^{N} \frac{p_i^{\;2}}{2m} +$$

short range interaction

$$+ H_{int} + H_{s.r.} - \sum_{\vec{k};\, \vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2} N$$

Quasi particles interacting via $H_{s.r.}$

$$H_{s.r.} = \frac{1}{2} \sum_{\vec{k};\, \vec{k}\neq\vec{0}}^{k>k_C} M_k^{\;2}\left(\rho_{\vec{k}}^{\;*}\rho_{\vec{k}} - N\right)$$

$$M_{\vec{k}}^{\;2} = \frac{4\pi e^2}{Vk^2}$$

$$H_{s.r.} = \sum_{\vec{k};\, \vec{k}\neq\vec{0}}^{k>k_C} \frac{2\pi e^2}{Vk^2}\left(\rho_{\vec{k}}^{\;*}\rho_{\vec{k}} - N\right)$$

Potential energy of the i^{th} electron due to **all the electrons** ***and*** the positive background:

$$\boxed{\vec{k} = \vec{0} \text{ terms } \rightarrow \textit{cancel the positive jellium}}$$

$$U(\vec{r}_i) = \frac{1}{V} \sum_{\substack{j=1 \\ j \neq i}}^{N} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} \frac{4\pi e^2}{k^2} e^{i\vec{k} \bullet (\vec{r}_i - \vec{r}_j)}$$

Total potential energy due to Coulomb interactions of **all the electrons** ***and*** the positive background:

$$\frac{1}{2} \sum_{i=1}^{N} U(\vec{r}_i) = \frac{1}{V} \sum_{\substack{j=1 \\ j \neq i}}^{N} \sum_{i=1}^{N} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} \frac{2\pi e^2}{k^2} e^{i\vec{k} \bullet (\vec{r}_i - \vec{r}_j)}$$

Sum over all the electrons, i=1,2,….N

Total potential energy due to Coulomb interactions of **all the electrons** ***and*** the positive background:

$$\frac{1}{2}\sum_{i=1}^{N} U(\vec{r}_i) = \frac{1}{V}\sum_{\substack{j=1\\ j\neq i}}^{N}\sum_{i=1}^{N}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{2\pi e^2}{k^2}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)}$$

add and subtract j=i terms

$$\frac{1}{2}\sum_{i=1}^{N} U(\vec{r}_i) = \frac{1}{V}\sum_{j=1}^{N}\sum_{i=1}^{N}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{2\pi e^2}{k^2}e^{i\vec{k}\bullet(\vec{r}_i-\vec{r}_j)} \boxed{-\frac{N}{V}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{2\pi e^2}{k^2}}$$

$$\rho_{\vec{k}} = \sum_{i=1}^{N} e^{-i\vec{k}\bullet\vec{r}_i}$$

$$\frac{1}{2}\sum_{i=1}^{N} U(\vec{r}_i) = \frac{1}{V}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{2\pi e^2}{k^2}\rho_{\vec{k}}^{\ *}\rho_{\vec{k}} - \frac{N}{V}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{2\pi e^2}{k^2}$$

$$\boxed{-\frac{N}{V}\sum_{\vec{k};\,\vec{k}\neq\vec{0}}\frac{2\pi e^2}{k^2} \quad self-energy}$$

$$\frac{1}{2}\sum_{i=1}^{N} U(\vec{r}_i) = \frac{1}{V}\sum_{\substack{\vec{k}\\ \vec{k}\neq\vec{0}}}\frac{2\pi e^2}{k^2}\left(\rho_{\vec{k}}^{\ *}\rho_{\vec{k}} - N\right)$$

Total potential energy due to Coulomb interactions of **all the electrons** ***and*** the positive background:

$$\frac{1}{2}\sum_{i=1}^{N} U(\vec{r}_i) = \frac{1}{V}\sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} \frac{2\pi e^2}{k^2}\left(\rho_{\vec{k}}^{\ *}\rho_{\vec{k}} - N\right)$$

$$H_{s.r.} = \frac{1}{V}\sum_{\substack{\boxed{k>k_c} \\ \vec{k};\,\vec{k}\neq\vec{0}}} \frac{2\pi e^2}{k^2}\left(\rho_{\vec{k}}^{\ *}\rho_{\vec{k}} - N\right)$$

$$FT \quad \text{of} \left(\frac{e^{-\mu r}}{r}\right)^{SC} = \frac{4\pi}{\mu^2 + k^2}$$

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

$$\boxed{k > k_c} \ \rightarrow \ \mu^2 + k^2 = \kappa^2$$

$$\kappa \geq \mu$$

“Screened Coulomb”

$H_{s.r.}$ = total potential energy due to SHORT RANGE interactions

$$H_{\text{int}} = -\frac{i}{2m}\sum_j \sum_{\substack{\vec{k} \\ \vec{k}\neq\vec{0}}} M_k Q_{\vec{k}}\ \vec{k}\bullet\left(2\vec{p}_j + \hbar\vec{k}\right)e^{-i\vec{k}\bullet\vec{r}_j}$$

RPA

$$\cancel{K} = \frac{1}{2m}\sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell}\ \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}}\ Q_{-\vec{k}}\, Q_{\vec{\ell}}\ \left(\vec{k}\bullet\vec{\ell}\right)\left\{\sum_j e^{-i\left(-\vec{k}+\vec{\ell}\right)\bullet\vec{r}_j}\right\}$$

RPA cancellation of H_{int}?

Because of these terms the cancellation is not obvious

Bohm and Pines:

FURTHER transformation of the Hamiltonian

$\mathfrak{H} = H_{new}$ can be carried out to account for H_{int}.

$$H_{\text{int}} = -\frac{i}{2m} \sum_{j} \sum_{\substack{\vec{k} \\ \vec{k} \neq \vec{0}}} M_k Q_{\vec{k}} \, \vec{k} \bullet \left(2\vec{p}_j + \hbar \vec{k} \right) e^{-i\vec{k} \bullet \vec{r}_j}$$

$$\mathfrak{H} = H_{new} = \boxed{\sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{\substack{\vec{k} \\ k \langle k_C}} \frac{1}{2} \left(P_{\vec{k}}^\dagger P_{\vec{k}} + \omega_p^2 Q_{\vec{k}}^\dagger \, Q_{\vec{k}} \right)}$$

$$- \sum_{\vec{k};\, \vec{k} \neq \vec{0}} \frac{2\pi e^2}{V k^2} N + \; H_{s.r.} + H_{\text{int}} + \cancel{K}$$

These two terms get modified as a result of this ***further*** transformation

Bohm and Pines:

FURTHER transformation of the Hamiltonian

can be carried out to account for H_{int}.

Raimes: Many Electron Theory; page 82

$$\mathfrak{H} = H_{new} = \boxed{\sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2}\left(P_{\vec{k}}^{\,\dagger} P_{\vec{k}} + \omega_p^{\,2} Q_{\vec{k}}^{\,\dagger}\ Q_{\vec{k}}\right)}$$

$$k_c = k_{\max} \approx \frac{\omega_p}{\mathrm{v}_f}$$

These two terms get replaced, on account of further transformation, by

$$-\sum_{\vec{k};\ \vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2} N + \ H_{s.r.} + H_{\text{int}} + \cancel{K}$$

$$\boxed{\sum_{i=1}^{N} \frac{p_i^{\,2}}{2m}\left(1 - \frac{\beta^2}{6}\right) + \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2}\left(P_{\vec{k}}^{\,\dagger} P_{\vec{k}} + \omega_k^{\,2} Q_{\vec{k}}^{\,\dagger}\ Q_{\vec{k}}\right)}$$

$$\textit{with}\ \ \beta = \frac{k_c}{k_F} \quad \text{and} \quad \omega_k^{\,2} = \omega_p^{\,2} + \frac{2}{m} E_F k^2 \rightarrow \omega = \omega(k)$$

$(\textit{see Slide}\ 156,\ L21)$

$\uparrow$ weak dispersion $\uparrow$.

$$\mathfrak{H} = H_{new} = \boxed{\sum_{i=1}^{N} \frac{p_i^{\ 2}}{2m} + \sum_{\substack{\vec{k} \\ k\langle k_c}} \frac{1}{2}\left(P_{\vec{k}}^{\ \dagger} P_{\vec{k}} + \omega_p^{\ 2} Q_{\vec{k}}^{\ \dagger}\ Q_{\vec{k}}\right)}$$

$$k_c = k_{\max} \approx \frac{\omega_p}{v_f}$$

These two terms get replaced, on account of further transformation, by

$$- \sum_{\vec{k};\ \vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2} N + \ H_{s.r.} + H_{\ldots}$$

← K.E. term

$$\boxed{\sum_{i=1}^{N} \frac{p_i^{\ 2}}{2m}\left(1 - \frac{\beta^2}{6}\right)} + \sum_{\vec{k}} \frac{1}{2}\left(P_{\vec{k}}^{\ \dagger} P \ldots Q_{\vec{k}}\right)$$

β≈0.7 for sodium, so K.E. diminishes by about 8%

with $\beta = \dfrac{k_c}{k_F}$ and … $\omega(k)$)

(*see Slide* 156, *L2*… …spersion ↑.

$$\mathfrak{H} = H_{new} = \sum_{\substack{\vec{k} \\ k \langle k_c}} \frac{1}{2}\left(P_{\vec{k}}^{\dagger} P_{\vec{k}} + \omega_p^{\ 2} Q_{\vec{k}}^{\dagger}\ Q_{\vec{k}} \right)$$

$$+ \sum_{i=1}^{N} \frac{p_i^{\ 2}}{2m} - \sum_{\vec{k};\ \vec{k} \neq \vec{0}} \frac{2\pi e^2}{Vk^2} N + H_{s.r.} \cancel{+ H_{\text{int}} + K}$$

$$\mathfrak{H} = H_{new} \approx \sum_{i=1}^{N} \frac{p_i^{\ 2}}{2m} + \sum_{\substack{\vec{k} \\ k \langle k_c}} \frac{1}{2}\left(P_{\vec{k}}^{\dagger} P_{\vec{k}} + \omega_p^{\ 2} Q_{\vec{k}}^{\dagger}\ Q_{\vec{k}} \right) - \sum_{\vec{k};\ \vec{k} \neq \vec{0}} \frac{2\pi e^2}{Vk^2} N + H_{s.r.}$$

Subsidiery condition:

$$\boxed{\left(P_k + M_k \rho_{\vec{k}} \right) \psi_{new} = 0 \quad \text{for } k < k_c}$$

What kind of a system does this Hamiltonian describe?

$$\mathfrak{H} = H_{new} \approx \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \sum_{\substack{\vec{k} \\ k \langle k_C}} \frac{1}{2}\left(P_{\vec{k}}^{\;\dagger} P_{\vec{k}} + \omega_p^{\;2} Q_{\vec{k}}^{\;\dagger}\; Q_{\vec{k}} \right)$$

$$- \sum_{\vec{k};\, \vec{k} \neq \vec{0}} \frac{2\pi e^2}{Vk^2} N + \; H_{s.r.}$$

Re-arrange the terms:

$$\mathfrak{H} = H_{new} \approx \sum_{\vec{k};\, k \langle k_C} \frac{1}{2}\left(P_{\vec{k}}^{\;\dagger} P_{\vec{k}} + \omega_p^{\;2} Q_{\vec{k}}^{\;\dagger}\; Q_{\vec{k}} \right)$$

$$+ \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \; H_{s.r.} \; - \sum_{\vec{k};\, \vec{k} \neq \vec{0}} \frac{2\pi e^2}{Vk^2} N$$

Raimes: Many Electron Theory; Eq.4.63, page 82

$$\mathfrak{H} = H_{new} = \boxed{\sum_{\vec{k};\, k\langle k_c} \frac{1}{2}\left(P_{\vec{k}}^{\dagger} P_{\vec{k}} + \omega_p^{\,2} Q_{\vec{k}}^{\dagger}\, Q_{\vec{k}}\right)} + \boxed{\sum_{i=1}^{N} \frac{p_i^{\,2}}{2m} + \; H_{s.r.}} - \boxed{\sum_{\vec{k};\, \vec{k}\neq\vec{0}} \frac{2\pi e^2}{Vk^2} N}$$

Subsidiery condition: $\left(P_k\right)_{new} \psi_{new} = 0 \;\; \text{for} \;\; k < k_c$

What kind of a system does this Hamiltonian describe?

SHO Hamiltonian

$$H = \frac{1}{2}\left(\frac{p^2}{m} + m\omega^2 x^2\right)$$

Plasma oscillations

Quasi particles interacting via $H_{s.r.}$

A constant term that is part of the electron self-energy which not accounted for in the plasma oscillations.

Long range interaction is accounted for by PLASMONS, and the short range part that remains is a screened Coulomb interaction.

“Random Phase Approximation” → “LINEARIZATION”

$$\cancel{K} = \frac{1}{2m} \sum_{\substack{-\vec{k} \\ k\langle k_c}}^{k\neq\ell} \sum_{\substack{\vec{\ell} \\ \ell\langle k_c}} M_{-\vec{k}}\, M_{\vec{\ell}} \left(\vec{k}\bullet\vec{\ell}\right) \left\{ \sum_{j} \left(Q_{-\vec{k}}\, e^{+i\vec{k}\bullet\vec{r}_j} \times Q_{\vec{\ell}}\, e^{-i\vec{\ell}\bullet\vec{r}_j} \right) \right\}$$

Bohm and Pines

Transformation of the Hamiltonian

Other paths to RPA ……

Equation of Motion method… Rowe (1968)

Greens function method ……Thouless (1961)

Diagrammatic perturbation theory ..

Questions:
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Linearized Time Dependent Hartree/Dirac Fock…

Alex Dalgaarno….. Walter Johnson →

RRPA