Metals: Ground State

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Outline

Introduction

- We'll cover material discussed in Lancaster 43.1 and 43.2.
- I find the treatment to be unsatisfactory, so will modify it somewhat.
- My version will follow Quantum Theory of Many Particle Systems by Fetter and Walecka, Chapter 1.
- This section examines the ground state energy of a metal.
  - *Jellium* Model: neutral system of interacting electrons in the field of a uniform positive distribution
  - Ground state is a bound state
  - Energy is measured by vaporization
- We'll show

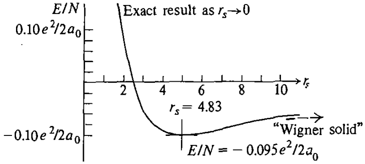
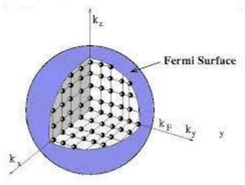


Fig. 3.2 Approximate ground-state energy [first two terms in Eq. (3.37)] of an electron gas in a uniform positive background.

where r_s is the dimensionless electron spacing.

Free electron ground state – a simple treatment



- Electrons are fermions: Pauli exclusion principle
  - Two electrons per momentum eigenstate – spin up,down
- Assume finite volume with periodic boundary conditions.
  - Momentum eigenstates are plane waves
  - $\sum_{p<p_F} \to \mathcal{V} \int_{p=0}^{p_F} \frac{d^3p}{(2\pi)^3}$
  - Then take $N \to \infty, \mathcal{V} \to \infty$ with fixed electron density $n_e = \frac{N}{\mathcal{V}}$.
  - Relate to inter-electron (nearest neighbor) distance r_e:

$$n_e = \frac{N}{\mathcal{V}} = \frac{3}{4\pi r_e^3} \approx \frac{3}{4\pi r_s^3 a_0^3}$$

$$\mathcal{V} = N\left(\frac{4\pi r_s^3 a_0^3}{3}\right)$$

where $r_s \equiv \frac{r_e}{a_0}$ and a_0 is the Bohr radius.

Free electron ground state – a simple treatment cont'd

- Compute the number of momentum-states with $|\mathbf{p}| \leq |\mathbf{p}_f|$.

$$\mathcal{V} \int_{p=0}^{p_F} \frac{d^3p}{(2\pi)^3} = \frac{4\pi}{(2\pi)^3} \mathcal{V} \int_{p=0}^{p_F} p^2 dp = \frac{4\pi}{3(2\pi)^3} \mathcal{V}(p_F)^3 = \frac{\mathcal{V} p_F^3}{6\pi^2}$$

- Multiply by 2 for the two spin states: $N = \frac{\mathcal{V} p_F^3}{3\pi^2}$
- Invert: $p_F = \left(3\pi^2 \frac{N}{\mathcal{V}}\right)^{\frac{1}{3}} = \left(3\pi^2 \left(\frac{3}{4\pi r_s^3 a_0^3}\right)\right)^{\frac{1}{3}}$
- Kinetic energy density:

$$\frac{W_0}{N} = 2\frac{\mathcal{V}}{N} \int_{p=0}^{p_F} \frac{d^3p}{(2\pi)^3} \frac{p^2}{2m} = \frac{8\pi}{(2\pi)^3} \frac{\mathcal{V}}{N} \int_{p=0}^{p_F} \frac{p^4 dp}{2m} = \frac{8\pi}{10m(2\pi)^3} \frac{\mathcal{V}}{N} (p_F)^5$$
$$\approx \frac{2.21}{r_s^2} \text{Ry}$$

where 'Ry' is an abbreviation for rydberg; 1 Ry $= \frac{e^2}{2a_0}$

- **Thus the kinetic energy-density is approximately $\frac{2.21}{r_s^2} \frac{\text{Ry}}{\text{electron}}$.**

Second quantization – general review

- Second quantization: helps manage symmetry and antisymmetry
- Wave function approach:
  - Single-particle basis functions: $\psi_{\mathbf{k}_1}(\mathbf{x}), \psi_{\mathbf{k}_2}(\mathbf{x}), ...$
  - $\psi_{\mathbf{k}_1\mathbf{k}_4}(\mathbf{x}_1, \mathbf{x}_2, ...) \propto (\psi_{\mathbf{k}_1}(\mathbf{x}_1)\psi_{\mathbf{k}_4}(\mathbf{x}_2)... \pm \psi_{\mathbf{k}_4}(\mathbf{x}_1)\psi_{\mathbf{k}_1}(\mathbf{x}_2)... + ...)$
  - The minus sign (antisymmetry) is for fermions
  - bra/ket notation: $\langle \mathbf{x} | \mathbf{k} \rangle \equiv \psi_{\mathbf{k}}(\mathbf{x})$, $|\mathbf{k}_1 \mathbf{k}_2\rangle \equiv |\mathbf{k}_1\rangle \otimes |\mathbf{k}_2\rangle$ etc.
- Annihilation and creation operators for fermions:
  - $a^\dagger_{\mathbf{k}}|0\rangle = |\mathbf{k}\rangle$, $a_{\mathbf{k}}|0\rangle = 0$, $a_{\mathbf{k}} a^\dagger_{\mathbf{k}'} + a^\dagger_{\mathbf{k}'} a_{\mathbf{k}} = \delta^3(\mathbf{k} - \mathbf{k}')$
  - So $a_{\mathbf{k}} a^\dagger_{\mathbf{k}'} = \delta^3(\mathbf{k} - \mathbf{k}') - a^\dagger_{\mathbf{k}'} a_{\mathbf{k}}$
- This formalism automatically takes care of antisymmetry.
  - For simplicity pretend $\mathbf{k}$ is an integer
  - Occupation number: $|n_1 n_2 ...\rangle = \prod_m \frac{1}{(n_m!)^{\frac{1}{2}}} \left(a^\dagger_m\right)^{n_m} |0\rangle$
  - Eg. if $n_i = 1$, $n_j = 1$, $n'_5 = 1$, $n'_7 = 1$; other n_m and n'_m are 0
    $\langle n'_1 n'_2 ... | n_1 n_2 ... \rangle = \langle 0 | a_5 a_7 a^\dagger_i a^\dagger_j | 0 \rangle = \delta(5 - j)\delta(7 - i) - \delta(7 - j)\delta(5 - i)$

Second quantization – e.g. of anti-commutation algebra

$$\begin{aligned}
\langle 0|a_5 a_7 a_i^\dagger a_j^\dagger|0\rangle &= \langle 0|a_5 \left(\delta(7-i) - a_i^\dagger a_7\right) a_j^\dagger|0\rangle \\
&= \delta(7-i)\langle 0|a_5 a_j^\dagger|0\rangle - \delta(7-j)\langle 0|a_5 a_i^\dagger|0\rangle + \langle 0|a_5 a_i^\dagger a_j^\dagger a_7|0\rangle \\
&= \delta(7-i)\langle 0|a_5 a_j^\dagger|0\rangle - \delta(7-j)\langle 0|a_5 a_i^\dagger|0\rangle \\
&= \delta(7-i)\delta(5-j)\langle 0|0\rangle - \delta(7-j)\delta(5-i)\langle 0|0\rangle - \\
&\qquad - \delta(7-i)\langle 0|a_j^\dagger a_5|0\rangle + \delta(7-j)\langle 0|a_i^\dagger a_5|0\rangle \\
&= \delta(5-j)\delta(7-i) - \delta(7-j)\delta(5-i)
\end{aligned}$$

where we have used the facts that $\langle 0|0\rangle = 1$, $a_5|0\rangle = 0$ and $a_7|0\rangle = 0$.

Interactions – the system Hamiltonian

- The jellium is a positive background with constant density $n(\mathbf{x}) = n_e = \frac{N}{\mathcal{V}}$
- $H = H_{\mathrm{K}} + H_{\mathrm{j}} + H_{\text{el-j}} + H_{\mathrm{el}}$
  - $H_{\mathrm{K}} = \sum_i \frac{\hat{p}_i^2}{2m}$ is the kinetic energy
  - $H_{\mathrm{j}} = \frac{1}{2} e^2 \int \int d^3x d^3x' \frac{n(\mathbf{x}) n(\mathbf{x}') e^{-\lambda|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|}$ is the jellium PE
  - $H_{\text{el-j}} = -e^2 \int d^3x \sum_{i=1,N} \frac{n(\mathbf{x}) e^{-\lambda|\mathbf{x}-\hat{\mathbf{r}}_i|}}{|\mathbf{x}-\hat{\mathbf{r}}_i|}$ is the jellium-electron PE
  - $H_{\mathrm{el}} = \frac{1}{2} e^2 \sum_{i \neq j} \frac{e^{-\lambda|\hat{\mathbf{r}}i-\hat{\mathbf{r}}_j|}}{|\hat{\mathbf{r}}_i-\hat{\mathbf{r}}_j|}$ is the electron-electron PE
- $\lambda \to 0$ at the end
- $H_{\mathrm{V}} = H_{\mathrm{j}} + H_{\text{el-j}} + H_{\mathrm{el}}$ is treated as a perturbation to the KE.
- The N-electron free theory (H_{K}) ground state is $|\Omega\rangle$.
  - $|\Omega\rangle = \prod_{|\mathbf{p}_i|<p_F} a_{\mathbf{p}_i}^{\mathrm{up}\dagger} a_{\mathbf{p}_i}^{\mathrm{down}\dagger} |0\rangle$
  - In future, suppress spins so write $|\Omega\rangle = \prod_{|\mathbf{p}_i|<p_F} a_{\mathbf{p}_i}^{\dagger} |0\rangle$.
  - Its energy was computed as $\frac{2.21}{r_s^2} \frac{\mathrm{Ry}}{\mathrm{electron}}$.
  - The perturbed energy is computed as $\Delta E = \langle \Omega | H_{\mathrm{V}} | \Omega \rangle$.

Interactions – the jellium potential

- Define $\mathcal{C} = e^2 \int d^3y \frac{e^{-\lambda|\mathbf{y}|}}{|\mathbf{y}|}$
- H_j is purely classical – a “number”, not an operator.
  - $E_\mathrm{j} \equiv \langle\Omega|H_\mathrm{j}|\Omega\rangle = H_\mathrm{j}$
  - Compute E_j

$$\begin{aligned}
E_\mathrm{j} &= \frac{1}{2}e^2 \int\int d^3x d^3x' \frac{n(\mathbf{x})n(\mathbf{x}')e^{-\lambda|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|} \\
&= \frac{e^2}{2}\left(\frac{N}{\mathcal{V}}\right)^2 \int\int d^3x d^3x' \frac{e^{-\lambda|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|} \\
&= \frac{1}{2}\left(\frac{N}{\mathcal{V}}\right)^2 \int d^3x \left(e^2 \int d^3y \frac{e^{-\lambda|\mathbf{y}|}}{|\mathbf{y}|}\right) \\
&= \left(\frac{N}{\mathcal{V}}\right)^2 \frac{1}{2} \int d^3x \mathcal{C} \\
&= \frac{1}{2}\left(\frac{N^2}{\mathcal{V}}\right)\mathcal{C}
\end{aligned}$$

  - **Summary:** $E_\mathrm{j} = \frac{1}{2}\left(\frac{N^2}{\mathcal{V}}\right)\mathcal{C}$

Interactions – the jellium-electron potential

- Follow Chapter 4.2's treatment of one-body potentials
- Consider electron potential $\hat{V}^{\mathbf{x}}$ caused by jellium at $\mathbf{x}$
    - Let $V^{\mathbf{x}}_{\mathbf{q}} = -\frac{e^2}{\mathcal{V}} n(\mathbf{x}) \int d^3y \frac{e^{-i\mathbf{y}\cdot\mathbf{q}} e^{-\lambda|\mathbf{y}-\mathbf{x}|}}{|\mathbf{y}-\mathbf{x}|}$
    - $V^{\mathbf{x}}_{\mathbf{q}} = -\frac{e^2}{\mathcal{V}} \frac{N}{\mathcal{V}} \int d^3y' \frac{e^{-i(\mathbf{y}'+\mathbf{x})\cdot\mathbf{q}} e^{-\lambda|\mathbf{y}'|}}{|\mathbf{y}'|} = -\frac{N}{\mathcal{V}} e^{-i\mathbf{x}\cdot\mathbf{q}} V^0_{\mathbf{q}}$
    - From Lancaster example 4.4, $\hat{V}^{\mathbf{x}} = \sum_{\mathbf{p}_1\mathbf{p}_2} V^{\mathbf{x}}_{\mathbf{p}_1-\mathbf{p}_2} a^\dagger_{\mathbf{p}_1} a_{\mathbf{p}_2}$.
- So $\hat{V}_{\text{el-j}} = -\frac{N}{\mathcal{V}} \sum_{\mathbf{p}_1\mathbf{p}_2} \int d^3x e^{-i(\mathbf{p}_1-\mathbf{p}_2)\cdot\mathbf{x}} V^0_{\mathbf{p}_1-\mathbf{p}_2} a^\dagger_{\mathbf{p}_1} a_{\mathbf{p}_2}$
  $= -\frac{N}{\mathcal{V}} \sum_{\mathbf{p}_1\mathbf{p}_2} \mathcal{V}\delta(\mathbf{p}_1 - \mathbf{p}_2) V^0_{\mathbf{p}_1-\mathbf{p}_2} a^\dagger_{\mathbf{p}_1} a_{\mathbf{p}_2} = -\frac{N}{\mathcal{V}}\mathcal{C} \sum_i a^\dagger_{\mathbf{p}_i} a_{\mathbf{p}_i}$
- Note that $\sum_i a^\dagger_{\mathbf{p}_i} a_{\mathbf{p}_i}$ is the number operator.
- So $\langle\Omega|\hat{V}_{\text{el-j}}|\Omega\rangle = -\frac{N}{\mathcal{V}}\mathcal{C}\langle\Omega|\sum_i a^\dagger_{\mathbf{p}_i} a_{\mathbf{p}_i}|\Omega\rangle = -\frac{N^2}{\mathcal{V}}\mathcal{C}$
- **Summary:** $E_{\text{el-j}} = -\left(\frac{N^2}{\mathcal{V}}\right)\mathcal{C}$

Interactions – the electron-electron potential

- Let $V_{\mathbf{q}} = \frac{e^2}{\mathcal{V}} \int d^3x \frac{e^{-i\mathbf{x}\cdot\mathbf{q}} e^{-\lambda|\mathbf{x}|}}{|\mathbf{x}|}$
- From Lancaster 4.63, $\hat{V}_{\text{el}} = \frac{1}{2} \sum_{\mathbf{pkq}} V_{\mathbf{q}} a^\dagger_{\mathbf{p}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}} a_{\mathbf{p}-\mathbf{q}}$.
- Should put spins back to get the right answer. See blue inserts.
- Re-order operators in $\hat{V}_{\text{el}}$ so that creation operators are on the right.
- $\hat{V}_{\text{el}} = \frac{1}{2} \sum_{\mathbf{pkq}} V_{\mathbf{q}} \left(\delta^3(\mathbf{q})\delta^3(\text{-}\mathbf{q}) - 2\delta^3(\mathbf{k}\text{-}\mathbf{p}+\mathbf{q})\delta^3(\mathbf{p}\text{-}\mathbf{k}\text{-}\mathbf{q})\right) +$ $V_{\mathbf{q}} \left(a_{\mathbf{k}+\mathbf{q}} a^\dagger_{\mathbf{p}} a_{\mathbf{p}\text{-}\mathbf{q}} a^\dagger_{\mathbf{k}} + \delta^3(-\mathbf{q}) a_{\mathbf{p}\text{-}\mathbf{q}} a^\dagger_{\mathbf{p}} - \delta^3(\mathbf{k}\text{-}\mathbf{p}+\mathbf{q}) a_{\mathbf{k}+\mathbf{q}} a^\dagger_{\mathbf{p}}\right)$
- Recall $|\Omega\rangle = \prod_{|\mathbf{p}|\le p_F} a^\dagger_{\mathbf{p}} |0\rangle$.
- If $|\mathbf{q}| > p_F$ then $\langle\Omega| a^\dagger_{\mathbf{q}} = 0$ $\implies$ if $|\mathbf{p}| > p_F$ or $|\mathbf{k}| > p_F$ then $\langle\Omega| a^\dagger_{\mathbf{p}} a^\dagger_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}} a_{\mathbf{p}-\mathbf{q}} |\Omega\rangle = 0$.
- If $|\mathbf{p}| \& |\mathbf{k}| \le p_F$ then $a^\dagger_{\mathbf{p}}|\Omega\rangle = 0$ and $a^\dagger_{\mathbf{k}}|\Omega\rangle = 0$.
- $\langle\Omega|\hat{V}_{\text{el}}|\Omega\rangle = \frac{1}{2} \sum_{\mathbf{p},\mathbf{k}\le p_F} V_{\mathbf{q}} \left(\delta^3(\mathbf{q})\delta^3(\text{-}\mathbf{q}) - 2\delta^3(\mathbf{k}\text{-}\mathbf{p}+\mathbf{q})\delta^3(\mathbf{p}\text{-}\mathbf{k}\text{-}\mathbf{q})\right) =$ $\frac{1}{2} \sum_{\mathbf{p},\mathbf{k}\le p_F} V_{\mathbf{0}} - \frac{1}{2} \sum_{\mathbf{p},\mathbf{k}\le p_F} V_{\mathbf{p}\text{-}\mathbf{k}} = \frac{1}{2} \frac{N^2}{\mathcal{V}} \mathcal{C} - \sum_{\mathbf{p},\mathbf{k}\le p_F} V_{\mathbf{p}\text{-}\mathbf{k}}$
- The term in red is the Hartree term. The other is the Fock term.

Interactions – the Hartree and Fock terms

- The Hartree term (*direct term*) is $\mathcal{H} = \frac{1}{2}\frac{N^2}{\mathcal{V}}\mathcal{C}$.
- $\mathcal{H}$ is "classical" and is the same as the jellium potential.
- The Fock term (*exchange term*) is $\mathcal{F} = -\sum_{\mathbf{p},\mathbf{k} \leq p_F} V_{\mathbf{p}\text{-}\mathbf{k}}$.
- $\mathcal{F}$ is quantum with no classical analogue.
- Recall $V_{\mathbf{p}\text{-}\mathbf{k}} = \frac{e^2}{\mathcal{V}} \int d^3x \frac{e^{-i\mathbf{x}\cdot\mathbf{q}} e^{-\lambda|\mathbf{x}|}}{|\mathbf{x}|}$.
- Lancaster Eq. (43.21) derives $V_{\mathbf{p}\text{-}\mathbf{q}} = \frac{4\pi e^2}{\mathcal{V}((|p|-|k|)^2+\lambda^2)}$.
- Recall $\sum_{q<p_F} \to \mathcal{V} \int_{q=0}^{p_F} \frac{d^3q}{(2\pi)^3}$.
- Then

$$\mathcal{F} \to \mathcal{V}^2 \int_{|p|=0}^{|p|=p_F} \frac{d^3p}{(2\pi)^2} \left(\int_{|k|=0}^{|k|=p_F} \frac{d^3k}{(2\pi)^2} \frac{4\pi e^2}{\mathcal{V}\left((|p|-|k|)^2+\lambda^2\right)} \right). \tag{1}$$

- Lancaster (p. 385) derives $\lim_{\lambda\to 0} \frac{\mathcal{F}}{N} = -\frac{3p_F}{4\pi} e^2 = -\frac{0.916}{r_s}$ Ry.

Interactions – total interaction energy

- Summary
  - jellium potential: $E_{\mathrm{j}} = \frac{1}{2}\left(\frac{N^2}{\mathcal{V}}\right)\mathcal{C}$.
  - jellium-electron potential: $E_{\text{el-j}} = -\left(\frac{N^2}{\mathcal{V}}\right)\mathcal{C}$
  - electron-electron $\mathcal{H}+\mathcal{F}$: $E_{\text{el-el}} = \frac{1}{2}\left(\frac{N^2}{\mathcal{V}}\right)\mathcal{C} - \frac{0.916}{r_s} N \text{ Ry}$.
- Add all these terms up. Take $\lambda \to 0$.
  - The terms proportional to $\mathcal{C}$ individually diverge.
  - But they add up to 0 so the divergences cancel.
  - The total is

$$\frac{E_{\text{interaction}}}{N} = -\frac{0.916}{r_s} Ry. \tag{2}$$

Interactions – sidebar on Lancaster

These notes are intended as clarification/correction of Lancaster p. 381.

- Consider fermion operators $A_1, A_2, ..., A_N$.
  - Suppose each A_i is either $a_{\mathbf{k}_i}$ or $a^\dagger_{\mathbf{k}_i}$.
  - Consider a product $P = A_1 A_2 ... A_N$.
  - By using anti-comm., change the order of terms in P.
  - Manipulate P until all terms T have creation operators to the left of annih. ops. Written $: P :$ and called *normal ordering*.
  - Define $\langle A_1 A_2 \rangle = A_1 A_2 \pm : A_1 A_2 :$ (plus sign to swap ops).
    - Example: $\langle a_{\mathbf{k}_i} a^\dagger_{\mathbf{k}_j} \rangle =: a_{\mathbf{k}_i} a^\dagger_{\mathbf{k}_j} : + \, \delta^{(3)}(\mathbf{k}_i - \mathbf{k}_j)$
- Wick's theorem is algorithm for normal ordering.
- Refer to Wikipedia on Wick's theorem, for algorithm and proof.
- Often, $a_{\mathbf{k}}|g\rangle = 0$ where $|g\rangle$ is a ground state.
- Then $: T : |g >= 0$ if T has at least one annih. op.
- Lancaster needs $: T : |\Omega >= 0$ but that **only works if the right-most operator is a creation op. That's not normal ordering**. His "Wick's theorem" is a variant for creation ops. on the right.

Wigner crystals – Introduction

- Our results are from 1st term in perturbation series
  - Born approximation: $\Delta E = \langle \psi_0 | V | \psi_0 \rangle$
  - ψ_0 is free ground state composed from plane waves
- 2nd term in perturbation series diverges as $\mathcal{V} \to \infty$ (Wigner).
- $E_G = \langle \Omega_G | H | \Omega_G \rangle \leq \langle \psi | H | \psi \rangle$ for all $|\psi\rangle$ iff $|\Omega_G\rangle$ is full-H ground state
- For large r_s, the kinetic energy is small. PE dominates.
- So $H \approx V$. Wigner guessed $\underline{\text{for large } r_s}$, $|\Omega_G\rangle$ looks like a crystal.
- Let $|\psi\rangle$ be an electron crystal wave function. We'll (sort of) show
  - $\langle \psi | V | \psi \rangle \approx -\frac{1.8 \text{ Ry}}{r_s}$
  - This is much less than the previously computed $-\frac{0.916 \text{ Ry}}{r_s}$

Wigner crystals – energy calculation

- Continue to approximate the positive charges by jellium.
- The electrons are localized at crystal positions $\mathbf{a}_j$. e.g. BCC
- $\psi_{BCC}(\mathbf{r}_1, \mathbf{r}_2, ...) \propto \sum_p (-1)^{\mathrm{sgn}(p)} \delta^3(\mathbf{r}_{p(1)} - \mathbf{a}_1)\delta^3(\mathbf{r}_{p(2)} - \mathbf{a}_2)...$
  - ψ_{BCC} is in the coordinate representation; p's are permutations
- Use the Wigner-Seitz approximation to compute energy
  - Imagine WS cell of radius r_e. Contains one electron.
  - Recall electron density $n_e = \frac{3}{4\pi r_e^3}$
  - Compute the electron-jellium energy in WS cell
  - Compute the jellium-jellium energy in WS cell
  - Only one electron so no energy contribution in WS cell
  - Cells are electrically neutral so inter-cell energy can be ignored
- $\frac{E_{ej}}{N} \approx -n_e e^2 \int_0^{|\mathbf{x}|=r_e} \frac{d^3x}{|\mathbf{x}|} = -\frac{3}{2}\frac{e^2}{r_e}$
- $\frac{E_{jj}}{N} \approx n_e e^2 \int_0^{|\mathbf{x}|=r_e} d^3x \frac{n(|\mathbf{x}|)}{|\mathbf{x}|}$ where $n(r) = \frac{4\pi r^3 n_e}{3}$, $\Longrightarrow \frac{E_{jj}}{N} \approx \frac{3}{5}\frac{e^2}{r_e}$
- $\frac{E_0}{N} = \frac{E_{ej}}{N} + \frac{E_{jj}}{N} \approx \frac{e^2}{r_e}\left(\frac{3}{5} - \frac{3}{2}\right) = -\frac{1.8}{r_s}\mathrm{Ry}.$

Wigner crystals – Interpretation of energy results

- But for low density (large r_s), $\frac{\langle \psi_{BCC} | H | \psi_{BCC} \rangle}{N} \approx -\frac{1.8}{r_s}$ Ry
  - Assume (I'm not sure why) that BCC gives lowest energy.
  - So (for large r_s) $\frac{E_0}{N} \approx -\frac{1.8}{r_s}$
- The Hartree-Fock (jellium) calculation was $\frac{E_{HF}}{N} = \left(\frac{2.2}{r_s^2} - \frac{0.916}{r_s}\right)$ Ry .
- Define the correlation energy $E_{\text{corr}} = E_0 - E_{HF}$
- At large r_s, $\frac{E_{\text{corr}}}{N} = -\frac{0.88}{r_s}$ Ry.
- At low r_s (high density) Gell-Mann and Bruekner used summing tricks to get

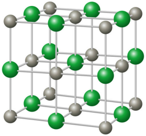
$$E_{\text{corr}} = -0.094 + 0.0622 \ln r_s \tag{3}$$

Electron energy summary

- The total energy density is $\frac{E}{N}$.
- $\frac{E}{N} = \left(\frac{2.2}{r_s^2} - \frac{0.916}{r_s}\right)\,\text{Ry} + \frac{E_{\text{corr}}}{N}$.
- $\lim_{r_s\to\infty} \frac{E_{\text{corr}}}{N} \approx -\frac{0.88}{r_s}\,\text{Ry}$.
- At low r_s (high density) Gell-Mann and Bruekner used summing tricks to get

$$\lim_{r_s\to 0} \frac{E_{\text{corr}}}{N} = (-0.094 + 0.0622 \ln r_s)\,\text{Ry} \tag{4}$$

Digression: NaCl – energy calculation



Salt crystal: grey balls are Na^+, green balls are Cl^-

- The ions (Na^+ and Cl^-) are in a FCC lattice at positions $\mathbf{a}_i$.
- The nearest-neighbor distance is r_e and the lattice spacing is $2r_e$.
- Let $E_i \equiv -z_i \sum_{j;j\neq i} \frac{e^2 z_j}{|\mathbf{a}_i - \mathbf{a}_j|}$; z_i $(= \pm 1)$ is charge of the ith ion
- Then $E = \frac{1}{2} \sum_i E_i = \frac{2N}{2} E_1 = NE_1$
  - $E_i = E_1$ for all i
  - Divide by 2 so we don't double-count
- Madelung computed $E_1 = -\frac{e^2}{r_e} M = -\frac{2M}{r_{sn}} \mathrm{Ry}$, where
  - $r_{sn} \equiv \frac{r_e}{a_0}$ where a_0 is the Bohr radius.
  - M is the *Madelung constant* and is crystal-dependent.

Digression: NaCl – energy calculation cont'd

- Energy is dominated by potential term for large r_s.
- The Madelung sum is *conditionally convergent*
    - Depends on order of summation
    - Physical principle is required – often boundary conditions
    - Regularization methods can be used
    - Lots of literature on the mathematics
- Click here for youtube derivation of the Madelung constant.
- Also see the wikipedia article on the Madelung constant.
- For salt $\frac{E_0}{N} \approx -\frac{1.7}{r_{sn}} \approx$ -0.6 Ry
    - $M = 1.7$
    - $r_{sn} \approx 6$
    - So $\frac{E_0}{N} = -\frac{2M}{r_{sn}}\text{Ry} \approx -\frac{2\times 1.7}{r_s} \approx -0.6$ Ry.