C&L CHAPTER 6

- Many electron interactions:

  . ~~Beyond~~ The independent e^- approximation: $e^- - e^-$ interaction.

recap:

$\Rightarrow$ One e^- Sch. eq:

$e^- - e^-$ interactions have been ignored so far. How good was this for solids? (for simple metals & semiconductors).

NoT so bad! Why? This is the subject of this chapter.

$\Rightarrow$ Let's start with The N-particle Sch. eq.

$$\chi \left\{ \{\vec{r}_n\} \underbrace{\{S_n\}}_{\text{spin}} \right\}$$

$$H\chi = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_i^2 \chi - Ze^2 \sum_{R}^{N} \frac{1}{|\vec{r}_i - \vec{R}|} \chi \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \chi = E\chi$$

Coulomb interaction

$\frac{1}{2}$ in a.u $\frac{1}{4\pi\varepsilon_0} = 1$

au $\begin{cases} m_e = 1 \\ \hbar = 1 \\ e = 1 \end{cases}$

$$H_{el} = -\sum_{k=1}^{k_F} \frac{\hbar^2}{2m} \vec{\nabla}_k^2 + \frac{1}{8\pi\varepsilon_0} \sum_{kk'} \frac{e^2}{|r_k - r_{k'}|} + H_{el-ion}$$

Jellium model : e^- gas embedded in a positive homogeneous charge medium.

Net charge = 0 (idealized model of a metal.

If interactions are neglected ⇒ Sommerfeld Model

$$H_0 = \sum_i \frac{p_i^2}{2m} + V^{e-n} = \sum_i H_0$$

positive background, constant.

$$\Psi_0 = \prod_i \phi_i(r_i, \sigma_i) \; ; \; \phi_i(r, \sigma) = \phi^0_{k\sigma} = \frac{1}{\sqrt{V}} e^{ikr} \chi_\sigma$$

spin function ↑ or ↓

$$N = 2 \sum_{k<k_F} 1 \; ; \; \varepsilon_0(k) = \frac{\hbar^2 k^2}{2m}$$

$$E_0 = 2 \sum_{k<k_F} \varepsilon_0(k)$$; only 1 variable in jellium : $n = \frac{N}{V}$

which is equivalent to $k_F = (3\pi^2 n)^{1/3}$

$r_s \longrightarrow \frac{4}{3}\pi r_s^3 =$ Vol per e^-, usually dimensionless, by dividing by Bohr radius a_0 $\Rightarrow r_s = \left(\frac{3}{4\pi}\right)^{1/3}\left(\frac{1}{n}\right)^{1/3} a_0^{-1}$

using r_s we have :

$$k_F = \frac{1.92}{r_s a_0} \qquad \mathcal{E}_F^0 = \frac{3.68}{r_s^2}\,(R_y)$$

$$\hbar\omega_p = \frac{3.46}{r_s^{3/2}}\,(R_y)$$ → plasma frequency

GG

Kinetic energy :

$$\langle E_{KE} \rangle = \frac{2}{N}\sum_{k<k_F} \varepsilon_k^0 = \frac{3}{5} E_F^0 = \frac{2.21}{r_s^2}\,(R_y)$$ ✓

$$\langle E_{pot} \rangle \simeq \frac{e^2}{r_s} = \frac{2}{r_s}\,(R_y)$$ ✓

$\frac{\hbar^2}{2ma} = 1$ $\quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$

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

so also $r_s \sim \frac{\langle E_{pot} \rangle}{\langle E_k \rangle}$ → measure of the ratio of average potential e⁻ to kin energy in the e⁻ gas.

$r_s < 1$ → high n, kinetic energy dominates

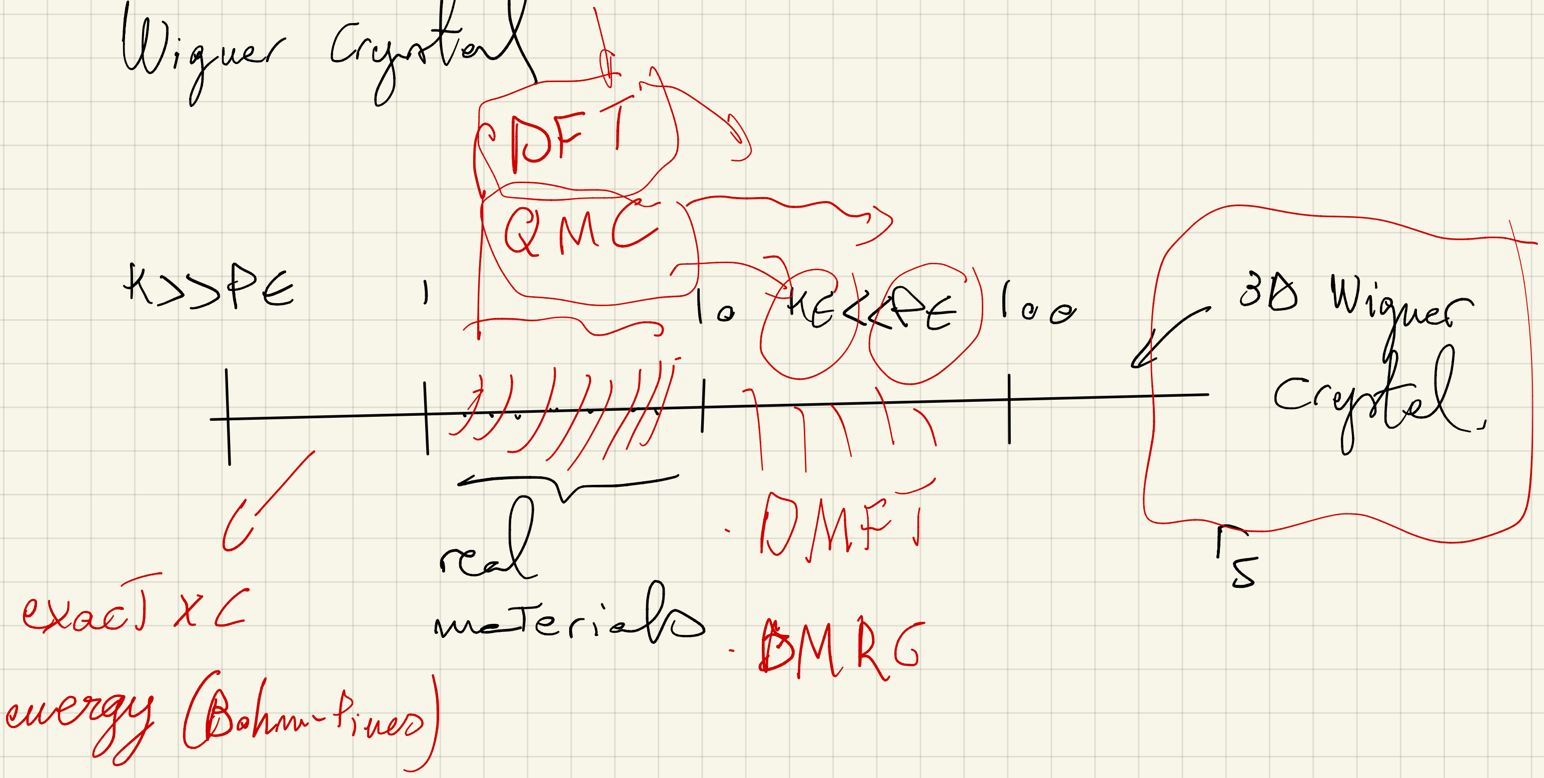
$r_s > 1$ low n, potential energy dominates

r_s, being $\sim$ Coulomb/Kinetic can be used as a small parameter to do perturbation theory ($r_s < 1$) to learn the effects of Coulomb interactions in the e^- gas.

(We can obtain the exact correlation energy in this limit, Bohm-Pines).

But for real materials $r_s \sim 1-5$ so, strongly interacting in 3D.

$r_s > 100 \rightarrow e^-$ correlation dominates $\Rightarrow e^-$ crystallize Wigner crystal



- if no e^-e^- interaction $\Rightarrow$ 1 body problem, $1e^-$ Sch. eq.

Can we still solve a $1e^-$ sh. eq. while includes parts of the e^-e^- interaction? $\Rightarrow$ $\underbrace{\text{Hartree}}$, $\underbrace{\text{Hartree-Fock}}$ approx.

$$H = \overbrace{-\sum_k \frac{\hbar^2}{2m}\vec{\nabla}_k^2}^{*} + \overbrace{\sum_{k,l} V(r_k - R_l)}^{*} + \overbrace{\frac{1}{2}\sum_{kk'} \frac{e^2}{|r_k - r_{k'}|}}^{**}$$

$$= \boxed{\sum_k H_k} + \boxed{\sum_{kk'} H_{kk'}}$$

* single e^- eq.

** 2 e^- eq.

If we neglect the strong e^-e^- interaction, we can separate the eq: $\sum_k H_k \chi = E\chi$

$$\chi(r_1 \ldots r_N) = \varphi_1(r_1) \ldots \varphi_N(r_N)$$

$E = \sum_k E_k$, but the term $H_{kk'}$ does not allow to do this.

$$\chi(r_1 \dots r_N) = \varphi_1(r_1)\cdot\varphi_2(r_2)\dots\varphi_N(r_N) \quad (1)$$

$$E = \langle \chi | H | \chi \rangle = \sum_k \langle \varphi_k | H_k | \varphi_k \rangle +$$

$$\frac{1}{2}\sum_{kk'} \left\langle \varphi_k \varphi_{k'} \left| \frac{e^2}{|r_k - r_{k'}|} \right| \varphi_k \varphi_{k'} \right\rangle$$

Those φ_k that minimize the Energy are the best set of functions of type (1) for groundstate.

$\Rightarrow$ variational principle $\delta\left[E - \sum_k \varepsilon_k \left(\langle \varphi_k | \varphi_k \rangle - 1\right)\right] = 0$

imposing normalization conditions.

Lagrange Multipliers

$$\sum_k \langle \delta\varphi_k | H_k | \varphi_k \rangle + \frac{e^2}{2}\sum_{k' \neq k} \left\langle \delta\varphi_k \varphi_{k'} \left| \frac{1}{|r_k - r_{k'}|} \right| \varphi_k \varphi_{k'} \right\rangle$$

$$- \varepsilon_k \langle \delta\varphi_k | \varphi_{k'} \rangle$$

$$\langle \underset{\sim}{\delta\varphi_k} | H_k + \frac{e^2}{2}\sum_{k'\neq k} \langle \varphi_{k'} | \frac{1}{|r_k - r_{k'}|} | \varphi_{k'} \rangle - E_k | \varphi_k \rangle = 0$$

This eq needs to be $= 0$. regardless the variation of $\delta\varphi_k$ $\Rightarrow$

$$\left[-\frac{\hbar^2}{2m} + e^2 \sum_{k'\neq k} \underbrace{\int \frac{|\varphi_k(r')|^2}{|r_k - r_{k'}|} d\vec{r}\,'}_{} + V^{ion}(\vec{r})\right]\varphi_k(r)$$

$$= E_k \varphi_k(r)$$

$\downarrow$

Hartree eq. Describes the eq. for an e^- at position r in the potential field $V(\vec{r})$ of the Lattice ions and in the Coulomb potential of an average distribution of all other e^-. The Lagrange parameters E_k can be interpreted as single e^- energies.

Hartree-Fock

$\chi = \prod_i \varphi_i(r)$ $\neq$ Pauli exclusion Principle

N. fermionic nature of e^-

$$\chi(k \to k') \Rightarrow \chi(k' \to k)$$

To include the fermionic nature : ↑ Make pause in here with cyrus notes

$$\chi = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \varphi_1(\vec{q}_1) & \cdots & \varphi_N(\vec{q}_1) \\ \vdots & & \\ \varphi_1(\vec{q}_N) & \cdots & \varphi_N(\vec{q}_N) \end{vmatrix} \quad \Bigg| \; \vec{q}_i = \vec{r}_i, \sigma_i$$

includes a sum over spin variables

$$E = \sum_k \int \varphi_k^*(q_1)\, H_k\, \varphi_k(q_1)\, dq_1 + \frac{e^2}{2} \sum_{kk'}{}^{\textcircled{\prime}} \int \frac{|\varphi_k(q_1)|^2 |\varphi_k(q_2)|^2}{|\vec{r}_1 - \vec{r}_2|} dq_1\, dq_2$$

$$- \frac{e^2}{2} \sum_{kk'} \int \frac{\varphi_k(q_1)\, \varphi_k(q_2)\, \varphi_{k'}(q_2)\, \varphi_{k'}(q_1)}{|r_1 - r_2|} dq_1\, dq_2$$

$$\delta\left[E - \sum_{kk'} \lambda_{kk'} \left(\langle\varphi_k|\varphi_{k'}\rangle - \delta_{kk'}\right)\right] = 0$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}_1^2 + V^{ion}(r_1)\right]\varphi_k(q_1) + \overbrace{e^2\sum_{k'}\frac{|\varphi_{k'}(q_2)|^2 dq_2}{|r_1-r_2|}}^{1e^- \text{ operator}}\varphi_k(q_1)$$

$$\overbrace{-e^2\sum_{k'}\int\frac{\varphi^*_{k'}(q_2)\varphi_k(q_1)}{|r_1-r_2|}}^{2e^- \text{ operator}}\underbrace{dq_2\,\varphi_{k'}(q_1)}_{(2)} =$$

$$= \cancel{\delta}\sum_{k'}\lambda_{kk'}\varphi_{k'}(q_1)$$

This is a Hermitian Hamiltonian, we can introduce a ~~Th~~ transformation $\varphi_i' = \sum_k U_{ik}\varphi_k$; $U_{ik} \Rightarrow$ unitary matrix That diagonalizes the matrix $\lambda_{kk'} \Rightarrow \lambda_{kk'} = E_k\delta_{kk'}$ in the new basis φ_i'. I will write φ_i for the new wave functions

Note: if we spin orbit coupling $\varphi(q) = \varphi(r,s) = \varphi(r)\,\varphi(s)$

so The spin appears as $\delta_{s_i s_j}$ in (2)

⇒ Hartree-Fock eq:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V^{ion}(r)\right]\varphi_j(r) + e^2\sum_{i\neq j}\overbrace{\int\frac{|\varphi_k(r')|^2}{|r-r'|}}^{(a)}dr'\,\varphi_j(r)$$

$$-e^2\sum_{k\neq j}\underbrace{\int\frac{\varphi_k(r')\varphi_j(r)}{|r-r'|}}_{(b)}dr'\,\varphi_k(r)\,\delta_{s_k s_j} = E_j\,\varphi_j(r)$$

Note (a) $V(r)\cdot\varphi(r)$

(b) $\int V(r,r')\varphi(r')\,dr'\cdot\varphi(r)$ ⇒ integral operator

E_i ⇒ energy needed To remove an e^- from the system.

$E_k - E_i$ ⇒ energy needed To Transfer an e^- from state i To state k

⇒ Koopmans Theorem. It's only correct if the removal of an e^- from the system does not alter The other φ_k $(k\neq i)$

$\Delta E = \langle\chi'|H|\chi'\rangle - \langle\chi|H|\chi\rangle$; $\chi' = \chi$ without The ith row and column of the determinant.

Hartree interaction => Classical Coulomb interaction

$$\sum_{k\neq j}\int\frac{|\varphi_k(r')|^2\,dr'}{|r-r'|}=\sum_{k}\int\frac{|\varphi_k(r')|^2\,dr'}{|r-r'|}-\int\frac{|\varphi_j(r')|^2}{|r-r'|}dr'$$

In the Hartree eq. the interaction of an e^- with its own space charge is substracted from the interaction of an e^- with all the others, including itself.

$$-e\int\frac{\rho_j^H(r')\,dr'}{|r-r'|}\cdot\varphi_j(r)$$ => energy of an e^- interacting with its own space cloud.

$$\rho_j^H(r)=-e|\varphi_j|^2\ ;\ \int\rho^H(r)\,dr=-e$$

In the H-F eq. we can include terms $k=j$ in both sums because these terms cancel themselves.
In DFT this is not the case and it's the origin of the self interaction error).

We can define a HF density :

$$e^2 \sum_{\substack{k \\ \text{spin} //}} \int \frac{\varphi_k^*(r')\,\varphi_j(r')}{|r-r'|}\,dr'\,\varphi_k(r) =$$

(same as s_i, s_j)

$$= -e \int \frac{\rho_j^{HF}(r,r')}{|r-r'|}\,dr'\,\varphi_j(r)$$

$$\rho_j^{HF} = -e \sum_{\substack{k \\ \text{spin} //}} \frac{\varphi_k^*(r')\,\varphi_j(r')\,\varphi_j^*(r)\,\varphi_k(r)}{\varphi_j^*(r)\,\varphi_j(r)}$$

$$\iint \rho^{HF}(r,r')\,dr\,dr' = -e$$

difference between ρ^H and ρ^{HF}

$\rho_i^H(r)$ → distributed along the crystal equally for all e^-

$\rho^{HF}(r,r')$ → depends on the location $\vec{r}$ of the e^- being considered → Motion of e^- of same spin is correlated !!

:-

It is not possible to obtain ρ^{HF} in the general case (Too hard). It can be evaluated exactly for free e^- (PW).

Final HF eq.

$$\Big[\Big[-\frac{\hbar^2}{2m}\nabla^2+V(r)-e\int\frac{\rho(r')-\rho_j^{HF}(r-r')}{|r-r'|}\,dr'\Big]\varphi_j(r)=E_j\varphi_j(r)$$

$\downarrow$

problem, the solution for φ_j depends on ρ_j^{HF} (which has φ_j inside) $\Rightarrow$ different HF eq. for each e^-

This can be solved using the Slater approximation that averages ρ_j^{HF} over all j

$$\bar{\rho}^{HF}=\frac{\sum_j \varphi_j^*(r)\varphi_j(r)\rho_j^{HF}(r,r')}{\sum_k \varphi_k^*(r)\varphi_k(r)}=-e\,\frac{\sum_{jk\parallel}\varphi_k^*(r')\varphi_j(r')\varphi_j^*(r)\varphi_k(r)}{\sum_k \varphi_k^*(r)\varphi_k(r)}$$

So

$$\Big[-\frac{\hbar^2}{2m}\nabla^2+V(r)-e\int\frac{\rho(r')-\bar{\rho}^{HF}(r,r')}{|r-r'|}\,dr'\Big]\varphi_j(r)=E_j\varphi_j(r)$$

$\downarrow$ One electron operator that contains important parts of the e^--e^- interaction

G. Grosso and G. Pastori Parravicini, Solid State Physics (Academic Press, 2000)

Chapter 4, sections on the electron gas.

$$\Psi_0 = A\{\phi_1\alpha\,\phi_1\beta\,\ldots\phi_m\alpha\,\phi_m\beta\ldots\phi_{N/2}\alpha\,\phi_{N/2}\beta\}\,, \qquad (30)$$

where $\phi_i(\mathbf{r})$ $(i = 1, 2, \ldots N/2)$ indicate orthonormal orbitals. Notice that the state Ψ_0 has total spin component S_z equal to zero and total spin S equal to zero.

The general Hartree–Fock equations (25), carrying out explicitly the summation over spin variables, take the form

$$\left[\frac{\mathbf{p}^2}{2m} + V_{\text{nucl}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}) + V_{\text{exch}}\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \qquad (31\text{a})$$

$(i = 1, 2, \ldots, N/2)$, with

↑ and ↓

$$V_{\text{coul}}(\mathbf{r}) = 2\sum_j^{N/2}\langle\phi_j(\mathbf{r}_2)\,|\,\frac{e^2}{|\mathbf{r}-\mathbf{r}_2|}\,|\,\phi_j(\mathbf{r}_2)\rangle \qquad (31\text{b})$$

only spin ∥ can exchange

$$V_{\text{exch}}\phi_i(\mathbf{r}) = -\sum_j^{N/2}\langle\phi_j(\mathbf{r}_2)\,|\,\frac{e^2}{|\mathbf{r}-\mathbf{r}_2|}\,|\,\phi_i(\mathbf{r}_2)\rangle\,\phi_j(\mathbf{r})\,. \qquad (31\text{c})$$

The Hartree–Fock equations of the homogeneous (interacting) electron gas can be solved exactly using plane waves $W(\mathbf{k}_i, \mathbf{r}) = (1/\sqrt{V})\exp(i\mathbf{k}_i \cdot \mathbf{r})$. The normal ground-state of the interacting gas is approximated with a single Slater determinant, formed by doubly occupied plane waves with wavevectors filling the Fermi sphere of radius k_F; we have

$$\Psi_0 = A\{W_{\mathbf{k}_1}\alpha\, W_{\mathbf{k}_1}\beta\ \dots W_{\mathbf{k}_{N/2}}\alpha\, W_{\mathbf{k}_{N/2}}\beta\}\ . \tag{38}$$

In the jellium model $V_{\text{nucl}}(\mathbf{r})$ and $V_{\text{coul}}(\mathbf{r})$ exactly cancel, and the Fock operator becomes

$$F = \frac{\mathbf{p}^2}{2m} + V_{\text{exch}}\ , \tag{39}$$

where V_{exch} is the exchange integral operator of type (31c) built with the occupied plane waves. In the case the Hartree approximation is considered, the exchange operator V_{exch} is omitted and one recovers the free-electron Sommerfeld model.

It is well known that the kinetic energy operator $\mathbf{p}^2/2m$ is diagonal in a plane wave representation. We now show that also the exchange integral operator, built up with plane waves, is diagonal in a plane wave representation. In fact we have

$$\begin{aligned} V_{\text{exch}} e^{i\mathbf{k}\cdot\mathbf{r}} &= -\sum_{\mathbf{q}}^{(\text{occ})} \frac{1}{\sqrt{V}} e^{i\mathbf{q}\cdot\mathbf{r}} \int \frac{1}{\sqrt{V}} e^{-i\mathbf{q}\cdot\mathbf{r}'} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} e^{i\mathbf{k}\cdot\mathbf{r}'}\, d\mathbf{r}' \\ &= -e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{V} \sum_{\mathbf{q}}^{(\text{occ})} \int e^{-i(\mathbf{k}-\mathbf{q})\cdot(\mathbf{r}-\mathbf{r}')} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' \\ &= -e^{i\mathbf{k}\cdot\mathbf{r}} \frac{1}{V} \sum_{q<k_F} \frac{4\pi e^2}{|\mathbf{k}-\mathbf{q}|^2}\ . \end{aligned} \tag{40}$$

$$V_{\mathrm{exch}} e^{i\mathbf{k}\cdot\mathbf{r}} = -\frac{2e^2 k_F}{\pi} F(\frac{k}{k_F})\, e^{i\mathbf{k}\cdot\mathbf{r}}$$

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

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m} - \frac{2e^2 k_F}{\pi} F(\frac{k}{k_F})$$

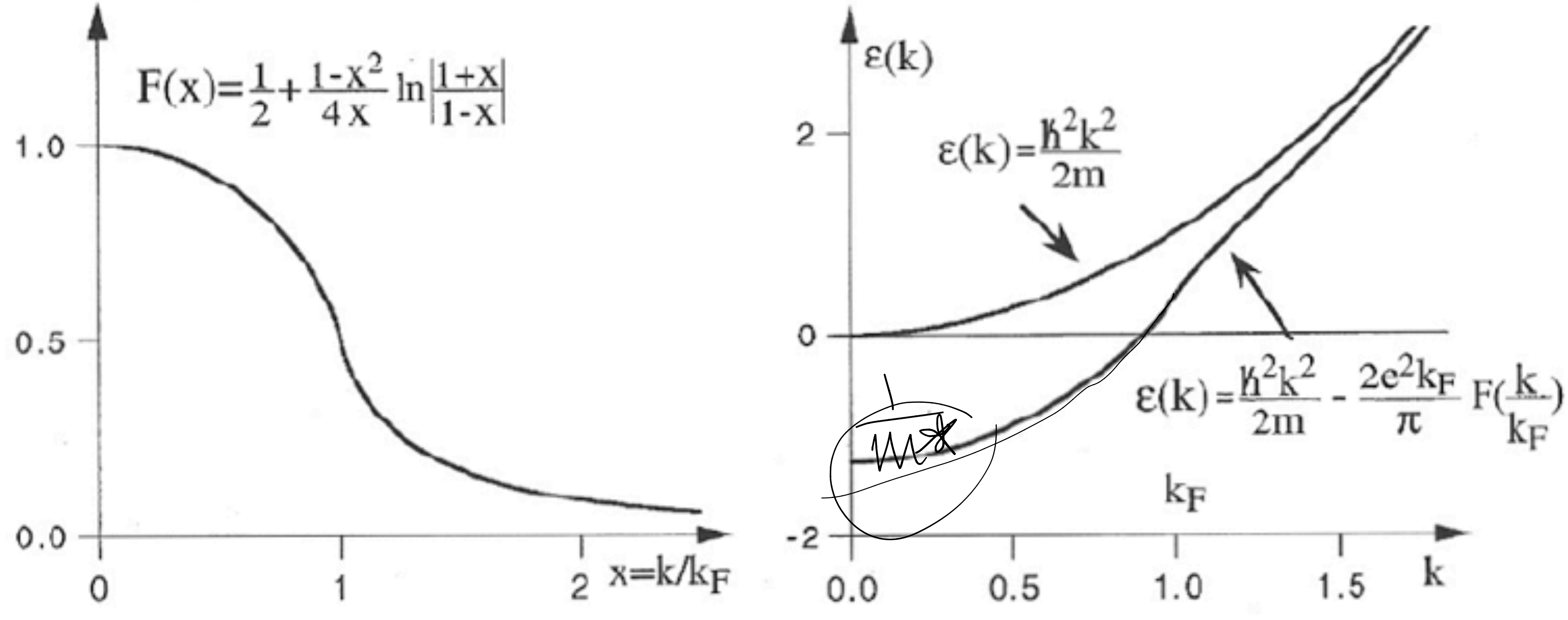


Fig. 4 (a) Schematic plot of the function $F(x)$. (b) Kinetic energy and Hartree–Fock orbital energy as a function of the wavevector k for the homogeneous electron gas. Energies are in Rydbergs, k is in units of a_{B}^{-1} (inverse Bohr radius), and we have taken $k_F = 1/a_{\mathrm{B}}$.

$$k_F a_{\mathrm{B}} = 1.92/r_s$$

$$E_0^{(\mathrm{HF})} = 2\sum_{k<k_F} \frac{\hbar^2 k^2}{2m} - \sum_{k<k_F} \frac{2e^2 k_F}{\pi} F(\frac{k}{k_F})$$

$$E_0^{(\mathrm{HF})} = N\left[\frac{3}{5}\frac{\hbar^2 k_F^2}{2m} - \frac{3}{4}\frac{e^2 k_F}{\pi}\right] = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} \text{ (in Rydberg)}$$

$r_s \to 0$ $+ 0.0622 \ln(r_s/a_0) - 0.096 + O(r_s/a_0)]$ Ry

Another interesting remark can be made on Eqs. (41). From Eq. (41b) we see that $F(x)$ varies smoothly (from one to one half) as k goes from zero to k_F. In the hypothetical case that we replace the function $F(x)$ by its average value 3/4 (see Eq. C5), we would have that the operator V_{exch} becomes a constant equal to

$$V_{\text{exch}}^{(\text{Slater})} = -\frac{3}{2}\frac{e^2}{\pi}k_F = -\frac{3}{2}\frac{e^2}{\pi}(3\pi^2 n)^{1/3} \ . \tag{45a}$$

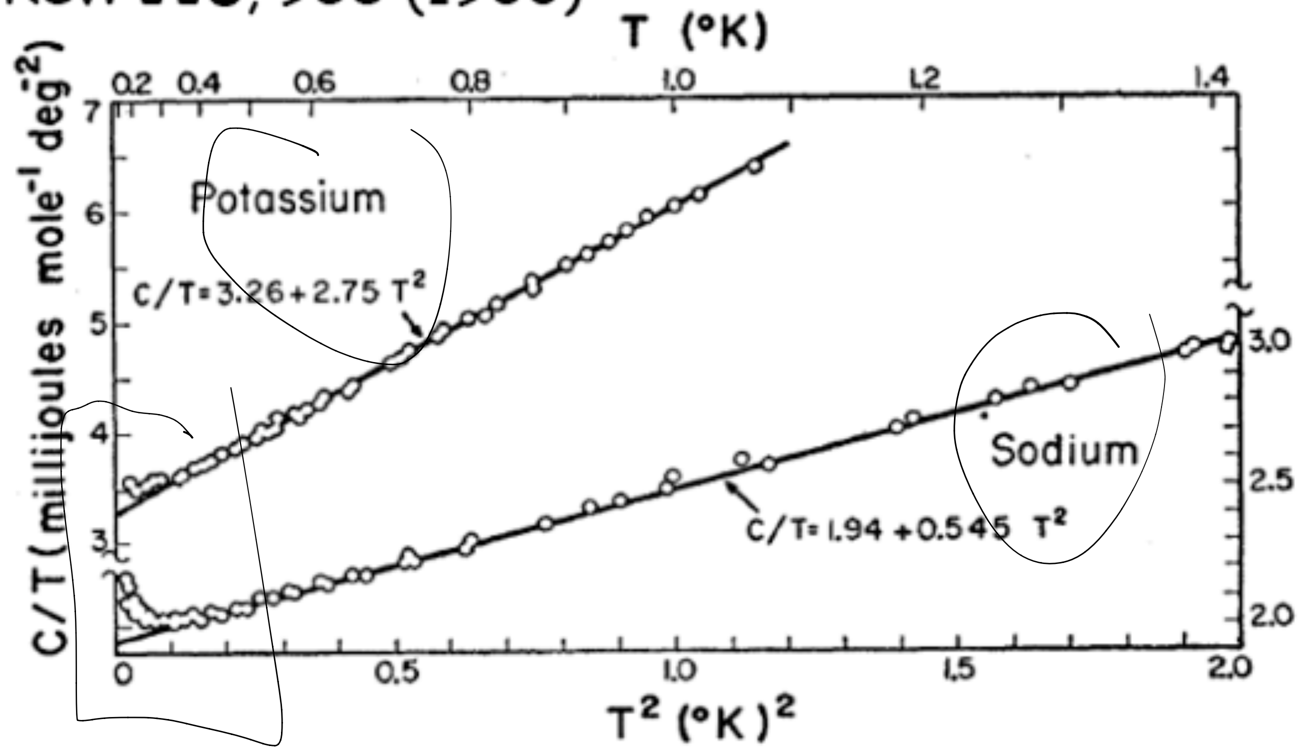
Slater suggested that expression (45a) could be adopted also for non-homogeneous electronic systems of *local density* $n(\mathbf{r})$, so obtaining the famous "$n^{1/3}$ local approximation" to the exchange operator

$$V_{\text{exch}}^{(\text{Slater})}(\mathbf{r}) = -\frac{3}{2}\frac{e^2}{\pi}[3\pi^2 n(\mathbf{r})]^{1/3} \ . \tag{45b}$$

$\boxed{\bar{V}^{x} \sim \rho^{1/3}}$

It is worthwhile to mention that the Slater local exchange approximation has had historically an important role in making many properties of actual materials accessible to the theory and to the interpretation; the reason is that the Hartree–Fock equations become ordinary differential equations, when the exchange operator is approximated with a local potential. In the literature, many attempts have been done to correct and improve the Slater expression (45b); among them we mention the once popular "X_α local approximation", where a semi-empirical parameter α multiplies the original Slater expression of Eq. (45b). All these attempts have come to an end with the advances of the density functional theory, mainly in the local density approximation

W. H. Lien and N. E. Phillips,
Heat Capacity of Sodium and Potassium at Temperatures below 1°K,
Phys. Rev. **118**, 958 (1960)



$$\gamma = \left(\frac{m_b}{m_e}\right)$$

FIG. 1. C/T vs T^2. C is the heat capacity of sample plus calorimeter per mole of sample. The corrections to C/T for the calorimeters were estimated from the known heat capacities of the material used (largely copper) and are $0.49+0.036T^2$ and $1.02+0.07T^2$ millijoules/mole deg² for sodium and potassium, respectively.

Sodium, Na

The data give values for the Debye temperature, γ, and the effective mass ratio of 156°K, 1.45×10^{-3} joules/mole deg², and 1.33, respectively.

Potassium, K

the Debye temperature, γ, and effective mass ratio 89.9°, 2.2×10^{-3} joules/mole deg² and 1.3, respectively.

"mass ratio" means $\gamma/\gamma_{\text{free electron}} = [D(E_F)_{\text{band}}/D(E_F)_{\text{free}}] \times (1+\lambda)$

Hartree Fock in the Jellium model

→ single orbitals are PW : $\phi_i^{HF} = \phi_{k\sigma} = \frac{1}{\sqrt{V}} e^{ikr} \sigma_{\eta}$

· Note that $V_{ion}(R) + V_H = 0$ in an homogeneous density, and a PW charge density is homogeneous.

$$\to -\frac{\hbar^2 k^2}{2m} \phi_{k\sigma}(r) - \frac{1}{V^{3/2}} \sum_{\substack{k'<k_F \\ \uparrow\uparrow}} \int dr' \frac{e^2}{|r-r'|} \underbrace{e^{-ik'r} e^{ik'r'} e^{ikr'}}_{e^{-i(k-k')(r-r')}} \times \frac{\sqrt{V}}{\sqrt{V}} e^{ikr} \sigma \to \phi_{k,\sigma}$$

new

$$= \varepsilon_\sigma \phi_{k\sigma}(r)$$

$$\Rightarrow -\frac{\hbar^2 k^2}{2m} \phi_{k\sigma}(r) - \frac{1}{V} \sum_{\substack{k'<k_F \\ \uparrow\uparrow}} \underbrace{\int dr' \frac{e^2}{|r-r'|} e^{-i(k-k')(r-r')}}_{\text{This is a F.T} = \frac{4\pi e^2}{|k-k'|^2}} \phi_{k\sigma}(r)$$

$$\left\{ -\frac{\hbar^2 k^2}{2m} - \int_{k'<k_F} \frac{dk'}{(2\pi)^3} \frac{4\pi e^2}{|k-k'|^2} \right\} \phi_{k\sigma}(r) = \varepsilon_\sigma(k) \phi_{k\sigma}(r)$$

This proves that plane waves are solutions of H.F eq in the homogeneous e^- gas

$$H_{HF}\,\phi_{k\sigma}(r) = \mathcal{E}_\sigma\,\phi_{k\sigma}(r)$$

drop σ (paramagnetic system)

$$\mathcal{E}_{HF}(k) = \frac{\hbar^2 k^2}{2m} - \int_{k'<k_F} \frac{dk'}{(2\pi)^3}\,\frac{4\pi e^2}{|k-k'|^2}$$

$$\mathcal{E}_{HF}(k) = \frac{\hbar^2 k^2}{2m} \overbrace{- \frac{2e^2}{\pi}\,k_F\,F\!\left(\frac{k}{k_F}\right)}^{\Sigma^{HF}(k)}$$

also called self energy

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

exchange and correlation energy:

$$\mathcal{E}_0(r) = e^2\int \frac{\rho(r')}{|r-r'|}\,dr'$$

← without $\boxed{xc}$ hole, i.e. Hartree

$$\mathcal{E}(r) = e^2\int \frac{\rho^{HF}(r)\,dr'}{|r-r'|} = e^2\int \frac{g(r,r')\,\rho(r')}{|r-r'|}\,dr'$$

. e^- density and pair correlation function.

$$\int |\Psi(x_1 \dots x_N)|^2 \, d^N x = 1$$

e^- density operators

$$\hat{\rho}(r) = \sum_i \delta(r-r_i)\,\delta_{\sigma_i \uparrow} + \sum_i \delta(r-r_i)\,\delta_{\sigma_i \downarrow} = \hat{\rho}_\uparrow(r) + \hat{\rho}_\downarrow(r)$$

$$\rho(r) = \langle \Psi | \hat{\rho} | \Psi \rangle = \sum_i \sum_\sigma \int \Psi^*(x_1 \dots x_N)\,\delta(r-r_i)\,\Psi(x_1 \dots x_N)\, d^N x$$

$$= N \sum_\sigma \int |\Psi(r\sigma, x_2 \dots x_N)| \, dx_2 \dots dx_N$$

$g(r,r')\rho(r')$ = density of e^- at r' when $1e^-$ is at r

$\rho(r)\,g(r,r')\,\rho(r')$ = distribution of particle pairs in the system.

$$\rho(r)\,g(r,r')\,\rho(r') = \langle \Psi | \sum_{i<j} \delta(r-r_i)\,\delta(r'-r_j) | \Psi \rangle$$

$$= \frac{N(N-1)}{2} \Big\langle \underbrace{\int |\Psi(r\sigma, r'\sigma', x_3 \dots x_N|^2 \, dx^3 \dots dx_N}_{\text{2 body DM} \to \rho_2(r,r')} \Big\rangle_{\text{spin of particles 1\&2}}$$

$$g(r,r') = \frac{N(N-1)}{2}\,\frac{\rho_2(r,r')}{\rho(r)\,\rho(r')}$$

$$\int g(r,r')\,\rho(r)\,\rho(r')\,dr\,dr' = \frac{N(N-1)}{2}$$ → all pairs in the system.

$g(r,r') = g(r',r)$ → in Homogeneous e^- gas.

$g(r, r' \to \infty) = 1$ (e^- are uncorrelated for long distances

$g(r,r') = g_{\uparrow\uparrow}(r,r') + g_{\downarrow\downarrow}(r,r')$ → only in H.E.G + only for H.Fock $+ g_{\uparrow\downarrow}(r,r') + g_{\downarrow\uparrow}(r,r')$

$g_{\uparrow\uparrow}(r_1, r_2) \to 0$ for $r_1 \to r_2$ for e^- or fermions.

but $g_{\uparrow\downarrow}(r,r')$ at $r=r'$ is system dependent

$$\int dr' [\overbrace{g(r,r') - 1]\,\rho(r')}^{\rho - \rho^{HF}} = -1$$ = exchange hole charge $= -1 \cdot (-e) \doteq +e$

In Jellium: $g(r,r') = g(|\underset{\downarrow}{r-r'}|)$

No exact position, only difference

→ Back To XC energy:

$$\varepsilon_{xc}(r) = \varepsilon(r) - \varepsilon_0(r) = e^2 \int \frac{[\rho^{HF}(r') - \rho(r')]}{r-r'}\, dr'$$

$$= e^2 \int \frac{[g(r,r')-1]\,\rho(r')}{|r-r'|}\, dr'$$

↙

interaction of an e^- with its xc hole which is positively charged with an integrated charge of "+e"

$\varepsilon_{xc}(r) \to$ X.C energy density

$$j_1(x) = \frac{\sin x - x\cos x}{x^2}$$

$$E_{xc} = \int \varepsilon_{xc}(r)\,\rho(r)\, dr$$

$$E_{xc}^{HF} = e^2 \rho_0 \int \frac{dr}{r}\left[g^{HF}(r) - 1\right] = -\frac{\cancel{6}\, e^2 k_F}{\pi} \int_0^{\infty} \frac{j_1(x)}{x}\, dx$$

$$= -\frac{3}{4}\, \frac{e^2 k_F}{\pi}$$

· We can estimate the cohesive energy

$$E_{coh} = E_{atom} - E_{GS \to solid}$$

$$E_{GS} = E_{KE} + E_{e^- - ion} + E_{ec}$$

$m_b > m_e$

$$E_{KE} = \frac{2.21}{r_s^2} \left(\frac{m_e}{m_b} \right)^{-1}$$

$$m_e = \left(\frac{\partial^2 E(k)}{\partial k_i \partial k_j} \right)^{-1} \cdot \frac{1}{3}$$

m_b → obtained from band structure

conduction band effective mass

$$E_{ee} = E_{Hartree} + E_x + \underbrace{E_{corr}}_{\text{Wigner interpolation formula}} \approx$$ → ~~a~~ write as function of r_s

$$E_{ee} = \frac{1.2}{r_s} + \left(-\frac{0.916}{r_s} \right) + \left(-\frac{0.88}{7.8 + r_s} \right) (Ry)$$

$$\left. \frac{\partial E_{gs}}{d r_s} \right|_{r_s = r_{eq}} = 0$$

Table 6.1

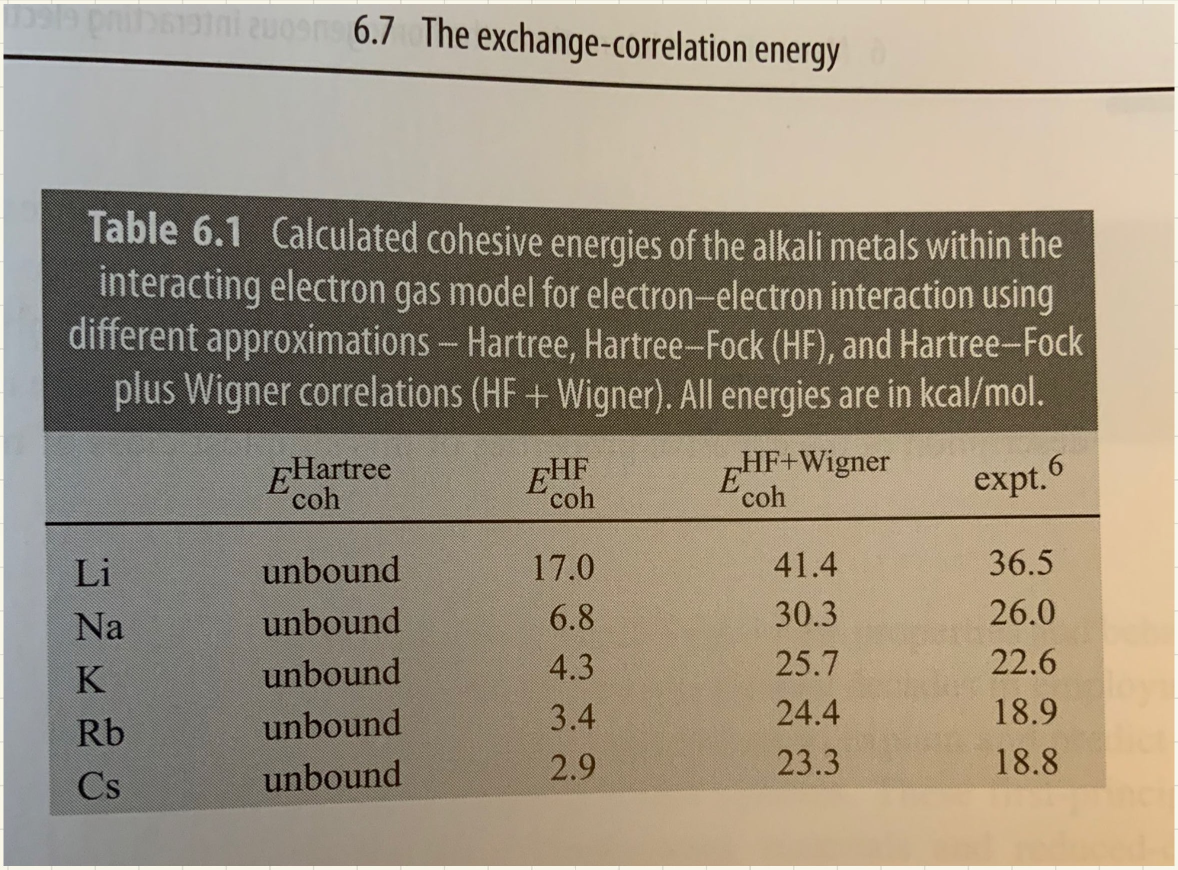


Table 6.1 Calculated cohesive energies of the alkali metals within the interacting electron gas model for electron–electron interaction using different approximations – Hartree, Hartree–Fock (HF), and Hartree–Fock plus Wigner correlations (HF + Wigner). All energies are in kcal/mol.

	$E_{\text{coh}}^{\text{Hartree}}$	$E_{\text{coh}}^{\text{HF}}$	$E_{\text{coh}}^{\text{HF+Wigner}}$	expt.[6]
Li	unbound	17.0	41.4	36.5
Na	unbound	6.8	30.3	26.0
K	unbound	4.3	25.7	22.6
Rb	unbound	3.4	24.4	18.9
Cs	unbound	2.9	23.3	18.8

Al → $Z = 13$, fcc 1 atom/cell

Basis size = TZDP → polarized → **N**umerical **A**tomic **O**rbital

Triple Zeta, double

Gaussian Basis set

Al

$1s^2$

$2s^2 \; 2p^6$ } Pseudopotential "Core"

$3s^2 \; 3p^1 \; 3d$ → Valence e^-

$$SZ \rightarrow \begin{cases} 3s \\ 3p^x \; p^y \; p^z \end{cases}$$

$$TZ \left(\begin{array}{lll} \overbrace{3s \; 3s' , 3s''}^{3} \\ 3p_x \; p'_x \; p''_x \\ \vdots \; p_y \\ \vdots \; p_z \end{array} \right) 9$$

$3d \rightarrow +5 +5$

orbitals TZDP(Al) = $3 + 9 + 10 = 22$