Jellium model

The jellium model consists of free electrons interacting with a uniform background positive charge and with themselves.

The Hamiltonian, in a plane-wave basis, is

$$\hat{H}_{\text{Jellium}} = \sum_{k\sigma} \frac{\hbar^2 k^2}{2m} c^\dagger_{k\sigma} c_{k\sigma} + \underbrace{\frac{4\pi e^2}{2V}}_{\text{count each pair only once}} \underbrace{\sum_{\substack{kk'\sigma\sigma' \\ q\neq 0}}}_{\text{cancellation of infinity at } q=0 \text{ from uniform positive background charge}} \frac{1}{q^2} c^\dagger_{k+q\sigma} c^\dagger_{k'-q\sigma'} c_{k'\sigma'} c_{k\sigma}$$

$$V(q) = \begin{cases} \dfrac{4\pi e^2}{q^2 V} & \text{for } q \neq 0 \\ 0 & \text{for } q = 0 \end{cases}$$

Study first with the variational principle.

Consider

$$E_{\text{trial}} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

we have always $E_{\text{trial}} \geq E_{gs}$

proof: $|\psi\rangle = \sum_n c_n |n\rangle$ $\quad \hat{H}|n\rangle = E_n |n\rangle$

$$E_{\text{trial}} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \geq \frac{\sum_n |c_n|^2 E_0}{\sum_n |c_n|^2} = E_{gs}$$

For our trial state, we will look at a single slater determinant.

Define $$\alpha^\dagger_{p\sigma} = \sum_\ell \underbrace{a_\ell^p}_{\text{numbers}} \underbrace{c^\dagger_{\ell\sigma}}_{\text{operator}}$$

and let $$|\psi\rangle = \prod_{\substack{\text{given set}\\ \text{of } p \text{ and } \sigma}} \alpha^\dagger_{p\sigma}|0\rangle$$

Note that

$$\left(\alpha^\dagger_{p\sigma}, \alpha_{p'\sigma'}\right)_+ = \sum_{\ell\ell'} a_\ell^p a_{\ell'}^{p'*} \left(c^\dagger_{\ell\sigma}, c_{\ell'\sigma'}\right)_+$$

$$= \sum_{\ell\ell'} a_\ell^p a_{\ell'}^{p'*} \delta_{\ell\ell'}\delta_{\sigma\sigma'}$$

$$= \sum_{\ell} a_\ell^p a_{\ell'}^{p'*} \delta_{\sigma\sigma'}$$

If we choose the a_ℓ^p vectors to be an orthonormal set,

then $\sum_\ell a_\ell^p a_\ell^{p'*} = \delta_{pp'}$

so $\left(\alpha^\dagger_{p\sigma}, \alpha_{p'\sigma'}\right)_+ = \delta_{pp'}$

Next, define a set of vectors b_ℓ^p such that

$$\sum_p b_\ell^p a_{\ell'}^p = \delta_{\ell\ell'}$$

Then $$\sum_p b_\ell^p \alpha^\dagger_{p\sigma} = \sum_p \sum_{\ell'} b_\ell^p a_{\ell'}^p c^\dagger_{\ell'\sigma} = c^\dagger_{\ell\sigma}$$

So we can now compute averages

$$\langle\psi| c^\dagger_{\ell\sigma} c_{\ell\sigma}|\psi\rangle = \sum_{pp'} b_\ell^p b_\ell^{p'*} \langle\psi|\alpha^\dagger_{p\sigma}\alpha_{p'\sigma}|\psi\rangle$$

$$= \sum_{pp'} b_\ell^p b_\ell^{p'*} \delta_{pp'}\, \delta(p,\sigma\in\psi)$$

$$= \sum_p |b_\ell^p|^2\, \delta(p,\sigma\in\psi)$$

$$\langle\psi| c^+_{l_1\sigma} c^+_{l_2\sigma'} c_{l_3\sigma'} c_{l_4\sigma} |\psi\rangle$$

$$= \sum_{p_1p_2p_3p_4} b^{p_1}_{l_1} b^{p_2}_{l_2} b^{p_3*}_{l_3} b^{p_4*}_{l_4} \langle\psi| \alpha^+_{p_1\sigma} \alpha^+_{p_2\sigma'} \alpha_{p_3\sigma'} \alpha_{p_4\sigma} |\psi\rangle$$

$$= \sum_{p_1p_2p_3p_4} b^{p_1}_{l_1} b^{p_2}_{l_2} b^{p_3*}_{l_3} b^{p_4*}_{l_4} \Big[\delta_{p_1p_4}\delta_{p_2p_3} \langle\psi| \alpha^+_{p_1\sigma}\alpha^+_{p_2\sigma'}\alpha_{p_2\sigma'}\alpha_{p_1\sigma}|\psi\rangle$$

$$+\delta_{p_1p_3}\delta_{p_2p_4}\delta_{\sigma\sigma'} \langle\psi|\alpha^+_{p_1\sigma}\alpha^+_{p_2\sigma}\alpha_{p_1\sigma}\alpha_{p_2\sigma}|\psi\rangle \Big]$$

note when $p_1=p_2$ and $\sigma=\sigma'$ we get 0 in both cases since $\alpha^2_{p\sigma}=0$.

so we can assume $p_1\neq p_2$

$$= \sum_{p_1p_2p_3p_4} b^{p_1}_{l_1} b^{p_2}_{l_2} b^{p_3*}_{l_3} b^{p_4*}_{l_4} \Big[\delta_{p_1p_4}\delta_{p_2p_3} \langle\psi| \alpha^+_{p_1\sigma}\alpha_{p_1\sigma}\alpha^+_{p_2\sigma'}\alpha_{p_2\sigma'}|\psi\rangle$$

$$- \delta_{p_1p_3}\delta_{p_2p_4}\delta_{\sigma\sigma'} \langle\psi|\alpha^+_{p_1\sigma}\alpha_{p_1\sigma}\alpha^+_{p_2\sigma}\alpha_{p_2\sigma}|\psi\rangle \Big]$$

since in this expression, the term with $p_1=p_2=p_3=p_4$ $\sigma=\sigma'$ cancels from both terms, we do not need to worry about the restriction $p_1\neq p_2$ anymore, since the total terms vanish when $p_1=p_2$.

$$= \sum_{p_1} b^{p_1}_{l_1} b^{p_1*}_{l_4} \delta(p_1^\sigma \in \psi) \sum_{p_2} b^{p_2}_{l_2} b^{p_2*}_{l_3} \delta(p_2^{\sigma'}\in\psi)$$

$$- \sum_{p_1} b^{p_1}_{l_1} b^{p_1*}_{l_3} \delta(p_1^\sigma\in\psi) \sum_{p_2} b^{p_2}_{l_2} b^{p_2*}_{l_2} \delta(p_2^\sigma\in\psi)\delta_{\sigma\sigma'}$$

Note that we have just shown that

$$\langle\psi| c^+_{l_1\sigma} c^+_{l_2\sigma'} c_{l_3\sigma'} c_{l_4\sigma}|\psi\rangle$$

$$= \langle\psi|c^+_{l_1\sigma}c_{l_4\sigma}|\psi\rangle\langle\psi|c^+_{l_2\sigma'}c_{l_3\sigma'}|\psi\rangle$$

$$- \langle\psi|c^+_{l_1\sigma}c_{l_3\sigma}|\psi\rangle\langle\psi|c^+_{l_2\sigma}c_{l_4\sigma}|\psi\rangle\delta_{\sigma\sigma'}$$

which is called Wick's theorem — replace averages of products of operators by products of averages of pairs of operators. Holds only for noninteracting / slater determinants.

Now we choose the a_k^p values. suppose we take

$$|\psi_{trial}\rangle = \prod_{\text{set } k,\sigma} c^\dagger_{k\sigma}|0\rangle \qquad \text{i.e. } a_k^p \sim \delta_{pk}$$

$$\hat{H} = \sum_{k\sigma} \frac{\hbar^2 k^2}{2m} c^\dagger_{k\sigma} c_{k\sigma} + \frac{1}{2} \sum_{\substack{kk'\sigma\sigma' \\ q\neq 0}} \frac{4\pi e^2}{Vq^2} c^\dagger_{k+q\sigma} c^\dagger_{k'-q\sigma'} c_{k'\sigma'} c_{k\sigma}$$

so

$$\langle\psi| c^\dagger_{k+q\sigma} c^\dagger_{k'-q\sigma'} c_{k'\sigma'} c_{k\sigma}|\psi\rangle$$
$$= \langle\psi|c^\dagger_{k+q\sigma} c_{k\sigma}|\psi\rangle\langle\psi|c^\dagger_{k'-q\sigma'} c_{k'\sigma'}|\psi\rangle - \langle\psi|c^\dagger_{k+q\sigma} c_{k'\sigma'}|\psi\rangle\langle\psi|c^\dagger_{k'-q\sigma'} c_{k\sigma}|\psi\rangle$$

The first term vanishes unless $q=0$. But when $q=0$, $V(q)=0$

so we neglect those terms for jellium.

The second requires $k'=k+q$ $\sigma'=\sigma$ or $q=k'-k$

so we find

$$\langle\psi|H|\psi\rangle = \sum_{k\sigma} \frac{\hbar^2 k^2}{2m}\langle\psi|c^\dagger_{k\sigma} c_{k\sigma}|\psi\rangle - \frac{1}{2}\sum_{k\neq k'\sigma} \frac{4\pi e^2}{|k'-k|^2 V}\langle\psi|c^\dagger_{k'\sigma} c_{k'\sigma}|\psi\rangle$$
$$* \langle\psi|c^\dagger_{k\sigma} c_{k\sigma}|\psi\rangle$$

Since $\frac{\hbar^2 k^2}{2m}$ is an increasing function of k, we minimize

the kinetic energy by filling the lowest k levels first.

This is called the "bath tub principle"

We use the state with minimum kinetic energy to estimate the ground state energy of jellium

If we have N particles $\Rightarrow \frac{N}{V} =$ density

Then we get

$$\sum_{\substack{k<k_F \\ \sigma}} 1 = N \Rightarrow \underset{\substack{\uparrow \\ \text{spin}}}{2} \underset{\substack{\uparrow \\ \text{dos in k space}}}{\frac{V}{(2\pi)^3}} \int_0^{k_F} \underset{\substack{\uparrow \\ \text{angular integral}}}{4\pi} k^2 dk = N$$

$$\text{so } n = \frac{N}{V} = \frac{2}{2\pi^2}\int_0^{k_F} k^2 dk = \frac{k_F^3}{3\pi^2} \Rightarrow \boxed{k_F = (3\pi^2 n)^{1/3}}$$

The kinetic energy becomes

$$2\sum_{k<k_F} \frac{\hbar^2 k^2}{2m} = \frac{2V}{(2\pi)^3}\cdot 4\pi \cdot \frac{\hbar^2}{2m}\int_0^{k_F} k^4 dk$$

$$= \frac{\hbar^2}{2m}\frac{k_F^5}{5\pi^2} V = V \cdot \frac{(3\pi^2 n)^{5/3}}{5\pi^2}\frac{\hbar^2}{2m}$$

the potential energy term becomes

$$\underset{\substack{\uparrow \\ \text{double counting}}}{-\frac{1}{2}} \cdot \underset{\substack{\uparrow \\ \text{spin}}}{2} \frac{V^2}{(2\pi)^6}\int_{k<k_F} d^3k \int_{k'<k_F} d^3k' \frac{4\pi e^2}{V|k'-k|^2}$$

Do k' integration first. choose z axis along $\vec{k}$ direction.

$$|\vec{k}'-\vec{k}|^2 = k'^2 - \vec{k}'\cdot\vec{k} + k^2 = k'^2 - 2k'k\cos\theta' + k^2 \quad \theta' = \text{angle bet } \vec{k} \text{ and } \vec{k}'$$

$$\int_0^{k_F} k'^2 dk' \int_{-1}^{1} d\cos\theta' \int_0^{2\pi} d\phi' \frac{1}{k^2 - 2kk'\cos\theta' + k'^2}$$

$$= 2\pi\int_0^{k_F} k'^2 dk' \left(-\frac{1}{2kk'}\right) \ln\left(k^2 - 2kk'\cos\theta + k'^2\right)\Big|_{-1}^{1}$$

$$= -\frac{\pi}{k}\int_0^{k_F} k' dk' \ln\left(\frac{k^2 - 2kk' + k'^2}{k^2 + 2kk' + k'^2}\right) = \frac{2\pi}{k}\int_0^{k_F} dk' k' \ln\left|\frac{k+k'}{k-k'}\right|$$

$$\underset{\text{integral tables}}{=} 2\pi\left\{\frac{k_F^2 - k^2}{2k}\ln\left|\frac{k_F+k}{k_F-k}\right| + k_F\right\}$$

Now do the k integral

$$= \frac{V^2}{(2\pi)^6} \frac{4\pi e^2}{V} \cdot 2\pi \cdot 4\pi \int_0^{k_F} dk \left[\frac{1}{2}(k k_F^2 - k^3) \ln\left|\frac{k_F+k}{k_F-k}\right| + k^2 k_F \right]$$

$$\underset{\text{mathematica}}{=} \frac{V e^2}{2\pi^3} \frac{k_F^4}{2}$$

so $$\frac{E_{total}}{V} = \left[\frac{\hbar^2}{2m} \frac{k_F^5}{5\pi^2} - \frac{e^2}{4\pi^3} k_F^4 \right]$$

recall $n = k_F^3/3\pi^2$ express energy in Rydbergs $= \frac{e^2}{2a_0} = \frac{e^4 m}{2\hbar^2}$

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

$$\frac{E}{N} = \frac{E}{V k_F^3/3\pi^2} = \left[\frac{3\hbar^2 k_F^2}{10m} - \frac{3e^2 k_F}{4\pi} \right]$$

$$= \frac{e^2}{2a_0} \left[\frac{3\hbar^2 k_F^2 a_0}{5me^2} - \frac{3 k_F a_0}{2\pi} \right]$$

define $r_s = r/a_0$ r = radius of sphere with one electron

$$\frac{4}{3}\pi r^3 = \frac{1}{n} \qquad r = \left(\frac{3}{4\pi n}\right)^{1/3}$$

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \frac{1}{a_0} = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{k_F a_0}$$

$$\frac{E}{N} = \frac{e^2}{2a_0} \left[\frac{3}{5}(k_F a_0)^2 - \frac{3}{2\pi}(k_F a_0) \right] = \left(\frac{3}{5}\left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2} - \frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \right) Ry$$

$$\boxed{\frac{E}{N} = \left(\frac{2.210}{r_s^2} - \frac{0.916}{r_s} \right) Ry}$$

going to higher orders gives

$$\frac{E}{N} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + 0.0622 \ln r_s - 0.142 + \cdots$$

$r_s \sim 1\text{-}10$ for most metals.