Phys 506 lecture 37: Jellium model

1 Introduction to the 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

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

$$V(q) = \begin{cases} \frac{4\pi e^2}{2Vq^2} & q \neq 0 \\ 0 & q = 0. \end{cases}$$

The potential vanishes when $q = 0$ due to the cancellation by the uniform positive background.

2 Variational principle

Study first with the variational principle. Consider

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

We always have $E_{\text{trial}} \geq E_{gs}$.

Proof: Start with $|\psi\rangle = \sum_n c_n |n\rangle$ where $\hat{H}|n\rangle = E_n |n\rangle$

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

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

$$\alpha^\dagger_{p\sigma} = \sum_l a^p_l c^\dagger_{l\sigma}$$

and let

$$|\psi\rangle = \prod_{p,\sigma} \alpha^\dagger_{p\sigma} |0\rangle$$

Note that

$$\{\alpha^\dagger_{p\sigma}, \alpha_{p'\sigma'}\} = \sum_{ll'} a^p_l a^{p'*}_{l'} \{c^\dagger_{l\sigma}, c_{l'\sigma'}\} = \sum_l a^p_l a^{p'*}_l \delta_{\sigma\sigma'}$$

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

$$\sum_l a_l^p a_l^{p'*} = \delta_{pp'}$$

so $\{\alpha^\dagger_{p\sigma}, \alpha_{p'\sigma'}\} = \delta_{pp'}$. Next, define a set of vectors b_l^p such that

$$\sum_p b_l^p a_{l'}^p = \delta_{ll'}$$

Then,

$$\sum_p b_l^p \alpha^\dagger_{p\sigma} = \sum_p \sum_{l'} b_l^p a_{l'}^p c^\dagger_{l'\sigma} = c^\dagger_{l\sigma}.$$

So, we can now compute averages.

$$\begin{aligned}\left\langle \psi \middle| c^\dagger_{l\sigma} c_{l\sigma} \middle| \psi \right\rangle &= \sum_{pp'} b_l^p b_l^{p'*} \left\langle \psi \middle| \alpha^\dagger_{p\sigma} \alpha_{p'\sigma} \middle| \psi \right\rangle \\ &= \sum_{pp'} b_l^p b_l^{p'*} \delta_{pp'} \delta(p, \sigma \in \psi) \\ &= \sum_p |b_l^p|^2 \delta(p, \sigma \in \psi)\end{aligned}$$

and

$$\begin{aligned}\left\langle \psi \middle| c^\dagger_{l_1\sigma} c^\dagger_{l_2\sigma'} c_{l_3\sigma'} c_{l_4\sigma} \middle| \psi \right\rangle &= \sum_{p_1p_2p_3p_4} b_{l_1}^{p_1} b_{l_2}^{p_2} b_{l_3}^{p_3*} b_{l_4}^{p_4*} \left\langle \psi \middle| \alpha^\dagger_{p_1\sigma} \alpha^\dagger_{p_2\sigma'} \alpha_{p_3\sigma'} \alpha_{p_4\sigma} \middle| \psi \right\rangle \\ &= \sum_{p_1p_2p_3p_4} b_{l_1}^{p_1} b_{l_2}^{p_2} b_{l_3}^{p_3*} b_{l_4}^{p_4*} \left[\delta_{p_1p_4} \delta_{p_2p_3} \left\langle \psi \middle| \alpha^\dagger_{p_1\sigma} \alpha^\dagger_{p_2\sigma'} \alpha_{p_2\sigma'} \alpha_{p_1\sigma} \middle| \psi \right\rangle \right. \\ &\quad \left. + \delta_{p_1p_3} \delta_{p_2p_4} \delta_{\sigma\sigma} \left\langle \psi \middle| \alpha^\dagger_{p_1\sigma} \alpha^\dagger_{p_2\sigma} \alpha_{p_2\sigma} \alpha_{p_1\sigma} \middle| \psi \right\rangle \right]\end{aligned}$$

Note when $p_1 = p_2$ and $\sigma = \sigma'$ we get zero in both cases since $\alpha^2_{p\sigma} = 0$. So, we can assume $p_1 \neq p_2$.

$$\begin{aligned}= \sum_{p_1p_2p_3p_4} b_{l_1}^{p_1} b_{l_2}^{p_2} b_{l_3}^{p_3*} b_{l_4}^{p_4*} &\left[\delta_{p_1p_4} \delta_{p_2p_3} \left\langle \psi \middle| \alpha^\dagger_{p_1\sigma} \alpha_{p_1\sigma} \alpha^\dagger_{p_2\sigma'} \alpha_{p_2\sigma'} \middle| \psi \right\rangle \right. \\ &\left. - \delta_{p_1p_3} \delta_{p_2p_4} \delta_{\sigma\sigma} \left\langle \psi \middle| \alpha^\dagger_{p_1\sigma} \alpha_{p_1\sigma} \alpha^\dagger_{p_2\sigma} \alpha_{p_2\sigma} \middle| \psi \right\rangle \right]\end{aligned}$$

Since in this expression, the term with $p_1 = p_2 = p_3 = p_4$ and $\sigma = \sigma'$ 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 $p_1 = p_2$.

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

Note that we have just shown

$$\left\langle \psi \middle| c^\dagger_{l_1\sigma} c^\dagger_{l_2\sigma'} c_{l_3\sigma'} c_{l_4\sigma} \middle| \psi \right\rangle = \left\langle \psi \middle| c^\dagger_{l_1\sigma} c_{l_4\sigma} \middle| \psi \right\rangle \left\langle \psi \middle| c^\dagger_{l_2\sigma'} c_{l_3\sigma'} \middle| \psi \right\rangle - \left\langle \psi \middle| c^\dagger_{l_1\sigma} c_{l_3\sigma'} \middle| \psi \right\rangle \left\langle \psi \middle| c^\dagger_{l_2\sigma'} c_{l_4\sigma} \middle| \psi \right\rangle$$

which is called *Wick's* theorem – replace averages of products of operators by products of averages of pairs of operators. Holds only for noninteracting particles/Slater determinants.

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

$$|\psi_{trial}\rangle = \prod_{k,\sigma} c^\dagger_{k\sigma} |0\rangle$$

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

so

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

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

$$\langle \psi | H | \psi \rangle \sum_{k\sigma} \frac{\hbar^2 k^2}{2m} \left\langle \psi \middle| c^\dagger_{k\sigma} c_{k\sigma} \middle| \psi \right\rangle - \sum_{k\neq k',\sigma} \frac{4\pi e^2}{|k'-k|^2 V} \left\langle \psi \middle| c^\dagger_{k'\sigma} c_{k'\sigma} \middle| \psi \right\rangle \left\langle \psi \middle| c^\dagger_{k\sigma} c_{k\sigma} \middle| \psi \right\rangle$$

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 "bathtub principle". We use the state with minimum kinetic energy to estimate the ground state energy of jellium.

3 Estimating the ground state

If we have N particles the density is N/V. Then we get

$$\sum_{k<k_F,\sigma} 1 = N \implies 2\frac{V}{(2\pi)^3} \int_0^{k_F} 4\pi k^2 \, dk = N$$

So,

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

The kinetic energy becomes

$$2 \sum_{k<k_F} \frac{\hbar^2 k^2}{2m} = \frac{2V}{(2\pi)^3} 4\pi \frac{\hbar^2}{2m} \int_0^{k_F} k^4 \, dk = \frac{\hbar^2}{2m} \frac{k_F^5}{5\pi^2} V = V \frac{(3\pi^2 n)^{5/3}}{5\pi^2} \frac{\hbar^2}{2m}$$

The potential energy term becomes

$$-\frac{1}{2} 2 \frac{V^2}{(2\pi)^6} \int_{k<k_F} d^3k \int_{k'<k_F} \frac{4\pi e^2}{V|k'-k|^2}$$

Do the k' integration first. Choose z-axis along $\mathbf{k}$ direction.

$$|\mathbf{k}' - \mathbf{k}|^2 = k'^2 - \mathbf{k}' \cdot \mathbf{k} + k^2 = k'^2 - 2k'k\cos\theta' + k^2$$

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

Now do the k integral.

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

So

$$\frac{E_{trial}}{V} = \frac{\hbar^2}{2m}\frac{k_F^5}{5} - \frac{e^2}{4\pi^3}k_F^4$$

Recall $n = \frac{k_F^3}{3\pi^2}$. Express energy in Rydbergs$= e^2/2a_0$.

$$E_N = \frac{E}{Vk_F^3/3\pi^2} = \frac{e^2}{2a_0}\left(\frac{3\hbar^2 k_F^2 a_0}{5me^2} - \frac{3k_F a_0}{2\pi}\right).$$

Define $r_s = r/a_0$ where r is the radius of a sphere with a single electron.

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

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

$$\frac{E}{N} = \frac{e^2}{2a_0}\left(\frac{3}{5}(k_F a_0)^2 - \frac{3}{2\pi}(k_F a_0)\right) = \left(\frac{2.210}{r_S^2} - \frac{0.916}{r_S}\right)\ \text{Ry}.$$