Notes on Thomas-Fermi model and Lindhard function

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Thomas - Fermi model

We consider to embed a nucleous with charge of $-Z$ at the origin in the jellium model with charge density of ρ_0, where the sign of electron density is taken to be positive. Based on the Thomas-Fermi model which applies the local density approximation (LDA) for the kinetic energy, the total energy is expressed as

$$E_{TF} = \int dr^3 \rho(\mathbf{r})\, t(\rho) - Z \int dr^3 \frac{\rho(\mathbf{r})}{r} + \frac{1}{2} \iint dr^3 dr'^3 \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$- \iint dr^3 dr'^3 \frac{\rho_0\, \rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2} \iint dr^3 dr'^3 \frac{\rho_0\, \rho_0}{|\mathbf{r}-\mathbf{r}'|} \quad \cdots\cdots (1)$$

$$t(\rho) = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \rho^{\frac{2}{3}} \quad \cdots\cdots (2)$$

Subject to a charge conservation condition:

$$N = \int dr^3 \rho(\mathbf{r}) \quad \cdots\cdots (3)$$

We variationally optimize E_{TF} with Lagrange's multiplier method:

$$F = E_{TF} - \mu_{TF} \left(\int dr^3 \rho(\mathbf{r}) - N \right) \quad \cdots\cdots (4)$$

$$\frac{\delta F}{\delta \rho} = 0 \rightarrow \frac{1}{2} (3\pi^2)^{\frac{2}{3}} \rho^{\frac{2}{3}}(\mathbf{r}) + V(\mathbf{r}) = \mu_{TF} \quad \cdots\cdots (5)$$
$$(T(\mathbf{r}) + V(\mathbf{r}) = \mu_{TF})$$

where

$$V(\mathbf{r}) = -\frac{Z}{r} + \int dr'^3 \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \cdots\cdots (6)$$

$$\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0 \quad \cdots\cdots (7)$$

Noting that the Fermi wave number k_F is given by

$$k_F = (3\pi^2 \rho_0)^{\frac{1}{3}} \quad \cdots\cdots (8)$$

and considering that the total system is infinitely large, one can equate μ_{TF} to the kinetic energy with k_{TF} as

$$\mu_{TF} = \frac{1}{2} k_F^2 = \frac{1}{2} (3\pi^2 \rho_0)^{\frac{2}{3}} \quad \cdots\cdots (9)$$

From Eq. (5), we have

$$\begin{aligned} T(\mathbf{r}) &= \frac{1}{2} (3\pi^2)^{\frac{2}{3}} \rho^{\frac{2}{3}}(\mathbf{r}) \\ &= \frac{1}{2} (3\pi^2)^{\frac{2}{3}} (\rho_0 + \rho(\mathbf{r}) - \rho_0)^{\frac{2}{3}} \\ &= \frac{1}{2} (3\pi^2)^{\frac{2}{3}} \rho_0^{\frac{2}{3}} \left(1 + \frac{\delta\rho(\mathbf{r})}{\rho_0}\right)^{\frac{2}{3}} = \mu_{TF} \left(1 + \frac{\delta\rho(\mathbf{r})}{\rho_0}\right)^{\frac{2}{3}} \\ &= \mu_{TF} \left(1 + \frac{2}{3}\left(\frac{\delta\rho(\mathbf{r})}{\rho_0}\right) - \frac{1}{9}\left(\frac{\delta\rho(\mathbf{r})}{\rho_0}\right)^2 + \cdots\cdots\right) \quad \cdots (10) \end{aligned}$$

Inserting Eq. (10) into Eq. (5) and taking the first order term, we obtain the following Eq.: linear response

$$\mu_{TF} + \frac{2}{3}\mu_{TF}\left(\frac{\delta\rho(\mathbf{r})}{\rho_0}\right) + V(\mathbf{r}) = \mu_{TF}$$

$$\longrightarrow \quad \delta\rho(\mathbf{r}) = -\frac{3\rho_0}{2\mu_{TF}} V(\mathbf{r}) \quad \cdots\cdots (11)$$

Since the total charge is given by

$$\rho_T(\mathbf{r}) = -Z\,\delta(\mathbf{r}) + \rho_0 \underbrace{-\rho_0}_{\text{background charge}} + \delta\rho(\mathbf{r}) \quad \cdots\cdots (12)$$

we can evaluate the potential of $V(\mathbf{r})$ by the Poisson Eq.:

$$\nabla^2 V(\mathbf{r}) = -4\pi \rho_T(\mathbf{r}) \quad \cdots\cdots (13)$$

Putting Eqs. (11) and (12) into Eq. (13), we have

$$\nabla^2 V(\mathbf{r}) = 4\pi Z \delta(\mathbf{r}) + k_{TF}^2 V(\mathbf{r}) \quad \cdots\cdots (14)$$

$$k_{TF} = \left(\frac{6\pi \rho_0}{\mu_{TF}}\right)^{\frac{1}{2}} = \left(\frac{192}{\pi}\rho_0\right)^{\frac{1}{6}} \quad \cdots\cdots (15)$$

Remembering that $V(\mathbf{r})$ and $\delta(\mathbf{r})$ can be Fourier-transformed as

$$V(\mathbf{r}) = \frac{1}{(2\pi)^3}\int dq^3\, V(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (16)$$

$$V(\mathbf{q}) = \int dr^3\, V(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (17)$$

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3}\int dq^3\, e^{i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (18)$$

and inserting Eqs. (16) and (18) into Eq. (14), we have

$$\frac{1}{(2\pi)^3}\int dq^3 V(\mathbf{q})(-q^2)\, e^{i\mathbf{q}\cdot\mathbf{r}} = \frac{4\pi Z}{(2\pi)^3}\int dq^3\, e^{i\mathbf{q}\cdot\mathbf{r}} + \frac{k_{TF}^2}{(2\pi)^3}\int dq^3\, V(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$\longrightarrow \quad -q^2 V(\mathbf{q}) = 4\pi Z + k_{TF}^2 V(\mathbf{q})$$

$$V(\mathbf{q}) = \frac{-4\pi Z}{q^2 + k_{TF}^2} \quad \cdots\cdots (19)$$

With Eq. (19), Eq. (16) is now expressed as

$$V(\mathbf{r}) = \frac{-4\pi Z}{(2\pi)^3}\int dq^3 \frac{1}{q^2 + k_{TF}^2}\, e^{i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (20)$$

By considering

$$dq^3 = d\theta \sin\theta\, d\phi\, q^2 dq$$

we evaluate the integral of Eq. (20)

$$V(\mathbf{r}) = \frac{-4\pi Z}{(2\pi)^3}\int_0^{\pi} d\theta \sin\theta \int_{-\pi}^{\pi} d\phi \int_0^{\infty} dq\, q^2 \frac{e^{iqr\cos\theta}}{q^2 + k_{TF}^2} \quad \cdots (21)$$

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$$V(\mathbb{r}) = \frac{-4\pi Z}{(2\pi)^3} \int_0^{\pi} d\theta \sin\theta \int_{-\pi}^{\pi} d\phi \int_0^{\infty} dq \cdot q^2 \frac{e^{iqr\cos\theta}}{q^2 + K_{TF}^2} \quad \cdots (21)$$

$$= \frac{-4\pi Z}{(2\pi)^3} \times (2\pi) \int_0^{\infty} dq \frac{q^2}{q^2 + K_{TF}^2} \int_{-1}^{1} dx \, e^{iqrx} \quad \leftarrow x = \cos\theta$$

$$= \frac{-Z}{\pi} \int_0^{\infty} dq \frac{q^2}{q^2 + K_{TF}^2} \left[\frac{e^{iqrx}}{iqr} \right]_{-1}^{1}$$

$$= \frac{-Z}{\pi} \frac{2}{r} \int_0^{\infty} dq \frac{q \sin qr}{q^2 + K_{TF}^2}$$

$$= -\frac{Z}{\pi} \cdot \frac{2}{r} \times \frac{\pi}{2} e^{-K_{TF} r} = -\frac{Z}{r} e^{-K_{TF} r}$$

Thus,

$$\boxed{V(\mathbb{r}) = -\frac{Z}{r} e^{-K_{TF} r}} \quad \cdots\cdots (22)$$

The Thomas - Fermi screening length λ_{TF} is given by

$$\lambda_{TF} = \frac{1}{K_{TF}} = \left(\frac{6\pi \rho_0}{\mu_{TF}} \right)^{-\frac{1}{2}} \quad \cdots\cdots (23)$$

Remembering $\mu_{TF} = \frac{1}{2} k_{TF}^2$, $k_F = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} (a_0 r_s)^{-1}$, $\rho_0^{-1} = \frac{4}{3}\pi (a_0 r_s)^3$,

one can calculate as

$$\lambda_{TF} = (6\pi)^{-\frac{1}{2}} \rho_0^{-\frac{1}{2}} \mu_{TF}^{\frac{1}{2}}$$

$$= (6\pi)^{-\frac{1}{2}} \left(\frac{4}{3}\pi\right)^{\frac{1}{2}} \times (a_0 r_s)^{\frac{3}{2}} \times \left(\frac{1}{2}\right)^{\frac{1}{2}} \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} (a_0 r_s)^{-1}$$

$$= (a_0 r_s)^{\frac{1}{2}} \left[\frac{1}{(6\pi)^3} \times \left(\frac{4\pi}{3}\right)^3 \times \frac{1}{8} \times \left(\frac{9\pi}{4}\right)^2 \right]^{\frac{1}{6}}$$

$$= (a_0 r_s)^{\frac{1}{2}} \left[\left(\frac{\pi}{12}\right)^2 \right]^{\frac{1}{6}} = (a_0 r_s)^{\frac{1}{2}} \left(\frac{\pi}{12}\right)^{\frac{1}{3}} \quad \cdots (24)$$

For Na with $r_s \simeq 4$ a.u., we have

$$\lambda_{TF} \text{ for Na} = \left(\frac{\pi}{12}\right)^{\frac{1}{3}} \times 4^{\frac{1}{2}} \simeq 1.3 \text{ a.u.} \quad \cdots (25)$$

which implies that the screening length is quite short.

By inserting Eq. (22) into Eq. (11), we have

$$\delta\rho(\mathbf{r}) = -\frac{3\rho_0}{2\mu_{TF}} V(\mathbf{r})$$

Eq. (15)

$$= -\frac{3}{2}\frac{1}{6\pi}\left[\left(\frac{6\pi\rho_0}{\mu_{TF}}\right)^{\frac{1}{2}}\right]^2 \times \left(-\frac{Z}{r}e^{-k_{TF}r}\right)$$

$$= \frac{Z}{4\pi}(k_{TF})^2 \frac{1}{r} e^{-k_{TF}r} \quad \cdots\cdots (26)$$

Integrating Eq. (26) over all the space, we see

$$\int dr^3 \delta\rho(\mathbf{r}) = \frac{Z}{4\pi}(k_{TF})^2 \times 4\pi \int_0^\infty dr \cdot r^2 \frac{1}{r} e^{-k_{TF}r}$$

$$= \frac{Z}{4\pi}(k_{TF})^2 \times 4\pi \times \frac{1}{(k_{TF})^2} = Z \quad \cdots (27)$$

From Eq. (27), it is confirmed that the screening is perfect and short range due to Eq. (26).

The static dielectric function $\varepsilon(q)$ is defined by

$$V(\mathbf{q}) = \frac{V_{ext}(\mathbf{q})}{\varepsilon(\mathbf{q})} \quad \cdots\cdots (28)$$

where

$$V_{ext}(\mathbf{q}) = \int dr^3 \left(\frac{-Z}{r}\right) e^{-\mathbf{q}\cdot\mathbf{r}} = \frac{-4\pi Z}{q^2} \quad \cdots\cdots (29)$$

This is also obtained from Eq. (19) with $k_{TF} = 0$.

By putting Eqs. (19) and (29) into Eq. (28), we have

$$\varepsilon_{TF}(q) = \frac{V_{ext}(q)}{V(q)} = \left(\frac{-4\pi Z}{q^2}\right) \times \left(\frac{-4\pi Z}{q^2 + k_{TF}^2}\right)^{-1}$$

$$= \frac{q^2 + k_{TF}^2}{q^2} = 1 + \frac{k_{TF}^2}{q^2}$$

Thus,

$$\boxed{\varepsilon_{TF}(q) = 1 + \frac{k_{TF}^2}{q^2}} \quad \cdots\cdots (30)$$

In the limit $q \to 0$, ε_{TF} is found to be divergent.

Later, we consider the Lindhard function.

So, we try to find general formula for $\delta\rho$.

Using Eq. (28), one can obtain $V(\mathbf{r})$ as

$$\boxed{V(\mathbf{r}) = \frac{1}{(2\pi)^3}\int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)} e^{i q\cdot\mathbf{r}}} \quad \cdots\cdots (31)$$

In case of $-\frac{Z}{r}$, $V_{ext}(q) = \frac{-4\pi Z}{q^2}$ ... (29),

The induced charge $\delta\rho(\mathbf{r})$ by a purturbed potential V_{ext} is found through the Poisson's eq. as

$$\nabla^2(V - V_{ext}) = -4\pi\,\delta\rho(\mathbf{r}) \quad \cdots\cdots (32)$$

From Eq. (31), Eq. (32) reads

$$\delta\rho(\mathbf{r}) = \frac{1}{(-4\pi)}\frac{1}{(2\pi)^3}\int dq^3 (-q^2)\left(\frac{1}{\varepsilon(q)} - 1\right) V_{ext}(q)\, e^{i q\cdot\mathbf{r}} \quad \cdots (33)$$

Inserting Eq. (29) into Eq. (33) we have

$$\boxed{\delta\rho(\mathbf{r}) = \frac{Z}{(2\pi)^3}\int dq^3\left(1 - \frac{1}{\varepsilon(q)}\right) e^{i q\cdot\mathbf{r}}} \quad \cdots\cdots (34)$$

Integrating the induced electron density over space,

$$\delta \rho(\mathbf{r}) = \frac{Z}{(2\pi)^3} \int dq^3 \left(1 - \frac{1}{\varepsilon(\mathbf{q})}\right) e^{i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (34)$$

one can obtain the total induced charge:

$$Q = \int dr^3 \, \delta \rho(\mathbf{r})$$

$$= \frac{Z}{(2\pi)^3} \int dq^3 \left(1 - \frac{1}{\varepsilon(\mathbf{q})}\right) \underbrace{\int dr^3 e^{i\mathbf{q}\cdot\mathbf{r}}}_{= (2\pi)^3 \delta(\mathbf{q})}$$

$$Q = Z\left(1 - \frac{1}{\varepsilon(0)}\right) \quad \cdots\cdots (35)$$

Thus, for $\varepsilon(0) \to \infty$ (metallic cases),

The total induced charge Q is found as

$$Q = Z \quad \cdots\cdots (36)$$

In summary,

$$\boxed{\begin{aligned} V(\mathbf{r}) &= \frac{1}{(2\pi)^3} \int dq^3 \frac{V_{ext}(\mathbf{q})}{\varepsilon(\mathbf{q})} e^{i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (31) \\ \delta \rho(\mathbf{r}) &= \frac{Z}{(2\pi)^3} \int dq^3 \left(1 - \frac{1}{\varepsilon(\mathbf{q})}\right) e^{i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (34) \\ Q &= Z\left(1 - \frac{1}{\varepsilon(0)}\right) \quad \cdots\cdots (35) \end{aligned}}$$

Static linear response theory

We consider a response of electrons by a perturbation theory. Within a linear response. Then, we start from

$$\delta\rho(q) = \chi(q)\, V(q) \quad \cdots\cdots (37)$$

where $\chi(q)$ is a linear response function.

As we already discussed in Eq. (28), we have

$$V(q) = V_{ext}(q) + \delta V(q) = \frac{V_{ext}(q)}{\varepsilon(q)} \quad \cdots\cdots (28)$$

It should be noted that we neglected the higher order terms in Eqs. (37) and (28), which is called linear response theory. The induced charge $\delta\rho$ will change the potential with respect to Hartree term $\delta V_H(q)$ and exchange-correlation term $\delta V_{xc}(q)$

$$\delta V(q) = \delta V_H(q) + \delta V_{xc}(q) \quad \cdots\cdots (38)$$

At this moment, we neglect δV_{xc}, which corresponds to ramdom phase approximation (RPA).

In this approximation, $\delta V = \delta V_H$. Thus, from Poisson eq. we have

$$\nabla^2 \delta V(\mathbf{r}) = -4\pi\, \delta\rho(\mathbf{r}) \longrightarrow \boxed{\delta V(q) = \frac{4\pi}{q^2}\,\delta\rho(q)} \quad \cdots\cdots (39)$$

Inserting Eqs. (37) and (39) into Eq. (28), we have

$$V(q) = V_{ext}(q) + \delta V(q)$$
$$= V_{ext}(q) + \frac{4\pi}{q^2}\delta\rho(q)$$
$$= V_{ext}(q) + \frac{4\pi}{q^2}\chi(q)V(q)$$

$\longrightarrow$

$$\left(1-\frac{4\pi}{q^2}\chi(q)\right)V(q) = V_{ext}(q)$$

$$V(q) = V_{ext}(q) \times \left(1-\frac{4\pi}{q^2}\chi(q)\right)^{-1} \quad \cdots\cdots (40)$$

Comparing Eq. (40) with Eq. (28), we obtain

$$\boxed{\varepsilon(q) = 1-\frac{4\pi}{q^2}\chi(q)} \quad \cdots\cdots (41)$$

Remembering that in the TF model, ε is given by,

$$\varepsilon_{TF}(q) = 1+\frac{k_{TF}^2}{q^2} \quad \cdots\cdots (30)$$

we see

$$\chi_{TF}(q) = -\frac{k_{TF}^2}{4\pi} \quad \cdots\cdots (42)$$

which is independent of q.

Lindhard response function

We evaluate the linear response function $\chi(q)$ under a weak perturbation potential $V(r)$

$$V(r) = V(q)\, e^{i q \cdot r} + \text{c.c.} \qquad \cdots\cdots (43)$$

To the first order, the perturbed one-particle wave function is given by

$$\varphi_k^{(1)}(r) = \varphi_k(r) + \sum_{k' \neq k} \frac{H'_{k'k}}{E_k - E_{k'}}\, \varphi_{k'}(r) \qquad \cdots\cdots (44)$$

$$\boxed{\begin{aligned} \varphi_k &= \frac{1}{\sqrt{V}}\, e^{i k \cdot r} \\ E_k &= \frac{1}{2}|k|^2 \end{aligned}}$$

where

$$\begin{aligned} H'_{k'k} &= \int dr^3\, \varphi_{k'}^{*}\, V(r)\, \varphi_k(r) \\ &= \frac{1}{V}\Big[\int dr^3\, V(q)\, e^{i(k+q-k')\cdot r} \\ &\quad + \int dr^3\, V^{*}(q)\, e^{i(k-q-k')\cdot r}\Big] \end{aligned}$$

$$\boxed{H'_{k'k} = V(q)\,\delta_{k',k+q} + V^{*}(q)\,\delta_{k',k-q}} \qquad \cdots\cdots (45)$$

Inserting Eq. (45) into Eq. (44) yields

$$\varphi_k^{(1)}(r) = \frac{1}{\sqrt{V}}\left[e^{i k\cdot r} + \frac{2V(q)}{k^2 - (k+q)^2}\, e^{i(k+q)\cdot r} + \frac{2V^{*}(q)}{k^2 - (k-q)^2}\, e^{i(k-q)\cdot r}\right] \qquad \cdots\cdots (46)$$

Thus, the change of electron density is given by

$$\delta\rho(r) = 2\sum_k \left[|\varphi_k^{(1)}(r)|^2 - |\varphi_k(r)|^2\right] f_k \qquad \cdots\cdots (47)$$

where the prefactor is due to spin degeneracy, and f_k is the occupation number for the state with k.

$$\varphi_{k}^{(1)}(r) = \frac{1}{\sqrt{V}}\left[e^{ik\cdot r} + \underbrace{\frac{2V(q)}{k^2-(k+q)^2}}_{\alpha} e^{i(k+q)\cdot r} + \underbrace{\frac{2V^*(q)}{k^2-(k-q)^2}}_{\beta} e^{i(k-q)\cdot r} \right] \quad \cdots\ (46)$$

To the first order, we see

$$|\varphi_{k}^{(1)}(r)|^2 = \frac{1}{V}\left(e^{-ik\cdot r} + \alpha V^*(q) e^{-i(k+q)\cdot r} + \beta V(q) e^{-i(k-q)\cdot r} \right)$$

$$\times \left(e^{ik\cdot r} + \alpha V(q) e^{i(k+q)\cdot r} + \beta V^*(q) e^{i(k-q)\cdot r} \right)$$

$$\simeq \frac{1}{V}\left(1 + \alpha V(q) e^{iq\cdot r} + \beta V^*(q) e^{-iq\cdot r} + \alpha V^*(q) e^{-iq\cdot r} + \beta V(q) e^{iq\cdot r} \right)$$

$$= \frac{1}{V}\left(1 + (\alpha+\beta) V(q) e^{iq\cdot r} + (\alpha+\beta) V^*(q) e^{-iq\cdot r} \right) \quad \cdots\ (47B)$$

Inserting Eq. (47B) into Eq. (47), we obtain

$$\delta\rho(r) = \left(\frac{4}{V}\sum_{k}\left[\frac{f_k}{k^2-(k+q)^2} + \frac{f_k}{k^2-(k-q)^2} \right] \right) \times \left(V(q) e^{iq\cdot r} + V^*(q) e^{-iq\cdot r} \right) \quad \cdots\ (48)$$

Noting

$$\sum_{k} \frac{f_k}{k^2-(k-q)^2} \overset{k' = k-q}{=} \sum_{k'} \frac{f_{k'+q}}{(k'+q)^2 - k'^2} = \sum_{k} \frac{-f_{k+q}}{k^2-(k+q)^2}$$

we can rewrite Eq. (48) as

$$\delta\rho(r) = \left(\frac{4}{V}\sum_{k} \frac{f_k - f_{k+q}}{k^2-(k+q)^2} \right) \times \left(V(q) e^{iq\cdot r} + V^*(q) e^{-iq\cdot r} \right) \quad \cdots\ (49)$$

Comparing Eq. (49) with Eq. (37), we have

$$\boxed{\chi(q) = \frac{4}{V}\sum_{k} \frac{f_k - f_{k+q}}{k^2-(k+q)^2}} \quad \cdots\cdots\ (50)$$

This is called the Lindhard response function.

The summations in Eq. (48) can be transformed to integrals, and evaluated analytically as follows:

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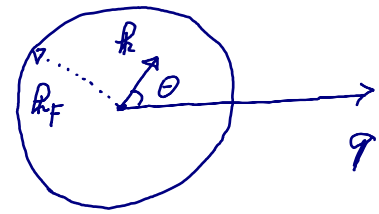
$$\sum_{k} \frac{f_k}{k^2-(k+q)^2} = \frac{V}{(2\pi)^3}\int dk^3 \, \frac{f_k}{k^2-(k+q)\cdot(k+q)}$$

$$= \frac{V}{(2\pi)^3}\int dk^3 \, \frac{f_k}{k^2-k^2-2kq\cos\theta-q^2}$$

$$= \frac{-V}{(2\pi)^3}\int dk^3 \, \frac{f_k}{2kq\cos\theta+q^2}$$



$$= \frac{-V}{(2\pi)^3}\int_0^{k_F} dk\, 2\pi k^2 \int_0^{\pi} d\theta \, \frac{f_k \sin\theta}{2kq\cos\theta+q^2}$$

$$= \frac{-V}{(2\pi)^3}\int_0^{k_F} dk\, 2\pi k^2 \times \left(\frac{1}{kq}\times\frac{1}{2}\ln\left|\frac{1+\frac{2k}{q}}{1-\frac{2k}{q}}\right|\right)$$

$$= \frac{-V}{8\pi^2 q}\int_0^{k_F} dk\, k \ln\left|\frac{q+2k}{q-2k}\right| = \frac{-V}{8\pi^2 q}\times\underbrace{\frac{1}{4}}_{\frac{1}{4q}}\left[\frac{-q^2}{2}\ln\left|\frac{1+\frac{2k_F}{q}}{1-\frac{2k_F}{q}}\right| + 2k_F\left(q-k_F\ln\left|1-\frac{4k_F}{2k_F+q}\right|\right)\right] \quad \cdots\cdots (51)$$

As well

$$\sum_{k} \frac{f_k}{k^2-(k-q)^2} = \frac{-V}{(2\pi)^3}\int_0^{k_F} dk\, 2\pi k^2 \int_0^{\pi} d\theta \, \frac{f_k \sin\theta}{-2kq\cos\theta+q^2}$$

$$= \frac{-V}{(2\pi)^3}\int_0^{k_F} dk\, 2\pi k^2 \times \left(\frac{1}{kq}\times\frac{1}{2}\ln\left|\frac{1+\frac{2k}{q}}{1-\frac{2k}{q}}\right|\right) \quad \cdots\cdots (52)$$

Thus, we see Eq. (52) is equivalent to Eq. (51).

By performing calculations in Eq. (51) as

$$\frac{1}{4q}\times\left[-\frac{q^2}{2}\ln\left(\frac{q+2k_F}{q-2k_F}\right)+2k_F q-2k_F^2\ln\left(\frac{q-2k_F}{q+2k_F}\right)\right]$$

$$= \frac{1}{4}\left[\left(2\frac{k_F^2}{q}-\frac{q}{2}\right)\ln\left|\frac{1+\frac{q}{2k_F}}{1-\frac{q}{2k_F}}\right| + 2k_F\right]$$

$$= k_F\left[\frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|+\frac{1}{2}\right], \quad \text{where } \eta=\frac{q}{2k_F} \quad \cdots\cdots (53)$$

we obtain

$$\sum_{k} \frac{f_k}{k^2-(k+q)^2} = \frac{-V}{8\pi^2} \times k_F \left[\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right] \quad \cdots\cdots (54)$$

Inserting Eq. (54) into Eq. (50), we see

$$\chi(q) = \frac{-k_F}{\pi^2} \left[\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right] \quad \cdots\cdots (55)$$

Remembering that See Eq. (15)

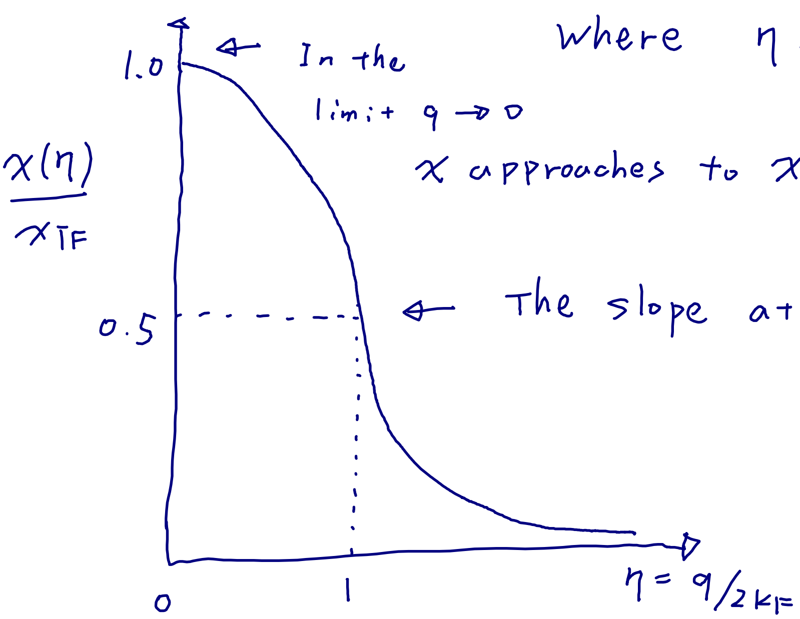
$$-\frac{k_F}{\pi^2} = -\frac{1}{\pi^2} \times (3\pi^2 \rho_0)^{\frac{1}{3}} = -\left(\frac{3}{\pi 4}\right)^{\frac{1}{3}} \rho_0^{\frac{1}{3}} = -\frac{k_{TF}^2}{4\pi} \quad \cdots (56)$$

and Eq. (42), $\chi_{TF} = -\frac{k_{TF}^2}{4\pi}$, we can rewrite Eq. (55) as

$$\boxed{\chi(q) = \left[\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right] \chi_{TF}} \quad \cdots\cdots (56)$$

Lindhard response function

where $\eta = \frac{q}{2k_F}$



Using Eq. (41), the dielectric function is given by

$$\boxed{\varepsilon(q) = 1 - \frac{4\pi}{q^2} \left[\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right] \chi_{TF}} \quad \cdots\cdots (57)$$

Friedel oscillation

With the Lindhard dielectric function of Eq. (57) and Eq. (34), we evaluate $\delta\rho(\mathbf{r})$.

$$\delta\rho(\mathbf{r}) = \frac{Z}{(2\pi)^3}\int dq^3 \left(1-\frac{1}{\varepsilon(q)}\right) e^{i\mathbf{q}\cdot\mathbf{r}}$$

$$= \frac{Z}{(2\pi)^3}\int_0^\infty dq\cdot q^2 \int_{-\pi}^{\pi} d\phi \int_0^\pi d\theta \sin\theta \left(1-\frac{1}{\varepsilon(q)}\right) e^{iqr\cos\theta}$$

$$= \frac{Z}{(2\pi)^2}\int_0^\infty dq\cdot q^2\left(1-\frac{1}{\varepsilon(q)}\right)\underbrace{\int_{-1}^{1} dx\, e^{iqrx}}_{\left[\frac{e^{iqrx}}{iqr}\right]_{-1}^{1} = \frac{2}{qr}\sin qr} \quad \leftarrow x = \cos\theta$$

$$= \frac{Z}{r}\int_0^\infty dq\; g(q)\sin qr \quad \text{---- (58)}$$

where

$$g(q) = \frac{q}{2\pi^2}\,\frac{\varepsilon(q)-1}{\varepsilon(q)} \quad \text{---- (59)}$$

$g(q)$ behaves as follows:

$$q\to 0 \qquad g(q)\to 0$$

$$q\to\infty \qquad g(q)\to 0, \quad g'(q)\to 0$$

$$q\to 2k_F \qquad g'(q)\to C\ln|q-2k_F|, \quad g''(q)\to\frac{C}{q-2k_F} \quad \text{---- (60)}$$

C is a constant.

Integrating Eq. (58) by parts two times, we see

$$(58) = \left[g(q)\left(\frac{-1}{r}\cos qr\right)\right]_0^\infty - \int_0^\infty dq\, g'(q)\left(\frac{-1}{r}\cos qr\right) = \frac{1}{r}\int_0^\infty dq\; g'(q)\cos qr$$

$$= \frac{1}{r}\left[g'(q)\frac{1}{r}\sin qr\right]_0^\infty - \frac{1}{r}\int_0^\infty dq\, g''(q)\frac{1}{r}\sin qr = -\frac{1}{r^2}\int_0^\infty dq\; g''(q)\sin qr$$

---- (61)

Let's consider the case of $r \to \infty$.

In this case, $q \to \infty$, $\sin qr$ will largely oscillate, and those contribution will cancel out. The leading term arises around $q = 2k_F$. Then, we can evaluate using Eqs. (58) – (61) as

$$\delta \rho(r) = \frac{-CZ}{r^3} \int_{2k_F - \Delta}^{2k_F + \Delta} dq \, \frac{1}{q - 2k_F} \sin qr \quad \cdots\cdots (62)$$

↑ odd with respect to $2k_F$

Remembering an addition theorem:

$$\sin qr = \underbrace{\sin[(q-2k_F)r]}_{\text{odd}} \cos 2k_F r + \underbrace{\cos[(q-2k_F)r]}_{\text{even}} \sin 2k_F r \quad \cdots (63)$$

inserting Eq. (63) into Eq. (62), and considering the parity of integrands, one can obtain the following Eq.

$$\delta \rho(r) = \frac{-CZ}{r^3} \cos 2k_F r \int_{2k_F - \Delta}^{2k_F + \Delta} dq \, \frac{\sin[(q-2k_F)r]}{q - 2k_F}$$

changing the variable $x \equiv (q - 2k_F) r$, we have

$$\delta \rho(r) = \frac{-CZ \cos 2k_F r}{r^3} \int_{-\Delta r}^{\Delta r} dx \, \frac{\sin x}{x} \quad \cdots\cdots (64)$$

In case of $r \to \infty$,

$$\int_{-\Delta r}^{\Delta r} dx \, \frac{\sin x}{x} \to \int_{-\infty}^{\infty} \frac{\sin x}{x} = \pi$$

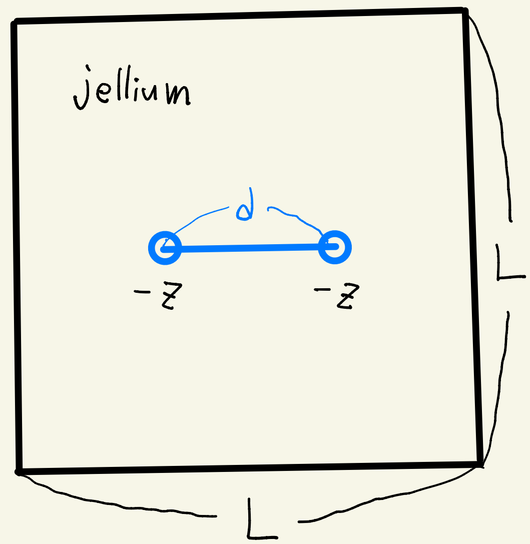
Thus, we obtain

$$\boxed{\delta \rho(r) = -\pi Z \frac{C \cos 2k_F r}{r^3}, \quad r \to \infty} \quad \cdots\cdots (65)$$

This is called the Friedel oscillation.

Embedding of two nuclei to jellium

We consider to embed two nuclei with a charge of $-Z$ into the jellium as shown in the right figure, where we assume $d \ll L$ and the Born-von Karman periodic boundary condition. The electron density is assumed to be ρ_0 before embedding the two nuclei.



Also the background compensation charge is still introduced. On top of the assumption, we embed the two nuclei.

Then the total energy of the system can be approximated as

$$E = E_0 + E_1 + E_2 + E_N \quad \cdots\cdots \quad (66)$$

E_0 zero-th order term evaluated by the jellium model

E_1 1st order correction

E_2 2nd order correction

E_N nuclei interaction

Evaluation of E_0

Using the kinetic energy density t and the exchange-correlation energy ε_{xc} of the jellium model, we evaluate E_0 as

$$E_0 = \int dr^3 \, \rho_0(r) \left(t(r) + \varepsilon_{xc}(r) \right) \quad \cdots\cdots \quad (67)$$

where

$$\rho_0(r) = \rho_0 \quad \text{constant} \qquad \rho_0 = \frac{3}{4\pi} r_s^{-3}$$

$$t(r) = \frac{3}{10}\left(\frac{9}{4}\pi\right)^{\frac{2}{3}} r_s^{-2} \quad \cdots\cdots \quad (68)$$

$$\varepsilon_{xc}(r) = \underbrace{-\frac{3}{4\pi}\left(\frac{9}{4}\pi\right)^{\frac{1}{3}} r_s^{-1}}_{\text{exchange}} + \underbrace{0.0622 \ln r_s - 0.094}_{\text{correlation}},$$

Since ρ_0 is constant. E_0 is also constant, and does not depend on the distance of d.

Evaluation of E_1

We embed the two nuclei into the jellium. The potential is given by

$$V_{ext}(\mathbf{r}) = \overbrace{\frac{-Z}{|\mathbf{r}+\frac{d}{2}|}}^{=V_N(\mathbf{r}-\tau_1)} + \overbrace{\frac{Z}{|\mathbf{r}-\frac{d}{2}|}}^{=V_N(\mathbf{r}-\tau_2)} \quad \cdots\cdots (70)$$

The one is placed at $\tau_1 = (-\frac{d}{2}, 0, 0)$, the other is placed at $\tau_2 = (\frac{d}{2}, 0, 0)$.

Since electrons screen the embeded nuclei potential, the resultant screened potential V_{scr} can be estimated as

$$V_{scr}(\mathbf{r}) = \frac{1}{(2\pi)^3}\int dq^3 \frac{V_{ext}(\mathbf{q})}{\varepsilon(\mathbf{q})} e^{i\mathbf{q}\cdot\mathbf{r}} \quad \cdots\cdots (69)$$

where we employed Eq. (31). $V_{ext}(\mathbf{q})$ is given by

$$\mathbf{r}' = \mathbf{r}-\tau_1 \qquad \mathbf{r}' = \mathbf{r}_2 - \tau_2$$

$$\begin{aligned}
V_{ext}(\mathbf{q}) &= \int dr^3\, V_N(\mathbf{r}-\tau_1)\, e^{-i\mathbf{q}\cdot\mathbf{r}} + \int dr^3\, V_N(\mathbf{r}-\tau_2)\, e^{-i\mathbf{q}\cdot\mathbf{r}} \\
&= \int dr'^3\, V_N(\mathbf{r}')\, e^{-i\mathbf{q}\cdot(\mathbf{r}'+\tau_1)} + \int dr'^3\, V_N(\mathbf{r}')\, e^{-i\mathbf{q}\cdot(\mathbf{r}'+\tau_2)} \\
&= e^{-i\mathbf{q}\cdot\tau_1}\int dr^3\, V_N(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}} + e^{-i\mathbf{q}\cdot\tau_2}\int dr^3\, V_N(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}} \\
&= e^{-i\mathbf{q}\cdot\tau_1} V_N(\mathbf{q}) + e^{-i\mathbf{q}\cdot\tau_2} V_N(\mathbf{q}) = \left(e^{iq_x\frac{d}{2}} + e^{-iq_x\frac{d}{2}}\right) V_N(\mathbf{q}) \\
&= 2\cos\frac{q_x d}{2}\, V_N(\mathbf{q}) \quad \cdots\cdots (70) \\
&= \left[\frac{1}{2}\sum_{i=1}^{2} e^{-i\mathbf{q}\cdot\tau_i}\right] 2V_N(\mathbf{q}) = \underbrace{S(\mathbf{q})}_{\text{Structure factor}} \times 2V_N(\mathbf{q}) \quad \cdots\cdots (70')
\end{aligned}$$

The dielectric function $\varepsilon(\mathbf{q})$ in (69) can be approximated by using the Lindhard function.

From the 1st order perturbation, E_1 is given by

$$E_1 = \underset{\text{spin degeneracy}}{2}\sum_{k} \langle \varphi_k | V_{scr} | \varphi_k \rangle \quad \cdots\cdots (71)$$

Rather than using the bare potential of V_{ext}, we employ V_{scr} to evaluate E_1. The treatment goes beyond the conventional the 1st order perturbation theory. The integral in (71) becomes

$$\langle \varphi_k | V_{scr} | \varphi_k \rangle = \frac{1}{V}\int dr^3\, e^{-ik\cdot r}\left[\frac{1}{(2\pi)^3}\int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)} e^{iq\cdot r}\right] e^{ik\cdot r}$$

From the Born-Von Karman condition,

$$= \frac{1}{V(2\pi)^3}\int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)} \underbrace{\int dr^3\, e^{i(-k+q+k)\cdot r}}_{=\,\delta_{q0}}$$

δ_{q0} ← Kronecker's delta

$$= \frac{1}{V(2\pi)^3}\int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)}\, \delta_{q0} \times V = \frac{1}{(2\pi)^3} \underbrace{(\Delta q)^3}_{\frac{(2\pi)^3}{L^3}} \frac{V_{ext}(0)}{\varepsilon(0)}$$

$$= \frac{1}{V}\frac{V_{ext}(0)}{\varepsilon(0)} \quad \cdots\cdots (72)$$

The integral can be evaluated in a different way as

$$= \frac{1}{V(2\pi)^3}\int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)} \underset{\text{delta function}}{\delta(q)} \times (2\pi)^3 = \frac{1}{V}\frac{V_{ext}(0)}{\varepsilon(0)}$$

This is equivalent to (72).

From (70), (29), (56), and (57), we have

$$V_{ext}(q) = 2\cos\frac{q_x d}{2}\, V_N(q) = -\frac{8\pi Z}{q^2}\cos\frac{q_x d}{2}$$

$$\simeq -\frac{8\pi Z}{q^2} \quad (q \to 0) \quad \cdots\cdots (73)$$

$$\varepsilon(q) = 1 - \frac{4\pi}{q^2}\left[\frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right]\chi_{TF}, \quad \eta = \frac{q}{2k_F}$$

$$\chi_{TF} = -\frac{k_{TF}^2}{4\pi}$$

$$\boxed{\ln\left|\frac{1+\eta}{1-\eta}\right| \simeq 2\eta + \frac{2}{3}\eta^3 + \cdots \quad (\eta \to 0)}$$

$$\simeq 1 - \frac{4\pi}{q^2}\left[\frac{1}{2} + \frac{1-\eta^2}{4\eta}\times 2\eta\right]\chi_{TF} = 1 - \frac{4\pi}{q^2}\left(1 - \frac{1}{2}\frac{q^2}{4k_F^2}\right)\chi_{TF}$$

$$= 1 - \frac{4\pi}{q^2}\chi_{TF} + \frac{\pi}{2k_F^2}\chi_{TF} = 1 - \frac{\cancel{4\pi}}{q^2}\times\left(-\frac{k_{TF}^2}{\cancel{4\pi}}\right) + \frac{\cancel{\pi}}{2k_F^2}\left(-\frac{k_{TF}^2}{4\cancel{\pi}}\right)$$

$$= 1 + \frac{k_{TF}^2}{q^2} - \frac{1}{8k_F^2}k_{TF}^2 \quad \cdots\cdots (74)$$

So,

$$\frac{V_{ext}(0)}{\varepsilon(0)} = \lim_{q\to 0}\frac{V_{ext}(q)}{\varepsilon(q)} = \lim_{q\to 0}\frac{-\frac{8\pi Z}{q^2}}{1-\frac{k_{TF}^2}{8k_F^2}+\frac{k_{TF}^2}{q^2}} = \lim_{q\to 0}\frac{-8\pi Z}{\left(1-\frac{k_{TF}^2}{8k_F^2}\right)q^2 + k_{TF}^2}$$

$$= -\frac{8\pi Z}{k_{TF}^2} \quad \cdots\cdots (75)$$

By inserting (75) into (72), we have

$$\langle\varphi_k|V_{scr}|\varphi_k\rangle = -\frac{8\pi Z}{V k_{TF}^2} \quad \cdots\cdots (76)$$

Eq. (71) can be evaluated as

$$E_1 = 2\sum_k^{occ}\langle\varphi_k|V_{scr}|\varphi_k\rangle$$

$$= 2\frac{V}{(2\pi)^3}\int dk^3\left(-\frac{8\pi Z}{V k_{TF}^2}\right) = \frac{4Z}{(2\pi)^3}\times\frac{4}{3}\pi k_F^3$$

$$= 2\frac{\cancel{V}}{(2\pi)^3}\times\left(-\frac{8\pi Z}{\cancel{V}k_{TF}^2}\right)\times\frac{4}{3}\pi k_F^3$$

$$= -\frac{\cancel{8\pi}\times\cancel{8\pi}}{\cancel{8\pi^3}}\times\frac{Z}{3k_{TF}^2}\times k_F^3 = -\frac{8Z k_F^3}{3\pi k_{TF}^2} \quad \cdots\cdots (77)$$

From (77), it turns out that E_1 does not depend on the distance of d between two nuclei.

Evaluation of E_2

The second order perturbation energy is given by

spin degeneracy

$$E_2 = 2 \sum_{k}^{occ.} \sum_{k' \neq k} \frac{|\langle \varphi_{k'} | V_{scr} | \varphi_k \rangle|^2}{E_k - E_{k'}} - E_2^{(dc)} \quad \cdots\cdots (78)$$

The double counting term $E_2^{(dc)}$ will be discussed later on.

The matrix elements can be evaluated as

$$\langle \varphi_{k'} | V_{scr} | \varphi_k \rangle = \frac{1}{V} \int dr^3\, e^{-ik' \cdot r} \left[\frac{1}{(2\pi)^3} \int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)} e^{iq \cdot r} \right] e^{ik \cdot r}$$

$$= \frac{1}{V(2\pi)^3} \int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)} \int dr^3\, e^{i(-k'+q+k)\cdot r}$$

$$= \frac{1}{V(2\pi)^3} \int dq^3 \frac{V_{ext}(q)}{\varepsilon(q)} \delta_{k', k+q} \times V = \frac{1}{\cancel{(2\pi)^3}} \frac{\cancel{(2\pi)^3}}{V} \frac{V_{ext}(q)}{\varepsilon(q)} \delta_{k', k+q} \quad \cdots\cdots (79)$$

So, we have

$$\langle \varphi_{k+q} | V_{scr} | \varphi_k \rangle = \frac{1}{V} \frac{V_{ext}(q)}{\varepsilon(q)} \quad \cdots\cdots (80)$$

Using (80), the first term in the R.H.S of Eq. (78) can be calculated as

q=0 is excluded.

$$2 \sum_{k}^{occ} \sum_{k' \neq k} \frac{|\langle \varphi_{k'} | V_{scr} | \varphi_k \rangle|^2}{E_k - E_{k'}} = \frac{2}{V^2} \sum_{k} \sum_{q}{}' \left[\frac{f_k}{\frac{1}{2}k^2 - \frac{1}{2}(k+q)^2} \right] \frac{|V_{ext}(q)|^2}{|\varepsilon(q)|^2} \quad \cdots\cdots (81)$$

From (54) and (55), we have

$$\sum_{k} \frac{2 f_k}{k^2 - (k+q)^2} = \cancel{-} \frac{2V}{8\cancel{\pi^2}} \times \cancel{k_F} \times \left(\cancel{-} \frac{\cancel{\pi^2}}{\cancel{k_F}} \right) \chi(q) = \frac{V}{4} \chi(q) \quad \cdots\cdots (82)$$

Using (82), (81) can be rewritten as

$$2 \sum_{k}^{occ} \sum_{k' \neq k} \frac{|\langle \varphi_{k'} | V_{scr} | \varphi_k \rangle|^2}{E_k - E_{k'}} = \frac{2}{V^2} \sum_{q}{}' \frac{|V_{ext}(q)|^2}{|\varepsilon(q)|^2} \times \frac{V}{4} \chi(q)$$

From (70'), $S(q) \times 2 V_N(q)$

$$= \boxed{\frac{1}{2V} \sum_{q}{}' \frac{|V_{ext}(q)|^2}{|\varepsilon(q)|^2} \chi(q)} = \frac{1}{2V} \sum_{q}{}' \frac{S^2 \times 4 V_N^2}{\varepsilon^2} \chi = \frac{2}{V} \sum_{q}{}' \frac{(S(q))^2 (V_N(q))^2}{(\varepsilon(q))^2} \chi(q) \quad \cdots\cdots (83)$$

It should be noted that (83) contains the double counting term in second order. This is given by

$$E_2^{(dc)} = \frac{1}{2}\iint dr^3 dr'^3 \frac{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad \cdots\cdots \quad (84)$$

Noting

$$\delta\rho(\mathbf{r}) = \frac{1}{V}\sum_q \delta\rho(q)\, e^{iq\cdot r}, \quad \delta\rho(q) = \int dr^3\, \delta\rho(\mathbf{r})\, e^{-iq\cdot \mathbf{r}} \quad \cdots \quad (85)$$

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{V^2}\sum_q\sum_{q'} |q\rangle\langle q| \frac{1}{|\mathbf{r}-\mathbf{r}'|} |q'\rangle\langle q'|$$

$$= \frac{1}{V^2}\sum_q\sum_{q'} e^{iq\cdot r}\, c(q,q')\, e^{-iq'\cdot r} \quad \cdots \quad (86)$$

$$c(q,q') = \iint dr^3 dr'^3 \frac{e^{-iq\cdot\mathbf{r}}\, e^{iq'\cdot\mathbf{r}'}}{|\mathbf{r}-\mathbf{r}'|}$$

$$= \iint dr^3 dr'^3 \frac{e^{-iq\cdot(r-r')}\, e^{-iq\cdot r'}\, e^{iq'\cdot r'}}{|\mathbf{r}-\mathbf{r}'|} = \int dr'^3\, \frac{4\pi}{q^2}\, e^{i(q'-q)\cdot r'}$$

$$= \frac{4\pi}{q^2}\,\delta(q'-q)\times(2\pi)^3 \quad \cdots \quad (87)$$

and inserting Eqs. (85) – (87) into Eq. (84), we have

$$E_2^{(dc)} = \frac{1}{2}\iint dr^3 dr'^3 \left[\frac{1}{V}\sum_{q_1}\delta\rho(q_1)\, e^{iq_1\cdot r}\right]\left[\frac{1}{V}\sum_{q_2}\delta\rho(q_2)\, e^{iq_2\cdot r'}\right]$$

$$\times \underbrace{\left[\frac{1}{V^2}\sum_{q_3}\sum_{q_4}\frac{4\pi}{q_3^2}\,\delta(q_4-q_3)\times(2\pi)^3\times e^{iq_3\cdot r}\, e^{-iq_4\cdot r'}\right]}$$

$$\frac{1}{V^2}\sum_{q_3}\frac{V}{(2\pi)^3}\times e^{iq_3\cdot r}\int dq_4^3\, \frac{4\pi}{q_3^2}\,\delta(q_4-q_3)\times(2\pi)^3\, e^{-iq_4\cdot r'}$$

$$= \frac{1}{V}\sum_{q_3} e^{iq_3\cdot r}\times\frac{4\pi}{q_3^2}\times e^{-iq_3\cdot r'} = \frac{4\pi}{V}\sum_{q_3}\frac{1}{q_3^2}\, e^{iq_3\cdot(r-r')}$$

$$= \frac{1}{2}\frac{1}{V^3}\sum_{q_1}\sum_{q_2}\sum_{q_3}\delta\rho(q_1)\,\delta\rho(q_2)\,\frac{4\pi}{q_3^2}\iint dr^3 dr'^3\, e^{i(q_1+q_3)\cdot r}\, e^{i(q_2-q_3)\cdot r'}$$

$$= \frac{1}{2V^3}\sum_{q_1}\sum_{q_2}\sum_{q_3}\delta\rho(q_1)\,\delta\rho(q_2)\,\frac{4\pi}{q_3^2}\int dr^3\, e^{i(q_1+q_3)\cdot r}\, \delta_{q_2 q_3}\times V$$

$$= \frac{1}{2V^3} \sum_{q_1} \sum_{q_2} \sum_{q_3} \delta\rho(q_1)\,\delta\rho(q_2)\,\frac{4\pi}{q_3^2}\left(\delta_{q_1,-q_3} \times V\right) \times \left(\delta_{q_2 q_3} \times V\right)$$

$$= \frac{1}{2V} \sum_q{}' \delta\rho(-q)\,\delta\rho(q)\,\frac{4\pi}{q^2} = \frac{1}{2V} \sum_q{}' \delta\rho^*(q)\,\delta\rho(q)\,\frac{4\pi}{q^2} \quad \cdots\cdots (88)$$

From (37) and (28), we have

$$\delta\rho(q) = \chi(q)\,V_{scr}(q) = \chi(q)\,\frac{V_{ext}(q)}{\varepsilon(q)} \quad \cdots\cdots (89)$$

Substituting $\delta\rho$ in (88) by (89), we have

$$E_2^{(dc)} = \frac{1}{2V} \sum_q{}' \frac{(\chi(q))^2}{(\varepsilon(q))^2}\left(V_{ext}(q)\right)^2 \frac{4\pi}{q^2} \quad \cdots\cdots (90)$$

Inserting (83) and (90) into (72) yields

$$E_2 = \frac{1}{2V} \sum_q{}' \frac{|V_{ext}(q)|^2}{|\varepsilon(q)|^2}\,\chi(q) - \frac{1}{2V} \sum_q{}' \frac{(\chi(q))^2}{(\varepsilon(q))^2}\left|V_{ext}(q)\right|^2 \frac{4\pi}{q^2}$$

$$= \frac{1}{2V} \sum_q{}' \frac{|V_{ext}(q)|^2}{(\varepsilon(q))^2}\,\chi(q)\overbrace{\left(1 - \frac{4\pi}{q^2}\chi(q)\right)}^{\varepsilon(q)}$$

$$\boxed{E_2 = \frac{1}{2V} \sum_q{}' \frac{\chi(q)}{\varepsilon(q)}\left|V_{ext}(q)\right|^2} \quad \cdots\cdots (91)$$

Evaluation of E_N

The nuclei interaction is simply given by

$$E_N = \frac{Z^2}{R}, \quad R = d \quad \cdots\cdots (92)$$

So, at the fixed volume V and the electron density ρ_0 we see that only E_2 and E_N depend on the distance $R=d$.

Real space representation of E_2

From (70), we have

$$V_{ext}(q) = \sum_{i=1}^{2} e^{-iq\cdot\tau_i} V_N(q) \quad \cdots\cdots (93)$$

$$\rightarrow \quad |V_{ext}(q)|^2 = \left(\sum_i e^{iq\cdot\tau_i} V_N^*(q)\right)\left(\sum_j e^{-iq\cdot\tau_j} V_N(q)\right)$$

$$= \sum_{i,j} e^{iq\cdot(\tau_i-\tau_j)} |V_N(q)|^2 \quad \cdots\cdots (94)$$

Inserting (94) to (91) yields

$$E_2 = \frac{1}{2V}\sum_q{}' \frac{\chi(q)}{\varepsilon(q)} \left(\sum_{ij} e^{iq\cdot(\tau_i-\tau_j)} |V_N(q)|^2\right)$$

$$= \frac{1}{2V}\sum_{ij}\sum_q{}' e^{iq\cdot(\tau_i-\tau_j)} \frac{\chi(q)}{\varepsilon(q)} |V_N(q)|^2 \quad \cdots\cdots (95)$$

Since χ, ε, V_N depends on $|q|$, the summation over q in (95) can be written as

$$\sum_q{}' e^{iq\cdot(\tau_i-\tau_j)} \frac{\chi(q)}{\varepsilon(q)} |V_N(q)|^2 \qquad R_{ij} = |\tau_i - \tau_j|$$

$$= \frac{V}{(2\pi)^3} \lim_{q_{min}\to 0} \int_{q_{min}}^{\infty} dq\cdot q^2 \cdot 2\pi \int_0^{\pi} d\theta \sin\theta d\theta \; e^{iqR_{ij}\cos\theta} \frac{\chi(q)}{\varepsilon(q)} |V_N(q)|^2 \quad \cdots (96)$$

Noting $\quad e^{iqR_{ij}\cos\theta} = 1 + iqR_{ij}\cos\theta + \cdots$

$$\varepsilon(q) = 1 - \frac{4\pi}{q^2}\chi(q) \quad \leftarrow \text{From (41)}$$

$$\rightarrow \frac{4\pi}{q^2}\chi(q) = 1 - \varepsilon(q) \rightarrow \frac{\chi(q)}{\varepsilon(q)} = \frac{q^2}{4\pi}\left(\frac{1-\varepsilon(q)}{\varepsilon(q)}\right)$$

$$\lim_{q\to 0} \varepsilon(q) = 1 + \frac{k_{TF}^2}{q^2} - \frac{1}{8p_F^2} k_{TF}^2 \quad \leftarrow \text{From (74)}$$

$$V_N(q) = -\frac{4\pi Z}{q^2} \quad \leftarrow \text{From (29)}$$

we can evaluate as

$$\lim_{q\to 0} e^{iqR_{ij}\cos\theta}\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2 = \lim_{q\to 0}\frac{q^2}{4\pi}\left(\frac{1-1-\frac{k_{TF}^2}{q^2}+\frac{k_{TF}^2}{8k_F^2}}{1+\frac{k_{TF}^2}{q^2}-\frac{1}{8k_F^2}k_{TF}^2}\right)\times\frac{16\pi^2 Z^2}{q^4}$$

$$= 4\pi Z^2\lim_{q\to 0}\frac{-\frac{k_{TF}^2}{q^2}+\frac{k_{TF}^2}{8k_F^2}}{\left(1-\frac{k_{TF}^2}{8k_F^2}\right)q^2+k_{TF}^2} = -\frac{4\pi Z^2}{q^2} \quad \cdots\cdots (97)$$

Therefore, we see

$$dq\cdot q^2\times\lim_{q\to 0} e^{iqR_{ij}\cos\theta}\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2 = -4\pi Z^2 dq \quad \cdots (98)$$

Since at $q=0$, the integrant is finite, we can write (96)

as $\sum_q{}' e^{iq\cdot(\tau_i-\tau_j)}\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2$ $\quad x=\cos\theta \quad \frac{dx}{d\theta}=-\sin\theta$

$$= \frac{V}{(2\pi)^3}\int_0^\infty dq\cdot q^2\cdot 2\pi\int_0^\pi d\theta\,\sin\theta\, e^{iqR_{ij}\cos\theta}\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2$$

$$= \frac{V}{4\pi^2}\int_0^\infty dq\cdot q^2\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2\int_{-1}^{1}dx\, e^{iqR_{ij}x}$$

$e^{iqR_{ij}} - e^{-iqR_{ij}} = 2i\sin qR_{ij}$

$$= \frac{V}{4\pi^2}\int_0^\infty dq\cdot q^2\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2\left[\frac{1}{iqR_{ij}}e^{iqR_{ij}x}\right]_{-1}^{1}$$

$$= \frac{V}{2\pi^2R_{ij}}\int_0^\infty dq\cdot q\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2\sin qR_{ij} \quad \cdots\cdots (99)$$

Inserting (99) into (95), we have

$$E_2 = \frac{1}{2}\sum_{ij}\Phi_{bs}(R_{ij}) \quad \cdots\cdots (100)$$

$$\Phi_{bs}(R_{ij}) = \frac{1}{2\pi^2R_{ij}}\int_0^\infty dq\cdot q\frac{\chi(q)}{\varepsilon(q)}|V_N(q)|^2\sin qR_{ij} \quad \cdots (101)$$

Noting

$$\varepsilon(q) = 1 - \frac{4\pi}{q^2}\chi(q) \quad \leftarrow \text{From (41)}$$

$$\rightarrow \frac{4\pi}{q^2}\chi(q) = 1 - \varepsilon(q) \rightarrow \frac{\chi(q)}{\varepsilon(q)} = \frac{q^2}{4\pi}\left(\frac{1-\varepsilon(q)}{\varepsilon(q)}\right)$$

$$V_N(q) = -\frac{4\pi Z}{q^2} \quad \leftarrow \text{From (29)}$$

Eq. (101) can be rewritten as

$$\Phi_{bs}(R_{ij}) = \frac{1}{2\pi^2 R_{ij}}\int_0^\infty dq \cdot q \cdot \frac{q^2}{4\pi}\left(\frac{1-\varepsilon(q)}{\varepsilon(q)}\right)\frac{16\pi^2 Z^2}{q^4}\sin qR_{ij}$$

$$= \frac{2Z^2}{\pi R_{ij}}\int_0^\infty dq\left(\frac{1-\varepsilon(q)}{\varepsilon(q)}\right)\frac{\sin qR_{ij}}{q} \quad \cdots\cdots \quad (102)$$

Here we define $\Phi(R_{ij})$ as

$$\Phi(R_{ij}) = \frac{Z^2}{R_{ij}} + \frac{2Z^2}{\pi R_{ij}}\int_0^\infty dq\left(\frac{1-\varepsilon(q)}{\varepsilon(q)}\right)\frac{\sin qR_{ij}}{q}$$

$$= \frac{Z^2}{R_{ij}} - \frac{2Z^2}{\pi R_{ij}}\int_0^\infty dq\,\frac{\sin qR_{ij}}{q} + \frac{2Z^2}{\pi R_{ij}}\int_0^\infty dq\,\varepsilon^{-1}(q)\frac{\sin qR_{ij}}{q}$$

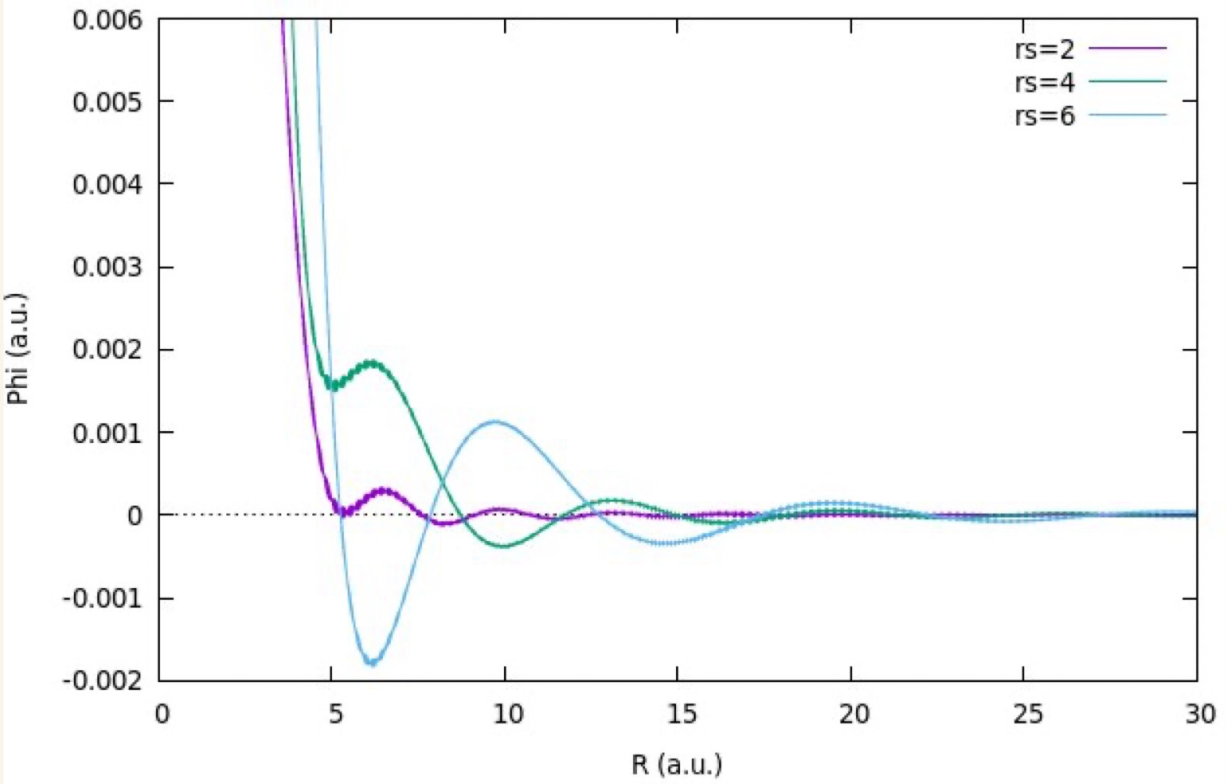
Dirichlet integral: $\int_0^\infty dq\,\frac{\sin q}{q} = \frac{\pi}{2}$

$$x = qR_{ij} \rightarrow \frac{dx}{dq} = R_{ij} \rightarrow dq = \frac{dx}{R_{ij}}, \quad q = \frac{x}{R_{ij}} \rightarrow \int_0^\infty dq\,\frac{\sin qR_{ij}}{q} = \int_0^\infty dx\,\frac{\sin x}{x} = \frac{\pi}{2}$$

$$= \frac{Z^2}{R_{ij}} - \frac{\cancel{2}Z^2}{\cancel{\pi}R_{ij}} \times \frac{\cancel{\pi}}{\cancel{2}} + \frac{2Z^2}{\pi R_{ij}}\int_0^\infty dq\,\frac{\sin qR_{ij}}{q\,\varepsilon(q)}$$

$$\boxed{\Phi(R_{ij}) = \frac{2Z^2}{\pi R_{ij}}\int_0^\infty dq\,\frac{\sin qR_{ij}}{q\,\varepsilon(q)}} \quad \cdots\cdots \quad (103)$$

By performing numerical integrations in Eq. (103), we obtain the following two body potentials for r_s = 2, 4, and 6.



The asymptotic behaviour of Φ for a large R is given by

$$\Phi(R) \propto \frac{\cos 2k_F R}{(2k_F R)^3} \quad \text{------} \quad (104)$$

The equation of (104) can be obtained by a similar analysis for the derivation of Friedel oscillation.

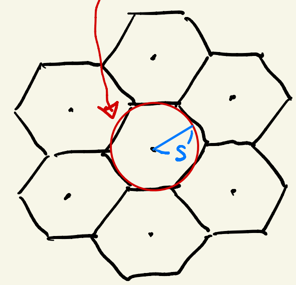
Note Although we started from the two nuclei in our model, the derivation is valid even for bulks, and one can obtain the same result for $\Phi(R)$ as (103).

Modelling of sp-valent materials

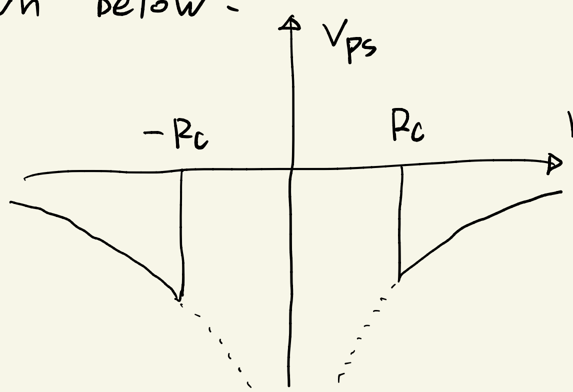
We model simple sp-valent materials by embedding pseudo potentials into the jellium model, and evaluate the energy by a perturbation theoy.

* In a crystal, the Wigner-Seiz cell is replaced by the Wigner-Seiz sphere whose volume is equivalent to that of the Wigner-Seiz cell.

$\Omega = \frac{4}{3}\pi S^3$



* As the embeded potential, we employ the Ashcroft's empty core pseudopotential as shown below:



$$V_{ps}(r) = 0 \qquad r \leq R_c$$

$$V_{ps}(r) = -\frac{Z}{r} \qquad R_c < r$$

* The total energy of the model is given by

$$E = E_0 + E_E + E_2 + E_N \qquad \cdots\cdots (105)$$

E_0 zero-th order energy evaluated by jellium model

E_E electro static term

E_2 2nd order correction for band energy

E_N nuclei interaction

E_0 The energy of E_0 is given by

$$E_0 = \int_\Omega dr^3 \rho_0 \left(\tau(\rho_0) + \varepsilon_{xc}(\rho_0) \right)$$

Within the Wigner - Seiz cell

Note that ρ_0 is a constant value every where.

$$= Z \rho_0 \left(\tau(\rho_0) + \varepsilon_{xc}(\rho_0) \right) \quad \cdots\cdots (106)$$

where τ and ε_{xc} are given by Eq. (68).

E_E E_E is evaluated by the following consideration: We assume that ρ_0 can be calculated by the superposition of partial densities associated with every Wigner - Seiz sphere.

$$\rho_0 = \sum_i \rho_0^{(i)} \quad \cdots\cdots (107)$$

Also the total pseudopotential V_{ps} can be written as

$$V_{ps}(\mathbf{r}) = \sum_i V_{ps}^{(i)}(\mathbf{r} - \mathbf{R}_i) \quad \cdots (108)$$

If the Wigner - Seiz sphere is charge neutral, the sum of two potentials:

$$V^{(i)}(\mathbf{r} - \mathbf{R}_i) = V_{ps}^{(i)}(\mathbf{r} - \mathbf{R}_i) + \int d\mathbf{r}'^3 \frac{\rho_0^{(i)}}{|\mathbf{r} - \mathbf{R}_i - \mathbf{r}'|} \quad \cdots\cdots (109)$$

becomes zero beyond the Wigner - Seiz radius of S because of the Gauss's law. Thus, E_E per atom can be calculated by

$$E_E = \int d\mathbf{r}^3 \rho_0^{(i)} V_{ps}^{(i)}(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r}^3 d\mathbf{r}'^3 \frac{\rho_0 \rho_0}{|\mathbf{r} - \mathbf{r}'|} \quad \cdots (110)$$

These integrations are performed within a Wigner - Seiz cell.

Since the electron density ρ_0 is given by

$$\rho_0 = \frac{Z}{\Omega} = \frac{Z}{\frac{4}{3}\pi S^3} \quad \cdots\cdots (111)$$

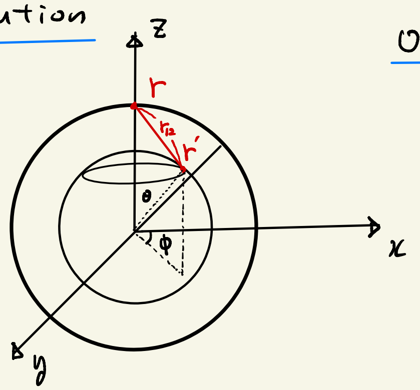
we can calculate as

$$\int \rho_0^{(i)} V_{ps}^{(i)}(\mathbf{r})\, d\mathbf{r}^3 = \frac{Z}{\frac{4}{3}\pi S^3} \times 4\pi \int_{R_c}^{S} dr \cdot r^2 \left(-\frac{Z}{r}\right)$$

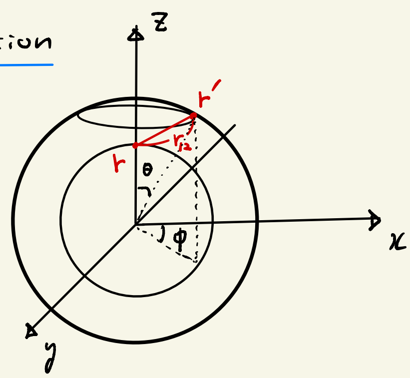
$$= \frac{-3Z^2}{S^3}\left[\frac{1}{2}r^2\right]_{R_c}^{S} = -\frac{3Z^2}{2S^3}(S^2 - R_c^2) = -\frac{3Z^2}{2S}\left[1 - \left(\frac{R_c}{S}\right)^2\right] \quad \cdots\cdots (112)$$

Calculation of $\frac{1}{2}\iint d\mathbf{r}^3 d\mathbf{r}'^3 \frac{\rho_0 \rho_0}{|\mathbf{r}-\mathbf{r}'|}$

Inner contribution



Outer contribution



$$r_{12}^2 = r^2 + r'^2 - 2rr'\cos\theta \quad \cdots (113)$$

$$2r_{12}\frac{dr_{12}}{d\theta} = 2rr'\sin\theta$$

$$\rightarrow \quad r'^2 \sin\theta = \frac{r' r_{12}}{r}\, dr_{12} \quad \cdots (114)$$

$$r_{12}^2 = r^2 + r'^2 - 2rr'\cos\theta$$

$$2r_{12}\frac{dr_{12}}{d\theta} = 2rr'\sin\theta$$

$$\rightarrow \quad r'^2 \sin\theta = \frac{r' r_{12}}{r}\, dr_{12}$$

So, we can calculate Inner contribution as

$$\int d\mathbf{r}'^3 \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \int \frac{1}{r_{12}} r'^2 \sin\theta\, dr'\, d\theta\, d\phi \quad \leftarrow \text{ using (114)}$$

$$= \int \frac{1}{r_{12}} \frac{r' r_{12}}{r}\, dr_{12}\, dr'\, d\phi = \frac{1}{r}\int r'\, dr_{12}\, dr'\, d\phi$$

$$= \frac{4\pi}{r}\int_0^r r'^2\, dr' = \frac{4\pi}{r}\left[\frac{1}{3}r'^3\right]_0^r = \frac{4\pi}{3}r^2 \quad \cdots (113)$$

$$\boxed{\begin{aligned} &\int d\phi = [\phi]_0^{2\pi} = 2\pi \\ &\int dr_{12} = [r_{12}]_{r-r'}^{r+r'} = 2r' \end{aligned}}$$

The outer contribution is calculated as

$$\int dr'^3 \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \int \frac{1}{r_{12}} r'^2 \sin\theta \, dr' d\theta d\phi = \frac{1}{r}\int r' dr_{12} dr' d\phi$$

$$\int d\phi = [\phi]_0^{2\pi} = 2\pi, \quad \int dr_{12} = [r_{12}]_{r'-r}^{r'+r} = 2r$$

$$= 4\pi \int_r^s r' dr' = 4\pi \left[\frac{1}{2} r'^2\right]_r^s = 2\pi(s^2 - r^2) \quad \cdots\cdots (114)$$

$$\frac{4-6}{3} = -\frac{2}{3}$$

So, the sum of (113) and (114) is given by

$$\frac{4}{3}\pi - 2\pi =$$

$$\int dr'^3 \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{4}{3}\pi r^2 + 2\pi(s^2 - r^2) = -\frac{2}{3}\pi r^2 + 2\pi s^2 \quad \cdots\cdots (115)$$

Using (115), one can calculate as

$$\frac{1}{2}\iint dr^3 dr'^3 \frac{\rho_0 \rho_0}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{2} \times \frac{Z^2}{\frac{16}{9}\pi^2 s^6} \times \int dr \cdot 4\pi r^2 \times \left(-\frac{2}{3}\pi r^2 + 2\pi s^2\right)$$

$$= \frac{9Z^2}{8s^6}\left[-\frac{2}{3}\int_0^s dr \cdot r^4 + 2s^2 \int_0^s dr \cdot r^2\right]$$

$$= \frac{9Z^2}{8s^6}\left[-\frac{2}{3}\left[\frac{1}{5}r^5\right]_0^s + 2s^2\left[\frac{1}{3}r^3\right]_0^s\right]$$

$$= \frac{9Z^2}{8s^6}\left(-\frac{2}{15}s^5 + \frac{2}{3}s^5\right) = \frac{\cancel{9}^{3} Z^2}{\cancel{8}_{1} \cancel{s^6}} \times \frac{\cancel{8}^{1}}{\cancel{15}_{5}} \cancel{s^5} = \frac{3Z^2}{5s} \quad \cdots\cdots (116)$$

Inserting (112) and (116) into (110) yields

$$E_E = -\frac{9Z^2}{10s} + \frac{3Z^2 R_c^2}{2s^3} \quad \cdots\cdots (117)$$

Here we consider to approximate the total energy by the sum of $E_0 + E_E$, and calculate $\frac{\partial E}{\partial s} = 0$.

Noting $\frac{4}{3}\pi(a_0 r_s)^3 = \rho_0^{-1} = \left(\frac{Z}{\frac{4}{3}\pi s^3}\right)^{-1}$

$$\longrightarrow \quad a_0 r_s = s Z^{-\frac{1}{3}}$$

One can perform the calculation of $\frac{\partial E}{\partial s} = 0$.

The following is the results with experiments for S

	Li	Na	Mg	Al	K	Zn	Ga	Ca
Calc	3.76	4.24	3.70	3.26	5.36	3.09	3.09	4.48
Expt.	3.26	3.93	3.34	2.98	4.86	2.90	3.15	4.12

We see that the equilibrium volume is mainly determined by $E_0 + E_E$.

Heine & Weaire
Solid State Physics
Vol. 24. (1970).

Evaluation of E_2

It should be noted that (91) is valid for crystals.

$$E_2 = \frac{1}{2V} \sum_q{}' \frac{\chi(\mathbf{q})}{\varepsilon(\mathbf{q})} \left| V_{ext}(\mathbf{q}) \right|^2 \quad \cdots (91)$$

In our model, V_{ext} is approximated by (108).

So, we have

$$V_{ext}(\mathbf{r}) = V_{ps}(\mathbf{r}) = \sum_i V_{ps}^{(i)}(\mathbf{r} - \mathbf{R}_i) \quad \cdots (118)$$

$$V_{ext}(\mathbf{q}) = V_{ps}(\mathbf{q}) = \sum_i \int dr^3\, V_{ps}^{(i)}(\mathbf{r} - \mathbf{R}_i)\, e^{-i\mathbf{q}\cdot\mathbf{r}} \quad \cdots (119)$$

$\mathbf{r}' = \mathbf{r} - \mathbf{R}_i$

$$= \sum_i \int dr'^3\, V_{ps}^{(i)}(\mathbf{r}')\, e^{-i\mathbf{q}\cdot(\mathbf{r}' + \mathbf{R}_i)}$$

$$= \sum_i e^{-i\mathbf{q}\cdot\mathbf{R}_i} \int dr^3\, V_{ps}^{(i)}(\mathbf{r})\, e^{-i\mathbf{q}\cdot\mathbf{r}}$$

$$= \frac{1}{N} \sum_i e^{-i\mathbf{q}\cdot\mathbf{R}_i} \times N\, V_{ps}(\mathbf{q}) \quad \cdots (120)$$

By introducing the structure factor

$$S(q) = \left[\frac{1}{N}\sum_i e^{-i q \cdot R_i}\right]\delta_{qG} \qquad \cdots\cdots (121)$$

One can write (119) as

$$V_{ext}(q) = S(q) \times N V_{ps}(q) \qquad \cdots\cdots (122)$$

Also, it should be noted that Eqs. (100) and (101), are valid for crystals.

So, even for bulks, we have

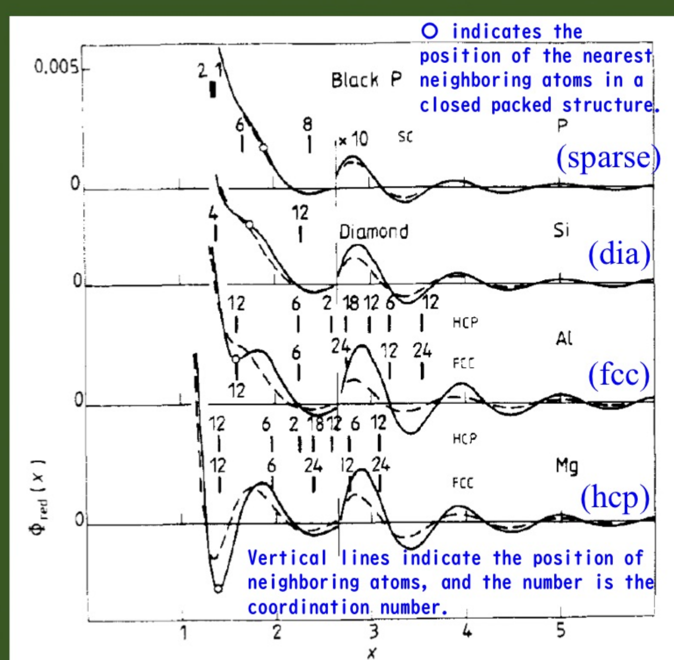
$$E_2 + E_N = \frac{1}{2}\sum_{i \neq j} \Phi(R_{ij}) \qquad \cdots\cdots (123)$$

$$\Phi(R) = \frac{Z^2}{R} + \frac{1}{2\pi^2 R}\int_0^\infty dq \cdot q^2 \frac{\chi(q)}{\varepsilon(q)} |V_{ps}(q)|^2 \sin qR \qquad \cdots (124)$$

$$= \frac{Z^2}{2R}\Phi_{red}(R)$$

$$\Phi(R) = \frac{Z^2}{R} + \Phi_{bs}(R) = \frac{Z^2}{2R}\Phi_{red}(R)$$

- The nearest neighbor positions of Mg and Al coincide with a dip.
- The hcp Mg has a relatively less distribution of atoms around the second peak, leading to hcp.
- The fcc Al has a less distribution of atoms around the second peaks, leading to fcc.
- In Si in the diamond structure, the 4 atoms get closer, and others get away, leading to a sparse structure. A similar behavior is found in P.



J. Hafner and V. Heine, J. Phys. F13, 2489 (1983).