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APPENDIX A

THE EXCHANGE AND SELF - POTENTIAL ENERGY CALCULATION^{17,20}

For the system of fermion such as electron, the total wave function must be antisymmetric in the coordinate including spin. It should be written as

$$\Psi = \frac{1}{\sqrt{N!}} \sum_p (-1)^p P \phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \dots \phi_N(\vec{x}_N) \quad , \quad (\text{A.1})$$

where p is the number of interchange in the permutation

P . $\phi(\vec{x})$ is defined as

$$\phi(\vec{x}) = \Psi(\vec{r})\alpha(\zeta) \quad \text{for spin up electron,}$$

and

$$\phi(\vec{x}) = \Psi(\vec{r})\beta(\zeta) \quad \text{for spin down electron.}$$

ζ is equal to plus or minus one according to the state of spin up or spin down respectively, and

$$\alpha(1) = 1 \quad , \quad \alpha(-1) = 0 \quad ,$$

and

$$\beta(1) = 0 \quad , \quad \beta(-1) = 1 \quad .$$

The Hamiltonian H for the system of monovalent metals, each atom having only one valence electron which can move through the fixed lattices of ion-cores, is therefore

$$H = - \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2 + \sum_i^N \sum_a^N V_a(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j}^N \sum_{a \neq b}^N \frac{e^2}{r_{ij}} + \frac{1}{2} \sum_{a \neq b}^N \sum_{ab}^N \frac{e^2}{R_{ab}}, \quad (\text{A.2})$$

here $V_a(\vec{r}_i)$ is the potential energy of the i^{th} electron in the field of ion-core in cell (a).

Since

$$E = \int \Psi^* H \Psi d\tau, \quad (\text{A.3})$$

and for a symmetric operator H and normalized determinantal wave function Ψ ,

we get

$$\int \Psi^* H \Psi d\tau = \sqrt{N!} \int \Psi^* H \Psi_0 d\tau, \quad (\text{A.4})$$

where $\Psi_0 = \phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \dots \phi_N(\vec{x}_N)$.

Using (A.1) to (A.4) altogether with the orthogonality condition, we have

$$E = \int \sum_p (-1)^p P \phi_1^*(\vec{x}_1) \phi_2^*(\vec{x}_2) \dots \phi_N^*(\vec{x}_N) \left(- \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2 + \sum_i^N \sum_a^N V_a(\vec{r}_i) \right. \\ \left. + \frac{1}{2} \sum_{i \neq j}^N \sum_{a \neq b}^N \frac{e^2}{r_{ij}} + \frac{1}{2} \sum_{a \neq b}^N \sum_{ab}^N \frac{e^2}{R_{ab}} \right) \phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \dots \phi_N(\vec{x}_N) d\tau,$$

$$\begin{aligned}
E = & \sum_i^N \int \phi_i^*(\vec{x}_i) \left(-\frac{\hbar^2}{2m} \nabla_i^2 + \sum_a^N V_a(\vec{r}_i) \right) \phi_i(\vec{x}_i) d\vec{x}_i \\
& + \frac{1}{2} \sum_{i \neq j}^N \sum_{i \neq j}^N \left(\left(\frac{e^2}{r_{ij}} |\phi_i(\vec{x}_i)|^2 |\phi_j(\vec{x}_j)|^2 d\vec{x}_i d\vec{x}_j \right. \right. \\
& \left. \left. - \frac{1}{2} \sum_{i \neq j}^N \sum_{i \neq j}^N \left(\frac{e^2}{r_{ij}} \phi_i^*(\vec{x}_j) \phi_j^*(\vec{x}_i) \phi_i(\vec{x}_i) \phi_j(\vec{x}_j) d\vec{x}_i d\vec{x}_j + \frac{1}{2} \sum_{a \neq b}^N \sum_{a \neq b}^N \frac{e^2}{R_{ab}} \right) \right) \right) .
\end{aligned} \tag{A.5}$$

For parallel spins ϕ_i and ϕ_j have spin functions as $\alpha(\zeta_i)$ and $\alpha(\zeta_j)$ or $\beta(\zeta_i)$ and $\beta(\zeta_j)$, (A.5) becomes

$$\begin{aligned}
E = & \sum_i^N \int \psi_i^*(\vec{r}_i) \left(-\frac{\hbar^2}{2m} \nabla_i^2 + \sum_a^N V_a(\vec{r}_i) \right) \psi_i(\vec{r}_i) d\vec{r}_i \\
& + \frac{1}{2} \sum_{i \neq j}^N \sum_{i \neq j}^N \left(\left(\frac{e^2}{r_{ij}} |\psi_i(\vec{r}_i)|^2 |\psi_j(\vec{r}_j)|^2 d\vec{r}_i d\vec{r}_j \right. \right. \\
& \left. \left. - \frac{1}{2} \sum_{i \neq j}^N \sum_{i \neq j}^N \left(\frac{e^2}{r_{ij}} \psi_i^*(\vec{r}_j) \psi_j^*(\vec{r}_i) \psi_i(\vec{r}_i) \psi_j(\vec{r}_j) d\vec{r}_i d\vec{r}_j + \frac{1}{2} \sum_{a \neq b}^N \sum_{a \neq b}^N \frac{e^2}{R_{ab}} \right) \right) \right) .
\end{aligned} \tag{A.6}$$

(// spins)

If ϕ_i and ϕ_j have opposite spins, the third term in (A.5) is vanished. Changing the variable \vec{r}_i and \vec{r}_j in (A.6), the expression for E is obtained as

$$\begin{aligned}
E = & \sum_1^N \left[\psi_1^*(\vec{r}_1) \left(-\frac{\hbar^2}{2m} \nabla_1^2 + \sum_a^N V_a(\vec{r}_1) \right) \psi_1(\vec{r}_1) \right] d\vec{r}_1 \\
& + \frac{1}{2} \sum_{i \neq j}^N \sum^N \left[\left[\frac{e^2}{r_{12}} |\psi_i(\vec{r}_1)|^2 |\psi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \right. \right. \\
& \left. \left. - \frac{1}{2} \sum_{i \neq j}^N \sum^N \left[\left[\frac{e^2}{r_{12}} \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) \psi_i(\vec{r}_2) \psi_j(\vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \sum_{a \neq b}^N \frac{e^2}{R_{ab}} \right. \right. \right. \\
& \left. \left. \left(// \text{ spins} \right) \right] \right] \quad (A.7)
\end{aligned}$$

If i is put equal to j , the integrands in the second and third terms of (A.7) cancel each other. Thus the condition $i \neq j$ can be omitted. Therefore (A.7) becomes

$$\begin{aligned}
E = & \sum_1^N \left[\psi_1^*(\vec{r}_1) \left(-\frac{\hbar^2}{2m} \nabla_1^2 + \sum_a^N V_a(\vec{r}_1) \right) \psi_1(\vec{r}_1) \right] d\vec{r}_1 \\
& + \frac{1}{2} \sum_i^N \sum_j^N \left[\left[\frac{e^2}{r_{12}} |\psi_i(\vec{r}_1)|^2 |\psi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \right. \right. \\
& \left. \left. - \frac{1}{2} \sum_{i,j}^N \sum^N \left[\left[\frac{e^2}{r_{12}} \psi_i^*(\vec{r}_1) \psi_j^*(\vec{r}_2) \psi_i(\vec{r}_2) \psi_j(\vec{r}_1) \right] d\vec{r}_1 d\vec{r}_2 \right. \right. \right. \\
& \left. \left. \left(// \text{ spins} \right) \right] \right] \\
& + \frac{1}{2} \sum_{a \neq b}^N \sum^N \frac{e^2}{R_{ab}} \quad (A.7a)
\end{aligned}$$

Using Hartree's method and the variational principle, the terms on the right hand side of the above equation which having concern with ψ_1 can be written in the form

$$\int \psi_1^*(\vec{r}_1) H_1 \psi_1(\vec{r}_1) d\vec{r}_1 \quad (A.8)$$

H_i is represented by

$$\begin{aligned}
 H_i = & -\frac{\hbar^2}{2m} \nabla_1^2 + \sum_a^N V_a(\vec{r}_1) + e^2 \sum_j^N \left(\frac{|\psi_j(\vec{r}_2)|^2}{r_{12}} \int d\vec{r}_2 \right. \\
 & \left. - e^2 \sum_j^N \int \frac{\psi_j^*(\vec{r}_2) \psi_i(\vec{r}_2) \psi_j(\vec{r}_1) d\vec{r}_2}{r_{12} \psi_i(\vec{r}_1)} \right) . \quad (A.9) \\
 & \text{(spin } j \\
 & \text{=spin } i)
 \end{aligned}$$

To obtain the ground state energy, ψ_i must be chosen so as to minimize (A.8). The variational principle tells that the corresponding energy of ψ_i is the lowest eigenvalue of the equation

$$H_i \psi_i = \epsilon_i \psi_i \quad (A.10)$$

Substituting (A.9) into (A.10) with the new subscript \vec{k} , \vec{k}' and sum \vec{k} over all the occupied orbital states. At absolute zero, each state contains two electrons with opposite spins. Thus (A.10) can be rewritten as

$$\begin{aligned}
 & \left(-\frac{\hbar^2}{2m} \nabla_1^2 + \sum_a^N V_a(\vec{r}_1) + e^2 \sum_{\vec{k}'}^N \left(\frac{|\psi_{\vec{k}'}(\vec{r}_2)|^2}{r_{12}} \int d\vec{r}_2 \right) \psi_{\vec{k}}(\vec{r}_1) \right. \\
 & \left. - e^2 \sum_{\vec{k}'}^N \left(\int \frac{\psi_{\vec{k}'}^*(\vec{r}_2) \psi_{\vec{k}}(\vec{r}_2) \psi_{\vec{k}'}(\vec{r}_1) d\vec{r}_2}{r_{12} \psi_{\vec{k}}(\vec{r}_1)} \right) \right) \psi_{\vec{k}}(\vec{r}_1) = \epsilon_{\vec{k}} \psi_{\vec{k}}(\vec{r}_1) . \quad (A.11) \\
 & \text{(spin } j \\
 & \text{=spin } i)
 \end{aligned}$$

The second and the third terms in the bracket represent the Hartree field. In free-electron gas, the approximation involved is that of replacing the actual charge distribution of the ion-cores by a uniform distribution of the same total charge which is sufficient to neutralize the charge of the electron. Thus the total Hartree field is zero. Equation (A.11) reduces to

$$\left(-\frac{\hbar^2}{2m} \nabla_1^2 - e^2 \sum_{\vec{k}'} \int \frac{\psi_{\vec{k}'}^*(\vec{r}_2) \psi_{\vec{k}}(\vec{r}_2) \psi_{\vec{k}'}(\vec{r}_1) d\vec{r}_2}{r_{12} \psi_{\vec{k}}(\vec{r}_1)} \right) \psi_{\vec{k}}(\vec{r}_1) = \epsilon_{\vec{k}} \psi_{\vec{k}}(\vec{r}_1). \quad (\text{A.12})$$

The normalized eigenfunction of the Hartree equation is

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}, \quad (\text{A.13})$$

and must also be eigenfunction of (A.12) with different corresponding eigenvalues. If the wave function (A.13) is used, the exchange term, the second term on the left hand side of the (A.12) becomes

$$-\frac{e^2}{V} \sum_{\vec{k}'} (e^{-i(\vec{k}-\vec{k}') \cdot \vec{r}_1} \int \frac{e^{i(\vec{k}-\vec{k}') \cdot \vec{r}_2}}{r_{12}} d\vec{r}_2) \psi_{\vec{k}}(\vec{r}_1). \quad (\text{A.14})$$

$$\text{The integral } e^{-i(\vec{k}-\vec{k}') \cdot \vec{r}_1} \int \frac{e^{i(\vec{k}-\vec{k}') \cdot \vec{r}_2}}{r_{12}} d\vec{r}_2 \quad (\text{A.15})$$

must be taken into the consideration. In order to evaluate this integral, the electrostatic theory is utilized. The function $e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$ is supposed to be the charge density distribution which creates potential $\phi(\vec{r})$ at the point \vec{r} . This is not a physically real distribution but must be treated for the purpose of the calculation. $\phi(\vec{r})$ should satisfy Poisson's equation

$$\nabla^2 \phi(\vec{r}) = -4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}$$

The required solution is $\phi(\vec{r}) = \frac{4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}}{|\vec{k} - \vec{k}'|^2}$,

or

$$\phi(\vec{r}_1) = \frac{4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_1}}{|\vec{k} - \vec{k}'|^2} \quad (\text{A.16})$$

The potential $\phi(\vec{r}_1)$ in terms of charge distribution is

$$\phi(\vec{r}_1) = \int \frac{\rho(\vec{r}_2) d\vec{r}_2}{r_{12}},$$

$$\phi(\vec{r}_1) = \int \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_2}}{r_{12}} d\vec{r}_2 \quad (\text{A.17})$$

Since (A.16) and (A.17) are equal, we have

$$\int \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_2}}{r_{12}} d\vec{r}_2 = \frac{4\pi e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_1}}{|\vec{k} - \vec{k}'|^2} \quad (\text{A.18})$$

The integral (A.15) becomes $\frac{4\pi}{|\vec{k} - \vec{k}'|^2}$, and the exchange term (A.14) may be written as $\epsilon_x(\vec{k}) \psi_{\vec{k}}(\vec{r}_1)$ with the exchange energy

$$\epsilon_x(\vec{k}) = -\frac{4\pi e^2}{V} \sum_{\vec{k}'} \frac{1}{|\vec{k} - \vec{k}'|^2} \quad (A.19)$$

Replacing the sum by an integral, (A.19) becomes

$$\epsilon_x(\vec{k}) = -\frac{4\pi e^2}{V} \cdot \frac{V}{8\pi^3} \int \frac{d\vec{k}'}{|\vec{k} - \vec{k}'|^2},$$

and the total energy E_x is

$$E_x = \sum_{\vec{k}} \epsilon_x(\vec{k}) = -\frac{e^2 V}{16\pi^5} \left(\int \frac{d\vec{k} d\vec{k}'}{k^2 \left(1 + \frac{k'^2}{k^2} - \frac{2k'}{k} \cos \theta\right)} \right) \quad (A.20)$$

Now with $\mu = \cos \theta$ and $s = \frac{k'}{k}$, we obtain

$$\frac{1}{k^2 \left(1 + \frac{k'^2}{k^2} - \frac{2k'}{k} \cos \theta\right)} = \frac{1}{k^2 (1 + s^2 - 2s\mu)}$$

For the half space $s < 1$, we have

$$\frac{1}{1 + s^2 - 2s\mu} = \left(\sum_{\ell} s^{\ell} P_{\ell}(\mu) \right)^2 = \sum_{\ell, \lambda} s^{\ell+\lambda} P_{\ell}(\mu) P_{\lambda}(\mu),$$

where $P_{\ell}(\mu)$ and $P_{\lambda}(\mu)$ are Legendre polynomials. Thus

$$E_x = - \frac{e^2 V}{16\pi^5} \left(2 \int_{k < k_0} d\vec{k} \int_{k' < k} 2\pi k'^2 dk' d\mu \sum_{\ell, \lambda} \left(\frac{k'}{k}\right)^{\ell+\lambda} \cdot \frac{1}{k^2} P_\ell(\mu) P_\lambda(\mu) \right),$$

where we have used the normalization condition

$$\int_{-1}^1 P_\ell(\mu) P_\lambda(\mu) d\mu = \frac{2}{2\ell+1} \delta_{\ell\lambda}$$

By counting the both space $k' < k$ and $k < k'$, we obtain

$$\begin{aligned} E_x &= - \frac{e^2 V}{2\pi^4} \left(\int_0^{k_0} d\vec{k} k \sum_{\ell} \frac{1}{(2\ell+1)(2\ell+3)} \right), \\ &= - \frac{e^2 V}{2\pi^4} k_0^4 \left(\sum_{\ell=0}^{\infty} \frac{1}{2} \left(\frac{1}{2\ell+1} - \frac{1}{2\ell+3} \right) \right), \\ E_x &= - \frac{e^2 V}{4\pi^3} k_0^4 \quad . \quad (A.21) \end{aligned}$$

Here k_0 is the magnitude of the wave vector at the Fermi sphere,

$$k_0 = \left(3\pi^2 \frac{N}{V} \right)^{\frac{1}{3}}, \quad (A.22)$$

N/V is the electron concentration. Since the atomic sphere volume is

$$\frac{4}{3} \pi r_s^3 = \frac{V}{N}, \quad (\text{A.23})$$

and making use of (A.22) and (A.23), the exchange energy becomes

$$E_x = -\frac{3e^2 N}{4} \left(\frac{9}{4\pi^2}\right)^{\frac{1}{3}} \cdot \frac{1}{r_s}.$$

The exchange energy per electron E_{xe} is

$$E_{xe} = -\frac{3}{2} \left(\frac{9}{4\pi^2}\right)^{\frac{1}{3}} \cdot \frac{1}{r_s},$$

$$E_{xe} = -\frac{0.916}{r_s} \text{ ryd.} \quad (\text{A.24})$$

According to (A.7), transforming this into the \vec{k} - notation and using the fact that at the absolute zero there are two electrons with opposite spins in each occupied orbital state $\psi_{\vec{k}}(\vec{r})$, we get

$$\begin{aligned} NE_0 = & 2 \sum_{\vec{k}} \int \psi_{\vec{k}}^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_a V_a(\vec{r}) \right) \psi_{\vec{k}}(\vec{r}) d\vec{r} \\ & + 2 \sum_{\vec{k}} \sum_{\vec{k}'} \left(\int \frac{e^2}{r_{12}} |\psi_{\vec{k}}(\vec{r}_1)|^2 |\psi_{\vec{k}'}(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \right. \\ & \left. - \sum_{\vec{k}} \sum_{\vec{k}'} \left(\int \frac{e^2}{r_{12}} \psi_{\vec{k}}^*(\vec{r}_1) \psi_{\vec{k}'}^*(\vec{r}_2) \psi_{\vec{k}}(\vec{r}_2) \psi_{\vec{k}'}(\vec{r}_1) d\vec{r}_1 d\vec{r}_2 \right) + \frac{1}{2} \sum_{a \neq b} \sum_{\vec{k}} \frac{e^2}{R_{ab}} \right), \end{aligned}$$

where $\Psi_{\vec{k}}(\vec{r})$ satisfies the equation

$$\nabla^2 \Psi_{\vec{k}}(\vec{r}) + \frac{2m}{\hbar^2} (\epsilon(\vec{k}) - V(\vec{r})) \Psi_{\vec{k}}(\vec{r}) = 0, \quad (\text{A.26})$$

and the spherically symmetric potential energy $V(\vec{r})$ due to an electron in the field of the ion-core is defined as

$$\begin{aligned} V(\vec{r}) &= \sum_a^N U_a(\vec{r}), \\ U_a(\vec{r}) &= \begin{cases} V_a(\vec{r}) & \text{within cell (a),} \\ 0 & \text{outside cell(a).} \end{cases} \end{aligned} \quad (\text{A.27})$$

If $\rho(\vec{r})$ denotes the number density of electrons with both kinds of spin at position \vec{r} , then

$$\rho(\vec{r}) = 2 \sum_{\vec{k}} |\Psi_{\vec{k}}(\vec{r})|^2, \quad (\text{A.28})$$

with $\Psi_{\vec{k}}(\vec{r})$ is assumed to be normalized to unity. It follows from (A.25), (A.26), (A.27) and (A.28) that the first term in (A.25) can be rewritten as

$$\begin{aligned} & 2 \sum_{\vec{k}} \int \Psi_{\vec{k}}^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + \sum_a^N V_a(\vec{r}) \right) \Psi_{\vec{k}}(\vec{r}) d\vec{r} \\ &= 2 \sum_{\vec{k}} \int \Psi_{\vec{k}}^*(\vec{r}) (\epsilon(\vec{k}) - V(\vec{r}) + \sum_a^N V_a(\vec{r})) \Psi_{\vec{k}}(\vec{r}) d\vec{r}, \\ &= 2 \sum_{\vec{k}} \epsilon(\vec{k}) + \int \rho(\vec{r}) \left(\sum_a^N V_a(\vec{r}) - V(\vec{r}) \right) d\vec{r}, \end{aligned}$$

$$\begin{aligned}
&= 2 \sum_{\vec{k}} \epsilon(\vec{k}) + \sum_a^N \int \rho(\vec{r}) (V_a(\vec{r}) - U_a(\vec{r})) d\vec{r} \quad , \\
&= 2 \sum_{\vec{k}} \epsilon(\vec{k}) + \sum_{b \neq a}^N \sum_{(b)}^N \int \rho(\vec{r}) V_a(\vec{r}) d\vec{r} \quad , \quad (\text{A.29})
\end{aligned}$$

by using the property of $U_a(\vec{r})$ in (A.27). Assuming that for all points outside cell (a) the potential energy of the interaction between the ion core in cell (a) of position \vec{R}_a and the valence electron charge distribution in cell (b) regarded as concentrated at the center of the cell is

$$V_a(\vec{r}) = - \frac{e^2}{|\vec{R}_b - \vec{R}_a|} \quad . \quad (\text{A.30})$$

The integration in (A.29) with (A.30) is therefore

$$\begin{aligned}
\int_{(b)} \rho(\vec{r}) V_a(\vec{r}) d\vec{r} &= - \int_{(b)} \frac{e^2}{|\vec{R}_a - \vec{R}_b|} \rho(\vec{r}) d\vec{r} \quad , \\
&= - \frac{e^2}{R_{ab}} \quad .
\end{aligned}$$

(A.29) becomes

$$2 \sum_{\vec{k}} \epsilon(\vec{k}) - \sum_{a \neq b}^N \sum_{(b)}^N \frac{e^2}{R_{ab}} \quad . \quad (\text{A.31})$$

The second term of the equation (A.25) or Coulomb term becomes

$$\begin{aligned}
 2 \sum_{\vec{k}} \sum_{\vec{k}'} \left(\int \int \frac{e^2}{r_{12}} |\psi_{\vec{k}}(\vec{r}_1)|^2 |\psi_{\vec{k}'}(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \right) &= \frac{1}{2} \left(\int \int \frac{e^2}{r_{12}} \rho(\vec{r}_1) \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \right), \\
 &= \frac{1}{2} \sum_{a \neq b}^N \sum^N \int_{(a)} \int_{(b)} \frac{e^2}{r_{12}} \rho(\vec{r}_1) \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 + \frac{N}{2} \int_{(a)} \int_{(a)} \frac{e^2}{r_{12}} \rho(\vec{r}_1) \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2, \\
 &= \frac{1}{2} \sum_{a \neq b}^N \sum^N \frac{e^2}{R_{ab}} + \frac{N}{2} \int_{(a)} \int_{(a)} \frac{e^2}{r_{12}} \rho(\vec{r}_1) \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad . \quad (\text{A.32})
 \end{aligned}$$

From (A.25), (A.31) and (A.32), we get

$$\begin{aligned}
 NE_0 &= 2 \sum_{\vec{k}} \epsilon(\vec{k}) + \frac{N}{2} \int_{(a)} \int_{(a)} \frac{e^2}{r_{12}} \rho(\vec{r}_1) \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\
 &\quad - \sum_{\vec{k}} \sum_{\vec{k}'} \left(\int \int \frac{e^2}{r_{12}} \psi_{\vec{k}}^*(\vec{r}_1) \psi_{\vec{k}}^*(\vec{r}_2) \psi_{\vec{k}}(\vec{r}_2) \psi_{\vec{k}'}(\vec{r}_1) d\vec{r}_1 d\vec{r}_2 \right) \quad . \quad (\text{A.33})
 \end{aligned}$$

Since

$$\epsilon(\vec{k}) = \epsilon_0 + \alpha \frac{\hbar^2 k^2}{2m} \quad ,$$

we have

$$2 \sum_{\vec{k}} \epsilon(\vec{k}) = N(\epsilon_0 + \alpha E_F) \quad ,$$

where $E_F = \frac{\hbar^2 k^2}{2m}$ is the free electron Fermi energy.

The second term in (A.33) is the self-potential energy

of a charge distribution of density $\rho(\vec{r})$ within an atomic polyhedron. In the free-electron approximation, the number density

$$\rho(\vec{r}) = \frac{N}{V} = \frac{3}{4\pi r_s^3} .$$

The self-potential energy term is $\frac{N}{2} \int_{(a)} \int_{(a)} e^2 \left(\frac{3}{4\pi r_s^3} \right)^2 \frac{1}{r_{12}} d\vec{r}_1 d\vec{r}_2$,

(A.34)

and it can be proved¹⁷ that

$$\begin{aligned} \iint \frac{d\vec{r}_1 d\vec{r}_2}{r_{12}} &= 32\pi^2 \int_0^{r_s} r dr \int_0^r r^2 dr , \\ &= 32\pi^2 \frac{r_s^5}{15} , \end{aligned}$$

then (A.34) becomes

$$\frac{9e^2 N}{2(4\pi r_s^3)^2} \cdot \frac{32\pi^2}{15} r_s^5 = \frac{3e^2 N}{5r_s} ,$$

or can be written in the atomic units as $\frac{1.2N}{r_s}$ ryd.

The self-potential energy per atom is $\frac{1.2}{r_s}$ ryd. (A.35)

The last term in (A.33) is the exchange energy which has been given in (A.24).

APPENDIX B



CORRELATION ENERGY^{17,21-24}

We present here procedure for obtaining the expressions for the correlation energy. The two methods which will be given are that of Wigner^{21,22}, and of Bohm and Pines^{23,24}. Wigner's approach will be introduced first. This approach can be separated into two cases, i.e., at high-density limit and at low-density limit. The former case will be considered first.

As is well known, the wave function for a system of electrons occupying n doubly-degenerate states can be written as the product of the Hartree-Fock determinants for spin up and spin down electrons :

$$\Psi = \frac{1}{n!} \begin{vmatrix} \psi_1(\vec{x}_1) \dots \psi_1(\vec{x}_n) \\ \vdots \\ \psi_n(\vec{x}_1) \dots \psi_n(\vec{x}_n) \end{vmatrix} \cdot \begin{vmatrix} \psi_1(\vec{y}_1) \dots \psi_1(\vec{y}_n) \\ \vdots \\ \psi_n(\vec{y}_1) \dots \psi_n(\vec{y}_n) \end{vmatrix}, \quad (\text{B.1})$$

where \vec{x} stands for three Cartesian coordinates of electrons with upward spin, and \vec{y} for those of electrons with downward spin. Wigner assumed that there is a statistical correlation between the positions of electrons with antiparallel spin. This led to an improvement of the wave function and

to a lowering of the energy value. The energy gained this way was called "the correlation energy". The new form of the wave function was²¹

$$\Psi = \frac{1}{n!} \begin{vmatrix} \psi_1(\vec{y}_1 \dots \vec{y}_n; \vec{x}_1) \dots \psi_1(\vec{y}_1 \dots \vec{y}_n; \vec{x}_n) \\ \vdots \\ \psi_n(\vec{y}_1 \dots \vec{y}_n; \vec{x}_1) \dots \psi_n(\vec{y}_1 \dots \vec{y}_n; \vec{x}_n) \end{vmatrix} \cdot \begin{vmatrix} \psi_1(\vec{y}_1) \dots \psi_1(\vec{y}_n) \\ \vdots \\ \psi_n(\vec{y}_1) \dots \psi_n(\vec{y}_n) \end{vmatrix} \quad (\text{B.2})$$

This form of wave function was used to calculate the expectation value of the energy. The energy was then minimized to give the values of y and E . In order to obtain $\psi_Y(\vec{x}, \vec{y})$, the second order Rayleigh-Schrödinger perturbation theory was employed. The normalization constant (Ψ^*, Ψ) is neglected. The expressions obtained are very complicated and were calculated numerically by Wigner. For $r_s = 1$, the correlation energy per electron turns out to be²³

$$E = - \frac{0.88}{7.8} \text{ ryd.} \quad (\text{B.3})$$

We next consider the low-density limit ($r_s \gg 20$) in which the electrons are in a uniform positive background. The potential energy of interaction between electrons go as $\frac{1}{r_s}$ while the kinetic energy behave as $\frac{1}{r_s^2}$. For large values of r_s , the kinetic energy is of very small magnitude when compared with the potential energy. In order to obtain the total energy of electron in solid, two

assumptions were made. One makes a cellular approximation and neglects the interaction between each cell²³.

The potential $V(r)$ at a distance r from the center due to the positive charge in the sphere of radius r_0 is

$$\begin{aligned} V(r) &= \left[e \int_{r' > r} \frac{d^3 r'}{|\vec{r}' - \vec{r}|} + e \int_{r' < r} \frac{d^3 r'}{|\vec{r}' - \vec{r}|} \right] \left(\frac{3}{4\pi r_s^3} \right) \\ &= \frac{3e}{2r_0} - \frac{e}{2r_0^3} r^2 \end{aligned} \quad (B.4)$$

The corresponding potential energy is therefore

$$PE = -\frac{3e^2}{2r_0} + \frac{e^2}{2r_0^3} r^2 \quad (B.5)$$

The Hamiltonian for the harmonic oscillator becomes

$$H = \frac{p^2}{2m} - \frac{3e^2}{2r_0} + \frac{e^2}{2r_0^3} r^2 \quad (B.6)$$

It can be seen that the frequency of oscillation is given by

$$\omega^2 = \frac{e^2}{mr_0^3} = \frac{\omega_p^2}{3},$$

where the plasma frequency ω_p and the density of electrons n are defined by

$$\omega_p^2 = \frac{4\pi n e^2}{m},$$

and

$$n = \frac{1}{\frac{4}{3} \pi r_s^3}$$

The lowest state energy in three directions of oscillation can be written²³ as

$$E = -\frac{3e^2}{2r_0} + \frac{\sqrt{3}}{2} \hbar\omega_p \quad (B.7)$$

The energy $\hbar\omega_p$ in atomic units is

$$\hbar\omega_p = \left[\frac{12}{r_s^3} \right]^{\frac{1}{2}} \text{ ryd.},$$

where $r_s = r_0/a_0$, a_0 is the Bohr radius. The total energy E is thus

$$E = -\frac{3}{r_s} + \frac{3}{r_s^{3/2}} \quad (B.8)$$

in atomic units.

Since the correlation energy is defined as the energy beyond that of Hartree-Fock¹⁷, the Hartree-Fock energy is obtained from the sum of the self-energy of electron, the interaction energy with the positive background and the exchange energy. The self-energy of the electron is $\frac{1.2}{r_s}$ according to (A.35) in appendix A. The interaction energy of electron with the positive background

is negative and twice the self-energy, i.e., $-\frac{2.4}{r_s}$. From (A.24) the exchange energy is $-\frac{0.92}{r_s}$. Therefore the Hartree-Fock energy is

$$E_{\text{HF}} = -\frac{2.4}{r_s} + \frac{1.2}{r_s} - \frac{0.92}{r_s} = -\frac{2.12}{r_s} \text{ ryd} \quad (\text{B.9})$$

Comparing the E_{HF} and the leading term in (B.8), we have

$$E_{\text{cor}} = -\frac{0.88}{r_s} \text{ ryd.} \quad (\text{B.10})$$

By interpolation of the correlation energy to between that high-densities limit and low-densities limit, we obtain the correlation energy of the metallic densities as²³

$$w = -\frac{0.88}{r_s + 7.8} \text{ ryd.} \quad (\text{B.11})$$

Another approach to the correlation energy calculation is the theory of plasma oscillations due to Bohm and Pines^{23,24}. This theory is based on the close resemblance to a classical plasmas. (Classical plasmas are highly ionized gas which are composed of electrons and positive charges with low densities and high temperatures^{17,23}.) Metal may also be regarded as a quantum plasmas since it is composed of the positive ions arrange on a crystal lattice with high densities and low temperatures^{17,23}. The conduction electrons are in fact quite mobile. In the case of free-electron approximation, the ion-core is replaced by the uniform

distribution of positive charges whose the density is equal to the average electronic density. The motion of electrons thus overshoot the charge in some regions. As a result, the imbalance remains, the electrons are attracted back and overshoot again, etc. Thus a longitudinal oscillation, plasma oscillation, is set up. The frequency²⁴ of this oscillation can be calculated by assuming that a charge imbalance is established in the plasma from the displacement of a slab of charge by a distance ξ . If it is assumed that the plasma is otherwise unaffected, the slab will behave like a condensor. An electric field is established in the interior to restore the charge balance and which the magnitude is $E = 4\pi\sigma$, σ is the excess surface charge density at either end and is given by $ne\xi$. Here n is average electron density. The equation of motion for an electron inside the slab is

$$m\ddot{\xi} = -eE = -4\pi ne^2\xi \quad . \quad (B.12)$$

This equation shows that the electrons will oscillate at a frequency ω_p , where

$$\omega_p = \frac{4\pi ne^2}{m} \quad , \quad (B.13)$$

which is called the plasma frequency.

However, this frequency ω_p is possible only when the wavelength is sufficiently long as will be shown. The potential energy due to the Coulomb interaction between the i^{th} and j^{th} electrons can be written¹⁷ in the Fourier series as

$$\frac{e^2}{r_{ij}} = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \quad , \quad (\text{B.14})$$

where

$$\vec{k} = 2\pi (n_1 \hat{e}_1 + n_2 \hat{e}_2 + n_3 \hat{e}_3) \quad ,$$

and $\hat{e}_1, \hat{e}_2, \hat{e}_3$ being unit vectors along three mutually orthogonal edges of the unit cubic metal and n_1, n_2, n_3 being integers. The sum is taken over all integral values of n_1, n_2, n_3 including zero. To determine the coefficients $C_{\vec{k}}$ we multiply both sides of (B.14) by $\exp [i\vec{k}' \cdot (\vec{r}_j - \vec{r}_i)]$ and integrate with respect to \vec{r}_j over the volume of the box. Thus we have

$$C_{\vec{k}} = \frac{4\pi e^2}{k^2} \quad , \quad (\text{B.15})$$

except for $k = 0$. C_0 is obtained by integrating (B.14), this gives

$$C_0 = e^2 \int \frac{d\vec{r}_j}{r_{ij}} \quad (\text{B.16})$$

which is the potential energy of the i^{th} electron due to a uniform distribution of one electronic charge throughout the box. From (B.14) the total potential energy of the i^{th} electron, $U(\vec{r}_i)$, due to the interaction with all other electrons and the positive background is

$$U(\vec{r}_i) = \sum_{j \neq i} \sum_{\vec{k}}' \frac{4\pi e^2}{k^2} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} , \quad (\text{B.17})$$

while the prime indicates that the term $k = 0$ is excluded since it is cancelled out by the positive background. Since the total force F_i exerted on the i^{th} electron is

$$F_i = - \text{grad}_i U(\vec{r}_i) .$$

We now have

$$\ddot{v}_i = - \frac{1}{m} \left[4\pi e^2 \sum_j \sum_{\vec{k}}' \frac{\vec{k}}{k^2} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \right] , \quad (\text{B.18})$$

If we can regard the electrons as point particles, the electronic charge density is then $-\rho(\vec{r})$, where

$$\rho(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i) . \quad (\text{B.19})$$

$\delta(\vec{r} - \vec{r}_i)$ being the Dirac delta function and the sum being over all the electrons. $\rho(\vec{r})$, the particle density, can be expanded in Fourier series within the box, i.e.,

$$\rho(\vec{r}) = \sum_{\vec{k}} \rho_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} , \quad (\text{B.20})$$

$$\rho_{\vec{k}} = \int \rho(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d\vec{r} \quad (B.21)$$

From (B.19), we have

$$\rho_{\vec{k}} = \sum_i e^{-i\vec{k}\cdot\vec{r}_i} \quad (B.22)$$

The Fourier coefficient ρ_0 from (B.21) is the average electron density n while the other coefficients represent the fluctuation about this average density. Equation (B.18) can be expressed in terms of the density fluctuation as

$$\ddot{\vec{v}}_i = -\frac{4\pi e^2}{m} \sum_{\vec{k}} \frac{\vec{k}}{k^2} \rho_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} \quad (B.23)$$

We have from (B.22)

$$\ddot{\rho}_{\vec{k}} = -\sum_i \left[(\vec{k}\cdot\vec{v}_i)^2 + i\vec{k}\cdot\dot{\vec{v}}_i \right] e^{i\vec{k}\cdot\vec{r}_i} \quad (B.24)$$

Substituting $\dot{\vec{v}}_i$ from (B.23) into (B.24), we get

$$\ddot{\rho}_{\vec{k}} = -\sum_i (\vec{k}\cdot\vec{v}_i)^2 e^{i\vec{k}\cdot\vec{r}_i} - \frac{4\pi e^2}{m} \sum_i \sum_{\vec{k}'} \frac{\vec{k}\cdot\vec{k}'}{k'^2} \rho_{\vec{k}'} e^{i(\vec{k}'-\vec{k})\cdot\vec{r}_i} \quad (B.25)$$

The last term of (B.25) can be considered as being composed of two parts, one with $\vec{k}' = \vec{k}$ and another with $\vec{k}' \neq \vec{k}$, i.e.,

$$-\frac{4\pi e^2}{m} \sum_i \sum_{\vec{k}'} \frac{\vec{k}\cdot\vec{k}'}{k'^2} \rho_{\vec{k}'} e^{i(\vec{k}'-\vec{k})\cdot\vec{r}_i} = -\frac{4\pi e^2 n}{m} \rho_{\vec{k}}$$

$$-\frac{4\pi e^2 n}{m} \sum_i \sum_{\vec{k}' \neq \vec{k}} \frac{\vec{k}\cdot\vec{k}'}{k'^2} \rho_{\vec{k}'} \rho_{\vec{k}-\vec{k}'} \quad (B.26)$$

The second term in the right hand side of (B.25) is now replaced by equation (B.26) and becomes

$$\ddot{\rho}_{\vec{k}} + \omega_p^2 \rho_{\vec{k}} = - \sum_i (\vec{k} \cdot \vec{v}_i)^2 e^{-i\vec{k} \cdot \vec{r}_i} - \frac{4\pi e^2}{m} \sum_i \sum_{\vec{k}' \neq \vec{k}} \frac{\vec{k} \cdot \vec{k}'}{k'}^2 \rho_{\vec{k}'} \rho_{\vec{k}-\vec{k}'}. \quad (\text{B.27})$$

It can be seen that $\rho_{\vec{k}}$ oscillate at a frequency ω_p provided that the two terms on the right hand side of (B.27) are neglected. $\rho_{\vec{k}}$ for $\vec{k} \neq 0$ are the density fluctuation of n and are expected to be small. The phase factor $\exp(-i\vec{k} \cdot \vec{r}_i)$ are complex numbers of unit modulus and $\rho_{\vec{k}}$ is the sum of these unit vectors with random phase directions in the complex plane. For each vector there are always vectors in nearly opposite direction so that the sum is small, and the time average of $\rho_{\vec{k}}$ is zero. Such an approximation is called the random phase approximation (RPA)¹⁷. The second term in the right hand side of (B.27) is the sum of the product of two Fourier coefficients and is small and may be neglected. Within the RPA, the condition for collective oscillatory behavior of $\rho_{\vec{k}}$ and therefore of the entire electron gas is

$$\frac{k^2 v_0^2}{\omega_p^2} \ll 1 \quad \text{or} \quad k^2 \ll k_c^2, \quad ,$$

where k_c is of the order of ω_p/v_0 and v_0 is the velocity at the top of the Fermi distribution. It is expected that the quantum plasmas behave collectively¹⁷ for $k \ll k_c$ with oscillation frequency near ω_p . For short-wavelength $k \gg k_c$ the plasma behaves like a system of free particles since the first term on the right hand side would be dominant. The interaction which is responsible for this case will now be discussed¹⁷.

The total potential energy due to the Coulomb interaction of electrons is

$$\frac{1}{2} \sum_{i \neq j} \sum \frac{e^2}{r_{ij}} \quad . \quad (B.28)$$

Using (B.17), (B.28) can be rewritten as

$$\frac{1}{2} \sum_i U(\vec{r}_i) = \sum_{i \neq j} \sum_{\vec{k}} \frac{2\pi e^2}{k^2} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \quad . \quad (B.29)$$

This expressions can be split into two terms. Substituting (B.22) into the above, we have

$$\frac{1}{2} \sum_i U(\vec{r}_i) = \sum_{\vec{k}} \frac{2\pi e^2}{k^2} (\rho_{\vec{k}}^* \rho_{\vec{k}} - n) \quad . \quad (B.30)$$

The interaction which account for the plasmon is that for $k \ll k_c$. The residual interaction H_{sr} is then responsible for the free electrons for the case $k \gg k_c$. We have

$$H_{sr} = \sum_{i \neq j} \sum_{\vec{k}} \frac{2\pi e^2}{k^2} e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \quad . \quad (B.31)$$

($k > k_c$)

If we consider $\sum_{\vec{k}} \frac{4\pi e^2}{k^2} e^{i\vec{k}\cdot\vec{r}}$ instead of (B.31) and replace
 $(k > k_c)$

the sum by an integral in the k -space, we get

$$\begin{aligned} \frac{1}{8\pi^3} \int_{(k > k_c)} \frac{4\pi e^2}{k^2} e^{i\vec{k}\cdot\vec{r}} d\vec{k} &= \frac{e^2}{2\pi^2} \int_{(k > k_c)} \frac{e^{i\vec{k}\cdot\vec{r}}}{k^2} d\vec{k} \\ &= \frac{2e^2}{\pi} \int_{k_c}^{\infty} \frac{\sin kr}{kr} dk \\ &= \frac{e^2}{r} F(k_c r) \quad , \quad (B.32) \end{aligned}$$

$$\begin{aligned} \text{where } F(k_c r) &= \frac{2}{\pi} \int_{k_c r}^{\infty} \frac{\sin x}{x} dx \quad , \\ &= 1 - \frac{2}{\pi} \text{Si}(k_c r) \quad , \quad (B.33) \end{aligned}$$

$$\text{with } \text{Si}(y) = \int_0^y \frac{\sin x}{x} dx \quad .$$

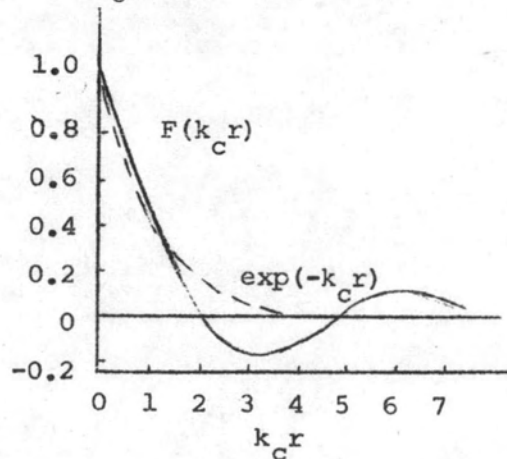


Fig. B.1¹⁷ The full curve represents the function $F(k_c r)$, equation (B.33), and the dash curve represents the function $\exp(-k_c r)$.

The graph of $F(k_c r)$ shown in figure (B.1) is similar to the graph of $\exp(-k_c r)$ for $k_c r$ less than 2. At large values of $k_c r$, the function $F(k_c r)$ oscillate with decreasing amplitude but when modulate by $\frac{e^2}{r}$, the oscillation are negligible. The remaining interaction which acts on the free electron is equivalent to the screened Coulomb interaction or short-range interaction with effective range or screening distance k_c^{-1} . The potential energy due to short-range interaction may be written as

$$H_{sr} = \frac{1}{2} \sum_{i \neq j} \sum \frac{e^2}{r_{ij}} F(k_c r_{ij}) \quad . \quad (B.34)$$

According to the plasma theory¹⁷, the system which consists of n electrons and a uniform distribution of positive charge in a box of unit volume can be described approximately by a set of n particles having a screened Coulomb interaction, together with a set of plasmons one for each k with $k < k_c$. The plasmon may be viewed as particles associated with the plasma oscillation in which the latter are represented approximately by a finite set of harmonic oscillators with frequency ω_p . The energy is $(N + \frac{1}{2}) \hbar \omega_p$, and so the ground state energy is $\frac{1}{2} \hbar \omega_p$. The number of plasmons is $\frac{k_c^3}{6\pi^2}$ which is the number of vector \vec{k} lying within a sphere of radius k_c . The density is $\frac{1}{8\pi^3}$.

Next, we have to find the exchange energy for the short-range interaction between free electrons. From appendix A, the exchange energy associated with the state \vec{k} can be written as

$$\epsilon_x(\vec{k}) = -\frac{e^2}{V} \sum_{\vec{k}'} \int \frac{1}{r} e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} d\vec{r} \quad . \quad (\text{B.35})$$

(The sum is over all the orbital state within the Fermi sphere of state \vec{k}_0 .) Since we are considering the unit volume, V is set to be unity. Substituting (B.17) into (B.35), we obtain

$$\epsilon_x(\vec{k}) = - \sum_{\substack{\vec{k}' \\ (|\vec{k}'| < k_0)}} \int e^{i(\vec{k}-\vec{k}') \cdot \vec{r}} d\vec{r} \sum_{\substack{\vec{k}'' \\ (|\vec{k}''| > k_c)}} \frac{4\pi e^2}{|\vec{k}''|^2} e^{i\vec{k}'' \cdot \vec{r}} \quad . \quad (\text{B.36})$$

We now change \vec{k}' and \vec{k}'' to \vec{k}_1 and \vec{k}_2 respectively. Thus equation (B.36) becomes

$$\epsilon_x(\vec{k}) = - \sum_{\vec{k}_1} \sum_{\vec{k}_2} \frac{4\pi e^2}{|\vec{k}_2|^2} \int e^{i(\vec{k}-\vec{k}_1+\vec{k}_2) \cdot \vec{r}} d\vec{r} \quad . \\ (|\vec{k}_1| < k_0) (|\vec{k}_2| > k_c)$$

Evaluating the integral, $\epsilon_x(\vec{k})$ becomes

$$\epsilon_x(\vec{k}) = -4\pi e^2 \sum_{\vec{k}_1} \frac{1}{|\vec{k}_1-\vec{k}|^2} \quad . \\ (|\vec{k}_1| < k_0 \\ |\vec{k}_1-\vec{k}| > k_c)$$

Replacing the sum by an integral in k -space, we get

$$\epsilon_x(\vec{k}) = -\frac{e^2}{2\pi^2} \int \frac{d\vec{k}_1}{|\vec{k}_1 - \vec{k}|^2}, \quad (\text{B.37})$$

where the integral is over the region defined by $|\vec{k}_1| < k_0$ and $|\vec{k}_1 - \vec{k}| > k_c$.

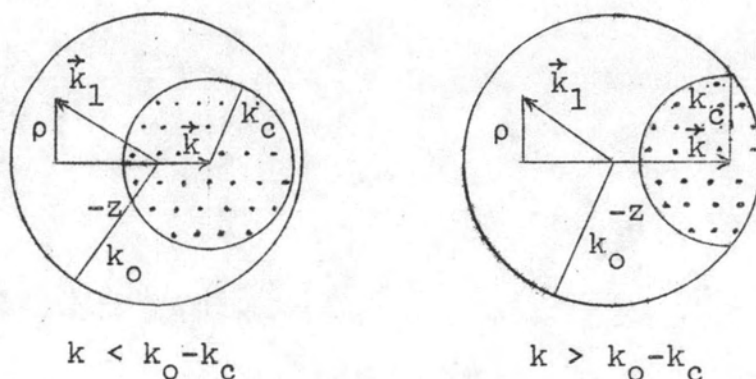


Fig B.2¹⁷ The region of integration for \vec{k}_1 lies inside the Fermi sphere and outside the shaded area.

If we use cylindrical coordinate (ρ, ϕ, z) with origin at k and z -axis is in the \vec{k} -direction. ρ being the perpendicular distance from \vec{k}_1 to the z -axis, we have

$$|\vec{k}_1 - \vec{k}|^2 = \rho^2 + z^2. \quad (\text{B.38})$$

The volume element being considered is $\rho d\rho d\phi dz$. Due to the azimuthal symmetry, the integrand is independent of

ϕ and the integration over $d\phi$ can be performed immediately to obtain 2π . Equation (B.37) for two cases¹⁷ is then given by

$$\epsilon_x(\vec{k}) = -\frac{e^2}{\pi} \int_{-(k+k_0)}^{k_0-k} dz \int_0^{[k_0^2-(z+k)^2]^{\frac{1}{2}}} \frac{\rho d\rho}{\rho^2+z^2} + \frac{e^2}{\pi} \int_{-k_c}^{k_c} dz \int_0^{(k_c^2-z^2)^{\frac{1}{2}}} \frac{\rho d\rho}{\rho^2+z^2}; \quad (\text{B.39})$$

for $k < k_0 - k_c$ and

$$\begin{aligned} \epsilon_x(\vec{k}) = & -\frac{e^2}{\pi} \int_{-(k+k_0)}^{-k_c} dz \int_0^{[k_0^2-(z+k)^2]^{\frac{1}{2}}} \frac{\rho d\rho}{\rho^2+z^2} \\ & - \frac{e^2}{\pi} \int_{-k_c}^{(k_0^2-k_c^2-k^2)/2k} dz \int_0^{[(k_0^2-(z+k)^2)^{\frac{1}{2}}]} \frac{\rho d\rho}{(k_c^2-z^2)^{\frac{1}{2}} \rho^2+z^2}. \end{aligned} \quad (\text{B.40})$$

for $k > k_0 - k_c$. As a result, we obtain for $k < k_0 - k_c$

$$\epsilon_x(\vec{k}) = -\frac{e^2}{2\pi} \left[2k_0 + \frac{k_0^2 - k^2}{k} \log \left(\frac{k_0 + k}{k_0 - k} \right) - 4k_c \right], \quad (\text{B.41})$$

and for $k > k_0 - k_c$

$$\epsilon_x(\vec{k}) = \left[-\frac{e^2}{2\pi} \left(k_0 + \frac{k_0^2 - k^2}{k} \log \left(\frac{k_0 + k}{k_c} \right) + \frac{3k^2 + k_c^2 - k_0^2}{2k} - 2k_c \right) \right]. \quad (\text{B.42})$$

The total exchange energy is nE_x , where E_x is the average exchange energy per electron. Thus we get

$$nE_x = \sum_{\vec{k}} \epsilon_x(\vec{k}) \quad , \quad (\text{B.43})$$

the sum is over all the orbital states within the Fermi sphere. For the purpose of this evaluation, we replace the sum by an integral

$$\begin{aligned} nE_x &= \frac{1}{2\pi^2} \int_0^{k_0} \epsilon_x(\vec{k}) k^2 dk \quad , \\ &= \frac{1}{2\pi^2} \int_0^{k_0-k_c} \epsilon_x(\vec{k}) k^2 dk + \frac{1}{2\pi^2} \int_{k_0-k_c}^{k_0} \epsilon_x(\vec{k}) k^2 dk \quad . \end{aligned} \quad (\text{B.44})$$

The integral has split into two parts;- in the first integral $\epsilon_x(\vec{k})$ must be represented by (B.41), while in the second integral, it is given by (B.42). The result is

$$nE_x = - \frac{3e^2 k_0 n}{4\pi} \left(1 - \frac{4\beta}{3} + \frac{\beta^2}{2} - \frac{\beta^4}{48} \right) \quad , \quad (\text{B.45})$$

where β stands for $\frac{k_c}{k_0}$. The average exchange energy per electron in atomic units is then

$$E_x = - \frac{0.916}{r_s} \left[1 - \frac{4\beta}{3} + \frac{\beta^2}{2} - \frac{\beta^4}{48} \right] \text{ ryd.} \quad . \quad (\text{B.46})$$

The total ground state energy of system considered to Bohm and Pines is expected to consist of the kinetic energy of

the particles, the exchange energy due to short-range interaction and the zero-point energy of the plasmons. In this theory the terms which have been neglected are the coupling between plasmons and electrons and the corrections other than the first order perturbation correction to the electron wave function due to the short range interactions H_{sr} . Since the potential energy of the complete Coulomb interaction is given by (B.30), the remainder of the equation (B.30) after the removal of the short-range interaction can be expressed as

$$\sum_{\vec{k}}' \frac{2\pi e^2}{k^2} \rho_{\vec{k}}^* \rho_{\vec{k}} - \sum_{\vec{k}}' \frac{2\pi e^2 n}{k^2} \quad . \quad (B.47)$$

$(k < k_c) \qquad \qquad \qquad (k < k_c)$

Since the density fluctuation $\rho_{\vec{k}}$ for $k < k_c$ are responsible for plasmons, the first term of (B.47) can be thought as the ground state energy. The zero-point energy of the plasmon is $\frac{1}{2} \hbar \omega_p$. Denoting E_{Bp} as the average energy per electron, the total energy of the system is

$$nE_{Bp} = nE_F + nE_x + \sum_{\vec{k}}' \left(\frac{\hbar \omega_p}{2} - \frac{2\pi e^2 n}{k^2} \right).$$

Replacing the sum by an integral, we get

$$nE_{Bp} = nE_F + nE_x + \frac{k_c^3}{6\pi^2} \left(\frac{\hbar \omega_p}{2} - \frac{2\pi e^2 n}{k^2} \right) \quad . \quad (B.48)$$

With the aid of (A.22) ($k_0^3 = 3\pi^2 n$ for unit volume) and of (B.45), we obtain

$$E_{Bp} = E_F - \frac{3e^2 k_0}{4\pi} \left(1 - \frac{4\beta}{3} + \frac{\beta^2}{2} - \frac{\beta^4}{48}\right) + \frac{\hbar\omega_p}{4} \beta^3 - \frac{e^2 k_0}{\pi} \beta$$

$$\text{with } \beta = \frac{k_c}{k_0}.$$

$$E_{Bp} = E_F - \frac{3e^2 k_0}{4\pi} \left(1 - \frac{\beta^2}{2} - \frac{\beta^4}{48}\right) + \frac{\hbar\omega_p}{4} \beta^3. \quad (\text{B.49})$$

From section (2.2) the Fermi energy for free electron

$$E_F = \frac{2.21}{r_s^2} \text{ ryd}, \text{ and the energy term for plasmon in atomic units}^{17} \quad \hbar\omega_p = \frac{2\sqrt{3}}{r_s^{3/2}} \text{ ryd}. \text{ Thus (B.49) can be written in atomic units as}$$

$$E_{Bp} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} \left(1 + \frac{\beta^2}{2} - \frac{\beta^4}{48}\right) + \frac{\sqrt{3}}{2r_s^{3/2}} \beta^3 \text{ ryd}$$

$$E_{Bp} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - \frac{0.458}{r_s} \beta^2 + \frac{0.866}{r_s^{3/2}} \beta^3 + \frac{0.019}{r_s} \beta^4 \text{ ryd}.$$

(B.50)

The first two terms are the average energy per electron E_{HF} in the Hartree-Fock theory.

The remaining terms represent the long-range correlation energy per electron w_ℓ which are not taken into account in the Hartree-Fock theory. Thus

$$w_{\ell} = - \frac{0.458}{r_s} \beta^2 + \frac{0.866}{r_s^{3/2}} \beta^3 + \frac{0.019}{r_s} \beta^4 \text{ ryd.} \quad (\text{B.51})$$

In the calculation of Bohm and Pines¹⁷, the second order perturbative correction due to H_{sr} (the short-range correlation energy) has been omitted. Denoting w_s as the short-range correlation energy per electron, we have¹⁷

$$w_s = - \frac{1}{n} \sum_{j \neq 0} \frac{|(H_{sr})_{oj}|^2}{E_j - E_0}, \quad (\text{B.52})$$

$$\text{where } (H_{sr})_{oj} = \int \Psi_0^* H_{sr} \Psi_j d\tau. \quad (\text{B.53})$$

The normalized wave functions Ψ_0 and Ψ_j are n^{th} -order determinants of free electron functions and represent respectively the ground state and the excited state of the unperturbed system. E_0 and E_j are the corresponding kinetic energies, i.e., the energies of the system of particles in the state Ψ_0 and Ψ_j when no interaction is present. The calculation of the matrix element is omitted here. We assume that the only non-zero matrix elements are those for which Ψ_j contains two excited one-electron functions. This means that Ψ_j is obtained from Ψ_0 by exciting two electrons to lie outside the Fermi sphere. These excited electrons can be either parallel spins or antiparallel spins. It has been founded that the excited electron must have the same spin state as initial state otherwise the matrix element is zero. Equation (B.52)

represents the short-range correlation energy of parallel spins and antiparallel spins. According to Pauli principle, the parallel spins are apart so that the short-range interaction for those can be treated as small quantity. Only the short-range correlation of antiparallel spin remains¹⁷.

Supposing that the two electrons which are raised from Ψ_0 to Ψ_j having the wave vector \vec{k}_1 and \vec{k}_2 with opposite spins. In the excited state, their wave vectors change to $(\vec{k}_1 + \vec{k})$ and $(\vec{k}_2 - \vec{k})$ which lie outside the Fermi sphere and $k > k_c$. However, the momentum of the system must be conserved. Thus we have

$$(H_{sr})_{0j} = \frac{4\pi e^2}{k^2}, \quad (\text{B.54})$$

$$\begin{aligned} E_j - E_0 &= \frac{\hbar^2}{2m} [(\vec{k}_1 + \vec{k})^2 + (\vec{k}_2 - \vec{k})^2 - \vec{k}_1^2 - \vec{k}_2^2] \\ &= \frac{\hbar^2}{2m} \vec{k} \cdot (\vec{k}_1 - \vec{k}_2 + \vec{k}), \end{aligned} \quad (\text{B.55})$$

and thus

$$w_s = -\frac{1}{n} \sum_{\vec{k}} \sum_{\vec{k}_1} \sum_{\vec{k}_2} \frac{m(4\pi e^2)^2}{\hbar^2 k^4 \vec{k} \cdot (\vec{k}_1 - \vec{k}_2 + \vec{k})}. \quad (\text{B.56})$$

Replacing the sums by integrals, we have

$$w_s = -\frac{1}{n} \frac{m(4\pi e^2)^2}{\hbar^2 (8\pi^3)^3} \iiint \frac{d\vec{k} d\vec{k}_1 d\vec{k}_2}{k^4 \vec{k} \cdot (\vec{k}_1 - \vec{k}_2 + \vec{k})}, \quad (\text{B.57})$$

where the regions of integrations are

$$|\vec{k}_1|, |\vec{k}_2| < k_0, k > k_c, |\vec{k}_1 + \vec{k}| > k_0, |\vec{k}_2 - \vec{k}| > k_0.$$

Changing all momenta in units of k_0 and the energy into rydbergs, we obtain

$$w_s = - \frac{3}{16\pi^5} \iiint \frac{d\vec{k} d\vec{k}_1 d\vec{k}_2}{k^4 \vec{k} \cdot (\vec{k}_1 - \vec{k}_2 + \vec{k})} \text{ ryd} \quad , \quad (\text{B.58})$$

where $|\vec{k}_1|, |\vec{k}_2| < 1, k > \beta, |\vec{k}_1 + \vec{k}_2| > 1, |\vec{k}_2 - \vec{k}| > 1$ and $k < 1$. The evaluation of the integral²⁴ in (B.58) yielded the the short-range correlation energy :

$$w_s = -(0.0254 - 0.0626 \log \beta + 0.00637 \beta^2) \text{ ryd} \quad (\text{B.59})$$

The total correlation energy, the sum of (B.51) and (B.59), is

$$w = - \frac{0.458}{r_s} \beta^2 + \frac{0.866}{r_s^{3/2}} \beta^3 + \frac{0.019}{r_s} \beta^4 - 0.0254 + 0.0626 \log \beta - 0.00637 \beta^2 \text{ ryd.} \quad (\text{B.60})$$

It can be seen that the correlation energy is expressed in terms of β . In order to obtain the value of β , Pine²⁴ proposed the minimization of w_ℓ . If the fourth order term of β is neglected, we get

$$\frac{\partial w_\ell}{\partial \beta} = - \frac{0.916}{r_s} \beta + \frac{2.598}{r_s^{3/2}} \beta^2 = 0.$$

The value of β becomes

$$\beta = 0.353 r_s^{\frac{1}{2}} .$$

Upon substitution of this value for β , we obtain the total correlation energy as

$$w = -0.115 + 0.031 \log r_s . \quad (\text{B.61})$$

APPENDIX C

FORTRAN IV PROGRAM FOR SOLVING THE LOWEST STATE ENERGY

The variables used in the expressions for solving the lowest state energy are denoted by the following symbols in the FORTRAN IV program.

	Variables	Symbols in Program
<u>MAIN PROGRAM</u>		
	E(energy)	P(1)
	l	P(2)
	α_l	P(3)
	n	P(9)
	Z_N	ZN
	f_i	Y(I)
	"	
	f_i	YY(I)
	Δr	H
	r_i	X(I)
	r_s	RS
	ΔE	DEL
<u>SUBROUTINE WAVEFT</u>		
	$\frac{f(r_s) - \frac{f(r_s + 10^{-12}) - f(r_s - 10^{-12})}{2 \times 10^{-12}}}{r_s}$	DIFF
<u>REAL FUNCTION FYY</u>		
	$V(r)$	V

MAIN PROGRAM

```

IMPLICIT REAL*8(A-H,O-Z)
COMMON X(1000),Y(1000),YY(1000)/GROUPA/P(10)/GROUPF/H/GROUPE/ZN
COMMON/GROUPG/RS
DIMENSION SUBT(3)
IR=1
IW=3
ERROR = 1. * 10. ** (-9)
5 READ (IR,102) SUBT,ZN
  IF (ZN.EQ.O.) STOP
  WRITE (IW,201) SUBT
  L=0
  P(2)=0
  READ (IR,103) RS,P(1),P(3),P(9)
  CALL WAVEFT(DEL,F2,0)
  DEL=DEL/5.
  X2=P(1)
  NOL=0
  SIGN=1.
1  XI=X2
  F1=F2
  X2=X2+DEL*SIGN
  P(1)=X2
  CALL WAVEFT(DEL,F2,1)
  X2=P(1)
  IF (DABS(F2).LT.ERROR) GOTO7
  NOL=NOL+1
  IF (F1/F2.LT.O.) GOTO2
  IF (DABS(F1).LT.DABS(F2)) SIGN=-SIGN
  IF (NOL.GT.50) GOTO5
  GOTO1
2  IF (DABS(F1/F2).GT.20.) F1=20.*F2 * (-1.)
  IF (DABS(F2/F1).GT.20.) F2=20.*F1 * (-1.)
  Q=(X1*F2-X2*F1)/(F2-F1)
  P(1)=Q
  CALL WAVEFT(DEL,F,1)
  Q=P(1)
  IF (F/F1.LT.O.) GOTO3
  F1=F
  X1=Q
  GOTO4
3  F2=F
  X2=Q
4  IF (DABS(F).LT.ERROR) GOTO6
  IF (DABS(X1-X2).GE.ERROR) GOTO2
6  P(1)=(X1*F2-X2*F1)/(F2-F1)
7  WRITE (IW,200) P(9),P(2),P(1),P(3),RS
  GOTO5

```

```
102 FORMAT(3A4,D8.0)
103 FORMAT(2D7.0,2D12.8)
200 FORMAT(1H0,2(8X,F3.0,5X),4(6X,D12.5))
201 FORMAT(1H1,3A4/1H0,13X,'QUANTUM NO. '/1H ,5X,'PRINCIPAL',9X,
1'ANGULAR',8X,'ENERGY VALUE',8X,'PARAMETER',8X,'ATOMIC RADIUS')
END
```



SUBROUTINE

```

SUBROUTINE WAVEFT(DEL,DIFF,NOP)
IMPLICIT REAL*8(A-H,O-Z)
COMMON X(1000),Y(1000),YY(1000)/GROUPA/P(10)/GROUPF/H/GROUPE/ZN
COMMON/GROUPG/RS
COMMON/GROUPH/N
LOGICAL LPO,LP1
H=2.5D-03/64./2./2.
LPO=.FALSE.
LP1=.FALSE.
X(1)=0.
Y(1)=0.
YY(1)=0.
L=P(2)
N1=P(9)
IF(NOP.GT.0)GOTO11
DEL=((ZN/(P(9)+P(2)))**2)/10.
11 DO 1I=2,5
X(I)=X(I-1)+H
Y(I)=(X(I)**(L+1))*DEXP(-X(I)*ZN/P(9))
XX=X(I)
YYY=Y(I)
1 YY(I)=FYY(XX,YYY)
KKL=0
NBL=0
NB6=0
9 H=2.5D-03/32./2./2./2.
KKL=KKL+1
N=5
NM=0
NO=0
CALL YNME(40,N,N1,L,NM,NO,&8,&7,&4)
DO 2I=1,8
2 CALL YNME(20,N,N1,L,NM,NO,&8,&7,&4)
DO 3I=1,14
3 CALL YNME(40,N,N1,L,NM,NO,&8,&7,&4)
10 IF(KKL.GT.19)GOTO4
IF(NO.EQ.N1-L-1.AND.NM.EQ.N1-L-1)GOTO7
IF(LPO.OR.LP1) DEL = DEL /3.
P(1) = P(1) - 2.*DEL/8.
IF(NOP.EQ.C)GOTO9
IF(.NOT.(LPO.OR.LP1)NBL=NBL+1
IF(NBL.EQ.3)DEL=DEL/4.
IF(NBL.EQ.3)NBL=0
GO TO 9
8 IF(KKL.GT.19)GOTO4
IF(NO.EQ.N1-L-1)GOTO6
IF(NO.LT.N1-L-1)GOTO10

```



```

4 F=FINTP(4,N,RS)
  RS1=RS-1.D-12
  RS2=RS+1.D-12
  F1=FINTP(4,N,RS1)
  F2=FINTP(4,N,RS2)
  DIFF=(F*2.D-12-RS*(F2-F1))/2.D-12/RS
  RETURN
6 EO=P(1)
  IF(LP1)P(1)=(E1+EO)/2.
  LPO=.TRUE.
  IF(.NOT.LP1)P(1)=P(1)+DEL/4.
  IF(NOP.EQ.0)GOTO9
  IF(.NOT.LP1)NB6=NB6+1
  IF(NB6.EQ.3)DEL=DEL/4.
  IF(NB6.EQ.3)NB6=0
  GOTO9
7 E1=P(1)
  IF(LPO)P(1)=(E1+EO)/2.
  LP1=.TRUE.
  IF(.NOT.LPO)P(1)=P(1)-DEL/4.
  IF(NOP.EQ.0)GOTO9
  IF(.NOT.LPO)NBL=NBL+1
  IF(NBL.EQ.3)DEL=DEL/4.
  IF(NBL.EQ.3)NBL=0
  GOTO9
END

SUBROUTINE YNME(NL,/N/,/N1/,/L/,/NM/,/NO/,*,*,*)
IMPLICIT REAL*8(A-H,0-Z)
COMMON X(1000),Y(1000),YY(1000)/GROUPF/H
COMMON/GROUPd/RS
NLL=NL+4
DO 1I=1,NLL
  CALL YNEX2(N)
  N=N+1
  IF(Y(N).GE.Y(N-1).AND.Y(N-1).LT.Y(N-2).OR.Y(N).LT.Y(N-1).AND.
2Y(N-1).GE.Y(N-2))NM=NM+1
  IF(Y(N)/Y(N-1).LT.0.)NO=NO+1
  IF(RS.LT.X(N).AND.NO.EQ.N1-L-1.AND.NM.EQ.NO)RETURN3
  IF(RS.LT.X(N).AND.NO.LT.N1-L-1)RETURN2
  IF(NM.GT.N1-L-1)RETURN1
  IF(DABS(Y(N)).GT.1.D+7)RETURN1
1 CONTINUE
  IF(2.*H.GT.1.)N=N-4
  IF(2.*H.GT.1.)GOTO3
  IF(Y(N).GE.Y(N-1).AND.Y(N-1).LT.Y(N-2).AND.Y(N).LT.Y(N-2).OR.
3Y(N).LT.Y(N-1).AND.Y(N-1).GE.Y(N-2).AND.Y(N).GT.Y(N-2))NM=NM-1
  N=N-8
  DO 2I=1,4

```

```

N=N+1
J=N+1
X(N)=X(J)
Y(N)=Y(J)
2 YY(N)=YY(J)
H=2.*H
3 RETURN
END

```

```

REAL FUNCTION FYY*8(X,Y)
IMPLICIT REAL*8(A-H,O-Z)
COMMON/GROUPA/P(10)/GROUPE/ZN
V=( (ZN-1.)*DEXP(-P(3)*X)+1.)/X
FYY=Y*(P(1)-2.*V+P(2)*(P(2)+1.)/X**2)
RETURN
END

```

```

SUBROUTINEYNEX1(N)
IMPLICIT REAL*8(A-H,O-Z)
COMMON X(1000),Y(1000),YY(1000)/GROUPC/E/GROUPF/H
Y(N+1)=Y(N)+Y(N-2)-Y(N-3)+H*H*(951.*YY(N)+156.*YY(N-1)-594.*
1YY(N-2)-204.*YY(N-3)+51.*YY(N-4))/720.
X(N+1)=X(N)+H
XX=X(N+1)
1 Z=Y(N+1)
YY(N+1)=FYY(XX,Z)
Y(N+1)=2.*Y(N)-Y(N-1)+H*H*(18.*YY(N+1)+209.*YY(N)+4.*YY(N-1)
2+14.*YY(N-2)-6.*YY(N-3)+YY(N-4))/240.
W=Y(N+1)
IF(DABS((W-Z)/W).GE.E)GOTO1
YY(N+1)=FYY(XX,W)
RETURN
END

```

```

SUBROUTINEYNEX2(N)
IMPLICIT REAL*8(A-H,O-Z)
COMMON X(1000),Y(1000),YY(1000)/GROUPC/E/GROUPF/H
E=1.D-12
CALL YNEX1(N)
K=N+1
1 Z=Y(K)
XX=X(K)
CALL YNEX1(K)
Y(N+1)=2.*Y(N)-Y(N-1)-H*H*(YY(N+2)+YY(N-2)-24.*(YY(N+1)+YY(N-1))
3-194.*YY(N))/240.
W=Y(N+1)
YY(N+1)=FYY(XX,W)
IF(DABS((W-Z)/W).GE.E)GOTO1
RETURN
END

```

```
REAL FUNCTION FINTP*8(L,N,RS)
IMPLICIT REAL*8(A-H,O-Z)
COMMON X(1000),Y(1000),YY(1000)/GROUPA/P(10)/GROUPF/H/GROUPE/ZN
FINTP=Y(N)
B=1.
U=(RS-X(N))/H
DO1I=1,L
B=B*(U+DFLOAT(I-1))/DFLOAT(I)
BACNEW=Y(N)
C=1.
DO2II=1,I
C=C*DFLOAT(I-II+1)/DFLOAT(II)*(-1.)
2 BACNEW=BACNEW+C*Y(N-II)
1 FINTP=FINTP+B*BACNEW
RETURN
END
```

VITA

My name is Sirinee Hongwisitkul. I was born in Nakornrajasima on 26th November 1953. I graduated from Chulalongkorn University with B.Sc. in Physics in 1975. During 1975 - 1977 , I got the scholarship from the University Development Commission, National Education Council.

