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HARTREE-FOCK METHOD FOR THE INTERACTION OF LATTICE VIBRATIONS WITH ELECTRONS IN A METAL*)

By

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§ 1. Introduction

It is an important problem in solid state physics accurately to calculate the absolute value of the conductivity and the vibrational frequencies of a metal. One of the difficulties in calculating the conductivity is to formulate exactly the interaction of a valence electron with lattice vibrations. The interaction matrix element is usually assumed[1] as $2/3a_q(\mathrm{e}_q\mathrm{q})C$, where a_q, e_q and q are the amplitude, the polarization vector and the wave number vector of a lattice vibration respectively, and C is the interaction constant introduced as a parameter. PETERSON and NORDHEIM[2] have first successfully calculated the interaction constant C theoretically, although several points of their treatments are open to criticism[3]. BARDEEN[3] treated the problem along their line by the HARTREE's self-consistent field method, taking the *Umklapp processes* into account. The theoretical values of the conductivities of alkali metals obtained by BARDEEN are, however, about twice the experimental values, which discrepancy might be attributed to the neglect of the effects of the exchange and the correlation energies of valence electrons.

The vibrational frequencies of a metal are calculated[4] on the other hand usually by introducing force constants between neighbouring atoms as arbitrary parameters and neglecting the effect of valence electrons.

It is now shown in the present paper that the contribution of the valence electrons to the adiabatic potential of the normal vibrations may be derived from first principles by an extention of the HARTREE-

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FOCK method without introducing any arbitrary parameters. The effects of the exchange energy on the adiabatic potential and on the interaction constant is discussed by substituting the exchange energy with SLATER's simplified expression[5], its validity being simultaneously verified. The conductivity thus derived is in good agreement with the experimental value and the compressibility formulated by the present method is found to be identical with the expression of WIGNER and SEITZ except the contribution from the correlation energy between the antiparallel spin electrons. In the following paper[6], we apply the results to the calculation of the frequencies of normal vitrations of sodium metal.

Further problems given below are left to subsequent papers:

(I) The non-adiabatic solution[7].
(II) The effects of the correlation energy on the interaction constant[7].
(III) The calculations of normal vibrations of Cu[8].
(IV) Anomalous electrical conductivity and DEBYE temperature of Li[8].
(V) The relative lattice stability of alkali metals.
(VI) Theoretical derivation of the GRÜNEISEN constants of alkali metals.
(VII) The conductivity of transition metals[9].

§ 2. HARTREE-FOCK Equation for a Vibrating Metal

The Hamiltonian for a monovalent metal is given, including only the contribution of valence electrons explicitly, as

$$\begin{aligned}\mathscr{H} &= (1/2m)\sum_{i}\mathbf{p}_i^2+(1/2)\sum_{i\neq j}e^2/|\mathbf{r}_i-\mathbf{r}_j|+\sum_{i,l}v_{\mathrm{I}}(\mathbf{r}_i-\mathbf{R}_l)\\ &\quad+(1/2)\sum_{l\neq l'}e^2/|\mathbf{R}_l-\mathbf{R}_{l'}|+(1/2)\sum_{l\neq l'}v_R(\mathbf{R}_l-\mathbf{R}_{l'})+\sum_{l}(M/2)\dot{\mathbf{R}}_l^2,\end{aligned} \tag{2.1}$$

where the first term is the kinetic energy of valence electrons $i, j, \cdots$, the second term coulomb repulsions between them, the third term electron-ion interactions, the fourth or the fifth term coulomb or exchange repulsions between ion-cores $l, l', \cdots$, respectively, and the last term is the kinetic energy of the ions; $\mathbf{p}_i$ or $\mathbf{r}_i$ is the momentum or the coordinate vector of the i-th electron, m or M the mass of an electron or an ion, and $\mathbf{R}_l$ or $\dot{\mathbf{R}}_l$ the coordinate or velocity vector of the l-th ion. The spin-orbit or spin-spin interactions are neglected here.

Let $\mathbf{R}_l^0$ be the equilibrium lattice point of the l-th ion, and $\mathbf{u}_l$ the displacement vector, so that

$$\mathbf{R}_l = \mathbf{R}_l^0 + \mathbf{u}_l \, . \tag{2.2}$$

The $\mathbf{u}_l$ are also expressed[10a)] in terms of normal coordinates a_q and a_q^*;

$$\begin{aligned} \mathbf{u}_l &= \sum_{\mathrm{q},\mathrm{e}_q} \mathbf{u}_{l;\mathrm{q}\mathrm{e}_q} \, , \\ \mathbf{u}_{l;\mathrm{q}\mathrm{e}_q} &= N^{-1/2} \mathbf{e}_q \left\{ a_q \exp(i\mathbf{q}\mathbf{R}_l^0) + a_q^* \exp(-i\mathbf{q}\mathbf{R}_l^0) \right\} \, , \end{aligned} \tag{2.3}$$

where N is the number of ions in unit volume, q the wave number vector, and $\mathbf{e}_q$ is the unit vector in the direction of polarization of the lattice wave, taken in the same sense as $\mathbf{e}_{-q}$, so that $a_q = a_{-q}^*$ by Eq. (2.3). It is frequently convenient[10a)] to define real $\bar{a}_q$ and $\bar{a}_{-q}$ by the relation

$$a_q = 1/\sqrt{2}\,(\bar{a}_q + i\bar{a}_{-q}) \, , \qquad a_q^* = 1/\sqrt{2}\,(\bar{a}_q - i\bar{a}_{-q}) \, . \tag{2.4}$$

We assume as an approximate wave function for the Hamiltonian (2.1),

$$\Phi(\mathbf{k}_1 \cdots \mathbf{k}_N; n_q \cdots) = (N!)^{-1/2} \det|\Psi(\mathbf{k}_i, \mathbf{r}_j; \bar{a}_q \cdots)| \cdot \prod_q Q(n_q, \bar{a}_q), \tag{2.5}$$

where $\mathbf{k}_i$ or n_q specifies the function Ψ or Q, and

$$\int \Psi^*(\mathbf{k}_i, \mathbf{r}; \bar{a}_q \cdots) \Psi^*(\mathbf{k}_i', \mathbf{r}; \bar{a}_q \cdots) d\mathbf{r} = \delta(\mathbf{k}_i, \mathbf{k}_i') \, , \tag{2.6}$$

$$\int Q^*(n_q, \bar{a}_q) Q(n_{q'}, \bar{a}_{q'}) d\bar{a}_q = \delta(n_q, n_{q'}) \, , \tag{2.7}$$

and hence,

$$\int \Phi^* \Phi \prod_{i,q} d\mathbf{r}_i d\bar{a}_q = \prod_{i,q} \delta(\mathbf{k}_i, \mathbf{k}_i') \delta(a_q, a_{q'}) \, . \tag{2.8}$$

The wave equation for Ψ is given from the variational theorem, in an adiabatic approximation, by the following equation,

$$\delta_\Psi \left[\int \det|\Psi^*(\mathbf{k}_i, \mathbf{r}_j; \bar{a}_q \cdots)| \cdot \mathscr{H}^E \det|\Psi(\mathbf{k}_i, \mathbf{r}_j; \bar{a}_q \cdots)| \, d\mathbf{r}_1 \cdots d\mathbf{r}_N \right] = 0 \tag{2.9}$$

with the auxiliary condition Eq. (2.6). In Eq. (2.9) $\mathscr{H}^E$ is the sum of such terms in $\mathscr{H}$ of Eq. (2.1), as to depend on the momenta and coordinates of valence electrons, *i. e.*,

$$\mathscr{H}^E = (1/2m) \sum \mathbf{p}_i^2 + (1/2) \sum_{i \neq j} e^2/|\mathbf{r}_i - \mathbf{r}_j| + \sum_{i,l} v_{\mathrm{I}}(\mathbf{r}_i - \mathbf{R}_l) \, . \tag{2.1E}$$

The equation for Ψ as derived from Eq. (2.9) is.

$$\left\{-\frac{\hbar^2}{2m}\Delta+V_i+V_\rho+V_{\mathrm{ex}}\right\}\Psi(\mathbf{k}_i,\mathbf{r};\bar{a}_q)$$
$$=\left\{E_0(\mathbf{k}_i)+\delta E(\mathbf{k}_i;\bar{a}_q)\right\}\Psi(\mathbf{k}_i,\mathbf{r};\bar{a}_q) \tag{2.10}$$

where

$$V_i(\mathbf{r}_i)=\sum_l v_{\mathrm{I}}(\mathbf{r}_i-\mathbf{R}_l)\,, \tag{2.11}$$

$$V_\rho(\mathbf{r}_i)=2\sum_{\mathbf{k}_j}\int(e^2/r_{ij})\,|\Psi(\mathbf{k}_j,\mathbf{r}_j)|^2d\mathbf{r}_j\,, \tag{2.12}$$

and

$$V_{\mathrm{ex}}\Psi(\mathbf{k}_i,\mathbf{r}_i)=\left\{-\sum_{\mathbf{k}_j}\int(e^2/r_{ij})\Psi^*(\mathbf{k}_j\mathbf{r}_j)\Psi(\mathbf{k}_i\mathbf{r}_j)d\mathbf{r}_j\right\}\Psi(\mathbf{k}_j,\mathbf{r}_i)$$
$$=-\sum_{\mathbf{k}_j}\frac{\int\Psi^*(\mathbf{k}_j\mathbf{r}_j)\Psi(\mathbf{k}_i\mathbf{r}_j)(e^2/r_{ij})\Psi^*(\mathbf{k}_i\mathbf{r}_i)\Psi(\mathbf{k}_j\mathbf{r}_i)dr_j}{\Psi^*(\mathbf{k}_i\mathbf{r}_i)\Psi(\mathbf{k}_i\mathbf{r}_i)}\Psi(\mathbf{k}_i\mathbf{r}_i). \tag{2.13}$$

The summations in Eqs. (2.12) and (2.13) extend over all occupied states. The factor 2 in Eq. (2.12) is the spin factor. The term $\mathbf{k}_i=\mathbf{k}_j$ is cancelled out in Eq. (2.10). V_ρ or V_{ex} depends generally on the electronic configuration $(\mathbf{k}_1,\cdots,\mathbf{k}_N)$, and V_{ex} on $\mathbf{k}_i$ of the valence electron i in question. However, Eq. (2.10) is solved by simplifying the exchange potential Eq. (2.13), as

$$V_{\mathrm{ex}}(\mathbf{r}_i)=-3e^2\left\{(3/8\pi)2\sum_{\mathbf{k}_j}\Psi^*(\mathbf{k}_j\mathbf{r}_i)\Psi(\mathbf{k}_j\mathbf{r}_i)\right\}^{1/3}, \tag{2.14}$$

according to SLATER[5]. V_ρ or V_{ex} depends now only on the electron configuration $(\mathbf{k}_1,\cdots,\mathbf{k}_N)$, so that the $N/2$ equations (2.10) reduces to a single wave equation, which is solved as an ordinary eigen-value problem. The accuracy of the approximation (2.14) will be discussed in §7.

The wave equations for $Q(n_q;\bar{a}_q)$ are readily derived by the variation theorem,

$$\delta_Q\int\Phi^*\mathscr{H}\Phi\prod_{i,q}d\mathbf{r}_i d\bar{a}_q=0\,. \tag{2.15}$$

They are ordinary harmonic oscillator equations, if terms higher than second order with respect to a_q or a_q^* are neglected.

Non-adiabatic approximation will be carried out in a later paper[7] by quantizing the normal coordinates (a_q, a_q^*) or $(\bar{a}_q, \bar{a}_{-q})$ by usual procedure. The correlation effects[7] of anti-parallel spin electrons will, furthermore, be taken into account there by starting from the wave equation

$$\bar{\Phi} = \sum c(\mathbf{k}_1 \cdots \mathbf{k}_N)\Phi(\mathbf{k}_1 \cdots \mathbf{k}_N ;\, n_q \cdots) \tag{2.16}$$

with auxiliary condition $\sum c^* c = 1$, instead of Eq. (2.5), diagonalizing the Hamiltonian matrix

$$\left(\Phi(\mathbf{k}_1' \cdots \mathbf{k}_N' ;\, n_q \cdots) \middle| \mathscr{H} \middle| \Phi(\mathbf{k}_1 \cdots \mathbf{k}_N ;\, n_q \cdots)\right) \,,$$

which is equivalent to determine the coefficients c's.

§3. The Self-consistent Solution of the Wave Fnnction

Eq. (2.10) in the foregoing section reduces to the wave equation for the perfect crystal when $\mathbf{u}_l = 0$ or $a_q = a_q^* = 0$, *i.e.*, each ion is in its equilibrium lattice point. In this case the wave function $\psi(\mathbf{k}, \mathbf{r})$ and its energy $E_0(\mathbf{k})$ are given respectively as

$$\psi(\mathbf{k}, \mathbf{r}) = U_0(\mathbf{r}) \cdot \exp(i\mathbf{k}\mathbf{r}) \,, \tag{3.1}$$

and

$$E_0(\mathbf{k}) = E_0 + (\hbar^2/2m)\, k^2 \,, \tag{3.2}$$

which are good approximations for alkali metals except for Li metal. E_0 includes the coulomb energy,

$$1.20\, e^2/r_s \,, \tag{3.2c}$$

and the exchange energy,

$$-0.916\, e^2/r_s \,, \tag{3.2 ex}$$

where r_s is the radius of a sphere of atomic volume.

The potential of ions, $V_i(\mathbf{r})$ given by (2.11), is expanded in power series of a_q and a_q^* as

$$V_i = V_i^0 + V_i^{\mathrm{I}} + V_i^{\mathrm{II}} \,,$$

where

$$V_i^{\mathrm{I}} = -N^{-1/2} \sum_l \left\{ a_q \cdot \exp(i\mathbf{q}\mathbf{R}_l^0) \cdot \mathbf{e}_q \cdot \mathrm{grad}\, v_{\mathrm{I}}(\mathbf{r} - \mathbf{R}_l^0) + \mathrm{comp} \cdot \mathrm{conj}. \right\} \,, \tag{3.3}$$

and

$$V_i^{\mathrm{II}} = \frac{1}{2N} \sum_l \left\{ a_q^2 \cdot \exp(2i\,\mathbf{q}\mathbf{R}_l^0) + a_q^* a_q + a_q a_q^* + a_q^{*2} \exp(-2i\,\mathbf{q}\mathbf{R}_l) \right\} \times \left\{ \frac{v_{\mathrm{I}}'(\mathbf{r} - \mathbf{R}_l)}{|\mathbf{r} - \mathbf{R}_l|} + \left(v_{\mathrm{I}}''(\mathbf{r} - \mathbf{R}_l) - \frac{v_{\mathrm{I}}'(\mathbf{r} - \mathbf{R}_l)}{|\mathbf{r} - \mathbf{R}_l|} \right) \cos^2(\mathbf{e}_q, \mathbf{r} - \mathbf{R}_l) \right\} \,, \tag{3.4}$$

v_{I}' or v_{I}'' being the first or the second derivative with respect to $|\mathbf{r} - \mathbf{R}_l|$.

The nonvanishing matrix elements are,

$$\left.\begin{aligned} V^{\mathrm{I}}_{ih+} &= \int \psi^*(\mathbf{k}+\mathbf{q}+\mathbf{K}_h, \mathbf{r})\, V^{\mathrm{I}}_i \psi(\mathbf{k}, \mathbf{r})\, d\mathbf{r}, \\ V^{\mathrm{I}}_{ih-} &= \int \psi^*(\mathbf{k}-\mathbf{q}-\mathbf{K}_h, \mathbf{r})\, V^{\mathrm{I}}_i \psi(\mathbf{k}, \mathbf{r})\, d\mathbf{r}, \end{aligned}\right\} \tag{3.5}$$

and

$$\left.\begin{aligned} V^{\mathrm{II}}_{ih+} &= \int \psi^*(\mathbf{k}+2\mathbf{q}+\mathbf{K}_h)\, V^{\mathrm{II}}_i \psi(\mathbf{k})\, d\mathbf{r}, \\ V^{\mathrm{II}}_{ih-} &= \int \psi^*(\mathbf{k}-2\mathbf{q}-\mathbf{K}_h)\, V^{\mathrm{II}}_i \psi(\mathbf{k})\, d\mathbf{r}, \\ V^{\mathrm{II}}_{ih} &= \int \psi^*(\mathbf{k}+\mathbf{K}_h)\, V^{\mathrm{II}}_i \psi(\mathbf{k})\, d\mathbf{r}, \end{aligned}\right\} \tag{3.6}$$

where $\mathbf{K}_h$ is a vector of lattice point in the reciprocal lattice space.

In the second order approximation, the contribution to the energy from V^{II}_i is $\int \psi(\mathbf{k}) V^{\mathrm{II}}_i \psi(\mathbf{k}) d\mathbf{r}$, *i.e.*, $V^{\mathrm{II}}_{ih=0}$ of Eq. (3.6), which is given by Eq. (3.4),

$$V^{\mathrm{II}}_{ih=0} = (4\pi e^2/3)\,|a_q|^2\,. \tag{3.7}$$

Perturbations $V^{\mathrm{I}}_p + V^{\mathrm{II}}_p$ accompanying the lattice deformation $\mathbf{u}_{l;q\mathbf{e}_q}$ consist, besides of $V^{\mathrm{I}}_i + V^{\mathrm{II}}_i$ of ionic field, of $V^{\mathrm{I}}_\rho + V^{\mathrm{II}}_\rho$ and $V^{\mathrm{I}}_{\mathrm{ex}} + V^{\mathrm{II}}_{\mathrm{ex}}$ of the valence electrons, and the appropriate perturbed wave function $\Psi(\mathbf{k})$ in Eq. (2.10) is expanded with respect to $\psi(\mathbf{k}')$ as

$$\begin{aligned} \Psi(\mathbf{k}\,\mathbf{r}) = {} & \Big[1-(1/2)\sum_h \big\{|b(\mathbf{k}h+)|^2 + |b(\mathbf{k}h-)|^2\big\}\Big]\psi(\mathbf{k}, \mathbf{r}) \\ & + \sum_h \big\{b(\mathbf{k}h+)\psi(\mathbf{k}+\mathbf{q}+\mathbf{K}_h, \mathbf{r}) + b(\mathbf{k}h-)\psi(\mathbf{k}-\mathbf{q}-\mathbf{K}_h, \mathbf{r})\big\} \\ & + \sum_{h\neq 0} c(\mathbf{k}h)\psi(\mathbf{k}+\mathbf{K}_h, \mathbf{r}) \\ & + \sum_h \big\{c(\mathbf{k}h+)\psi(\mathbf{k}+2\mathbf{q}+\mathbf{K}_h, \mathbf{r}) + c(\mathbf{k}h-)\psi(\mathbf{k}-2\mathbf{q}-\mathbf{K}_h, \mathbf{r})\big\}\,, \end{aligned} \tag{3.8}$$

where the coefficients b's are themselves of the first order with respect to a_q or a_q^*, given as

$$b(\mathbf{k}h+) = V^{\mathrm{I}}_{ph+}\big\{E_0(\mathbf{k}) - E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\big\}^{-1}, \tag{3.9}$$

$$b(\mathbf{k}h-) = V^{\mathrm{I}}_{ph-}\big\{E_0(\mathbf{k}) - E_0(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\big\}^{-1}, \tag{3.10}$$

with

$$V^{\mathrm{I}}_{ph+} = \int \psi^*(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\, V^{\mathrm{I}}_p \psi(\mathbf{k})\, d\mathbf{r},$$

and

$$V^{\mathrm{I}}_{ph-} = \int \psi^*(\mathbf{k}-\mathbf{q}-\mathbf{K}_h) V^{\mathrm{I}}_p \psi(\mathbf{k})\, d\mathbf{r} \ ,$$

and are determined from the self-consistency of V^{I}_ρ or $V^{\mathrm{I}}_{\mathrm{ex}}$. The c's are of the second order with respect to a_q and a_q^*, which are not explicitly given here, they falling out from the final expression of the second order perturbation energy.

The electron density $\rho(\mathbf{r})$ are given by Eq. (3.8) as,

$$\begin{aligned}\rho(\mathbf{r}) &= 2\sum_k \Psi^*(\mathbf{kr})\Psi(\mathbf{kr}) \\ &= \rho_0(\mathbf{r}) + \rho_{\mathrm{I}}(\mathbf{r}) + \rho_{\mathrm{II}}(\mathbf{r}) \ ,\end{aligned} \tag{3.11}$$

where

$$\rho_0(\mathbf{r}) = 2\sum_k \psi^*(\mathbf{kr})\psi(\mathbf{kr}) \ , \tag{3.12}$$

$$\rho_{\mathrm{I}}(\mathbf{r}) = \sum_h \left\{\rho^{\mathrm{I}}_{h+} \exp\left[i(\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right] + \rho^{\mathrm{I}}_{h-} \exp\left[-i(\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right]\right\}, \tag{3.13}$$

with

$$\rho^{\mathrm{I}}_{h+} = 2\sum_k U_0^2 \left\{b(\mathbf{kh}+) + b^*(\mathbf{kh}-)\right\} \ , \tag{3.14}$$

$$\rho^{\mathrm{I}}_{h-} = 2\sum_k U_0^2 \left\{b^*(\mathbf{kh}+) + b(\mathbf{kh}-)\right\} \ , \tag{3.15}$$

and

$$\begin{aligned}\rho_{\mathrm{II}} = {} & 2\sum_h \sum_{h'} \sum_k U_0^2 \Big\{b(\mathbf{kh}+)b^*(\mathbf{kh}'-)\exp\left[i(2\mathbf{q}+\mathbf{K}_h+\mathbf{K}_{h'})\mathbf{r}\right] \\ & + b^*(\mathbf{kh}+)\,b(\mathbf{kh}'-)\exp\left[-i(2\mathbf{q}+\mathbf{K}_h+\mathbf{K}_{h'})\mathbf{r}\right]\Big\} \\ & + 2\sum_h \sum_k U_0^2 \Big\{\left[c(\mathbf{kh}+) + c^*(\mathbf{kh}-)\right]\exp\left[i(2\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right] \\ & + \left[c^*(\mathbf{kh}+) + c(\mathbf{kh}-)\right]\exp\left[-i(2\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right]\Big\} \\ & + 2\sum_{h\neq 0}{}' U_0^2 c(\mathbf{kh})\exp\left[i\mathbf{K}_h\mathbf{r}\right] .\end{aligned} \tag{3.16}$$

V^{I}_ρ is given by the POISSON's equation $\Delta V^{\mathrm{I}}_\rho = -4\pi e^2 \rho_{\mathrm{I}}$ and Eqs. (3.13), (3.14) and (3.15) with the approximation $U_0^2 = 1$ as

$$V^{\mathrm{I}}_\rho = \sum_h \left\{V^{\mathrm{I}}_{\rho h+} \exp\left[i(\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right] + V^{\mathrm{I}}_{\rho h-} \exp\left[-i(\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right]\right\} \ , \tag{3.17}$$

where

$$V^{\mathrm{I}}_{\rho h+} = (8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2) \sum_k \left\{b(\mathbf{kh}+) + b^*(\mathbf{kh}-)\right\} \ , \tag{3.18}$$

and

$$V^{\mathrm{I}}_{\rho h-} = (8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2)\sum_k\left\{b^*(\mathbf{kh}+)+b(\mathbf{kh}-)\right\}. \tag{3.19}$$

The contribution from V^{II}_ρ to the energy vanishes, since V^{II}_ρ, as well as ρ_{II}, does not include constant terms.

$V^{\mathrm{I}}_{\mathrm{ex}}$ and $V^{\mathrm{II}}_{\mathrm{ex}}$ are also readily derived by Eqs. (2.14), (3.12), (3.13), (3.14) as

$$V^{\mathrm{I}}_{\mathrm{ex}} = \sum_h\left\{V^{\mathrm{I}}_{\mathrm{ex}h+}\cdot\exp\left[i(\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right]+V^{\mathrm{I}}_{\mathrm{ex}h-}\cdot\exp\left[-i(\mathbf{q}+\mathbf{K}_h)\mathbf{r}\right]\right\}, \tag{3.20}$$

where

$$\left.\begin{aligned} V^{\mathrm{I}}_{\mathrm{ex}h+} &= -(2e^2/N)(3N/8\pi)^{1/3}\sum_k\left\{b(\mathbf{kh}+)+b^*(\mathbf{kh}-)\right\} \\ V^{\mathrm{I}}_{\mathrm{ex}h-} &= -(2e^2/N)(3N/8\pi)^{1/3}\sum_k\left\{b^*(\mathbf{kh}+)+b(\mathbf{kh}-)\right\} \end{aligned}\right\}, \tag{3.21}$$

and

$$\begin{aligned} V^{\mathrm{II}}_{\mathrm{ex}} = (4e^2/3N^2)(3N/8\pi)^{1/3}&\sum_h\left\{\sum_k\left[b(\mathbf{kh}+)+b^*(\mathbf{kh}-)\right]\right\} \\ &\times\left\{\sum_k\left[b^*(\mathbf{kh}+)+b(\mathbf{kh}-)\right]\right\}. \end{aligned} \tag{3.22}$$

The terms with coefficients c's in Eq. (3.8) do not contribute to the second order perturbation energy as mentioned above.

The coefficients $b(\mathbf{kh}+)$ and $b(\mathbf{kh}-)$ are now determined from the self-consistency of V^{I}_ρ and $V^{\mathrm{I}}_{\mathrm{ex}}$ as follows.[3] The first order perturbation matrices V^{I}_p are the sum of V^{I}_i, V^{I}_ρ and $V^{\mathrm{I}}_{\mathrm{ex}}$, and hence, from Eqs. (3.9) and (3.10),

$$\begin{aligned} \Sigma\left\{b(\mathbf{kh}+)+b^*(\mathbf{kh}-)\right\} &= \left\{V^{\mathrm{I}}_{ih+}+V^{\mathrm{I}}_{\rho h+}+V^{\mathrm{I}}_{\mathrm{ex}h+}\right\} \\ &\quad\times 2\sum_k\left\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\right\}^{-1}. \end{aligned} \tag{3.23}$$

Substituting Eq. (3.23) into Eqs. (3.18) and (3.21), we have

$$\begin{aligned} V^{\mathrm{I}}_{\rho h+} &= \left[(8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2)\cdot 2\sum_k\left\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\right\}^{-1}\right] \\ &\quad\times\left\{V^{\mathrm{I}}_{ih+}+V^{\mathrm{I}}_{\rho h+}+V^{\mathrm{I}}_{\mathrm{ex}h+}\right\}, \end{aligned} \tag{3.24}$$

and

$$\begin{aligned} V^{\mathrm{I}}_{\mathrm{ex}h+} &= -\left[(2e^2/N)(3N/8\pi)^{1/3}\cdot 2\sum_k\left\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\right\}^{-1}\right] \\ &\quad\times\left\{V^{\mathrm{I}}_{ih+}+V^{\mathrm{I}}_{\rho h+}+V^{\mathrm{I}}_{\mathrm{ex}h+}\right\}, \end{aligned} \tag{3.25}$$

and hence,

$$
\begin{aligned}
V^{\mathrm{I}}_{ph+} &= V^{\mathrm{I}}_{ih+} + V^{\mathrm{I}}_{\rho h+} + V^{\mathrm{I}}_{\mathrm{ex}h+} \\
&= V^{\mathrm{I}}_{ih+}\left\{1+S(\mathbf{q}+\mathbf{K}_h)\right\}^{-1},
\end{aligned}
\tag{3.26}
$$

where

$$
\begin{aligned}
S(\mathbf{q}+\mathbf{K}_h) = \Big[-\left\{8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2-(2e^2/N)(3N/8\pi)^{1/3}\right\}\cdot \\
\times 2\sum_k \left\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\right\}^{-1}\Big].
\end{aligned}
\tag{3.27}
$$

Self-consistent values of $V^{\mathrm{I}}_{\rho h+}$ and $V^{\mathrm{I}}_{\mathrm{ex}h+}$ are now given by Eqs. (3.24) and (3.25) by substituting their last factor $\{V^{\mathrm{I}}_{ih+}+V^{\mathrm{I}}_{\rho h+}+V^{\mathrm{I}}_{\mathrm{ex}h+}\}$ with Eq. (3.26). Self-consistent $V^{\mathrm{I}}_{\rho h-}$, $V^{\mathrm{I}}_{\mathrm{ex}h-}$ and V^{I}_{ph-} are similary derived, and henceforth we have

$$
\begin{aligned}
V^{\mathrm{II}}_{\mathrm{ex}} = (3e^2/3N^2)(3N/8\pi)^{1/3}\sum_h \Big[|V^{\mathrm{I}}_{ph+}|^2\cdot 2\sum_k \left\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\right\}^{-1} \\
+ |V^{\mathrm{I}}_{ph-}|^2\cdot 2\sum_k \left\{E_0(\mathbf{k})-E_0(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\right\}^{-1}\Big].
\end{aligned}
\tag{3.28}
$$

The orthogonality is obvious for $\Psi(\mathbf{k})$ and $\Psi(\mathbf{k}')$, where $\mathbf{k}\neq\mathbf{k}'$ and $\mathbf{k}\pm(\mathbf{q}+\mathbf{K}_h)\neq\mathbf{k}'$, and the same is true for $\Psi(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)$ or $\Psi(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)$ and $\Psi(\mathbf{k})$ because of the equality,

$$
b(\mathbf{k}\mathbf{h}+)+b^*(\mathbf{k}+\mathbf{q}+\mathbf{K}_h,\mathbf{h}-)=0\,,
\tag{3.29}
$$

or

$$
b(\mathbf{k}\mathbf{h}-)+b^*(\mathbf{k}-\mathbf{q}-\mathbf{K}_h,\mathbf{h}+)=0\,,
\tag{3.30}
$$

which are readily verified by Eqs. (3.9), (3.10) and $V^*_{ih\pm}=V_{ih\pm}$.

§4. The Adiabatic Potential of Valence Electrons

We now evaluate the mean value $\bar{\mathscr{H}}^E$ of $\mathscr{H}^E$ of Eq. (2.1*E*), *i. e.*

$$
\int (N!)^{-1/2}\det|\Psi(\mathbf{k}_i,\mathbf{r}_j;\bar{a}_q)|\cdot\mathscr{H}^E\cdot(N!)^{-1/2}\det|\Psi(\mathbf{k}_i,\mathbf{r}_j;\bar{a}_q)|\prod_i d\mathbf{r}_i
\tag{4.1}
$$

with the wave functions Ψ derived in the foregoing section. $\mathscr{H}^E$ is expressed as

$$
\mathscr{H}^E=\mathscr{H}^E_1+\mathscr{H}^E_2+\mathscr{H}^E_3\,,
\tag{4.2}
$$

where

$$
\mathscr{H}^E_1=\sum_i\left\{-\frac{\hbar}{2m}\Delta_i+V_0(\mathbf{r}_i)+V^{\mathrm{I}}_p(\mathbf{r}_i)+V^{\mathrm{II}}_p(\mathbf{r}_i)\right\},
\tag{4.3}
$$

$$\mathscr{H}_2^E = (1/2) \sum_{i,j(i \neq j)} (e^2/\mathbf{r}_{ij}) \,, \tag{4.4}$$

and

$$\mathscr{H}_3^E = -\sum_i \left\{ V_\rho^0(\mathbf{r}_i) + V_{\mathrm{ex}}^0(\mathbf{r}_i) + V_\rho^{\mathrm{I}}(\mathbf{r}_i) + V_{\mathrm{ex}}^{\mathrm{I}}(\mathbf{r}_i) + V_{\mathrm{ex}}^{\mathrm{II}}(\mathbf{r}_i) \right\} , \tag{4.5}$$

with

$$\begin{aligned} V_0 &= V_i^0 + V_\rho^0 + V_{\mathrm{ex}}^0 \,, \\ V_p^{\mathrm{I}} &= V_i^{\mathrm{I}} + V_\rho^{\mathrm{I}} + V_{\mathrm{ex}}^{\mathrm{I}} \,, \\ V_p^{\mathrm{II}} &= V_i^{\mathrm{II}} + V_{\mathrm{ex}}^{\mathrm{II}} \,. \end{aligned}$$

We have hence, in accordance with Eqs. (2.10), (3.7), (3.26) and (3.30),

$$\begin{aligned} \bar{\mathscr{H}}^E &= 2 \sum_k \Big(E_0(\mathbf{k}) + \delta E_0(\mathbf{k}, a_q) \Big) \\ &= 2 \sum_k \Big(E_0 + (\hbar/2m) k^2 \Big) + 2 \sum_h \sum_k \Big[|V_{ph+}^{\mathrm{I}}|^2 \cdot \Big\{ E_0(\mathbf{k}) - E_0(\mathbf{k} + \mathbf{q} + \mathbf{K}_h) \Big\}^{-1} \\ &\quad + |V_{ph-}^{\mathrm{I}}|^2 \Big\{ E_0(\mathbf{k}) - E_0(\mathbf{k} - \mathbf{q} - \mathbf{K}_h) \Big\}^{-1} \Big] + N(V_{ih=0}^{\mathrm{II}} + V_{\mathrm{ex}}^{\mathrm{II}}) \,, \end{aligned} \tag{4.6}$$

and

$$\begin{aligned} \bar{\mathscr{H}}_2^E &= 2 \sum_k \sum_{k'} \int \Psi^*(\mathbf{k}\mathbf{r}_i) \Psi(\mathbf{k}\mathbf{r}_i) (e^2/r_{ij}) \Psi^*(\mathbf{k}'\mathbf{r}_j) \Psi(\mathbf{k}'\mathbf{r}_j) \, d\mathbf{r}_i d\mathbf{r}_j \\ &\quad - \sum_k \sum_{k'} \int \Psi^*(\mathbf{k}'\mathbf{r}_i) \Psi(\mathbf{k}\mathbf{r}_i) (e^2/r_{ij}) \Psi^*(\mathbf{k}\mathbf{r}_j) \Psi(\mathbf{k}'\mathbf{r}_j) \, d\mathbf{r}_i d\mathbf{r}_j \\ &= (1/2) \int \rho(\mathbf{r}_i) \Big\{ V_\rho(\mathbf{r}_i) + V_{\mathrm{ex}}(\mathbf{r}_i) \Big\} \, d\mathbf{r}_i \,, \end{aligned}$$

with the same simplification of the exchange term resorted to in deriving Eq. (2.14) from Eq. (2.13). $\bar{\mathscr{H}}_3^E$ is given from Eq. (4.5) as

$$\bar{\mathscr{H}}_3^E = -\int \rho(\mathbf{r}_i) \Big\{ V_\rho(\mathbf{r}_i) + V_{\mathrm{ex}}(\mathbf{r}_i) \Big\} \, d\mathbf{r}_i \,,$$

and hence with reference to (3.2*c*) and (3.2 ex)

$$\begin{aligned} \bar{\mathscr{H}}_2^E + \bar{\mathscr{H}}_3^E &= -(1/2) \int \rho(\mathbf{r}_i) \Big\{ V_\rho(\mathbf{r}_i) + V_{\mathrm{ex}}(\mathbf{r}_i) \Big\} \, d\mathbf{r}_i \\ &= -0.60 \, Ne^2/r_s + 0.458 \, Ne^2/r_s \\ &\quad - 2 \sum_h \sum_k \Big[V_{ph+}^{\mathrm{I}*} (V_{\rho h+}^{\mathrm{I}} + V_{\mathrm{ex}h+}^{\mathrm{I}}) \Big\{ E_0(\mathbf{k}) - E_0(\mathbf{k} + \mathbf{q} + \mathbf{K}_h) \Big\}^{-1} \\ &\quad + V_{ph-}^{\mathrm{I}*} (V_{\rho h+}^{\mathrm{I}} + V_{\mathrm{ex}h+}^{\mathrm{I}}) \Big\{ E_0(\mathbf{k}) - E_0(\mathbf{k} - \mathbf{q} - \mathbf{K}_h) \Big\}^{-1} \Big] - (1/2) N V_{\mathrm{ex}}^{\mathrm{II}} \,. \end{aligned} \tag{4.7}$$

$\bar{\mathscr{H}}^E$ is now given from (4.6) and (4.7) as,

$$\bar{\mathscr{H}}^E = \bar{\mathscr{H}}_0^E + \delta\bar{\mathscr{H}}^E ,$$

where

$\bar{\mathscr{H}}_0^E =$ (The electronic energy for a perfect crystal including the coulomb and exchange energies)

$$\delta\bar{\mathscr{H}}^E = -2\sum_h\sum_k\Big[V^{\mathrm{I}*}_{ph+}V^{\mathrm{I}}_{ih+}\big\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\big\}^{-1}$$
$$+V^{\mathrm{I}*}_{ph-}V^{\mathrm{I}}_{ih-}\big\{E_0(\mathbf{k})-E_0(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\big\}^{-1}\Big]+N(V^{\mathrm{II}}_{i,h=0}+V^{\mathrm{II}}_{\mathrm{ex}}/2). \tag{4.8}$$

The contribution from $V^{\mathrm{II}}_{\mathrm{ex}}$ may be incorporated into the second term, by replacing $V^{\mathrm{I}}_{ph\pm}$ by $V^{\mathrm{I}'}_{ph\pm}$, *i.e.*

$$V^{\mathrm{I}'}_{ph\pm} = V^{\mathrm{I}}_{ih\pm}\big\{1+S'(\mathbf{q}+\mathbf{K}_h)\big\}^{-1} \tag{4.9}$$

where

$$S'(\mathbf{q}+\mathbf{K}_h) = -\big\{8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2-(5/6)(2e^2/N)(3N/8\pi)^{1/3}\big\}\cdot$$
$$\times 2\sum_k\big\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\big\}^{-1}, \tag{4.10}$$

which differs from $S(\mathbf{q}+\mathbf{K}_h)$ given by Eq. (3.27) just in the coefficient 5/6 of the second term in the first factor. We have thus for the second order perturbation energy as

$$\delta\bar{\mathscr{H}}^E = -2\sum_h\sum_k\Big[V^{\mathrm{I}'*}_{ph+}V^{\mathrm{I}}_{ih+}\big\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\big\}^{-1}$$
$$+V^{\mathrm{I}'*}_{ph-}V^{\mathrm{I}}_{ih-}\big\{E_0(\mathbf{k})-E_0(\mathbf{k}-\mathbf{q}-\mathbf{K}_h)\big\}^{-1}\Big]+(4\pi Ne^2/3)|a_q|^2 . \tag{4.11}$$

§ 5. Electrical Conductivity of Monovalent Metals

The V^{I}_{ih+} in Eq. (3.26) is expressed, according to BARDEEN[3], by the approximations Eqs. (3.1) and (3.2) for $\psi(\mathbf{k})$ and $E_0(\mathbf{k})$ as

$$V^{\mathrm{I}}_{ih+} = \int\psi^*(\mathbf{k}+\mathbf{q}+\mathbf{K}_h,\mathbf{r})\,V^{\mathrm{I}}_i\psi(\mathbf{k},\mathbf{r})\,d\mathbf{r}$$
$$= iN^{-1/2}a_q(\mathbf{e}_q,\mathbf{q}+\mathbf{K}_h)\left\{\frac{4\pi Ne^2}{|\mathbf{q}+\mathbf{K}_h|^2}+\gamma(V(r_s)-E_0)\right\}g(x)\,, \tag{5.1}$$

where $g(x)=3(\sin x-x\cos x)/x^3$, $x=r_s|\mathbf{q}+\mathbf{K}_h|$, and $\gamma=U_0^2(r_s)$. $V(r_s)$ is the HARTREE-FOCK potential at the surface of an atomic sphere of radius r_s. We have on the other hand for the summation in Eq. (3.27),

$$2\sum_k\big\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\big\}^{-1} = -(3N/4\zeta_0)f(t) \tag{5.2}$$

where $\zeta_0=(\hbar^2/2m)\cdot k_F^2$ is the Fermi energy, k_F being the wave number of an electron at the Fermi surface given by $1.92/r_s$, $t=|\mathbf{q}+\mathbf{K}_h|/2k_F$ and

$$f(t) = \frac{1}{2}+\frac{1-t^2}{4t}\log\left|\frac{1+t}{1-t}\right| . \tag{5.3}$$

The self-consistent matrix element V^{I}_{ph+} is given, from Eqs. (3.26), (3.27), (5.1) and (5.3), as

$$V^{\mathrm{I}}_{ph+} = i(2/3)N^{-1/2}a_q\cdot\cos(\mathbf{e}_q, \mathbf{q}+\mathbf{K}_h)\cdot|\mathbf{q}+\mathbf{K}_h|\cdot G(t)F(t)^{-1}\zeta_0 , \tag{5.4}$$

where,

$$G(t) = \left\{1+\gamma(V(r_s)-E_0)(3t^2/\beta\zeta_0)\right\} g(3.84t), \tag{5.5}$$

$\beta=e^2k_F/\pi\zeta_0$, and

$$F(t) = (2t^2/\beta)+(1-3t^2/2)f(t) . \tag{5.6}$$

At high temperatures, $T\gg\Theta$ (Θ : the Debye characteristic temperature), the amplitude of the vibration is given by

$$|a_q|^2 = \kappa T/2M\omega_q^2 , \tag{5.7}$$

where κ is the Boltzmann constant, M the mass of the atom and ω_q the angular frequency of the vibration. According to the treatment of Debye, ω_q is given by

$$\omega_q = (\kappa\Theta/\hbar)(q/q_m) \tag{5.8}$$

where q_m is the largest value of q. The amplitude $|a_q|$ for transitions $K_h\neq 0$ (*Umklapp processes*) is assumed to be equal to $|a_{q_m}|$ according to Bardeen, *i.e.*

$$|a_{q_m}|^2 = \kappa T/2M\omega_{q_m}^2 . \tag{5.9}$$

The interaction constant C, as defined by Sommerfeld and Bethe, is now given by

$$C^2 = 4t_m^{-4}\left[\int_0^{t_m}\left\{G(t)F(t)^{-1}\zeta_0\right\}^2 t^3dt + \int_{t_m}^1\left\{(t/t_m)G(t)F(t)^{-1}\zeta_0\right\}^2 t^3dt\right] , \tag{5.10}$$

where $t_m=q_m/2k_F=2^{-2/3}$ is the largest value of t; the second term arises from the *Umklapp processes*, while the factor t/t_m there from the assumption Eq. (5.9).

The conductivity σ at high temperatures is given in terms of the interaction constant C as

$$\sigma = Me^2(\hbar\pi)^{-3}k_F(dE_0/dk)_F^2(\kappa\Theta^2/T)C^{-2}, \tag{5.11}$$

which may be written in the form,

$$(C/\zeta_0)^{-2} = \pi\sigma m h T / 4\beta M \kappa \Theta^2 , \tag{5.12}$$

using the relation

$$k_F (dE_0/dk)_F = 2\zeta_0 .$$

Table I shows the interaction constants of alkali metals evaluated by Eq. (5.10) as well as those by HARTREE approximation in comparison with the experimental values determined by Eq. (5.12) from the observed conductivities.

TABLE I. Theoretical interaction constants C of monovalent metals, including exchange effects by SLATER's simplified HARTREE-FOCK method.

	Li	Na	K	Rb	Cs
$\sigma \times 10^{-16}$ c.g.s. units at 0°C	10.7	22.8	18.2	8.6	6.0
extrapol. from σ_{exp} at (T°K)†	(250)	(150)	(80)	(50)	(35)
$r_s \times 10^{8}$ cm	1.72	2.12	2.56	2.81	3.13
β	1.08	1.33	1.60	1.77	1.90
ζ_0 (eV)	4.72	3.16	2.06	1.79	1.53
Θ °K†	330–360	180–202	114	65	45
$(C/\zeta_0)_{\text{exp.}}$	1.26–1.34	0.92–1.04	0.92	1.25	1.25
$(V(r_s)-E_0)$*eV	-0.8	0.08	-0.02	0.03	0.00
C/ζ_0 with exchange effects.	0.78	1.14	1.23	1.28	1.30
C/ζ_0 HARTREE approx.	0.50	0.73	0.75	0.80	0.80

*) H. BROOKS, Phys. Rev. **91**, 1027 (1953); F. S. HAM, *Solid State Physics* Vol I. 185 (1955). †) D. K. C. MACDONALD, *Handbuch der Physik* Band XIV, 175 (1956)

As seen from Table I, the theoretical values are considerably improved upon those of the HARTREE approximation, by taking the exchange effects into account, indicating an important part played by them through the electron-phonon interaction. For Li metal the assumptions of Eqs. (3.1) and (3.2) are only poor approximations as referred to before; detailed discussions will be given in later papers.

§ 6. Compressibility of Alkali Metals

The validity of Eq. (4.10) is now examined by deriving from it the compressibility of alkali metals, and by comparing the result with that obtained from the cohesion energy of the WIGNER-SEITZ theory.

The second order perturbation energy $\delta\bar{\mathscr{W}}^E$ of Eq. (4.11) is expressed, substituting Eqs. (5.1), (5.2) and (5.4) into Eq. (4.10), as

$$\delta\bar{\mathscr{W}}^E = |a_q|^2 Ne^2 \left\{4\pi/3 - 4\pi \sum_h \cos^2(\mathbf{e}_q, \mathbf{q}+\mathbf{K}_h) G^2(t) F'(t)^{-1} f(t)\right\}, \tag{6.1}$$

where

$$F'(t) = 2t^2/\beta + (1-1.25\,t^2) f(t). \tag{6.2}$$

Eq. (6.1) is an even function of $t = |\mathbf{q}+\mathbf{K}_h|/2k_F$, which is expanded with respect to q^2, for the case of the longitudinal vibration of long wave length (*i.e.* $q \approx 0$ and $\cos(\mathbf{e}_q, \mathbf{q}) = 1$), neglecting terms $h \neq 0$, as

$$\begin{aligned}\delta\bar{\mathscr{W}}^E = |a_q|^2 N\Big[&-4\pi Ne^2 + (4\pi/3)Ne^2 \\ &+ \left\{-2(V(r_s)-E_0) + (2/3)\zeta_0 + +0.60\,e^2/r_s - 0.254\,e^2/r_s\right\} q^2\Big], \end{aligned}\tag{6.3}$$

where the third or the fourth term of the coefficient of q^2 in Eq. (6.3) is the contribution from the coulomb or the exchange energy of valence electrons respectively.

The circular frequency ω of the longitudinal vibration of long wave length $q \approx 0$ in the direction of (1, 0, 0) is obtained from Eq. (2.15), as[6)]

$$|a_q|^2 M\omega^2 = \{\delta\bar{\mathscr{W}}^E + \delta\bar{\mathscr{W}}^C\}, \tag{6.4}$$

where $\delta\bar{\mathscr{W}}^E$ is given by Eq. (6.3) and $\delta\bar{\mathscr{W}}^C$ is the contribution from the coulomb repulsions between ions. For the simplicities' sake the exchange repulsions between ion-cores are here neglected, which is unimportant for the present discussion of examining the validity of Eq. (4.11). The $\delta\bar{\mathscr{W}}^C$ for the mode under consideration is evaluated as

$$\delta\bar{\mathscr{W}}^C = |a_q|^2 N\left\{(8\pi/3)Ne^2 - (0.368\,e^2/r_s)\,q^2 + \cdots\right\}. \tag{6.5}$$

The circular frequency of the mode is related, on the other hand, to the elastic constant c_{11} as

$$M\omega^2 = Nc_{11}q^2. \tag{6.6}$$

We have now from Eqs. (6.3), (6.4), (6.5) and (6.6),

$$c_{11} = N\left\{-2(V(r_s)-E_0) + (2/3)\zeta_0 + (0.60-0.368)e^2/r_s - 0.254e^2/r_s\right\}, \tag{6.7}$$

and for the reciprocal of compressibility $1/\kappa$,

$$\begin{aligned} 1/\kappa &= c_{11}-(2/3)(c_{11}-c_{12}) \\ &= N\left\{-2(V(r_s)-E_0)+(2/3)\zeta_0+(0.60-0.368-0.032)e^2/r_s-0.254\,e^2/r_s\right\}, \end{aligned} \tag{6.8}$$

where $c_{11}-c_{12} = 0.048\,Ne^2/r_s$.

The expression (6.8) for $1/\kappa$ is compared with that derived from the cohesion energy E_c as follows. The cohesion energy of alkali metals is expressed, according to the theory of WIGNER-SEITZ, as

$$E_c(r_s) = E_0(r_s)+(3/5)\zeta_0-0.60\,e^2/r_s+0.458\,e^2/r_s-0.288\,e^2/(r_s+5.1\,a_H), \tag{6.9}$$

where a_H is the BOHR radius and the third, fourth and fifth terms are the coulomb, exchange and correlation energies of valence electrons respectively. The reciprocal of the compressibility is hence given (Appendix I) as

$$\begin{aligned} 1/\kappa &= (1/12\pi r_s)(d^2E_c/dr_s^2) \\ &= N\Big[-2(V(r_s)-E_0)+(2/3)\zeta_0+0.2\,e^2/r_s-0.204\,e^2/r_s \\ &\qquad -(0.064\,e^2/r_s)\left\{1+(1+5.1\,a_H/r_s)^{-1}\right\}(1+5.1\,a_H/r_s)^{-2}\Big], \end{aligned} \tag{6.10}$$

referring to the equilibrium condition $(dE_c/dr_s)=0$, and to the relation,

$$dE_0/dr_s = (3/r_s)\left\{(V(r_s)-E_0)-0.2\,e^2/r_s+0.306\,e^2/r_s\right\}, \tag{6.11}$$

derived by FROELICH$^{11)}$ and BARDEEN.$^{12)}$

We see, by comparing the expressions (6.8) and (6.10) for $1/\kappa$, that the former adequately reproduces the latter except the exchange and correlation terms. The contribution $-0.254\,Ne^2/r_s$ from the exchange energy in Eq. (6.8) is about 20% larger than that $-0.204\,N^2e/r_s$ in Eq. (6.10), which excess may be attributed, as shown in the next section, to the simplification Eq. (2.14) of the exchange energy. The contribution from the correlation energy is not included in Eq. (6.8) as the consequence of the underlying wave function of Eq. (2.5) without configurational interactions. The correlation energy is incorporated by starting from the wave function Eq. (2.16) instead, as mentioned before.

§ 7. The Validity of the Simplified Exchange Energy

The perturbing ionic field V_i^I accompanying the lattice deformation is screened or compensated by the redistribution of valence electrons.

One of the effects of the exchange energy on the screening field is that through the density of energy levels of valence electrons. This reduction of the level density has been ignored altogether in the forgoing treatment of simplified exchange energy of Eq. (2.14), which is independent of k.

The V_{ex}^0 depends on the wave number of an electron as

$$V_{\mathrm{ex}}^0 = -1.224 \frac{e^2}{r_s} \left\{ \frac{1}{2} + \frac{1-(k/k_F)^2}{4(k/k_F)} \log \left| \frac{1+k/k_F}{1-k/k_F} \right| \right\}, \tag{7.1}$$

which has the singularity[10b)]

$$dV_{\mathrm{ex}}^0/dk = \infty \qquad \text{at} \qquad k = k_F, \tag{7.2}$$

that reduces the level density at the FERMI surface abnormally. Such anomaly as expected from (7.2) is not, however, observed with the experimental values of the electronic specific heat or the paramagnetic susceptibility, which depends directly on the level density at the FERMI surface. SEITZ and SAMPSON[13)] has suggested in this regard that the correlation energy of electrons of anti-parallel spins might have tendency to compensate the anomaly. Recent theoretical investigations[14)] have shown actually that the resultant reduction of the level density amounts only about to 10%, taking the exchange and correlation effects into account at the same time.

The effect may be approximately included by replacing the summation (5.2), *i.e.*, $2\sum_k \{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\}^{-1}$, by

$$D/D_0 \cdot 2\sum_k \left\{E_0(\mathbf{k})-E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)\right\}^{-1}, \tag{7.3}$$

where D or D_0 is the density of energy levels at the FERMI surface with or without the exchange and correlation effects. The contribution from the effect is now the addend

$$N \cdot (2/3)\zeta_0(1-D/D_0) \tag{7.4}$$

to $1/\kappa$ of Eq. (6.8).

More important is the other effect of exchange energy which has been taken into account by the second term of the first factor in Eq. (3.27) or Eq. (4.10). This effect is physically interpreted as reducing the screening field of valence electrons, which are redistributed to compensate the pertubing ionic field of lattice deformation, by keeping them more apart from each other than corresponding to HARTREE approximation. The correlation energy of anti-parallel spins is also expected to have the similar effect by the same reason which will be discussed in a later paper, its magnitude being about 10% of that of the exchange effect as estimated from Eq. (6.10).

The simplified exchange energy of Eq. (2.14) over-estimates the latter effect by 20% for $q \ll q_m$ as shown in the forgoing section.

The validity of Eq. (2.14) for $q=(2^{-1/3})\,q_m=k_F$ is examined by comparing the exchange energy of the deformed crystal

$$-\frac{1}{2}\sum_{k}\sum_{k'}\iint \Psi^*(\mathbf{k}'\,\mathbf{r}_j)\,\Psi(\mathbf{k}\,\mathbf{r}_j)(e^2/r_{ij})\Psi^*(\mathbf{k}\mathbf{r}_i)\Psi(\mathbf{k}'\mathbf{r}_i)d\mathbf{r}_i d\mathbf{r}_j \qquad (7.5)$$

with its simplified expression,

$$-(3e^2/2)\left\{\frac{3}{8\pi}\cdot 2\sum_{k'}\Psi(\mathbf{k}'\,\mathbf{r}_i)\,\Psi(\mathbf{k}'\mathbf{r}_i)\right\}^{1/3}, \qquad (7.6)$$

where $\Psi(\mathbf{k})$ is given by Eqs. (3.8), (3.9) and (3.10), neglecting the third and fourth terms in Eq. (3.8) according to the conclusion in §4. The zeroth order term of (7.5) or (7.6) with regard to ionic displacement is $-0.458\,Ne^2/r_s$, which corresponds to the exchange energy of the metal without deformation, while the term $q=k_F$ and $K_h=0$ in (7.5) or (7.6) is*)

$$-0.10\,Ne^2/r_s\left\{|V_{p,h=0,+}|^2+|V_{p,h=0,-}|^2\right\}\zeta_0^{-2} \qquad (7.7)$$

or

$$-0.17\,Ne^2/r_s\left\{|V_{p,h=0,+}|^2+|V_{p,h=0,-}|^2\right\}\zeta_0^{-2} \qquad (7.8)$$

respectively.

The comparison of (7.7) with (7.8) shows that the simplified exchange energy overestimates the second term due to the lattice deformation by *ca.* 60%, which makes about 15% difference of V^I_{ph+} of Eq. (3.26) or of $\delta\mathscr{W}^E$ of Eq. (4.9).

The simplified exchange energy is also a good approximation for $\mathbf{q}=(\pi/r_0, 0, 0)$ ($2r_0$; lattice constant), as shown in the following paper, by comparing the frequency of the vibration of the mode $\mathbf{e}_q=(1,0,0)$ or $\mathbf{e}_q=(0,1,0)$, derived from Eq. (4.11), with that obtained by cellur method[6].

We might, thus, conclude that the exchange term in Eq. (3.26) or in Eq. (4.11) is a good approximation for all range of q, provided that they are corrected for the over-estimation mentioned above as well as for the reduction of the level density.

The effective matrix element, modified by taking into consideration

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*) See Appendix II.

the corrections discussed above as well as the effect of correlation interactions between valence electrons, will be given as[7],

$$V_{ph+} = V_{ih+}\left\{1+S(\mathbf{q}+\mathbf{K}_h)\right\}^{-1} \tag{7.9}$$

with

$$S(\mathbf{q}+\mathbf{K}_h) = \left\{8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2-2B(\mathbf{q}+\mathbf{K}_h)\pi e^2/k_F^2\right\}$$
$$\times (D/D_0)2\sum_k \left\{E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)-E_0(\mathbf{k})\right\}^{-1} \tag{7.10}$$

where the $B(\mathbf{q}+\mathbf{K}_h)$ is more or less independent of $\mathbf{q}+\mathbf{K}_h$ and the factor D/D_0 is due to the reduction of the level density at the FERMI surface. The contribution from the exchange and correlation energies to the $1/\kappa$ is now

$$-N\left\{B(\mathbf{q}+\mathbf{K}_h=0)\cdot 0.204e^2/r_s+(2/3)\cdot\zeta_0(D/D_0-1)\right\}. \tag{7.11}$$

Table II gives the interaction constants evaluated by Eq. (7.9) where B's are assumed constant and determined by equating Eq. (7.11) with the fourth and fifth terms of Eq. (6.10).

TABLE II. Interaction constants C of monovalent metals, taking the exchange and correlation effects into account.

	Na	K	Rb	Cs
$B(\mathbf{q}=0)$	1.25	1.21	1.18	1.18
(D/D_0)*)	0.90	0.935	0.945	0.965
(C/ζ_0) by Eq. (7.9)	1.08	1.12	1.20	1.20
$(C/\zeta_0)_{\text{exp.}}$	1.02~1.15	0.98	1.32	1.29

*) D. PINES, Phys. Rev. **92**, 626 (1954).

The experimental values $(C/\zeta_0)_{\text{exp}}$ in Table II is evaluated by the equation†)

$$(C/\zeta_0)^{-2}_{\text{exp}} = (D/D_0)^2(\pi\sigma mhT/4\beta M\kappa\Theta^2), \tag{7.13}$$

instead of Eq. (5.12), taking into account the reduction of the level density at the FERMI surface.

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†) The conclusion of E. J. BLATT (Phys Rev. **99**, 1735 (1955)) or R. BARRIE (*ibid.*, **103**, 1581 (1956)) is not correct. Cf. M. TSUJI, J. Phys. Soc. Japan, **12**, 828 (1957).

§ 8. Discussion

Recently Bardeen and Pines[15)] investigated the role of electron-electron interactions in the electron-lattice vibration interaction in metals by extending the Bohm-Pines collective description method. They concluded that the exchange and correlation effects on the effective matrix element V_{ph+} and on the adiabatic potential $\delta\overline{\mathscr{W}}^{E}$, which depends on V_{ph+}, are negligible for small wave number vector q, in deviation from the present conclusion.

Their conclusion might, however, be questioned in that the effective matrix element of the electron-lattice vibration interaction is, according to Bardeen and Pines,

$$V_{ph+} = V_{ih+}\left[1+(8\pi e^2/|\mathbf{q}+\mathbf{K}_h|^2)\cdot 2\sum_{k}\left\{E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_h)-E_0(\mathbf{k})\right\}^{-1}\right]^{-1}, \tag{8.1}$$

which is given by Eq. (3.26) by cancelling the exchange term in the $S(q)$ of Eq. (3.27). Eq. (8.1) leads similarly as in §6, to the expression of $1/\kappa$, *i.e.*,

$$1/\kappa = N\left\{-2(V(r_s)-E_0)+(2/3)\zeta_0+0.2e^2/r_s\right\}, \tag{8.2}$$

which differs from that of Eq. (6.10) in dispensing with the exchange and correlation terms. Numerically, (8.1) and (6.8) give respectively $1.39\cdot 10^{11}$ dynes/cm^2 and $0.72\cdot 10^{11}$ dynes/cm^2, or including the contribution from the ion-core exchange repulsions, $1.47\cdot 10^{11}$ dynes/cm^2 or $0.80\cdot 10^{11}$ dynes/cm^2, which is compared with the experimental value $\sim 0.80\cdot 10^{11}$ dynes/cm^2. The effects of the exchange and correlation energies on the $c_l = c_{11}+2c_{44}$ are similarly expressed as $1/\kappa$, inasmuch as both $c_{11}-c_{12}$ and c_{44} do not include the effects. The value of c_l for Na derived by Bardeen and Pines is 15% larger than the experimental value, or even 25% larger, if one takes the ion-core exchange repulsions into account, whereas the effects of the exchange and correlation energies given by Eq. (7.11) just covers the discrepancy as readily be seen.

This comparison shows the exchange and correlation terms are indispensable. The interaction constants in Table I or II also show the important role of the exchange and correlation effects on the effective matrix element of electron-lattice vibration interactions.

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Appendix I

Eq. (6.10) is derived as follows. We have from Eq. (6.9)

$$\frac{dE_c}{dr_s}=\frac{dE_0}{dr_s}-\frac{6}{5}\frac{\zeta_0}{r_s}+0.6\frac{e^2}{r_s^2}-\frac{0.458e^2}{r_s^2}+\frac{0.288e^2}{(r_s+5.1a_H)^2}, \qquad \text{(AI.1)}$$

assuming $\alpha(r_s)=m/m^*=1$ and $d\alpha(r_s)/dr_s=0$, or

$$\frac{dE_c}{dr_s}=\frac{3}{r_s}(V(r_s)-E_0)-\frac{6}{5}\frac{\zeta_0}{r_s}+\frac{0.458e^2}{r_s^2}+\frac{0.288e^2}{(r_s+5.1a_H)^3}, \qquad \text{(AI.2)}$$

substituting dE_0/dr_s from Eq. (6.11). Differentiation of Eq. (AI.2) gives

$$\frac{d^2E_c}{dr_s^2}=-\frac{3}{r_s^2}(V(r_s)-E_0)+\frac{3}{r_s}\left\{\frac{dV}{dr_s}-\frac{dE_0}{dr_s}\right\}$$
$$+\frac{6}{r_s^2}\frac{3\zeta_0}{5}-\frac{0.916e^2}{r_s^3}-\frac{0.576e^2}{(r_s+5.1a_H)^3}. \qquad \text{(AI.3)}$$

The Hartree-Fock potential $V_0(r)$ is given as,

$$V_0(r)=v_I(r)+\left(\frac{3e^2}{2r_s}-\frac{e^2r^2}{2r_s^3}\right)-\frac{0.916e^2}{r_s},$$

and hence admitting that $v_I(r)$ tends to $-e^2/r$ in the neighbourhood of $r=r_s$,

$$V_0(r_s)=-\frac{0.916e^2}{r_s}. \qquad \text{(AI.4)}$$

We have from Eqs. (AI.4), (6.11) and (AI.3),

$$\frac{d^2E_c}{dr_s^2}=-\frac{12}{r_s^2}(V(r_s)-E_0)+\frac{6}{r_s^2}\frac{3\zeta_0}{5}+\frac{1.8e^2}{r_s^3}-\frac{0.916e^2}{r_s^3}-\frac{0.576e^2}{(r_s+5.1a_H)^3},$$

and hence

$$\frac{1}{\kappa}=\frac{1}{12\pi r_s}\frac{d^2E_c}{dr_s^2}$$
$$=N\left\{-\frac{4}{3}(V(r_s)-E_0)+\frac{2}{5}\zeta_0+\frac{0.2e^2}{r_s}-\frac{0.102e^2}{r_s}-\frac{0.064e^2r_s^2}{(r_s+5.1a_H)^3}\right\},$$

or

$$\frac{1}{\kappa}=N\left\{-2(V(r_s)-E_0)+\frac{2}{3}\zeta_0\right.$$
$$\left.+\frac{0.2e^2}{r_s}-\frac{0.204e^2}{r_s}-\frac{0.064e^2r_s}{(r_s+5.1a_H)}\left(1+\frac{r_s}{r_s+5.1a_H}\right)\right\}, \qquad \text{(AI.5)}$$

with reference to the equilibrium condition $dE_c/dr_s=0$, *i.e.*,

$$-\frac{2}{3}(V(r_s)-E_0)+\frac{4}{15}\zeta_0-\frac{0.102e^2}{r_s}-\frac{0.064e^2r_s}{(r_s+5.1a_H)^2}=0\ .$$

Appendix II

The exchange energy of valence electrons is given as

$$-(1/2)\sum_k\sum_{k'}\iint\Psi^*(\mathbf{k}'\mathbf{r}_j)\Psi(\mathbf{k}\mathbf{r}_j)(e^2/r_{ij})\Psi^*(\mathbf{k}\mathbf{r}_i)\Psi(\mathbf{k}'\mathbf{r}_i)d\mathbf{r}_i d\mathbf{r}_j$$

$$=-0.458\frac{Ne^2}{r_s}-\sum_h\frac{\pi}{4}\frac{e^2}{(2\pi)^4}\frac{m^2}{\hbar^4}\frac{k_F^2}{|\mathbf{q}+\mathbf{K}_h|^2}\left\{|V_{ph+}|^2+|V_{ph-}|^2\right\}h(\mathbf{q}+\mathbf{K}_h), \tag{AII. 1}$$

where the second term of the right hand side arises from the deformation accompanying the lattice vibration and the $h(q)$ is given as

$$h(\bar{q})=\int_{-1}^{1}\int_{-1}^{1}S(\bar{q},x,y)\,dx\,dy\ , \tag{AII. 2}$$

where

$$S(\bar{q},x,y)=S_1(\bar{q},x,y)+S_2(\bar{q},x,-y)+S_2(\bar{q},-x,y)\ ,$$

$$S_1(\bar{q},x,y)=-\frac{2(x-y)^2}{(\bar{q}^2/4-x^2)(\bar{q}^2/4-y^2)}\left\{\frac{\bar{q}^2}{4}(x+y)^2+\frac{\bar{q}^2}{4}+xy\right\}$$

$$\times\begin{Bmatrix}(1-x^2)\log\dfrac{1+x}{x-y}+(1-y^2)\log\dfrac{1-y}{x-y}-(1-x)(1+y) & \text{for}\quad x>y\\[2ex] (1-x^2)\log\dfrac{1-x}{y-x}+(1-y^2)\log\dfrac{1+y}{y-x}-(1+x)(1-y) & \text{for}\quad x<y\end{Bmatrix},$$

and

$$S_2(\bar{q},x,-y)=\frac{(\bar{q}+x-y)^2}{(\bar{q}/2+x)^2\,(\bar{q}/2-y)^2}\left\{(1-x^2)\log\left[\frac{\sqrt{A}+(\bar{q}+x-y)^2+x^2-y^2}{2(\bar{q}+x-y)^2}\right]\right.$$

$$+(1-y^2)\log\left[\frac{\sqrt{A}+(\bar{q}+x-y)^2-x^2+y^2}{2(\bar{q}+x-y)^2}\right]$$

$$\left.+\frac{1}{2}\sqrt{A}-1+xy-\bar{q}(x-y)-\frac{\bar{q}^2}{2}\right\}$$

with abbreviations $\bar{q}=q/k_F$ and

$$A=(\bar{q}+x-y)^4+2(\bar{q}+x-y)^2(2-x^2-y^2)+(x^2-y^2)^2.$$

The integrand $S(\bar{q},x,y)$ of (AII. 2) is singular along the lines $x=\pm\bar{q}/2$ and $y=\pm\bar{q}/2$, it being meant by the appropriate integral that

$$\lim_{\varepsilon\to 0}\left\{\int_{-1}^{-\frac{\bar{q}}{2}-\varepsilon}\int_{-1}^{-\frac{\bar{q}}{2}-\varepsilon}+\int_{-\frac{\bar{q}}{2}+\varepsilon}^{\frac{\bar{q}}{2}-\varepsilon}\int_{-1}^{-\frac{\bar{q}}{2}-\varepsilon}+\int_{\frac{\bar{q}}{2}+\varepsilon}^{1}\int_{-1}^{-\frac{\bar{q}}{2}-\varepsilon}+\int_{-1}^{-\frac{\bar{q}}{2}-\varepsilon}\int_{-\frac{\bar{q}}{2}+\varepsilon}^{\frac{\bar{q}}{2}-\varepsilon}\right.$$

$$\left.+\cdots\cdots+\int_{\frac{\bar{q}}{2}+\varepsilon}^{1}\int_{\frac{\bar{q}}{2}+\varepsilon}^{1}\right\},$$

which converges as is readily verified. The integral $h(q)$ is estimated at 13.1 for $q=k_F$, giving the expression (7.6).

The exchange energy in the simplified expression is, instead of Eq. (A II. 1),

$$\begin{aligned}&-(3/2)e^2\Big\{(3/8\pi)2\sum_k \Psi(\mathbf{kr}_i)\Psi(\mathbf{kr}_i)\Big\}^{1/3}\\&=-0.458\frac{Ne^2}{r_s}-\sum_h\frac{7}{6}Ne^2\left\{\frac{3}{8\pi}N\right\}^{1/3}\left\{|V_{ph+}|^2+|V_{ph-}|^2\right\}\\&\qquad\times\Big\{2\sum_k(E_0(\mathbf{k}+\mathbf{q}+\mathbf{K}_k)-E_0(\mathbf{k}))^{-1}\Big\}^2\ .\end{aligned}\tag{A II. 3}$$

The term $q=k_F$ and $\mathbf{K}_h=0$ is given by Eq. (5.2) as the expression (7.7).

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