written in the Bloch form

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_k(\vec{r}) \quad . \qquad \text{(IV-25)}$$

We write the matrix elements as

$$U_{kk'} = -\sum_{\vec{l}} \vec{R}(\vec{l}) \cdot \int_{\text{crystal}} \psi_{k'}^{*}(\vec{r})\, \nabla V \psi_k(\vec{r})\, d\vec{r} \qquad \text{(IV-26)}$$

and by changing the origin to the lattice point at $\vec{l}$ so that $\vec{r}' = \vec{r} - \vec{l}$

$$U_{kk'} = -\sum_{\vec{l}} \vec{R}(\vec{l})\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{l}} \int \psi_{k'}^{*}(\vec{r}')\, \nabla V \psi_k(\vec{r}')\, d\vec{r}' \quad . \qquad \text{(IV 26a)}$$

Bailyn [11] has computed the integral in Eq. (IV-26a) in a calculation that uses the Hartree-Fock equation for the electrons. We follow his notation and express the integral as

$$\int_{\text{crystal}} \psi_{k'}^{*}(\vec{r})\, \nabla V(\vec{r}) \psi_k(\vec{r})\, d\vec{r} = \hat{s}\,[JS] \qquad \text{(IV-27)}$$

where $\hat{s} = \dfrac{\vec{k} - \vec{k}'}{|\vec{k} - \vec{k}'|}$ .

We are ignoring normalization factors. J denotes the contribution to the matrix element of the ion core alone and S denotes a shielding factor which includes the effect of the electron cloud about the core and the exchange hole.

If we now express the displacement $\vec{R}(\vec{l})$ in terms of lattice waves, we have

$$\vec{R}(\vec{l}) = \sum_{p} \sum_{\vec{q}} \hat{e}_{\vec{q},p}\, a_{\vec{q},p}\, e^{-i\vec{q}\cdot\vec{l}} \qquad \text{(IV-28)}$$

where $\hat{e}_{\vec{q},p}$ is a unit vector which depends on $\vec{q}$, the lattice vibration or phonon wave number and the polarization p. $a_{\vec{q}}$ is the amplitude of the vibration.

Then

$$U_{kk'} = - \sum_{\vec{q}} \sum_{\vec{l}} e^{-i(\vec{k} - \vec{k'} + \vec{q}) \cdot \vec{l}} \, a_{\vec{q},p} \sum_{p} \hat{e}_{\vec{q},p} \cdot \hat{s} \, [JS(\theta)] \quad . \qquad \text{(IV-29)}$$

the sum over $\vec{l}$ yields the condition

$$\vec{k} - \vec{k'} + \vec{q} = \begin{cases} \vec{K}, \text{ a reciprocal lattice vector} \\ 0 \end{cases} \qquad \text{(IV-30)}$$

and a value N, the number of ions.

Since $\vec{k}$ and $\vec{k'}$ are specified and we have restricted $\vec{q}$ to lie in the 1st Brillouin zone, $\vec{q}$ is specified and the sum over $\vec{q}$ reduces to a single term.

The value of $a_{\vec{q}}$ comes from the matrix element for a phonon annihilation (creation) operator and is given by [ 12]

$$a_{\vec{q},p} = \left[ \frac{\hbar}{2NM \nu_{\vec{q},p}} \right]^{1/2} \times \begin{cases} (\bar{n}_{\vec{q},p})^{1/2} & \text{annihilation of phonon} \\ \text{or} & \\ (\bar{n}_{\vec{q},p} + 1)^{1/2} & \text{creation of phonon} \end{cases} \qquad \text{(IV-31)}$$

where M is the mass of the ion and $\nu_{\vec{q},p}$ the frequency of the phonon $\vec{q}$ .

$\bar{n}_{\vec{q}}$ the equilibrium occupation number is given by the Bose-Einstein factor;

$$\bar{n}_{\vec{q}} = \frac{1}{e^{h\nu_{\vec{q}}/kT} - 1} \quad . \qquad \text{(IV-32)}$$

For the high temperature limit $h\nu/kT \ll 1$ and $a_{\vec{q}}$ becomes

$$a_{\vec{q}} = \left[ \frac{\hbar}{2NM\nu_{\vec{q}}} \; \frac{kT}{h\nu_{\vec{q}}} \right]^{1/2} \quad \text{High Temperature Limit} \quad , \qquad \text{(IV-33)}$$

We write this as

$$a_{\vec{q},p} = \frac{B^{1/2}}{N\omega_{\vec{q},p}} \qquad \text{(IV-34)}$$