Effective Mass Theory in Solids from a Many-Particle Standpoint*

W. KOHN†
Carnegie Institute of Technology, Pittsburgh, Pennsylvania, and Bell Telephone Laboratories, Murray Hill, New Jersey
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Effective-mass equations for electrons and holes in solids are usually derived by means of the independent-particle model. It is shown in the present paper that for the case of an extra electron or a hole in an insulator, or semiconductor, moving under the action of a weak Coulomb field, an effective-mass equation,

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2-\frac{qe}{\kappa r}\right)F=EF,$$

can be derived from some very general properties of the entire many-particle system (m^*=effective mass, q=external charge, κ=static dielectric constant). The effects of exchange and correlation are automatically included without approximation. It is suggested that the same type of result can be derived for the motion of electrons and holes in arbitrary slowly varying and weak electromagnetic fields.

1. INTRODUCTION

THE notion of "effective mass" is widely used by solid state physicists. It offers a convenient and often suggestive way of describing experimental results: Suppose a physical quantity Q (specific heat, cyclotron resonance frequency, etc.) is given by the expression

$$Q=f(m) \tag{1.1}$$

for free electrons (m=electron mass). Then if for some real solid it is found empirically to have the value Q^*, the corresponding effective mass m^* is defined by

$$Q^*=f(m^*); \tag{1.2}$$

i.e., m^* is that value which, when introduced into the free-electron formula, gives agreement with experiment.

From the theoretical side, the effective-mass concept can be made plausible by the model which treats the electrons as independent and satisfying a Schrödinger equation of the form

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V(\mathbf{r})\right)\psi=E\psi, \tag{1.3}$$

where $V(\mathbf{r})$ is an effective periodic potential. The solutions of this equation are the familiar Bloch waves

$$\psi_{\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}), \tag{1.4}$$

whose eigenvalues are[1]

$$E_{\mathbf{k}}=E_0+E_2k^2 \tag{1.5}$$

for sufficiently small values of k. Comparison with the free electron expression for the energy, $(\hbar^2/2m)k^2$, leads to the following definition of m^*:

$$\hbar^2/2m^*=E_2. \tag{1.6}$$

With the same model one can then show that, at least for small values of k, the behavior of the electrons in solids is equivalent to that of free electr ns with an altered effective mass m^*.

Now clearly the usefulness of the concept of effective mass depends entirely on whether, for a given material, the *same* value of m^* describes correctly several different empirical properties. Many instances can be cited where this is found to be approximately true. Let us take one—donor states in silicon.

Consider a perfect crystal of Si at the absolute zero of temperature. Add a charge $+e$ to one of the nuclei, converting it into a P nucleus. This extra charge will produce an additional mean potential

$$U=e/\kappa r, \tag{1.7}$$

at large distances, where κ is the static dielectric constant of Si. Now add an extra electron. This may be caught in a bound state. If the orbit is large enough one can show—on the basis of the one-particle model—that this state can be described by the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2-\frac{e^2}{\kappa r}\right)F=EF, \tag{1.8}$$

where m^* is the effective mass of the conduction band.[2] But m^* can be independently measured by a cyclotron resonance experiment[3] where, again on the basis of the one-particle model, the resonance frequency is given by

$$\omega=eH/m^*c; \tag{1.9}$$

here H is the static magnetic field. Also κ can be independently measured. When these empirical values of m^* and κ are used in (1.8) to compute the energy spectrum of the donors, excellent agreement with

* Supported in part by the Office of Naval Research.
† Permanent address: Carnegie Institute of Technology, Pittsburgh, Pennsylvania.
[1] For the sake of simplicity we assume here, and in the rest of this paper, that the solid has cubic symmetry, that the band in question is nondegenerate, and that there are no spin-dependent forces.
[2] This type of equation was first obtained by G. H. Wannier, Phys. Rev. **52**, 191 (1937).
[3] Dresselhaus, Kip, and Kittel, Phys. Rev. **95**, 568 (1954); B. Lax *et al.*, Phys. Rev. **93**, 1418 (1954).

experiment is found for sufficiently large orbits[4]—a success of the effective-mass equation (1.8).

This surprisingly good agreement suggests that the validity of Eq. (1.8) may be better than the rather crude independent-particle model by which it is theoretically justified. In the present paper we shall in fact show that this equation can be derived from some very general properties of the entire many-electron wave function, without any recourse to the one-particle picture.

More precisely, we shall derive the following theorem: Consider a perfect insulating crystal, with nuclei held rigidly in place, and at $T=0$. Now introduce a *small* point charge q and an additional electron into the crystal. Then *all* low-lying energy states of the system are described rigorously by the one-particle equation (1.8), where m^* is an effective mass and κ is the static dielectric constant.[1] In other words, all the complicated effects of the interactions of electrons with the nuclei and with each other are completely represented by the two phenomenological constants m^* and κ.

The nature of the derivation of this result leads one to believe that it is a special case of the following more general theorem: Take again the above-described insulating crystal. Add one electron and consider the response of the entire system to an external electromagnetic field $A_\mu(\mathbf{r},t)$, which varies slowly in the following senses:

$$\left|\frac{\partial A_\mu}{\partial x_i}\right| \Big/ |A_\mu| \ll \frac{1}{a}, \quad \left|\frac{\partial A_\mu}{\partial t}\right| \Big/ |A_\mu| \ll \frac{\Delta E}{\hbar}, \tag{1.10}$$

where a is the lattice parameter and ΔE is a characteristic energy of the order of electron volts. For motions in which the energy of the system is changed from its unperturbed ground state energy by an amount $\ll\Delta E$, its response to the field can be rigorously described by a one-particle equation involving the three phenomenological constants m^*, κ, and χ; here χ is the static magnetic susceptibility, and m^* and κ are as defined above. We hope to come back to this conjecture at a later time.

The entire situation is completely analogous for the case of a so-called "hole" where an electron has been removed from a perfect insulating crystal.

In any actual physical situation the conditions which we have imposed will be more or less violated. But in many cases the actual state of affairs differs only very slightly from our idealized one and our conclusions are then of real significance. The most important fact is that our results do not depend on the quite unrealistic assumption of a weak electron-electron interaction.

[4] Picus, Burstein, and Henvis, Bull. Am. Phys. Soc. Ser. II, 1, 126 (1956). W. Kohn, Phys. Rev. 98, 1856 (1955). Actually, in Si, the mass is anisotropic and appropriate modifications have to be made to interpret the experimental data.

2. EFFECTIVE MASS AND DIELECTRIC CONSTANT

We consider our perfect insulating crystal plus one electron, a total of $N+1$ electrons. We choose atomic units, e, $\hbar$, and m equal to 1. The Hamiltonian of our system is

$$H=-\sum_{i=1}^{N+1}\tfrac{1}{2}\nabla_i^2-\sum_{i,l}\frac{Z_l}{|\mathbf{r}_i-\mathbf{R}_l|}+\tfrac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}, \tag{2.1}$$

where $\mathbf{R}_l$ and Z_l are the position vector and charge of the lth nucleus and $\mathbf{r}_i$ is the position vector of the ith electron.

This Hamiltonian commutes with the total translation operators T_α, which are defined by

$$T_\alpha f(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_{N+1}) = f(\mathbf{r}_1+\boldsymbol{\tau}_\alpha, \mathbf{r}_2+\boldsymbol{\tau}_\alpha, \cdots \mathbf{r}_{N+1}+\boldsymbol{\tau}_\alpha), \quad \alpha=1, 2, 3, \tag{2.2}$$

where the $\boldsymbol{\tau}_\alpha$ are the fundamental translation vectors of the lattice. Hence the (normalized) eigenfunctions of H can be chosen to be also eigenfunctions of T_α. It is convenient to write them in the form

$$\Psi_{n,\mathbf{K}}=e^{i\mathbf{K}\cdot\mathbf{r}_1}\Phi_{n,\mathbf{K}}, \tag{2.3}$$

where $\Phi_{n,\mathbf{K}}$ is a strictly periodic function in the sense that

$$T_\alpha\Phi_{n,\mathbf{K}}=\Phi_{n,\mathbf{K}}. \tag{2.4}$$

The vector $\mathbf{K}$ is restricted to lie in the first Brillouin zone, and n denotes the set of quantum numbers which, besides $\mathbf{K}$, specify the state. We denote the eigenvalues of H by $E_{n,\mathbf{K}}$:

$$H\Psi_{n,\mathbf{K}}=E_{n,\mathbf{K}}\Psi_{n,\mathbf{K}}. \tag{2.5}$$

We shall now characterize our system by a certain property of the energy spectrum $E_{n,\mathbf{K}}$. Let us assume for simplicity that the ground state of our system corresponds to $\mathbf{K}=0$ and let us denote the corresponding n by $n=0$.[5] The property in question is then that

$$E_{n,0}-E_{0,0}\geq\Delta E, \quad n\neq 0, \tag{2.6}$$

where ΔE is a finite energy, independent of the size of the crystal, if sufficiently large. Figure 1 illustrates the meaning of (2.6) by means of the one-particle model. Evidently the usual independent-particle model of an insulator satisfies (2.6); that of a metal, however, does not. That a *real* insulator (with electron-electron interactions) also has this property, is evidenced most directly by the following empirical fact: When only a few extra electrons are present, optical radiation, which causes transitions between states of the same $\mathbf{K}$, is not absorbed, until the quantum of energy reaches a certain threshold.[6] For our purposes we shall *define* an insulator by the requirement that (2.6) is satisfied.

[5] Actually the ground state has a double degeneracy due to spin. However, since we have assumed spin-independent forces this is of no consequence, and we may for definiteness assume that the z component of the total spin is $+\frac{1}{2}$.

[6] Of course, due to imperfections, *slight* absorption does in fact take place even for very small photon energies.

Near $\mathbf{K}=0$, the energy $E_{0,\mathbf{K}}$ can be expanded as

$$E_{0,\mathbf{K}}=E_{0,0}+\alpha_{ij}K_iK_j+\cdots. \tag{2.7}$$

Linear terms in K_i are absent since $E_{0,0}$ was taken to be the absolute minimum of energy. For simplicity, we consider a cubic crystal where by symmetry we may write (2.7) in the form

$$E_{0,\mathbf{K}}=E_{0,0}+(1/2m^*)K^2; \tag{2.8}$$

m^* is by definition the effective mass. We plan in a future publication to show that this m^* is what one measures in a cyclotron resonance experiment.

We now turn to the effective dielectric constant κ^*. Let us consider the inner product

$$(\Psi_{0,\mathbf{K}}e^{-i\mathbf{K}\cdot\mathbf{r}_1},\Psi_{0,\mathbf{K}'}e^{-i\mathbf{K}'\cdot\mathbf{r}_1})=(\Phi_{0,\mathbf{K}},\Phi_{0,\mathbf{K}'}). \tag{2.9}$$

For $\mathbf{K}=\mathbf{K}'$ it has the value 1. One might expect that for $|\mathbf{K}-\mathbf{K}'|a\ll 1$ (a=lattice parameter), it would have a value close to 1. This is not so. In the independent-particle model it has the value $(N+1)^{-1}$, where $N+1$ is the total number of electrons, and when the Coulomb interaction is treated by perturbation methods (see Appendix) one finds the value $[(N+1)\kappa]^{-1}$, where κ is the static dielectric constant of the perfect insulator (N electrons). Clearly, the N dependence of this product is not altered when the Coulomb interaction is strong. Also this scalar product must tend to a definite limit when K and K' are $\ll a^{-1}$, so that we are led to introduce the effective dielectric constant κ^* by the equation,

$$\frac{1}{\kappa^*}=(N+1)\lim_{\substack{\mathbf{K},\,\mathbf{K}'\to 0\\ \mathbf{K}\neq\mathbf{K}'}}(\Phi_{0,\mathbf{K}},\Phi_{0,\mathbf{K}'}). \tag{2.10}$$

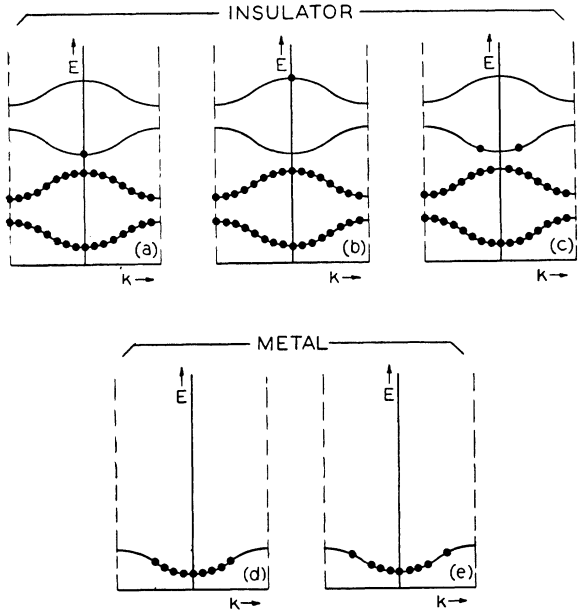

FIG. 1. One-particle spectra of insulators and metals. (a) is the insulator ground-state with $\mathbf{K}=0$. All excited states with $\mathbf{K}=0$, such as (b) and (c), exceed it in energy by at least ΔE. (d) is the metallic ground state; some excited states, such as (e), exceed it in energy by infinitesimal amounts.

We shall show in Sec. 4 that this κ^* is in fact the static dielectric constant κ of the perfect insulator (N electrons).

3. IMPURITY STATE PROBLEM

We now introduce into our $N+1$ electron system a small point charge q at the origin producing a perturbation potential

$$U=-q\sum_i\frac{1}{r_i}+q\sum_l\frac{Z_l}{R_l}. \tag{3.1}$$

What are the eigenfunctions and eigenvalues of the new Hamiltonian?

We expand the new eigenfunctions in terms of the $\Psi_{n,\mathbf{K}}$:

$$\Psi=\sum_{n,\mathbf{K}}A_{n,\mathbf{K}}\Psi_{n,\mathbf{K}}, \tag{3.2}$$

and substitute into the Schrödinger equation

$$(H+U-E)\Psi=0. \tag{3.3}$$

This gives the system of equations:

$$(E_{0,\mathbf{K}}-E)A_{0,\mathbf{K}}+\sum_{\mathbf{K}'}(0\mathbf{K}|U|0\mathbf{K}')A_{0,\mathbf{K}'}+\sum_{\mathbf{K}'}\sum_{n'\neq 0}(0\mathbf{K}|U|n'\mathbf{K}')A_{n',\mathbf{K}'}=0, \tag{3.4a}$$

$$(E_{n,\mathbf{K}}-E)A_{n,\mathbf{K}}+\sum_{\mathbf{K}'}(n\mathbf{K}|U|0\mathbf{K}')A_{0,\mathbf{K}'}+\sum_{\mathbf{K}'}\sum_{n'\neq 0}(n\mathbf{K}|U|n'\mathbf{K}')A_{n',\mathbf{K}'}=0 \quad (n\neq 0), \tag{3.4b}$$

where we have explicitly displayed the terms with $n=0$. Since q is infinitesimal we expect solutions for which

$$|E-E_{0,0}|\ll\Delta E, \quad \text{and} \quad A_{n,\mathbf{K}}\neq 0 \text{ only if } Ka\ll 1. \tag{3.5}$$

We can then solve (3.4b) for $A_{n,\mathbf{K}}$ to first order in q:

$$A_{n,\mathbf{K}}=\frac{1}{E_{0,0}-E_{n,0}}\sum_{\mathbf{K}'}(n\mathbf{K}|U|0\mathbf{K}')A_{0,\mathbf{K}'}, \quad n\neq 0. \tag{3.6}$$

Substitution into (3.4a) gives

$$(E_{0,\mathbf{K}}-E)A_{0,\mathbf{K}}+\sum_{\mathbf{K}'}\left[(0\mathbf{K}|U|0\mathbf{K}')+\sum_{\mathbf{K}''}\sum_{n''\neq 0}\frac{(0\mathbf{K}|U|n''\mathbf{K}'')(n''\mathbf{K}''|U|0\mathbf{K}')}{E_{0,0}-E_{n'',0}}\right]A_{0,\mathbf{K}'}=0. \tag{3.7}$$

As the second term in the square bracket is of order q^2, it can be neglected in comparison with the first, so that we finally obtain

$$(E_{\mathbf{K}}-E)A_{\mathbf{K}}+\sum_{\mathbf{K}'}(\mathbf{K}|U|\mathbf{K}')A_{\mathbf{K}'}=0; \tag{3.8}$$

here and in what follows we suppress the common quantum number $n=0$, to simplify the notation.

We now study the matrix elements of U. By (3.1), the diagonal elements are

$$(\mathbf{K}|U|\mathbf{K})=-q(N+1)\left(\Phi_{\mathbf{K}},\frac{1}{r_1}\Phi_{\mathbf{K}}\right)+q\sum_l\frac{Z_l}{R_l}. \quad (3.9)$$

Let us denote the operation of performing, in an inner product, all spin sums and all integrations except that over $\mathbf{r}_1$ by $(\ )'$; and let us define

$$\rho_{\mathbf{K}}(\mathbf{r}_1)\equiv(N+1)(\Phi_{\mathbf{K}},\Phi_{\mathbf{K}})'. \quad (3.10)$$

This is the charge density in the state $\Psi_{\mathbf{K}}$. Clearly

$$\rho_{\mathbf{K}}(\mathbf{r}_1)=\rho_0(\mathbf{r}_1)+\frac{1}{N}\rho'_{\mathbf{K}}(\mathbf{r}_1), \quad (3.11)$$

where $\rho_0(\mathbf{r}_1)$ is the charge density of the perfect insulator (N electrons), and $(1/N)\rho_{\mathbf{K}}'(\mathbf{r}_1)$ is the additional charge density due to the extra electron. With these definitions (3.9) becomes

$$(\mathbf{K}|U|\mathbf{K})=q\left(\sum_l\frac{Z_l}{R_l}-\int\frac{\rho_0(\mathbf{r})}{r}d\mathbf{r}\right)+\frac{q}{N}\int\frac{\rho'_{\mathbf{K}}(\mathbf{r})}{r}d\mathbf{r}. \quad (3.12)$$

The term in parentheses is the potential at $\mathbf{r}=0$ in the perfect insulator, independent of $\mathbf{K}$ and of the same order of magnitude as ΔE, namely, electron volts. Let us denote it by W. As the second term vanishes for large N, we have simply

$$(\mathbf{K}|U|\mathbf{K})=qW. \quad (3.13)$$

For $\mathbf{K}\neq\mathbf{K}'$,

$$(\mathbf{K}|U|\mathbf{K}')=-q\int\rho_{\mathbf{K},\mathbf{K}'}(\mathbf{r}_1)\frac{e^{i(\mathbf{K}'-\mathbf{K})\cdot\mathbf{r}_1}}{r_1}d\mathbf{r}_1, \quad (3.14)$$

where

$$\rho_{\mathbf{K},\mathbf{K}'}(\mathbf{r}_1)=(N+1)(\Phi_{\mathbf{K}},\Phi_{\mathbf{K}'})', \quad (3.15)$$

Since $\rho_{\mathbf{K},\mathbf{K}'}$ is a completely periodic function of $\mathbf{r}_1$ it can be expanded as follows:

$$\rho_{\mathbf{K},\mathbf{K}'}(\mathbf{r}_1)=\sum_\nu\rho_{\mathbf{K},\mathbf{K}'}^{(\nu)}\exp(i\mathbf{K}_\nu\cdot\mathbf{r}_1), \quad (3.16)$$

where the $\mathbf{K}_\nu$ are the reciprocal lattice vectors. Substitution into (3.14) gives the series

$$(\mathbf{K}|U|\mathbf{K}')=-4\pi q\sum_\nu\rho_{\mathbf{K},\mathbf{K}'}^{(\nu)}\frac{1}{|\mathbf{K}'-\mathbf{K}+\mathbf{K}_\nu|^2}. \quad (3.17)$$

For small K and K' we need retain only the term with $\nu=0$ and can replace $\rho_{\mathbf{K},\mathbf{K}'}^{(0)}$ by its limiting value for small K and K', which by (2.10) is just $1/V\kappa^*$, V being the volume of the crystal. Thus, finally

$$(\mathbf{K}|U|\mathbf{K}')=-\frac{q}{\kappa^*}\frac{4\pi}{V}\frac{1}{|\mathbf{K}'-\mathbf{K}|^2}, \quad \mathbf{K}\neq\mathbf{K}'. \quad (3.18)$$

With these matrix elements (3.13), (3.18), and the definition of our effective mass, (2.8), we now go back to the Schrödinger equation (3.8) which becomes

$$\left(\frac{1}{2m^*}K^2-E^*\right)A_{\mathbf{K}}-\frac{q}{\kappa^*}\frac{4\pi}{V}\sum_{\mathbf{K}'\neq\mathbf{K}}\frac{1}{|\mathbf{K}-\mathbf{K}'|^2}A_{\mathbf{K}'}=0, \quad (3.19)$$

where

$$E^*=E-E_{00}-qW. \quad (3.20)$$

To transform this into a Schrödinger equation in coordinate space, we define

$$F(\mathbf{r})\equiv\frac{1}{V^{\frac{1}{2}}}\sum_{\mathbf{K}}A_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}}. \quad (3.21)$$

Multiplying (3.19) by $e^{i\mathbf{K}\cdot\mathbf{r}}$ and summing over $\mathbf{K}$ gives

$$\left(-\frac{1}{2m^*}\nabla^2-E^*\right)F(\mathbf{r})-\frac{q}{\kappa^*}\int\Delta(\mathbf{r}-\mathbf{r}')\frac{1}{r'}F(\mathbf{r}')d\mathbf{r}'=0, \quad (3.22)$$

where

$$\Delta(\mathbf{r}-\mathbf{r}')=\frac{1}{V}\sum_{\mathbf{K}}e^{i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}')}. \quad (3.23)$$

$\Delta(\mathbf{r}-\mathbf{r}')$ is a "spread-out δ function" extending over dimensions of the order of a.[7] Therefore, if F does not vary appreciably over a lattice spacing—as we can verify at once—we can replace (3.22) by

$$\left(-\frac{1}{2m^*}\nabla^2-\frac{q}{\kappa^*r}\right)F(\mathbf{r})=E^*F(\mathbf{r}), \quad (3.24)$$

which is of course the familiar hydrogen-like effective-mass equation.

It remains to verify that the conditions (3.5) under which these equations were derived are indeed satisfied. Consider first the negative-energy solutions of (3.24). For these,

$$E^*=-\frac{m^*q^2}{2\kappa^{*2}}\frac{1}{n^2}, \quad K\lesssim\frac{qm^*}{\kappa^*}, \quad (3.25)$$

so that, for small enough q, (3.4) is fulfilled. It remains fulfilled for positive energy solutions of (3.24) for which $E^*\ll\Delta E$.

It is obvious that an identical derivation leads to an effective-mass equation for a hole.

4. DISCUSSION OF DIELECTRIC CONSTANT

As our theory deals with the entire system it is not surprising that, in contrast to the more elementary discussions, the effective dielectric constant κ^* is not introduced through intuitive considerations but rather

[7] If the summation in (3.23) were carried out over all $\mathbf{K}$, instead of the first Brillouin zone only, (3.23) would be a sharp δ function.

emerges quite naturally from the equations themselves. In Eq. (2.10) we defined the effective dielectric constant by

$$\frac{1}{\kappa^*}=(N+1)\lim_{\substack{\mathbf{K},\,\mathbf{K}'\to 0\\ \mathbf{K}\neq\mathbf{K}'}}(\Phi_{\mathbf{K}},\Phi_{\mathbf{K}'}). \tag{4.1}$$

We shall now show that this κ^* is equal to the static dielectric constant κ of the medium.

The most natural definition of κ would refer to the perfect insulator (N electrons) and be as follows: Consider two small point charges q_1 and q_2 in the medium, at a distance $R\gg a$ from each other. The energy of the entire system will then contain a term proportional to q_1 and q_2 of the form

$$E_{q_1,\,q_2}=q_1q_2/\kappa R. \tag{4.2}$$

The constant κ is the dielectric constant. In the appendix we verify explicitly that, in the case of weak electron-electron interactions, the constant κ^* in Eq. (4.1) is identical with the static dielectric constant κ defined by Eq. (4.2).

However, when the electron-electron interactions are not weak, it is difficult to identify the effective dielectric constant κ^*, defined by (4.1) in terms of $N+1$ particle functions, with the static dielectric constant κ as defined in (4.2) in terms of the N-electron system. We therefore use instead of (4.2) the following definition of κ which enables us to prove in general its equality with κ^*. We consider the $N+1$ electron system with two infinitesimal point charges $q_1>0$ and $q_2<0$ at a large distance R. This system has discrete energy states (electron bound to q_1). We then expect on physical grounds that the energy of the system will contain a term falling off as $1/R$ and given by

$$\tilde{E}=(q_1-1)q_2/\kappa R, \tag{4.3}$$

where κ is the same dielectric constant as that defined by (4.2).[8] We may therefore define the dielectric constant κ by the following relation:

$$\tilde{E}\to -q_2/\kappa R, \quad \text{for} \quad q_1,\,q_2\to 0. \tag{4.4}$$

We shall now show that the κ^*, Eq. (4.1), is equal to κ as defined by (4.4).

Begin by setting $q_2=0$ and take q_1 at $\mathbf{R}=0$. The wave function of the $N+1$ electron system is then

$$\Psi=\sum_{\mathbf{K}} A_{\mathbf{K}}\Psi_{\mathbf{K}}, \tag{4.5}$$

where we neglect terms proportional to q_1. The first-order perturbation energy due to q_2, located at $\mathbf{R}$, is

$$E^{(1)}=(\Psi,U_2\Psi), \tag{4.6}$$

where

$$U_2=-q_2\sum_i\frac{1}{|\mathbf{r}_i-\mathbf{R}|}+q_2\sum_l\frac{Z_l}{|\mathbf{R}_l-\mathbf{R}|}. \tag{4.7}$$

(We can neglect the term q_1q_2/R because of its proportionality to q_1.) Therefore

$$E^{(1)}=\sum_{\mathbf{K}}|A_{\mathbf{K}}|^2(\Psi_{\mathbf{K}},U_2\Psi_{\mathbf{K}}) + \sum_{\mathbf{K}\neq\mathbf{K}'}A_{\mathbf{K}}^*A_{\mathbf{K}'}(\Psi_{\mathbf{K}},U_2\Psi_{\mathbf{K}'}). \tag{4.8}$$

Now, as in the discussion following (3.8), we find that $(\Psi_{\mathbf{K}},U_2\Psi_{\mathbf{K}})$ is q_2 times the electrostatic potential $W(\mathbf{R})$ existing at $\mathbf{R}$ in the perfect insulator (N electrons). $W(\mathbf{R})$ is of course a periodic function of $\mathbf{R}$. The first term in (4.8) is then just $q_2W(\mathbf{R})$. It describes the interaction of q_2 with its surroundings in the perfect insulator (N electrons) and is of no further interest. We now calculate the second term in (4.8):

$$\begin{aligned}\sum_{\mathbf{K}\neq\mathbf{K}'}A_{\mathbf{K}}^*A_{\mathbf{K}'}&\left(\Psi_{\mathbf{K}},\,-q_2\sum\frac{1}{|\mathbf{r}_i-\mathbf{R}|}\Psi_{\mathbf{K}'}\right)\\ &=-q_2(N+1)\sum_{\mathbf{K}\neq\mathbf{K}'}A_{\mathbf{K}}^*A_{\mathbf{K}'}\\ &\qquad\times\left(\Phi_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}_1},\frac{1}{|\mathbf{r}_1-R|}\Phi_{\mathbf{K}'}e^{i\mathbf{K}'\cdot\mathbf{r}_1}\right)\\ &=-q_2\frac{(N+1)}{V}4\pi\sum_{p\neq 0}\frac{e^{-i\mathbf{p}\cdot\mathbf{R}}}{p^2}G(\mathbf{p}),\end{aligned} \tag{4.9}$$

where

$$G(\mathbf{p})=\sum_{\mathbf{K}\neq\mathbf{K}'}A_{\mathbf{K}}^*A_{\mathbf{K}'}(\Phi_{\mathbf{K}}e^{i\mathbf{K}\cdot\mathbf{r}_1},e^{i\mathbf{p}\cdot\mathbf{r}_1}\Phi_{\mathbf{K}'}e^{i\mathbf{K}'\cdot\mathbf{r}_1}). \tag{4.10}$$

For large R, we require $G_0=\lim_{\mathbf{p}\to 0}G(\mathbf{p})$:

$$\begin{aligned}G_0&=\lim_{\mathbf{p}\to 0}\sum_{\mathbf{K}\neq\mathbf{K}'}A_{\mathbf{K}}^*A_{\mathbf{K}'}\delta_{\mathbf{K},\,\mathbf{p}+\mathbf{K}'}(\Phi_{\mathbf{K}'+\mathbf{p}},\Phi_{\mathbf{K}'})\\ &=\lim_{\mathbf{p}\to 0}\sum_{\mathbf{K}'}A_{\mathbf{K}'+\mathbf{p}}^*A_{\mathbf{K}'}\frac{1}{(N+1)\kappa^*}\\ &=\frac{1}{(N+1)\kappa^*}.\end{aligned} \tag{4.11}$$

Substituting into (4.9) gives, for large $\mathbf{R}$,

$$-\frac{q_2}{\kappa^*}\frac{4\pi}{V}\sum_{\mathbf{p}\neq 0}\frac{e^{-i\mathbf{p}\cdot\mathbf{R}}}{p^2}=-\frac{q_2}{\kappa^*R}. \tag{4.12}$$

Thus, finally,

$$E^{(1)}=q_2\left(W(\mathbf{R})-\frac{1}{\kappa^*R}\right). \tag{4.13}$$

Comparison with (4.4) gives the required equality, $\kappa^*=\kappa$.

[8] No formal proof for (4.3) has been found so far, except for the case of weak electron-electron interaction, where the identity of κ and κ^* can be explicitly demonstrated (see Appendix). However in the author's opinion, there is no reasonable doubt that (4.3) is in fact strictly correct. It simply expresses the fact that the long-range field around the electron trapped by the charge q_1 is $(q_1-1)/\kappa R$.

5. CONCLUDING REMARKS

In this paper we have proved the effective mass equation for a very special case, namely that of a weak Coulomb field. Evidently generalizations are called for, e.g., to the actual motion in excited impurity states, where the trapped electron moves in a very large orbit about a *finite* external charge; or to motions in other kinds of weak external fields.

But the simple case studied here already exhibits a characteristic feature. The motion of the electrons is highly correlated. Loosely speaking we can say that the conduction band electron carries with itself a polarization cloud, which partially cancels its charge. Because of this high degree of correlation, a solution of the Hartree-Fock equations would lead to qualitatively wrong results. However, in spite of the complete inapplicability of this method, which is usually employed to derive approximate one-particle equations, we have seen that the low-lying states of our system are nevertheless strictly described by a single-electron type of equation.

A brief comment should be made on deviations from the effective-mass equation. It would seem that they can be conveniently studied by means of Eq. (3.7), which for a finite external charge q represents a much better approximation than the effective-mass equation (3.24).

APPENDIX. EXPLICIT EVALUATION OF κ AND κ^* FOR THE CASE OF WEAK ELECTRON-ELECTRON INTERACTION

In the systems of interest in the present paper, a weak Coulomb interaction between the electrons can be treated by perturbation theory, because a finite energy is required to excite a pair of electrons. This enables us to verify explicitly, to zeroth and second order in the charge of the electrons, the equality of κ^*, the effective dielectric constant of Sec. 2, and κ, the usual static dielectric constant (see Sec. 4).

No Electron-Electron Interaction

We begin with the trivial case of no Coulomb interactions between the electrons. For consistency the potential due to the ions must then also be made short range. Thus we may consider the following zero-order Hamiltonian:

$$H_0=-\sum_i \frac{\hbar^2}{2m}\nabla_i^2-\sum_{i,l}\frac{Z_l}{|\mathbf{r}_i-\mathbf{R}_l|}e^{-\alpha|\mathbf{r}_i-\mathbf{R}_l|}, \quad \text{(A.1)}$$

where α is some artificial screening constant.

Since in this approximation the electrons are uncharged, the static dielectric constant of the medium is obviously

$$\kappa=1. \quad \text{(A.2)}$$

Next we calculate κ^* according to its definition by Eq. (2.10). The appropriate eigenfunctions of H_0 are Slater determinants of Bloch waves. Let $\chi(\alpha)$ be the normalized determinant describing the perfect insulator (full bands) with the N electrons, other than the αth, and let $\psi_{0,\mathbf{K}}(\alpha)=u_{0,\mathbf{K}}(\alpha)\exp(i\mathbf{K}\cdot\mathbf{r}_\alpha)$ be the normalized Bloch waves in the lowest conduction band. With an appropriate choice of the phases of $\chi(\alpha)$, the normalized wave function $\Psi_{0,\mathbf{K}}$ of the $(N+1)$-electron system is then

$$\Psi_{0,\mathbf{K}}=\frac{1}{(N+1)^{\frac{1}{2}}}\sum_{\alpha=1}^{N+1}\chi(\alpha)u_{0,\mathbf{K}}(\alpha)\exp(i\mathbf{K}\cdot\mathbf{r}_\alpha). \quad \text{(A.3)}$$

By (2.10), we have

$$\begin{aligned}1/\kappa^*&=(N+1)\lim(\Phi_{0,\mathbf{K}},\Phi_{0,\mathbf{K}'})\\&=(N+1)\lim(\Psi_{0,\mathbf{K}}e^{-i\mathbf{K}\cdot\mathbf{r}_1},\Psi_{0,\mathbf{K}'}e^{-i\mathbf{K}'\cdot\mathbf{r}_1})\\&=\lim[(u_{0,\mathbf{K}}(1),u_{0,\mathbf{K}'}(1))+\sum_{\alpha,\beta}{}'(\chi(\alpha)\psi_{0,\mathbf{K}}(\alpha)^{-i\mathbf{K}\cdot\mathbf{r}_1},\\&\qquad\chi(\beta)\psi_{0,\mathbf{K}'}(\beta)e^{-i\mathbf{K}'\cdot\mathbf{r}_1})],\end{aligned} \quad \text{(A.4)}$$

where "lim" denotes the limit defined in (2.10) and $\sum'$ means that $\alpha=\beta=1$ is excluded. Clearly the first term in the square bracket of (A.4) gives 1; the others give 0 by integration over $\mathbf{r}_\alpha$ or $\mathbf{r}_\beta$. This establishes the required value for κ^*,

$$\kappa^*=1, \quad \text{(A.5)}$$

equal to κ.

Weak Electron-Electron Interaction

We now discuss the explicit calculation of κ and κ^* in the case of the weak electron-electron interactions. We begin with κ. Let $\Psi_{n,\mathbf{K}}$ be the wave functions of the perfect insulator, with the ground state denoted by $n=0$, $\mathbf{K}=0$. If two point charges q_1 and q_2 are immersed in the medium, at $\mathbf{r}=0$ and $\mathbf{R}$, respectively, they produce a perturbation

$$U=-q_1\sum_i\frac{\epsilon}{r_i}-q_2\sum_i\frac{\epsilon}{|\mathbf{R}-\mathbf{r}_i|}. \quad \text{(A.6)}$$

Here the electronic charge ϵ is regarded as small, and the interaction with the nuclei which is irrelevant for what follows has been omitted. The second-order perturbation energy, proportional to q_1 and q_2, is

$$E_{q_1,q_2}{}^{(2)}=q_1q_2\epsilon^2\sum_{n',\mathbf{K}'}\times\frac{\left(00\left|\sum_i\frac{1}{r_i}\right|n'\mathbf{K}'\right)\left(n'\mathbf{K}'\left|\sum_i\frac{1}{|\mathbf{R}-\mathbf{r}_j|}\right|00\right)+\text{c.c.}}{E_{00}-E_{n',\mathbf{K}'}}. \quad \text{(A.7)}$$

To evaluate (A.7), let us begin by Fourier analyzing the partial scalar product $(\Psi_{0,0},\Psi_{n',\mathbf{K}'})'$:

$$(\Psi_{0,0},\Psi_{n',\mathbf{K}'})'=\frac{1}{N}\sigma_{n',\mathbf{K}'}(\mathbf{r}_1)e^{i\mathbf{K}'\cdot\mathbf{r}_1}$$

$$=\frac{1}{N}\sum_{\nu}\sigma_{n',\mathbf{K}'}{}^{(\nu)}\exp(\mathbf{K}_\nu\cdot\mathbf{r}_1)e^{i\mathbf{K}'\cdot\mathbf{r}_1}, \quad (A.8)$$

where $\sigma_{n',\mathbf{K}'}(\mathbf{r}_1)$ is some periodic function of $\mathbf{r}_1$ which is Fourier-expanded in the following step. Therefore

$$\left(00\left|\sum_i\frac{1}{r_i}\right|n'\mathbf{K}'\right)=4\pi\sum_\nu\sigma_{n',\mathbf{K}'}{}^{(\nu)}\frac{1}{|\mathbf{K}_\nu+\mathbf{K}'|^2}, \quad (A.9)$$

and similarly

$$\left(n'\mathbf{K}'\left|\sum_j\frac{1}{|\mathbf{r}_j-\mathbf{R}|}\right|00\right)$$

$$=4\pi\sum_{\nu'}\sigma_{n',\mathbf{K}'}{}^{(\nu')*}\frac{\exp[-i(\mathbf{K}_{\nu'}+\mathbf{K}')\cdot\mathbf{R}]}{|\mathbf{K}_{\nu'}+\mathbf{K}'|^2}. \quad (A.10)$$

Therefore (A.7) becomes

$$E_{q_1,q_2}{}^{(2)}=q_1q_2\epsilon^2 16\pi^2\Bigg[\sum_{n'\mathbf{K}'}\sum_{\nu\nu'}\frac{\sigma_{n',\mathbf{K}'}{}^{(\nu)}\sigma_{n',\mathbf{K}'}{}^{(\nu')*}}{E_{0,0}-E_{n',\mathbf{K}'}}$$

$$\times\frac{\exp[-i(\mathbf{K}_{\nu'}+\mathbf{K}')\cdot\mathbf{R}]}{|\mathbf{K}_\nu+\mathbf{K}'|^2|\mathbf{K}_{\nu'}+\mathbf{K}'|^2}+\text{c.c.}\Bigg]. \quad (A.11)$$

We shall show below that, for small K',

$$\lim_{\mathbf{K}'\to0}(-8\pi V)\sum_{n'}\frac{\sigma_{n',\mathbf{K}'}{}^{(0)}\sigma_{n',\mathbf{K}'}{}^{(0)*}}{(K')^2(E_{0,0}-E_{n',\mathbf{K}'})}=\gamma, \quad (A.12)$$

where γ is a characteristic constant. Then for large R, we obtain from (A.11)

$$E_{q_1,q_2}{}^{(2)}=-q_1q_2\epsilon^2\gamma\frac{4\pi}{V}\frac{1}{2}\Bigg[\sum_{\mathbf{K}'}\frac{e^{-i\mathbf{K}'\cdot\mathbf{R}}}{(K')^2}+\frac{e^{i\mathbf{K}'\cdot\mathbf{R}}}{(K')^2}\Bigg]$$

$$=-q_1q_2\epsilon^2\gamma(1/R). \quad (A.13)$$

When this is added to the direct Coulomb interaction between q_1 and q_2, one finds for the total interaction energy,

$$E_{q_1,q_2}=(q_1q_2/R)(1-\gamma\epsilon^2), \quad (A.14)$$

so that the dielectric constant is

$$1/\kappa=1-\gamma\epsilon^2, \quad (A.15)$$

where γ is defined in (A.12).

We now evaluate γ explicitly for the case of weak Coulomb interactions. As (A.11) contains an explicit factor ϵ^2, it is permissible to evaluate the $\sigma_{n',\mathbf{K}'}{}^{(0)}$ with the independent-particle eigenfunctions of H_0. Clearly $\sigma_{n',\mathbf{K}'}{}^{(0)}$ will vanish unless $\Psi_{n',\mathbf{K}'}$ differs from $\Psi_{0,0}$ by the excitation of a single electron from a previously occupied state, m, $\mathbf{k}$ to a previously unoccupied state m', $\mathbf{k}'$. Neglecting the states near the zone boundary, which in the limit where $K'\to0$ play no role, we have of course $\mathbf{k}'=\mathbf{k}+\mathbf{K}'$, so that for small K'

$$\sigma_{n',\mathbf{K}'}{}^{(0)}=\frac{1}{V}(u_{m,\mathbf{k}},u_{m',\mathbf{k}+\mathbf{K}'})$$

$$=\frac{1}{V}\sum_{\alpha=1}^{3}\left(u_{m,\mathbf{k}},\frac{\partial}{\partial k_\alpha}u_{m',\mathbf{k}}\right)K_\alpha'. \quad (A.16)$$

Therefore, by (A.12)

$$\gamma=8\pi V\sum_{m,\mathbf{k}}\sum_{m'}\frac{1}{(K')^2}\frac{1}{\epsilon_{m',\mathbf{k}}-\epsilon_{m,\mathbf{k}}}\frac{1}{V^2}$$

$$\times\sum_{\alpha,\beta}\left(u_{m,\mathbf{k}},\frac{\partial}{\partial k_\alpha}u_{m',\mathbf{k}}\right)\left(u_{m,\mathbf{k}},\frac{\partial}{\partial k_\beta}u_{m',\mathbf{k}}\right)^*K_\alpha'K_\beta'$$

$$=\frac{1}{\pi^2}\sum_m\sum_{m'}\int d\mathbf{k}\frac{\left|\left(u_{m,\mathbf{k}},\frac{\partial}{\partial k_1}u_{m',\mathbf{k}}\right)\right|^2}{(\epsilon_{m',\mathbf{k}}-\epsilon_{m,\mathbf{k}})}, \quad (A.17)$$

where m and m' run, respectively, over the occupied and unoccupied bands. Cubic symmetry has been used in the last step.

Next we calculate the effective dielectric constant κ^* to second order in ϵ. According to (2.10), it is defined in terms of the $(N+1)$-particle functions $\Psi_{0,\mathbf{K}}$ by

$$1/\kappa^*=(N+1)\lim(\Psi_{0,\mathbf{K}},\Psi_{0,\mathbf{K}'}e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_1}). \quad (A.18)$$

For weak electron-electron interaction, we have

$$\Psi_{0,\mathbf{K}}=\Psi_{0,\mathbf{K}}{}^{(0)}+\epsilon^2\Psi_{0,\mathbf{K}}{}^{(1)}+\cdots, \quad (A.19)$$

where $\Psi_{0,\mathbf{K}}{}^{(0)}$ is a Slater determinant of Bloch waves and $\epsilon^2\Psi_{0,\mathbf{K}}{}^{(1)}$ is the first-order perturbation function due to the perturbation

$$\epsilon^2H'=\epsilon^2\Bigg[\frac{1}{2}\sum_{i,j}{}'\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}$$

$$-\sum_{i,l}\frac{Z_l}{|\mathbf{r}_i-\mathbf{R}_l|}(1-e^{-\alpha|\mathbf{r}_i-\mathbf{R}_l|})\Bigg]. \quad (A.20)$$

Substituting (A.19) into (A.18) gives

$$1/\kappa^*=1-\epsilon^2\gamma^*, \quad (A.21)$$

where

$$\gamma^*=-(N+1)\lim[(\Psi_{0,\mathbf{K}}^{(0)},\Psi_{0,\mathbf{K}'}^{(1)}e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_1}) + (\Psi_{0,\mathbf{K}}^{(1)},\Psi_{0,\mathbf{K}'}^{(0)}e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_1})] = -2(N+1)\lim(\Psi_{0,\mathbf{K}}^{(0)},\Psi_{0,\mathbf{K}'}^{(1)}e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_1}). \quad (A.22)$$

Our object is to show that this γ^* is equal to the γ of Eq. (A.17).

The function $\Psi_{0,\mathbf{K}}^{(0)}$ is, by (A.3),

$$\Psi_{0,\mathbf{K}}^{(0)}=\frac{1}{(N+1)^{\frac{1}{2}}}\sum_{\alpha=1}^{N+1}\chi(\alpha)\psi_{0,\mathbf{K}}(\alpha). \quad (A.23)$$

The first-order perturbation function $\Psi_{0,\mathbf{K}'}^{(1)}$ can be evaluated from the usual expression

$$\Psi_{0,\mathbf{K}'}^{(1)}=\sum_n \Psi_{n,\mathbf{K}'}\frac{(\Psi_{n,\mathbf{K}'},H'\Psi_{0,\mathbf{K}'})}{E_{0,\mathbf{K}'}-E_{n,\mathbf{K}'}}. \quad (A.24)$$

To evaluate the matrix elements in (A.24), we Fourier analyze H'. Apart from an irrelevant additive constant, we obtain

$$H'=\frac{4\pi}{V}\sum_{\mathbf{p}}{}'\left[\frac{1}{p^2}\left(\tfrac{1}{2}\sum_{i,l}{}'e^{i\mathbf{p}\cdot(\mathbf{r}_i-\mathbf{r}_j)}-\sum_{i,j}Z_l e^{i\mathbf{p}\cdot(\mathbf{r}_i-\mathbf{R}_l)}\right) + \sum_{i,l}\frac{1}{p^2+\alpha^2}Z_l e^{i\mathbf{p}\cdot(\mathbf{r}_i-\mathbf{R}_l)}\right] = \frac{2\pi}{V}\sum_{\mathbf{p}}{}'\sum_{i,j}{}'\frac{1}{p^2}e^{i\mathbf{p}\cdot(\mathbf{r}_i-\mathbf{r}_j)}-\frac{4\pi NZ_l}{V}\sum_i\sum_\nu{}'\frac{\exp(i\mathbf{K}_\nu\cdot\mathbf{r}_i)}{K_\nu^2} + \frac{4\pi NZ_l}{V}\sum_i\sum_\nu\frac{\exp(i\mathbf{K}_\nu\cdot\mathbf{r}_i)}{K_\nu^2+\alpha^2}, \quad (A.25)$$

where $\sum_{\mathbf{p}}{}'$ means that $\mathbf{p}=0$ is omitted; $\sum_{i,j}{}'$ means that $i\neq j$; $\sum_\nu{}'$ means that $\nu=0$ is omitted. The last two terms in (A.21) represent a periodic potential and do not contribute to γ^*. The remaining term causes the scattering of two electrons. A little consideration shows that the only states which contribute to γ^* are those $\Psi_{n,\mathbf{K}'}$ which differ from $\Psi_{0,\mathbf{K}'}$ in that one electron has been scattered from $\psi_{0,\mathbf{K}'}$ to $\psi_{0,\mathbf{K}}$ while another electron is scattered from $\psi_{m,\mathbf{k}}$ to $\psi_{m',\mathbf{k}+\mathbf{K}'-\mathbf{K}}$, where m and m' denote occupied and unoccupied bands, respectively.

For such a state, the expansion coefficient of (A.24) is

$$C_{n,\mathbf{K}'}\equiv\frac{(\Psi_{n,\mathbf{K}'},H'\Psi_{0,\mathbf{K}'})}{E_{0,\mathbf{K}'}-E_{n,\mathbf{K}'}} = \frac{4\pi}{V}\frac{1}{|\mathbf{K}'-\mathbf{K}|^2}(u_{0,\mathbf{K}},u_{0,\mathbf{K}'})(u_{m',\mathbf{k}+\mathbf{K}'-\mathbf{K}},u_{m,\mathbf{k}}) \times\frac{1}{\epsilon_{0,\mathbf{K}'}+\epsilon_{m,\mathbf{k}}-\epsilon_{0,\mathbf{K}}-\epsilon_{m',\mathbf{k}+\mathbf{K}'-\mathbf{K}}} \rightarrow\frac{4\pi}{V}\frac{1}{|\mathbf{K}'-\mathbf{K}|^2}\left(\frac{\partial}{\partial k_\alpha}u_{m',\mathbf{k}},u_{m,\mathbf{k}}\right)\frac{(K_\alpha'-K_\alpha)}{\epsilon_{m,\mathbf{k}}-\epsilon_{m',\mathbf{k}}}, \quad (A.26)$$

where in the last line we have used the fact that K and K' are small.

The contribution of one such state to γ^* is, by (A.26),

$$-2(N+1)\lim C_{n,\mathbf{K}'}\frac{1}{N+1}(\psi_{0,\mathbf{K}}(2),\psi_{0,\mathbf{K}}(2)) \times(\psi_{m,\mathbf{k}}(1),\psi_{m',\mathbf{k}+\mathbf{K}'-\mathbf{K}}(1)e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_1}) = -2\lim C_{n,\mathbf{K}'}\left(u_{m,\mathbf{k}},\frac{\partial}{\partial k_\beta}u_{m',\mathbf{k}}\right)(K_\beta'-K_\beta) = \frac{8\pi}{V}\frac{\left|\left(u_{m,\mathbf{k}},\dfrac{\partial}{\partial k_1}u_{m',\mathbf{k}}\right)\right|^2}{\epsilon_{m',\mathbf{k}}-\epsilon_{m,\mathbf{k}}}. \quad (A.23)$$

Summing over all appropriate m and m' and integrating over $\mathbf{k}$ gives

$$\gamma^*=\frac{1}{\pi^2}\sum_m\sum_{m'}\int d\mathbf{k}\frac{\left|\left(u_{m,\mathbf{k}},\dfrac{\partial}{\partial k_1}u_{m',\mathbf{k}}\right)\right|^2}{\epsilon_{m',\mathbf{k}}-\epsilon_{m,\mathbf{k}}}, \quad (A.24)$$

which is identical with γ.

This completes the demonstration that up to second order in ϵ, $\kappa=\kappa^*$.

Note added in proof.—A paper by T. I. Liberberg and K. B. Tolpygo (Zhur. Eksptl. i Teort. Fiz. **26**, 35 (1954) has been brought to my attention, which deals with the impurity state problem from a many electron point of view. This paper is based on the approximation of tightly bound polarizable ions and conduction electrons which are localizable on a single ion. Exchange and correlation effects are, of course, only partly included in such a treatment.