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PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Quantum Transport Theory of Impurity-Scattering-Limited Mobility in n-Type Semiconductors Including Electron-Electron Scattering*

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The Kubo formula is employed to obtain an expression for ionized-impurity mobility, including higher-order impurity scattering effects and electron-electron scattering effects for nondegenerate semiconductors. Without electron-electron scattering, the lowest-order term of the mobility, as has been previously demonstrated, is found to be the same as the well-known Brooks-Herring formula for ionized-impurity mobility. The form of the higher-order impurity scattering terms has also been previously given. We have evaluated these terms and found them to be negligibly small for the range of impurity concentration and temperature considered here. Electron-electron scattering is calculated by a single-particle approximation from the time-independent Hartree-Fock theory, taking the electron-impurity scattering as the basic mechanism and treating the electron-electron interactions as perturbations. An impurity-scattered electron in our model is found to interact only with other independent electrons not interacting with impurities. Taking into account the correction of electron-electron scattering effects, the Brooks-Herring formula is found to be reduced by a factor which can be expressed in closed form as $1-e^{-1}$. This factor of 0.632 agrees well with other theoretical calculations using the Boltzmann transport theory.

I. INTRODUCTION

Two theoretical treatments have been proposed to describe ionized-impurity-scattering-limited mobility in semiconductors: the Conwell-Weisskopf[1] and Brooks-Herring[2–6] treatments. These two different approaches yield nearly the same result. While these formulas are qualitatively correct, there are refinements by which they may be improved. One of these improvements involves taking into account the electron-electron scattering.[3–5] When ionized-impurity scattering is dominant in determining mobility, the momentum redistribution among the electrons through electron-electron interactions tends to reduce the mobility.[7–9]

A classical approach to calculating the electron-electron scattering of a completely ionized gas was given by Spitzer and Härm.[10] Starting from the Boltzmann equation with the help of the Fokker-Planck equation, they found that the electron conductivity is reduced by a factor of 0.5816. Another calculation has been made by Appel.[11] Appel used a variational principle with electron-electron scattering a small perturbation. He took the interaction between electrons to be a shielded Coulomb potential. Starting from the Boltzmann equation and calculating up to the second-order terms, Appel found that the electron-electron scattering reduced the Brooks-Herring mobility by a factor of 0.573, independent of temperature.

In this paper, we start from the Kubo formula.[12] As discussed in Fujita,[13] the Kubo formula is reduced to a simpler form which enables us to calculate the ionized-impurity mobility including higher-order scattering effects. Fujita has discussed the general expressions for the conductivity derived from the Kubo formula, including higher-order impurity scattering effects. We use his general expressions to evaluate the effects of high-order impurity scattering in detail, extend his work to derive expressions for the mobility, including electron-electron scattering in all orders, and calculate these effects in detail.

In Sec. II we discuss the Kubo formula briefly and present the results of higher-order impurity

scattering effects without the correction of electron-electron collisions. In Sec. III we calculate the effects of electron-electron scattering, and in Sec. IV we present some conclusions drawn from this study.

All formulas in this paper are in the mks system of units and the meanings of all symbols in this paper are listed in the Appendix.

II. HIGHER-ORDER IMPURITY SCATTERING

It is possible to solve some nonequilibrium transport problems such as electric conductivity without going through the traditional Boltzmann transport equation, and to formulate the macroscopic behavior in microscopic terms. This was first demonstrated by Kubo[12] in his microscopic, exact formulation of an electric-conductivity tensor. Fujita has rewritten the original Kubo formula in a slightly different form[13]

$$\sigma_{\mu\nu}(\omega)=\lim_{\vec{u}\to 0}\frac{\partial}{\partial u_\nu}\int_0^\infty dt\, e^{-i\omega t}\lim_{\Omega\to\infty}\frac{1}{\Omega}\,\mathrm{Tr}[\rho' I_\mu(t)]\,, \tag{1}$$

$$\rho'\equiv\frac{e^{-\beta H+\beta\vec{I}\cdot\vec{u}}}{\mathrm{Tr}(e^{-\beta H+\beta\vec{I}\cdot\vec{u}})}\,. \tag{2}$$

Fujita has used this formula to evaluate the conductivity for a system of noninteracting electrons in an impurity potential such that the time-independent Hamiltonian of the system (without external field) is composed of the sum of single-particle Hamiltonians. This reduces the many-body problem to a one-body problem. Expanding the conductivity in ascending powers of n_s (the ionized-impurity or scatterer concentration), the lowest-order mobility term is found to be the well-known Brooks-Herring formula for mobility (denoted by μ_{BH})

$$\mu^{(-1)}=\frac{\sigma^{(-1)}}{ne}=\mu_{BH}$$
$$=\frac{2^{7/2}(4\pi\epsilon)^2(K_B T)^{3/2}}{\pi^{3/2}m^{*1/2}Z^2e^3n_s}\left(\ln(1+b)-\frac{b}{1+b}\right)^{-1}, \tag{3}$$

$$b=\frac{24m^*\epsilon K_B^2T^2}{ne^2\hbar^2}\,, \tag{4}$$

where we have used a Boltzmann distribution for the electrons as appropriate to a nondegenerate semiconductor, and we have used the screened Coulomb potential for the interaction between electron and ion as in the Brooks-Herring treatment. Fujita's expression for conductivity is in terms of the Fermi distribution function, and Fujita has set $\hbar$ equal to unity.

Fujita[13] has also given expressions for the second-order conductivity terms. These involve scattering from two impurities which may or may not be interacting. We have evaluated these second-order expressions in detail and (after lengthy calculations) found them to be very small—in fact, negligible—for nondegenerate semiconductors.

III. ELECTRON-ELECTRON SCATTERING

Suppose that the total Hamiltonian for a system of N electrons interacting via two-body forces and interacting with ionized impurities is given by

$$H=H_1+H_2\,, \tag{5}$$

$$H_1=\sum_j h_0^{(j)}+\sum_{j,\alpha}V_\alpha^{(j)}=\sum_j h^{(j)}\,, \tag{6}$$

$$H_2=\frac{1}{2}\sum_{l=1}^{N}\sum_{\substack{m=1\\ m\neq l}}^{N}V_{lm}=\frac{1}{2}\sum_{l=1}^{N}h_{ee}\,. \tag{7}$$

For H_1, the single-particle part, $h_0^{(j)}$ is the kinetic energy of electron j and $V_\alpha^{(j)}=V(r^{(j)}-R_\alpha)$ is the potential between the electron at a position $r^{(j)}$ and the infinitely heavy impurity at the fixed position R_α. For H_2, the two-body part, V_{lm} is the interaction potential between electron l at a position r_l and electron m at r_m.

Employing the single-particle approximation from the time-independent Hartree-Fock theory,[14] we can transform the many-body Hamiltonian H into a single-particle-like Hamiltonian H_s:

$$H\to H_s=\textstyle\sum_k h_s^{(K)}\,, \tag{8}$$

$$h_s=h_0+\textstyle\sum_\alpha V_\alpha+h_{ee}\,. \tag{9}$$

The eigenvalues of $h_s^{(K)}$ are[14]

$$E_s^{(K)}=\epsilon_K+\sum_{K'}\left(\langle K'K|V_{KK'}|K'K\rangle\right.$$
$$\left.-\langle KK'|V_{KK'}|K'K\rangle\right)\,, \tag{10}$$

where the ϵ_K are the eigenvalues of $h^{(K)}$, the electron-impurity part of H. The $E_s^{(K)}$ are termed the self-consistent energies of the levels.

This is to say that, in this single-particle-like approximation, we take one electron as a basic particle and treat the other electrons as contributing to the perturbing potential. Note that the perturbation term in (10) will cancel out if $K'=K$, since an electron does not act on itself.

In this way the two-body problem is reduced to an equivalent one-body problem, and we can transform (1) and (2) into

$$\sigma_{\mu\nu}(\omega)=\lim_{\vec{u}\to 0}\lim_{\Omega\to\infty}\frac{\partial}{\partial u_\nu}\int_0^\infty dt\, e^{-i\omega t}\,\frac{1}{\Omega}$$
$$\times\mathrm{Tr}\left(i_\mu e^{-(i/\hbar)th_s}n' e^{(i/\hbar)th_s}\right)\,, \tag{11}$$

$$n' = \frac{1}{1+e^{\beta(h_s-\vec{1}\cdot\vec{u})}} , \tag{12}$$

respectively. Following the same procedure as Fujita for the single-electron problem and setting $\omega = 0$ and $\mu = \nu = x$, we can express the static conductivity in the $\vec{P} - \vec{K}$ representation[15] as

$$\sigma \equiv \sigma_{xx}(0) = -\frac{ih}{(2\pi\hbar)^3}\frac{e}{m^*}\int d^3P\, P_x \times \int d^3K \,(0|\frac{1}{h_s - i\hbar a}|\vec{K})\frac{\partial}{\partial u_x} n'_{\vec{K}}(\vec{P}) , \tag{13}$$

where we omit the two limit symbols with the understanding that $\vec{u} \to 0$ and $a \to 0$ where a is a positive number. In (13) the matrix element $n'_{\vec{K}}(\vec{P})$ is defined by

$$n'_{\vec{K}}(\vec{P}) = \langle \vec{P} + (\vec{K}/2)|n'|\vec{P} - (\vec{K}/2)\rangle \tag{14}$$

in the $\vec{P} - \vec{K}$ representation.[13,15] The expression of the form $(0|h|\vec{K})$ in (13) is a matrix element which is itself an operator. A general definition is

$$(\vec{K}|h(\vec{P})|\vec{K}') \equiv \eta^{\vec{K}'} h_{\vec{K}-\vec{K}'}(\vec{P})\,\eta^{-\vec{K}} - \eta^{-\vec{K}'} h_{\vec{K}-\vec{K}'}(\vec{P})\,\eta^{\vec{K}} , \tag{15}$$

where $h_{\vec{K}-\vec{K}'}(\vec{P})$ is in the same form as (14), and $\eta^{\pm\vec{K}}$ is a displacement operator acting only on a function of $\vec{P}$ in the $\vec{P} - \vec{K}$ representation such that[13]

$$\eta^{\pm\vec{K}} f(\vec{P}) = f(\vec{P} \pm \vec{K}/2)\,\eta^{\pm\vec{K}} . \tag{16}$$

The actual operator in the $\vec{K} - \vec{K}'$ element is $(h-l)^{-1}$ $(l = i\hbar a)$. Fujita expands this resolvent operator in a perturbation series[13]

$$R_l \equiv \frac{1}{h-l} = \frac{1}{h_0 - l - g_l} , \tag{17}$$

$$g_l = -V + \sum_{K=1}^{\infty}\left(-V\frac{1}{h_0 - l}\right)^K (-V) , \tag{18}$$

where $V = \sum_\alpha V_\alpha$.

In this section we expand the resolvent operator $(h_s - l)^{-1}$ in such a way that

$$\frac{1}{h_s - l} = R_l - R_l h_{ee} R_l + R_l h_{ee} R_l h_{ee} R_l - + \cdots . \tag{19}$$

Since we consider the electron-electron interactions as the perturbation potential, we can calculate the $\vec{K} - \vec{K}'$ elements of h_{ee} in the $\vec{P} - \vec{K}$ representation in the same way as we do those of the electron-ion potential, by means of a Fourier transformation.[13]

Examining all elements of $(h_s - l)^{-1}$, we find that those terms containing odd numbers of h_{ee} vanish and only those terms containing an even number of h_{ee} give contributions. Therefore, two h_{ee} together should describe a certain interacting process between two electrons and we may write

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \cdots \tag{20}$$

or

$$\mu = \mu_1 + \mu_2 + \mu_3 + \cdots , \tag{21}$$

where the first term corresponds to R_l in (19), the second term corresponds to the second nonvanishing term in (19), $R_l h_{ee} R_l h_{ee} R_l$, and so on. Thus, the subscripts indicate the number of electrons involved.

The matrix element $n'_{\vec{K}}(\vec{P})$ in (13) is related to the distribution function of conduction electrons. We assume that the electron distribution is not influenced by the electron-electron or electron-ion interactions, and hence we can replace h_s in (12) by h_0. After manipulations the expression

$$\frac{\partial}{\partial u_x} n'_{\vec{K}}(\vec{P})$$

in (13) can be reduced to the Boltzmann distribution function as appropriate to a nondegenerate semiconductor.

From our calculations we have concluded that, except for the lowest-order term $\mu^{(-1)}$, all higher-order terms in the impurity scattering are negligibly small. Hence, in this section we will take only one impurity into account as a scatterer, and g_l will be set equal to the first nonvanishing term in (18), or $g_l = V(1/h_0 - l)V$.

The first term in the expansions of (13) can be identified immediately as the first-order term of Fujita.[13] Therefore, we have

$$\mu_1 = \mu_{BH} , \tag{22}$$

as it should since this term is the contribution without electron-electron scattering (electron-impurity scattering being the only scattering mechanism).

We may represent components of the perturbation expansion (19) by a set of diagrams. Let the impurity be represented by a point (a cross ×) in the diagram, the perturbation arising from the impurity be indicated by a dotted line (corresponding to V), the interaction between electrons be denoted by a wavy line (corresponding to h_{ee}), and the propagation of the electron be represented by a horizontal solid line. If we set the electron-impurity potential $V = 0$ in (18), then R_l becomes a term corresponding to the propagation of an electron "free" with respect to the impurity. In this way we find that there are two kinds of diagrams contributing to σ_2, as shown in Fig. 1, where electron 1 is the basic electron in our model (this convention is continued hereafter). Note that we break the solid line of electron 1 into two parts for convenience in writing down the mathematical expressions from the diagrams. In Fig. 1(a) electron 2 is free, corresponding to $R_l = 1/(h_0 - l)$. In both

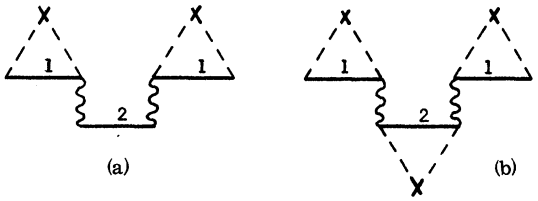

FIG. 1. Diagrams representing two interacting electrons. (a) One of the electrons is free with respect to the impurity. (b) Both electrons are scattered by the impurities.

diagrams, the triangle represents the term R_l of (17), corresponding to the situation in which the electron is scattered by an impurity, and the ordering in the triangle helps us to write down the mathematical expression of the quantity g_l, i.e., $g_l = V[1/(h_0 - l)]V$.

The Coulomb force between any two electrons is a long-range force. We will cut off this interaction force by surrounding any given electron by a virtual hole. This hole has the effect of a positive charge, which screens out the electric potential of the electron at all but very short distances. Two electrons can then only interact if they come very close. Such a screened potential occurs naturally in any system where a cloud of electrons is available to spread itself out about a Coulomb source. The effective charge Ze of the ionized-impurity atom is $Z = 1$ in most cases in elemental semiconductors like silicon and germanium, and the density of these virtual holes is just the density of electrons. Thus, the potential between electrons has the same form as the electron-impurity potential, the screened Coulomb potential,

$$V(r) = \pm \frac{Ze^2}{4\pi\epsilon} \frac{1}{r} e^{-\lambda r} , \tag{23}$$

$$\frac{1}{\lambda} = \left(\frac{\epsilon K_B T}{e^2 n} \right)^{1/2} , \tag{24}$$

where the + sign is for an electron-electron potential, the − sign is for an electron-impurity potential, and r stands for the distance between electrons or electron and ion, according to circumstances.

For a cloud of n electrons there are $n!$ similar diagrams describing the same contribution, since electrons are indistinguishable particles. If we calculate the contribution of Fig. 1(a), corresponding to μ_A, we get

$$\mu_A = -\frac{1}{2!} \frac{n}{n_s} \mu_{BH} . \tag{25}$$

For the contribution corresponding to Fig. 1(b), we find that the integrand is zero, and hence Fig. 1(b) contributes nothing to the mobility. Therefore, an electron being scattered by an impurity and interacting with another electron which is free with respect to impurities is the only contribution to the electron-electron scattering involving two electrons. For the case of three electrons, whenever the supplemental electrons are interacting with each other or with an impurity, we find these terms to be zero. The corresponding diagrams are shown in Fig. 2.

The only nonzero term involving three electrons is that in which the basic electron is being scattered by an impurity and is interacting with two other independent electrons free with respect to the impurity. The corresponding diagram is shown in Fig. 3. The contribution of this diagram is found

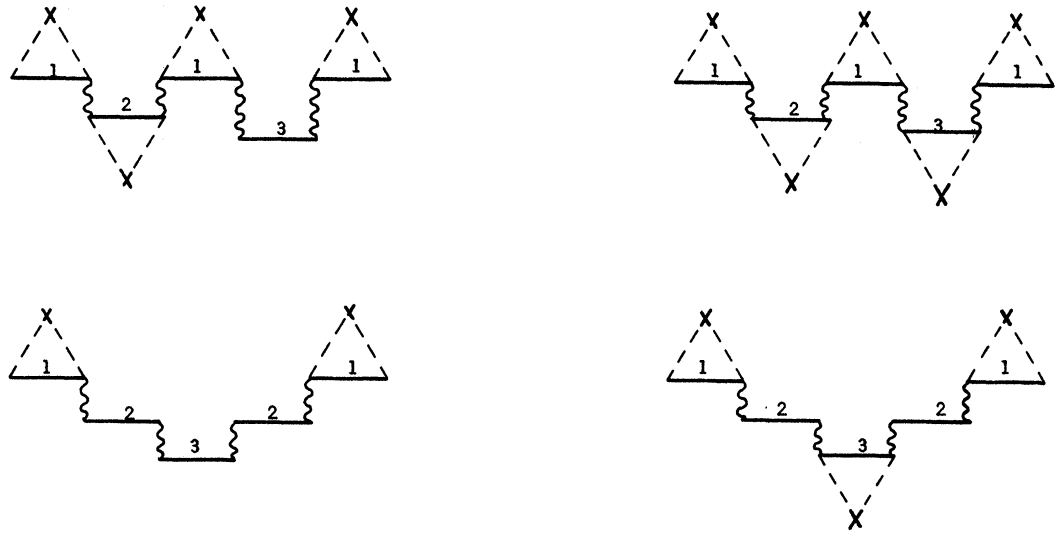

FIG. 2. Diagrams representing three interacting electrons which contribute nothing to the conduction.

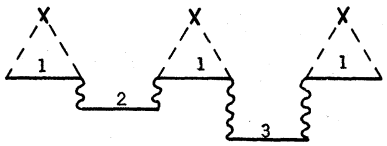

FIG. 3. Diagram representing nonzero term of the conduction involving three interacting electrons.

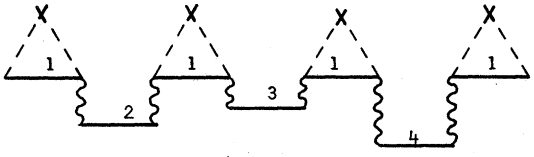

FIG. 4. Diagram representing four interacting electrons with nonzero contribution to the conduction.

to be

$$\mu_3 = \frac{1}{3!}\frac{n^2}{n_s^2}\mu_{BH} . \tag{26}$$

Since for two and three electrons our basic electron interacts only with other independent free electrons, we assume that our basic electron will interact only with other independent free electrons for all higher-order terms of electron-electron scattering. With this assumption, it is easy to calculate the contribution of four interacting electrons from the diagram as shown in Fig. 4; thus we have

$$\mu_4 = \frac{1}{4!}\frac{n^3}{n_s^3}\mu_{BH} . \tag{27}$$

Continuing the same argument, we obtain

$$\mu = \left(1 - \frac{1}{2!}\frac{n}{n_s} + \frac{1}{3!}\frac{n^2}{n_s^2} - \frac{1}{4!}\frac{n^3}{n_s^3} + \cdots\right)\mu_{BH} . \tag{28}$$

When the ionized-impurity scattering is the dominant scattering mechanism in n-type semiconductors, the donor impurity atoms are practically all ionized. If we assume there is only one kind of impurity atoms, then the concentration of ionized impurities n_s is equal to the concentration of conduction electrons n. Thus, (28) reduces to

$$\mu = (1 - e^{-1})\,\mu_{BH} \tag{29}$$

for the correction due to electron-electron scattering in all orders.

IV. CONCLUSIONS

Starting from the Kubo formula and extending the results of Fujita[13] for electron-impurity scattering, we have evaluated the effects of electron-electron scattering on ionized-impurity mobility by a single-particle-like approximation from the time-independent Hartree-Fock theory. With the correction of electron-electron interactions, the existing Brooks-Herring formula is reduced by a factor which can be expressed in closed form as $1 - e^{-1}$. This reduction factor of 0.632 is temperature independent, reflecting the similarity between ion and electron potentials. This correction factor is in reasonably close agreement with previous predictions[10,11] using Boltzmann's theory.

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APPENDIX

The meanings of the symbols used in this study are σ, electric conductivity; ω, frequency of the external electric field; $\vec{u}$, a vector (c number) independent of the particle coordinates; t, time coordinate; Ω, volume of the system; Tr, trace; $I(t)$, $e^{(i/\hbar)tH} I e^{-(i/\hbar)tH}$; I/Ω, total-current density operator; H, total Hamiltonian of the system without external (electric) field; $\hbar$, $h/2\pi$ (with h being Planck's constant); β, $1/K_B T$; K_B, Boltzmann's constant; T, the absolute temperature; μ, mobility limited by ionized impurities; ϵ, dielectric constant of the semiconductor; m^*, effective mass of electron; Ze, effective charge of each ionized-impurity atom; n, the conduction-electron density; n_s, the ionized-impurity or scatterer concentration; $h_0^{(j)}$, the kinetic energy of electron j; $V_\alpha^{(j)}$, the electron-impurity potential; h, the single-particle Hamiltonian without electron-electron interactions; V_{lm}, interaction potential between electron l and electron m; H_s, the total single-particle-like Hamiltonian; h_s, the single-particle-like Hamiltonian; E_s, the eigenvalues of h_s; ϵ_k, the eigenvalues of h; η, the displacement operator defined in the $\vec{P} - \vec{K}$ representation; R_l, the resolvent operator; l, $i\hbar a$; a, a positive number; $1/\lambda$, the potential screening distance.

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Experimental Investigation of the Band Structure of Graphite

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Photoemission and secondary electron emission (SEE) measurements have been used to investigate the band structure of graphite. The energy distribution curves obtained from both types of measurements reveal identical features for those transitions to conduction-band states occurring up to 5 eV above the vacuum level. Two minima in the σ_1 conduction band, located at critical points Γ_{3u}^+ and Q_{1u}^+, have been observed at 7.5 and 8.6 eV above the Fermi level. Emission from these final states is observed for $\vec{E} \parallel c$ orientation due to the relaxation of electrons initially excited to P_3^+; this $\vec{E} \parallel c$ transition, which is observed at 14.5 ± 0.5 eV, is in good agreement with the predicted value of 13.5 eV assigned to transitions $P_3^- \rightarrow P_3^+$. The σ-band gap at the Brillouin-zone center has been measured for $\vec{E} \perp c$ to be 11.5 ± 0.1 eV and the separation of the σ bands increases to 15.0 eV at Q in good agreement with the optical reflectivity data. The observation and assignment of interband transitions at higher SEE energies provide additional evidence in support of the two-dimensional band structure proposed by Painter and Ellis. The photoemission measurements give detailed information concerning the nature of the π-band structure at points along the three-dimensional Brillouin-zone face. The splitting of the π bands at P and Q is observed to be 0.8 eV, which gives rise to $\vec{E} \perp c$ transitions at 4.76 and 4.82 eV associated with the saddle-point nature of the π bands at Q, and a value of 0.42 eV for the Slonczewski and Weiss parameter γ_1. The SEE results locate P_3^- below the Fermi level, which provides evidence for electron occupancy at the center of the Brillouin-zone edge in agreement with recent Fermi-surface studies.

I. INTRODUCTION

Graphite is a highly anisotropic crystal of space group C_{6v}^4, with an interlayer spacing (3.37 Å) which is large compared with the interatomic spacing in any single layer (1.42 Å). Consequently most theoretical calculations[1-4] of the electronic band structure have used, as a first approximation, a single two-dimensional layer model which neglects any interaction between successive layers. The electron states may be separated into σ and π bands analogous to the sp^2-hybridized atomic eigenstates, the former referring to states which are even with respect to reflection in the layer plane and the latter to those which are odd. The π bands may be regarded as arising from the overlap of p_z atomic orbitals which are oriented normal to the layer plane. Each energy band in the single-layer approximation splits into two closely spaced states upon including the interaction between successive planes. Since the π bands are related to those atomic orbitals directed normal to the basal plane, it follows that these bands will be particularly sensitive to the interlayer interaction, and the magnitude of the splitting is expected to be greater than that for the σ bands. This splitting of the π bands is responsible for the π valence and conduction bands overlapping at the Brillouin-zone edge which, in turn, determines the complex nature of the Fermi surface and the semimetallic properties of graphite. The π-band structure has, therefore, been the subject of numerous theoretical[5,6] and experimental[7] studies.

Since the interlayer forces are weak, the selection rules determined for interband transitions in the two-dimensional structure remain essentially