Expressio ns for the Current in the Bloch Approximation of "Tight Binding" for Metallic Electrons

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Various approximate methods have been used for the calculation of metallic wave functions.\(^1\) Of these, the most important are: (1) the approximation of "tight binding" in which it is assumed that the atoms are relatively far away from one another, so that the overlap of the wave functions of the electrons in neighboring atoms is small;\(^2\) (2) the opposite limiting case, the approximation of nearly free electrons, in which it is assumed that the variations in the potential energy are small in comparison with the kinetic energy of the metallic electrons\(^3\) and (3) the method of Wigner and Seitz\(^4\) and its extensions by Slater,\(^5\) which is the most accurate of all. We wish to discuss the expressions for the current in the first of these methods. In this method, the Bloch wave functions are approximated by a linear combination of atomic wave functions.

The Bloch form for the wave function of a metallic electron is \(\psi_k = \)
exp(i\(\mathbf{k} \cdot \mathbf{r}\))\(u_k(\mathbf{r})\), where \(u_k(\mathbf{r})\) has the translational period of the crystal lattice. The vector \(\mathbf{k}\) is the propagation vector of the electron wave, and is in magnitude \(2\pi/\lambda\), where \(\lambda\) is the wave-length. The standard expression for, say, the \(x\)-component of the current carried by an electron in this state is:

\[
i_x = -ev_x = -(\hbar e/4\pi\mu i)\int |\psi_k^* (\partial \psi_k/\partial x) - \psi_k (\partial \psi_k^*/\partial x)| d\tau. \tag{1}
\]

The Bloch expression for the same component of the current is\(^6\)

\[
i_x = -(2\pi e/\hbar)(\partial E/\partial k_x) \tag{2}
\]

where \(E\) is the energy, expressed as a function of the propagation vector \(k\). These two expressions are, of course, equal if \(\psi_k\) is an exact solution of the Schrödinger equation:

\[
-(\hbar^2/8\pi^2\mu) \Delta \psi_k + V(\mathbf{r})\psi_k = E_k\psi_k \tag{3}
\]

in which \(V(\mathbf{r})\) is the periodic potential of the crystal lattice. If \(\psi_k\) is determined by some approximate method, there is no reason to suppose that (1) and (2) will give the same result. In fact, if hydrogen-like atomic wave functions, \(e^{-\alpha r}\), are used for the calculation of the Bloch wave functions in the approximation of “tight-binding” it is found, as will be shown more explicitly later, that (1) is just one-third of (2).\(^7\)

Such disagreement on the current is perhaps at first surprising, because one might expect that, at least in the limiting case when the distance between the atoms is very large, the approximate wave function so derived will be very close to the exact wave function, obtained by solution of the Schrödinger equation. However, in this limit the current goes to zero, and while both (1) and (2) approach zero, the ratio between them does not approach unity.

It is the purpose of the present paper to point out this discrepancy, explain somewhat its causes and to examine the type of wave function for which exact agreement is to be expected.

Let us first examine the nature of the field in which the electron moves. We may assume that the potential in the crystal lattice is fairly constant in the regions between the atoms, and, without loss of generality, this constant potential may be taken equal to zero. If the potential in the neighborhood of any atom is \(U(\mathbf{r})\), the total potential in the crystal is\(^8\)

\[
V(\mathbf{r}) = \sum_i U(|\mathbf{r} - \mathbf{r}_i|), \tag{4}
\]

where the sum is over all lattice points (designated by the vectors \(\mathbf{r}_i\)). Here \(U(\mathbf{r})\) cannot be taken to be the true atomic potential (i.e., the field of the ion about which the valence electron of the free atom moves), as is generally assumed, because the latter will fall off as \(1/r\) for large \(r\), and the sum (4) will be infinite for an infinite lattice. Rather, one should use a screened field which in the neighborhood of any atom is very nearly equal.
to the field of the ion, but which falls off exponentially instead of as $1/r$ at large distances. The screening of course is due to all the valence electrons except the one under consideration. These considerations indicate that to compute the Bloch functions one should use, instead of the true atomic wave functions, functions which are determined from a screened ionic field. We show below that if this is done the expressions (1) and (2) give the same value for the current, at least in the limiting case when the atoms are far apart. The disagreement on the current mentioned above, which occurs if true atomic wave functions are used, thus seems to be connected with the choice of the crystalline potential.

We proceed with the mathematical proof of the foregoing statements. The equation for the "atomic" wave functions $\varphi(r)$ from which we will construct the Bloch wave function is

$$-(\frac{h^2}{8\pi^2\mu}) \Delta \varphi(r) + U(r)\varphi(r) = E_0\varphi(r).$$

For simplicity we assume that $\varphi(r)$ is a radial ($s$) function. We also assumed that $U(r)$ falls off much more rapidly than $1/r$ for large $r$, so that the asymptotic form for $\varphi(r)$ which holds if $U(r) \approx 0$ is:

$$\varphi(r) \sim e^{-\alpha r}/r,$$

in which $\alpha$ is determined from

$$E_0 = -\alpha^2 h^2 / 8\pi^2\mu.$$  

The true atomic wave function would instead have the asymptotic form $e^{-\alpha r}$, which is appropriate for an electron moving in a coulomb field.

The wave function of an electron moving in the crystal lattice is formed from an appropriate linear combination of the "atomic" wave functions:

$$\psi_k = \sum I \exp[i k \cdot \rho_I] \varphi(|r - \rho_I|),$$

the sum running over all lattice points.

In this approximation the energy, $E_k$, is:

$$E_k = E_0 + \sum I \exp[-i k \cdot \rho_I] \int \varphi(|r - \rho_I|) \left(V(r) - U(r)\right)\varphi(r) d\tau.$$  

The Bloch expression for the velocity of an electron in the state $k$ is

$$v_x = \frac{2\pi}{h} \left(\frac{\partial E}{\partial k_x}\right) = -(2\pi/h) \sum I \exp[-i k \cdot \rho_I],$$

in which $I$ is the integral:

$$I = \int \varphi(|r - \rho_I|) \left(V(r) - u(r)\right)\varphi(r) d\tau$$

$$= \int \varphi(|r - \rho_I|) \left(\sum \delta(|r - \rho_m|)\right)\varphi(r) d\tau.$$  

The second form follows from the first by substitution of the expression (4) for $V(r)$. Since we are assuming that $U(|r - \rho_m|)$ is small except in
the neighborhood of \( \rho_m \), the only significant term in the sum over \( m \) is that for which \( m = l \), so that

\[
I_l \simeq \int \varphi(|x - \rho_1|) U(|x - \rho_1|) \varphi(r) dr. \tag{12}
\]

Using the Schrödinger equation (5) for \( \varphi(r) \), we see that \( I_l \) may be written in the form:

\[
I_l \simeq \int \left\{ \left( \frac{\hbar^2}{8\pi^2 \mu} \right) \Delta + E_0 \right\} \varphi(|x - \rho_1|) \varphi(r) dr. \tag{13}
\]

Since

\[
\Delta \varphi(|x - \rho_1|) = \Delta_r \varphi(|x - \rho_1|), \tag{14}
\]

(the second Laplacian is taken with \( \rho_1 \) as the variable) we may express \( I_l \) in terms of the overlap integral

\[
g(\rho) = \int \varphi(|x - \rho|) \varphi(r) dr. \tag{15}
\]

Thus

\[
I_l = \left\{ \frac{\hbar^2}{8\pi^2 \mu} \Delta \right\} + E_0 \right\} g(\rho)
\]

\[
= \left\{ \frac{\hbar^2}{8\pi^2 \mu} \frac{d^2 g}{d\rho^2} + \frac{2}{\rho} \frac{dg}{d\rho} + E_0 g \right\} \bigg|_{\rho = \rho_1}. \tag{16}
\]

To obtain the second form we have made use of the fact that \( \varphi(r) \) and consequently \( g(\rho) \) are radial functions.

The ordinary expression for the velocity is obtained by substituting the expression (8) for \( \psi_k \) into equation (1). We then have:

\[
v_x = \frac{\hbar}{2\pi \mu} \Sigma \exp[-iK \cdot \rho_1] \int \varphi(r)(\partial \varphi(|x - \rho_1|)/\partial x) dr. \tag{17}
\]

Now

\[
\frac{\partial \varphi(|x - \rho_1|)}{\partial x} = - \frac{\partial \varphi(|x - \rho_1|)}{\partial (\rho_1)_x}, \tag{18}
\]

so that

\[
v_x = -(i\hbar/2\pi \mu) \Sigma \left[ \frac{\partial g(\rho_1)}{\partial (\rho_1)_x} \exp[-iK \cdot \rho_1] \right.
\]

\[
= -(i\hbar/2\pi \mu) \sum [d g(\rho_1)/d \rho_1] [d g(\rho_1)/d \rho_1] \exp[-iK \cdot \rho_1]. \tag{19}
\]

In view of (16), the two expressions (10) and (19) for the velocity will be equal only if

\[
\frac{\hbar^2}{8\pi^2 \mu} \left[ \frac{d^2 g}{d\rho^2} + \frac{2}{\rho} \frac{dg}{d\rho} \right] + E_0 g = \frac{\hbar^2}{8\pi^2 \mu} \left( \frac{2}{\rho} \frac{dg}{d\rho} \right), \tag{20}
\]

or if (cf. Eq. (7))

\[
d^2 g/d\rho^2 - \alpha^2 g = 0. \tag{21}
\]
Thus we must have

$$g = ce^{-\alpha r}$$  \hspace{1cm} (22)$$

where $c$ is a constant.

The overlap integral $g(\rho)$ will have this form if the major contribution to the integral comes from the region where the potential is fairly constant (and, by assumption, equal to zero) because in this region the wave function will have the form $e^{-\alpha r}/r$. It is not difficult to show that the overlap integral,

$$\int e^{-a|\mathbf{r}-\mathbf{\rho}|} e^{-\alpha r} \frac{e^{-\alpha r}}{r} \, dr,$$

is proportional to $e^{-\alpha r}$, and thus has the desired form.

On the other hand, for hydrogen-like wave functions of the form $e^{-ar}$, the overlap integral is proportional to

$$e^{-\alpha r} \{1 + \alpha \rho + \frac{1}{2} \alpha \rho^2\},$$

and with this expression (19) is just one-third of (10).


5 J. C. Slater, Ibid., 45, 794 (1934).


7 Analogous considerations apply to the corresponding two ways of computing the diamagnetic current induced by a magnetic field. If the diamagnetism is computed directly from an integral similar to (1) rather by differentiation with respect to the field strength [the analog of (10)] and if hydrogenic wave functions are used, London's estimate of the resonance integral necessary to account for the diamagnetism of aromatic compounds is raised from 4.4 to 13.2 electron volts. The fact that the latter value is unreasonably high need not cause concern, as the hydrogenic model is not really applicable. Anyway, the change by a factor of three cancels out in computing the relative amounts of diamagnetism of different aromatic substances, so that the ability of his theory to predict the variation of diamagnetism with chemical composition is not affected.

8 Cf. Mott and Jones (reference 1), p. 65 and following.