

The Work Done by an External Field

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Abstract.

From the change in kinetic energy induced by an external field, we discuss the applicable conditions for the Mott-Davis and Moseley-Lukes form of the Kubo-Greenwood formula (KGF) for the electrical conductivity which has been implemented in *ab initio* codes. We show that the simplified KGF is suitable only for computing the AC conductivity at sufficiently high frequency and when the gradient of the carrier density is small.

Keywords: Kubo-Greenwood formula, DC conductivity, longitudinal field, transverse field.

PACS numbers: 05.60.Gg, 72.10.Bg, 72.20.Dp

1. Introduction

The Kubo-Greenwood formula (KGF) is widely adopted to compute AC conductivity for amorphous semiconductors and to estimate the DC conductivity from an extrapolation procedure[1, 2]. Greenwood[3] based his derivation on a kinetic expression for current density which is only justified when the gradient of the carrier concentration is small[4]. Mott and Davis[1], Moseley and Lukes[5] developed a simplified version of KGF without using an explicit expression for the current density, but they made two implicit assumptions: (1) the Joule heat produced by a sample per unit time is $\Omega \mathbf{j} \cdot \mathbf{E}$, where Ω is the volume of sample, \mathbf{E} the strength of external electric field, \mathbf{j} is the current density; and (2) identifying the power $\Omega \mathbf{j} \cdot \mathbf{E}$ of current as the absorption energy per unit time Γ from AC field:

$$\Gamma = \sum_{fi} \hbar \omega_{fi} (w_{fi} P_i - w_{if} P_f), \quad (1)$$

where P_i is the occupation probability of the initial state $|i\rangle$, w_{fi} is the transition probability per unit time from initial state $|i\rangle$ to final state $|f\rangle$, $\hbar \omega_{fi}$ is the energy difference between $|f\rangle$ and $|i\rangle$. The conductivity is read off from

$$\frac{\Omega}{2} \sum_{\alpha, \beta} \sigma_{\alpha\beta} E_\alpha E_\beta = \Gamma, \quad \alpha, \beta = x, y, z, \quad (2)$$

where the factor 1/2 in the L.H.S comes from averaging the power of current over one period of the AC field. The AC conductivity at frequency ω is[1, 5]

$$\sigma(\omega) = \frac{2\pi e^2 \hbar^3 \Omega}{m^2} \int dE \frac{[f(E) - f(E + \hbar\omega)] |D|_{av}^2 N(E) N(E + \hbar\omega)}{\hbar\omega}, \quad (3)$$

where Ω is the volume of sample, f is the Fermi distribution function, $N(E)$ is the density of states, $D_{E',E} = \int d^3x \psi_{E'}^* \partial \psi_E / \partial x$, and 'av' represents an average over all states having energy near $E' = E + \hbar\omega$. The DC conductivity is obtained by taking the $\omega \rightarrow 0$ limit in (3)[1]:

$$\sigma_{dc} = \frac{2\pi e^2 \hbar^3 \Omega}{m^2} \int dE |D|_{av}^2 [N(E)]^2 \frac{df}{dE}. \quad (4)$$

Since w_{fi} contains an energy-conserving delta function $\delta(E_f - E_i - \hbar\omega)$, the assumption (2) means that the system is driven by a radiation field with frequency $\omega = \omega_{fi}$. The photon energy for a DC field is zero, so that the absorbed energy of the system from a DC field should vanish. According to (2), σ_{dc} would be zero. However a DC voltage does produce Joule heat in a conductor or a semiconductor. One may conclude that (i) (3) is not suited to AC fields with low frequencies; and (ii) (4) is not consistent with (2), although the limiting procedure from (3) to (4) seems legitimate. On the other hand, (3) has been used to compute AC conductivity and extrapolate σ_{dc} in liquid carbon[2]. (4) is implemented in SIESTA[6] to calculate σ_{dc} for a-Si and a-Si:H. The DC conductivities obtained fall in the range of observed values in different systems. Therefore extrapolation from (3) and (4) must represent the correct σ_{dc} to some extent.

The aim of this paper is to explore and resolve these controversial issues. In Sec.2, we derive the rate dK/dt of change kinetic energy from the time-dependent Schrödinger equation. This rigorous expression of power is applicable to an arbitrary electromagnetic field, and leads to a proper current density[7, 8, 4]. Using the approximation implied by assumption (1), the rigorous current density reduces to the kinetic expression used by Greenwood[3]. Thus the simplified derivations[1, 5] suffer the same error as the original one: the formula is suitable only when the gradient of the carrier density is small, a condition derived from the current operator[4].

To find the connection between dK/dt (well defined for any electromagnetic field) and Γ which is only defined for a radiation field, we calculate dK/dt for three successively more complex cases: DC voltage, AC voltage and arbitrary field. For both DC and low frequency AC voltages (i.e. any field described by a scalar potential), dK/dt comes from the work done by the internal force. When a time-dependent vector potential appears, there is an additional $\partial K/\partial t$ term contributing to the change in kinetic energy which results from the time dependence of vector potential $\partial \mathbf{A}/\partial t$.

A DC voltage described by a time-independent scalar potential can be described from both stationary perturbation theory (SPT) and time-dependent theory (TDPT). Sec.3 will show that in TDPT only when we introduce the interaction with the time-independent scalar potential in a specified way (physically reasonable), are the descriptions of states and dK/dt in TDPT consistent with those in SPT. This is a natural requirement for a self-consistent theory. In Sec.4, we show that the Joule heat from a low frequency AC field described by a time-dependent scalar potential is the work done by the internal force. As expected, when $\omega = 0$, the result for AC voltage reduces to the DC result. This is possible because we consistently use a scalar potential to describe the interaction with a low frequency external field. If we adopt a different gauge, both scalar potential and vector potential are needed. In Sec.5, we calculate the rate of change of the kinetic energy induced by a general electromagnetic field described by both vector and scalar potentials. We will see that assumption (2) renders the simplified KGF[1, 5] (3) only suitable for computing conductivity at sufficiently high frequency, i.e for a radiation field. This is the origin of the confusion: viewing Γ as the unique reason for change in kinetic energy[1, 5] dK/dt and taking the $\omega \rightarrow 0$ limit in (3)[1] are not valid. Our formulation is applicable to an arbitrary electromagnetic field in any gauge: applying Greenwood's gauge $\mathbf{A} = -\mathbf{E}t$ for a DC voltage in the $\partial K/\partial t$ term of our strict formula does lead to (4). However (4) neglected the contribution from the work done by the internal force.

2. Rate of change in kinetic energy

We will use the Schrödinger picture. Consider a system with N electrons + \mathcal{N} nuclei in an external electromagnetic field (\mathbf{A}, ϕ) , at time t , and the state of system is described by $\Psi'(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t)$. To save space, we will not write out the nuclear coordinates

explicitly. Ψ' satisfies the Schrödinger equation

$$i\hbar\partial\Psi'/\partial t = H'\Psi', \quad (5)$$

where $H' = H + H_{mf}(t)$, $H_{mf}(t)$ is the interaction between system and external field (\mathbf{A}, ϕ) . The time dependence of $H_{mf}(t)$ comes from the external field. H is the Hamiltonian of the system without external field: $H|m\rangle = \varepsilon_m|m\rangle$, we use $|m\rangle$ or Ψ_m to denote the m^{th} stationary state of the system. If the system is in a thermal bath at temperature T , before introducing external field, the probability that the system is in state Ψ_m is $P_m = e^{-\beta\varepsilon_m}/Z$, where $Z = \sum_n e^{-\beta\varepsilon_n}$ is the partition function.

For a system in external field (\mathbf{A}, ϕ) , the velocity operator \mathbf{v}_i for the i^{th} electron is[9] $\mathbf{v}_i = m^{-1}\mathbf{p}_i^m$, where $\mathbf{p}_i^m = -i\hbar\nabla_{\mathbf{r}_i} - e\mathbf{A}(\mathbf{r}_i; t)$ and \mathbf{r}_i are the mechanical momentum and position operators of the i^{th} electron, $e = -1.6 \times 10^{-19}\text{C}$ is the charge of electron. Similarly $\mathbf{v}_\alpha = \mathbf{p}_\alpha^m/M_\alpha$ is the velocity of the α^{th} nucleus, $\mathbf{p}_\alpha^m = -i\hbar\nabla_{\mathbf{R}_\alpha} + Z_\alpha e\mathbf{A}(\mathbf{R}_\alpha; t)$ and \mathbf{R}_α are the mechanical momentum and position operators of the α^{th} nucleus, $-Z_\alpha e$ is the charge of the α^{th} nucleus. The average kinetic energy of the system in state $\Psi'(t)$ is

$$K_{\Psi'}(t) = \int d\tau \Psi'^*(t) \widehat{K}(t) \Psi'(t), \quad (6)$$

where $d\tau = d\mathbf{r}_1 d\tau'$, $d\tau' = d\mathbf{r}_2 \cdots d\mathbf{r}_N$, the arguments of Ψ' are $(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N; t)$, and

$$\widehat{K}(t) = \sum_i \frac{(\mathbf{p}_i^m)^2}{2m} + \sum_\alpha \frac{(\mathbf{p}_\alpha^m)^2}{2M_\alpha} \quad (7)$$

is the kinetic energy operator of the whole system in an external field. The time dependence in $\widehat{K}(t)$ arises from that of \mathbf{A} . To compute the macroscopic response to a mechanical perturbation, the coarse-grained average and ensemble average can be done in the final stage[7, 8, 4]. In this paper we only discuss the average over the state of the system.

With the help of (5), the rate of change in the average kinetic energy is[9]

$$\frac{d}{dt}K_{\Psi'}(t) = \frac{1}{i\hbar} \int d\tau \Psi'^*(t) [\widehat{K}, H'] \Psi'(t) + \int d\tau \Psi'^*(t) \frac{\partial \widehat{K}(t)}{\partial t} \Psi'(t). \quad (8)$$

The Hamiltonian H' of system in external field can be written as

$$H' = \widehat{K}(t) + V_\phi + H_2, \quad (9)$$

where

$$V_\phi = \sum_i e\phi(\mathbf{r}_i; t) - \sum_\alpha Z_\alpha e\phi(\mathbf{R}_\alpha; t), \quad (10)$$

is the potential energy of the system in an external field (\mathbf{A}, ϕ) , and

$$H_2 = \frac{1}{2} \sum_{ij} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i\alpha} V_1(\mathbf{r}_i, \mathbf{R}_\alpha) + \frac{1}{2} \sum_{\alpha\beta} U_2(\mathbf{R}_\alpha, \mathbf{R}_\beta), \quad (11)$$

represents the internal interactions of the system, $V_1(\mathbf{r}_i, \mathbf{R}_\alpha)$ is the interaction energy of the i^{th} electron and α^{th} nucleus, $V_2(\mathbf{r}_i, \mathbf{r}_j)$ is the interaction energy between the i^{th}

electron and the j^{th} electron, $U_2(\mathbf{R}_\alpha, \mathbf{R}_\beta)$ is the interaction energy between the α^{th} and the β^{th} nuclei. The 1st term in (8) can be changed to:

$$[\widehat{K}, H'] = [\widehat{K}, H_2] + [\widehat{K}, V_\phi]. \quad (12)$$

Here $(i\hbar)^{-1}[\widehat{K}, H_2]$ represents the power due to the internal force:

$$\frac{1}{i\hbar}[\widehat{K}, H_2] = \sum_i \{\mathbf{f}_i \cdot \mathbf{v}_i - \frac{i\hbar}{2m} \nabla_{\mathbf{r}_i} \cdot \mathbf{f}_i\} + \sum_\alpha \{\mathbf{f}_\alpha \cdot \mathbf{v}_\alpha - \frac{i\hbar}{2M_\alpha} \nabla_{\mathbf{R}_\alpha} \cdot \mathbf{f}_\alpha\}, \quad (13)$$

where

$$\mathbf{f}_\alpha = -\{\nabla_{\mathbf{R}_\alpha} [\sum_i V_1(\mathbf{r}_i, \mathbf{R}_\alpha) + \frac{1}{2} \sum_\beta U_2(\mathbf{R}_\alpha, \mathbf{R}_\beta)]\}, \quad (14)$$

is the internal force on the α^{th} nucleus, and

$$\mathbf{f}_i = -\{\nabla_{\mathbf{r}_i} [\frac{1}{2} \sum_j V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_\alpha V_1(\mathbf{r}_i, \mathbf{R}_\alpha)]\}, \quad (15)$$

is the internal force on the i^{th} electron. From now on we will not write out the corresponding terms for nuclei which are similar to those for electrons. The second term of (12) represents the power due to the electric field described by the scalar potential:

$$\frac{1}{i\hbar}[\widehat{K}, V_\phi] = \sum_i e[-\nabla_{\mathbf{r}_i} \phi(\mathbf{r}_i; t)] \cdot \mathbf{v}_i + \sum_i \frac{e}{2m} i\hbar [\nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_i} \phi(\mathbf{r}_i; t)]. \quad (16)$$

To calculate the 2nd term in (8), one should notice that $[\mathbf{p}_i^m, \partial \mathbf{p}_i^m / \partial t] \neq 0$ and $[\mathbf{p}_\alpha^m, \partial \mathbf{p}_\alpha^m / \partial t] \neq 0$:

$$\frac{\partial \widehat{K}(t)}{\partial t} = \sum_i [-e \frac{\partial \mathbf{A}(\mathbf{r}_i; t)}{\partial t}] \cdot \mathbf{v}_i + \sum_i \frac{1}{2m} i\hbar e [\nabla_{\mathbf{r}_i} \cdot \frac{\partial \mathbf{A}(\mathbf{r}_i; t)}{\partial t}]. \quad (17)$$

Substituting (13,16,17) into (8), one finds

$$\begin{aligned} \frac{d}{dt} K_\Psi(t) &= \int d\tau \Psi'^*(t) \sum_i e \mathbf{E}(\mathbf{r}_i; t) \cdot \mathbf{v}_i \Psi'(t) \\ &+ \int d\tau \sum_i \frac{1}{2m} [e \mathbf{E}(\mathbf{r}_i; t)] \cdot [i\hbar \nabla_{\mathbf{r}_i} \Psi'(t) \Psi'^*(t)] \\ &+ \int d\tau \Psi'^*(t) \sum_i \mathbf{f}_i \cdot \mathbf{v}_i \Psi'(t) + \int d\tau \frac{1}{2m} \sum_i \mathbf{f}_i \cdot [i\hbar \nabla_{\mathbf{r}_i} \Psi'(t) \Psi'^*(t)], \end{aligned} \quad (18)$$

where $\mathbf{E}(\mathbf{r}_i; t) = -\nabla \phi(\mathbf{r}_i; t) - \partial \mathbf{A}(\mathbf{r}_i; t) / \partial t$ is the electric field at \mathbf{r}_i . To obtain the 2nd and 4th terms in (18), we integrated by parts. (18) is a form of the Ehrenfest theorem: the rate of change in kinetic energy equals the work done per unit time by the external electric field (the first two terms) and the internal force (the last two terms). The 1st and 3rd terms are the corresponding quantum average values of the powers in classical mechanics. The 2nd and 4th terms are produced by the commutation relation between momentum and position: they will disappear in classical limit.

In the first two terms of (18), exchanging the integration variables $\mathbf{r}_k (k = 2, 3, \dots, N) \leftrightarrow \mathbf{r}_1$, using the antisymmetry of the many-electron wave function and changing \mathbf{r}_1 to \mathbf{r} , they become $\int_{\Omega} d\mathbf{r} [\mathbf{E}(\mathbf{r}; t)] \cdot \mathbf{j}_m(\mathbf{r}; t)$:

$$\mathbf{j}_m(\mathbf{r}; t) = Ne \int d\tau' \Psi'^* \mathbf{v} \Psi' + \frac{i\hbar e}{2m} \nabla_{\mathbf{r}} n'(\mathbf{r}; t), \quad (19)$$

where the arguments of Ψ' are $(\mathbf{r}, \mathbf{r}_2 \mathbf{r}_3 \dots \mathbf{r}_N; t)$, $n'(\mathbf{r}; t) = N \int d\tau' \Psi' \Psi'^*$ is the carrier density. \mathbf{j}_m defined by (19) is the same as the rigorous microscopic current density obtained from the microscopic response method[7] and polarization density[8]. Only when the gradient of the carrier density is small, can one neglect the second term in (19) and replace $\int_{\Omega} d\mathbf{r} \mathbf{E} \cdot \mathbf{j}_m$ with $\Omega \mathbf{j} \cdot \mathbf{E}$. By means of the equivalence between the microscopic response method and the Kubo formula[4], the first term in (19) corresponds to the kinetic expression $e \text{Tr}[\rho'(t) \mathbf{v}]$ of Greenwood[3], where $\rho'(t)$ is the density matrix of the system in external field. Thus assumption (1) is equivalent to using $e \text{Tr}[\rho'(t) \mathbf{v}]$, the kinetic expression for the current density.

3. DC voltage

Let us adopt the common gauge in which a DC field is solely described by a time-independent scalar potential. In this gauge, both stationary perturbation theory (SPT) and time-dependent perturbation theory (TDPT) can be used, and they should give the same results for any observable quantities. As we will see, the first nonzero contribution to the rate of change of kinetic energy is second order in V (consistent with our macroscopic experience), so to formulate a consistent approximation, we will carry out perturbation theory to second order in V .

Applying a DC voltage on a piece of conductor or semiconductor, after a short transient period, the system will evolve to a steady state if the system is in good thermal contact with the environment such that the Joule heat evolved can be completely removed from the system. The constant external voltage establishes a time-independent electric field *inside* the system. The system is described by a Hamiltonian $H' = H + V$, where H is the Hamiltonian of system without external DC voltage, V is given by (10) with a steady scalar potential ϕ .

If the system is initially in an eigenstate Ψ_j of H with eigenvalue ε_j , after the short transient period, the system will be in the stationary state Ψ'_j of H' with eigenvalue ε'_j . Denote $V_{kj} = \langle \Psi_k | V | \Psi_j \rangle$, then one can easily compute[9] Ψ'_j and ε'_j to second order in V :

$$\Psi'_j = \Psi_j + \sum_{p=1,2} \left\{ \sum_{m(\neq j)} c_{mj}^{(p)} \Psi_m + c_{jj}^{(p)} \Psi_j \right\}. \quad (20)$$

Since H' is time-independent, the time evolution of system is given by

$$\Psi'_j(t) = e^{-it\varepsilon'_j/\hbar} \Psi'_j. \quad (21)$$

Substituting Ψ'_j and ε'_j obtained from SPT into (21), to second order in V ,

$$\Psi'_j(t) = e^{-it\varepsilon_j/\hbar}\Psi_j + e^{-it\varepsilon_j/\hbar} \sum_{p=1,2} \left\{ \sum_{m(\neq j)} b_{mj}^{(p)}\Psi_m + b_{jj}^{(p)}\Psi_j \right\}, \quad (22)$$

where

$$b_{mj}^{(1)} = \frac{V_{mj}}{\varepsilon_j - \varepsilon_m} \quad \text{for } m \neq j, \quad b_{jj}^{(1)} = -\frac{it}{\hbar}V_{jj} \quad (23)$$

and

$$b_{mj}^{(2)} = \sum_{k(\neq j)} \frac{V_{mk}V_{kj}}{(\varepsilon_j - \varepsilon_k)(\varepsilon_j - \varepsilon_m)} \quad (24)$$

$$-V_{jj}\frac{V_{mj}}{(\varepsilon_j - \varepsilon_m)^2} - \frac{it}{\hbar}V_{jj}\frac{V_{mj}}{\varepsilon_j - \varepsilon_m} \quad \text{for } m \neq j,$$

and

$$b_{jj}^{(2)} = -\frac{1}{2} \sum_{k(\neq j)} \frac{|V_{kj}|^2}{(\varepsilon_j - \varepsilon_k)^2} - \frac{it}{\hbar} \sum_{k(\neq j)} \frac{|V_{kj}|^2}{\varepsilon_j - \varepsilon_k} - \frac{t^2 V_{jj}^2}{2\hbar^2}. \quad (25)$$

Now consider the viewpoint of TDPT, in which the perturbation V causes transitions from Ψ_j to other eigenstates Ψ_k of H . Using the familiar expansion[9]

$$\Psi'_j(t) = \Psi_j e^{-it\varepsilon_j/\hbar} + \sum_{p=1,2} \left[\sum_{m(\neq j)} a_{mj}^{(p)}(t) e^{-it\varepsilon_m/\hbar} \Psi_m + a_{jj}^{(p)}(t) e^{-it\varepsilon_j/\hbar} \Psi_j \right], \quad (26)$$

the first order expansion coefficients satisfy

$$i\hbar \frac{da_{mj}^{(1)}(t)}{dt} = e^{it(\varepsilon_m - \varepsilon_j)/\hbar} V_{mj} \quad \text{for } m \neq j, \quad (27)$$

and

$$i\hbar \frac{da_{jj}^{(1)}(t)}{dt} = V_{jj}. \quad (28)$$

To make (26) consistent with (22) at order V , we have to integrate (27) by adiabatically introducing the interaction $\int_{-\infty}^t dt' e^{\lambda t'}$ ($\lambda \rightarrow 0^+$) and integrate (28) by $\int_0^t dt'$. This procedure is reasonable because the system is initially in state Ψ_j , the transition from Ψ_j to another state Ψ_m ($m \neq j$) requires some time. On the other hand, the probability amplitude of state Ψ_j begins to decrease immediately.

The second order expansion coefficients satisfy

$$i\hbar \frac{da_{mj}^{(2)}(t)}{dt} = \sum_{k(\neq j)} a_{kj}^{(1)}(t) e^{it(\varepsilon_m - \varepsilon_k)/\hbar} V_{mk} + a_{jj}^{(1)}(t) e^{it(\varepsilon_m - \varepsilon_j)/\hbar} V_{mj}, \quad (29)$$

and

$$i\hbar \frac{da_{jj}^{(2)}(t)}{dt} = \sum_{k(\neq j)} a_{kj}^{(1)}(t) e^{it(\varepsilon_j - \varepsilon_k)/\hbar} V_{jk} + a_{jj}^{(1)}(t) V_{jj}. \quad (30)$$

If we integrate (29) by adiabatically introducing interaction $\int_{-\infty}^t dt' e^{\lambda t'}$ ($\lambda \rightarrow 0^+$), integrate (30) by $\int_0^t dt'$ and in $a_{jj}^{(2)}$ drop one term with wrong time factor $e^{-it\varepsilon_k/\hbar}$, we almost reproduce (22) except without the 1/2 factor in the first term of $b_{jj}^{(2)}$.

There are two differences between SPT and TDPT of concern to us here. In SPT no equation exists to determine $c_{jj}^{(p)}$ ($p = 1, 2$) in (20). The perturbed wave function (20) is not normalized, if one does not include $\sum_{p=1,2} c_{jj}^{(p)} \Psi_j$. $c_{jj}^{(p)}$ ($p = 1, 2$) are determined from the normalization of Ψ'_j to the corresponding order[9]. In TDPT, $a_{jj}^{(p)}(t)$ ($p = 1, 2$) are determined by (28,30). Using (5), one can easily find $(d/dt)[\int d\tau \Psi_j'^*(t) \Psi'_j(t)] = 0$. Thus the perturbed wave function (26) is normalized if $\int d\tau \Psi_j^* \Psi_j = 1$. If in (26), we only considered $a_{mj}^{(1)}(t)$ for $m \neq j$, and used the normalization condition of $\Psi'_j(t)$ to determine $a_{jj}^{(p)}(t)$ ($p = 1, 2$), we would not reproduce (22). Therefore the suggested means of introducing the interaction is necessary to make TDPT consistent with SPT.

When the DC field is described by a time-independent scalar potential, the rate of change in kinetic energy can be written as

$$\frac{d}{dt} K_{\Psi'_j(t)} = \frac{1}{i\hbar} \int d\tau \Psi_j'^*(t) [K_0, H] \Psi'_j(t) + \frac{1}{i\hbar} \int d\tau \Psi_j'^*(t) [H, V] \Psi'_j(t), \quad (31)$$

where K_0 is the kinetic energy when vector potential is zero. Because $[K_0, H] = [K_0, H_2]$ and $[H, V] = [K_0, V]$, after a comparison with (13,16), one may say that the first term in (31) is the power due to the internal force, and the second term in (31) is the power due to the external force. Of course, the effect of external field is also reflected in $\Psi'_j(t)$. With the help of (26), one can easily show that to order V^2 , the second term in (31) is zero. (31) becomes

$$\begin{aligned} \frac{d}{dt} K_{\Psi'_j(t)} &= \frac{1}{i\hbar} \int d\tau \Psi_j'^*(t) [K_0, H] \Psi'_j(t) \\ &= \frac{1}{i\hbar} \sum_{kl} a_{kj}^{(1)*} a_{lj}^{(1)} [\varepsilon_l - \varepsilon_k] K_{0kl} + \frac{1}{i\hbar} \sum_l [\varepsilon_l - \varepsilon_j] [a_{lj}^{(2)} K_{0jl} - a_{lj}^{(2)*} K_{0lj}], \end{aligned} \quad (32)$$

where $K_{0jl} = \langle j | K_0 | l \rangle$ and $a_{lj}^{(p)} = a_{lj}^{(p)}(t) e^{i(\varepsilon_j - \varepsilon_l)t/\hbar}$ ($p = 1, 2$). The change in kinetic energy is produced by the power of the internal force. It is easy to check that without an external field, the internal force does no work, the average kinetic energy $K_{\Psi_j(t)} = \int d\tau \Psi_j^*(t) K_0 \Psi_j(t)$ in stationary state $\Psi_j(t)$ does not change with time:

$$\frac{d}{dt} K_{\Psi_j(t)} = \frac{1}{i\hbar} \int d\tau \Psi_j^*(t) [K_0, H] \Psi_j(t) = 0. \quad (33)$$

The Joule heat comes from a steady voltage which changes the state of system.

4. Low frequency AC voltage

We will use a gauge in which a low frequency AC field is solely described by a time-dependent scalar potential. The interaction of system with an AC voltage is given by (10) with a periodic scalar potential ϕ :

$$V(t) = F e^{-i\omega t} + F^\dagger e^{i\omega t}. \quad (34)$$

An AC voltage will produce a time-dependent current. According to Ampere's law, the time-dependent current will produce a time-dependent magnetic induction. Therefore a time-dependent vector potential $\mathbf{A}(\mathbf{r}, t)$ must accompany the AC voltage. (34) is only suitable for low frequency $\omega \ll \sigma/\epsilon_0$, where σ is the DC conductivity for the system.

When the frequency of an AC voltage approaches zero, its properties should be the same as those of DC voltage. Therefore we must integrate the equations of probability amplitudes $a_{lj}^{(p)}(t)$ ($p = 1, 2$) for $V(t)$ in the same way as those for the DC voltage:

$$a_{lj}^{(1)}(t) = -\frac{F_{lj}e^{i(\omega_{lj}-\omega)t}}{\hbar(\omega_{lj}-\omega)} - \frac{F_{jl}^*e^{i(\omega_{lj}+\omega)t}}{\hbar(\omega_{lj}+\omega)} \quad \text{for } l \neq j, \quad (35)$$

and

$$a_{jj}^{(1)}(t) = \frac{F_{jj}(e^{-i\omega t} - 1)}{\hbar\omega} - \frac{F_{jj}^*(e^{i\omega t} - 1)}{\hbar\omega}. \quad (36)$$

We will not write down the expressions for $a_{lj}^{(2)}(t)$ and $a_{jj}^{(2)}(t)$, they are too long. To the 2nd order in $V(t)$, the state of system is

$$\Psi'_j(t) = \Psi_j e^{-it\varepsilon_j/\hbar} + \sum_{p=1,2} \sum_l a_{lj}^{(p)}(t) \Psi_l e^{-it\varepsilon_l/\hbar}. \quad (37)$$

The rate of change in kinetic energy is

$$\frac{d}{dt} K_{\Psi'_j}(t) = \frac{1}{i\hbar} \int d\tau \Psi'_j{}^*(t) [K_0, H] \Psi'_j(t) + \frac{1}{i\hbar} \int d\tau \Psi'_j{}^*(t) [H, V(t)] \Psi'_j(t), \quad (38)$$

For an AC voltage, to obtain the dissipated energy, we must average (38) over a period $T = 2\pi/\omega$ of the AC voltage[10]: $T^{-1} \int_0^T dt$. Using $a_{lj}^{(p)}(t)$ and $a_{jj}^{(p)}(t)$ ($p = 1, 2$), one can show that to 2nd order in $V(t)$,

$$T^{-1} \int_0^T dt \frac{1}{i\hbar} \int d\tau \Psi'_j{}^*(t) [H, V(t)] \Psi'_j(t) = 0. \quad (39)$$

The time-averaged power of the external force is zero. Thus the change in kinetic energy is due to the internal force:

$$\begin{aligned} \frac{1}{T} \int_0^T dt \frac{d}{dt} K_{\Psi'_j}(t) &= \frac{1}{T} \int_0^T dt \frac{1}{i\hbar} \int d\tau \psi'_j{}^*(t) [K_0, H] \psi'_j(t) \\ &= \frac{1}{i\hbar} \sum_{m(\neq j)} \{ K_{jm} \sum_{k(\neq j)} \left[\frac{F_{mk} F_{jk}^*}{\hbar(\omega_{kj} + \omega)} + \frac{F_{km}^* F_{kj}}{\hbar(\omega_{kj} - \omega)} \right] + \frac{(F_{mj} F_{jj}^* - F_{jm}^* F_{jj}) K_{jm}}{\hbar\omega} \\ &\quad - K_{mj} \sum_{k(\neq j)} \left[\frac{F_{mk}^* F_{jk}}{\hbar(\omega_{kj} + \omega)} + \frac{F_{km} F_{kj}^*}{\hbar(\omega_{kj} - \omega)} \right] - \frac{(F_{mj}^* F_{jj} - F_{jm} F_{jj}^*) K_{mj}}{\hbar\omega} \} \\ &\quad + \frac{1}{i\hbar} \sum_{kl(k \neq l)} K_{lk} (\varepsilon_k - \varepsilon_l) \left\{ \frac{F_{kj} F_{lj}^*}{\hbar(\omega_{kj} - \omega) \hbar(\omega_{lj} - \omega)} + \frac{F_{jk}^* F_{jl}}{\hbar(\omega_{kj} + \omega) \hbar(\omega_{lj} + \omega)} \right\}. \end{aligned} \quad (40)$$

For an AC voltage, because $[K_0, H] = [K_0, H_2]$, we may say that the Joule heat comes from the power of the internal force. For $\omega = 0$, Eq.(40) reduces to Eq.(32), the Joule heat for DC voltage.

5. Electromagnetic field

In Sec.3 and 4, a special gauge is used: both DC voltage and low frequency AC voltage are described by scalar potentials. The rates of change kinetic energy are given in (31,38). Now consider the system interacting with a general electromagnetic field described by (\mathbf{A}, ϕ) which may or may not change with time. We will not restrict ourselves to any special gauge. The kinetic energy operator of the system is $\widehat{K}(t)$ rather than K_0 . If vector potential \mathbf{A} changes with time, there is one more term $\partial\widehat{K}(t)/\partial t$ in $dK_{\Psi'_j}(t)/dt$ (8). $\partial\widehat{K}(t)/\partial t$ results from the time dependence of vector potential $\partial\mathbf{A}(\mathbf{r}, t)/\partial t$.

To apply TDPT to compute $dK_{\Psi'_j}(t)/dt$, we notice that $H_{mf} = V_A + V_\phi$, where $V_A = V_{A1} + V_{A2}$ is the interaction involving vector potential \mathbf{A} , V_{A1} presents the terms which are first order in \mathbf{A} , V_{A2} presents the terms which are second order in \mathbf{A} . V_{A2} is only a function of coordinates and does not include differential operators. Notice $\widehat{K} = K_0 + V_A$ and $H = K_0 + H_2$, the commutator in the first term of (8) can be transformed to

$$[\widehat{K}, H'] = [\widehat{K}, H] + [H, H_{mf}] + [V_{A1}, V], \quad (41)$$

where $V = V_\phi + H_2$ and

$$\frac{1}{i\hbar}[V_{A1}, V] = \sum_i m^{-1}[e\mathbf{A}(\mathbf{r}_i, t) \cdot \nabla_{\mathbf{r}_i} V] - \sum_\alpha M_\alpha^{-1}[Z_\alpha e\mathbf{A}(\mathbf{R}_\alpha, t) \cdot \nabla_{\mathbf{R}_\alpha} V]. \quad (42)$$

Since $-\nabla_{\mathbf{r}_i} V = \mathbf{f}_i + [-e\nabla_{\mathbf{r}_i} \phi(\mathbf{r}_i, t)]$, $-e\mathbf{A}(\mathbf{r}_i, t)/m$ is the part of velocity due to field of the i^{th} electron, the first term in (42) is the power of the field momentum due to scalar potential ϕ and the internal force. The 2^{nd} term is the power of the field momentum of nuclei. Substituting (41) into (8), one has

$$\begin{aligned} \frac{d}{dt}K_{\Psi'_j}(t) &= \frac{1}{i\hbar} \int d\tau \Psi_j'^*(t) ([\widehat{K}, H] + [H, H_{mf}(t)]) \Psi_j'(t) \\ &+ \int d\tau \Psi_j'^*(t) \left(\frac{\partial\widehat{K}(t)}{\partial t} + \frac{1}{i\hbar}[V_{A1}, V] \right) \Psi_j'(t). \end{aligned} \quad (43)$$

For an electromagnetic field with several frequencies ω_n , the matrix element of the interaction has form:

$$[H_{mf}(t)]_{lj} = \sum_n [F_{lj}^n e^{-i\omega_n t} + F_{jl}^{n*} e^{i\omega_n t}]. \quad (44)$$

With the same method for an AC voltage described by a scalar potential, one can show to 2^{nd} order in $H_{mf}(t)$, $(i\hbar)^{-1} \int d\tau \Psi_j'^*(t) [H, H_{mf}] \Psi_j'(t) = 0$. The first term in (43) can be similarly obtained as (40) for AC voltage:

$$\begin{aligned} \frac{1}{i\hbar} \int d\tau \Psi_j'^*(t) [\widehat{K}, H] \Psi_j'(t) &= \frac{1}{i\hbar} \sum_{p=1,2} \left\{ \sum_{l(\neq j)} (\varepsilon_j - \varepsilon_l) [a_{lj}^{(p)*}(t) e^{it(\varepsilon_l - \varepsilon_j)/\hbar} K_{lj} \right. \\ &\left. - a_{lj}^{(p)}(t) e^{it(\varepsilon_j - \varepsilon_l)/\hbar} K_{jl}] \right\} + \frac{1}{i\hbar} \sum_{kl(k \neq l)} a_{lj}^{(1)*}(t) a_{kj}^{(1)}(t) e^{it(\varepsilon_l - \varepsilon_k)/\hbar} K_{lk} (\varepsilon_k - \varepsilon_l), \end{aligned} \quad (45)$$

where the matrix elements of the kinetic energy are calculated with $\widehat{K}(t)$ rather than K_0 , the transition probability amplitudes are computed for $H_{mf}(t)$. After average over one period of external field, the order V term in the curly bracket is zero. We see from (17) that $\partial\widehat{K}(t)/\partial t$ is first order in vector potential. To second order in $H_{mf}(t)$,

$$\begin{aligned} \int d\tau \Psi_j'^*(t) \frac{\partial\widehat{K}(t)}{\partial t} \Psi_j'(t) &= \int d\tau \Psi_j^* \frac{\partial\widehat{K}(t)}{\partial t} \Psi_j \\ &+ \sum_l [a_{lj}^{(1)*}(t) e^{it(\varepsilon_l - \varepsilon_j)/\hbar} \int d\tau' \Psi_l^* \frac{\partial\widehat{K}(t)}{\partial t} \Psi_j + a_{lj}^{(1)}(t) e^{-it(\varepsilon_l - \varepsilon_j)/\hbar} \int d\tau' \Psi_j^* \frac{\partial\widehat{K}(t)}{\partial t} \Psi_l]. \end{aligned} \quad (46)$$

For many choices of gauge, $\partial\widehat{K}(t)/\partial t$ is Hermitian, the second term in the square bracket is the complex conjugate of the first term. Combining (42,45,46), the rate $dK_{\Psi_j}(t)/dt$ of change in kinetic energy in (43) is determined.

We analyze the conditions which lead to KGF for this general case. If (i) the gradient of the carrier density is small; and (ii) the wavelength of vector potential is larger than the characteristic length of the considered sample, the first term in (46) is zero. One can see this from (17): under conditions (i) and (ii), the second term in (17) is ignored, and the first term in (46) becomes $[-\partial\mathbf{A}(\mathbf{r};t)/\partial t] \sum_i \int d\tau \Psi_j^* \mathbf{v}_i \Psi_j$. But the average velocity $\int d\tau \Psi_j^* \mathbf{v}_i \Psi_j$ in a stationary state Ψ_j of H is zero. Now only the square bracket term is left in (46). Each term represents the power due to part of electric field described by vector potential:

$$-\partial\mathbf{A}(\mathbf{r};t)/\partial t = -\partial\mathbf{A}_\perp(\mathbf{r};t)/\partial t - \partial\mathbf{A}_\parallel(\mathbf{r};t)/\partial t, \quad (47)$$

the longitudinal and transverse parts satisfy $\nabla \times \mathbf{A}_\parallel = 0$ and $\nabla \cdot \mathbf{A}_\perp = 0$ respectively. The contribution from $-\nabla\phi$ is absent from (46).

Greenwood used a special gauge: $\mathbf{A}(t) = -t\mathbf{E}$ and $\phi = 0$ to describe a DC voltage[3]. Then $V_{A1} = t\mathbf{E} \cdot \mathbf{v}$, according to TDPT, $\langle l|e\mathbf{E}t \cdot \mathbf{v}|j\rangle \sim (\varepsilon_l - \varepsilon_j)a_{lj}^{(1)}/t$. If the interaction time is long enough that transition probability per unit time is well defined, then a typical term in the square bracket of (46) becomes $\sum_l (\varepsilon_l - \varepsilon_j)|a_{lj}^{(1)}|^2/t$. Averaging (46) over the occupation probability of the initial state Ψ_j , one obtains (4). From (18,19) and (43), (4) missed the contributions from (42) and (45). Although the momentum due to field i.e. (42) is negligible, the contribution (45) is same order as (46): $|(V_{A1})_{lj}|^2/\hbar$.

If we consider only the radiation field in (47), $\partial\mathbf{A}_\perp(\mathbf{r};t)/\partial t \sim \omega A_\perp$. Then $a_{lj}^{(1)}(t) = -\langle l|e\mathbf{A}_\perp \cdot \mathbf{v}|j\rangle e^{i(\omega_{lj} - \omega)t + \lambda t} [\hbar(\omega_{lj} - \omega - i\lambda)]^{-1}$. If the interaction time is long enough, the square bracket in (46) becomes $\sum_l \hbar\omega |a_{lj}^{(1)}(t)|^2/t$ i.e. (1). For a zero frequency radiation field, the absorbed energy from field is zero. Thus we understand that although the limit procedure from (3) to (4) is not legitimate, (4) can be obtained in Greenwood gauge (a longitudinal field), and contains part of the conductivity. The power (45) induced by the internal force on system always exists, no matter longitudinal field or transverse field. The applicable lower limit frequency of (3) is at least $\omega \gg \sigma/\epsilon_0$. For intrinsic Si[11], $\sigma = 1.2 \times 10^{-5} \text{Scm}^{-1}$, the simplified version[1, 5] of Kubo-Greenwood formula wok only when the frequency of external field is higher than $\sigma/\epsilon_0 \sim 1.4 \times 10^8 \text{Hz}$.

Numerical calculations[2, 12, 13, 14, 15] have shown $\sigma(\omega)$ approaches zero with ω below a resonance absorption frequency ω_r which is roughly the splitting from the maximum of density of states in the valence band to the edge of conduction band. This agrees with our analysis. Sometimes researchers extrapolate[2] σ_{dc} from $\sigma(\omega_r)$. Because of the existence of (4), if the velocity matrix elements are not very sensitive to the energies of states, extrapolation will deliver reasonable results.

6. Conclusion

In summary, from the rate of change in kinetic energy, we obtained a rigorous expression for the power done by an arbitrary electromagnetic field in any gauge. It leads to a proper current density which has been proved by the continuity equation[7], polarization density[8] and current operator[4]. We show the simplified derivation of KGF by Mott-Davis and Moseley-Lukes suffers the same approximations used by Greenwood. The work done by the internal force is missed in (3,4), they are same order as the terms in KGF. Using (4) or extrapolation from (3) can obtain a significant part of the DC conductivity, but a stricter calculation based on the rigorous current density would deliver more accurate, possibly even qualitatively new results.

Acknowledgments

We thank the Army Research Office for support under MURI W91NF-06-2-0026, and the National Science Foundation for support under grant DMR 09-03225.

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