# The Theory of Direct Transitions in Semiconductors

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*The problem of direct interband transitions in semiconducting crystals is considered in detail. The solution of the problem is shown to lead to a system of simultaneous coupled nonlinear differential equations. These equations do not distinguish between static and dynamic fields, and are obtained without recourse to any approximation procedures. They therefore apply for electromagnetic fields of arbitrary amplitude. It is shown, finally, that the linearization of these equations correctly predicts the fundamental optical absorption edge and the photoconductive rate equations which result in photomixing phenomena.*

## I. INTRODUCTION

Within the past year there has been an increasing interest in semiconductor behavior, resulting from the development of the optical maser. In addition to the fact that the semiconductor can be used as an optically active medium, this interest results, in part, from a variety of nonlinear effects which can occur in semiconductors at infrared and optical frequencies.

Optical masers are capable of providing very high-intensity fields at photon energies corresponding to the energy gap between valence and conduction bands. Since nonlinear effects generally vary as some power of field strength, the laser has stimulated keen interest in semiconductor nonlinear phenomena. Examples of such phenomena are the Franz-Keldysh[1,2] effect and the multiple-photon process.[3] Closely allied with these nonlinear interband effects is the process of photomixing[4,5] (photoconductivity), where two coherent optical signals are beat together to produce a photosignal which is proportional to the instantaneous density of photoexcited electrons and hence contains sum and difference frequency terms.

The aforementioned phenomena have been analyzed previously by calculating the interband transition probabilities from time-dependent perturbation theory[1-3] for the case where an electrostatic and electromagnetic field act on an electron in a crystal. This approach involves discarding quadratic terms in the vector potential in the Hamiltonian (the static and dynamic fields are treated differently), and neglecting higher-order nonlinearities in the population distribution.

In this article, a more general theory of direct transitions in semiconductors is presented. A semiclassical approach is used, wherein the semiconductor properties are quantized and the electromagnetic field is treated classically. A set of rather simple coupled nonlinear differential equations is obtained for the equations of motion governing the fundamental absorption process, without resorting to any perturbation or approximation procedures. In contrast to the usual method of analysis, these equations do not distinguish between static and dynamic fields. The linearization of the nonlinear equations correctly predicts the fundamental optical absorption, and is shown to lead to the photoconductive rate equation for the generation of conduction band electrons.

## II. SOLUTION TO THE WAVE EQUATION

The equation of motion for an electron in a crystal is the wave equation

$$\mathcal{H}\psi = i\hbar(\partial\psi/\partial t), \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian operator and $\psi$ is the one-electron wave function. Without the presence of the radiation or static fields the Hamiltonian, $\mathcal{H}_0$, is

$$\mathcal{H}_0 = (\mathbf{p}^2/2m) + V(\mathbf{r}).$$

Here $m$ is the electron mass, $V(\mathbf{r})$ is the lattice potential, and $\mathbf{p}$ is the momentum operator. With $\mathcal{H}_0$ as the operator in (1), the eigenfunctions of $\mathcal{H}_0$ are the Bloch functions:

$$\mathcal{H}_0\{u_N(\mathbf{r};\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r})\} = \mathcal{E}_N(\mathbf{k})u_N(\mathbf{r};\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}), \tag{2}$$

where

$$\varphi_N(\mathbf{r};\mathbf{k}) = u_N(\mathbf{r};\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}),$$

are the Bloch functions, and $\mathcal{E}_N(\mathbf{k})$ are the energy eigenvalues. The subscript $N$ refers to the different energy bands, and the function $u_N(\mathbf{r};\mathbf{k})$, which is normalized over the volume of the unit cell, has the periodicity of the lattice. In the presence of a static and dynamic field, the Hamiltonian becomes

$$\mathcal{H} = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + V(\mathbf{r}) - \mathbf{F}\cdot\mathbf{r}, \tag{3}$$

where $e$ is the electronic charge, $c$ is the vacuum light velocity, $\mathbf{A}$ is the vector potential for the dynamic field (the gauge $\Phi = 0$ and $\nabla\cdot\mathbf{A} = 0$ is chosen), and $\mathbf{F} = e\mathbf{E}_0$ is the force due to the static field $\mathbf{E}_0$. The static and dynamic fields enter differently in (3), because of the fact that the vector potential for the static field increases linearly with time. It will be shown, however, that in the solution there is no distinction between the two fields.

With the Hamiltonian given by (3), the wave function $\psi$ is chosen so that the equation of motion (1) does not contain secular terms, and so that the solution to the wave equation [(7) and (8) below] takes a relatively simple form in which the time-dependent and time-independent fields both appear. A normalized wave function that satisfies these two criteria is given by

$$\begin{aligned}\psi(\mathbf{r},t) = {}& \frac{\Delta^{\frac{1}{2}}}{(2\pi)^{\frac{3}{2}}}\sum_N \int d^3k a_N(t;\mathbf{k})u_N[\mathbf{r};\mathbf{K}(t)] \\ & \times \exp i\left\{\mathbf{k}\cdot\mathbf{r} + \frac{1}{\hbar}\mathbf{F}\cdot\mathbf{r}t - \frac{1}{\hbar}\int_0^t \mathcal{E}_N[\mathbf{K}(\tau)]\,d\tau + S_N(t;\mathbf{k})\right\},\end{aligned} \tag{4}$$

where $\Delta$ is the volume of a unit cell, and where, for the sake of simplicity, the function $S_N(t;\mathbf{k})$ has been defined as

$$S_N(t;\mathbf{k}) = i\frac{e}{\hbar}\int_0^t d\tau\,\mathbf{E}\cdot\int dv_0 u_N^*(\mathbf{r};\mathbf{K})\nabla_K u_N(\mathbf{r};\mathbf{K}). \tag{5}$$

Here $\nabla_K$ is the gradient operator in $\mathbf{K}$-space and the asterisk denotes the complex conjugate. One result of the added force on the electron, determined by the total electric field vector

$$\mathbf{E} = \mathbf{E}_0 - \frac{1}{c}\frac{\partial\mathbf{A}}{\partial t},$$

is to change the electron wave vector from the constant value $\mathbf{k}$ to the time-varying value

$$\mathbf{K}(t) = \mathbf{k} + \frac{1}{\hbar}\mathbf{F}t - \frac{e}{\hbar c}\mathbf{A}(t), \tag{6}$$

which describes the intraband electronic motion. The integral over $\mathbf{k}$-space entering in (4) extends over all values of the wave number within an energy band, and the volume integral over coordinate space appearing in (5) extends over the volume of a unit cell. It should be noted that the dc field does not appear symmetrically with the time-varying field in (4); this is due to the fact that the Hamiltonian has a different form for static and time-dependent fields. The form of the wave function given by (4) was suggested by Houston's choice of wave function for an applied dc field.[6]

It is assumed now that the wavelength of the applied radiation is much greater than the dimensions of the unit cell, and that the electron wave vector **k** has the same value for the lowest state in the conduction band as for the highest state in the valence band. Thus the electron momentum vector for the final state is the same as the momentum vector for the initial state (direct transitions). In Appendix A, it is shown that the substitution of the wave function $\psi$ from (4) into the wave equation (1) yields a differential equation for the undetermined probability coefficients $a_N(t;\ \mathbf{k})$. Considering only direct transitions between valence and conduction bands, there results [see (29)]

$$\begin{aligned} \partial a_c/\partial t &= -Qa_v \\ \partial a_v/\partial t &= Q^* a_c\,, \end{aligned} \tag{7}$$

where

$$Q = i\,\frac{e}{m}\,\frac{\mathbf{E}\cdot\mathbf{M}}{\omega_{cv}}\exp i\left[\int_0^t \omega_{cv}d\tau - (S_c - S_v)\right]. \tag{8}$$

The subscripts $c$ and $v$ refer, respectively, to the conduction and valence bands; **M** is the matrix element for transitions between the two bands,

$$\mathbf{M} = \int dv_0 u_c^* \nabla u_v;$$

and $\omega_{cv}$ is an angular frequency given by

$$\omega_{cv} = \frac{\mathcal{E}_c - \mathcal{E}_v}{\hbar}.$$

In taking the complex conjugate of $Q$ it should be noted that the function $S_N$ defined by (5) is real. This follows from the fact that the electric field **E** is chosen to be real, and that the integral

$$\int dv_0 u_N^* \nabla_K u_N$$

is imaginary, since

$$\nabla_K \int u_N^* u_N dv_0 = \nabla_K \delta_{NN} = 0.$$

The interaction between the semiconductor and the electromagnetic field results in the generation of a probability current density in the crystal. The expectation value of this current, in turn, acts as a source of radiation in the Maxwell equation for the curl of **H**. Therefore a complete solution of the problem of the interaction between the semiconductor and radiation field requires an evaluation of this current source. The expectation value of the probability current density, **J**, can be expressed as follows, by noting that the canonical momentum operator **p** is Hermitian,

$$\mathbf{J} = \frac{e}{mV}\left\langle \mathbf{p} - \frac{e}{c}\mathbf{A} \right\rangle, \tag{9}$$

where $V$ is the crystal volume and the angular brackets denote averaging over the volume $V$.

It is now convenient to define a vector **j** by

$$\mathbf{J} = \int d^3k\mathbf{j}$$

such that **j** is the averaged current density per unit volume in **k**-space. In Appendix B it is shown that **j** satisfies the simple relationship [see (36)]

$$\mathbf{j}\cdot\mathbf{E} = \partial W/\partial t, \tag{10}$$

where $W$ is the energy of the system per unit volume, i.e.,

$$W = (1/V)(\,|\,a_c\,|^2\mathcal{E}_c + |\,a_v\,|^2\mathcal{E}_v). \tag{11}$$

Equation (10) is just the statement of conservation of power flow, for the left-hand side of this equation is the power transferred into the semiconductor, as given by the scalar product of current density and *total* electric field. The right-hand side of (10) is, of course, the resultant rate of increase of energy density in the quantized semiconductor system.

Equations (7), (10), and (11) contain the necessary information to solve various types of semiconductor problems involving direct transitions. The derivation of these equations did not require discarding $\mathbf{A}^2$ terms in the Hamiltonian, and the solution for the unknown amplitudes $a_N$ did not necessitate using perturbation or approximation methods. It should be emphasized at this point that the results do not distinguish between static and dynamic fields. The set of equations (7), (10), and (11) is nonlinear and may be solved to any order in the electric field **E** to determine the various nonlinear interband phenomena. The remainder of this paper will be devoted to a detailed treatment of the linear solutions, which will be shown to lead to the rate equation for the generation of electron-hole pairs (photoconductivity).

## III. SMALL-SIGNAL SOLUTIONS AND DERIVATION OF THE PHOTOCONDUCTIVE RATE EQUATION

The equations of motion for optical interband transitions [(7), (10), and (11)] can be greatly simplified by seeking solutions for $a_c$ and $a_v$ correct to first order in the electric field $\mathbf{E}$. Under this condition, which applies when the external electromagnetic force influencing the electronic motion in the crystal is small, the wave vector $\mathbf{K}(t)$ can be replaced by $\mathbf{k}$, so that $\omega_{cv}$ becomes time-independent. It is then easy to show from (7) and (8) that the solutions for $a_c$ and $a_v$ correct to first order are:

$$\begin{aligned} a_c &= a_c^{(0)} - a_v^{(0)} \frac{ie}{m\omega_{cv}} \mathbf{M} \cdot \int \mathbf{E} e^{i\omega_{cv}t}\, dt \\ a_v &= a_v^{(0)} - a_c^{(0)} \frac{ie}{m\omega_{cv}} \mathbf{M}^* \cdot \int \mathbf{E} e^{-i\omega_{cv}t}\, dt. \end{aligned} \tag{12}$$

The superscript (0) indicates the zero-order solutions which, for this example, are independent of time. For the case where the crystal is in thermal equilibrium at 0°K, the constant amplitudes $a_c^{(0)}$ and $a_v^{(0)}$ can be determined by noting that the electrons are confined to states in the valence band only, i.e.,

$$| a_c^{(0)} |^2 = 0, \tag{13a}$$

and

$$| a_v^{(0)} |^2 d^3k = \rho(\mathbf{k}) d^3k, \tag{13b}$$

where $\rho(\mathbf{k})$ is the density of states. Integrating (13b) over a spherical shell gives for the number of states in a range $dk$

$$| a_v^{(0)} |^2 dk = (V/\pi^2) k^2 dk, \tag{13c}$$

in which $V$ is the crystal volume.

A second-order linear differential equation can now be derived for the crystal current density $\mathbf{j}$. Since the external forces are assumed to be small, $\mathbf{K}(t) \approx \mathbf{k}$, whereupon one obtains from (10) and (11)

$$\mathbf{j} \cdot \mathbf{E} = \frac{\hbar\omega_{cv}}{V} \frac{\partial | a_c |^2}{\partial t}, \tag{14}$$

where use has been made of the relation $| a_c |^2 + | a_v |^2 = \text{constant}$. By substituting the first-order solution for $a_c$ from (12) into (14), it is found after some manipulation that $\mathbf{j}$ satisfies the equation of motion for a forced harmonic oscillator, i.e.,

$$\frac{\partial^2 \mathbf{j}}{\partial t^2} + \omega_{cv}^2 \mathbf{j} = G \frac{\partial \mathbf{E}}{\partial t}, \tag{15}$$

where

$$G = \frac{2\hbar}{\omega_{cv} V} \left(\frac{e}{m}\right)^2 | M_E |^2 | a_v^{(0)} |^2, \tag{16}$$

and $M_E$ is the component of $\mathbf{M}$ in the direction of the electric field $\mathbf{E}$.

The validity of (15) may be checked by calculating the absorption coefficient $\alpha(\omega)$ for the fundamental absorption edge. It is assumed that the semiconductor has spherical energy surfaces with the same reduced effective mass, $1/m^* = 1/m_c^* - 1/m_v^*$, along all crystal axes, and that in consequence

$$\omega_{cv} \approx \omega_0 + (\hbar/2m^*)k^2, \tag{17}$$

where $\hbar\omega_0$ is the minimum energy gap between the two bands. By making use of (13c) for $| a_v^{(0)} |^2$ and (17) for $\omega_{cv}$, the observable crystal current density $\mathbf{J}$ can be found by integrating $\mathbf{j}$, as determined from (15), over $\mathbf{k}$-space. The resultant expression is given by the following constitutive relation between $\mathbf{J}$ and $\mathbf{E}$

$$\mathbf{J} = \frac{1}{\pi} \sqrt{\frac{2}{\hbar}} \left(\frac{e}{m}\right)^2 | M_E |^2 (m^*)^{\frac{3}{2}} \frac{\sqrt{\omega - \omega_0}}{\omega} \mathbf{E}, \tag{18}$$

where $\omega$ is angular oscillation frequency of the radiation field. The absorption coefficient can now be found directly by observing that in the frequency domain the coefficient of $\mathbf{E}$ in (18) is the macroscopic conductivity, $\sigma$, of the solid and is related to the absorption coefficient by

$$\alpha = 4\pi\sigma/n_0 c,$$

in which $n_0$ is the index of refraction of the crystal. The value for $\alpha$ obtained in this manner from (18) is the same as that given elsewhere.[7]

The photoconductive rate equation for generation of conduction electron-hole pairs also follows from the small-signal solution. If $n$ is the number of conduction electrons per unit volume (equal to the number of holes), then one may express $n$ as the $\mathbf{k}$-space integral of $| a_c |^2$:

$$n = \int d^3k \, \frac{|a_c|^2}{V}. \tag{19}$$

The rate of increase of conduction electrons is obtained from (14), whereby

$$\frac{\partial n}{\partial t} = \mathbf{E} \cdot \int d^3k \, \frac{\mathbf{j}}{\hbar\omega_{cv}} . \tag{20}$$

In order to account for lattice collisions which produce intraband transitions and eventual interband recombinations, it is necessary to add a phenomenological loss term to (20). This is accomplished by adding a term $n/\tau_n$ to the left-hand side of (20), where $\tau_n$ is the lifetime of an electron in the excited states of the conduction band. Equation (20) then leads to the photoconductive rate equation

$$\frac{\partial n}{\partial t} + \frac{n}{\tau_n} = \mathbf{E} \cdot \int d^3k \, \frac{\mathbf{j}}{\hbar\omega_{cv}} . \tag{21}$$

A situation of particular interest is where **E** is an optical field made up of several coherent frequencies. Combining (15) and (21) then results in the rate equation for photomixing

$$\frac{\partial n}{\partial t} + \frac{n}{\tau_n} = \frac{n_0 c}{4\pi} \sum_{p,q} \frac{\alpha_p}{\hbar\omega_p} \mathbf{E}_p \cdot \mathbf{E}_q . \tag{22}$$

In this equation the subscripts $p$ and $q$ enumerate the different frequency components in the incident radiation. It is seen from (22) that $n$ contains the sum and difference beat frequencies of the incoming radiation. This equation may be used to calculate the optical mixing properties of semiconductor crystals, where the mixing process results from photoconductivity.[8]

## IV. CONCLUSIONS

The analysis of the problem of direct transitions in semiconductors has led to several simultaneous nonlinear differential equations. Linearization of these equations correctly predicts the fundamental optical absorption and photoconductive mixing effects. Nonlinear effects such as might result from the time dependence of $\omega_{cv}$ (Franz-Keldysh effect), or from the time dependence of $|a_c|^2$ and $|a_v|^2$ (multiple-photon effects) can be predicted by appropriate higher-order approximation procedures.

## V. ACKNOWLEDGMENT

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## APPENDIX A

### *Derivation of the Equations of Motion Governing Direct Transitions*

Equation (2) can be rewritten as

$$\left[\frac{\mathbf{p}^2}{2m} + V(\mathbf{r})\right] u_N(\mathbf{r};\,\mathbf{k}) \exp\,(i\mathbf{k}\cdot\mathbf{r}) = \mathcal{E}_N(\mathbf{k}) u_N(\mathbf{r};\,\mathbf{k}) \exp\,(i\mathbf{k}\cdot\mathbf{r}), \quad (23)$$

where $u_N(\mathbf{r};\,\mathbf{k}) \exp i\mathbf{k}\cdot\mathbf{r}$ are the stationary Bloch functions, and $\mathbf{p}$ is the operator $-i\hbar\nabla$. It follows directly from (23) that in the presence of an electromagnetic field

$$\left[\frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + V(\mathbf{r})\right] u_N(\mathbf{r};\,\mathbf{K}) \exp i\left(\mathbf{k} + \frac{1}{\hbar}\mathbf{F}t\right)\cdot\mathbf{r} = \mathcal{E}_N(\mathbf{K}) u_N(\mathbf{r};\,\mathbf{K}) \exp i\left(\mathbf{k} + \frac{1}{\hbar}\mathbf{F}t\right)\cdot\mathbf{r}. \quad (24)$$

Equation (24) can be verified by performing the indicated operations and invoking (23).

The substitution of the wave function $\psi(\mathbf{r}, t)$ from (4) into the wave equation with the Hamiltonian of (3) yields, with the help of (24),

$$0 = \sum_N \int d^3k \left\{\frac{\partial a_N}{\partial t} u_N(\mathbf{r};\,\mathbf{K}) + a_N\left[\frac{\partial \mathbf{K}}{\partial t}\cdot\nabla_K u_N(\mathbf{r};\,\mathbf{K}) + i\,\frac{\partial S_N}{\partial t} u_N(\mathbf{r};\,\mathbf{K})\right]\right\} \exp i(\mathbf{r}, t, \mathbf{k}, N), \quad (25)$$

where $\exp i(\mathbf{r},t,\mathbf{k},N)$ is an abbreviation for the exponential function

$$\exp i\left\{\mathbf{k}\cdot\mathbf{r} + \frac{1}{\hbar}\mathbf{F}\cdot\mathbf{r}t - \frac{1}{\hbar}\int_0^t \mathcal{E}_N(\mathbf{K})\,d\tau + S_N(t;\,\mathbf{k})\right\}.$$

Equation (25) is now multiplied by

$$u_{N'}{}^*(\mathbf{r};\,\mathbf{K}') \exp -i(\mathbf{r},t,\mathbf{k}',N'),$$

and integrated over all coordinate space. The resulting equation is then simplified by making use of the lemma[9]

$$\int_{\text{all space}} dv \int d^3k\Phi(\mathbf{r};\, \mathbf{k},\mathbf{k}') \exp i(\mathbf{k} - \mathbf{k}')\cdot\mathbf{r} = \frac{(2\pi)^3}{\Delta} \int dv_0 \Phi(\mathbf{r};\, \mathbf{k},\mathbf{k}),$$

where $\Phi(\mathbf{r};\, \mathbf{k},\mathbf{k}')$ is a lattice periodic function. Recall that the volume integral on the right-hand side of this expression extends over the volume of a unit cell.

The result of performing the above operations on (25) is

$$\frac{\partial a_L}{\partial t} + ia_L \frac{\partial S_L}{\partial t} = -\sum_N a_N \frac{\partial \mathbf{K}}{\partial t}\cdot\left\{\int dv_0 u_L^* \nabla_K u_N\right\} \times \exp i\left[\int_0^t \omega_{LN}\, d\tau + (S_N - S_L)\right], \tag{26}$$

where $\hbar\omega_{LN} = \mathcal{E}_L - \mathcal{E}_N$. It can be shown from the definition of $S_L$ [see (5)] that the time derivative, $\partial S_L/\partial t$, is

$$\frac{\partial S_L}{\partial t} = i\frac{\partial \mathbf{K}}{\partial t}\cdot \int dv_0 u_L^* \nabla_K u_L ,$$

so that (26) may be rewritten as

$$\frac{\partial a_L}{\partial t} = -{\sum_N}' a_N \frac{\partial \mathbf{K}}{\partial t}\cdot\left\{\int dv_0 u_L^* \nabla_K u_N\right\} \times \exp i\left[\int_0^t \omega_{LN}\, d\tau + (S_N - S_L)\right], \tag{27}$$

where ${\sum_N}'$ indicates that $N = L$ is excluded from the sum.

There is a rather simple relationship between the matrix element of the gradient operator in **K**-space and in coordinate space, which for $N \neq L$, can be expressed as[9]

$$\int dv_0 u_L^* \nabla_K u_N = \frac{i\hbar}{m\omega_{LN}} \int dv_0 u_L^* \nabla u_N . \tag{28}$$

By combining (27) and (28) and noting from (6) that $\partial\mathbf{K}/\partial t = e\mathbf{E}/\hbar$, the results

$$\frac{\partial a_L}{\partial t} = -i\frac{e}{m}\mathbf{E}\cdot{\sum_N}' a_N \frac{1}{\omega_{LN}}\left\{\int dv_0 u_L^* \nabla u_N\right\} \times \exp i\left[\int_0^t \omega_{LN}\, d\tau + (S_N - S_L)\right]. \tag{29}$$

For transitions between valence and conduction bands only, (29) reduces to (7).

## APPENDIX B

### *The Relationship between Current Density and Energy*

The expectation value, or volume average, of the probability current density in the presence of an electromagnetic field is given by

$$\mathbf{J} = \frac{e}{mV} \langle \mathbf{p} - \frac{e}{c} \mathbf{A} \rangle. \tag{30}$$

Considering only transitions between the valence and conduction bands for the wave function of (4), the current density determined from (30) becomes

$$\begin{aligned} \mathbf{J} = -i \frac{e\hbar}{mV} \int d^3k \Big\{ & i\mathbf{K}(|a_c|^2 + |a_v|^2) + |a_c|^2 \int dv_0 u_c^* \nabla u_c \\ & + |a_v|^2 \int dv_0 u_v^* \nabla u_v + a_c^* a_v \mathbf{M} \exp i \left[ \int_0^t \omega_{cv}\, d\tau + (S_v - S_c) \right] \\ & - a_c a_v^* \mathbf{M}^* \exp -i \left[ \int_0^t \omega_{cv}\, d\tau + (S_v - S_c) \right] \Big\}. \end{aligned} \tag{31}$$

Equation (31) can be simplified considerably by making use of the relationship[9]

$$i \frac{m}{\hbar^2} \nabla_K \mathcal{E}_N(\mathbf{K}) = i\mathbf{K} + \int dv_0 u_N^*(\mathbf{r}; \mathbf{K})\, \nabla u_N(\mathbf{r}; \mathbf{K}). \tag{32}$$

Combining (31) and (32) results in the expression

$$\begin{aligned} \mathbf{J} = -i \frac{e\hbar}{mV} \int d^3k \Big\{ & i \frac{m}{\hbar^2} (|a_c|^2 \nabla_K \mathcal{E}_c + |a_v|^2 \nabla_K \mathcal{E}_v) \\ & + a_c^* a_v \mathbf{M} \exp i \left[ \int_0^t \omega_{cv}\, d\tau + (S_v - S_c) \right] \\ & - a_c a_v^* \mathbf{M}^* \exp -i \left[ \int_0^t \omega_{cv}\, d\tau + (S_v - S_c) \right] \Big\}. \end{aligned} \tag{33}$$

The energy density, $W$, for the quantized semiconductor system is given by (11). By differentiating $W$ with respect to time, one has

$$\begin{aligned} \frac{\partial W}{\partial t} = \frac{1}{V} \Big[ & |a_c|^2 \frac{\partial \mathbf{K}}{\partial t} \cdot \nabla_K \mathcal{E}_c + |a_v|^2 \frac{\partial \mathbf{K}}{\partial t} \cdot \nabla_K \mathcal{E}_v \\ & + \left( a_c^* \frac{\partial a_c}{\partial t} + a_c \frac{\partial a_c^*}{\partial t} \right) \mathcal{E}_c + \left( a_v^* \frac{\partial a_v}{\partial t} + a_v \frac{\partial a_v^*}{\partial t} \right) \mathcal{E}_v \Big]. \end{aligned} \tag{34}$$

Now, from the preceding work in Appendix A the time dependences of $a_c$ and $a_v$ are known and, for the present situation, are given by (7). Thus by combining (7) with (34) and noting that $\partial \mathbf{K}/\partial t = e\mathbf{E}/\hbar$, one obtains the following formula for $\partial W/\partial t$:

$$\begin{aligned}\frac{\partial W}{\partial t} = \frac{1}{V}\frac{e}{\hbar}\mathbf{E}\cdot\Bigg\{&| a_c |^2 \nabla_K \mathcal{E}_c + | a_v |^2 \nabla_K \mathcal{E}_v \\ &- i\frac{\hbar^2}{m} a_c{}^* a_v \mathbf{M} \exp i\left[\int_0^t \omega_{cv}\, d\tau + (S_v - S_c)\right] \\ &+ i\frac{\hbar^2}{m} a_c a_v{}^* \mathbf{M}^* \exp -i\left[\int_0^t \omega_{cv}\, d\tau + (S_v - S_c)\right]\Bigg\}.\end{aligned} \tag{35}$$

A comparison of (33) and (36) illustrates the desired relationship between current density and energy density, viz.,

$$\mathbf{j}\cdot\mathbf{E} = \partial W/\partial t, \tag{36}$$

where $\mathbf{J} \equiv \int d^3k\mathbf{j}$.

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