PHYSICAL REVIEW B VOLUME 48, NUMBER 16 15 OCTOBER 1993-II

Nonlinear optical response of semiconductors in the independent-particle approximation

J. E. Sipe
Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7
and Ontario Laser and Lightwave Research Centre, University of Toronto, Toronto, Ontario, Canada M5S 1A7

Ed Ghahramani
Physica Computing, 2700 Thimens, Suite 416, St. Laurent, Quebec, Canada H4R 2C4

(Received 15 December 1992)

We present a formalism for the calculation of the optical response of semiconductors in the independent-particle approximation. The unphysical divergences at zero frequency that plagued earlier approaches are eliminated by a careful treatment of interband and intraband motion, yet the calculations can be made in a way very analogous to usual perturbation theory. The general formalism is illustrated by deriving an expression for the response coefficient for second-harmonic generation.

I. INTRODUCTION

The simplest treatment of the optical response of a crystal, at the level of a full band-structure calculation, proceeds via an independent-particle approximation. In the so-called "long-wavelength limit," where the variation of the macroscopic Maxwell field over distances on the order of the lattice spacing is neglected, the Hamiltonian is taken to be

$$\mathcal{H}=\sum_i\left[\frac{\left[\mathbf{p}_i-\frac{e}{c}\mathbf{A}(t)\right]^2}{2m}+V(\mathbf{x}_i)\right] , \tag{1.1}$$

where as usual $e=-|e|$ and m denote the electron charge and mass, the subscript i labels the electrons in the crystal, $\mathbf{x}_i$ and $\mathbf{p}_i$ are, respectively, the coordinates and momenta, and $V(\mathbf{x})$ is the effective periodic crystal potential. Equation (1.1) is written as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2 , \tag{1.2}$$

where

$$\mathcal{H}_0=\sum_i\mathcal{H}_{0i} , \tag{1.3}$$

with

$$\mathcal{H}_{0i}=\frac{\mathbf{p}_i^2}{2m}+V(\mathbf{x}_i) , \tag{1.4}$$

and

$$\begin{aligned}\mathcal{H}_1&=-\frac{e}{mc}\mathbf{A}(t)\cdot\sum_i\mathbf{p}_i ,\\ \mathcal{H}_2&=\frac{e^2}{2mc^2}N\,\mathbf{A}^2(t) ,\end{aligned} \tag{1.5}$$

where N is the total number of electrons in the normalization volume Ω of the crystal. The eigenstates of $\mathcal{H}_{0i}$ are the Bloch states $\psi_u(\mathbf{k};\mathbf{x}_i)$, where $\mathbf{k}$ labels the crystal momentum, and u the band index; in terms of the Bloch states the many-particle eigenstates of $\mathcal{H}_0$ can be constructed. In the long-wavelength limit the effect of $\mathcal{H}_2$ is only to introduce a time-dependent phase factor for all the eigenstates, so it may be neglected; perturbation theory may be employed to treat $\mathcal{H}_1$, and at the end of the calculation $\mathbf{E}=-c^{-1}\dot{\mathbf{A}}(t)$ is identified as the macroscopic Maxwell field. Although local-field effects are obviously neglected in such a treatment, results in good qualitative and often even good quantitative agreement with experiment over a wide frequency range can be obtained for a host of semiconductors.[1]

Yet even at the reasonably simplistic level of such a treatment, calculations of nonlinear response coefficients of semiconductors are plagued by unphysical divergences as $\omega\rightarrow 0$, where ω is the frequency of the incident light. A number of years ago, Aspnes[2] discussed such a divergence in the calculation of the nonlinear response coefficient for second-harmonic generation, $\overleftrightarrow{\chi}^{(2)}(-2\omega;\omega,\omega)$. He was able to show, for crystals with cubic symmetry, that the divergence is indeed only an apparent divergence: a factor multiplying the divergent term in fact equals zero. It is only recently that this has been verified for arbitrary crystal class by the derivation of a new sum rule.[3]

The source of the apparent divergences can be illustrated by the derivation of an expression for the *linear* susceptibility $\overleftrightarrow{\chi}(-\omega;\omega)$. Applying straightforward perturbation theory in $\mathcal{H}_1$,[4] we calculate the expectation value of the current density operator

$$\mathbf{J}=\frac{e}{\Omega m}\sum_i\left[\mathbf{p}_i-\frac{e}{c}\mathbf{A}(t)\right] , \tag{1.6}$$

in the presence of an electric field

$$\mathbf{E}(t)=\mathbf{E}(\omega)e^{-i\omega t}+\text{c.c.} , \tag{1.7}$$

where we assign a small positive imaginary part to ω to describe turning the field on from zero at $t=-\infty$. Writing the expectation value of the current density as $d\mathcal{P}/dt$, where $\mathcal{P}$ is an effective polarization, we find $\mathcal{P}(t)$ is of the form (1.7). Denoting Cartesian components by superscripts, we write

$$\mathcal{P}^a(\omega)=\chi^{ab}(-\omega;\omega)E^b(\omega)\ , \tag{1.8}$$

where repeated Cartesian components are summed over, and identify the linear susceptibility $\overleftrightarrow{\chi}(-\omega;\omega)$; we find

$$\chi^{ab}(-\omega;\omega)=\frac{e^2}{m^2\omega^2\hbar}\frac{1}{\Omega}\sum_{uv\mathbf{k}}\frac{f_{uv}(\mathbf{k})p^a_{uv}(\mathbf{k})p^b_{vu}(\mathbf{k})}{\omega_{vu}(\mathbf{k})-\omega} -\frac{e^2n}{m\omega^2}\delta^{ab}\ , \tag{1.9}$$

where δ^{ab} is the Kronecker delta. Here $n\equiv N/\Omega$ is the electron density; $\mathbf{p}_{uv}(\mathbf{k})$ is the matrix element $\langle u\mathbf{k}|\mathbf{p}|u\mathbf{k}\rangle$, where $\langle \mathbf{x}|u\mathbf{k}\rangle=\psi_u(\mathbf{k};\mathbf{x})$; $\omega_{vu}(\mathbf{k})\equiv\omega_v(\mathbf{k})-\omega_u(\mathbf{k})$, where $\hbar\omega_u(\mathbf{k})$ is the single-particle energy eigenvalue of $\psi_u(\mathbf{k};\mathbf{x})$; $f_{uv}(\mathbf{k})\equiv f_u(\mathbf{k})-f_v(\mathbf{k})$, where $f_u(\mathbf{k})$ is the Fermi factor of band u at crystal momentum $\mathbf{k}$. The term involving n in Eq. (1.9) results from the term involving $\mathbf{A}(t)$ in Eq. (1.6).

Certainly Eq. (1.9) appears to diverge as $\omega\to0$; in fact, with a bit of algebra Eq. (1.9) can be written so as to display the nature of the divergence:

$$\chi^{ab}(-\omega;\omega)=\omega^{-2}A^{ab}+\omega^{-1}B^{ab}+C^{ab}(\omega)\ , \tag{1.10}$$

where

$$C^{ab}(\omega)=\frac{1}{\Omega}\sum_{uv\mathbf{k}}\frac{e^2}{\hbar m^2}\frac{f_{uv}(\mathbf{k})p^a_{uv}(\mathbf{k})p^b_{vu}(\mathbf{k})}{\omega^2_{vu}(\mathbf{k})[\omega_{vu}(\mathbf{k})-\omega]} \tag{1.11}$$

is finite as $\omega\to0$, and the coefficients of the divergent terms are

$$A^{ab}=\frac{1}{\Omega}{\sum_{uv\mathbf{k}}}'\frac{e^2f_u(\mathbf{k})}{m^2\hbar}\frac{p^a_{uv}(\mathbf{k})p^b_{vu}(\mathbf{k})+p^a_{vu}(\mathbf{k})p^b_{uv}(\mathbf{k})}{\omega_{vu}(\mathbf{k})} -\frac{e^2n}{m}\delta^{ab} \tag{1.12}$$

$$B^{ab}=\frac{1}{\Omega}\sum_{uv\mathbf{k}}\frac{e^2}{m^2\hbar}\frac{f_{uv}(\mathbf{k})p^a_{uv}(\mathbf{k})p^b_{vu}(\mathbf{k})}{\omega^2_{vu}(\mathbf{k})}\ ,$$

where the prime on the sum in the first of Eq. (1.12) indicates that terms for which $f_u(\mathbf{k})=f_v(\mathbf{k})$ are to be excluded.

Of the two "dangerous" coefficients A^{ab} and B^{ab}, it is easier to dispose of B^{ab}. Using time-reversal symmetry $[\mathbf{p}_{uv}(-\mathbf{k})=-\mathbf{p}_{vu}(\mathbf{k}),\ \omega_u(\mathbf{k})=\omega_u(-\mathbf{k}),\ f_u(-\mathbf{k})=f_u(\mathbf{k})]$ a change of dummy indices shows immediately that $B^{ab}=0$. To treat A^{ab}, we substitute the expression for the inverse effective mass,[5]

$$\left[\frac{1}{m^*_u(\mathbf{k})}\right]^{ab}=\frac{\delta^{ab}}{m}-\sum_{v\neq u}\frac{p^a_{uv}(\mathbf{k})p^b_{vu}(\mathbf{k})+p^b_{uv}(\mathbf{k})p^a_{vu}(\mathbf{k})}{\hbar m^2\omega_{vu}(\mathbf{k})}\ , \tag{1.13}$$

where $[1/m^*_u(\mathbf{k})]^{ab}$ are the Cartesian components of the inverse effective-mass tensor of band u at crystal momentum $\mathbf{k}$, in the first of Eqs. (1.12) to write

$$A^{ab}=-\frac{e^2}{\Omega}\sum_{u\mathbf{k}}f_u(\mathbf{k})\left[\frac{1}{m^*_u(\mathbf{k})}\right]^{ab}\ . \tag{1.14}$$

Now for a clean, cold semiconductor we have $f_u(\mathbf{k})=f_u=0$ or 1, independent of $\mathbf{k}$. We refer to this situation, of primary interest in this paper, as the special case of "filled bands." Since

$$\left[\frac{1}{m^*_u(\mathbf{k})}\right]^{ab}=\frac{1}{\hbar}\frac{\partial^2\omega_u(\mathbf{k})}{\partial k^a\partial k^b}\ , \tag{1.15}$$

in the case of filled bands, the integral over the Brillouin zone that (1.14) becomes, in the limit of an infinite crystal, vanishes because $\omega_u(\mathbf{k})$ is periodic in the Brillouin zone. Thus $\chi^{ab}(-\omega;\omega)=C^{ab}(\omega)$, which, in fact, yields the usual result for the susceptibility of a clean, cold semiconductor[6] (see Sec. III).

For a metal, of course, A^{ab} in general does not vanish, and $\chi^{ab}(-\omega;\omega)$ *does* diverge as $\omega\to0$, simply because free electrons have a resonance at $\omega=0$ and no scattering is included in this simple perturbation treatment. But in a clean, cold semiconductor, where the bands are filled, there are no "free" electrons, no resonance at $\omega=0$, and $\overleftrightarrow{\chi}(-\omega;\omega)$ is finite there. More generally (recall $B^{ab}=0$), we have [cf. Eq. (1.10)]

$$\chi^{ab}(-\omega;\omega)=-\frac{e^2n}{\omega^2}\left[\frac{1}{N}\sum_{u\mathbf{k}}f_u(\mathbf{k})\left[\frac{1}{m^*_u(\mathbf{k})}\right]^{ab}\right] +\frac{1}{\Omega}\sum_{uv\mathbf{k}}\frac{e^2}{\hbar m^2}\frac{f_{uv}(\mathbf{k})p^a_{uv}(\mathbf{k})p^b_{vu}(\mathbf{k})}{\omega^2_{vu}(\mathbf{k})[\omega_{vu}(\mathbf{k})-\omega]}\ . \tag{1.16}$$

Physically, the first term on the right-hand side of Eq. (1.16) clearly describes the effects of *intraband* motion; the term in parentheses is an average inverse effective mass. The second term, as we argue in detail in Sec. II, describes *interband* motion. It is because matrix elements of $\mathcal{H}_1$ only involve states at the same crystal momentum that these two physically distinct contributions are "entangled" in the straightforward calculation leading to Eq. (1.9); sum rules such as Eq. (1.13) must be used to disentangle them. Indeed, it was with the use of a new sum rule that those intraband contributions to $\overleftrightarrow{\chi}^{(2)}(-2\omega;\omega,\omega)$ resonant at zero frequency were shown to vanish for a clean, cold semiconductor, rendering that quantity finite as $\omega\to0$.[3]

But with respect to the future calculation of other nonlinear optical response coefficients, such a situation is clearly undesirable. Simply at a practical level, for each new coefficient to be calculated it would appear necessary to find a new sum rule, or set of sum rules, to isolate the intraband contributions. This is both tedious and inelegant. A method of calculation which separates the intraband and interband motion from the start would obviously be preferable. This is what we develop in this paper.

Such an approach was introduced many years ago by Genkin and Mednis.[7] The differences between our development and theirs are matters more of implementation than spirit, but they are important. The resonant intraband contributions at $\omega=0$ were of central importance to Genkin and Mednis, who dealt with partially filled bands. One of our goals is to show how such terms vanish for filled bands, so we must be more careful to relate quantities which appear to our calculation to definitions of the Bloch functions which are periodic over the Brillouin zone. A second difference is that while Genkin and Mednis developed a single-particle formalism, we have developed ours in second quantized notation to allow for generalization beyond the independent-particle approximation. Even at the level of the independent-particle approximation, we note that the derivation of expressions for nonlinear optical coefficients is simplified by the use of second-quantized notation.[8]

Another difference, related to the periodicity in the Brillouin zone mentioned above, concerns the development of the perturbation series in the interband motion. Both of us, in a sense, describe the intraband motion of the electrons in their original bands to all orders in the zeroth order of our perturbation expansion. But while Genkin and Mednis then develop iteratively a unitary transformation to describe the interband motion, our treatment of that motion is done more analogously to usual perturbation theory. This is possible because of our choice of wave functions describing the interband motion. We take these to be instantaneous eigenstates of the time-dependent Hamiltonian, essentially wave functions which describe adiabatic intraband motion including the Berry's phase. A result of this is that the interaction then describing the interband motion has the form of a dipole moment interaction, with Blount's[9] representation of the position operator—*but without its diagonal piece*—playing the role of the position operator. This connection allows us to physically identify in a clearer way the aspects of interband and intraband motion that appear in all stages of the calculation, particularly in the expression for the induced current density [see the discussion after Eq. (2.72)].

Finally, we are more concerned than were Genkin and Mednis in reducing our expressions to a form suitable for numerical analysis. Nonetheless, our work is clearly in the general direction they established; as well, it relies heavily on the insights of Blount[9] and Lax.[10]

The goal of this paper is to establish the general formalism and give a few illustrative examples. We plan to present the application of the formalism we develop here to the numerical calculation of a number of nonlinear response coefficients in later communications. The basic formalism is presented in Sec. II: in Sec. II A we present the instantaneous single-particle eigenstates we employ in our calculation, and discuss their parametric time dependence. In Sec. II B we discuss the corresponding many-particle states, and in Sec. II C we discuss the expansion of single-particle operators in terms of both the instantaneous single-particle states and the usual basis states. Section II D details the unitary transformation between these two bases, and in Sec. II E we discuss the electron dynamics in the instantaneous eigenstate basis.

Section III is devoted to perturbation calculations. In Sec. III A, we introduce an interaction picture, the zeroth order of which describes intraband motion of the electrons in their original bands to all orders, and present the perturbation scheme to describe interband effects. Since each order of this perturbation scheme involves intraband motion to all orders, to calculate nonlinear susceptibilities it is convenient to expand in both interband and intraband effects. This is done in Sec. III B, and in Sec. III C the forms of the susceptibilities are presented to second order; the generalization to higher order is straightforward. As a particular example, we work out the expression for $\overleftrightarrow{\chi}^{(2)}(-2\omega;\omega,\omega)$, and discuss how it reduces to an expression obtained earlier for that coefficient. In Sec. III D, we discuss the different contributions to $\overleftrightarrow{\chi}^{(2)}(-2\omega;\omega,\omega)$ with the help of a full band-structure calculation. A discussion and summary of our results are presented in Sec. IV.

II. GENERAL FORMALISM

A. Single-particle Hamiltonians

We shall require certain properties of the eigenstates of single-particle Hamiltonians, which we state here for reference. For a Hamiltonian of the form

$$\mathcal{H}_0=\frac{\mathbf{p}^2}{2m}+V(\mathbf{x}) \ , \tag{2.1}$$

where $V(\mathbf{x})$ is periodic, $V(\mathbf{x})=V(\mathbf{x}+\mathbf{R})$ where $\mathbf{R}$ is any lattice vector, Bloch's theorem guarantees the eigenstates $|\alpha\rangle$ can be labeled by a band index n and wave vector $\mathbf{k}$, $\alpha=(n\mathbf{k})$, and is chosen to be of the form

$$\langle \mathbf{x}|\alpha\rangle \equiv \psi_n(\mathbf{k};\mathbf{x})=\Omega^{-1/2}u_n(\mathbf{k};\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}} \ , \tag{2.2}$$

where Ω is the normalization volume of the crystal, $u_n(\mathbf{k};\mathbf{x})=u_n(\mathbf{k};\mathbf{x}+\mathbf{R})$, and $\mathbf{k}$ can be restricted to the first Brillouin zone; we denote the eigenvalues by $\hbar\omega_n(\mathbf{k})$. Allowing for the possibility of points and lines of degeneracy in reciprocal space, but assuming that planes of degeneracy do not exist, it is possible to uniquely define the bands in such a way that $\omega_n(\mathbf{k})$and $\psi_n(\mathbf{k};\mathbf{x})$ are continuous in $\mathbf{k}$, and even differentiable in $\mathbf{k}$ at all general points; then[10]

$$\begin{aligned}&\psi_n(\mathbf{k}+\mathbf{G};\mathbf{x})=\psi_n(\mathbf{k};\mathbf{x})\\&\omega_n(\mathbf{k}+\mathbf{G})=\omega_n(\mathbf{k}) \ ,\end{aligned} \tag{2.3}$$

where $\mathbf{G}$ is any reciprocal-lattice vector, and

$$i\frac{\partial u_n(\mathbf{k};\mathbf{x})}{\partial \mathbf{k}}=\sum_m u_m(\mathbf{k};\mathbf{x})\xi_{mn}(\mathbf{k}) \tag{2.4}$$

for points $\mathbf{k}$ where the band n is nondegenerate. The $\xi_{mn}(\mathbf{k})$ satisfy the Hermiticity condition, $\xi^*_{mn}(\mathbf{k})=\xi_{nm}(\mathbf{k})$, and for $m\neq n$ are given by

$$\xi_{mn}(\mathbf{k})=\frac{\mathbf{v}_{mn}(\mathbf{k})}{i\omega_{mn}(\mathbf{k})} \ , \tag{2.5}$$

where

$$\mathbf{v}_{mn}(\mathbf{k})\equiv\int\psi_m^*(\mathbf{k};\mathbf{x})\frac{\hbar}{im}\nabla\psi_n(\mathbf{k};\mathbf{x})d\mathbf{x}\ ,$$
$$\omega_{mn}(\mathbf{k})\equiv\omega_m(\mathbf{k})-\omega_n(\mathbf{k})\ . \tag{2.6}$$

The phases of $\xi_{mn}(\mathbf{k})$ ($m\neq n$), and the functions $\xi_{nn}(\mathbf{k})$, are chosen so that the periodicity conditions (2.3) are satisfied.[11] We further require

$$\frac{\partial}{\partial\mathbf{k}}\cdot\xi_{nn}(\mathbf{k})=0\ , \tag{2.7}$$

which guarantees that the $\xi(\mathbf{k})$ are uniquely determined, except for transformations related to shifts in the origin of the unit cell in real space.

Next we consider the single-particle Hamiltonian

$$\mathcal{H}(t)=\frac{[\mathbf{p}+\hbar\mathbf{K}(t)]^2}{2m}+V(\mathbf{x})\ , \tag{2.8}$$

where in our applications we shall have

$$\mathbf{K}(t)=-\frac{e}{\hbar c}\mathbf{A}(t)\ , \tag{2.9}$$

where $\mathbf{A}(t)$ is the vector potential; in the long-wavelength limit this is taken to be uniform, and to describe the full electric field,

$$\mathbf{E}(t)=-\frac{1}{c}\dot{\mathbf{A}}(t)\ . \tag{2.10}$$

Our development will employ a set of instantaneous eigenfunctions $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ of $\mathcal{H}(t)$,

$$\mathcal{H}(t)\bar{\psi}_n(\mathbf{k};\mathbf{x})=\hbar\omega_n(\mathbf{k}+\mathbf{K})\bar{\psi}_n(\mathbf{k};\mathbf{x})\ , \tag{2.11}$$

where all quantities with overbars depend implicitly on time, and $\mathbf{K}=\mathbf{K}(t)$ is given by Eq. (2.9). Since

$$\mathbf{p}+\hbar\mathbf{K}=e^{-i\mathbf{K}\cdot\mathbf{x}}\mathbf{p}e^{i\mathbf{K}\cdot\mathbf{x}}\ , \tag{2.12}$$

it follows that

$$\mathcal{H}(t)=e^{-i\mathbf{K}\cdot\mathbf{x}}\mathcal{H}_0e^{i\mathbf{K}\cdot\mathbf{x}}\ , \tag{2.13}$$

and if we have a set of solutions $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ of Eq. (2.11) we may also write

$$\mathcal{H}_0[\bar{\psi}_n(\mathbf{k};\mathbf{x})e^{i\mathbf{K}\cdot\mathbf{x}}]=\hbar\omega_n(\mathbf{k}+\mathbf{K})[\bar{\psi}_n(\mathbf{k};\mathbf{x})e^{i\mathbf{K}\cdot\mathbf{x}}]\ . \tag{2.14}$$

That is, $\bar{\psi}_n(\mathbf{k};\mathbf{x})\exp(i\mathbf{K}\cdot\mathbf{x})$ is a state with crystal momentum $\mathbf{k}+\mathbf{K}$. To discuss the parametric dependence of the $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ on time we first demonstrate a lemma: If an orthonormal set $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ satisfies Eq. (2.11) at time t, then the same equations are satisfied at time $t+dt$ if

$$i\hbar\frac{d}{dt}\bar{\psi}_n(\mathbf{k};\mathbf{x})=\sum_q{}'\,\bar{\psi}_q(\mathbf{k};\mathbf{x})\boldsymbol{\mu}_{qn}(\mathbf{k};t)\cdot\mathbf{E}(t) \tag{2.15}$$

for each n, and if

$$\mathbf{E}(t)\cdot\mathbf{V}_{ln}(\mathbf{k};t)=0 \tag{2.16}$$

for each n and any state $\bar{\psi}_l(\mathbf{k};\mathbf{x})$ for which $\omega_l(\mathbf{k}+\mathbf{K})=\omega_n(\mathbf{k}+\mathbf{K})$. Here

$$\mathbf{V}_{ln}(\mathbf{k};t)\equiv\frac{1}{m}\int\bar{\psi}_l^*(\mathbf{k};\mathbf{x})\left[\frac{\hbar}{i}\nabla+\hbar\mathbf{K}\right]\bar{\psi}_n(\mathbf{k};\mathbf{x})d\mathbf{x}$$
$$=\frac{1}{m}\int\bar{\psi}_l^*(\mathbf{k};\mathbf{x})e^{-i\mathbf{K}\cdot\mathbf{x}}\left[\frac{\hbar}{i}\nabla\right][\bar{\psi}_n(\mathbf{k};\mathbf{x})e^{i\mathbf{K}\cdot\mathbf{x}}]d\mathbf{x}\ , \tag{2.17}$$

and the prime on the summation in Eq. (2.15) indicates the sum is over states $\bar{\psi}_q(\mathbf{k};\mathbf{x})$ for which $\omega_q(\mathbf{k}+\mathbf{K})\neq\omega_n(\mathbf{k}+\mathbf{K})$, and the expression for $\boldsymbol{\mu}_{qn}(\mathbf{k};t)$ will be given below. To confirm the lemma we must show that

$$\frac{d}{dt}[\mathcal{H}(t)\bar{\psi}_n(\mathbf{k};\mathbf{x})-\hbar\omega_n(\mathbf{k}+\mathbf{K})\bar{\psi}_n(\mathbf{k};\mathbf{x})]=0 \tag{2.18a}$$

or

$$\left[\mathcal{H}(t)-\hbar\omega_n(\mathbf{k}+\mathbf{K})\right]\frac{d\bar{\psi}_n(\mathbf{k};\mathbf{x})}{dt}$$
$$=e\mathbf{E}(t)\cdot\left[\frac{\partial\omega_n(\mathbf{k}+\mathbf{K})}{\partial\mathbf{k}}-\frac{1}{m}\left[\frac{\hbar}{i}\nabla+\hbar\mathbf{K}\right]\right]\bar{\psi}_n(\mathbf{k};\mathbf{x}) \tag{2.18b}$$

for all n, if Eqs. (2.15) and (2.16) are satisfied. Using Eq. (2.15) in Eq. (2.18b) we find

$$-i\sum_q{}'\,\omega_{qn}(\mathbf{k}+\mathbf{K})\boldsymbol{\mu}_{qn}(\mathbf{k};t)\cdot\mathbf{E}(t)[\bar{\psi}_q(\mathbf{k};\mathbf{x})e^{i\mathbf{K}\cdot\mathbf{x}}]$$
$$=e\mathbf{E}(t)\cdot\left[\frac{\partial\omega_n(\mathbf{k}+\mathbf{K})}{\partial\mathbf{k}}-\frac{\hbar}{mi}\nabla\right][\bar{\psi}_n(\mathbf{k};\mathbf{x})e^{i\mathbf{K}\cdot\mathbf{x}}]\ , \tag{2.19}$$

the validity of which we must confirm. The functions on both sides of Eq. (2.19) are spanned by functions of crystals momentum $\mathbf{k}+\mathbf{K}$. To show that Eq. (2.19) is satisfied, we must therefore establish that its projection onto $\bar{\psi}_l(\mathbf{k};\mathbf{x})\exp(i\mathbf{K}\cdot\mathbf{x})$ is satisfied for all l. For $l=n$ we find that the left-hand side of the projection is zero ($q\neq n$), and the right-hand side is also, since

$$\mathbf{V}_{nn}(\mathbf{k};t)=\frac{\partial\omega_n(\mathbf{k}+\mathbf{K})}{\partial\mathbf{k}}\ , \tag{2.20}$$

[cf. Eqs. (2.14) and (2.17)]. Projecting Eq. (2.19) now onto a $\bar{\psi}_l(\mathbf{k};\mathbf{x})\exp(i\mathbf{K}\cdot\mathbf{x})$ such that $\omega_l(\mathbf{k}+\mathbf{K})\neq\omega_n(\mathbf{k}+\mathbf{K})$, the resulting equation requires

$$\boldsymbol{\mu}_{ln}(\mathbf{k};t)=\frac{e\mathbf{V}_{ln}(\mathbf{k};t)}{i\omega_{ln}(\mathbf{k}+\mathbf{K})}\ ,$$
$$\omega_{ln}(\mathbf{k}+\mathbf{K})\neq0\ , \tag{2.21}$$

the expression we adopt for $\boldsymbol{\mu}_{ln}$. Finally, if there is an l such that $\omega_l(\mathbf{k}+\mathbf{K})=\omega_n(\mathbf{k}+\mathbf{K})$, the projection of Eq. (2.19) onto $\bar{\psi}_l(\mathbf{k};\mathbf{x})\exp(i\mathbf{K}\cdot\mathbf{x})$ leads to the condition (2.16), which is guaranteed by assumption. This completes the demonstration of the lemma, and identifies $\boldsymbol{\mu}_{ln}$.

We now explore the consequences of the evolution prescription (2.15). Consider first the simple choice of a $\mathbf{k}$ and n such that $\omega_n(\mathbf{k})$ is nondegenerate, and suppose

$\mathbf{A}(t)$ vanishes for $t < t_0$. Then, at least for times $t > t_0$ such that $\omega_n(\mathbf{k}+\mathbf{K})$ remains nondegenerate, it is easy to verify that Eqs. (2.15) and (2.21) are satisfied by

$$\bar{\psi}_n(\mathbf{k};\mathbf{x}) = \Omega^{-1/2}\bar{u}_n(\mathbf{k};\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}} , \tag{2.22}$$

where

$$\bar{u}_n(\mathbf{k};\mathbf{x}) = e^{-i\phi_n(\mathbf{k};t)}u_n(\mathbf{k}+\mathbf{K};\mathbf{x}) , \tag{2.23}$$

with

$$\phi_n(\mathbf{k};t) = -\int_{\mathbf{k}}^{\mathbf{k}+\mathbf{K}(t)} \xi_{nn}(\boldsymbol{\kappa}')\cdot d\boldsymbol{\kappa}' , \tag{2.24}$$

where the path of integration in the Brillouin zone depends on the evolution of $\mathbf{K}$, with $\boldsymbol{\kappa}' = \mathbf{k}+\mathbf{K}(t')$. Equation (2.21) then leads to

$$\boldsymbol{\mu}_{ln}(\mathbf{k};t) = e\xi_{ln}(\mathbf{k}+\mathbf{K})e^{i\phi_{ln}(\mathbf{k};t)} , \tag{2.25}$$

with

$$\phi_{ln}(\mathbf{k};t) = \phi_l(\mathbf{k};t) - \phi_n(\mathbf{k};t) . \tag{2.26}$$

More generally, if $\omega_n(\mathbf{k})$ is degenerate, Eqs. (2.22)–(2.26) satisfy Eqs. (2.15) and (2.21) *and* Eq. (2.16) as long as we choose the eigenfunctions at the point $\mathbf{k}$ of degeneracy such that Eq. (2.16) is satisfied as $\mathbf{A}(t)$ increases from zero. Thus, we see that the $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ satisfying Eq. (2.11) evolve such that their crystal momenta remain at $\mathbf{k}$ [see Eq. (2.22)], but the periodic part of the functions are associated with crystal momentum $\mathbf{k}+\mathbf{K}(t)$ [see Eq. (2.23)].

We now consider what happens to these $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ as $\mathbf{k}+\mathbf{K}(t)$ approaches a point of degeneracy, at say $\mathbf{k}+\mathbf{K}_d$, $\mathbf{K}_d \equiv \mathbf{K}(t_d)$. For example, we look at a simple scenario where two bands are degenerate at $\mathbf{k}+\mathbf{K}$, but are nondegenerate at $\mathbf{k}+\mathbf{K}(t)$ for ranges of times t before and after t_d. For such t less than t_d, then, putting Eqs. (2.22) in Eq. (2.15) yields

$$i\hbar\frac{d}{dt}\hat{u}_n(\mathbf{k}+\mathbf{K};\mathbf{x}) = \sum_q{}' \hat{u}_q(\mathbf{k}+\mathbf{K};\mathbf{x})\boldsymbol{\mu}_{qn}(\mathbf{k};t)\cdot\mathbf{E}(t) , \tag{2.27}$$

where

$$\hat{u}_n(\mathbf{k}+\mathbf{K};\mathbf{x}) \equiv u_n(\mathbf{k}+\mathbf{K};\mathbf{x})e^{-i\phi_n(\mathbf{k};t)} . \tag{2.28}$$

Note that Eqs. (2.27) are the "usual" $\mathbf{k}\cdot\mathbf{p}$" equations[12] that would be expected for the periodic part of the Bloch function as $\boldsymbol{\kappa} = \mathbf{k}+\mathbf{K}(t)$ evolves through points $\boldsymbol{\kappa}$ in the Brillouin zone where $\omega_n(\boldsymbol{\kappa})$ is nondegenerate. Now we digress for a moment and consider the periodic functions $\hat{u}_n(\mathbf{k}+\mathbf{K};\mathbf{x})$ at points where $\mathbf{K}$ is in the neighborhood of $\mathbf{K}_d$, $\hat{u}_n(\mathbf{k}+\mathbf{K}_d - e\hbar^{-1}\mathbf{E}(t_d)\Delta t + \ldots;\mathbf{x})$, where $t = t_d + \Delta t$. To write these in terms of the $\hat{u}_n(\mathbf{k}+\mathbf{K}_d;\mathbf{x})$ we must choose the correct set of basis functions at t_d, since the $\hat{u}_n(\mathbf{k}+\mathbf{K}_d;\mathbf{x})$ are degenerate.[13] Using Eqs. (2.17) (2.22), (2.23), and (2.28), we see that the correct set satisfies precisely Eq. (2.16) at $t = t_d$, and that with this choice the $\hat{u}_n(\mathbf{k}+\mathbf{K};\mathbf{x})$ will evolve precisely according to Eq. (2.27), for times both earlier and later than t_d. Thus, in particular, considering the earlier times, the $\hat{u}_n(\mathbf{k}+\mathbf{K};\mathbf{x})$ are generated from those at $\mathbf{K}_d$ must match up with the $\hat{u}_n(\mathbf{k}+\mathbf{K};\mathbf{x})$ that followed from t_0, except perhaps for phase factors, since at an intermediate time $t_0 < t < t_d$ we have assumed there is no degeneracy. This guarantees that, as the $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ evolve according to Eq. (2.15), Eq. (2.16) will be satisfied at points $\mathbf{k}+\mathbf{K}_d$ of degeneracy, $t = t_d$. Thus, by our lemma these $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ will continue to satisfy Eq. (2.11), even as $\mathbf{k}+\mathbf{K}$ moves through such points of degeneracy.

Examples such as the above indicate that the $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ evolving according to Eqs. (2.15) will always satisfy Eq. (2.11), as long as at points $\mathbf{k}$ of degeneracy the bands are initially labeled correctly as $\mathbf{A}(t)$ initially increases from zero. One proviso is necessary: since the wave functions $\psi_n(\mathbf{k};\mathbf{x})$ are not analytic functions of $\mathbf{k}$ at points of degeneracy,[13] a wave function $\bar{\psi}_n(\mathbf{k};\mathbf{x})$ can apparently change to a wave function labeled by a band index different from its original index as $\mathbf{k}+\mathbf{K}$ moves through a point of degeneracy. Thus, the $\omega_n(\mathbf{k}+\mathbf{K})$ appearing in Eq. (2.11) should really be written as $\omega_{\bar{n}}(\mathbf{k}+\mathbf{K})$, where $\bar{n}$ depends not only on n and $\mathbf{K}$ but on the entire history $\mathbf{K}(t)$. Likewise, ϕ_n and u_n in Eq. (2.23) must be redefined accordingly. Specifying this dependence in detail would involve a greater study of the topology of the band structure than we wish to embark upon here. Furthermore, it is not necessary for our purposes. *The crucial point is that the states* $|\alpha\rangle$, *where*

$$\langle \mathbf{x}|\alpha\rangle \equiv \bar{\psi}_n(\mathbf{k};\mathbf{x}) , \tag{2.29}$$

form a complete set of eigenstates of $\mathcal{H}(t)$ *for any t, and can thus be used as a basis at any time t.* Our primary interest in this paper is in the special case of filled bands. By this we mean any initial distribution of electrons which $f_n(\mathbf{k}) = f_n = 0$ or 1, independent of $\mathbf{k}$, where $f_n(\mathbf{k})$ is the Fermi factor for band n at wave vector $\mathbf{k}$. This is the appropriate limit to describe a clean, cold semiconductor, and in this limit $f_{\bar{n}} = f_n$ for the $\bar{n}$ discussed above. It will become clear that no confusion will result in our derived expressions of interest if we omit the bar in $\omega_{\bar{n}}(\mathbf{k}+\mathbf{K})$, $\phi_{\bar{n}}(\mathbf{k};t)$, and $u_{\bar{n}}(\mathbf{k}+\mathbf{K};\mathbf{x})$. With this simplification in notation we rewrite Eq. (2.14) as an unrestricted sum,

$$i\hbar\frac{d\bar{\psi}_n(\mathbf{k};\mathbf{x})}{dt} = \sum_q \bar{\psi}_q(\mathbf{k};\mathbf{x})\boldsymbol{\mu}_{qn}(\mathbf{k};t)\cdot\mathbf{E}(t) , \tag{2.30}$$

where we henceforth define [cf. Eq. (2.25)]

$$\begin{aligned} \boldsymbol{\mu}_{qn}(\mathbf{k};t) &= e\mathbf{r}_{qn}(\mathbf{k}+\mathbf{K})e^{i\phi_{qn}(\mathbf{k};t)} , \\ \mathbf{r}_{qn}(\boldsymbol{\kappa}) &\equiv \xi_{qn}(\boldsymbol{\kappa}) \quad \text{if } \omega_q(\boldsymbol{\kappa}) \neq \omega_n(\boldsymbol{\kappa}) \\ &\equiv 0 \quad \text{if } \omega_q(\boldsymbol{\kappa}) = \omega_n(\boldsymbol{\kappa}) \end{aligned} \tag{2.31}$$

and where

$$\bar{\psi}_n(\mathbf{k};\mathbf{x}) = \Omega^{-1/2}u_n(\mathbf{k}+\mathbf{K};\mathbf{x})e^{-i\phi_n(\mathbf{k};t)}e^{i\mathbf{k}\cdot\mathbf{x}} . \tag{2.32}$$

B. Many-particle Hamiltonians

We now consider the many-particle Hamiltonians, corresponding to $\mathcal{H}_0$ and $\mathcal{H}$, and their eigenstates. For the

Hamiltonian

$$H_0=\sum_i \left[\frac{\mathbf{p}_i^2}{2m}+V(\mathbf{x}_i)\right] \tag{2.33}$$

describing a system of fermions, we denote the many-particle eigenstates by $|S\rangle$, where S labels a sequence of occupation numbers $s_1,s_2,\dots$, the s_α either 0 or 1, and α specifies a state $(n\mathbf{k})$ described by the wave function (2.2). Then

$$H_0|S\rangle=E_S|S\rangle\ , \tag{2.34}$$

where

$$E_S=\sum_\alpha s_\alpha\hbar\omega_\alpha\ , \tag{2.35}$$

with $\omega_\alpha\equiv\omega_n(\mathbf{k})$. In the usual way[14] we introduce fermion raising and lowering operations, $a_\alpha^\dagger$ and a_α, satisfying the anticommutation relations

$$\begin{aligned}&\{a_\alpha,a_\beta\}=\{a_\alpha^\dagger,a_\beta^\dagger\}=0\ ,\\&\{a_\alpha,a_\beta^\dagger\}=\delta_{\alpha\beta}\ .\end{aligned} \tag{2.36}$$

Then,

$$H_0=\sum_\alpha \hbar\omega_\alpha a_\alpha^\dagger a_\alpha=\sum_{n\mathbf{k}}\hbar\omega_n(\mathbf{k})a_{n\mathbf{k}}^\dagger a_{n\mathbf{k}}\ . \tag{2.37}$$

Since we are neglecting spin-orbit coupling in Eq. (2.33), and Eq. (2.38) below, we may neglect spin variables except for accounting for the spin degeneracy at the end of our calculations.

Correspondingly, for the many-particle Hamiltonian

$$H(t)=\sum_i\left[\frac{[\mathbf{p}_i+\hbar\mathbf{K}(t)]^2}{2m}+V(\mathbf{x}_i)\right]\ , \tag{2.38}$$

we can introduce many-particle eigenstates $\overline{|S\rangle}$, where again S labels a set of occupation numbers $s_1,s_2,\dots$, with, however, the s_α now referring to states described by the wave functions (2.35). Here,

$$H(t)\overline{|S\rangle}=\bar{E}_S\overline{|S\rangle}\ , \tag{2.39}$$

where

$$\bar{E}_S=\sum_\alpha s_\alpha\hbar\bar{\omega}_\alpha\ , \tag{2.40}$$

and $\bar{\omega}_\alpha\equiv\omega_n[\mathbf{k}+\mathbf{K}(t)]$. Associated with these states we introduce fermion raising and lowering operators $b_\alpha^\dagger$ and b_α, satisfying

$$\begin{aligned}&\{b_\alpha,b_\beta\}=\{b_\alpha^\dagger,b_\beta^\dagger\}=0\ ,\\&\{b_\alpha,b_\beta^\dagger\}=\delta_{\alpha\beta}\ ,\end{aligned} \tag{2.41}$$

where, like the quantities with overbars, the b_α, $b_\alpha^\dagger$ are implicit functions of time through the dependence of the wave functions (2.32) on time. Corresponding to Eq. (2.37), we may write

$$H(t)=\sum_\alpha\hbar\bar{\omega}_\alpha b_\alpha^\dagger b_\alpha=\sum_{n\mathbf{k}}\hbar\omega_n[\mathbf{k}+\mathbf{K}(t)]b_{n\mathbf{k}}^\dagger b_{n\mathbf{k}}\ . \tag{2.42}$$

C. Operators

We shall be primarily interested in single-particle operators, e.g.,

$$\Theta=\sum_i f_\Theta(\mathbf{x}_i)\ . \tag{2.43}$$

Then, in the usual way,[14] we find

$$\Theta=\sum_{\alpha\beta}a_\alpha^\dagger a_\beta\Theta_{\alpha\beta}=\sum_{\alpha\beta}b_\alpha^\dagger b_\beta\bar{\Theta}_{\alpha\beta}\ , \tag{2.44}$$

with

$$\begin{aligned}&\Theta_{\alpha\beta}=\int\psi_{n_1}^*(\mathbf{k}_1;\mathbf{x})f_\Theta(\mathbf{x})\psi_{n_2}(\mathbf{k}_2;\mathbf{x})d\mathbf{x}\ ,\\&\bar{\Theta}_{\alpha\beta}=\int\bar{\psi}_{n_1}^*(\mathbf{k}_1;\mathbf{x})f_\Theta(\mathbf{x})\bar{\psi}_{n_2}(\mathbf{k}_2;\mathbf{x})d\mathbf{x}\ ,\end{aligned} \tag{2.45}$$

where $\alpha=(n_1\mathbf{k}_1)$, $\beta=(n_2\mathbf{k}_2)$. If $f_\Theta(\mathbf{x})$ has only nonzero matrix elements between states of the same $\mathbf{k}$, Eq. (2.44) simplifies to

$$\begin{aligned}\Theta&=\sum_{nm\mathbf{k}}a_{n\mathbf{k}}^\dagger a_{m\mathbf{k}}\Theta_{nm}(\mathbf{k})\ ,\\&=\sum_{nm\mathbf{k}}b_{n\mathbf{k}}^\dagger b_{m\mathbf{k}}\bar{\Theta}_{nm}(\mathbf{k})\ ,\end{aligned} \tag{2.46}$$

where

$$\begin{aligned}&\Theta_{nm}(\mathbf{k})=\int\psi_n^*(\mathbf{k};\mathbf{x})f_\Theta(\mathbf{x})\psi_m(\mathbf{k};\mathbf{x})d\mathbf{x}\ ,\\&\bar{\Theta}_{nm}(\mathbf{k})=\int\bar{\psi}_n^*(\mathbf{k};\mathbf{x})f_\Theta(\mathbf{x})\bar{\psi}_m(\mathbf{k};\mathbf{x})d\mathbf{x}\ .\end{aligned} \tag{2.47}$$

As an example, we consider the current density operator $\mathbf{J}$,

$$\mathbf{J}=\frac{e}{\Omega}\sum_i\frac{1}{m}\left[\mathbf{p}_i-\frac{e}{c}\mathbf{A}(t)\right]\ . \tag{2.48}$$

Using the first of Eq. (2.6) and the orthogonality of the $\psi_n(\mathbf{k};\mathbf{x})$, we have

$$\mathbf{J}=\frac{e}{\Omega}\sum_{nm\mathbf{k}}a_{n\mathbf{k}}^\dagger a_{m\mathbf{k}}\left[\mathbf{v}_{nm}(\mathbf{k})-\frac{e}{mc}\delta_{nm}\,\mathbf{A}(t)\right]\ . \tag{2.49}$$

Alternatively, we evaluate

$$\frac{1}{m}\int\bar{\psi}_n^*(\mathbf{k};\mathbf{x})\left[\frac{\hbar}{i}\nabla-\frac{e}{c}\mathbf{A}(t)\right]\bar{\psi}_m(\mathbf{k};\mathbf{x})d\mathbf{x} =e^{i\phi_{nm}(\mathbf{k};t)}\mathbf{v}_{nm}(\mathbf{k}+\mathbf{K})\ , \tag{2.50}$$

where we have used the definitions (2.6) and (2.32), and Eq. (2.17); so we can write the same operator appearing in Eq. (2.49) as

$$\mathbf{J}=\frac{e}{\Omega}\sum_{nm\mathbf{k}}b_{n\mathbf{k}}^\dagger b_{m\mathbf{k}}e^{i\phi_{nm}(\mathbf{k};t)}\mathbf{v}_{nm}(\mathbf{k}+\mathbf{K})\ . \tag{2.51}$$

Defining

$$\mathbf{j}_{nm}(\mathbf{k}+\mathbf{K})\equiv\frac{e}{\Omega}\mathbf{v}_{nm}(\mathbf{k}+\mathbf{K})\ , \tag{2.52}$$

we can write Eq. (2.51) as

$$\mathbf{J}=\sum_{nm\mathbf{k}}b_{n\mathbf{k}}^\dagger b_{m\mathbf{k}}\mathbf{j}_{nm}(\mathbf{k}+\mathbf{K})e^{i\phi_{nm}(\mathbf{k};t)}\ . \tag{2.53}$$

D. The unitary transformation

We now introduce a unitary transformation

$$U=\sum_S |S\rangle\overline{\langle S|}\ ,$$
$$U^\dagger=\sum_S \overline{|S\rangle}\langle S|\ , \tag{2.54}$$

where the sum is over all sets of occupation numbers S $(s_1,s_2,\ldots)$; the states $|S\rangle$ and $\overline{|S\rangle}$ involve the same occupation numbers, although in $|S\rangle$ they refer to the states described by the wave functions (2.2), while in $\overline{|S\rangle}$ they refer to those described by the wave functions (2.32). We use U to introduce transformed operators

$$\Theta'=U\Theta U^\dagger\ . \tag{2.55}$$

In particular,

$$\begin{aligned} b'_\alpha &= Ub_\alpha U^\dagger\ ,\\ &=\sum_{ST}|T\rangle\overline{\langle T|}b_\alpha\overline{|S\rangle}\langle S|\ , \end{aligned} \tag{2.56}$$

so

$$\langle T|b'_\alpha|S\rangle=\overline{\langle T|}b_\alpha\overline{|S\rangle}\ , \tag{2.57}$$

and thus we identify $b'_\alpha=a_\alpha$. A similar result holds for $b_\alpha^\dagger$, so we have

$$\begin{aligned} a_\alpha&=Ub_\alpha U^\dagger\ ,\\ a_\alpha^\dagger&=Ub_\alpha^\dagger U^\dagger\ . \end{aligned} \tag{2.58}$$

This implies that for operators of the form, e.g., of Eq. (2.46) we have

$$\Theta'=\sum_{nm\mathbf{k}} a_{n\mathbf{k}}^\dagger a_{m\mathbf{k}}\overline{\Theta}_{nm}(\mathbf{k})\ . \tag{2.59}$$

So, in particular, we have

$$\begin{aligned} H'&=\sum_{n\mathbf{k}} a_{n\mathbf{k}}^\dagger a_{n\mathbf{k}}\hbar\omega_n(\mathbf{k}+\mathbf{K})\ ,\\ \mathbf{J}'&=\sum_{nm\mathbf{k}} a_{n\mathbf{k}}^\dagger a_{m\mathbf{k}}\mathbf{j}_{nm}(\mathbf{k}+\mathbf{K})e^{i\phi_{nm}(\mathbf{k};t)}\ , \end{aligned} \tag{2.60}$$

where we have used Eqs. (2.42) and (2.53). Now the operators U and $U^\dagger$ depend on time because of the time dependence of $\overline{\langle S|}$ and $\overline{|S\rangle}$. Look first at

$$\frac{d}{dt}U^\dagger=\sum_S\frac{d\overline{|S\rangle}}{dt}\langle S|\ . \tag{2.61}$$

To evaluate the time derivative in Eq. (2.61), we note that the configuration-space representation of $|\bar{S}\rangle$ is[15]

$$\langle\mathbf{x}_1,\mathbf{x}_2\cdots\mathbf{x}_N\overline{|S\rangle}=\frac{1}{\sqrt{N!}}\sum_P\delta_P\mathcal{P}[\bar{\psi}_{\lambda_1}(\mathbf{x}_1)\bar{\psi}_{\lambda_2}(\mathbf{x}_2)\times\cdots\bar{\psi}_{\lambda_n}(\mathbf{x}_n)]\ , \tag{2.62}$$

where

$$N=\sum_\alpha s_\alpha\ , \tag{2.63}$$

the P's label the $N!$ permutations of N objects, the δ_P are the parities of the permutations, and the $\mathcal{P}$ are the associated operators; $\bar{\psi}_{\lambda_1}(\mathbf{x}_1)$, e.g., is short for $\bar{\psi}_{n_1}(\mathbf{k}_1;\mathbf{x}_1)$.

Using Eqs. (2.30) and (2.32) one can form the time derivatives of the $\bar{\psi}_{\lambda_i}(\mathbf{x}_i)$ and, using the properties of the raising and lowering operators,[14] identify

$$\frac{d}{dt}\overline{|S\rangle}=\frac{-i}{\hbar}\sum_{nm\mathbf{k}}b_{n\mathbf{k}}^\dagger b_{m\mathbf{k}}\boldsymbol{\mu}_{nm}(\mathbf{k};t)\cdot\mathbf{E}(t)\overline{|S\rangle}\ . \tag{2.64}$$

So, introducing the Hermitian operator

$$\begin{aligned} \mathbf{P}&\equiv\frac{1}{\Omega}\sum_{nm\mathbf{k}}b_{nk}^\dagger b_{m\mathbf{k}}\boldsymbol{\mu}_{nm}(\mathbf{k};t)\\ &=\frac{e}{\Omega}\sum_{nm\mathbf{k}}b_{n\mathbf{k}}^\dagger b_{m\mathbf{k}}\mathbf{r}_{nm}(\mathbf{k}+\mathbf{K})e^{i\phi_{nm}(\mathbf{k};t)}\ , \end{aligned} \tag{2.65}$$

we find, using Eqs. (2.61) and (2.64), and their adjoints,

$$\begin{aligned} \frac{d}{dt}U^\dagger&=-\frac{i\Omega}{\hbar}\mathbf{E}(t)\cdot\mathbf{P}U^\dagger\ ,\\ \frac{d}{dt}u&=\frac{i\Omega}{\hbar}U\mathbf{P}\cdot\mathbf{E}(t)\ . \end{aligned} \tag{2.66}$$

E. Dynamics

Describing the many-particle system by a density operator ρ, the dynamics are specified by the equation

$$i\hbar\dot{\rho}=[H,\rho]\ . \tag{2.67}$$

If we work instead with the transformed operator $\rho'\equiv U\rho U^\dagger$, using the cyclic property of the trace, and the fact that U is unitary, we find that the expectation value of any operator Θ is given as well by

$$\langle\Theta\rangle\equiv\mathrm{Tr}(\rho\Theta)=\mathrm{Tr}(\rho'\Theta')\ . \tag{2.68}$$

From Eq. (2.67), and the time dependence of the operators U and $U^\dagger$ [Eq. (2.66)], we readily find that the evolution of ρ' is specified by the equation

$$i\hbar\dot{\rho}'=[H'+H'_d,\rho']\ , \tag{2.69}$$

where H' is given by Eq. (2.60), and

$$\begin{aligned} H'_d&=-\Omega\mathbf{P}'\cdot\mathbf{E}(t)\\ &=-\sum_{nm\mathbf{k}}a_{n\mathbf{k}}^\dagger a_{m\mathbf{k}}\boldsymbol{\mu}_{nm}(\mathbf{k};t)\cdot\mathbf{E}(t)\ . \end{aligned} \tag{2.70}$$

In deriving Eq. (2.69) we have essentially effected a separation between the intraband and interband dynamics. The Hamiltonian H' describes the electrons as if they were unperturbed by the electric field, except that their energies change as they would if the electrons were moving within their original bands as driven by the field.[16] All interband dynamics are driven by H'_d, which takes a form familiar from atomic physics, with $\Omega\mathbf{P}'$ playing the role of a dipole moment operator.

That dipole moment operator formally appears to be associated with a number of "atoms," each labeled by $\mathbf{k}$, with dipole matrix elements $\boldsymbol{\mu}_{nm}$ connecting different "atomic states"—really the different bands. The only difference from the usual atomic dipole interaction Hamiltonian is that here the dipole matrix elements associated with the atoms—really of course the electrons—vary because of the intraband motion. The formal structure of the total Hamiltonian $H'+H_d'$ encourages one to think of the electrons as entities with translational (intraband) degrees of freedom, with dynamics described by H', and internal (interband) degrees of freedom coupled through H_d' to the electric field via a dipole moment, which is however adiabatically modified by the translational motion.

This rough physical picture cannot be pushed too far, of course; the system really consists simply of electrons in a periodic potential driven by an electric field: there are no real "internal degrees of freedom" (besides of course spin) of the electrons. This is reflected in the formalism by the fact that the different Cartesian components of the effective dipole moment operators are not kinematically independent. Putting $\boldsymbol{\mu}_{nm} \equiv e\mathbf{q}_{nm}$ [cf. Eq. (2.31)], it is easy to derive from Eqs. (2.4), (2.24), and (2.26) that[17]

$$\sum_{p} (q^a_{np}q^b_{pm} - q^b_{np}q^a_{pm}) = i \left[\frac{\partial q^a_{nm}}{\partial K^b} - \frac{\partial q^b_{nm}}{\partial K^a} \right] , \tag{2.71}$$

where the superscripts a and b denote Cartesian components; if $\mathbf{q}$ described a true displacement (position) operator, of course, we would have $|q^a,q^b]=0$ and the left-hand side of Eq. (2.71) would vanish.

Nonetheless, the conceptual separation of intraband and interband motion is useful in that it provides a physical interpretation of various contributions to terms of interest. For example, as we show in detail in Appendix A, we have

$$\langle \mathbf{J} \rangle = \langle \mathbf{J}_A \rangle + \frac{d}{dt}\langle \mathbf{P} \rangle , \tag{2.72}$$

where $\mathbf{J}$ is the current density operator (2.48), (2.49), (2.51), and (2.53), and $\mathbf{P}$ is the operator (2.65), which in line with the discussion above we refer to as the polarization operator. Here,

$$\mathbf{J}_A = \frac{e}{\Omega} \sum_{nm\mathbf{k}} b^\dagger_{n\mathbf{k}} b_{m\mathbf{k}} \hbar^{-1} \frac{\partial \mathcal{E}_{nm}(\mathbf{k};t)}{\partial \mathbf{K}} \tag{2.73}$$

with

$$\mathcal{E}_{nm}(\mathbf{k};t) \equiv \delta_{nm}\hbar\omega_n(\mathbf{k}+\mathbf{K}) - \boldsymbol{\mu}_{nm}(\mathbf{k};t)\cdot\mathbf{E}(t) , \tag{2.74}$$

can be physically identified as an intraband current density operator. The physical significance of the terms contributing to $\mathbf{J}_A$ can be seen by noting that

$$\begin{aligned} \mathcal{E} &\equiv \sum_{nm\mathbf{k}} b^\dagger_{n\mathbf{k}} b_{m\mathbf{k}} \mathcal{E}_{nm}(\mathbf{k};t) \\ &= \left[\sum_{n\mathbf{k}} b^\dagger_{n\mathbf{k}} b_{n\mathbf{k}} \hbar\omega_n(\mathbf{k}+\mathbf{K}) \right] - \Omega \mathbf{P}\cdot\mathbf{E}(t) \end{aligned} \tag{2.75}$$

can be thought of as the sum of the kinetic and potential energy of the electrons as they move through their bands, plus a polarization energy associated with the interband motion, itself modulated by the dependence of the dipole-moment-like operators on the intraband motion of the electrons. The derivative appearing in Eq. (2.73) is thus simply an effective group velocity (matrix) associated with the intraband electron motion, but as modulated by the polarization energy associated with the interband motion. The form (2.72) for the expectation value of the current density operator $\mathbf{J}$ is particularly useful for calculating that quantity, to which we turn in the following section.

III. PERTURBATION CALCULATION

A. Interaction picture

Returning to the Eqs. (2.69) and (2.70) governing the dynamics of the system, we can now construct a formal interaction picture which implicitly takes into account the intraband motion described by H', Eq. (2.60). To do this, note that although H' is time dependent the $a^\dagger_{n\mathbf{k}}$are not, so even unequal time commutators of H' vanish,

$$[H'(t_1),H'(t_2)]=0 . \tag{3.1}$$

Defining the unitary operator

$$W(t) \equiv \exp\left[\frac{i}{\hbar} \int_{-\infty}^{t} H'(t')dt' \right] , \tag{3.2}$$

we then have

$$\begin{aligned} \frac{dW(t)}{dt} &= \frac{i}{\hbar} W(t)H'(t) \\ &= \frac{i}{\hbar} H'(t)W(t) , \end{aligned} \tag{3.3}$$

and the interaction picture density operator,

$$\tilde{\rho} = W\rho' W^\dagger \tag{3.4}$$

is readily found to satisfy the dynamical equation

$$i\hbar\dot{\tilde{\rho}} = [\tilde{H}_d,\tilde{\rho}] , \tag{3.5}$$

where

$$\begin{aligned} \tilde{H}_d &\equiv WH_d'W^\dagger \\ &= -\sum_{nm\mathbf{k}} \tilde{a}^\dagger_{n\mathbf{k}}(t)\tilde{a}_{m\mathbf{k}}(t)\boldsymbol{\mu}_{nm}(\mathbf{k};t)\cdot\mathbf{E}(t) , \end{aligned} \tag{3.6}$$

with, for example,

$$\tilde{a}_{m\mathbf{k}}(t) \equiv Wa_{m\mathbf{k}}W^\dagger . \tag{3.7}$$

Since $a_{m\mathbf{k}}$ is time independent, it is easy to confirm that $\tilde{a}_{m\mathbf{k}}(t)$ satisfies the differential equation

$$i\hbar\frac{d\tilde{a}_{m\mathbf{k}}(t)}{dt} = [\tilde{a}_{m\mathbf{k}}(t),\tilde{H}(t)] , \tag{3.8}$$

where

$$\begin{aligned} \tilde{H}(t) &= WH'W^\dagger \\ &= \sum_{n\mathbf{k}} \tilde{a}^\dagger_{n\mathbf{k}}(t)\tilde{a}_{n\mathbf{k}}(t)\hbar\omega_n[\mathbf{k}+\mathbf{K}(t)] . \end{aligned} \tag{3.9}$$

Working out the commutator in Eq. (3.8) and formally integrating, we then have

$$\tilde{a}_{m\mathbf{k}}(t) = a_{m\mathbf{k}}e^{-i\nu_m(\mathbf{k};t)} , \tag{3.10}$$

where

$$\nu_m(\mathbf{k};t)=\int_{-\infty}^{t}\omega_m[\mathbf{k}+\mathbf{K}(t')]dt' , \tag{3.11}$$

For any specified vector potential $\mathbf{A}(t)$, $\mathbf{K}(t)=-(e/\hbar)\mathbf{A}(t)$, the interaction picture takes into account in the operators $\tilde{a}_{m\mathbf{k}}(t)$ the variation of the energies of the electrons as they move within their original bands under the action of the applied field. The only dynamics remaining in Eq. (3.5) is then that of the interband motion. We can describe this in perturbation theory by iterating Eq. (3.5) in the usual way,[18]

$$\begin{aligned}\tilde{\rho}(t)=\rho_0&+\frac{1}{i\hbar}\int_{-\infty}^{t}[\tilde{H}_d(t'),\rho_0]dt'\\&+\frac{1}{(i\hbar)^2}\int_{-\infty}^{t}\int_{-\infty}^{t'}[\tilde{H}_d(t'),[\tilde{H}_d(t''),\rho_0]]\\&\times dt''dt'+\cdots\end{aligned} \tag{3.12}$$

where $\rho_0=\tilde{\rho}(t=-\infty)=\rho'(t=-\infty)$. For any operator Θ we then have [cf. Eq. (2.68)]

$$\begin{aligned}\langle\Theta\rangle&=\mathrm{Tr}(\rho'\Theta')=\mathrm{Tr}(\tilde{\rho}\tilde{\Theta})\\&=\mathrm{Tr}(\rho_0\hat{\Theta}) ,\end{aligned} \tag{3.13}$$

where

$$\begin{aligned}\hat{\Theta}(t)=\tilde{\Theta}(t)&+\frac{1}{i\hbar}\int_{-\infty}^{t}[\tilde{\Theta}(t),\tilde{H}_d(t)]dt'\\&+\frac{1}{(i\hbar)^2}\int_{-\infty}^{t}\int_{-\infty}^{t'}[[\tilde{\Theta}(t),\tilde{H}_d(t')],\tilde{H}_d(t'')]\\&\times dt''dt'+\cdots\\&\equiv\hat{\Theta}_0(t)+\hat{\Theta}_1(t)+\hat{\Theta}_2(t)+\cdots .\end{aligned} \tag{3.14}$$

In arriving at the last form of Eq. (3.13) we have used the cyclic property of the trace to "unravel" the commutators.[19] For operators of the form (2.46) and (2.49) we have

$$\begin{aligned}\tilde{\Theta}&=\sum_{nm\mathbf{k}}\tilde{a}^{\dagger}_{n\mathbf{k}}\tilde{a}_{m\tilde{\mathbf{k}}}\Theta_{nm}(\mathbf{k}+\mathbf{K})e^{i\phi_{nm}(\mathbf{k};t)} ,\\&\equiv\sum_{nm\mathbf{k}}\tilde{a}^{\dagger}_{n\tilde{\mathbf{k}}}\tilde{a}_{m\mathbf{k}}\theta_{nm}(\mathbf{k};t) .\end{aligned} \tag{3.15}$$

Using Eq. (3.10) and Eq. (3.15) in Eq. (3.14), to determine $\langle\Theta\rangle$ we then require

$$\begin{aligned}&\mathrm{Tr}(\rho_0 a^{\dagger}_{n\mathbf{k}}a_{m\mathbf{k}})=\delta_{nm}f_n(\mathbf{k}) ,\\&\mathrm{Tr}(\rho_0[a^{\dagger}_{n\mathbf{k}}a_{m\mathbf{k}},a^{\dagger}_{p\mathbf{k}'}a_{q\mathbf{k}'}])=\delta_{\mathbf{k}\mathbf{k}'}f_{nm}(\mathbf{k})\delta_{nq}\delta_{mp} ,\\&\ldots ,\end{aligned} \tag{3.16}$$

where $f_n(\mathbf{k})$ is the Fermi factor for band n at wave vector $\mathbf{k}$, $f_{nm}(\mathbf{k})=f_n(\mathbf{k})-f_m(\mathbf{k})$, etc. The second of Eq. (3.16), and the more complicated expressions which appear in the higher order contributions to Eq. (3.13), follow from the anticommutation relations (2.36) and the first of Eq. (3.16). From the sum (3.14) we find we can then write

$$\langle\Theta\rangle=\langle\Theta\rangle_{(0)}+\langle\Theta\rangle_{(1)}+\langle\Theta\rangle_{(2)}+\cdots , \tag{3.17}$$

where

$$\begin{aligned}\langle\Theta\rangle_{(0)}&=\sum_{n\mathbf{k}}f_n(\mathbf{k})\Theta_{nn}(\mathbf{k}+\mathbf{K}) ,\\\langle\Theta\rangle_{(1)}&=-\frac{1}{i\hbar}\sum_{nm\mathbf{k}}f_{nm}(\mathbf{k})\theta_{nm}(\mathbf{k};t)e^{i\nu_{nm}(\mathbf{k};t)}\int_{-\infty}^{t}e^{i\nu_{mn}(\mathbf{k};t')}\boldsymbol{\mu}_{mn}(\mathbf{k};t')\cdot\mathbf{E}(t')dt' ,\\\langle\Theta\rangle_{(2)}&=-\frac{1}{\hbar^2}\sum_{\substack{nmq\\\mathbf{k}}}\theta_{nm}(\mathbf{k};t)f_{nq}(\mathbf{k})e^{i\nu_{nm}(\mathbf{k};t)}\int_{-\infty}^{t}e^{i\nu_{mq}(\mathbf{k},t')}\boldsymbol{\mu}_{mq}(\mathbf{k};t')\cdot\mathbf{E}(t')\\&\qquad\times\int_{-\infty}^{t'}e^{i\nu_{qn}(\mathbf{k};t'')}\boldsymbol{\mu}_{qn}(\mathbf{k};t'')\cdot\mathbf{E}(t'')dt''dt'\\&\quad-\frac{1}{\hbar^2}\sum_{\substack{nmq\\\mathbf{k}}}\theta_{nm}(\mathbf{k};t)f_{mp}(\mathbf{k})e^{i\nu_{nm}(\mathbf{k};t)}\int_{-\infty}^{t}e^{i\nu_{pn}(\mathbf{k};t')}\boldsymbol{\mu}_{pn}(\mathbf{k};t')\cdot\mathbf{E}(t')\\&\qquad\times\int_{-\infty}^{t'}e^{i\nu_{mp}(\mathbf{k};t'')}\boldsymbol{\mu}_{mp}(\mathbf{k};t'')\cdot\mathbf{E}(t'')dt''dt' ,\\&\vdots\end{aligned} \tag{3.18}$$

with

$$\nu_{nm}(\mathbf{k};t)\equiv\nu_n(\mathbf{k};t)-\nu_m(\mathbf{k};t) . \tag{3.19}$$

The expansion (3.18) is an iteration in the interband motion, but in each step the intraband motion of the electrons is included to all orders. We may see this in detail by looking at the zeroth order term in the expansion. Since

$$\mathbf{P}'=\frac{1}{\Omega}\sum_{nm\mathbf{k}}a^{\dagger}_{n\mathbf{k}}a_{m\mathbf{k}}\boldsymbol{\mu}_{nm}(\mathbf{k};t) \tag{3.20}$$

[cf. Eqs. (2.55) and (2.65)] and $\mu_{nm}=0$ if $n=m$ [Eq. (2.31)], we have $\langle \mathbf{P}\rangle_{(0)}=0$. On the other hand, the current density does not in general vanish to zeroth order. Using the second of Eq. (2.60) and Eq. (2.52), we have

$$\begin{aligned}\langle \mathbf{J}\rangle_{(0)}&=\sum_{n\mathbf{k}} f_n(\mathbf{k})\mathbf{j}_{nn}(\mathbf{k}+\mathbf{K})\\&=\frac{e}{\Omega}\sum_{n\mathbf{k}} f_n(\mathbf{k})\mathbf{v}_{nn}[\mathbf{k}+\mathbf{K}(t)]\ ,\end{aligned}\tag{3.21}$$

where in the second of Eq. (3.21) we have explicitly indicated the time dependence of $\mathbf{K}(t)$ [Eq. (2.9)]. Even for an $\mathbf{E}(t)$ [Eq. (2.10)] consisting of a single frequency, Eq. (3.21) will in general contain all higher harmonics as the electrons fully undergo their intraband motion. This can be seen by expanding the $\mathbf{v}_{nn}$ in Eq. (3.21) about $\mathbf{K}=0$. Denoting Cartesian components by superscripts and summing over them when repeated, we have

$$\begin{aligned}\langle J^a\rangle_{(0)}=&\frac{e}{\Omega}\sum_{n\mathbf{k}} f_n(\mathbf{k})v^a_{nn}(\mathbf{k})+\frac{e}{\Omega}\sum_{n\mathbf{k}} f_n(\mathbf{k})\frac{\partial v^a_{nn}(\mathbf{k})}{\partial k^b}K^b(t)\\&+\frac{e}{2\Omega}\sum_{n\mathbf{k}} f_n(\mathbf{k})\frac{\partial^2 v^a_{nn}(\mathbf{k})}{\partial k^b\partial k^c}K^b(t)K^c(t)+\cdots\ .\end{aligned}\tag{3.22}$$

Taking the electric field to be in general sum of frequency components,

$$\mathbf{E}(t)=\sum_{\beta}\mathbf{E}(\omega_\beta)e^{-i\omega_\beta t}\ ,\tag{3.23}$$

where each frequency ω_β contains a small positive imaginary part so that $\mathbf{E}(t)$ vanishes at $t\rightarrow-\infty$, using Eq. (2.10) we find

$$\begin{aligned}\langle J^a\rangle_{(0)}=&\frac{e}{\Omega}\sum_{n\mathbf{k}} f_n(\mathbf{k})v^a_{nn}(\mathbf{k})\\&+\frac{ie^2}{\Omega}\sum_{\substack{n\mathbf{k}\\ \beta}}\frac{f_n(\mathbf{k})}{\hbar\omega_\beta}\frac{\partial v^a_{nn}(\mathbf{k})}{\partial k^b}E^b(\omega_\beta)e^{-i\omega_\beta t}\\&-\frac{e^3}{2\Omega}\sum_{\substack{n\mathbf{k}\\ \beta\gamma}}\frac{f_n(\mathbf{k})}{\hbar^2\omega_\beta\omega_\gamma}\frac{\partial^2 v^a_{nn}(\mathbf{k})}{\partial k^b\partial k^c}E^b(\omega_\beta)E^c(\omega_\gamma)\\&\times e^{-i(\omega_\beta+\omega_\gamma)t}+\cdots\ .\end{aligned}\tag{3.24}$$

The first term in Eq. (3.24) quite generally vanishes, since for most initial conditions of interest $f_n(\mathbf{k})=f_n(-\mathbf{k})$, and $\mathbf{v}_{nn}(-\mathbf{k})=\mathbf{v}_{nn}(\mathbf{k})$. The second term in Eq. (3.24) in general does not vanish; since $\hbar^{-1}\partial v^a_{nn}(\mathbf{k})/\partial k^b$ is the inverse effective-mass tensor for an electron at crystal momentum $\hbar\mathbf{k}$ in band n, we identify this term as the current density that would be expected from a collection of free electrons, but with the inverse free-electron mass replaced by the appropriate inverse effective-mass tensor for each electron. This term diverges as $\omega_\beta\rightarrow0$, simply because the intraband motion of the electrons is resonant at zero frequency in the absence of any scattering terms. The third and higher terms in Eq. (3.24), which are nonlinear contributions due to the variation in the effective masses of the electrons as they undergo intraband motion, also diverge at zero frequency.

Our special case of interest is the situation where $f_n(\mathbf{k})=f_n=0$ or 1; see the discussion after Eq. (2.29). In that limit the second and third terms in Eq. (3.24) vanish, since $\mathbf{v}_{nn}(\mathbf{k})$ is a periodic function in reciprocal space [see Eq. (2.3)], and gradients of such functions integrated over the Brillouin zone vanish.[20] More generally, we see from Eq. (3.21) that

$$\langle \mathbf{J}\rangle_{(0)}=0\quad\text{(filled bands)}\tag{3.25}$$

to *all* orders in the electric field, since regardless of the value of $\mathbf{K}(t)$ the sum over $\mathbf{k}$ in the first Brillouin zone involves the set of vectors $\mathbf{k}+\mathbf{K}(t)$ which are equivalent, when used as the argument of $\mathbf{v}_{nn}$, to the set of vectors $\mathbf{k}$. So, as expected, we find that there is no net current density due to purely intraband motion in the case of filled bands.

B. Expansion in powers of the electric field

We now return to Eq. (3.18) and consider $\langle\Theta\rangle_{(1)}$, which describes the first-order interband response. The intraband motion is taken into account fully here, which leads to a complicated integrand to evaluate, with $\mathbf{A}$ appearing in $v_{mn}(\mathbf{k};t')$. For some special applied fields, it may be appropriate to evaluate $\langle\Theta\rangle_{(1)}$ directly. But it is also possible to use the expression to generate a series in powers of $\mathbf{E}(t)$ which involves iteration in *both* the interband *and* intraband motion. For the calculation of nonlinear susceptibilities, this is generally what is required. To generate this expansion, use Eq. (3.23) in Eq. (3.18) to write

$$\begin{aligned}\langle\Theta\rangle_{(1)}=&-\frac{1}{i\hbar}\sum_{nm\mathbf{k}} f_{nm}(\mathbf{k})\theta_{nm}(\mathbf{k};t)e^{i\nu_{nm}(\mathbf{k};t)}\\&\times\left[\int_{-\infty}^{t}e^{i[\nu_{mn}(\mathbf{k};t')-\omega_\beta t']}\right.\\&\qquad\left.\times\mu^b_{mn}(\mathbf{k};t')dt'\right]E^b(\omega_\beta)\ ,\end{aligned}\tag{3.26}$$

where we henceforth take repeated frequency components, as well as Cartesian components, to be summed over. To approximate the integral which appears, use the exact relation

$$e^{S(t)}L(t)=\frac{d}{dt}\left[e^{S(t)}\frac{L(t)}{\dot S(t)}\right]-e^{S(t)}\frac{d}{dt}\left[\frac{L(t)}{\dot S(t)}\right]\ ,\tag{3.27}$$

with

$$\begin{aligned}&L(t)=\mu^b_{mn}(\mathbf{k};t)\ ,\\&S(t)=i[\nu_{mn}(\mathbf{k};t)-\omega_\beta t]\ .\end{aligned}\tag{3.28}$$

Then, defining

$$\begin{aligned}&\boldsymbol{\kappa}=\mathbf{k}+\mathbf{K}(t)\ ,\\&\boldsymbol{\kappa}'=\mathbf{k}+\mathbf{K}(t')\ ,\\&\vdots\end{aligned}\tag{3.29}$$

we have $\dot{S}(t)=i[\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta]$ [see Eq. (3.11)], and the integral appearing in Eq. (3.26) becomes

$$\int_{-\infty}^{t} e^{i[\nu_{mn}(\mathbf{k};t')-\omega_\beta t']}\mu_{mn}^{b}(\mathbf{k};t')dt'=\frac{e^{i[\nu_{mn}(\mathbf{k};t)-\omega_\beta t]}\mu_{mn}^{b}(\mathbf{k};t)}{i[\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta]}-\frac{e}{i\hbar}\int_{-\infty}^{t} e^{i[\nu_{mn}(\mathbf{k};t')-\omega_\beta t']}\frac{\partial}{\partial\kappa'^{c}}\left[\frac{\mu_{mn}^{b}(\mathbf{k};t')}{\omega_{mn}(\boldsymbol{\kappa}')-\omega_\beta}\right]E^{c}(t')dt' , \tag{3.30}$$

which is exact. We have used the fact that $\mu_{mn}^{b}(\mathbf{k};t')$ and $\omega_{mn}(\boldsymbol{\kappa}')$ depend on time only through their dependence on $\mathbf{K}(t')$ [Eqs. (2.24), (2.31), and (3.29)], and $d\mathbf{K}(t')/dt'=e\hbar^{-1}\mathbf{E}(t')$ [Eqs. (2.9) and (2.10)]. Finally expanding $\mathbf{E}(t')$ in Eq. (3.30) in frequency components [Eq. (3.23)], we apply Eq. (3.27) again, this time to the integrand on the right-hand side of Eq. (3.30). Putting the result into Eq. (3.26), we find

$$\langle\Theta\rangle_{(1)}=\langle\Theta\rangle_{(1,0)}+\langle\Theta\rangle_{(1,1)}+\cdots , \tag{3.31}$$

where

$$\begin{aligned}\langle\Theta\rangle_{(1,0)}&=\sum_{nm\mathbf{k}}\frac{f_{nm}(\mathbf{k})}{\hbar}\frac{\theta_{nm}(\mathbf{k};t)\mu_{mn}^{b}(\mathbf{k};t)}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta}e^{-i\omega_\beta t}E^{b}(\omega_\beta) ,\\ \langle\Theta\rangle_{(1,1)}&=\sum_{nm\mathbf{k}}\frac{ief_{nm}(\mathbf{k})}{\hbar^2}\frac{\theta_{nm}(\mathbf{k};t)}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta-\omega_\gamma}\frac{\partial}{\partial\kappa^{c}}\left[\frac{\mu_{mn}^{b}(\mathbf{k};t)}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta}\right]e^{-i(\omega_\beta+\omega_\gamma)t}E^{b}(\omega_\beta)E^{c}(\omega_\gamma) .\end{aligned} \tag{3.32}$$

Here, $\langle\Theta\rangle_{(i,j)}$ involves an ith-order expansion in the interband motion, with a total expansion in the electric field of order $(i+j)$. Similarly, turning to the third expression in Eq. (3.18), we proceed in the same way to find

$$\langle\Theta\rangle_{(2)}=\langle\Theta\rangle_{(2,0)}+\langle\Theta\rangle_{(2,1)}+\cdots , \tag{3.33}$$

where, for example,

$$\begin{aligned}\langle\Theta\rangle_{(2,0)}=\frac{1}{\hbar^2}\sum_{\substack{nml\\ \mathbf{k}}}\frac{1}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta-\omega_\gamma}&\left[\frac{f_{nl}(\mathbf{k})\theta_{nm}(\mathbf{k};t)\mu_{ml}^{b}(\mathbf{k};t)\mu_{ln}^{c}(\mathbf{k};t)}{\omega_{ln}(\boldsymbol{\kappa})-\omega_\gamma}+\frac{f_{ml}(\mathbf{k})\theta_{nm}(\mathbf{k};t)\mu_{ml}^{c}(\mathbf{k};t)\mu_{ln}^{b}(\mathbf{k};t)}{\omega_{ml}(\boldsymbol{\kappa})-\omega_\gamma}\right]\\ &\times e^{-i(\omega_\beta+\omega_\gamma)t}E^{b}(\omega_\beta)E^{c}(\omega_\gamma) .\end{aligned} \tag{3.34}$$

Note that the summands in Eqs. (3.32) and (3.34) still depend on time. But the time dependence associated with the phases $\phi(\mathbf{k};t)$ can immediately be seen to vanish. In the first of Eq. (3.32), for example, we have

$$\begin{aligned}\theta_{nm}(\mathbf{k};t)\mu_{mn}^{b}(\mathbf{k};t)&=[\Theta_{nm}(\boldsymbol{\kappa})e^{i\phi_{nm}(\mathbf{k};t)}][er_{mn}^{b}(\boldsymbol{\kappa})e^{i\phi_{mn}(\mathbf{k};t)}]\\ &=e\Theta_{nm}(\boldsymbol{\kappa})r_{mn}^{b}(\boldsymbol{\kappa}) .\end{aligned} \tag{3.35}$$

Turning to the second of Eqs. (3.32), we can easily confirm from the definition of $\mathbf{r}_{mn}(\boldsymbol{\kappa})$ that

$$\begin{aligned}e^{-i\phi_{mn}(\mathbf{k};t)}\frac{\partial}{\partial\kappa^{c}}[r_{mn}^{b}(\boldsymbol{\kappa})e^{i\phi_{mn}(\mathbf{k};t)}]&=\frac{-[r_{mn}^{b}(\boldsymbol{\kappa})\Delta_{mn}^{c}(\boldsymbol{\kappa})+r_{mn}^{c}(\boldsymbol{\kappa})\Delta_{mn}^{b}(\boldsymbol{\kappa})]}{\omega_{mn}(\boldsymbol{\kappa})}\;\frac{-i\sum_p[\omega_{mp}(\boldsymbol{\kappa})r_{mp}^{b}(\boldsymbol{\kappa})r_{pn}^{c}(\boldsymbol{\kappa})-\omega_{pn}(\boldsymbol{\kappa})r_{mp}^{c}(\boldsymbol{\kappa})r_{pn}^{b}(\boldsymbol{\kappa})]}{\omega_{mn}(\boldsymbol{\kappa})}\\ &\equiv r_{mn;c}^{b}(\boldsymbol{\kappa}) ,\end{aligned} \tag{3.36}$$

where

$$\boldsymbol{\Delta}_{mn}(\boldsymbol{\kappa})\equiv\mathbf{v}_{mm}(\boldsymbol{\kappa})-\mathbf{v}_{nn}(\boldsymbol{\kappa}) , \tag{3.37}$$

and the difference in Fermi factors $[f_{nm}(\mathbf{k})]$ appearing in the second of Eqs. (3.32) ensures that, in our case of filled bands, we need only consider the derivative appearing in Eq. (3.36) for $\omega_{mn}(\boldsymbol{\kappa})\neq 0$. Using Eq. (3.36) we may then write

$$f_{nm}(\mathbf{k})\theta_{nm}(\mathbf{k};t)\frac{\partial}{\partial\kappa^{c}}\left[\frac{\mu_{mn}^{b}(\mathbf{k};t)}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta}\right]=ef_{nm}(\mathbf{k})\Theta_{nm}(\boldsymbol{\kappa})\left[\frac{r_{mn}^{b}(\boldsymbol{\kappa})}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta}\right]_{;c} , \tag{3.38}$$

where

$$\left[\frac{r_{mn}^{b}(\boldsymbol{\kappa})}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta}\right]_{;c}\equiv\frac{r_{mn;c}^{b}(\boldsymbol{\kappa})}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta}+r_{mn}^{b}(\boldsymbol{\kappa})\frac{\partial}{\partial\kappa^{c}}\left[\frac{1}{\omega_{mn}(\boldsymbol{\kappa})-\omega_\beta}\right] . \tag{3.39}$$

When Eqs. (3.35) and (3.38) are used in Eq. (3.32), the only remaining time dependence is due to the dependence on time of $\boldsymbol{\kappa}$ for each $\mathbf{k}$ [Eq. (3.29)]. But in the case of filled bands this time dependence vanishes, by virtue of the argument given after Eq. (3.25), and we can write

$$\begin{aligned}\langle\Theta\rangle_{(1,0)}&=\sum_{nm\mathbf{k}}\frac{ef_{mn}}{\hbar}\frac{\Theta_{nm}(\mathbf{k})r^{b}_{mn}(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega_\beta}e^{-i\omega_\beta t}E^{b}(\omega_\beta)\ ,\\ \langle\Theta\rangle_{(1,1)}&=\sum_{nm\mathbf{k}}\frac{ie^2f_{nm}}{\hbar^2}\frac{\Theta_{nm}(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega_\beta-\omega_\gamma}\left[\frac{r^{b}_{mn}(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega_\beta}\right]_{;c}e^{-i(\omega_\beta+\omega_\gamma)t}E^{b}(\omega_\beta)E^{c}(\omega_\gamma)\ ,\\ \langle\Theta\rangle_{(2,0)}&=\frac{1}{\hbar^2}\sum_{\substack{nml\\ \mathbf{k}}}\frac{e^2}{\omega_{mn}(\mathbf{k})-\omega_\beta-\omega_\gamma}\left[\frac{f_{nl}\Theta_{nm}(\mathbf{k})r^{b}_{ml}(\mathbf{k})r^{c}_{ln}(\mathbf{k})}{\omega_{ln}(\mathbf{k})-\omega_\gamma}+\frac{f_{ml}\Theta_{nm}(\mathbf{k})r^{c}_{ml}(\mathbf{k})r^{b}_{ln}(\mathbf{k})}{\omega_{ml}(\mathbf{k})-\omega_\gamma}\right]\\ &\quad\times e^{-i(\omega_\beta+\omega_\gamma)t}E^{b}(\omega_\beta)E^{c}(\omega_\gamma)\ .\end{aligned}\tag{3.40}$$

For the rest of this paper we shall restrict ourselves to the case of filled bands, leaving aspects of the more general problem to later communications.

We close this section by collecting all terms of a given order in the electric field together. That is, we put

$$\begin{aligned}\langle\Theta\rangle_{\rm I}&=\langle\Theta\rangle_{(1,0)}\ ,\\ \langle\Theta\rangle_{\rm II}&=\langle\Theta\rangle_{(2,0)}+\langle\Theta\rangle_{(1,1)},\ \text{etc.}\ ,\end{aligned}\tag{3.41}$$

where

$$\begin{aligned}\langle\Theta\rangle_{\rm I}&=R^{b}_{\rm I}(-\omega_\beta;\omega_\beta)E^{b}(\omega_\beta)e^{-i\omega_\beta t}\ ,\\ \langle\Theta\rangle_{\rm II}&=R^{bc}_{\rm II}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)E^{b}(\omega_\beta)E^{c}(\omega_\gamma)e^{-i(\omega_\beta+\omega_\gamma)t}\ ,\end{aligned}\tag{3.42}$$

with

$$\begin{aligned}R^{b}_{\rm I}(-\omega_\beta;\omega_\beta)&=\sum_{nm\mathbf{k}}\frac{ef_{nm}}{\hbar}\frac{\Theta_{nm}(\mathbf{k})r^{b}_{mn}(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega_\beta}\ ,\\ R^{b}_{\rm II}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)&=\sum_{\substack{nml\\ \mathbf{k}}}\frac{e^2}{\hbar^2[\omega_{mn}(\mathbf{k})-\omega_\beta-\omega_\gamma]}\left[\frac{f_{nl}\Theta_{mn}(\mathbf{k})r^{b}_{ml}(\mathbf{k})r^{c}_{ln}(\mathbf{k})}{\omega_{ln}(\mathbf{k})-\omega_\gamma}+\frac{f_{ml}\Theta_{nm}(\mathbf{k})r^{c}_{ml}(\mathbf{k})r^{b}_{ln}(\mathbf{k})}{\omega_{ml}(\mathbf{k})-\omega_\gamma}\right]\\ &\quad+\sum_{nm\mathbf{k}}\frac{ie^2}{\hbar^2}\frac{f_{nm}\Theta_{nm}(\mathbf{k})}{[\omega_{mn}(\mathbf{k})-\omega_\beta-\omega_\gamma]}\left[\frac{r^{b}_{mn}(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega_\beta}\right]_{;c}\ .\end{aligned}\tag{3.43}$$

Although it is possible to symmetrize $R_{\rm II}$ so that it satisfies intrinsic permutation symmetry,[21] $R^{bc}_{\rm II}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)=R^{cb}_{\rm II}(-\omega_\beta-\omega_\gamma;\omega_\gamma,\omega_\beta)$, we have not done that in Eq. (3.43) for simplicity. These expressions will serve as the basis of our calculation of susceptibilities in the following section.

C. Susceptibilities

As an example, we now use the perturbation formalism derived in the preceding sections to evaluate the linear and second-harmonic susceptibilities of a crystal with filled bands. The first of these is of course a well-known result;[6] the second has only been recently derived for a general crystal class,[3] utilizing a sum rule to eliminate an unphysical divergence. In the present formalism, such divergences do not even appear.

We have already seen that the expectation value of **J** vanishes to zeroth order [Eq. (3.25)], and to evaluate it to higher order it is convenient to calculate $\langle\mathbf{P}\rangle$ and $\langle\mathbf{J}_A\rangle$ separately [see Eq. (2.72)]. Referring to the final results of Sec. III B, we see that we can expect expansions of the form

$$\begin{aligned}\langle\mathbf{P}\rangle&=\langle\mathbf{P}\rangle_{\rm I}+\langle\mathbf{P}\rangle_{\rm II}+\cdots\ ,\\ \langle\mathbf{J}_A\rangle&=\langle\mathbf{J}_A\rangle_{\rm I}+\langle\mathbf{J}_A\rangle_{\rm II}+\cdots\ ,\end{aligned}\tag{3.44}$$

with

$$\begin{aligned}\langle P^{a}\rangle_{\rm I}&=\chi^{ab}_{\rm I}(-\omega_\beta;\omega_\beta)E^{b}(\omega_\beta)e^{-i\omega_\beta t}\ ,\\ \langle P^{a}\rangle_{\rm II}&=\chi^{abc}_{\rm II}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)E^{b}(\omega_\beta)E^{c}(\omega_\gamma)e^{-i(\omega_\beta+\omega_\gamma)t}\ ,\end{aligned}\tag{3.45}$$

and

$$\begin{aligned}\langle J^{a}_A\rangle_{\rm I}&=\sigma^{ab}_{\rm I}(-\omega_\beta;\omega_\beta)E^{b}(\omega_\beta)e^{-i\omega_\beta t}\ ,\\ \langle J^{a}_A\rangle_{\rm II}&=\sigma^{abc}_{\rm II}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)E^{b}(\omega_\beta)E^{c}(\omega_\gamma)\\ &\quad\times e^{-i(\omega_\beta+\omega_\gamma)t}\ ,\end{aligned}\tag{3.46}$$

where as before both Cartesian components and frequency components are to be summed over if repeated. It is easy to verify that $\sigma^{ab}_{\rm I}(-\omega;\omega)$ vanishes for a crystal with filled bands, so the entire linear response is due to interband transitions, real and virtual. Using the result (3.42), with $\Theta=P^{a}$, we find

$$\chi_{\rm I}^{ab}(-\omega;\omega)=\frac{1}{\Omega}\sum_{nm\mathbf{k}}\frac{e^2 f_{nm}}{\hbar}\frac{r_{nm}^a(\mathbf{k})r_{mn}^b(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega}\,, \tag{3.47}$$

exactly the result we would find for a set of atoms labeled by $\mathbf{k}$ [see discussion after Eq. (2.70)]. Note that at this point the phase of the wave functions used to calculate $\mathbf{r}_{nm}(\mathbf{k})$ and $\mathbf{r}_{mn}(\mathbf{k})$ is irrelevant, since multiplying $\psi_n(\mathbf{k};\mathbf{x})$ or $\psi_m(\mathbf{k};\mathbf{x})$ by any (uniform) phase will not change the product in the numerator of Eq. (3.47). Thus, any convenient set of wave functions may be chosen; they need not satisfy the first of Eq. (2.3). Defining the dielectric constant

$$\epsilon^{ab}(\omega)=\delta^{ab}+4\pi\chi_{\rm I}^{ab}(-\omega;\omega) \tag{3.48}$$

and writing the $\mathbf{r}(\mathbf{k})$ in terms of the $\mathbf{v}(\mathbf{k})$ [Eqs. (2.5) and (2.31)], we have

$$\epsilon^{ab}(\omega)=\delta^{ab}+\frac{4\pi e^2}{\Omega\hbar}\sum_{nm\mathbf{k}}\frac{f_{nm}v_{nm}^a(\mathbf{k})v_{mn}^b(\mathbf{k})}{\omega_{mn}^2(\mathbf{k})[\omega_{mn}(\mathbf{k})-\omega-i\eta]}\,, \tag{3.49}$$

where we explicitly indicate the small positive imaginary part $i\eta$ of the frequency [see discussion after Eq. (3.23)]. Passing to the limit of an infinite crystal we take

$$\frac{1}{\Omega}\sum_{\mathbf{k}}\to 2\int\frac{d\mathbf{k}}{8\pi^3} \tag{3.50}$$

the factor of 2 to include the spin degeneracy, and we find

$$\mathrm{Im}[\epsilon^{ab}(\omega)]=\frac{e^2}{\hbar\pi}\sum_{nm}\int d\mathbf{k}\frac{f_{nm}v_{nm}^a(\mathbf{k})v_{mn}^b(\mathbf{k})}{\omega_{mn}^2(\mathbf{k})}\times\delta[\omega-\omega_{mn}(\mathbf{k})]\,, \tag{3.51}$$

the usual result. The numerical evaluation of Eq. (3.51), for a given calculated band structure, is usually done directly; $\mathrm{Re}[\epsilon^{ab}(\omega)]$ can then be obtained from that result using the Kramers-Kronig relation.

We now turn to the (second order) nonlinear response. Here, both $\langle \mathbf{J}_A\rangle_{\rm II}$ and $\langle \mathbf{P}\rangle_{\rm II}$ will contribute to $\langle \mathbf{J}\rangle_{\rm II}$ through Eq. (2.72). Introducing an effective polarization potential $\mathcal{P}$ through the relation

$$\langle \mathbf{J}\rangle=\dot{\mathcal{P}}\,, \tag{3.52}$$

and expanding $\mathcal{P}$ as in Eqs. (3.44), we introduce an effective nonlinear susceptibility $\chi^{abc}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)$ by

$$\mathcal{P}^a=\chi^{abc}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)E^b(\omega_\beta)E^c(\omega_\gamma)e^{-i(\omega_\beta+\omega_\gamma)t}\,. \tag{3.53}$$

From Eqs. (2.72), (3.45), (3.46), (3.52), and (3.53) we then find

$$\chi^{abc}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)=\chi_{\rm II}^{abc}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)+\frac{i\sigma_{\rm II}^{abc}(-\omega_\beta-\omega_\gamma;\omega_\beta,\omega_\gamma)}{(\omega_\beta+\omega_\gamma)}\,. \tag{3.54}$$

As an example, we work out the effective susceptibility for second-harmonic generation, $\chi^{abc}(-2\omega;\omega,\omega)$. Using the second of Eq. (3.42) with $\Theta=P^a$ we easily find

$$\chi_{\rm II}^{abc}(-2\omega;\omega,\omega)=\frac{e^3}{\hbar^2\Omega}\sum_{\substack{nml\\ \mathbf{k}}}\frac{1}{\omega_{mn}(\mathbf{k})-2\omega}\left[\frac{f_{nl}r_{nm}^a(\mathbf{k})\{r_{ml}^b(\mathbf{k})r_{ln}^c(\mathbf{k})\}}{\omega_{ln}(\mathbf{k})-\omega}+\frac{f_{ml}r_{nm}^a(\mathbf{k})\{r_{ml}^b(\mathbf{k})r_{ln}^c(\mathbf{k})\}}{\omega_{ml}(\mathbf{k})-\omega}\right]$$
$$+\frac{ie^3}{2\hbar^2\Omega}\sum_{\substack{nml\\ \mathbf{k}}}\frac{f_{nm}r_{nm}^a(\mathbf{k})}{\omega_{mn}(\mathbf{k})-2\omega}\left[\left[\frac{r_{mn}^c(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega}\right]_{;b}+\left[\frac{r_{mn}^b(\mathbf{k})}{\omega_{mn}(\mathbf{k})-\omega}\right]_{;c}\right]\,, \tag{3.55}$$

where when we use the curly brackets { } with the matrix elements we mean a symmetrized form with respect to Cartesian components $\{r_{ml}^b(\mathbf{k})r_{ln}^c(\mathbf{k})\}\equiv\frac{1}{2}[r_{ml}^b(\mathbf{k})r_{ln}^c(\mathbf{k})+r_{ml}^c(\mathbf{k})r_{ln}^b(\mathbf{k})]$; we have defined $\chi^{abc}(-2\omega;\omega,\omega)$ so that it satisfies intrinsic permutation symmetry,[21] $\chi_{\rm II}^{acb}(-2\omega;\omega,\omega)=\chi_{\rm II}^{abc}(-2\omega;\omega,\omega)$. Next we turn to $\sigma_{\rm II}^{abc}(-2\omega;\omega,\omega)$ [Eq. (3.46)]. From Eq. (2.73) for the operator $\mathbf{J}_A$ we see that there will be two contributions due to the two terms contributing to $\mathcal{E}_{nm}$. To obtain second-order terms in $\langle \mathbf{J}_A\rangle$, the first must be taken to second order in the perturbation expansion [Eqs. (3.42)], but the second only to first order. Gathering up both terms, we find

$$\frac{i\sigma_{\rm II}^{abc}(-2\omega;\omega,\omega)}{2\omega}=-\frac{e^3}{4\hbar^2\Omega\omega^2}\sum_{\substack{nm\\ \mathbf{k}}}\left[\frac{f_{nm}v_{nn}^a(\mathbf{k})\{r_{nm}^b(\mathbf{k})r_{mn}^c(\mathbf{k})\}}{\omega_{mn}(\mathbf{k})-\omega}+\frac{f_{nm}v_{nn}^a(\mathbf{k})\{r_{mn}^b(\mathbf{k})r_{nm}^c(\mathbf{k})\}}{\omega_{nm}(\mathbf{k})-\omega}\right]$$
$$-\frac{ie^3}{4\hbar^2\Omega\omega}\sum_{\substack{nm\\ \mathbf{k}}}\frac{f_{nm}}{\omega_{mn}(\mathbf{k})-\omega}[r_{nm;a}^b(\mathbf{k})r_{mn}^c(\mathbf{k})+r_{nm;a}^c(\mathbf{k})r_{mn}^b(\mathbf{k})]\,. \tag{3.56}$$

The sum of the expressions in Eqs. (3.55) and (3.56) gives the effective nonlinear susceptibility for second-harmonic generation, $\chi^{abc}(-2\omega;\omega,\omega)$ [Eq. (3.54)]. In Appendix B we discuss how expressions such as (3.55) and (3.56) may be reduced to forms amenable for numerical analysis. Here we only note that the expression for $\chi_{\text{II}}^{abc}(-2\omega;\omega,\omega)$ is obviously finite as $\omega\rightarrow 0$, and the expression for $i(2\omega)^{-1}\sigma_{\text{II}}^{abc}(-2\omega;\omega,\omega)$ is easily shown to be finite as $\omega\rightarrow 0$ using only time-reversal symmetry (Appendix B). Thus, the formally divergent terms that appear in more usual derivations of $\chi^{abc}(-2\omega;\omega,\omega)$,[22] and must be eliminated by sum rules,[3] do not appear in this approach. Nonetheless, after a certain amount of algebra, the expression derived here for $\chi^{abc}(-2\omega;\omega,\omega)$ can be shown to be equivalent to the usual expression, as discussed in Appendix B.

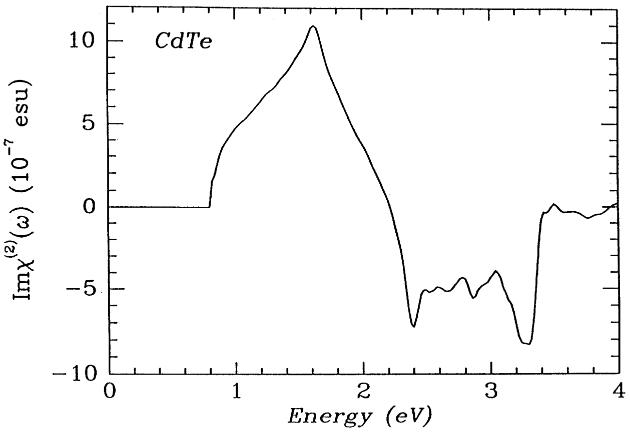

FIG. 1. Im$[\chi^{xyz}(-2\omega;\omega,\omega)]$ for CdTe. See Ghahramani, Moss, and Sipe (Ref. 23).

D. Second-harmonic generation in CdTe

As a simple example, in this section we present the different contributions to $\tilde{\chi}^{(2)}(-2\omega;\omega,\omega)$ for CdTe from a full band-structure calculation. The energy bands and velocity matrix elements are calculated using basis orbitals ($1s$-$5p$) for Cd and Te in a minimal linear combination of Gaussian orbitals (MLCGO) technique, in conjunction with the $X\alpha$ method for constructing the potentials of each material.[23] The local single-site effective potentials and basis orbitals are constructed by adjusting the α's to produce the correct lowest band gap; interactions up to ninth nearest neighbor are included to ensure convergence. This technique has been widely discussed and employed by us[1] and others.[24] Although not an *a priori* method, it generally gives good qualitative and often good quantitative agreement with experiment when used to calculate the optical response of semiconductors.[25] Typically, relativistic effects, such as spin-orbit coupling, are neglected, so the formalism developed here can be applied without extension.

The results for CdTe have already been presented in the literature and compared with experiment;[23] for reference we give the frequency dependence of the imaginary part of $\chi^{xyz}(-2\omega;\omega,\omega)$ in Fig. 1. For cubic symmetry this component, and those equal to it by symmetry, are the only nonvanishing components. We denote it by $\chi^{(2)}(\omega)$. The real part of $\chi^{(2)}(\omega)$ can be determined from the imaginary part by a Kramers-Kronig relation.[26]

Figure 1 was calculated using the standard approach sketched in the Introduction, extended to second order;[22]a sum rule[3] was used to eliminate an apparent divergence at zero frequency. With the approach developed in this paper no such divergence appears (see Sec. III C), and the physical different contributions to Im$\chi^{(2)}(\omega)$ may be identified [see Eq. (3.54)].

These different contributions are plotted in Fig. 2. The solid line is the contribution from the first term on the right-hand side of Eq. (3.55) [see Eq. (B4)]. It represents the purely interband contribution that would result if one thought of the system as only a set of effective atoms labeled by their crystal momenta **k** [see the discussion after Eq. (2.70)]. Although this term can be nonvanishing for photon energies $\hbar\omega=E>\frac{1}{2}E_G$, where E_G is the (direct) band gap [see Eq. (B4)], and the computed values of this term for $\frac{1}{2}E_G>E>E_G$ indeed seem to be larger than the inevitable numerical noise, our results indicate the term is only significant when $E>E_G$. It is clear from a comparison of Figs. 1 and 2 that this pure interband term is only part of the physics.

The dashed line in Fig. 2 is the contribution from the second term in Eq. (3.55) [see Eq. (B13)], and describes the portion of Im$\chi^{(2)}(\omega)$ that results from the modulation of the linear susceptibility by the intraband motion of the electrons [refer back to Eq. (3.26); this term follows from the second expression in Eq. (3.32) with $\Theta=P^a$]. For $E<E_G$ this is the largest contribution to Im$\chi^{(2)}(\omega)$. Finally, the dashed-dotted line in Fig. 2 is the contribution from $i(2\omega)^{-1}\sigma_{\text{II}}^{xyz}$, Eq. (3.56) [see Eqs. (B6b) and (B17)]. This is the portion of Im$\chi^{(2)}(\omega)$ resulting from the modification of intraband motion by the polarization energy associated with the interband motion [see Eqs. (2.73)

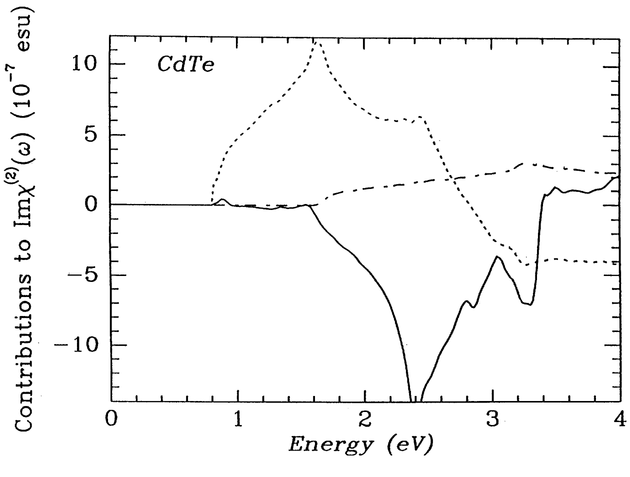

FIG. 2. The different contributions to Im$[\chi^{xyz}(-2\omega;\omega,\omega)]$. Solid line: pure interband term; dashed line: modulation of interband term by intraband motion; dashed-dotted line: modulation of intraband current by interband polarization. See text.

and (2.74); the first sum in Eq. (3.56) vanishes (see discussion before Eq. (B14)]. This term only appears for $E > E_G$.

The three curves in Fig. 2, when summed, lead to the curve in Fig. 1, as they should. We note that some particular contributions [those from Eqs. (B12a) and (B16b)] vanish identically for the special case of cubic symmetry considered here, although in general they would be nonzero. And while there is still much to be interpreted in how all these different contributions relate to the underlying features of the band structures of semiconductors, it is clear that the formalism established here at least allows them to be identified as different physical effects, and calculated. We plan to return to matters of more detailed interpretation in future communications.

IV. SUMMARY

We have presented a formalism for the calculation of nonlinear optical response coefficients of crystals within the independent particle approximation. Our particular emphasis has been on the case of *filled bands,* where all bands are either completely filled or completely empty. None of the apparent divergences which plagued earlier formalisms appear here. Although we have presented detailed expressions and a sample calculation only for second harmonic generation, the formalism can be easily applied to find expressions for response coefficients for other nonlinear processes. The second-quantized form in which the theory is developed will facilitate generalization beyond the independent-particle approximation.

The hallmark of the technique is the separation of the interband and intraband motion of the electrons, both in calculating the evolution of the density operator [Eqs. (2.69) and (2.70)], and in evaluating the induced current density [Eqs. (2.72)–(2.74)]. Although for the evaluation of the usual response coefficients one wants a perturbation expansion in both interband and intraband motion, the formalism treats these effects in quite different ways.

The intraband motion is taken into account by expanding in terms of eigenstates of the instantaneous Hamiltonian [cf. Eq. (2.11)]. In the limit of low frequency—the adiabatic limit—these become exact single-particle wave functions describing the evolution of the system. Note that we have defined these wave functions such that they are orthogonal to their parametric time derivatives [see Eq. (2.15)]. This guarantees that the Berry's phase is *included* in these wave functions;[27] in fact, it is related to the ξ_{mm} [see Eqs. (2.22)–(2.24), and the recent work of Zak and co-workers[28]]. For the usual nonlinear response coefficients, we expect the results to be independent of these Berry's phases for filled bands, as we have seen here for the special case of second harmonic generation. After all, such coefficients could be calculated by the more usual approach (recall the discussion in Sec. I) where only momentum matrix elements would appear. The possible appearance of the Berry's phases in more general optical response calculations is still a matter for investigation.

By defining the instantaneous eigenstates so that they are orthogonal to their parametric time derivatives, we guarantee that the rest of the physics involves only matrix elements between different bands [see Eqs. (2.31), (2.69), and (2.70)], i.e., it is the interband motion. A perturbation theory was developed in terms of the interband motion and, although for our application here we also expanded in terms of the intraband motion, one could use the perturbation calculation of the interband motion taking the intraband motion into account to all orders [Eq. (3.18)].

Of the contributions to the response coefficients, a "purely" interband term can be identified, which is the only contribution that would appear in a simple model where the crystal is considered as a set of n-level atoms, each associated with a different $\mathbf{k}$ point.[29] Since we can also calculate the other contributions, one of the issues this formalism will allow us to address is the question of just how good a description of the true nonlinear optical response follows from such a simple and attractive physical model. To this, and the host of the other issues in this paper we have relegated to future communications, we now plan to turn.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada, and the Ontario Laser and Lightwave Research Centre. We wish to thank Dr. D. J. Moss and Professor H. M. van Driel for fruitful discussions on the matters discussed herein.

APPENDIX A

In this appendix we confirm Eq. (2.72). We begin, using Eqs. (2.65) and (2.68), with

$$\langle \mathbf{P} \rangle = \mathrm{Tr}(\rho \mathbf{P}) = \mathrm{Tr}(\rho' \mathbf{P}') = \frac{1}{\Omega} \mathrm{Tr} \left[\rho' \sum_{nm\mathbf{k}} a^{\dagger}_{n\mathbf{k}} a_{m\mathbf{k}} \boldsymbol{\mu}_{nm}(\mathbf{k};t) \right] . \tag{A1}$$

We then find

$$\frac{d\langle P^a \rangle}{dt} = T_1 + T_2 + T_3 , \tag{A2}$$

where the superscript a denotes a Cartesian component, and

$$\begin{aligned} T_1 &= \frac{1}{i\hbar\Omega} \mathrm{Tr} \left[[H', \rho'] \sum_{nm\mathbf{k}} a^{\dagger}_{n\mathbf{k}} a_{m\mathbf{k}} \mu^a_{nm}(\mathbf{k};t) \right] , \\ T_2 &= \frac{1}{i\hbar\Omega} \mathrm{Tr} \left[[H'_d, \rho'] \sum_{nm\mathbf{k}} a^{\dagger}_{n\mathbf{k}} a_{m\mathbf{k}} \mu^a_{nm}(\mathbf{k};t) \right] , \\ T_3 &= \frac{1}{\Omega} \mathrm{Tr} \left[\rho' \sum_{nm\mathbf{k}} a^{\dagger}_{n\mathbf{k}} a_{m\mathbf{k}} \frac{\partial \mu^a_{nm}(\mathbf{k};t)}{\partial K^b} \right] \frac{dK^b}{dt} , \end{aligned} \tag{A3}$$

where b also denotes a Cartesian component, and we have used Eq. (2.69); repeated Cartesian components are to be summed over. Using the trace property

$$\mathrm{Tr}([A,B]C) = \mathrm{Tr}(B[C,A]) , \tag{A4}$$

the expressions for T_1 and T_2 may be rewritten as involving the commutators of $a^{\dagger}_{n\mathbf{k}} a_{m\mathbf{k}}$ with H' and H'_d, respectively. From the anticommutation relations of $a_{n\mathbf{k}}$ and

$a^\dagger_{m\mathbf{k}'}$ it is easy to verify that

$$[a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}},a^\dagger_{p\mathbf{k}'}a_{q\mathbf{k}'}]=a^\dagger_{n\mathbf{k}}a_{q\mathbf{k}}\delta_{mp}\delta_{\mathbf{k}\mathbf{k}'}-a^\dagger_{p\mathbf{k}}a_{m\mathbf{k}}\delta_{nq}\delta_{\mathbf{k}\mathbf{k}'}\ , \tag{A5}$$

so immediately

$$[a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}},H']=-\hbar\omega_{nm}(\mathbf{k}+\mathbf{K})a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}}\ , \tag{A6}$$

and

$$\begin{aligned}T_1&=-\frac{1}{i\Omega}\mathrm{Tr}\left[\rho'\sum_{nm\mathbf{k}}\omega_{nm}(\mathbf{k}+\mathbf{K})\mu^a_{nm}(\mathbf{k};t)a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}}\right]\\&=\frac{e}{\Omega}\mathrm{Tr}\left[\rho'\sum_{\substack{n,m\neq n,\\ \mathbf{k}}}v^a_{nm}(\mathbf{k}+\mathbf{K})e^{i\phi_{nm}(\mathbf{k};t)}a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}}\right]\\&=\langle J^a\rangle-\frac{e}{\Omega}\sum_{n\mathbf{k}}\mathrm{Tr}[\rho' v^a_{nn}(\mathbf{k}+\mathbf{K})a^\dagger_{n\mathbf{k}}a_{n\mathbf{k}}]\ ,\end{aligned} \tag{A7}$$

where we have used Eqs. (2.31), (2.52), (2.60), and (2.68). Similarly, using Eq. (A5) to evaluate $[a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}},H'_d]$, we find

$$T_2=-\frac{e}{\hbar\Omega}\mathrm{Tr}\left[\rho'\sum_{nm\mathbf{k}}a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}}\left[\frac{\partial\mu^a_{nm}(\mathbf{k};t)}{\partial K^b}-\frac{\partial\mu^b_{nm}(\mathbf{k};t)}{\partial K^a}\right]\right]E^b(t), \tag{A8}$$

where we have used Eq. (2.71). Finally using Eqs. (2.9) and (2.10), we have

$$T_3=\frac{e}{\hbar\Omega}\mathrm{Tr}\left[\rho'\sum_{nm\mathbf{k}}a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}}\frac{\partial\mu^a_{nm}(\mathbf{k};t)}{\partial K^b}\right]E^b(t)\ . \tag{A9}$$

Using Eqs. (A7)–(A9) in Eq. (A2), we find

$$\begin{aligned}\langle J^a\rangle=&\frac{d}{dt}\langle P^a\rangle+\frac{e}{\Omega}\mathrm{Tr}\left[\rho'\sum_{n\mathbf{k}}v^a_{nn}(\mathbf{k}+\mathbf{K})a^\dagger_{n\mathbf{k}}a_{n\mathbf{k}}\right]\\&-\frac{e}{\Omega\hbar}\mathrm{Tr}\left[\rho'\sum_{nm\mathbf{k}}\frac{\partial\mu^b_{nm}(\mathbf{k};t)}{\partial K^a}a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}}\right]E^b(t)\ .\end{aligned} \tag{A10}$$

Defining

$$\mathbf{J}'_A=\frac{e}{\Omega}\sum_{nm\mathbf{k}}a^\dagger_{n\mathbf{k}}a_{m\mathbf{k}}\frac{1}{\hbar}\frac{\partial\mathcal{E}_{nm}(\mathbf{k};t)}{\partial\mathbf{K}}\ , \tag{A11}$$

where $\mathcal{E}_{nm}(\mathbf{k};t)$ is given by Eq. (2.74), and using Eq. (2.68) we find Eq. (2.72) from Eq. (A10).

APPENDIX B

In this appendix we discuss the simplification of expressions (3.55) and (3.56). The only symmetry property we employ is the time reversal symmetry of the Hamiltonian (2.1), from which it follows[30] that

$$\mathbf{v}_{mn}(\mathbf{k})=-\mathbf{v}_{nm}(-\mathbf{k})\ , \tag{B1}$$

so

$$\mathbf{r}_{mn}(\mathbf{k})=\mathbf{r}_{nm}(-\mathbf{k}) \tag{B2}$$

[see Eqs. (2.5) and (2.31)] and

$$r^a_{nm;b}(-\mathbf{k})=-r^a_{mn;b}(\mathbf{k}) \tag{B3}$$

[see Eq. (3.36)]. The goal of the kind of simplifications we seek is to reduce expressions to be computed to a form which involves only one factor of the form $[\omega_{ln}(\mathbf{k})-\omega]^{-1}$ or $[\omega_{ln}(\mathbf{k})-2\omega]^{-1}$ [see, e.g., Eq. (3.42)]. Then, restoring the small positive imaginary part to the frequency the factor can be written as a principal value part of a Dirac δ function. The contribution from the latter can be computed directly, and then the other obtained by a Kramers-Kronig relation.[26]

We begin with the first term on the right-hand side of Eq. (3.55). Here the factors $(\omega_{mn}-2\omega)^{-1}(\omega_{ln}-\omega)^{-1}$ and $(\omega_{mn}-2\omega)^{-1}(\omega_{ml}-\omega)^{-1}$ may be broken up by the method of partial fractions. Two terms proportional to $(\omega_{mn}-2\omega)^{-1}$ result, which may be combined, as well as terms proportional to $(\omega_{ln}-\omega)^{-1}$ and $(\omega_{ml}-\omega)^{-1}$. The final result is

$$\frac{e^3}{\hbar^2\Omega}\frac{r^a_{nm}\{r^b_{ml}r^c_{ln}\}}{(\omega_{ln}-\omega_{ml})}\left[\frac{2f_{nm}}{(\omega_{mn}-2\omega)}+\frac{f_{ml}}{(\omega_{ml}-\omega)}+\frac{f_{ln}}{(\omega_{ln}-\omega)}\right]\ . \tag{B4}$$

Here, and in the rest of this appendix, we do not explicitly indicate the $\mathbf{k}$ dependence of terms such as $r^a_{nm}(\mathbf{k})$ and $\omega_{nm}(\mathbf{k})$, and we understand all band indices, as well as crystal momenta $\mathbf{k}$, to be summed over. Note that (B4) is of the form desired, except for possible difficulties with an "accidental degeneracy" if $\omega_{ln}=\omega_{ml}$ at some point in the Brillouin zone. Although the possibility and nature of such accidental degeneracies has not been studied in detail analytically, the evidence from numerical calculation is that they do not present a problem.[31]

Now we turn to the second sum in Eq. (3.55). To effect a decomposition by partial fractions, we work out the derivatives to find that the net term to be summed may be written as

$$\frac{ie^3}{2\hbar^2\Omega}\frac{f_{nm}r^a_{nm}}{\omega_{mn}-2\omega}\left[\frac{r^b_{mn;c}}{(\omega_{mn}-\omega)}-\frac{r^b_{mn}\Delta^c_{mn}}{(\omega_{mn}-\omega)^2}+(b\leftrightarrow c)\right]\ , \tag{B5}$$

where $(b\leftrightarrow c)$ indicates the preceding term(s) should be written with b and c exchanged. We have used

$$\frac{\partial\omega_{mn}}{\partial k^c}=v^c_{mm}-v^c_{nn}\equiv\Delta^c_{mn} \tag{B6}$$

[cf. Eq. (3.37)]. Decomposing Eq. (B5) by partial fractions we find

$$\begin{aligned}\frac{ie^3}{2\hbar^2\Omega}f_{nm}r^a_{nm}&\left[\frac{2r^b_{mn;c}}{\omega_{mn}(\omega_{mn}-2\omega)}-\frac{r^b_{mn;c}}{\omega_{mn}(\omega_{mn}-\omega)}\right.\\&-\frac{4r^b_{mn}\Delta^c_{mn}}{\omega^2_{mn}(\omega_{mn}-2\omega)}+\frac{2r^b_{mn}\Delta^c_{mn}}{\omega^2_{mn}(\omega_{mn}-\omega)}\\&\left.+\frac{r^b_{mn}\Delta^c_{mn}}{\omega_{mn}(\omega_{mn}-\omega)^2}+(b\leftrightarrow c)\right]\ .\end{aligned} \tag{B7}$$

To handle the terms proportional to $(\omega_{mn}-\omega)^{-2}$ we note that

$$-\frac{r^b_{mn}}{\omega_{mn}}\frac{\partial}{\partial k^c}\left[\frac{1}{\omega_{mn}-\omega}\right]=\frac{r^b_{mn}\Delta^c_{mn}}{\omega_{mn}(\omega_{mn}-\omega)^2}\ , \tag{B8}$$

so we may partially integrate such terms over the Brillouin zone, the net contributions at the edges of course vanishing.[20] Returning for a moment to Eq. (3.36), we see that

$$\begin{aligned}\frac{\partial}{\partial \kappa^6}[r^a_{mn}(\boldsymbol{\kappa})r^b_{nm}(\boldsymbol{\kappa})]&=\frac{\partial}{\partial \kappa^c}[r^a_{mn}(\boldsymbol{\kappa})e^{i\phi_{mn}(\mathbf{k};t)}r^b_{nm}(\boldsymbol{\kappa})e^{i\phi_{nm}(\mathbf{k};t)}]\\&=r^a_{mn;c}(\boldsymbol{\kappa})r^b_{nm}(\boldsymbol{\kappa})+r^a_{mn}(\boldsymbol{\kappa})r^b_{nm;c}(\boldsymbol{\kappa})\ ,\end{aligned} \tag{B9}$$

so in the result of the above-mentioned partial integration we may put

$$\frac{\partial}{\partial k^c}[r^a_{mn}r^b_{nm}]=r^a_{mn;c}r^b_{nm}+r^a_{mn}r^b_{nm;c}\ . \tag{B10}$$

Doing this and collecting all terms, we find that the summand (B7) may be replaced by

$$\begin{aligned}\frac{ie^3}{2\hbar^2\Omega}f_{nm}\Bigg[&\frac{2r^a_{nm}}{\omega_{mn}(\omega_{mn}-2\omega)}\left(r^b_{mn;c}-\frac{2r^b_{mn}\Delta^c_{mn}}{\omega_{mn}}\right)\\&+\frac{r^b_{mn}}{\omega_{mn}(\omega_{mn}-\omega)}\left(r^a_{nm;c}+\frac{r^a_{nm}\Delta^c_{mn}}{\omega_{mn}}\right)\\&+(b\leftrightarrow c)\Bigg]\ .\end{aligned} \tag{B11}$$

Using expressions for $r^b_{mn;c}$ and $r^a_{nm;c}$ [see again Eq. (3.36)] in Eq. (B11), we look first at the terms involving only two bands; we find they may be collected into two terms with different resonant denominators,

$$\frac{-8ie^3}{\hbar^2\Omega}\frac{f_{nm}r^a_{nm}}{\omega^2_{mn}(\omega_{mn}-2\omega)}\{\Delta^b_{mn}r^c_{mn}\} \tag{B12a}$$

and

$$\frac{-ie^3}{\hbar^2\Omega}\frac{f_{nm}\Delta^a_{mn}}{\omega^2_{mn}(\omega_{mn}-\omega)}\{r^b_{mn}r^c_{nm}\}\ . \tag{B12b}$$

Applying time-reversal symmetry [Eqs. (B1) and (B2)], Eq. (B12b) is seen to vanish. The terms involving three bands that result when Eq. (3.36) is used in Eq. (B11) can likewise be written as the sum of two terms with different resonant denominators,

$$\frac{2e^3}{\hbar^2\Omega}\frac{f_{nm}r^a_{nm}(\omega_{ml}-\omega_{ln})\{r^b_{ml}r^c_{ln}\}}{\omega^2_{mn}(\omega_{mn}-2\omega)} \tag{B13a}$$

and

$$\frac{e^3}{\hbar^2\Omega}\left[\frac{f_{nl}}{\omega^2_{ln}(\omega_{ln}-\omega)}-\frac{f_{lm}}{\omega^2_{ml}(\omega_{ml}-\omega)}\right]\omega_{mn}r^a_{nm}\{r^b_{ml}r^c_{ln}\}\ . \tag{B13b}$$

Neither (B13a) nor (B13b) vanishes. Thus the final result for $\chi^{abc}_{\mathrm{II}}(-2\omega;\omega,\omega)$ [Eq. (3.55)] is the sum of terms coming from expressions (B4), (B12a), (B13a), and (B13b). All expressions are to be summed over the Brillouin zone, and (B4) and (B12a) are to be summed also over band indices n and m, while (B13a) and (B13b) are to be summed also over band indices n, m, and l.

Next we turn to the simplification of Eq. (3.56). The first sum in that expression vanishes from time reversal symmetry: writing that sum as half the sum over $\mathbf{k}$ and half that over $-\mathbf{k}$, and using Eqs. (B1) and (B2), it is seen to vanish. When the same procedure is applied to the second sum in Eq. (3.56), we find

$$\begin{aligned}-\frac{ie^3}{4\hbar^2\Omega\omega}&\left[\frac{f_{nm}}{\omega_{mn}-\omega}-\frac{f_{mn}}{\omega_{nm}-\omega}\right]\{r^b_{nm;a}r^c_{mn}\}\\&=-\frac{ie^3}{4\hbar^2\Omega}\left[\frac{f_{nm}}{\omega_{mn}}\left(\frac{1}{\omega_{mn}-\omega}+\frac{1}{\omega_{mn}+\omega}\right)\right]\\&\quad\times\{r^b_{nm;a}r^c_{mn}\}\end{aligned} \tag{B14}$$

as an equivalent summand, which confirms that $i(2\omega)^{-1}\sigma^{abc}_{\mathrm{II}}(-2\omega;\omega,\omega)$ is finite as $\omega\rightarrow 0$. Writing the term in expression (B14) involving $(\omega_{mn}+\omega)^{-1}$ as a sum over $-\mathbf{k}$ and using Eqs. (B2) and (B3), it may be combined with the first term in the second line of (B14) to give a summand

$$\frac{-ie^3}{2\hbar^2\Omega}\frac{f_{nm}}{\omega_{mn}(\omega_{mn}-\omega)}\{r^b_{nm;a}r^c_{mn}\} \tag{B15}$$

equivalent to the summand (B14). Referring back to Eq. (3.36), we see that when it is used in the expression (B15) both two-band and three-band terms will be generated. The two-band term is the sum of two contributions,

$$-\frac{ie^3}{2\hbar^2\Omega}\frac{f_{nm}\Delta^a_{nm}\{r^b_{mn}r^c_{nm}\}}{\omega^2_{mn}(\omega_{mn}-\omega)} \tag{B16a}$$

and

$$\frac{ie^3}{2\hbar^2\Omega}\frac{f_{nm}r^a_{nm}\{r^b_{mn}\Delta^c_{mn}\}}{\omega^2_{mn}(\omega_{mn}-\omega)}\ . \tag{B16b}$$

Using time-reversal symmetry, the sum over $\mathbf{k}$ of expression (B16a) is easily seen to vanish. The three-band terms that result from using Eq. (3.36) in the expression (B15) can be written as

$$\frac{e^3}{2\hbar^2\Omega}\frac{f_{nm}}{\omega^2_{mn}(\omega_{mn}-\omega)}[\omega_{nl}r^a_{lm}\{r^b_{mn}r^c_{nl}\}-\omega_{lm}r^a_{nl}\{r^b_{lm}r^c_{mn}\}]\ . \tag{B17}$$

The final result for $i(2\omega)^{-1}\sigma^{abc}_{\mathrm{II}}(-2\omega;\omega,\omega)$ is thus the sum over terms coming from expressions (B16b) and (B17). Both expressions are to be summed over the Brillouin zone, and (B16b) is to be summed also over band indices n and m, while Eq. (B17) is to be summed over band indices n, m, and l.

This completes our simplification of Eqs. (3.55) and (3.56). When the described results are combined,

$$\chi^{abc}(-2\omega;\omega,\omega)=\chi_{\mathrm{II}}^{abc}(-2\omega;\omega,\omega)+\frac{i\sigma_{\mathrm{II}}^{abc}(-2\omega;\omega,\omega)}{2\omega} \tag{B18}$$

[cf. Eq. (3.54)], we obtain an expression which, after some straightforward algebra, is found equivalent to the expression for $\chi^{abc}(-2\omega;\omega,\omega)$ obtained earlier, by usual perturbation theory, for a crystal with filled bands.[3]

---

[1] See, e.g., D. J. Moss, E. Ghahramani, and J. E. Sipe, Phys. Status Solidi B **164**, 587 (1991); E. Ghahramani and J. E. Sipe, Phys. Rev. B **46**, 1831 (1992), and references cited therein.

[2] D. E. Aspnes, Phys. Rev. B **6**, 4648 (1972).

[3] E. Ghahramani, D. J. Moss, and J. E. Sipe, Phys. Rev. B **43**, 8990 (1991).

[4] D. J. Moss, E. Ghahramani, J. E. Sipe, and H. M. van Driel, Phys. Rev. B **41**, 1542 (1990).

[5] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, 1976), Chap. 12, Appendix E.

[6] See, e.g., F. Wooten, *Optical Properties of Solids* (Academic, New York, 1976), Chap. 7.

[7] V. N. Genkin and P. M. Mednis, Fiz. Tverd. Tela (Leningrad) **10**, 3 (1968) [Sov. Phys. Solid State **10**, 1 (1968)]; Zh. Eksp. Teor. Fiz. **54**, 1137 (1968) [Sov. Phys. JETP **27**, 609 (1968)].

[8] The second quantized calculation leads directly to terms involving the difference in Fermi factors [see, e.g., Eq. (3.16)], reducing the number of terms to be calculated.

[9] E. I. Blount, in *Solid State Physics, Advances in Research and Applications,* edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 305, and references cited therein.

[10] M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Wiley, New York, 1974).

[11] *Symmetry Principles in Solid State and Molecular Physics* (Ref. 10), Chap. 7.

[12] See the discussion in Ref. 10, p. 215.

[13] See, e.g., G. L. Bir and G. E. Pikus, *Symmetry and Strain-induced Effects in Semiconductors* (Wiley, New York, 1974), for a discussion.

[14] See, e.g., J. W. Negele and H. Orland, *Quantum Many-Particle Systems* (Addison-Wesley, New York, 1988).

[15] *Quantum Many-Particle Systems* (Ref. 14), Chap. 1.

[16] See the early discussion by W. V. Houston, Phys. Rev. **57**, 184 (1940).

[17] See also the discussion in Ref. 9.

[18] See, e.g., G. D. Mahan, *Many-Particle Physics,* 2nd ed. (Plenum, New York, 1990), Chap. 3.

[19] See, e.g., Ref. 4, Appendix.

[20] Reference 5, Appendix I.

[21] See, e.g., R. W. Boyd, *Nonlinear Optics* (Academic, New York, 1992).

[22] See, e.g., D. J. Moss, J. E. Sipe, and H. M. van Driel, Phys. Rev. B **36**, 9708 (1987).

[23] E. Ghahramani, D. J. Moss, and J. E. Sipe, Phys. Rev. B **43**, 9700 (1991).

[24] M. Z. Huang and W. Y. Ching, J. Phys. Chem. Solids **46**, 977 (1985).

[25] For example, compare E. Ghahramani, D. J. Moss, and J. E. Sipe, Phys. Rev. Lett. **64**, 2815 (1990), and Phys. Rev. B **43**, 8990 (1991), with U. Schmid, N. E. Christensen, M. Alouani, and M. Cardona, *ibid.* **43**, 14 597 (1991).

[26] See, e.g., Ref. 3. For another use of Kramers-Kronig relations in nonlinear optics, see the work of Van Stryland *et al.*, e.g. M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, IEEE J. Quantum Electron. **26**, 760 (1990).

[27] M. V. Berry, Proc. R. Soc. London Ser. A **392**, 45 (1984).

[28] J. Zak, Phys. Rev. Lett. **62**, 2747 (1989); Europhys. Lett. **9**, 615 (1989); L. Michel and J. Zak, *ibid.* **18**, 239 (1992).

[29] See, e.g., M. Lindberg and S. W. Koch, Phys. Rev. B **38**, 3342 (1988).

[30] See, e.g., J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1974).

[31] Such terms also appear in the calculation of other parametric processes such as third-harmonic generation, see, e.g., Ref. 4.