PHYSICAL REVIEW B VOLUME 50, NUMBER 24 15 DECEMBER 1994-II

Third-order optical nonlinearities in semiconductors: The two-band model

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

M. Sheik-Bahae
Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

E. W. Van Stryland
Center for Research and Education in Optics and Lasers and Department of Physics and Electrical Engineering, University of Central Florida, Orlando, Florida 32826

(Received 8 September 1994)

We calculate the coherent electronic contributions to the third-order optical response $\chi^{(3)}(-\omega;\omega,\Omega,-\Omega)$ of bulk semiconductors in the independent-particle approximation using a simple two-band model. The formalism used to derive this response coefficient naturally accounts for all relevant contributions and, in contrast to existing results in the literature, leads to physically realistic, nondivergent expressions in the limits $\omega,\Omega \rightarrow 0$. Such well behaved infrared limits imply that the imaginary part of our $\chi^{(3)}$ correctly describes the dispersion of nondegenerate absorption; indeed for $\Omega = 0$ our results are consistent with predictions from Franz-Keldysh theory. Complementing these results, we can now also unambiguously extract from the real part of $\chi^{(3)}$ the below band gap, two-band model predictions for the nonlinear refractive index, the dc Kerr effect, and the virtual photoconductivity; all of these predict a finite, real $\chi^{(3)}(0;0,0,0)$ as physically expected for clean, cold semiconductors. Finally, our specific results help expose more general consequences of the gauge choice when employing common approximate band-structure models.

I. INTRODUCTION

Bulk semiconductor optical nonlinearities play a central role in many optical devices and optical systems.[1-3] In particular, the nonlinear refractive index $n_2(\omega)$ has potential use for fast all-optical switching, which has led to intense study of third-order nonlinearities in semiconductors.[4-10] Simple band-structure models cannot only lead to a better understanding of such nonlinear responses, but are also often essential for the efficient design and analysis of practical devices. A two-band crystal, an analog of the familiar two-level atom, is perhaps the simplest such model, and so its suitability in calculating physically realistic optical response coefficients should be well understood.

A two-band model has recently been employed in a transition rate calculation of the third-order nonlinear absorption $\Delta\alpha(\omega,\Omega)$ (the change in absorption at ω due to the presence of light at Ω), from which $n_2(\omega)$ is then obtained via a Kramers-Kronig relation.[8-10] While that work has been very successful in explaining the universal dispersion of $n_2(\omega)$ below the band gap, certain aspects of the calculation deserve further investigation. Perhaps most striking is the result that the expression for $n_2(\omega)$ is formally divergent as $\omega \rightarrow 0$; on physical grounds, this is certainly not expected for cold, intrinsic semiconductors (insulators). The origin of the unphysical divergences was associated with a divergence in $\Delta\alpha(\omega,\Omega \rightarrow 0)$, and suspected to be due to the use of the velocity gauge. While the divergences in the $n_2(\omega)$ expression can in the end be removed "by hand," the necessity of such a heuristic adjustment is clearly unsatisfactory. A better understanding of the origins of such divergences, and how to avoid them in general, would be quite helpful. Not only would this reveal the actual $n_2(\omega)$ and $\Delta\alpha(\omega,\Omega)$ relevant here, but would also insure that similar problems do not enter in future studies employing more sophisticated band-structure models, or in studies of entirely different nonlinear processes.[11-13] Second, we note that the "quadratic Stark effect" enters the previous calculation quite differently than all other contributions. We instead desire a formalism that more symmetrically and naturally includes all contributions, so that consistent approximations can be more transparently applied. This also insures that as new problems are studied one does not accidentally neglect any relevant terms. Finally, although the transition rate approach is adequate for the calculation of many nonlinear coefficients, we are interested in a more generally applicable susceptibility formalism.

In recent work[14-16] we have presented a general susceptibility formalism that can address the various points outlined above, and we thus apply it here. From our calculation of $\chi^{(3)}(-\omega;\omega,\Omega,-\Omega)$ one can obtain both the nondegenerate absorption $\Delta\alpha(\omega,\Omega)$ and $\Delta n(\omega,\Omega)$, the third-order change in refraction at ω due to the presence of light at Ω. Our formalism automatically includes all distinct contributions to nonlinear coefficients, and so accounts for all Stark effect terms in $\chi^{(3)}$. More importantly, as we have previously discussed, our approach also

0163-1829/94/50(24)/18073(10)/$06.00

avoids the unphysical infrared divergences which generally plague the calculation of optical susceptibilities of insulators.[14–16] Hence, denoting the electric field as $|E_\Omega|$, we can extract a $n_2(\omega) \equiv \Delta n(\omega,\omega)/|E_\Omega|^2$, which is finite for $\omega \rightarrow 0$, in contrast to the previous work. Further, we also obtain two-band model predictions for the dc Kerr effect $\Delta n(\omega, 0)$, and the virtual photoconductivity $\Delta n(0,\Omega)$ discussed elsewhere,[17] both finite as $\omega, \Omega \rightarrow 0$. These refractive coefficients are well behaved since our $\Delta\alpha(\omega,\Omega)$ is itself finite as $\Omega \rightarrow 0$, implying that our results correct the Ω and ω dispersions of absorption previously quoted. Illustrative of this is that our $\Delta\alpha(\omega, 0)$ is consistent with the "second-order" contribution to the established Franz-Keldysh theory, which describes the change of absorption at ω due to a dc field.[18–20]

Our main emphasis in this paper is to understand the origin of the unphysical dispersions in the previous work, and how to correct them as simply as possible. Hence, we adopt a similar two-band model and also only consider the diagonal tensor component $\chi^{(3)}_{zzzz}$. So, in the limit of small linear absorption,[21] we find

$$\Delta n(\omega,\Omega) = I_\Omega \frac{24\pi^2}{c n_\omega n_\Omega} \mathrm{Re}\, \chi^{(3)}_{zzzz}(-\omega;\omega,\Omega,-\Omega), \qquad (1)$$

$$\Delta \alpha(\omega,\Omega) = I_\Omega \frac{48\pi^2 \omega}{c^2 n_\omega n_\Omega} \mathrm{Im}\, \chi^{(3)}_{zzzz}(-\omega;\omega,\Omega,-\Omega), \qquad (2)$$

where I_Ω is the irradiance of light at Ω, and n_ω, n_Ω are the relevant linear refractive indices. The formalism which we present, however, can be implemented with more sophisticated band structures, and to study other tensor components.[6,22] In the end, we show that it is primarily our use of the length gauge which leads to the various well behaved expressions, a gauge consequence reminiscent of findings in many atomic system studies.[23,24]

After reviewing the general formalism and describing the adopted two-band model in Sec. II, we explicitly derive the predicted expressions for the various $\chi^{(3)}$ contributions in Sec. III. In Sec. IV we include a discussion and compare to previously published results. We summarize in Sec. V.

II. GENERAL FORMALISM

A. Optical susceptibilities for crystals

The optical properties of solids are commonly studied theoretically in the velocity gauge, where the interaction enters as $-(e/mc)\mathbf{p}\cdot\mathbf{A}$, rather than the $-e\mathbf{r}\cdot\mathbf{E}$ appearing in the length gauge.[23] This is mainly because extended crystalline states cause complications when working with the position operator. Nevertheless, there are benefits to using the length gauge, and we have shown how its implementation need be no more difficult.[15,16] The essential points of our approach, which is similar to other formulations,[20,25,26] are summarized here.

The troublesome nature of the position operator in crystals can be illustrated by considering its Bloch state matrix elements $\langle n\mathbf{k}|\mathbf{r}|m\mathbf{k}'\rangle$; here $\langle \mathbf{r}|n\mathbf{k}\rangle \equiv e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$ is an eigenstate of bulk crystal Hamiltonian H_0 for band n energy $\hbar\omega_n(\mathbf{k})$, with normalization $\langle n\mathbf{k}|m\mathbf{k}'\rangle = \delta_{nm}\delta(\mathbf{k}-\mathbf{k}')$. It is convenient to separate $\mathbf{r}$ into intraband $\mathbf{r}_i$ and interband $\mathbf{r}_e$ pieces, $\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e$, where for crystals of interest here[27]

$$\langle n\mathbf{k}|\mathbf{r}_i|m\mathbf{k}'\rangle = \delta_{nm}\left[\delta(\mathbf{k}-\mathbf{k}')\xi_{nn} + i\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')\right], \qquad (3)$$

$$\langle n\mathbf{k}|\mathbf{r}_e|m\mathbf{k}'\rangle = (1-\delta_{nm})\delta(\mathbf{k}-\mathbf{k}')\xi_{nm}. \qquad (4)$$

The soon-to-be-discussed vectors ξ_{nm} have an implicit $\mathbf{k}$ dependence (to simplify notation, we suppress such $\mathbf{k}$ labels). The highly singular nature of $\mathbf{r}_i$, involving $\nabla_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}')$, generally makes $\mathbf{r}$ more difficult to manipulate than the momentum operator; note that $\langle n\mathbf{k}|\mathbf{p}|m\mathbf{k}'\rangle$ is simply

$$\langle n\mathbf{k}|\mathbf{p}|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')\mathbf{p}_{nm}, \qquad (5)$$

involving only $\delta(\mathbf{k}-\mathbf{k}')$ regardless of n and m. Further, all $\mathbf{p}_{nm}$ can be easily calculated from integrals over the unit cell volume V_c,

$$\mathbf{p}_{nm}(\mathbf{k}) = -i\hbar \int_{V_c} d^3r \;\; \psi^*_{n\mathbf{k}}(\mathbf{r})\nabla_{\mathbf{r}}\psi_{m\mathbf{k}}(\mathbf{r}), \qquad (6)$$

while the less familiar ξ_{nn} have an ambiguous phase sensitivity, and cannot be as conveniently calculated.[27]

In the end, however, these difficulties in the position operator need not prove troublesome. For example, to identify $\mathbf{r}_e$ define $\mathbf{r}_{nm} = (1-\delta_{nm})\xi_{nm}$, and use the commutator relation $[H_0, \mathbf{r}] = \frac{\hbar}{im}\mathbf{p}$ to discover the familiar relationship

$$\mathbf{r}_{nm} = \frac{\mathbf{p}_{nm}}{im\omega_{nm}}, \qquad (7)$$

where $\omega_{nm} \equiv \omega_n - \omega_m$.[28] Secondly, $\mathbf{r}_i$ is in practice no more difficult to deal with than $\mathbf{p}$ because one can arrange that $\mathbf{r}_i$ only appears in commutators with *simple* operators S [*simple* here is defined as meaning that matrix elements of S are analogous to Eq. (5)]. Such commutators $[\mathbf{r}_i, S]$ have matrix elements of the form

$$\langle n\mathbf{k}|[\mathbf{r}_i, S]|m\mathbf{k}'\rangle = \delta(\mathbf{k}-\mathbf{k}')i(S_{nm})_{;\mathbf{k}}, \qquad (8)$$

where the $;\mathbf{k}$ operation indicates the generalized derivative

$$(S_{nm})_{;\mathbf{k}} = \frac{\partial S_{nm}}{\partial \mathbf{k}} - iS_{nm}(\xi_{nn} - \xi_{mm}). \qquad (9)$$

This shows that if S is a simple operator the commutator $[\mathbf{r}_i, S]$ is also simple, and can be as easily manipulated as $\mathbf{p}$. Finally, as we later show, the diagonal elements ξ_{nn} never actually need to be explicitly calculated.

These realizations allow one to easily implement standard perturbation theory for the density operator ρ in the length gauge for crystals.[16] One can then obtain the mean microscopic current $\langle \mathbf{j}\rangle = \mathrm{Tr}(\mathbf{j}\rho)$ whose local spatial average $\langle\langle \mathbf{j}\rangle\rangle$ provides the macroscopic polarization density $\mathbf{P}$, since $d\mathbf{P}/dt \equiv \langle\langle \mathbf{j}\rangle\rangle$. From this one extracts the third-order susceptibility tensor, $P_d = \chi^{(3)}_{dcba}E_cE_bE_a$. The general expression is presented elsewhere[16] and shows that a diagonal element $\chi^{(3)}_{zzzz}(-\omega_d;\omega_c,\omega_b,\omega_a)$, where $\omega_d \equiv \omega_c + \omega_b + \omega_a$, can be most conveniently written as the sum of four contributions $\chi^{(3)} = \chi^{ee} + \chi^{ie} + \chi^{ei} + \chi^{ii}$. Here, we assume that only two bands exist, a filled valence band v and an empty conduction band c, and in the long-wavelength limit we find[16]

$$\chi^{ee} = \frac{e^4}{\hbar^3}\left(\frac{2}{\omega_3\omega_2}\right)\sum_{\mathbf{k}} |r^z_{cv}|^4\omega_{cv}\left[\left(\frac{1}{\omega_{cv}+\omega_3}-\frac{1}{\omega_{cv}-\omega_3}\right)\left(\frac{1}{\omega_{cv}-\omega_1}-\frac{1}{\omega_{cv}+\omega_1}\right)\right], \tag{10}$$

$$\chi^{ie} = \frac{e^4}{\hbar^3}\left(\frac{1}{\omega_3^2\omega_2}\right)\sum_{\mathbf{k}}\left(\frac{p^z_{cc}-p^z_{vv}}{m}\right)\left(\frac{|r^z_{cv}|^2}{\omega_{cv}-\omega_1}-\frac{|r^z_{cv}|^2}{\omega_{cv}+\omega_1}\right)_{;k^z}, \tag{11}$$

$$\chi^{ei} = \frac{e^4}{\hbar^3}\left(\frac{1}{\omega_3^2}\right)\sum_{\mathbf{k}}\left(\frac{p^z_{vv}-p^z_{cc}}{m}\right)\left[\frac{r^z_{vc}}{\omega_{cv}-\omega_2}\left(\frac{r^z_{cv}}{\omega_{cv}-\omega_1}\right)_{;k^z}+\frac{r^z_{cv}}{\omega_{cv}+\omega_2}\left(\frac{r^z_{vc}}{\omega_{cv}+\omega_1}\right)_{;k^z}\right], \tag{12}$$

$$\begin{aligned}\chi^{ii} = \frac{e^4}{\hbar^3}\left(\frac{1}{\omega_3}\right)\sum_{\mathbf{k}}\Bigg[&\left(\frac{\omega_{cv}r^z_{vc}}{\omega_{cv}-\omega_3}\right)_{;k^z}\frac{1}{\omega_{cv}-\omega_2}\left(\frac{r^z_{cv}}{\omega_{cv}-\omega_1}\right)_{;k^z}\\ &-\left(\frac{\omega_{cv}r^z_{cv}}{\omega_{cv}+\omega_3}\right)_{;k^z}\frac{1}{\omega_{cv}+\omega_2}\left(\frac{r^z_{vc}}{\omega_{cv}+\omega_1}\right)_{;k^z}\Bigg].\end{aligned} \tag{13}$$

In these expressions $\omega_1 = \omega_a$, $\omega_2 = \omega_b + \omega_a$, and $\omega_3 = \omega_c + \omega_b + \omega_a$; intrinsic permutation symmetry is yet to be incorporated. Divergences for ω_1, ω_2, or ω_3 approaching zero are apparent here. These are similar to the secular divergences discussed elsewhere[29] since, as we show in Sec. IV, the properly symmetrized expressions are finite in these limits for the cases of interest here. Lastly, we comment that while the splitting of the total $\chi^{(3)}$ into the above four terms is primarily for convenience here, there are some conceptual advantages to such a decomposition as well.[14,16]

B. Two-band model details

In order to evaluate the above expressions we must model the $\mathbf{k}$ dependent ω_{cv}, r^z_{cv}, p^z_{nn}, and in principle the ξ_{nn}. These quantities should be determined so that they are consistent among themselves, and with the two-band assumption. These requirements can best be illustrated by considering the commutator identity $[r^a, p^b] = i\hbar\delta^{ab}$. That is, decompose $\mathbf{r}$ into intraband and interband components, and then take matrix elements of the relation, $\langle n\mathbf{k}|[r^a,p^b]|m\mathbf{k}'\rangle = i\hbar\delta^{ab}\delta_{nm}\delta(\mathbf{k}-\mathbf{k}')$. Such matrix elements, and some simple algebra, lead to the following two-band relations,

$$\frac{1}{\hbar}\frac{\partial^2\omega_c}{\partial k^a\partial k^b} = \frac{1}{m}\delta^{ab} + \frac{\omega_{cv}}{\hbar}\left(r^a_{cv}r^b_{vc}+r^a_{vc}r^b_{cv}\right), \tag{14}$$

$$\frac{1}{\hbar}\frac{\partial^2\omega_v}{\partial k^a\partial k^b} = \frac{1}{m}\delta^{ab} - \frac{\omega_{cv}}{\hbar}\left(r^a_{cv}r^b_{vc}+r^a_{vc}r^b_{cv}\right), \tag{15}$$

$$(r^b_{cv})_{;k^a} = -\frac{1}{\omega_{cv}}\left(r^a_{cv}\frac{\partial\omega_{cv}}{\partial k^b}+r^b_{cv}\frac{\partial\omega_{cv}}{\partial k^a}\right), \tag{16}$$

where we have used Eq. (7) and the fact that $p^b_{nn}/m = \partial\omega_n/\partial k^b$. Equations (14) and (15) are familiar as just the (possibly $\mathbf{k}$ dependent) inverse electron effective mass tensors m_c^{-1} and m_v^{-1}. Adding Eqs. (14) and (15) shows that the two-band assumption imposes a certain symmetry, $m_c^{-1} + m_v^{-1} = 2m^{-1}$, on these bands. Note, more importantly, that the less familiar Eq. (16) can be used in Eqs. (10)–(13) so that strictly the ξ_{nn} never need to be explicitly calculated.

Equations (14)–(16) represent the self-consistent two-band model equations for ω_c, ω_v, and $\mathbf{r}_{cv}$. Rather than obtaining a solution to these equations, it is more common to adopt a simple model which mirrors the actual bands of interest. Hence one often adopts constant diagonal effective mass tensors (consistent with $m_c^{-1}+m_v^{-1} = 2m^{-1}$), which leads to the parabolic, isotropic dispersion

$$\hbar\omega_{cv} = E_g + \frac{\hbar^2k^2}{2m_{cv}}, \tag{17}$$

where $m_{cv}^{-1} \equiv m_c^{-1} - m_v^{-1}$. Further, the involved valence band is considered to be light-hole-like so that the vector $\mathbf{r}_{cv}$ is taken to be in the radial $\hat{\mathbf{k}}$ direction;[9] its magnitude is then inferred from Eqs. (14) and (15),

$$|\mathbf{r}_{cv}|^2 = \left(\frac{\hbar}{4m_{cv}\omega_{cv}}\right). \tag{18}$$

One often also approximates the ω_{cv} in the denominator above by simply $E_g/\hbar$. Unfortunately, although the above described model is often used, it is strictly not consistent with the exact two-band expressions of Eqs. (14)–(16). One minor problem is the parabolicity of Eq. (17). For example, consider the one-dimensional case, and apply another $;k$ operation to Eqs. (14) and (15) (equivalently, these are matrix elements of a "higher-order" commutator, $\langle nk|[r_i,[r,p]]|nk'\rangle = 0$), subtract the results, and use Eq. (16) to find that

$$\frac{\partial^3\omega_{cv}}{\partial k^3} = -12|r_{cv}|^2\frac{\partial\omega_{cv}}{\partial k}. \tag{19}$$

This implies that a parabolic dispersion cannot be exact, which is not surprising since a solution of Eqs. (14)–(16) is analogous to solving a coupled two-band problem; such an analysis shows that parabolicity is only valid for small enough k. A second problem with the dispersion in Eq. (17) and the assumed radial $\mathbf{r}_{cv}$ is the three-dimensional isotropicity it implies. This is also inconsistent with Eqs. (14)–(16). For example, with this model a diagonal element (say, $a = b = z$) of Eq. (14) has a left-hand side which is the constant m_c^{-1}, while the right-hand side is angularly dependent since $|r^z_{cv}|^2 \propto |\hat{z}\cdot\hat{\mathbf{k}}|^2$.

This shows that, even in the parabolic limit, the isotropic dispersion in Eq. (17) is strictly not a possible solution to Eqs. (14)–(16).[30]

Recalling that Eqs. (14)–(16) originate from the commutator $[r^a, p^b] = i\hbar\delta^{ab}$, the above inconsistencies can be restated more dramatically: the parabolic, isotropic two-band model does not formally satisfy $[r^a, p^b] = i\hbar\delta^{ab}$. Indeed, Eqs. (14)–(16) can be considered sum rules, and the above statement is completely analogous to the breakdown of the Thomas-Reiche-Kuhn sum rule which strictly occurs for the two level atom.[31] Further considerations show that the problem can also be viewed as the fact that matrix elements of $[\mathbf{r}_i, \mathbf{p}_i]$, $[\mathbf{r}_i, \mathbf{p}_e]$, and $[\mathbf{r}_e, \mathbf{p}_i]$ are being treated at a different level of approximation than matrix elements of $[\mathbf{r}_e, \mathbf{p}_e]$. Despite these problems we choose to adopt the simple parabolic, isotropic two-band model for several reasons. First, we would like to compare to previous work[9,10] and so should employ a similar band-structure model. Second, the bands of interest are well represented by the parabolic, isotropic dispersions, while dispersions more consistent with Eqs. (14)–(16) are qualitatively different. Lastly, this parabolic, isotropic two-band model illustrates the common, general situation: even in more sophisticated models the band structure is approximated as best as possible, and usually does not represent a self-consistent solution to the analogs of Eqs. (14)–(16).

Hence, aware of the problems with this model, we cautiously proceed and identify possible problems as they arise. Realize, however, that we are not limited to this simple band-structure model, and our technique could be used in the future with more sophisticated band structures. Indeed, while the isotropic model used here may give an adequate description of the diagonal $\chi^{(3)}_{zzzz}$ components, more accurate band structures should obviously be used to study other tensor components.[6,7]

III. EVALUATION OF $\chi^{(3)}(-\omega;\omega,\Omega,-\Omega)$

A. Nondegenerate absorption $\Delta\alpha(\omega,\Omega)$

The third-order nondegenerate absorption $\Delta\alpha(\omega,\Omega)$ can be obtained by investigating the resonances in the imaginary part of $\chi^{(3)}(-\omega;\omega,\Omega,-\Omega)$. Equations (10)–(13) show that resonances occur when $\omega_{cv}{=}\omega_1$, ω_2, or ω_3, which were defined as one, a sum of two, or a sum of three of the frequencies involved, respectively. Here, as in the previous work,[9,10] we are interested in $\hbar\Omega < E_g$, and for definiteness we take both $\omega, \Omega \geq 0$. Hence, resonances can occur for $\omega_{cv}{=}\omega - \Omega$, ω, or $\omega + \Omega$; these are labeled the electronic Raman effect, Stark effect, and two-photon absorption, respectively. Since some of the manipulations involving the $;\mathbf{k}$ operation are not standard, we describe the calculation in some detail.

Consider first the ω_2 resonances, which lead to the two-photon absorption and electronic Raman effects and are the easiest to obtain and describe. Such ω_2 resonances are clearly only possible in the χ^{ei} and χ^{ii} terms of Eqs. (12) and (13). In these equations a $;k^z$ operator does not act on the ω_2 resonant factors, and so does not complicate the evaluation significantly; one only need use Eq. (16) to reveal the relevant $;k^z$ affected matrix elements. Hence, since we have already implicitly assumed the limit of infinite crystal volume V, each $\mathbf{k}$ sum in Eqs. (10)–(13) is interpreted in the standard way, accounting for spin, as representing

$$\frac{1}{V}\sum_{\mathbf{k}} = \frac{2}{8\pi^3}\int d^3k. \tag{20}$$

The resonances are also treated in the usual way since we have assumed that frequencies have a small imaginary component, and use the identity

$$\lim_{\epsilon\to 0}\frac{1}{E+i\epsilon} = \mathcal{P}\frac{1}{E} - i\pi\delta(E). \tag{21}$$

Still leaving the incorporation of permutation symmetry as a last step, this leads to ω_2 resonant contributions

$$\mathrm{Im}\,\chi^{ei} = 6C\frac{(\omega_2 - E_g/\hbar)^{\frac{3}{2}}}{\omega_3^2\omega_2\omega_{21}}\left(\frac{2}{\omega_2} + \frac{1}{\omega_{21}}\right), \tag{22}$$

$$\mathrm{Im}\,\chi^{ii} = -6C\frac{(\omega_2 - E_g/\hbar)^{\frac{3}{2}}}{\omega_3\omega_{32}\omega_{21}}\left(\frac{1}{\omega_2} - \frac{1}{\omega_{32}}\right)\left(\frac{2}{\omega_2} + \frac{1}{\omega_{21}}\right), \tag{23}$$

where $\omega_{ij} \equiv \omega_i - \omega_j$ and the constant

$$C = \frac{e^4}{\pi\hbar^2 30\sqrt{2\hbar m_{cv}}}. \tag{24}$$

Now for two-photon absorption $\omega_2 = \omega + \Omega$, so ω_1 is either ω or Ω; both must be considered to insure intrinsic permutation symmetry. Adding all terms we get that the dispersion of two-photon absorption is given by

$$(\mathrm{Im}\,\chi)^T = C\frac{(\omega+\Omega)^3}{\omega^4\Omega^4}(\omega + \Omega - E_g/\hbar)^{\frac{3}{2}}. \tag{25}$$

The electronic Raman effect is obtained by simply changing Ω to $-\Omega$, this gives

$$(\mathrm{Im}\,\chi)^R = C\frac{(\omega-\Omega)^3}{\omega^4\Omega^4}(\omega - \Omega - E_g/\hbar)^{\frac{3}{2}}. \tag{26}$$

Here our only comment is that if we went beyond a simple parabolic approximation in Eq. (17) then higher-order powers (> 3/2) would be introduced.

Obtaining the Stark terms requires much more algebra, but is not difficult. Resonances at ω can come from both ω_3 and ω_1 for this case of $\chi^{(3)}(-\omega;\omega,\Omega,-\Omega)$, and all four terms $\chi^{ee}, \chi^{ie}, \chi^{ei}, \chi^{ii}$ have Stark contributions. Further, one must now deal with the possibility that the $;k^z$ operator acts on a resonant factor, which complicates the situation by introducing higher-order poles since

$$\frac{\partial}{\partial k^z}\left(\frac{1}{\omega_{cv}-\omega}\right) = -(\omega_{cv}-\omega)^{-2}\frac{\partial\omega_{cv}}{\partial k^z}. \tag{27}$$

Strictly, we could avoid this problem by using partial integrations to move the k^z derivative (one can easily show that the entire $;k^z$ operator can be moved in this way) away from the resonant factor of interest; in fact, such manipulations were used to obtain the particular form of χ^{ei}, χ^{ii} in Eqs. (12) and (13), which we have seen simplifies the ω_2 resonance evaluation. However, one must be careful about such partial integrations in general since the resulting different expressions, although formally equivalent, can lead to different answers in a model calculation. This discrepancy arises since, as discussed in Sec. II B, the parabolic, isotropic two-band model treats matrix elements of $[\mathbf{r}_e, \mathbf{p}_e]$ differently than those of $[\mathbf{r}_i, \mathbf{p}_e]$, $[\mathbf{r}_e, \mathbf{p}_i]$, and $[\mathbf{r}_i, \mathbf{p}_i]$; although not obvious, this implies that distinct approximations will be introduced into the (partial integration) related expressions. Nevertheless, we can avoid significant problems in our scheme by not performing any partial integration rearrangements of the adopted expressions. For example, the Stark contributions of χ^{ei}, χ^{ii} are evaluated from the same expressions [Eqs. (12) and (13)] used to derive Eqs. (25) and (26). This insures that the two-photon absorption, electronic Raman, and Stark effects are evaluated at the same level of approximation, and that the $\Omega = 0$ limit is then well described; for $\Omega = 0$ the three effects are indistinguishable.

Hence, whenever higher-order poles appear,[32] we treat them instead by using relations such as

$$\left(\frac{1}{\omega_{cv} - \omega}\right)^{n+1} = \frac{1}{n!}\frac{\partial^n}{\partial\omega^n}\left(\frac{1}{\omega_{cv} - \omega}\right), \tag{28}$$

which again let the $\mathbf{k}$ sum be easily done for the simple pole, and leaving derivatives to be applied in the end. This outlines a method which consistently applies similar approximations to each of the Raman, Stark and two-photon absorption contributions. We admit, however, that it is still open to the nontrivial objection that different, formally equivalent expressions (those related by partial integrations) lead to different answers. We do not regard this as too troublesome since it is clear that the discrepancies are due to the model inconsistencies; this is very similar to the situation in a two-level atom calculation.[31] Further, the answers which arise from the formally equivalent expressions are not drastically different; either constants arising from angular integrations in $\mathbf{k}$ space are slightly modified, or extra terms arise which can be ignored in light of the parabolic approximation. Again, since our main goal here is to compare to the previous work, we proceed and discuss these points further in Sec. IV.

We simply state our Stark results here, but quote the $\chi^{ee}, \chi^{ie}, \chi^{ei}, \chi^{ii}$ contributions separately in order to allow independent verification. From χ^{ee} we find

$$(\mathrm{Im}\,\chi^{ee})^S = 2C\frac{(\omega - E_g/\hbar)^{\frac{1}{2}}}{\omega^2(\omega+\Omega)(\omega-\Omega)} - C\frac{(\omega - E_g/\hbar)^{-\frac{1}{2}}}{\omega(\omega+\Omega)(\omega-\Omega)}. \tag{29}$$

We do remark that to obtain the above result one must be careful to avoid the $\omega_2 = 0$ secular divergences discussed elsewhere.[29] Next we find from χ^{ei} and χ^{ie}

$$(\mathrm{Im}\,\chi^{ie})^S = -6C\frac{(\omega - E_g/\hbar)^{\frac{3}{2}}}{\omega^3(\omega+\Omega)(\omega-\Omega)} - 3C\frac{(\omega - E_g/\hbar)^{\frac{1}{2}}}{\omega^2(\omega+\Omega)(\omega-\Omega)}, \tag{30}$$

$$(\mathrm{Im}\,\chi^{ei})^S = -2C\frac{(\omega - E_g/\hbar)^{\frac{3}{2}}}{\omega^3\Omega^2}, \tag{31}$$

while from χ^{ii} we have the contribution

$$\begin{aligned}(\mathrm{Im}\,\chi^{ii})^S = {} & 2C\frac{(\omega - E_g/\hbar)^{\frac{3}{2}}}{\omega^3(\omega+\Omega)(\omega-\Omega)} \\ & -3C\frac{(\omega - E_g/\hbar)^{\frac{1}{2}}}{\omega^2(\omega+\Omega)(\omega-\Omega)} \\ & -4C\frac{(\omega - E_g/\hbar)^{\frac{3}{2}}}{\omega^3\Omega^2} - 2C\frac{(\omega - E_g/\hbar)^{\frac{3}{2}}}{\omega\Omega^4} \\ & -9C\frac{(\omega - E_g/\hbar)^{\frac{1}{2}}}{\omega^2\Omega^2} - 3C\frac{(\omega - E_g/\hbar)^{-\frac{1}{2}}}{4\omega\Omega^2}.\end{aligned} \tag{32}$$

We have found the algebra is simplified by introducing permutation symmetry only as a last step, but that it is convenient to consider the case $\omega_1 = \omega_3$ separately from $\omega_1 \neq \omega_3$. The total Stark effect contribution to Im $\chi^{(3)}$ is then $(\mathrm{Im}\,\chi)^S$, which is the sum of Eqs. (29)–(32).

We can now obtain $\Delta\alpha(\omega,\Omega)$ from Eq. (2) using the result that $\mathrm{Im}\,\chi^{(3)} = (\mathrm{Im}\,\chi)^R + (\mathrm{Im}\,\chi)^S + (\mathrm{Im}\,\chi)^T$. We find that each of the two-photon absorption, electronic Raman, and Stark effects can be written in the form

$$\Delta\alpha(\omega,\Omega) = 2K\frac{\sqrt{E_p}}{n_\omega n_\Omega E_g^3}F_2(\hbar\omega/E_g, \hbar\Omega/E_g)I_\Omega, \tag{33}$$

where[33]

$$K = \frac{4}{5}\left(\frac{\pi e^4}{c^2\sqrt{m}}\right). \tag{34}$$

As previously noticed, this form displays the material scaling properties since $F_2(x,y)$ is a dimensionless function of dimensionless variables, and $E_p \equiv 2|p_{cv}^0|^2/m$ is common for many materials; here $|p_{cv}^0|^2$ denotes the value of $|p_{cv}|^2$ at $\mathbf{k} = 0$.[9] Our results for $F_2(x,y)$ are summarized in Table I, and will be discussed further in Sec. IV.

B. Nondegenerate refraction $\Delta n(\omega,\Omega)$

The real part of $\chi^{(3)}(-\omega;\omega,\Omega,-\Omega)$ or the nondegenerate refraction $\Delta n(\omega,\Omega)$ could in principle be obtained directly from Eqs. (10)–(13). However, we can also use a Kramers-Kronig transformation since we have already calculated the imaginary part of $\chi^{(3)}$. In this latter approach, we find that all three of $(\mathrm{Im}\,\chi)^R$, $(\mathrm{Im}\,\chi)^S$, and $(\mathrm{Im}\,\chi)^T$ provide a contribution which can be written as

$$\Delta n(\omega,\Omega) = K\frac{\hbar c\sqrt{E_p}}{n_\omega n_\Omega E_g^4}G_2(\hbar\omega/E_g, \hbar\Omega/E_g)I_\Omega, \tag{35}$$

where $G_2(x,y)$ is again a dimensionless function,

$$G_2(x,y) = \frac{2}{\pi}\mathcal{P}\int_0^\infty \frac{F_2(z,y)}{z^2 - x^2}dz. \tag{36}$$

TABLE I. Nondegenerate absorption dispersion function $F_2(x,y)$ as derived in this paper. The analogous results from Ref. 10, scaled by a constant factor, are also shown.

Contribution	$F_2(x,y)$ derived here	$F_2(x,y)$ of Ref. 10
Two-photon absorption $x+y \geq 1$	$\frac{(x+y)^3}{x^3y^4}(x+y-1)^{\frac{3}{2}}$	$\frac{(x+y)^2}{x^3y^4}(x+y-1)^{\frac{3}{2}}$
Raman $x-y \geq 1$	$\frac{(x-y)^3}{x^3y^4}(x-y-1)^{\frac{3}{2}}$	$\frac{(x-y)^2}{x^3y^4}(x-y-1)^{\frac{3}{2}}$
Stark $x \geq 1$	$-4\frac{(x-1)^{\frac{3}{2}}}{x^2(x+y)(x-y)} - 4\frac{(x-1)^{\frac{1}{2}}}{x(x+y)(x-y)} - \frac{(x-1)^{-\frac{1}{2}}}{(x+y)(x-y)}$ $-2\frac{(x-1)^{\frac{3}{2}}}{y^4} - 6\frac{(x-1)^{\frac{3}{2}}}{x^2y^2} - 9\frac{(x-1)^{\frac{1}{2}}}{xy^2} - \frac{3}{4}\frac{(x-1)^{-\frac{1}{2}}}{y^2}$	$\frac{(x-1)^{\frac{1}{2}}}{x(x+y)^2(x-y)^2}$ $-2\frac{(x-1)^{\frac{3}{2}}}{xy^4} + \frac{1}{2}\frac{(x-1)^{\frac{1}{2}}}{xy^2(x+y)(x-y)} - \frac{1}{4}\frac{(x-1)^{-\frac{1}{2}}}{y^2(x+y)(x-y)}$

This is similar to the results of Sheik-Bahae *et al.*,[9] and all of the relevant integrals can be performed as described there.[34] Our results for the $G_2(x,y)$ expressions are summarized in Table II and also discussed further in the next section.

IV. DISCUSSION

In this section we will compare our derived $\Delta\alpha(\omega,\Omega)$ and $\Delta n(\omega,\Omega)$ to those previously quoted in the literature. Along with understanding the differences in these expressions, we also wish to illustrate how our general nondegenerate dispersions are consistent with physical expectations and with certain well-known results in the limits $\Omega \to 0$ and/or $\omega \to 0$. We begin by comparing our $\Delta\alpha(\omega,\Omega)$ with that obtained by Sheik-Bahae *et al.*,[9,10] both results are given in Table I. We contrast these dispersions in Fig. 1 by plotting their respective degenerate two-photon absorption, $F_2(x,x)$, below the band gap; for the comparison we have normalized these curves to the same peak value. We can identify two distinct reasons for the differences in Table I. The first minor difference arises since in the previous work[9,10] one or more factors of ω_{cv} have effectively been approximated as simply $E_g/\hbar$; these factors arise from the value for $|\mathbf{r}_{cv}|^2$, or analogously $|\mathbf{p}_{cv}|^2$, as in Eq. (18). Such an approximation is often adopted and not completely inappropriate here as it does lead to the correct material scaling prediction. However, the predicted dispersions are modified by this approximation; if we "correct" the results

TABLE II. Nondegenerate refraction dispersion function $G_2(x,y)$. We are interested in $x<1$ and $y<1$ here and it is to be understood that the $(1-x-y)^{\frac{3}{2}}$ term in $T(x,y)$ only contributes for $1-x-y \geq 0$.

Contribution	$G_2(x,y)$ derived here
Two-photon absorption	$T(x,y)+T(-x,y)$
Raman	$T(x,-y)+T(-x,-y)$
Stark	$S(x,y)+S(-x,y)+S(x,-y)+S(-x,-y)$

where
$$T(x,y) = \frac{(x+y)^3}{y^4x^4}(1-x-y)^{\frac{3}{2}} - \left[\frac{1}{yx^4} + \frac{3}{y^3x^2}\right](1-y)^{\frac{3}{2}} + \frac{9}{2y^2x^2}(1-y)^{\frac{1}{2}} - \frac{3}{8yx^2}(1-y)^{-\frac{1}{2}}$$

and
$$S(x,y) = -\left[\frac{1}{y^4x} + \frac{3}{y^2x^3}\right](1-x)^{\frac{3}{2}} + \frac{9}{2y^2x^2}(1-x)^{\frac{1}{2}} - \frac{3}{8y^2x}(1-x)^{-\frac{1}{2}} - \frac{4}{y^2x^2}$$
$$+\frac{1}{x^2-y^2}\left[\frac{2}{y^3}(1-y)^{\frac{3}{2}} - \frac{2}{x^3}(1-x)^{\frac{3}{2}} - \frac{2}{y^2}(1-y)^{\frac{1}{2}} + \frac{2}{x^2}(1-x)^{\frac{1}{2}} + \frac{1}{2y}(1-y)^{-\frac{1}{2}} - \frac{1}{2x}(1-x)^{-\frac{1}{2}}\right]$$

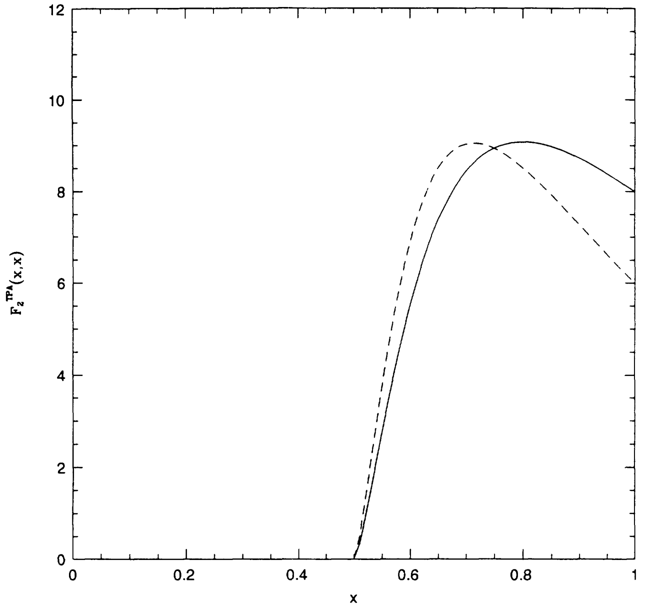

FIG. 1. The two-photon absorption dispersion function $F_2^{\mathrm{TPA}}(x,x)$ versus x of this paper (solid) is compared to previous results of Ref. 10 (dashed), which have been normalized to the same peak height.

of Sheik-Bahae *et al.*[9,10] for this approximation we find that their two-photon and electronic Raman dispersions agree with our results. In contrast, the similarly "corrected" Stark effect dispersions still differ from our results, and so a second reason for discrepancies must be found. Perhaps the most striking illustration of these remaining discrepancies is that the total (corrected or uncorrected) $\Delta\alpha(\omega,\Omega)$ of Sheik-Bahae *et al.*[9,10] diverges as $\Omega \rightarrow 0$, while our $\Delta\alpha(\omega,0)$ is finite. Indeed, we physically expect this to be finite for insulators. This quantity, or Im $\chi^{(3)}(-\omega;\omega,0,0)$, should be related to the relevant (second order in the dc field) contribution to the Franz-Keldysh effect. This situation is also similar to recent findings in a Pockels effect study[11] where an analogous quantity, Im $\chi^{(2)}(-\omega;\omega,0)$, has also been shown to be finite in clean, cold semiconductors.

The unphysical divergence which plagues the $\Delta\alpha(\omega,\Omega)$ of Sheik-Bahae *et al.*[9,10] as $\Omega \rightarrow 0$ also infects their $\Delta n(\omega,\Omega)$. In fact, both are examples of a very common problem which we have discussed at length elsewhere.[14,16] We have shown that such problems are a consequence of using approximate band structures and opting to work in the velocity gauge. This can be described schematically by considering $\chi_{\mathbf{p}\cdot\mathbf{A}}$ and $\chi_{\mathbf{r}\cdot\mathbf{E}}$, the susceptibilities obtained through the velocity and length gauges, respectively. We find that

$$\chi_{\mathbf{p}\cdot\mathbf{A}} = \chi_{\mathbf{r}\cdot\mathbf{E}} + \mathcal{R}, \tag{37}$$

where as expected by gauge invariance $\mathcal{R}$ is strictly zero. However, it is easy to show that the vanishing of $\mathcal{R}$ relies on commutator identities, such as $[r^a, p^b] = i\hbar\delta^{ab}$, $[r^c,[r^a,p^b]] = 0$, and so on. Hence, the implied breakdown of such commutators (as discussed in Sec. II B) in our approximate two-band model leads to dramatic qualitative problems when using the velocity gauge. That is, $\mathcal{R}$ does not vanish, which proves very troublesome since $\mathcal{R}$ is also proportional to powers of the vector potential, $Ae^{-i\Omega t} = Ee^{-i\Omega t}/\Omega$, and so diverges for $\Omega \rightarrow 0$. Hence, this unphysical divergence is introduced into $\chi_{\mathbf{p}\cdot\mathbf{A}}$ through Eq. (37). In contrast, we employ the length gauge and find that the formal loss of identities such as $[r^a, p^b] = i\hbar\delta^{ab}$ in this two-band model lead only to much subtler problems. [For example, recall the discussion in Sec. III regarding the ambiguity in the evaluation of Eqs. (10)–(13) if partial integrations are performed; similar ambiguities have been noted in a model calculation for a two-level atom.[31]] Quite distinct effects seen in other systems can also be interpreted as manifestations of these same issues.[16,23,24,31,35] In general, the problems seen here would be avoided if one could instead employ an approximate band structure which *is* consistent with $[r^a, p^b] = i\hbar\delta^{ab}$, as both gauges would then lead to the same divergence-free expressions. As discussed in Sec. II B, this is not our main goal and regardless, the expressions we derive can be considered realistic, physically well-behaved approximations.

Proceeding, we find that after taking the limit $\Omega \rightarrow 0$ we are left with a $\Delta\alpha(\omega,0)$ described by

$$\begin{aligned} F_2(x,0) = &-\frac{4}{x^4}(x-1)^{\frac{3}{2}} - \frac{1}{x^3}(x-1)^{\frac{1}{2}} \\ &+\frac{5}{4x^2}(x-1)^{-\frac{1}{2}} - \frac{3}{8x}(x-1)^{-\frac{3}{2}} \\ &+\frac{3}{64}(x-1)^{-\frac{5}{2}}, \end{aligned} \tag{38}$$

which of course is only valid above the band gap, $x \geq 1$. Note that the last term above leads to a strong positive band-edge divergence, as illustrated in Fig. 2. This

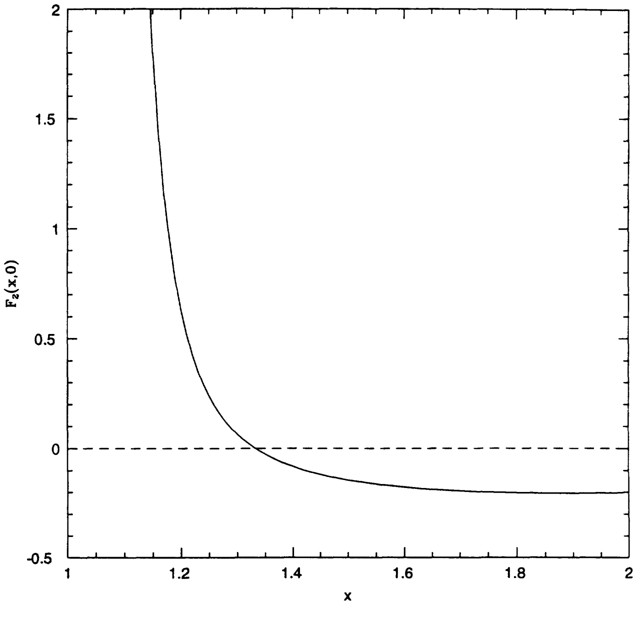

FIG. 2. A plot of the dispersion of the nonlinear absorption change $F_2(x,0)$ versus x above the band gap.

is qualitatively in agreement with the Franz-Keldysh effect,[18,19] which predicts absorption into the band gap, similar to a redshift of the band edge. Note also how this constrasts with the band-edge blueshift associated with the Stark effect indicated by the negative band-edge divergence of $F_2(x,y)$ for $y \neq 0$.[9] Further, we can even compare our results somewhat quantitatively with the Franz-Keldysh predictions. Of course, the Franz-Keldysh theory is formulated by treating the intraband perturbation of the dc field exactly, but the weak dc field limit of the Franz-Keldysh effect (to second order in the dc field) has also been discussed by Aspnes and Rowe.[20] There it is shown that the strong band-edge divergence indeed has a $(\hbar\omega - E_g)^{-\frac{5}{2}}$ dependence, in agreement with our results in Eq. (38). This dispersion eventually leads to the familiar result that electroreflectance resembles the third derivative of the linear absorption or joint density of states. The additional terms of $F_2(x,0)$ which we find in Eq. (38) are not described by Aspnes and Rowe[20] since there many small contributions were neglected. We only comment that the alternating signs in the band-edge resonant terms of Eq. (38) are already suggestive at this second-order level of the the absorption oscillations seen in the strong field Franz-Keldysh effect;[36] this is also illustrated by the sign reversal in Fig. 2.

We next consider the nondegenerate refraction $\Delta n(\omega,\Omega)$ and its comparison to the previously quoted expressions. Again we find that the expressions of Sheik-Bahae *et al.*[9,10] have certain zero divergences which our expressions lack. In the previous work, such divergences were realized to be unphysical and were removed in each of the electronic Raman, two-photon absorption, and Stark effect terms separately. However, our results show that such a removal is somewhat unphysical as these three terms need not be separately finite. Hence, this artificial divergence removal makes a direct term by term comparison of earlier results[9,10] with our expressions meaningless. Further, even the total "divergence-free" $\Delta n(\omega,\Omega)$ from the previous work will differ substantially from our results due to its use of the $\omega_{cv} \approx E_g/\hbar$ approximation which we have discussed above. For these reasons we instead concentrate on graphical comparisons between our results here, and quote the physically well-behaved expressions for $\Delta n(\omega,\omega)$, $\Delta n(\omega,0)$, and $\Delta n(0,\Omega)$ which we can obtain.

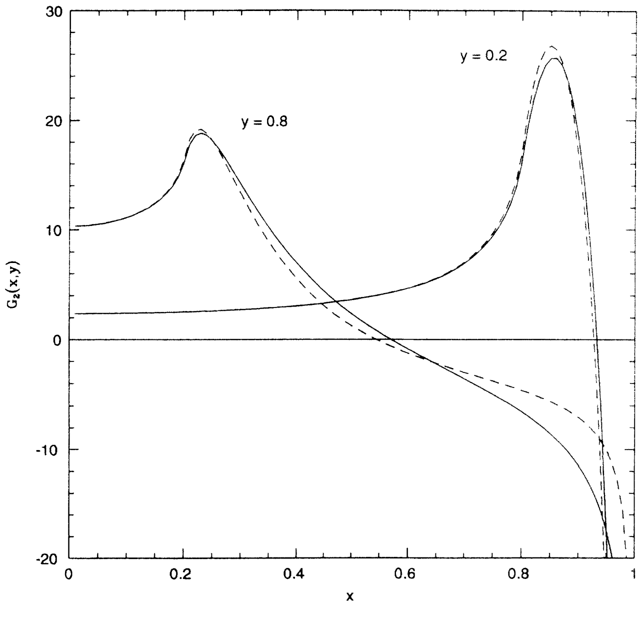

FIG. 3. The dispersion of nondegenerate nonlinear refraction $G_2(x,y)$ versus x for two values $y = 0.2$ and $y = 0.8$ is shown by the solid lines. The dashed lined lines corresponds to the results in Ref. 10, which have been normalized at zero frequency.

Our general nondegenerate refraction $\Delta n(\omega,\Omega)$ is illustrated in Fig. 3 for the particular choices $\hbar\Omega = 0.2E_g$ and $\hbar\Omega = 0.8E_g$. We have also plotted the corresponding curves from Sheik-Bahae *et al.*,[10] where for comparison purposes their expressions are normalized to ours at zero frequency. These curves are seen to be qualitatively similar, with the most significant difference being the behavior near the band edge. Consider next the special case of the degenerate nonlinear refractive index ($\Omega = \omega$), which is equivalent to the $n_2(\omega)$ coefficient, $\Delta n(\omega) \equiv \Delta n(\omega,\omega)/2 \equiv n_2(\omega)|E_\omega|^2/2$.[9] We find that the dispersion of this nonlinear self-refractive effect is described by $G_2(x,x) = g(x) + g(-x)$, where

$$g(x) = -\frac{8}{x^4} - \frac{10}{x^5}(1-x)^{\frac{3}{2}} + \frac{8}{x^5}(1-2x)^{\frac{3}{2}} + \frac{17}{x^4}(1-x)^{\frac{1}{2}} - \frac{2}{x^3}(1-x)^{-\frac{1}{2}} - \frac{1}{4x^2}(1-x)^{-\frac{3}{2}}. \tag{39}$$

Again, this expression is finite at $\omega = 0$, and the expression for $n_2(0)$ is similar to a previous estimate.[37] In contrast, the $n_2(\omega)$ of Sheik-Bahae *et al.*[9,10] formally diverges, and the divergence had to be removed by hand; we compare this against our result (again normalized at zero frequency) in Fig. 4. We again see the qualitative agreement of the two curves, which is reassuring since the previous results are in excellent agreement with experimental results for many materials.[9,10] New behavior in our $n_2(\omega)$ near the band edge may help explain some of the experimental data for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$,[38,9] but one should remember the crudeness of this two-band model and the independent-particle approximation. Indeed, even though our results modify the predicted $\Delta n(\omega,\Omega)$, as in the earlier work[9,10] we also find that absolute agreement with experiments requires a more sophisticated model (for example, including the heavy holes[6,7] and possibly excitonic effects[10]). Other many body effects which will introduce dephasing times and broadening may also be important.

Our physically well-behaved expressions also allow us to unambiguously evaluate $\Delta n(\omega,0)$, which describes the dc Kerr effect, or the change in the refractive index at ω to second order in the dc field. Again we note that the results of Sheik-Bahae *et al.*[9,10] are formally divergent in this $\Omega \to 0$ limit, but here we find $G_2(x,0) = k(x) + k(-x)$, where

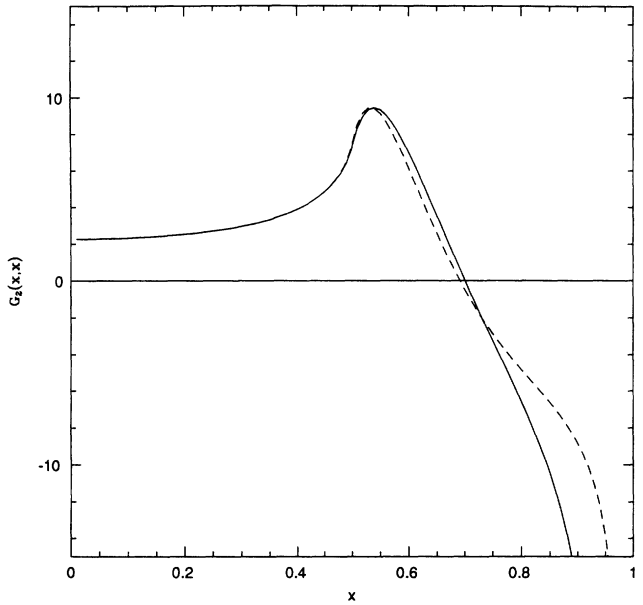

FIG. 4. The nonlinear refraction dispersion $G_2(x,x)$ versus x predicted in this paper (solid) and from Ref. 10 (dashed), which has been normalized at zero frequency.

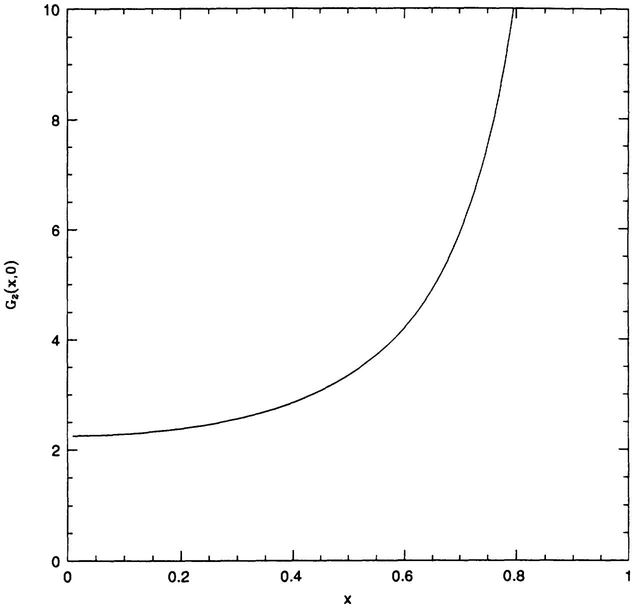

FIG. 5. A plot of the below band-gap dc Kerr effect $G_2(x,0)$ versus x.

$$\begin{aligned} k(x) = &-\frac{7}{x^4} - \frac{5}{8x^2} - \frac{4}{x^5}(1-x)^{\frac{3}{2}} + \frac{1}{x^4}(1-x)^{\frac{1}{2}} \\ &+\frac{5}{4x^3}(1-x)^{-\frac{1}{2}} + \frac{3}{8x^2}(1-x)^{-\frac{3}{2}} \\ &+\frac{3}{64x}(1-x)^{-\frac{5}{2}}. \end{aligned} \tag{40}$$

As we now expect, this expression is itself finite in the limit $x \to 0$. Further, Eq. (40) is consistent with the Franz-Keldysh-type predictions which also display the $\omega^{-2}(E_g - \hbar\omega)^{-\frac{5}{2}}$ band-edge divergence.[20] We have plotted this dc Kerr effect dispersion in Fig. 5; a comparison would show the general similarity of this dispersion to the below band gap clamped lattice calculation for $\chi^{(2)}(-\omega;\omega,0)$ of Ghahramani and Sipe.[11] A quantitative comparison of this curve with experiment would be interesting, although again this simple model employing only two bands and neglecting excitonic effects may not be able to account for the absolute magnitude of the effect.

Lastly, we can also obtain from our general nondegenerate nonlinear refraction an expression for $G_2(0,y)$, which describes the virtual photoconductivity effect $\chi^{(3)}(0;0,-\Omega,\Omega)$ discussed elsewhere.[17] Yablonovitch *et al.*[17] argued that one should expect a formal similarity between $G_2(0,y)$ and the dc Kerr effect, $G_2(x,0)$. In fact, if we evaluate the virtual photoconductivity from our $\Delta n(\omega,\Omega)$ in the $\omega = 0$ limit, we do indeed find that $G_2(0,y) = G_2(y,0)$, as given in Eq. (40). This might have been expected from the more general symmetry between x and y shown in Table II, which is consistent with an overall permutation symmetry in this crystal problem.[39] We end by noting that since $G_2(0,y)$ is finite, a dc polarization exists but that strictly there is no dc current here for $y \leq 1$.[16]

V. SUMMARY

We have shown how physically realistic expressions for the coherent third-order optical response of semiconductors can be rigourously obtained in the length gauge using a simple two-band model. The length gauge has allowed us to obtain the nondegenerate absorption and refraction, $\Delta\alpha(\omega,\Omega)$ and $\Delta n(\omega,\Omega)$, in a form which exposes their true behavior at $\omega = 0$ and/or $\Omega = 0$. This has led us to obtain the third-order contributions corresponding to the Franz-Keldysh effect, the nonlinear refractive index, the dc Kerr effect, and the virtual photoconductivity, as well as identifying the finite two-band model prediction for $\Delta n(0,0)$.

In addition, the manipulations involved here have more clearly exposed the consistency requirements of simple band-structure models, and clarified some of the consequences of the gauge choice. Although we have explicitly described only a two-band model, even multiple-band formulations often encounter unexpected unphysical divergences whose origin can be explained by the same issues considered here. Further note that, while here our division of $\chi^{(3)}$ into χ^{ee}, χ^{ie}, χ^{ei}, and χ^{ii} components is mainly for convenience, elsewhere[16] we have shown how this can be used to better understand the relationship between the optical response of crystals and the analogous responses of atomic and free electron gas systems. Finally, we state that our technique can also be used in conjunction with more sophisticated band structures in order to look at other $\chi^{(3)}$ tensor components, as well as entirely different nonlinear properties. Several such applications are currently being developed.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Ontario Laser and Lightwave Research Centre. Two of us (C.A. and J.E.S.) appreciate the hospitality of the faculty and staff at CREOL, where some of this work was accomplished. C.A. would also like to thank the Department of Physics and the University of Toronto for financial support.

---

[1] G. Assanto *et al.*, Appl. Phys. Lett. **62**, 1323 (1993).

[2] A. Villeneuve *et al.*, Appl. Phys. Lett. **62**, 2465 (1993).

[3] K. Al-hemyari *et al.*, Appl. Phys. Lett. **63**, 3562 (1993).

[4] M. D. Dvorak *et al.*, IEEE J. Quantum Electron **30**, 256 (1994).

[5] B. S. Wherrett, J. Opt. Soc. Am. B **1**, 67 (1984).

[6] D. C. Hutchings and E. W. Van Stryland, J. Opt. Soc. Am. B **9**, 2065 (1992).

[7] D. C. Hutchings and B. S. Wherrett, Phys. Rev. B **49**, 2418 (1994).

[8] M. Sheik-Bahae, D. J. Hagan, and E. W. Van Stryland, Phys. Rev. Lett. **65**, 96 (1990).

[9] M. Sheik-Bahae *et al.*, IEEE J. Quantum Electron. **27**, 1296 (1991).

[10] M. Sheik-Bahae, J. Wang, and E. W. Van Stryland, IEEE J. Quantum Electron. **30**, 249 (1994).

[11] E. Ghahramani and J. E. Sipe, Appl. Phys. Lett. **64**, 2421 (1994).

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

[13] D. J. Moss *et al.*, Phys. Rev. B **41**, 1542 (1990).

[14] J. E. Sipe and E. Ghahramani, Phys. Rev. B **48**, 11 705 (1993).

[15] Some of this work was presented at the Interdisciplinary Laser Science Conference (ILS-IX) 1993, Toronto, Canada.

[16] C. Aversa and J. E. Sipe (unpublished).

[17] E. Yablonovitch *et al.*, Phys. Rev. Lett. **63**, 976 (1989).

[18] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **34**, 1138 (1958) [Sov. Phys. JETP **34**, 788 (1958)].

[19] D. E. Aspnes, Phys. Rev. **153**, 972 (1967).

[20] D. E. Aspnes and J. E. Rowe, Phys. Rev. B **5**, 4022 (1972).

[21] D. C. Hutchings *et al.*, Opt. Quantum Electron. **24**, 1 (1992).

[22] M. I. Dykman and Y. G. Rubo, Phys. Rev. B **45**, 5926 (1992).

[23] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms: Introduction to Quantum Electrodynamics* (Wiley, New York, 1989).

[24] F. Bassani, J. J. Forney, and A. Quattropani, Phys. Rev. Lett. **39**, 1070 (1977).

[25] V. M. Genkin and P. Mednis, Sov. Phys. Solid State **10**, 1 (1968).

[26] G. P. Agrawal, C. Cojan, and C. Flytzanis, Phys. Rev. B **17**, 776 (1978).

[27] E. I. Blount, *Solid State Physics* (Academic, New York, 1962), Vol. 13.

[28] In the case that $n \neq m$ but $\omega_{nm} = 0$, one chooses the wave functions at these degeneracies such that the relevant components of $\mathbf{p}_{cv}$ and $\mathbf{r}_{cv}$ vanish.

[29] D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Free Atoms and Molecules* (Springer-Verlag, Berlin, 1979).

[30] Indeed, an isotropic dispersion in the conduction and light-hole bands only arises after realizing the triplet nature (of cubic symmetry) of the valence bands.

[31] G. Barton, J. Phys. B **7**, 2134 (1974).

[32] We note that nonsimple poles can also arise for the case $\omega_1 = \omega_3 = \omega$ and quite independent of the $;k^z$ operator, for example, in χ^{ee}.

[33] The leading factor of 2 in Eq. (33) can be modified depending on the particular details of ω, Ω being equal and/or zero. For example, see Ref. 39.

[34] A subtlety deserves comment. In this unphysical model of infinite bands, the absorption strictly continues to infinite frequencies, so the integral in Eq. (36) may not be separately finite for each of the two-photon absorption, electronic Raman, and Stark effects. However, we find the "infinities" from each term cancel in the sum, which is the physically relevant quantity, and so are not considered further. Ironically, the approximations adopted in Refs. 9 and 10, which lead to incorrect $F_2(x,y)$, "soften" the absorption and such infinities do not occur.

[35] R. Zeyher, H. Bilz, and M. Cardona, Solid State Commun. **19**, 57 (1976).

[36] Reference 20 shows that dephasing mechanisms should be considered to correctly describe the experimental results. Our use of the full susceptibility approach and density operator dynamics is useful for the theoretical treatment of such effects.

[37] J. A. Van Vechten and D. E. Aspnes, Phys. Lett. **30A**, 346 (1969).

[38] M. J. LaGasse *et al.*, Appl. Phys. Lett. **56**, 417 (1990).

[39] Butcher and Cotter, *Elements of Nonlinear Optics* (Cambridge University Press, Cambridge, 1990).