

Miller's rule and the static limit for second-harmonic generation

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We formulate a simplified model for the second-harmonic generation susceptibility, using recently derived sum rules to determine the relevant parameters. We show that Miller's empirical rule can be obtained from this model in a natural way and Miller's constant can be computed for many semiconductors using the well-known empirical pseudopotential parameters. The resulting static limit is consistently found to be in agreement with experiments.

I. INTRODUCTION

A large number of papers have been recently published on the theoretical calculation of the second-harmonic generation susceptibility function $\chi^{(2)}(\omega, \omega)$ in semiconductors without a center of inversion.¹ They are all founded on the calculation of the relevant matrix elements on the basis of the known band structure. Calculations have also been performed recently on asymmetric quantum wells,² where the effect of the lack of specular symmetry is considered, in addition to the contribution originating from the lack of inversion symmetry. All the above calculations display strong peaks in correspondence to single transition resonances and to double transition resonances, but fail, in most cases, to reproduce the correct static limit $\chi^{(2)}(0, 0)$. Furthermore, no satisfactory theoretical explanation has ever been given for the approximate validity of the Miller's rule,³ which allows the expression of the second-order susceptibility in terms of the first-order one as

$$\chi_{ijk}^{(2)}(\omega, \omega) = \Delta_{ijk} \chi_{ii}^{(1)}(2\omega) \chi_{jj}^{(1)}(\omega) \chi_{kk}^{(1)}(\omega) , \quad (1)$$

where the tensorial indices give the directions of polarization and applied fields, and Δ_{ijk} is a constant when the frequencies ω and 2ω are in the transparency region. Miller's rule would also require Δ to be the same for different materials, but this has been found not to be strictly correct.⁴ Theoretically, the validity of this rule has been proved only in the simple case of the anharmonic oscillator.⁵

We think that the shortcomings of the existing sophisticated theories are due both to the extreme sensitivity of $\chi^{(2)}$ to the constituent parameters (matrix elements and energy differences), and to the fact that a limited number of matrix elements are selected, where a sum on a complete basis set would be required. Both limitations have been shown to be a large source of errors in two-photon processes⁶ since the requirement of gauge invariance is violated. In the case of $\chi^{(2)}(\omega, \omega)$ a number of very stringent requirements have been recently obtained as a consequence of time causality,⁷ which are expected to be violated in any approximate calculation. They are summarized in the following seven sum rules:

$$\chi^{(2)}(0, 0) = \frac{2}{\pi} \int_0^\infty \frac{\text{Im}\chi^{(2)}(\omega', \omega')}{\omega'} d\omega' , \quad (2)$$

$$\int_0^\infty \omega^n \text{Re}\chi^{(2)}(\omega, \omega) d\omega = 0 , \quad (3)$$

with $n = 0, 2, 4$;

$$\int_0^\infty \omega^n \text{Im}\chi^{(2)}(\omega, \omega) d\omega = 0 , \quad (4)$$

with $n = 1, 3$; and finally

$$\int_0^\infty \omega^5 \text{Im}\chi_{ijk}^{(2)}(\omega, \omega) d\omega = -\frac{\pi}{16} \frac{Ne^3}{m^3} \left\langle \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right\rangle_0 , \quad (5)$$

where N is the electron density, $V(\mathbf{x})$ is the external potential experienced by the electrons, and the average is performed in the ground state of the system.

In this paper we propose a simplified model for $\chi^{(2)}(\omega, \omega)$, which is based on the choice of a single resonance frequency, but can be forced to satisfy the above described sum rules. We will show that imposing the sum rule requirement provides a justification for Miller's rule, allows a calculation of Miller's constant, and leads to values of the static limit $\chi^{(2)}(0, 0)$ which are consistently in agreement with the experimental values. In Sec. II we will describe our simplified model and show how imposing the sum rules leads to Miller's formula (1). In Sec. III we will show how Miller's constant and the static limit can be computed from crystal pseudopotential theory, and will give examples for a large number of materials. Conclusions and discussions are presented in Sec. IV.

II. SIMPLIFIED MODEL FOR THE SECOND-HARMONIC SUSCEPTIBILITY

From the general theory of the nonlinear susceptibilities we have

$$\chi_{ijk}^{(2)}(\omega, \omega) = \frac{e^3}{V\hbar^2} \sum_{m,n} \left[\frac{\langle \psi_g | x_i | \psi_m \rangle \langle \psi_m | x_j | \psi_n \rangle \langle \psi_n | x_k | \psi_g \rangle}{(\omega_m - \omega_g - 2\omega - i\gamma)(\omega_n - \omega_g - \omega - i\gamma)} + \frac{\langle \psi_g | x_j | \psi_m \rangle \langle \psi_m | x_k | \psi_n \rangle \langle \psi_n | x_i | \psi_g \rangle}{(\omega_n - \omega_g + 2\omega + i\gamma)(\omega_m - \omega_g + \omega + i\gamma)} \right. \\ \left. + \frac{\langle \psi_g | x_k | \psi_m \rangle \langle \psi_m | x_i | \psi_n \rangle \langle \psi_n | x_j | \psi_g \rangle}{(\omega_m - \omega_g + \omega + i\gamma)(\omega_n - \omega_g - \omega - i\gamma)} \right], \quad (6)$$

where V is the volume of the system, ψ_n are the stationary states with energy $E_n = \hbar\omega_n$, g labels the ground state, and \mathbf{x} is the dipole operator. The positive broadening $\gamma \rightarrow 0^+$ accounts for the causal behavior of the response.

After straightforward algebra, expression (6) can be reduced to the following form:

$$\chi_{ijk}^{(2)}(\omega, \omega) = \sum_n \frac{\alpha_1^n}{(\omega_n - \omega_g - \omega - i\gamma)} + \frac{\alpha_2^n}{(\omega_n - \omega_g - 2\omega - i\gamma)} + \sum_{n'} \frac{\alpha_3^{n'}}{(\omega_{n'} - \omega_g - \omega - i\gamma)^2} + (\omega \rightarrow -\omega)^*, \quad (7)$$

where n' labels all "doubly resonant" states, i.e., states for which another state n'' exists such that $\omega_{n'} - \omega_{n''} = \omega_{n''} - \omega_g$. While in atomic or molecular systems these states are unlikely to occur, in crystalline solids the presence of bands ensures their existence in most cases. The real coefficients α are given by appropriate sums over a complete set of intermediate states and do not depend on the frequency ω . No approximations have been introduced in deriving (7). In our simplified model we consider a single resonant frequency ω_0 , so that expression (7) reduces to

$$\chi_{ijk}^{(2)}(\omega, \omega) = \frac{\alpha_1}{(\omega_0 - \omega - i\gamma)} + \frac{\alpha_2}{(\omega_0 - 2\omega - i\gamma)} + \frac{\alpha_3}{(\omega_0 - \omega - i\gamma)^2} + (\omega \rightarrow -\omega)^*. \quad (8)$$

We can now impose all the above described sum rules. We obtain that the oscillator strengths α_i must satisfy the following linear system of equations:

$$\frac{\omega_0}{4} \alpha_1 + \omega_0 \alpha_2 + \alpha_3 = 0, \\ \frac{\omega_0^3}{16} \alpha_1 + \omega_0^3 \alpha_2 + 3\omega_0^2 \alpha_3 = 0, \quad (9) \\ \frac{\omega_0^5}{64} \alpha_1 + \omega_0^5 \alpha_2 + 5\omega_0^4 \alpha_3 = c,$$

where

$$c = -\frac{1}{16} \frac{e^3}{m^3} \left\langle \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right\rangle_0. \quad (10)$$

The solutions of (9) are

$$\alpha_1 = \frac{64}{9} \frac{c}{\omega_0^5}, \quad \alpha_2 = -\frac{22}{9} \frac{c}{\omega_0^5}, \quad \alpha_3 = \frac{2}{3} \frac{c}{\omega_0^4}. \quad (11)$$

We can now substitute the above expressions (11) into (8), to find that the susceptibility takes the form

$$\chi_{ijk}^{(2)}(\omega, \omega) = \frac{Ne^3}{2m^3} \left\langle \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right\rangle_0 \frac{1}{(4\omega^2 - \omega_0^2)(\omega^2 - \omega_0^2)^2}. \quad (12)$$

The above expression can be written in terms of the linear susceptibilities, recalling that their expressions for the single resonance model are

$$\chi_{ii}^{(1)}(\omega) = \frac{Ne^2}{m} \frac{1}{(\omega_0^2 - \omega^2)}. \quad (13)$$

We finally obtain

$$\chi_{ijk}^{(2)}(\omega, \omega) = -\frac{\left\langle \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right\rangle_0}{2N^2 e^3} \chi_{ii}^{(1)}(2\omega) \chi_{jj}^{(1)}(\omega) \chi_{kk}^{(1)}(\omega), \quad (14)$$

which is an explicit expression for Miller's rule, with a specific definition of Miller's constant. Since expression (14) has been derived in the single pole approximation, it is expected to be satisfied at frequencies far below or above the typical transition frequencies of the considered system. The resonance pole ω_0 may be identified, following, e.g., Phillips,⁸ as the average gap between valence and conduction bands. We stress, however, that ω_0 enters expression (14) only via the linear susceptibility, which is a well-defined measurable quantity and can be taken from experiments. Then the only remaining problem is to compute Miller's constant.

III. STATIC LIMIT

The static limit can be obtained from expression (14) by taking the limit $\omega \rightarrow 0$. We obtain

$$\chi_{ijk}^{(2)}(0, 0) = -\frac{\left\langle \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right\rangle_0}{2N^2 e^3} \chi^{(1)}(0)^3, \quad (15)$$

where the static susceptibility factor $\chi^{(1)}(0)^3$ automatically includes local-field effects, which are difficult to estimate and account for a few percent of the total.⁹

The calculation of the expectation value of the third derivative of the crystal pseudopotential can be carried out by considering the fact that the contributions to the static limit originate from the valence electrons, and the potential to which they respond is in effect the pseudopotential.¹⁰ Since we have demonstrated⁷ that the

TABLE I. Parameters used in the computation of the static limit of $\chi^{(2)}$. The lattice constant a can be obtained from the cation-anion spacing d (Å) as $a = 4d/\sqrt{3}$. The linear susceptibility is taken from the dielectric constant ϵ_∞ (in order to rule out vibrational effects) as $\chi^{(1)}(0) = (\epsilon_\infty - 1)/4\pi$. The last four columns report the computed and the experimental values (Refs. 13–16) of $\chi^{(2)}(0,0)$ and Δ in units of 10^{-8} esu.

	d	ϵ_∞	Δ (th)	Δ (exp)	$\chi^{(2)}(0,0)$ (th)	$\chi^{(2)}(0,0)$ (exp)
GaSb	2.65	14.4	103	104	125	130 ± 13
GaAs	2.45	10.9	94	92	46	43 ± 2
InSb	2.81	15.7	134	112	216	174 ± 16
GaP	2.36	9.1	128	82	34	20 ± 2
InAs	2.61	12.3	154	118	112	86 ± 9
ZnSe	2.45	5.9	217	180	12.8	10.6 ± 1

electron-electron interaction does not contribute to the sum rule constant, the bare (or unscreened) pseudopotential $V_p(\mathbf{r})$ is needed. Assuming that the pseudopotential is taken in local form in the case of III-V and II-VI compounds, we can write

$$V_p(\mathbf{r}) = \sum_{\mathbf{G}} V_p(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}, \quad (16)$$

where \mathbf{G} denotes the reciprocal lattice vectors. The desired expectation value is given by

$$\left\langle \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k} \right\rangle_0 = -\Omega \sum_{\mathbf{G}} iG_i G_j G_k n^*(\mathbf{G}) V_p(\mathbf{G}), \quad (17)$$

where Ω is the unit-cell volume, and $n(\mathbf{G})$ is the Fourier transform of the electron density.

We observe, however, that in the definition of the pseudopotentials the screening due to the interaction between valence electrons is often taken into account. If this is the case we must subtract the Hartree contribution due to the electron density so that, in reciprocal space,

$$V_p(\mathbf{G}) = V_p^{(s)}(\mathbf{G}) - \frac{4\pi e^2}{G^2} n(\mathbf{G}), \quad (18)$$

where $V_p^{(s)}$ is the screened pseudopotential. The Hartree correction to (17), however, turns out to vanish because of time reversal symmetry.

For the purpose of illustration we have carried out a calculation of the static limit $\chi^{(2)}(0,0)$, using expressions (15) and (17). We have considered a large number of III-V and II-VI compounds for which the pseudopotential parameters $V_p(\mathbf{G})$ and the valence electron densities $n(\mathbf{G})$ have been known for a long time, and experimental data of $\chi^{(1)}(0)$ and $\chi^{(2)}(0,0)$ are available. Specifically, the pseudopotential parameters are taken from Cohen and Bergstresser¹¹ and the density transforms $n(\mathbf{G})$ from Chelikowski and Cohen.¹² Moreover, we report in Table I the experimental values of $\chi^{(1)}(0)$ and $\chi^{(2)}(0,0)$.

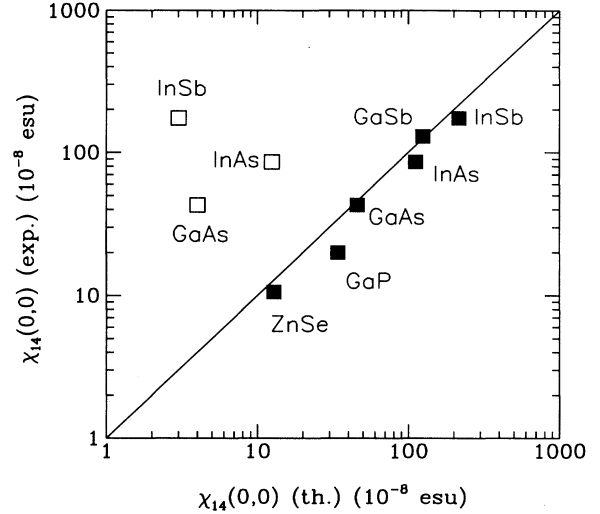


FIG. 1. Comparison between theoretical and experimental results for $\chi^{(2)}(0,0)$. Full squares: this work. Empty squares: Fong and Shen's results (Ref. 18), obtained with the same empirical pseudopotentials. Observe that the results are reported on a logarithmic scale.

The experimental values of the only nonzero element $\chi_{14}^{(2)}(0,0) = \chi_{xyz}^{(2)}(0,0)$ for GaP,^{13,14} GaAs,^{13,14} GaSb,¹⁴ InAs,¹⁴ InSb,¹⁵ and ZnSe (Ref. 16) are converted using the Levine-Bethea¹³ scale, as recommended in Ref. 17.

The comparison between the computed and the experimental values of $\chi^{(2)}(0,0)$ shows a remarkably good agreement in all the materials investigated. As shown in Fig. 1, this compares very favorably with the theoretical calculations of Fong and Shen¹⁸ based on the same pseudopotentials. The reason is due to the fact that their calculations do not allow for the separation given in expression (15) between Miller's constant, which depends weakly on the material, and the first-order static susceptibility, which in our case is taken from experiments. The origin of such a strong simplification must be traced to the sum rule constraint in our simplified model.

IV. CONCLUSIONS

We have shown that the sum rules of the second-harmonic susceptibility can be used in a simple model based on a resonant state to derive an explicit expression which verifies Miller's rule. Miller's constant is evaluated from the pseudopotential parameters appropriate to a number of zinc-blende compounds. When this is combined with the experimental first-order susceptibilities, remarkable agreement is found with the experimental values of $\chi^{(2)}(0,0)$.

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