

THE FLOQUET METHOD APPLIED TO SOLIDS

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ABSTRACT

We apply the Floquet method to study the interaction of a monochromatic periodic field with a crystal. In particular, equations for the field modified bands and for the transition probabilities among them are obtained. An application is presented to investigate the role of intermediate states in two-photon absorption in a model crystal. Qualitative comparison is made with experiment.

RESUMO

Aplicamos o método de Floquet ao estudo de interações de um campo periódico monocromático com um cristal. Em particular, equações para as bandas de energia modificadas pelo campo e para as probabilidades de transição entre elas são obtidas. Apresentamos uma aplicação na qual o efeito de estados intermediários na absorção de dois fótons num cristal modelo é investigado. Apresentamos comparação qualitativa dos nossos resultados com a experiência.

1. INTRODUCTION

Electromagnetic radiation has been an important tool in the study of the properties of matter. The development of lasers opened new perspectives due to the generation of new phenomena originated by intense radiation fields. There has been extensive studies concerning the interaction of laser fields with atoms, molecules and, in less extension, with solids [1–5].

The theoretical approaches may be generally divided in two groups: perturbation theory and “non-perturbative” methods. Although oversimplified, this classification helps the discussion of the present situation. Perturbation theory is adopted when the electromagnetic laser field may be considered a perturbation to the internal fields of matter.

If one considers intense fields, perturbation theory, even in high order, does not converge properly and is quite complicated. An alternative approach are the so called “non-perturbative” schemes which try to avoid the intrinsic difficulties of high order perturbation theory by treating approximately the field in all orders. Many recent experimental results must be interpreted in the light of these late approaches [6–8], which have been mainly developed to study non-linear processes involving laser interaction with atoms and molecules.

Keldysh [9] was the first to try to describe an “exact” S matrix, by approximately incorporating in the initial and final states of an electron in a solid, the effect

of the electromagnetic field in all orders. Unfortunately this method, which leads to simple analytical results cannot be justified from first principles. Modifications to this scheme have been suggested in the literature but all suffer some formal difficulties [10–12].

A treatment used successfully in atoms and molecules is the Floquet method [5–13] which treats the interaction of a quantized system with a time periodic electromagnetic field. The solution of the time dependent Schrodinger equation may be obtained from an infinite time independent matrix (Floquet’s matrix).

In this work we develop a “non-perturbative” scheme based in the Floquet method, to treat the interaction of light with solids. Due to the multiple periodicities of the Hamiltonian, this method applied to solids generalizes naturally the Bloch approach for the crystalline structure generating Brillouin zones in higher dimensions and offers an immediate interpretation for modifications in the band structure of the solid due to the field. The time evolution operator is easily calculated from the Floquet’s matrix leading to the inter bands transition probabilities.

The derivation in Sec. 2 is the Floquet version of the field quantized approach developed earlier by the authors [14]. In Sec. 3 we apply the method to investigate the role of intermediate states in two-photon absorption in solids.

2. THE FLOQUET METHOD

The Floquet formalism is applied below to treat the electronic excitations induced in a solid by laser light. The total time dependent Hamiltonian in the dipole approximation is

$$H(\vec{x}, t) = \frac{1}{2} (\vec{p} + \alpha \vec{A}(t))^2 + V(\vec{x}), \quad (1)$$

where atomic units, $e = \hbar = m = 1$, have been used and $\alpha = 1/137$.

For linearly polarized light the vector potential $\vec{A}(t)$ may be written as

$$\vec{A}(t) = -\vec{A}_0 \cos \omega t. \quad (2)$$

If one considers a crystal potential which has spatial periodicity \vec{a} , it is obvious that the Hamiltonian (1) satisfies, with $\tau = 2\pi/\omega$,

$$H(\vec{x} + \vec{a}, t + \tau) = H(\vec{x}, t). \quad (3)$$

The electromagnetic field may be formally incorporated in the crystal potential by an unitary transformation θ such that

$$\psi(\vec{x}, t) = \exp -i \left[\int_0^t \alpha \vec{p} \cdot \vec{A}(t') dt' + \frac{\alpha^2}{2} \int_0^t A^2(t') dt' \right] \phi(\vec{x}, t) \equiv \theta(t) \phi(\vec{x}, t). \quad (4)$$

The time dependent Schrodinger equation satisfied by ϕ is

$$\left[\frac{p^2}{2} + V(\vec{x}, t) \right] \phi(\vec{x}, t) = i \frac{\partial \phi}{\partial t}(\vec{x}, t) \quad (5.a)$$

where

$$V(\vec{x}, t) = V(\vec{x} + \alpha \int_0^t \vec{A}(t') dt'), \quad (5.b)$$

is the transformed potential which has space-time periodicity. The potential $V(\vec{x}, t)$ may be expanded in a generalized Fourier series

$$V(\vec{x}, t) = \sum_{\vec{G}, n} V_{\vec{G}, n} \exp [i(\vec{G} \cdot \vec{x} - n\omega t)]. \quad (6.a)$$

In this equation, $V_{\vec{G}, n}$ incorporates the coefficients $V_{\vec{G}}$ of usual Bloch expansion in terms of the reciprocal lattice vectors and those related to the Floquet index n :

$$V_{\vec{G}, n} = V_{\vec{G}} J_n \left(\frac{\alpha}{\omega} \vec{G} \cdot \vec{A}_0 \right). \quad (6.b)$$

The solutions of Eq. 5.a may be conveniently expanded in Bloch-Floquet components given by

$$\phi_{\vec{q}\vec{k}}(\vec{x}, t) = \exp [i(\vec{k} \cdot \vec{x} - qt)] u_{\vec{q}\vec{k}}(\vec{x}, t), \quad (7.a)$$

where $u_{\vec{q}\vec{k}}$ has space-time periodicity:

$$u_{\vec{q}\vec{k}}(\vec{x}, t) \equiv \sum_{\vec{G}, n} u_{\vec{G}, n} \exp [i(\vec{G} \cdot \vec{x} - n\omega t)]. \quad (7.b)$$

In Eq.7 (q, \vec{k}) belongs to a four-dimensional volume where \vec{k} , the wave vector, is in a three dimensional Brillouin zone and q , usually called the quasi-energy, may be chosen in the range $0 < q \leq \omega$.

The coefficients $u_{\vec{G}, n}$ depend on (q, \vec{k}) and obey the following equation:

$$\langle \vec{G}_n | H_F(\vec{k}) | \vec{G}'_n \rangle u_{\vec{G}'_n}(\vec{k}) = q u_{\vec{G}_n}(\vec{k}) \quad (8)$$

where

$$\begin{aligned} \langle \vec{G}_n | H_F(\vec{k}) | \vec{G}'_n \rangle &= V_{\vec{G}-\vec{G}', n-n'} + \\ &+ \frac{1}{2} [(\vec{k} + \vec{G})^2 - n\omega] \delta_{\vec{G}\vec{G}', n-n'} \delta_{nn'} \end{aligned} \quad (9)$$

are, by definition, the components of the so-called "Floquet Hamiltonian" in the basis $\{|\vec{G}, n\rangle\}$. The Bloch-Floquet states fully incorporate the symmetries of the original Hamiltonian: \vec{G} and n are associate to the eigenvalues of the discrete space translations of the lattice vectors and time translations of period τ , respectively. In the \vec{x}, t representation these states are proportional to $\exp [i(\vec{G} \cdot \vec{x} - n\omega t)]$.

It is clear that $u_{\vec{G}, n}(q) \equiv \langle \vec{G}, n | q0 \rangle$ are the components of the eigenvectors $|q0\rangle$ associate to the eigenvalues q 's, in the range $(0, \omega)$. From Eqs. (8) and (9) one can immediately show that

$$\begin{aligned} |qm\rangle &= \sum_{\ell=-\infty}^{\infty} |\vec{G}, \ell\rangle u_{\vec{G}\ell-m} = \\ &= \sum |\vec{G}, \ell\rangle \langle \vec{G}, \ell - m | q0 \rangle \end{aligned} \quad (10)$$

are eigenvectors of H_F with eigenvalues $q + m\omega$. Therefore the expansion coefficients of $|qm\rangle$ in the basis $|\vec{G}, \ell\rangle$ satisfy the translation properties

$$\langle \vec{G}, \ell | qm \rangle = \langle \vec{G}, \ell - m | q0 \rangle = u_{\vec{G}\ell-m} \quad (11)$$

The transition probability between a valence band state $|v_{\vec{k}}\rangle$ and a conduction band state $|c_{\vec{k}}\rangle$ is given in terms of the time evolution operator $U(t, t_0)$, by

$$P_{v \rightarrow c}(t, t_0) = |\langle c_{\vec{k}} | U(t, t_0) | v_{\vec{k}} \rangle|^2. \quad (12)$$

The initial and final states are Bloch functions which can be expanded as:

$$\langle \vec{x} | b_{\vec{k}} \rangle = \sum_{\vec{G}} b_{\vec{G}} e^{i\vec{G} \cdot \vec{x}} \quad (13)$$

The transition amplitude is expressed in terms of the Floquet Hamiltonian and of its eigenvectors. The calculations are presented in the Appendix and one has

$$\begin{aligned} \langle c_{\vec{k}} | U(t, t_0) | v_{\vec{k}} \rangle &= \left| \sum_{\substack{\vec{G}_1, \vec{G}_2 \\ s, r, n}} c_{\vec{G}_1}^* v_{\vec{G}_2} \langle \vec{G}_1, n | e^{-iH_F(t-t_0)} | \vec{G}_2, 0 \rangle \right. \\ &\times J_s \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{G}_1 + \vec{k}) \right) e^{i(s-n)\omega t} J_r \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{G}_2 + \vec{k}) \right) e^{-ir\omega t_0} \left. \delta_{\vec{k}\vec{k}} \right| \end{aligned} \quad (14)$$

where J_n is the Bessel function of order n .

The transition probability expressed by Eqs. 12 and 14 depends on t_0 , the initial time, or yet the initial phase of the field. Since this parameter is not fixed experimentally, an average over t_0 is performed, keeping the interaction time $(t - t_0)$ constant. Therefore one has

$$\begin{aligned} P_{v \rightarrow c} &= \sum_m \left| \sum_{\vec{G}_1, \vec{G}_2, n, p} c_{\vec{G}_1}^* v_{\vec{G}_2} \langle \vec{G}_1, n | e^{-i(H_F - p\omega)(t-t_0)} | \vec{G}_2, 0 \rangle \right|^2 \end{aligned}$$

$$\times J_{p+n} \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{k} + \vec{G}_1) \right) J_{p-m} \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{k} + \vec{G}_2) \right) |^2. \quad (15)$$

The asymptotic behavior of the transition probability is conveniently calculated using the Laplace transform given by

$$P_{v \rightarrow c}(\vec{k}) = \lim_{\Gamma \rightarrow \infty} \frac{1}{\Gamma} \int_0^\infty d(t - t_0) \exp \left[-\frac{(t - t_0)}{\Gamma} \right] P_{v \rightarrow c}(t - t_0). \quad (16)$$

The quantity Γ has dimensions of time and may be interpreted as the average relaxation time of the system.

Following Thomas [15] the average probability is

$$\vec{P}_{v \rightarrow c}(\vec{k}) = \sum_q S_{cq} S_{qv} \quad (17.a)$$

where

$$S_{cq} = \sum_N \left| \sum_{\vec{G}_1, \ell} c_{\vec{G}_1}^* \langle \vec{G}_1, \ell | q0 \rangle J_{\ell-N} \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{k} + \vec{G}_1) \right) \right|^2, \quad (17b)$$

and S_{qv} is expressed similarly replacing c by v .

3. TWO-PHOTON PROCESSES IN SOLIDS

In order to investigate the role of intermediate resonances in multiphoton processes in solids, we consider two-photon processes in a model crystal such that an intermediate resonant state may be reached by proper tuning of the laser frequency. This calculation is motivated by the measurements in Cu_2O [16] under strong pump field which indicates that the direct two-photon absorption coefficient is weakly enhanced by intermediate exciton resonances.

The purpose here is to present qualitative arguments justifying the role played by intermediate state, therefore we choose a simple model potential, of the Kronig-Penney (KP) type, to describe the solid:

$$V(z) = -\sigma a \sum_m \delta(z - ma) \quad (18)$$

where a is the lattice parameter and σ the potential strength.

Calculations are performed for $\sigma = 0.3$ and we diagonalize the Hamiltonian following Ref. 14. The bare KP spectrum is shown in Fig. 1. Transitions between the lower (v) and upper (c) bands are studied in the frequency range $\omega_1 \leq \omega \leq \omega_2$ shown in the same figure. The intermediate state resonant situation occurs at $\omega = \omega_r$, with absorption of two-photons.

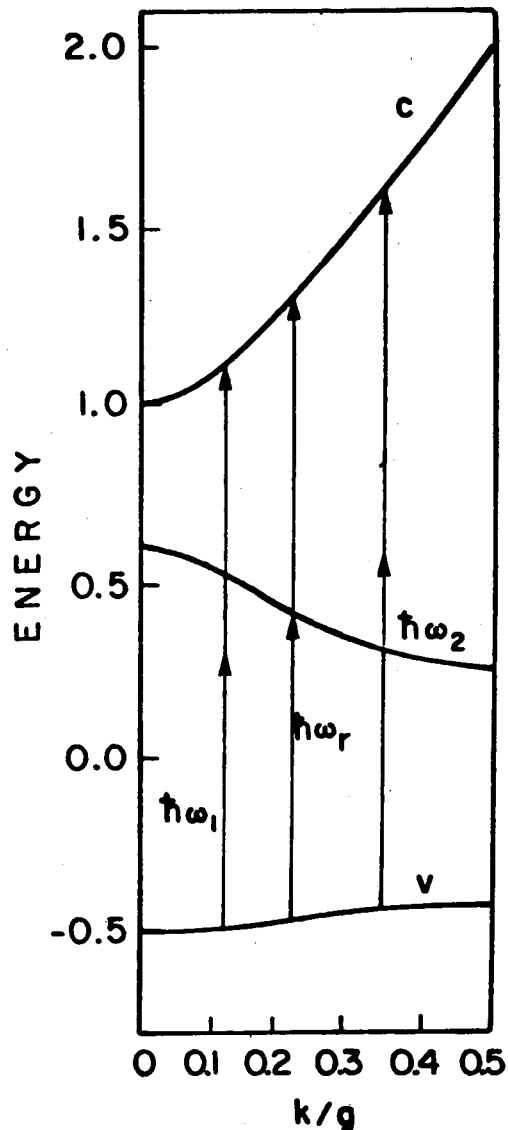


Fig. 1 - Undressed energy bands of the Kronig-Penney model in a truncated basis with 3 reciprocal lattice vectors and corresponding to the potential strength $\sigma = 0.3$. The energy is given in units of ϵ (see text). Some two-photon transitions are schematically indicated by arrows.

The experimentally accessible quantity for the $v \rightarrow c$ transition is the total time average probability:

$$P_T(\omega) = \int P_{v \rightarrow c}(k) \frac{a}{2\pi} dk \quad (19)$$

In Fig. 2, this quantity is plotted as function of the laser frequency for two different amplitudes of the field, which is characterized by the parameter

$$X = \frac{eaE_0}{\pi\epsilon} \quad (20)$$

where E_0 is the electric field amplitude and $\epsilon = 2\pi^2 \hbar^2 / ma^2$.

Antonetti et al [16] have observed a small enhancement factor, of the order of 3, in Cu_2O , using a fixed pump laser with $\hbar\omega \times 2\text{eV}$ and intensity $I_0 \approx 10^{11} \text{W/cm}^2$, which correspond to $X \approx 0.1$ (Fig. 2b). The intermediate state

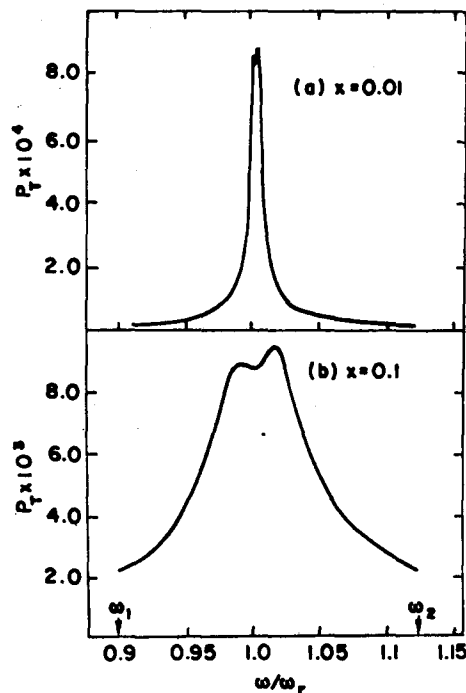


Fig. 2 - Integrated time-average transition probability between bands v and c as a function of ω/ω_r for field amplitudes $X = 0.01$ (a) and $X = 0.1$ (b).

resonance was reached experimentally by varying the temperature.

A qualitative interpretation of their results is obtained analysing Fig. 2, where it is clear that the transition probability at resonance (ω_r) is considerably modified with respect to a "background" value (ω_b) which corresponds to about 10% detuning in frequency. A measure of this modification may be obtained defining an enhancement factor

$$\eta = P_T(\omega_r)/P_T(\omega_b) \quad (21)$$

and taking arbitrarily $\omega_b/\omega_r = 0.9$. For $X = 0.01$, $\eta \approx 50$ while for field values compatible with the experimental conditions [16], $\eta \approx 4$, which corresponds to a relatively weak enhancement, as obtained experimentally.

4. CONCLUSIONS

The Floquet Method provides an adequate non perturbative formalism for the study of the interaction of light with solids. It also allows the calculation of the quasi-energy spectrum of bands in the presence of a laser field, which is useful in understanding several properties of the physical system.

Although this method leads to results equivalent to those obtained from a field-quantized approach derived recently [14], the presentation in Sec. 2 is based in the standard derivations, and the connection with the classical Floquet method is straightforward [13, 17].

The simple example in Sec. 3 illustrates the potentiality and flexibility of the method, but for a quantitative comparison, more realistic models for the crystal potential must be considered.

Appendix A

The time evolution operator may be expressed as

$$U(t, t_0) = \theta(t) U'(t, t_0) \theta^{-1}(t_0) \quad (A.1)$$

where θ is defined in Eq. 4 and

$$U'(t, t_0) = \sum_{\vec{g}, \vec{k}} |\phi_{\vec{q}\vec{k}}(t)\rangle \langle \phi_{\vec{q}\vec{k}}(t_0)| \quad (A.2)$$

where the state $|\phi_{\vec{q}\vec{k}}(t)\rangle$ is defined from the wave function $\phi_{\vec{q}\vec{k}}(\vec{x}, t) = \langle \vec{x} | \phi_{\vec{q}\vec{k}}(t) \rangle$.

From Eqs. 7.a and 7.b one has

$$|\phi_{\vec{q}\vec{k}}(t)\rangle = \sum_{\vec{G}, n} u_{\vec{G}, n} e^{-i(\vec{q} + n\omega)t} |\vec{G} + \vec{k}\rangle \quad (A.3b)$$

where $|\vec{G} + \vec{k}\rangle$ is a quasi-momentum eigenstate of the lattice.

Substituting Eq. A.3 in A.2 and using Eq. 10 one has

$$U'(t, t_0) = \sum_{\vec{q}\vec{k}, \vec{G}\vec{G}', n\vec{m}} |\vec{G} + \vec{k}\rangle \langle \vec{G}', n | qm \rangle e^{-i(\vec{q} - m\omega)(t - t_0)} \langle qm | \vec{G}', 0 \rangle e^{-in\omega t} \langle \vec{G}' + \vec{k} | \quad (A.4a)$$

From the definition of the Floquet Hamiltonian, the time evolution operator $U'(t, t_0)$ may be expressed as:

$$U'(t, t_0) = \sum_{\vec{k}\vec{G}\vec{G}', n} |\vec{G} + \vec{k}\rangle \langle \vec{G}', n | \exp[-iH_F(t - t_0)] |\vec{G}', 0\rangle e^{-in\omega t} \langle \vec{G}' + \vec{k} | \quad (A.4b)$$

The initial and final states can be expand as:

$$|v_{\vec{k}}\rangle = \sum_{\vec{G}} v_{\vec{G}} |\vec{G} + \vec{k}\rangle \quad (A.5a)$$

$$|c_{\vec{k}}\rangle = \sum_{\vec{G}} c_{\vec{G}} |\vec{G} + \vec{k}\rangle \quad (A.5b)$$

From Eq. A.1, using $I = \sum_{\vec{G}, \vec{k}} |\vec{G} + \vec{k}\rangle \langle \vec{G} + \vec{k}|$, one has

$$\begin{aligned} \langle c_{\vec{k}} | U(t, t_0) | v_{\vec{k}} \rangle &= \sum_{\vec{G}_1, \vec{k}_1, \vec{G}_2, \vec{k}_2} \langle c_{\vec{k}} | \theta(t) | \vec{G}_1 + \vec{k}_1 \rangle \\ &\times \langle \vec{G}_1 + \vec{k}_1 | U'(t, t_0) | \vec{G}_2 + \vec{k}_2 \rangle \langle \vec{G}_2 + \vec{k}_2 | \theta^{-1}(t_0) | v_{\vec{k}} \rangle \end{aligned} \quad (A.6)$$

The first and the last term in the RHS of Eq. (A.6) may be easily evaluated since $|\vec{G} + \vec{k}\rangle$ is an eigenstate of the operator p :

$$\langle c_{\vec{k}} | \theta(t) | \vec{G} + \vec{k} \rangle = e^{-i\varphi(t)} c_{\vec{G}}^* \exp \left[i \frac{\vec{A}_0 \cdot (\vec{G} + \vec{k})}{\alpha \omega} \sin \omega t \right] \quad (\text{A.7a})$$

where

$$\varphi(t) = \alpha \int_0^t A^2(t') dt'. \quad (\text{A.7b})$$

It is possible to expand (A.7) into a Fourier series:

$$\langle c_{\vec{k}} | \theta(t) | \vec{G}_1 + \vec{k}_1 \rangle = e^{-i\varphi(t)} c_{\vec{G}_1}^* \sum_s J_s \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{G}_1 + \vec{k}_1) \right) e^{is\omega t} \delta_{\vec{k}, \vec{k}_1}. \quad (\text{A.8})$$

The common phase $e^{-i\varphi(t)}$ cancels out the in transition probability calculation and is omitted below. From Eq. A.4b

$$\langle \vec{G}_1 + \vec{k}_1 | U(t, t_0) | \vec{G}_2 + \vec{k}_2 \rangle = \sum_n$$

$$\langle \vec{G}_{1,n} | \exp [-iH_F(t, t_0)] | \vec{G}_2, 0 \rangle e^{-in\omega t} \delta_{\vec{k}_1, \vec{k}_2}, \quad (\text{A.9})$$

and therefore

$$\begin{aligned} \langle c_{\vec{k}} | U(t, t_0) | v_{\vec{k}'} \rangle &= \left[\sum_{\vec{G}_1, \vec{G}_2, n, s, r} c_{\vec{G}_1}^* \vec{G}_2 \right. \\ &\langle \vec{G}_{1,n} | \exp [-iH_F(t, t_0)] | \vec{G}_2, 0 \rangle \\ &\times J_s \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{G}_1 + \vec{k}') \right) e^{i(s-n)\omega t} \\ &\left. \times J_r \left(\frac{\alpha \vec{A}_0}{\omega} \cdot (\vec{G}_2 + \vec{k}) \right) e^{-ir\omega t_0} \right] \delta_{\vec{k}, \vec{k}'}, \quad (\text{A.10}) \end{aligned}$$

which leads to Eqs. (14) and (15).

REFERENCES

1. P. Lambropoulos, *Adv. Atom. Mol. Phys.* **12**, 87 (1976).
2. J.E. Bayfield, *Phys. Reports*, **51**, 317 (1979).
3. F. Ehlotzky, *Can. J. Phys.* **59**, 1200 (1981).
4. M.H. Mittelman. *Introduction to the Theory of Laser-atom Interactions.* (Plenum Press, New York) (1982).
5. S.I. Chu, *Adv. Atom. Mol. Phys.* **21**, 197 (1984).
6. L.A. Lompré, G. Mainfray, C. Manus, S. Repoux and J. Thebault, *Phys. Rev. Lett.* **36**, 949 (1976).
7. K.G.H. Baldwin and B.W. Borenham, *J. Appl. Phys.* **52**, 2627 (1981).
8. S.L. Chin, F. Yergeau and P. Lavigne, *J. Phys. B: At. Mol. Phys.* **18**, L213 (1985).
9. L.V. Keldysh, *Z. Eksp. Teor. Fiz.* **47**, 1945 (1964) [*Sov. Phys. JETP* **20**, 1307 (1965)].
10. H.D. Jones and H.R. Reiss, *Phys. Rev.* **B16**, 2466 (1977).
11. H.S. Brandi, Ginette Jalbert and O.L. Malta, *Phys. Stat. Sol. (b)* **124**, 147 (1984).
12. H.S. Brandi, Ginette Jalbert and O.L. Malta, *Revista Brasileira de Física* **13**, 633 (1983).
13. J.H. Shirley, *Phys. Rev.* **B138**, 979 (1965).
14. G. Jalbert, B. Koiller, H.S. Brandi and N. Zagury, *J. Phys. C: Solid State Phys.* **19**, 5745 (1986).
15. G. Thomas, *J. Chem. Phys.* **79**, 4912 (1983).
16. A. Antonetti, R. Astier, J.L. Martin, A. Migus, D. Hulin and A. Mysyrowicz, *Optics Comm.* **38**, 431 (1981).
17. N. Tzoar and J.I. Gersten, *Phys. Rev.* **B12**, 1132 (1975).