Optical Nonlinearity Induced by Giant Dipole Moment of Wannier Excitons

Akira Shimizu

Canon Inc. Research Center, 5 Morinosato-Wakamiya, Atsugi, Kanagawa 243-01, Japan

(Received 16 October 1987)

A new mechanism for enhancing optical nonlinearities in quantum well structures, subject to an electric field normal to the layers, is investigated. It is found that large nonlinearities are induced by virtual transitions of Wannier excitons with "giant dipole moments." In contrast to other mechanisms, this enhancement mechanism is independent of correlations between excitons, for *any* order of nonlinearities. This fact results in a resonant enhancement at *half* the excitonic energy, and an ultrafast response, even faster than other virtual-process–induced mechanisms.

PACS numbers: 71.35.+z, 42.65.Bp, 78.65.−s

The recent advance of the physics of semiconductor superlattices and quantum well structures (QWS's)[1] has revealed the possibility of the enhancement of optical nonlinearities in these systems over those in bulk crystals.[2-9] The purpose of this Letter is to propose a new mechanism for the enhancement of optical nonlinearities due to *interband virtual* transitions.

To achieve fast response, one has to use virtual excitations (i.e., the photon energy should be less than the absorption edge),[4-7] rather than real excitations for which very large nonlinearities can be obtained at the expense of speed of the response time (>1 ns).[3] The dominant mechanism of optical nonlinearities due to virtual processes in usual QWS's is the optical (or ac) Stark effect,[4] which is due to many-body correlations between virtual excitations.[5] To obtain *larger* nonlinearities, one should utilize some "modified" QWS's for which some *additional* effects for enhancement can be expected. A possible candidate is biased QWS's, i.e., QWS's in a static electric field, F_{bias}, normal to the layers.

Biased QWS's have been investigated in connection with the quantum confined Stark effect, which can be represented as a strong dependence of the *linear* susceptibility, $\chi^{(1)}$, on F_{bias}.[8] To consider nonlinear responses, we focus on the effects of excitons, since optical properties of semiconductors near the band edge are mostly determined by excitons. Then, most characteristic of the biased QWS's is the very large static dipole moment of excitons, which is hardly obtainable in bulk crystals.[8,9] This field-induced static dipole moment may be called "the giant dipole moment" (GDM) in the sense that, as explained below, the GDM is much larger than a possible static dipole moment of any of the usual excitations in inorganic semiconductors.

The virtual charge-induced optical nonlinearity (VCON), found by Yamanishi[6] and by Chemla, Miller, and Schmitt-Rink,[7] can be viewed as a result of the GDM of excitons. That is, the GDM of virtually excited excitons gives rise to static polarization, which is second order in the light field. In my notation of the nth-order nonlinear susceptibility $\chi^{(n)}$, this nonlinearity is represented by $\chi^{(2)}(0;\omega,-\omega)$. Furthermore, this static polarization creates a depolarization field, F_{dpl}, against F_{bias}. Then, excitons feel $F_{\text{bias}}+F_{\text{dpl}}$, instead of just F_{bias}. This results in changes of both the energy and the oscillator strength of the excitons, which cause changes of the dielectric function. This nonlinearity is represented by $\chi^{(3)}$. Note that excitons could *not* affect themselves if there were no many-body correlations between them. This simply means an absence of self-energy for noninteracting particles. In the case of VCON, it can be shown that excitons themselves "feel" F_{dpl} through the dipole-dipole interaction between GDM's of excitons. Thus, for $n\geq 3$, VCON, as well as the optical Stark effect and any other enhancement mechanisms, relies upon correlations between excitons, although VCON for $n=2$ is independent of the correlations.

In this Letter I propose a new mechanism for the enhancement of $\chi^{(n)}$, which is *independent of any correlations between excitions,* for *any* n. This mechanism may be called "the direct GDM effect," or simply "the GDM effect," since this enhancement can be understood as a direct result of the GDM of excitons, as shown below. For $\chi^{(2)}$ and $\chi^{(3)}$, the direct GDM causes resonant enhancement *both* at E_{ex} (the excitonic energy) and at $E_{\text{ex}}/2$, whereas both VCON and the optical Stark effect cause enhancement near E_{ex} *only*. The enhancement at $E_{\text{ex}}/2$ is important for practical applications, because the QWS is essentially transparent (i.e., *linear* absorption is absent) for this photon energy, and we can fully utilize large $\chi^{(n)}$ simply by avoiding the peak of the corresponding *nonlinear* absorption. (Note that at a practical intensity of light of, say, a laser diode, the nonlinear absorption is much smaller than the linear one.) By contrast, linear absorption would occur at E_{ex}, when the optical pulse is so short that the energy spectrum is broad and extends to the absorption edge,[10] and/or when the absorption spectrum has a long tail due to, e.g., nonuniformity of F_{bias} in a multiple QWS (MQWS). Furthermore, in this case the response of VCON and the optical Stark effect becomes slow as a result of lifetime limitations, because real excitations occur.[10] On the other hand, the direct GDM is basically free from lifetime limitations *even in the above case,* because it does not

rely on correlations between excitons, and thus is basically independent of (low density) real populations. Also, the real excitation itself can be suppressed by the use of a photon energy near $E_{ex}/2$. Thus, the response of the direct GDM is *faster* than the other two mechanisms. Details on the above points will be given elsewhere.

First of all, let us define the GDM of excitons. The electric dipole moment of an excitonic state $|ex\rangle$ can be written as the sum of two terms: $\langle ex|\mathbf{P}_t|ex\rangle = e\mathbf{l}_{cell} + e\mathbf{l}_{env}$. Here, $\mathbf{P}_t$ denotes the total electric polarization operator, e is the unit charge, $e\mathbf{l}_{cell}$ represents the polarization due to the cell-periodic parts, and $e\mathbf{l}_{env}$ is the GDM of the exciton. They are defined by

$$\mathbf{l}_{cell} \equiv \frac{1}{v}\int_{cell} d^3\rho\,\boldsymbol{\rho}(|u_v(\boldsymbol{\rho})|^2 - |u_c(\boldsymbol{\rho})|^2), \tag{1}$$

$$\mathbf{l}_{env} \equiv \int d^3r_e \int d^3r_h (\mathbf{r}_h - \mathbf{r}_e)\,|\psi_{env}(\mathbf{r}_e,\mathbf{r}_h)|^2, \tag{2}$$

where u_c (u_v) is the cell-periodic part of the electron (hole), v is the volume of a unit cell, $\boldsymbol{\rho}$ represents the position vector within a unit cell, $\mathbf{r}_e$ ($\mathbf{r}_h$) denotes the position of the electron (hole), and ψ_{env} is the excitonic envelope function. For usual excitonic states $\mathbf{l}_{env}=0$ since ψ_{env} is highly symmetric, and excitonic dipole moments, if any, are provided solely by the cell term $\mathbf{l}_{cell}$. Because of the lattice periodicity, the magnitude of l_{cell} is always less than the lattice constant a. On the other hand, for biased QWS's ψ_{env} is "deformed" (because of the bias field), resulting in a finite l_{env} of the order of the excitonic Bohr radius a_B^*, which dominates the above term since

$$l_{env} \sim a_B^* (\sim 120\ \text{Å for GaAs}) \gg a (\sim 5\ \text{Å}) > l_{cell}.$$

It should be noted that $\mathbf{l}_{env}$ is basically independent of the component materials of the system since $\mathbf{l}_{env}$ depends on neither u_c nor u_v. Therefore, $\mathbf{l}_{env}$ (and $\chi^{(2)}$) can be finite even for QWS's based on centrosymmetric crystals for which $l_{cell}=\chi^{(2)}=0$.

According to nonlinear-response theories,[11-13] the microscopic expression for $\chi^{(n)}$, in electric dipole approximation, contains a product of matrix elements of a form

$$\langle g|\mathbf{P}_t|m_1\rangle\langle m_1|\mathbf{P}_t|m_2\rangle\langle m_2|\mathbf{P}_t|m_3\rangle\cdots\langle m_n|\mathbf{P}_t|g\rangle,$$

where $|g\rangle$ stands for the ground state of the system, and the $|m_i\rangle$'s are many-body excited states. We consider the excitonic contribution to $\chi^{(n)}$ in direct-gap semiconductors. By the selection rule, single $\mathbf{P}_t$ can change the number of excitons by ± 1 or 0. Then, there exist terms whose $|m_i\rangle$'s are all single-exciton states, $|ex_i\rangle$. This means that no exciton-exciton correlation is involved in these terms. The magnitude of the product $\langle g|\mathbf{P}_t|ex_1\rangle\langle ex_n|\mathbf{P}_t|g\rangle$ is determined by the oscillator strength f. We focus on $n-1$ matrix elements of the form $\langle ex_i|\mathbf{P}_t|ex_j\rangle$. As discussed above, the magnitude of its diagonal elements is $e\mathbf{l}_{cell}$ for the usual excitons, whereas it is $e\mathbf{l}_{env}$ for excitons with GDM. Thus, the contribution of the above terms to $\chi^{(n)}$, if any, is proportional to fl_{cell}^{n-1} for the usual systems, whereas it is proportional to fl_{env}^{n-1} for the excitonic system with GDM, resulting in very large values of $\chi^{(n)}$. This is the direct GDM term.

For $n \geq 3$, there are other terms for which some $|m_i\rangle$'s are states of two or more excitons $|ex_1 ex_2 \ldots\rangle$. These terms give rise to nonlinearities only when the $|ex_1 ex_2 \ldots\rangle$ are deviates from the simple product of single-exciton states.[13] [By contrast, the GDM effect utilizes the anomalous property (i.e., the GDM) of the single-exciton states.] The deviation is caused by various correlations between excitons,[13] e.g., dipole-dipole interaction in the case of VCON. The $\chi^{(n)}$ with $n \geq 3$ is the sum of all such correlation-related contributions (i.e., VCON and the optical Stark effect, etc.) and the direct GDM contribution.

Although the difference between the direct GDM and the other mechanisms is obvious for $n \geq 3$ from the above argument, care is needed for $n=2$ because the above definition of the direct GDM terms *includes* $\chi^{(2)}(0;\omega,-\omega)$ due to VCON. Thus, for $n=2$, what is newly found is the enhancement of $\chi^{(2)}(2\omega;\omega,\omega)$ shown below. In particular, the enhancement of $\chi^{(2)}$ at $E_{ex}/2$ can be shown to come from the nonlinear interaction of GDM with the light field, which was disregarded in previous work.[6,7] This interaction causes a modulation of the energy of virtual excitons by the light field, which results in optical nonlinearities. It can be shown that all the direct GDM terms for $n \geq 3$ come from this interaction, although a *part* of the contribution to $\chi^{(2)}(2\omega;\omega,\omega)$ at E_{ex} is independent of this interaction. Thus, in a slightly narrower sense, the direct GDM mechanism is the effect of this interaction.

Let us calculate $\chi^{(n)}$, both for bound and unbound excitons, of the GaAs/AlGaAs MQWS under F_{bias} normal to the layers, along the z direction. Barriers are assumed to be sufficiently high and thick that each well can be treated separately. The excitonic envelope function ψ_{env} is assumed to be of the form

$$\psi_{env}(\mathbf{r}_e,\mathbf{r}_h) = G(\mathbf{R}_\parallel)W(\mathbf{r}_\parallel,z_e,z_h),$$

where $\mathbf{R}_\parallel$ and $\mathbf{r}_\parallel$ are the center-of-mass and relative coordinates, respectively, of an electron-hole pair for two-dimensional motion in the x-y plane. For bound excitons,[14] G may be written as

$$G_{\mathbf{R}_\parallel^0}(\mathbf{R}_\parallel) = (2/\pi\xi^2)^{1/2}\exp(-|\mathbf{R}_\parallel - \mathbf{R}_\parallel^0|/\xi),$$

where $\mathbf{R}_\parallel^0$ denotes the position of a bound center (say, a QW imperfection), and ξ is the localization length. For unbound excitons, G is given by a plane wave. As for W, we use the variational form[15] which is described by the (lowest) subband envelope functions, ϕ_e (for electrons) and ϕ_h (for holes), and the $1S$-like function with two variational parameters α and β, which correspond to the inverse of the anisotropic excitonic Bohr radius. With the above envelope function, $\mathbf{l}_{env}$ is along the z direction,

and the z component is given by

$$l_{\rm env}=(1/I_z)\int dz_e\int dz_h\, e^{-2\beta|z_e-z_h|}(2\beta|z_e-z_h|+1)|\phi_e(z_e)|^2|\phi_h(z_h)|^2(z_h-z_e), \tag{3}$$

where I_z has appeared from the normalization of W, and is given by our dropping the factors $1/I_z$ and z_h-z_e in this equation.

For the second-harmonic generation, resonantly large values of $\chi^{(2)}$ [$\equiv\chi^{(2)}(2\omega;\omega,\omega)$] are obtained when the photon energy (either $\hbar\omega$ or $2\hbar\omega$) is close to the excitonic energy, $E_{\rm ex}$. The calculated result for $\chi^{(2)}$, slightly below the one-photon resonance (i.e., $\hbar\omega=E_{\rm ex}-\Delta$, $0<\Delta\ll E_{\rm ex}$), is given by

$$\chi^{(2)}_{ijk}=\frac{e^3}{4}\frac{2\Xi}{L_z+L_B}\frac{2a^2|I_{eh}|^2}{\pi I_z}\frac{l_{\rm env}}{E_g\Delta}[(R_k^*R_j+R_j^*R_k)\delta_{i,z}-2(R_i^*R_k\delta_{j,z}+R_i^*R_j\delta_{k,z})], \tag{4}$$

where i,j,k ($=x,y,z$) denote the tensor indices, and the R_i's are the transition matrix elements:

$$R_i\equiv(1/v)\int_{\rm cell}d^3\rho\,\rho_i u_c^*(\rho)u_v(\rho).$$

In Eq. (4), L_z (L_B) is the well (barrier) thickness, E_g ($\approx E_{\rm ex}$) denotes the band-gap energy of the well, δ is the Kronecker delta, $\Xi=1$ for unbound excitons while $\Xi=8\pi\xi^2/\sigma$ for bound excitons, with σ^{-1} being the areal number density of bound centers, and $I_{eh}\equiv\int dz\,\phi_e^*(z)\phi_h(z)$ is the overlap integral of a free electron-hole pair. On the right-hand side of Eq. (4), the second factor comes from the sum over excitonic states (2 is the spin degeneracy), the third factor and the R's are from the oscillator strength, and the δ's are due to the direction of $\mathbf{l}_{\rm env}$.

For the bulk GaAs crystal, $\chi^{(2)}_{i'j'k'}$ is nonzero only if the i',j',k' are all different, because of the symmetries of the zinc-blende structure,[16] where i',j',k' ($=1,2,3$) refer to the crystallographic axes (which do not necessarily agree with the QW axes). This is not the case for the present system. Disregarding the anisotropy of $\mathbf{R}$, i.e., setting $R_i\equiv R$, independent of i, we find that the nonvanishing components of $\chi^{(2)}_{ijk}$ are as follows:

$$\chi^{(2)}_{\eta zz}=2\chi^{(2)}_{zzz}=2\chi^{(2)}_{\eta\eta' z}=2\chi^{(2)}_{\eta z\eta'}=-2\chi^{(2)}_{z\eta\eta'},$$

where η and η' are x or y. For $L_z=120$ Å, $L_B=80$ Å, and $F_{\rm bias}=100$ kV/cm, we obtain $\chi^{(2)}_{\eta zz}\approx-8\times10^{-6}$ esu, by using the values[15] $|R|^2=(3\ \text{Å})^2$, $\Xi=1$, $a\approx1.2/a_B^*\approx(100\ \text{Å})^{-1}$, $|I_{eh}|^2\approx0.5$, $l_{\rm env}\approx0.5L_z$, $I_z\approx0.7$, $E_g=1.5$ eV, and $\Delta=1$ meV. This value of $|\chi^{(2)}|$ is about 10 times larger than the observed value[16] of $(7\pm2)\times10^{-7}$ esu for $|\chi^{(2)}_{123}|$ of bulk GaAs.

In the case of the two-photon resonance (i.e., $2\hbar\omega=E_{\rm ex}-\Delta$), the formula for $\chi^{(2)}$ is obtained by replacement of the factor in the square brackets in Eq. (4) by $4(R_i^*R_k\delta_{j,z}+R_i^*R_j\delta_{k,z})$. The nonvanishing components are then $\chi^{(2)}_{izz}=2\chi^{(2)}_{i\eta z}=2\chi^{(2)}_{iz\eta}\approx16\times10^{-6}$ esu, where $i=x,y,z$. This value is about 20, 400, and 5000 times larger than those for bulk GaAs, $LiNbO_3$, and potassium dihydrogen phosphate crystals,[16] respectively.

Similar calculations can be made for higher n. Note that the factor of enhancement is larger for higher n because $\chi^{(n)}\propto l_{\rm env}^{n-1}$. For $n=3$, $\chi^{(3)}$ can be shown to be 10–10^3 times greater than the value for bulk crystals, both at $E_{\rm ex}$ and at $E_{\rm ex}/2$.

I shall now discuss possible corrections to the above results. We have calculated the contribution to $\chi^{(n)}$ only from the $1S$ heavy-hole exciton composed of the lowest subbands. Although there must be other contributions such as that from ionized excitons, one expects that the former is dominant near the (lowest) excitonic resonance in the present system, since in QWS's the $1S$ heavy-hole excitonic resonance peak is very sharp and well separated from the other contributions.[17] I have assumed low temperature. Since in QWS's the excitonic peak is known to be stable even at the room temperature,[17] for which the full width Γ is several millielectronvolts, one expects the calculation to remain valid as long as $\Delta\gtrsim\Gamma/2$. The maximum values of $|\chi^{(n)}|$ would be obtained at $|\Delta|\approx\Gamma/2$. The anisotropy in $\mathbf{R}$ can modify the numerical factors in the relations between different tensor components, such as 2 in $\chi^{(2)}_{\eta zz}=2\chi^{(2)}_{zzz}$. The local field correction may slightly increase the magnitude of $\chi^{(n)}$. Despite our taking all these corrections into account, however, the estimated order of magnitude of $|\chi^{(n)}|$ would remain unchanged.

Note that the above MQWS is not the optimized one. As for L_z and $F_{\rm bias}$, for example, larger L_z or $F_{\rm bias}$ would result in larger $l_{\rm env}$ and smaller $|I_{eh}|^2/(L_z+L_B)$ in Eq. (4). Thus, optimum values should exist. Furthermore, modified QWS's, such as the graded-gap QWS,[6] can lead to larger $\chi^{(n)}$. These optimizations should be a future problem. I also note that the GDM effects can be realized in any quantum microheterostructures, such as quantum lines or boxes, of any (direct-gap) semiconductors or insulators. And also, the polarization of the envelope function can be supplied by other means, say, by a built-in potential or by the gradual change of the composition of a type-II-staggered superlattice[1] with barrier layers inserted.

Let us compare the present mechanism, for $n=2$, with the dc-electric-field-induced second-harmonic generation for *bulk* crystals (or gases),[18] which is the enhancement of $\chi^{(2)}$, observed for some bulk materials, by the application of the dc bias field. I first note that the *absence* of that enhancement was confirmed for GaAs *bulk* crystals.[18] Let us discuss the advantage of the present mechanism from a more general point of view. For usual (non-small-gap) semiconductors, the dc second-harmonic generation is due to polarization of immobile electrons.[18]

Then, only a small enhancement is expected for noncentrosymmetric crystals since electrons are already polarized before the application of F_{bias}, while the *relative* increase of $\chi^{(2)}$ is drastic for centrosymmetric crystals since $\chi^{(2)}(\text{no bias})=0$. We should note that the *absolute* magnitude of the resulting dipole moment for each electron is still less than the lattice constant (because of the lattice periodicity), which is much smaller than GDM obtained in QWS's. Furthermore, QWS's are also needed in order to utilize excitons, since excitons are unstable in bulk crystals.[8,9] The advantages of our using excitons[19] are that (a) we can utilize strong resonance since the excitonic state is localized in energy, in contrast to band electrons, and (b) an excitonic state has much larger oscillator strength than a free electron-hole pair. Therefore, we can state quite generally that $\chi^{(2)}(\text{bulk}) \leq \chi^{(2)}(\text{biased bulk}) \ll \chi^{(2)}(\text{biased QWS})$.

Both the direct GDM mechanism and VCON are closely related to large nonlinearities observed in some organic materials, for which the nonlinearities are considered to be due to the "GDM" of *excited states of the molecules.*[20] For organic materials, excitons are usually localized, say, as Frenkel excitons, so that l_{env} (if any) cannnot exceed l_{cell} by much. However, the GDM can be provided by the asymmetry of the molecular orbitals, which correspond to l_{cell}, since the molecular orbitals can become very long as compared with the lattice constant of inorganic semiconductors. In this sense, each quantum well corresponds to a two-dimensional array of long molecules. A Wannier exciton with GDM corresponds to a Frenkel exciton of the long asymmetric (polarized) molecules. The large optical nonlinearities of organic materials, especially those of layered ones, may be understood more clearly with the concepts of VCON and the direct GDM mechanism.

Finally, I comment on the experimental situation. To my knowledge, no experiments corresponding to the present prediction have yet been performed. Presumably, the easiest way to observe the GDM effect is to measure $\chi^{(2)}$ or $\chi^{(3)}$ of a GaAs/AlGaAs MQWS, both with and without F_{bias}, near the two-photon resonance (to avoid VCON, the optical Stark effect, and linear absorption), at low temperatures.

In conclusion, I have found a new excitonic nonlinear mechanism, the direct GDM effect, which provides the possibility of QWS's (or quantum lines or boxes) as new nonlinear materials with (1) large $\chi^{(n)}$ ($\propto f l_{\text{env}}^{n-1}$), (2) ultrafast response (<1 ps), and (3) transparency for light (especially, at $E_{\text{ex}}/2$). These properties suggest wide potential applications.

Helpful discussions with Professor H. Sakaki and Professor D. C. Tsui are gratefully acknowledged. Hearty thanks are also due to T. Sawada, T. Utsumi, and I. Endo for constant encouragement.

[1]L. Esaki, IEEE J. Quantum Electron. **22**, 1611 (1986).

[2]Y. C. Chang, J. Appl. Phys. **58**, 499 (1985), and references therein.

[3]S. Schmidtt-Rink, D. S. Chemla, and D. A. B. Miller, Phys. Rev. B **32**, 6601 (1985).

[4]A. Mysyrowicz, D. Hulin, A. Antonetti, A. Migus, W. T. Masselink, and H. Morkoc, Phys. Rev. Lett. **56**, 2748 (1986).

[5]S. Schmitt-Rink and D. S. Chemla, Phys. Rev. Lett. **57**, 2752 (1986).

[6]M. Yamanishi, Phys. Rev. Lett. **59**, 1014 (1987).

[7]D. S. Chemla, D. A. B. Miller, and S. Schmitt-Rink, Phys. Rev. Lett. **59**, 1018 (1987).

[8]D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Wiegmann, T. H. Wood, and C. A. Burrus, Phys. Rev. Lett. **53**, 2173 (1984). Although, some authors represent the quantum confined Stark effect by $\chi^{(2)}(\omega;\omega,0)$, where "0" corresponds to F_{bias}, I will not use such a notation here; i.e., I consider F_{bias} as a given parameter.

[9]Bulk excitons are unstable against the bias field because of (a) lower binding energy, (b) field ionization (see Ref. 8), and (c) the impact ionization by free carriers [W. Bludau and E. Wagner, Phys. Rev. B **13**, 5410 (1976)]. However, for very pure crystals at very low temperatures, both (a) and (c) could be irrelavent. As for (b), using standard formulas for the linear polarizability and tunneling probability, we can estimate the field ionization time as $\tau \approx 4/E_b$ ps, under F_{bias} needed to produce $l_{\text{env}} \approx a_B^*/2$. Here E_b is the exciton binding energy measured in millielectronvolts. For typical direct-gap semiconductors, E_b is 2–40 meV, and τ is 2–0.1 ps, which is comparable to the transverse relaxation time of the system. The smallness of the oscillator strength of the bulk excitons as compared with the QW excitons is also a disadvantage of the bulk. Considering also the sensitivity of τ on F_{bias}, we should state that the situation is marginal; the GDM effect in bulk crystals, if any, might be observed only by very careful experiment, which would be a challenging problem.

[10]M. Yamanishi, M. Kurosaki, Y. Osaka, and S. Datta, in Proceedings of the Sixth International Conference on Ultrafast Phenomena, Mt. Hiei, Japan, July 1988 (Springer-Verlag, New York, to be published).

[11]R. Kubo, J. Phys. Soc. Jpn. **12**, 1 (1957), Eq. (2.28).

[12]Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984), Chap. 2, and references therein.

[13]E. Hanamura, Phys. Rev. B **37**, 1273 (1988).

[14]J. Hegarty and M. D. Sturge, J. Opt. Soc. Am. **2**, 1143 (1985), and references therein.

[15]M. Matsuura and T. Kamizato, Phys. Rev. B **33**, 8385 (1986).

[16]A. Yariv, *Optical Electronics* (CBS College Publishing, New York, 1985), Chap. 8.

[17]D. S. Chemla, D. A. B. Miller, P. W. Smith, A. C. Gossard, and W. Wiegmann, IEEE J. Quantum Electron. **20**, 265 (1984).

[18]R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Lett. **8**, 404 (1962), J. H. McFee, Appl. Phys. Lett. **11**, 228 (1967); R. S. Finn and J. F. Ward, Phys. Rev. Lett. **26**, 285 (1971).

[19]After the submission of this Letter, there appeared a discussion of $\chi^{(2)}$ of asymmetric QWS's [J. Khurgin, Appl. Phys. Lett. **51**, 2100 (1987)]. Since Khurgin did not consider excitonic effects, the values of $\chi^{(2)}$ obtained are much smaller than those predicted here. He did not consider $\chi^{(n)}$ for $n \geq 3$.

[20]N. C. Kothari and T. Kobayashi, IEEE J. Quantum Electron. **20**, 418 (1984).