Excitons in semiconductor superlattices: Heuristic description of the transfer between Wannier-like and Frenkel-like regimes

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In this paper, we present a straightforward model calculation, based on a heuristic approach, which gives a satisfactory description of excitons in quantum-confined heterostructures, varying continuously from isolated quantum wells to superlattices. In particular, we show how it is possible to account for the progressive crossing from a Wannier-like regime, for short periods, to a Frenkel-like behavior, when the quantum wells become decoupled. We propose a comparison with previous variational approaches.

With recent developments in semiconductor technology, the growth of systems consisting of alternate thin layers of two different semiconductors with controlled thicknesses has become possible. Thus, during the past few years, heterostructures such as heterojunctions, quantum wells, and superlattices have stimulated new research in semiconductor physics. In particular, a considerable amount of work has been devoted to the optical properties of such quantum-confined heterostructures. The ability to produce a strong spatial localization of electrons and holes between high-quality interfaces made it possible to observe efficient intrinsic excitonic lines, even at room temperature. It is now well established that the size-quantization field deeply alters the binding energy and oscillator strength of free excitons. This point was intensively studied from both the experimental[1-7] and theoretical[7-22] points of view. However, the mathematical description of these systems was recently submitted to a kind of "inflation" in the complexity, in order to take account of more and more intimate details of the band structure of the host materials. Consequently, the spectroscopist often finds himself in a comfortless situation: properly unraveling intricate optical spectra needs to estimate the total effect of confinement. First, one needs to calculate the energies of subband-to-subband transitions; this is rather straightforward using the envelope function formalism. But some difficulty may arise from the correct inclusion of Coulombic effects. The most accurate calculations[7-22] are variational: they have the advantage of providing a rigorous lower bound on the binding energies as well as estimates for the oscillator strengths. Nevertheless, such theories, although not really tedious, may fall outside the scope of some experimentalists. Leavitt and Little[23] recently fitted to the dimensionless result of a variational calculation by the ratio of two polynomials, which is a valuable simplification.

In this Brief Report, we present a straightforward model, based on heuristic considerations of dimensionality, which gives a satisfactory description of excitons in quantum-confined heterostructures, varying continuously from isolated quantum wells to superlattices.

It is well known that these systems are somewhere in between a bidimensional (2D) and a tridimensional (3D) system, so that neither the 3D nor the 2D model is a good one. As a result, the existing mathematical solutions, which all use a 3D model, are tedious. The original method proposed by He[24] consists in stating that, because the real problem is neither purely 3D nor purely 2D, a fractional-dimensional space should be used to simplify the mathematical treatments. In this model, the anisotropic interactions in the 3D space are treated as isotropic ones in an α-dimensional space, where the dimension α is determined by the degree of anisotropy. In other words, the fractional-dimensional model consists in solving the Schrödinger equation in an αD space where the interactions actually experience an isotropic environment. Within this formalism, the exciton binding energy is given by

$$E_b = E_0 \left[\frac{2}{\alpha - 1} \right]^2 , \tag{1}$$

where E_0 is the value of the 3D effective Rydberg. Setting $\alpha = 3$, 2, or 1 allows us to obtain the well-known results for the integer-dimensional models. Of course, the present formalism is only relevant when an anisotropic medium surrounds the exciton, and not when a perturbating potential breaks its internal structure, as could occur in type-II systems. In previous works,[25,26] we have shown that, for a type-I single quantum well, very satisfactory values for E_b could be obtained by just using a model of the "compression" undergone by the unit vector along the quantization axis of the quantum well. From the consideration of the physical respective sizes of the quantum well and of the 3D exciton, we can infer[26] the following expression for α:

$$\alpha = 3 - e^{-L_w^*/2a_0} , \tag{2}$$

where $L_w^* = L_w + 2/k_b$ is the "effective width" of the quantum well, i.e., the real width L_w plus the spreading of the carriers into the barriers at both sides of the well. By a simple envelope function calculation of the electron and hole confined states in the quantum well, we can esti-

mate this spreading as twice the quantity $1/k_b$, where $k_b^{-1}=k_{b_e}^{-1}+k_{b_h}^{-1}$, k_{b_e} and k_{b_h} being the "wave vectors" characteristic of the vanishing of electrons and holes, respectively, in the barriers. This model can even be improved[26] by inclusion of additional ingredients (band nonparabolicities, dielectric constant mismatch between host materials, . . .) and converges towards a unique 3D value for light- and heavy-hole exciton binding energies on both limits of infinitely wide and vanishingly narrow quantum wells. In any case, our results compare very favorably to those of other calculations and to experimental findings.

Now, let us consider the case of superlattices. A superlattice is a kind of effective semiconductor with a strongly anisotropic Brillouin zone, which one has the opportunity to vary at will, since the width of this zone along the growth axis is inversely proportional to the period. When the width of the Brillouin zone is large, comparing with $1/a_0$ (a_0 is the Bohr radius of the exciton), the Coulombic potential is slowly varying relative to the period of the superlattice. This corresponds to the criterion for validity of the Wannier approximation.[27] On the other hand, when the well are decoupled, this criterion is no longer fulfilled, and another type of treatment is necessary. The variational calculation of Ref. 7, which uses a rather simple trial function, nicely exhibits the boundary between both regimes: both in-plane and on-axis extension parameters present a discontinuity at this point. Within our formalism, the dimensionality α should account for the gradual crossing from a quasi-3D case—for thin periods or, at least, thin barriers—to a strongly anisotropic situation. We make the following proposal:

$$\alpha=3-(1-\beta)\ , \tag{3}$$

where β is an anisotropy parameter defined as $\beta=\mu_{0z}/\mu_z$. μ_{0z} and μ_z are the on-axis reduced effective masses in the 3D crystal and in the superlattice, respectively. The latter is obtained by calculating the curvatures of the electron and hole first minibands at the zone center. The reason for this choice is the following: we need a variation of α from 3 for periods near zero ($\beta\rightarrow 1$), to 2 when the period (or simply the barrier) becomes larger, i.e., when μ_z becomes infinite ($\beta\rightarrow 0$). This means that the dispersion relations of the superlattice run from a 3D to a 2D situation. Then, from Eq. (1), the binding energy should consequently vary from one time to four times the effective 3D Rydberg.

Recently, Pereira *et al.*[19] presented a theory which is, in principle, comparable to ours. In this model, the superlattice is considered as an effective semiconductor with strongly anisotropic dispersion relations. The on-axis reduced effective mass of the electron-hole pair is compared to its analog for the in-plane motion, so that the ratio of the two constitutes an anisotropy parameter γ. Figure 1 displays a comparison of the results of Ref. 19 with our calculation performed by using exactly the same numerical parameters: the binding energy of the confined exciton follows rather similar variations in both models. However, a slight difference exists between their respective slopes, our model giving a faster increase of

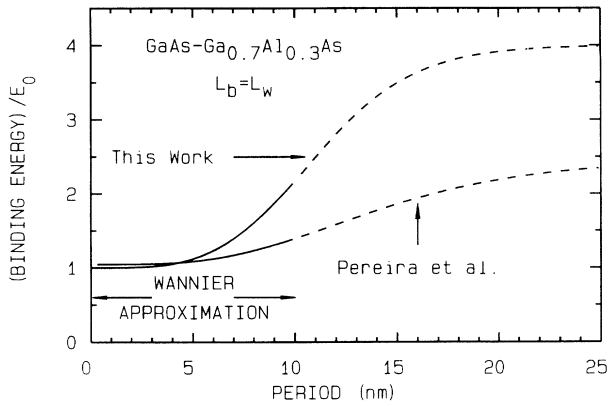

FIG. 1. Plot of the binding energy of the 1*s* exciton involving the first heavy-hole and electron subbands in a GaAs-$Ga_{0.7}Al_{0.3}As$ superlattice with equal well and barrier widths ($L_w=L_b$), vs the period. The result of our calculation using Eqs. (1) and (3) is compared to the one of the model of Ref. 19. Solid lines show the range of validity of these models, while dashed lines allow comparison of their asymptotic behaviors for wide periods, which explain the observed difference of slopes.

the binding energy versus the period. Note that β in our model is different from γ used in Ref. 19. Our choice is motivated by the anisotropy of dispersion relations in valence bands, which appears as soon as the fourfold degeneracy is lifted, as in quantum wells. When reducing the period down to zero, one should expect to recover a three-dimensional isotropic medium, rather than an artificially anisotropic one. In order to avoid such an artifact, we thus prefer to compare the effective mass in the superlattice to what this mass would be in the 3D equivalent alloy. This alloy corresponds to mixing both semiconductors rather than making up a heterostructure, keeping the same proportions. This should "naturally" describe the threshold of occurrence of the coupling—or decoupling—between the quantum wells, which controls the anisotropy of the superlattice. Indeed, this way of computing α takes advantage of characteristics of the whole heterostructure, such as effective masses or potential discontinuities, in a global way. Thus the variation of α from 3 to 2 should occur at the same "rate" as the continuous crossing from a situation with coupled quantum wells to a situation with quasi-isolated ones.

In fact, the limit of validity of both models is similar to the criterion for validity of the Wannier approximation in bulk semiconductors; in the present case, the exciton Bohr radius should be compared to the period of the superlattice, rather than to that of the host crystal. This is why we refer to a "Wannier-like" regime. Practically, for superlattices with equal well and barrier thicknesses, and for usual materials (e.g., GaAs-$Ga_{0.7}Al_{0.3}As$) this approximation is only valid for periods lower than about 10 nm. Increasing the period, at some value the quantum wells become decoupled, which implies that the excitons which could appear tend to be localized within one given well. In other words, the "size" of the exciton becomes smaller than the period of the superlattice. Then, we can no longer consider that the exciton "sees" the superlattice as

an effective medium, since the motion of the carriers along the z axis is inhibited. In other words, decoupling the quantum wells makes the system transfer from a "Wannier-like" regime into a "Frenkel-like" regime, where the exciton only "sees" one elementary cell.

As clearly demonstrated in earlier works,[7,18] progressively increasing the barrier widths in the superlattice, or the period, leads to a situation similar to the one of single quantum wells. As stated above, our model has proven to give a correct description of excitonic features, in this case. In fact, the really questionable point is again how to predict the exact threshold between the "Wannier-like" and "Frenkel-like" regimes and the shape of the corresponding onset. The variational approach proposed by Dignam and Sipe,[18] using a basis of "two-well" exciton states predicts a sensitive effect of interwell coupling for periods below 15 nm, in the model case of symmetrical GaAs-$Ga_{0.7}Al_{0.3}As$ superlattices. An excellent agreement is found with available experimental data[7] down to about 6 nm of period, below which the calculated Rydberg becomes vanishingly small. Although this model is very accurate, it is clear, from the reading of Ref. 18, that it needs the use of quite tedious calculations and thus of computational facilities, which may not be at the disposal of every spectroscopist. Figure 2 illustrates the principle of our method: we propose to combine, by a simple multiplication, the reductions of dimensionality obtained from Eqs. (2) and (3). The resulting expression is then

$$\alpha = 3 - (1-\beta)e^{-L_w^*/2a_0} . \tag{4}$$

In Fig. 2 we have plotted the calculated binding energy of the 1s exciton in symmetrical GaAs-$Ga_{0.7}Al_{0.3}As$ superlattices, versus the period. Two dashed lines labeled W and F correspond, respectively, to the application of Eq. (3) ("Wannier-like") and Eq. (2) ("Frenkel-like"), and the full line is the result of Eq. (4). Curve W is discussed above, while curve F just accounts for the variation of the well width, ignoring the effect of the barrier thickness.

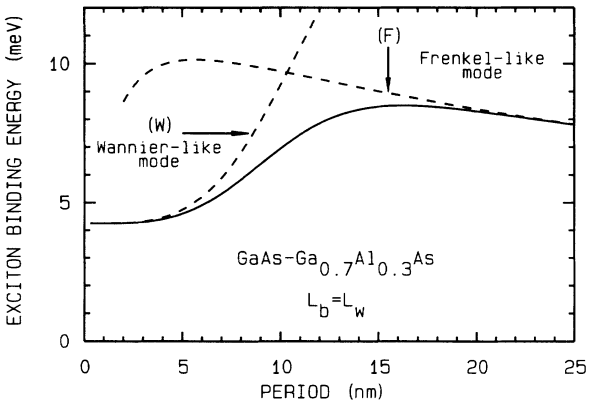

FIG. 2. The same as Fig. 1, but the dashed line labeled W corresponds to the application of Eq. (3) (Wannier approximation), i.e., the interwell effect. The dashed line labeled F is obtained via Eq. (2) (single-well approximation) and rather represents the intrawell effect. The solid line shows the result of superimposing both regimes as in Eq. (4). Note that both effects show competing contributions for periods between 5 and 20 nm.

We see that two fundamental conditions are fulfilled by the calculation via Eq. (4): (i) convergence of the Rydberg to 3D values at infinitely wide (value for the bulk well material) and vanishingly narrow (bulk equivalent alloy) layer thicknesses, (ii) appearance of the effect of interwell coupling at 15 nm of period. The most remarkable observation is that a purely "Wannier-like" approximation only stands for very short periods (lower than 5 nm), while the "single-well" regime is only valid for very wide periods (larger than 20 nm). An intermediate regime rules the major part of the figure, i.e., the most commonly encountered values of the period.

In order to check the adequacy of our model, we propose, in Fig. 3, a comparison between our calculation and the ones of Refs. 18 and 19, taking exactly the same values for basic parameters (we took the ones from Ref. 18). We have also plotted the experimental data from Ref. 7. We notice that our results nicely fit the ones of both other theories in their respective zone of maximum validity: the difference between them never exceeds 0.7 meV. Now concerning the comparison with experimental results, the agreement is excellent since our evaluation rarely falls outside the error bars, corresponding to the experimental uncertainty. A better agreement could be found by using another set of parameters or by including some of the effects[26] quoted above, but this is not really the purpose of this work. At last, we remark that the variation of the Rydberg predicted in Ref. 19 is very different from the one experimentally measured, especially for periods larger than 10 nm, which considerably shortens the range of validity of this theory.

We have presented a simple method for calculating the properties of excitons in semiconductor superlattices, from an estimation of the noninteger dimensionality. This estimation is based on a careful analysis of the various physical ingredients which rule the behavior of electrons and holes in such systems. Other elaborate models, of reasonable accuracy, present finite domains of validity and often remain out of the scope of most experimentalists. We have demonstrated that our formalism allows us to avoid such problems. In particular, we have proposed

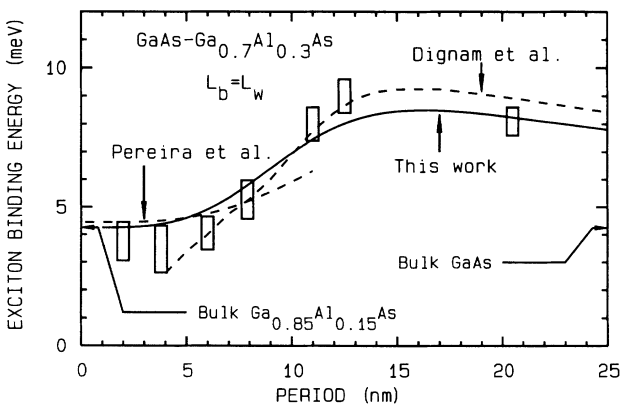

FIG. 3. Comparison between our calculation and the ones by Pereira *et al.* (Ref. 19), and by Dignam and Sipe (Ref. 18). Rectangles represent experimental data obtained by Chomette *et al.* (Ref. 7) via temperature-dependent photoluminescence excitation spectroscopy.

a successful way of accounting for the superimposition of interwell and intrawell effects, which together rule the behavior of anisotropic excitons. Although we do not intend to compete with more elaborate theories, we wish to point out that our model is based on a heuristic physical reasoning and that it may be really convenient when no computational facilities are available. Moreover, the simplicity of this approach should allow a rather straightforward extension to systems of still lower dimensionality, such as quantum wires or quantum dots.

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