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Exciton-free-layer depth as a function of the electron-hole mass ratio

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An analytical approximation for the wave functions of heavy-mass excitons in semi-infinite crystals is developed, and extends the validity of previous results reported for light-mass excitons. The new wave functions (where a homogeneous exciton-free layer appears together with a transition layer) fit the numerical solutions in the range of mass ratio $0.03 \leq m_e/m_h \leq 0.32$. This makes it possible to calculate the reflectance of heavy-mass excitons. A fair agreement between theory and experiment is obtained for GaAs and InP, which were not so well described in a previous microscopic approach.

I. INTRODUCTION

Although it has now been three decades since the fundamental issue of excitonic reflectivity was addressed by Pekar,[1] some problems still remain unsolved. In particular, the depth of the exciton-free layer is still an object of debate. In this paper we show that the exciton-free-layer depth is a function of the electron-hole mass ratio m_e/m_h, ranging from $0.8a_B$ (where a_B is the excitonic radius) for mass ratio of order 1 to about $2a_B$ for m_e/m_h much lower than unity. This finding reconciles the different determinations of the exciton-free-layer depth for different materials with each other, and all of them with theory.

The concept of an exciton-free layer was originally introduced to account for the exciton repulsion from the surface arising from the image potential.[2] Even if the image potential is neglected, an exciton-free layer must occur due to the very fact that the exciton center of mass cannot reach the surface if both the electron and hole have to stay inside the crystal.[3] On the other hand, since the exciton-free layer lowers the excitonic reflectivity peaks, its depth can be obtained from experiment by carefully reproducing the absolute value of the reflectivity structure. As a matter of fact, the experimental depths determined in this way (in units of a_B) are quite different from each other even for different samples of the same material.[4] This situation originates from the presence, in some cases, of extrinsic exciton-free layers due to built-in electric fields or to damaged subsurface regions. It originates also from the great sensitivity of the fit to the value of the peak reflectivity (so that even a few percent error in the latter can yield a 100% error in the exciton-free layer depth). Such depth, as well as the relative amplitude of the two propagating polaritons [the so-called additional boundary condition (ABC)], can also be derived from the knowledge of the exciton wave functions and of the related microscopic dielectric susceptibility at the surface.[5–7] Along these lines a numerical determination of exciton wave functions by D'Andrea and Del Sole[3,8] showed the occurrence (rather than of a homogeneous exciton-free layer where the excitons are not allowed to stay) of an inhomogeneous transition layer, where the probability of finding an exciton changes from the vacuum value (zero) to the bulk value. In the range $m_e/m_h \geq 0.2$,[3] the depth of the transition layer appeared slightly smaller than a_B, and all theoretical reflectivity spectra computed from these wave functions were found to be in satisfactory agreement with the experimental results collected for materials, such as CdS, where the above inequality is fulfilled.[8]

Computation of the reflectivity spectra was carried out also for cubic semiconductors[9] by neglecting the valence-band degeneracy. In this case a single excitonic branch, with a suitable average mass[10] (which fulfills the above inequality), was assumed. The comparison between theory and experiment for GaAs and InP, however, did not show a very good agreement and a thicker exciton-free layer, of the order of $2a_B$, was introduced to reproduce the experimental reflectivity spectra.[9] Since the main contribution to the optical properties in degenerate-band materials comes from the heavy-mass exciton which does not fulfill the inequality $m_e/m_h \geq 0.2$ in GaAs and InP, it is not surprising that the microscopic theory outlined above[3,6,8,9] cannot be so easily applied.

The purpose of this paper is to compute exciton wave functions and optical properties in the range of mass ratio $m_e/m_h \leq 0.2$, where the exciton wave function is well described by the adiabatic approximation.[3] We mimic the calculated wave functions in terms of a homogeneous exciton-free layer plus a transition layer. We show that the exciton-free layer depth d is particularly large for small mass ratio m_e/m_h and compute, from our model wave functions, the dielectric susceptibility and the reflectivity spectra. These are found to be in satisfactory agreement with experiments in the cases of GaAs and InP.

II. EXCITON WAVE FUNCTIONS

We solve the effective-mass Schrödinger equation for an exciton in the half-space $z > 0$, with the "no-escape" boundary conditions at the surface.[6] The image potential, as it was assumed in our previous works on the same topic,[3,6,8,9,11] is neglected. A numerical solution can be obtained by (i) expanding the wave function in terms of products of hydrogenic orbitals $\varphi_{nlm}(\mathbf{r})$ (where $\mathbf{r}$ is the electron-hole relative coordinate) times plane waves in the center-of-mass coordinate Z, and (ii) choosing the coefficients to satisfy the no-escape boundary conditions.[3] Alternatively, for small values of m_e/m_h, the adiabatic separation of the fast relative electron-hole (e-h) motion (characterized by the reduced mass μ) from the slow center-of-mass motion (characterized by the total mass M) can be done. Along these lines an accurate solution of the fast-motion equation was obtained by modifying Satpathy's[12] exact approach to the impurity problem while the center-of-mass problem was solved numerically.[3] The two methods have been found to be in excellent agreement at $m_e/m_h=0.2$, which is the lower limit of validity of the former approach.[3]

Consider in more detail the simple analytical approximation developed in the range $m_e/m_h \geq 0.2$.[3,6,9,11] For the wave function at $r=0$, which is the one that is important for the determination of the optical properties, one obtains

$$\Psi(0,Z)=(2\pi)^{-1/2}[e^{-iK_z Z}+Ae^{iK_z Z}-(1+A)e^{-PZ}]\phi_{100}(0)\ , \quad (1)$$

with

$$A=-\frac{P-iK_Z}{P+iK_Z}\ . \quad (2)$$

This formula describes an exciton traveling towards the surface ($Z=0$) with wave vector $-K_Z$. It is completely back-reflected ($|A|^2=1$) into the state of the wave vector K_Z, and generates an evanescent wave. In Eq. (1) $K_Z=(2ME_{\mathrm{c.m.}}/\hbar^2)^{1/2}$ is the z component of the center-of-mass wave vector and P is a fitting parameter. In Ref. 3, P was found to depend on m_e/m_h in the mass range $0.2 \leq m_e/m_h \leq 1$ which is typical of the values appropriate for light-mass excitons. (We assume $m_e \leq m_h$. In the opposite case it is sufficient to interchange the e and h labels.) Unfortunately, the analytical approximation (1) does not satisfactorily reproduce the results of calculation carried out within the adiabatic approximation[3] in the range of effective masses $m_e/m_h \leq 0.2$, appropriate for heavy-mass excitons.

In order to avoid this shortcoming, we consider here a modified version of (1):

$$\begin{aligned}\Psi_h(0,Z)&=0 \quad \text{if } 0 \leq Z \leq d\ ,\\ \Psi_h(0,Z)&=\Psi(0,Z-d) \quad \text{if } Z>d\ .\end{aligned} \quad (3)$$

In other words, there are now a homogeneous exciton-free layer d and a transition layer of depth $1/P$. Both d and P are found using a best-fit procedure aimed at reproducing the numerical wave functions in the range $0.03 \leq m_e/m_h \leq 0.3$ (the adiabatic wave functions for $m_e/m_h \leq 0.2$ and those calculated according to the method of Ref. 3 for $m_3/m_h \geq 0.2$). A comparison of numerical and model wave functions is given in Fig. 1. d and $1/P$, divided by the effective Bohr radius a_B, have been plotted in Fig. 2. The parameter d/a_B is a strongly decreasing function of m_e/m_h and reduces to zero for values of m_e/m_h larger than 0.3. In this case (relevant for light-mass excitons) only the transition layer is present. This agrees well with the previous formulation of D'Andrea and Del Sole.[3] However, while in the previous formulation only the transition layer occurred (for $m_e/m_h \geq 0.2$), now a small homogeneous exciton-free layer *and* the transition layer coexist for $0.2 \leq m_e/m_h \leq 0.3$. Since it has been shown that the

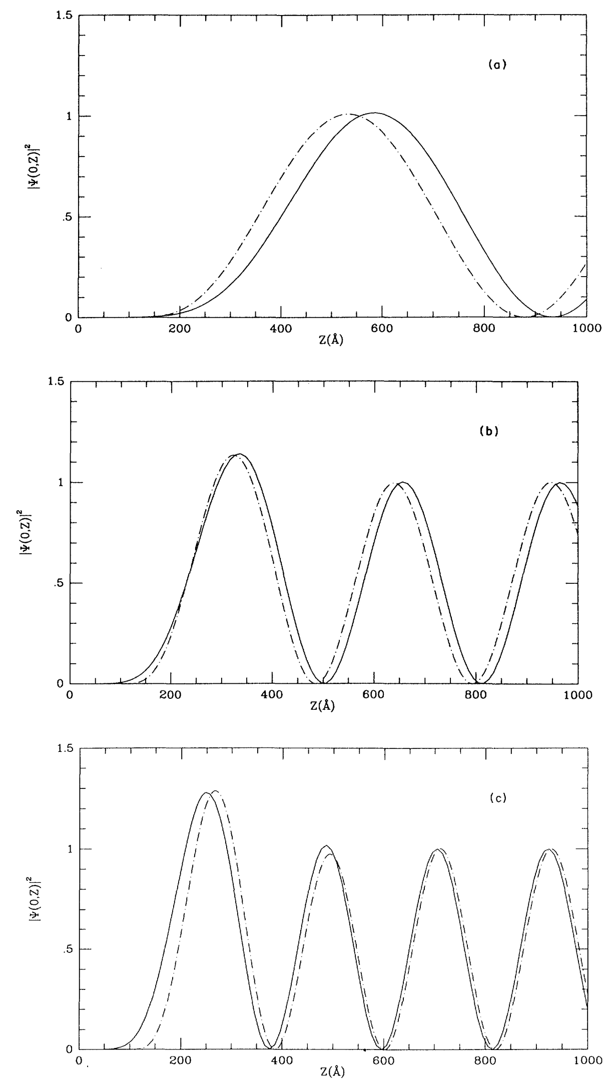

FIG. 1. Square modulus of heavy-exciton wave function $|\Psi(0,Z)|^2\pi^2 a_B^3$, for center-of-mass energies: (a) 0.1 meV, (b) 0.5 meV, and (c) 1 meV. We have used mass parameters similar to those of the heavy exciton in GaAs ($\mu=0.05$ m, $M=0.79$ m, $m_e/m_h=0.07$). Solid lines are the adiabatic wave functions from Ref. 3. Dot-dashed lines are the wave functions calculated according to the analytic approximation (3) with $d=100$ Å and $1/P=95$ Å.

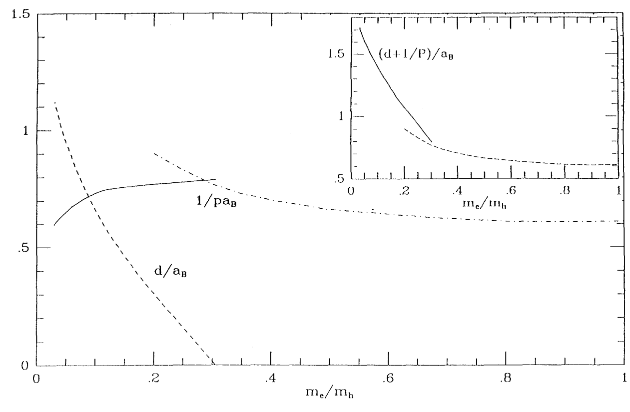

FIG. 2. Dashed line: the homogeneous exciton-free layer d of the analytical wave function (3) as a function of the mass ratio m_e/m_h. Full line: transition-layer depth $1/P$ of the analytical wave function (3). Dot-dashed line: transition-layer depth from Fig. 3 of Ref. 3. Inset: $d+1/P$ of the analytical wave function (3) (solid line); $1/P$ from Fig. 3 of Ref. 3 (dashed line).

effect of a *small* transition layer on optical properties is equivalent to that of exciton-free layer of the same depth,[8] this discrepancy is only apparent. Therefore we can compare, getting similar results, the sum of the exciton-free and transition-layer depths (this work) with the transition-layer depth of the previous formulation. This is shown in the inset of Fig. 2. For instance, at $m_e/m_h=0.2$, we get $d+1/P=1.14a_B$ in the present formulation, and $1/P=0.95a_B$ in the previous one. The same argument explains the relatively large mismatch between $1/P$ values of the two formulations in the range where they do coexist: a better agreement is found comparing in the inset $d+1/P$ of the present formulation (full line) with $1/P$ of the previous one (dashed line).

In conclusion, in the range of overlap $0.2\le m_e/m_h\le 0.3$, the two formulations appear to be very similar: The sum of the exciton-free *plus* transition-layer depths in the new formulation is only slightly larger (at most 20%) than the transition-layer depth of the old formulation. Such a difference leads to negligible changes in the optical spectra. On the other hand, when the ratio of effective masses m_e/m_h approaches zero, the exciton-free layer becomes deeper than the transition layer and their sum approaches twice the exciton radius. This corresponds to heavy-mass excitons in GaAs and InP.

III. EXCITONIC REFLECTIVITY

Our model wave function allows an easy calculation of the reflectivity spectra. In the case of a single-exciton branch, we have to deal with three regions: vacuum ($z\le 0$), exciton-free layer ($0\le z\le d$), and "bulk" ($z\ge d$). The last region including the transition layer, the dielectric susceptibility assumes therein the form derived in Ref. 6. The equations for light propagation can be solved in a straightforward, yet cumbersome way, by matching the electric and magnetic fields at the boundaries according to Maxwell's boundary conditions.[6] No ABC is required, since it is embodied in the form of the nonlocal dielectric susceptibility in the bulk region. More complicated situations would occur in the case of more exciton branches, since both the exciton-free layer and transition-layer depths would be different.

The reflectivity spectrum calculated in the case of the heavy-mass exciton in GaAs is shown and compared with experiments, in Fig. 3. Since heavy-mass excitons bear $\frac{3}{4}$ of the total oscillator strength,[13] the neglect of the light-mass exciton is expected not to affect the calculated reflectivity strongly. We computed the heavy-exciton masses according to Eqs. (66) and (67) of Ref. 14, in terms of the electron effective mass and of Luttinger's parameters γ_1, γ_2, γ_3. These were taken from Ref. 15 for GaAs ($\gamma_1=7.1$, $\gamma_2=2.02$, $\gamma_3=2.91$). We obtained $M_h=0.79$ m and $\mu=0.045$ m. From the values of μ and M_h we computed an e-h mass ratio appropriate to heavy excitons: $m_e/m_h=0.064$. The values of d and P were taken from Fig. 2: $d=125.8$ Å and $1/P=102$ Å. A fair agreement between theory and experiment[16] is found. It is more satisfactory than the one found in the calculation of Ref. 9 (dot-dashed line in Fig. 3), including only the transition layer. The inclusion of light-mass excitons altogether yields hardly noticeable changes in reflectivity line shapes.[17] The agreement between theory and experiment, however, is not yet perfect. In particular, the steep rise of the reflectivity on the high-frequency side is still underestimated by theory. A similar calculation has been carried out for InP: again a fair agreement with experiment[18] is obtained. In this case, however, the improvement with respect to Ref. 9 is minor, since a smaller

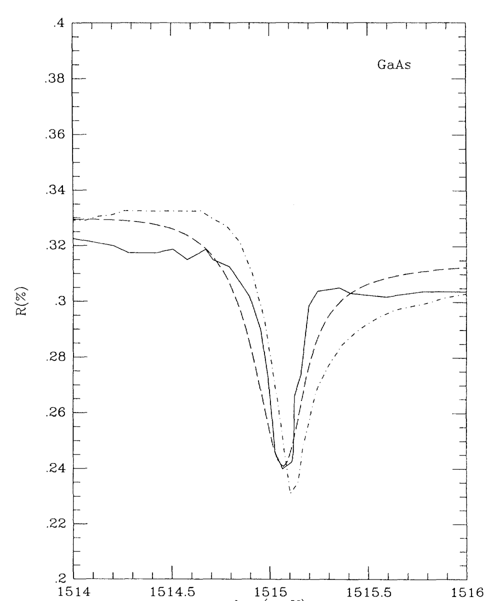

FIG. 3. Normal-incidence reflectance in GaAs. Experiment from Ref. 16: full line. Our calculation: dashed line. Excitonic parameters used in the calculation: $\hbar\omega_0=1.515$ eV, $4\pi\alpha=0.22\times10^{-2}$, $\epsilon=12.6$, $M=0.79$ m, $m_e/m_h=0.064$, $d=125.8$ Å, $1/P=102$ Å, and $\Gamma=0.095$ meV. Dot-dashed line: calculation from Ref. 9, with $d=0$, $1/P=65$ Å, $M=0.298$ m.

discrepancy between theory and experiment was apparent.

IV. CONCLUSIONS

In conclusion, we have extended the theory of D'Andrea and Del Sole[3,6,8,9,11] concerning the microscopic calculation of the excitonic reflectivity to small electron-hole ratios $m_e/m_h \leq 0.2$. An exciton-free layer has been found, in addition to the transition layer of the previous formulation, for $m_e/m_h \leq 0.3$. In the range of overlap, $0.2 \leq m_e/m_h \leq 0.3$, the two formulations give nearly identical results. However, when the mass ratio m_e/m_h approaches zero, the exciton-free layer becomes deeper than the transition layer, and their sum approaches twice the exciton radius. This is the case in the range of mass ratios relevant for heavy-mass excitons in GaAs and InP. In both cases the calculated reflectivity spectra are in satisfactory agreement with experiments. (Calculations based on the transition-layer alone yielded poorer line shapes.) The agreement with experiment is still not perfect. It is worth speculating on the origin of this remaining discrepancy. We believe that it arises from the neglect of the image potential, based on the picture that the exciton is a neutral entity.[6] In this case, its internal structure (and therefore the image potential) can be neglected as far as the electron-hole separation is smaller than their average distance from the surface. However, although the image potential cannot drastically modify the exciton properties, it can slightly change the calculated exciton-free layer depth and the details of the reflectivity spectra. A concurring reason might be the presence of extrinsic exciton-free layers in the samples involved in the experiments. Both additional investigations and an adiabatic calculation of the exciton wave function, where the image potential is treated perturbatively, should help in solving this issue.

Finally, let us point out that we have a coherent picture of all exciton features in semi-infinite semiconductors. The puzzle of the occurrence of two types of exciton-free (or transition) layers with a depth of about a_B or $2a_B$, respectively, has been solved. The computed reflectivity is in fair agreement with experiments both for large exciton-free materials such as GaAs and InP, as well as for CdS, ZnS, etc. already accounted for by the simple transition-layer approach. Remaining discrepancies in the reflectivity line shapes occur for GaAs and (to a minor extent) for InP. They can be explained in terms of the neglected image potential.[19]

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