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Binding energy of ionized-donor-bound excitons in two-dimensional semiconductors

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The ground-state energies of the two-dimensional ionized-donor-bound exciton (D^+,X) have been calculated variationally for all values of the effective electron-to-hole mass ratio σ. They are compared with those obtained in the three-dimensional case using the same 55-term wave function. We found that in the two-dimensional case the (D^+,X) complex remains stable until $\sigma=0.88$, which is about two times larger than the value obtained in the three-dimensional case.

I. INTRODUCTION

Recently much interest has been devoted to the electronic states of semiconductor microstructures, surfaces, and interfaces, mainly due to the possible applications to optoelectronic devices.[1,2]

The exciton states play an important part in the optical properties of these structures. In particular, their binding energies[3,4] in the two-dimensional (2D) semiconductors are considerably enhanced compared to the situation in the three-dimensional (3D) bulk semiconductors.

In the 3D semiconductors, the properties of excitons bound to neutral or ionized impurities have been extensively studied[5,6] during the last few years. In particular it has been proven[7] by means of variational calculations and within the effective-mass approximation that the exciton–ionized-donor complex (D^+,X) is stable only for values of the electron-to-hole effective mass ratio σ less than a critical value $\sigma_c=0.426$.

In the 2D case, the bound excitons are expected to exhibit higher values of their binding energies[8] so that they may be observed at room temperature. Actually, some experimental evidences of bound excitons in semiconductor superlattices has been reported recently.[9] In particular, we expect also a more extended range of the stability of the (D^+,X) complex, though, to our knowledge, no theoretical study has been devoted to this subject.

We present here a variational calculation of the binding energy of the (D^+,X) complex in two-dimensional semiconductors. This situation corresponds to the limiting case of very thin quantum-well semiconductor superlattices. This study may also be used to understand what happens at doped semiconductor surfaces.

In the following section we specify our wave function and describe our variational method of solution of the Schrödinger equation relative to the ground state of the complex. In Sec. III we present and discuss the results of our calculations.

II. FORMULATION OF THE PROBLEM OF THE BOUND STATES OF THE COMPLEX AND TRIAL WAVE FUNCTION

In the effective-mass approximation, the Hamiltonian of the system consisting of an electron (e) and a hole (h) bound to an ionized donor (D^+) in an isotropic two-dimensional semiconductor is given by

$$H=-\frac{1}{2}\Delta_e-\frac{\sigma}{2}\Delta_h+\left[\frac{1}{r_h}-\frac{1}{r_e}-\frac{1}{r_{eh}}\right]. \tag{1}$$

ϵ is an appropriate dielectric constant taking into account possible polarization effects whereas $\sigma=m_e^*/m_h^*$, defines the electron-to-hole effective mass ratio. We use the unit of length $a=\epsilon\hbar^2/m_e^*e^2$ and the unit of energy $e^2/\epsilon a$. The latter corresponds to twice the 3D donor binding energy.

To solve the problem of the bound states of the exciton–ionized-donor complex, we have to find the wave functions ψ satisfying the wave equation

$$H\psi=E\psi\ . \tag{2}$$

We restrict our study to the ground state, corresponding to the lowest energy value E, determined by means of variational calculations. From the 3D case studies,[7,10,11] it appears that the electron-to-hole and electron-to-ionized-donor Coulomb interactions give essential contributions to the binding of the complex. Therefore, it is important to take the distances r_e and r_{eh} into account in the wave function. We choose a Hylleraas-type trial function[12] centered on the electron rather than on the ionized donor. It reads

$$\begin{aligned}\psi(s,t,u)&=\phi(ks,kt,ku)\ ,\\ \phi(s,t,u)&=\sum_{l,m,n}C_{lmn}|lmn\rangle\ ,\end{aligned} \tag{3}$$

where $|lmn\rangle=\alpha_{lmn}e^{-s/2}s^lu^mt^n$ are basis functions normalized to unity.

s, t, u are elliptic coordinates:

$$s=r_e+r_{eh},\quad t=r_e-r_{eh},\quad u=r_h$$

with $0\leq s\leq\infty$, $-u\leq t\leq u$, $0\leq u\leq s$.

k is a scaling factor; l, m, n are positive integers or zero. The C_{lmn} are variational coefficients. In order to satisfy the variation condition, which sets

$$E=\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle \tag{4}$$

to a minimum, we rewrite the energy E,

$$E=\frac{M}{N}k^2-\frac{L}{N}k\ , \tag{5}$$

in terms of the quadratic forms

$$M=\mathbf{C}^{+}\mathbf{T}\mathbf{C},\quad L=-\mathbf{C}^{+}\mathbf{V}\mathbf{C},\quad N=\mathbf{C}^{+}\mathbf{S}\mathbf{C}\ , \tag{6}$$

where **C** denotes the column matrix of the linear coefficients C_{lmn}. The matrices **T**, **V**, and **S** are defined with respect to the basis functions $|lmn\rangle$ by

$$T_{lmn}^{l'm'n'}=\left\langle l'm'n'\left|-\frac{1}{2}\Delta_e-\frac{\sigma}{2}\Delta_h\right|lmn\right\rangle\ ,$$

$$V_{lmn}^{l'm'n'}=\left\langle l'm'n'\left|\frac{1}{r_h}-\frac{1}{r_e}-\frac{1}{r_{eh}}\right|lmn\right\rangle\ , \tag{7}$$

$$S_{lmn}^{l'm'n'}=\langle l'm'n'|lmn\rangle\ .$$

All these matrix elements may be expressed in terms of the integrals $J_{lmn}^{l',m'n'}(\lambda,\mu,\nu)$ defined by

$$\begin{aligned}J_{lmn}^{l'm'n'}(\lambda,\mu,\nu)&=2\pi\int_0^{\infty}e^{-s}s^{l+l'+\lambda}ds\int_0^{s}\frac{u^{m+m'+\mu}}{(s^2-u^2)^{1/2}}du\int_0^{\mu}\frac{t^{n+n'+\nu}}{u^2-t^2}dt\\&=2\pi(l+l'+\lambda+m+m'+\mu+n+n'+\nu)!I_{m+m'+\mu+n+n'+\nu}I_{n+n'+\nu}\ .\end{aligned} \tag{8}$$

with

$$I_{2n}=\frac{(2n)!\pi}{(n!)^2 2^{2n+1}},\quad I_{2n+1}=\frac{(n!)^2 2^{2n}}{(2n+1)!}\ .$$

The expressions of $T_{lmn}^{l'm'n'}$, $V_{lmn}^{l'm'n'}$, and $S_{lmn}^{l'm'n'}$ obtained in this way are given in Appendix A.

The variational condition (4) becomes then

$$\frac{\partial E}{\partial k}=0,\quad \frac{\partial E}{\partial C_{lmn}}=0 \tag{9}$$

for any of the indices l, m, n. The first of Eqs. (9) leads to the relation

$$k=\frac{L}{2M} \tag{10}$$

from which we deduce

$$E=-\epsilon k^2,\quad \text{where } \epsilon=M/N\ , \tag{11}$$

whereas the last equations are equivalent to the system

$$(k^2\mathbf{T}+k\mathbf{V}-E\mathbf{S})\mathbf{C}=0\ . \tag{12}$$

With $E=-k^2\epsilon$, we are finally left with the eigenvalue problem

$$(\mathbf{A}-k\mathbf{B})\mathbf{C}=0\ , \tag{13}$$

where **A** and **B** denote the matrices $\mathbf{T}+k\mathbf{N}$ and $-\mathbf{V}$, respectively, whereas k plays the role of the eigenvalue and **C** that of the eigenvector of components C_{lmn}.

We solve equation (13) by means of iterations on ϵ until the desired accuracy on the energy is obtained. The initial value of ϵ is deduced from the asymptotic behavior

$$E_{\text{asymp}}=-\frac{k^2}{4}\left[1+\frac{\sigma}{2}\right]=-k^2\epsilon_{\text{asymp}}\ ,$$

$$\epsilon_{\text{asymp}}=\frac{1}{4}\left[1+\frac{\sigma}{2}\right]\ . \tag{14}$$

III. RESULTS AND DISCUSSION

We have calculated the binding energy of the (D^+,X) complex in a two-dimensional (2D) semiconductor for several values of σ by using 55 terms characterized by the condition $l+m+n\leq 6$ in the trial wave function (3). The (D^+,X) complex is only stable if its energy E is lower than the energy $E_D^{(2D)}$ of the 2D neutral donor. The variation of the ratio of the energy E to $E_D^{(2D)}$ versus σ is shown in Fig. 1. We can see that the (D^+,X) complex is stable in a 2D semiconductor if the mass ratio σ is lower than $\sigma_c^{(2D)}=0.88$.

In the 3D case, a critical mass ratio $\sigma_c^{(3D)}\simeq 0.426$ has

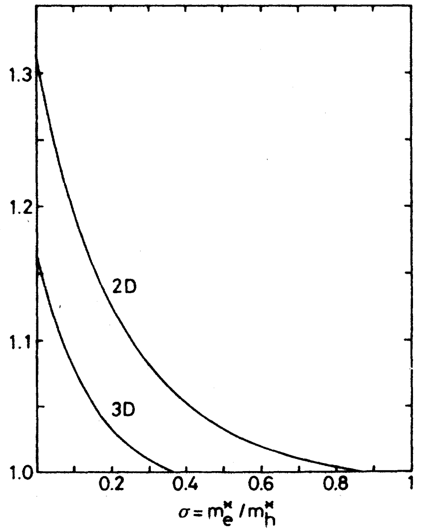

FIG. 1. Ratio of the ground-state energy E of the (D^+,X) complex to the neutral donor energy E_D as a function of $\sigma=m_e^*/m_h^*$ in the 2D and 3D cases, with $E_D^{(2D)}=4E_D^{(3D)}$.

been obtained[7] using a more elaborated function. In order to test the validity of our trial wave function (3), we have calculated the binding energies of the (D^+,X) complex in the 3D case by using a method similar to that presented in Sec. II and in the same function (3). The corresponding matrix elements are reported in Appendix B. The same 55-term development leads to a critical mass ratio $\sigma_c^{(3D)} \simeq 0.365$ close to the value of 0.426 reported above (Fig. 1).

Our wave function (3) constitutes therefore a good approximation in the 3D case. We can reasonably think that the same conclusion holds in the 2D case. Moreover, the relative simple form of this function allows the application of the present method to the study of other properties of the complex. The comparison between the critical mass ratios $\sigma_c^{(2D)}$ and $\sigma_c^{(3D)}$ shows that for a given σ mass ratio, the (D^+,X) complex is by far more stable in the 2D than in the 3D case. We expect a comparable accuracy of our 2D and 3D results. Thus our 2D critical mass ratio $\sigma_c^{(2D)}=0.88$ is certainly lower than that which one may obtain by using the more elaborate wave function of Ref. 7. Therefore the range of stability of the (D^+,X) complex is probably extended up to σ values of the order of unity. The 2D energies are about four times greater than those obtained in the 3D case. In particular, in the limit of a zero mass ratio, the 2D- and 3D-energy values are respectively equal to 2.6314 and 0.5731 in units of two times the 3D donor energy.

These results seem to show that more favorable conditions for the detection of the (D^+,X) complex are realized in strictly 2D semiconductors and quantum-well (QW) superlattices (SL) than in bulk semiconductors. Indeed the energies of the quantum-well superlattices are expected to be between the 2D and 3D limits. This conclusion holds as long as $\sigma^{(SL)}=\sigma^{(3D)}$. In fact, in the quantum-well superlattices, the valence-band offset leads to a modification of the band structure and of the effective mass of the uppermost heavy-hole valence band. If $\sigma^{(SL)}<\sigma^{(3D)}$, the (D^+,X) complex is certainly more stable in the quantum-well superlattices than in the bulk semiconductors. However, when $\sigma^{(SL)}>\sigma^{(3D)}$, as in the case of the GaAs-Al$_x$Ga$_{1-x}$As system, this conclusion remains true so far as

$$\frac{E}{E_D}(\sigma_{SL}) > \frac{E}{E_D}(\sigma_{3D}) \ .$$

The exact value of $\sigma^{(SL)}$ depends in all cases on the magnitude of the band offset and on the quantum-well width.

APPENDIX A: MATRIX ELEMENTS IN THE 2D CASE

We use the notation (λ,μ,ν) instead of $J_{lmn}^{l'm'n'}(\lambda,\mu,\nu)$ [expression (8)]:

$$(S)_{lmn}^{l'm'n'}=\tfrac{1}{2}[1+(-1)^{n+n'}][(2,1,0)-(0,1,2)] \ ,$$

$$(V)_{lmn}^{l'm'n'}=\tfrac{1}{2}[1+(-1)^{n+n'}][(2,0,0)-(0,0,2)-4(1,1,0)] \ ,$$

$$(T)_{lmn}^{l'm'n'}=(T_e)_{lmn}^{l'm'n'}+\sigma(T_h)_{lmn}^{l'm'n'} \ ,$$

$$\begin{aligned}(T_e)_{lmn}^{l'm'n'}=\tfrac{1}{2}[1+(-1)^{n+n'}][&-2(l^2-n^2)(0,1,0)+(2l+1)(1,1,0)-\tfrac{1}{2}(2,1,0)+\tfrac{1}{2}(0,3,0)\\ &-2l(-1,3,0)+2l(l-1)(-2,3,0)-2n(n-1)(0,3,-2)] \ ,\end{aligned}$$

$$\begin{aligned}(T_h)_{lmn}^{l'm'n'}=\tfrac{1}{2}[1+(-1)^{n+n'}]&\left[-\tfrac{1}{8}(2,1,0)+\tfrac{1}{8}(0,1,2)-\frac{(l-n)}{2}(l+n+2m+1)(0,1,0)\right.\\ &+\tfrac{1}{2}(l+m+1)(1,1,0)-\frac{m(m+2n)}{2}(2,-1,0)+\frac{m(m+2l)}{2}(0,-1,2)\\ &\left.-\frac{l}{2}(-1,1,2)+\frac{l}{2}(l-1)(-2,1,2)-\frac{n}{2}(n-1)(2,1,-2)-\frac{m}{2}(1,-1,2)\right]\\ +\tfrac{1}{2}[1+(-1)^{n+n'+1}]&\left[-\frac{n}{2}(2,1,-1)+\frac{(m+n+1)}{2}(0,1,1)+n(l+m+1)(1,1,-1)\right.\\ &\left.-l(m+n+1)(-1,1,1)-\frac{m}{2}(2,-1,1)+m(l-n)(1,-1,1)\right] \ .\end{aligned}$$

APPENDIX B: MATRIX ELEMENTS IN THE 3D CASE

We use the notation (λ,μ,ν) instead of $I_{lmn}^{l'm'n'}(\lambda,\mu,\nu)$, where

$$\begin{aligned}I_{lmn}^{l'm'n'}(\lambda,\mu,\nu)&=\int_0^\infty e^{-s}s^{l+l'+\lambda}ds\int_{-s}^{s}t^{n+n'+\nu}dt\int_{|t|}^{s}u^{m+m'+\mu}du\\ &=\frac{(l+l'+\lambda+m+m'+\mu+n+n'+\nu+2)![1+(-1)^{n+n'+\nu}]}{(n+n'+\nu+1)(n+n'+\nu+m+m'+\mu+2)} \ ,\end{aligned}$$

$$(S)_{lmn}^{l'm'n'}=8\pi^2[(2,1,0)-(0,1,2)]\ ,$$

$$(V)_{lmn}^{l'm'n'}=8\pi^2[(2,0,0)-(0,0,2)-4(1,1,0)]\ ,$$

$$(T)_{lmn}^{l'm'n'}=(T_e)_{lmn}^{l'm'n'}+\sigma(T_h)_{lmn}^{l'm'n'}\ ,$$

$$\begin{aligned}(T_e)_{lmn}^{l'm'n'}=8\pi^2\{&2(l+1)(1,1,0)+2l(l-1)(-2,3,0)-2l(-1,3,0)-2n(n-1)(0,3,-2)\\&-\tfrac{1}{2}(2,1,0)+\tfrac{1}{2}(0,3,0)-[2l(l+1)-2n(n+1)](0,1,0)\}\ ,\end{aligned}$$

$$\begin{aligned}(T_h)_{lmn}^{l'm'n'}=8\pi^2\Bigg[&-\frac{m}{2}(m+2n+1)(2,-1,0)+\frac{m}{2}(m+2l+1)(0,-1,2)+\tfrac{1}{2}(2+l+m)(1,1,0)\\&+\tfrac{1}{2}(2+m+n)(0,1,1)-l(m+n+2)(-1,1,1)+n(m+l+2)(1,1,-1)+\frac{l}{2}(l-1)(-2,1,2)\\&-\frac{l}{2}(-1,1,2)-\tfrac{1}{8}(2,1,0)+\tfrac{1}{8}(0,1,2)-\frac{n(n-1)}{2}(2,1,-2)-\frac{n}{2}(2,1,-1)\\&-\frac{m}{2}(2,-1,1)-\frac{m}{2}(1,-1,2)-m(n-l)(1,-1,1)-\frac{(l-n)}{2}(l+n+2m+3)(0,1,0)\Bigg]\ .\end{aligned}$$

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