Excitonic exchange splitting in bulk semiconductors

Huaxiang Fu, Lin-Wang Wang, and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

~Received 18 September 1998!

We present an approach to calculate the excitonic fine-structure splittings due to electron-hole short-range exchange interactions using the local-density approximation pseudopotential method, and apply it to bulk semiconductors CdSe, InP, GaAs, and InAs. Comparing with previous theoretical results, the current calculated splittings agree well with experiments. Furthermore, we provide an approximate relationship between the short-range exchange splitting and the exciton Bohr radius, which can be used to estimate the exchange splitting for other materials. The current calculation indicates that a commonly used formula for exchange splitting in quantum dot is not valid. Finally, we find a very large pressure dependence of the exchange splitting: a factor of 4.5 increase as the lattice constant changes by 3.5%. This increase is mainly due to the decrease of the Bohr radius via the change of electron effective mass. @S0163-1829~99!02407-8#

I. INTRODUCTION

When an electron is excited from a fully occupied valence band of a semiconductor to an empty conduction band, the electron spin can be either parallel or antiparallel to the spin of the particle ~i.e., hole! left behind. This produces a fine structure of ''singlet'' and ''multiplet'' ~e.g., triplet! excitons, separated by the exchange splitting.[1-5] The exchange interaction contains both a short-range ~SR! part and a long-range ~LR! part.[1] The short-range part can be defined in real space as the electron-hole exchange integral within a Wigner-Seitz unit cell, and the long-range part is defined as the contribution to the exchange integral coming from different cells. The exchange interaction can also be divided in k space into analytical part and nonanalytical part.[6,7] These two ways of dividing are closely related, but not exactly the same ~the LR part can contain some analytical components!.[6,7] We study in this paper the analytical part of the exchange splitting ~but we will also use the phrase ''SR'' to mean the same thing, in a loose sense!. The LR exchange splitting of bulk exciton originates from the interaction between electron-hole dipoles located at different bulk unit cells. This causes a longitudinal-transverse excitonic splitting, which further lifts the degeneracy of the excitonic multiplet state. In direct-gap zinc-blende semiconductors, for example, the eightfold degenerate $\Gamma_{8v} \rightarrow \Gamma_{6c}$ fundamental excitonic transition splits via the SR exchange interaction into a fivefold and a threefold degenerate excitons ~Fig. 1!.

There, quantum confinement is expected[15] to sharply en-

$F^{\sim a!} \sim \mathbf{r}_h, \mathbf{r}$

to the crystal field. The calculated spin-orbit splitting D_{SO} and crystal-field splitting D_{CF} are given in Table II. They agree well with experiment.[42–46]

We next study the fine structure of bulk exciton with exciton wave vector $\mathbf{k}_{ex}=0$. In the calculation of exciton fine structure for zinc-blende materials, six ~counting spin degeneracy! highest valence bands $N_v=6$ ~including spin-orbit split-off bands! and two lowest conduction bands $N_c=2$ are used in constructing the exciton wave functions @upper bound sum in Eqs. ~8! and ~9!#. For wurzite CdSe, the two spin-orbit split-off bands are not included in this basis because they are rather removed from the VBM. Including these split-off bands changes the exchange splitting by less than 0.01%. Figures 1~b! and 1~c! show schematically the excitonic energy levels obtained from solving the secular equation @Eq. ~9!#. Our calculation shows that, the lowest exciton in Fig. 1~c! is fivefold degenerate in the zinc-blende structure, and twofold degenerate in the wurzite structure. The level splittings due to exchange interaction are labeled as $D_x^{(i)}$ ($i=1,2,3$) in Fig. 1~c!. Table II gives the exchange splittings $D_x^{(i)}$ ($i=1,2,3$) shown in Fig. 1~c!, in comparison with the available experimental data.[10,14] We see from Table II the following.

~i! Our calculated exchange splittings $D_x^{(1)}$ are generally in fair agreement with experiment for different materials. Compared with previous theoretical calculations on[12] GaAs and on[13] CdSe, which gave, respectively, exchange splittings $D_x^{(1)}$ of 380 and 1600 meV, our results of 9.61 and 49.78 meV are in much closer agreement with experimental values[10,14] 20⊖ 8 and 130 meV, respectively. We note, however, that our theoretical exchange splittings are *systematically* smaller than the experimental values. There are two possible reasons for this discrepancy: ~1! We have used the pseudopotential wave functions. Had we used the all-electron wave functions, which have more large $\mathbf{G}$ components in the summation of Eq. ~10! due to the rapid wave function oscillations near the nuclei. This might possibly increase our exchange splitting. ~2! Since our exchange splitting is proportional to $1/a_B^3$ ~see below!, an experimental uncertainty of a_B by 20% may cause the error of our calculated exchange splitting by a factor of 2. To accurately describe a_B and its effect, we need to go beyond the simple model of the exciton in Eq. ~7!. Specifically, we need to use a 4⊃4 $\mathbf{k \cdot p}$

model to describe the exciton wave functions,[47] and to consider the local field effects on the exciton solution.[48] Considering the simple exciton model used here @Eq. ~7!#, our results are quite good.

~ii! For zinc-blende materials, the exchange splitting $D_x^{(2)}$

splitting D_x^{bulk} is unknown in many cases. As a result, D_x^{bulk} is often used as a fitting parameter. For example, to fit the experimental splittings in InAs quantum dots, Banin *et al.*[18] has to use $D_x^{bulk} \simeq 2.5$ *m*eV in Eq. ~1!, which is unrealistically larger than our predicted value $D_x^{bulk} \simeq 0.29$ *m*eV for the same material. The main reason for this difference is the invalidity of Eq. ~1! in describing the total exchange interaction in dots.

In a strong confinement dot, the exciton wave function can be written as the product of the electron and hole single-particle wave functions $f_{iv}^*(\mathbf{r}_h$

due to the reduced dielectric constant.

Figure 4-b! shows the exchange splitting $D_x^{(1)}$ vs the pressure, demonstrating a dramatic increase. The exchange magnitude is 4.5 times of the equilibrium value when the lattice constant decreases by 3.5%. The lattice constant can be converted into pressure using the state equation:

$$B_0 1 aP5 2 V\frac{dP}{dV}, \qquad \text{~13!}$$

where $B_0 5 76.0$ GPa is[55] the bulk moduli of InP at zero pressure, and $a5 4.5$ is[55] the linear pressure-dependence coefficient of bulk moduli. We obtain the pressure-dependence coefficient of exchange splitting

$$]D_x^{-1!}/]P5 2 \frac{1}{B}]D_x^{-1!}/] \ln V5 6.2 \ me\text{V/GPa}, \qquad \text{~14!}$$

for bulk InP. This predicted strong enhancement of the bulk-exciton exchange splitting needs to be tested experimentally.

Since the enhancement of the bulk exchange splitting results mainly from the pressure-induced reduction of exciton radius, we expect that this pressure-induced enhancement will be absent in small dots. This expectation is based on the fact that the exciton wave function in small dots (R, a_B) is confined mainly by the quantum dot size ~rather than by the e-h interaction!, which will not be affected by the applied pressure.

VI. SUMMARY

The electron-hole exchange splitting in bulk semiconductors is studied using the first-principle pseudopotential method within the LDA scheme. The calculated exchange magnitudes agree fairly well with experiments. One formula is provided to estimate bulk exciton exchange splitting for other zinc-blende materials based on their exciton radii. This formula is quite useful since the measured exchange splitting is often not known due to its small magnitude. Our calculation indicates that the commonly used formula ɶEq. ~1!#

Willoughby, IOP Conf. Proc. No. 24 ~Institute of Physics, London, 1975!, p. 275.

[37] J. S. Blakemore, J. Appl. Phys. **53**, R123 ~1982!.

[38] J. V. Ozolinsh, G. K. Averkieva, A. F. Ilvins, and N. A. Goryunova, Kristallografiya **7**, 850 ~1962! @Sov. Phys. Crystallogr. **7**, 691 ~1963!#.

[39] L. M. Kanskaya, S. I. Kokhanovskii, R. P. Seisyan, Al. L. Efros, and V. A. Yukish, Fiz. Tekh. Poluprovodn. **17**, 718 ~1983! @Sov. Phys. Semicond. **17**, 449 ~1983!#.

[40] J. Takayama, K. Shimomae, and C. Hamaguchi, Jpn. J. Appl. Phys. **20**, 1265 ~1981!.

[41] M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 ~1962!.

[42] V. V. Sobolev, V. I. Donetskina, and E. F. Zagainov, Fiz. Tekh. Poluprovodn. **12**, 1089 ~1978! @Sov. Phys. Semicond. **12**, 646 ~1978!#.

[43] O. Goede, D. Hennig, and L. John, Phys. Status Solidi B **96**, 671 ~1979!.

[44] J. Camassel, P. Merle, L. Bayo, and H. Mathieu, Phys. Rev. B **22**, 2020 ~1980!.

[45] D. E. Aspnes and A. A. Studna, Phys. Rev. B **7**, 4605 ~1973!.

[46] C. R. Pidgeon, S. H. Groves, and J. Feinleib, Solid State Commun. **5**, 677 ~1967!.

[47] A. Baldereschi and N. O. Lipari, Phys. Rev. B **3**, 439 ~1971!.

[48] R. Bonneville and G. Fishman, Phys. Rev. B **22**, 2008 ~1980!.

[49] K. Ehara and K. Cho, Solid State Commun. **44**, 453 ~1982!.

[50] H. Fu and A. Zunger, Phys. Rev. B **55**, 1642 ~1997!.

[51] This does not mean that the results from Eq. ~3! can be compared with experimentally observed values. For more detailed discussion about this issue, please see Refs. 23 and 24.

[52] H. Haken, Nuovo Cimento **10**, 1230 ~1956!.

[53] V. Ozolins ~private communication!.

[54] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 ~1991!.

[55] D. N. Nichols, D. S. Rimai, and R. J. Sladek, Solid State Commun. **36**, 667 ~1980!.