Applicability of the k·p method to the electronic structure of quantum dots

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The **k·p** method has become the ''standard model'' for describing the electronic structure of nanometer-size quantum dots. In this paper we perform parallel **k·p** ~6⊃3⊃6 and 8⊃3⊃8! and direct-diagonalization pseudopotential studies on spherical quantum dots of an ionic material—CdSe, and a covalent material—InP. By using an equivalent input in both approaches, i.e., starting from a given atomic pseudopotential and deriving from it the Luttinger parameters in **k·p** calculation, we investigate the effect of the different underlying wavefunction representations used in **k·p** and in the more exact pseudopotential direct diagonalization. We find that ~i! the 6⊃3⊃6 **k·p** envelope function has a distinct ~odd or even! parity, while atomistic wave function is parity-mixed. The 6⊃3⊃6 **k·p** approach produces an incorrect order of the highest valence states for both InP and CdSe dots: the p-like level is above the s-like level. ~ii! It fails to reveal that the second conduction state in small InP dots is folded from the L point in the Brillouin zone. Instead, all states in **k·p** are described as Γ-like. ~iii! The **k·p** overestimates the confinement energies of both valence states and conduction states. A wavefunction projection analysis shows that the principal reasons for these **k·p** errors in dots are ~a! use of restricted basis set, and ~b! incorrect *bulk* dispersion relation. Error ~a! can be reduced only by increasing the number of basis functions. Error ~b! can be reduced by altering the **k·p** implementation so as to bend upwards the second lowest bulk band, and to couple the conduction band into the s-like dot valence state. Our direct diagonalization approach provides an accurate and practical replacement to the standard model in that it is rather general, and can be performed simply on a standard workstation. @S0163-1829~98!03112-9#

I. INTRODUCTION

Nanometer-size semiconductor quantum dots can now be made either by colloidal techniques[1–8] or by controlled coarsening of thin films grown via the Stranski-Krastanov mode.[9–12] Colloidally-grown dots of CdSe,[1–4] InP,[5–7] or InAs ~Ref. 8! are nearly spherical, unstrained objects with diameters ranging from 20 to 70 Å, whose surfaces are passivated by organic ligands. The size distribution is so uniform that up to 10 excited electron-hole states can be observed in photoluminescence excitation spectroscopy.[2,8] Quantum dots fabricated by controlled coarsening ~''self-assembled''!, on the other hand, appear in flattened pyramidal ~or sometimes pancake! shapes with confining dimensions ~height!

$P_n^{(N_b)}(\mathbf{k}) \approx (\sum_{m=1}^{N_b} |\langle u_{m,\mathbf{G}}|u_{n,\mathbf{k}}\rangle|^2$. The closer $P_n^{(N_b)}(\mathbf{k})$ is to 1, the more complete is the representation of $u_{n,\mathbf{k}=0}(\mathbf{r})$ via the set $\{u_{m,\mathbf{G}}($

It is now straightforward to compute the screened pseudo-potential $v_a(\mathbf{r})$ from an atomistic mean-field electronic theory ~e.g., density functional![31,32] and to solve Eqs. ~1! and ~2! by a standard diagonalization method.[33] However, in this approach, the computational effort scales as the *cube* power of the number of atoms per unit cell ~due to the need to orthogonalize each c_i to the lower states!, so the method is limited to small systems containing , 100 atoms per cell. Another approach is thus needed for quantum dots with ; 30–50 Å diameter (' 1000–5000 atoms). We propose to build on the fact that in such nanostructures one is often interested only in the states near the valence-band maximum ~VBM! and the conduction-band minimum ~CBM!. Hence, it makes no computational sense to have to orthogonalize these states to many lower-energy states that are physically unin-teresting. It is more reasonable[34] to ''fold'' the spectrum of Eq. ~1! around a reference energy e_{ref}

$$\left[\frac{\mathbf{P}^2}{2m_0} + V(\mathbf{r}) - e_{ref}\right]^2 c(\mathbf{r}) = (e - e_{ref})^2 c(\mathbf{r}), \qquad \text{~5!}$$

so that the lowest eigenvalue is now the one nearest to e_{ref}. By placing e_{ref} in the region of physical interest ~the band gap!, one can thus find the highest occupied dot orbit ~HODO! and the lowest unoccupied dot orbit ~LUDO! with-out having to search and orthogonalize many lower eigen-states that are now shifted outside the ''window of interest.'' This linearly-scaling ''folded spectrum method'' has been applied

$$H_{nso}(\mathbf{k}) = \begin{pmatrix} e_{c,0}+A'k^2 & iPk_x+B'k_yk_z & iPk_y+B'k_xk_z & iPk_z+B'k_xk_y \\ -iPk_x+B'k_yk_z & Ak_x^2+B(k_y^2+k_z^2) & Ck_xk_y & Ck_xk_z \\ -iPk_y+B'k_xk_z & Ck_xk_y & Ak_y^2+B(k_x^2+k_z^2) & Ck_yk_z \\ -iPk_z+B'k_xk_y & Ck_xk_z & Ck_yk_z & Ak_z^2+B(k_x^2+k_y^2) \end{pmatrix} \tag{9}$$

$$Q_{so}=\frac{\Delta_0}{3}\begin{pmatrix}0&0&0&0\\0&0&-i&0\\0&i&0&0\\0&0&0&0\end{pmatrix}, \quad R_{so}=\frac{\Delta_0}{3}\begin{pmatrix}0&0&0&0\\0&0&0&1\\0&0&0&-i\\0&-1&i&0\end{pmatrix}, \tag{10}$$

where $k^2 = k$

An almost universally adopted approximation[2,7,15,16,19] in the application of $\mathbf{k} \cdot \mathbf{p}$ to quantum dots is to take $A \, 5 \, B \, 1 \, C$ in Eq. ~8! @

$$k_d 5 \sqrt{\frac{2m_0}{\backslash^2} \frac{e 2\, e_g}{v \sim e!}},$$

$$k_b 5 \sqrt{\frac{2m_0}{\backslash^2} \sim 2\, e\, 1\, e_g\, 1\, DE_c!} \qquad \sim 22!$$

are the wave vectors in the dot and in the barrier, respectively.

E. Summary of $\mathbf{k} \cdot \mathbf{p}$ approximations

The $\mathbf{k} \cdot \mathbf{p}$ approximations for quantum dots are:

~a! The truncation of the number of G-like Bloch bases, and the use of second-order perturbation to correct this. In practice, these approximations are mitigated by treating the $\mathbf{k} \cdot \mathbf{p}$ parameters as adjustable parameters fitted to the observed bulk effective masses. The extent to which these parameters work for systems other than fitted ~e.g., nanometer dots! remains unknown.

~b! The valence states and conduction states are calculated in a decoupled way. The $8 \ominus 8$ model then breaks into $6 \ominus 6$ valence-only plus $2 \ominus 2$ conduction-only matrice.

~c! The isotropic approximation is used for the dot valence states ~i.e., $g_2 5 g_3$!, and then the dispersion $e_{n\mathbf{k}}^{\mathbf{k} \cdot \mathbf{p}}$ depends only on the amplitude of $\mathbf{k}$.

~d! The method does not consider the existence of real dot surface states or interface states at the dot's boundary.

IV. RESULTS AND DISCUSSIONS

InP and CdSe colloidal quantum dots were studied extensively both experimentally[1-7] and theoretically.[2,15,16] In particular, the observed photoluminescence spectra were interpreted by $\mathbf{k} \cdot \mathbf{p}$ models.[1-4,7,15,16] For CdSe dots, the $\mathbf{k} \cdot \mathbf{p}$ was also used to assign the observed high excited transitions,[2] however, the $\mathbf{k} \cdot \mathbf{p}$ parameters were adjusted to fit the experimental data of the *dot*.[2,4] For InP dots, the $6 \ominus 6$ $\mathbf{k} \cdot \mathbf{p}$ predicted that the lowest valence-to-conduction transition is dipole forbidden.[7,15] This was used to explain the carrier dynamics.[7] We are interested in these two materials for an additional reason, namely, that InP and CdSe have quite different magnitudes of spin-orbit splitting: $D_0 5 0.11$ eV for InP and $D_0 5 0.42$ eV for CdSe. Therefore, we can investigate how this difference will affect the applicability of $\mathbf{k} \cdot \mathbf{p}$ model to quantum dots.

For the purpose of a consistent comparison between the direct diagonalization ⒜Eqs. ~1! and ~5!⒥ and $\mathbf{k} \cdot \mathbf{p}$ model ⒜Eqs. ~16!–~22!⒥, the $\mathbf{k} \cdot \mathbf{p}$ Luttinger parameters are all calculated from the curvature of the *bulk-material* dispersion obtained by direct diagonalization using the same pseudopotential employed in dot calculations. These screened atomic pseudopotentials[31,32] are derived from local-density-approximation ~LDA! calculation, and are able to reproduce the LDA wave functions and the *experimentally observed* ~not LDA! bulk transition energies, effective masses, deformation potentials. The kinetic energy cutoff in dot calculation is taken the same as in deriving the potential from bulk solids, i.e., 6.8 Ry for InP and 6.88 Ry for CdSe. The lattice constants for InP and CdSe are 5.83 Å and 6.08 Å, respectively. After the effective masses of zincblende bulk materials are calculated by the pseudopotential approach ~see results in Table I!, the Luttinger parameters $\S g_1, g_2, g_3 \%$ are obtained from Eqs. ~B4! and ~B5! in Appendix B. The average $\bar{g}_2 5 (2g_2 1 3g_3)/5$ is used to replace the value of g_2 in the isotropic $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian.[44] Table I lists the pseudopotential effective masses and the ensuing

pseudopotential theory agree well with experiments.[45–49] Since CdSe exists experimentally in the wurzite ~

fined,'' i.e., it decreases abruptly from the dot's center to the dot's boundary. However, the wave function computed with a finite barrier exhibits a kink at the dot's boundary. This reflects the requirement of current conservation and mass discontinuity. Furthermore, the wave function is rather flat inside the dot ~implying a much weaker confinement!. In contrast, the radial wave function squared obtained by direct diagonalization is intermediate in terms of confinement, and smoothly decays into the vacuum without any unphysical kink. The large amplitude ~which is the quantity plotted in Fig. 4 multiplied by radius squared! of finite-barrier $\mathbf{k} \cdot \mathbf{p}$ wave function near the dot's boundary may cause incorrect electron-hole wave-function overlap, hence, incorrect Coulomb and exchange interactions.

2. Valence states of InP dots

The direct-diagonalization approach predicts for the valence states of InP dots that the HODO has a mostly s-like envelope function symmetry, and the next state below has a mostly p-like envelope function symmetry ~Fig. 3!. Note that the notation for the envelope here reflects only the majority angular character. The HODO has also p,d character, and thus is parity-mixed. Both states are threefold degenerate when $D_0 5 0$, and twofold degenerate when $D_0 Þ 0$. The symmetries can be gleaned from Fig. 4~b! that illustrates the radial wave function squared as obtained by the pseudopotential calculation. The radial wave function of the HODO has nonzero value at the origin ~the dot's center!, and the envelope can be described by spherical Bessel function $j_{L 5 0}(ar)$, thus being s-like. In contrast, the next valence state below the HODO has a zero amplitude at the origin, and its envelope can be described by $j_{L 5 1}(ar)$, thus being p-like. We find that, when we change the surface passivation potential ~to simulate different ligands in experiments!, the order of these s and p valence levels does not change. This reflects the fact that the wave-function amplitudes at the dot surface are very small @see Fig. 4~b!#.

One may wonder whether the electron-hole Coulomb energy, which is different for s-like and for p-like hole states, can reverse the s/p order. We calculate the Coulomb energy, and find that, for the $D 5 34.8$ Å dot, the Coulomb energy of s-like hole with s-like electron is about 10 meV *larger* than that of p-like hole. Therefore, the inclusion of Coulomb interaction will not alter the s-above-p conclusion obtained in our direct diagonalization.

In contrast with the result of the direct diagonalization, the $\mathbf{k} \cdot \mathbf{p}$ model gives the opposite order of valence level, i.e., the HODO is p-like and the next state below is s-like ~Fig. 3!. One may ask at what dot size the s/p order in $\mathbf{k} \cdot \mathbf{p}$ will become correct. Our calculation shows that the $\mathbf{k} \cdot \mathbf{p}$-predicted p-above-s level order is not changed even for dot size as large as 250 Å diameter, where the energy difference of s- and p-like states is negligible ~0.3 meV!. This indicates that $\mathbf{k} \cdot \mathbf{p}$ gives the incorrect s/p level order all the dot sizes. This p-above-s order was also found in previous $\mathbf{k} \cdot \mathbf{p}$

dot valence states, while a $2 \ominus 2$ model with both infinite and finite barriers is used for the dot conduction states. The finite barrier height is taken to be the work function of InP material ($D E_c 5 5.9$ eV).

1. Conduction states of InP dots

The $\mathbf{k} \cdot \mathbf{p}$ prediction for the lowest conduction state using infinite barrier significantly overestimates the *electron* confinement energy compared with the exact direct diagonalization. Using a finite barrier reduces the confinement energy, in closer agreement with the results of direct diagonalization. Fitting the energies of the lowest conduction states of different size dots gives ~e_c^{dot} in units of eV relative to the bulk VBM energy, D in units of Å!

$$e_c^{\text{dot}} 5 \begin{cases} 1.45 1 15.10/D^{0.93} & \text{~direct diagonalization!;} \\ 1.45 1 84.52/D^{1.26} & \text{~}\mathbf{k} \cdot \mathbf{p} \text{ with infinite barrier!;} \\ 1.45 1 26.25/D^{1.09} & \text{~}\mathbf{k} \cdot \mathbf{p} \text{ with finite barrier!.} \end{cases}$$

~23!

Figure 4~a! shows the radial wave function squared $*\upsilon c(\mathbf{r})\upsilon^2 d\upsilon d f$ of the lowest dot conduction state as obtained from $\mathbf{k} \cdot \mathbf{p}$ model either with infinite ~dotted line! or with finite ~dashed line! barriers. It can be seen that the $\mathbf{k} \cdot \mathbf{p}$ wave function corresponding to infinite barrier is strongly ''con-

ordering obtained by $\mathbf{k} \cdot \mathbf{p}$ has been used to explain the carrier dynamical process involving a transition-forbidden lowest exciton state.

This L-derived indirect dot conduction state cannot be described by the usual $\mathbf{k} \cdot \mathbf{p}$ model.

2. Valence states of InP dots

Considering next the dot valence states, Table III and Fig. 5~b! show that

~i! the s-like dot valence state has a significant (; 20%) contribution from bulk band bb$_2$ ~i.e., light-hole band! whereas the p-like dot valence state has nearly no contribution from this bulk band. Since $\mathbf{k} \cdot \mathbf{p}$ overestimates the down-dispersion of bulk lh band ~Fig. 2!, it will also overestimate the confinement of the dot s-like valence state.

~ii! The contribution from the lowest bulk conduction band (bb$_5$) to the s-like dot state is larger than to the

is insufficient even if the bulk dispersions of these three bands are exact. Like our direct pseudopotential result, a recent tight-binding calculation[54] on Si dots including the valence-conduction coupling also gives a s-like HODO state except for very small dots ~less than 87 atoms! where the surface effect can not be neglected. Not surprisingly, in Table V, when we replace the pseudopotential bulk bands by an equivalent number of $\mathbf{k} \cdot \mathbf{p}$ bands ~column 5!, the estimated energy levels seriously differ from column 4 ~also from column 2! due to the difference in bulk band dispersion.

E. Improving k·

approximated well by a single band if, and only if this is the exact bulk band. Otherwise, ~viz. the $\mathbf{k} \cdot \mathbf{p}$! many more bands are needed.

Table V shows analogous results to Table IV but for the dot's valence states ~both s-like and p-like!. Column 3 shows that when we use $M_b 5 8$ pseudopotential bulk bands, the estimated energy levels are quite close to the direct calculation ~column 2!, and the HODO state is s-like. However, when we use only the three highest bulk valence bands in Eq. ~27!, the order of s and p levels changes, and the estimated energies ~column 4! are now significantly different from the direct result ~column 2!, especially for the s-like dot valence states. This is due to the fact that the s-like dot state is more sensitive to the valence-conduction coupling. This shows that in order to have a correct prediction about the s/p level order, *inclusion of the three highest bulk valence bands*

derived from our pseudopotential bulk band structure. The $6 \widetilde{3} 6$ $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian is diagonalized using the basis of $\mathrm{u}F, F_z, J, L\&_{u,f} j_L(k_{Lm}r)$, where $k_{Lm} \widetilde{5} X_{Lm}/R$ and X

By comparing Fig. 8 ~CdSe! with Fig. 2 ~InP!, it can be seen that, the energy difference between the $\mathbf{k} \cdot \mathbf{p}$ and the pseudopotential bulk valence bands is generally smaller in CdSe

ard *et al.*[15] ~iii! The overall agreement between the $\mathbf{k} \cdot \mathbf{p}$ and the direct diagonalization results for valence states is better in CdSe dots ~Fig. 9! than in InP dots ~Fig. 3!.

The bulk band contribution $\widetilde{A}_i(n)$ ⊕Eq. ~26!# to the near-edge states of CdSe dots are illustrated in Table VII. In this table, the contributions from two bulk bands split by spin-orbit coupling are summed, and the summed contribution is assigned to one band in order to facilitate a direct comparison with Table III for InP dots. The projection distributions in Table VII for CdSe are quite similar to those in Table III for InP, i.e., the lowest dot conduction state has a dominant contribution from the lowest bulk conduction band, while the dot valence states come mainly from the three highest bulk valence bands. The significant difference is that, the contribution of the bulk band bb_2 to the s-like dot valence state in CdSe is significantly smaller than in InP ~Table III!. This is due to the large spin-orbit splitting D_0 in CdSe, moving bb_2 to deeper energies. Since bb_2 has a large error in bulk $\mathbf{k} \cdot \mathbf{p}$ ~Fig. 8!, the smaller participation of bb_2 in forming the dot's s-like state alleviates the $\mathbf{k} \cdot \mathbf{p}$ error in this dot state.

The projection amplitude into specific bulk bands and different $\mathbf{k}$ points are shown in Fig. 10. Again, we see that the bulk band bb_2 in CdSe ~Fig. 10! does not contribute as significantly as in InP ~Fig. 5! in forming the dot s-like valence state.

The above comparison between CdSe and InP quantum dots shows that the $\mathbf{k} \cdot \mathbf{p}$ performance on CdSe dots is better than on InP dots for two reasons: ~i! Considering the bulk band structures, the more ionic nature of CdSe flattens the band dispersion relation, so the overall difference between the predictions of the $\mathbf{k} \cdot \mathbf{p}$ bulk bands and the pseudopotential bulk bands is smaller; ~ii! Considering the bulk wave function contribution to the dot states, the large spin-orbit splitting in CdSe moves the poorly-described bulk band bb_2 to deeper energies, and reduces its contribution ~and error! to the dot's s-like state.

V. SUMMARY AND CONCLUSIONS

The $\mathbf{k} \cdot \mathbf{p}$ method and the direct-diagonalization pseudopotential method are used to calculate in parallel the electronic structures of InP and CdSe quantum dots. By using the pseudopotential-derived $\mathbf{k} \cdot \mathbf{p}$ &1.6rp78i00 2.i singuresdiAgj /F14 1 Tfdot'6

energy difference between $\mathbf{k} \cdot \mathbf{p}$ bands relative to the exact ones. Nevertheless, the $\mathbf{k} \cdot \mathbf{p}$ bulk bands depart significantly from the pseudopotential bands away from the Brillouin-zone origin. ⁞1

Figure 9 compares the $\mathbf{k} \cdot \mathbf{p}$ and the direct-diagonalization results on the orbital energies of CdSe dots of different sizes. For the LUDO, we see that ~i! the infinite barrier $\mathbf{k} \cdot \mathbf{p}$ model predicts much higher confinement energies than the exact diagonalization method, while the finite barrier $\mathbf{k} \cdot \mathbf{p}$ calculation improves the result. ~ii! Using pseudopotential-derived $\mathbf{k} \cdot \mathbf{p}$ parameters ~Table I!, we find that, similar to InP, the HODO in $\mathbf{k} \cdot \mathbf{p}$ calculation is p-like while the HODO in pseudopotential calculation is s-like. This holds using our *bulk*-derived $\mathbf{k} \cdot \mathbf{p}$ parameters $g_1 5 2.52$ and $\bar{g}_2 5 0.83$ ~Table I!. Using instead the $\mathbf{k} \cdot \mathbf{p}$ parameters[2] fit by Norris and Bawendi to the *experimental data on dots* ~$g_1 5 2.04$, $\bar{g}_2 5 0.58$! gives the s-like level above the p-like level just like our direct diagonalization. While the two sets of parameters give similar effective masses ~see Table II!, the ensuing electronic structures of dots can be, however, quite different. This illustrates how sensitive the $\mathbf{k} \cdot \mathbf{p}$ calculations are to the Luttinger parameters for CdSe dots as pointed out by Rich-

be accurately described by a small number of G-like Bloch basis set. This kind of error can only be reduced by increasing the size of the basis.

~vi! Error ~b! results specifically from ~1! the fact that the *s*-like dot valence state has a significant contribution from bulk band bb$_2$, which the **k·p** model predicts at too deep energies; ~2! the fact that the *p*-like dot valence state has large contribution from off-G part of bulk band structure whose dispersion is poorly described by **k·p**; ~3! inclusion of the valence-conduction coupling affects differently the energies of the *s*-like and *p*-like dot states, thus changing their energy separation.

~vii! **k·p** errors in CdSe dots appear to be smaller than in InP dots due to the more ionic nature and the large spin-orbit splitting of CdSe material.

~viii! The wave function and energy analysis suggests that in order to improve the **k·p** performance in quantum dots, one needs to ~1! correct the second lowest bulk band, and

make it less deeper; ~2! couple the valence bands to the conduction bands. However, direct-diagonalization provides an accurate and practical replacement to the **k·p**.

APPENDIX A: k·p HAMILTONIAN MATRIX FOR BULK IN z$J,J_z\rangle$ BASES

Using the bases uJ,J_z& in Eq. ~12!, the **k·p** Hamiltonian ₢Eq. ~7!# can be obtained, after a unitary transform of the matrix in Eq. ~8!, as follows:

$$
\begin{array}{cccccccc}
|\tfrac{1}{2},\tfrac{1}{2}\rangle_e & |\tfrac{1}{2},-\tfrac{1}{2}\rangle_e & |\tfrac{3}{2},\tfrac{3}{2}\rangle_h & |\tfrac{3}{2},\tfrac{1}{2}\rangle_h & |\tfrac{3}{2},-\tfrac{1}{2}\rangle_h & |\tfrac{3}{2},-\tfrac{3}{2}\rangle_h & |\tfrac{1}{2},\tfrac{1}{2}\rangle_h & |\tfrac{1}{2},-\tfrac{1}{2}\rangle_h \\
Y & 0 & -\sqrt{3}V^* & \sqrt{2}U & V & 0 & U & -\sqrt{2}V \\
 & Y & 0 & V^* & \sqrt{2}U & \sqrt{3}V & -\sqrt{2}V^* & U \\
 & & -T-Q & -S & R & 0 & -\tfrac{1}{\sqrt{2}}S & -\sqrt{2}R \\
 & & & -T+Q & 0 & -R & \sqrt{2}Q & \sqrt{\tfrac{3}{2}}S \\
 & & & & -T+Q & -S & -\sqrt{\tfrac{3}{2}}S^* & \sqrt{2}Q \\
 & & & & & -T-Q & \sqrt{2}R^* & -\tfrac{1}{\sqrt{2}}S^* \\
 & & & & & & Z & 0 \\
 & & & & & & 0 & Z
\end{array}
\qquad \text{~A1!}
$$

Here, the related parameters \$Y,U,V,T,Q,R,S,Z% are functions of the ensemble \$$g_1$, g_2, g_3, A8, P and D$_0$%in Eqs. ~9! and ~10!, and are explicitly written as

$$Y5\, e_{c,0}1 A8\text{-}k_x^2 1 k_y^2 1 k_z^2!5\, e_g 1 A8\text{-}k_x^2 1 k_y^2 1 k_z^2!,$$

$$U5\, \sqrt{\tfrac{1}{3}}\,iPk_z,$$

$$V5\, \sqrt{\tfrac{1}{6}}\,iP\text{-}k_x 2 ik_y!,$$

$$T5\, 1\, \frac{D_0}{3}1 \tfrac{1}{2}g_1\text{-}k_x^2 1 k_y^2 1 k_z^2!5 \tfrac{1}{2}g_1\text{-}k_x^2 1 k_y^2 1 k_z^2!,$$

$$Q5\, \tfrac{1}{2}g_2\text{-}k_x^2 1 k_y^2 2 2k_z^2!,$$

$$R52\, \frac{)}{2}\,@g_2\text{-}k_x^2 2 k_y^2! 2 2ig_3 k_x k_y#,$$

$$S5)\ g_3 k_z\text{-}k_x 2 ik_y!,$$

$$Z5 2 \tfrac{2}{3}D_0 2 \tfrac{1}{2}g_1\text{-}k_x^2 1 k_y^2 1 k_z^2!5 2 D_0 2 \tfrac{1}{2}g_1\text{-}k_x^2 1 k_y^2 1 k_z^2!,$$

$$\text{~A2!}$$

where e_g is band gap. After the spin-orbit coupling, the valence-band maximum becomes $1 \tfrac{1}{3}D_0$, and is taken as energy zero point in the most right-hand-side equations for parameters Y, T, and Z. Equations ~A1! and ~A2! constitute the 8⋅8 bulk **k·p** method, cast in uJ,J_z& representation.

APPENDIX B: SUBMATRICE OF ISOTROPIC k·p HAMILTONIAN

In the irreducible representation uF,F_z,J,L& ₢Eq. ~15!#, the isotropic Hamiltonian ~with $g_2 5 g_3 5 \bar{g}_2$! is block-diagonal for different \$$F,F_z$% By using Eqs. ~13! and ~15! and Eq. ~A1!, the submatrix H_{F,F_z} corresponding to $F 5 \tfrac{1}{2}$

can be obtained, by some derivation, as

$$H\tfrac{1}{2}, 6\tfrac{1}{2}5 \int^H$$

culations with $(\Delta_0 \neq 0)$ and without spin-orbit coupling $(\Delta_0 = 0)$ are very close ~with difference less than 5%! for InP. The four equations with three unknowns give g_1 value with an uncertainty of less than 1%. The relationships between the 838 and the 636 $\mathbf{k}\cdot\mathbf{p}$ parameters, providing consistent hole effective masses, are:

$$g_1^{838} = g_1^{636} + \frac{2}{3}\frac{P^2}{E_g},$$

$$\bar{g}_2^{838} = \bar{g}_2^{636} + \frac{1}{3}\frac{P^2}{E_g}.$$

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