



7 ca dUf]gcb'cZ h Y \_ ' d' UbX' h Y' X]fY W h X]U[ cbU']nUh]cb' UddfcUW X Yg' Zcf'XYgW]V]b[ ' h Y  
Y'Y W fcb]Wghfi W h fY'cZei Ubh a ' Xchg

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5fh]WYg'mci 'a UmVY']bhYfYghYX']b

[Electronic structure and optical gain saturation of InAs  \$1 - x\$  N  \$x\$  /GaAs quantum dots](#)

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# Comparison of the $k$ - $p$ and the direct diagonalization approaches for describing the electronic structure of quantum dots

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It is shown that the standard ~decoupled!  $6\text{ }6\text{ }k\text{-}p$  effective-mass approach for semiconductor quantum dots overestimates significantly the hole and electron confinement energies, and, for dots made of materials with small spin-orbit coupling ~e.g., phosphides, sulphides! produces a reverse order of  $s$ - and  $p$ -like valence states. By contrasting the electronic structures of dots as obtained by a direct diagonalization ~multiband! pseudopotential approach and by its  $k\text{-}p$  approximation, we are able to trace the systematic errors of  $k\text{-}p$  in dots to the  $k\text{-}p$  errors in the underlying bulk solids. This suggests a ‘‘diagnostic tool’’ and a strategy for improving the  $k\text{-}p$ . © 1997 American Institute of Physics. ©S0003-6951-97!00449-X#

It is now possible to produce via techniques of colloidal chemistry<sup>1</sup> nearly spherical quantum dots of a variety of semiconductor materials ~CdSe,<sup>2,3</sup> InP,<sup>4</sup> InAs,<sup>5</sup> Si<sup>6</sup>!, with typical diameters of 30–60 Å and good surface passivation. The rich spectroscopy<sup>2–5</sup> of such dots has been analyzed, almost universally, using a theoretical model that is so common that we term it the ‘‘standard model.’’ This ‘‘ $k\text{-}p$  effective mass approach,’’<sup>3,5,7–12</sup> expands the wave functions of the dot in terms of a linear combination of  $N_b$  bulk Bloch functions at the Brillouin zone center ~ $\mathbf{k}\text{ }0$ , or  $\Gamma$  point!. The most sophisticated version applied widely to quantum dots is<sup>3,5,9,10</sup> the  $6\text{ }6\text{ }k\text{-}p$  ~i.e.,  $N_b\text{ }6$ !. We know, however, that the loss of translational periodicity in all three dimensions could lead in a quantum dot to coupling between many ( $N_b\text{ }1$ ) bulk bands, and that this coupling could extend in momentum space well beyond the Brillouin zone center. This physical need for a large number of bulk basis functions is mitigated in the ~small basis  $N_b\text{ }6$ ! standard model by the introduction of empirical matrix elements ~‘‘Luttinger parameters’’! drawn from the corresponding bulk solid. The rapid increase in the number of such energy parameters as the basis size  $N_b$  increases, and the fact that some of the parameters are not physical observables, limit one’s ability to improve the standard model by raising  $N_b$  systematically. Thus, the model itself does not provide an intrinsic, reflective mechanism for judging when more bands and more parameters are needed to correctly describe a given quantum dot system.

We have recently developed an alternative theoretical approach<sup>13–15</sup> that includes, at the outset, a converged number of bands without the need to introduce redundant empirical parameters. We solve via direct diagonalization ~DD! the single particle Schrodinger equation

$$\left\{ \frac{1}{2} \text{ }^2 \text{ } 1 \left( \sum_n \left( v_a \text{-} \mathbf{r} \text{ } \mathbf{R}_n \text{ } \mathbf{2} \mathbf{d}_a \right) \right\} c^{-i} \text{ } 5 \text{ } e c^{-i}, \quad \sim 1!$$

where  $v_a(r)$  is the screened nonlocal pseudopotential of atom of type  $a$  ~both the dot material and its passivating layer! located at ‘‘cell’’  $n$  and site  $\mathbf{d}_a$ . This pseudopotential is derived<sup>14</sup> from *ab initio* local density approximation

~LDA! calculations on the underlying bulk solid and includes adjustments to correct the LDA error in bulk band energies. The wavefunctions  $c^{(i)}$  are expanded in a plane wave basis, and matrix elements of  $v_a$  are computed essentially exactly via numerical Fourier transformation. For periodic bulk solids, Eq. ~1! is solved using conventional matrix diagonalization techniques. This produces the Bloch function  $c_{n\mathbf{k}}(\mathbf{r}) \text{ } 5 \text{ } e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$  of band  $n$  and wavevector  $\mathbf{k}$ , and the bulk band structure dispersion  $e_{n\mathbf{k}}$ .

For ;  $10^3$ -atom quantum dot, conventional diagonalization techniques are impractical, so we solved Eq. ~1! via the novel ‘‘folded spectrum method’’ ~FSM!,<sup>15</sup> that provides exact eigen solutions of the near-edge states at a computational cost that increases only linearly with the system’s size. Unlike the standard model, surface effects are treated explicitly and effective mass approximations are not invoked. Unlike tight-binding model,<sup>16</sup> the dot wavefunctions  $c\text{-}\mathbf{r}$ ! are known explicitly, and a variationally flexible basis set is used. Our method was previously applied to nanostructures of Si,<sup>13</sup> CdSe,<sup>17,18</sup> GaAs,<sup>18</sup> and InP.<sup>19</sup> We propose to use here

calculations that are equivalent to our pseudopotential direct diagonalization method, we need to determine the Luttinger parameters from our pseudopotential. To do so, we first solve Eq. 1 via direct diagonalization, obtaining the bulk dispersion  $e_{n\mathbf{k}}$  and the effective masses. For InP, we find that in the absence of spin-orbit coupling (i.e.,  $D_0 = 0$ ),  $m_{\text{hh}}(001) = 0.474$ ,

$$e_i^{\text{dot}} \approx \sum_n \left( \sum_{\mathbf{k}} e_{n,\mathbf{k}}^{\text{bulk}} |c_{n,\mathbf{k}}^i|^2 \right). \quad (4)$$

The orbital energies of the  $s$ -,  $p$ -like valence states, and the lowest conduction state of the InP dot with 34.8 Å diameter as obtained by direct diagonalization are in eV, respectively,  $(e_s, e_p, e_{cb}) \approx (2.017, 2.022, 1.199)$  while  $k \cdot p$

deep an energy over confinement!. This is indeed borne out by Fig. 2.

(b) The  $s$ -like dot valence band has a significant contribution from  $\Gamma$  point ( $\mathbf{k} \approx 0$ ), whereas the  $p$ -like dot valence state has no contribution from  $\mathbf{k} \approx 0$ . Also, the  $\mathbf{k}$  points which contribute most significantly to the dot  $p$ -like state are generally more distant from  $\mathbf{k} \approx 0$  than those  $\mathbf{k}$  points which contribute significantly to the dot  $s$ -like state. Given that the  $k \cdot p$  approach does not describe well the bulk dispersion away from  $\Gamma$ -Fig. 1!, we expect that the  $k \cdot p$  model will not describe the  $p$ -like dot valence state well either. This is also borne out by Fig. 2.

(c) The  $s$ -like dot valence state has a larger contribution from the bulk conduction band than the  $p$ -like dot valence state, indicating that the  $s$ -like dot valence state is more affected by the neglect of coupling with the conduction bands in the standard  $k \cdot p$  model. Effects (a)–(c) explain why the 636  $k \cdot p$  produces an incorrect order of  $s$  and  $p$  valence states while over estimating the global confinement.

(d) The lowest  $s$ -like dot conduction state has a large contribution from the lowest bulk conduction band away from the  $\mathbf{k} \approx 0$  zone center. Since the  $k \cdot p$  overestimates significantly the up dispersion of the bulk conduction band (Fig. 1!), we expect it also to over estimate the dot's conduction state energy. This is indeed borne out by our direct calculation (Fig. 2!).

The above arguments can be quantified. We can approximately model the orbital energies of the *dot* as a linear combination of the orbital energies of the underlying *bulk*, using our spectral coefficients of Eq. (3) as weights: