Linear combination of bulk bands method for large-scale electronic structure calculations on strained nanostructures

bolic kinetic energy term; adding a state mixing term at the interface,[20] introducing nonlinear strain effects, etc. The formalism can get very complicated, and the rapid increase in the number of parameters makes it quite intractable.

An alternative approach[21] to this problem, which is more along the lines of *ab initio* methods, is to avoid the decomposition of the wave function in Eq. (1) into envelope functions. Instead, the wave function is described by a variationally flexible plane wave basis, and the potential is described as a superposition of atomic potentials[22] $v_a(\mathbf{r})$. This guarantees that the physical symmetry of the system is preserved, and affords an atomistic description of surfaces, interfaces, and strain. Since the basis set is not drawn from Γ-like Bloch states, an off-Γ character in the wave functions can be readily described. In this approach, the single-particle Schrödinger equation is constructed as

$$\left[-\frac{1}{2}\nabla^2 + \sum_{R,a} W_a(\mathbf{R}) v_a(\mathbf{x}-\mathbf{R}-\mathbf{d}_a(R)) \right] c(\mathbf{x})$$

$$\equiv H c(\mathbf{x}) = e c(\mathbf{x}), \qquad (2)$$

where $c(\mathbf{x})$ is the single-particle wave function, $\mathbf{R}$ denotes the position of the primary cell, and $\mathbf{d}_a(R)$ is the displacement of atom of type a inside the primary cell $\mathbf{R}$. $v_a(\mathbf{x})$ is a screened, spherical atomic pseudopotential that can be extracted from local density-approximation (LDA) calculations on bulk systems, and then adjusted empirically so as to fit the measured bulk band properties while keeping LDA quality wave functions.[22] In this work, we will deal with local pseudopotentials $v_a(\mathbf{x})$ only. The weight function $W_a(\mathbf{R})$ is used to denote whether an atom of type a occupies site $\mathbf{R} + \mathbf{d}_a(R)$. The atomic positions $\{\mathbf{R}+\mathbf{d}_a(R)\}$ are relaxed with respect to their "ideal" positions (e.g., perfect zinc-blende crystal structure) to minimize the strain energy. For strain-dependent pseudopotentials,[23,24] $W_a(\mathbf{R})$ could deviate from 0 or 1, being instead a function of local strain. $c(\mathbf{x})$ is expanded in a fixed plane-wave basis set

$$c(\mathbf{x}) = \sum_k A(k) e^{ik\cdot\mathbf{x}}. \qquad (3)$$

This approach (1) includes, via $\{\mathbf{R}+\mathbf{d}_a(R)\}$, the true atomistic symmetry of the heterostructure; (2) is able to describe the multivalley (e.g., Γ-X) mixing *via* the ability to describe the whole Brillouin zone (BZ) Bloch states; (3) could be used to study very small nanostructures, beyond the region of parabolic approximation of the band structure, and beyond the region of linear strain dependence; (4) retains interfacial properties pertaining to the atomic structures; and (5) given the atomistic (i.e., nonenvelope) nature of the wave functions $c(\mathbf{x})$, this method can also be used to calculate explicitly the Coulomb interaction and the exchange interactions.[18,17]

This approach has been used to study quantum wells, superlattices, disordered superlattices, quantum wires, colloidal quantum dots, embedded pyramidal quantum dots, and composition modulations in alloys. Excellent agreements with the experiment have been obtained for single-particle energy levels,[11] exchange splittings,[18] optical-absorption spectra[25] and the magnitudes of Γ-X coupling.[13]

The disadvantage of the expansion of Eq. (3) is that it does not lend itself to systematic approximations: The plane-wave basis $\{e^{ik\cdot\mathbf{x}}\}$ of Eq. (3) is classified only in terms of the kinetic energy $\frac{1}{2}k^2$. In contrast, the EMA expansion of Eq. (1) is "intuitive," in that one can classify the basis set in terms of physical Bloch functions $\{u_{\Gamma,n}e$

only as a continuum model for the envelope functions. In contrast, the LCBB method [1] retains the full atomistic structure of the wave functions, enabling the use of the Hamiltonian of Eq. (2) without parametrization; Eq. (2) describes the bulk band structure correctly throughout the BZ, *even if only a single band ($N_B = 1$) is used in Eq. (5).* Thus the method can be used to describe Γ-*X* couplings, nonparabolic effects around the Γ

atomic positions be denoted as

$^{\wedge}f_{k,n}$⨆H_1

Substituting these structure factors into Eq. ~22!, we obtain

$$
\^{\mathbf{k}+\mathbf{G}}uH_2u\mathbf{k}8+\mathbf{G}8\&= \sum_a e^{i\mathbf{q}\cdot\mathbf{d}_a^0}\Big[V_a\~{q}^2! W^a\~{\mathbf{k}-\mathbf{k}8!} + iV_a\~{q}^2!\,\mathbf{q}\cdot\mathbf{W}_d^a\~{\mathbf{k}-\mathbf{k}8!} + V_a^8\~{q}^2!\,\mathbf{q}\cdot\hat{W}_x^a\~{\mathbf{k}-\mathbf{k}8!}\cdot\mathbf{q}
$$

$$
+\frac{1}{2}V_a^9\~{q}^2!\sum_{i1,\ldots,i4} q_{i1}q_{i2}q_{i3}q_{i4}W^a_{i1,i2,i3,i4}\~{\mathbf{k}-\mathbf{k}8}
$$

error increases to

e.g., $(_n \| C_{k,n} \|^2 > 1 \times 10^{-3}$ ~above the dashed line in Fig. 3!, the number of **k** points is almost independent of m. This important feature of the LCBB and SLCBB methods makes their computational efforts scale almost as $O(N^0)$ ~see Sec. IV!

the anion atoms are used to represent the position of the primary cell. In Eq. ~17!, we have used the averaged $\hat{e} \cdot \hat{e}$ from the cation and anion atoms.

The calculation of Eqs. ~24! and ~25! can be further speeded up by carefully rearranging the ''do loops'' in the program over $\mathbf{k}$, $\mathbf{k8}$, $\mathbf{G}$, $\mathbf{G8}$ and n, $n8$. The idea is that Eq. ~24! @and the major part of Eq. ~A6!# depends only on $\mathbf{q} = \mathbf{k} - \mathbf{k8} + \mathbf{G} - \mathbf{G8}$. Thus, for the same $\mathbf{q}$, the time-consuming multiplications need not be repeated. In practice, instead of doing a double loop over $\mathbf{k}$ and $\mathbf{k8}$, one can have an outer loop over all possible $\mathbf{k} - \mathbf{k8}$ values, and an inner loop over the possible $\mathbf{k}$ for each $\mathbf{k} - \mathbf{k8}$. Within each loop for the same $\mathbf{k} - \mathbf{k8}$ value, we can then store the results of Eq. ~24! for each $\mathbf{G} - \mathbf{G8}$, and use them for different $\mathbf{G}$ and $\mathbf{k}$ values. In doing so, we have effectively reduced a major part of the $(N_B \times N_k \times N_G)^2$ scaling to N_B^2 ++ > =

in Eq. ~23!; 21 min to evaluate the matrix elements in Eq. ~25! @or Eq. ~A6!#; and 10 min to diagonalize the 3018 ×3018 matrix. Thus, in total it takes about 34 min to calculate the electron states of the quantum dot. This is about 1000 times faster than the direct calculation using the FSM. Should the system be larger, this ratio could also be. This is because the time for the current approach will not change, while the time of FSM will increase linearly with the size of the system.

Figure 4 shows the electron wave function and energies of the pyramidal InAs dot. We see that the SLCBB CBM energy has an error of 12 meV compared with the exact FSM results. The energy of SLCBB CBM+3 has a larger error of 29 meV. Notice that the SLCBB energy is slightly higher than the exact energy. This is an indication that the energy error comes from a limited SLCBB basis set @rather than from the matrix element evaluation error in Eq. ~24!#. A strong restriction on the basis set is the number of k points. With the limited k points, it is difficult to describe the more complicated wave functions of CBM+3, causing a larger energy error for this state. Notice also that the energy splitting between states has been reproduced accurately by the SLCBB method. The largest error for the energy splitting is 9 meV. So, in this regard, the result of SLCBB is quite satisfactory. The wave functions of the SLCBB and the direct calculation are quite similar. There are some small dif-

ferences, like the size of the isosurface. However, the SLCBB wave function plotted in Fig. 4 is only an approximate one. That is, to plot Fig. 4, we have projected the wave function $c(\mathbf{x})$ in Eq. ~15! to $u_{G,n}(\mathbf{x})$ @with a multiplication envelope function $F_n(\mathbf{x})$#. The use of $u_{G,n}(\mathbf{x})$ instead of $f_{k,n}(\mathbf{x})$ introduces some small errors in the plotted wavefunction amplitude ($_n$Ɱ$F_n(\mathbf{x})$Ɪ^2. Thus the small isosurface difference between SLCBB and direct calculation in Fig. 3 should not be taken too literally.

Next we calculate the hole states. Here more basis functions are needed to describe the degenerated top of the valence band. Like the conduction state calculation, an unrelaxed reference system with a lattice constant of 5.879 Å is used. The same four strained bulk systems and the same k-point selections are used as for the electron state calculation. However, more bands are taken in the basis set for each strained system. For the first bulk system of natural GaAs, four bands are taken, from the first to the fourth (G_{1v} and G_{15v}). For the other three systems, the three top valence

developed based on the current formalism. The SLCBB results differ from the exact diagonalization results only by $\lesssim 20$ meV in absolute energy levels, and $\lesssim 10$ meV in the energy splittings. The wave functions of the SLCBB are very similar to those obtained in direct diagonalization. However, for a system containing a quarter of a million atoms, the SLCBB is 100–1000 times faster than the direct FSM calcu-

nodes. These wave functions cannot be estimated without explicit calculation. If the error of our approximation were on the order of 100 meV, instead of the current 10-meV value ๏for example, by removing the second-order term $W_{i1,i2,i3,i4}^{a}$ in Eq. ~24! or by using only a single strained bulk system in the basis set#, completely different hole wave functions will result, bearing no resemblance to the states shown in Fig. 5.

VI. CONCLUSIONS

We have presented a strained, linear combination of bulk band ๏SLCBB! method for calculating single-particle wave-functions and energies of nanosystems. This method represents an extension of the LCBB method to the strained heterostructure systems. This method correctly treats the effects of strain on the electronic structure up to a major part of the second order. Unlike the conventional $\mathbf{k} \cdot \mathbf{p}$ method, no explicit strain deformation potential parameters are used to represent this strain effect. What is needed are the atomic positions and the atomic pseudopotentials. Sufficient details are presented in this paper, so that a workable program can be

where E_{cut} is a cutoff energy, usually about 5–8 Ry in our calculations.

A smooth cutoff function $v(|\mathbf{k}+\mathbf{G}|^2)$ can be defined as[22]

$$v(|\mathbf{k}+\mathbf{G}|^2) = \begin{cases} 1 & \text{if } E(\mathbf{k}+\mathbf{G}) < bE_{cut} \\ \sin^2\left[\dfrac{\pi(E_{cut}-E(\mathbf{k}+\mathbf{G}))}{2(1-b)E_{cut}}\right] & \text{if } bE_{cut} < E(\mathbf{k}+\mathbf{G}) < E_{cut}, \end{cases} \tag{A2}$$

where $b < 1$ is a control factor ($b = 0.8$ is used in the current calculation).

To use this smooth cutoff function, the potential part H_2 of the Hamiltonian will be changed to a nonlocal operator

$$H_2(\mathbf{x}_1,\mathbf{x}_2) = \int v(\mathbf{x}-\mathbf{x}_1)\prod_{R,a}\left(v_a(\mathbf{x}-\mathbf{R}-\mathbf{d}_a(R))#W_a(R)\right] v(\mathbf{x}-\mathbf{x}_2)d^3\mathbf{x}, \tag{A3}$$

where $v(\mathbf{x})$ is the Fourier transformation of $v(|\mathbf{k}+\mathbf{G}|^2)$ in real space, and is a short-range function. Then the matrix element $\langle \mathbf{k}+\mathbf{G}|H_2|\mathbf{k}'+\mathbf{G}'\rangle$ can be written as

$$\langle \mathbf{k}+\mathbf{G}|H_2|\mathbf{k}'+\mathbf{G}'\rangle = \frac{1}{V_0}\int A\overline{J(\mathbf{x}_1)}e^{-(\mathbf{k}+\mathbf{G})\cdot m(\mathbf{x}_1)}v(\mathbf{x}-\mathbf{x}_1)\prod_{i,a}\left(v_a(\mathbf{x}-\mathbf{R}-\mathbf{d}_a(R))#W_a(R)\right]$$

$$\times v(\mathbf{x}-\mathbf{x}_2)A\overline{J(\mathbf{x}_2)}e^{(\mathbf{k}'+\mathbf{G}')\cdot m(\mathbf{x}_2)}d^3\mathbf{x}_1 d^3\mathbf{x}_2 d^3\mathbf{x}. \tag{A4}$$

Using the same approximation as we did in Eq. (19)

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