

# Modeling of Gas-Surface Interactions Using Molecular Dynamics Simulations

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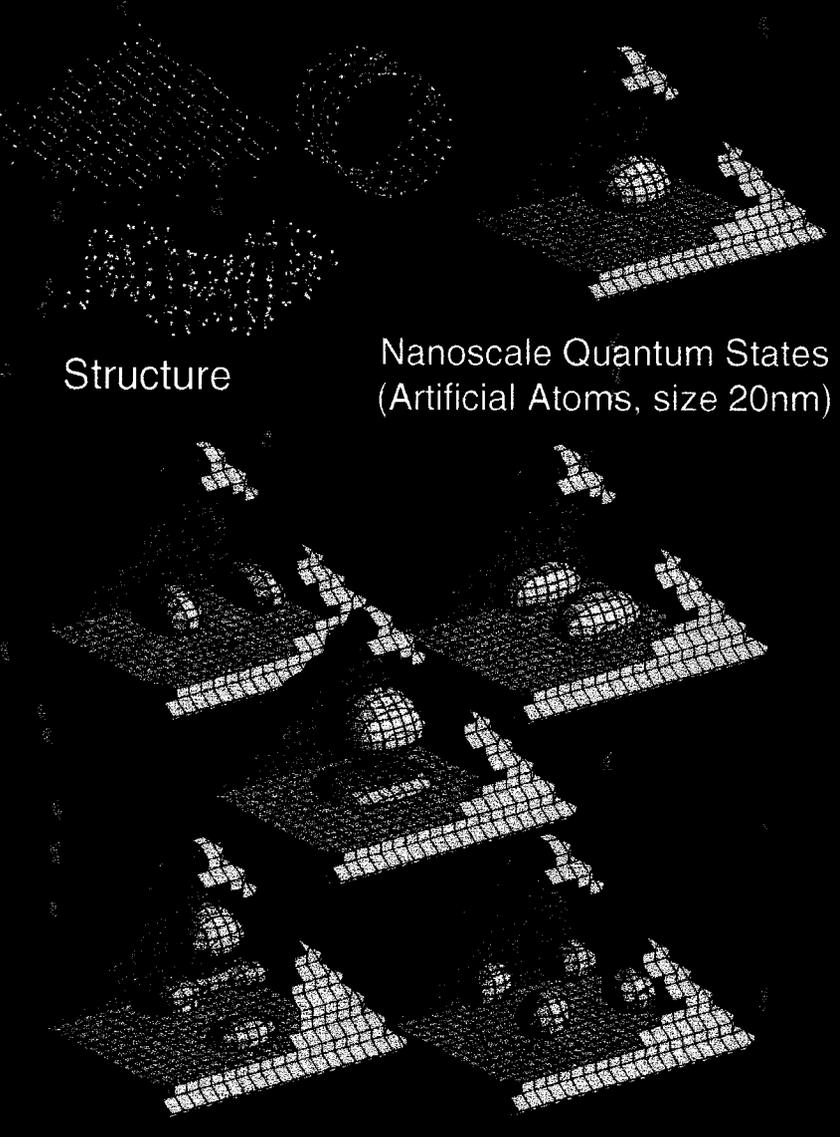
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Web: <http://hpc.jpl.nasa.gov/PEP/gekco/nemo3D>





Structure

Nanoscale Quantum States  
(Artificial Atoms, size 20nm)

### **Parameterization:**

- TB parameters determined from genetic algorithm to match experimentally measured band edges and masses.

### **Mechanical Strain:**

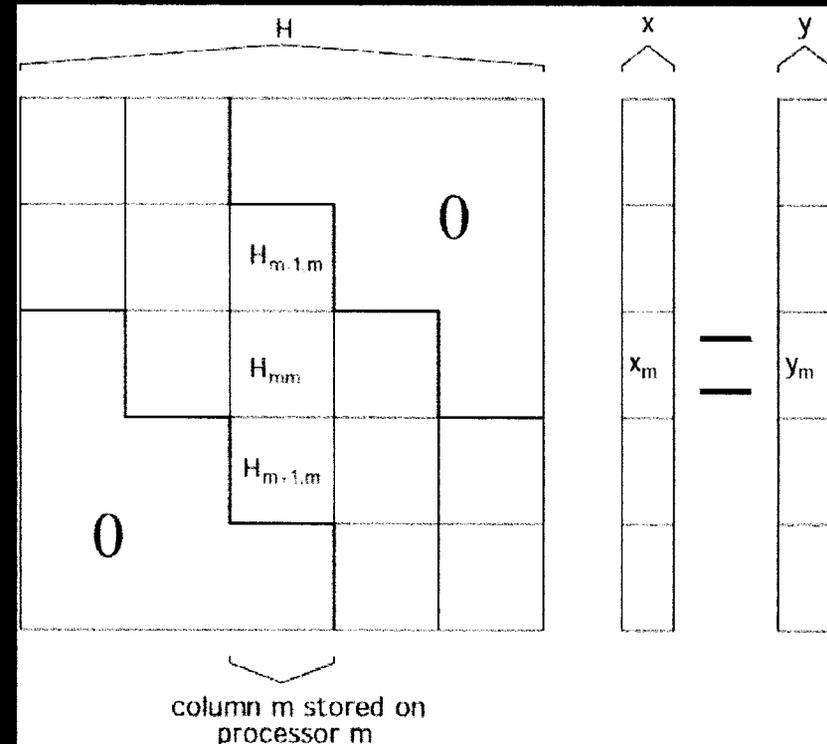
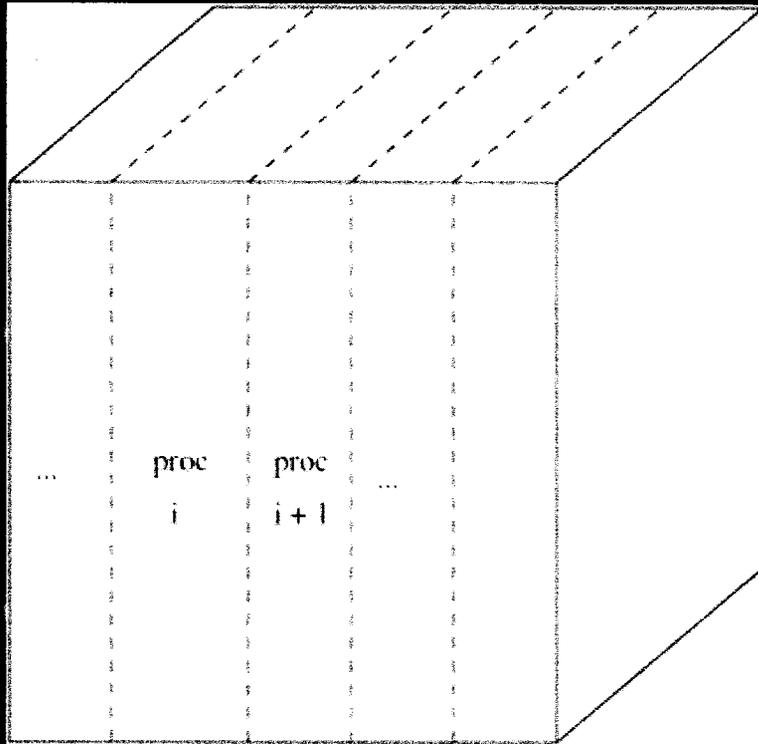
- CG-based minimization of mechanical strain to determine atomic positions

### **Electronic Structure:**

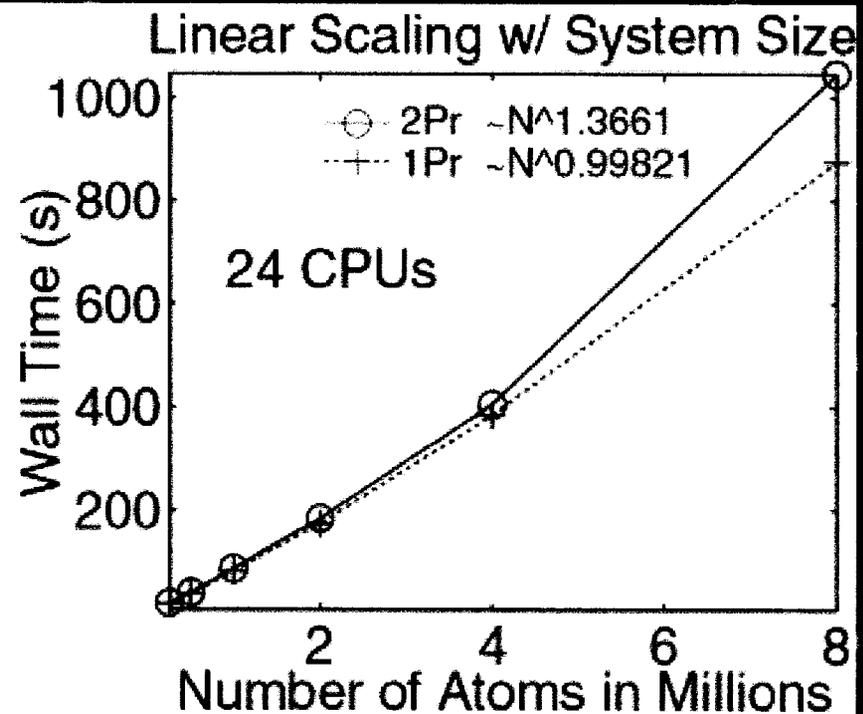
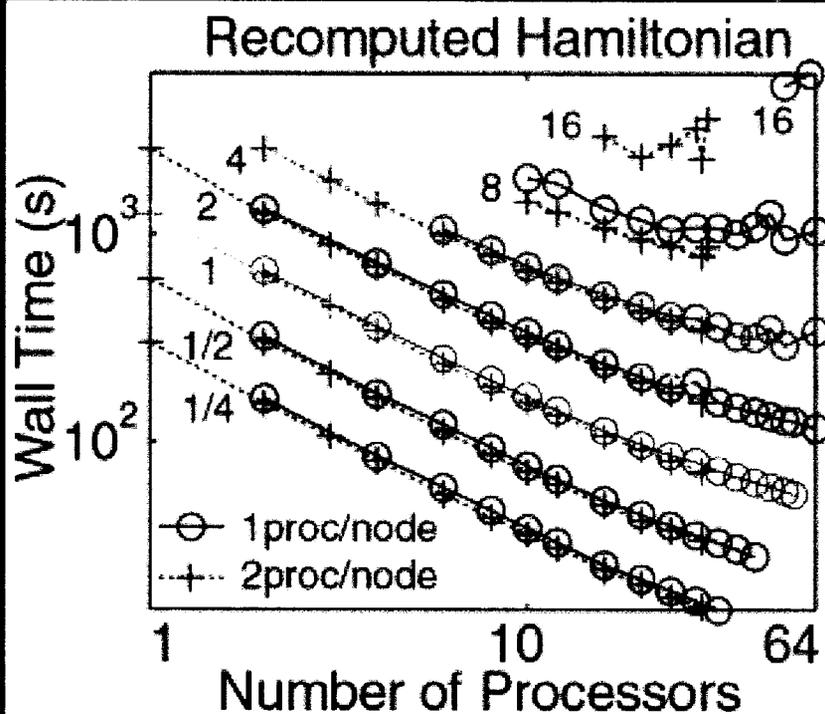
- Custom Lanczos eigenvalue solver

### **Numerical Simulation:**

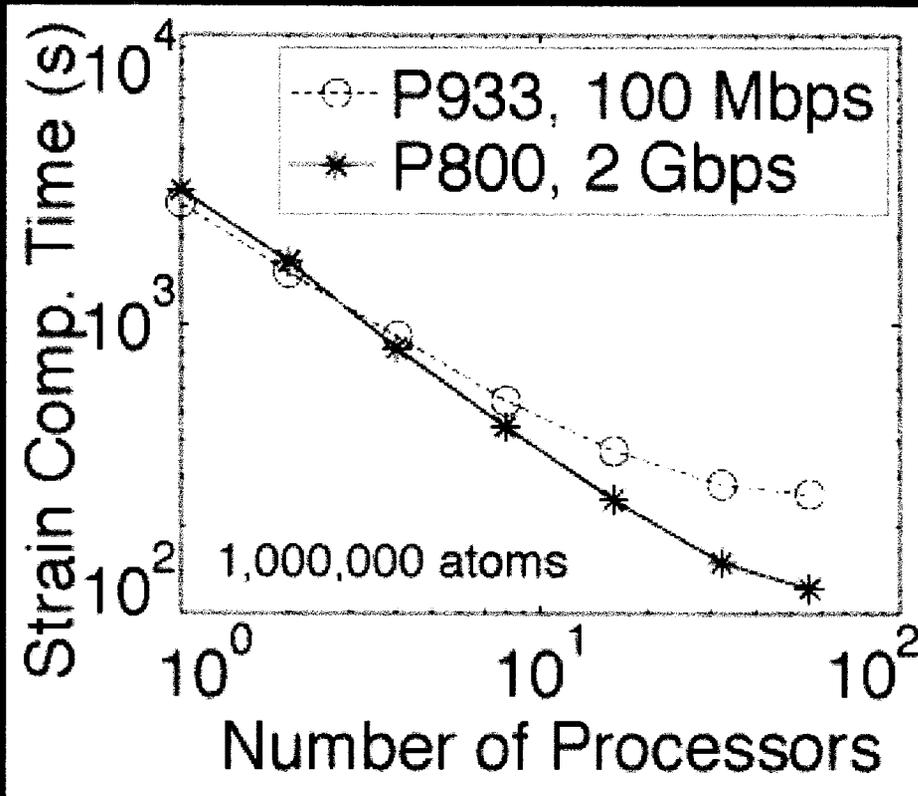
- Problem size is large: 100 GB is typical storage requirement for Hamiltonian
- Parallel implementation of both strain and electronic structure calculation is necessary!
- 1D data decomposition



- Divide Simulation domain into slices.
- Communication only from one slice to the next (nearest neighbor)
- Communication overhead across the surfaces of the slices.
- Limiting operation: sparse matrix-vector multiplication
- Enable Hamiltonian storage or re-computation on the fly.



- Eigenvalue computation ranging from 1/4 to 16 million atoms
- Large problems are too big for a single CPU (memory requirements)
- sp3s\* basis set , Matrix sizes up to  $1.6 \cdot 10^8 \times 1.6 \cdot 10^8$
- Recompute Hamiltonian matrix on the fly.
- Measure time for 30 Lanczos iterations, Full problem 1000-5000 iterations
- 1million atoms 5000 iteration 1 CPU: ~48 hours 20 CPUs: ~3.4 hours
- Computation time linear in system size.



Problem (1million atoms):

- Serial strain computation:  
~43 min.
- Serial electronic structure calculation (1000 iterations):  
~ 9.6 hours
- Parallel electronic structure computation on 20 CPUs:  
~41 min.

Solution:

- Parallelize strain calculation as well

Result:

- Reduce time to 2-5 minutes on a parallel machine.
- See difference between a fast 2Gbps and a 100Mbps network.
- Do not see that difference in the electronic structure calculation.
- Parallel strain computation is more communication dependent than the electronic structure calculation.

**Bulk Semiconductors are described by:**

- Conduction and valence bands, bandgaps (direct, indirect), effective masses
- 10-30 physically measurable quantities

**Tight Binding Models are described by:**

- Orbital interaction energies.
- 15-30 theoretical parameters

- Match experimental data in various electron transport areas of the Brillouin zone:

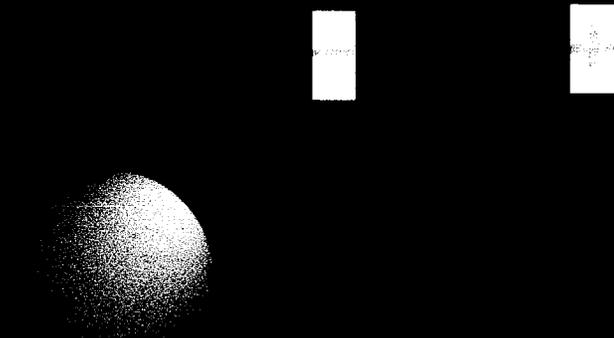
- Effective masses of electrons at  $\Gamma$ , X and L
- Effective masses of holes at  $\Gamma$
- Band edges at  $\Gamma$ , X and L

**Analytical approach:**

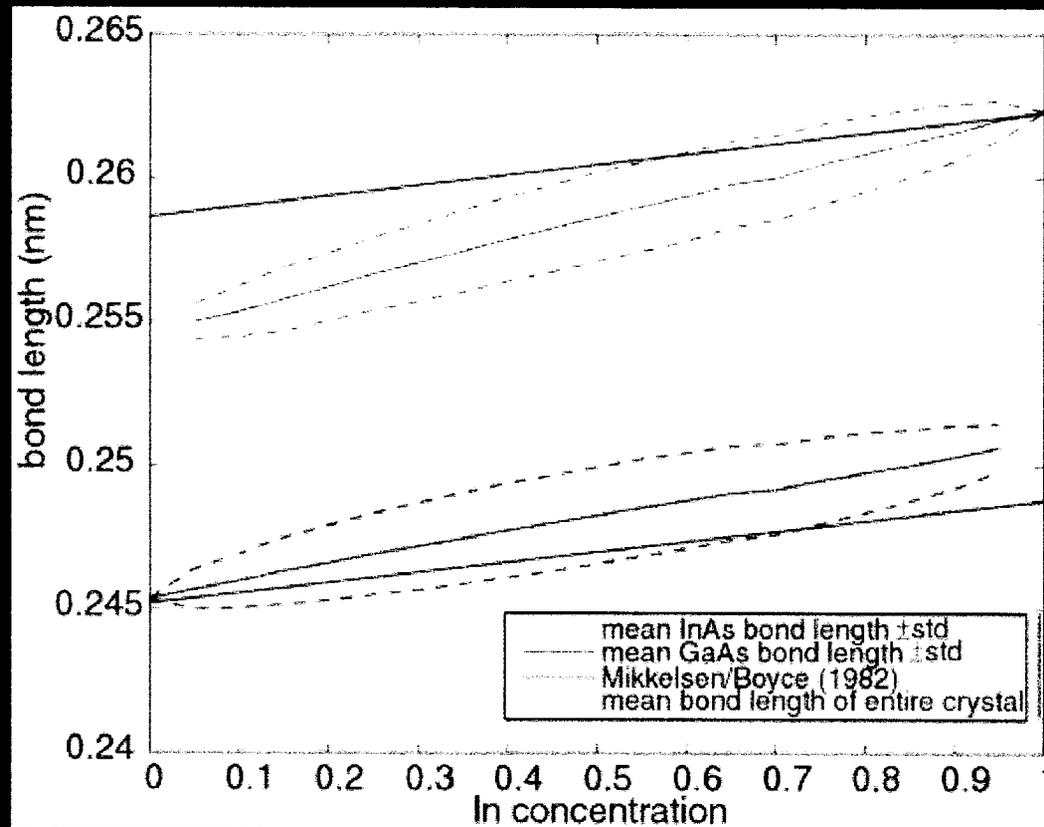
- Exact diagonalization at  $\Gamma$  for  $sp^3d^5s^*$
- Formulas developed by Tim Boykin at UAH (subcontract) for effective masses and bandgaps from interaction energies

**Numerical approach:**

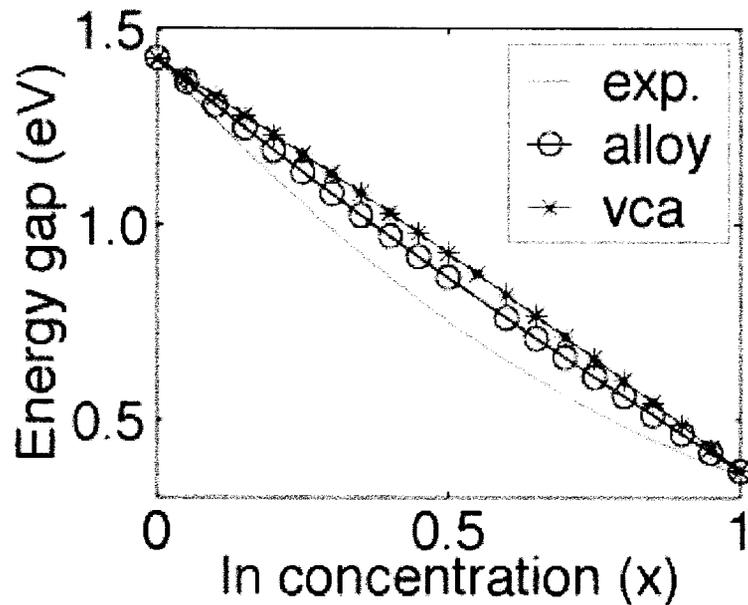
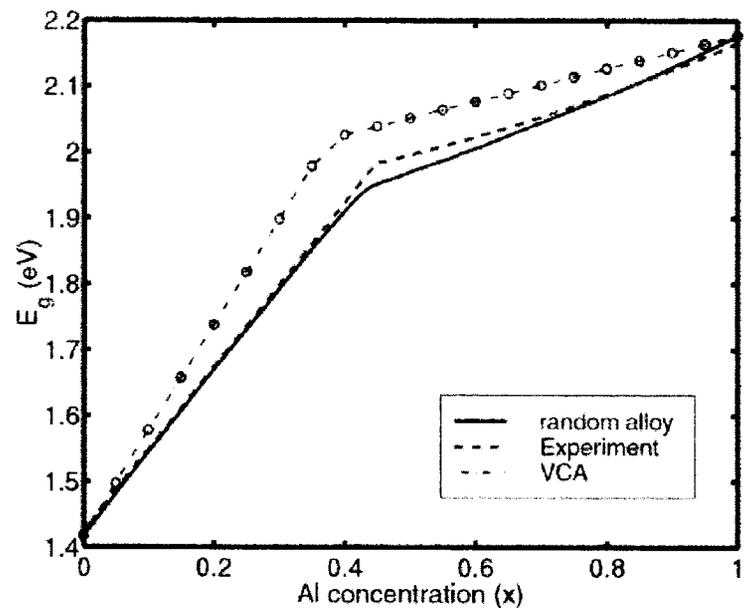
- Use a genetic algorithm to do fitting.



15-30 theoretical interaction energies



- Total strain energy (computed from Keating model) is minimized through CG-based algorithm
- Periodic boundary conditions require relaxation of the period
- InGaAs bond length distribution:
  - VCA on the bond length is incorrect
  - Locally, InAs and GaAs (mostly) maintain their bond length character



### Problem:

- VCA provides generally a linear bandgap if interpolated from the binaries GaAs, AlAs, and InAs.

### Approach:

- sp<sup>3</sup>s\* tight binding model
- Perform 3-D alloy simulation of the bandedges.
- Represent each individual atom in the chunk of material
- 3-D random alloy simulation matches experimental data well.

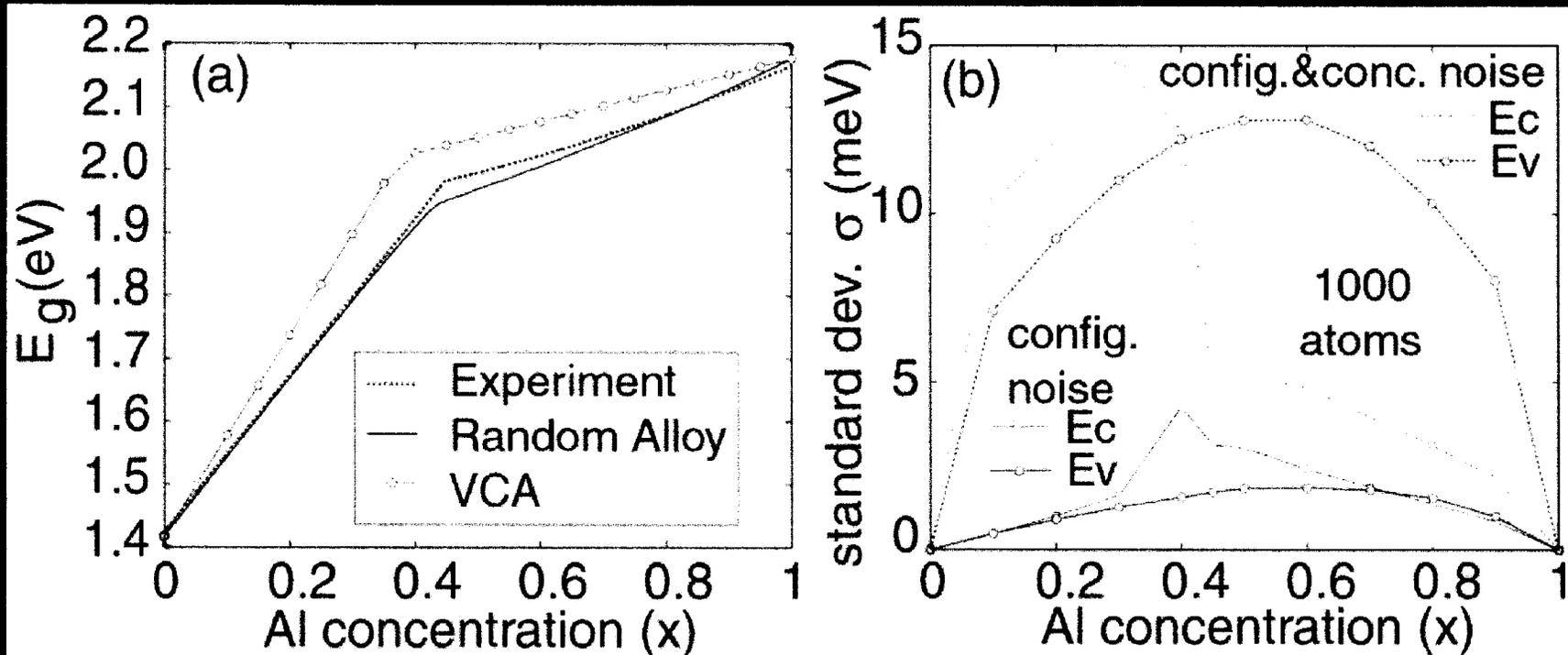
### AlGaAs:

- VCA derived from pure GaAs and AlAs results in an wrong bandgap.
- 3-D simulation gives the correct bowing.

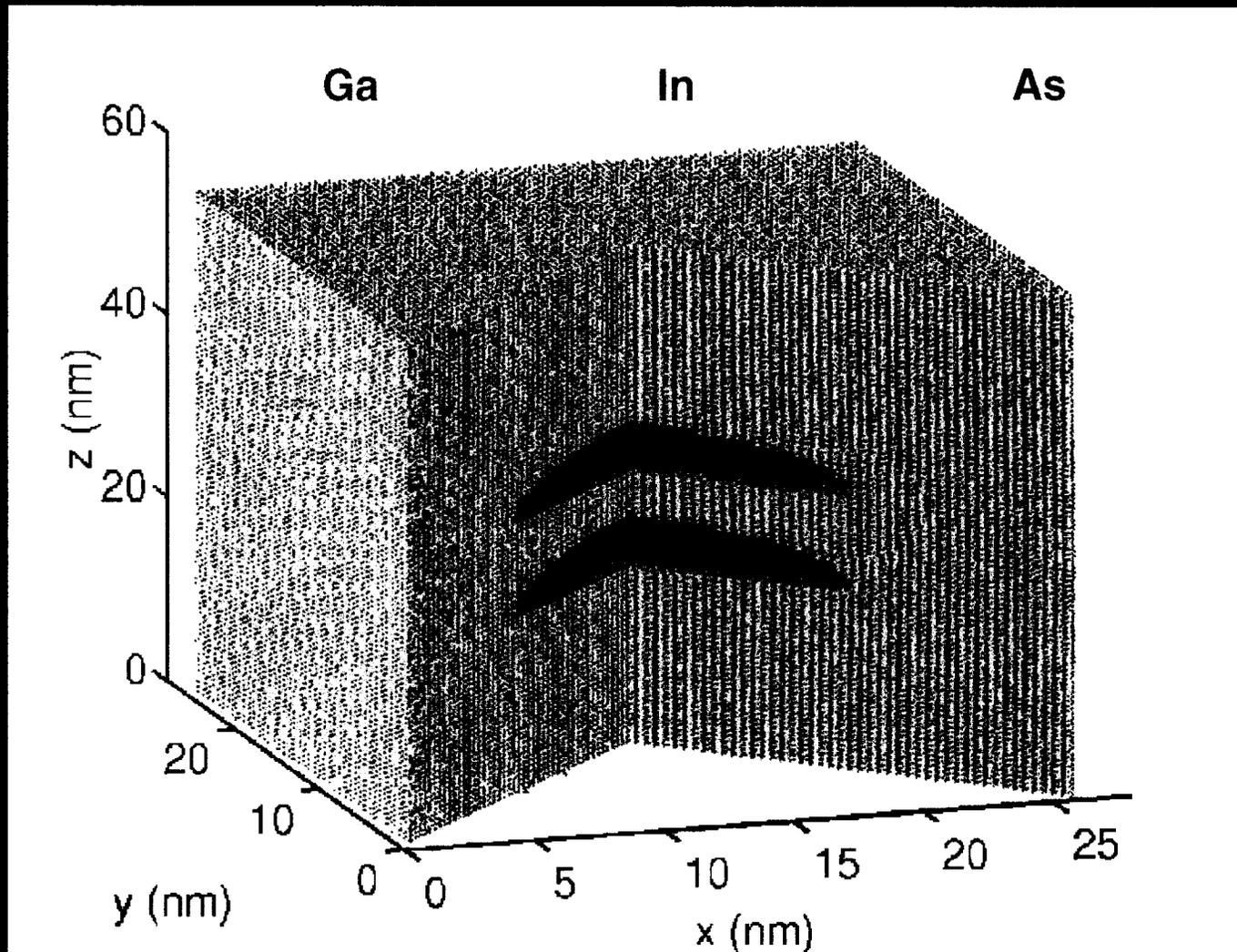
### InGaAs:

- Improved bowing versus the VCA.
- Still a problem with over estimating the band gap  
-> parameterization dependent

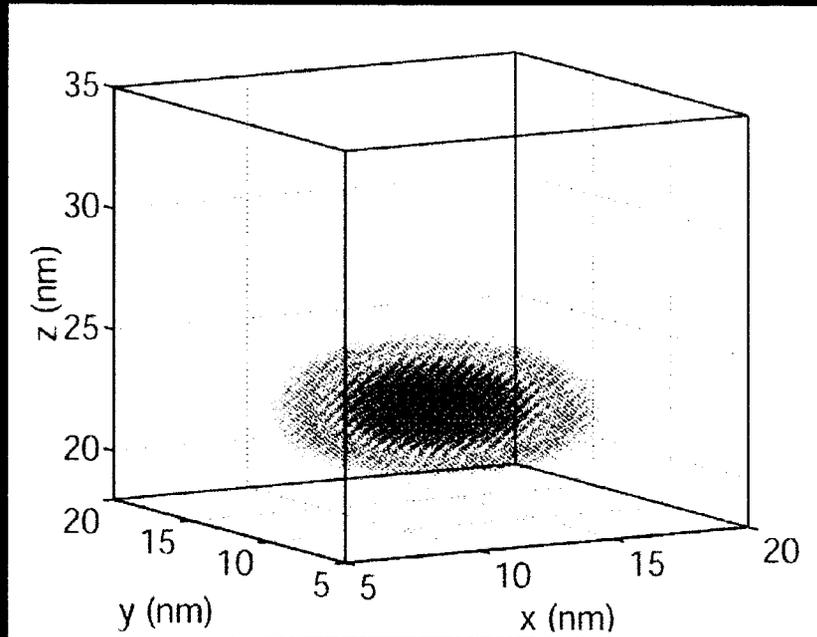
# Configuration and Concentration Noise



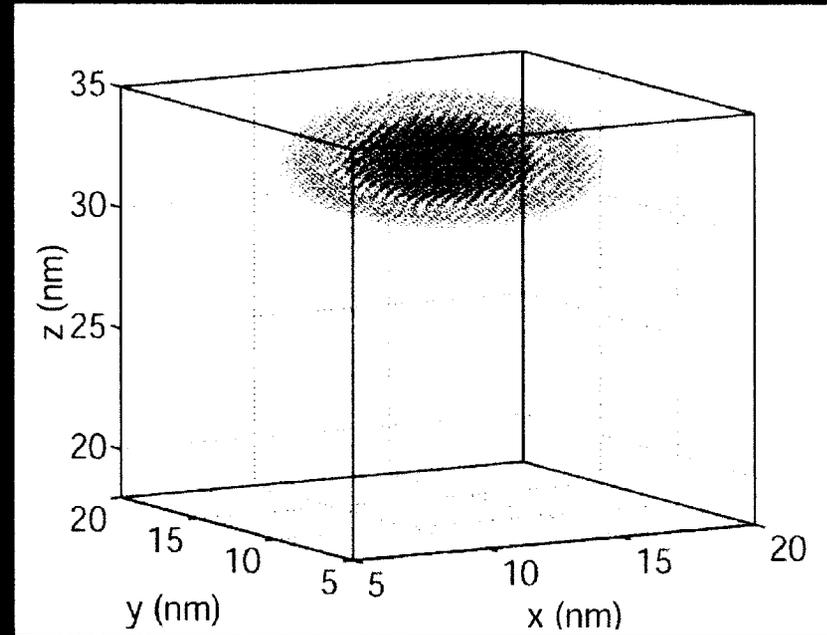
- Concentration may vary stochastically as well.
- Concentration noise is larger than configuration noise.
- For a system containing 1000 atoms, the variation is about 10-15 meV
  - Conduction band noise shows a significant feature at the  $\Gamma$ -X transition (Al~0.45)
  - Valence band dependence is much smoother.



- Cutaway of simulation domain
- Coupled InAs QDs: Diameter = 18 nm; QD separation = 5 nm



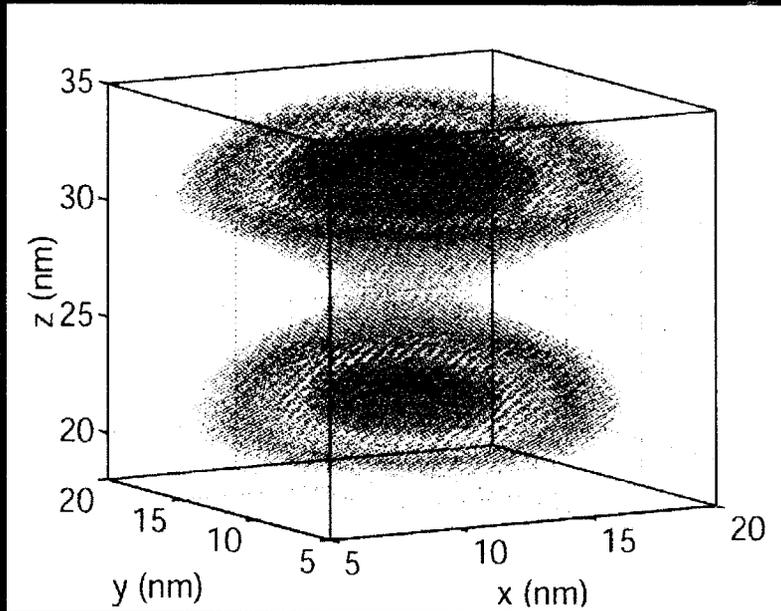
$$E = 0.828 \text{ eV}$$



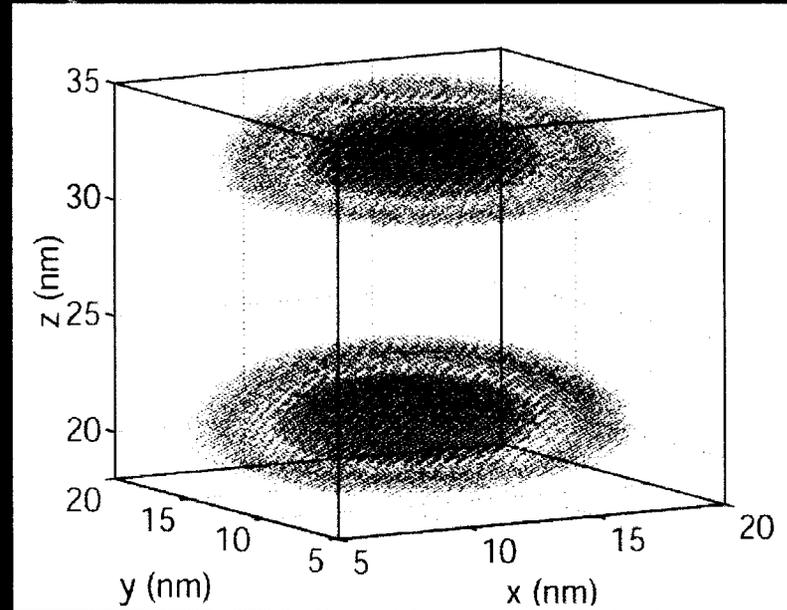
$$E = 0.835 \text{ eV}$$

### Unstrained system:

- Slight variation in the geometry of the two QDs breaks degeneracy.
- Compressive strain on the QD effectively raises  $E_c$  within QD. Without strain, potential well confining electrons is deeper and essentially decouples the two QDs.



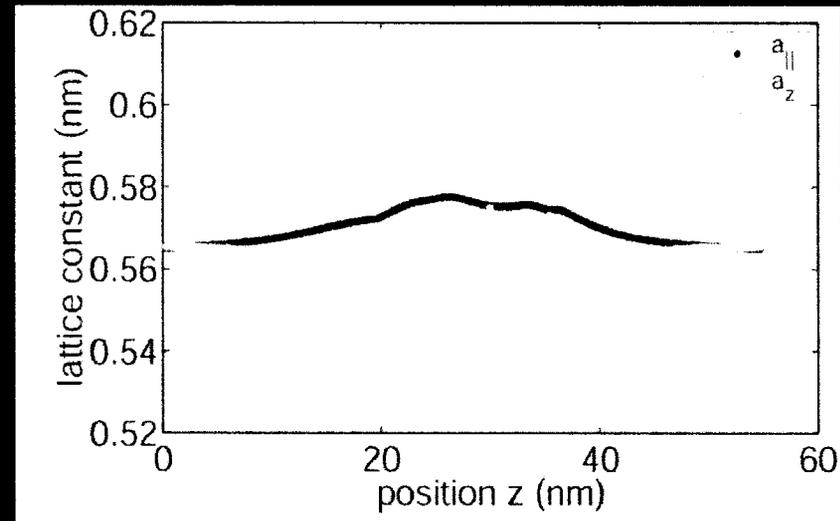
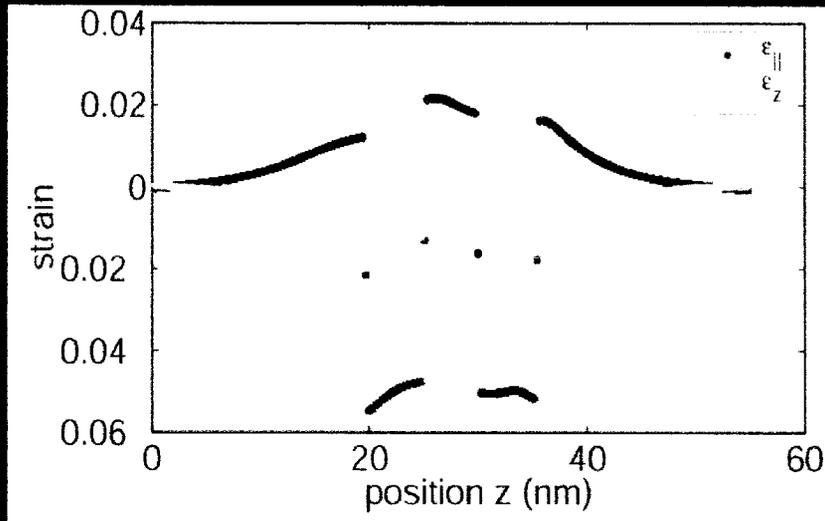
$E = 1.364 \text{ eV}$



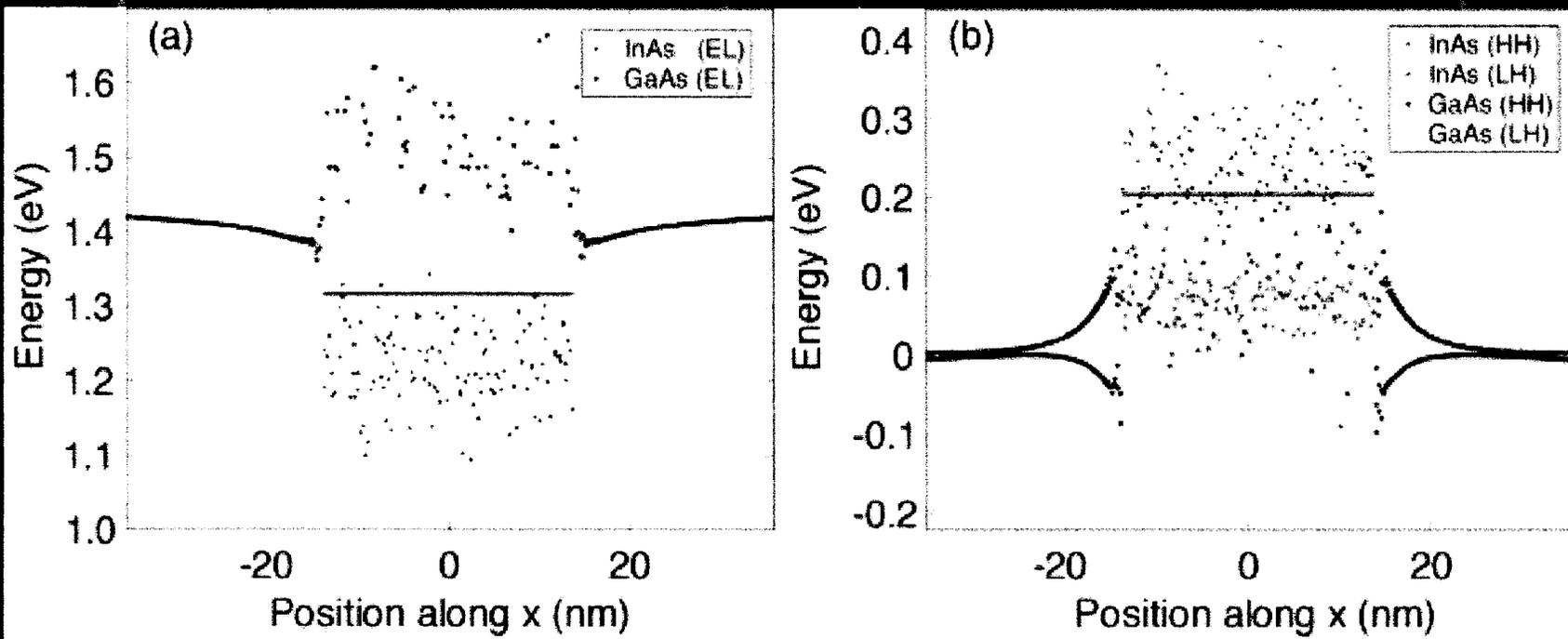
$E = 1.381 \text{ eV}$

### Strained Coupled QD:

- In absence of electron-electron interaction, ground state is bonding state; first excited state is anti-bonding state.
- Energy split (17 meV) is dependent on wave function overlap.
- Proper inclusion of strain is necessary to obtain correct eigenstates!



- Examine strain along major symmetry axis ( $z$ ) for primitive cells centered about As atoms
- Tensile bi-axial strain outside QD ( $\epsilon_{||} > 0$ ) due to stretching of GaAs to match InAs. Compressive strain in QD.
- Lattice constants follows same trends.

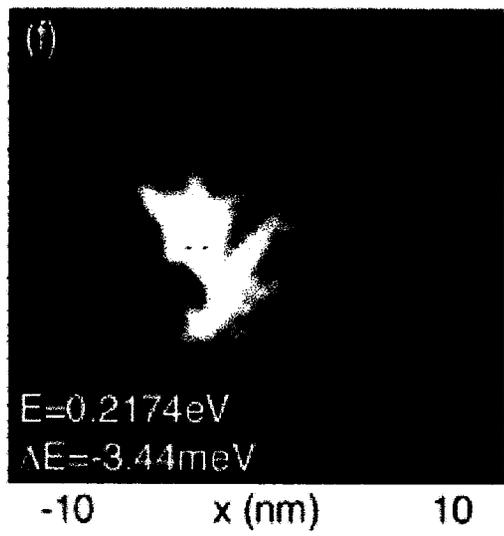
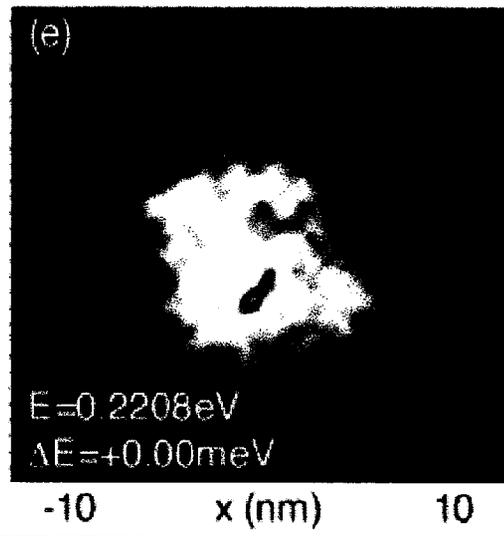
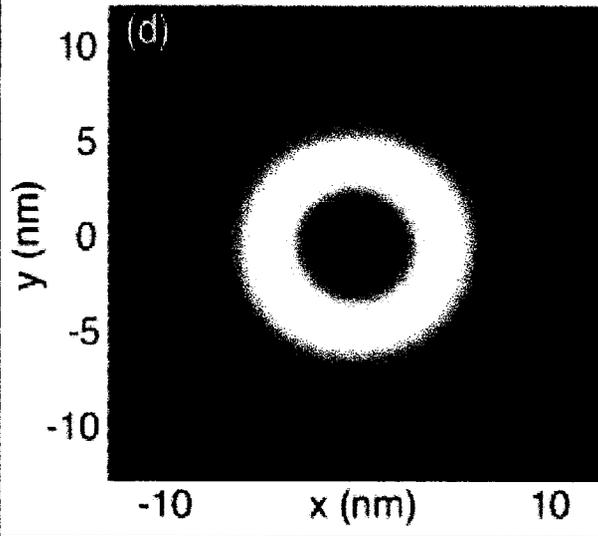
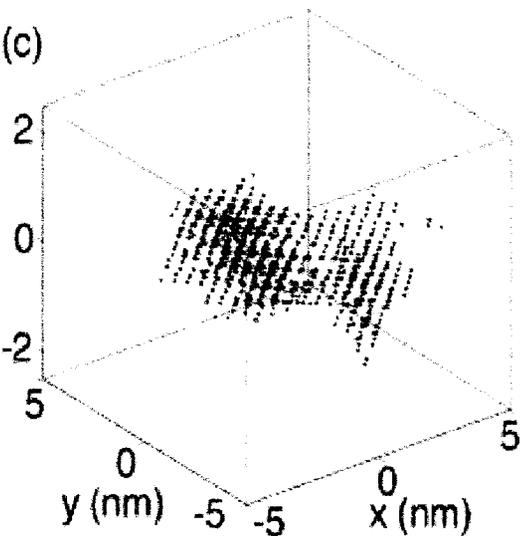
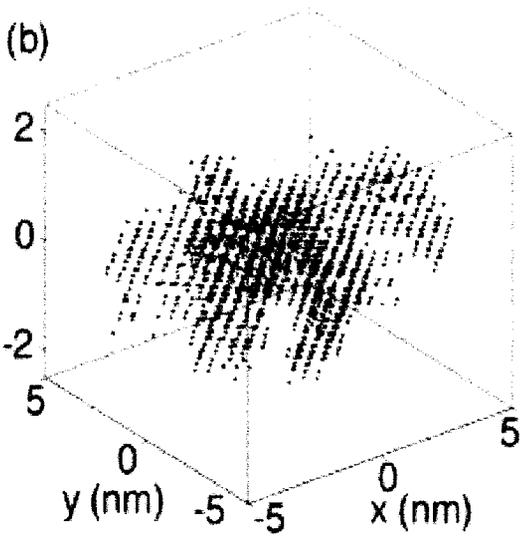
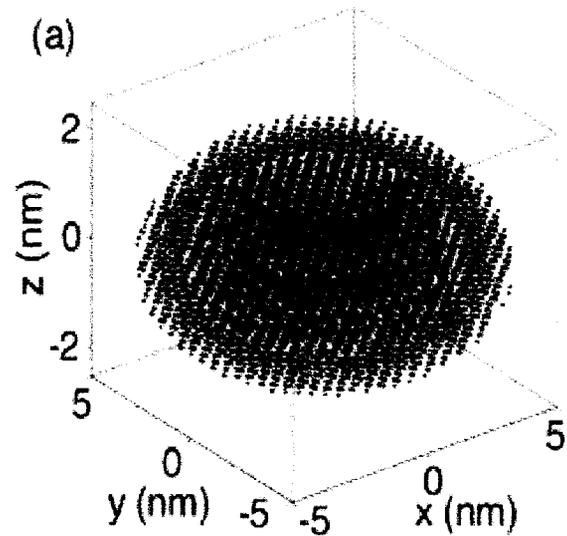


### In-As bonds compressed in x-y

- >  $E_c$  raised from bulk value of  $\sim 0.58\text{eV}$  to  $\sim 1.2\text{eV}$
- >  $E_v$  HH raised from bulk value of  $\sim 0.22\text{eV}$  to  $\sim 0.3\text{eV}$

### Ga-As bonds compressed in x-y and stretched in z inside dot

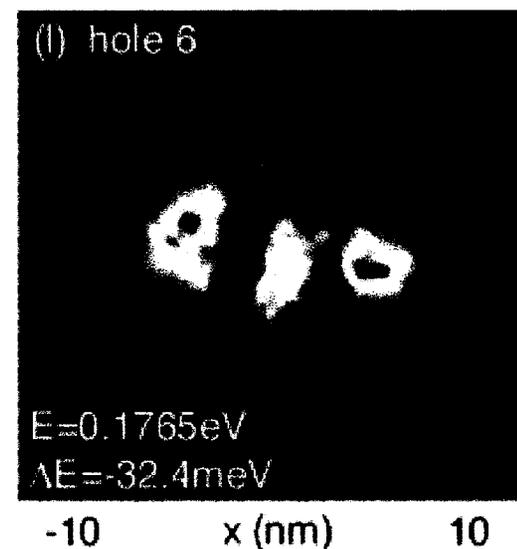
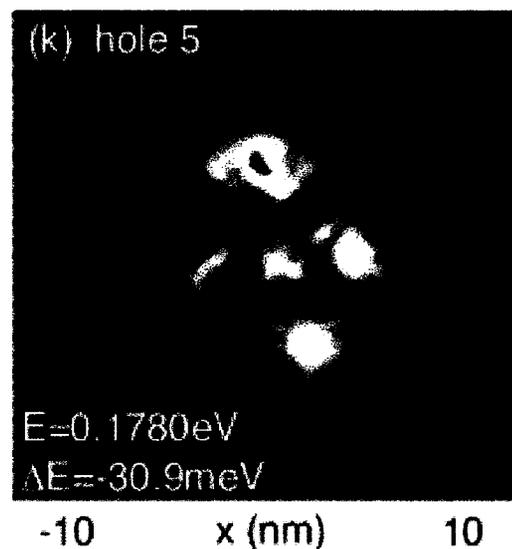
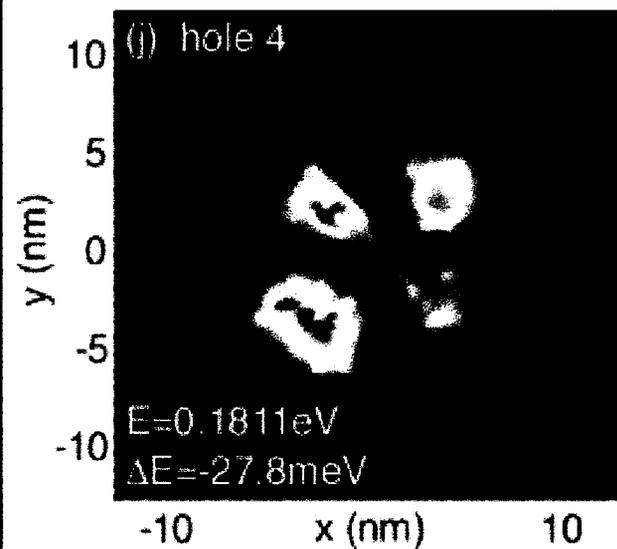
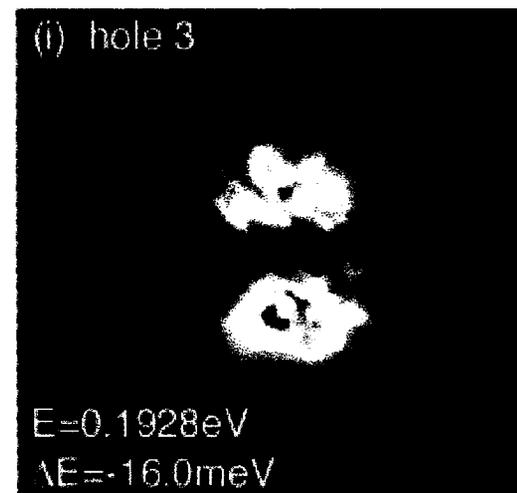
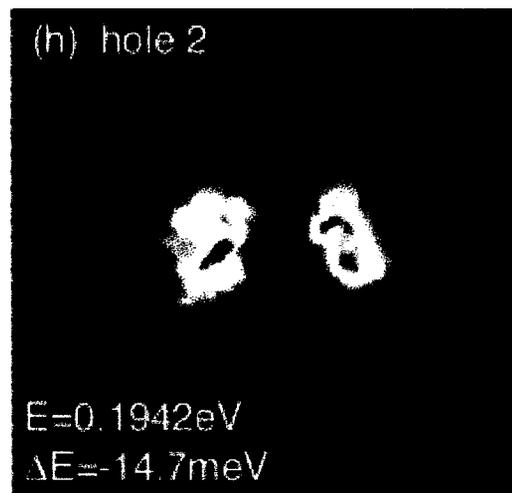
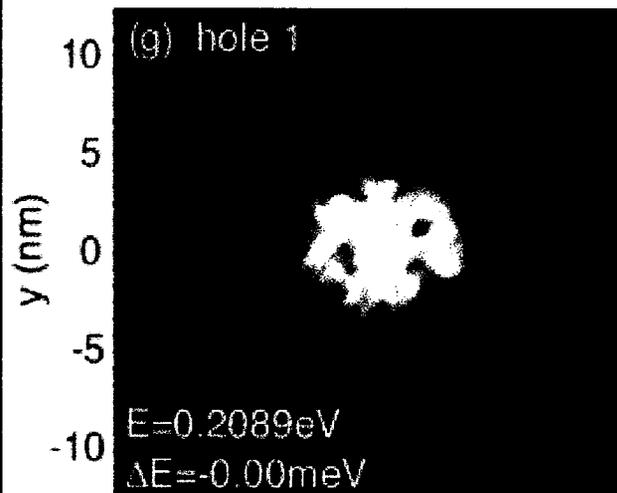
- >  $E_c$  raised from bulk value of  $\sim 1.42\text{eV}$  to  $\sim 1.55\text{eV}$
- >  $E_v$  raised from bulk value of  $0\text{eV}$  to  $\sim 0.1\text{eV}$

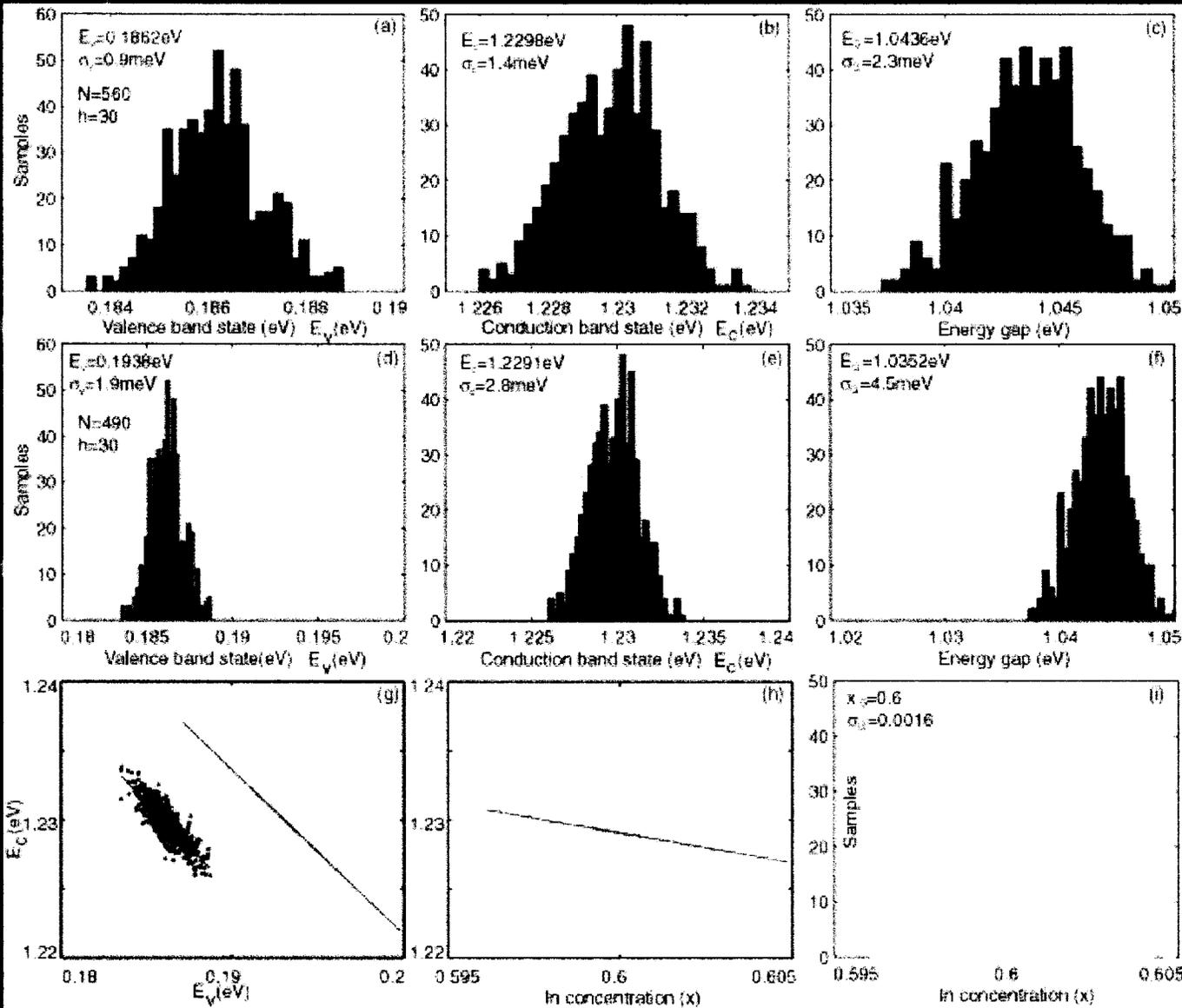


VCA / no Disorder

Disorder Sample 1

Disorder Sample 2





- Atomistic granularity  
 $\sigma = 2.3\text{meV}$

- Cell granularity  
 $\sigma = 4.5\text{meV}$

- $E_c$  and  $E_v$  strongly correlated

- $E_c$  and  $x$  weakly correlated

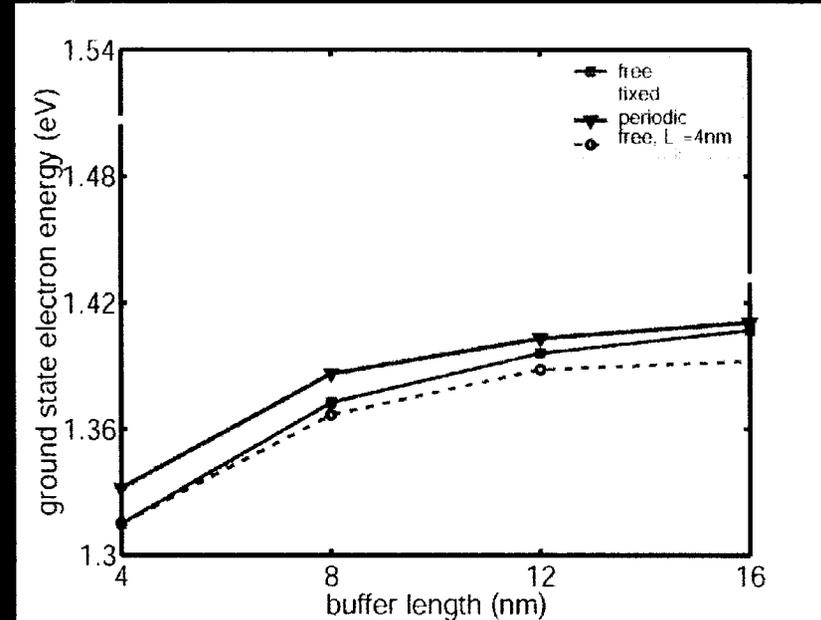
## Effect on ground state electron energy:

- System: Dome-shaped  $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}$  QD  
15nm radius; 5.4 nm height

*BC*: no constraints on QD; strain and ground state energy are underestimated

*BC*: QD boundary pinned; strain and ground state energy are overestimated

*BC* ( $k_{\text{supercell}}=0$ ): Eigenvalues lie in between free and fixed case, but results are much closer to case of free *BC*.



## Conclusions:

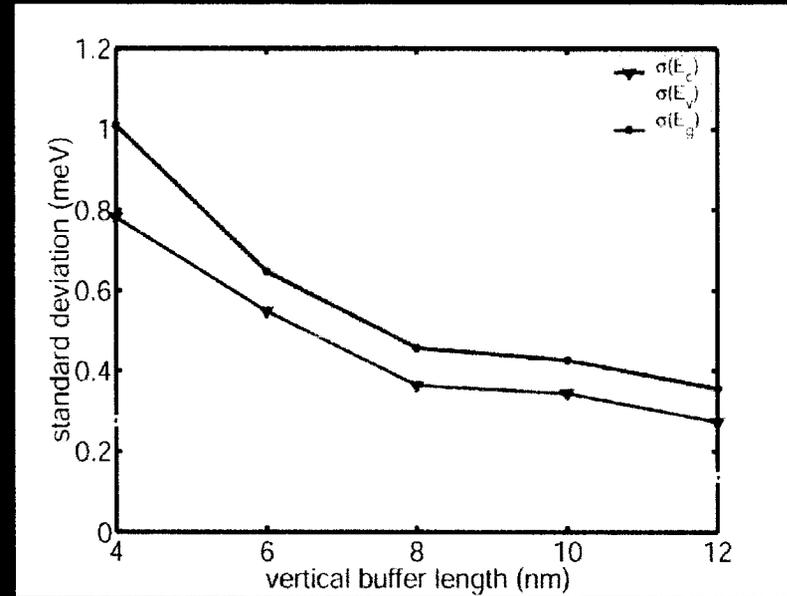
- Overall convergence is slow.
- Varying only vertical buffer size gives a good approximation.

## Question: What is the contribution of alloy disorder to linewidth broadening?

- Previous PL experimental results have found large contributions due to inhomogeneous broadening ( $\sim 30$  meV) [R. Leon et al., PRB, 60, pR8517]
- Single QD PL measurements have found narrow linewidths ( $\sim 0.9$  meV) [Nagamune, APL, 67, p3257]

### Computation:

- Use a 'direct sampling method' (roughly 100-200 samples)
- Assume no correlation between location of In, Ga cations within the QD



### Results:

- Convergence is slow but can place an upper bound of 0.35 meV, so the effect is small.
- Caveats:
  - Have not included interface interdiffusion
  - Variation is larger if there is short-range order (clustering).