

A Pilgrim's Guide to Semiconductor Energy Bands

David K. Ferry
Arizona State University



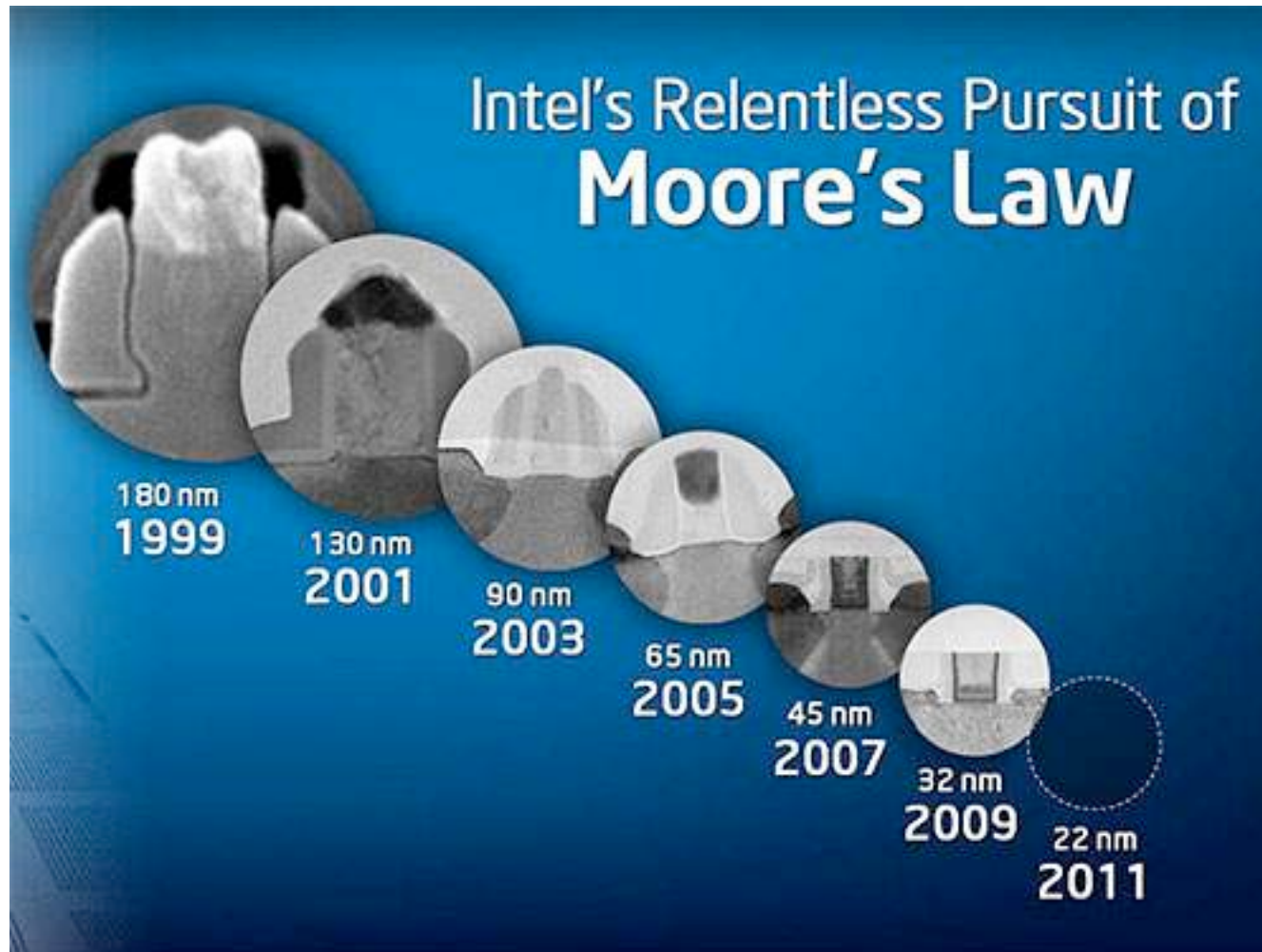
Of course, the question of the moment is:

“Why do we care about this?”

The details of the band structure have become very important to modern nano-technology, even to the semiconductor industry. It is also important in understanding transport measurements.

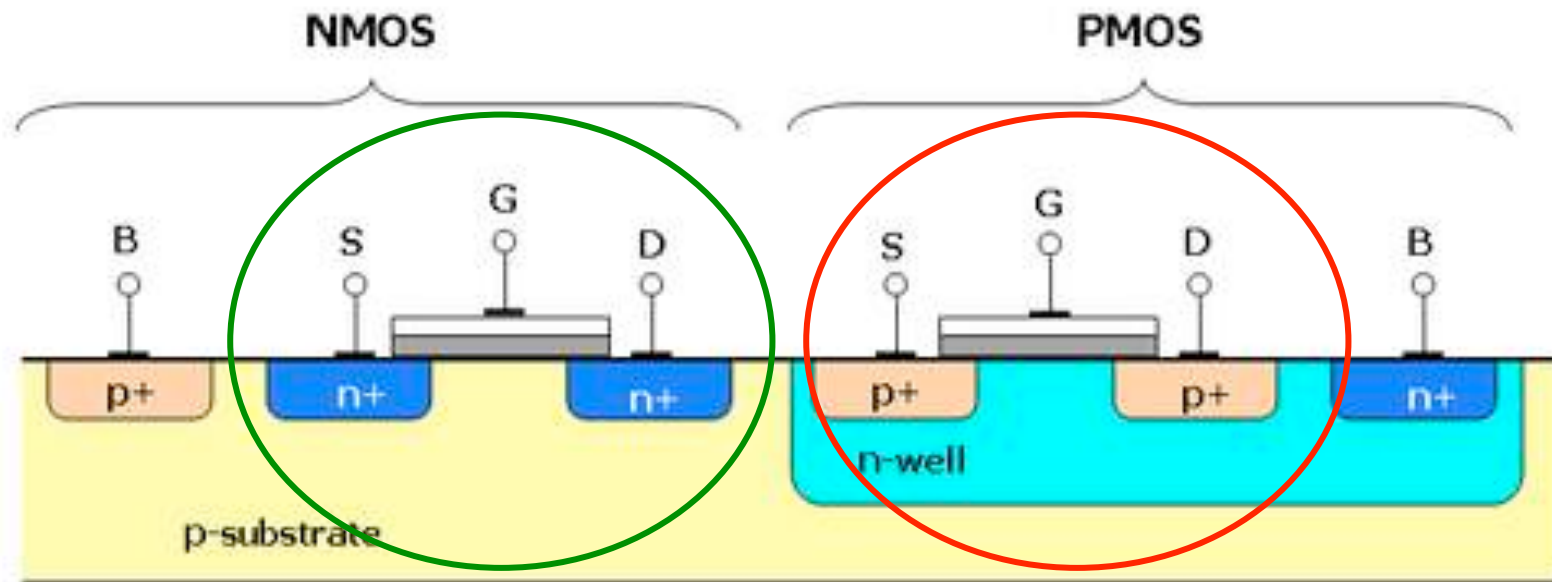


Progress in Moore's Law Depends Upon Deep Understanding of the Material Properties

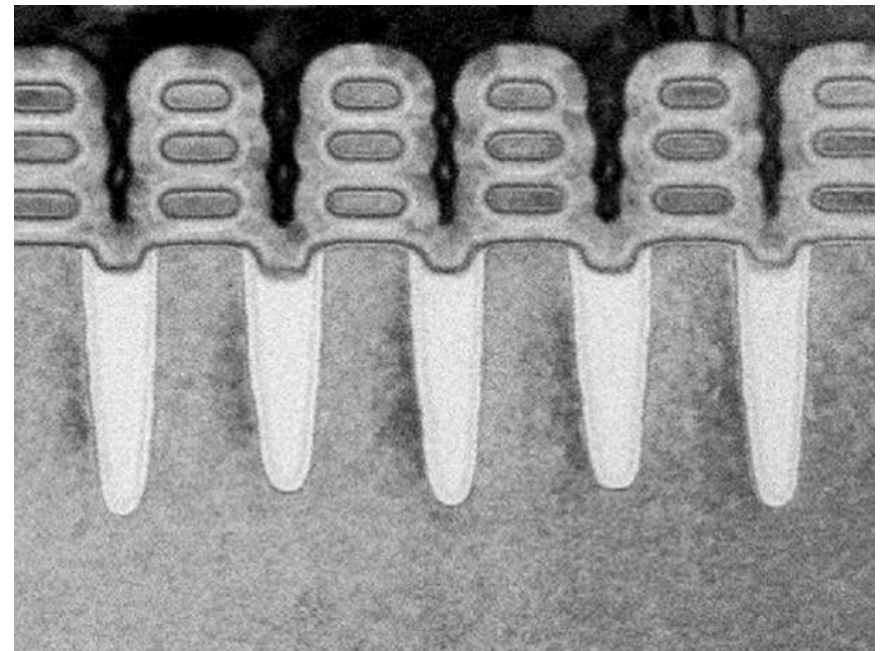
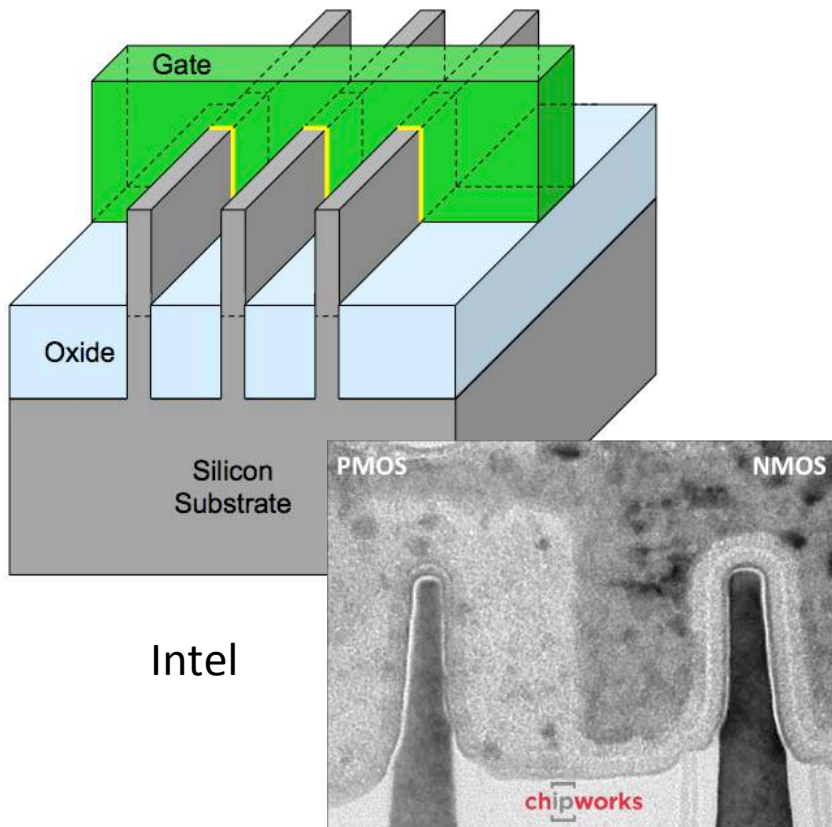


The NMOS device is *tensilely* strained to split the conduction bands and improve the mobility

The PMOS device is *compressively* strained to warp the valence bands and improve the mobility



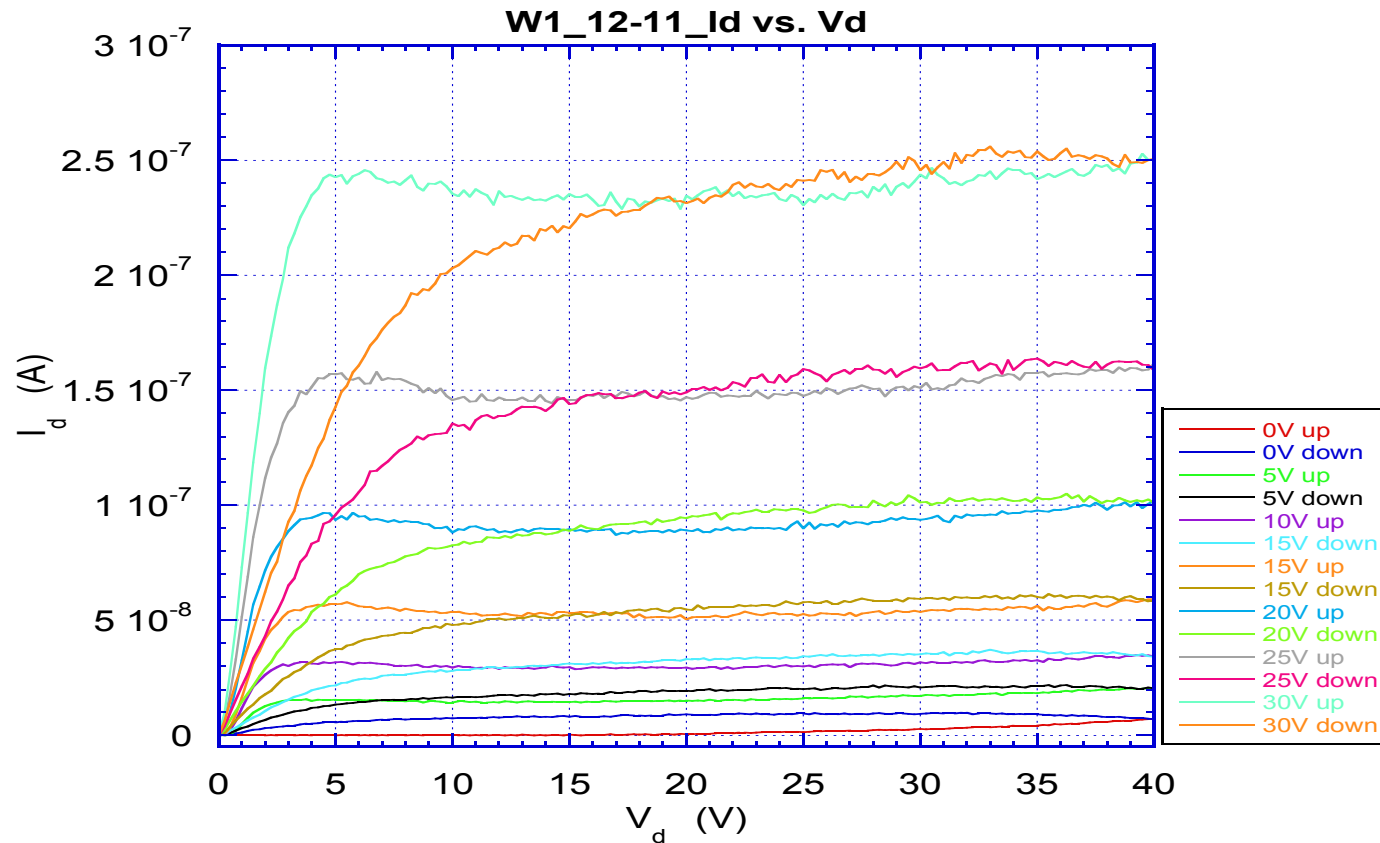
This knowledge is even more important for today's tri-gate devices (left) and the future nanowire devices (right)

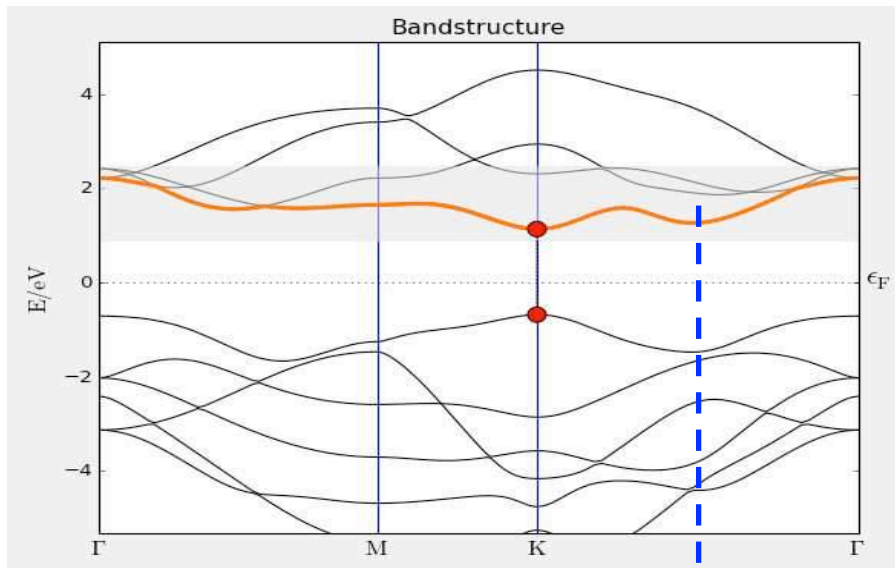


IBM

Data from Prof. Jon Bird's group (Buffalo) on WSe₂ monolayer.

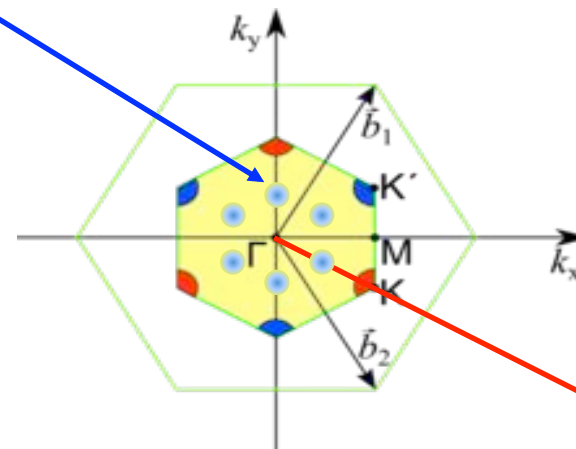
This behavior goes away if the material is annealed (heated) for a long period of time.



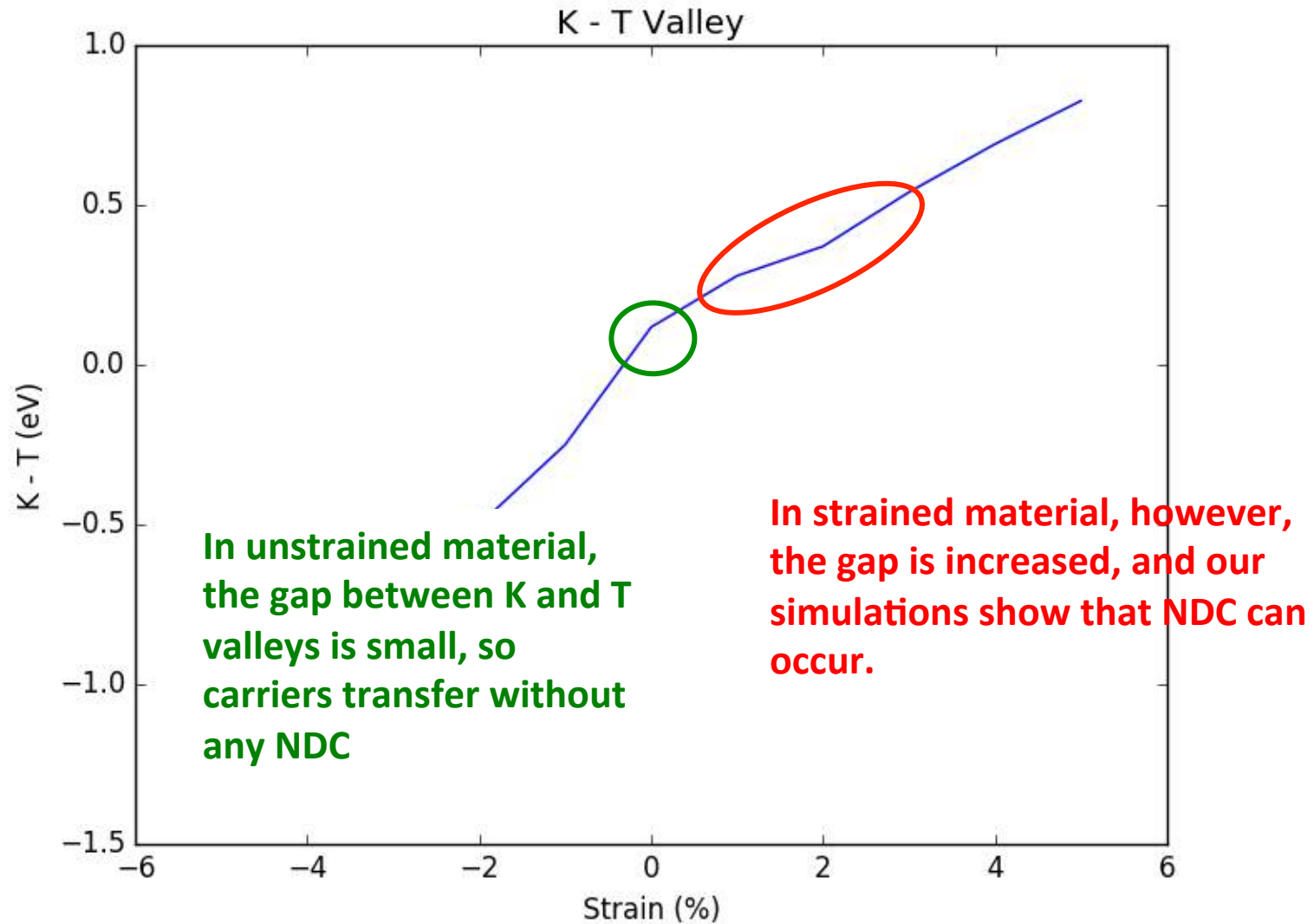


The main minimum of the CB and maximum of the VB are at K . However, there exist subsidiary minima at T in the BZ (~half way between Γ and K).

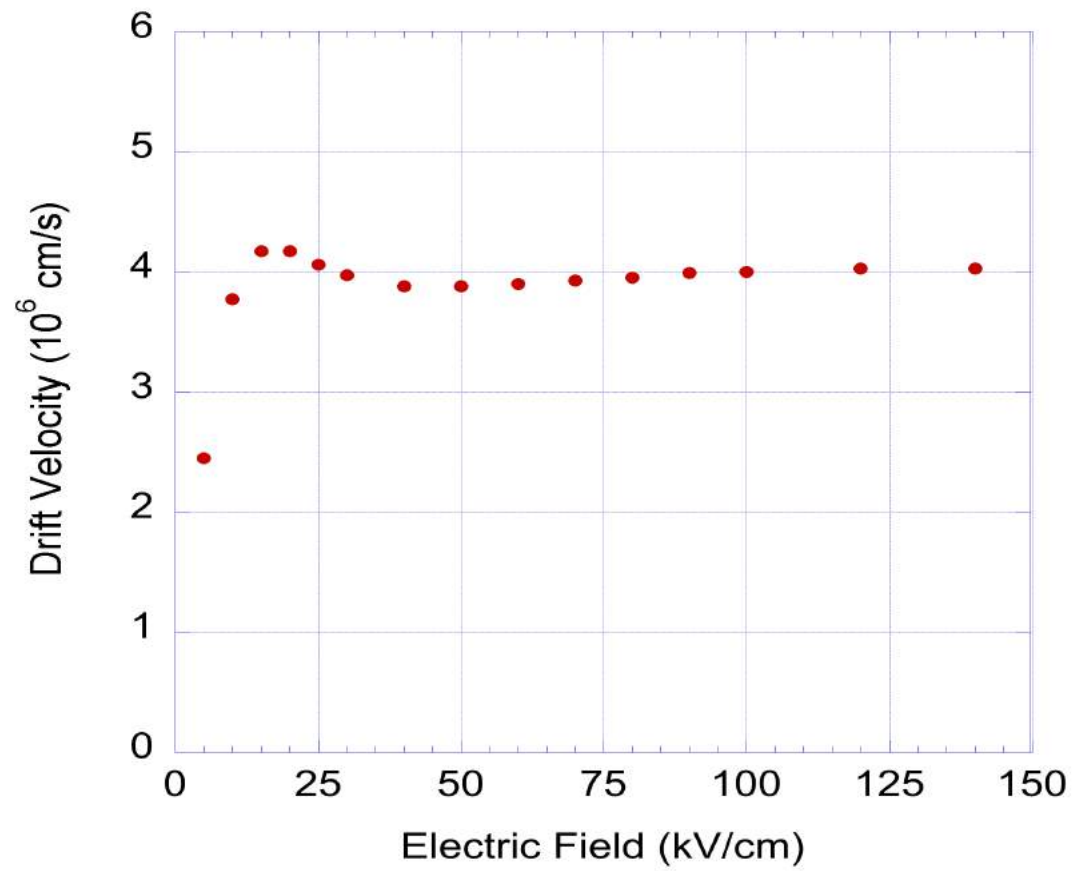
These secondary minima make the material more like GaAs.



Band structure for a monolayer of WSe₂ found from a DFT calculation.



NDC in strained WS_2 (with T-K ~ 115 meV; 1% strain)



*So, now you need to learn
about band structure! Where
do we begin?*



Discover how easy it is to
grasp the basics of band theory

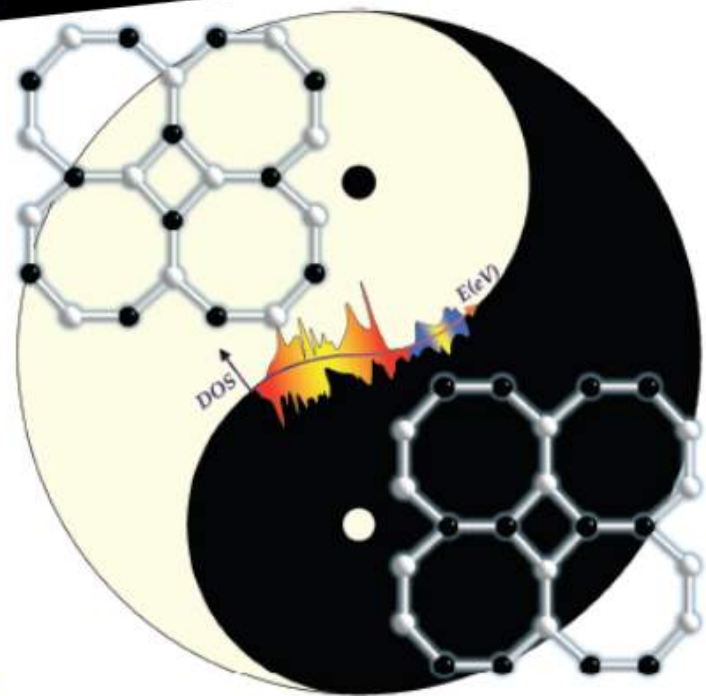
Band Theory FOR DUMMIES

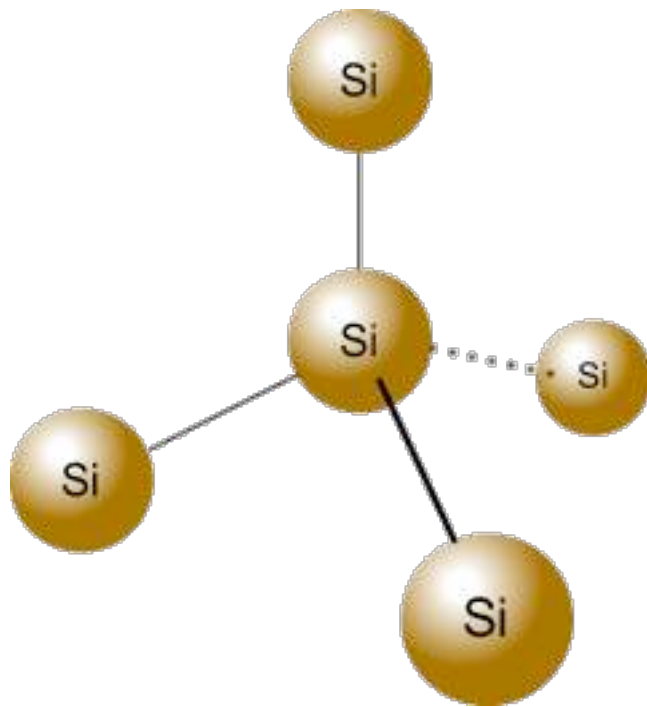
Jean-François Halet and Jean-Yves Saillard

Institut des Sciences Chimiques de Rennes

CNRS - Université de Rennes 1

E-mail: halet@univ-rennes1.fr, saillard@univ-rennes1.fr





Si, and most semiconductors, are covalently bonded with their 4 valence electrons.

The outer electrons are 1 *s* state and 3 *p* states, which form *hybrids*.

The hybrids form a tetrahedral, which is due to the repulsion between the hybrids.

Naturally, there are two 'Gods' of band theory:



Walter Kohn



John C. Slater



John Slater went to Cambridge and Copenhagen after finishing his Ph.D. He remarked about Bohr's

“...hand-waving approach to anything. I had supposed, when I went to Copenhagen, that although Bohr's papers looked like hand-waving, they were just covering up all the mathematics and careful thought that had gone on underneath. The thing I convinced myself of after a month, was that there was nothing underneath. It was all just hand waving.”

He returned to Harvard, then took over MIT's physics department. In the subsequent decades, he wrote the *Bible*: 5 books on quantum theory of atoms, molecules, and solids.



Walter Kohn came later. But, it was he who received the Nobel prize in 1998 for developing modern density functional theory.

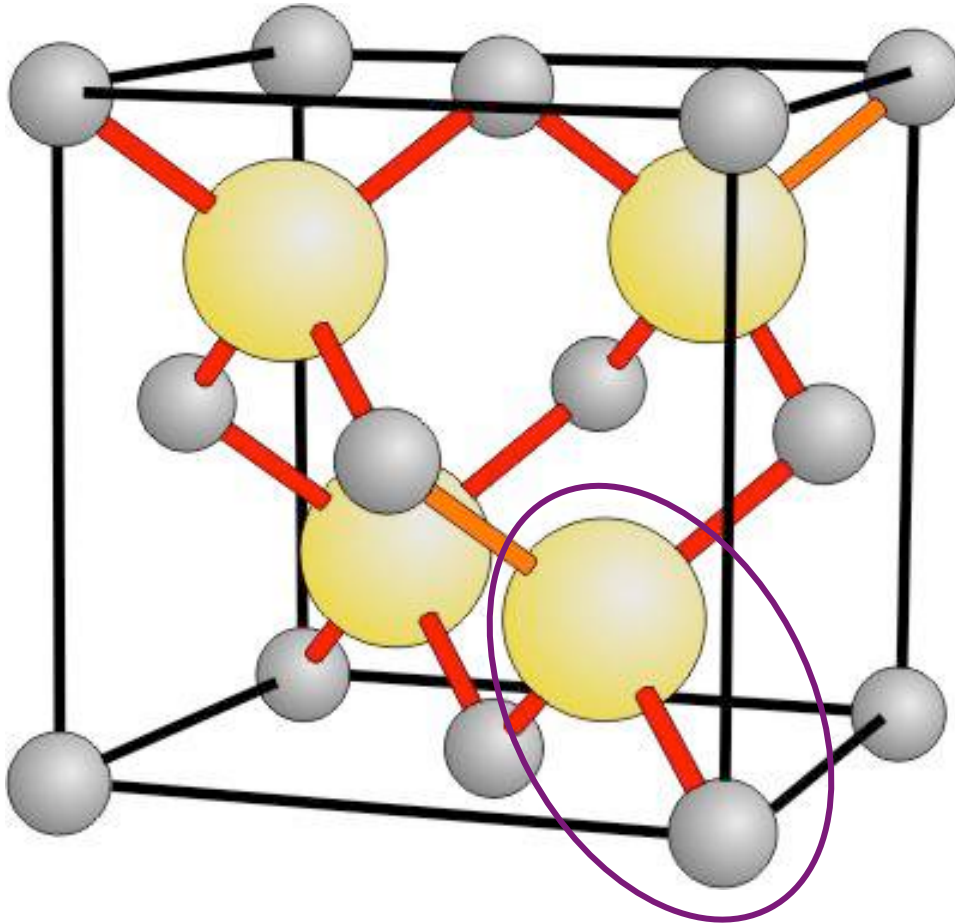
An Austrian, he left in 1938 for England, then Canada, and finally the US. Associated with Bell Labs as well as his university appointments, he delved heavily into condensed matter physics, and computational approaches to the theories of electronic structure.

Kohn is responsible for DFT. He (and Hohenberg) showed that the many-body interactions could be represented by a linear response functional of the local density (hence the D in DFT).

We will find that this is a mean-field theory and needs some corrections.



To do band structure, we really need two things: We need to know the atoms, and we need to know the crystal structure.



Nearly all tetrahedrally coordinated semiconductors have the face-centered cubic cell (which actually includes eight unit cells).

There are two atoms per unit cell in this structure.

These two atoms define the “structure factor.”

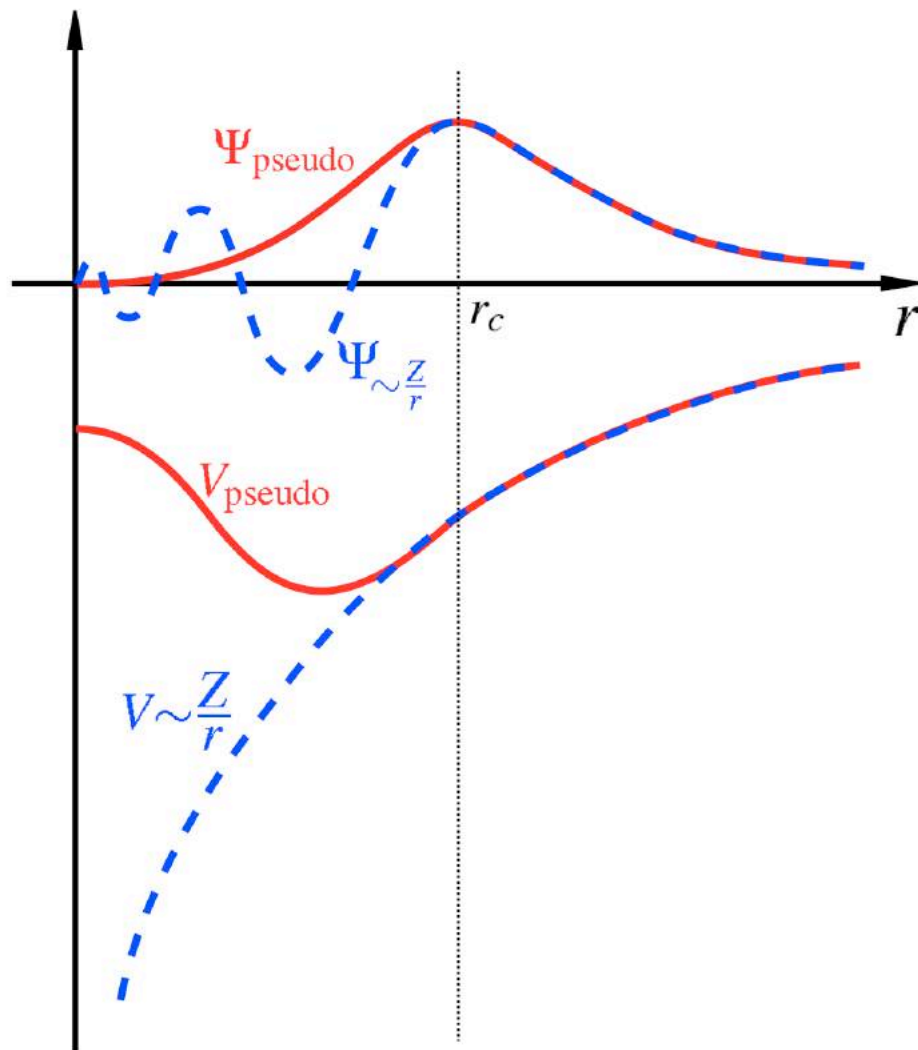
To do band structure, we really want to ignore the core electrons of the inner shells of the atoms---e.g., deal only with the bonding valence electrons. To do this, we use pseudo-potentials.

$$W(r) = V(r) + \sum_{t,j} (E - E_{t,j}) |t,j\rangle \langle t,j|.$$

Pseudo-potential

real atomic-potential

Core energies and wave functions
which are taken out of the real
potential.



This produces a smoothed potential and wave function which is far easier to handle, as we can avoid rapid oscillations and divergences (both of which multiply computing time).

To this, we add an exchange-correlation potential, which is a functional of the density; for example the Dirac exchange and Perdew-Zunger correlation:

$$V_{XC}(\rho) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \rho^{1/3} + \frac{\gamma}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s}, \quad r_s > 1$$

$$r_s = \left(\frac{3}{4\pi\rho} \right)^{1/3}$$

Density Functional Theory

In density functional theory, we are going to solve for the shape of the pseudo-potential and the pseudo-wave functions self consistently. That is, we alternate between the potential, which gives the wave functions through Schrödinger's equation, which then give the charge density, which then defines the new potential through Poisson's equation.

There are two approaches to this: (1) real space, and (2) momentum space. In each case, we have to make some approximation to the exchange and correlation energies for the electrons.

Density Functional Theory

Real space approaches

Atomic wave functions
Pseudo-potential in real space

SIESTA, FIREBALL

Density Functional Theory

Real space approaches

Atomic wave functions
Pseudo-potential in real space

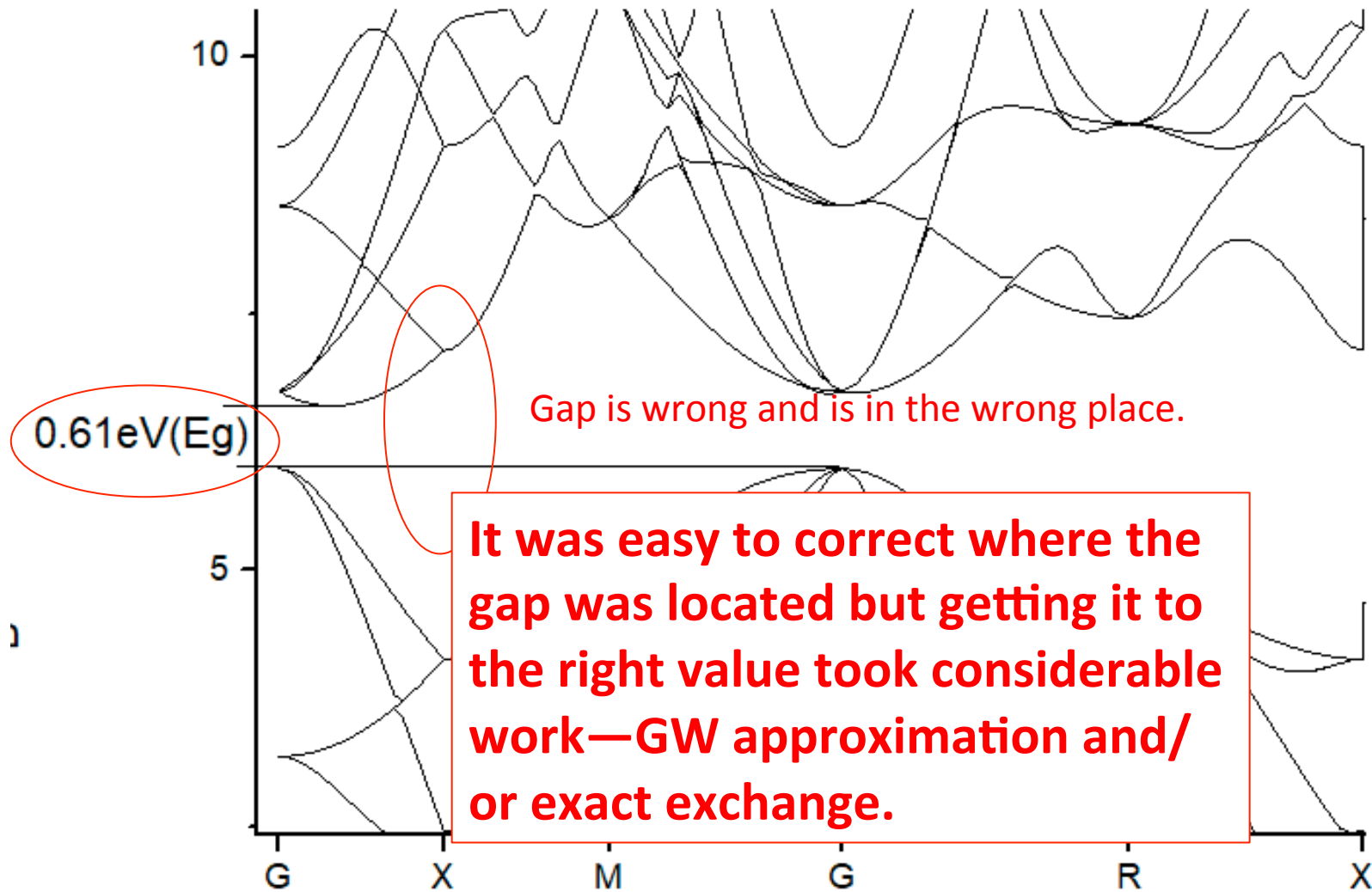
SIESTA, FIREBALLS

Momentum space approaches

Plane waves defined by the
reciprocal lattice vectors
Fourier transform of pseudo-
potential

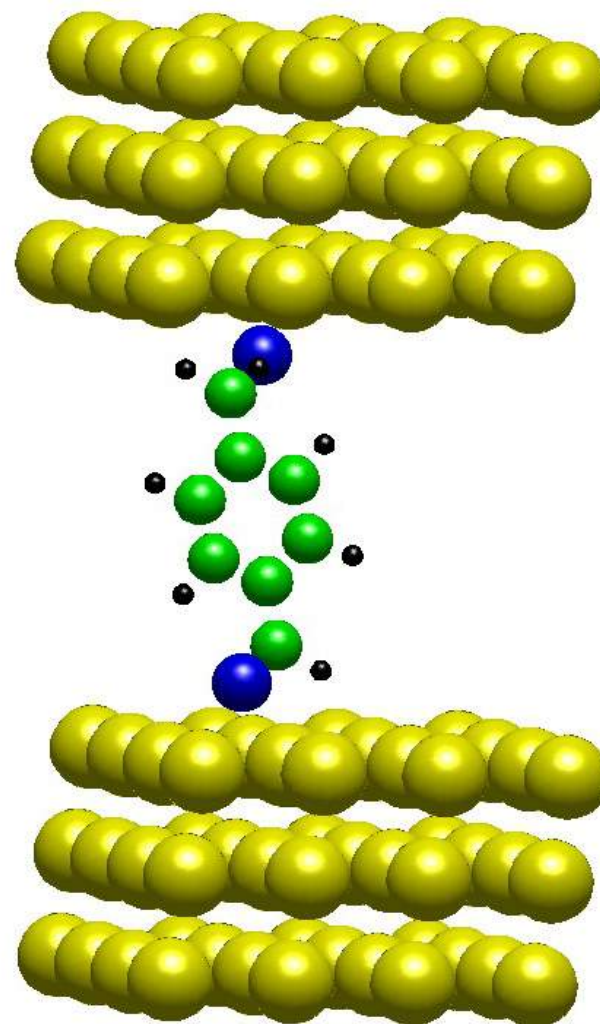
VASP, QUANTUM ESPRESSO

Unfortunately, DFT doesn't work very well for most semiconductors. This one is silicon.

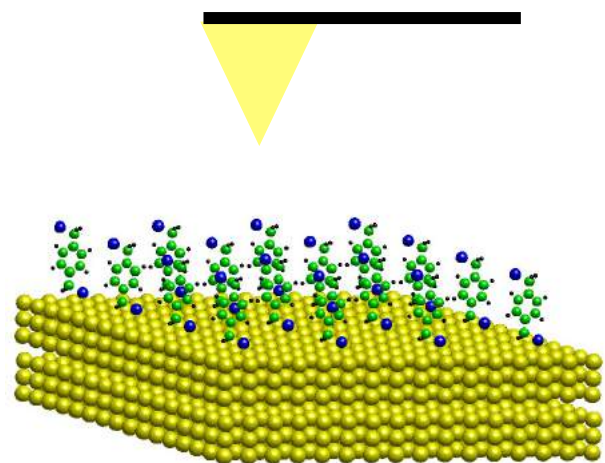


Theoretical Methods – Energy Spectrum

- DFT underestimates excitation energies for π -conjugated systems.
- Further underestimation in systems where considerable charge transfer occurs.
- Electron correlations in bond dissociation calculations inadequate.
- In general, Hartree-Fock calculations better for inter-atomic bond distances.

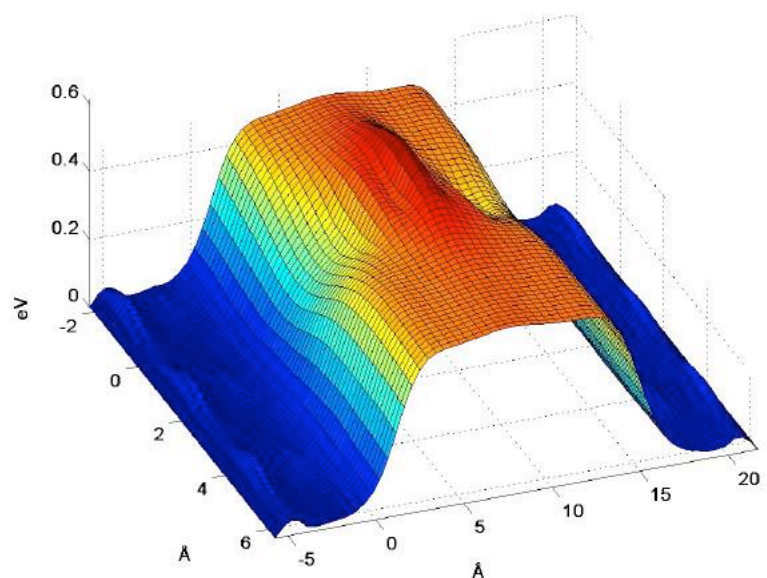


Background — Experimental Results



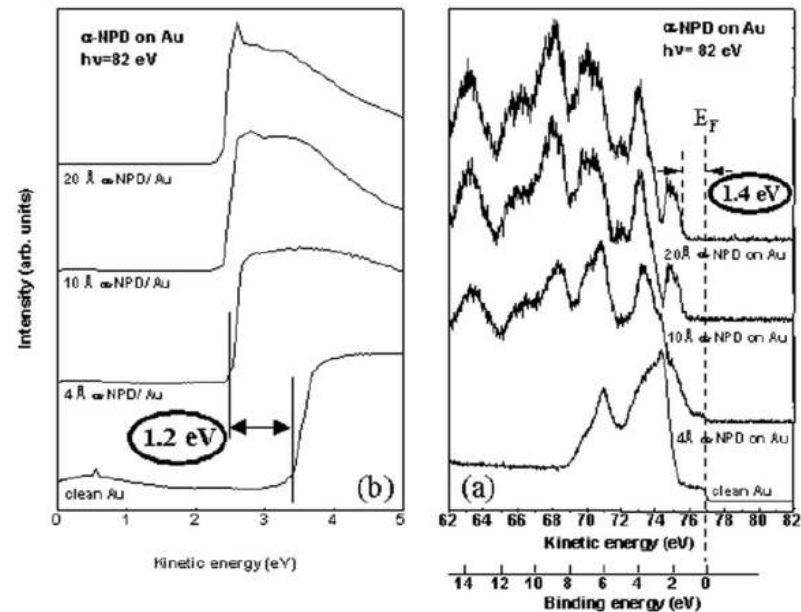
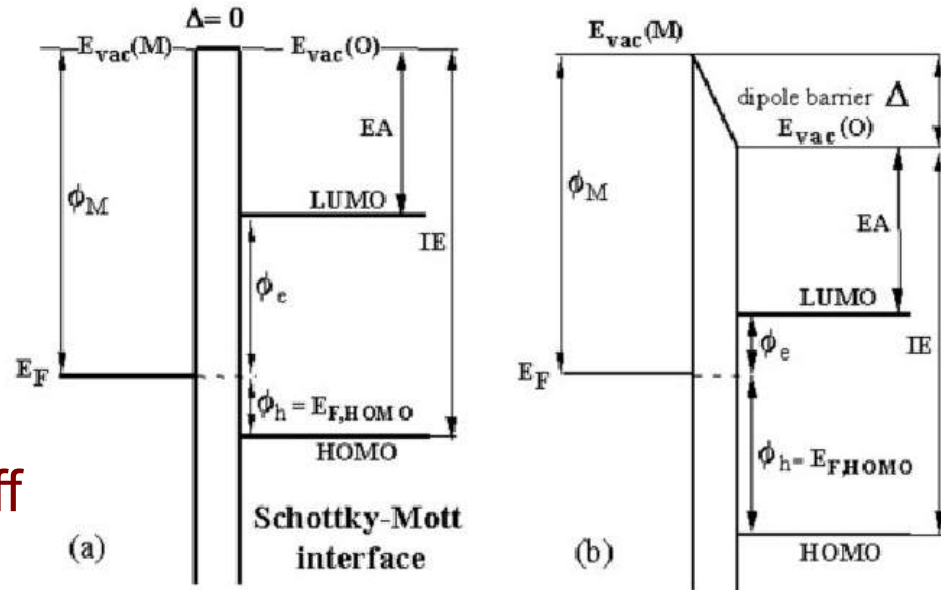
- AFM tip lowered onto SAM on Au substrate forming nanowire. Stretch begins.
- Photodiode measures deflection of cantilever arm (force). Conductance measured simultaneously.
- Over many repetitions, method can be used to isolate conductance of individual molecules.

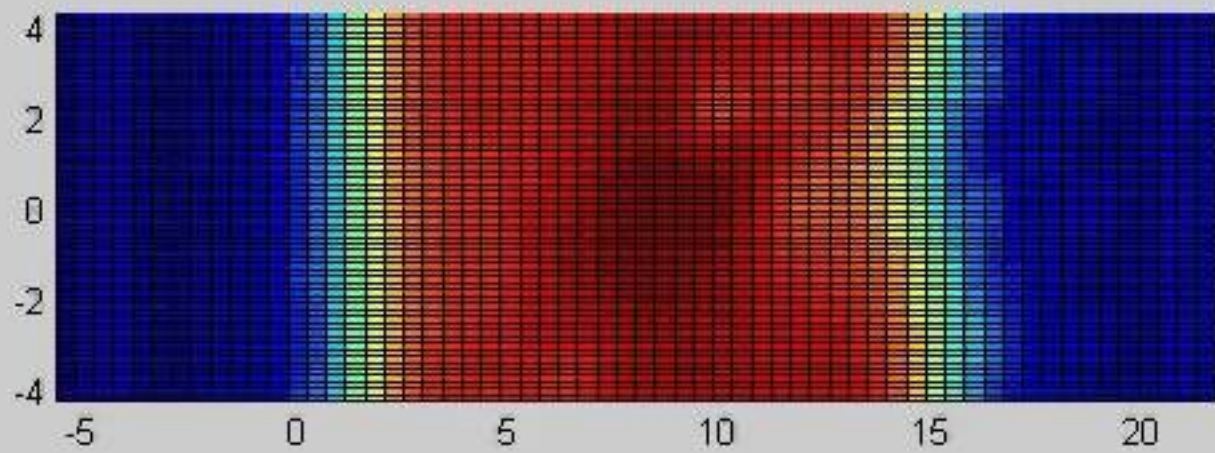
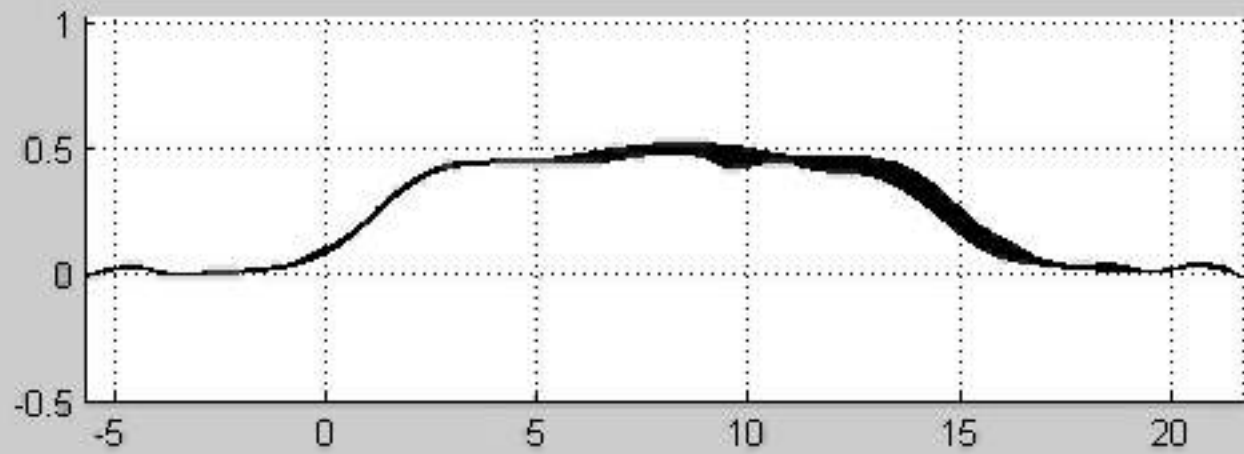
- Data gathered from point of contact (Au wire) through molecular bridge until wire breaks.
- Fluctuations at each plateau reveal interesting conductance behavior of stretched molecule.



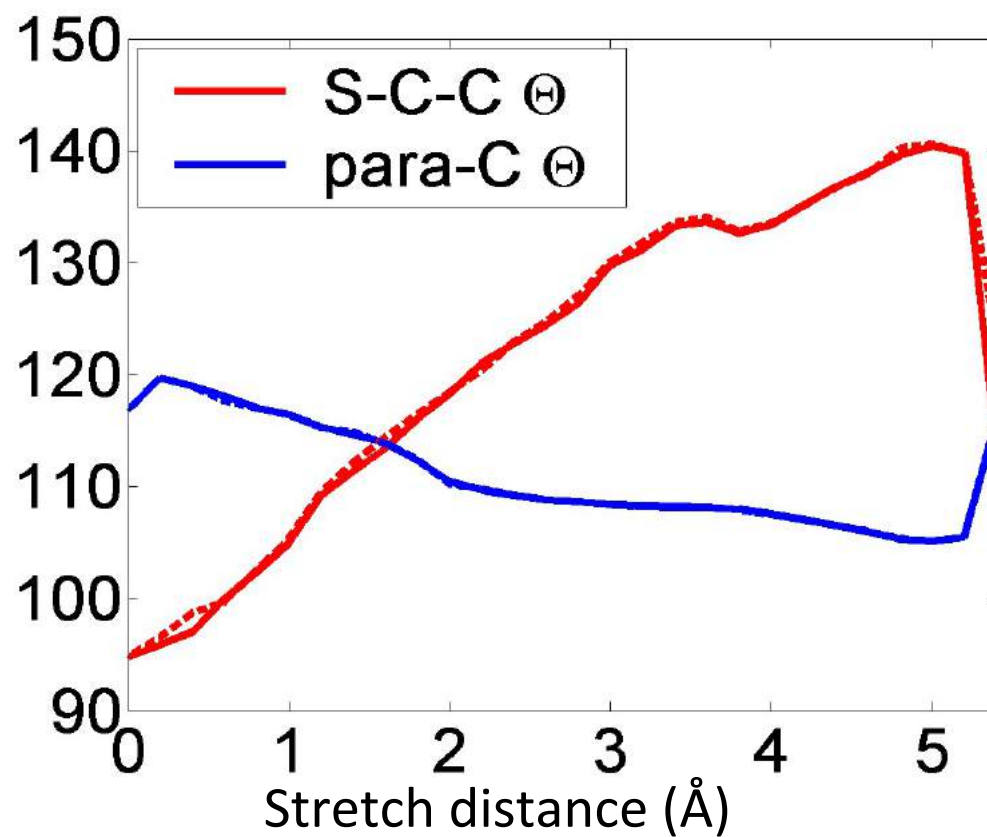
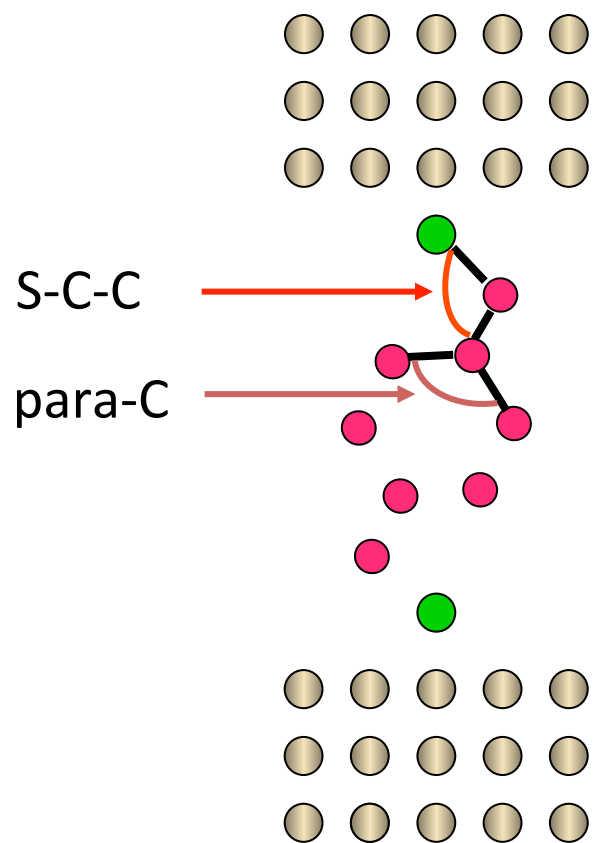
Organic- Metal Interface

- Schottky-Mott interface model doesn't work
- Charge transfer across interface causes vacuum level shift, Δ .
- UPS used to determine shift – photoemission cutoff gives Δ .
- Measure K.E.'s closer to photon energy to get Fermi energy and HOMO, LUMO levels to get ϕ_h .
- Extent of charge transfer vs. effect on metal surface dipole.

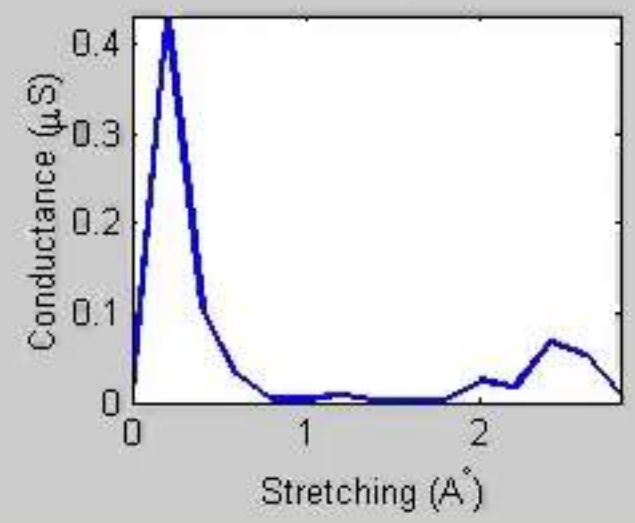
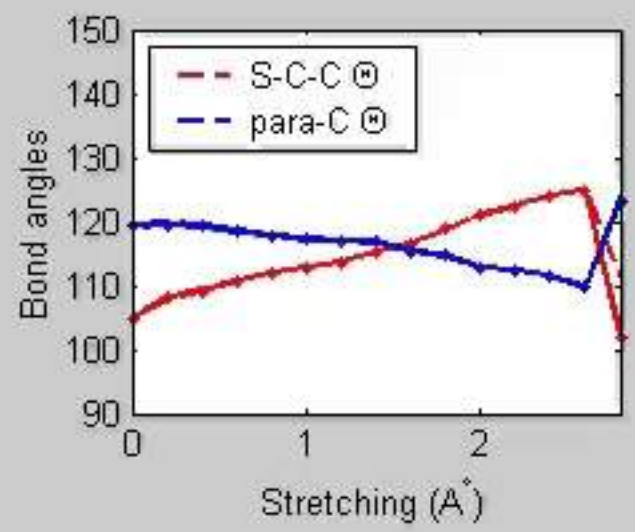
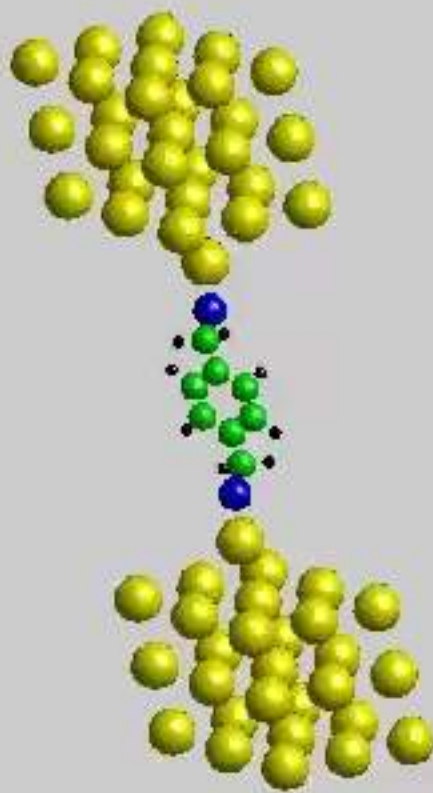




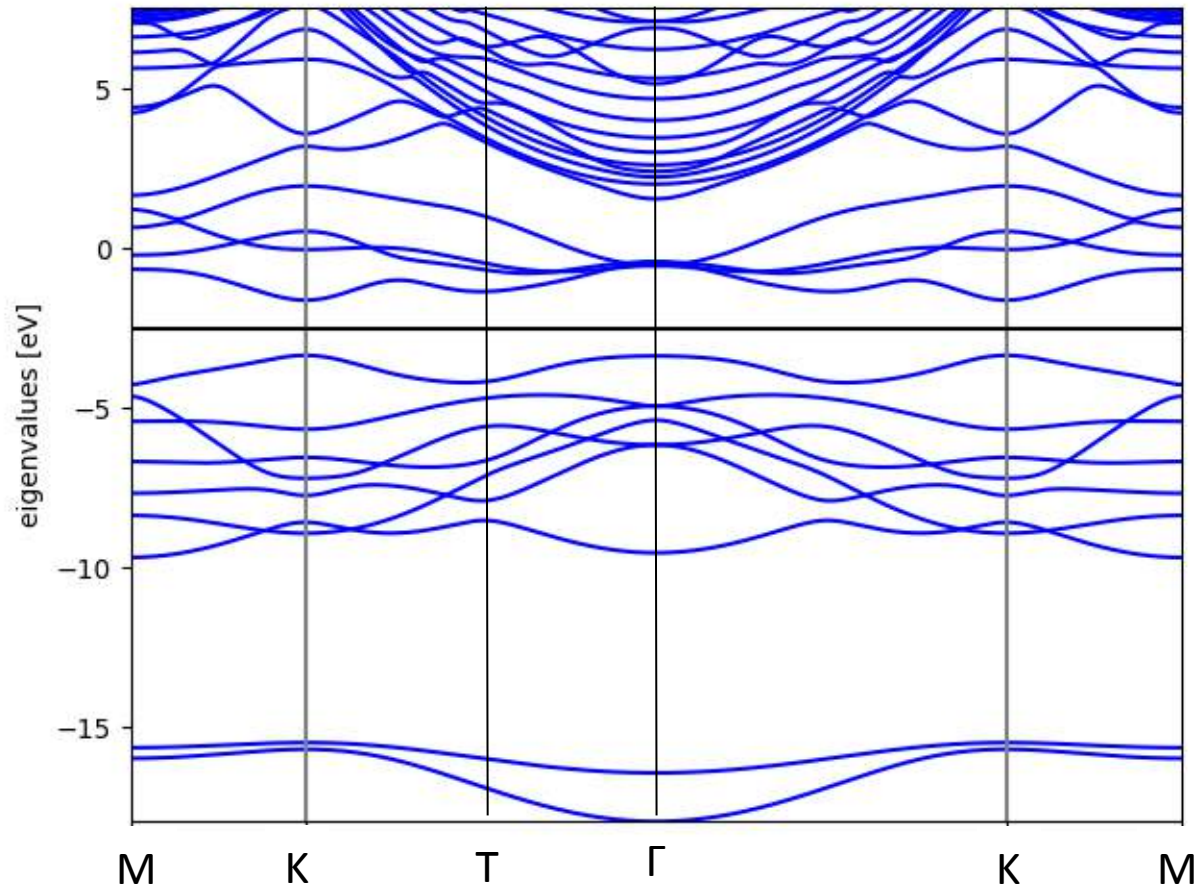
Analysis of distortion of the molecule



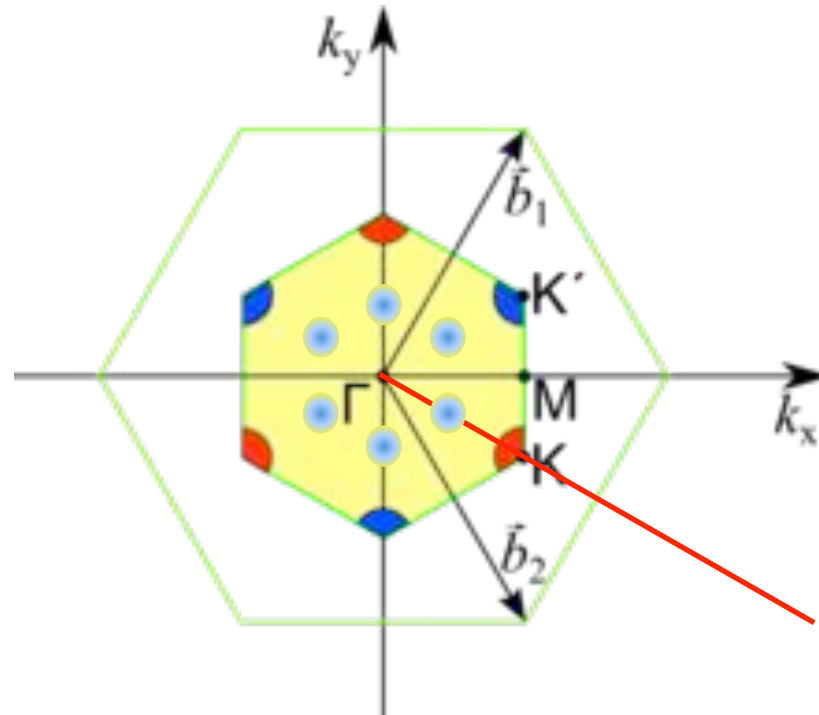
- Contacts separated gradually at each simulation step, allowing nuclei to relax in new position for new Hamiltonian calculation
- Sulfur-pivot carbon-paracarbon angle (S-C-C), ortho-para-orthocarbon angle (para-C) tracked. Gold atoms kept static.



Example of DFT band structure for MoS₂, a transition metal dichalcogenide monolayer

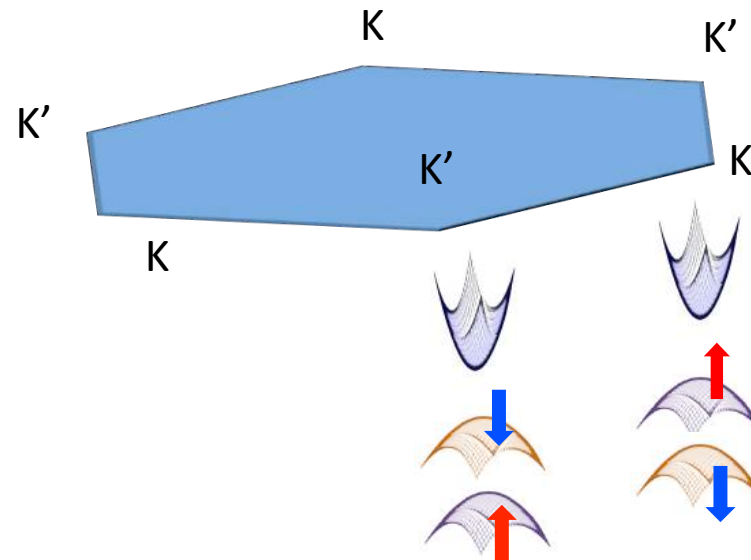


These materials also have the hexagonal form of the Brillouin zone, with minima at the K, K' points.



These are the T valleys of the conduction band. These are the lowest CB valley in bulk, and down to about 2 layers. In the monolayer, the K, K' valleys are the lowest.

One interesting aspect of the TMDCs is the fact that the spin-orbit interaction is oppositely directed in the two valleys of the conduction or valence bands. This gives interesting spin-valley coupling and can produce an effect like the spin Hall effect.



Density Functional Theory

So, we find that DFT is *first principles* band theory.

But, it is very compute intensive, taking perhaps days to reach convergence, the choice for the exchange and correlation potential is varied and using one is hard. Even then the results *may not match what we know from experiment*.



Density Functional Theory

So, we find that DFT is *first principles* band theory.

But, it is very compute intensive, taking perhaps days to reach convergence, the choice for the exchange and correlation potential is varied and using one is hard. Even then the results *may not match what we know from experiment.*

Wait, I am a practical person (engineer) and I just want to know the shape of the bands. After all, the gaps should match what has been measured for years...



Density Functional Theory

Empirical Methods

Real space approaches

Atomic wave functions
Pseudo-potential in real space

SIESTA, FIREBALLS

Momentum space approaches

Plane waves defined by the
reciprocal lattice vectors
Fourier transform of pseudo-
potential

VASP, QUANTUM ESPRESSO

Empirical Methods

Empirical means forget all that first principles stuff; we are going to use experimental data (data always has all the exchange, correlation, and many-body stuff included, even if I don't recognize it).

We now adjust the values of wave function overlap integrals between adjacent atoms (real space) or the Fourier coefficients of the pseudo-potential (momentum space) to fit the observed energies for the band structure.



Density Functional Theory

Empirical Methods

Real space approaches

Atomic wave functions
Pseudo-potential in real space

Semi-empirical tight binding
(Slater-Koster)

SIESTA, FIREBALLS

NEMO 1,2,3, OMEN

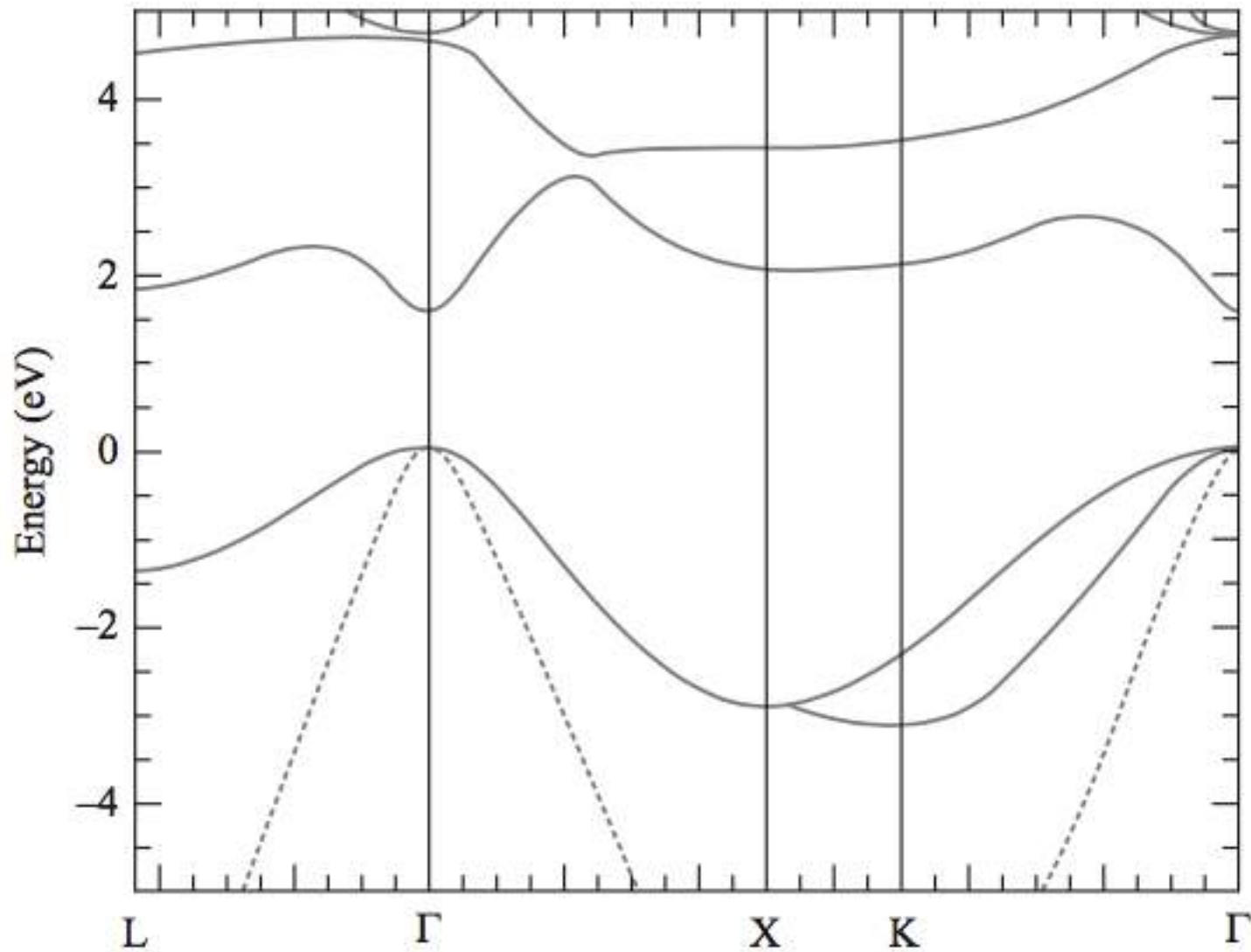
Momentum space approaches

Plane waves defined by the
reciprocal lattice vectors
Fourier transform of pseudo-
potential

VASP, QUANTUM ESPRESSO



Band structure of GaAs using sp^3s^* orbitals, without spin-orbit coupling, via the SETBM method



Density Functional Theory

Empirical Methods

Real space approaches

Atomic wave functions
Pseudo-potential in real space

Semi-empirical tight binding
(Slater-Koster)

SIESTA, FIREBALLS

NEMO 1,2,3, OMEN

Momentum space approaches

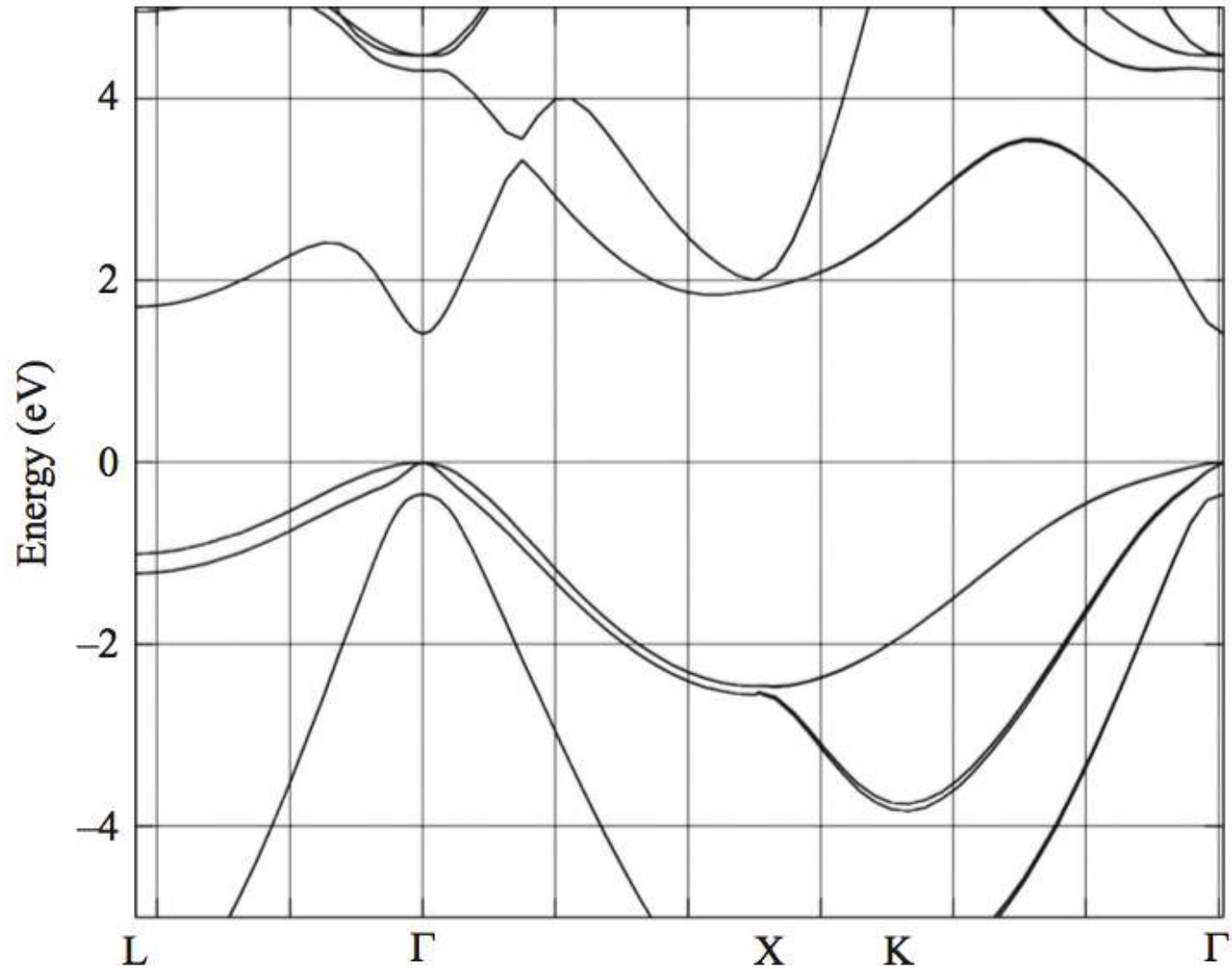
Plane waves defined by the
reciprocal lattice vectors
Fourier transform of pseudo-
potential

Empirical pseudo-potentials

VASP, QUANTUM ESPRESSO



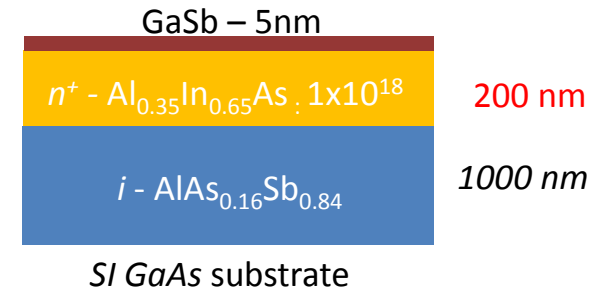
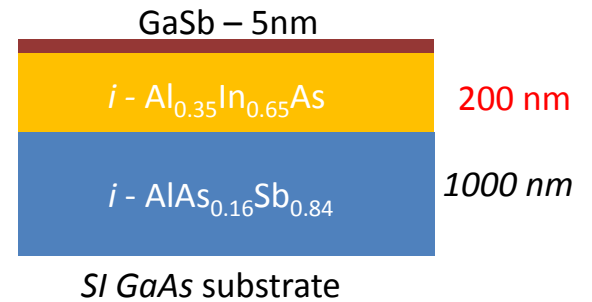
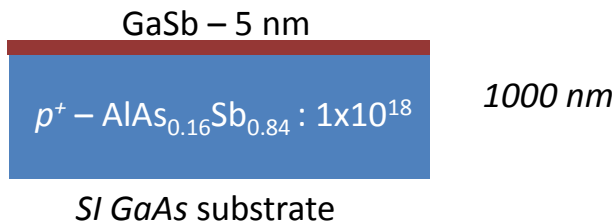
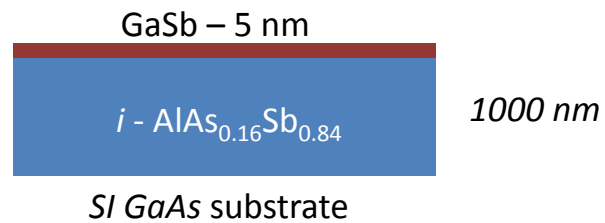
Band structure of GaAs using EPM, including nonlocal (p-state angular momentum) and spin-orbit interaction directly



Well, there appears to be some interest locally in the alloys AlAsSb and InAlAs...

Calibration/Test structures

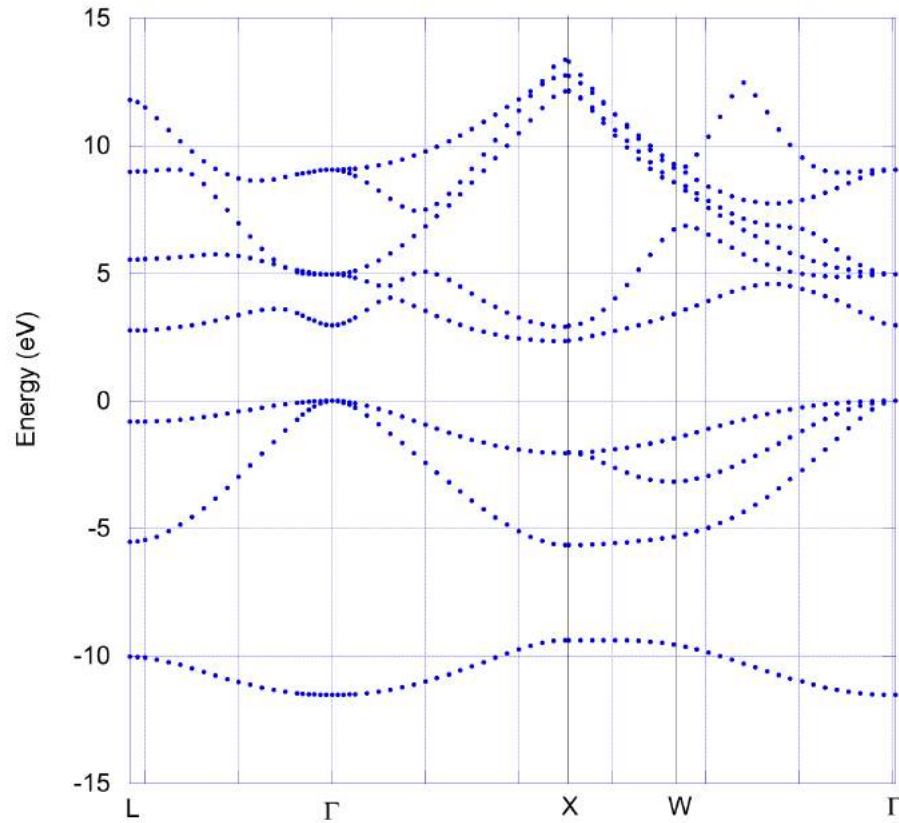
- Intrinsic and p-type AlAsSb for TD PL, TD Hall, XRD, TD Reflectivity, and TD Raman
- Intrinsic and n-type AlInAs for TD PL, TD Hall, XRD, TD Reflectivity, and TD Raman



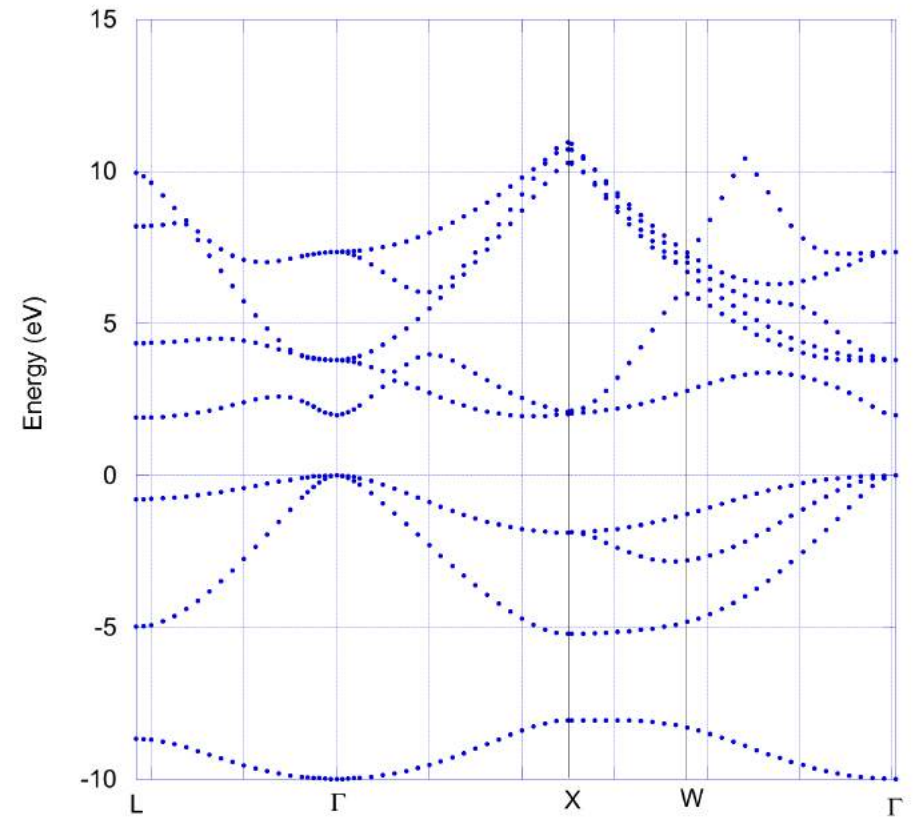
GaSb, InAs (buffer and substrate), and full structures (T673) will also be compared by Photoluminescence, Raman, XRD, and Reflectivity

The first step is to fit the bands of the binaries to get an idea of the Fourier coefficients

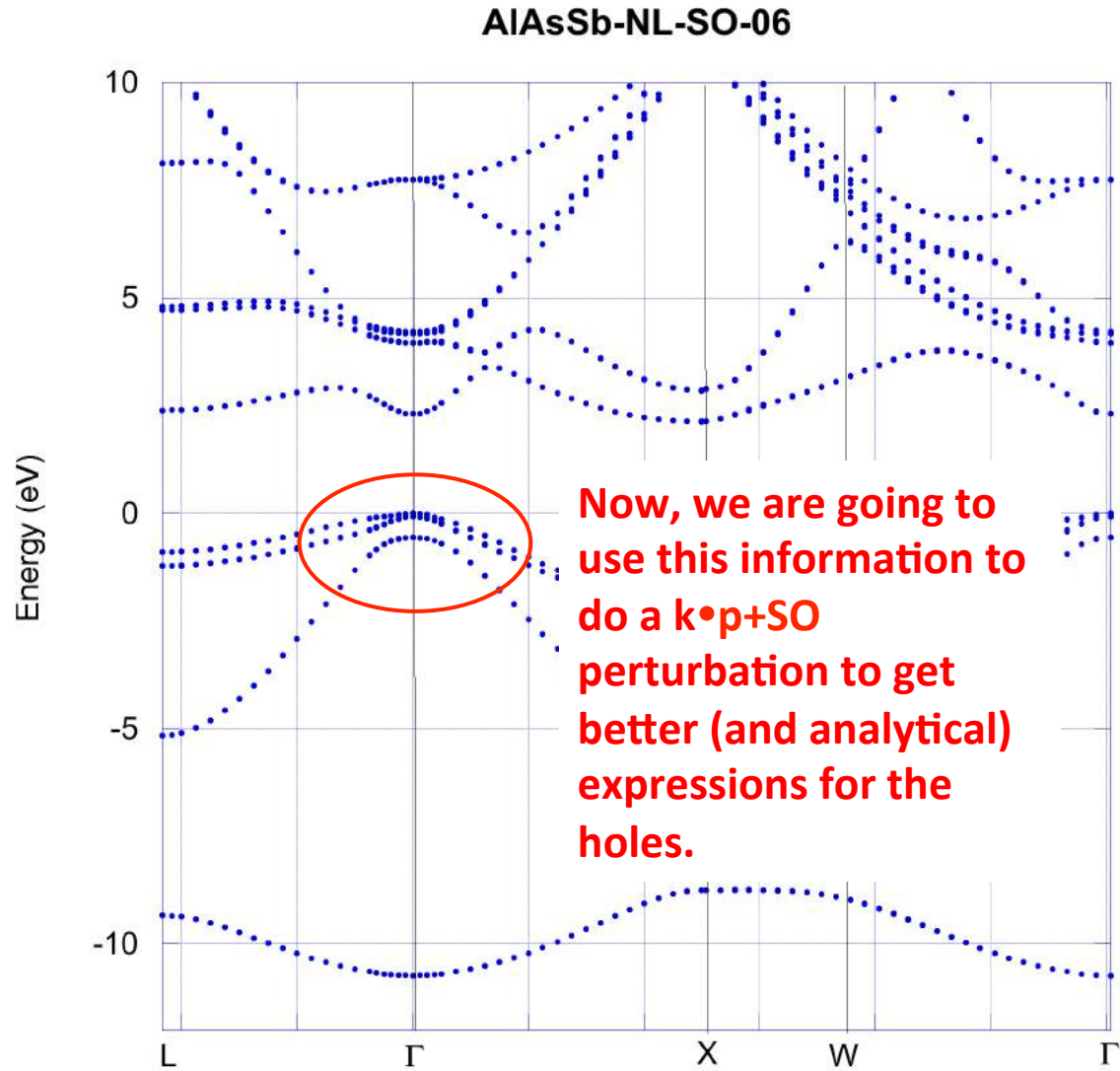
AiAs-L-EPM-012



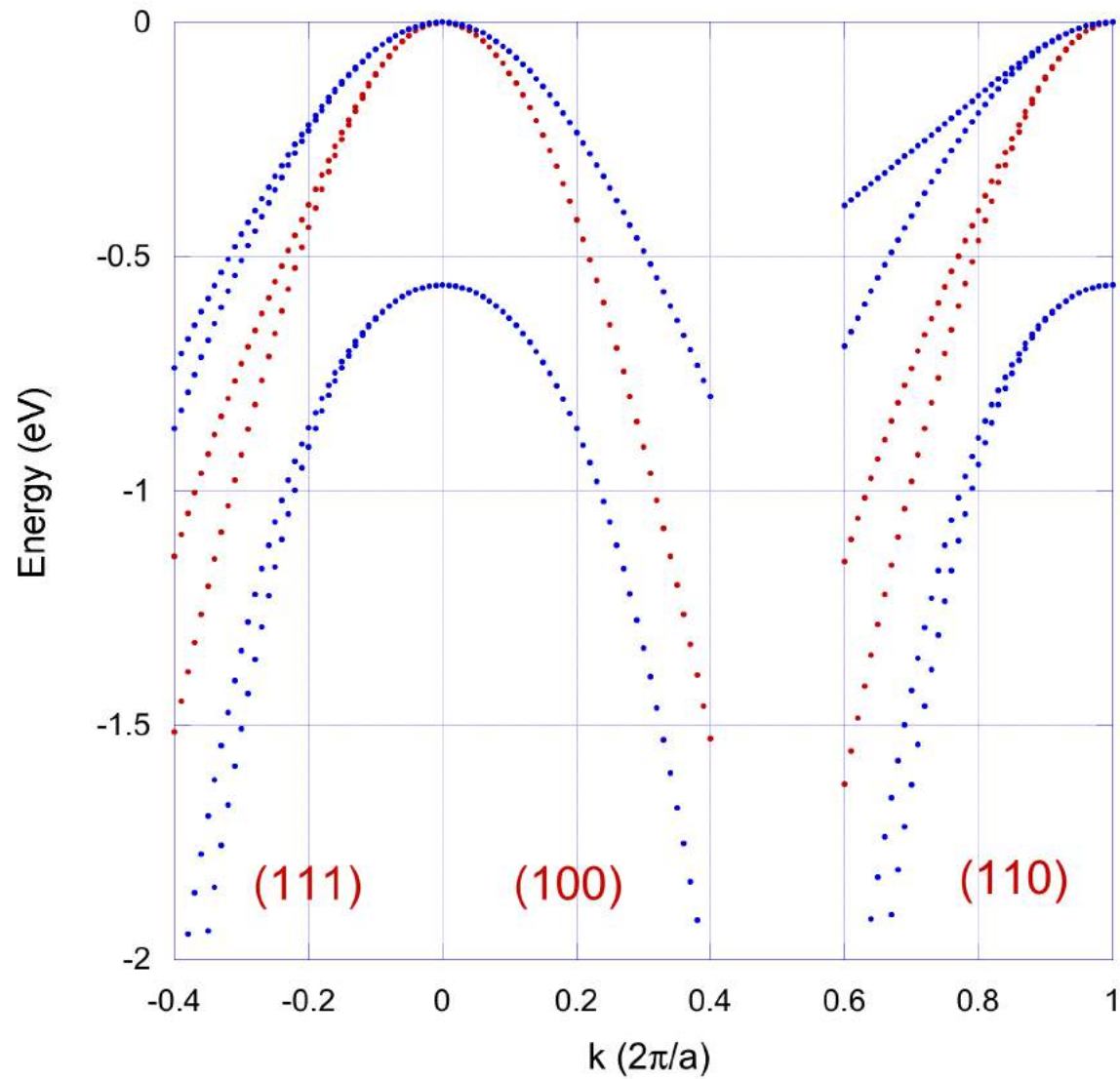
AISb-L-EPM-010



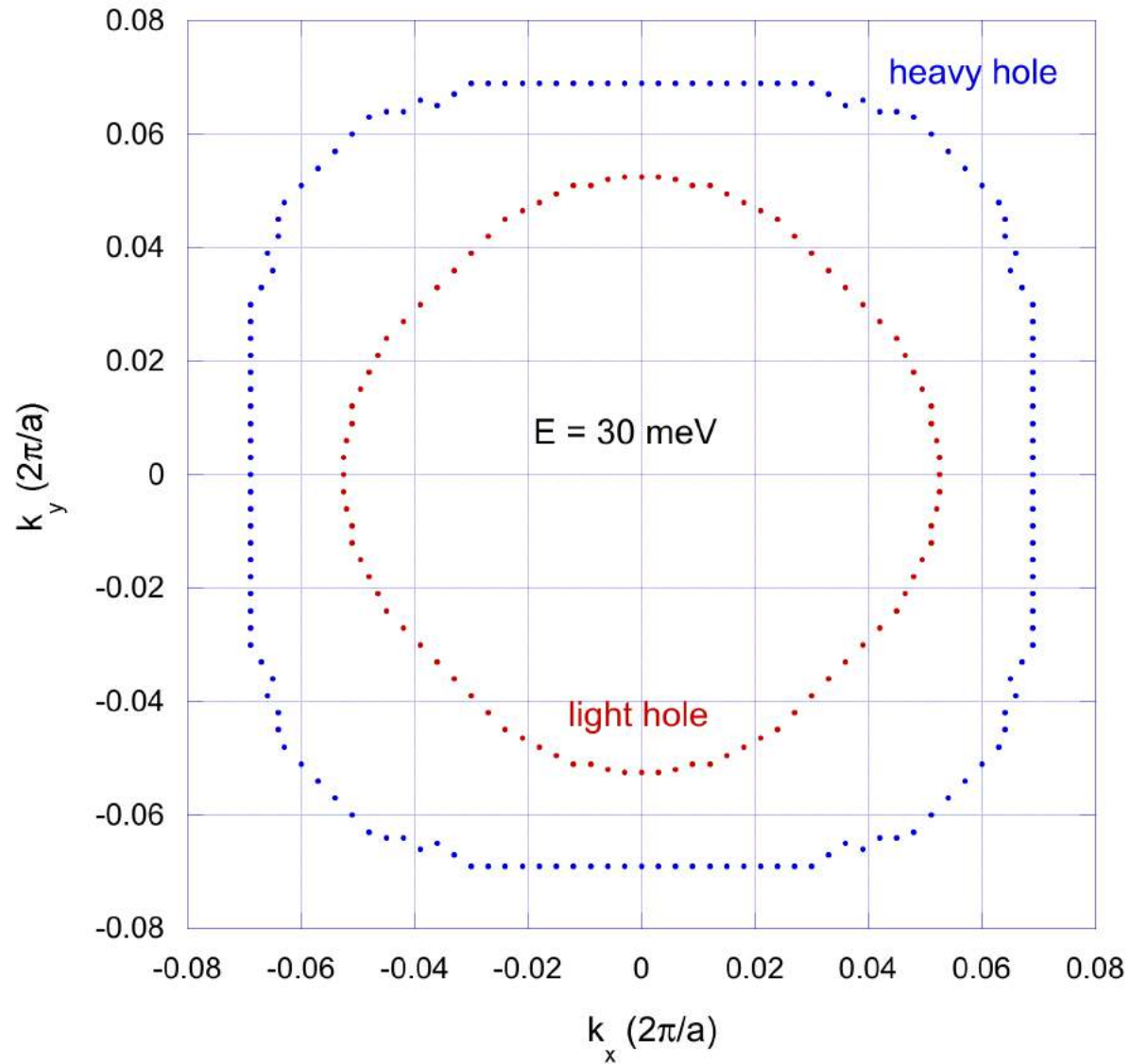
Then we proceed to the ternary, adding nonlocal and spin-orbit coupling



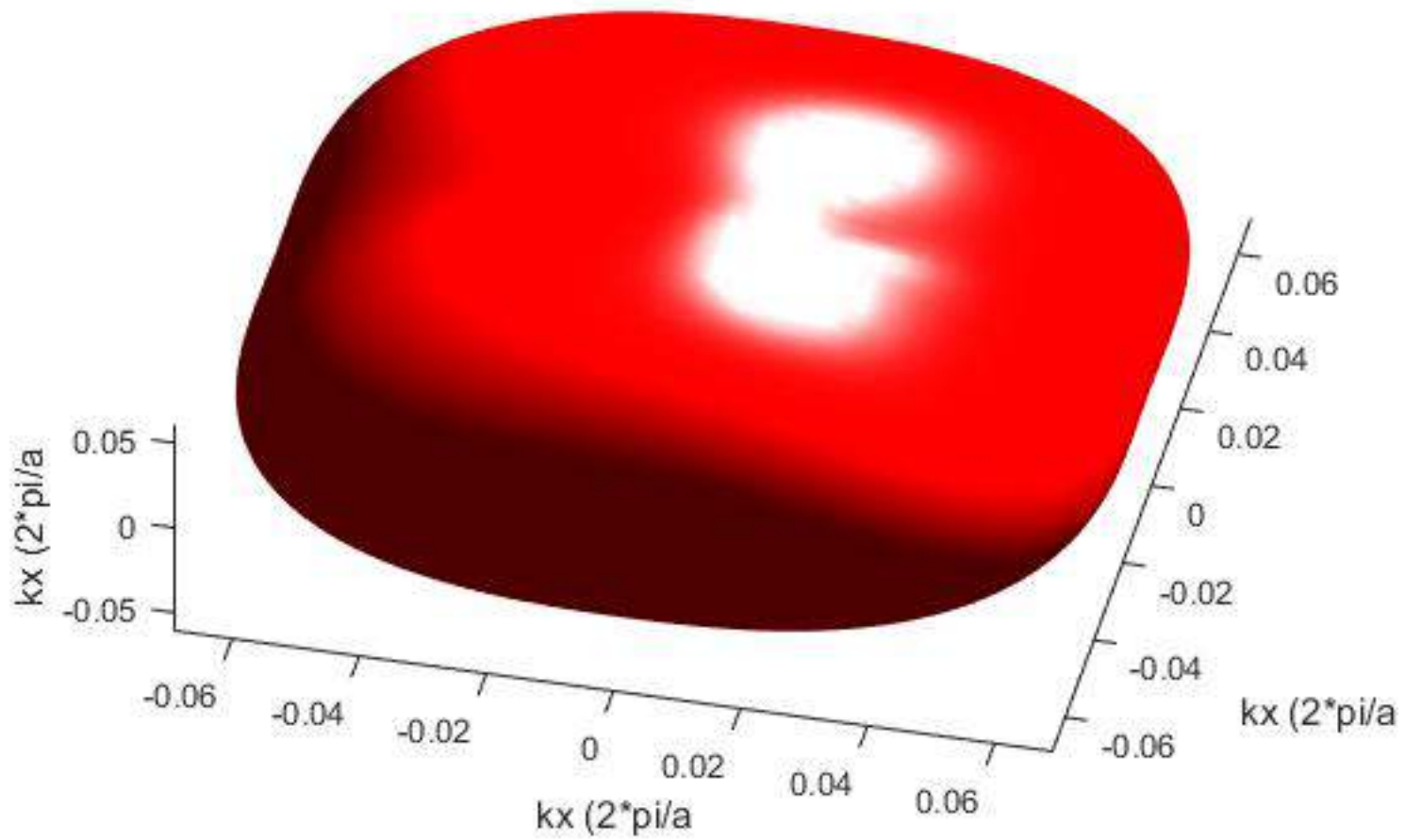
From these curves we can now determine the effective masses for the various hole states



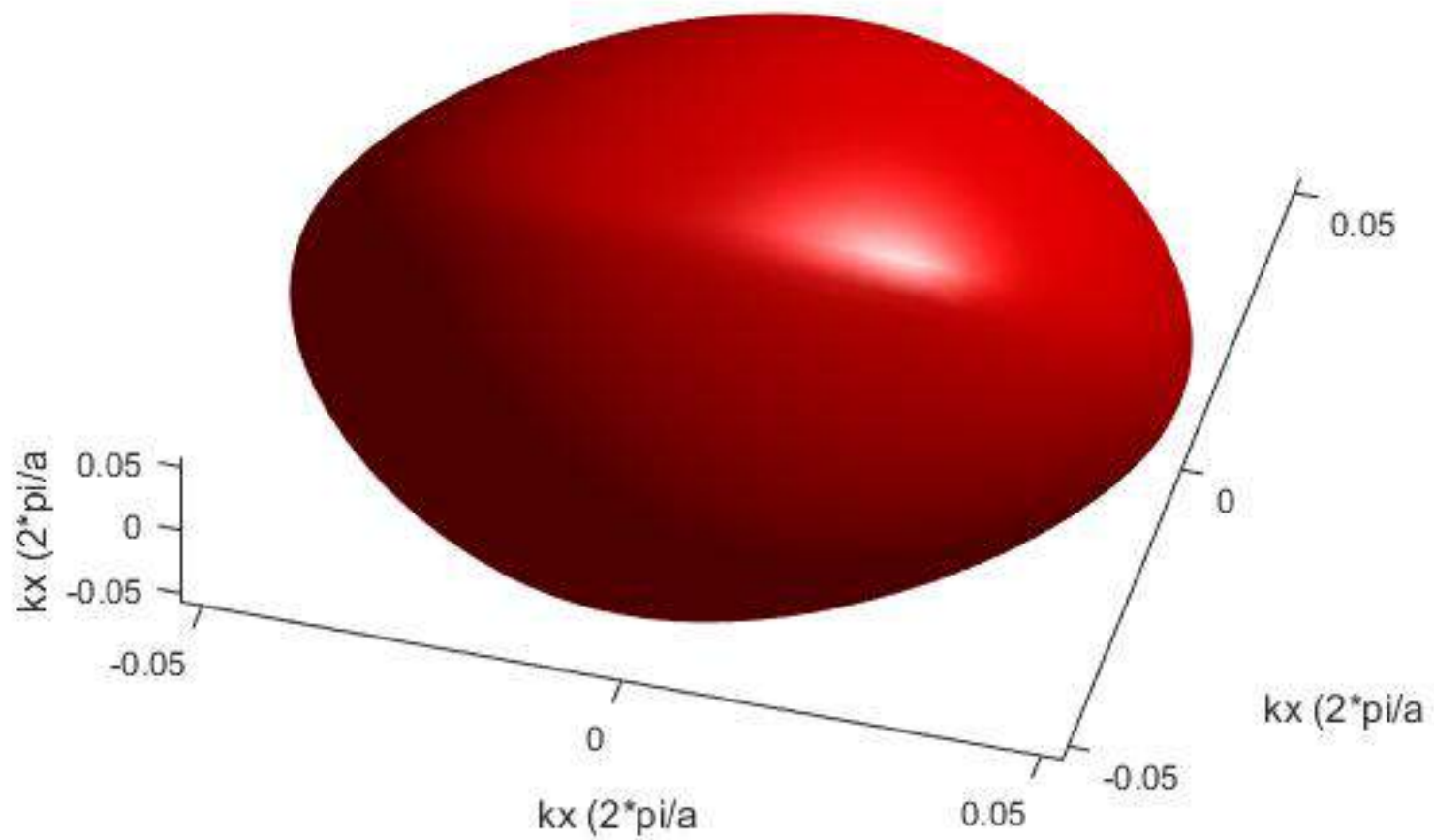
Constant energy contour for the top heavy and light hole bands, projected onto the (001) plane



Heavy Hole E = 30 meV



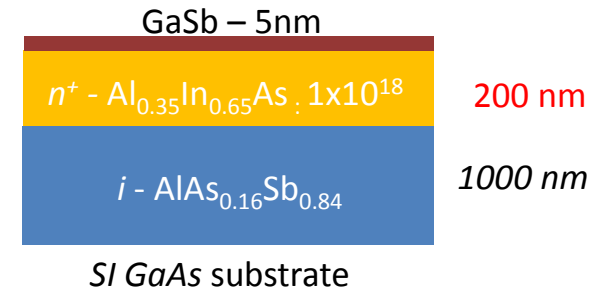
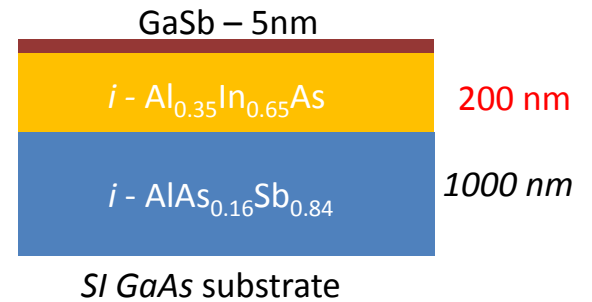
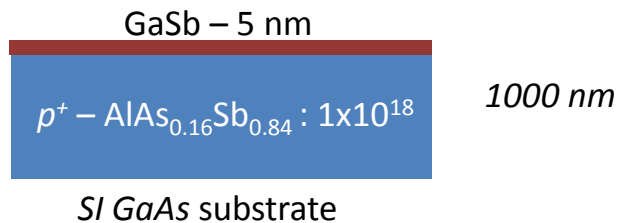
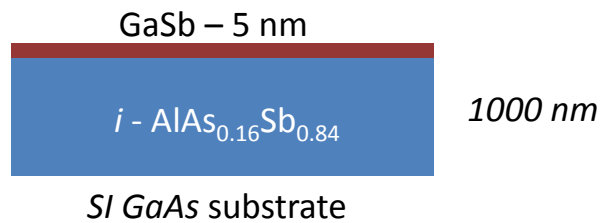
Light Hole $E = 30$ meV



Well, there appears to be some interest locally in the alloys AlAsSb and InAlAs...

Calibration/Test structures

- Intrinsic and p-type AlAsSb for TD PL, TD Hall, XRD, TD Reflectivity, and TD Raman
- Intrinsic and n-type AlInAs for TD PL, TD Hall, XRD, TD Reflectivity, and TD Raman



GaSb, InAs (buffer and substrate), and full structures (T673) will also be compared by Photoluminescence, Raman, XRD, and Reflectivity

Finally, the strained (to InAs) bands of the $\text{In}_{0.65}\text{Al}_{0.35}\text{As}$ alloy

