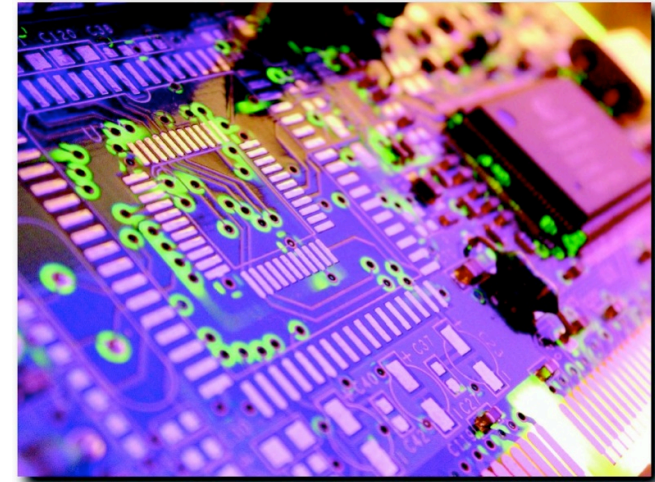


Electronic Properties of Materials from Quantum Monte Carlo

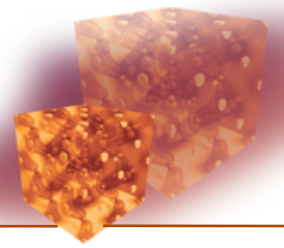
Richard G. Hennig

rg27@cornell.edu

- What are electronic properties?
- Band structure of perfect crystals
- Dopants and defects in semiconductors
- What can we calculate in Quantum Monte Carlo?



Electronic Properties of Materials



All materials:

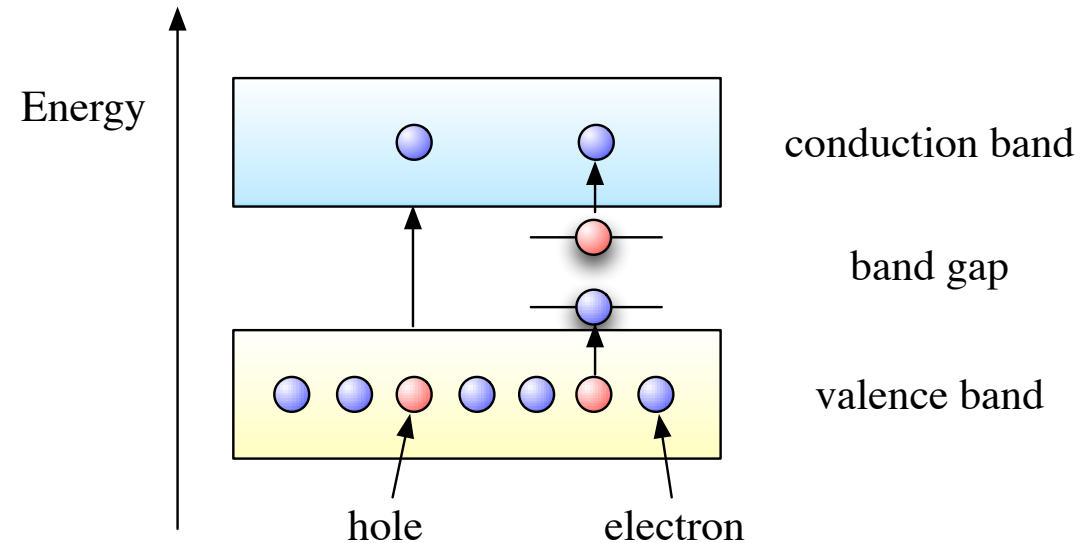
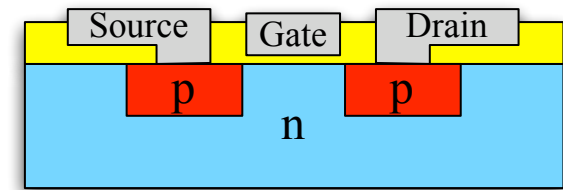
- Electronic density of states and bandgaps
- Electronic and thermal conductivity

Minerals under pressure

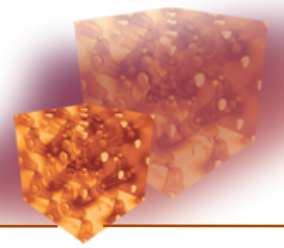
- Metal/insulator transitions affects Earth's magnetic field

Semiconductors

- Electron and hole mobility
- Effective masses
- Electronic transition levels of dopants
- Dopant diffusion
- Optical properties, excitons
- Band offsets for heterostructures

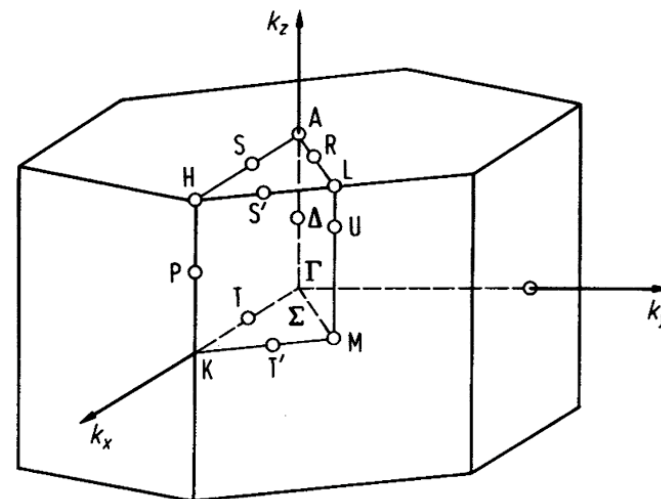
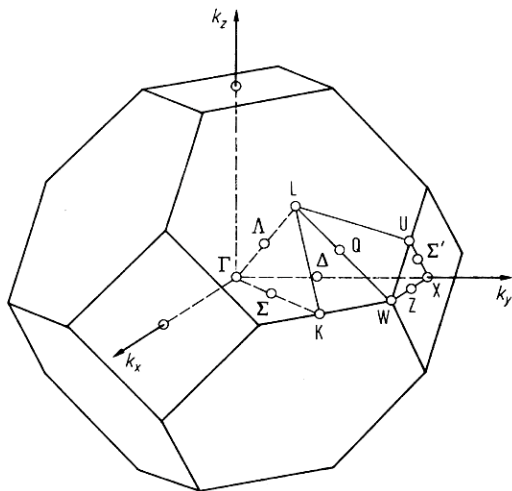


Band structure of crystals (1)

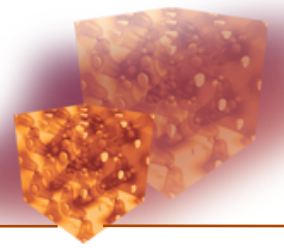


Bloch states and Brillouin zones

- Crystal structures defined by Bravais lattice $\{\mathbf{a}_i\}$ and basis
- Periodic density \Rightarrow Bloch theorem $\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r}) \cdot \exp(i\mathbf{k} \cdot \mathbf{r})$
- Fourier transformation $n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \cdot \exp(i\mathbf{G} \cdot \mathbf{r})$
- Reciprocal lattice $\mathbf{b}_{\mathbf{k}} = 2\pi \cdot \frac{\mathbf{a}_1 \times \mathbf{b}_m}{\mathbf{b}_{\mathbf{k}} \cdot (\mathbf{b}_1 \times \mathbf{b}_m)}$
- Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice



Band structure of crystals (2)



Diffraction picture for origin of the energy gap

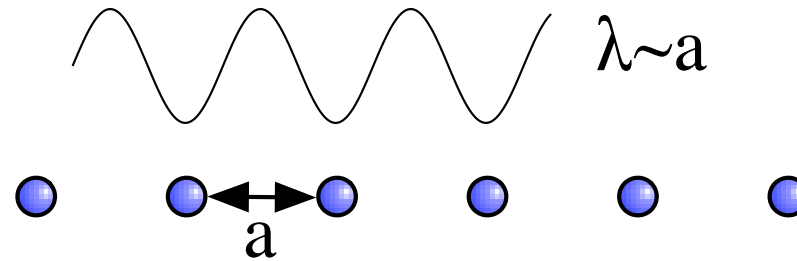
- Start with a 1D crystal and consider diffraction of electron wave

$$n\lambda = 2d \cdot \sin \theta \quad \text{with } d = a \text{ and } \sin \theta = 1$$

$$n\lambda = 2a$$

$$k = \frac{2\pi}{\lambda}$$

$$k = \frac{n\pi}{a}$$



- Take lowest order ($n = 1$) and consider incident and reflected electron wave

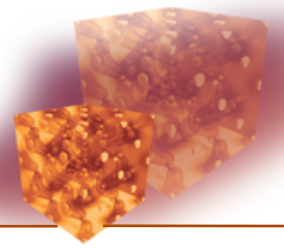
$$\psi_i = e^{ikx} = e^{i\frac{\pi}{a} \cdot x} \quad \text{and} \quad \psi_r = e^{-i\frac{\pi}{a} \cdot x}$$

- Total wave function for electrons with diffracted wave length

$$\psi = \psi_i \pm \psi_r \quad \Rightarrow \quad \psi_+ = \psi_i + \psi_r = 2 \cos \frac{\pi x}{a} \quad \text{and} \quad \psi_- = \psi_i - \psi_r = 2 \sin \frac{\pi x}{a}$$

- Only two solutions for $k = \pi/a$: Electron density on atoms or between
- No traveling wave solution

Band structure of crystals (3)



Diffraction picture for origin of the energy gap

- If ion potential is a weak perturbation U , the electrons near diffraction condition have two possible solutions

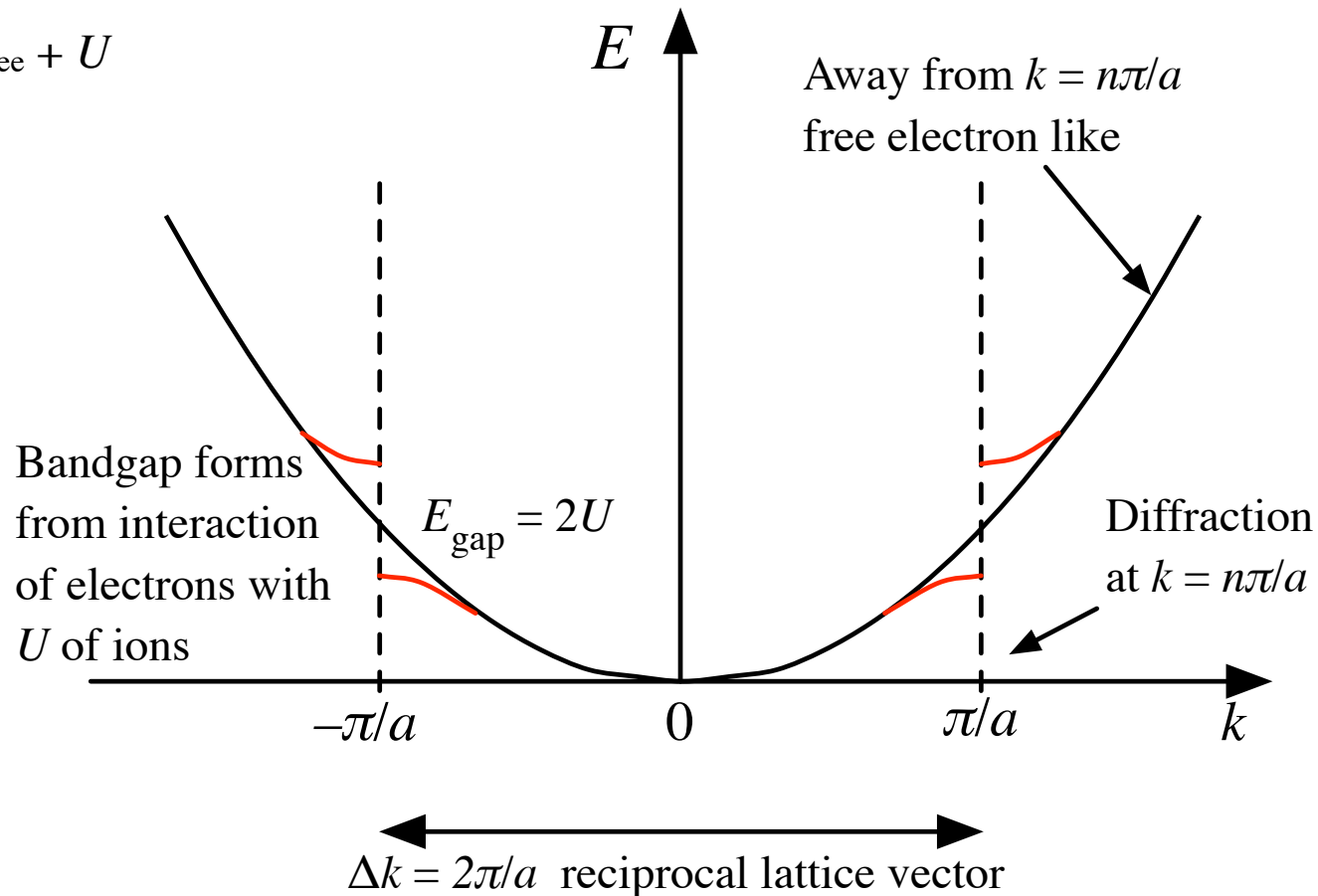
▶ Electron density between ions: $E = E_{\text{free}} - U$

▶ Electron density on ions: $E = E_{\text{free}} + U$

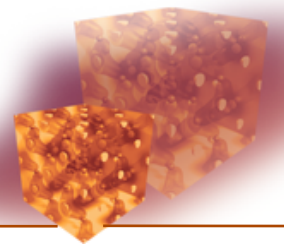
▶ Near diffraction condition energy is parabolic in k ,
 $E \propto k^2$

▶ Electron near diffraction conditions are not free

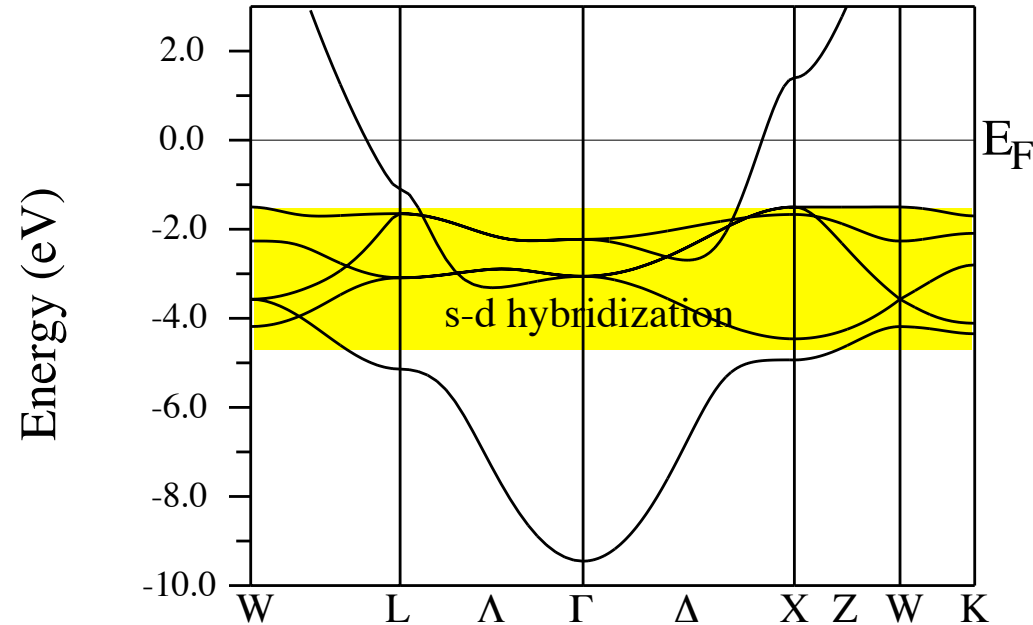
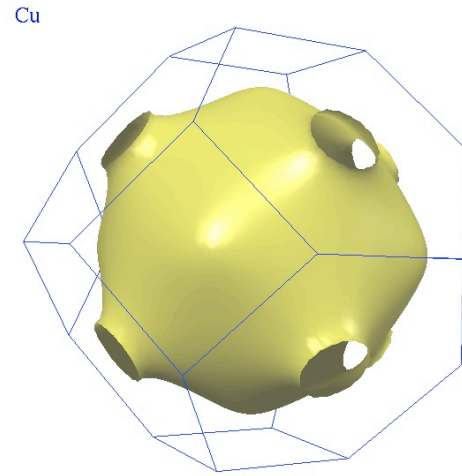
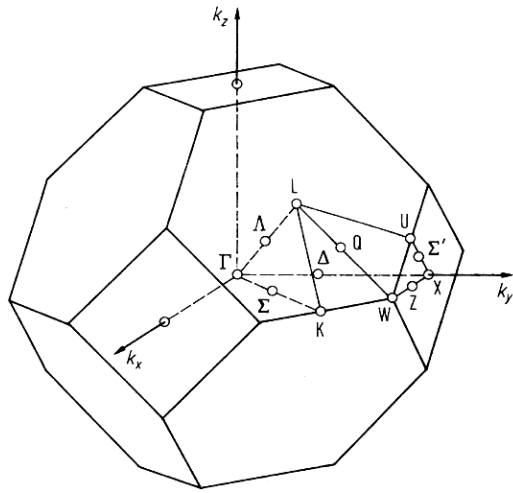
▶ Their properties can still be described as “free” with an *effective mass* m^*



Example of metallic band structure: Cu

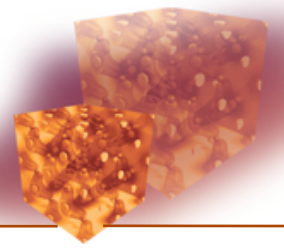


- Copper: Band structure calculated with Wien2k



- *Nearly free electron s-band* dominates at low and high energies
- Electron near diffraction conditions have different effective mass
- *Hybridization* between *nearly-free s* and *atomic-like d* orbitals at intermediate energies
- Necking of Fermi surface in [111] directions \Rightarrow *Hume-Rothery stabilization*

The bandgap problem of DFT

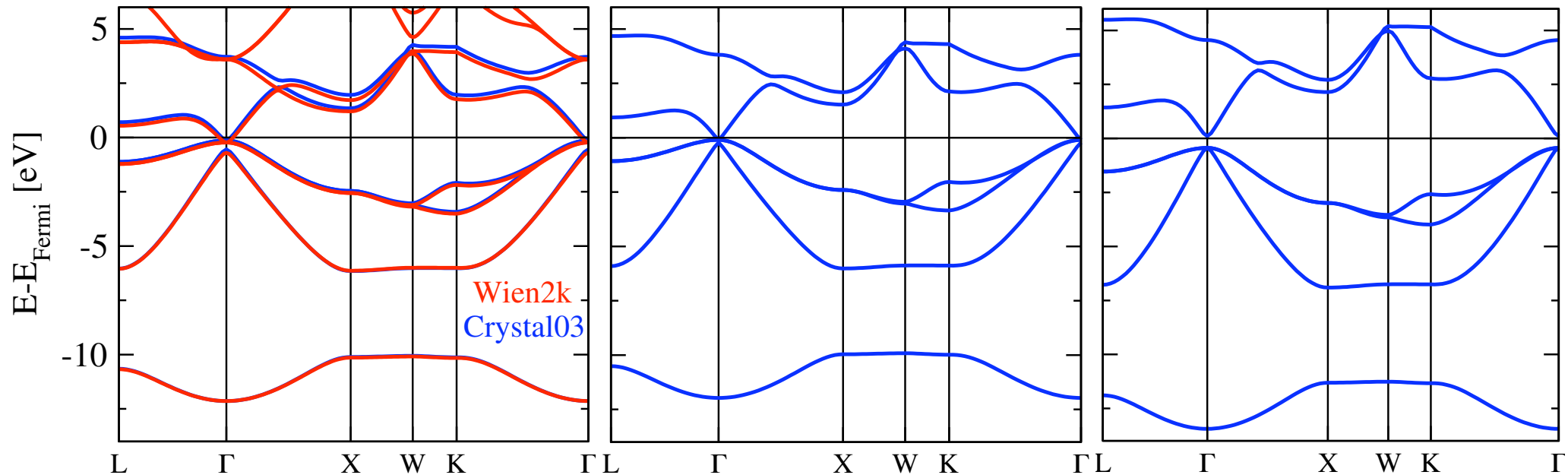


Example: Bandstructure of InAs

LDA, no gap: -0.42 eV

PBE, no gap: -0.13 eV

B3LYP 20%, gap: 0.54 eV

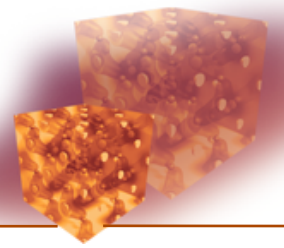


- Experimental bandgap: 0.41 eV

Band gap problem: LDA and GGA yield a metallic ground state!

- Practical solution: **Hybrid functionals B3LYP & HSE (0.39 eV)**
- Better solution: **GW approximation or QMC methods**

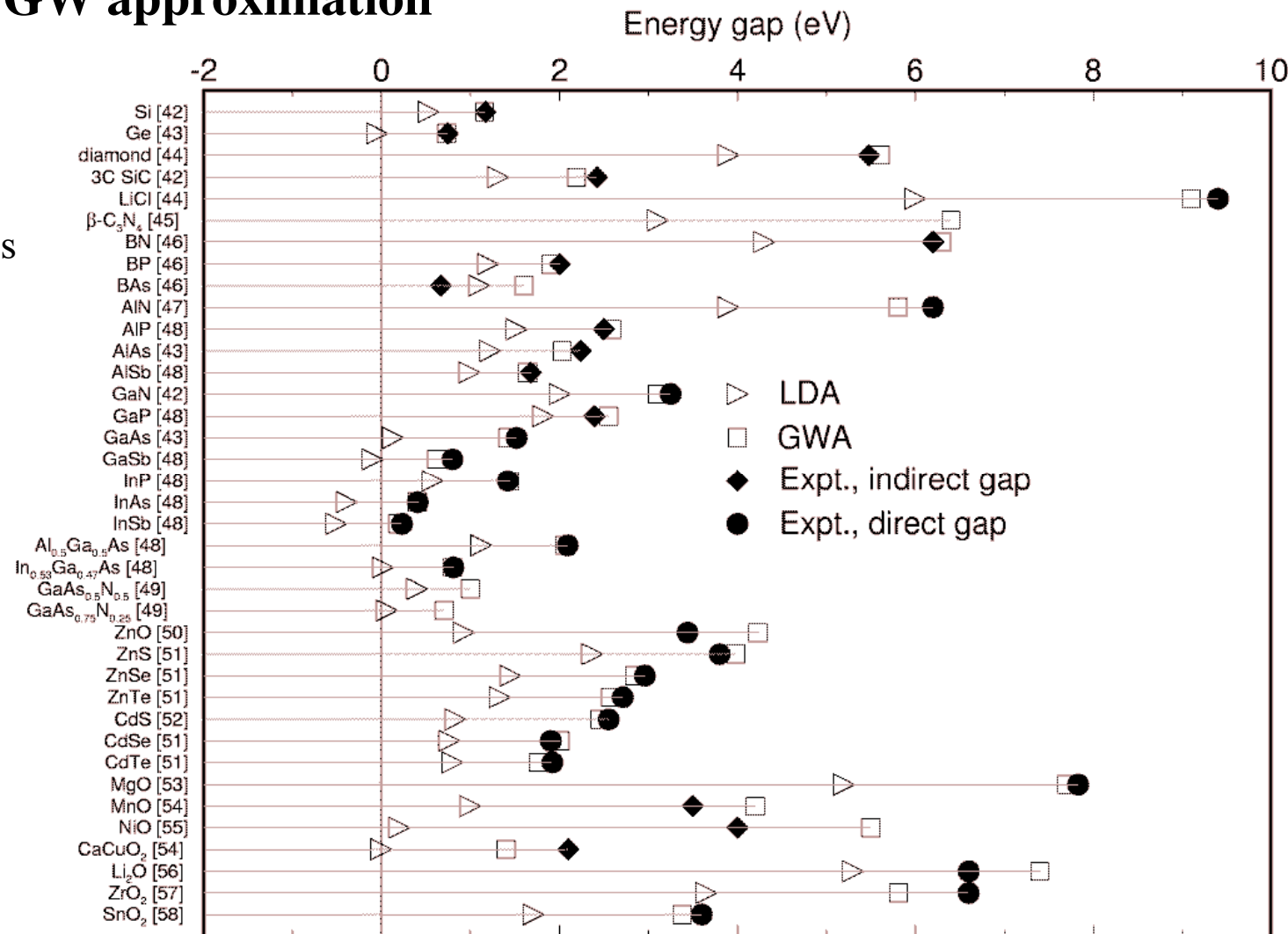
GWA calculation of band structures



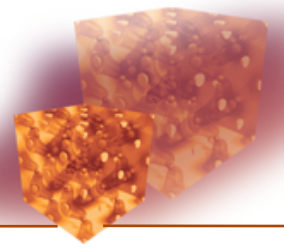
- Density functional methods provide a fast way of getting band structures
- However many functionals suffer from the **band gap problem**
- More accurate method: **GW approximation**

- ▶ Based on electronic Green's function
- ▶ Many-body correction of DFT quasiparticle energies
- ▶ Accurate band structures
- ▶ Computationally more demanding than DFT, implemented in abinit

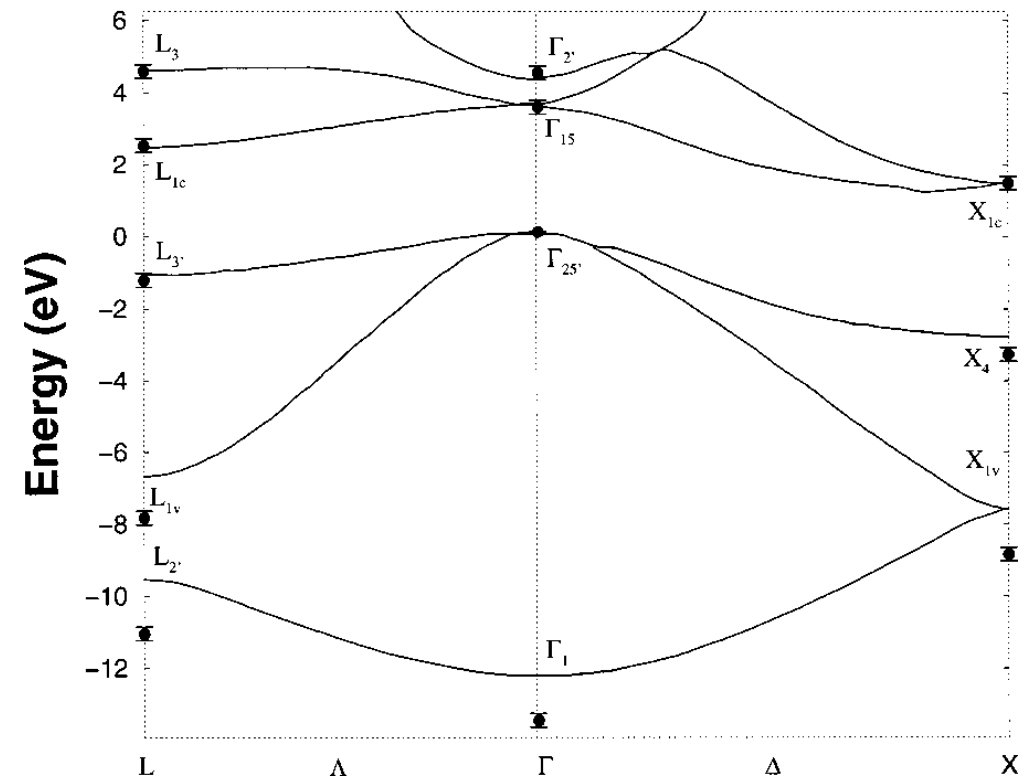
Aulbur *et al.*
Solid State Phys. 54, 1 (2000)



Calculation of band structures (QMC)

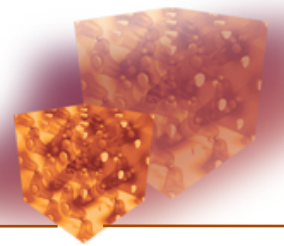


- Quantum Monte Carlo
 - ▶ Variational for ground state of respective symmetry
 - ▶ Combined optimization of ground and excited states to keep wave functions orthogonal (Schultz *et al.*, J. Chem. Phys. 121, 5836)
 - ▶ Silicon band structure shown
- Comparison QMC vs. GWA
 - ▶ Similar accuracy
 - ▶ Both computationally expensive
 - ▶ QMC much less tested than GWA
- For molecular systems, quantum chemistry methods such as MCSCF are very powerful

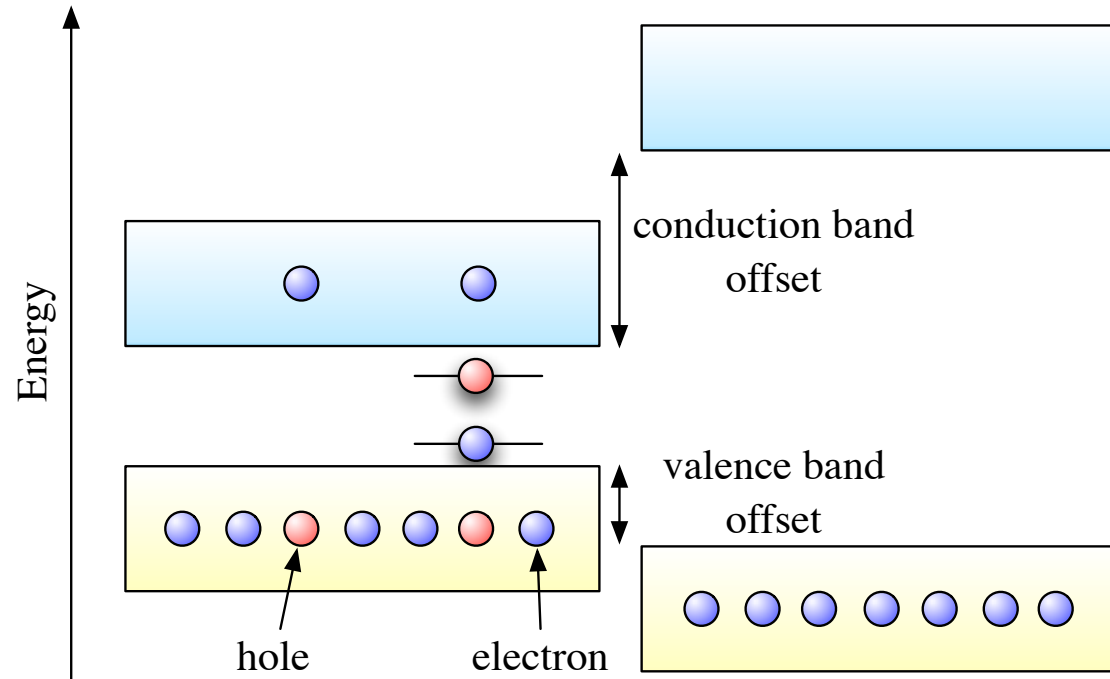


Williamson *et al.* PRB 57, 12140 (1998)

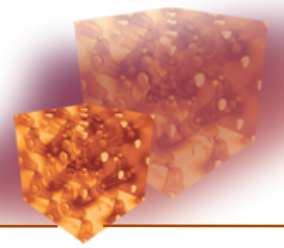
Electronic Properties of Semiconductors



- Density of states and bandgaps
- Intrinsic and extrinsic semiconductors (p and n doping)
- Heterostructures
 - Fabrication by MBE or MOCVD
 - Electronic properties controlled by band offsets
 - Examples:
 - (1) Laser diodes from II-VI and III-V heterostructures
 - (2) Heterojunction bipolar and high electron mobility transistor
- Calculation of defect levels and band offsets
 - Similar to calculation for crystal
 - DFT bandgap problem \Rightarrow Use GWA or QMC methods for improved accuracy



Dopants and Defects in Semiconductors



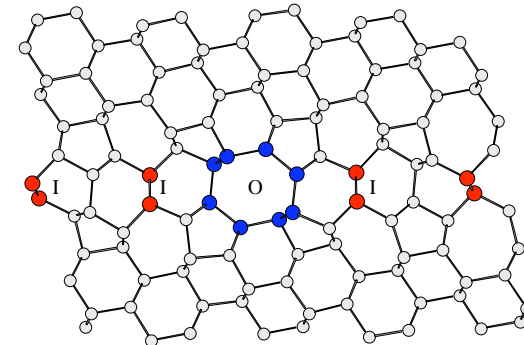
- Where are they?
 - ▶ Small concentrations and small sizes of dopants and defects
⇒ Experimental observations difficult
- What are they doing?
 - ▶ Dopants and defects can lead to electronic levels in the band gap
 - ▶ n-type donor states (P, As, Sb in Si)
 - ▶ p-type acceptor states (B in Si)

Computational methods can link experimental electronic properties to dopant and impurity structures

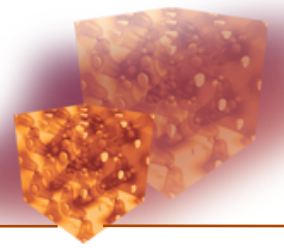
**{311} defect
in B doped Si**



Theory
→
Kim *et al.*



Structure of Defects and Dopants



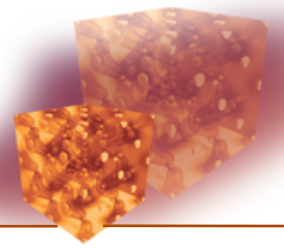
Harmonic transitions state theory

- Calculation of diffusion constant and reaction rates

$D_i = \frac{a_i^2}{6} \cdot \beta_i \cdot f_i \cdot \Gamma_i$	a_i – Jump length
$\Gamma_i = \Gamma_0 \cdot \exp\left(-\frac{\Delta H}{kT}\right)$	β_i – Availability factor (i.e. vacancy concentration)
$\Gamma_0 = \frac{\prod_{i=1}^{3N-3} \nu_i}{\prod_{i=1}^{3N-4} \nu'_i}$	f_i – Correlation factor (due to back jumps)
	Γ_i – Jump frequency
	ΔH – Enthalpy barrier of saddle point
	Γ_0 – Prefactor
	ν_i – Phonon frequency at minimum
	ν'_i – Phonon frequency at saddle point

- Jump length determined by geometry
- Availability factor determined by concentration of available sites
- Correlation factor requires at least forward and backward rate
- How to calculate phonon frequencies (see talk and lab by Dario Alfe)
- How to determine the saddle point structure?

Structure of Defects and Dopants



Determining saddle points

- **Nudged elastic band method**

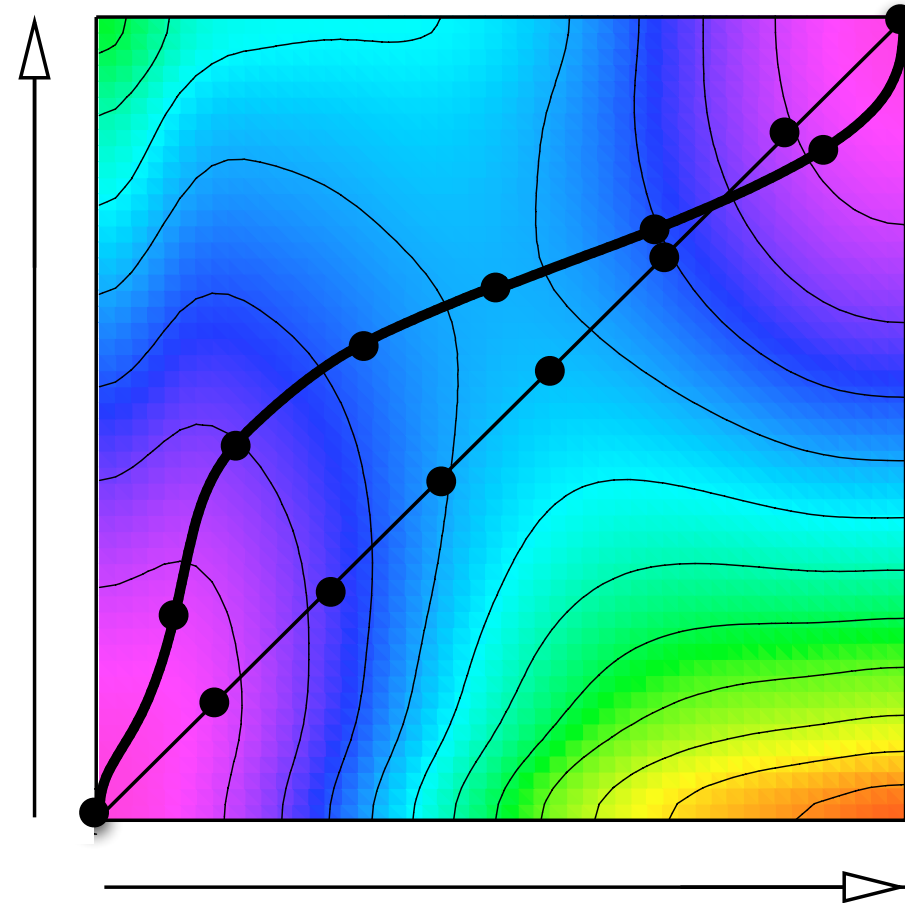
(Jonsson et al. 1998)

- ▶ Chain of $3N$ -dim configurations connected by "springs"
- ▶ Relaxation \Rightarrow Minimum energy path
- ▶ Implemented in PWSCF

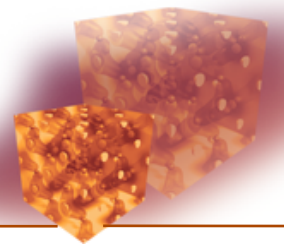
- **Dimer method**

(Henkelman and Jonsson, JCP (1999))

- ▶ Optimize rotation angle of the vector between pair of configurations \Rightarrow lowest curvature mode
- ▶ Follow direction uphill minimizing all other directions
- ▶ Very efficient first-derivative-only *saddle search method*



Diffusion of silicon interstitials



- Diffusion path only known for single but not larger interstitials
- Experiment: Diffusion activation 4.7–5.0 eV, barrier 0.3–1.8 eV
- Energy units: Room temperature = 0.024 eV

Multiscale approach: DFT & TB

DFT-GGA	I ₁	I ₂	I ₃	I _n ^{chain}
Formation [eV/atom]	3.8	2.8	2.4	1.7
Barrier [eV]	0.3	0.3	0.5	

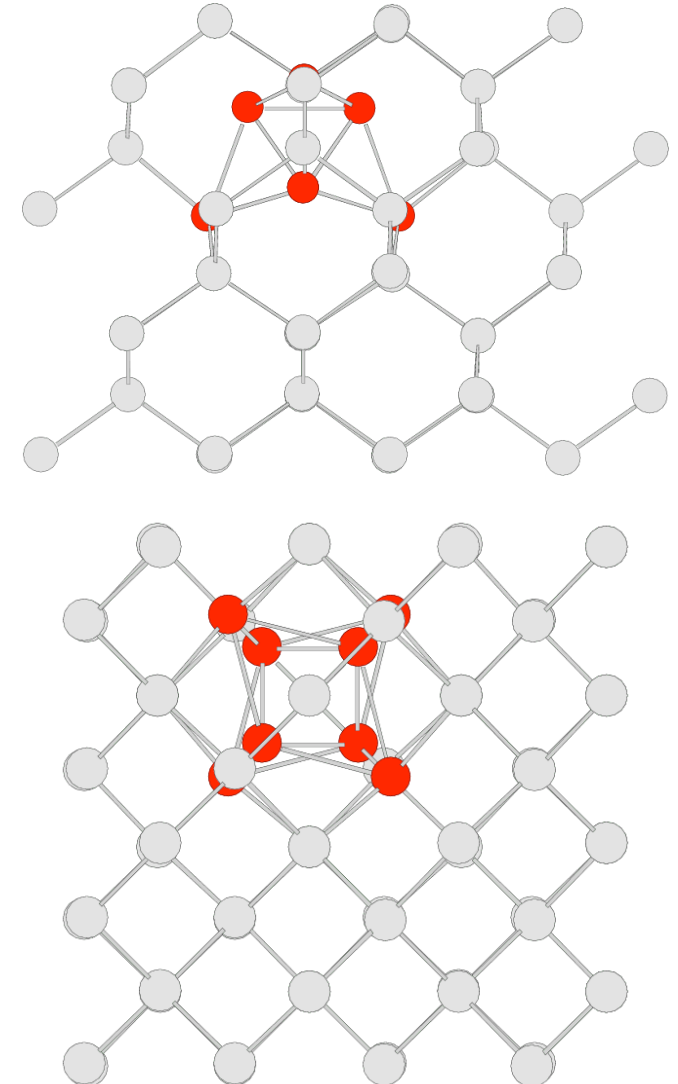
Results:

Fast diffusion of interstitials

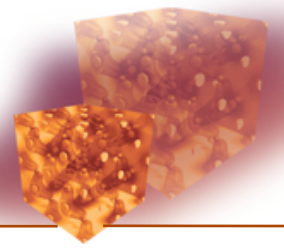
Single interstitials dominate

Driving force to form defect precipitates

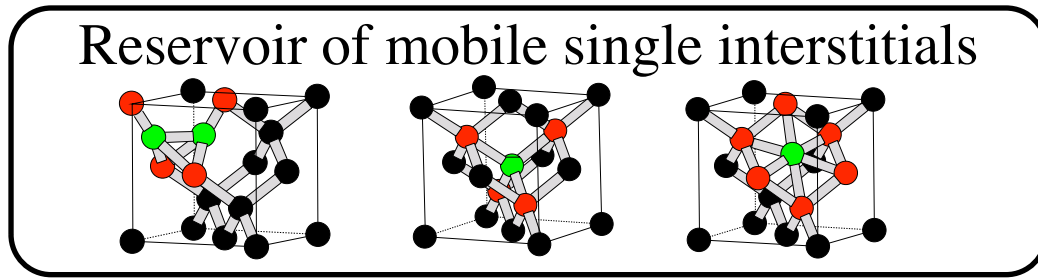
Defect charge states can lower diffusion barrier



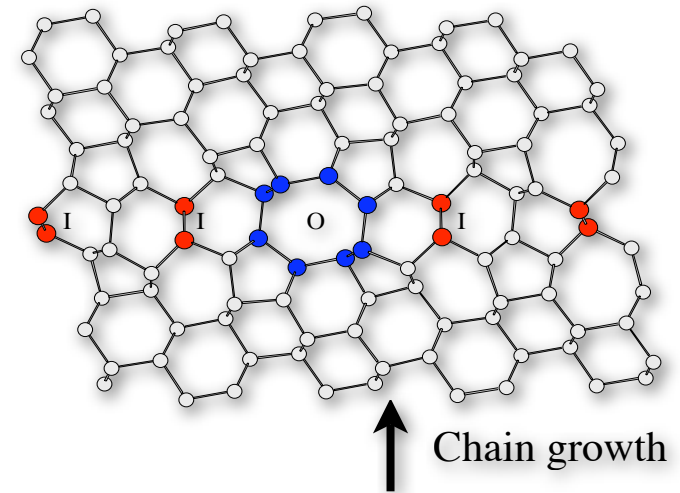
From compact to extended defect structures



Ion Implantation



Planar {311} defect

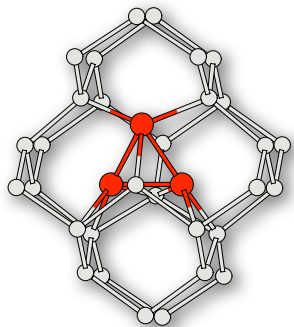


-2.0eV

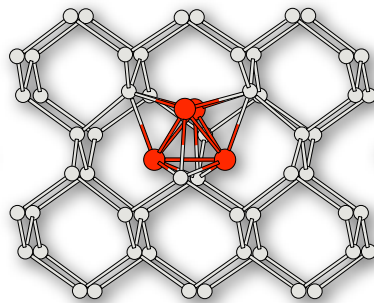
Thermal Annealing

Di-interstitials

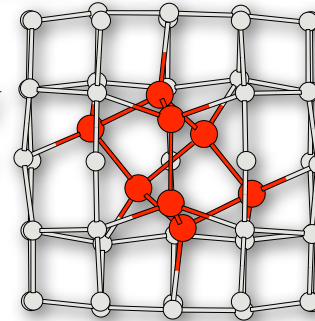
Tri-interstitials



-2.4eV

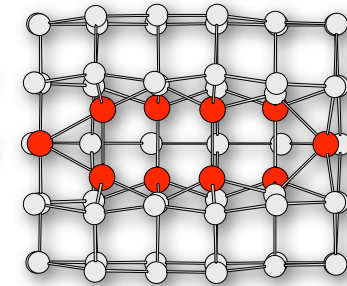


-0.3eV



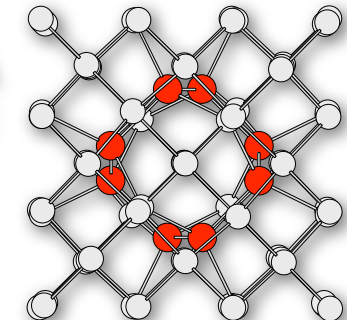
-0.7eV

Four-interstitials



chain

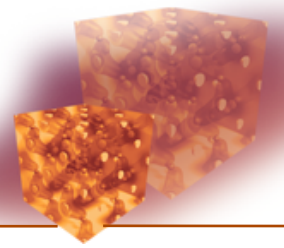
-2.2eV



compact

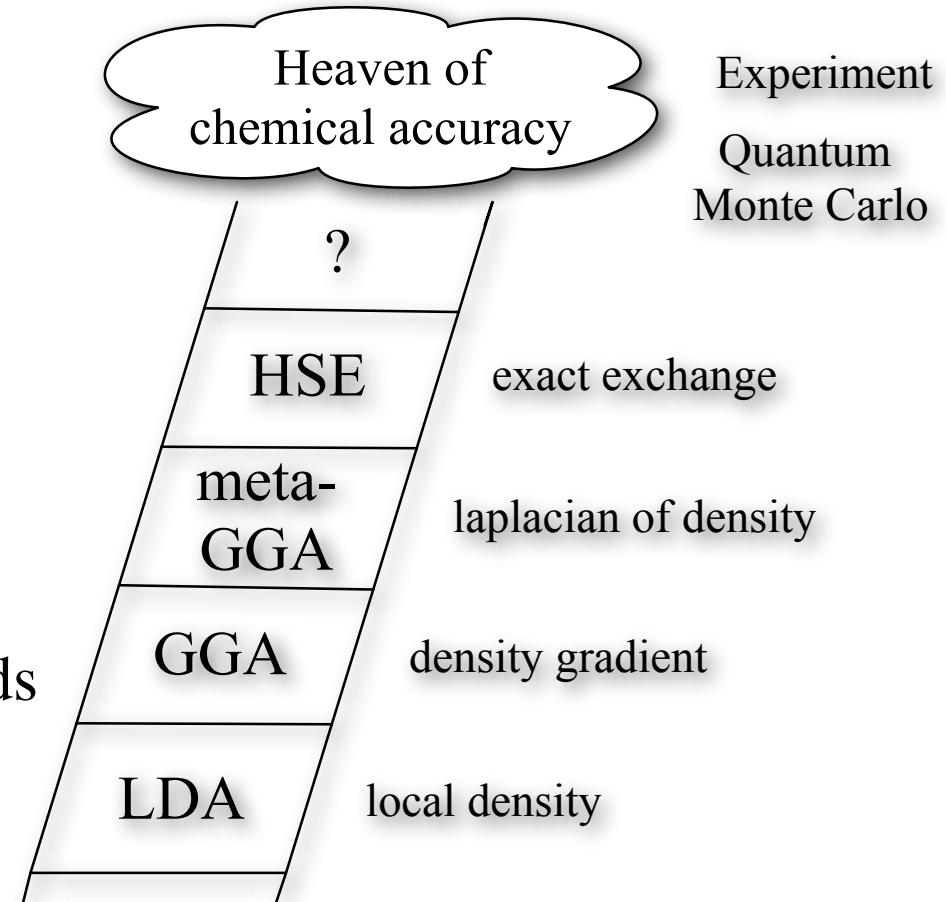
Rate limiting step

Jacobs ladder of density functionals

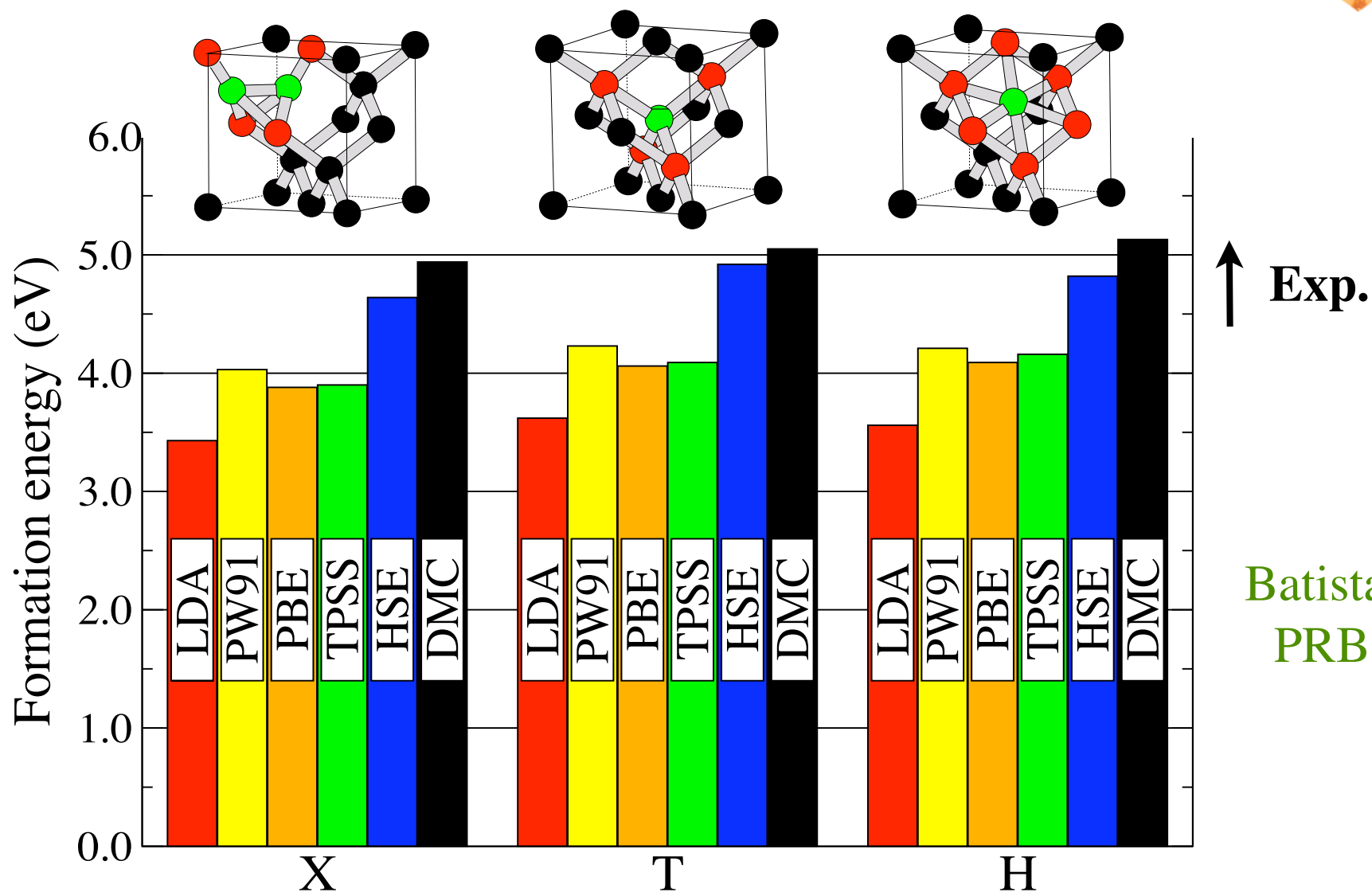
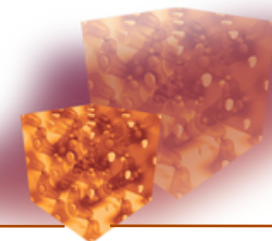


Approximations for unknown density functional

- Climbing “Jacob’s ladder” to heaven of chemical accuracy (Perdew *et al.* PRL 2003)
- Comparison to experiment or quantum chemistry
- Difficulties:
 - Experimental energies of defects
 - Quantum chemistry methods for solids
- Benchmark calculations by quantum Monte Carlo

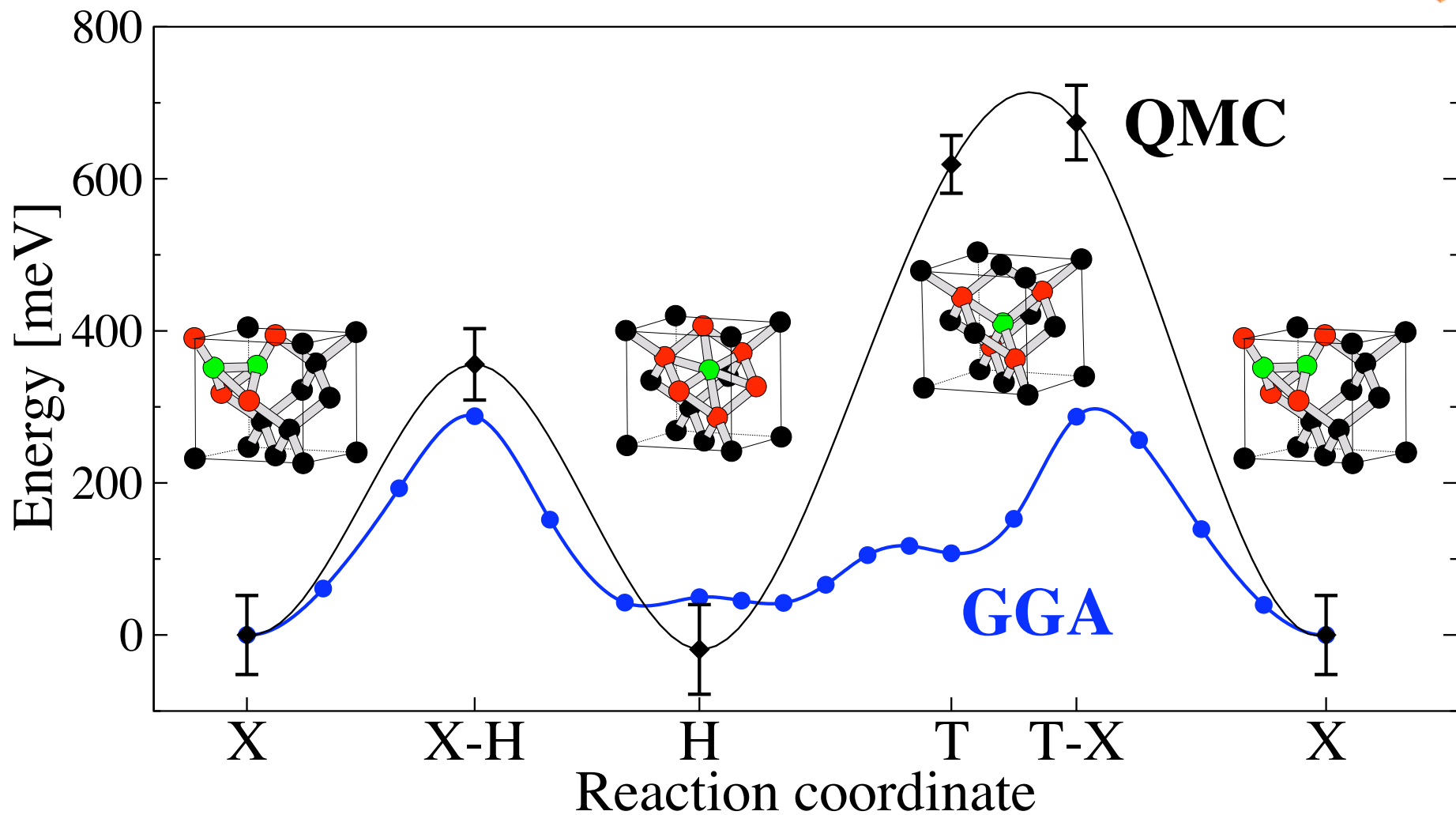
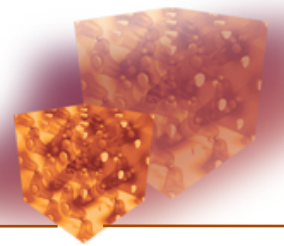


Accuracy of defect energies



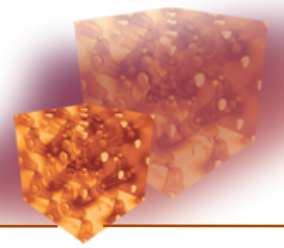
Climbing “Jacob’s ladder” of density functionals improves the accuracy for defect formation energies. The highest rung–hybrids–agree with QMC.

Accuracy of diffusion barriers



**Lowest energy barrier from X to H defect is similar in QMC and DFT.
The T defect and its barrier are higher in QMC.**

Electronic Transition Levels of Dopants



- Formation energy of defect X with charge q

$$E_f[X_q] = E_{\text{tot}}[X_q] - E_{\text{tot}}[\text{bulk}] - \sum_i n_i \cdot \mu_i + q[E_f + E_v + \Delta V]$$

$E_{\text{tot}}[X_q]$ Energy for charged defect (using uniform background charge)

$E_{\text{tot}}[\text{bulk}]$ Energy of ideal crystal

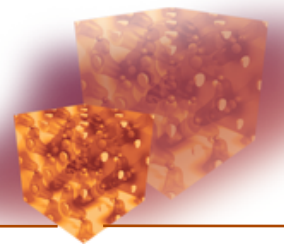
n_i, μ_i Number of defect atoms and their chemical potential

E_f Fermi energy relative to reference (valence band maximum)

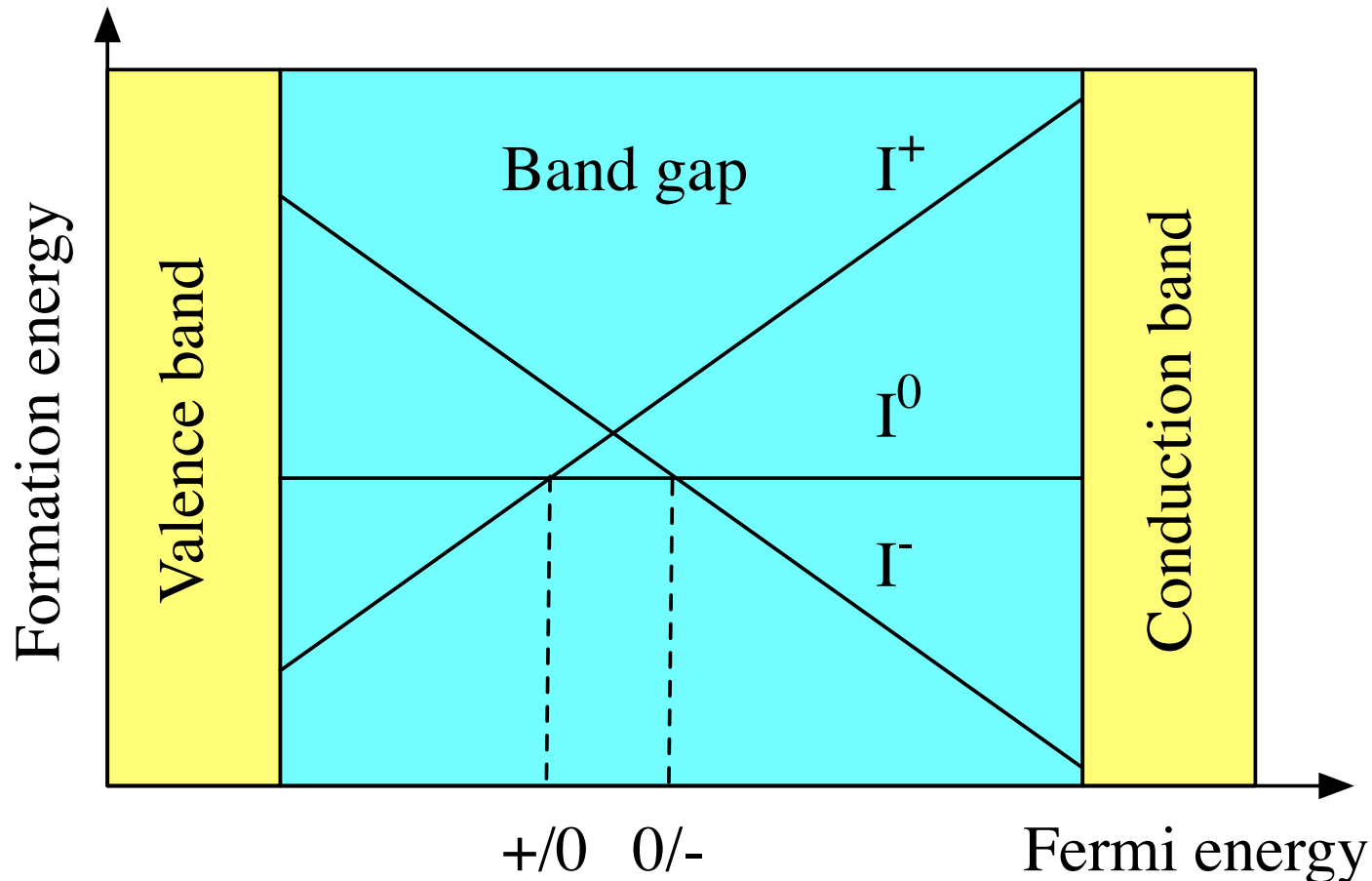
E_v Energy of reference

ΔV Alignment of electrostatic potentials of defect and crystal cell

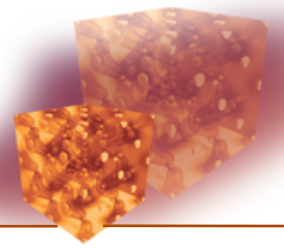
Electronic Transition Levels of Dopants



- Charge of defects changes as a function of Fermi level
- Change of defect charge for increasing Fermi level $++/+$ $+/0$ $0/-$ $-/--$
- *Thermodynamic* transition levels: Include relaxations of final state
- *Optical* transition levels: Final and initial charge state for same geometry



Calculations of Electronic Properties



Summary: What can we calculate with which method?

Property	DFT	GWA	QMC
Band gap	not always accurate ¹	very accurate	accurate
Effective mass	yes	yes	no
Transition levels	yes	very accurate	not done
Band offsets	not always accurate ¹	very accurate	not done
Defect energies	not always accurate ¹	no	accurate
Barriers	not always accurate ¹	no	accurate

¹ Improved accuracy for hybrid functionals

