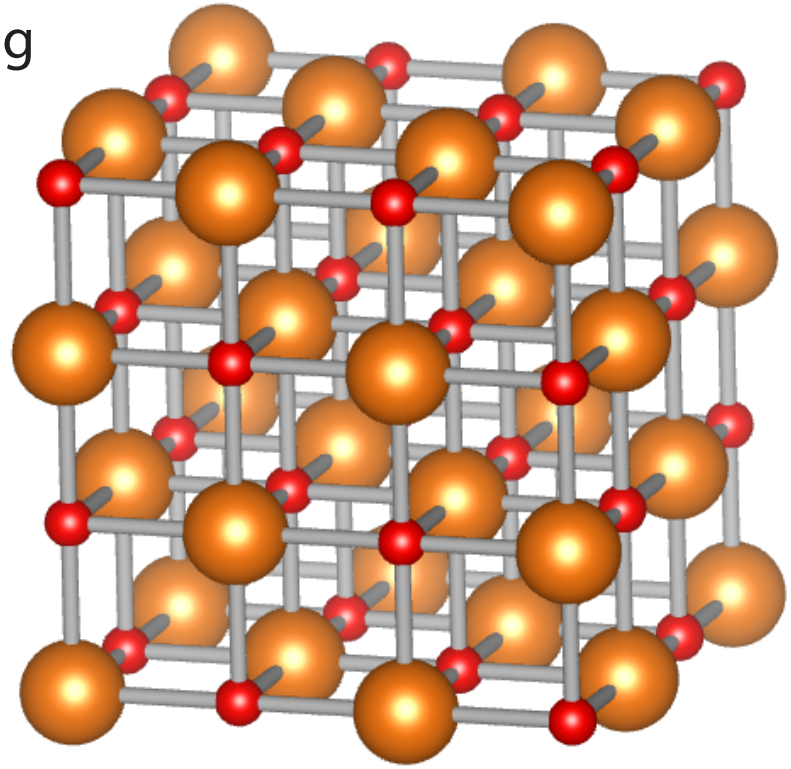
QMC for point defects in semiconductors and wide band-gap oxides

Elif Ertekin
Mechanical Science & Engineering, University of Illinois

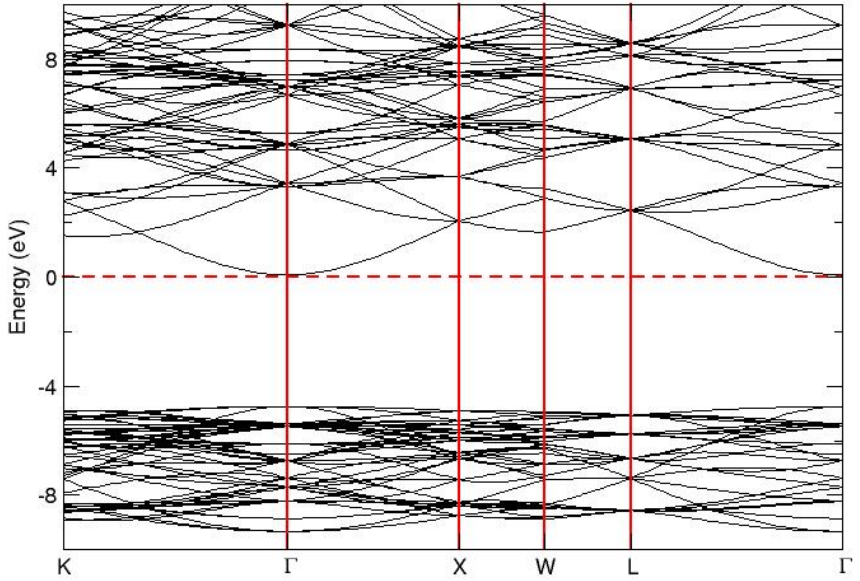
QMC@TTI, Vallico Sotto Italy. July 31 2013

Example: F-center Defect in MgO

Mg
O



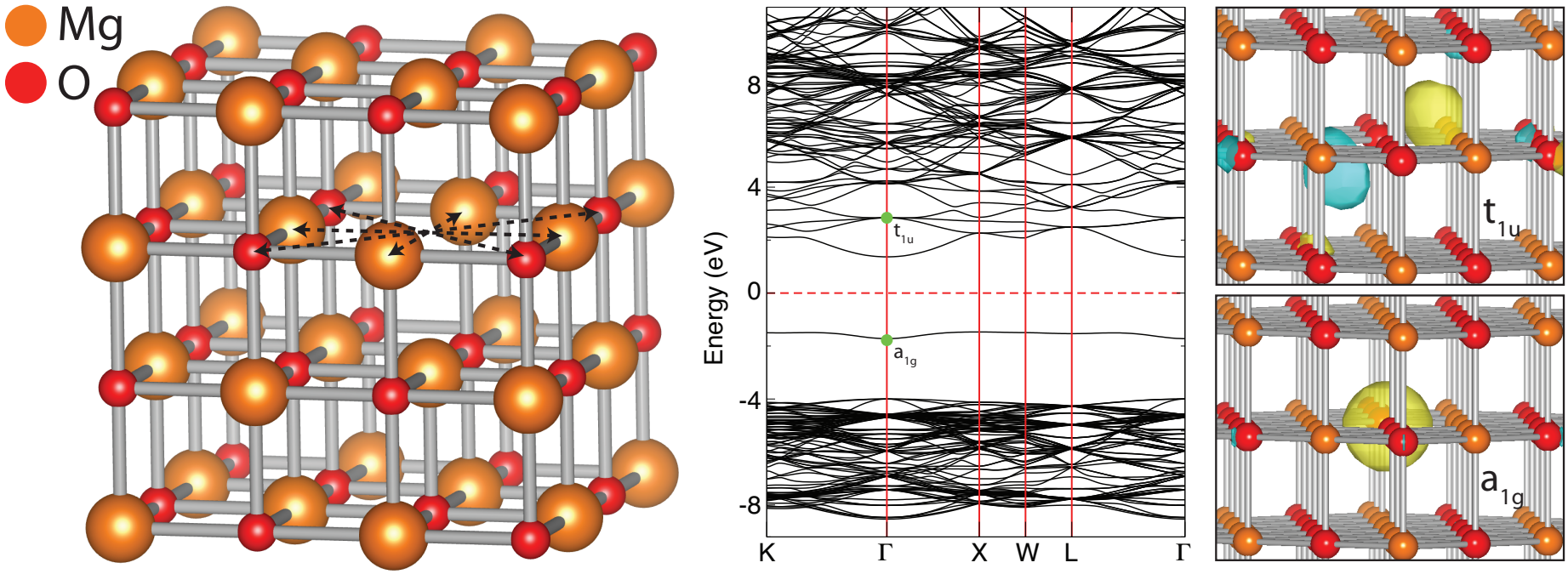
Electronic Band Structure from DFT-GGA



Experimental Gap: 7.81 eV
DFT Gap: 4.83 eV

Example: F-center Defect in MgO

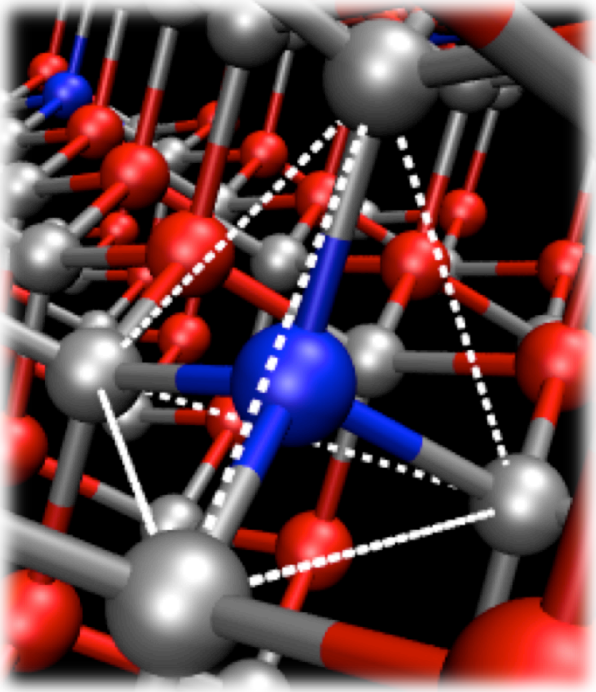
F-center Defect: Anion (O) Vacancy



A good hint why DFT struggles with point defect calculations: point defects introduce localized states into systems that otherwise have bulk-like (delocalized) states. DFT is unable to treat both types on an even footing – we need a theory that can.

Goal

example: Nitrogen impurities in ZnO



Explore the quantum Monte Carlo approach to calculating point defect properties

Zoo of Techniques

Method	Computational Scaling	Directly based on Schrödinger Equation?	Accurate Band Gap?	Accurate Total Energy?
DFT	~ CN_e^3	No	No	Sometimes
Hybrid DFT	~ $5*CN_e^{3-4}$	No	Often	Often
DFT+U	~ CN_e^3	No	When Fitted	Sometimes
GW	~ CN_e^4	Yes	Often	No
QMC	~ $100*CN_e^3$	Yes	Yes	Yes

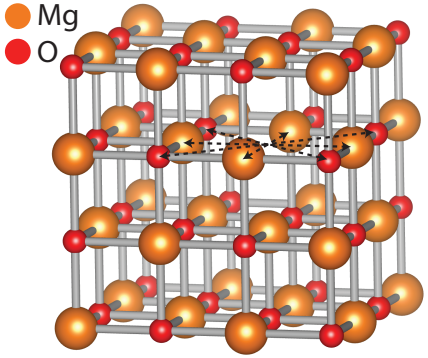
Point Defect Calculations in QMC

- **vacancy in diamond** :
  - R. Hood, P. Kent, R. Needs, P. Briddon. Phys. Rev. Lett. 91 035206 (2003)
- **magnesium oxide** :
  - Schottky Defect: D. Alfe, M. J. Gillan. Phys. Rev. B Rap. Commun. 71 (2005)
  - F-center defect: E. Ertekin, L. K. Wagner, J. C. Grossman, Phys. Rev. B (2013)
- **self-interstitials in silicon** :
  - Batista et al. Phys. Rev. B 74 121102 (2006)
  - Leung et al. Phys. Rev. Lett. 83 (1999)
  - Parker, Hennig. Phys. Stat. Sol. (2010)
- **vacancies, interstitials in alumimum**
  - R. Q. Hood, P. R. C. Kent, & F. A. Reboredo. *Phys. Rev. B* 85, (2012)
- **insulator-to-metal transition in highly-doped silicon**
  - E. Ertekin, M. T. Winkler, D. Recht, A. J. Said, M. J. Aziz, T. Buonassisi, J. C. Grossman. Phys. Rev. Lett. 108 026401 (2012).

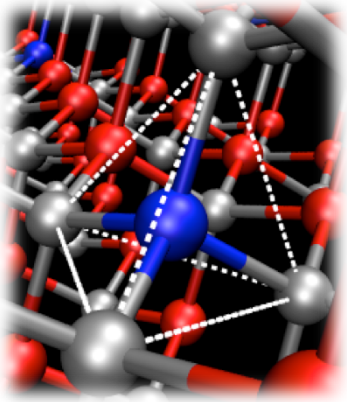
Discussion Topics

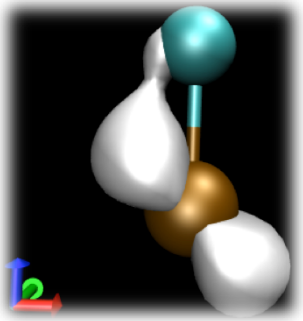
Thermal and Optical Ionization Energies of Point Defects

in Magnesium Oxide

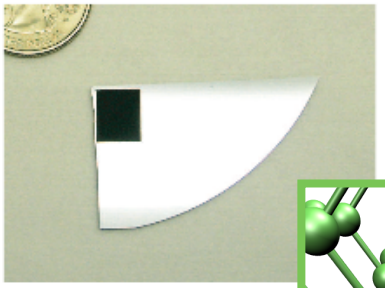


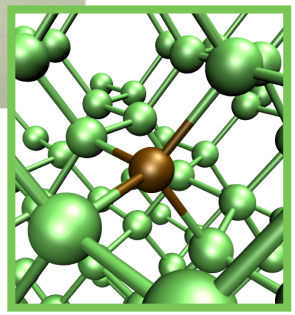
in Zinc Oxide

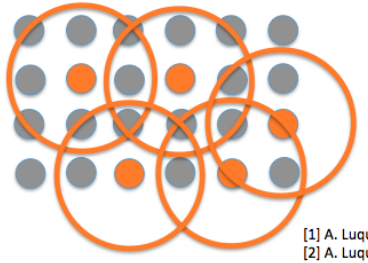




Metal-Insulator Transition in Chalcogen-Hyperdoped Silicon





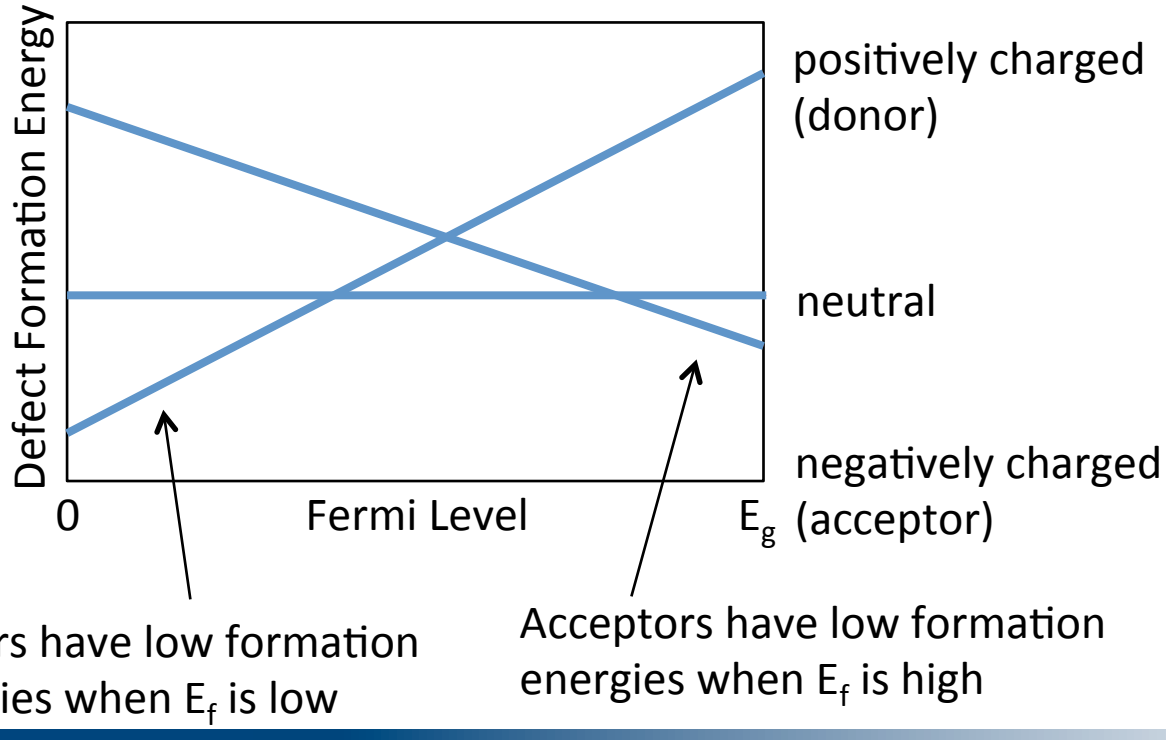


[1] A. Luque
[2] A. Luque

3 Properties of Interest

- Defect Formation Energies
- Thermal Ionization Energies
- Optical Ionization Energies

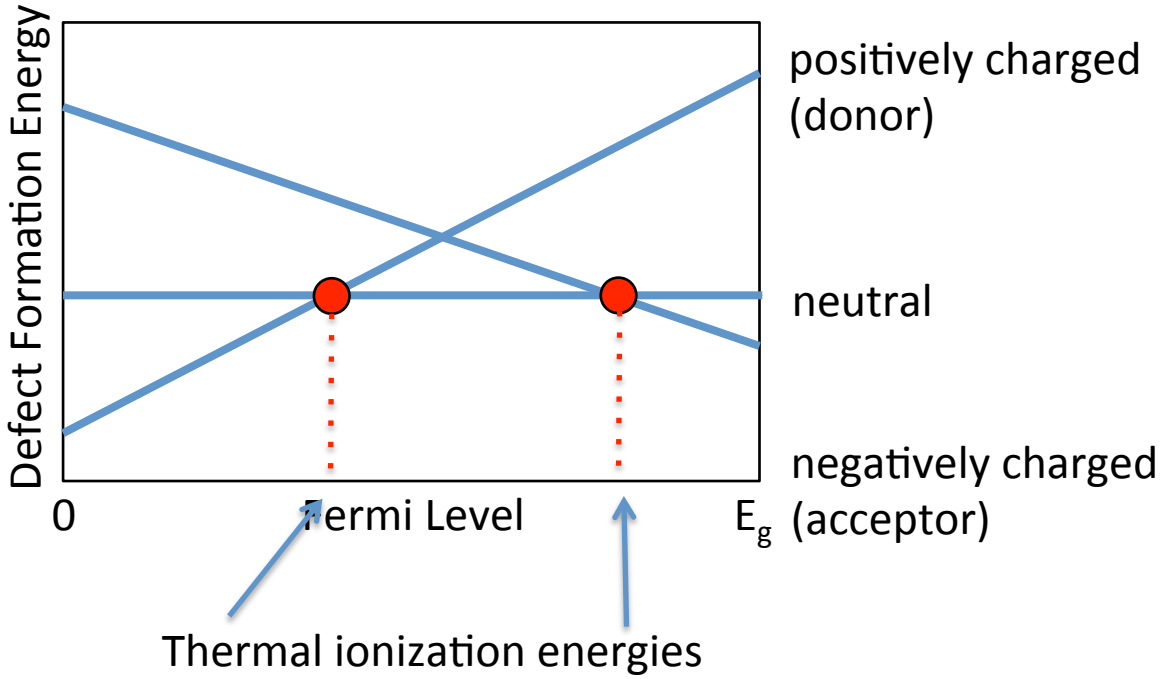
$$\Delta E_f = (E_{D,q} - E_{perf}) + \sum_i n_i \mu_i + q(E_V + E_F)$$



3 Properties of Interest

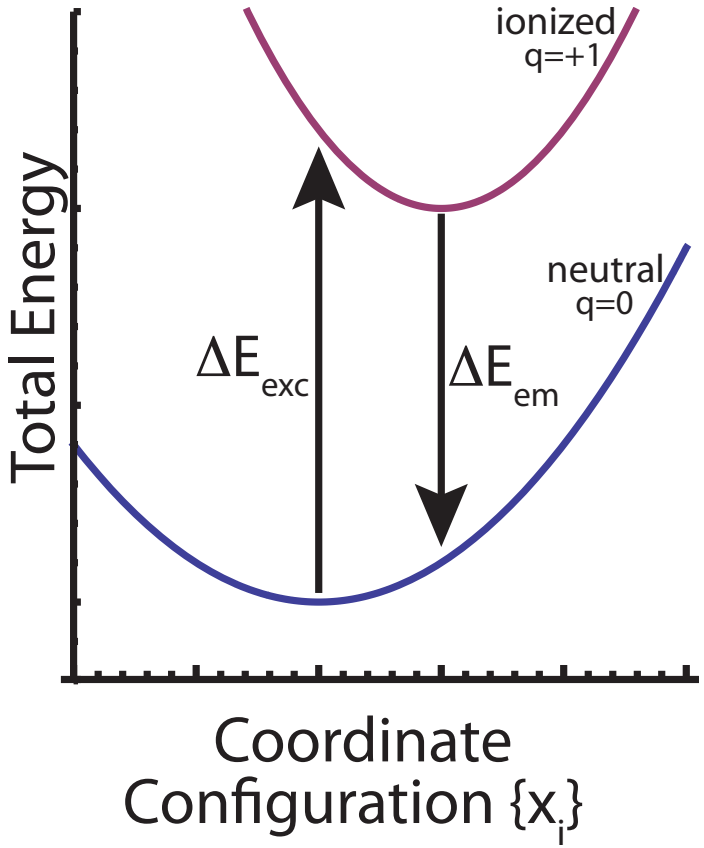
- Defect Formation Energies
- Thermal Ionization Energies
- Optical Ionization Energies

$$\Delta E_f = (E_{D,q} - E_{perf}) + \sum_i n_i \mu_i + q(E_V + E_F)$$



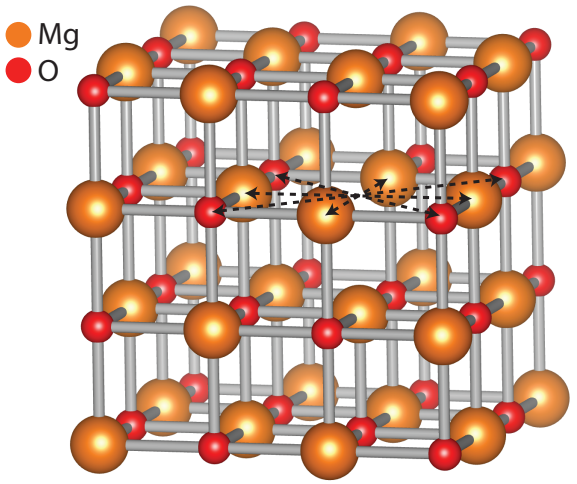
Properties of Interest

- Defect Formation Energies
- Thermal Ionization Energies
- Optical Ionization Energies



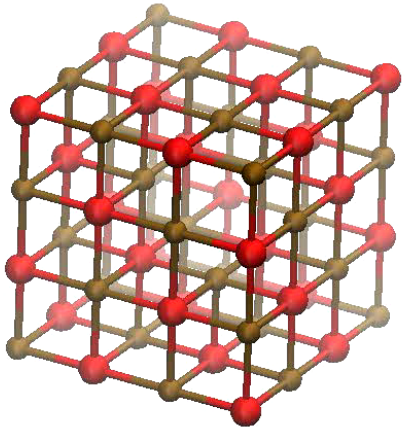
Geometries of MgO F-Centers

	Pure	F	F^+	F^{+2}
Mg-Mg distance (A)	2.98			
O-O distance (A)	5.96			
Relaxation Energy (eV)	--			



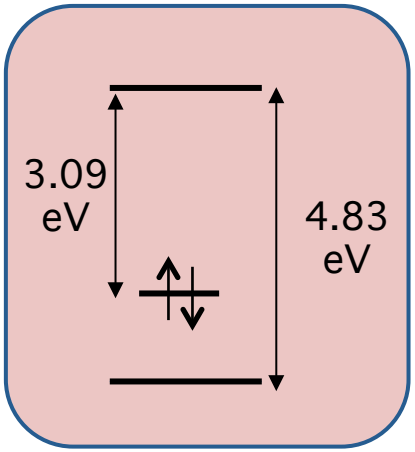
Geometries of MgO F-Centers

F - Center



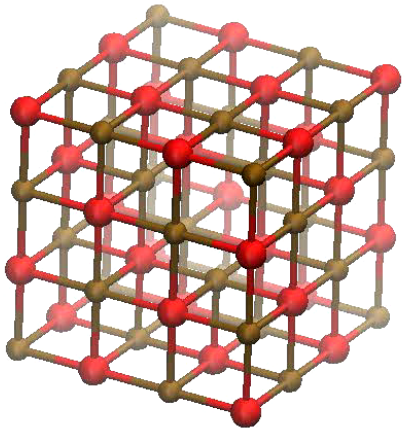
	Pure	F	F^{+}	F^{+2}
Mg-Mg distance (A)	2.98	2.97		
O-O distance (A)	5.96	5.97		
Relaxation Energy (eV)	--	0.003		

Exp: 5.00 eV

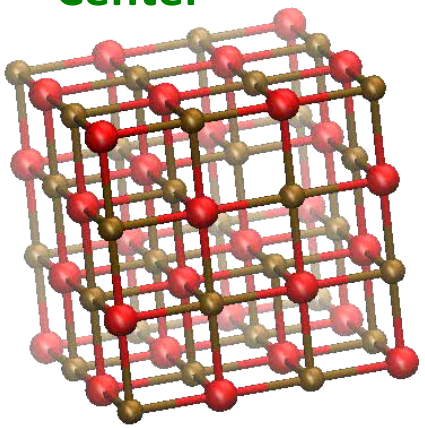


Geometries of MgO F-Centers

F - Center

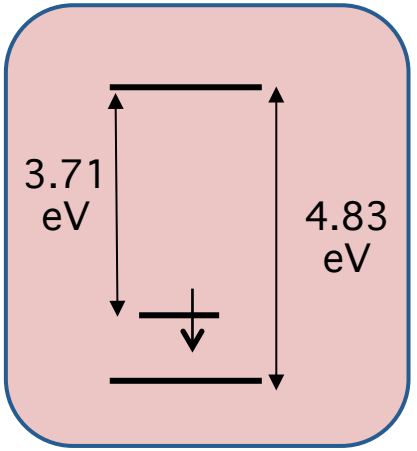


F^+ - Center



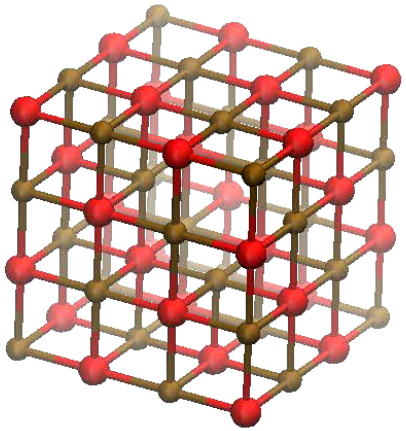
	Pure	F	F^+	F^{+2}
Mg-Mg distance (A)	2.98	2.97	3.09	
O-O distance (A)	5.96	5.97	5.89	
Relaxation Energy (eV)	--	0.003	0.545	

Exp: 4.95 eV

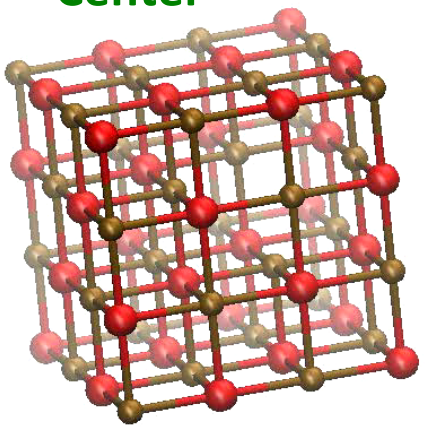


Geometries of MgO F-Centers

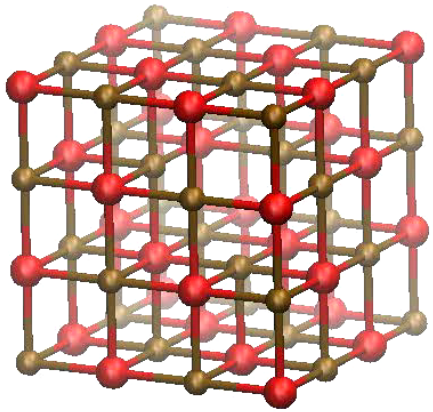
F - Center



F^{+} - Center

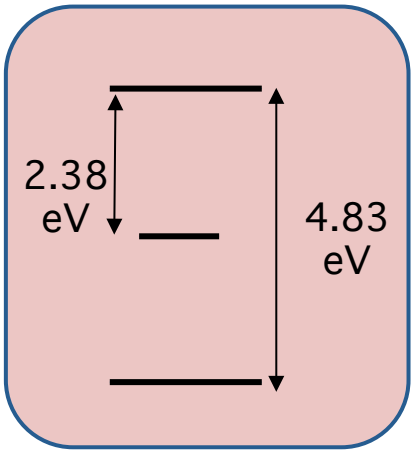


F^{+2} - Center



	Pure	F	F^{+}	F^{+2}
Mg-Mg distance (A)	2.98	2.97	3.09	3.18
O-O distance (A)	5.96	5.97	5.89	5.82
Relaxation Energy (eV)	--	0.003	0.545	1.182

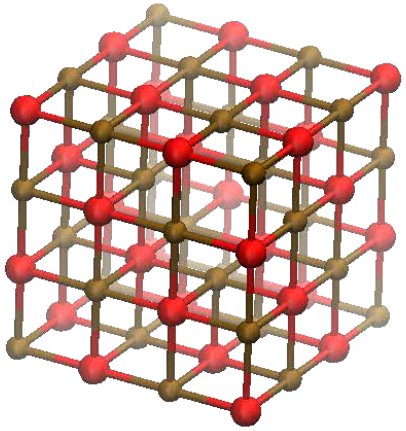
Exp: 2.3 eV



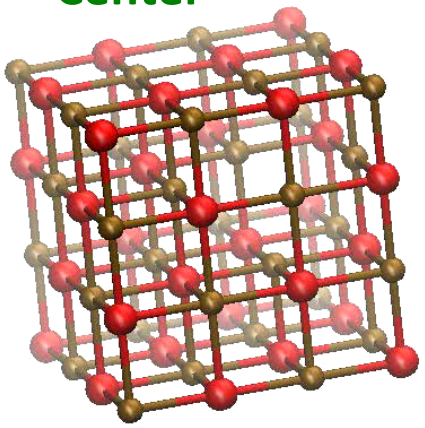
Geometries of MgO F-Centers

Approach for QMC: Use the DFT-optimized geometries for F, F^{+}, F^{+2}, and then find the corresponding energies in FN-DMC

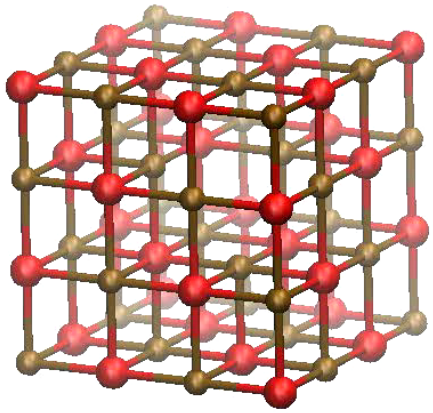
F - Center



F^{+} - Center



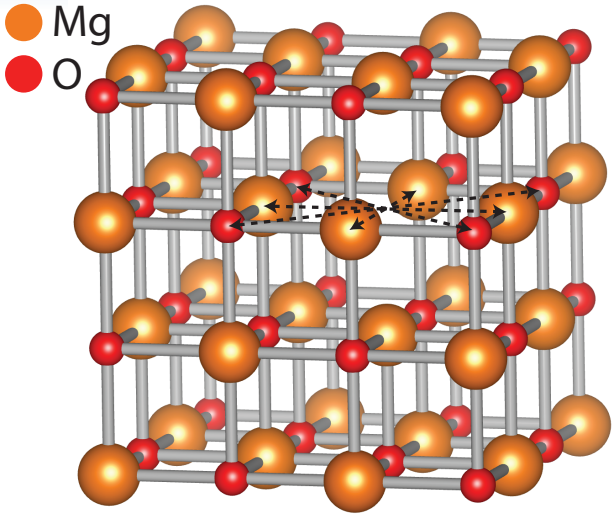
F^{+2} - Center



	Pure	F	F^{+}	F^{+2}
Mg-Mg distance (A)	2.98	2.97	3.09	3.18
O-O distance (A)	5.96	5.97	5.89	5.82
Relaxation Energy (eV)	--	0.003	0.545	1.182

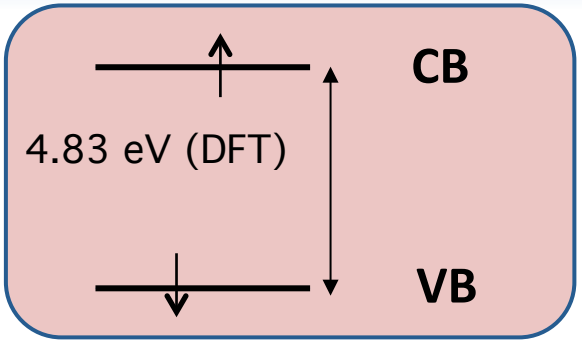
DFT-computed geometric parameters

MgO Optical Properties



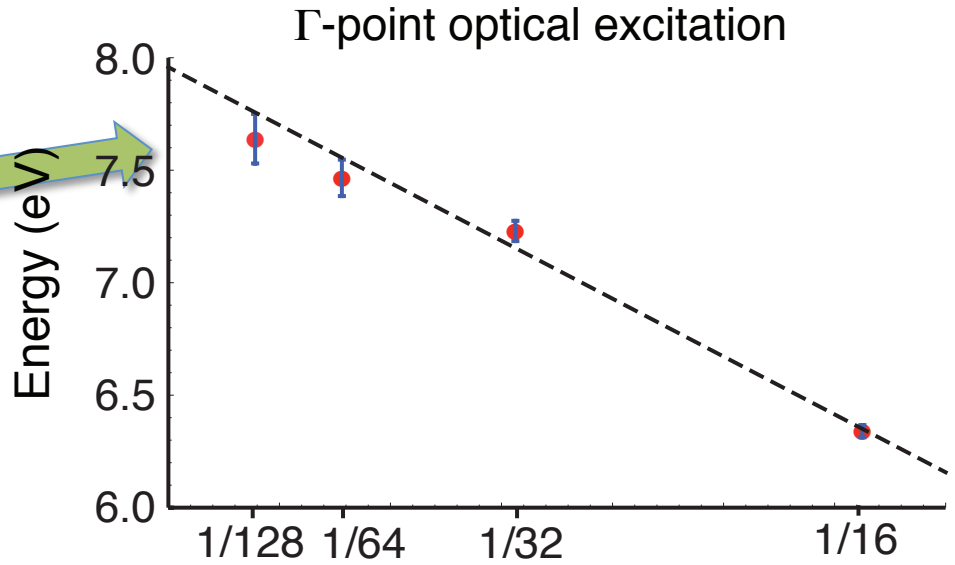
Optical Gap : 7.81 eV (experimental)

DFT description:



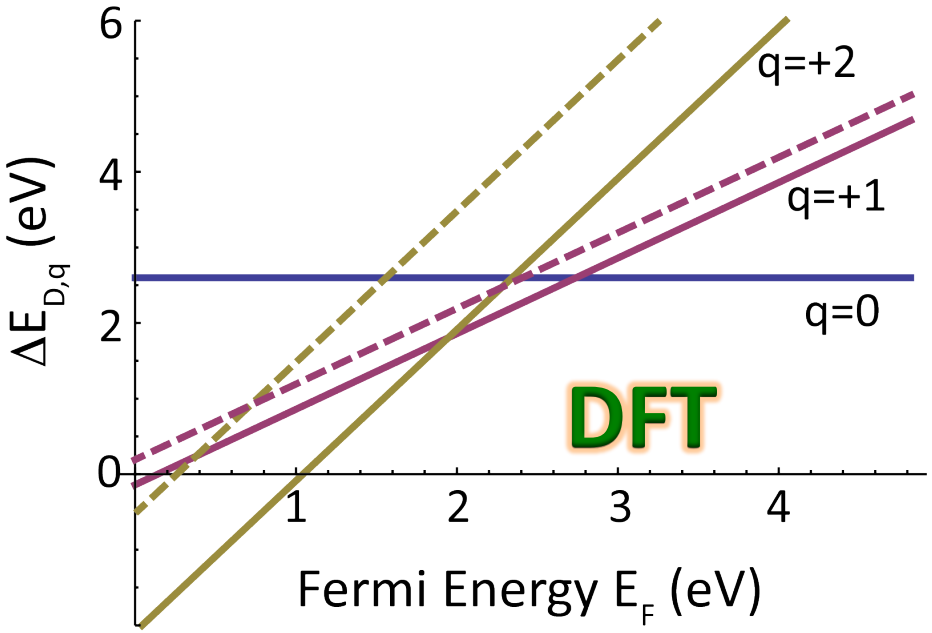
QMC description:

- Calculating of a gap requires many calculations for cells of different sizes in QMC, coupled with an extrapolation to infinite size
- Extrapolated value is 7.96(0.06) eV
- NB: I use a similar extrapolation scheme to obtain IP, EA



Thermal Ionization Energies

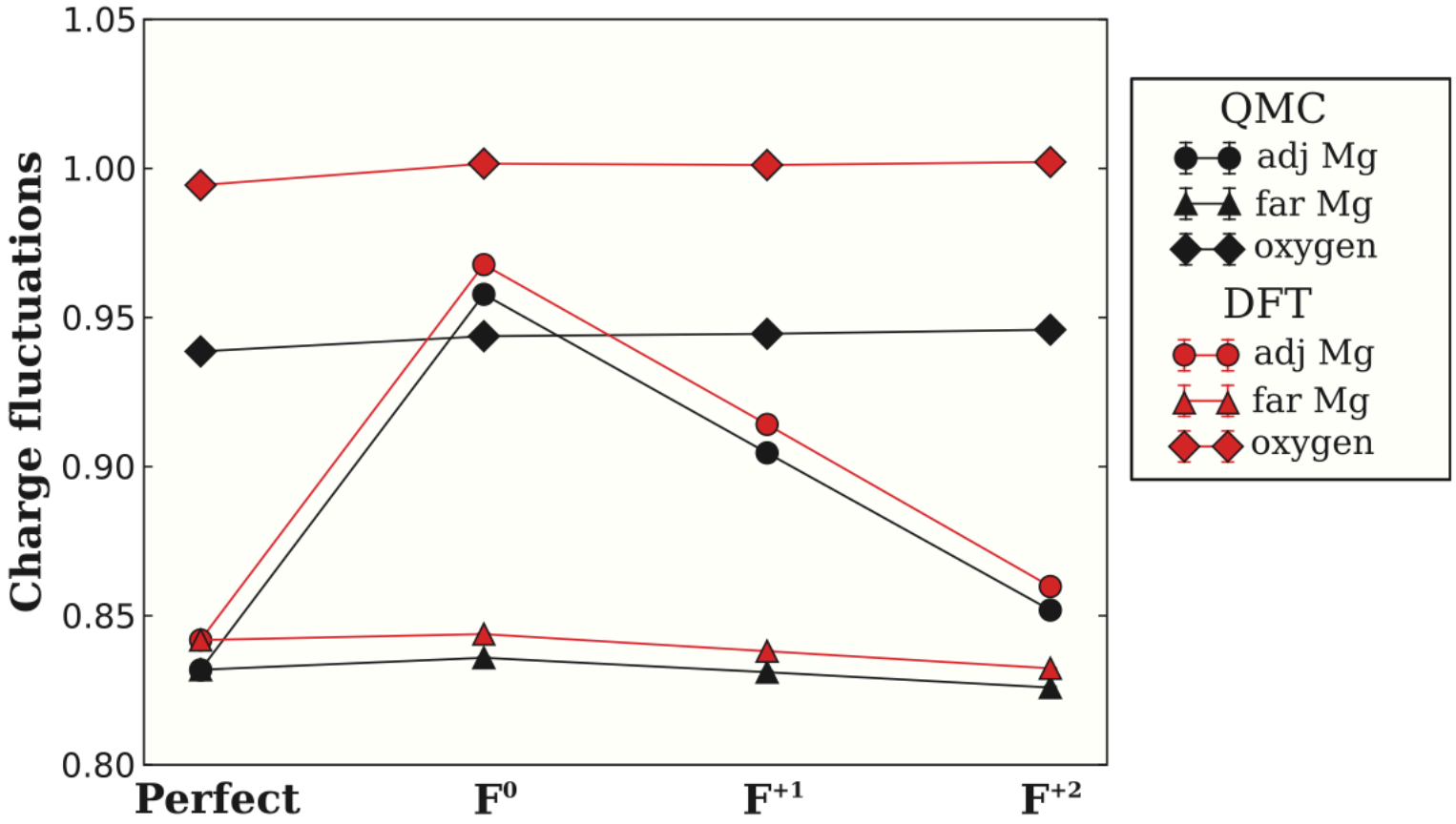
- Starting many-body wave functions for QMC calculations are constructed via Slater determinants, using single-particle Kohn-Sham orbitals from DFT



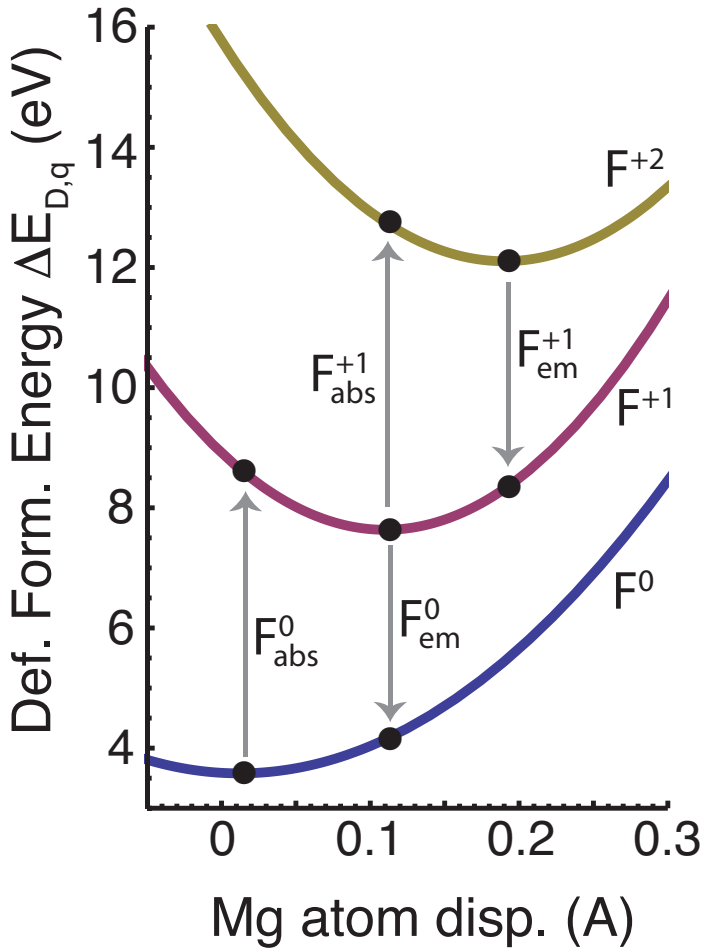
- In this case, both descriptions put the transition levels in the middle of the gap
- Note large difference in the range for the Fermi energy
- Charged image interaction problems

analysis

site-resolved charge fluctuations $\langle \psi | \left(n_i - \langle n_i \rangle \right)^2 | \psi \rangle$

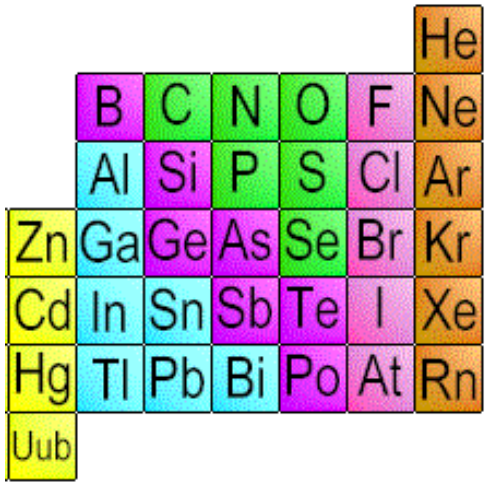


Optical Transitions



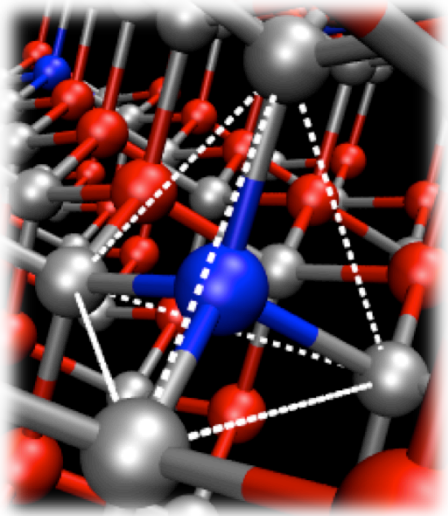
* *Rinke, Schleife, et al., PRL 2012*

Doping in Zinc Oxide

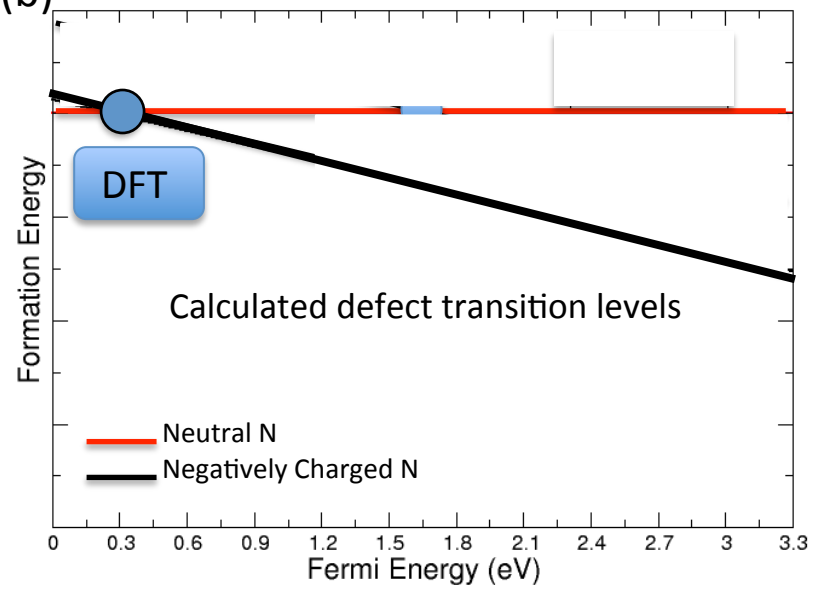


- Nitrogen : candidate for p-type ZnO
- Lots of experimental scatter in the literature
- Conventional DFT: N is a shallow acceptor in ZnO
- Hybrid functionals and GW results put the level deep in the gap

(a)

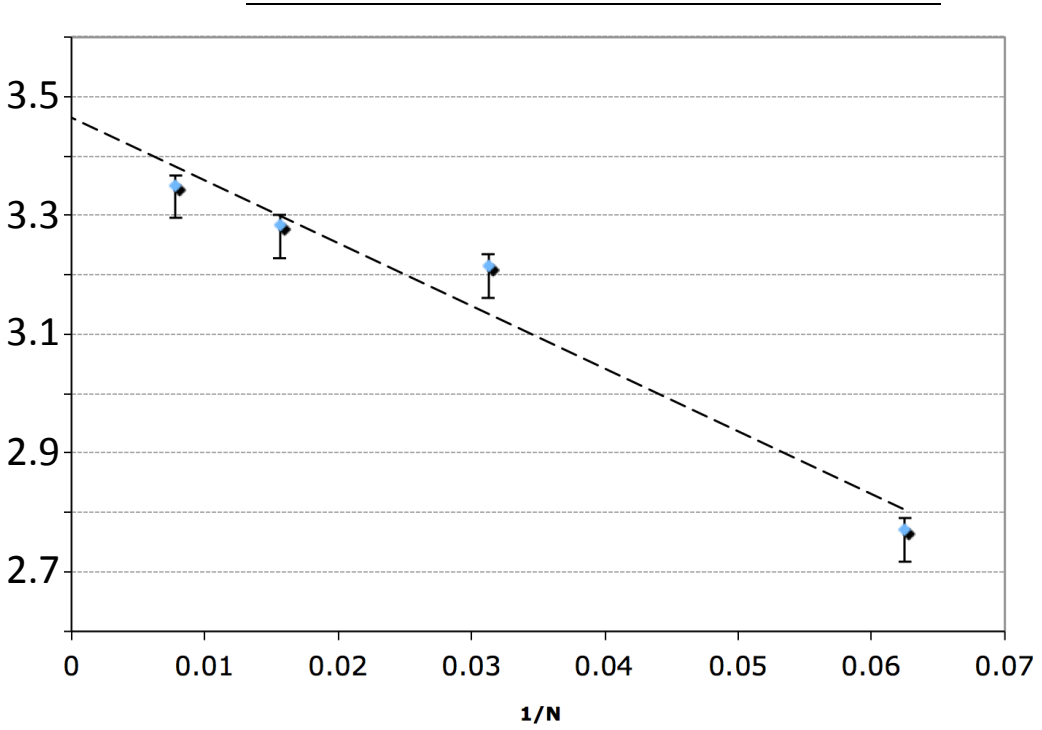


(b)



ZnO : challenging

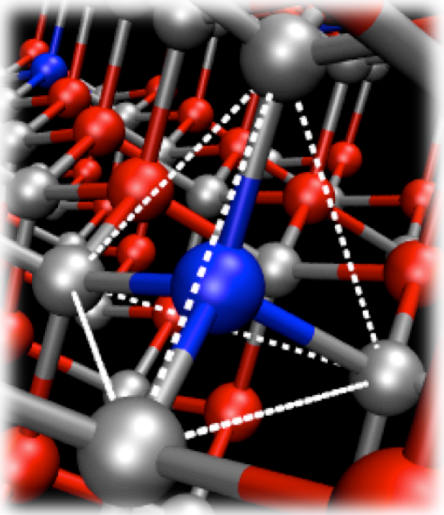
- d-orbitals from Zn atoms, p-orbitals from O atoms
- d-p hybridization – similar to what we heard before
- results in over-metallic description, and a DFT-PBE gap of 0.74 eV (vs. 3.4 in exp)
- compare to the QMC gap of 3.4(1) eV.



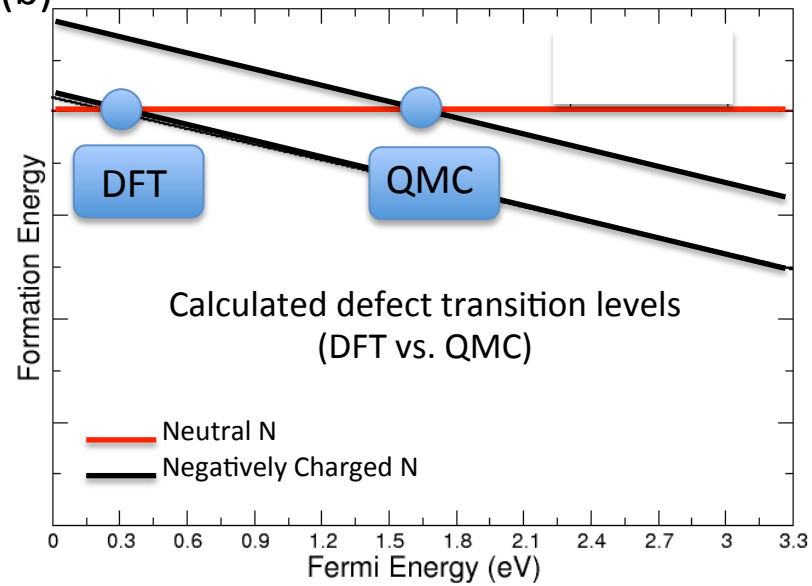
- **Approach: Use the DFT-optimized geometries, and compute the corresponding energies for the N and N^- defects via QMC**
- **For now, we use DFT-based estimates of charged image interactions (obtained via finite size extrapolation)**

N in ZnO According to QMC

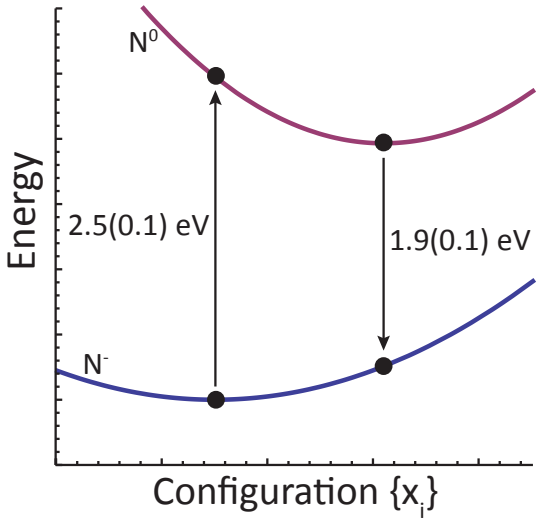
(a)



(b)



(c)

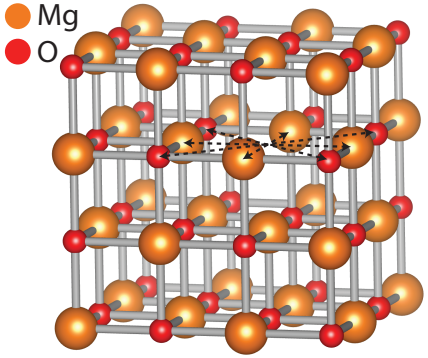


- According to QMC, N is deep
  - defect level occurs at 1.62(0.14) eV above the VBM
- Unlike MgO, in this case QMC changes the nature of the defect
- QMC results compare favorably to recent experiments and to other high-accuracy approaches:
  - 1.3 eV (Hybrid, van de Walle 2009), 1.6 eV (GW, Lany and Zunger 2010)
- Some caveats: 48 atom supercells (finite size effects < 0.3 eV)

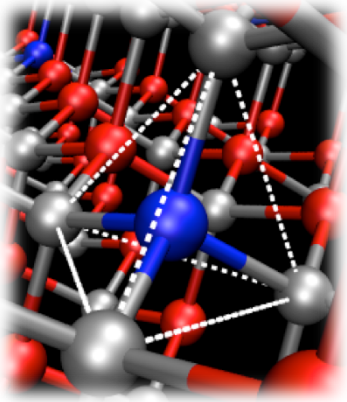
Discussion Topics

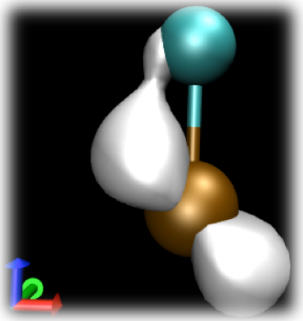
Thermal and Optical Ionization Energies of Point Defects

in Magnesium Oxide

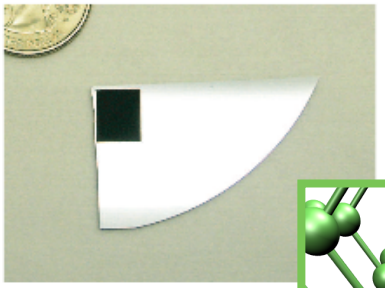


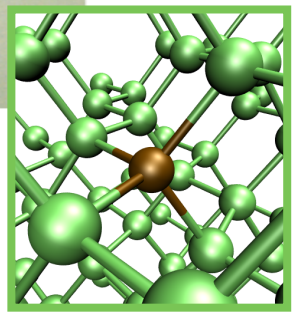
in Zinc Oxide

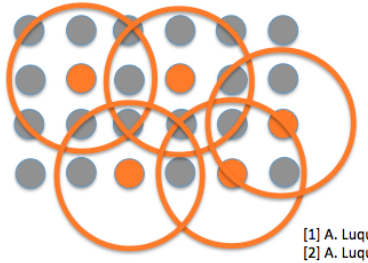




Metal-Insulator Transition in Chalcogen-Hyperdoped Silicon







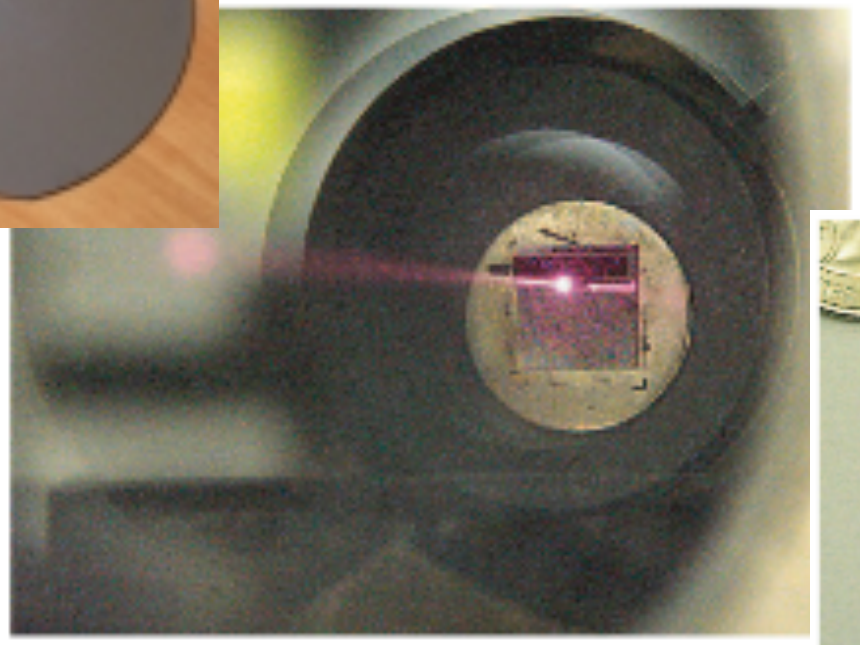
[1] A. Luque
[2] A. Luque

Laser Hyperdoping of Silicon

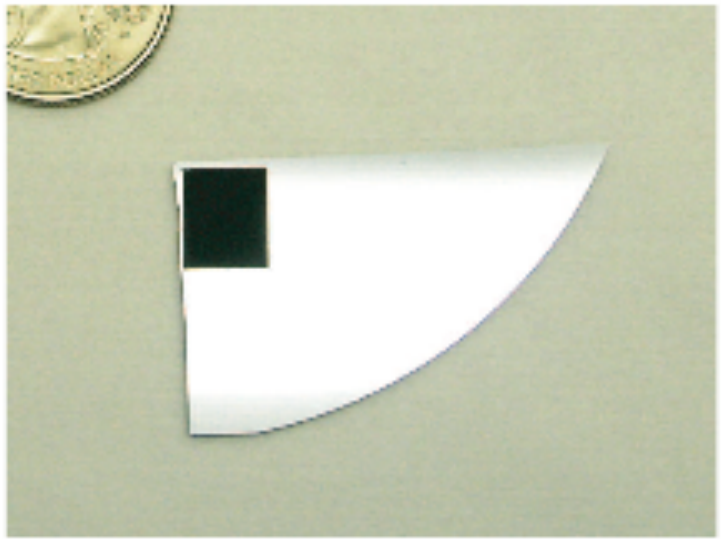
Experimental: Tonio Buonassisi Group, MIT, Mike Aziz (Harvard)

Start with c-Si wafer

Micro-structured with femtosecond or nanosecond laser pulses

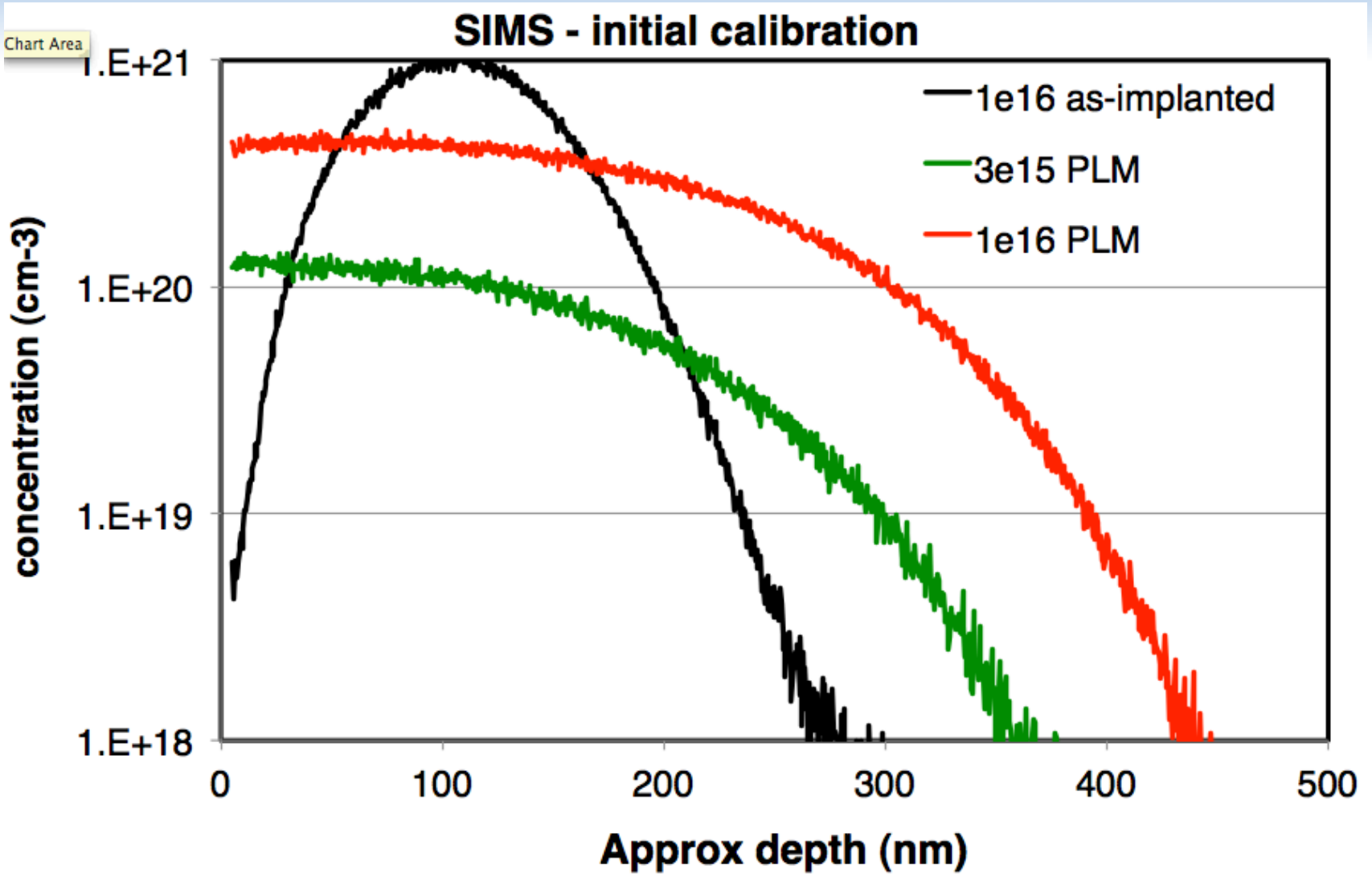


In the presence of a source of S, Se, or Te atoms



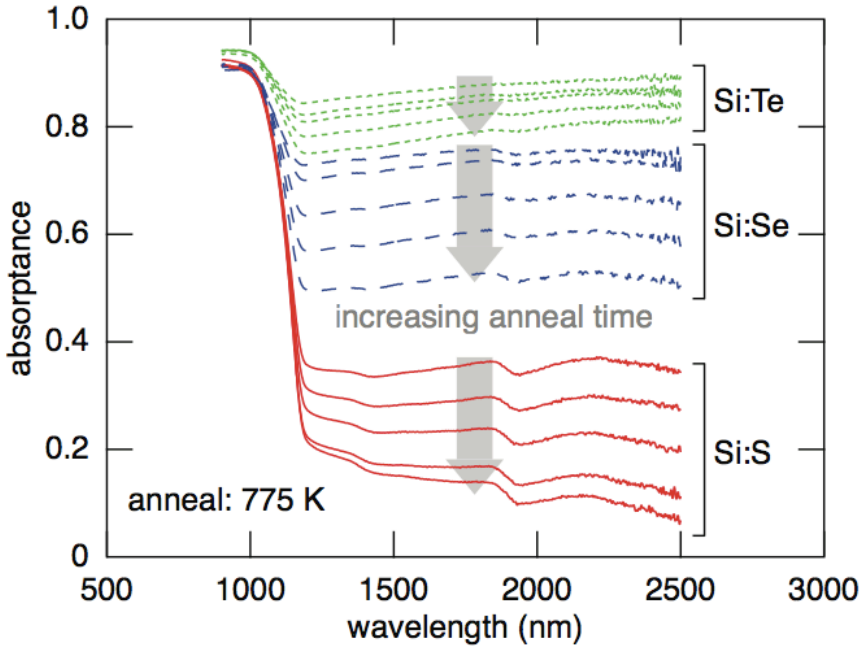
See: E. Ertekin, M. T. Winkler, et al., Phys. Rev. Lett. 2012.

Doping Concentration

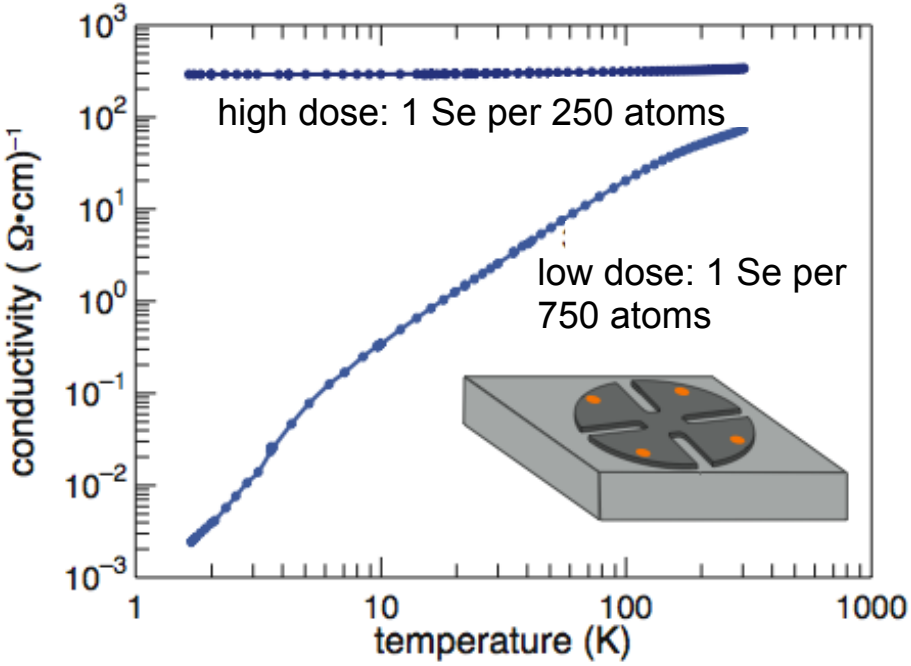


Silicon Hyperdoped with Selenium

experimentally measured properties ...



Tull, Winkler, Mazur. App. Phys. A 96 (2009)



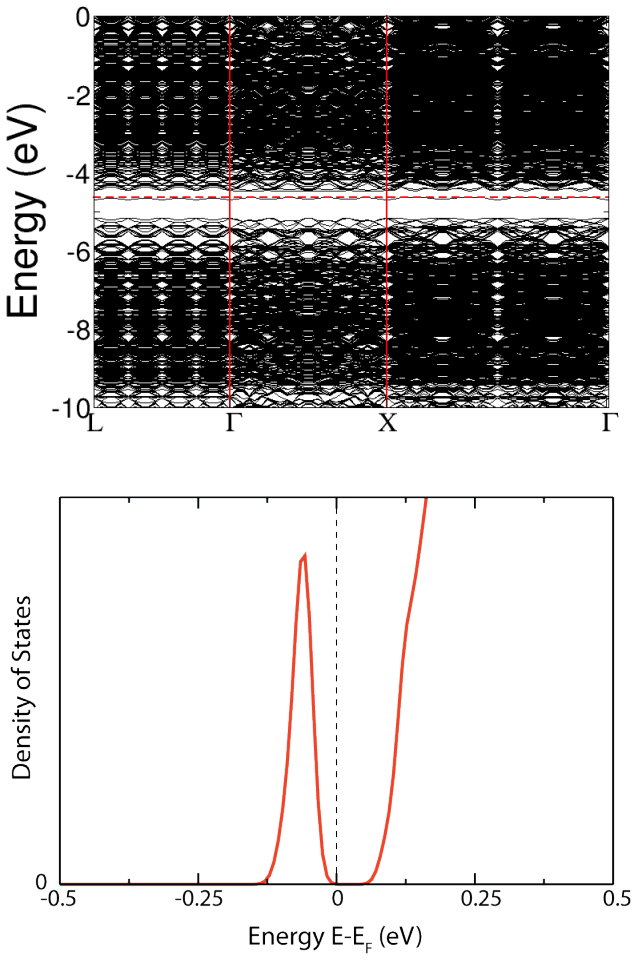
Courtesy: Mark Winkler, Tonio Buonassisi

- Enhanced optical absorption down to photon energies ~ 0.5 eV

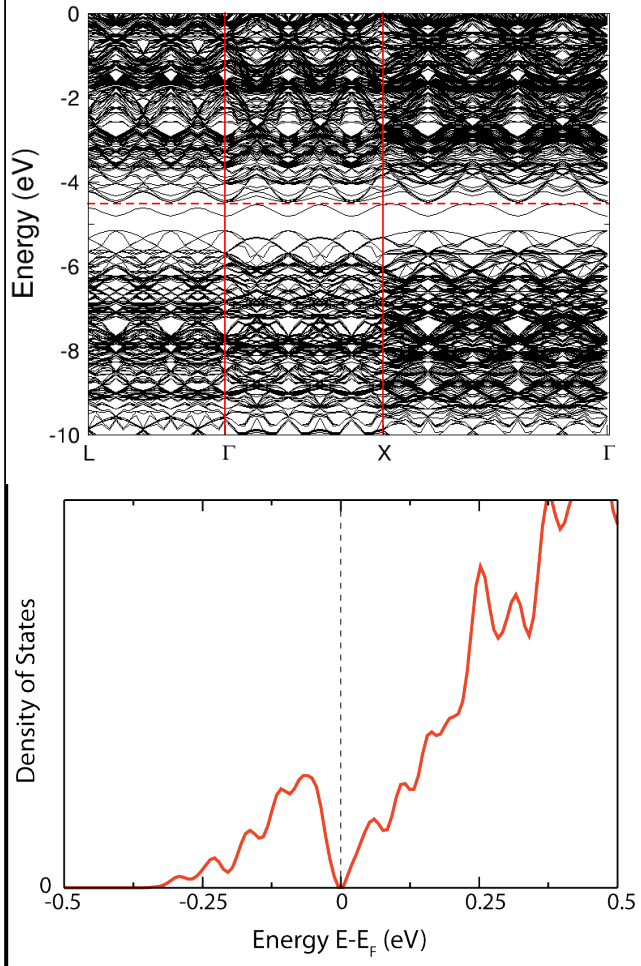
- Non-zero conductivity down to temperatures around T = 2K.

Band Structure/Density of States

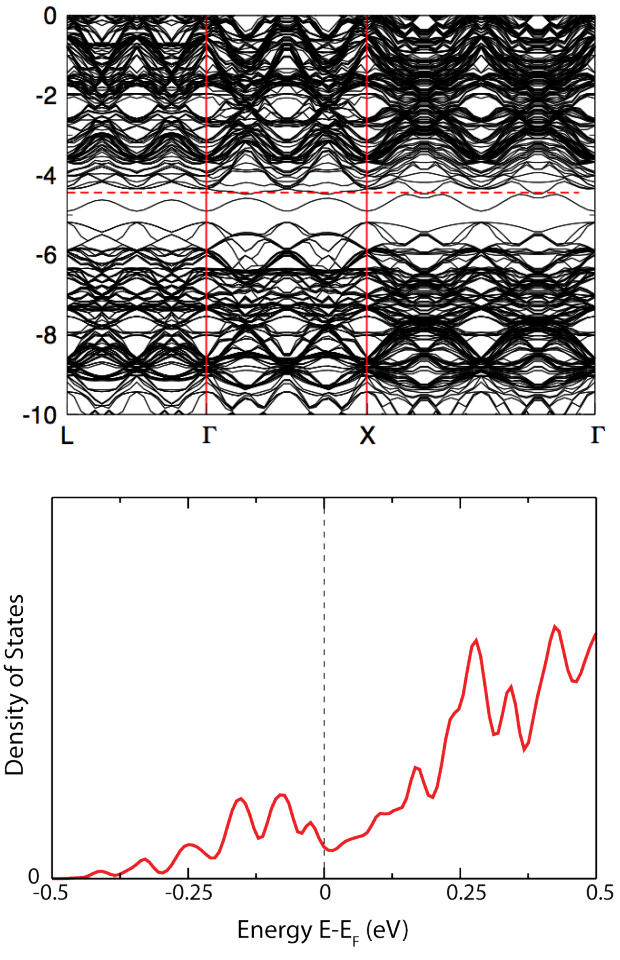
$Si_{1023}Se_1$



$Si_{249}Se_1$

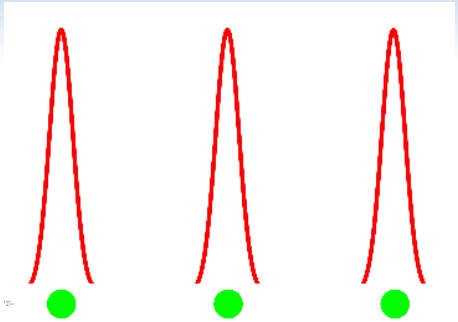


$Si_{127}Se_1$



Mott Metal Insulator Transition

Detailed mechanism for the observed behavior?



Low defect density:

- isolated, localized defect states.
- insulating character, electrons bound to impurity sites

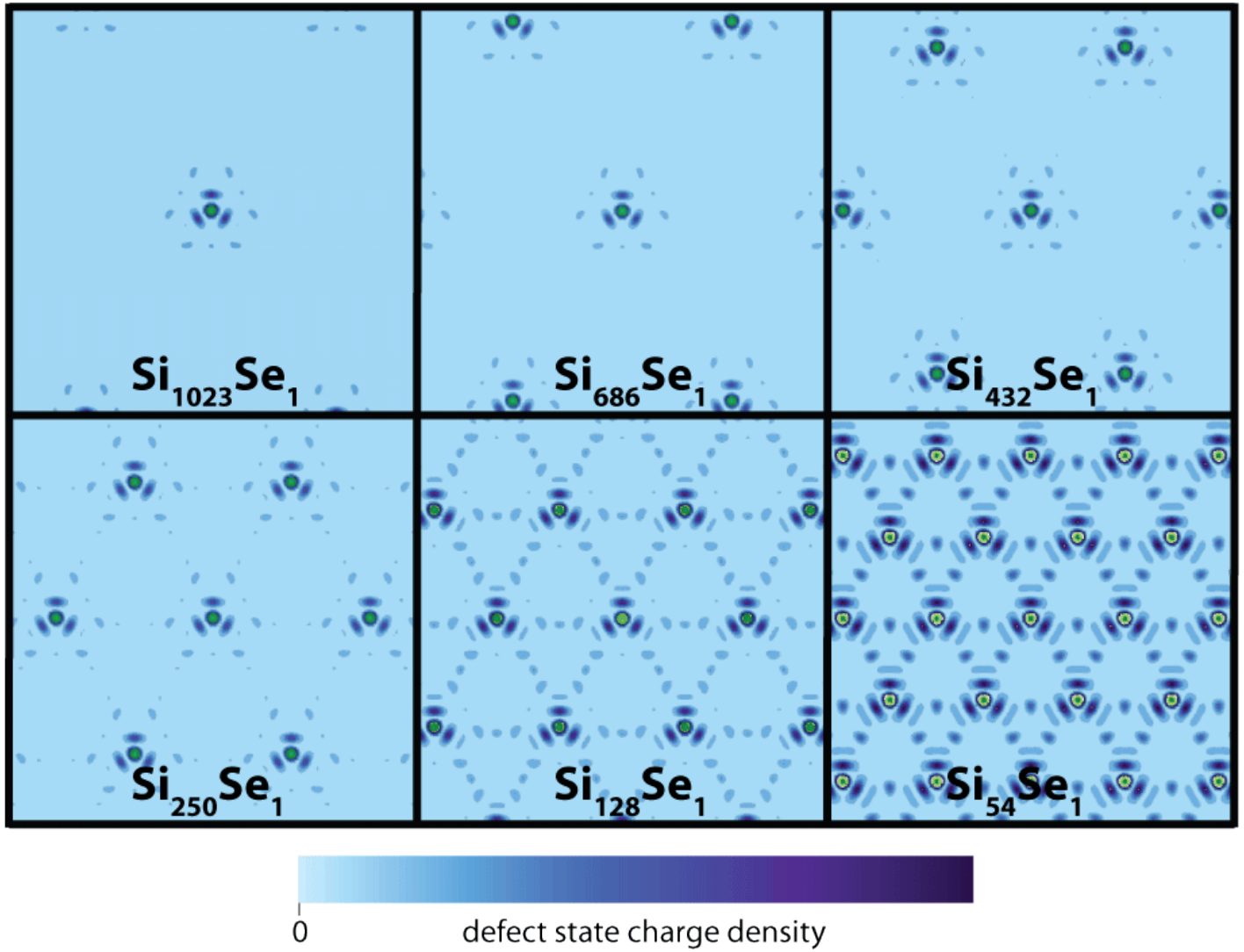
well-characterized for shallow defects in Si: P, Al, B, etc.

Mott

or Not(t)?

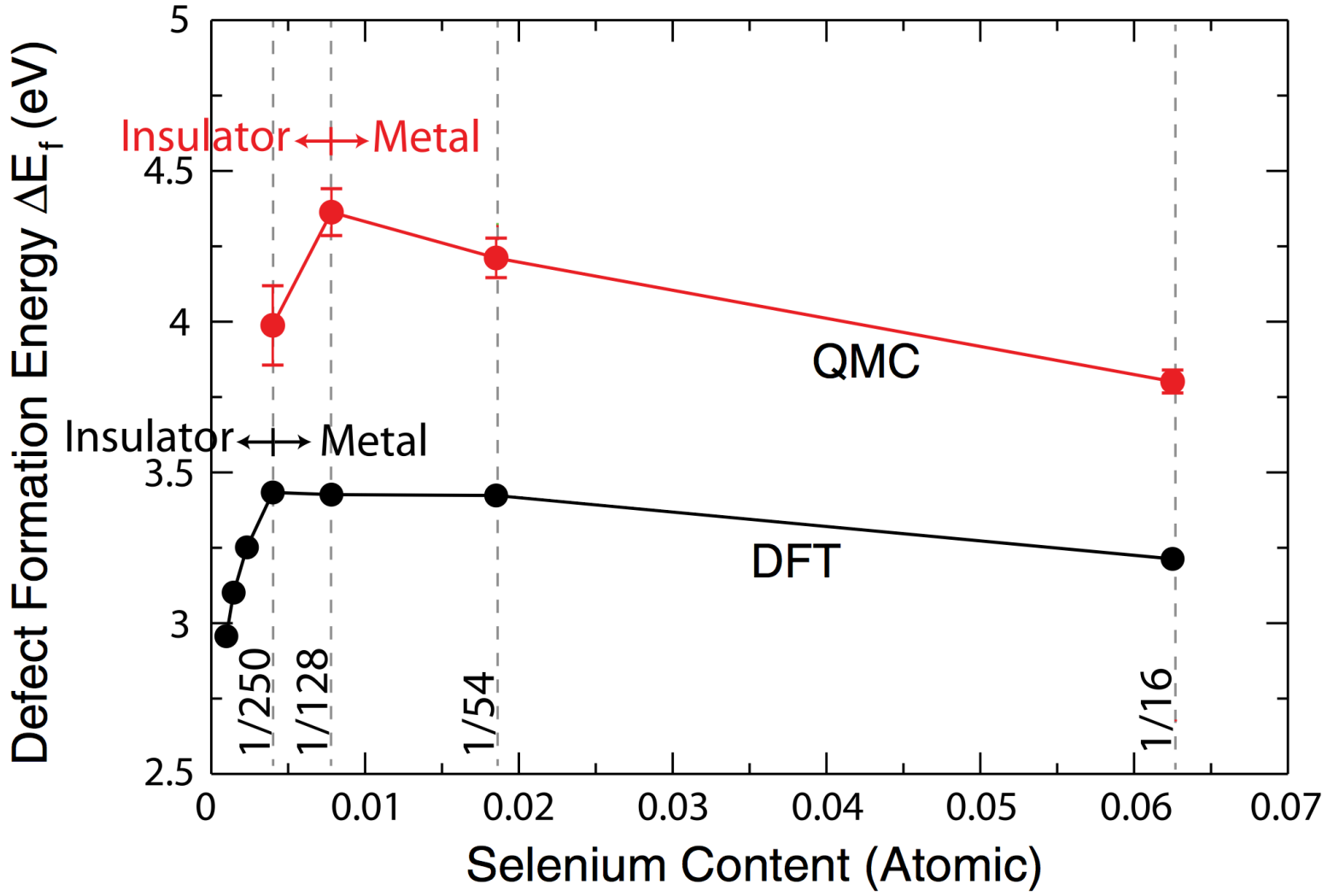
On the transition to metallic conduction in semiconductors
N. F. Mott, *Canadian Journal of Physics* **34** 12A pp. 1356 (1956).

Impurity State Charge Density



Defect Formation Energies

clues to the role of electron correlation at different defect densities



Conclusions

- Our preliminary efforts to apply this technique to point-defects in solids MgO, ZnO, and Si give promising results that compare favorably to experiment and/or other high-accuracy methods
- They also reveal some challenges
- Future Work: (lots … !)
  - QMC estimate of image-charge interactions
  - Application to other materials of interest
  - Physics-based studies of the DFT single vs. QMC many –particle descriptions

…THANK YOU FOR YOUR ATTENTION!

Computational resources: NERSC, XSEDE Extreme Science and Engineering Discovery Environment, NCSA

Work funded by: U.S. DEPARTMENT OF ENERGY