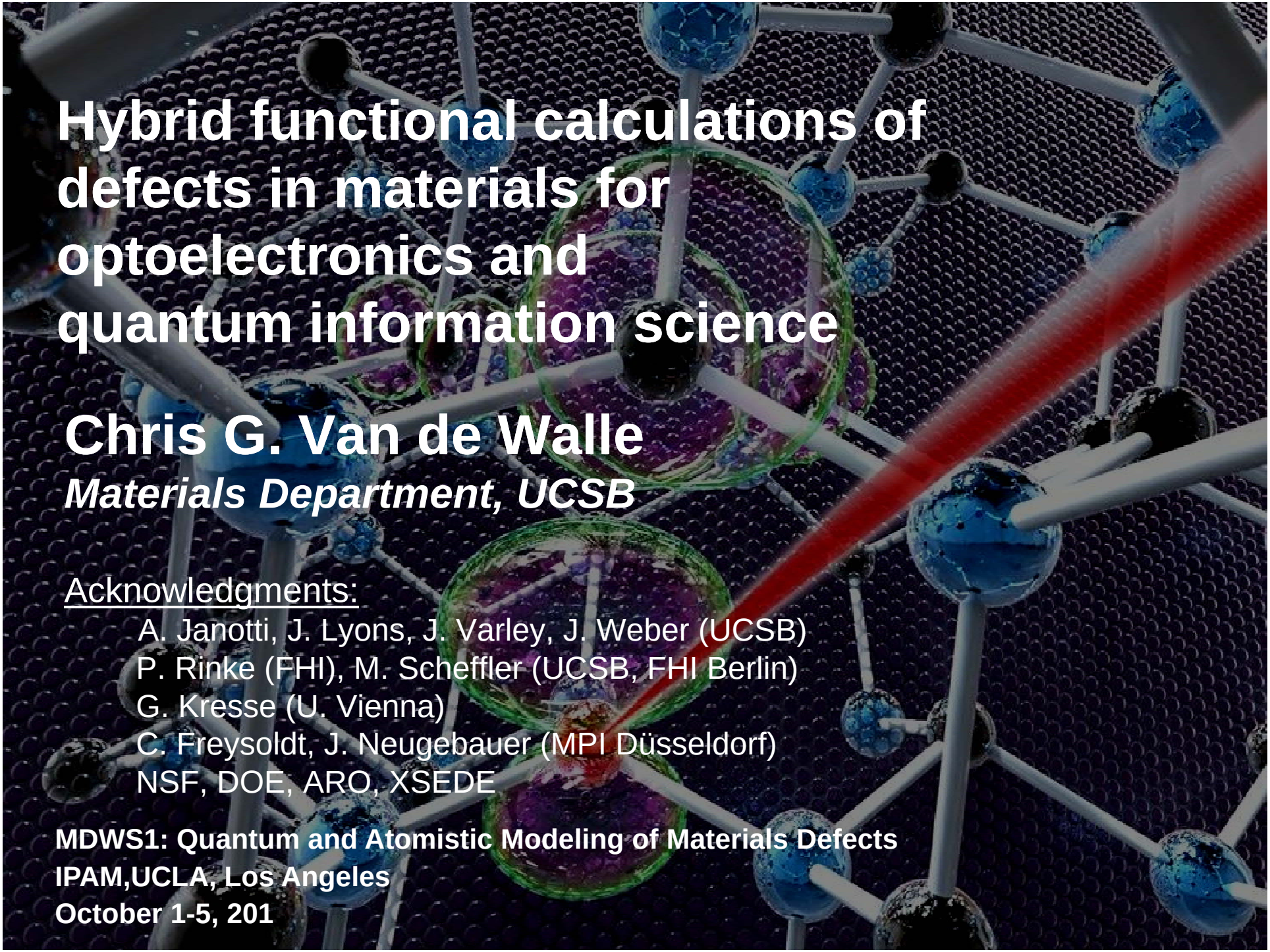

Hybrid functional calculations of defects in materials for optoelectronics and quantum information science

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A. Janotti, J. Lyons, J. Varley, J. Weber (UCSB)
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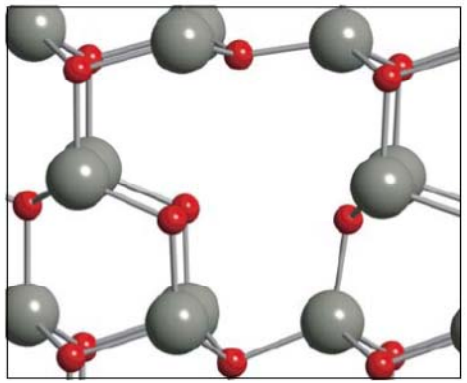
G. Kresse (U. Vienna)
C. Freysoldt, J. Neugebauer (MPI Düsseldorf)
NSF, DOE, ARO, XSEDE

MDWS1: Quantum and Atomistic Modeling of Materials Defects
IPAM,UCLA, Los Angeles
October 1-5, 201

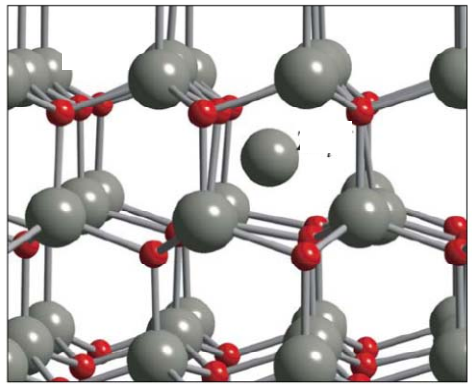
Why study defects?

- **"Defects"**
  - Extended defects
    - » dislocations
  - Point defects:
    - » Native defects
    - » Impurities
- **Defects often determine the properties of materials**
  - Doping and its limitations
  - Device degradation
  - Diffusion
    - » Mediated by point defects

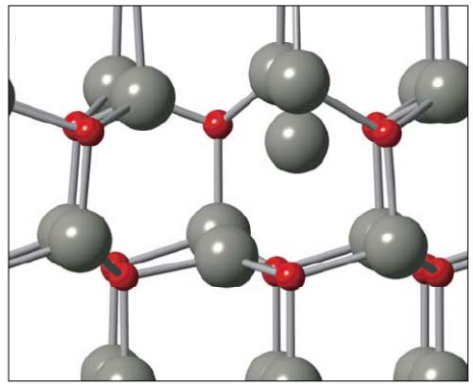
Vacancy



Interstitial



Antisite



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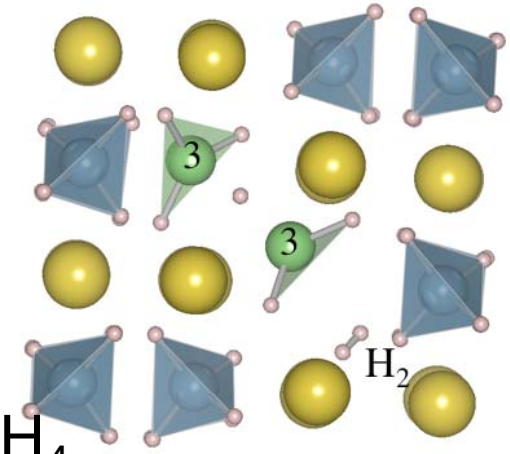
Technological significance

- **Semiconductors**
  - Achieve higher doping levels
    - » *p*-type doping of AlN would allow UV lasers
  - Controllably dope materials *p*-type and *n*-type
    - » Oxides
- **Photovoltaics**
  - $CuIn_xGa_{1-x}Se_2$
- **Hydrogen storage materials**
  - Kinetics of hydrogen release in $NaAlH_4$
- **Embrittlement of structural metals**



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First-Principles Calculations

- **Solve complex many-body problem for electrons in solid**
  - Nuclei treated classically (Born-Oppenheimer)
- **Replace with a single-particle problem:**

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

with $v_{\mathrm{KS}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_{\mathrm{H}}(\mathbf{r}) + v_{\mathrm{XC}}(\mathbf{r})$

potential due to nuclei

potential due to other electrons (Hartree)

exchange-correlation potential; captures many-body effects; functional of charge density

- **Density-functional theory (DFT)**
  - Highly valuable tool for studying defects
  - Very reliable for total energies and atomic structure

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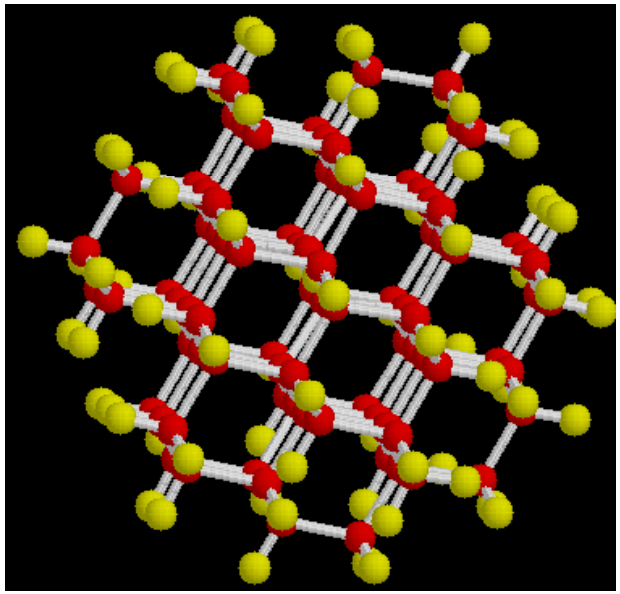
Defect calculations: geometry



- **Green's functions**
  - Implementation difficult
  - Non-intuitive
- **Clusters**
  - Surface effects
  - Not "bulk" (quantum confinement)
- **Supercells: Periodic Boundary Conditions**
  - Need rigorous treatment of electrostatic interactions in dielectric media
    - » C. Freysoldt, J. Neugebauer, and C. G. Van de Walle, Phys. Rev. Lett. **102**, 106402 (2009).

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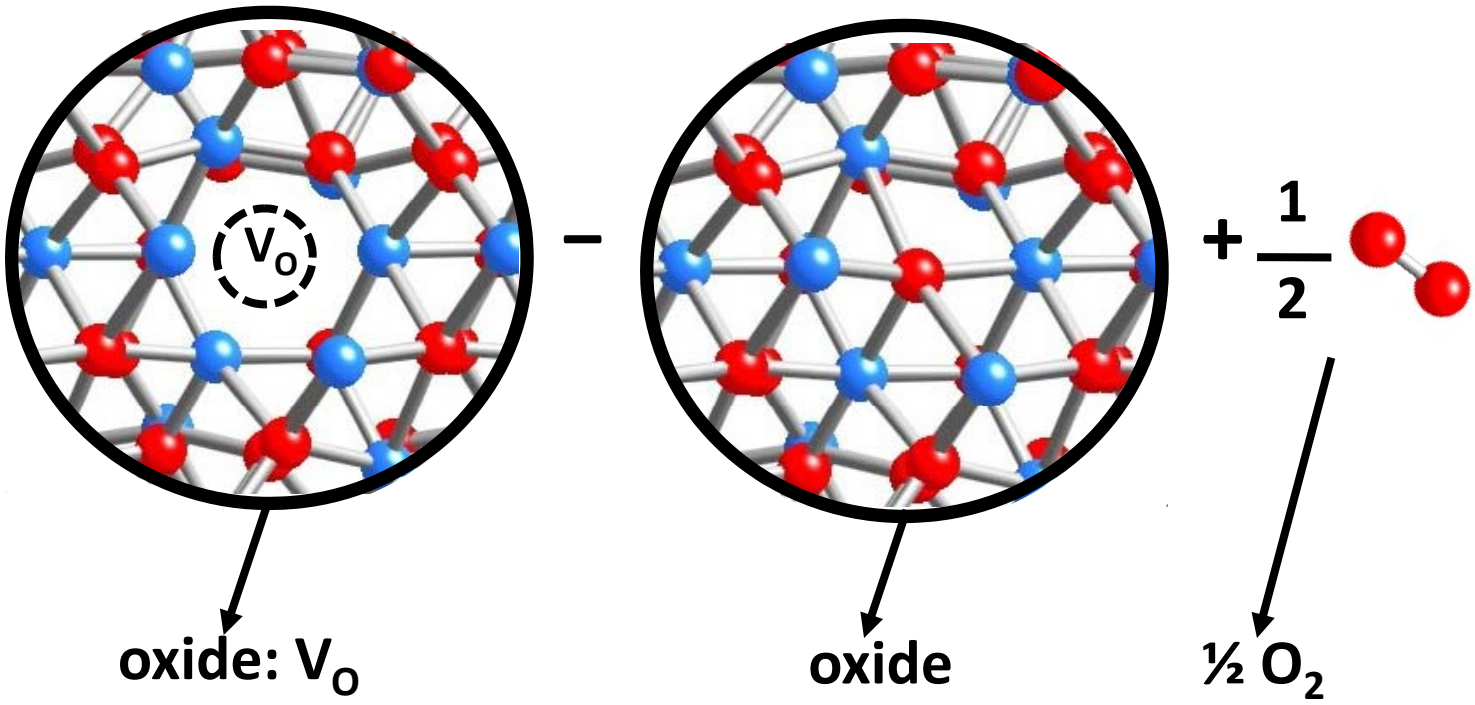
Defect Formation Energies

Example: oxygen vacancy (V_O) in ZnO



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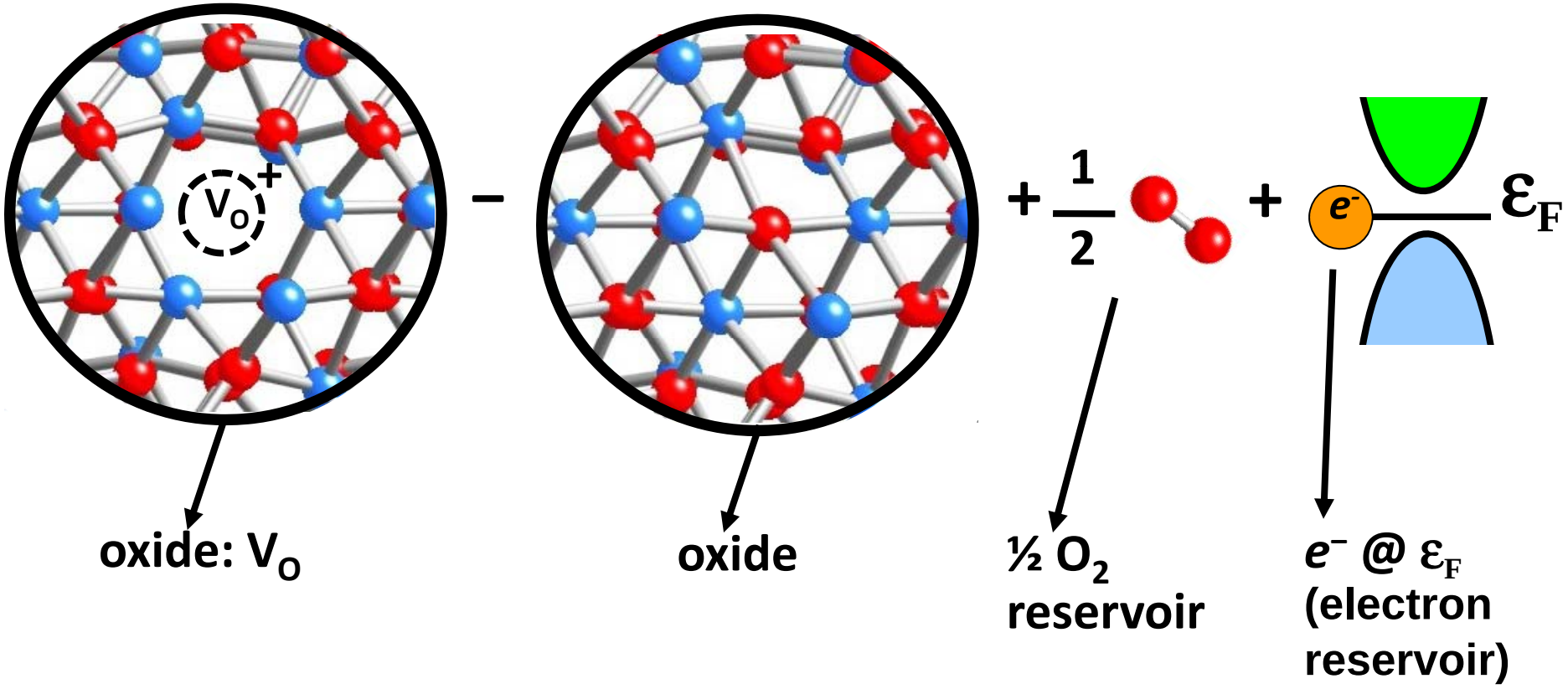
Defect Formation Energies

Example: oxygen vacancy (V_O) in ZnO



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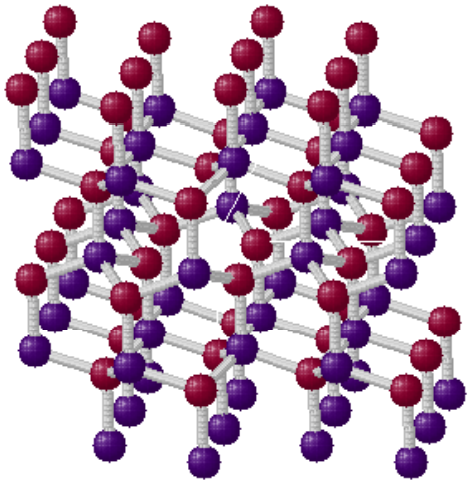
Formalism



- **E_{form}: formation energy**

  Concentration of defects or impurities:

  $C = N_{sites} \exp [- E_{form}/kT]$

- **Example: oxygen vacancy in ZnO**

  $E_{form}(V_O^+) = E_{tot}(V_O^+) - E_{tot}(\text{bulk}) + \mu_O + E_F$

  μ_O: energy of oxygen in reservoir, i.e., oxygen chemical potential

  E_F: energy of electron in its reservoir, i.e., the Fermi level

- **General expression**

  $E_{form}(D^q) = E_{tot}(D^q) - E_{tot}(\text{bulk}) + n_i \mu_i + qE_F$

  n_i: number of atoms being exchanged to form the defect

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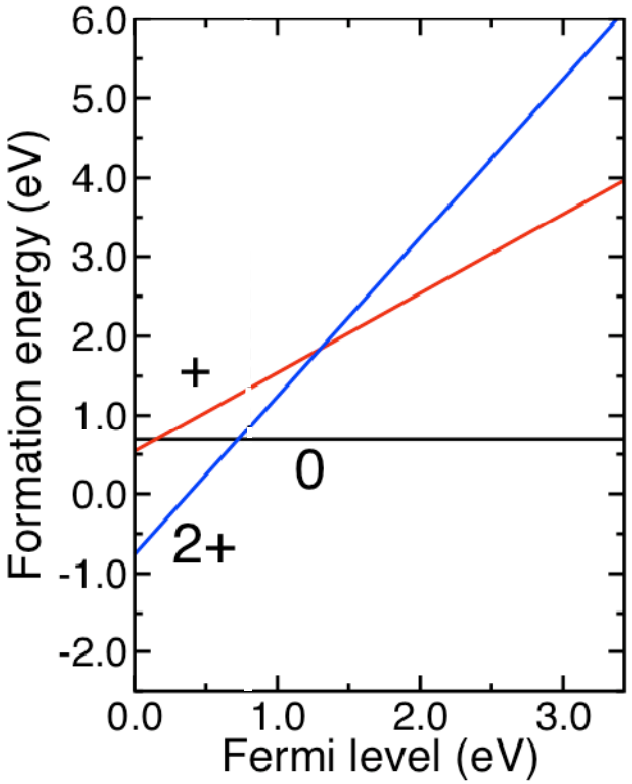
Formation energy



- V_O in ZnO
- DFT
- Local Density Approximation

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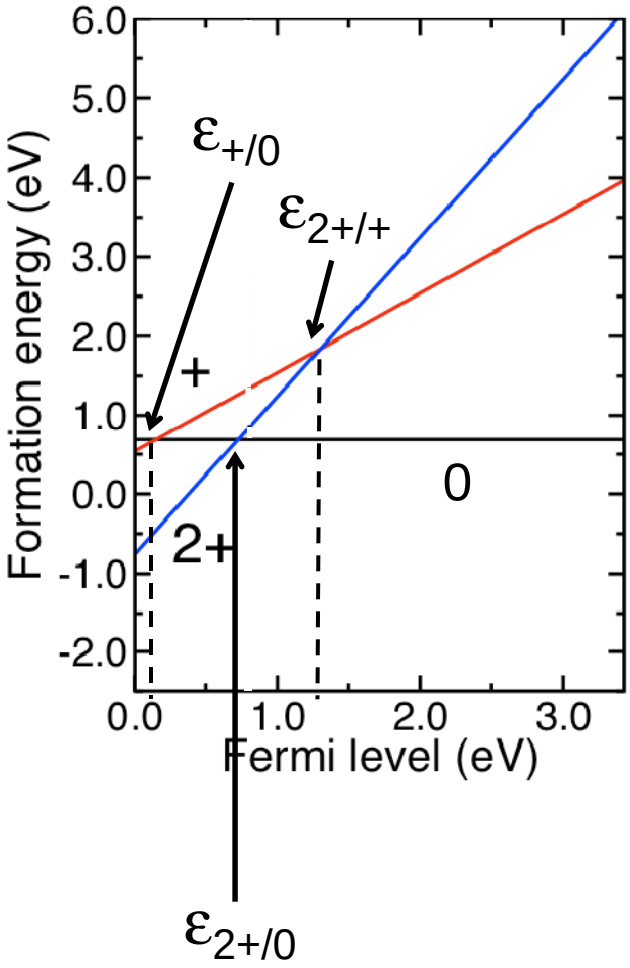
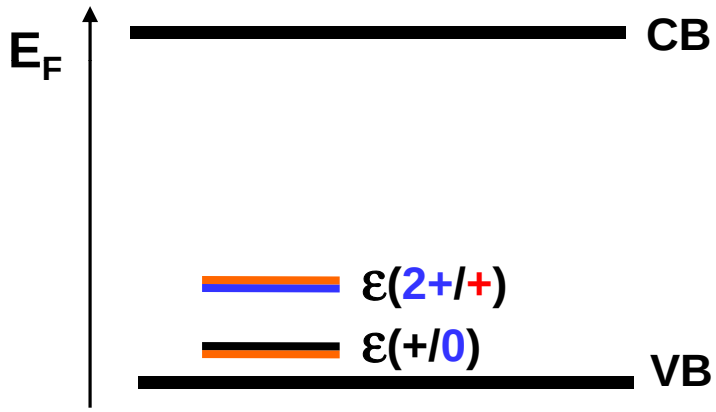
Transition levels



Charge-state transition levels



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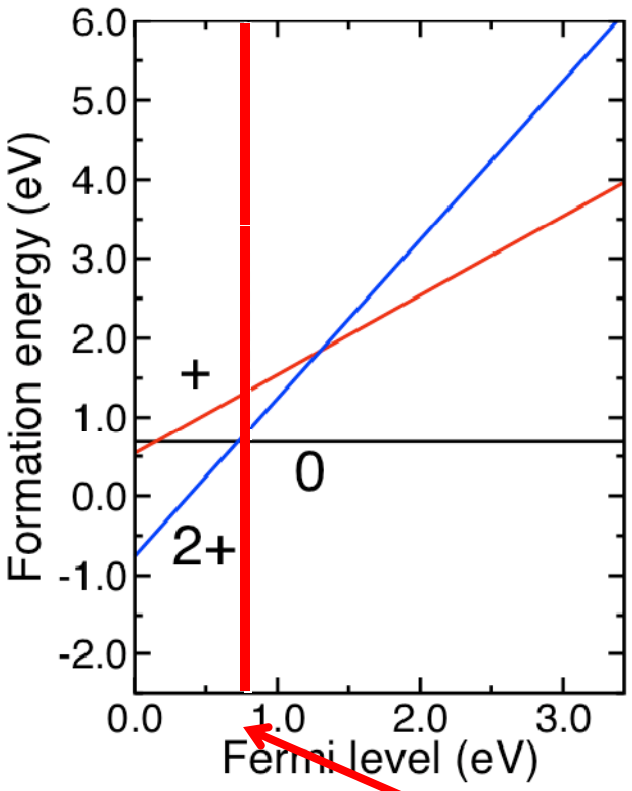
Issues...



- **Band gap problem**
  - DFT
    - » Local Density Approximation (LDA)
    - » Generalized Gradient Approximation (GGA)
- **Affects formation energies and transition levels**
  - Even for neutral charge states, if defect-induced Kohn-Sham states are occupied with electrons

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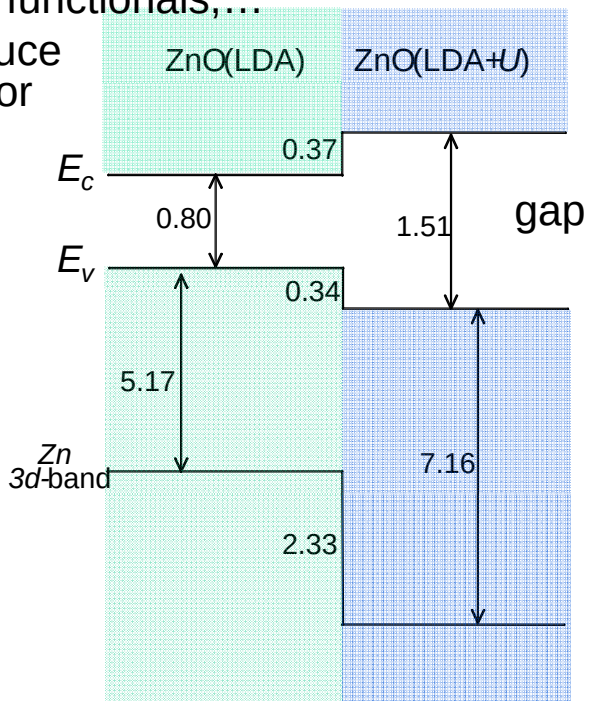
Band-gap corrections

- **Empirical corrections**
  - *Ad hoc* corrections
    - » "Scissors operator"
    - » "Modified pseudopotentials"
    - » Issues
      - Hard to control
      - Unintended consequences (indirect *vs*. direct gaps, …)
  - Extrapolating calculations that yield different gaps
    - » Different plane-wave cutoffs, exchange-correlation functionals,…
    - » Issue: different choices of parameter not only produce different gap, but also different levels of accuracy for description of defect
- **Physically meaningful corrections**
  - Self-interaction corrections
  - "LDA+*U*" approach
    - » Issues:
      - Determination of *U*
      - Band gap not fully corrected



Band-gap corrections: Hybrid functionals

- **Mixing of Hartree-Fock (exact exchange) and GGA**
  - A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
- **Functionals mix in ~25% of exact exchange**
  - PBE0
    - » J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
  - HSE
    - » Exact exchange only for short-range interactions
    - » J. Heyd, G. E. Scuseria and M. Enzernhof, J. Chem. Phys. **118**, 8207 (2003).
- **Obtain very good description of many properties**
  - Structural properties as good as, or better, than with LDA/GGA
  - Band gaps close to experiment
  - Better description of charge localization

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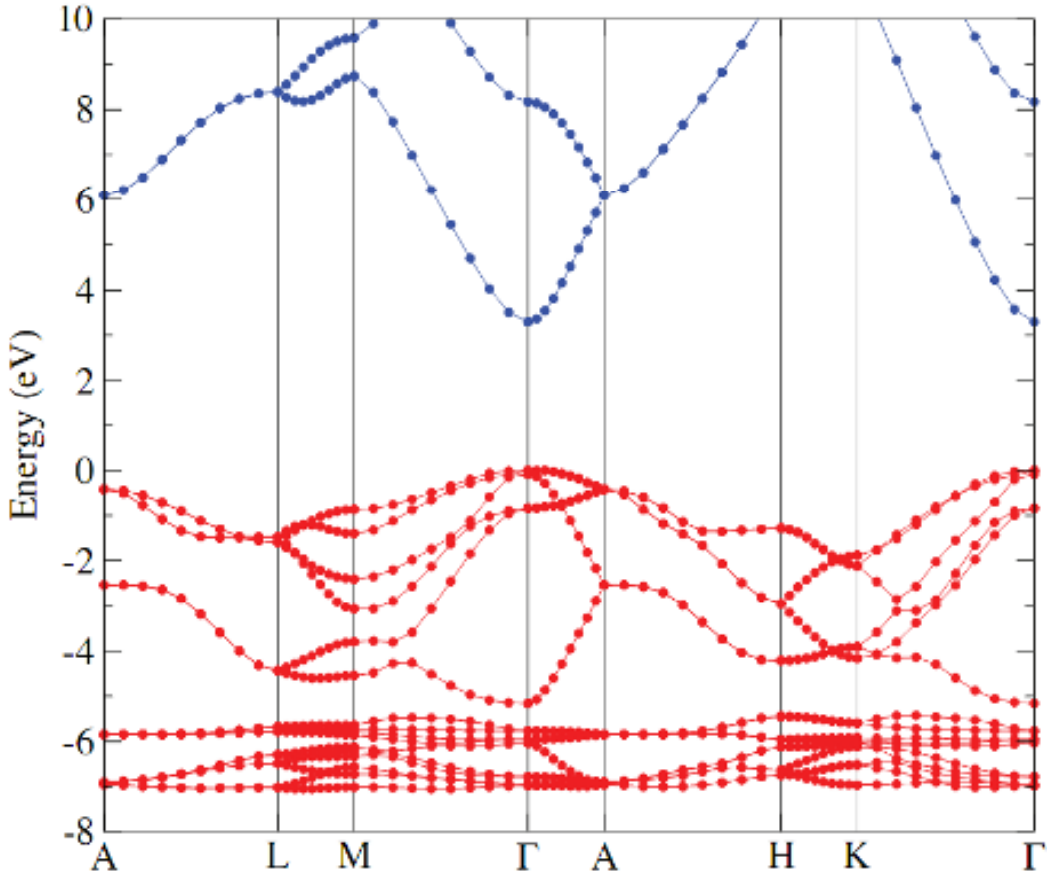
HSE calculations for ZnO



		PBE	HSE	Exp.
ZnO	a (Å)	3.28	3.23	3.25
	c (Å)	5.28	5.24	5.21
	E_g (eV)	0.73	3.35	3.40
	ΔH_f(eV)	-2.93	-3.66	-3.64

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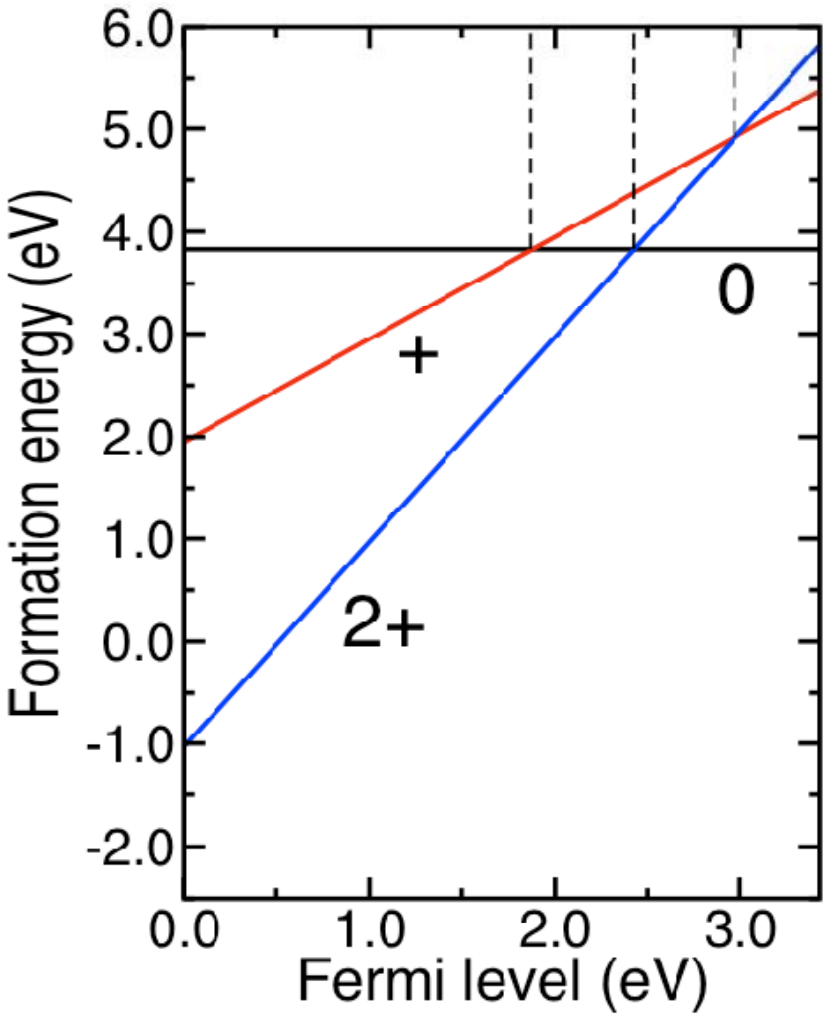
Example: V_O in ZnO



Value of formation energy :

- High formation energy
- Unlikely to form
  - » Experiment: electron spin resonance detects no oxygen vacancies in as-grown ZnO

Transition levels:

- Not a shallow donor!
- Not a source of conductivity

➔ Unintentional conductivity due to impurities

p-type doping of ZnO

- **Numerous reports of *p*-type ZnO**
  - Using N and other group-V impurities (Sb, As, P)
- **Reliability? Reproducibility?**
- **No *pn* junctions**
- **Nitrogen is often regarded as most suitable hole dopant**
  - Shallow acceptor in ZnSe

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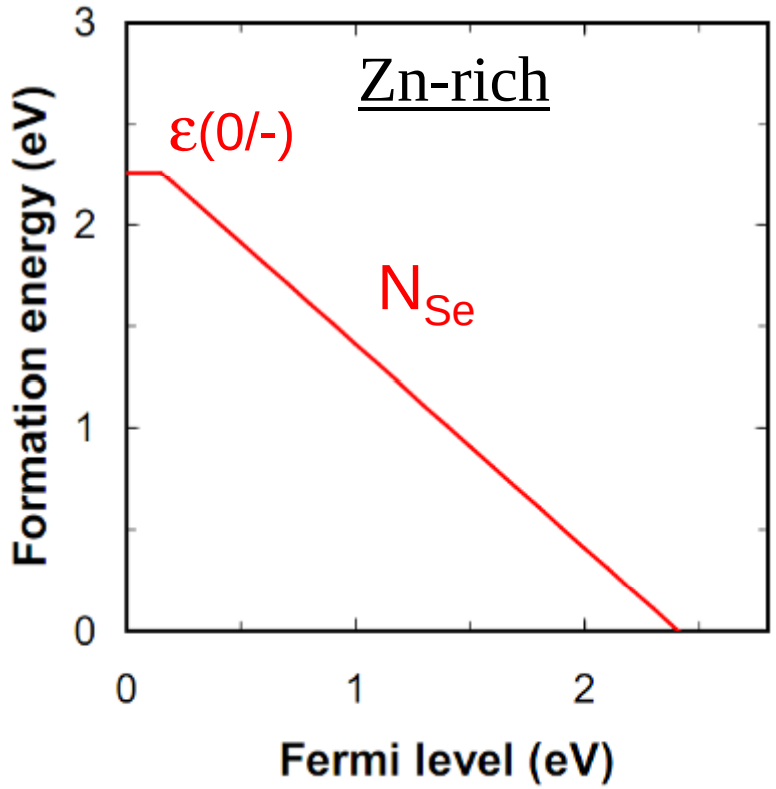
Test case: N_{Se} in ZnSe

- **Similar semiconductor**
- **N_{Se} known shallow acceptor in ZnSe**
- **Effective *p*-type dopant**
- **Results agrees well with experimental values**
  - Theory: E_A = 150 meV
  - Exp.: E_A = 110-130 meV



		PBE	HSE	Exp.
ZnSe	a (Å)	5.73	5.69	5.67
	E_g (eV)	1.19	2.80	2.82
	ΔH_f(eV)	-1.43	-1.74	-1.69

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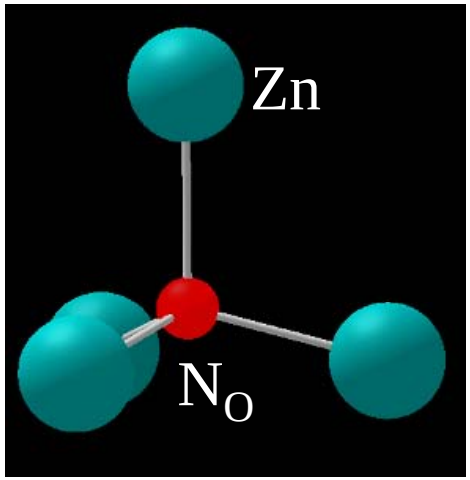
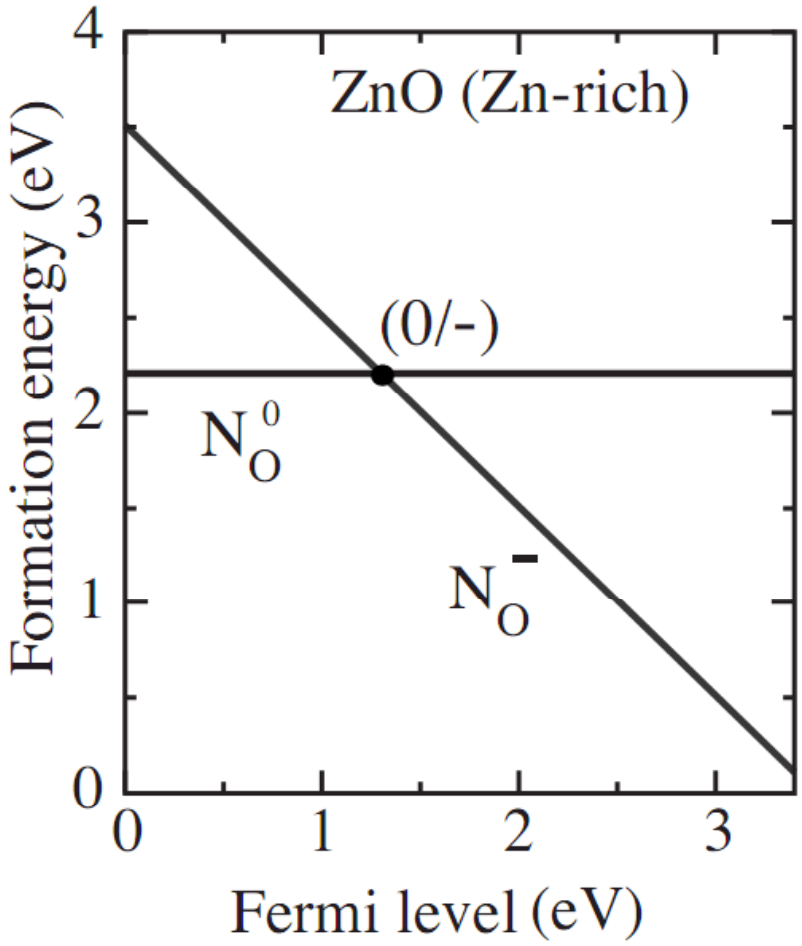
Nitrogen acceptor in ZnO

Deep acceptor
Large ionization energy: 1.3 eV
Off-center relaxation
Localized wavefunction



Axial bond = 2.12 Å
Planar bonds = 1.94 Å



J. L. Lyons, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. **95**, 252105 (2009).

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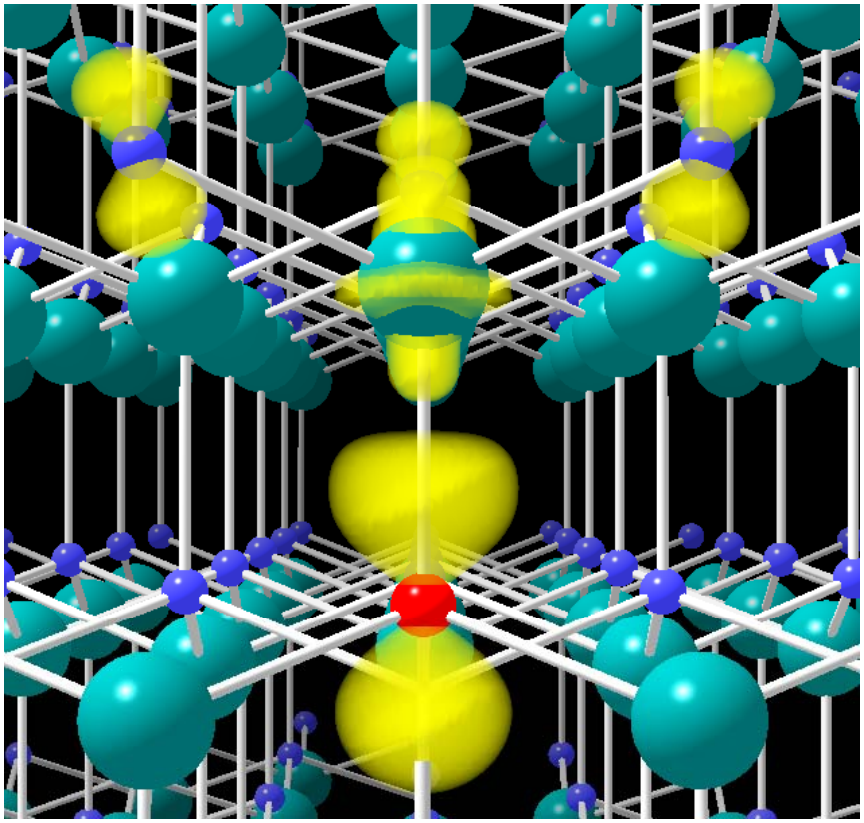
N_O acceptor: experiment

Localization on N atom

Directed towards axial zinc neighbor

Agrees with EPR signals



Spin density of nitrogen state
(Isosurface is 5% of maximum density)

W.E. Carlos, E.R. Glaser, and D.C. Look, Physica B **308**, 976 (2001).

N. Y. Garces *et al.*, Appl. Phys. Lett. **80**, 1334 (2002).

LDA does *not* produce this localized wave function!

Need hybrid functional!

"Why nitrogen cannot lead to *p*-type conductivity in ZnO", J. L. Lyons, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. **95**, 252105 (2009).

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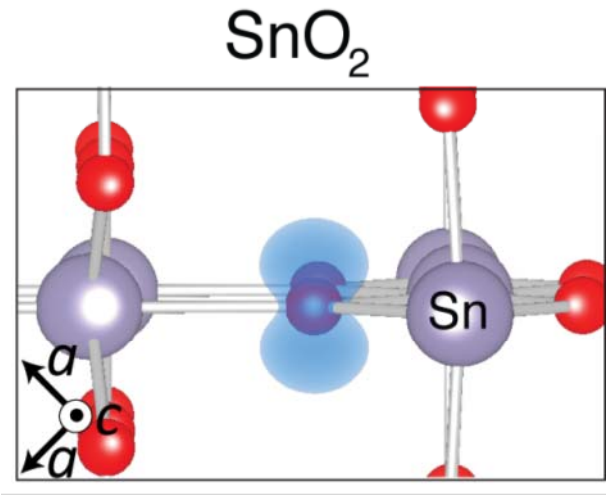
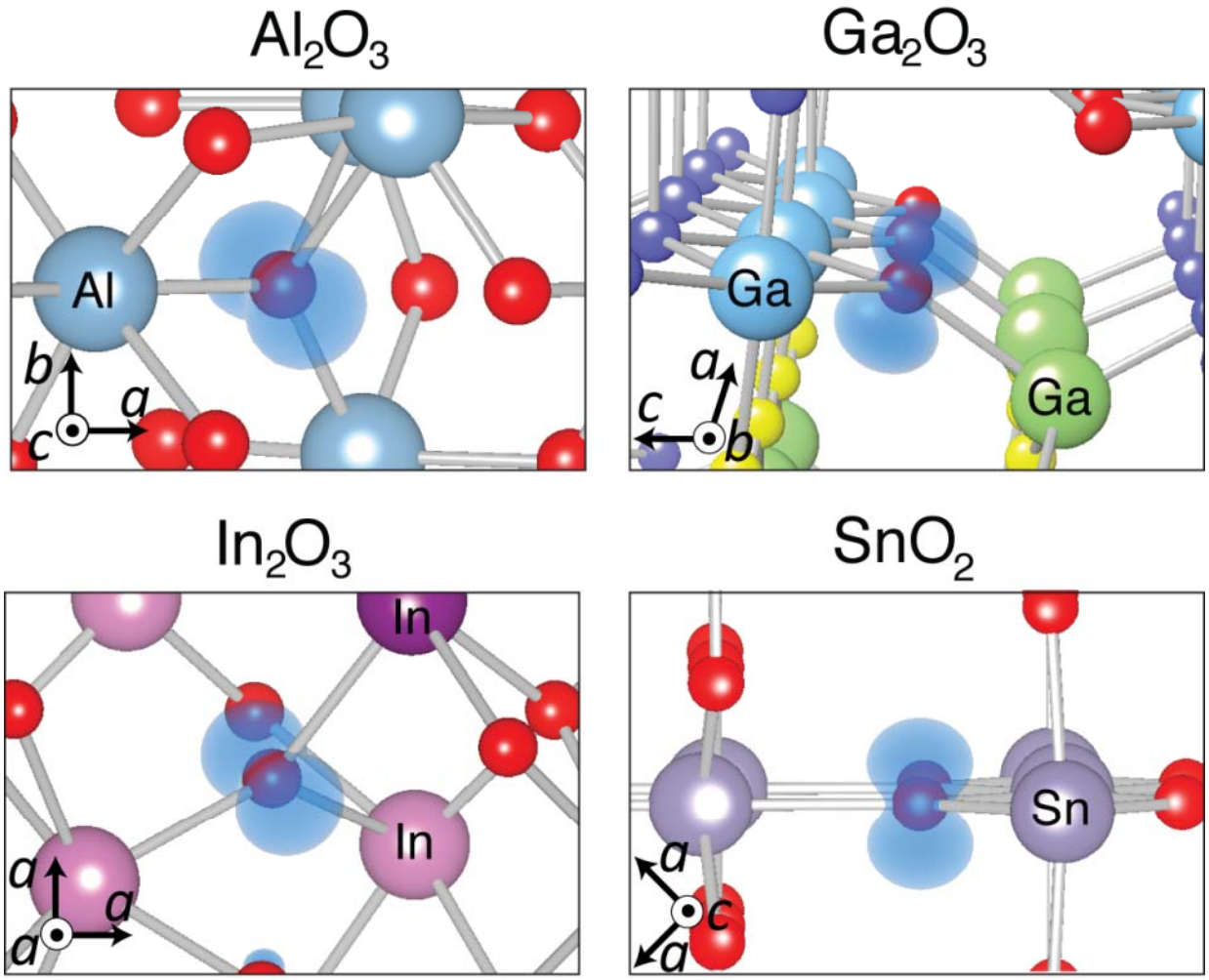
Conductivity: *p* type
Broader problem: self-trapping

- **In ZnO, holes are trapped in a localized state bound to acceptor impurities**
  - Rather than a delocalized, extended effective mass state
- **Localization of holes occurs in many oxides**
- **Polarons**
  - Presence of a charge in the valence band leads to large distortion of the lattice
  - Hole becomes trapped
  - "Self-trapping"



- **Major obstacle for *p*-type doping!**
  - Even if can get holes in the valence band, they will have very low mobility

Self-trapped holes



J. Varley, A. Janotti, C. Franchini, and C. G. Van de Walle, Phys. Rev. B **85**, 081109(R) (2012).

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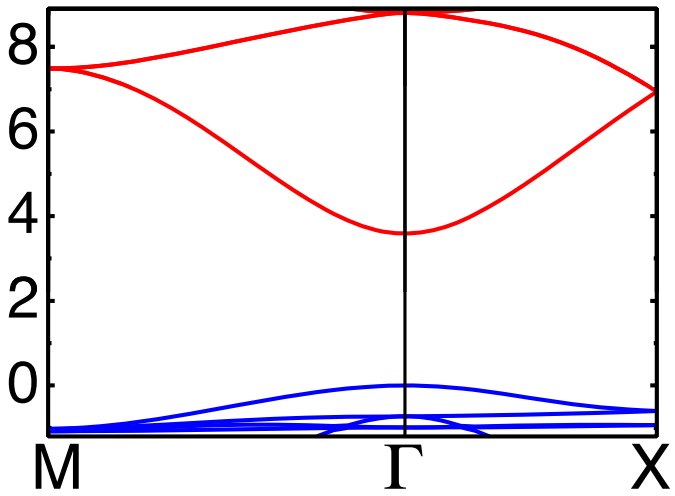
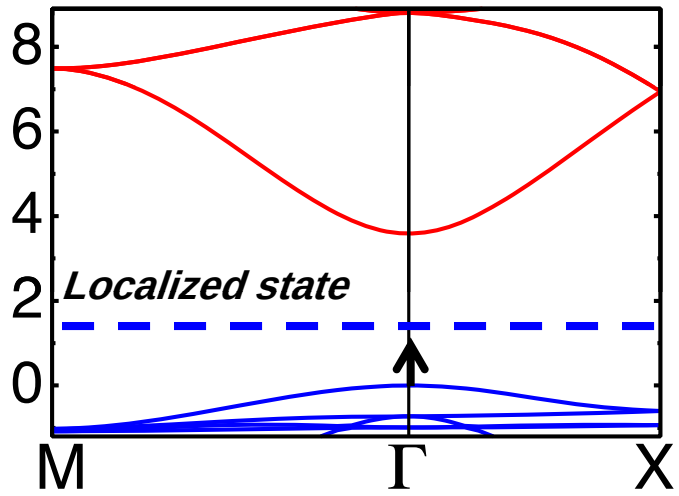
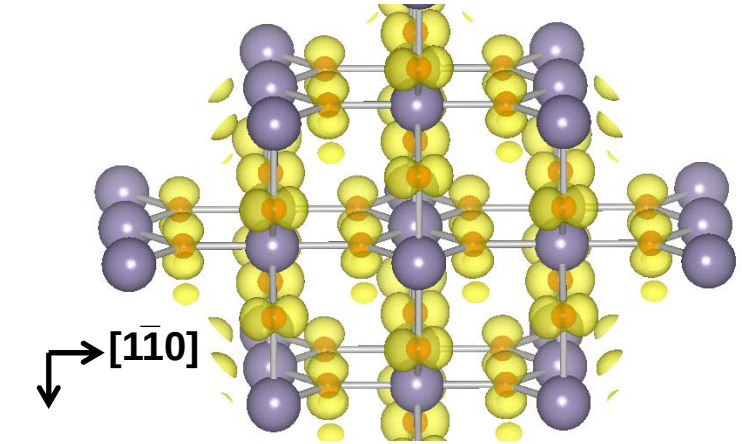
Signatures of self-trapped holes

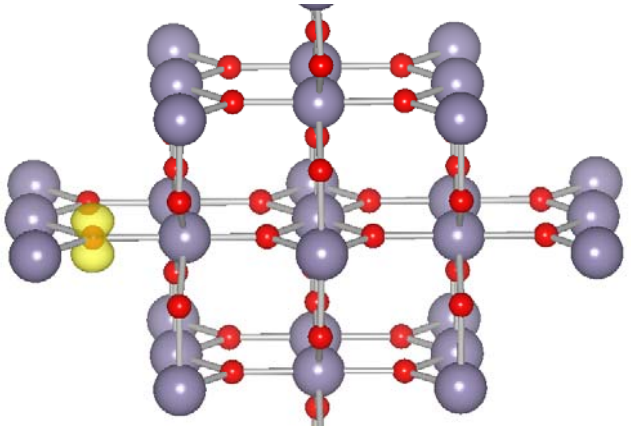
SnO_2







Self-trapping



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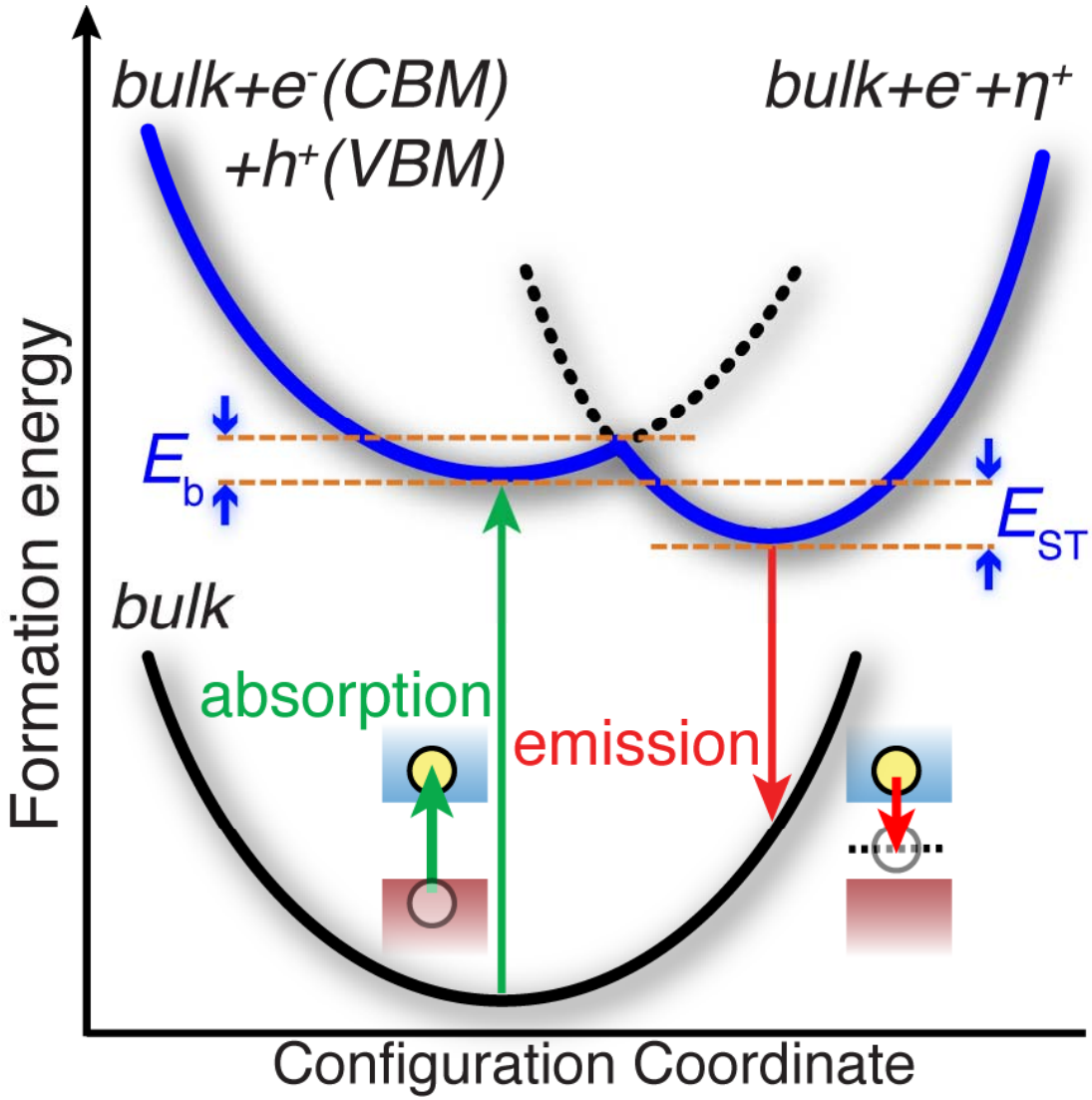
Energy barriers & optical signatures



- Need hybrid functional! LDA/GGA do not produce localization!
- Explains broad luminescence peaks observed in many oxide semiconductors
- Tendency to form small hole polarons is an obstacle to *p*-type conductivity

J. Varley, A. Janotti, C. Franchini, and C. G. Van de Walle, *Phys. Rev. B* **85**, 081109(R) (2012)

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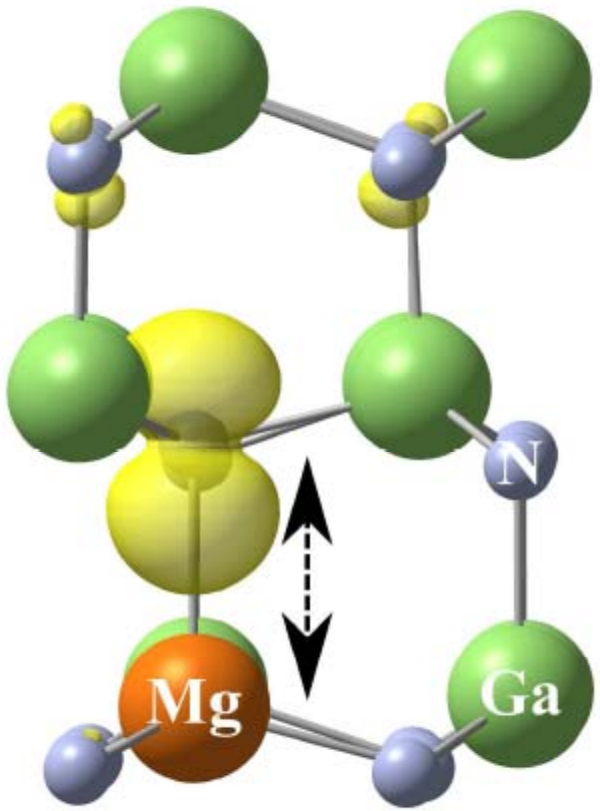
Magnesium acceptor in GaN

- **Mg incorporates on Ga site**
- **Only known effective *p*-type dopant for GaN**
- ***p*-type doping is still limiting factor for devices**
- **150-300 meV ionization energy**
  - Few percent ionization of acceptors

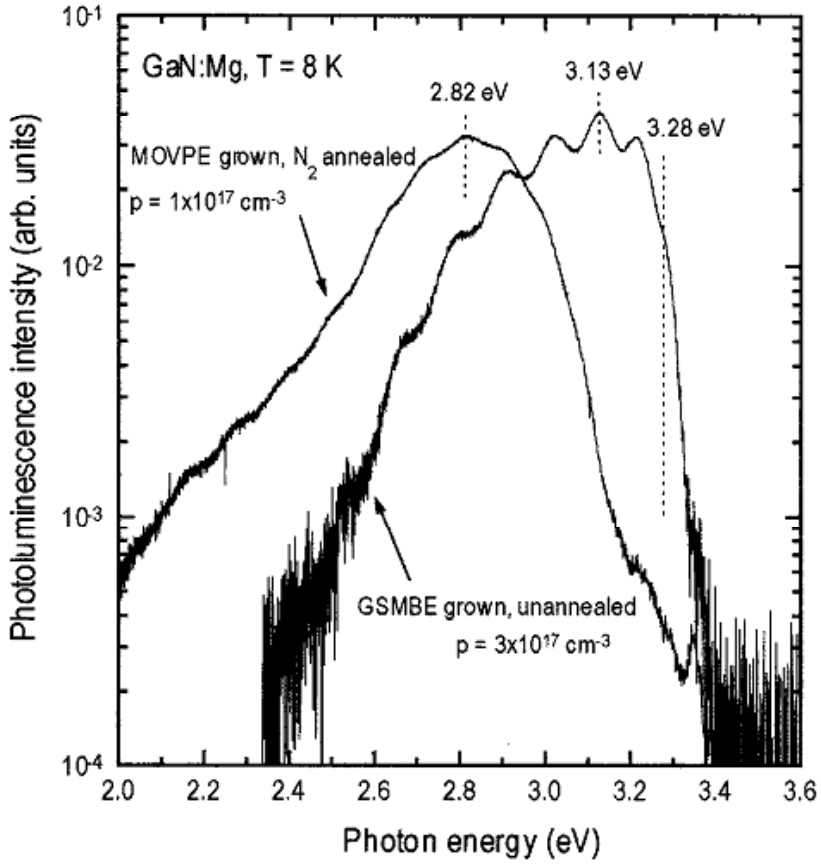
- **Optical behavior?**



Mg-related optical signals in GaN

- **Two photoluminescence (PL) signals observed in GaN:Mg**
- **3.27 eV "donor-acceptor pair" (DAP)**
  - Acceptor "A1"

    B. Monemar *et al.,* Phys. Rev. Lett. 102, 235501 (2009).
  - Unannealed, Mg-doped GaN
- **~2.8 eV blue luminescence**
  - Annealed, *p*-type GaN:Mg



C. Leroux *et al*., JAP 86, 3726 (1999).

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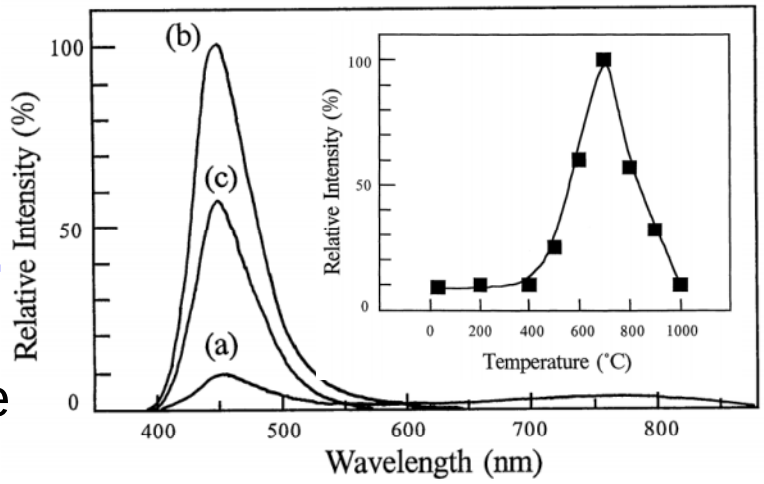
2.8 eV Blue Luminescence (BL)

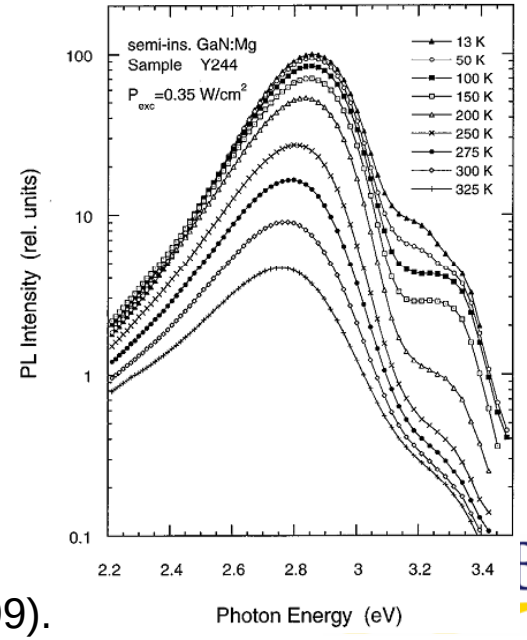
- **Strong increase in intensity after post-growth anneal**

- **Previous proposals: deep donor**
  - But: no deep donor signal from optically detected magnetic resonance (ODMR)
  - Instead: Mg acceptor signal…

    E. R. Glaser *et al.*, Phys. Rev. B 65, 085312 (2002)



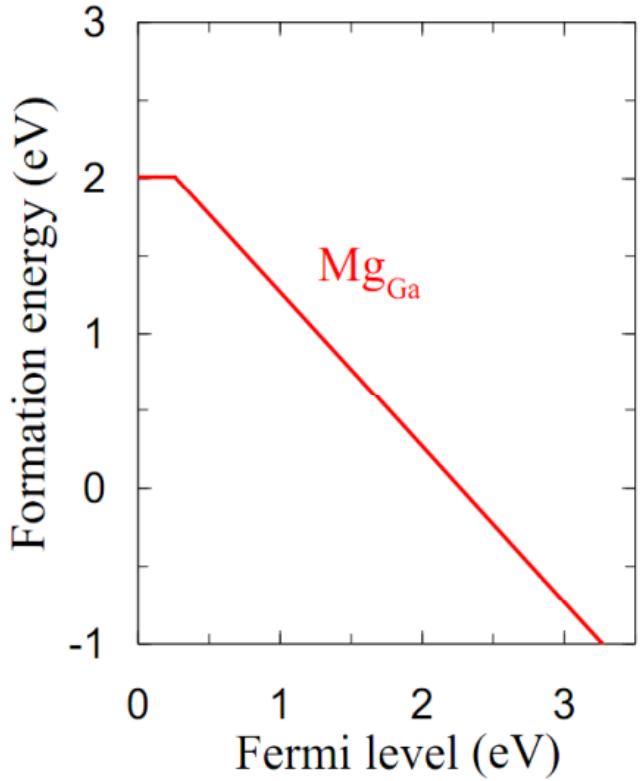
S. Nakamura *et al.*, JJAP 31, L139 (1992).

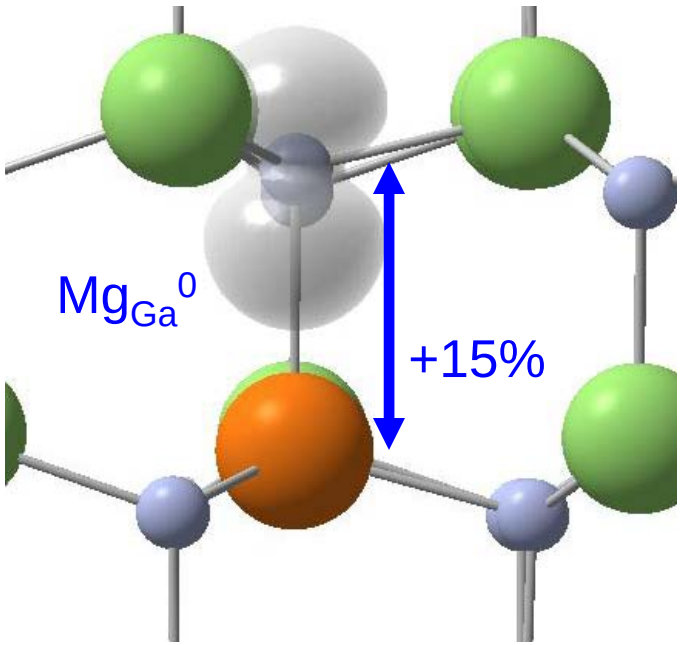


M. A. Reshchikov *et al.*, PRB 59, 13176 (1999).

Results: Mg_{Ga} in GaN

- **Mg_{Ga}: acceptor, ionization energy of 260 meV**
- **Hole for Mg_{Ga}^{0} is localized on nitrogen neighbor**
- **Large distortion in neutral charge state**
  - Axial Mg-N bond increases by 15%
  - See also Lany and Zunger, Appl. Phys. Lett. 96, 142114 (2010).





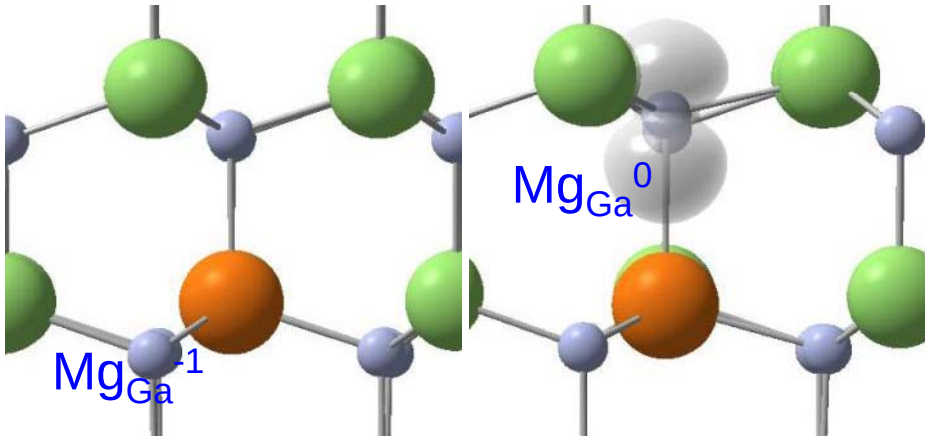
Spin density of Mg_{Ga}^{0}.
Isosurface shows the localized hole.

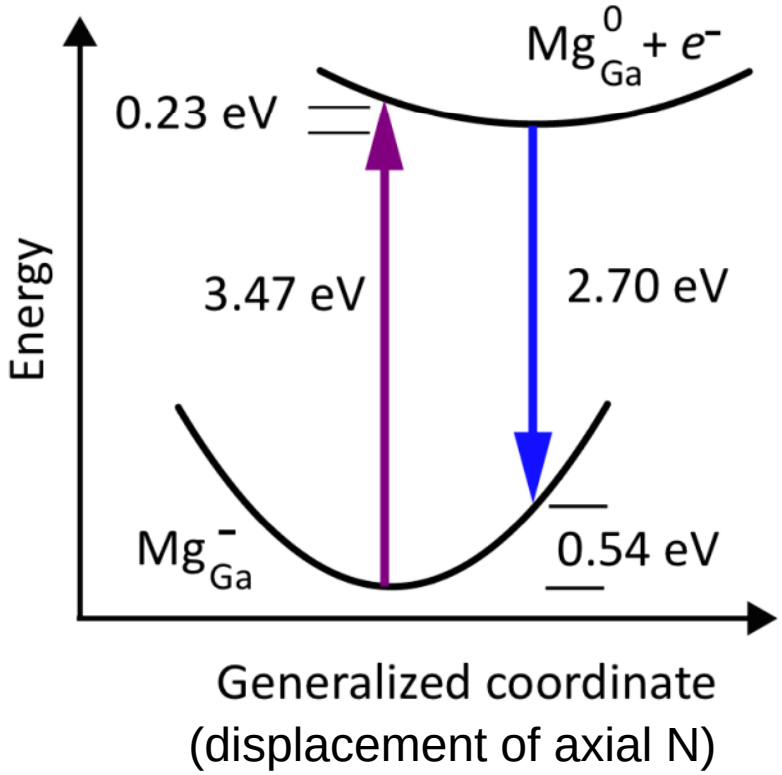
Results: optical signals of Mg_{Ga}

- **Large relaxations**

  → broad lines

- **Electron recombining (from CBM or shallow donor) with Mg_{Ga}^{0} leads to <u>blue</u> luminescence!**





J. L. Lyons, A. Janotti, and C. G. Van de Walle,
Phys. Rev. Lett. **108**, 156403 (2012)

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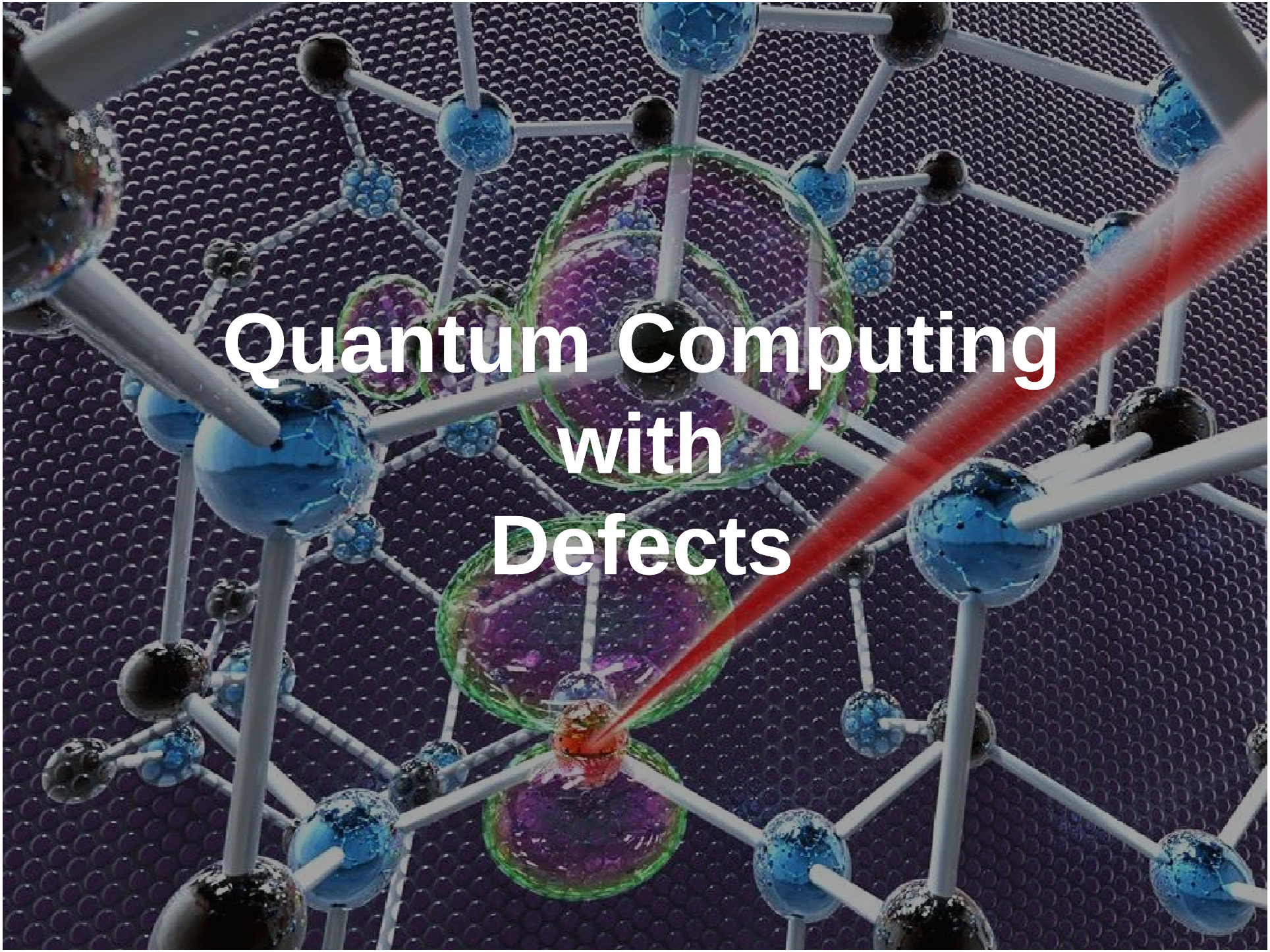
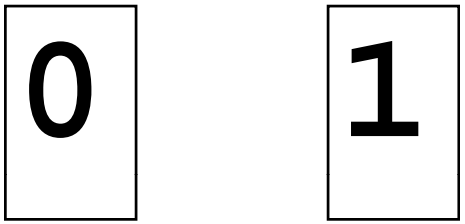
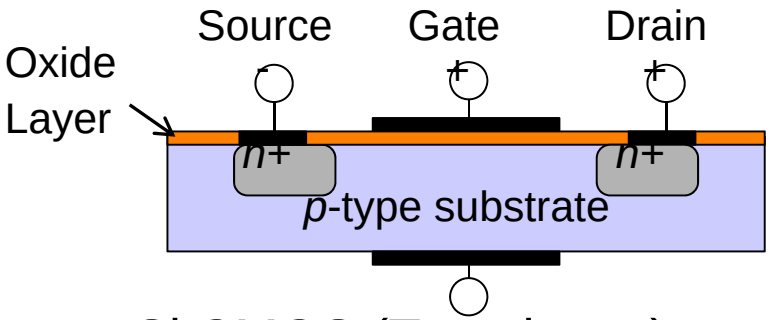

Quantum Computing
with
Defects

Paradigm shift

Classical Computing

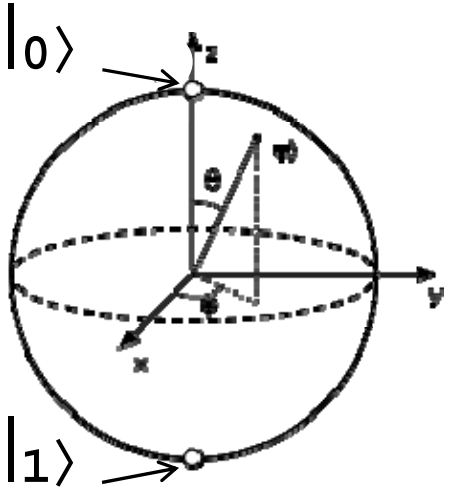


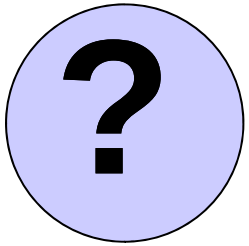


Si CMOS (Transistors)

- Discrete states
- On (1) or Off (0) states
- Classical bits (0 or 1)

Quantum Computing





Qubits (Quantum bits)

- Quantum states
- Superposition of $|0\rangle$ and $|1\rangle$
- Bloch sphere

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Qubit Requirements

- **Isolated**
  - design atomic-like state
- **Addressable**
  - can initialize, manipulate, and read out the quantum state
- **Engineerable**
  - create qubits in controlled and systematic manner

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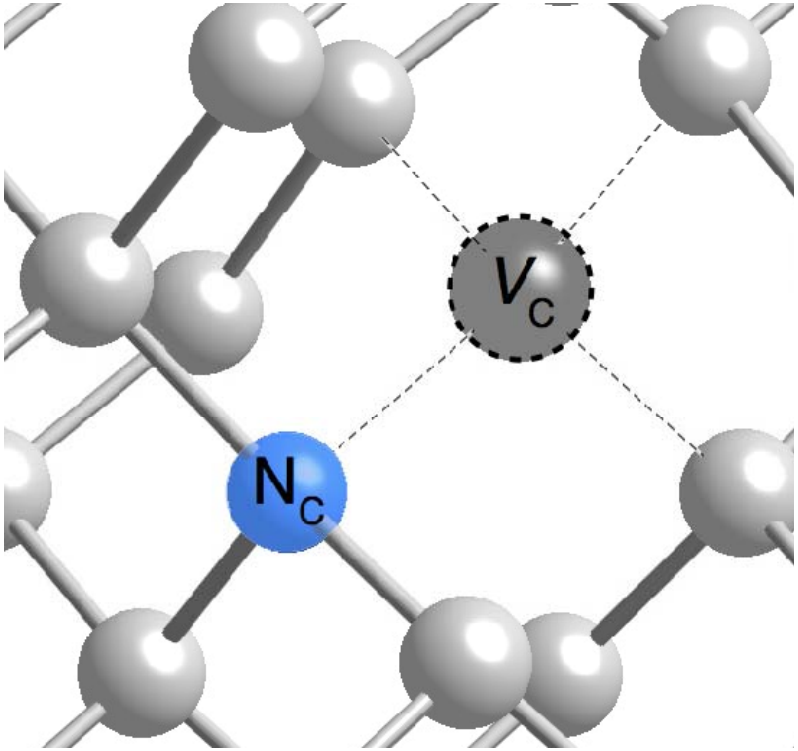
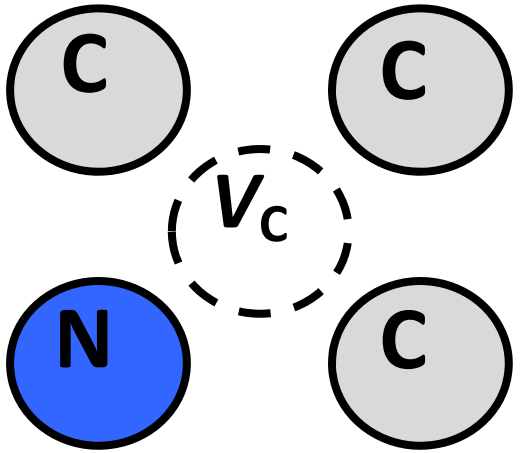
The NV center in Diamond





- **A "defect" with many desirable properties**
  - Room temperature qubit
  - Optically addressable single spin
  - Millisecond spin coherence times

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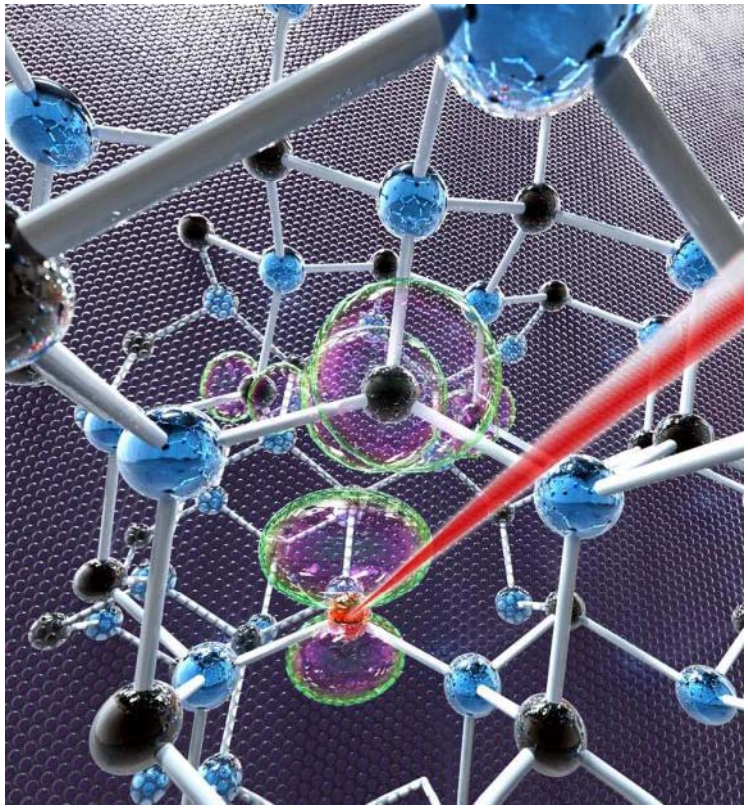
Other Defects with Similar Properties?

- **Diamond: difficult to grow and process**
- **Do similar defects exist in a more technologically mature material?**
- **If so, how do we find them?**
- **Propose a set of physical criteria for host material and defect**
- **Develop a framework for testing criteria**
- **Illustrate criteria by example**



– vacancies and complexes in other semiconductors

Quantum computing with defects, J. R. Weber, et al., Proc. Natl. Acad. Sci. 107, 8515-8518 (2010).

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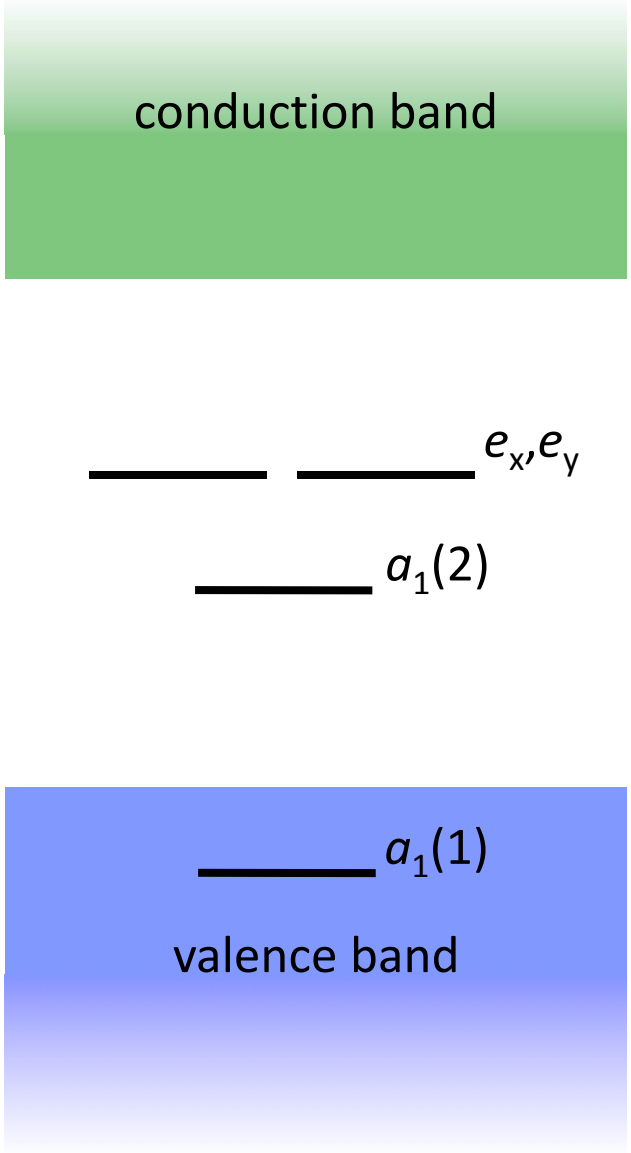
Important Host Criteria



- **Wide band gap**
  - Avoid coupling to bulk states
- **Small spin-orbit coupling**
  - Avoid unwanted spin flips
- **Constituent elements with no net nuclear spin (if possible)**
  - Avoid spin bath effects
- **High quality crystals/thin films**
  - Experimentally feasible to address individual defects

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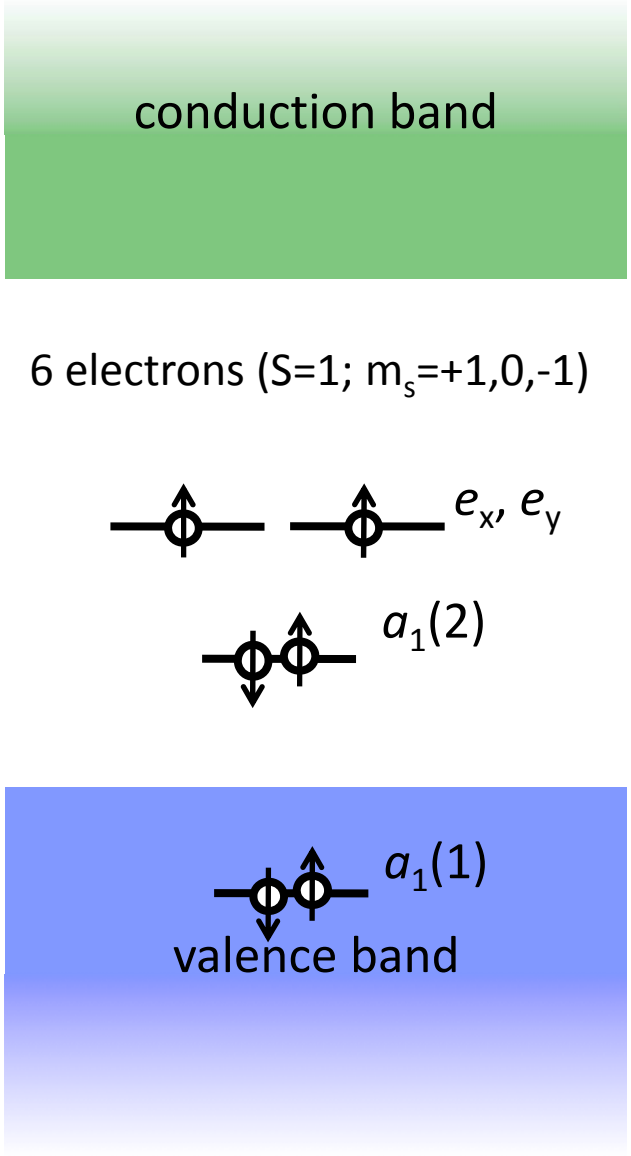
Important Defect Criteria



- **Defect states well localized within band gap**
  - Avoid coupling to bulk states
- **Splitting between defect levels not too small**
  - Avoid thermal coupling
- **Spin state capable of behaving as qubit**
  - Exploit spin sublevels
  - Form qubit states

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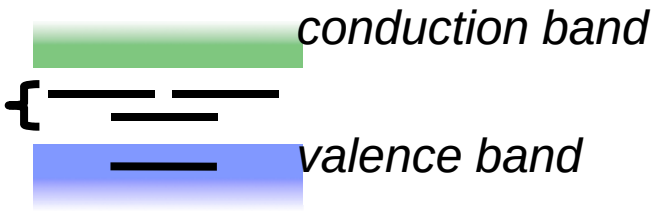
Calculations Give Insight Into:

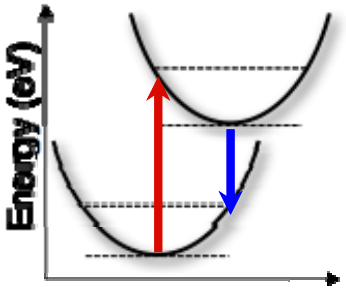
- Location of defect levels relative to band edges

  single-particle states

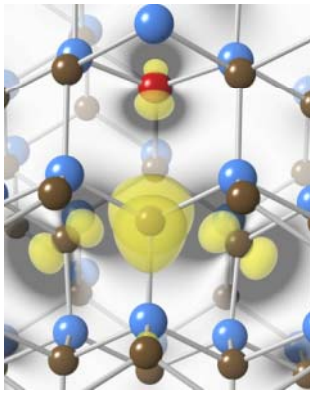


- Excitation properties associated with the defect

  configuration-coordinate diagrams

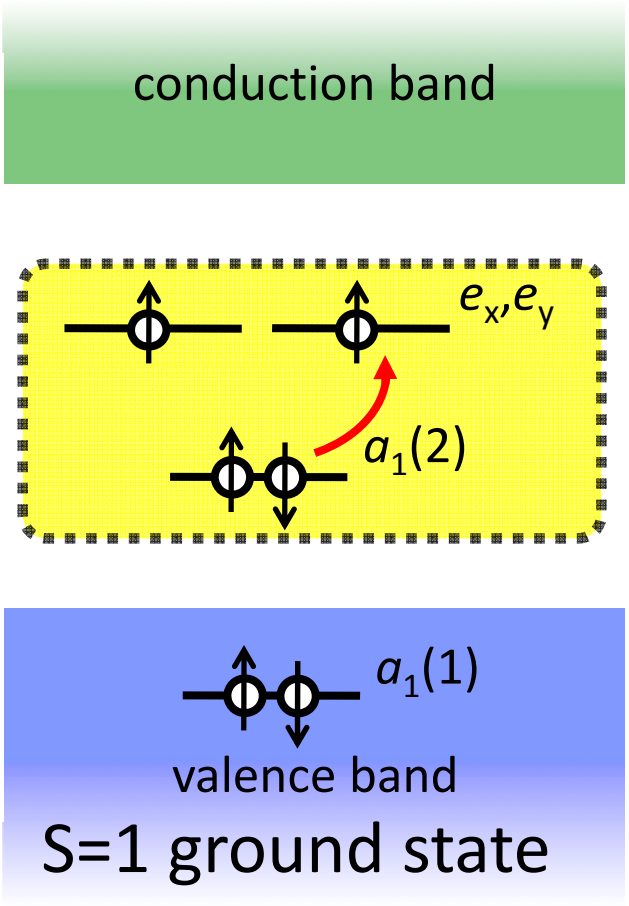


- **Defect stability: spin states, charge states, and binding energies**
  - formation energies



Calculated NV^{-1} Defect Levels

Single-particle picture



- Spin polarized calculation
  - Spin-majority and minority channels
- Excitation of $a_1(2)$ spin-minority electron
- Promoting $a_1(2)$ electron to higher lying empty state

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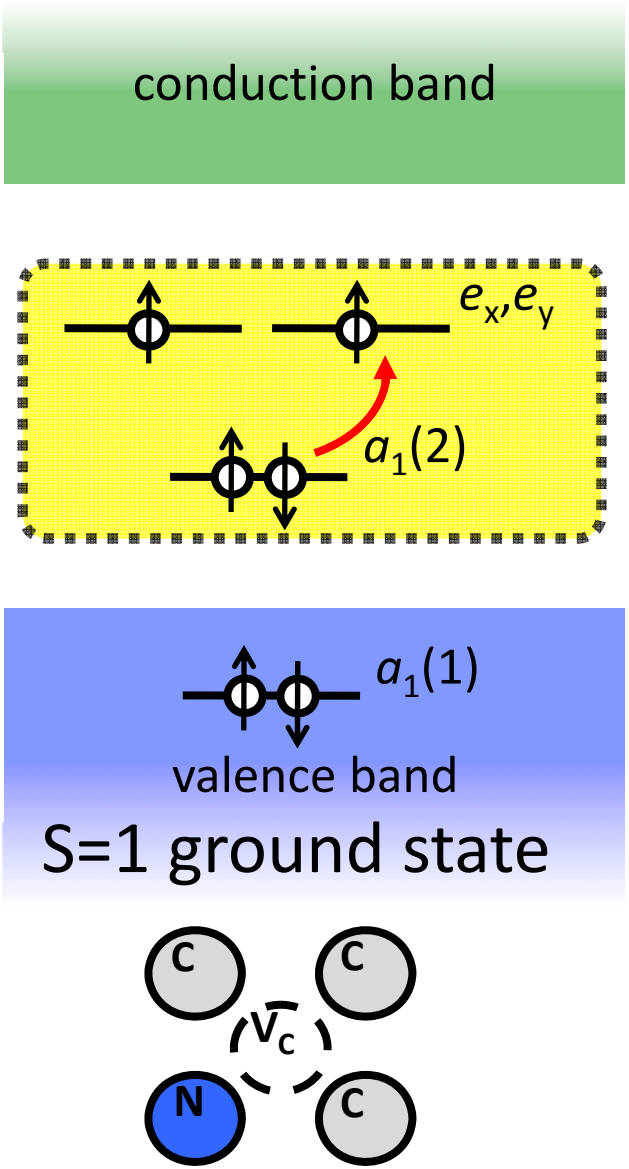
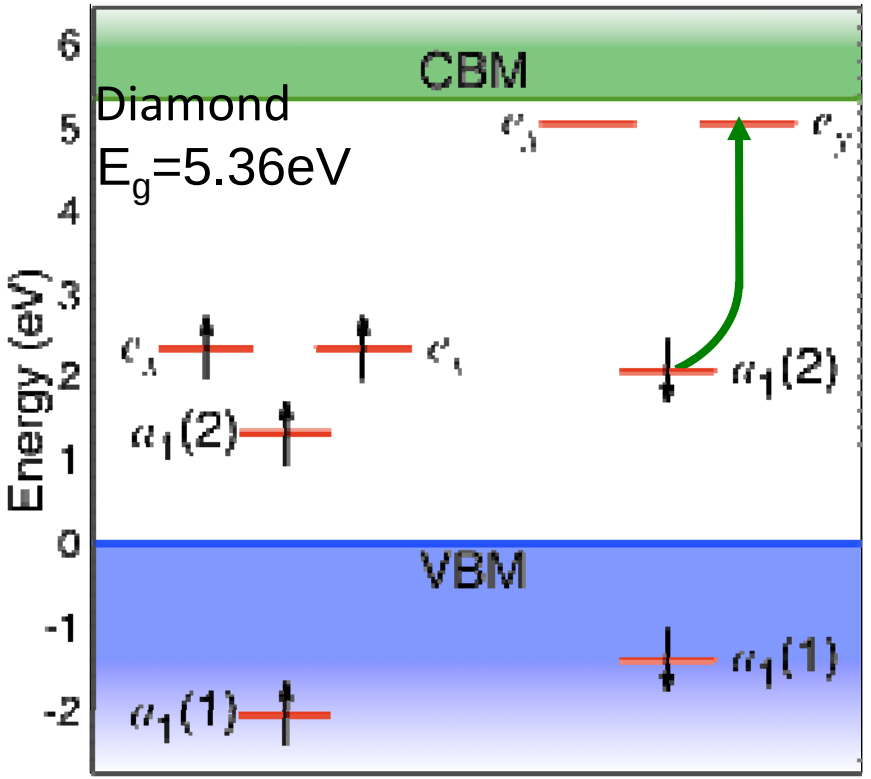
Calculated NV^{-1} Defect Levels

Single-particle picture





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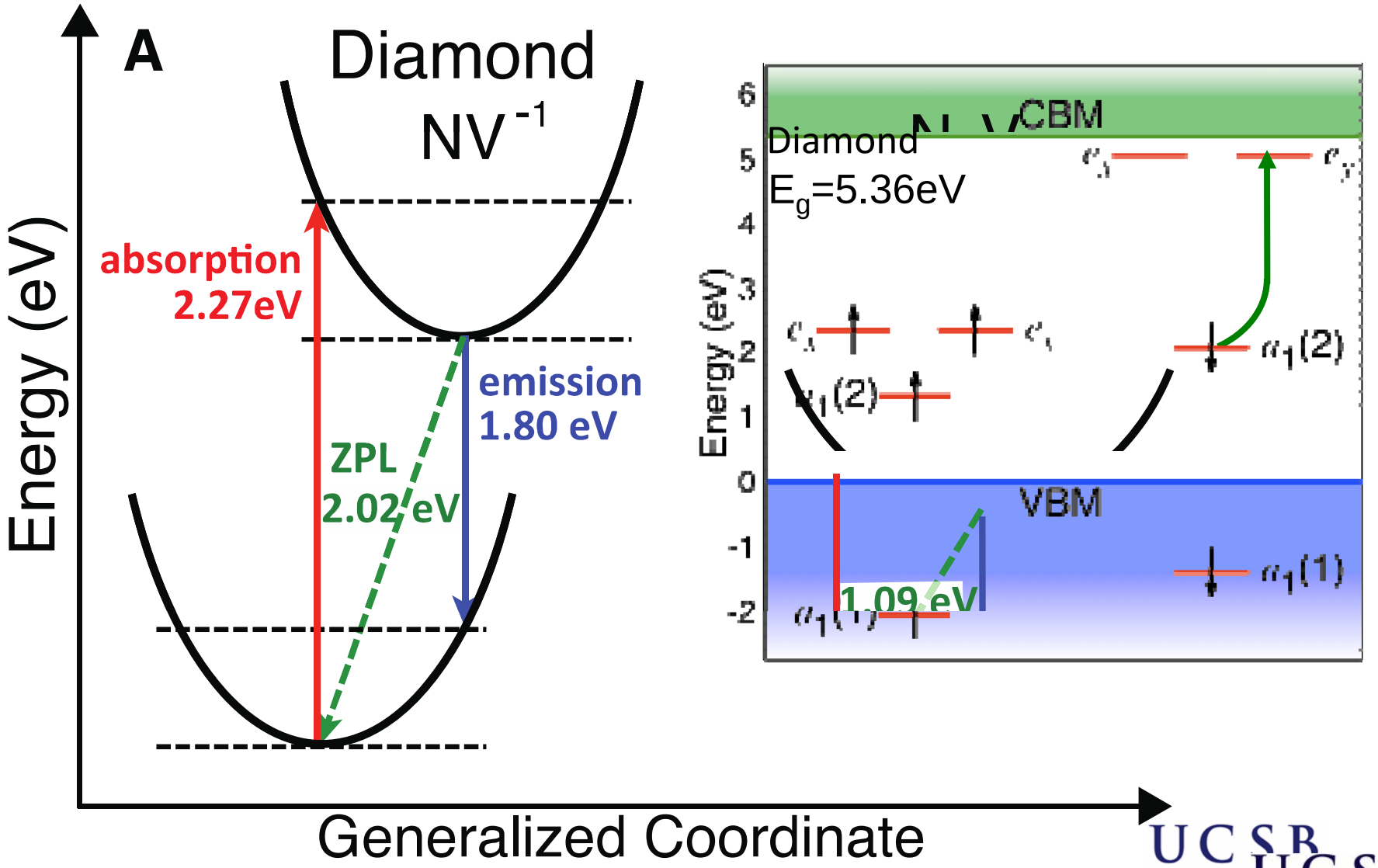
Calculated NV^{-1} Defect Levels



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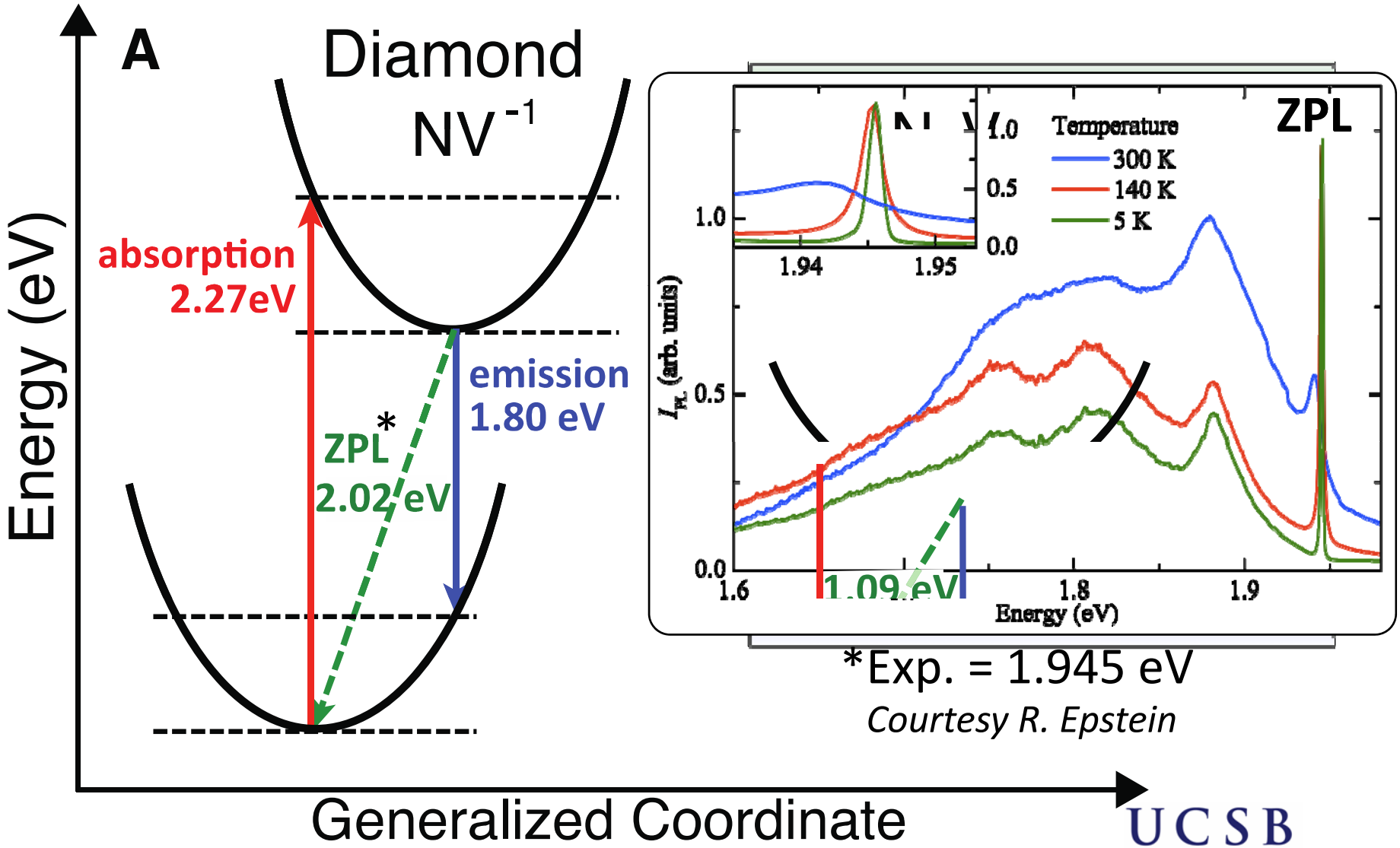
Calculated NV^{-1} Defect Levels



*Exp. = 1.945 eV

Courtesy R. Epstein

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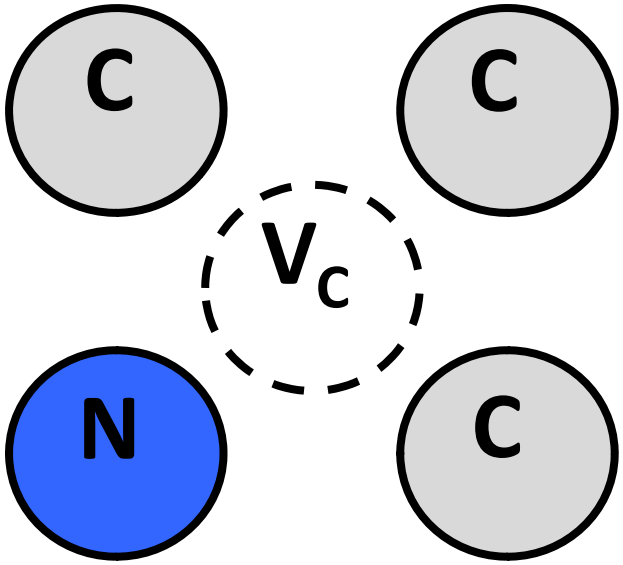
What About Other Defects?

NV: Diamond



$E_g = 5.36$ eV

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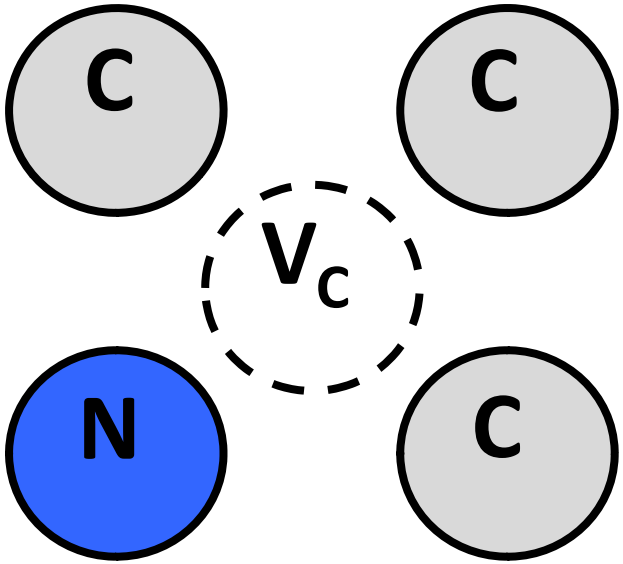
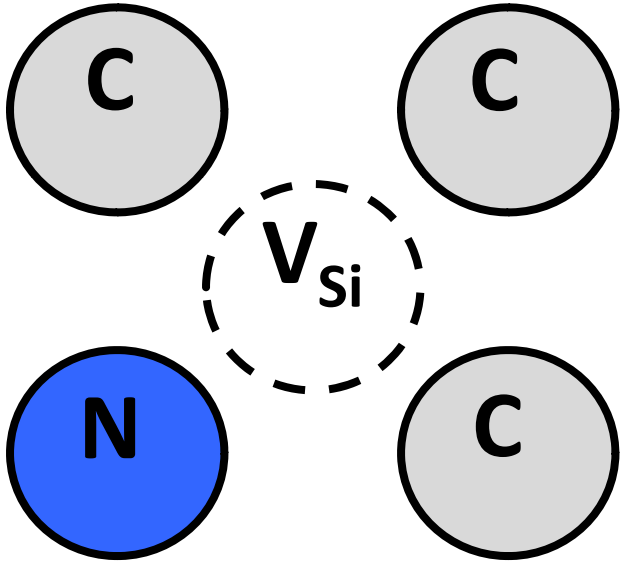
What About Other Defects?

NV: Diamond



E_g = 5.36 eV

$N_C V_{Si}$: SiC (4H)



E_g = 3.17 eV

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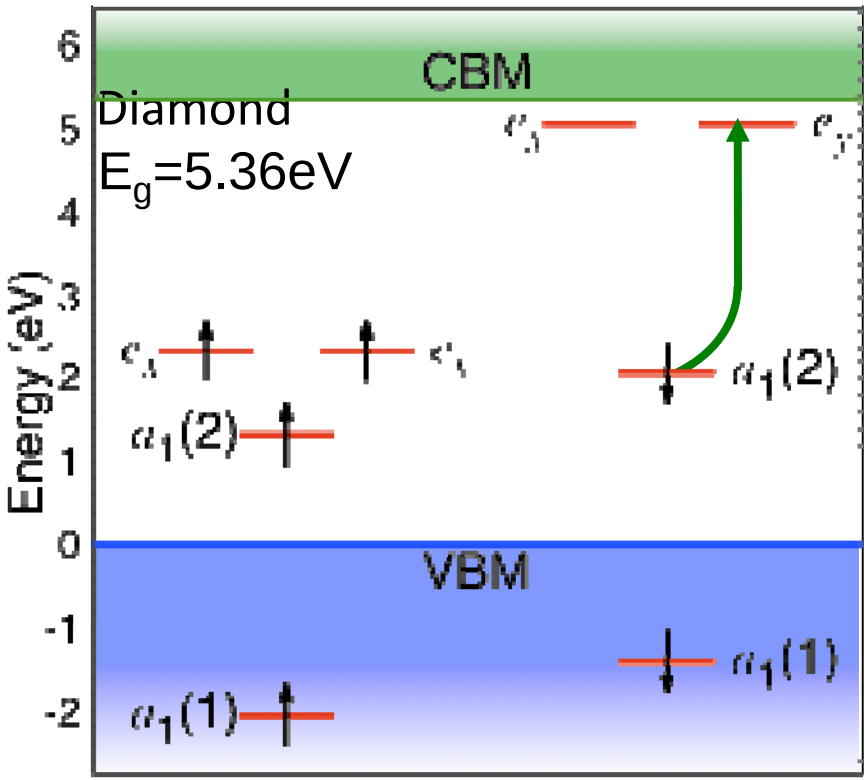
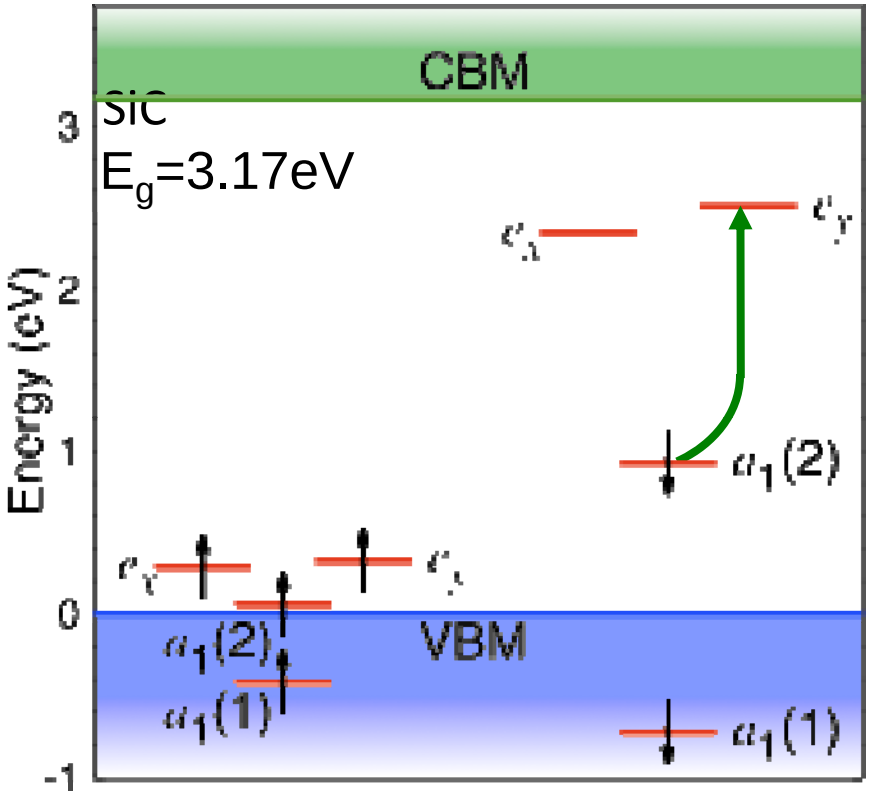
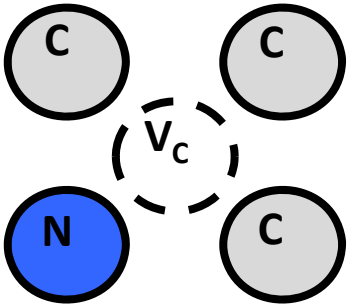
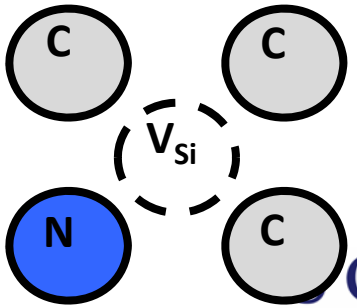
Calculated NV^{-1} Defect Levels









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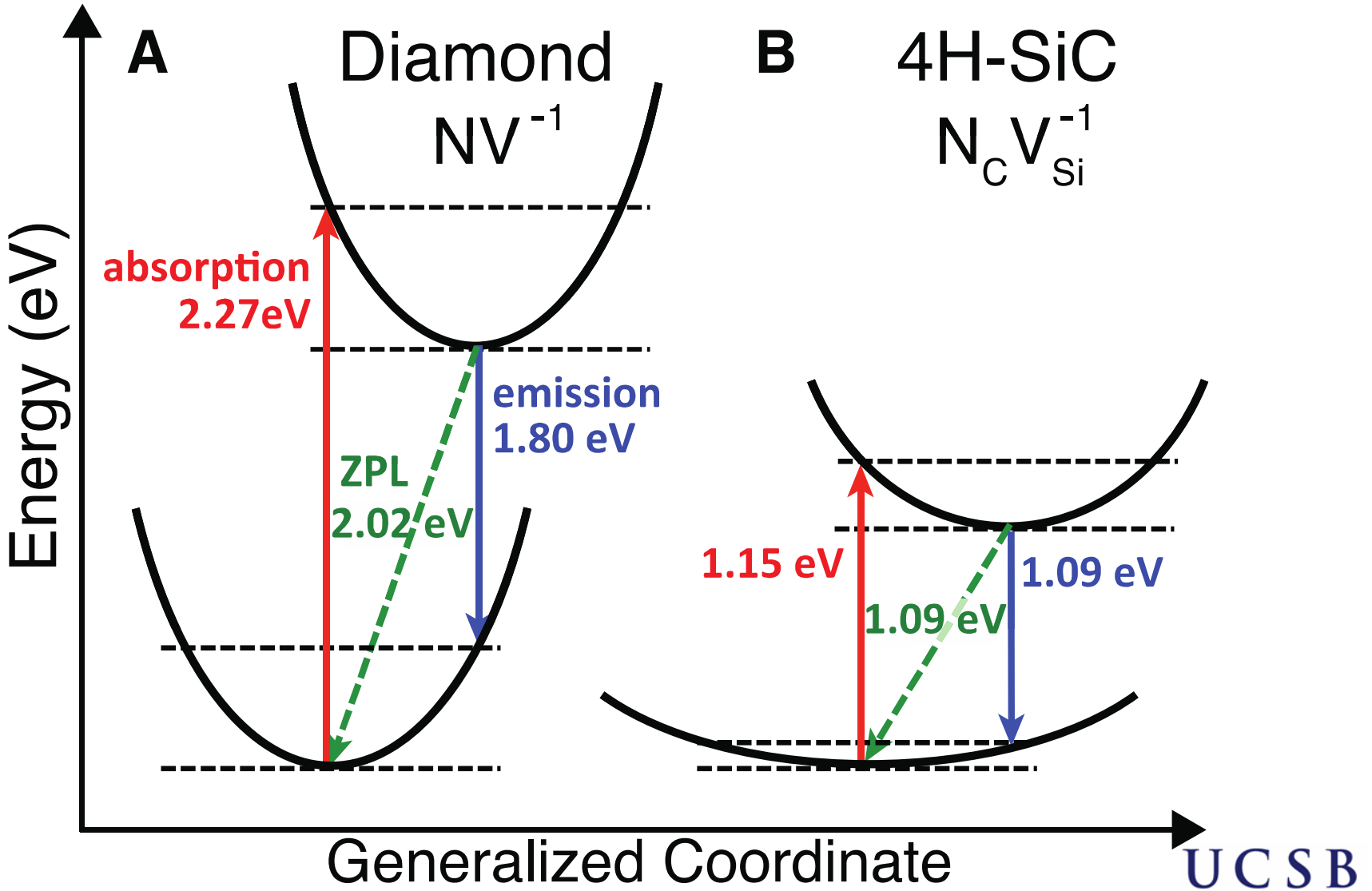
Calculated NV^{-1} Excitation Energies



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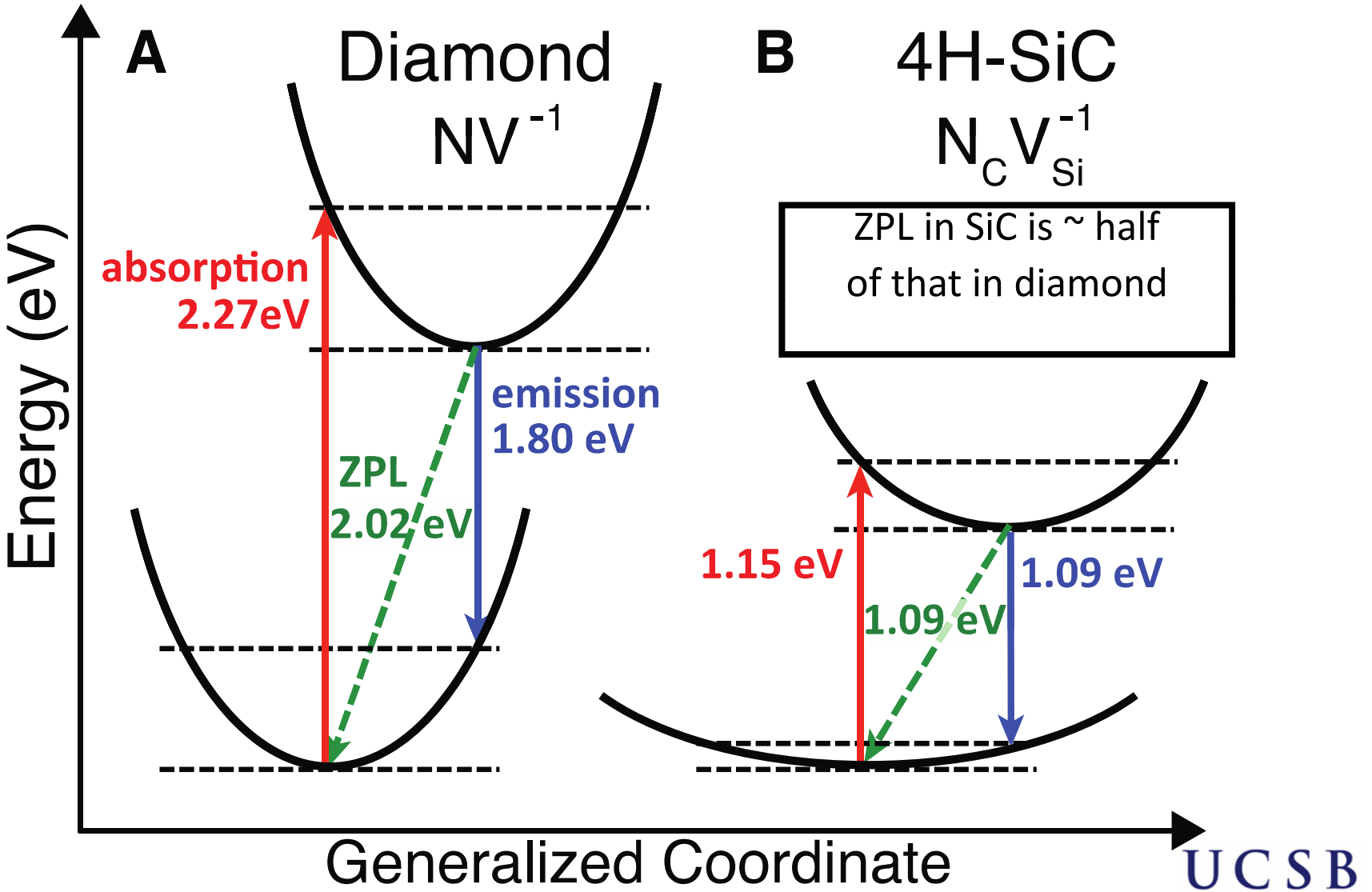
Calculated NV^{-1} Excitation Energies



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Summary

- **Understanding of point defects**
- **Examples where hybrid functionals are crucial for correct physics**
- **Point defects not responsible for unintentional conductivity**
  - Unintentional incorporation of impurities
- **Problems achieving *p*-type conductivity in wide-band-gap materials**
- **Transport limited by polarons**
- **Defects can be useful!**
  - Qubits for quantum computing

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