SAND2017-13128C

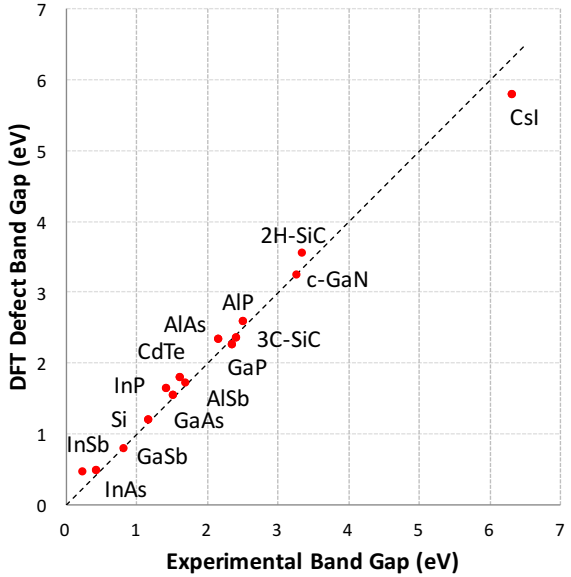
From narrow gap to ultra-wide band gap systems: End of band gap problem excuses for defect calculations

Peter A. Schultz

Sandia National Laboratories. Albuquerque NM 87185 USA

A. H. Edwards, R. M. Van Ginhoven, A.C. Pineda

U.S. Air Force Research Laboratory, Kirtland AFB, NM 87117 USA



MRS Fall Meeting 2017

SAND2017-xxxx
Unlimited Release

U.S. DEPARTMENT OF ENERGY

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Sandia National Laboratories

Why model defects in semiconductors and insulators?

Peter A. Schultz

Radiation effects in electronics

Process modeling for semiconductors

Defect chemistry for energy applications

Goals:

(1) Qualitative understanding - *Forensics*

Augment experiments

- incomplete, inconclusive, unavailable, expensive

(2) Quantitative characterization - *Predictive*

Predictive simulations, inform coarser models

- not just publishable, but defensible to engineers

The DFT defect shibboleths

Peter A. Schultz

- **"If you do not have the right band gap, you cannot hope to get the defect levels right"**

- **If you have the right band gap, you will get accurate defect levels**

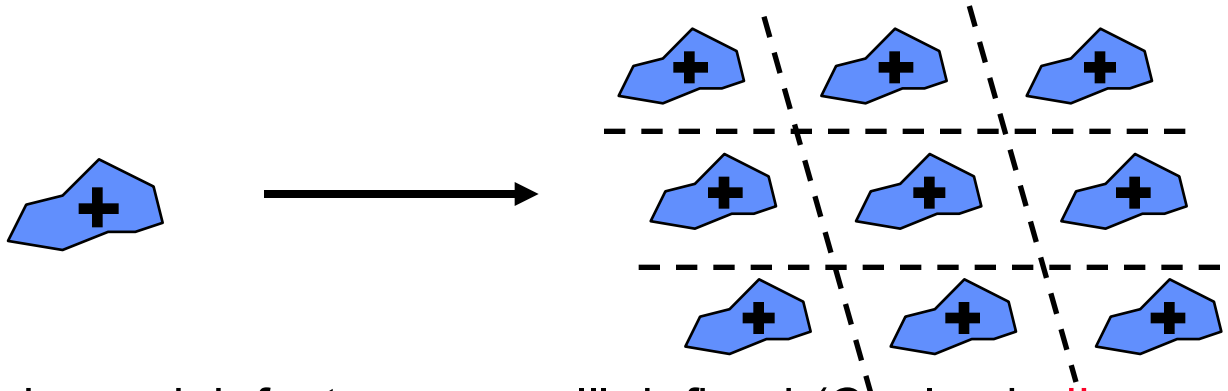
By the end of this talk …

- the Kohn-Sham gap mostly irrelevant to defect levels
- boundary-conditions/finite-size-errors matter more
- accuracy *proven* with standard semi-local functionals

Challenges for density functional theory

Peter A. Schultz

- **Conventional DFT fails for defect levels in semiconductors**
  - (1) Physical accuracy: e.g., "band gap problem"
  - (2) Computational model size limitations
  - (3) Shortage of good data for validation
  - (4) Supercell problem for charged defects:



Finite charged defect

Ill-defined (Coulomb divergence)

Lots of DFT calculations, no robust, predictive method

A supercell theory of defect energies

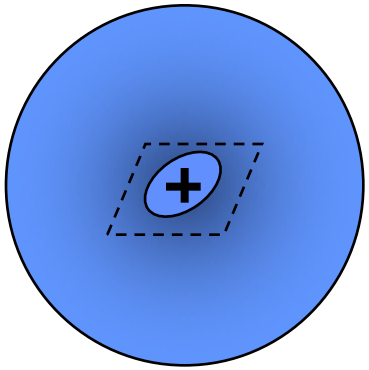
Peter A. Schultz, Phys. Rev. Lett. **96**, 246401 (2006).

Target system: isolated defect

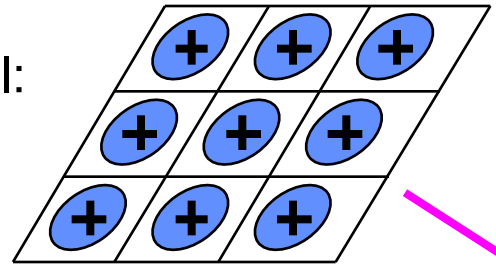
=

Computational model for isolated defect

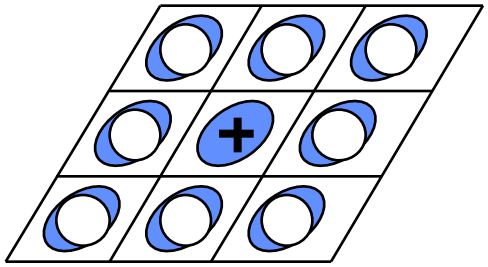
(+ DDO for defect banding)



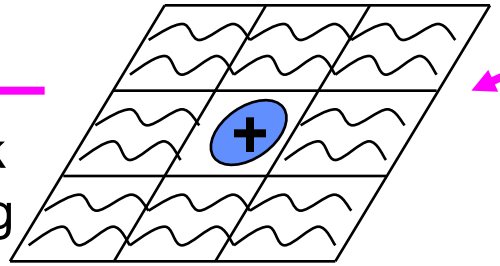
Standard DFT model: Supercell



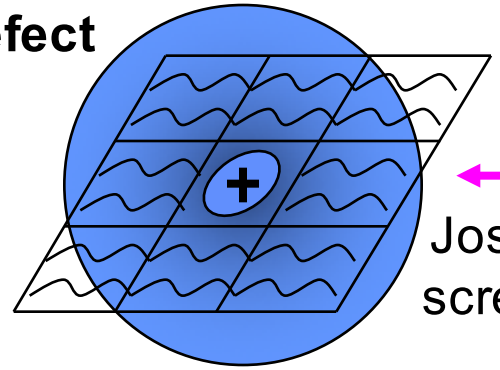
LMCC to fix boundary conditions



Crystal embedding to fix μ_e



Jost Bulk screening



Finite Defect Supercell Model

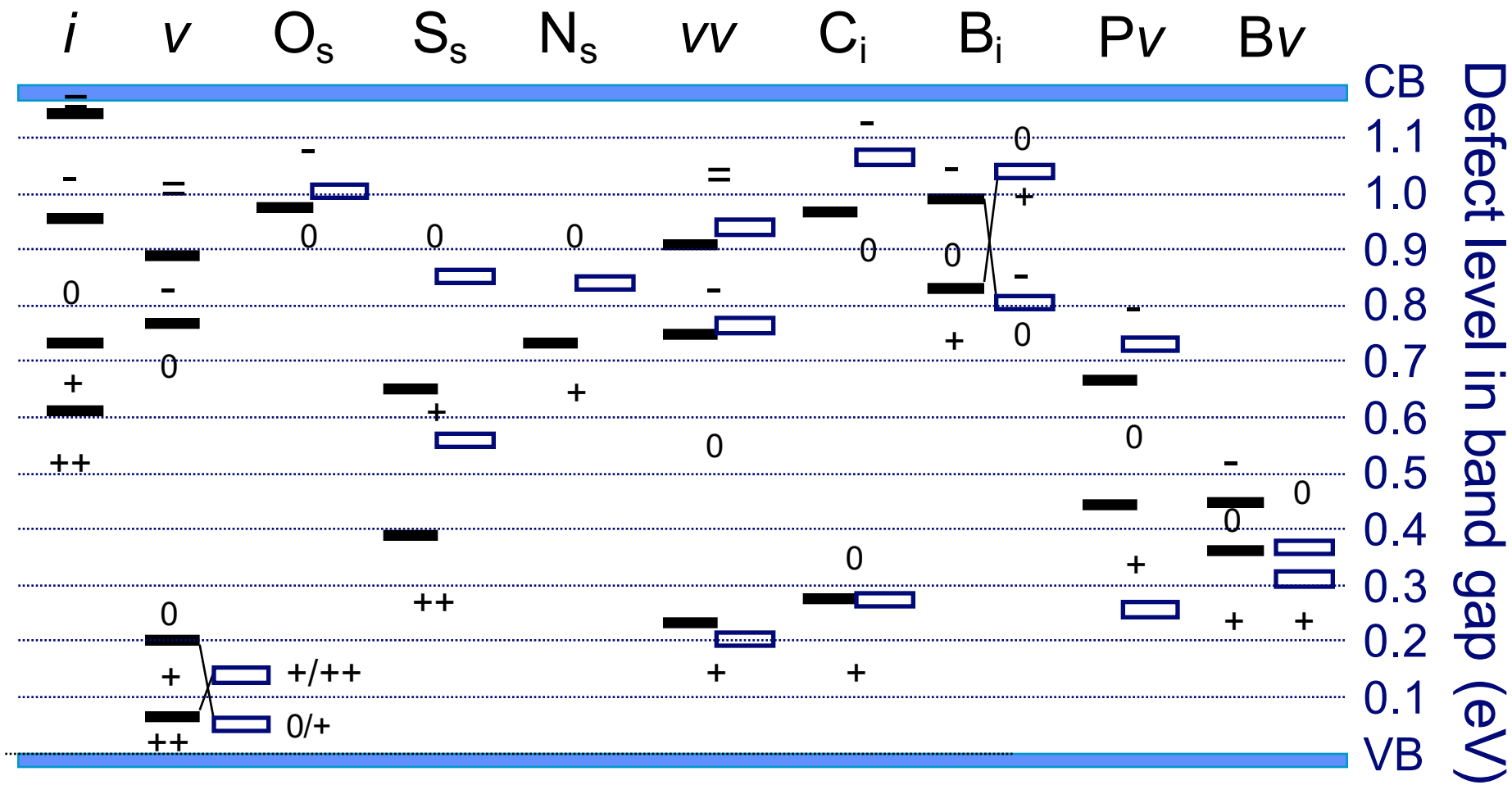
"Ab initio" computational model – connect model to physics
Calculations with rigorous control of charge boundary conditions

(*i.e.*,not jellium-based)

Si: DFT/LDA vs. Experimental Levels

Peter A. Schultz

Peter A. Schultz, Phys. Rev. Lett. **96**, 246401 (2006).



LDA: max error=0.25 eV, mean |error|= 0.10 eV

Intrinsic, first-row, second-row, and complexes across gap

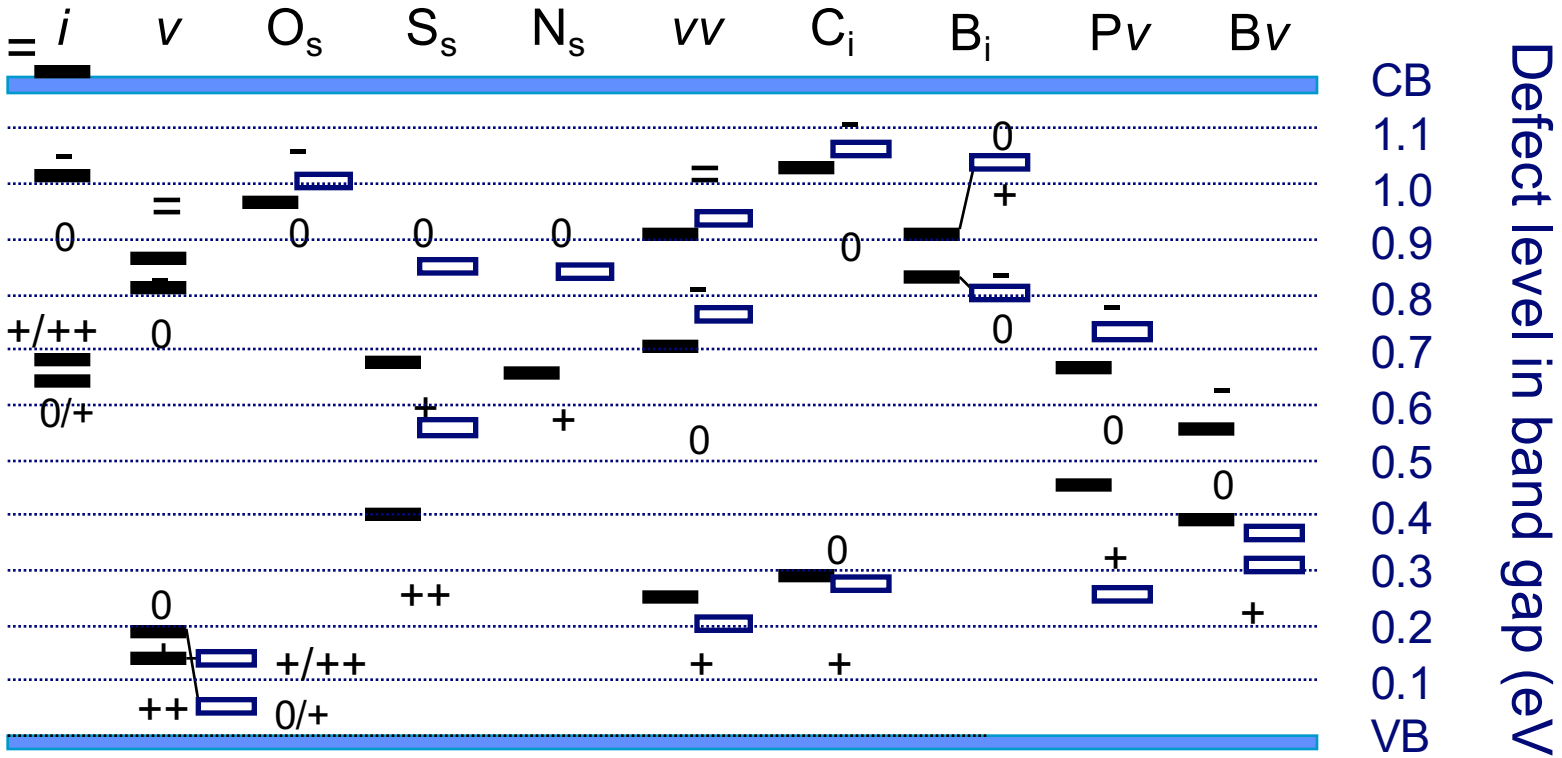
LDA Kohn-Sham gap is only 0.5 eV

Sandia National Laboratories

Si: DFT/PBE vs. Experimental Levels

Peter A. Schultz

P.A. Schultz and A.H. Edwards, NIMB **327**, 2-8 (2014).



… and several other defects

DFT/PBE defect level max |error|=0.20 eV, mean |error|=0.10 eV

DFT "defect gap" matches experiment (KS gap: 0.6 eV)

Absence of validated HSE/hybrid functional results

Sandia National Laboratories

Computational methods – III-V's

Peter A. Schultz

- **General purpose DFT code SeqQuest** (http://dft.sandia.gov/Quest)
  - well-converged (contracted-Gaussian) local orbital basis
  - both LDA and PBE functionals
  - converged norm-conserving pseudopotentials (Ga,In both Z_{val}=3,13)
  - full force relaxed (<1 meV total energies)
  - full FDSM … robust control of boundary conditions

- **Large bulk simulation supercells**
  - a_0=a_0(theory); GaAs: 5.60Å(LDA), 5.63Å(3d), 5.74Å(PBE); a_0(expt)=5.65 Å)
  - Up to 1000-atom supercells; cubic: 64-, 216-, 512-, 1000-site
  - ***k***-sampling: 3^3 for 64-site cells, 2^3 for larger (up to 1000-site) supercells,
  - explicit bulk screening
  - all these computational parameters are ***tested*** for convergence

Comparable to methods that yielded 0.1 eV accuracy in Si

Sandia National Laboratories

Simple intrinsic defects in GaAs: LDA

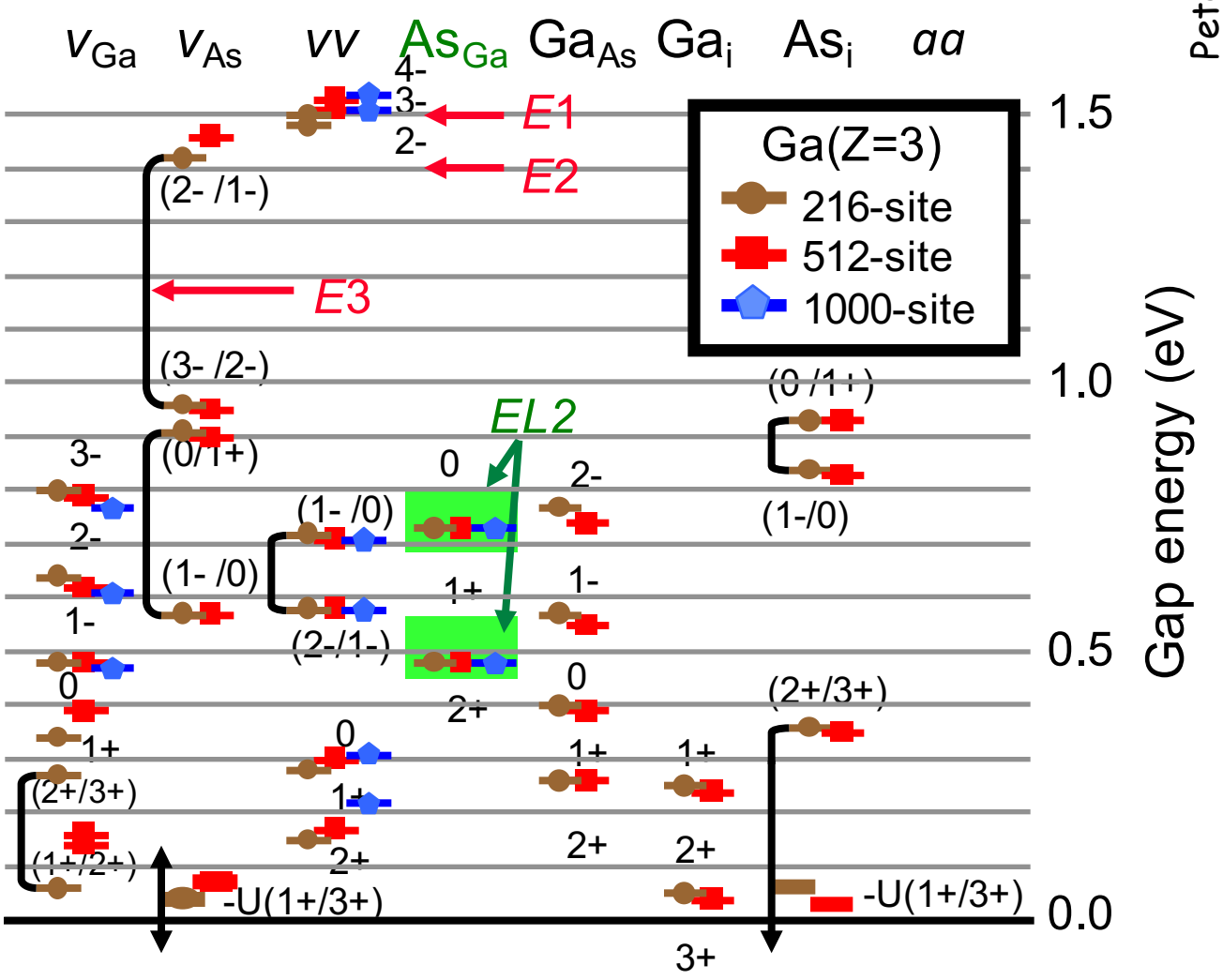
P.A. Schultz and O.A. von Lilienfeld, MSMSE **17**, 084007 (Dec. 2009).

216- = 512- = 1000-site
Verification: cell-converged

LDA-3d = LDA to ≤0.1eV
Verification: PP converged

LDA~PBE; spin <0.05 eV
Verification: functionals

As_{Ga} levels = *EL2* levels
v_{Ga} levels below midgap
Validation: levels < 0.1 eV



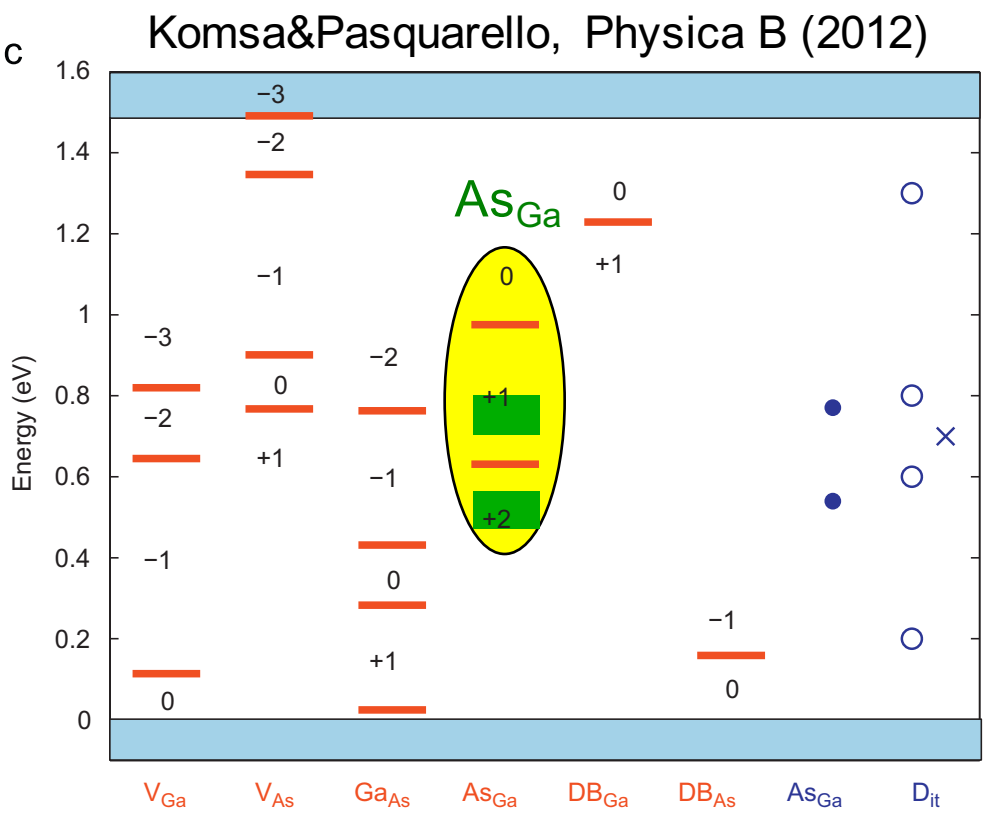
DFT+FDSM: Apparent accuracy of ~0.1 eV

Peter A. Schultz

Sandia National Laboratories

HSE for GaAs defects?

Peter A. Schultz



HSE gives ***worse*** results for EL2/As_{Ga}

(but: huge HSE computational cost … small cell, large-core PP)

Sandia National Laboratories

*E*1-*E*2 radiation center is the GaAs divacancy

P.A. Schultz, J. Phys.: Condens. Matter **27**, 075801 (2015).

Peter A. Schultz

Old (experimental) lore, back to 1988:

*E*1, *E*2 center = v_{As}(-/0), v_{As}(0/+)

*E*3 = v_{As} + *i*

vv is dismissed

Level structure reassigned with DFT:

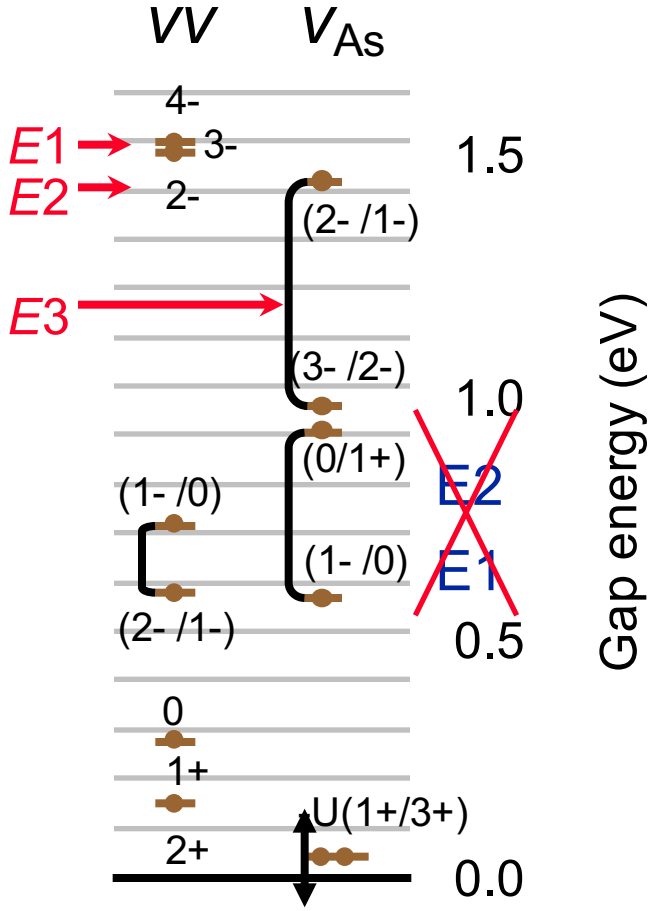
v_{As}(-/+) is mid-gap negative-U (only *one* level)

v_{As}(3-/1-) is upper-gap -U (*one* level)

vv(4-/3-/2-) near conduction band

vv is major radiation defect: *E*1-*E*2

v_{As}(3-/1-) transition is the *E*3



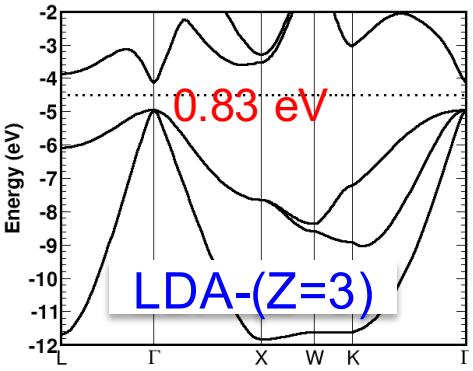
DFT-SeqQuest+FDSM levels good enough to identify defects based on ***quantitative*** defect level calculations

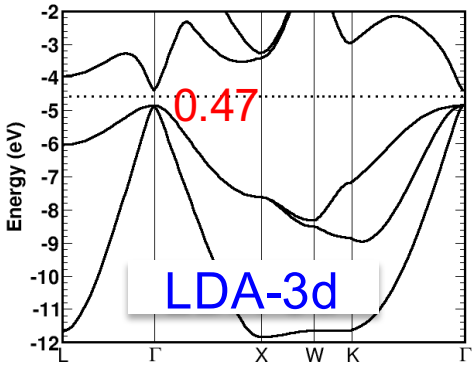
Sandia National Laboratories

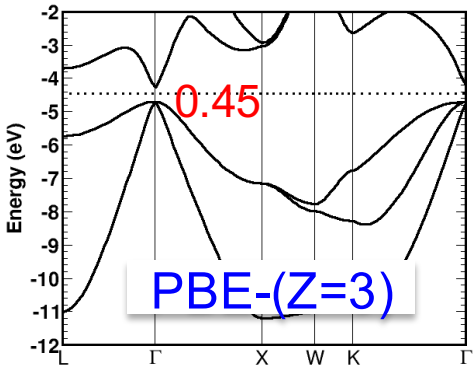
GaAs: A theoretical band gap laboratory

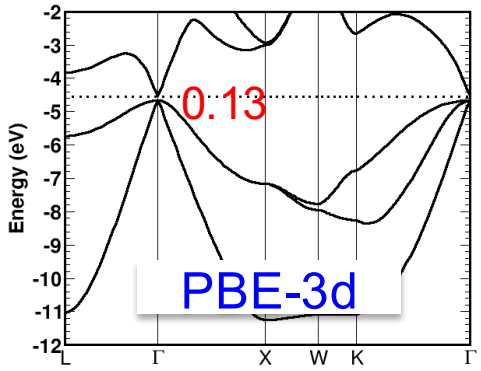
P.A. Schultz and A.H. Edwards, NIMB **327**, 2-8 (2014).

Change the Ga pseudopotential and the functional, and the KS band gap shrinks…









from 0.83 eV, LDA, Ga(Z=3) pseudopotential (PP) …

… to 0.13 eV, PBE-3d, Ga(Z=13) pseudopotential (PP)

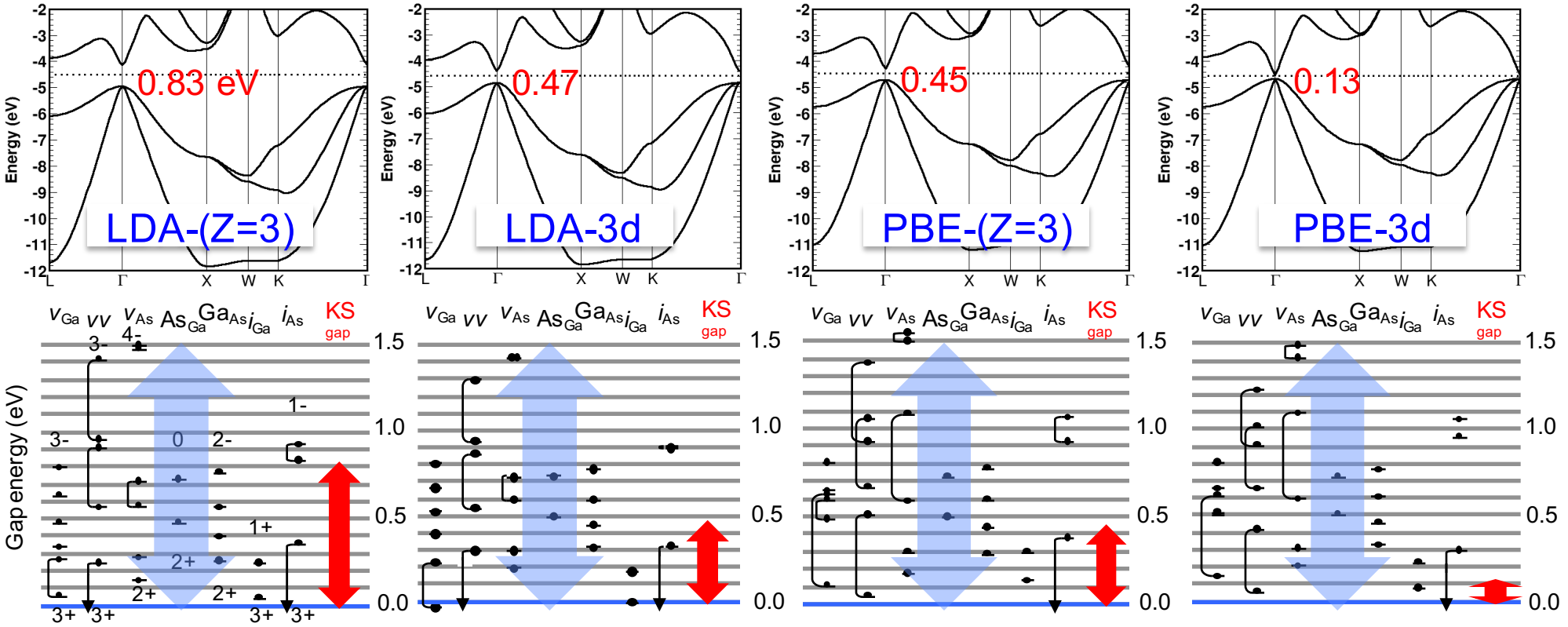
Sandia National Laboratories

GaAs: A theoretical laboratory

Peter A. Schultz

P.A. Schultz and A.H. Edwards, NIMB **327**, 2-8 (2014).

Change the Ga pseudopotential and the functional, and the KS band gap changes …



… but span of (total-energy-based) defect levels, the “defect band gap”, does not

Defect levels/gap ***insensitive*** to size of Kohn-Sham gap!

Sandia National Laboratories

The DFT "Defect band gap"

Peter A. Schultz

- Kohn-Sham gap: ***outside*** bounds of VB to CB *band* ***eigenvalues***
- Defect band gap: ***inside*** bounds of transition ***energies*** for defect levels

Band gaps: **experiment**, Kohn-Sham, DFT defect gap

Si	**1.17 eV**	
	KS	Defect
lda	0.49	1.2
pbe	0.62	1.2

AlAs	**2.16^{i} eV**	
	KS	Defect
lda	1.37	2.3
pbe	1.53	2.3

AlP	**2.51 eV**	
	KS	Defect
lda	1.48	2.55
pbe	1.67	2.55

GaAs	**1.52 eV**	
	KS	Defect
lda	0.83	1.54
lda-3d	0.47	1.52
pbe	0.45	1.50
pbe-3d	0.13	1.50

GaP	**2.35^{i} eV**	
	KS	Defect
lda	1.51	2.35
lda-3d	1.47	2.35
pbe	1.74	2.35
pbe-3d	1.52	n/c

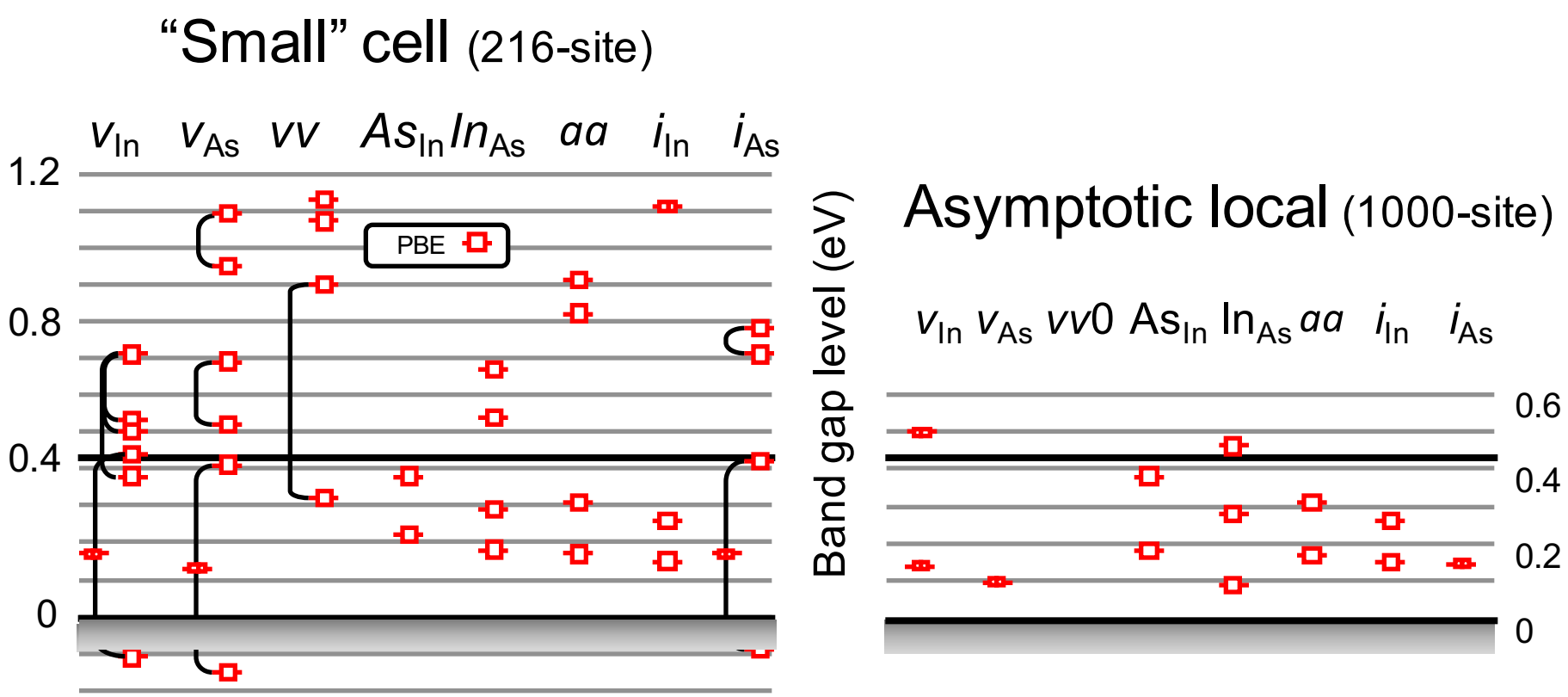
InP	**1.42 eV**	
	KS	Defect
lda	0.67	1.7
lda-3d	0.66	1.7
pbe	0.47	1.7
pbe-3d	0.46	n/c

Defect band gap matches (overshoots?) experiment

Sandia National Laboratories

InAs – no KS-DFT gap, no defects?

Peter A. Schultz



Too many defects!

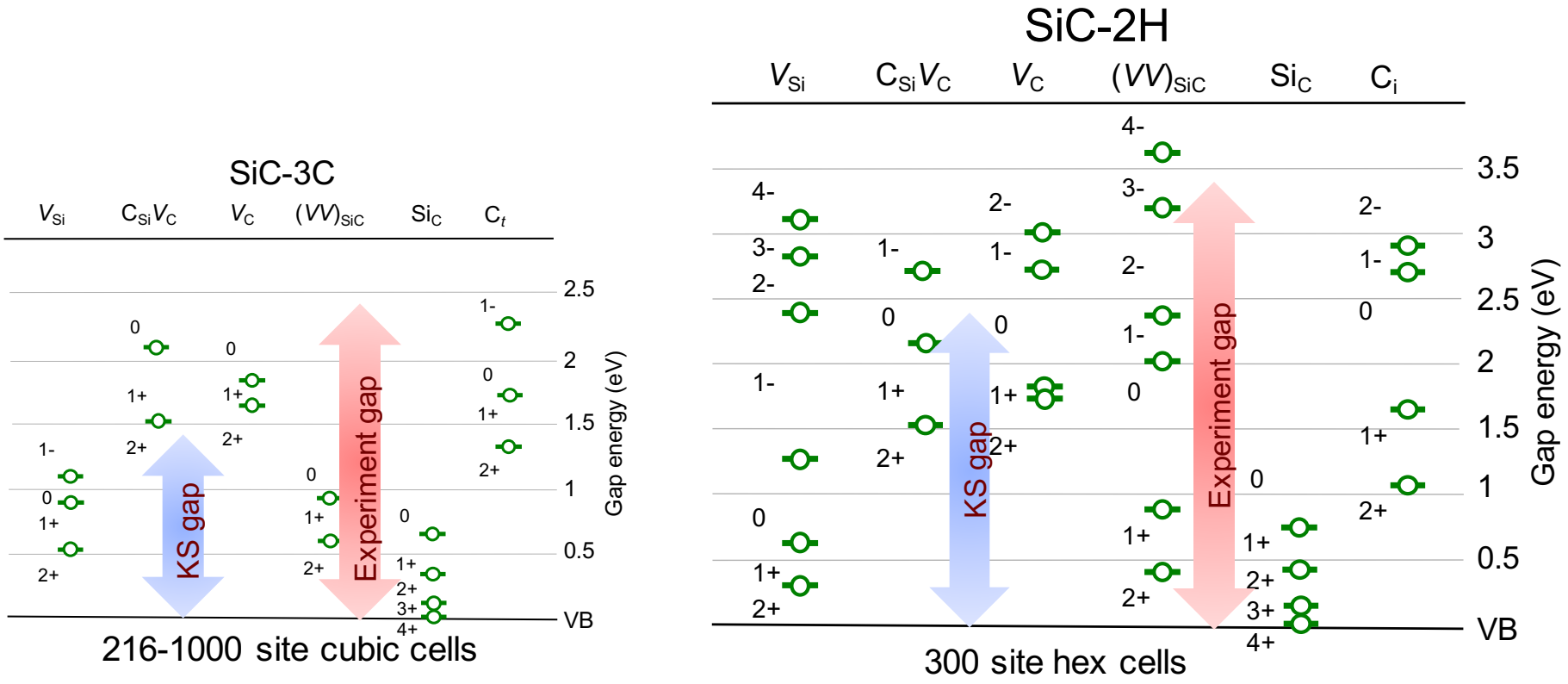
Need ***1000-site*** supercells to discriminate localized defects

Need to resolve finite-size errors near band edges

Sandia National Laboratories

SiC – polymorphs

Peter A. Schultz



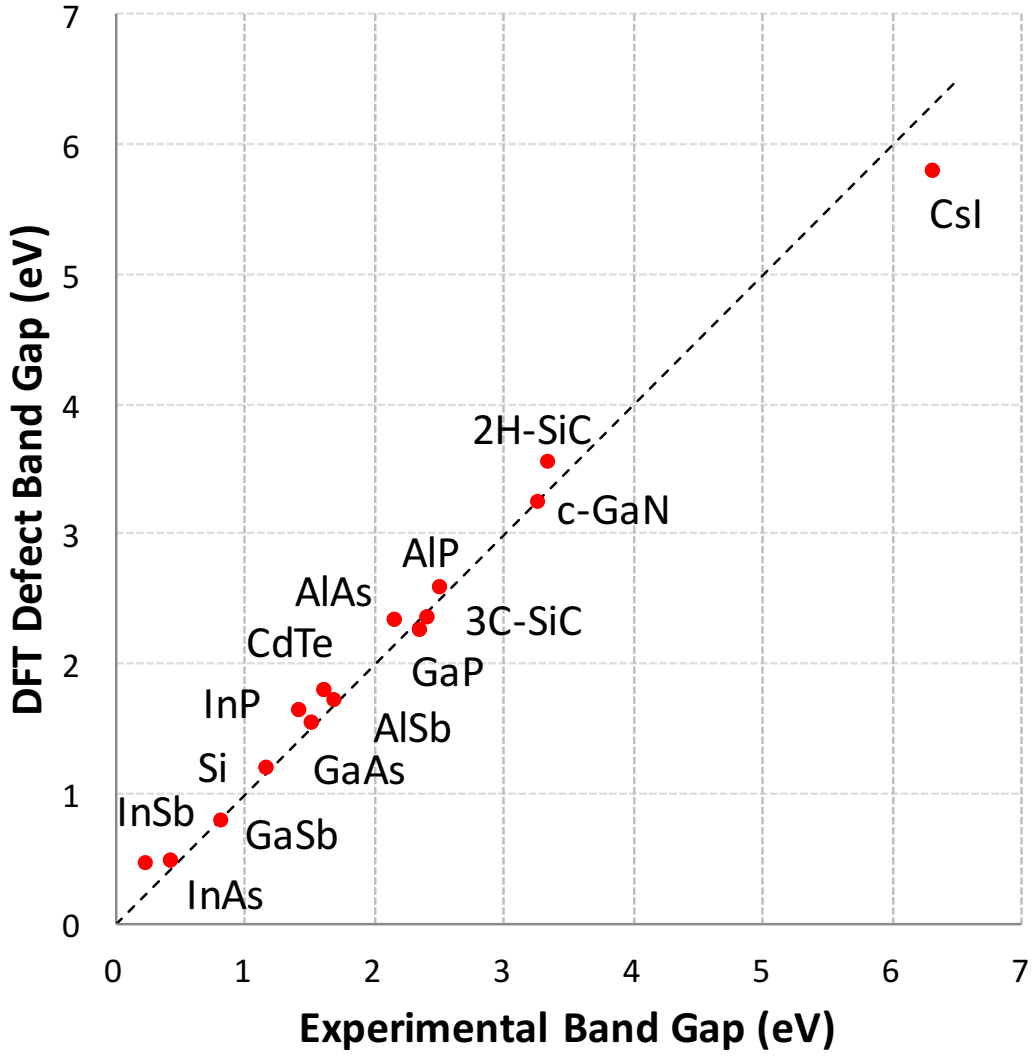
Total-energy-based defect levels

Predicts correct defect band gap for 3C-SiC *and* 2H-SiC

Sandia National Laboratories

The PBE Defect Gap vs. the Band Gap

Peter A. Schultz



PBE defect gap = experiment, *despite a band gap problem*

Sandia National Laboratories

Conclusions

Peter A. Schultz

- **"If you do not have the right band gap, you cannot hope to get the defect levels right"** ?

- **Defect band gap** predicts experimental band gap, despite KS-DFT band gap error

- Insensitive to change in functional (LDA vs. PBE), or pseudopotential
- Varied KS-DFT gap (GaAs "laboratory") → no change in levels or defect gap
- Zero KS-DFT band gap (InSb, InAs, GaSb) → good defect band gap
- Insensitive to k-sample gap (Si k-sample gap = KS gap)
- Semilocal DFT+FDSM - quantitative (~0.1 eV) for defect levels (where HSE fails)

→ importance of boundary conditions and finite size (supercell) effects

--------- Supporting slides ---------

CsI defect level spectrum - DFT

Peter A. Schultz

R. M. Van Ginhoven and P.A. Schultz, J.Phys.: Cond. Matter **25**, 495504 (2013)

250-site results = 432-,686-site
Verification: cell-converged

v_I levels match experiment
Validation of accuracy

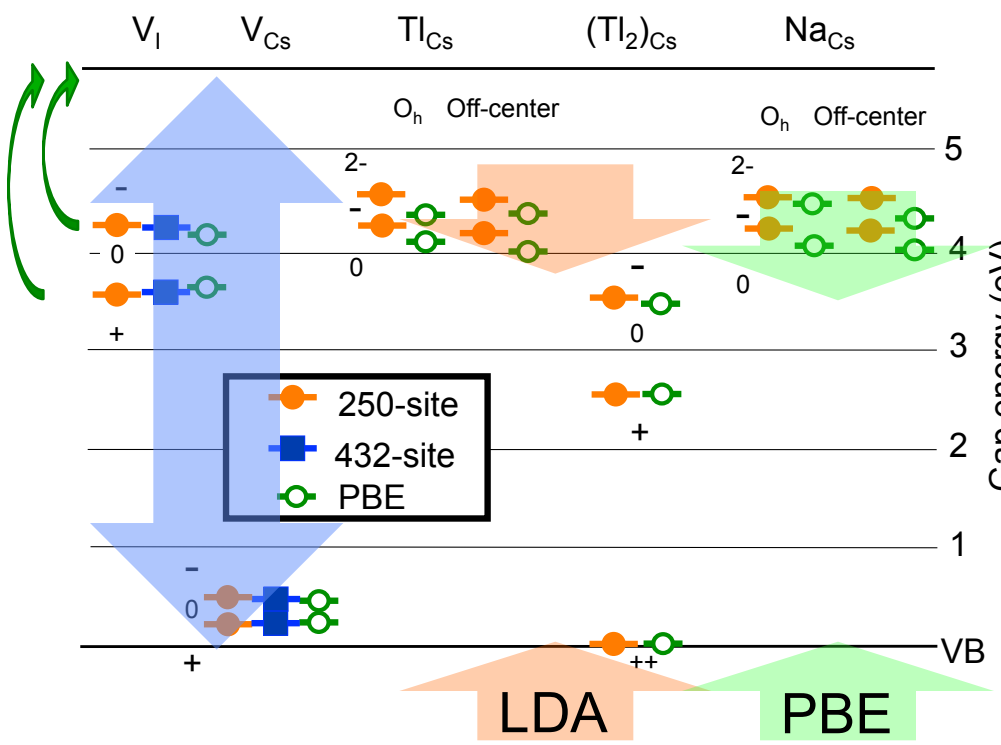
CsI band gap

KS-LDA: 3.80 eV

KS-PBE: 3.58

Defect span: >5.8 eV

Experiment: 6.3 eV

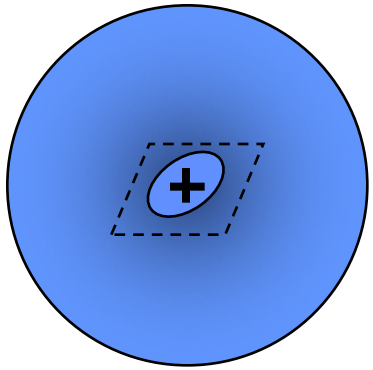


Not a band ***gap*** problem, a ***band edge problem***—
where are they cf. total energy defect levels?

Sandia National Laboratories

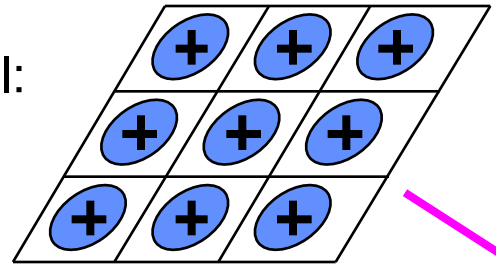
A supercell theory of defect energies

Peter A. Schultz, Phys. Rev. Lett. **96**, 246401 (2006).

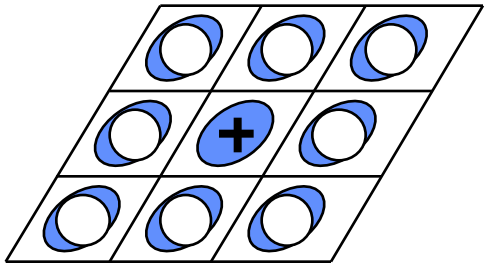


Target system: isolated defect = Computational model for isolated defect

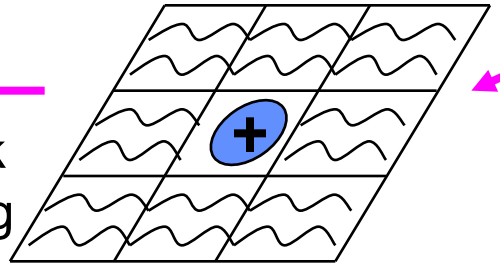
Standard DFT model: Supercell



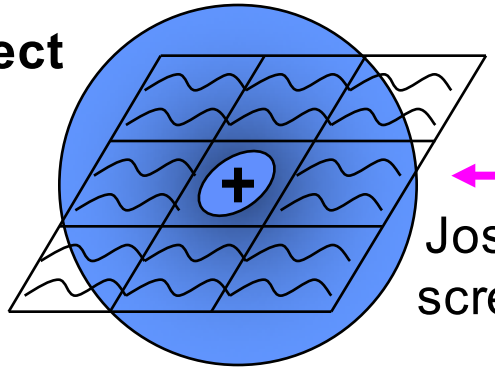
LMCC to fix boundary conditions



Crystal embedding to fix μ_e



Jost Bulk screening



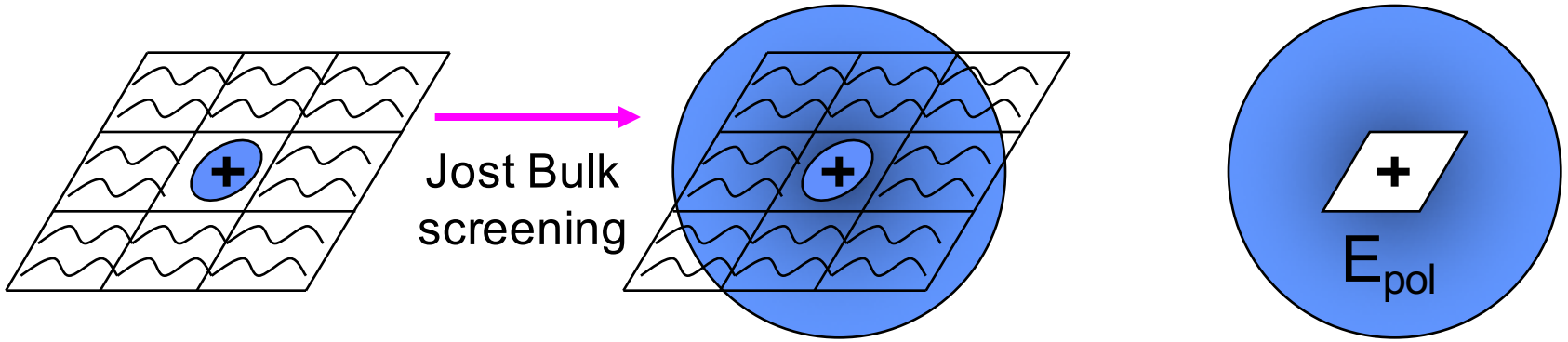
(+ DDO for defect banding)

Finite Defect Supercell Model

FDSM: *Ab initio computational model* – connect model to physics
Calculations with rigorous control of charge boundary conditions

The polarization model

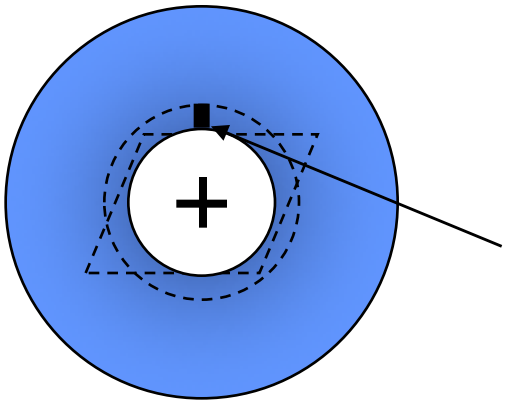
Peter A. Schultz



For extrapolation to bulk, need energy of screening outside of supercell: E_{pol}

Jost model: $$E_{pol} = \frac{(1 - 1/\varepsilon_0)\, q^2}{R_{jost}}$$

$R_{jost} = R_{vol} - R_{skin}$
q = charge on defect
$R_{jost} = R_{vol} - R_{skin}$
R_{vol} = radius of volume sphere



Two parameters for any material

R_{skin} = unscreened volume **inside** cell.
fit: =1.3-1.7 Bohr

ε_0 = static dielectric constant - expt

Si	GaAs	InP	GaP	AlAs	InAs
11.8	13	12.5	11.2	10.1	15.15