SAND2016-9983PE

Modeling charged defects and defect levels in semiconductors and oxides with DFT:
An improved inside-out perspective

Peter A. Schultz

Center For Computing Research: Multiscale Science, Dept. 1425

Sandia National Laboratories. Albuquerque NM 87185 USA

(With special thanks to Art Edwards at Air Force Research Laboratory)

October, 2016

SAND2015-3847-RE
Unlimited Release

U.S. DEPARTMENT OF ENERGY

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. .

Sandia National Laboratories

Why model defects in semiconductors and oxides?

Radiation effects in electronics

Process modeling for semiconductors

Radiation detectors

Defect chemistry in nuclear fuels and nuclear waste

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

Defects: from atoms to devices

Peter A. Schultz

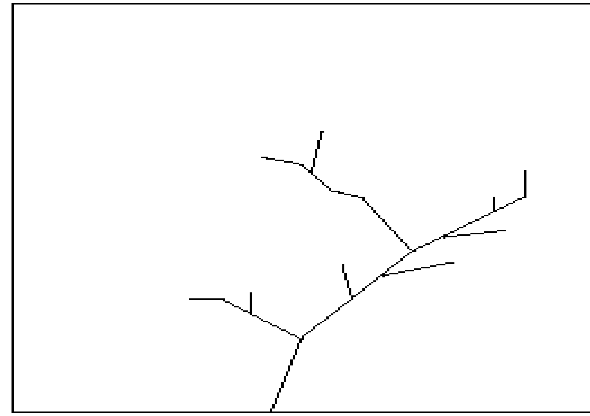
Initial defect distribution

Radiation creates displacement damage:

$$R \rightarrow V + I$$

and charge carriers (electrons and holes)

$$R \rightarrow n + p$$



Thx: Harry Hjalmarson (Sandia)

Defect evolution

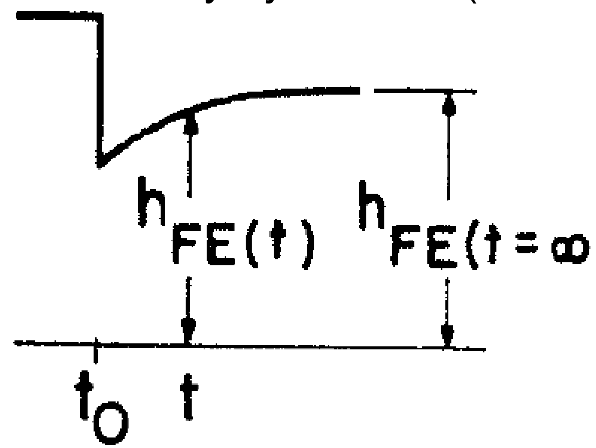
Defects react with each other, and with other dopants and impurities:

$$V + I \rightarrow Si_{Si}$$

Defects recombine electrons and holes, modifying currents:

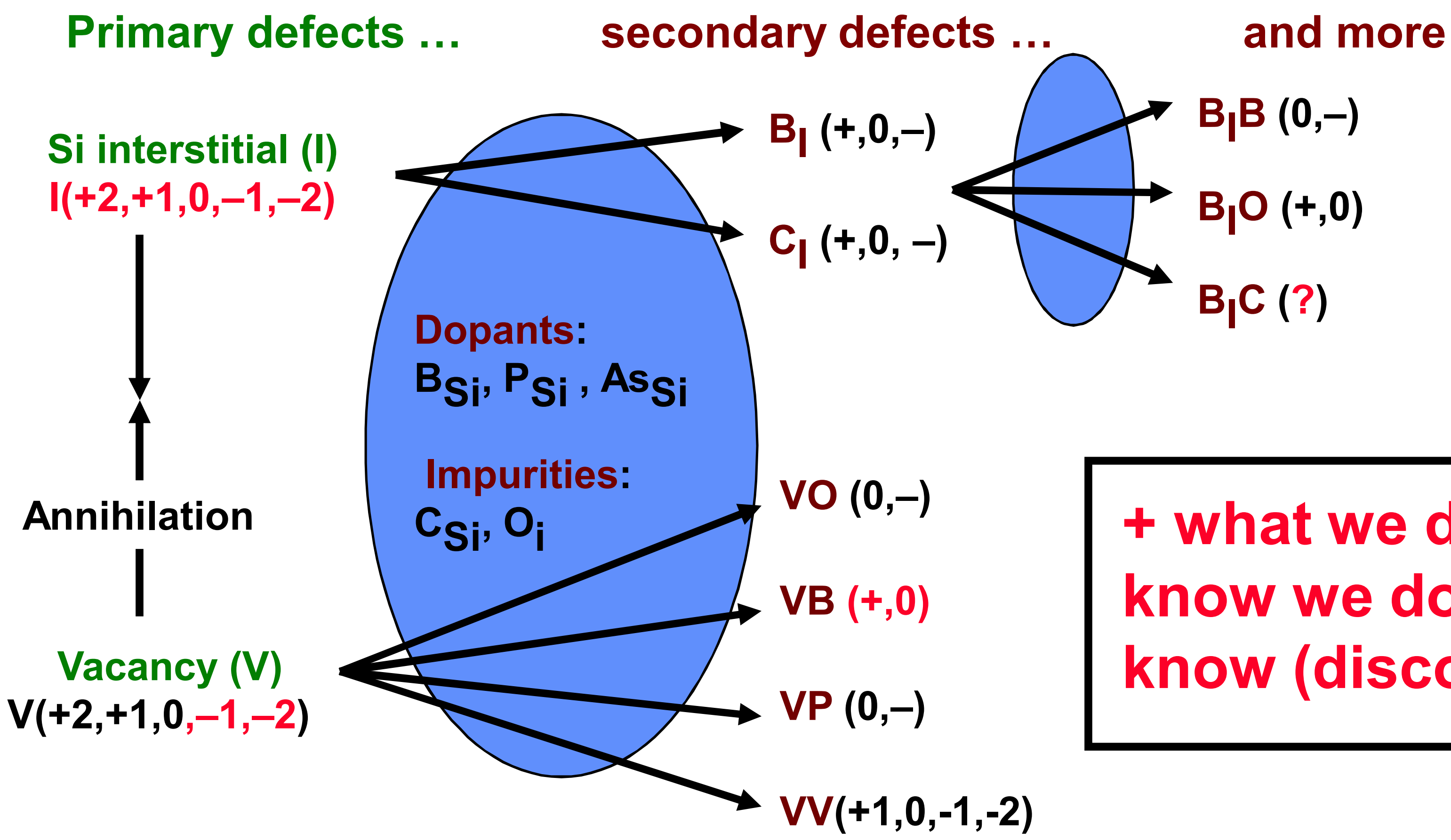
$$T^0 + n \rightarrow T^-$$

$$T^- + p \rightarrow T^+$$



Radiation/implant/processing creates evolving chemistry of defects. Those defects govern the performance of electronic devices.

The radiation effect defect universe: Si



+ what we don't know we don't know (discovery)

Need DFT - density functional theory - to fill gaps in defect physics: defect band gap energy levels, diffusion activation

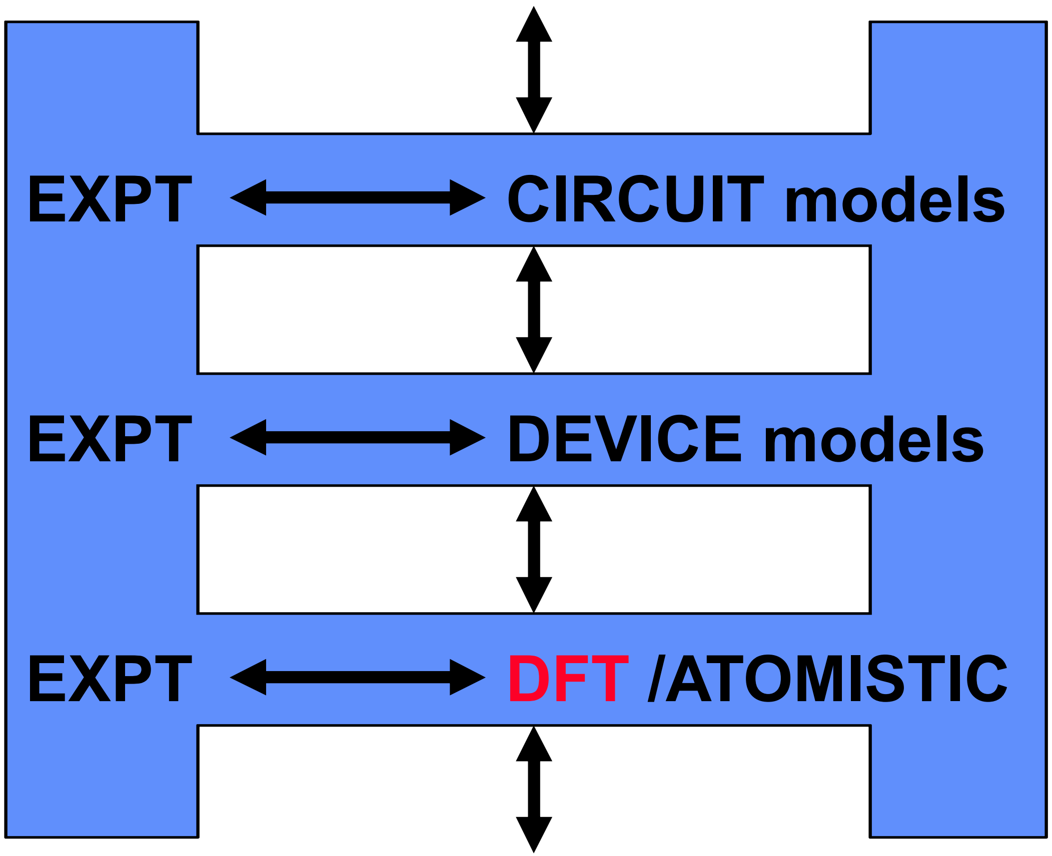
Peter A. Schultz

Sandia National Laboratories

Multiscale ladder for radiation damage

Peter A. Schultz

Electrical system response



Radiation damage

Require: quantitative confidence

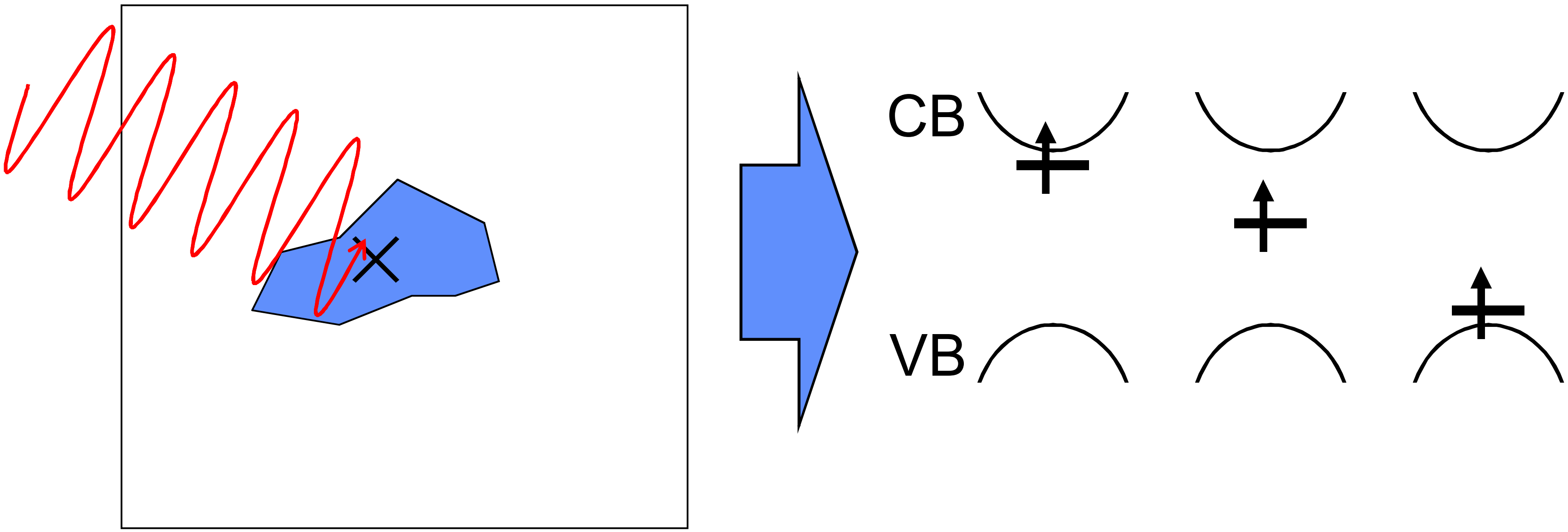
Verification, validation, uncertainty

Sandia National Laboratories

Radiation damage and defect levels

Peter A. Schultz

Radiation damage …



produces defects … and introduces electronic transitions

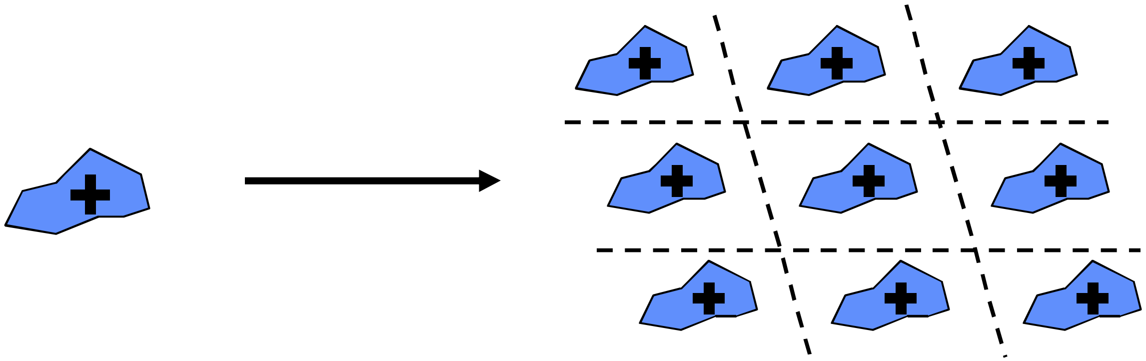
… and we need to quantify these transitions; DFT

Sandia National Laboratories

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

DFT "band gap problem"

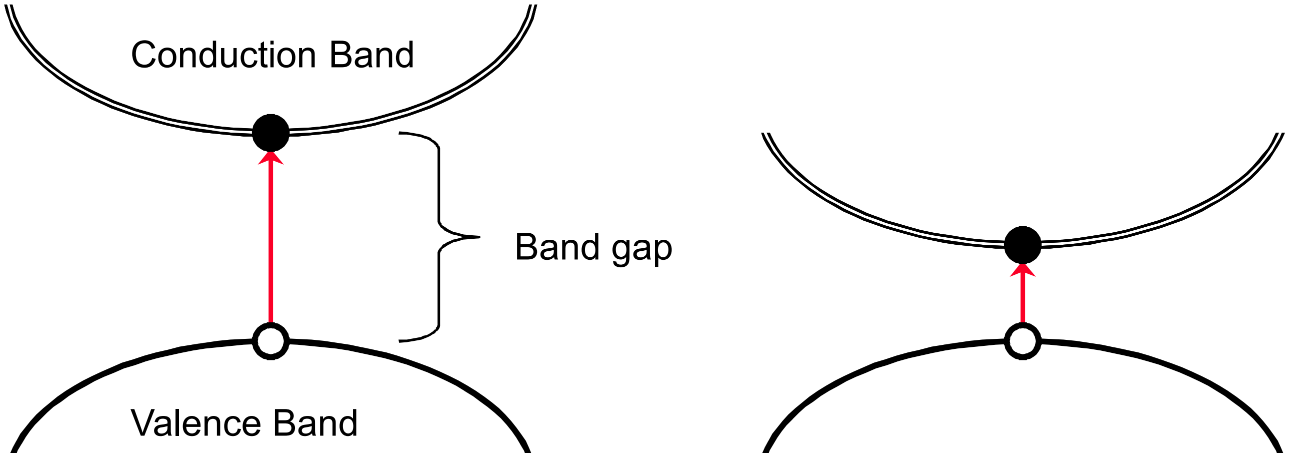
Peter A. Schultz

DFT gap. i.e., in KS eigenvalues, significantly underestimates experiment

[L.J. Sham and M. Schlüter, PRL **51**, 1888 (1983); PRB **32**, 3883 (1985)]

Si: expt: 1.2 eV, DFT/LDA: 0.5 eV

GaAs: expt. 1.5 eV, DFT/LDA: 0.5 eV



Experiment

Kohn-Sham (KS) eigenvalue spectrum

The band gap defines the energy scale for defect levels

Fundamental impediment to quantitative predictions?

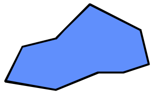
Sandia National Laboratories

The Supercell Approximation

Fast Fourier Transforms are convenient means to solve 3D Poisson Equation.

DFT codes typically assume periodic boundary conditions.

However, our finite defect is not periodic …



Finite defect

Peter A. Schultz

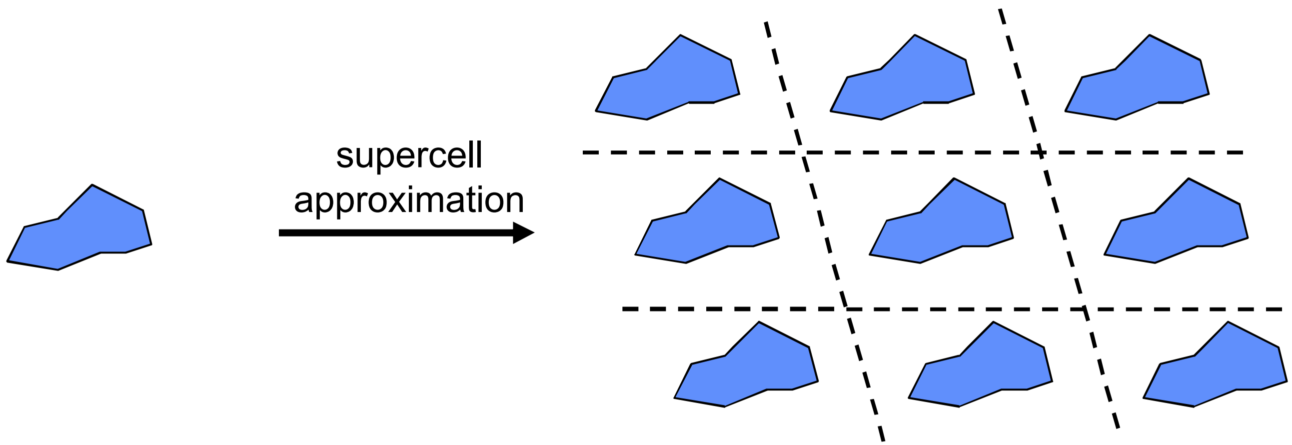
The Supercell Approximation

Peter A. Schultz

Fast Fourier Transforms are convenient means to solve 3D Poisson Equation.

DFT codes typically assume periodic boundary conditions.

However, our finite defect is not periodic …



Finite defect

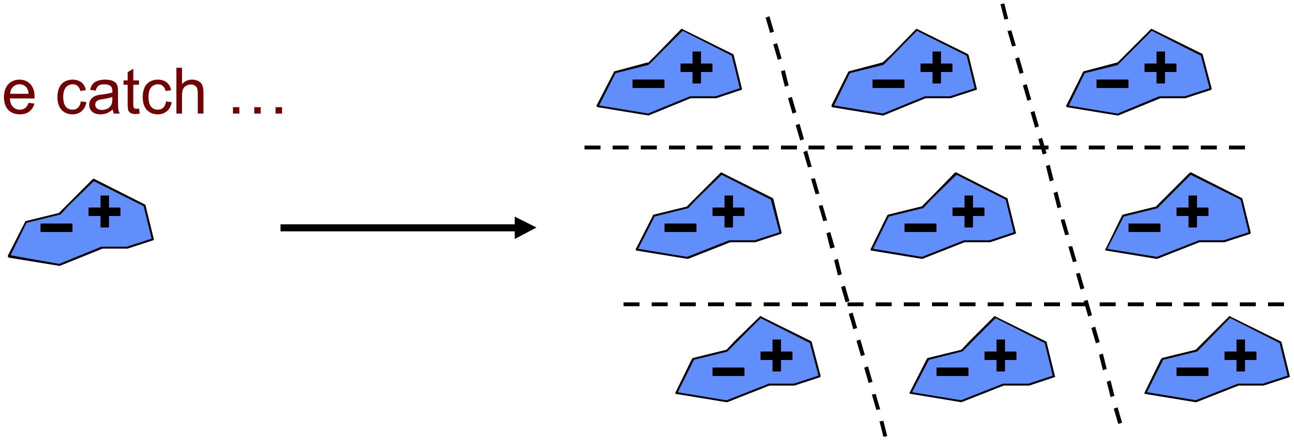
Periodic (interacting?) defects

The supercell Idea:
Surround perturbed defect region with enough material to buffer defects.
In the limit of *large enough* supercells … approach an isolated defect.

The Supercell Approximation

Peter A. Schultz

the catch …



Finite defect with dipole

Periodic (interacting) defects

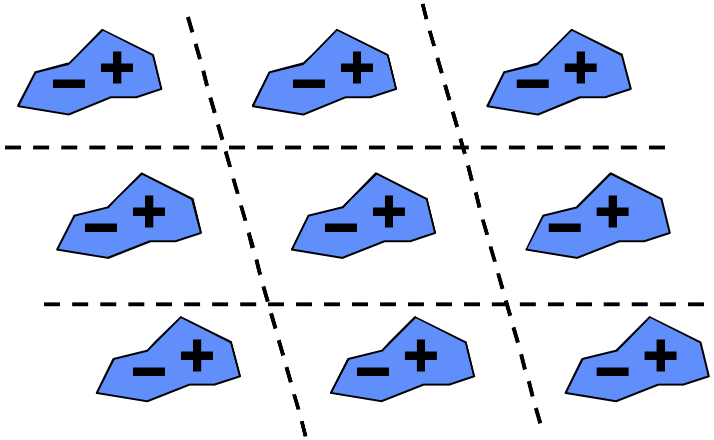
DFT expense limits size of supercell - defects interact

Sandia National Laboratories

The supercell approximation

Peter A. Schultz

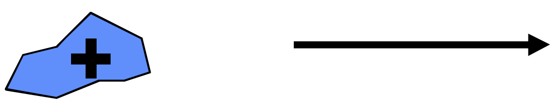
A problem …

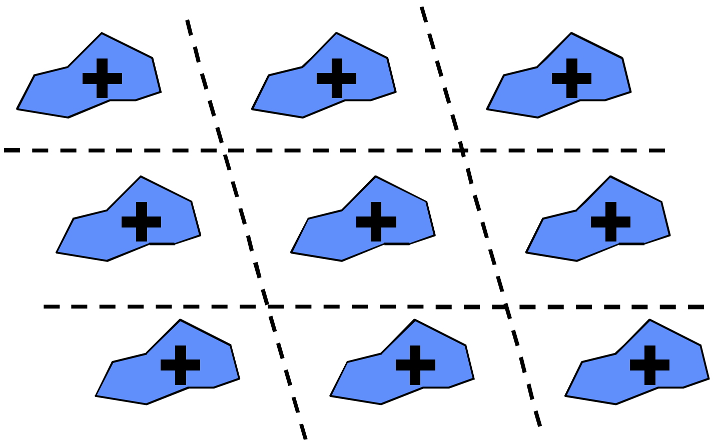


Finite defect with dipole

Periodic (interacting) defects

even worse …





Finite charged defect

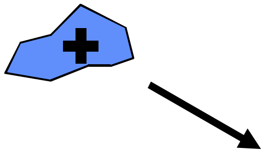
Ill-defined (Coulomb divergence)

Interactions and divergence are key issues

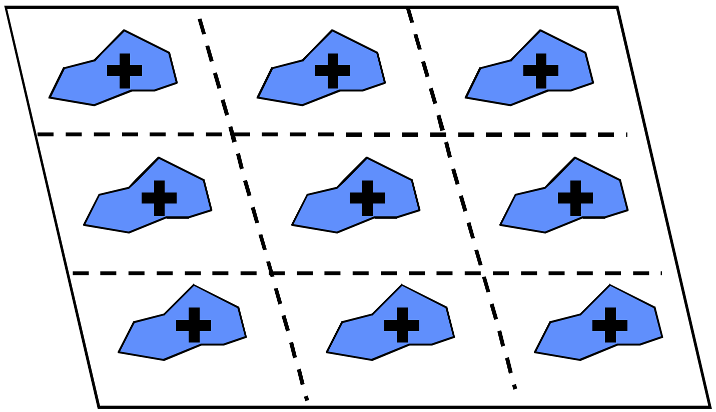
Sandia National Laboratories

Jellium to eliminate divergence?

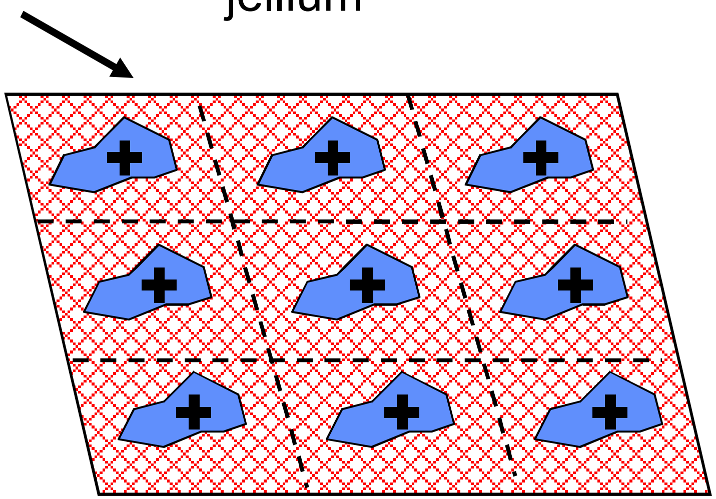
Isolated defect …



Apply supercell approximation …

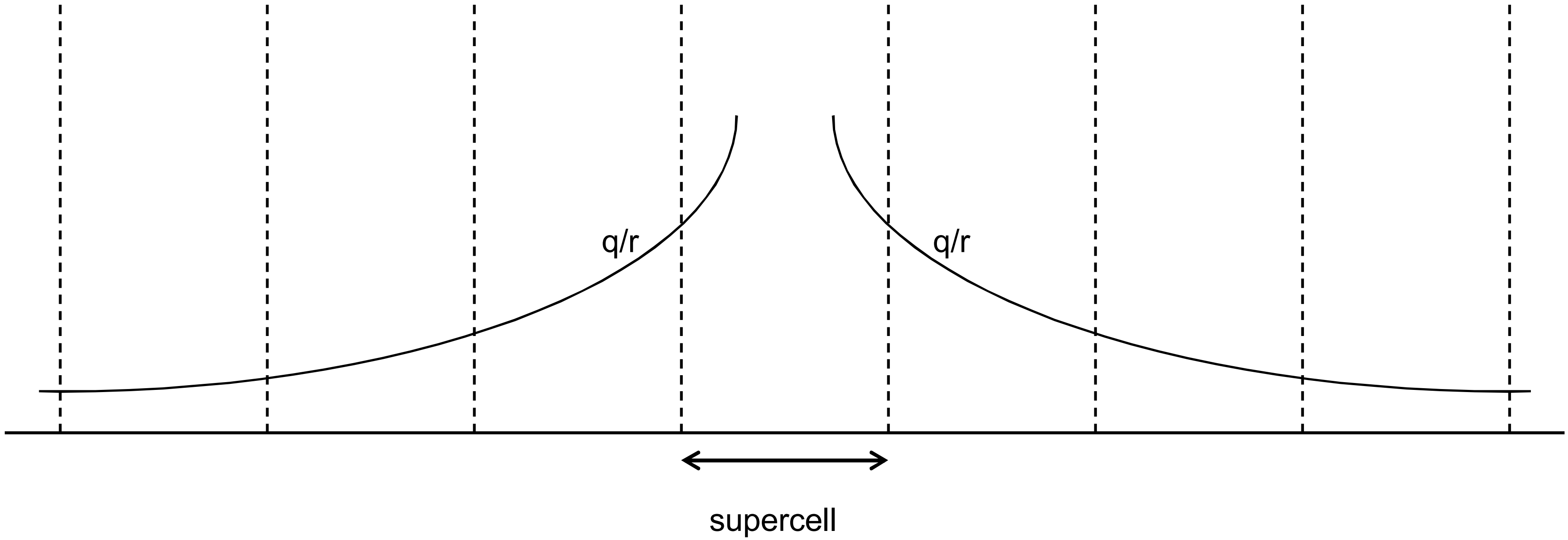


Neutralize with flat background charge: “jellium”



Peter A. Schultz

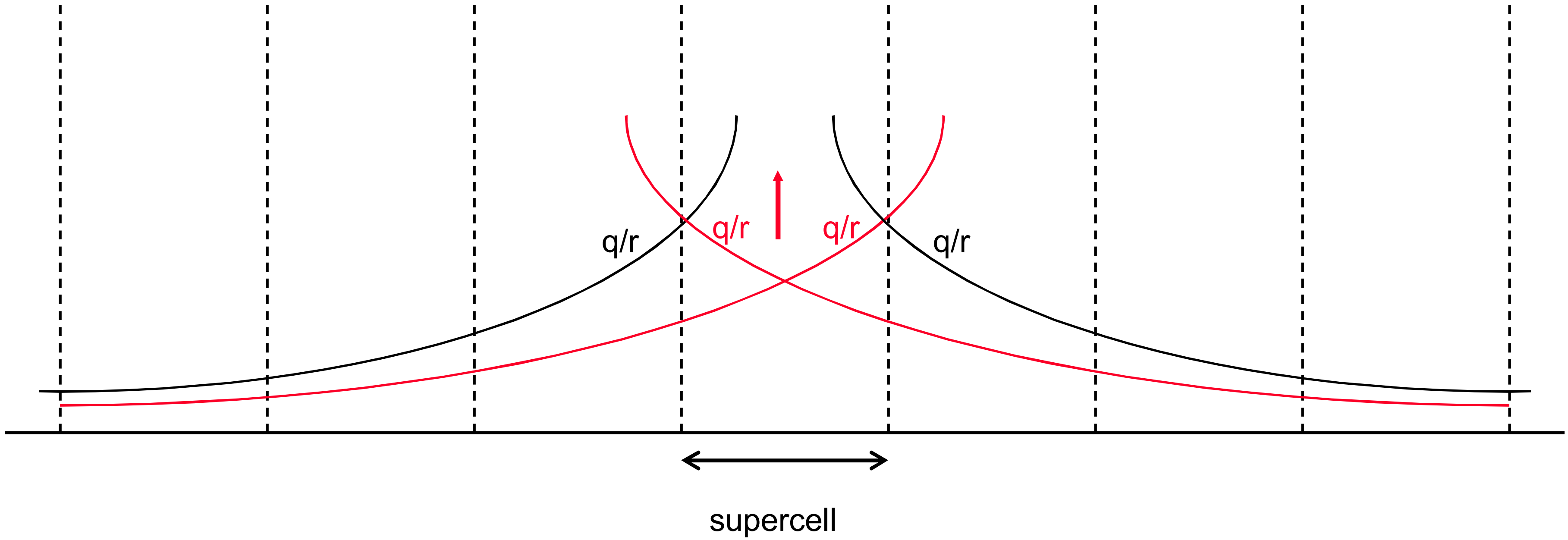
Whence the divergence?



Peter A. Schultz

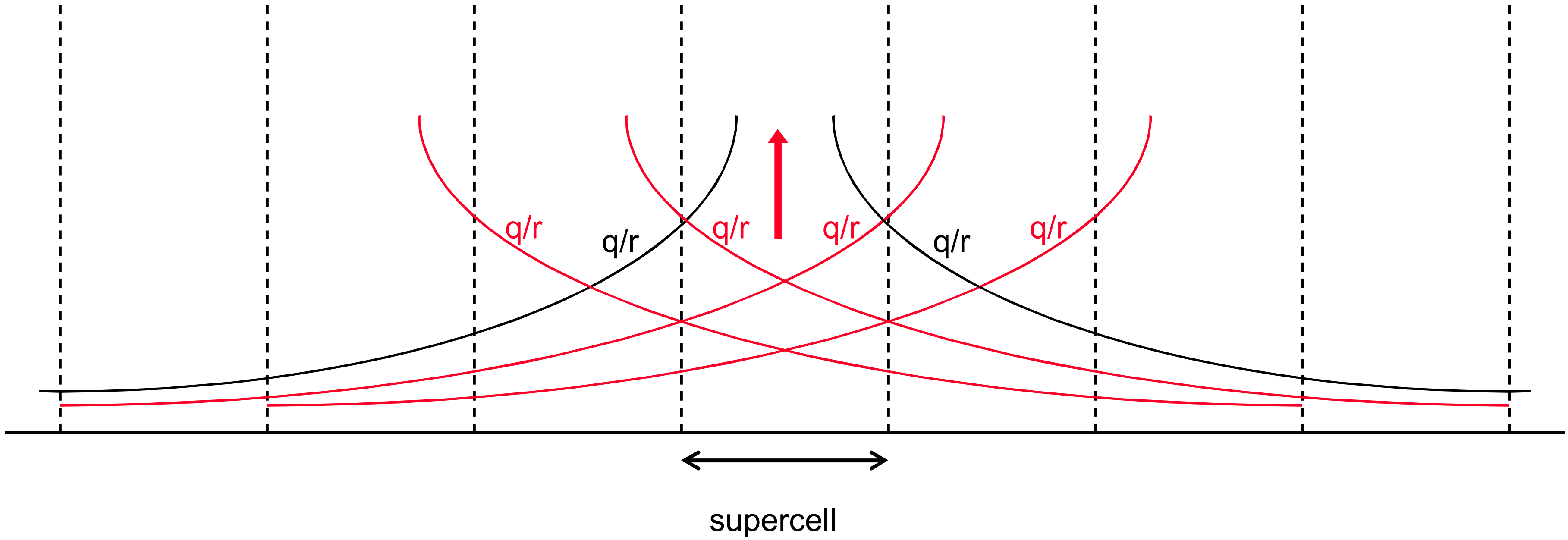
Whence the divergence?

Peter A. Schultz



Whence the divergence?

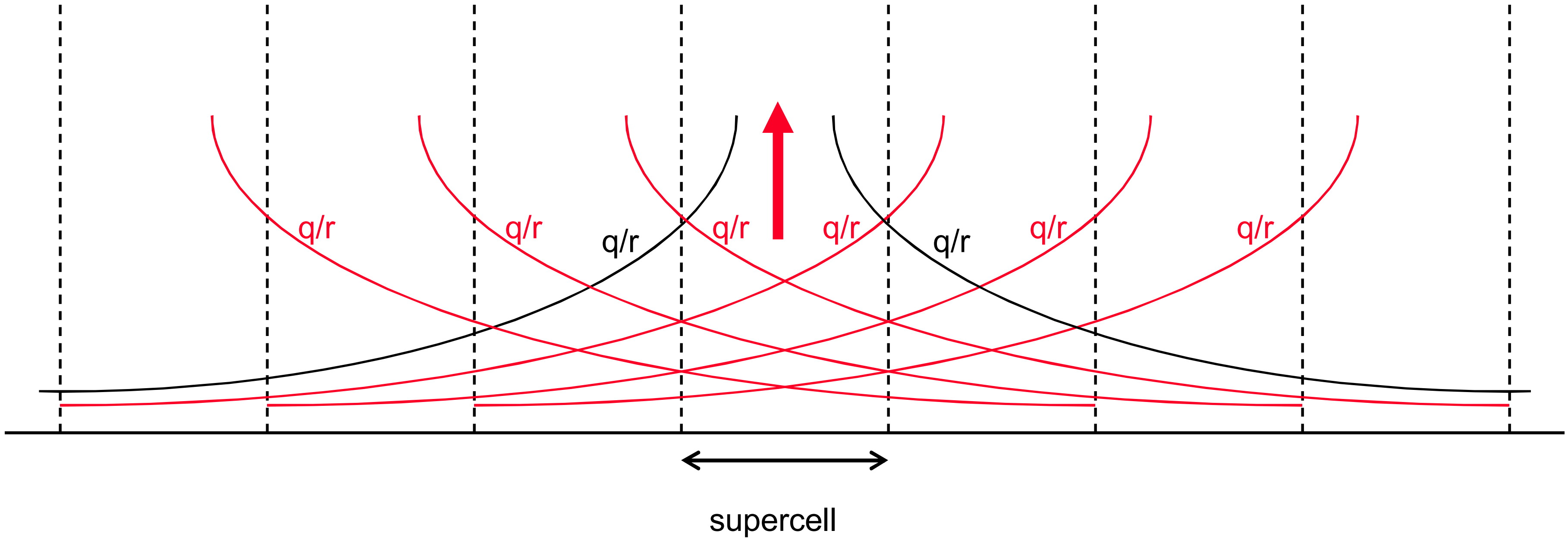
Peter A. Schultz



Sandia National Laboratories

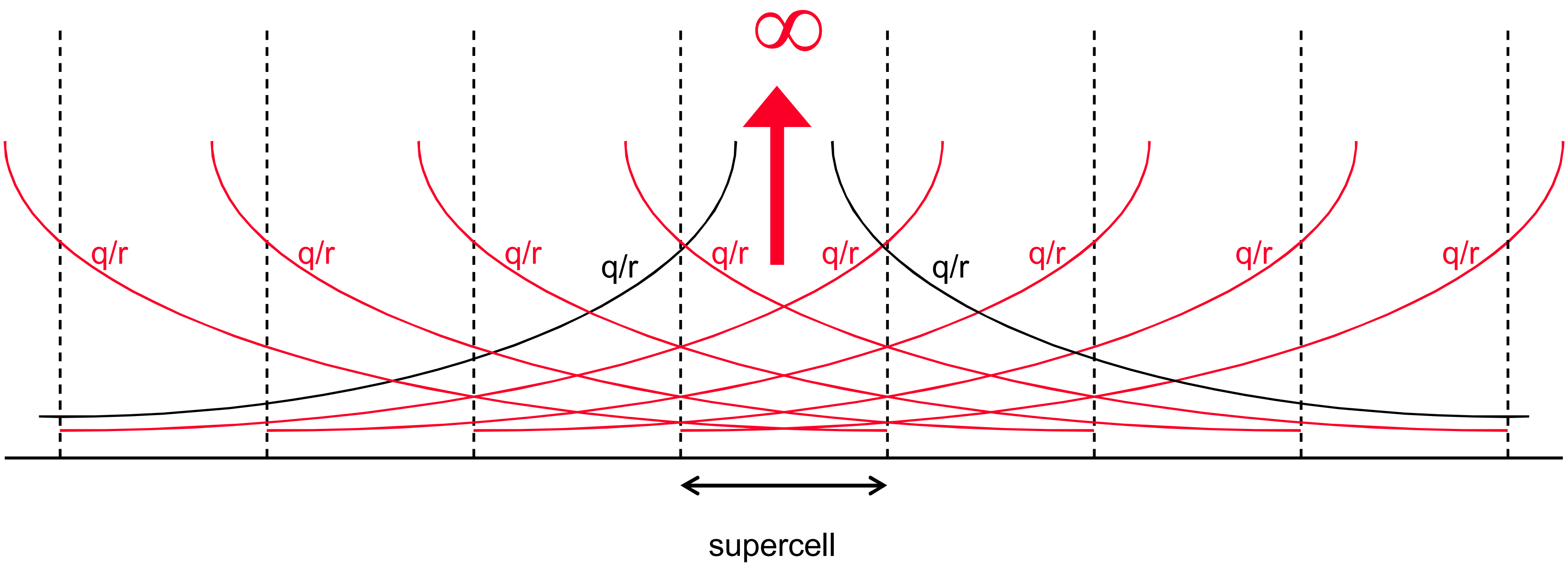
Whence the divergence?

Peter A. Schultz



Whence the divergence?

Peter A. Schultz



Divergence arises from infinite-ranged q/r potentials from periodic images

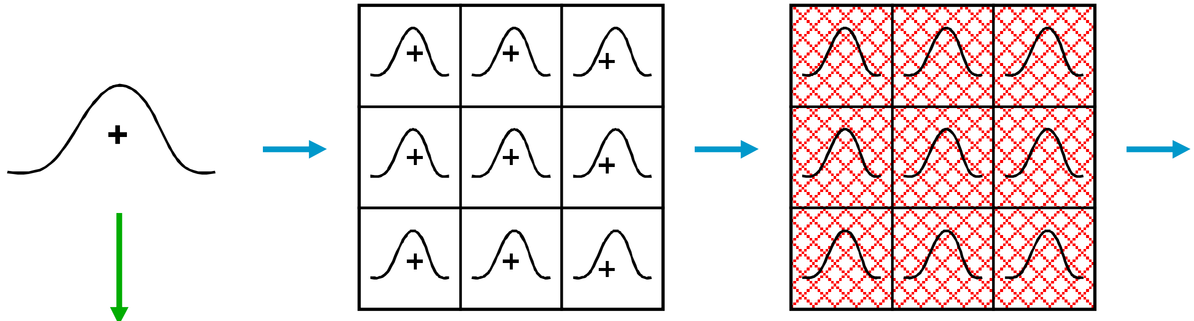
Divergence is not flat

Sandia National Laboratories

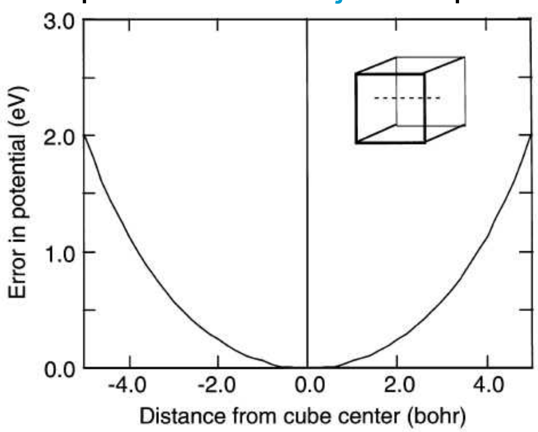
Net charge boundary conditions - jellium

Peter A. Schultz

Take isolated charge density… → create cubic supercell … → neutralize with "jellium" → Solve Poisson Equation for potential using periodic boundary conditions



Compare exact and jellium potential



Error in electrostatic potential over volume of supercell

Potential error goes as 1/L (length)!

L (Bohr)	Cell size	Potential Errors (V)
10.2	8 atoms	2.0 V
20.4	64	1.0
30.6	216	0.67
40.8	512	0.50
51.0	1000	0.40

Si band gap: 1.2 eV (expt.), 0.5 eV (DFT)

Standard jellium method has large O(1/L) error in potential
Error propagated into density distribution and into energy

Sandia National Laboratories

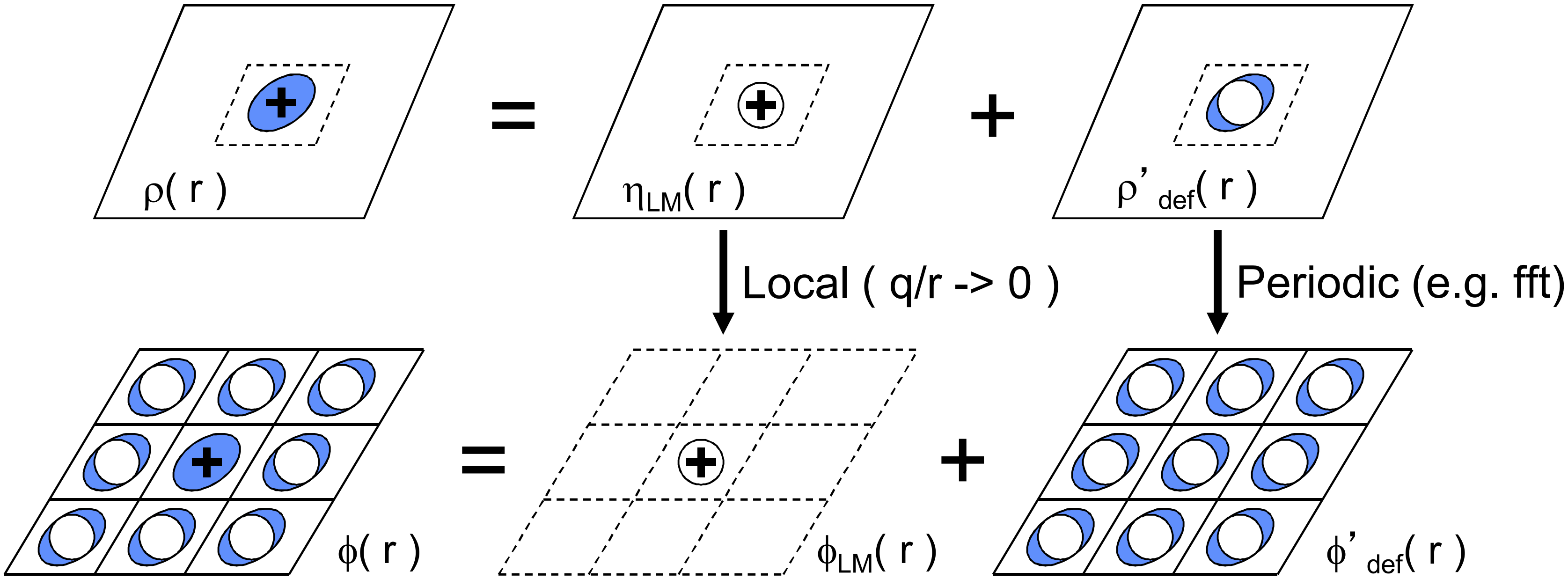
Local Moment CounterCharge (LMCC)

P.A. Schultz, PRB **60**, 1551 (1999)

- Solution of Poisson Equation is linear in the density
- LMCC: split total density $\rho(r)$ into two pieces …

(1) model local density $\eta_{LM}(r)$ matching multipole (charge) of $\rho(r)$

(2) remainder (momentless) density $\rho'(r) = \rho(r) - \eta_{LM}(r)$



Gives proper $r \rightarrow \infty$ asymptotic boundary condition
Avoid (not ignore!) Coulomb divergence

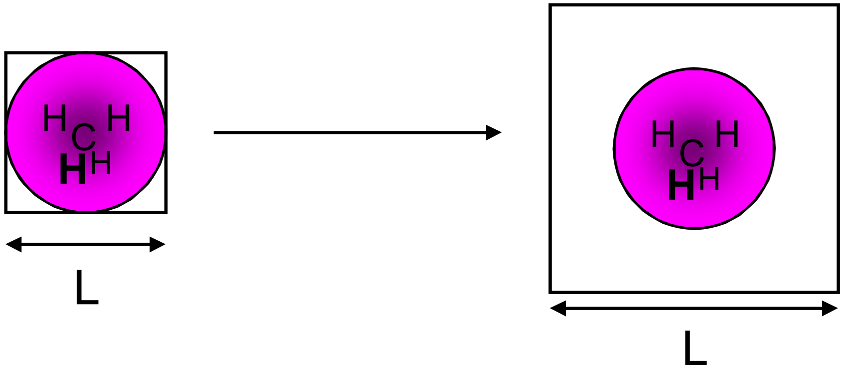
Sandia National Laboratories

Peter A. Schultz

Charged cell convergence - LMCC

Peter A. Schultz

P.A. Schultz, PRB **60**, 1551 (1999)



Charged, no dipole: $CH_4 \rightarrow CH_4[+]$ … Ionization Potential

L = 18.0 - 30.0 bohr (9.5-15.9 Å) IP varies < 10^{-5} eV

Dipole, no charge: Na–Cl diatomic molecule … Total Energy

L = 16.8 - 30.0 bohr (8.9-15.9 Å) TE varies < 10^{-5} eV

Dipole, charge: OH → OH[-] … Electron Affinity

L = 18.0 - 30.0 bohr (9.5-15.9 Å) EA varies < 10^{-3} eV

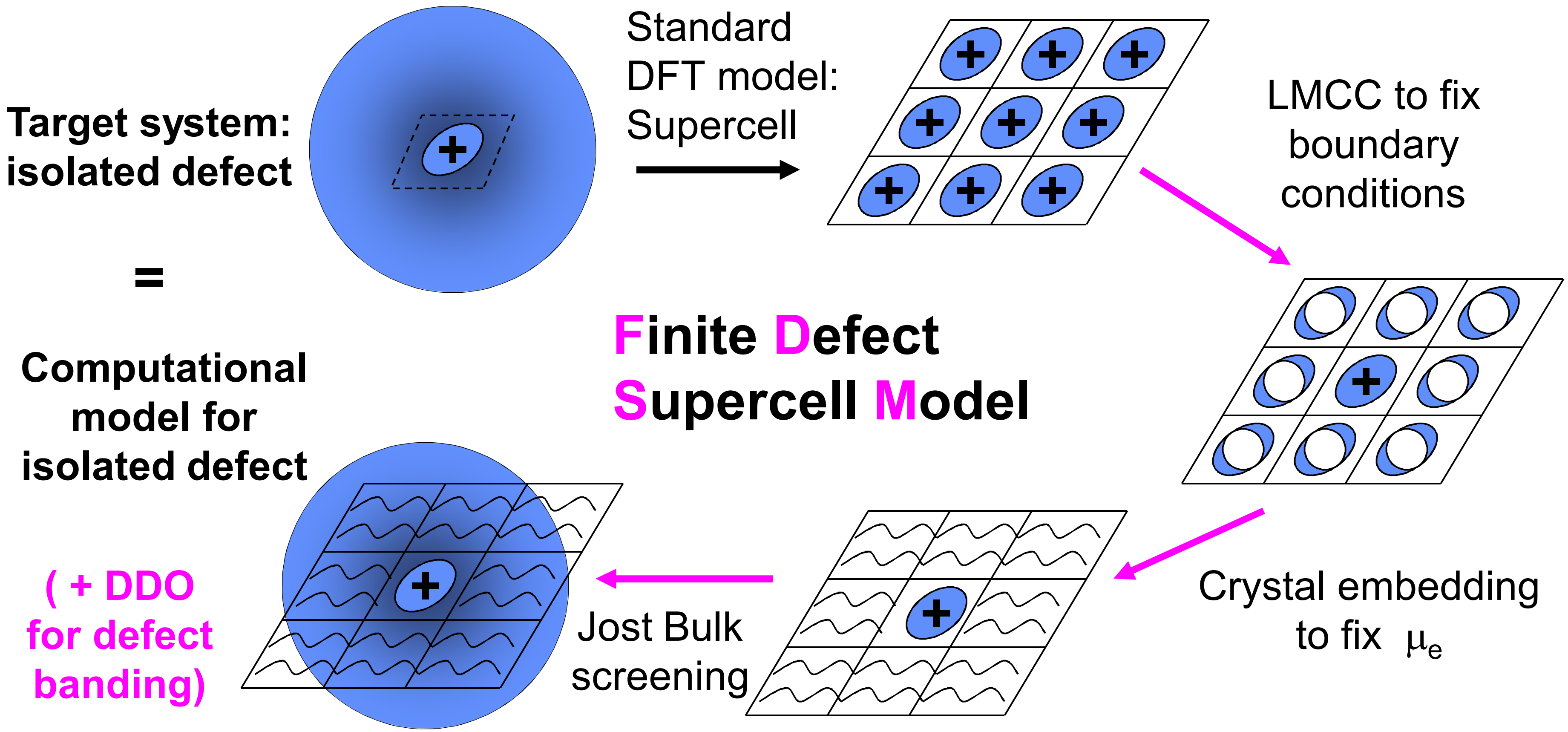
Total energy, levels, i.e. full Hamiltonian are all immediately converged.
-> electrostatic *potential* correctly represented by LMCC, not just energy

Sandia National Laboratories

A supercell theory of defect energies

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

Peter A. Schultz



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

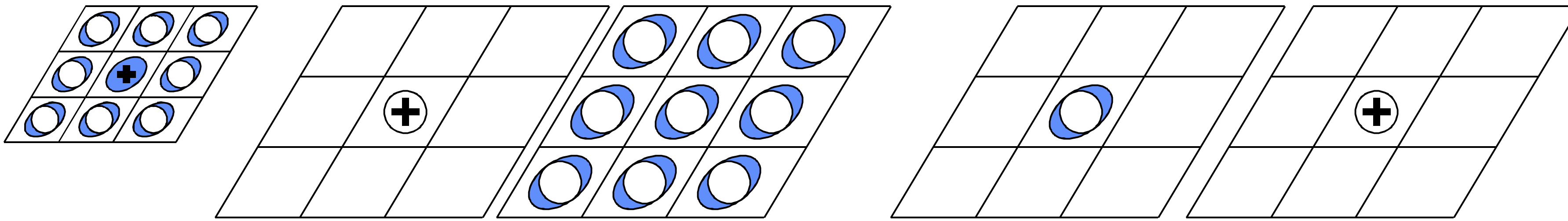
(*i.e.*,not jellium-based)

Sandia National Laboratories

A fixed chemical potential μ_e

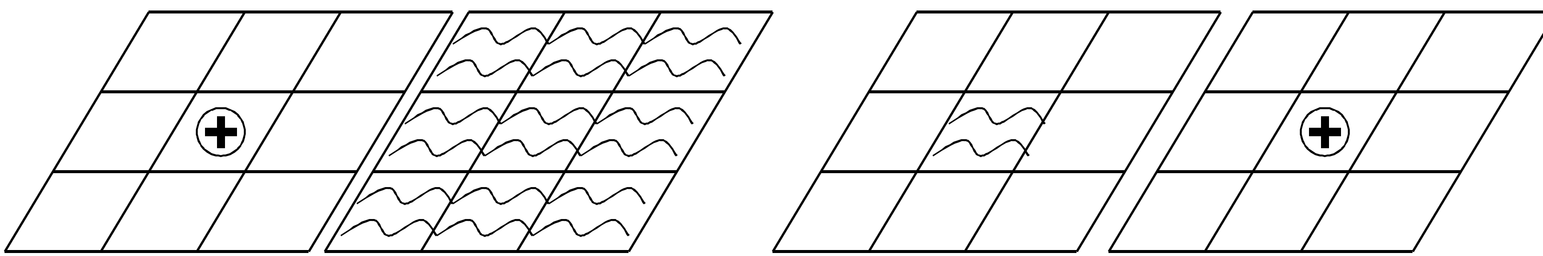
Replace interaction of net charge with periodic defect potential …

$$E_{\mu 0} = -\int dr\ \eta^{+}_{LM}\,(\phi'_{def} + C'_{def}) \quad + \int_{UC} dr\ \phi^{+}_{LM}\ \rho'_{def}$$



… with crystal potential:

$$+\int dr\ \eta^{+}_{LM}\,(\phi_{xtal} + C_{xtal}) \quad - \int_{UC} dr\ \phi^{+}_{LM}\ \rho_{xtal}$$



Replace ***variable*** defect cell C'_{def}, with ***fixed*** crystal C_{xtal} reference

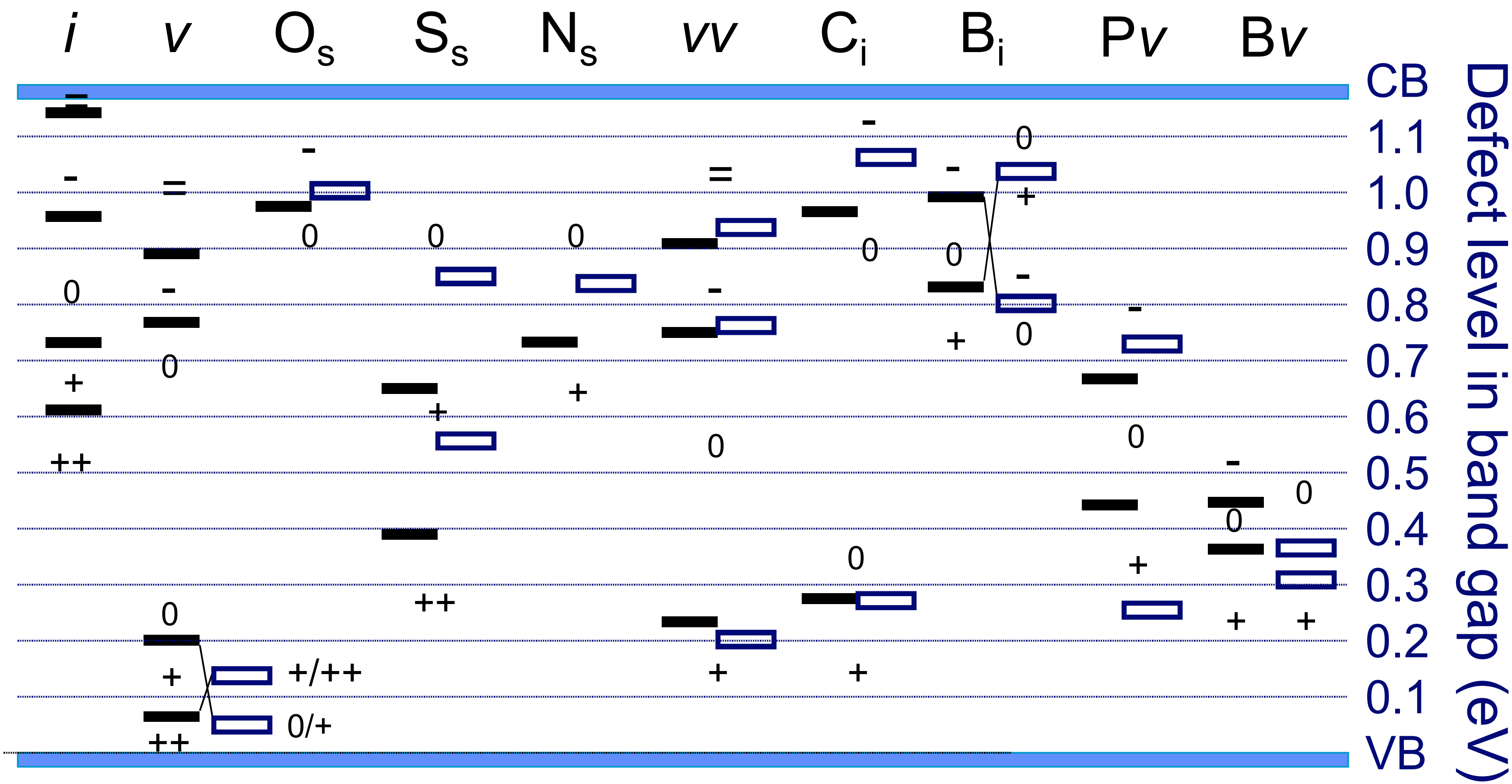
Chemical potential equivalent to matching potential at $R=\infty$

Peter A. Schultz

Sandia National Laboratories

Si: DFT/LDA vs. Experimental Levels

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



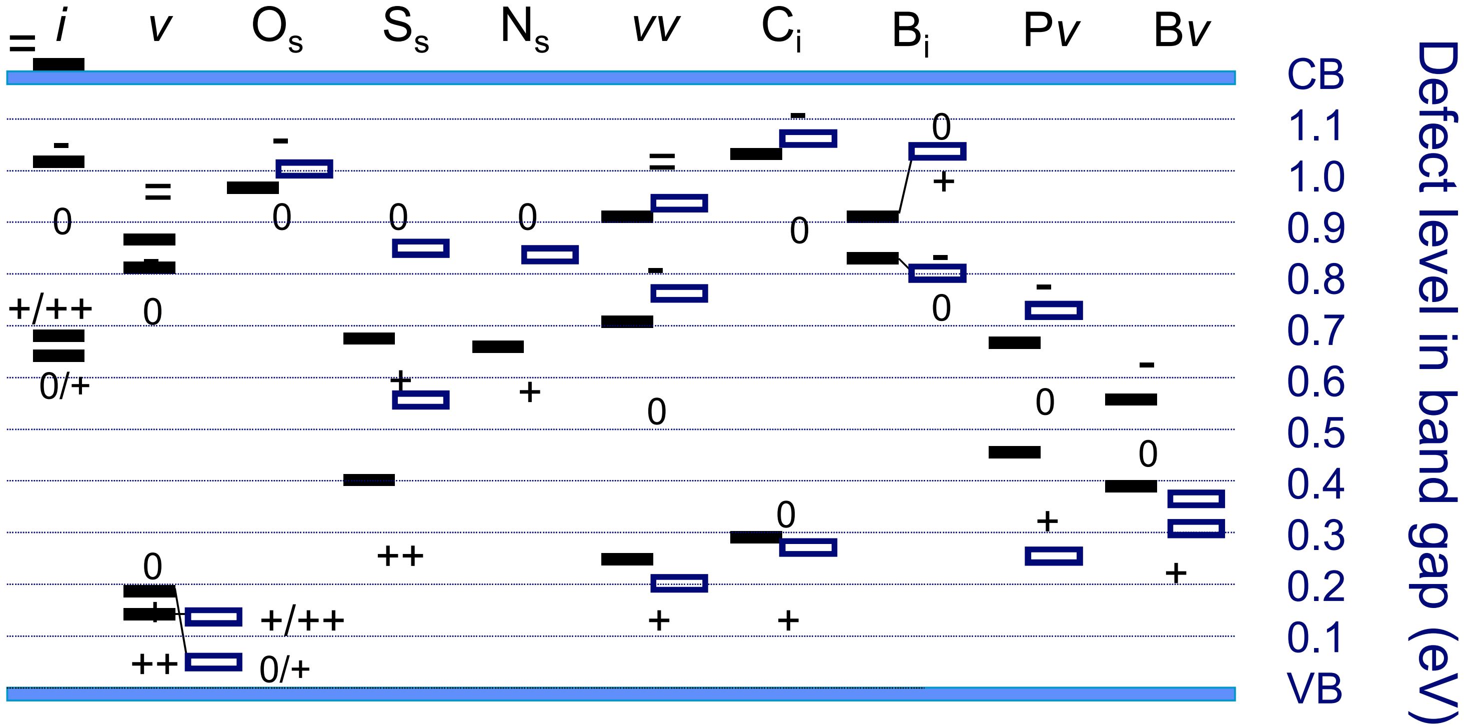
LDA: max error=0.25 eV, mean |error|= 0.10 eV
Intrinsic, first-row, second-row, and complexes across gap
LDA Kohn-Sham gap is only 0.5 eV

Peter A. Schultz

Sandia National Laboratories

Si: DFT/PBE vs. Experimental Levels

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



… and some 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)
Band gap problem not seen in **total-energy-based** defect levels

Is silicon a magical material for theory, too?

Peter A. Schultz

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)
  - –Cubic supercells: 64-, 216-, 512-, 1000-site
  - –***k***-sampling: 3^3 for 64-site cells, 2^3 for 216-, 512-, 1000-site cells,
  - –fully calibrated polarization model
  - –all these computational parameters are tested for convergence

Comparable method that yielded 0.1 eV accuracy in Si

Sandia National Laboratories

Simple intrinsic defects in GaAs: LDA

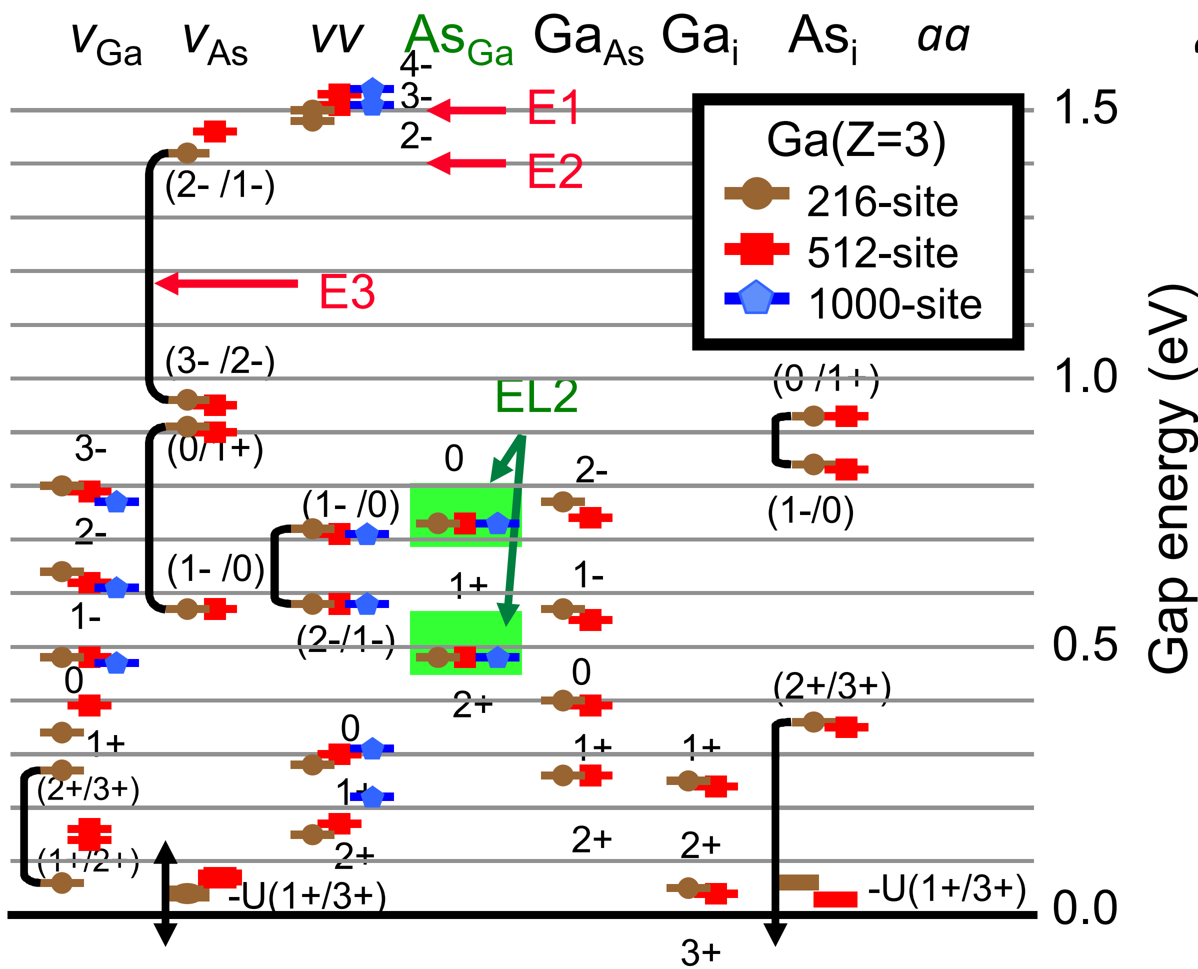
P.A. Schultz and O.A. von Lilienfeld, MSMSE **17**, 084007 (Dec. 2009).

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



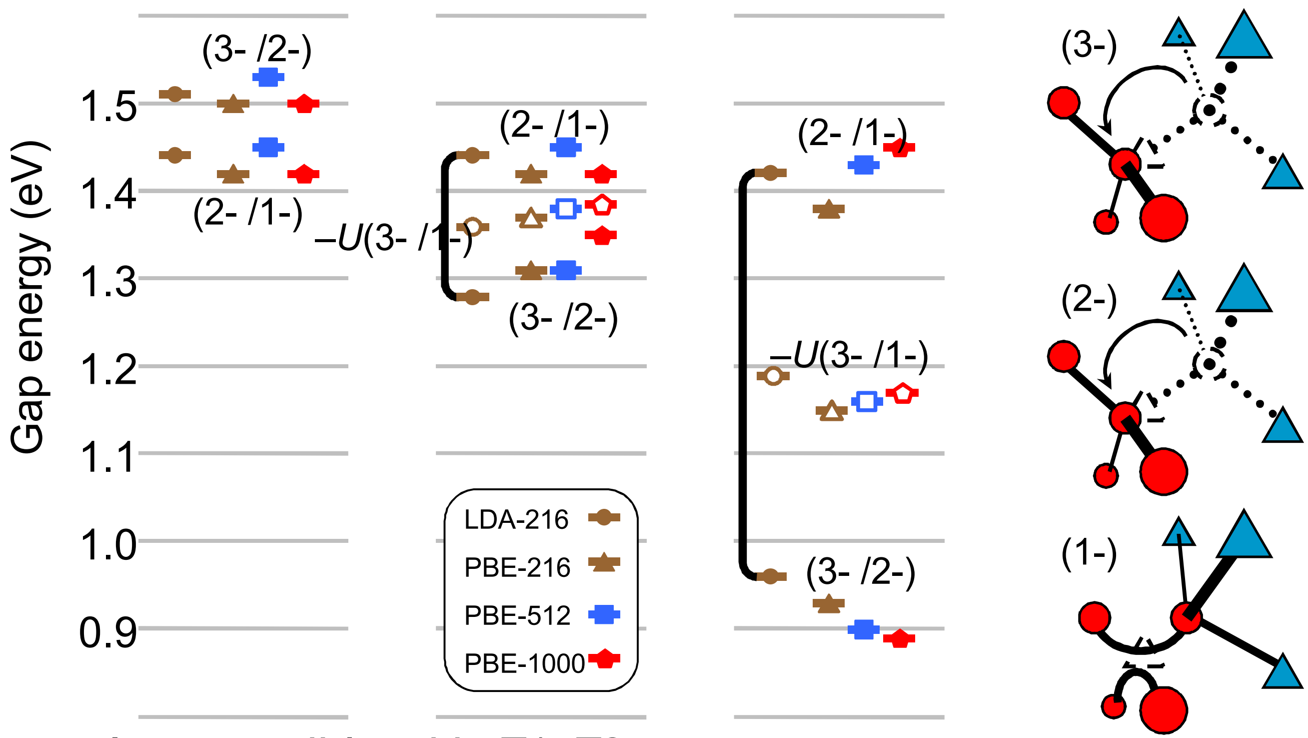
DFT+FDSM: Apparent accuracy of ~0.1 eV

Peter A. Schultz

Sandia National Laboratories

The v_{As} is *not* the E1-E2 center

Simple	*Complex*	*Site-shift*
v'_{As}	v'_{As}	v_{As}
T_d	$pD_{2d} \leftrightarrow rD_{2d}$	$v'_{As} \leftrightarrow v^{*}_{As}$



Incompatible with *E*1-*E*2 positron annihilation

Matches *E*3 (*DX*-like, level position)

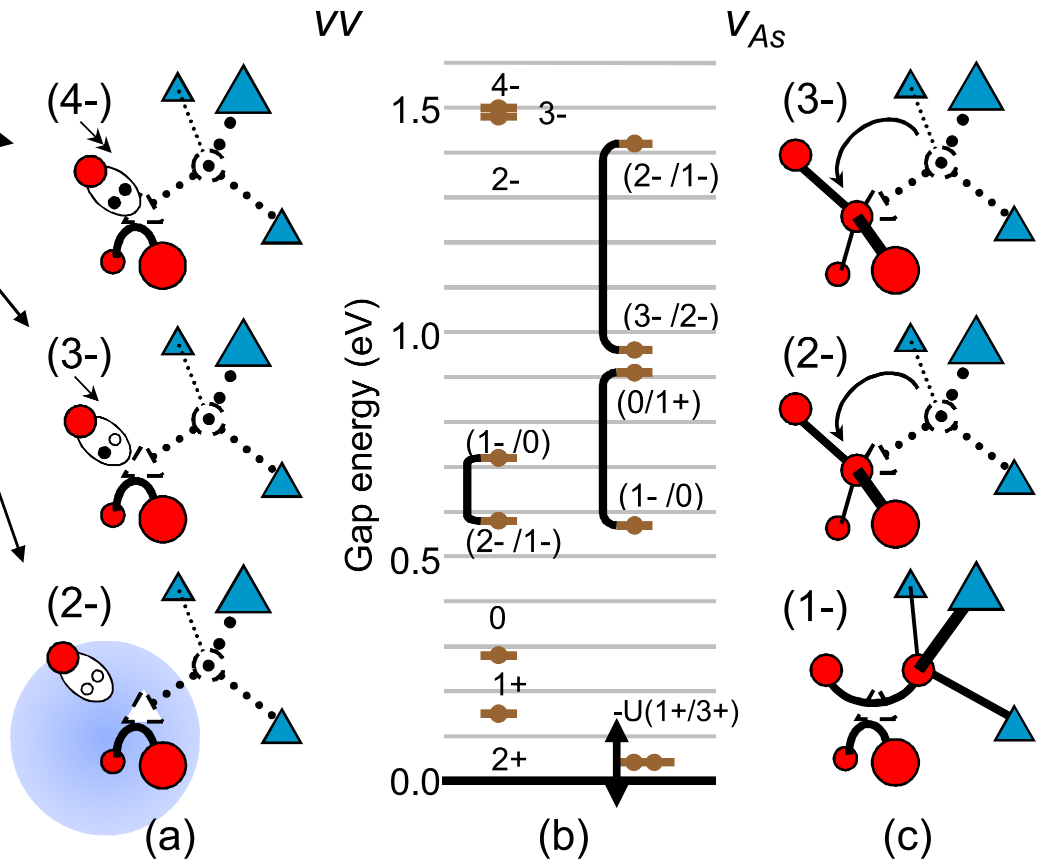
Peter A. Schultz

Sandia National Laboratories

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

Peter A. Schultz

Larger charge states

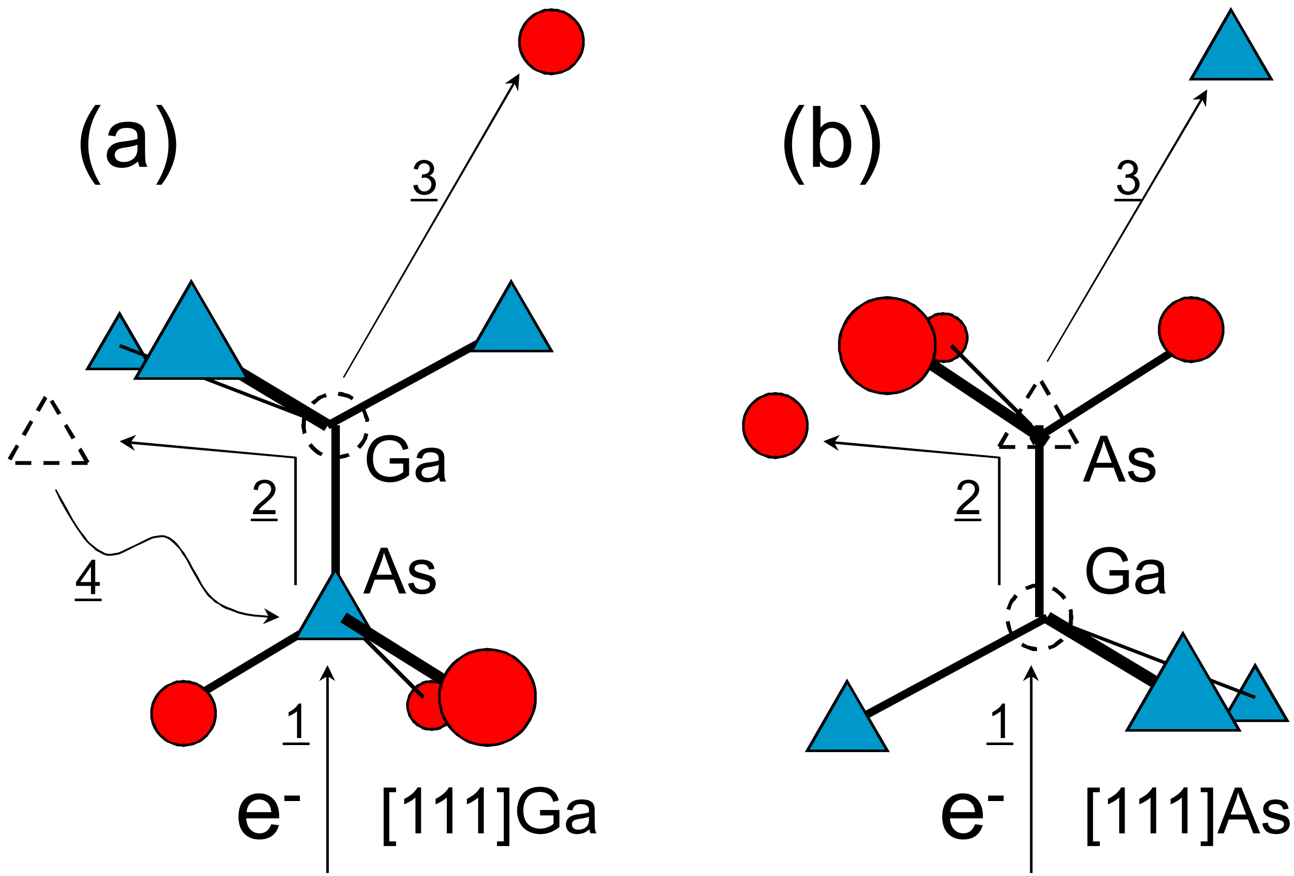


PAS explained on v_{As} side

Sandia National Laboratories

The GaAs divacancy *is* the E1-E2 center

Peter A. Schultz



vv appears to be a threshold defect, on the As site (same annihilation kinetics cf. As_i, and v_{Ga} invisible)

Sandia National Laboratories

The GaAs divacancy is the E1-E2 radiation center

Peter A. Schultz

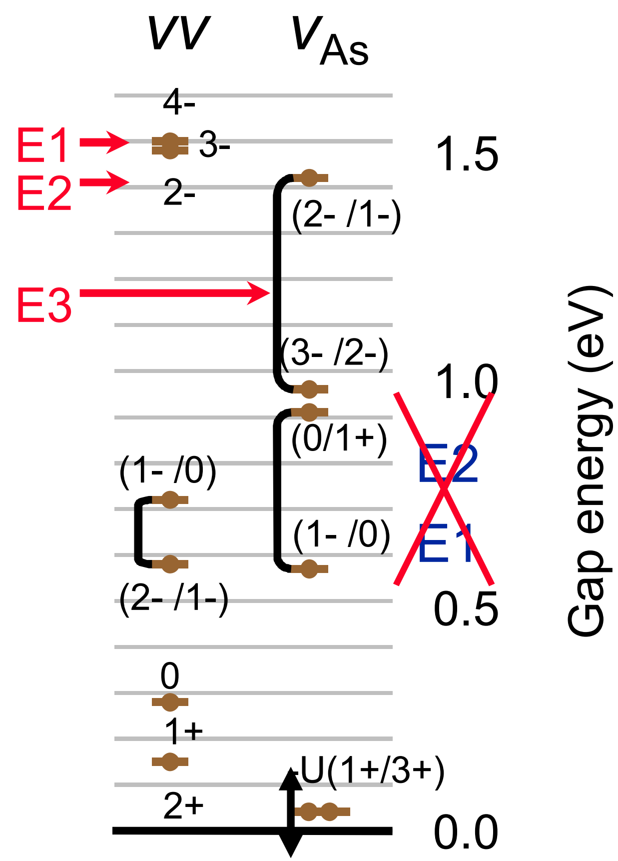
P.A. Schultz, J. Phys.: Condens. Matter **27**, 075801 (2015).

Old (experimental) lore, back to 1988:

- E1, E2 center = v_{As}(-/0), v_{As}(0/+)
- E3 = 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

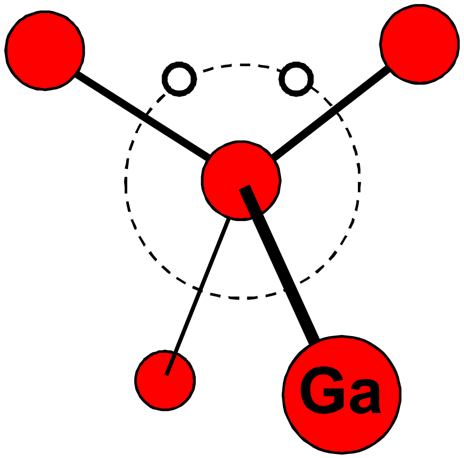


vv is major radiation defect: E1-E2
v_{As}(3-/1-) transition is the E3

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

Sandia National Laboratories

Discriminating a deep defect from shallow acceptors in supercell calculations: Gallium antisite in GaAs



PAS, PRB **93**, 125201 (2016)

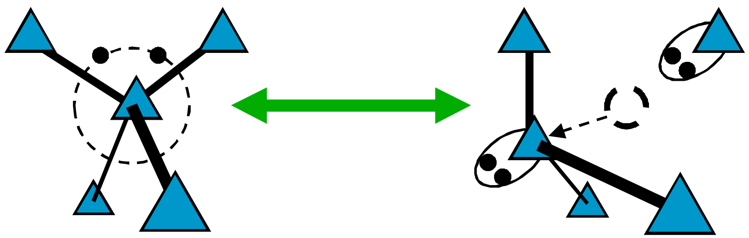
UUR
SAND2016-2676C

Sandia National Laboratories

GaAs - defect physics poorly known

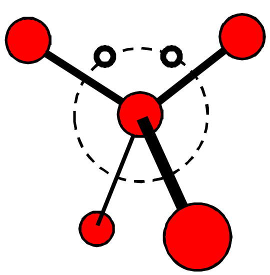
Peter A. Schultz

As_{Ga} = *EL2* Well characterized – deep double donor



Theory crucial in characterization:
Dabrowski &Scheffler, PRL 1988
Chadi & Chang, PRL1988

Ga_{As} = *???* Remains elusive



Experiment: Never definitively identified

Theory: Never definitively characterized
- supercell problem: deep or shallow?

Crucial to distinguish if defect shallow or deep

Ga_{As} history

Peter A. Schultz

Experiment: Ga-rich GaAs (>0.53 Ga) → "78/203" defect

Elliott 1982,1983; Yu 1982

- *p*-type
- **residual shallow double acceptor at 78 meV and 203 meV**
- no distortion from T_d
- Ga-rich and shallow double acceptor → Ga antisite

Doubts about 78/203: inadvertent B-contamination?

Kiessling, et al. 2008 – grown boron-free

- **semi-insulating, no residual acceptor**

→ shallow double acceptor = B_{As} antisite

Defect levels in GaAs: LDA

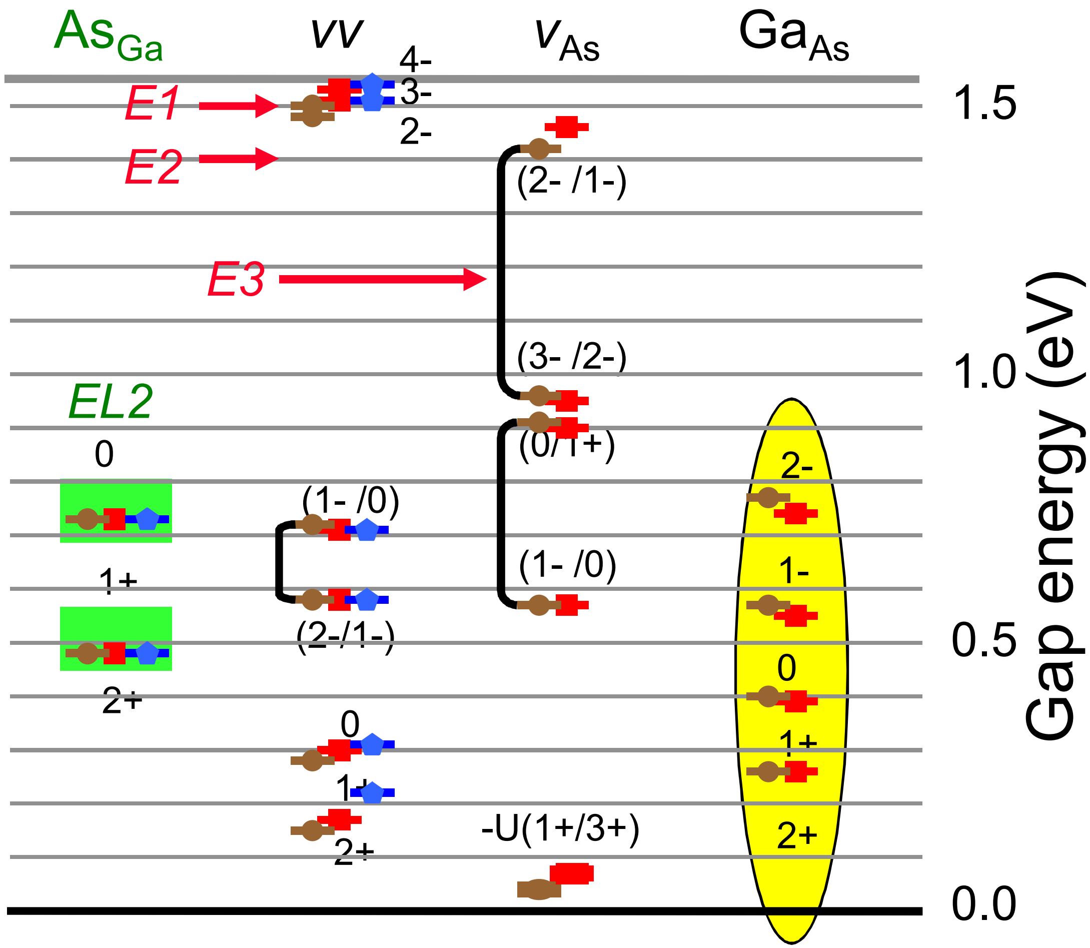
P.A.S. and O.A. von Lilienfeld, MSMSE **17**, 084007 (2009)
P.A.S., JPCM **27**, 075801 (2015)

DFT with SeqQuest

- Gaussian basis pseudopotentials
- LDA and PBE
- 216,512,1000-atom supercells
- Converged model parameters
- LMCC charge boundary conditions
- 216-, = 512- = 1000-atom levels

DFT matches experiment

EL2 = As_{Ga}
E1-E2 = divacancy
E3 = v_{As}(3-/1-)
Accuracy ~ 0.1 eV



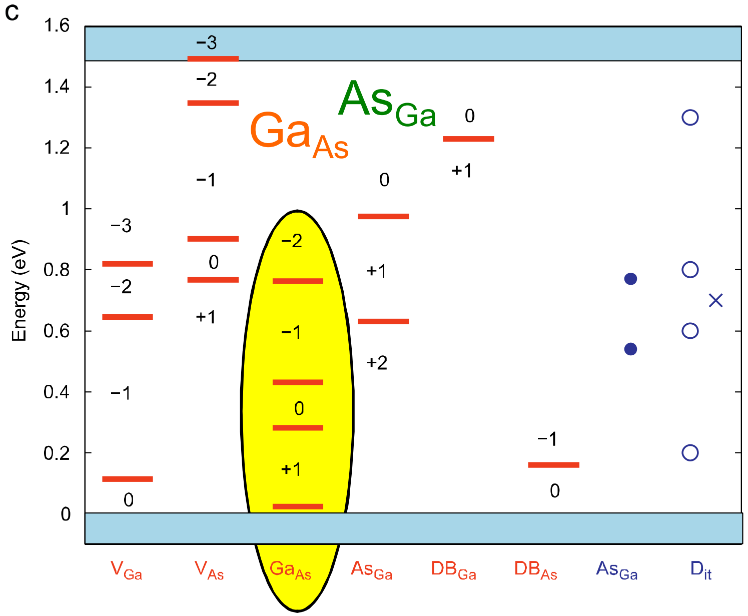
Ga antisite: two deep acceptors, two donors?

Sandia National Laboratories

Theory also inconclusive

Peter A. Schultz

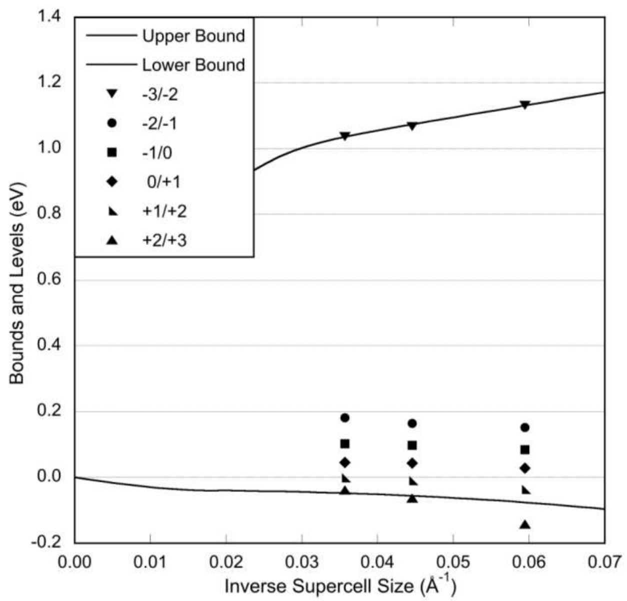
Komsa&Pasquarello, Physica B (2012)



HSE, 64-atom cells

Deep: two acceptor & two donor states

Wright&Modine, PRB (2015)



LDA, 216-,512-,1000-atom cells

Shallow double acceptor

HSE study agrees … … newer bounds analysis does not

Is Ga_{As} deep defect a supercell artifact?

Discriminating shallow/deep acceptors

Peter A. Schultz

Shallow: state and its charge delocalized, **supercell fails**

- defect banding, states entangled in VB
- less/no structural distortions

Deep: state and its charge localized, **DFT is valid**

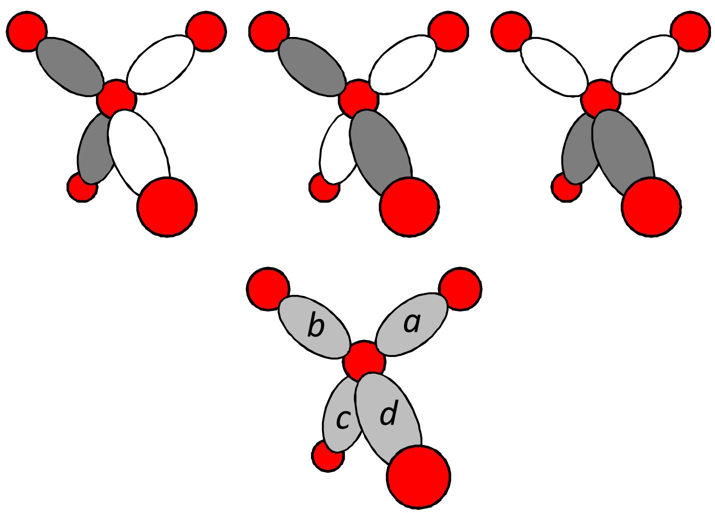
- eigenstates distinct from VBE
- greater structural distortions
- greater spin polarization

Sandia National Laboratories

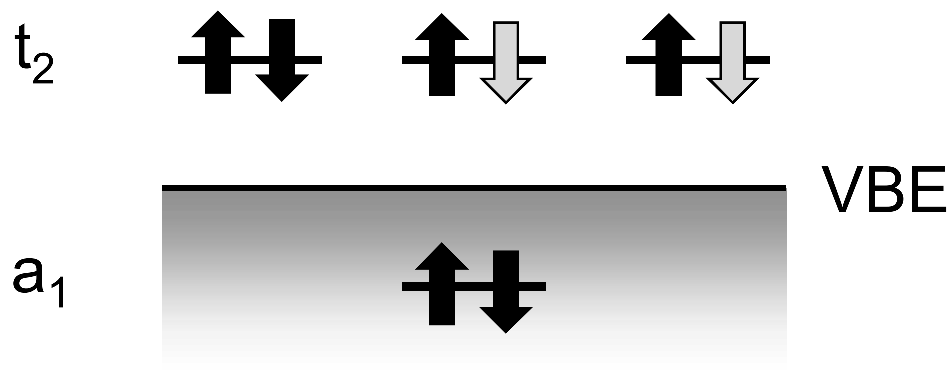
A conceptual model of Ga_{As}

Peter A. Schultz

Ga_{As}: LCAO-MO model
(thank you, George Watkins!)

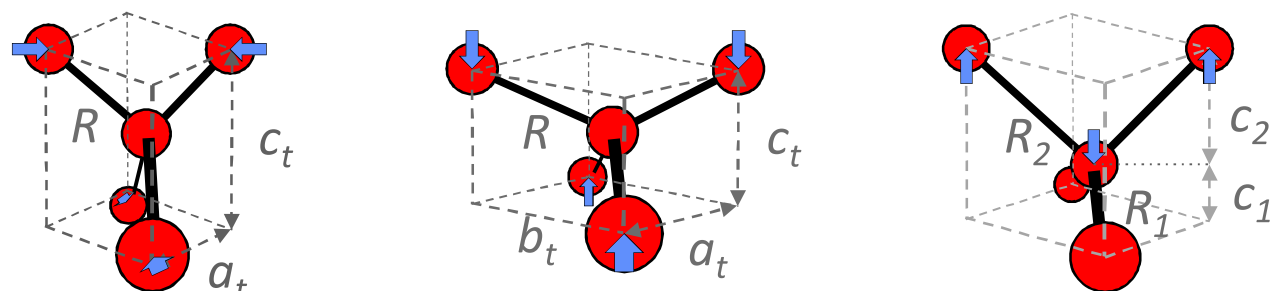


$Ga_{As}(0)$



Jahn-Teller instabilities

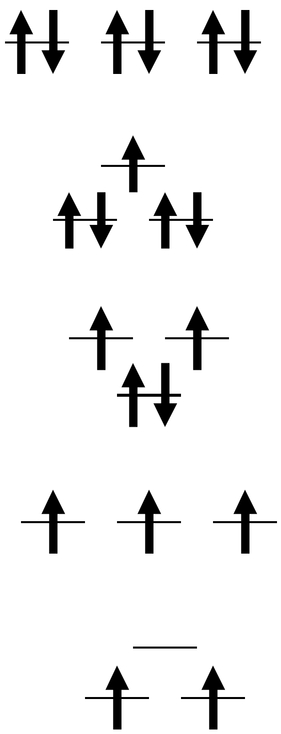
Occupation level patterns determine proper distortion/spin states



pD_{2d} rD_{2d} C_{2v}

$Ga_{As}(q)$ ground states

Peter A. Schultz



	Ground state		ΔE(T_d, meV)
(2-)		T_d	0
(1-)		rD_{2d}	-71
(0)		pD_{2d}	-102
(1+)		T_d	-95
(2+)		rD_{2d}	-25

(1000-atom PBE)

rD_{2d}(1-)

Relaxation energy (meV)

3x3x3	-15
4x4x4	-23
5x5x5	-30

Spin energy (meV)

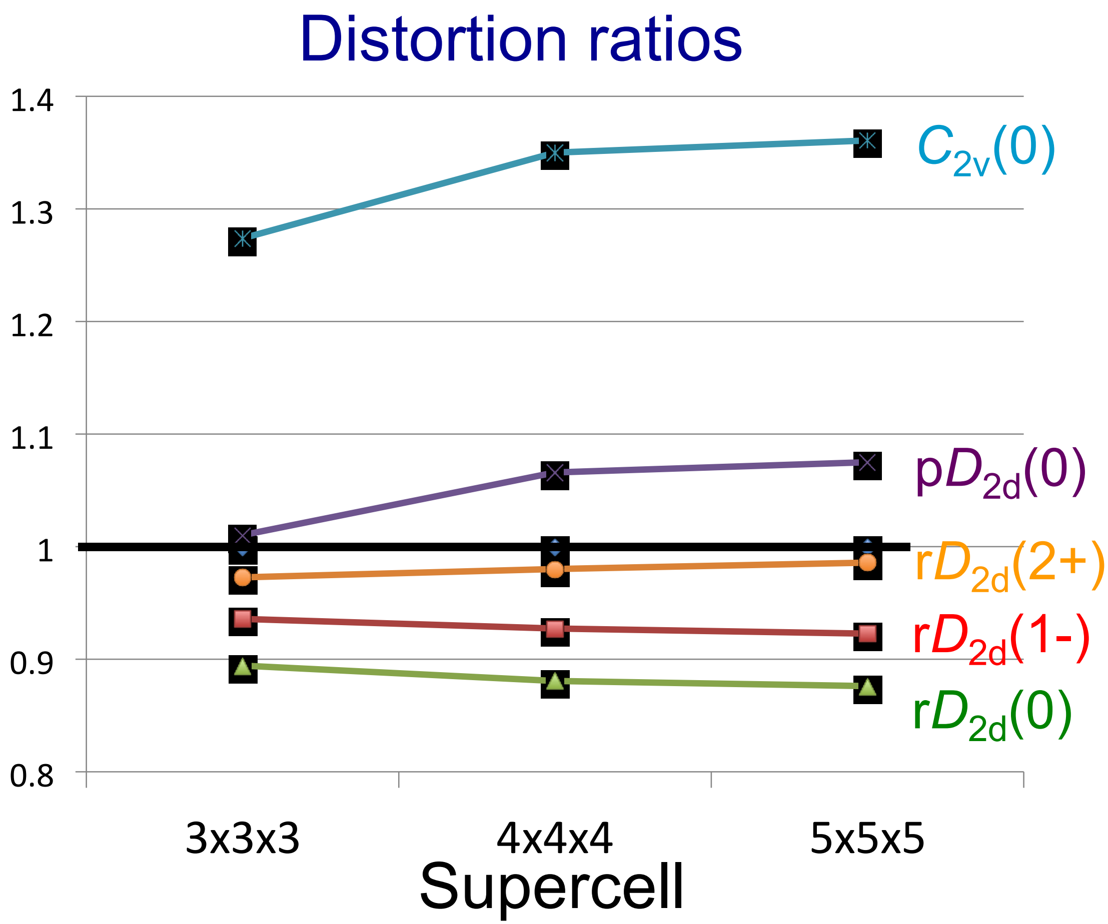
3x3x3	-33
4x4x4	-38
5x5x5	-41

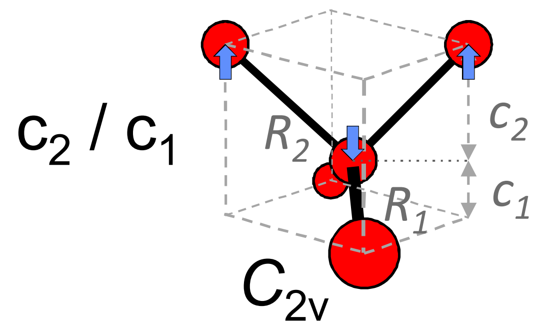
All ground states distort from (spinless) T_d

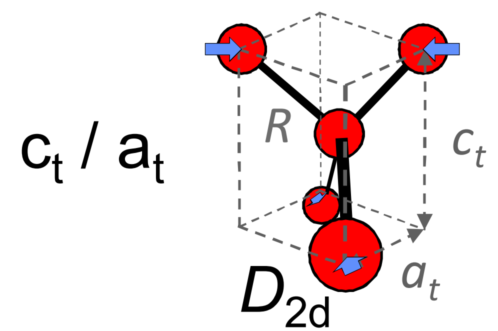
Relaxation, and spin polarization energy increase with cell size

Ga_{As} distortions magnify with cell size

Peter A. Schultz







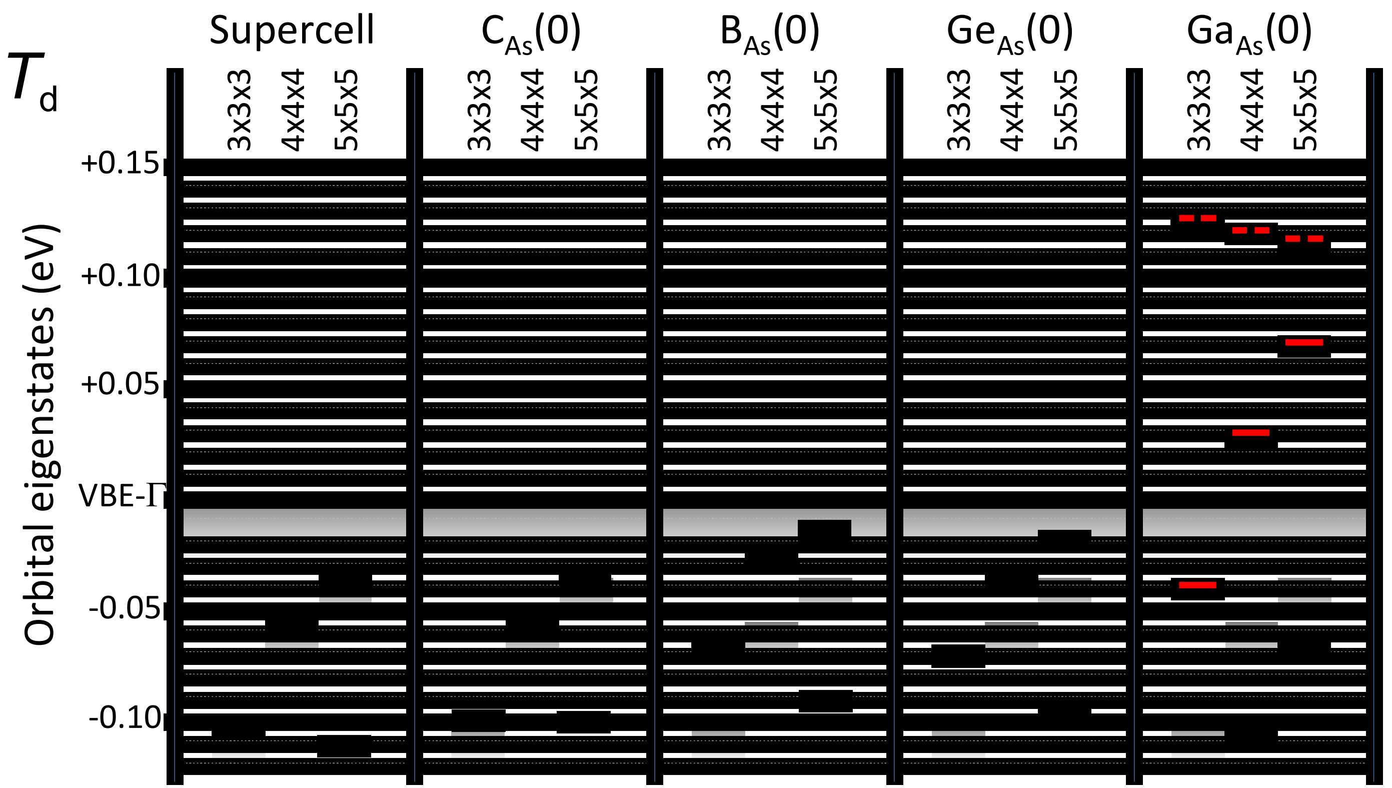
… except for $pD_{2d}(2+)$, which is only barely distorted

Sandia National Laboratories

What do X_{As} shallow acceptor supercells look like?

Peter A. Schultz

C_{As} = shallow acceptor
B_{As} = shallow double acceptor
Ge_{As} = shallow acceptor
Ga_{As} = ????



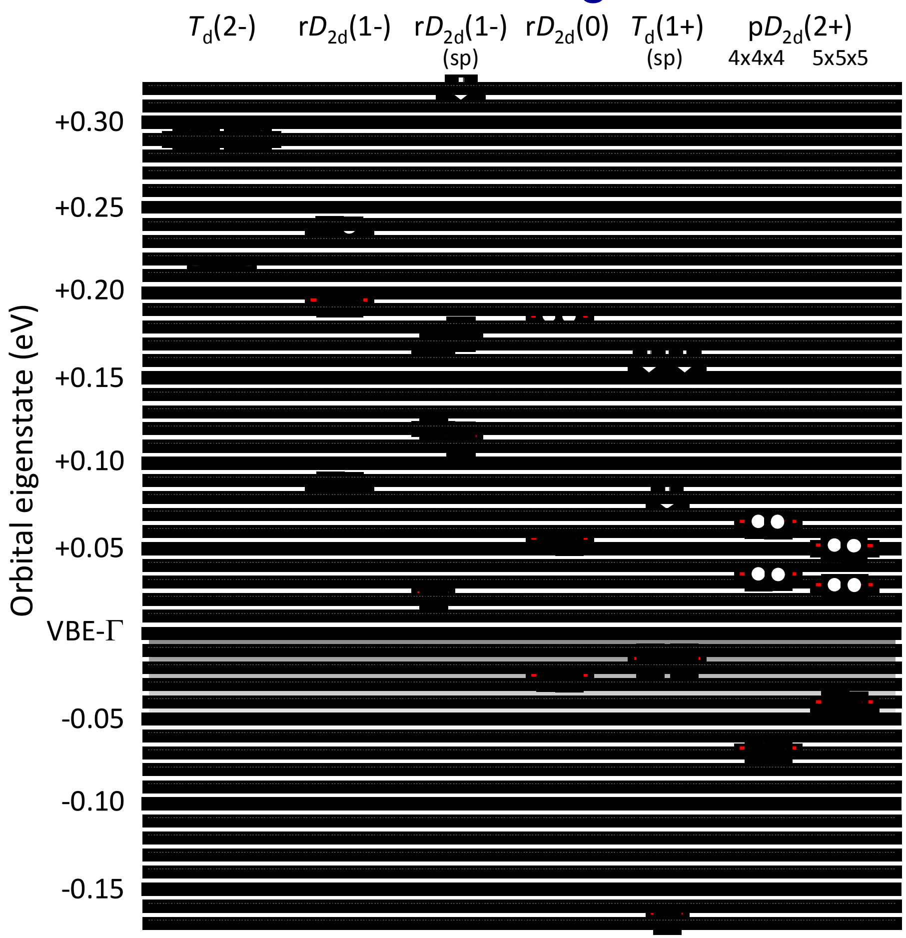
C_{As}, B_{As}, Ge_{As}: no distortions (<1meV)
no spin polarization (<3 meV)
no new defect eigenstates in "small" cells

Ga_{As} is *different* – Ga_{As} is not an effective mass state

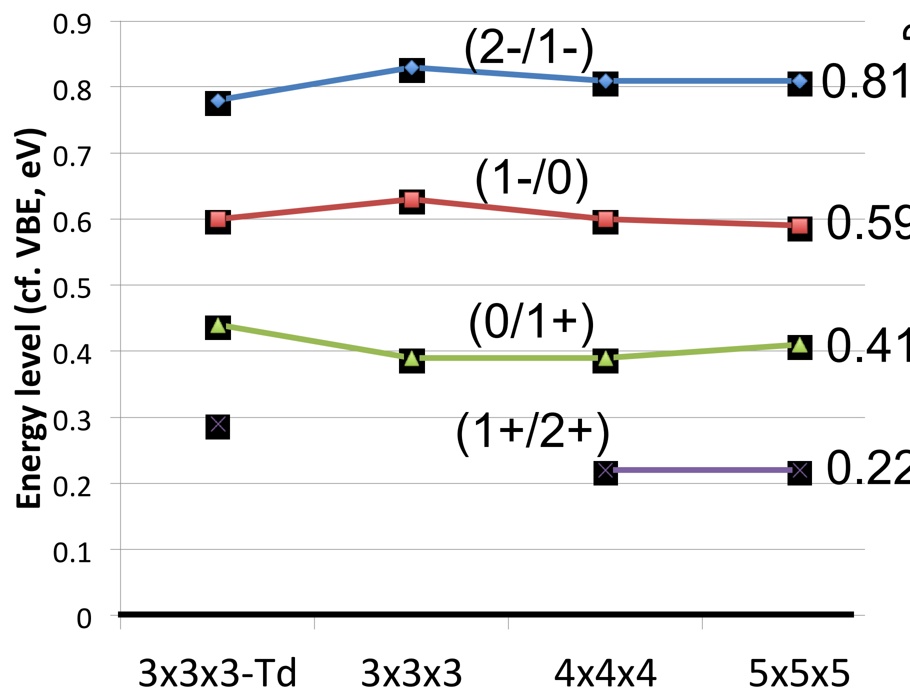
Ga_{As} eigenstates and energy levels

Peter A. Schultz

Kohn-Sham eigenstates



DFT **total energy** defect levels



Converged to ~0.01 eV

KS eigenstates cleanly within global Kohn-Sham gap

Energy levels converged to ~0.01 eV with supercell

Eigenstates ≠ energy levels: **levels expanded**

Sandia National Laboratories

The Ga antisite summarized

Recently published: P.A.S. PRB **93**, 125201 (2016)

Peter A. Schultz

Shallow states in supercells: C_{As}, B_{As}, Ge_{As}

- no distortions (<1 meV)
- small, decreasing spin energy (< 3 meV)
- KS states entangled in VB in small supercells, "small" > 1000 atoms!

Ga_{As} is localized: two deep donor, two acceptor states

- large, increasing distortions, increasing spin, clean KS spectrum
- distinct from behavior of known shallow acceptors

Ga_{As} is not the 78/203 shallow double acceptor

- shallow-Ga_{As} is high-energy defect in Ga-rich p-type GaAs
- low-energy defects Ga_i, v_{As}, and deep- Ga_{As} are donors → semi-insulating

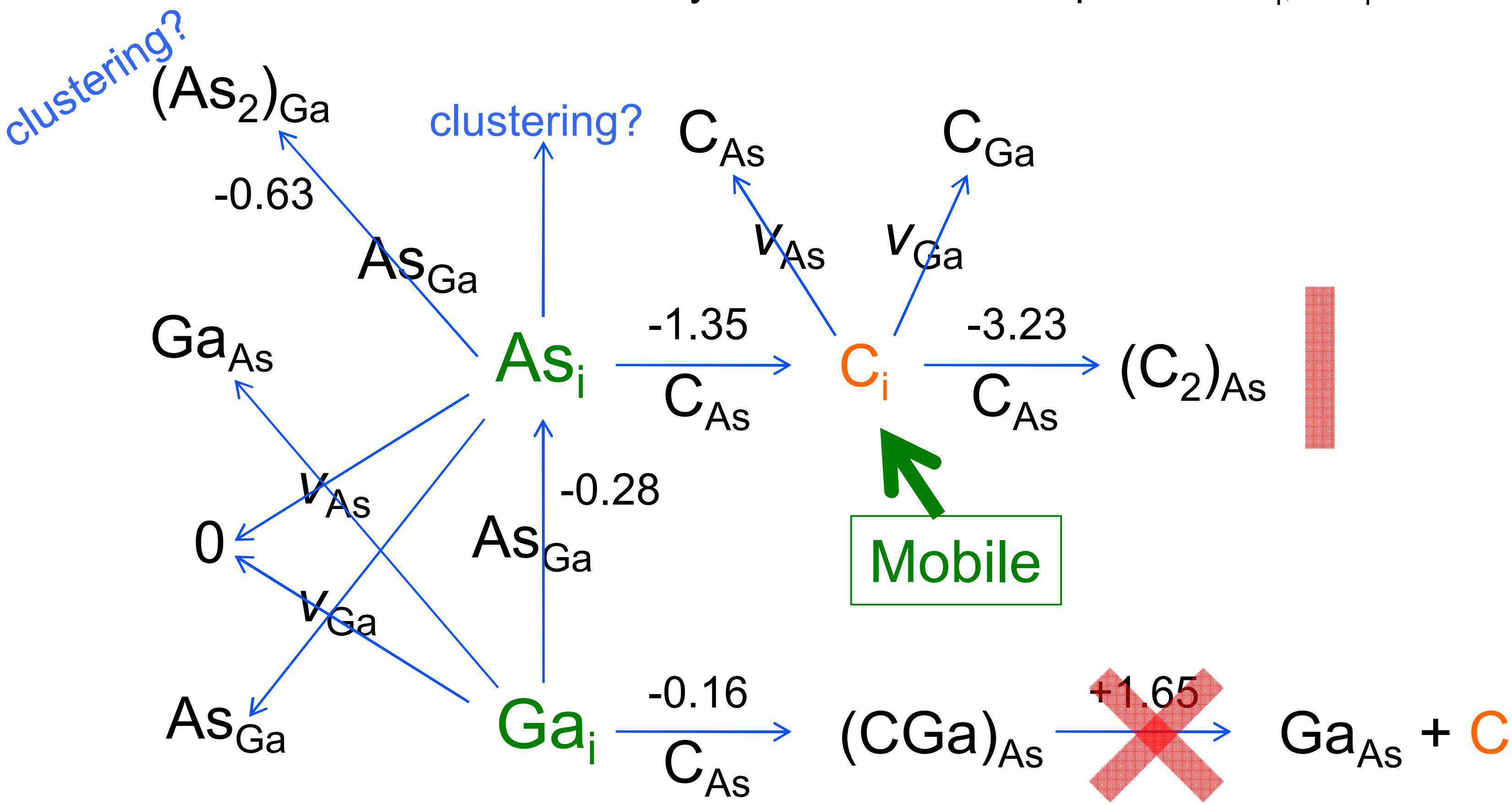
Energy level scale expanded compared to KS eigenstates

- "band gap problem" is … not a problem

GaAs: C-doped reaction network

P.A. Schultz, J. Res. Eng: Rad. Effects **30**, 257 (2012).

SeqQuest, LDA, 216-site, thermodynamic energy with E_f=VBE (p-type)
Reaction networks initiated by identified mobile species: As_i, Ga_i



Reliable defect levels means reliable chemistry

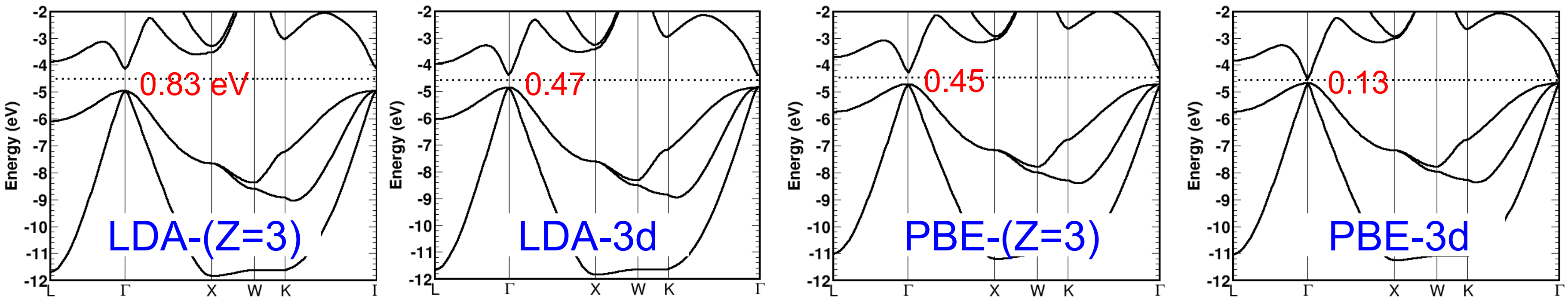
Peter A. Schultz

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 shrinks…



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

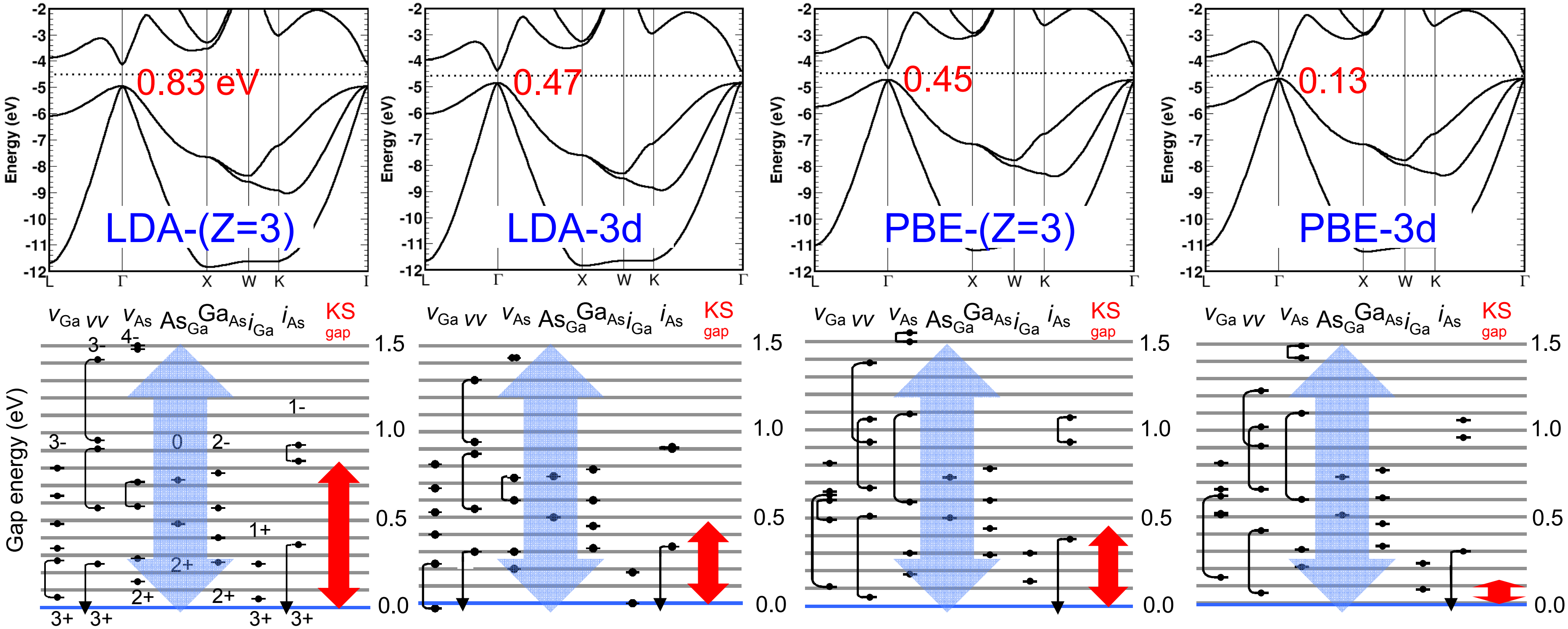
… to 0.13 eV, PBE-3d, Ga(Z=13) pseudopotential (PP)

GaAs: A theoretical laboratory

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

Peter A. Schultz

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

GaAs Computational model lessons

Peter A. Schultz

- KS band gap not a problem for Si and GaAs defects

- Defect levels insensitive to size of Kohn-Sham gap!
  - total-energy differences vs. eigenvalue-referenced
  - GaAs is ideal theoretical laboratory for testing methods

- Detailed control of boundary conditions crucial: FDSM works

- Is this unique to Si and GaAs?

Simple intrinsic defects in AlAs: Energy levels

MRS Symposia Proceedings **1370**, (MRS Spring 2011); SAND2012-2938 (April 2012)

ter A. Schultz

Verified cell-convergence

Calibrated: $v_{Al}^{(u)}$

Checked: As_{Al}

Verified: vv

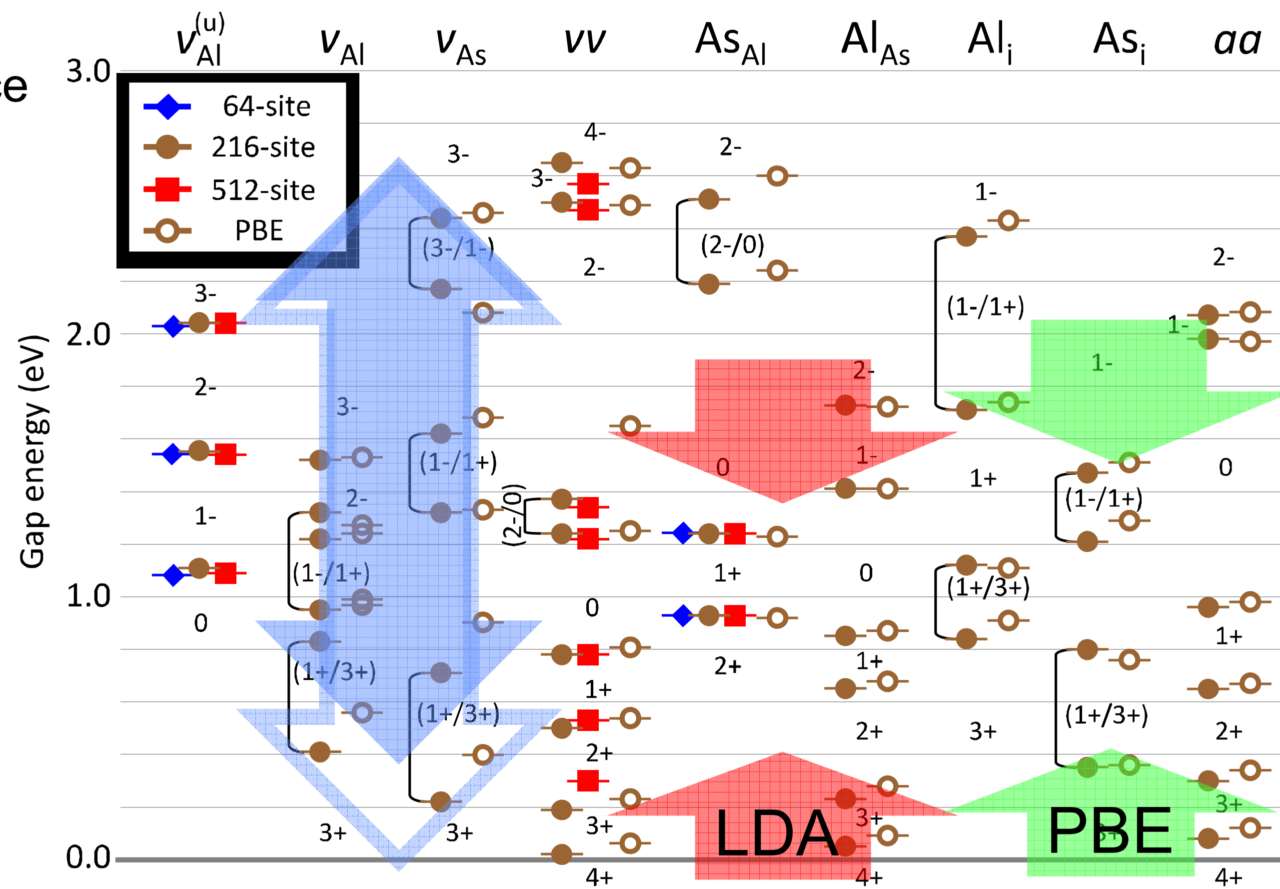
AlAs band gap

KS-LDA: 1.37 eV

KS-PBE: 1.53 eV

Defect span: 2.3 eV

Experiment: 2.16[i] eV



Very similar to GaAs defects, with some new features

A reverse band gap problem?

Sandia National Laboratories

GaP intrinsic defects

Peter A. Schultz

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

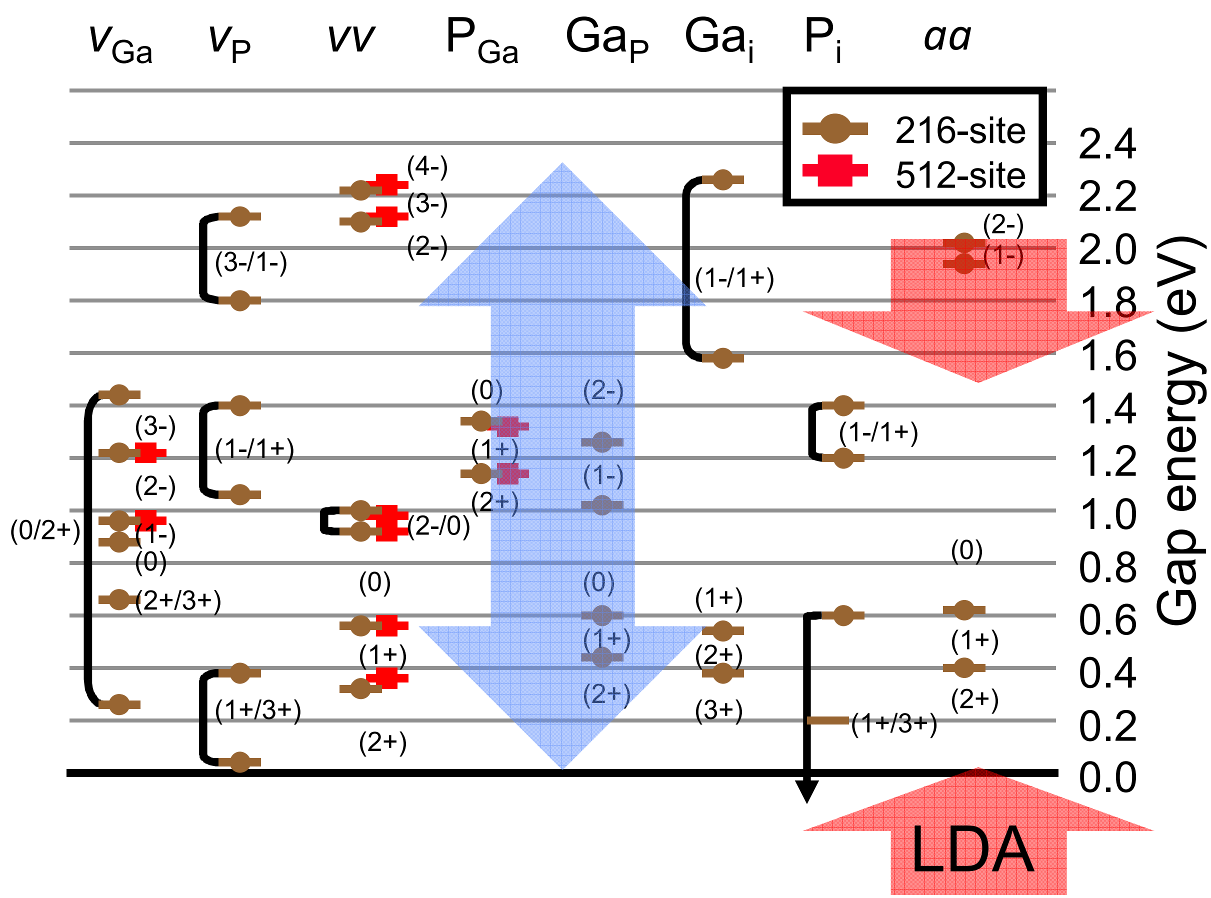
GaP band gap

KS-LDA: 1.51[i] eV

Defect span: 2.35 eV

Experiment: 2.35[i] eV

GaP defect levels: LDA, Ga(Z=3) PP



Sandia National Laboratories

InP intrinsic defects

Peter A. Schultz

216-site results = 512-site

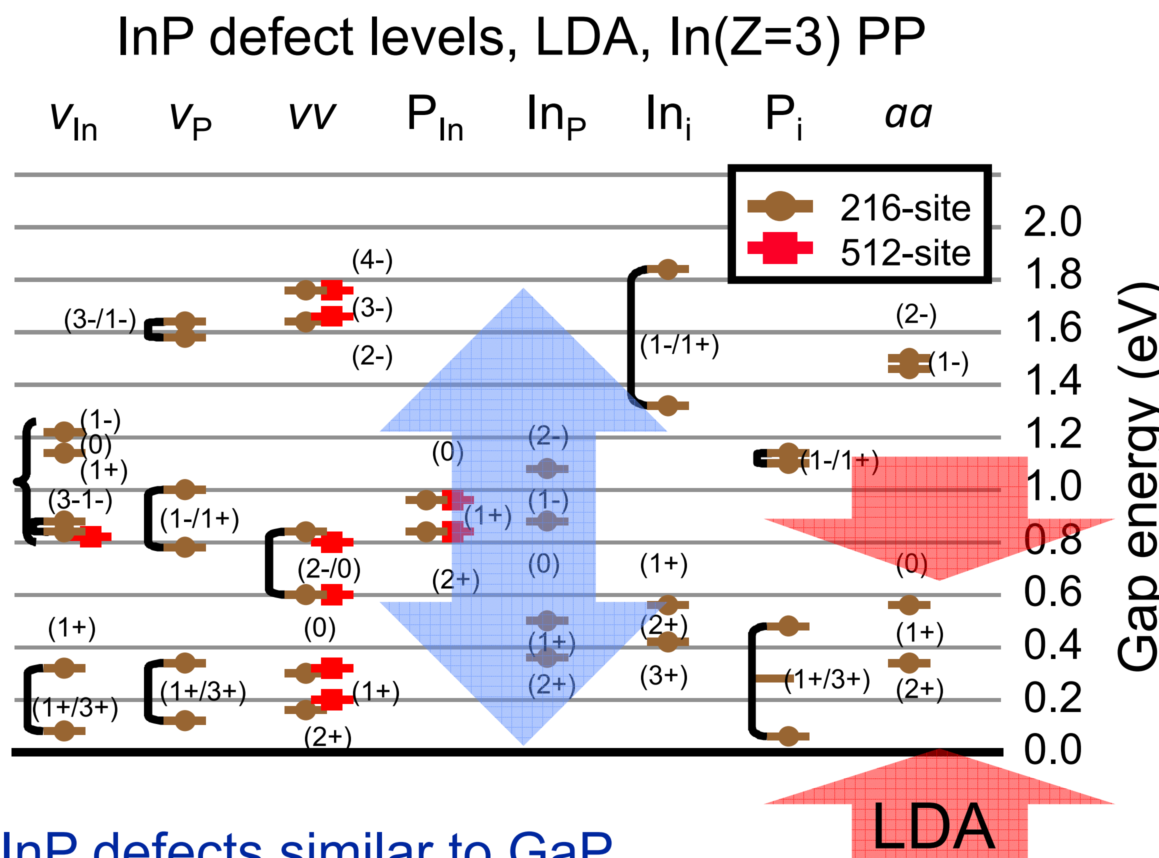
Verification: cell-converged

InP band gap

KS-LDA: 0.67 eV

Defect span: 1.7 eV

Experiment: 1.42 eV



InP defects similar to GaP

Augurs well for InGaP alloys?

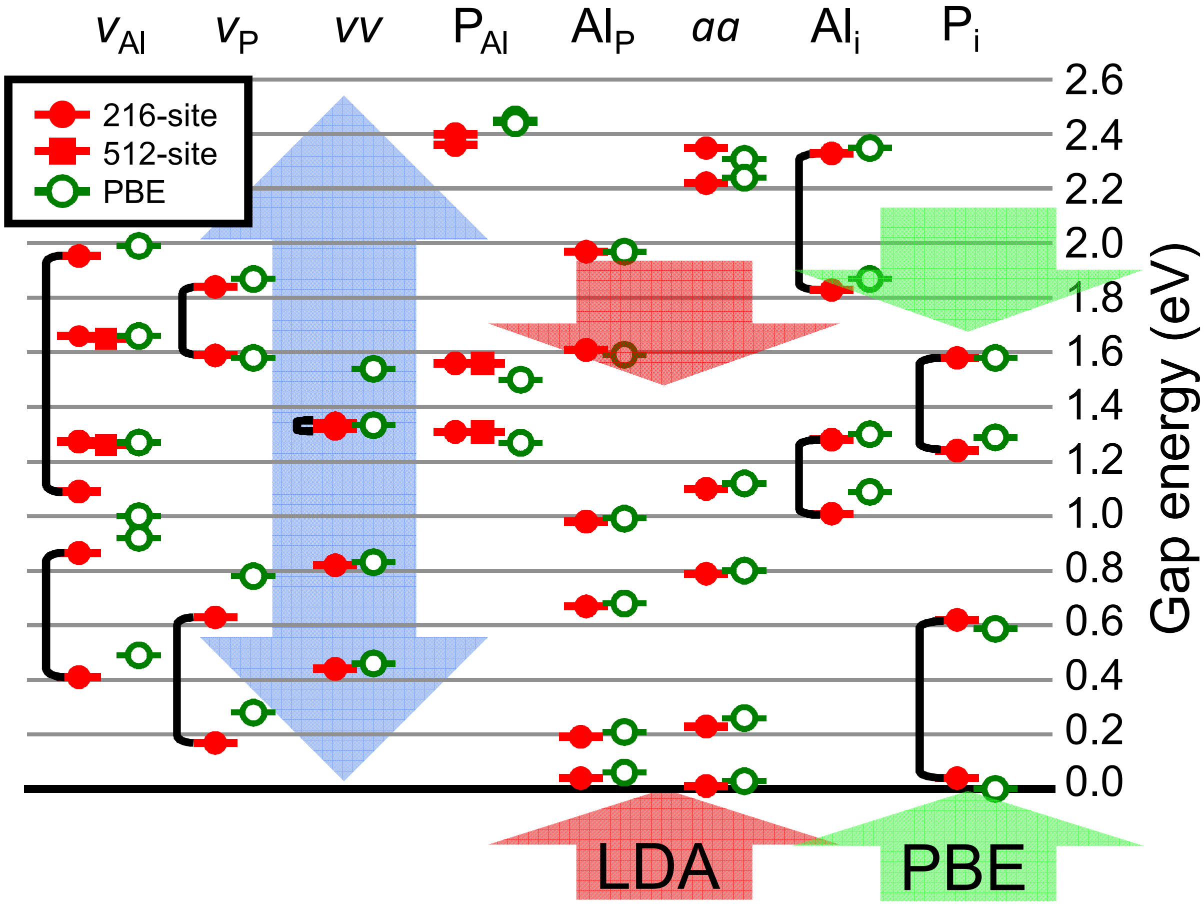
Sandia National Laboratories

AlP intrinsic defects

Peter A. Schultz

A.H.Edwards, H.Barnaby, A.C. Pineda, P.A. Schultz, IEEE-Trans. Nucl. Sci. **60**, 4109 (2013)

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



AlP band gap

KS-LDA: 1.48 eV

KS-PBE: 1.67 eV

Defect span: 2.55 eV

Experiment: 2.51 eV

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		AlAs	2.16[i] eV		AlP	2.51 eV	
	KS	Defect		KS	Defect		KS	Defect
lda	0.49	1.2	lda	1.37	>2.3	lda	1.48	2.55
pbe	0.62	1.2	pbe	1.53	>2.3	pbe	1.67	2.55

GaAs	1.52 eV		GaP	2.35[i] eV		InP	1.42 eV	
	KS	Defect		KS	Defect		KS	Defect
lda	0.83	1.54	lda	1.51	2.35	lda	0.67	1.7
lda-3d	0.47	1.52	lda-3d	1.47	2.35	lda-3d	0.66	1.7
pbe	0.45	1.50	pbe	1.74	2.35	pbe	0.47	1.7
pbe-3d	0.13	1.50	pbe-3d	1.52	n/c	pbe-3d	0.46	n/c

Total energy defect gap insensitive to Kohn-Sham gap
Defect band gap matches (overshoots?) experiment

Other examples

IV-IV: 3C-SiC (cubic)

GGA/PBE KS Gap:	1.38 eV
Defect Gap (PBE):	**~2.4**
Experimental Gap:	**2.40**

II-VI: CdTe (3d-valence)

LDA KS Gap:	0.81 eV
PBE KS Gap:	0.69 eV
Defect Gap (LDA&PBE):	**~1.6**
Experimental band gap:	**1.60**

Close correlation of the **defect gap** with **experiment band gap**

What about a crystal that is not tetrahedral, and a large gap?

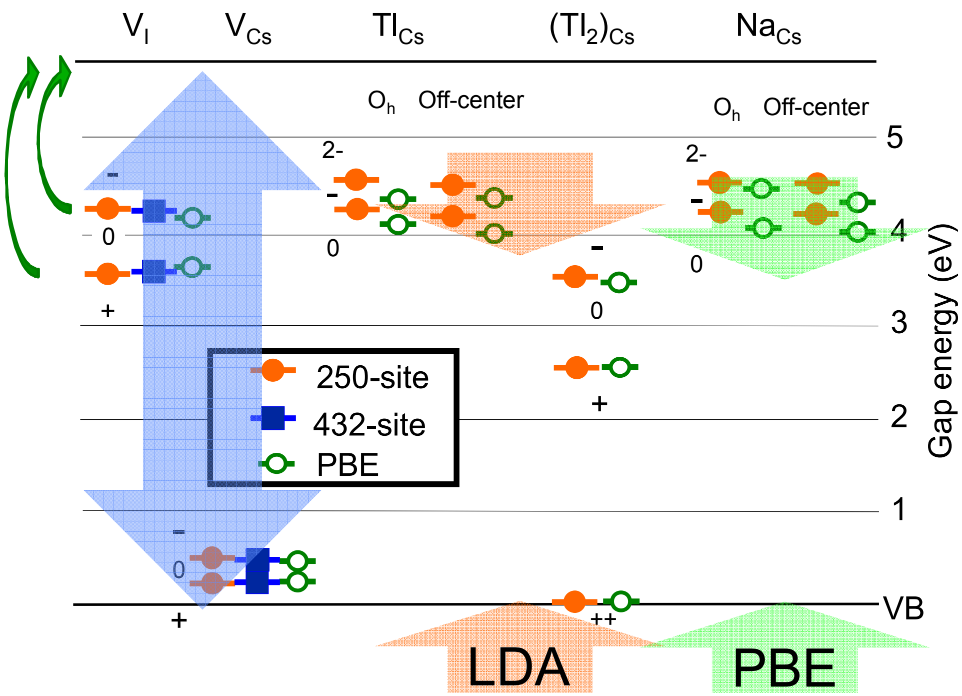
CsI defect level spectrum - DFT

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

Peter A. Schultz

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

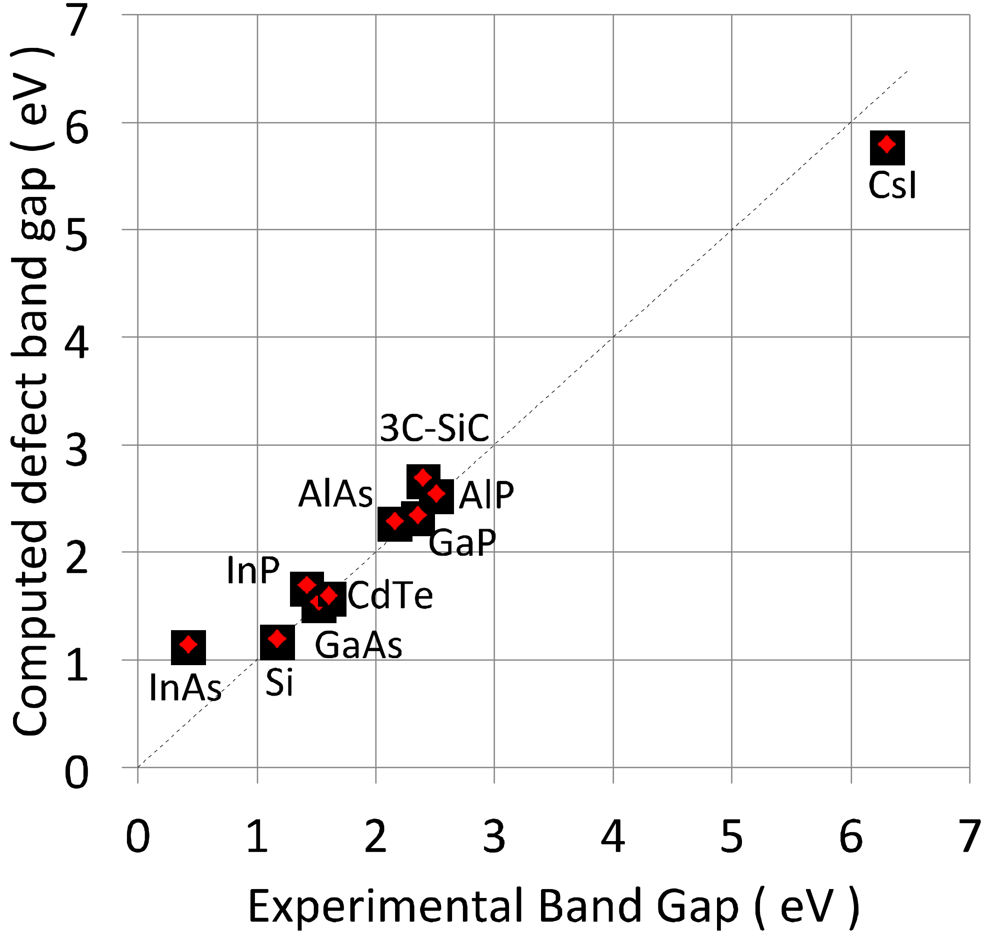
Experiment: 6.3 eV

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

Sandia National Laboratories

The Defect Gap vs. the Band Gap

Peter A. Schultz

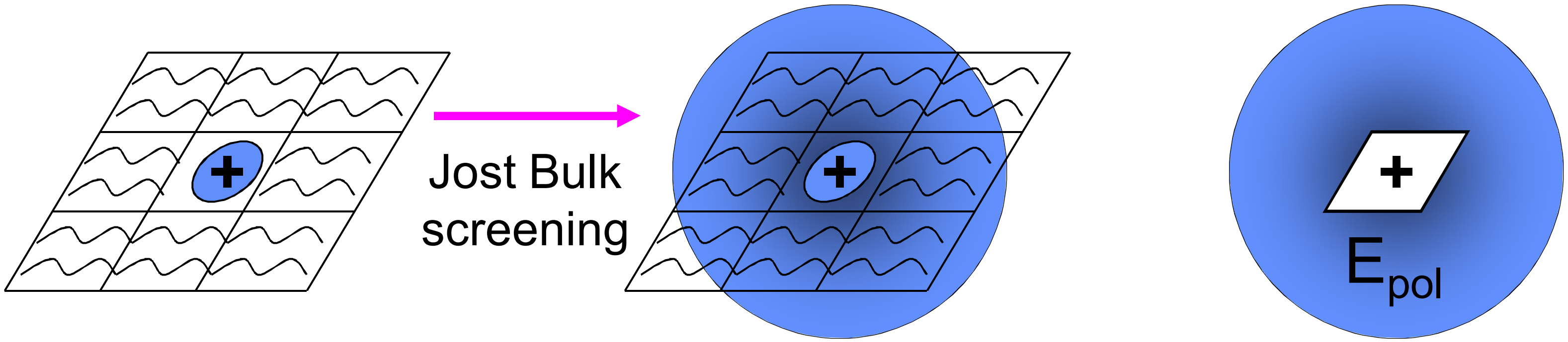


Defect gap = experiment, despite a band gap problem

Sandia National Laboratories

The polarization model

Peter A. Schultz

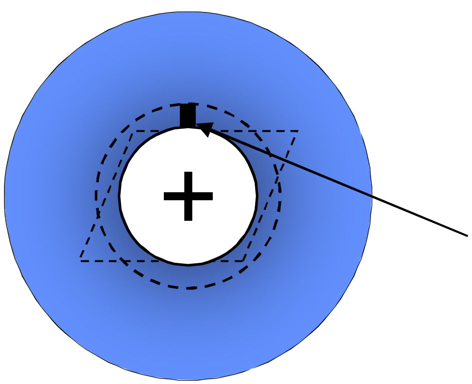


For extrapolation to bulk, need energy of screening outside of supercell: E_{pol}

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



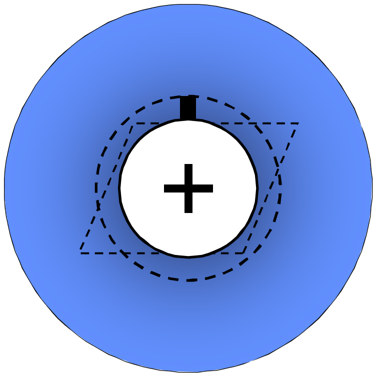
R_{skin} = unscreened volume **inside** cell.
fit: =1.3-1.7 Bohr

ε_0 = static dielectric constant - expt

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

Sandia National Laboratories

How big is bulk screening?



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

Defects mostly converged at 64-site cells

E_{pol} mostly insensitive to ε_0 at 10-15, use GaAs (LDA)

Charge *q*=	+1,-1	+2,-2	+3,-3	+4,-4
Screening:	1.09 eV	4.36 eV	9.81 eV	17.43 eV

This is lower bound on classical screening energy

Bulk classical screening outside defect is **huge**

Key insight to understanding KS gap *vs.* defect gap

Peter A. Schultz

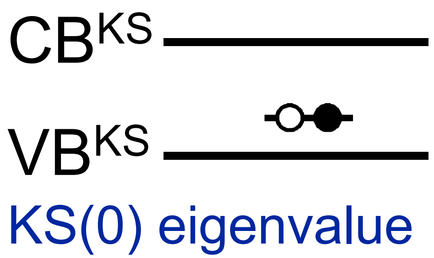
Sandia National Laboratories

How is a good defect band gap possible?

Peter A. Schultz

Conventional picture:

Defect state depicted as eigenvalue inside KS eigenvalue gap



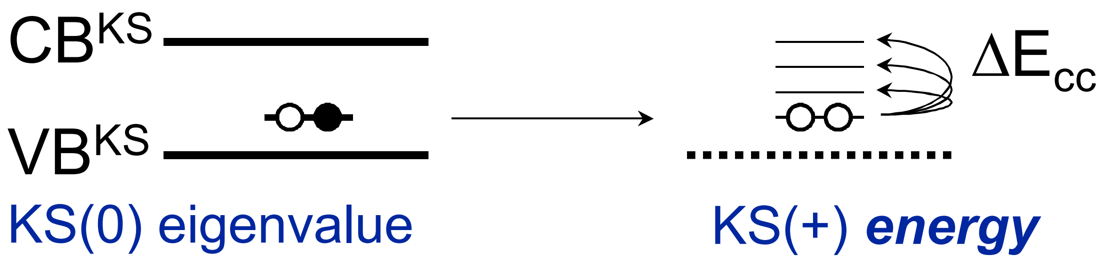
Sham and Kohn [Phys. Rev. **145**, 561 (1966)]
the KS eigenfunctions and eigenenergies are auxiliary functions of the KS equations, and **"must *not* be interpreted as corresponding to elementary excitations."**

How is a good defect band gap possible?

Peter A. Schultz

What about:
final state effects?

Effective level shift



Central cell electronic relaxation (quantum): ΔE_{cc}

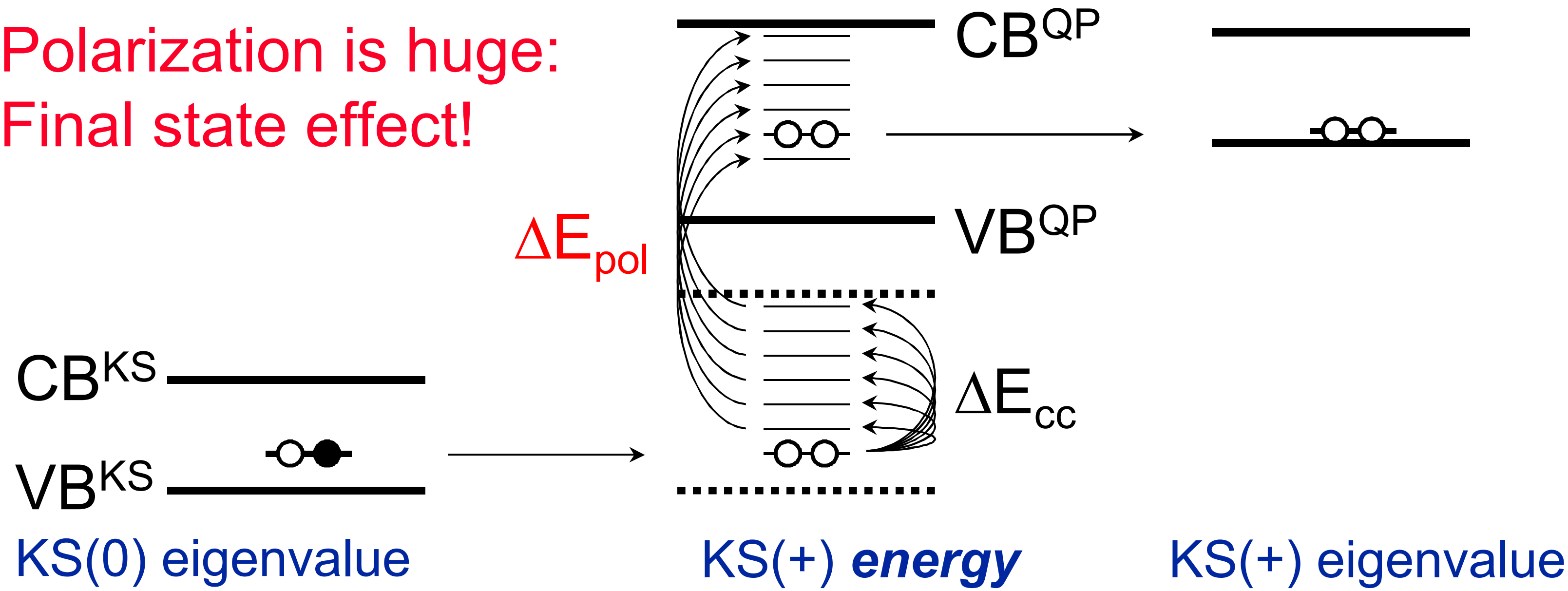
Sham and Kohn [Phys. Rev. **145**, 561 (1966)]
the KS eigenfunctions and eigenenergies are auxiliary functions of the KS equations, and **"must *not* be interpreted as corresponding to elementary excitations."**

Sandia National Laboratories

How is a good defect band gap possible?

Peter A. Schultz

Polarization is huge:
Final state effect!



Central cell relaxation (quantum): ΔE_{cc}
Long range screening (classical): $\Delta E_{pol} > E_g$
Defect levels bounded by (**screened**) quasiparticle gap, not eigenvalue gap

Sham and Kohn [Phys. Rev. **145**, 561 (1966)]
the KS eigenfunctions and eigenenergies are auxiliary functions of the KS equations, and "must *not* be interpreted as corresponding to elementary excitations."
Not only eigenvalues but eigenstates are meaningless

Conclusions

Peter A. Schultz

- ***Total energy*** DFT defect levels not constrained by KS band gap problem
- Semilocal DFT+FDSM - quantitative (~0.1 eV) for defect levels in semiconductors
- **Defect band gap** is good predictor of experimental band gap

- KS interpretation of band gap is not-even-wrong for defect levels
  - Sham and Kohn's ignored warning about misinterpreting KS eigenvalues
- **Rigorous charge boundary conditions** more crucial than KS band gap
  - ***band edge problem*** — where are they? — is the more serious question
- Path to better functionals: "fixing" using KS gap as primary metric is misguided
- **Diligence in credibility — verification/validation/UQ — crucial to predictive DFT**

Thanks to Arthur H. Edwards (AFRL) and also Renee M. Van Ginhoven (AFRL/RDHEC)

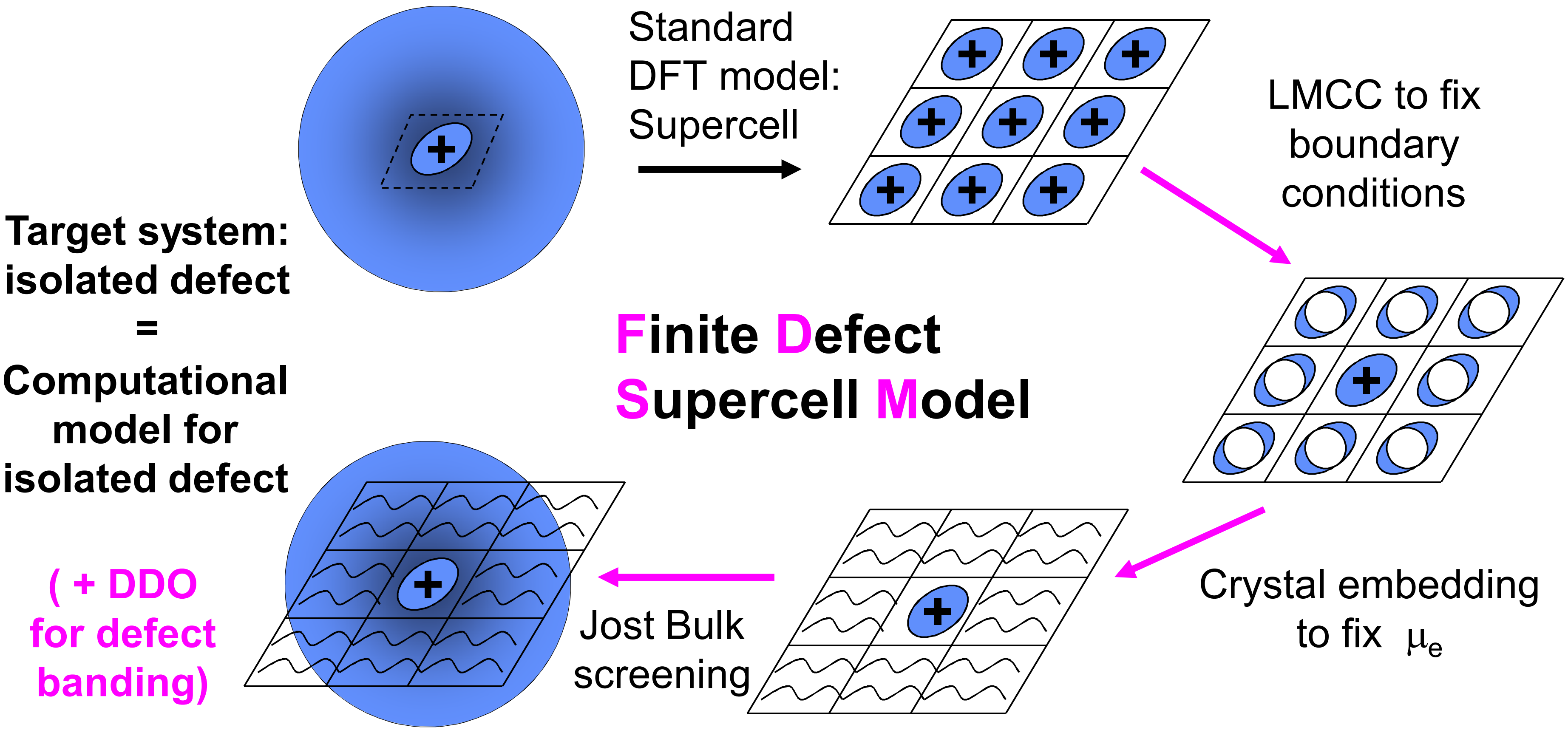
Quest DFT code information: http://dft.sandia.gov/Quest

paschul@sandia.gov http://www.cs.sandia.gov/~paschul

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

A supercell theory of defect energies

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



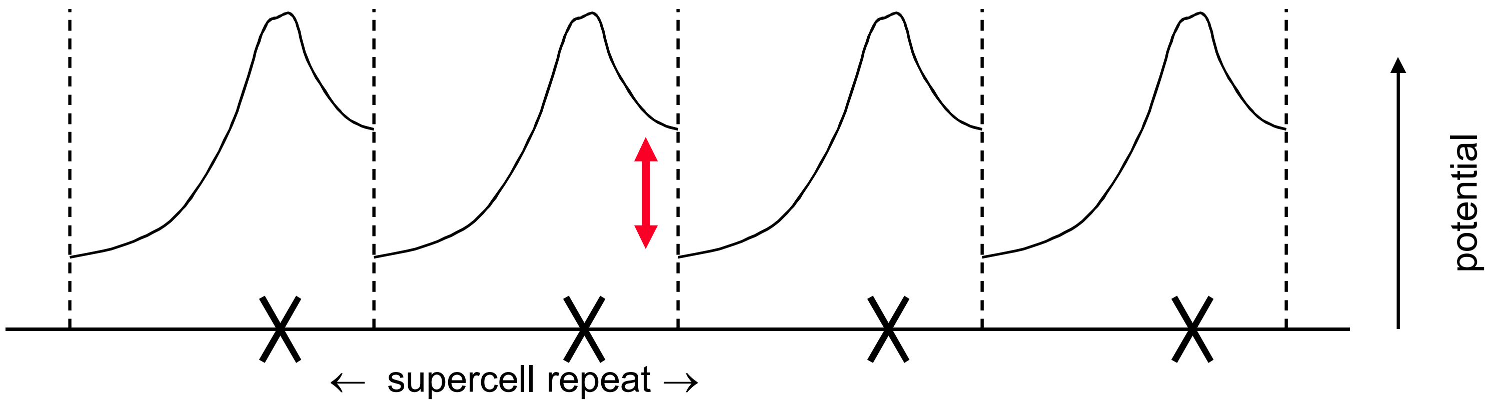
FDSM*: Ab initio computational model* – connect model to physics
Calculations with rigorous control of charge boundary conditions

Peter A. Schultz

LMCC potential in bulk systems

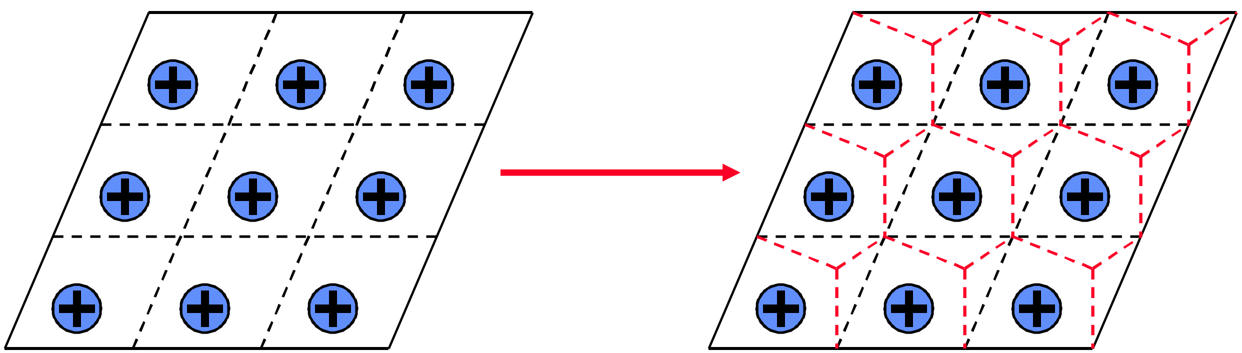
Peter A. Schultz

A complication in bulk systems …



Discontinuity in potential from LMCC at supercell boundary!

… is solved by using Wigner-Seitz cells around LMCC positions



With Wigner-Seitz local volume, LMCC potential is continuous

The electron chemical potential μ_e

Peter A. Schultz

- **Standard E_{form} of charged defects needs electron reservoir:**

$$E_{form}(q) = E_{defect}(q) - E_{xtal}(0) - \Sigma N_i \mu_i + q \mu_e$$

linked

- **Supercells with charge: $\phi_{def}(r) = \phi_{pbc}(r) + C_{def}$**

Periodic potential $\phi_{def}(r)$ only known to within a constant C_{def}

C_{def} = fcn{defect type, configuration, cell shape, cell size, …}

$E_{defect}(q)$ has qC_{def} term in its internal energy

- **Standard ad hoc workarounds unsatisfactory - unquantitative**
  - **matching VB,CB edge, band structure features, average potentials …**
  - **Issue: renormalizing infinities, defect modified bands, band-bending, …**
  - **calibration uncertainty of "few tenths of eV" (Garcia & Northrup) - best case**

Needed a more rigorous scheme to fix electron reservoir

Defect energy and level calculation

Peter A. Schultz

Finite Defect Supercell Model Formation Energy

$$E_{form}(q) = E_{defect}(q) - E_{xtal}(0) - \Sigma N_i \mu_i + E_{\mu 0}(q) + E_{pol}(q)$$

$E_{defect}(q)$: DFT energy with LMCC potential
- $E_{xtal}(0) - \Sigma N_i \mu_i$: match number of each type of atom
$E_{\mu 0}(q)$: fix chemical potential μ_e to common electron resevoir
$E_{pol}(q)$: bulk polarization response

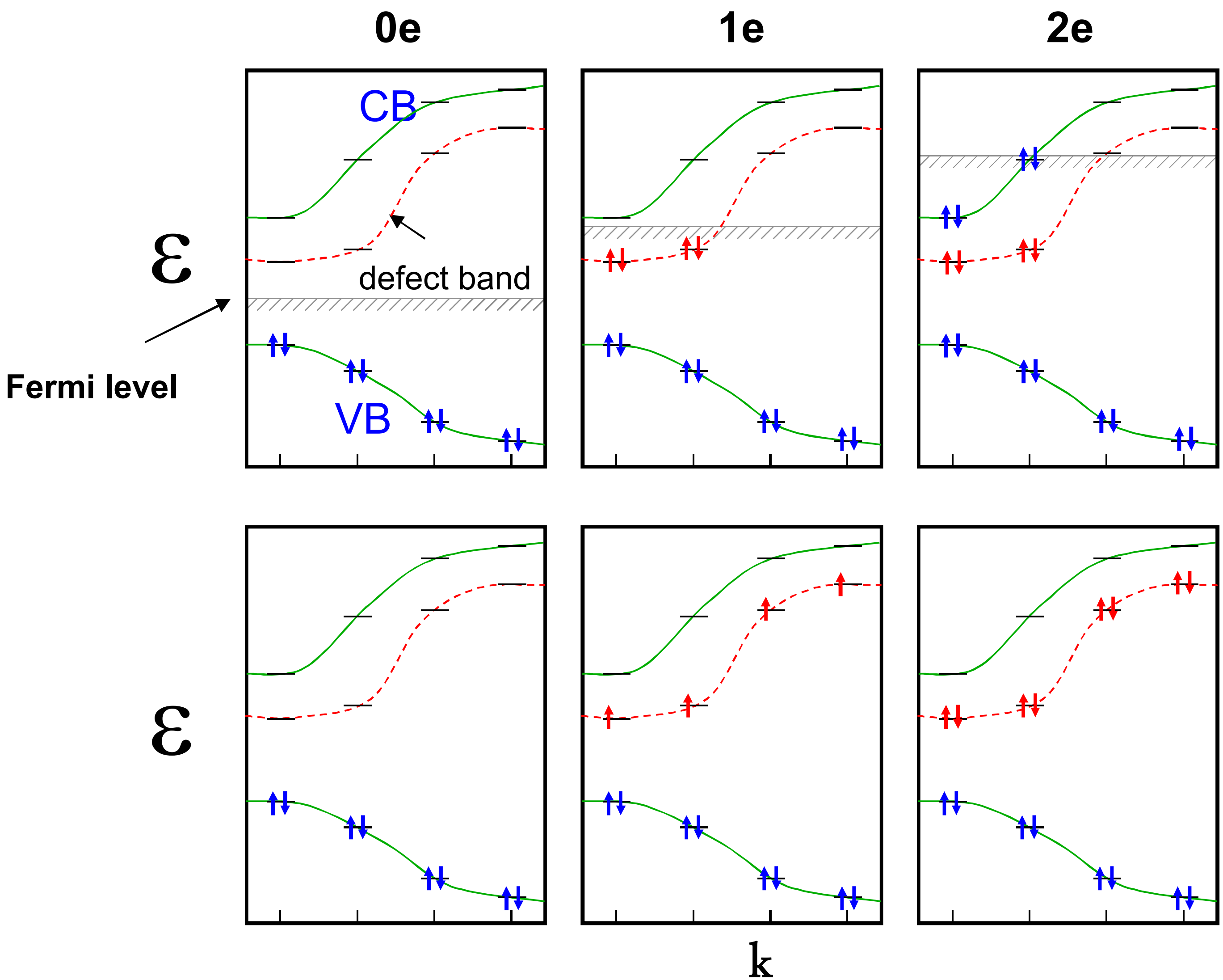
Defect level calculation

$$\Delta E(q/q\text{-}1) = E_{form}(q) - E_{form}(q\text{-}1)$$

Need to set spectrum vs. VB/CB by single marker.
All defect levels for all defects then fixed by continuity.

Defect banding: Discrete Defect Occupations

Peter A. Schultz



Standard methods: metallic, poor model of defect.

DDO: valid model of defect state with 0,1,2 electrons

Charged cell convergence - Jellium

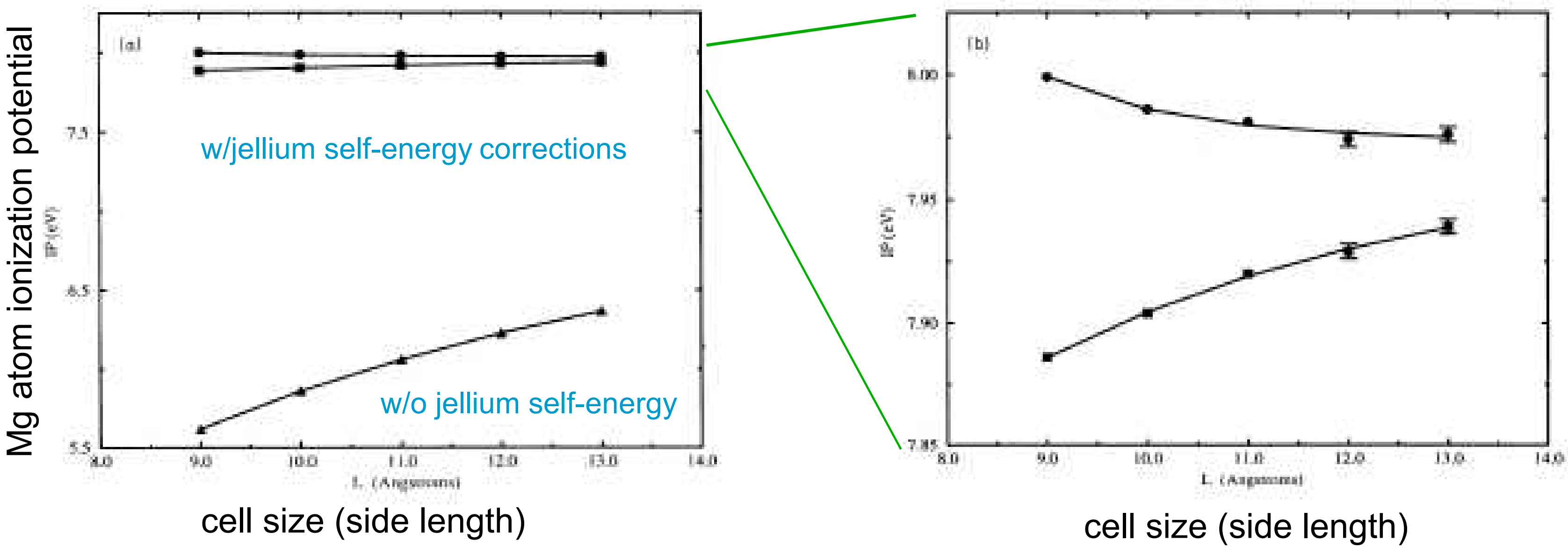
Peter A. Schultz

PHYSICAL REVIEW B VOLUME 51, NUMBER 7 15 FEBRUARY 1995-I

Periodic boundary conditions in *ab initio* calculations

G. Makov and M. C. Payne
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom
(Received 19 July 1994)

Figure 3

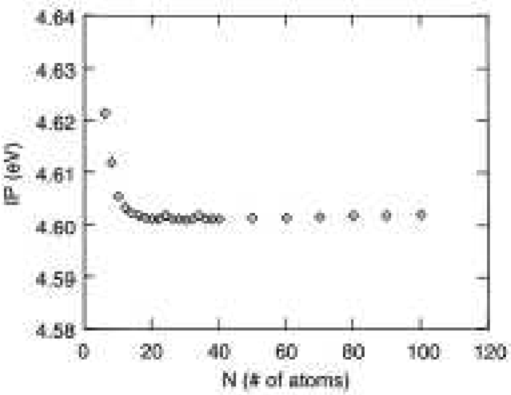


Variation in computed total energy due to incorrect charge potential

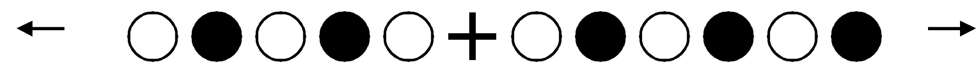
LMCC: NaCl - Cl vacancy ionization

Peter A. Schultz

1D chain

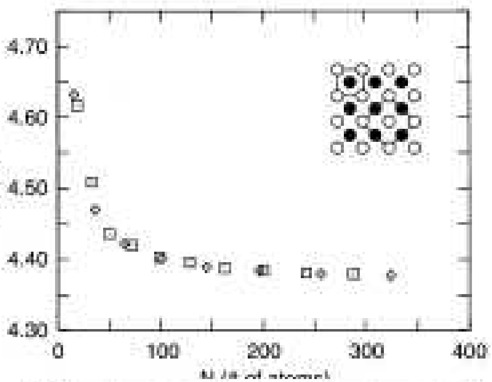


1D:



Supercell size dependence due to polarization.
Larger supercell -> more polarization
Apparent L^{-3} scaling = 1D classical dielectric screening

2D sheet

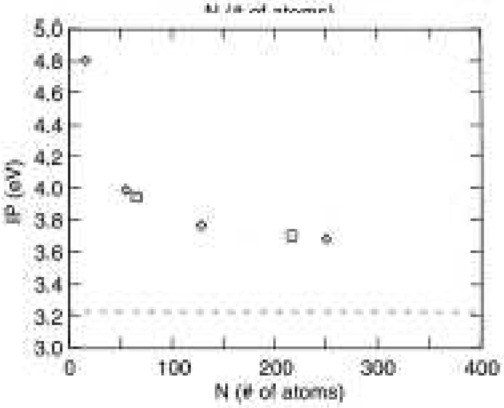


2D: single-layer 2D square sheet (polar&non-polar)

Apparent L^{-2} scaling = 2D classical dielectric screening

Insensitive to cell type, polar vs. non-polar

3D bulk

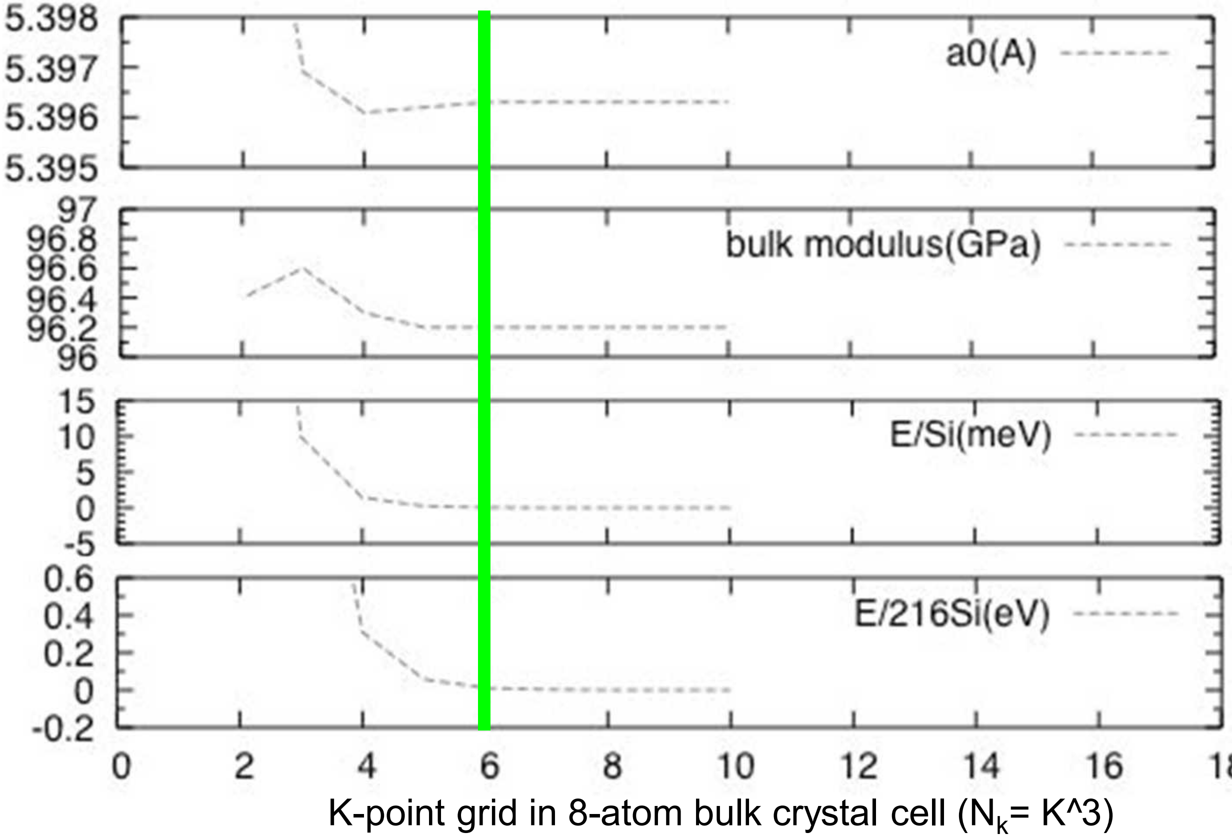


3D: bulk-layer 3D square sheet (fcc&sc cells)

Apparent L^{-1} scaling = 3D classical dielectric screening
Strictly screening due to large supercell volume
Insensitive to cell shape

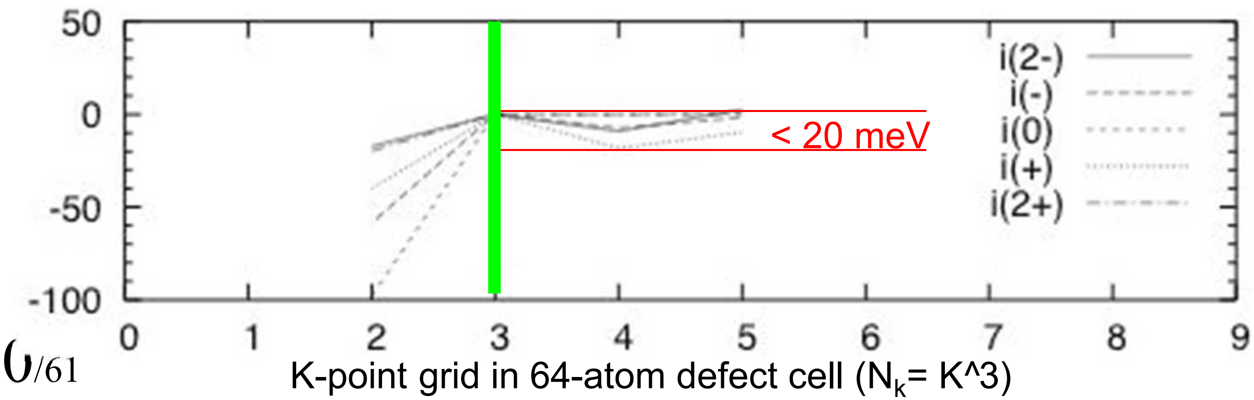
Sandia National Laboratories

BZ convergence: Si self-interstitial



Bulk properties (a_0,B,E/Si,E_{tot}) converge quickly: at 6^3 k w/8-cell = 3^2 k w/64-cell = 2^3 k w/216-cell

Defect energies should not vary faster than bulk, IF computational model is valid.



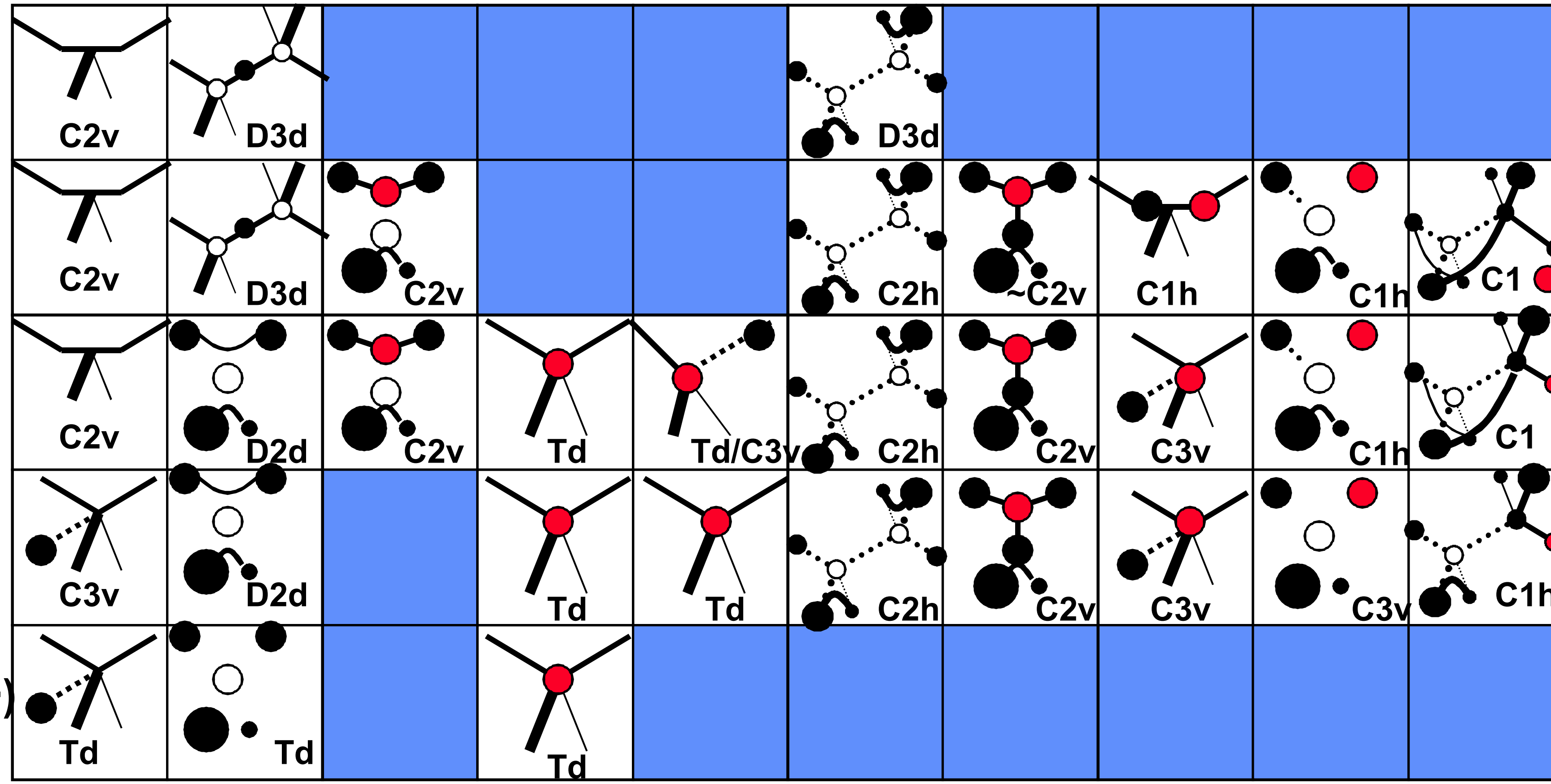
Interstitial formation energies in 64-site cell vary <20 meV {10 meV w/o I(+)} beyond equivalent of 6^3 k-grid in 8-site.

Peter A. Schultz

Sandia National Laboratories

Silicon defect structures

Peter A. Schultz



	i	*v*	O_s	S_s	N_s	*vv*	C_i	B_i	P*v*	B*v*
(2-)	C2v	D3d				D3d				
(-)	C2v	D3d	C2v			C2h	~C2v	C1h	C1h	C1
(0)	C2v	D2d	C2v	Td	Td/C3v	C2h	C2v	C3v	C1h	C1
(+)	C3v	D2d		Td	Td	C2h	C2v	C3v	C3v	C1h
(2+)	Td	Td		Td						

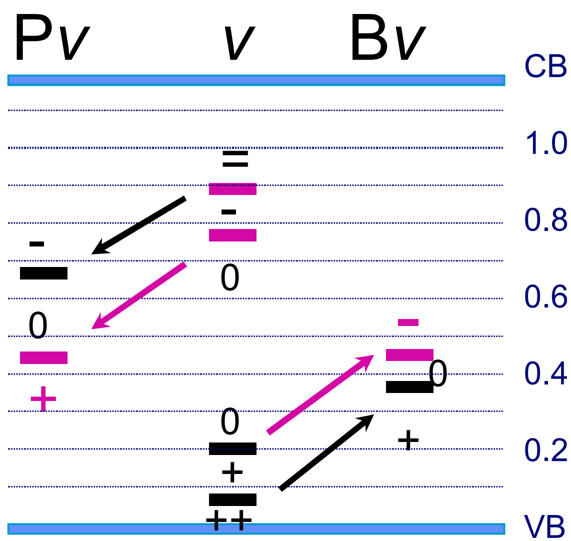
GGA: E(C2v) < E(D3d) for *v*(-)

Si: new P-v and B-v charge states

Peter A. Schultz

- Silicon level calculations - over 15 defects with levels

  i(=/-/0/+/++), *v(=/-/0/+/++)*, *vv(=/-/0/+)*, C_i(-/0/+), B_i(-/0/+), P*v*, B*v*
  O_s(A-center), O_i, N_s, S_s, v_2O, v_2O_2, H_i, vP_2, v_2P, …
  DFT "defect band gap" matches experiment (1.2 eV)
  DFT: mean |error| = 0.10 eV, max error~0.2 eV



Task: Theory quantified v(=/-), v(-/0)

Discovery: Theory *predicted* Pv(+) and Bv(-)

"Absolute prediction"
new levels >0.4 eV from band edge
validation error: 0.2
P*v*(0/+) subsequently confirmed in experiment
[Larsen, et al PRL 97, 106402 (2006)]

VALIDATION is key to quantitative DISCOVERY - GaAs is ALL discovery

Calibrating the polarization model: v_{Ga}

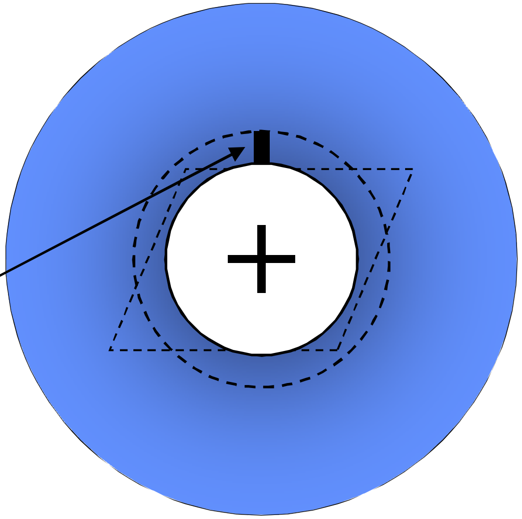
Peter A. Schultz

Jost model:

$$E_{pol} = \frac{(1 - 1/\varepsilon_0)\, q^2}{R_j}$$

$$R_j = R_{vol} - R_{skin}$$

R_{skin} accounts for unscreened volume **inside** supercell



Need ε_0 (use 13), and R_{skin} (fit)

Why use v_{Ga}?

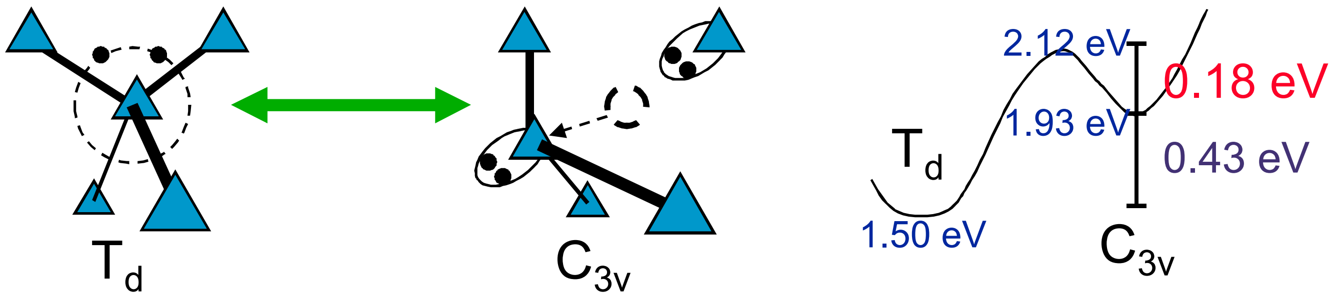
Need higher charge states (0 to -3), best if not strongly distorted (near T_d)

Energy(eV)	$v_{Ga}(0)$	E(2-/1-)-E(1-/0)	E(3-/2-)-E(2-/1-)	aAs: E(0/+)-E(+/2+)
64-site	2.81	0.167	0.174	0.231
216-site	2.69	0.168	0.152	0.246
512-site	2.75	0.162	0.141	0.252

GaAs EL2 and the As antisite

Peter A. Schultz

EL2 = antisite $As_{Ga}(0)$



216-site =
512-site
(~ 64-site)

	Experiment -EL2	**SeqQuest/FDSM - As_{Ga}**
EL2(0/1+)	E_c -0.74 eV	E_c -0.81 eV
EL2(1+/2+)	E_v+0.54 eV	E_v +0.48 eV
Splitting:	0.24 eV (E_g=1.52)	0.25 eV
EL2*	no donor states	no donor states
Reorientation:	~0.3 eV	~0.2 eV

Verification: 64-216-512-1000-site supercell results match

Validation: DFT matches experiment for EL2 w/in 0.1eV