

# **Modeling charged defects and defect levels in semiconductors and oxides with DFT:**

## ***An improved inside-out perspective***

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**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)**

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# Why model defects in semiconductors and oxides?

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**Radiation effects in electronics**

**Process modeling for semiconductors**

**Radiation detectors**

**Defect chemistry in nuclear fuels and nuclear waste**

Goals:

(1) Qualitative understanding

Augment experiments

- incomplete, inconclusive, unavailable, expensive

(2) Quantitative characterization

Predictive simulations, inform coarser models

- not just publishable, but defensible to engineers

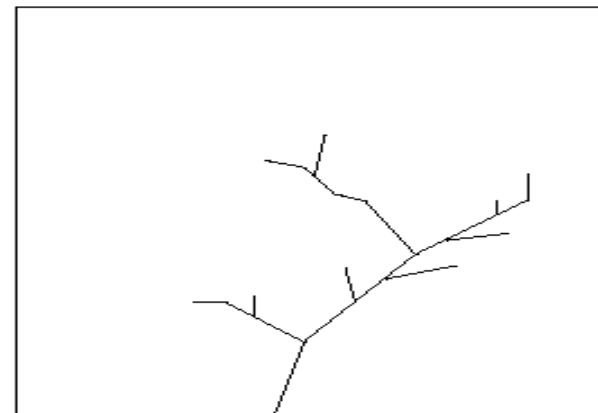
# Defects: from atoms to devices

Initial defect distribution

**Radiation creates displacement damage:**

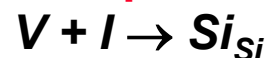


**and charge carriers (electrons and holes)**

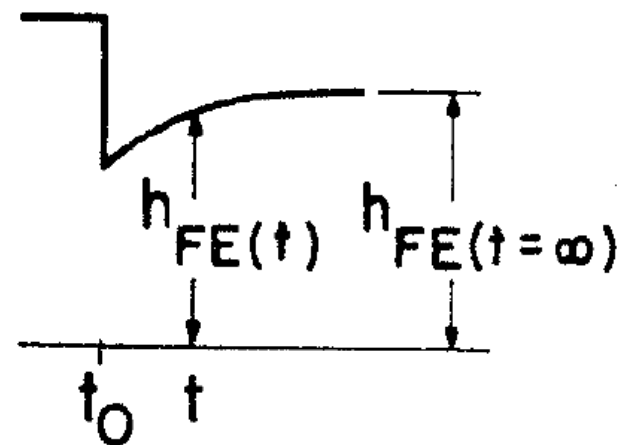
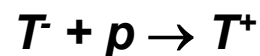


Defect evolution

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

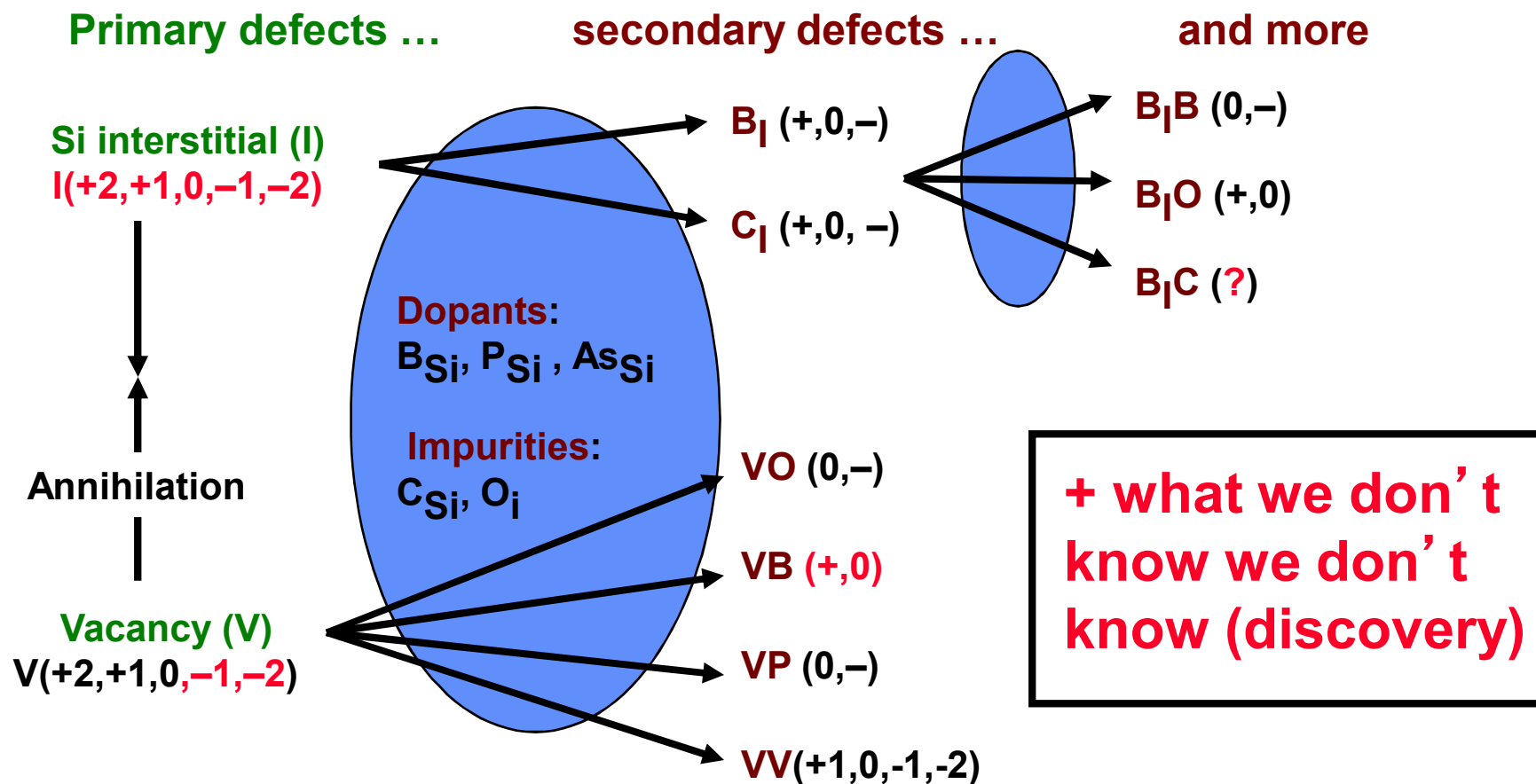


**Defects recombine electrons and holes, modifying currents:**



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

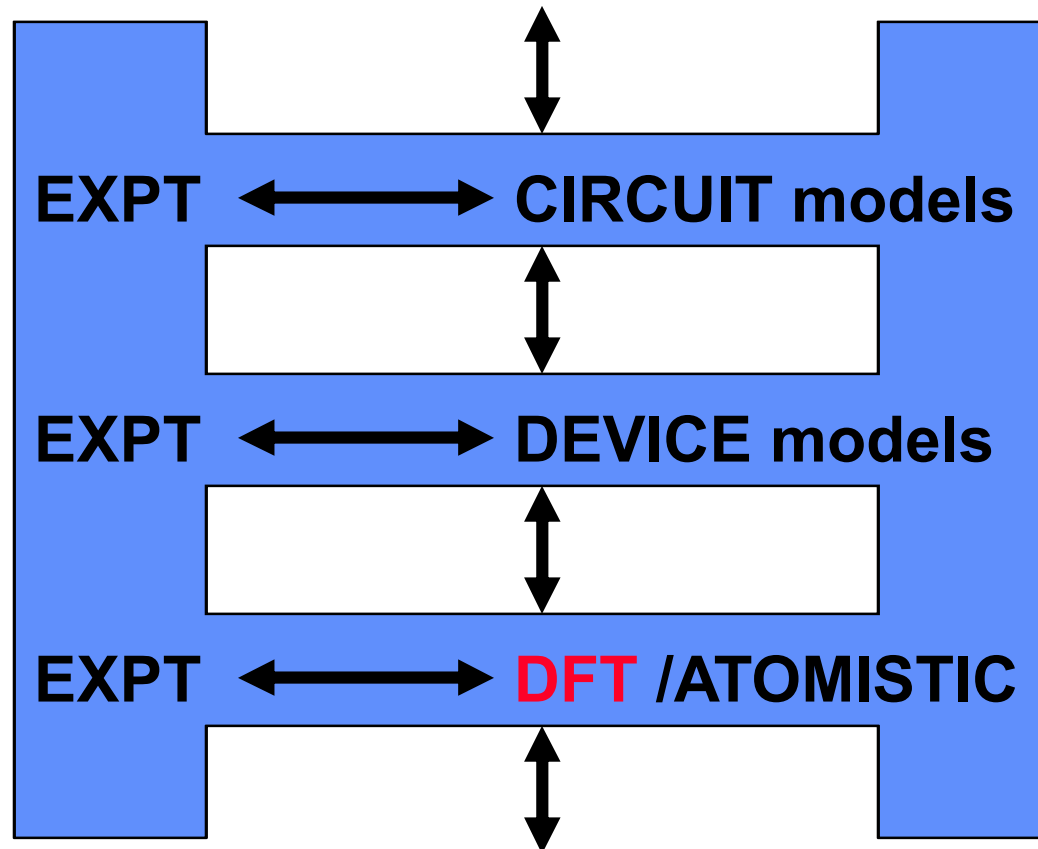
# The radiation effect defect universe: Si



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

# Multiscale ladder for radiation damage

**Electrical system response**

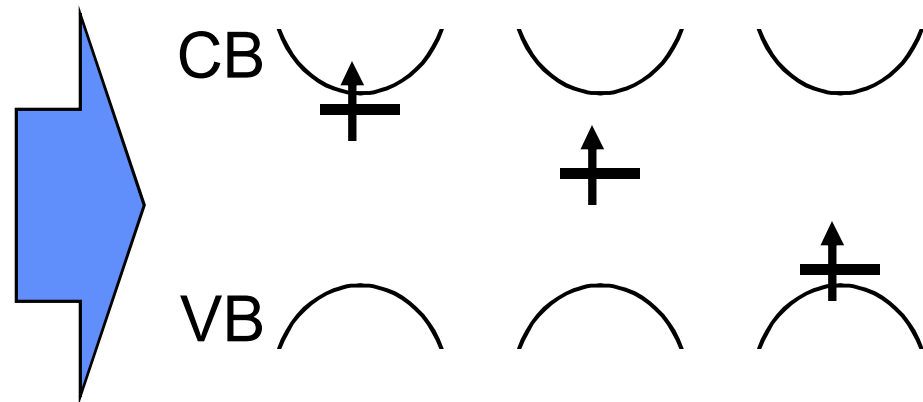
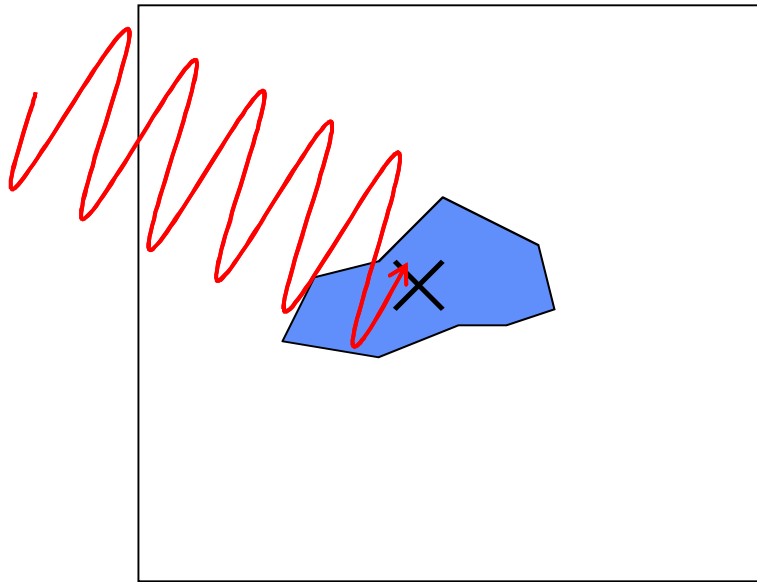


**Radiation damage**

**Require: quantitative confidence**  
**Verification, validation, uncertainty**

# Radiation damage and defects levels

Radiation damage ...



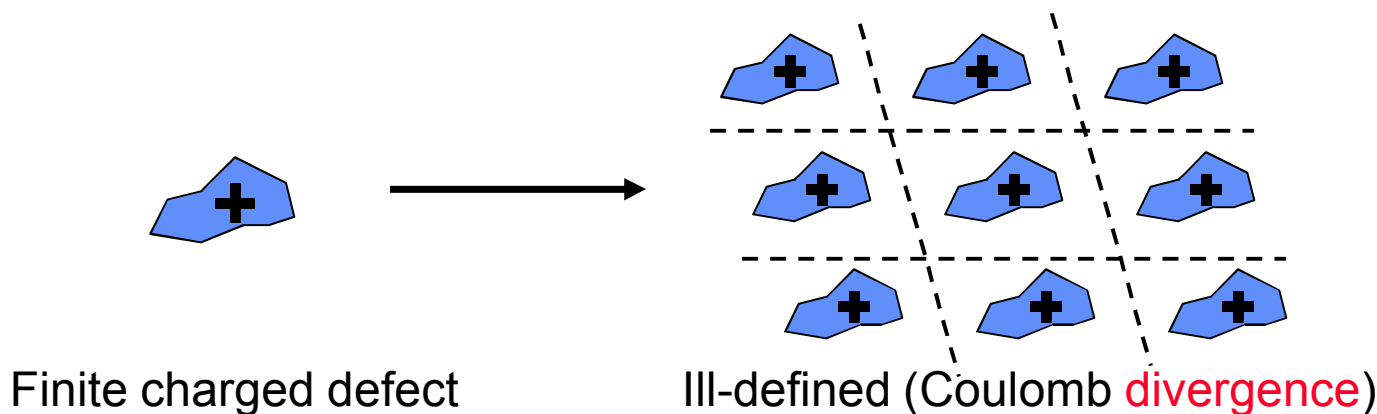
produces defects ... and introduces electronic transitions

... and we need to quantify these transitions; DFT

# Challenges for density functional theory

- **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:



Lots of DFT calculations, no robust, predictive method

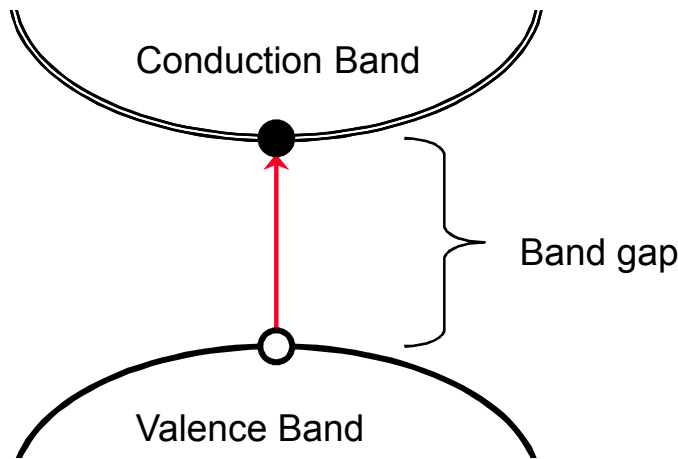
# DFT “band gap problem”

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

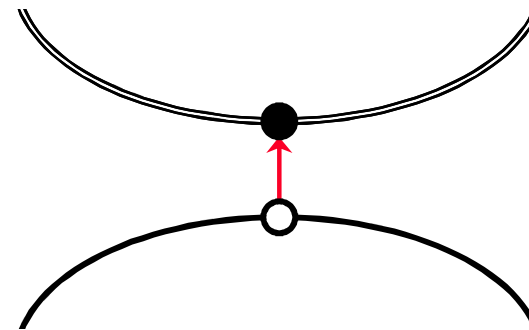
[L.J. Sham and M. Schlüter, PRL **51**, 1888 (1983); PRB **32**, 3883 (1985)]

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?**



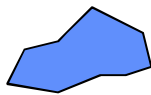
# The Supercell Approximation

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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 ...



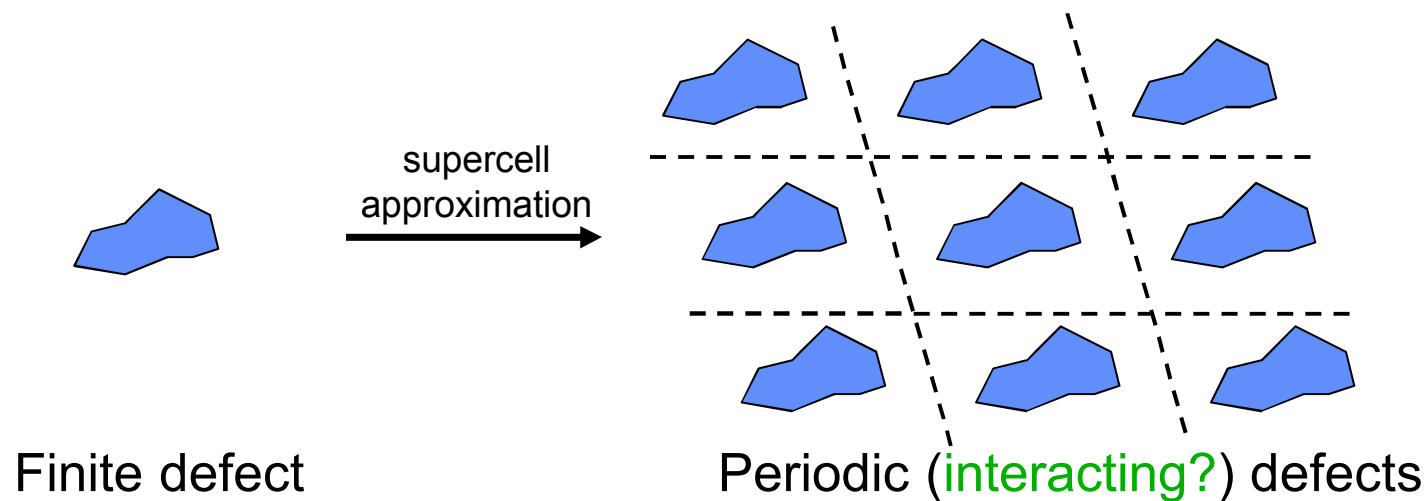
Finite defect

# 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 ...



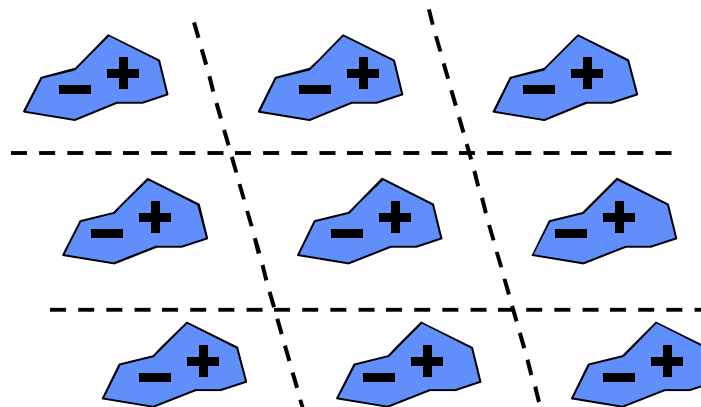
## The supercell Idea:

Surround perturbed defect region with enough material to buffer defects.

In the limit of large enough supercells approach an isolated defect.

# The Supercell Approximation

the catch ...



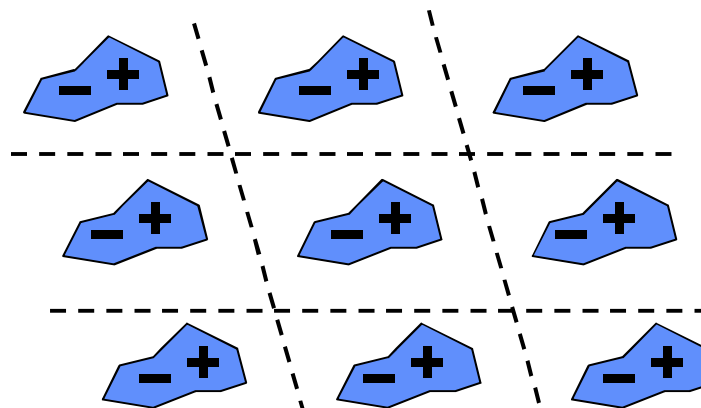
Finite defect with dipole

Periodic (**interacting**) defects

DFT expense limits size of supercell - defects interact

# The supercell approximation

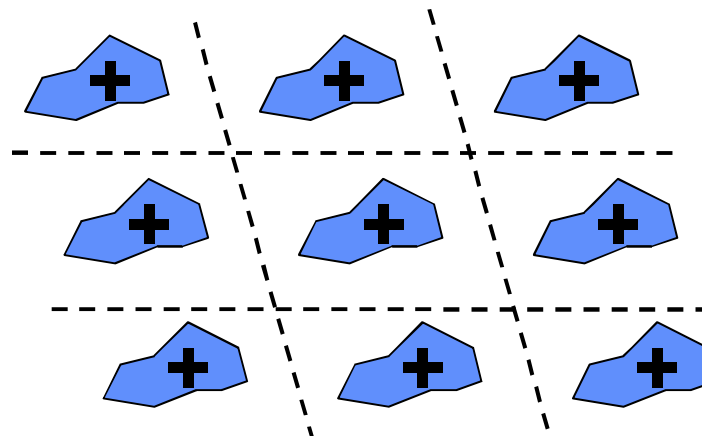
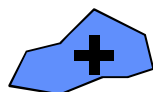
A problem ...



Finite defect with dipole

Periodic (interacting) defects

even worse ...



Finite charged defect

Ill-defined (Coulomb divergence)

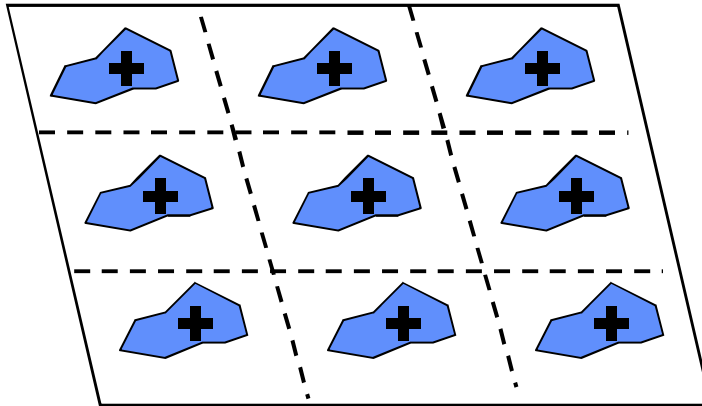
Interactions and divergence are key issues

# Jellium to eliminate divergence?

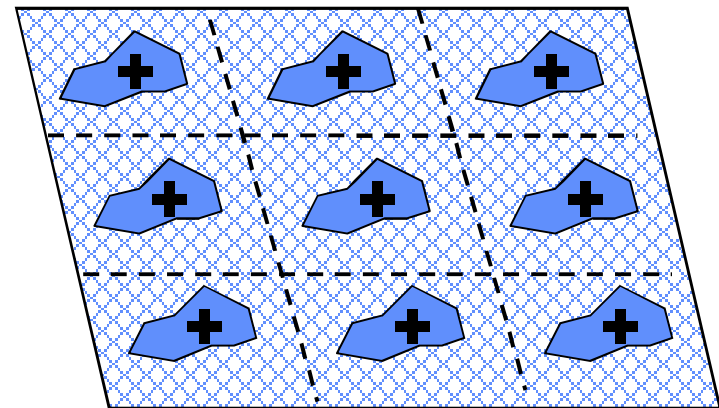
Isolated defect ...



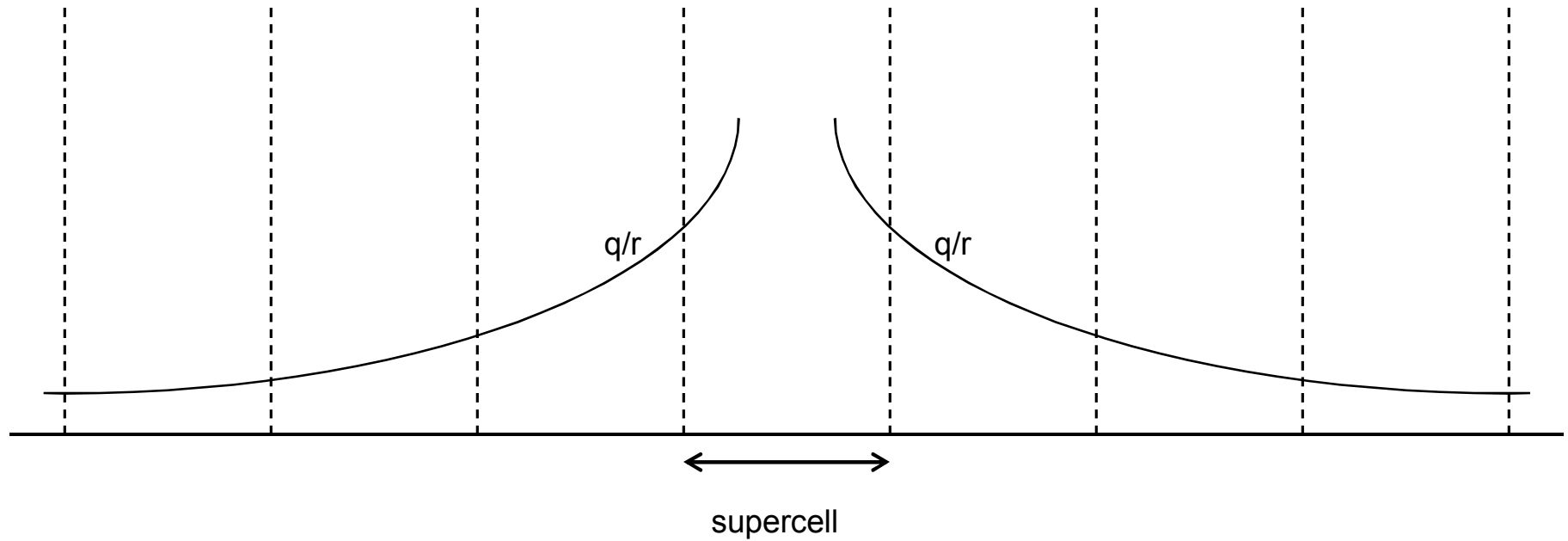
Apply supercell approximation ...



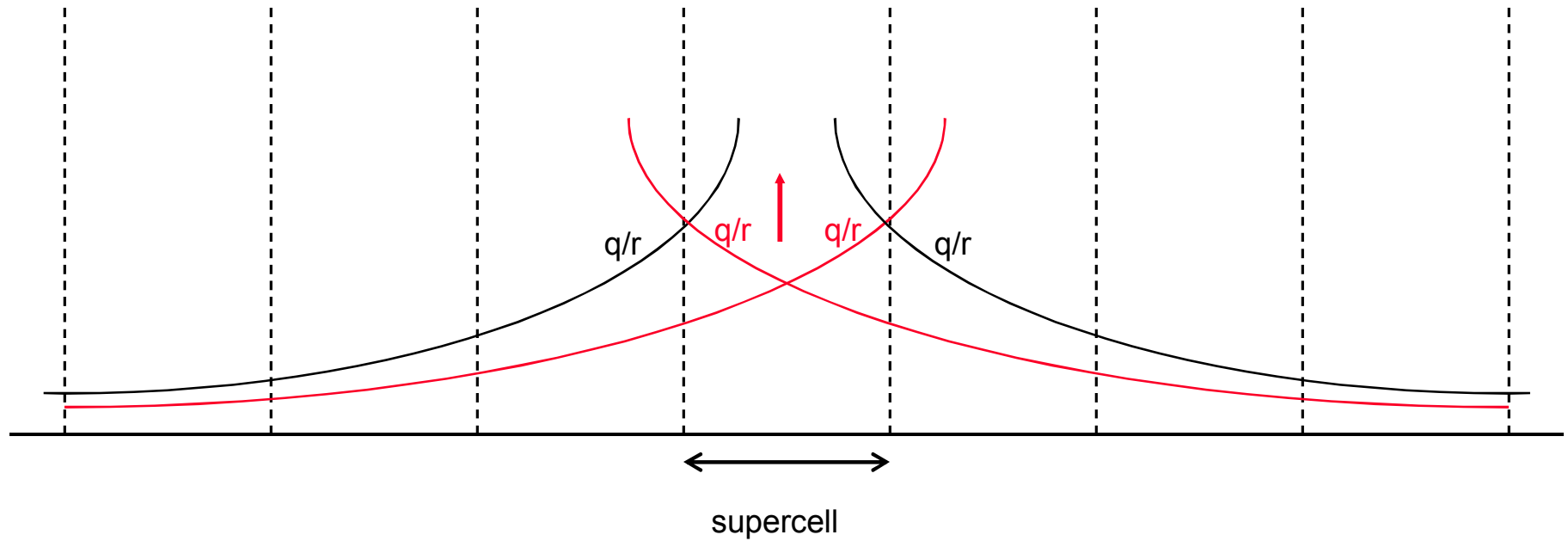
Neutralize with flat  
background charge:  
“jellium”



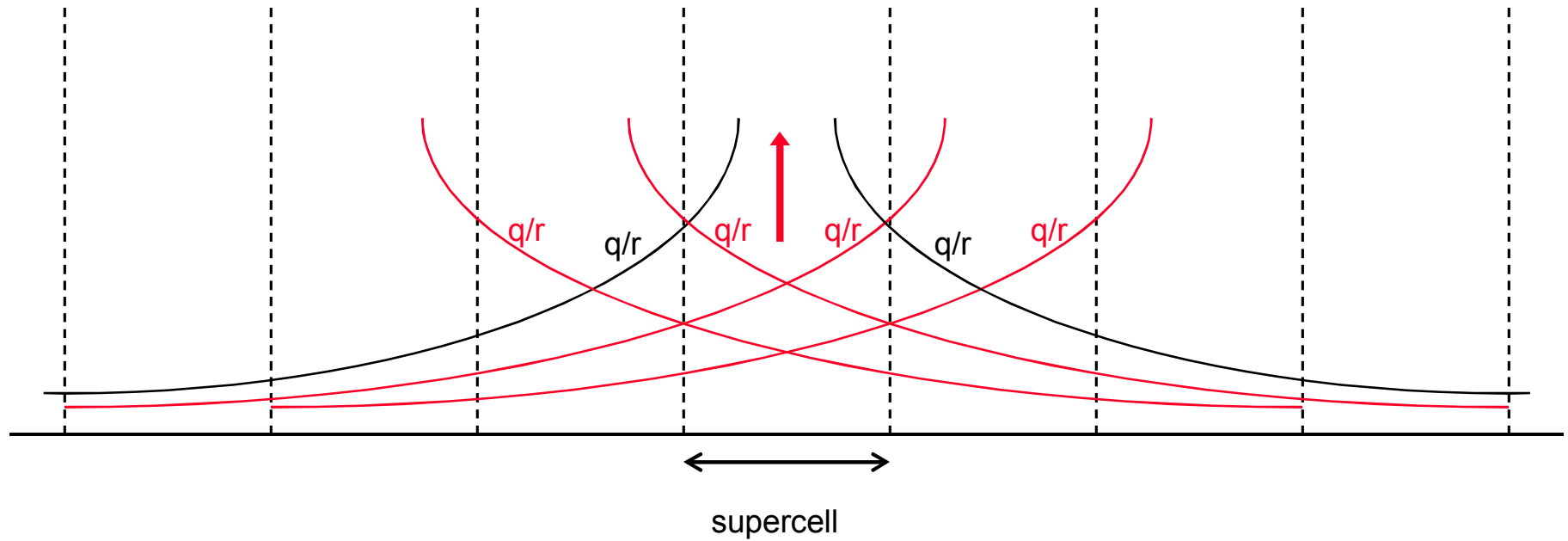
# Whence the divergence?



# Whence the divergence?

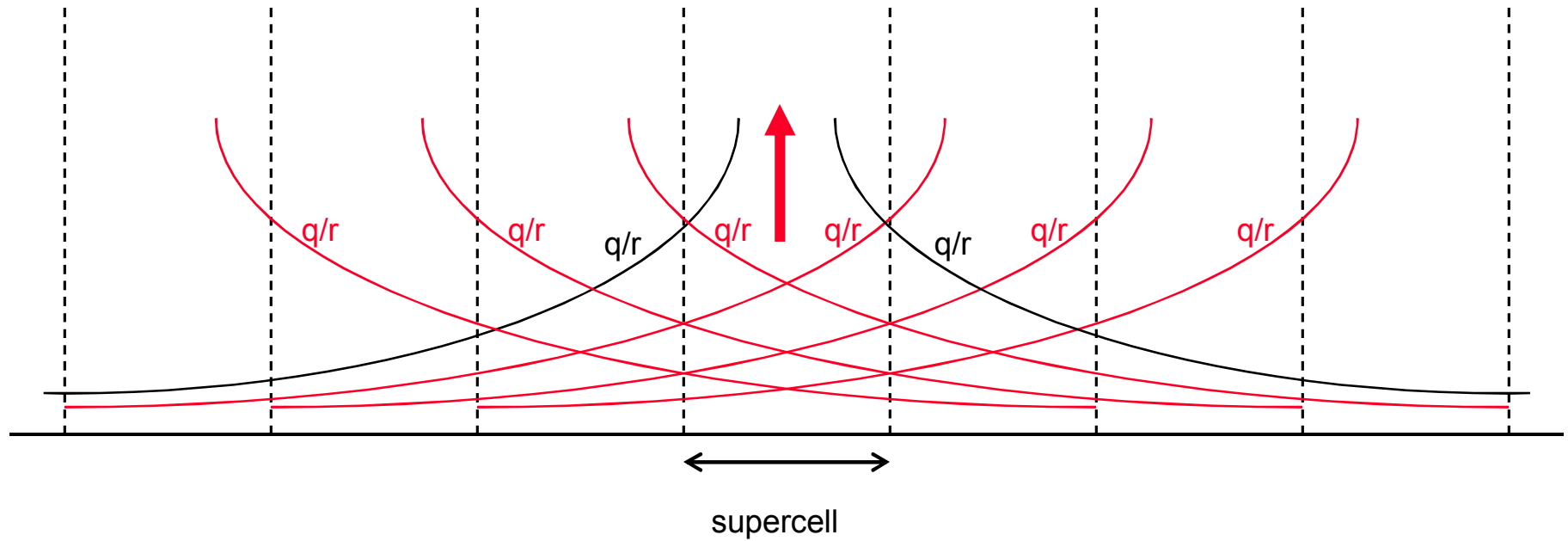


# Whence the divergence?

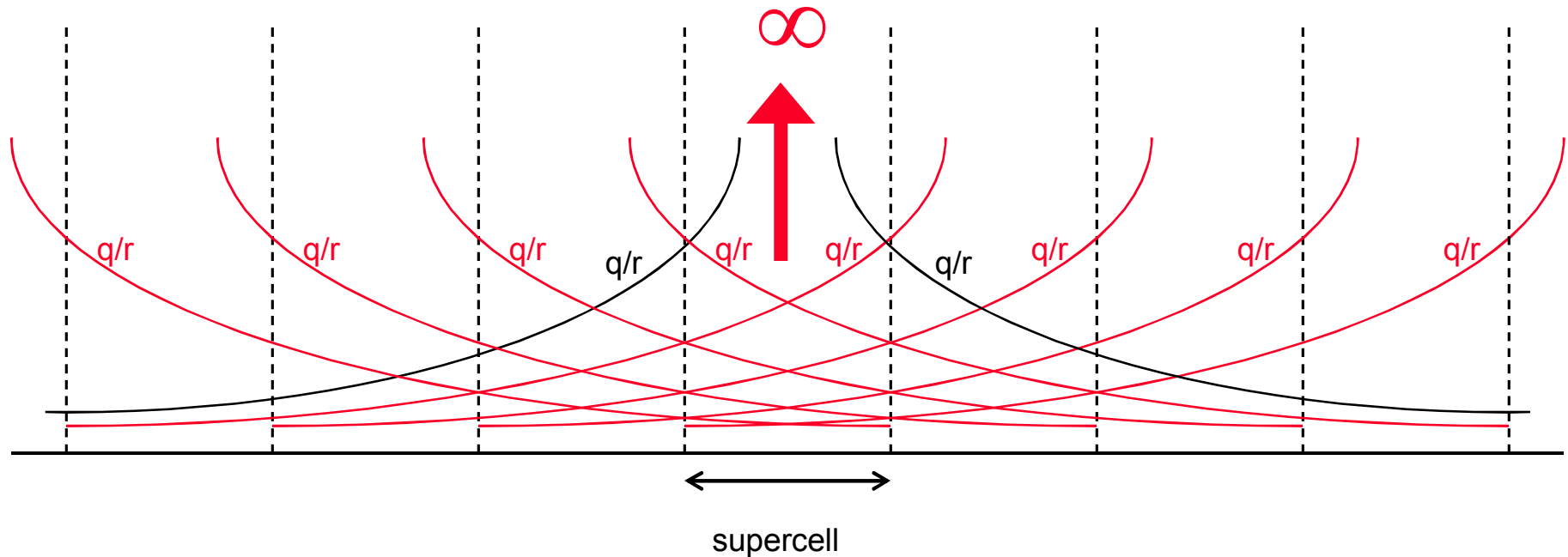




# Whence the divergence?



# Whence the divergence?

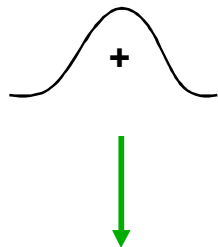


Divergence arises from infinite-ranged  $q/r$  potentials from periodic images

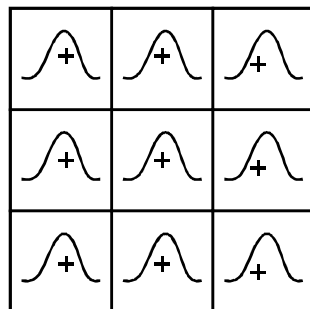
**Divergence is not flat**

# Net charge boundary conditions - jellium

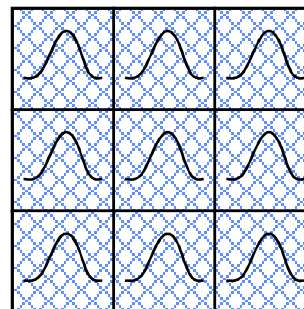
Take isolated charge density...



create cubic supercell ...

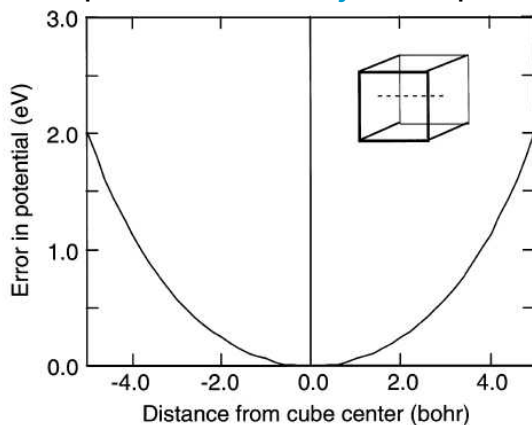


neutralize with "jellium"



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
20.4	64	1.0
30.6	216	0.67
40.8	512	0.50
51.0	1000	0.40

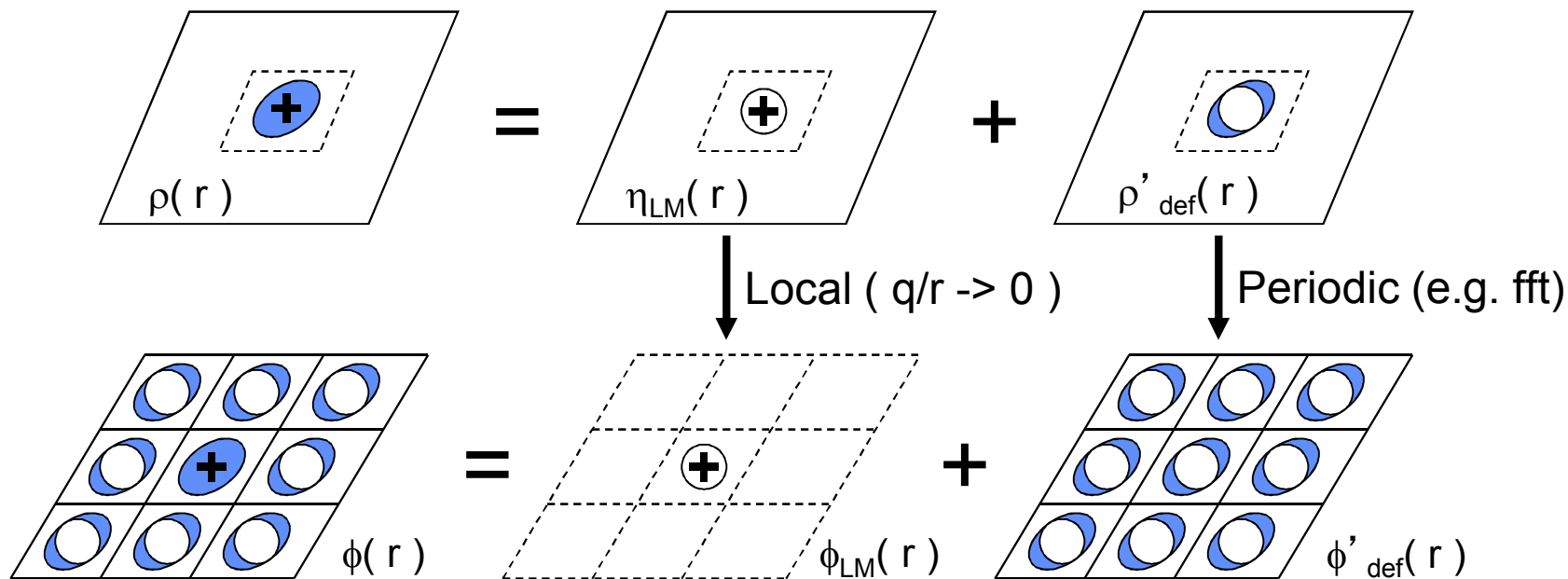
Si band gap: 1.2 eV (expt.), 0.5 eV (DFT)

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

# Local Moment CounterCharge (LMCC)

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

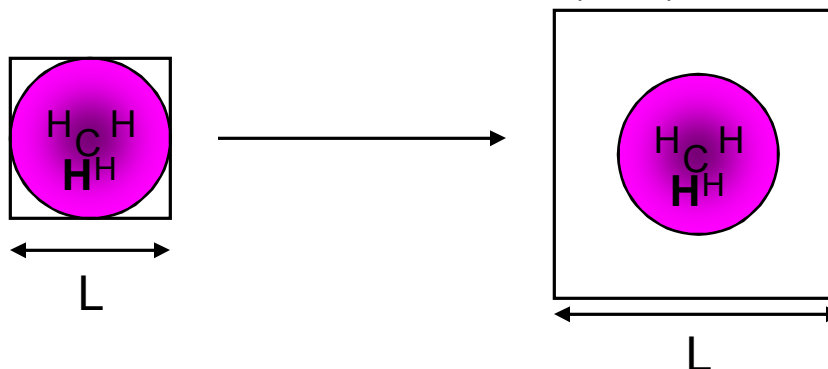
- Solution of Poisson Equation is linear in the density
- LMCC: split total density  $\rho(\mathbf{r})$  into two pieces ...
  - (1) model local density  $\eta_{\text{LM}}(\mathbf{r})$  matching multipole (charge) of  $\rho(\mathbf{r})$
  - (2) remainder (momentless) density  $\rho'(\mathbf{r}) = \rho(\mathbf{r}) - \eta_{\text{LM}}(\mathbf{r})$



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

# Charged cell convergence - LMCC

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



Charged, no dipole:  $\text{CH}_4 \rightarrow \text{CH}_4[+]$  ... Ionization Potential

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

Dipole, no charge:  $\text{Na-Cl}$  diatomic molecule ... Total Energy

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

Dipole, charge:  $\text{OH} \rightarrow \text{OH}[-]$  ... Electron Affinity

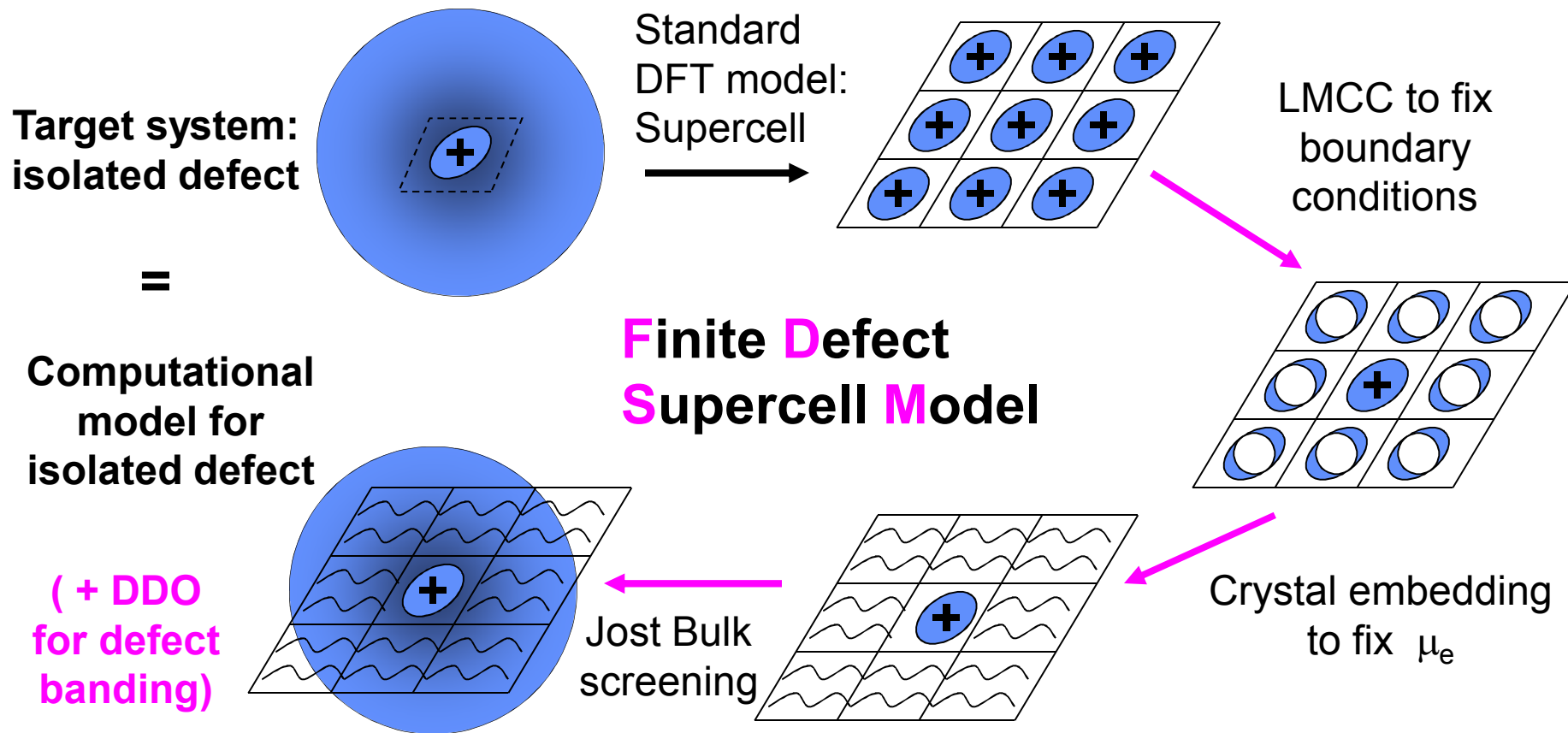
$L = 18.0 - 30.0$  bohr (9.5-15.9 Å)    **EA varies  $< 10^{-3}$  eV**

Total energy, levels, i.e. full Hamiltonian are all immediately converged.

-> electrostatic *potential* correctly represented by LMCC, not just energy

# A supercell theory of defect energies

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



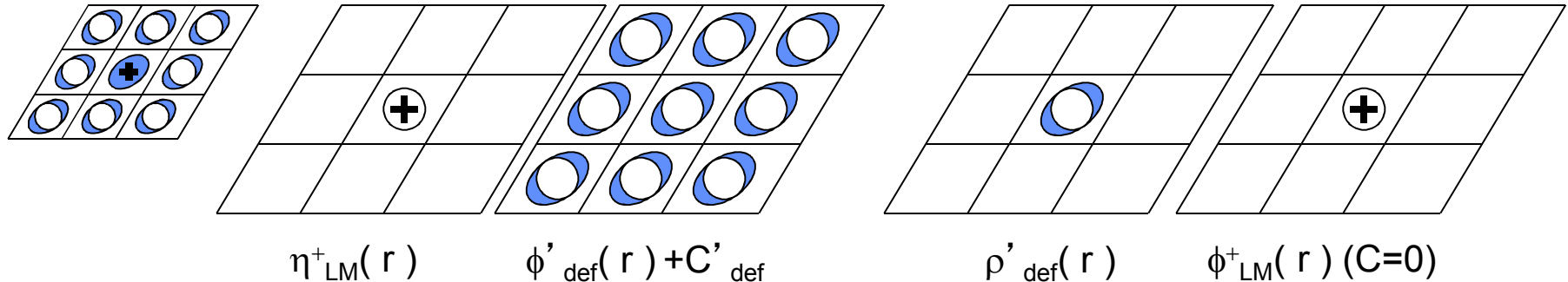
*“Ab initio” computational model – connect model to physics*  
Calculations with rigorous control of charge boundary conditions

(i.e., not jellium-based)

# A fixed chemical potential $\mu_e$

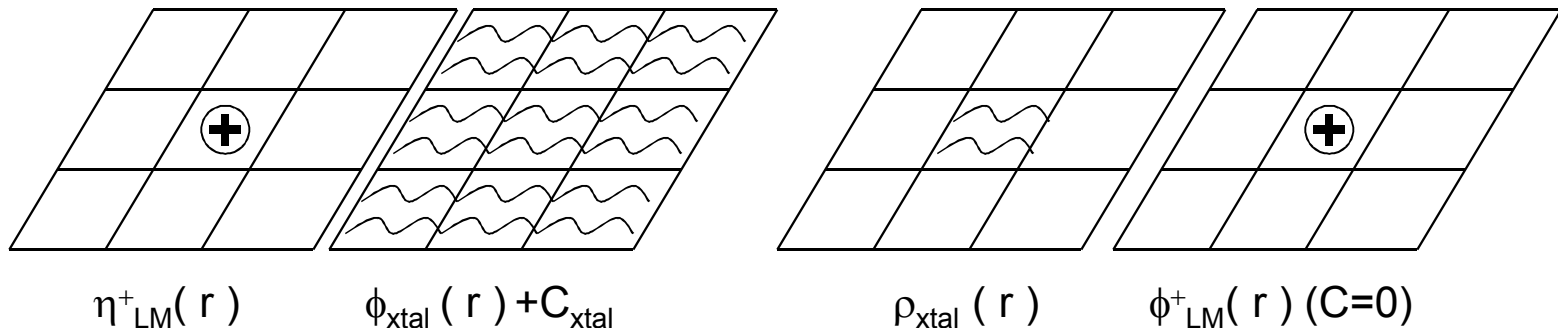
Replace interaction of net charge with periodic defect potential ...

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



... with crystal potential:

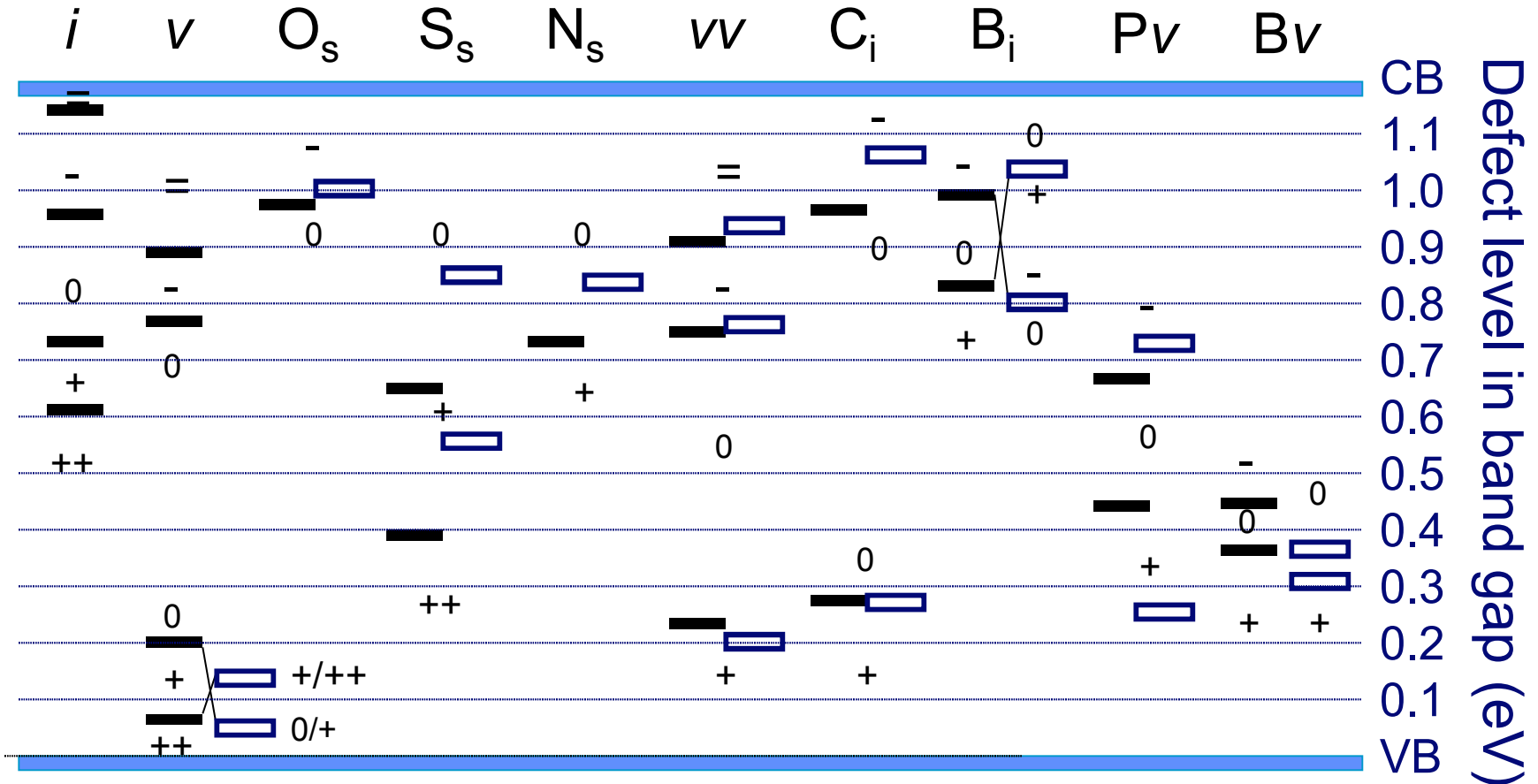
$$+ \int dr \eta_{LM}^+ (\phi_{xtal} + C_{xtal}) - \int_{UC} dr \phi_{LM}^+ \rho_{xtal}$$



Replace **variable** defect cell  $C'_{def}$ , with **fixed** crystal  $C_{xtal}$  reference  
 Chemical potential equivalent to matching potential at  $R=\infty$

## Si: DFT/LDA vs. Experimental Levels

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



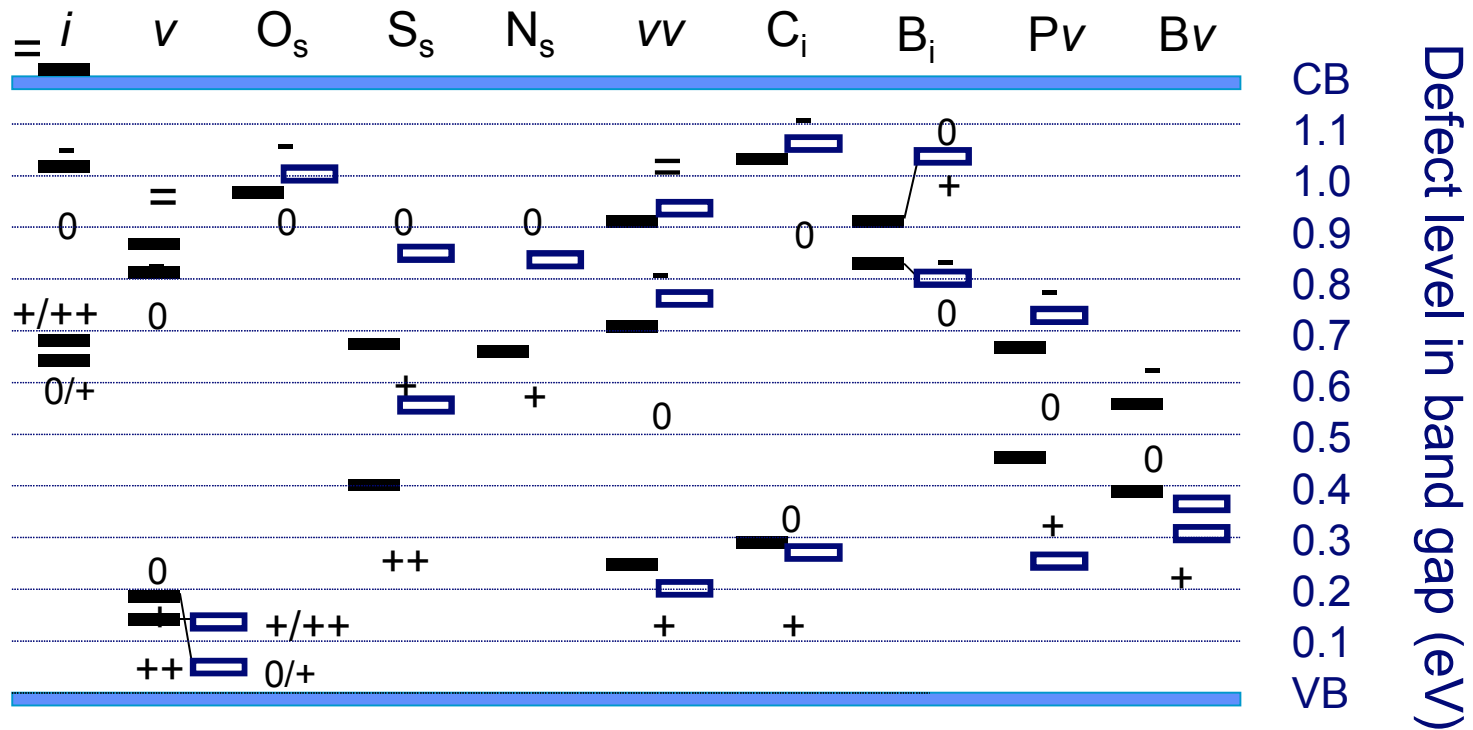
LDA: max error=0.25 eV, mean |error|= 0.10 eV

Intrinsic, first-row, second-row, and complexes across gap  
LDA Kohn-Sham gap is only 0.5 eV



# Si: DFT/PBE vs. Experimental Levels

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



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?

# Computational methods – III-V's

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- **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  $Z_{\text{val}}=3,13$ )
  - full force relaxed ( $<1$  meV total energies)
  - full FDSM ... robust control of boundary conditions
- **Large bulk simulation supercells**
  - $a_0=a_0(\text{theory})$ ; GaAs: 5.60Å(LDA), 5.63Å(3d), 5.74Å(PBE);  $a_0(\text{expt})=5.65$  Å
  - Cubic supercells: 64-, 216-, 512-, 1000-site
  - $\mathbf{k}$ -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

Peter A. Schultz

216- = 512- = 1000-site

LDA-3d = LDA to  $\leq 0.1\text{eV}$

LDA~PBE; spin <0.05 eV

As<sub>Ga</sub> levels = EL2 levels

$v_{Ga}$  levels below midgap



# The GaAs divacancy is the E1-E2 radiation center

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:

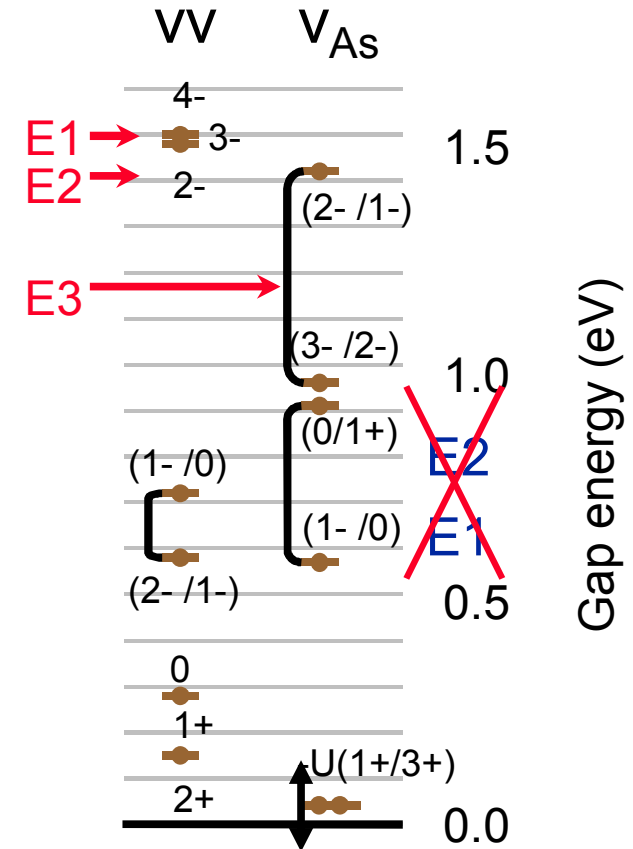
$v_{As}(-/+)$  is mid-gap negative-U (only *one* level)

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

$vv(\textcolor{red}{4}/\textcolor{red}{3}/\textcolor{red}{2}-)$  near conduction band

$vv$  is major radiation defect: E1-E2

$v_{As}(\textcolor{red}{3}/\textcolor{red}{1}-)$  transition is the E3

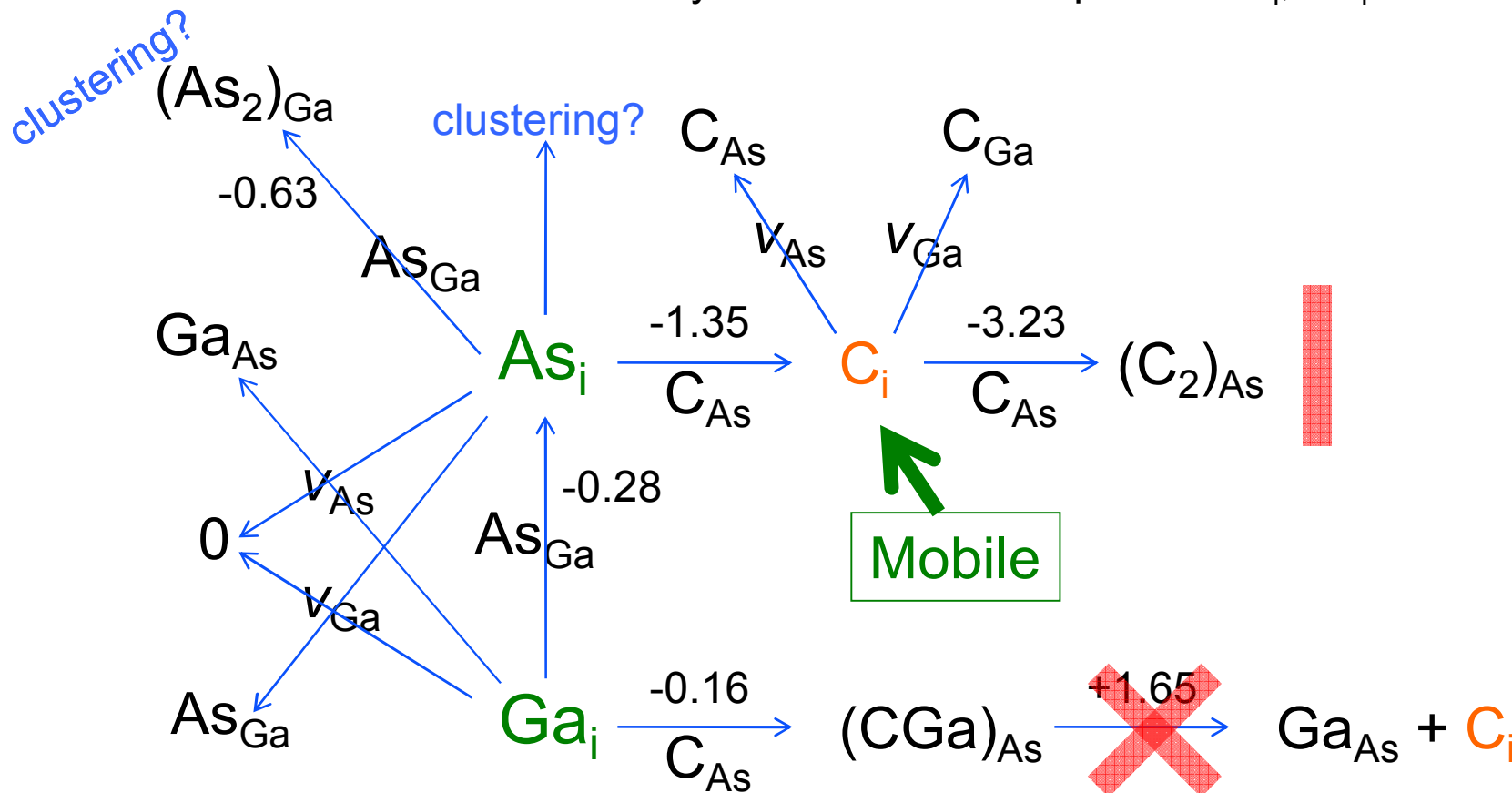


DFT-SeqQuest+FDSM levels good enough to identify defects strictly on **quantitative** defect level calculations

# GaAs: C-doped reaction network

P.A. Schultz, J. Res. Eng: Rad. Effects **30**, 257 (201).

SeqQuest, LDA, 216-site, thermodynamic energy with  $E_f = \text{VBE}$  (p-type)  
Reaction networks initiated by identified mobile species:  $\text{As}_i$ ,  $\text{Ga}_i$

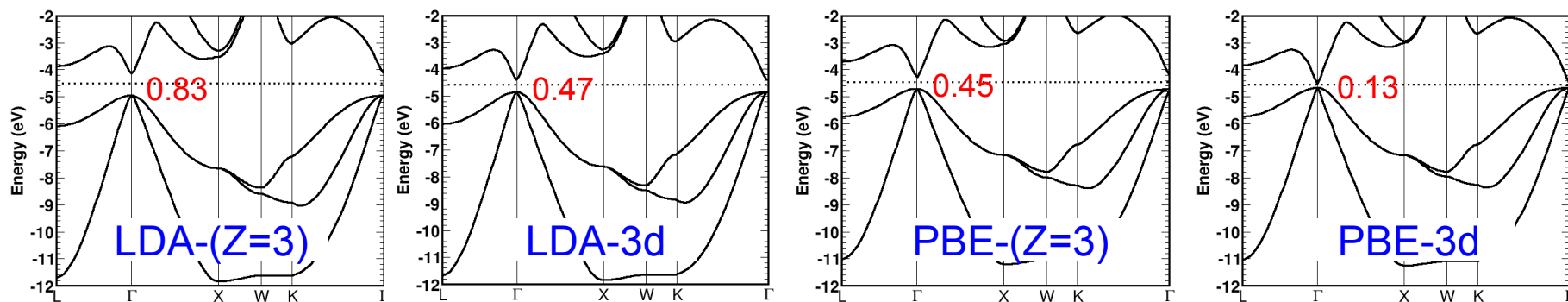


Reliable defect levels means reliable chemistry

# GaAs: A theoretical 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) ...

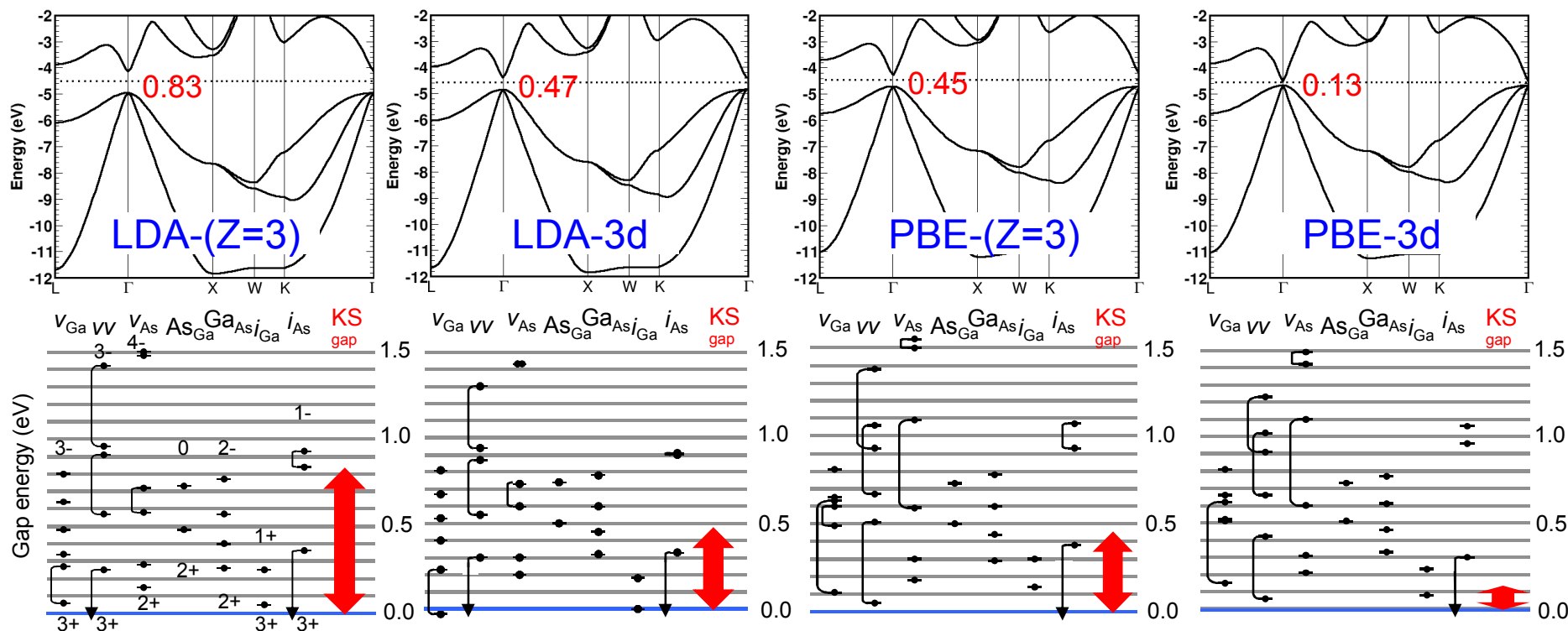
... to **0.13 eV**, PBE-3d, Ga(Z=13) pseudopotential (PP)

# GaAs: A theoretical 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** changes ...

Peter A. Schultz



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

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

# GaAs Computational model lessons

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- 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)

Verified cell-convergence

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

Checked:  $\text{As}_{\text{Al}}$

Verified:  $vv$

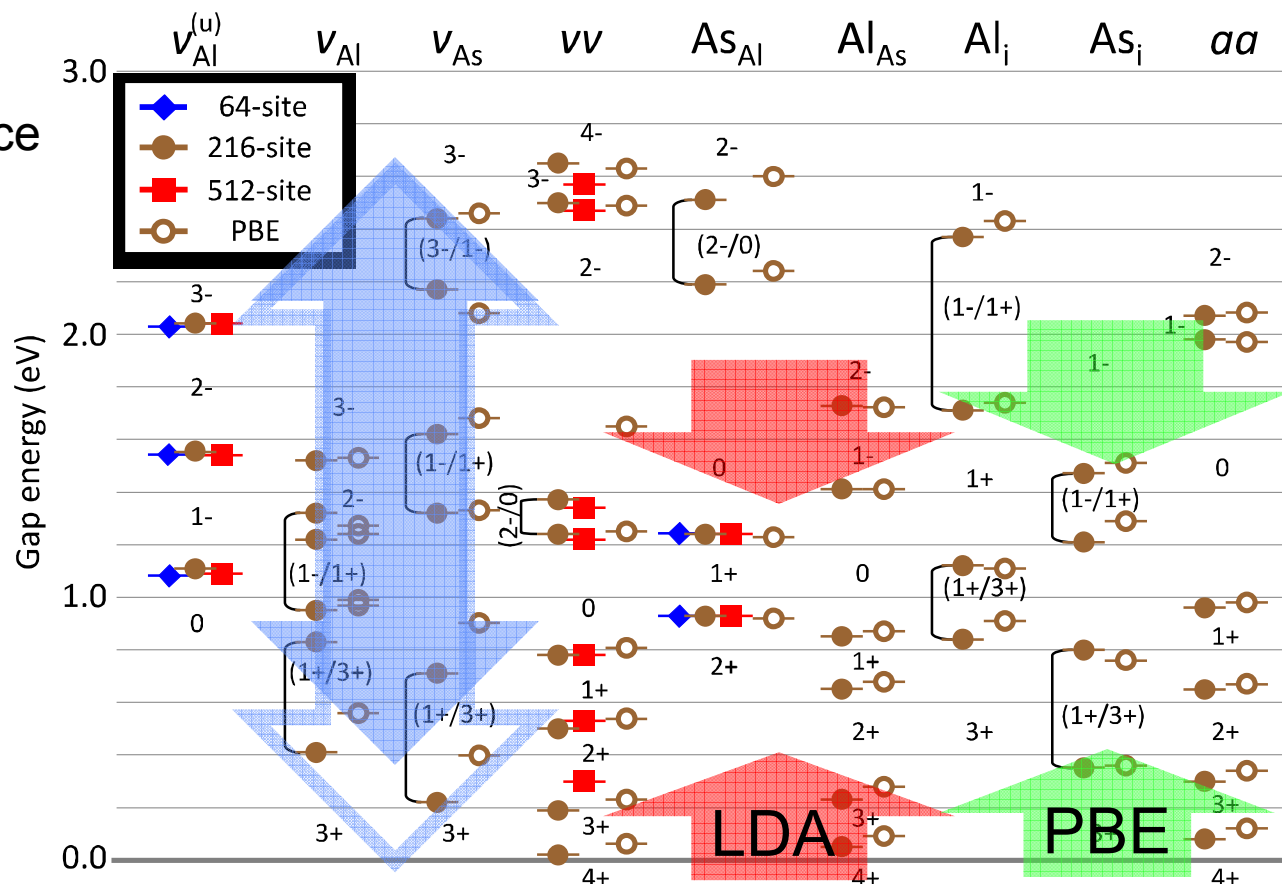
AlAs band gap

KS-LDA: 1.37 eV

KS-PBE: 1.53 eV

Defect span: 2.3 eV

Experiment: 2.16<sup>i</sup> eV



Very similar to GaAs defects, with some new features  
A reverse band gap problem?

# GaP intrinsic defects

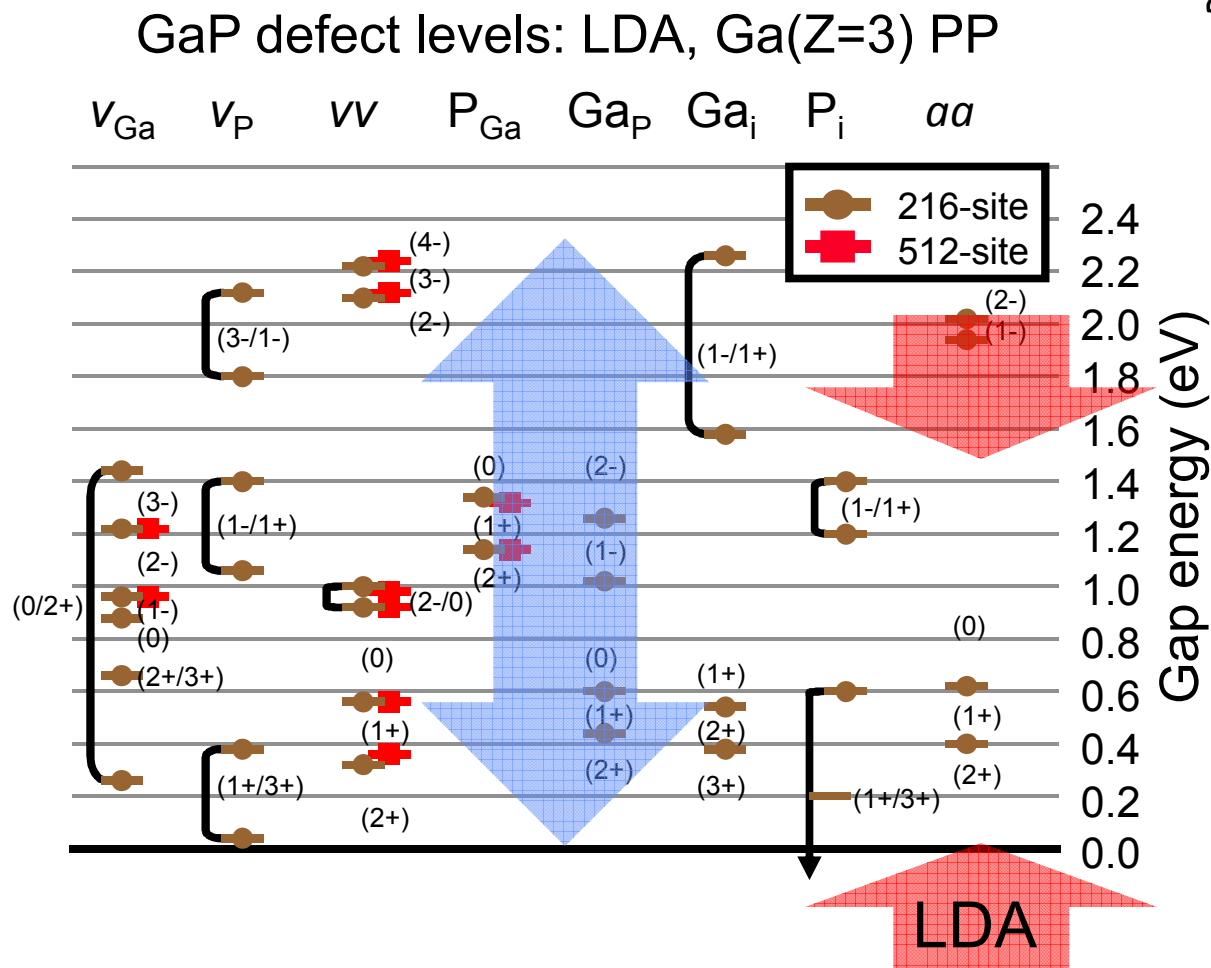
216-site results = 512-site  
Verification: cell-converged

GaP band gap

KS-LDA: 1.51<sup>i</sup> eV

Defect span: 2.35 eV

Experiment: 2.35<sup>i</sup> eV



# InP intrinsic defects

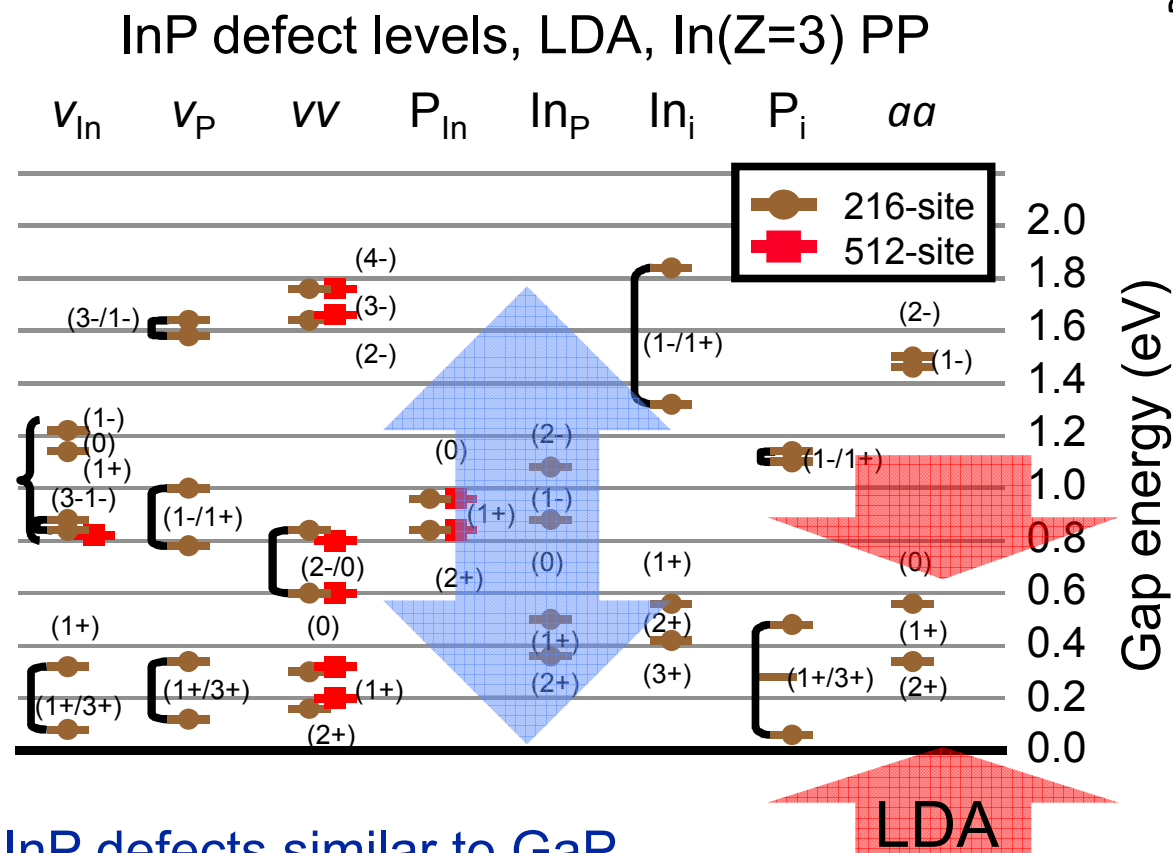
216-site results = 512-site  
Verification: cell-converged

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?

# AIP intrinsic defects

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

Peter A. Schultz

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

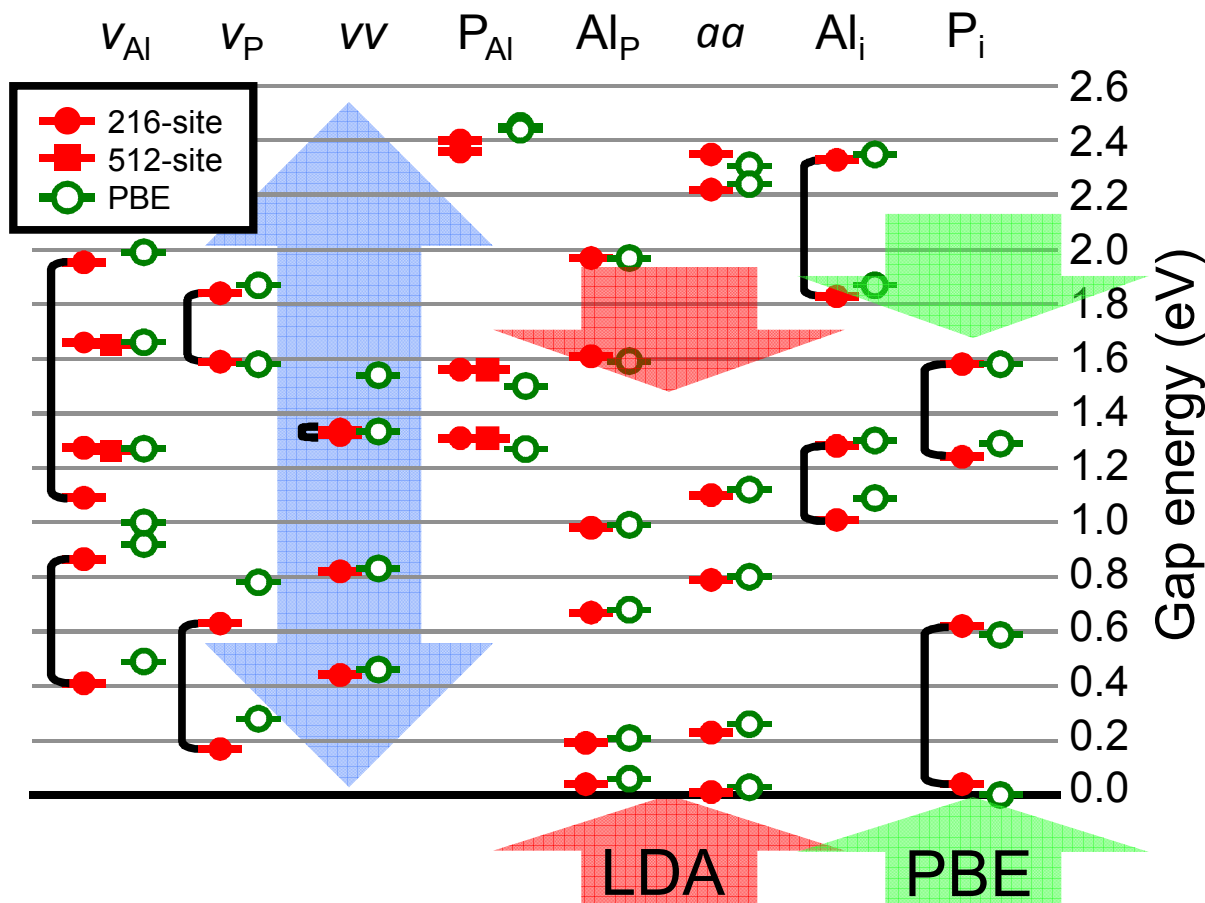
AIP band gap

KS-LDA: 1.48 eV

KS-PBE: 1.67 eV

Defect span: 2.55 eV

Experiment: 2.51 eV



# The DFT “Defect band gap”

- 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			AlAs			AlP		
1.17 eV			2.16 <sup>i</sup> eV			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			GaP			InP		
1.52 eV			2.35 <sup>i</sup> eV			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

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## IV-IV: 3C-SiC (cubic)

GGA/PBE KS Gap:	1.38 eV
<b>Defect Gap (PBE):</b>	<b>~2.7</b>
<b>Experimental Gap:</b>	<b>2.40</b>

## II-VI: CdTe (3d-valence)

LDA KS Gap:	0.81 eV
PBE KS Gap:	0.69 eV
<b>Defect Gap (LDA&amp;PBE):</b>	<b>~1.6</b>
<b>Experimental band gap:</b>	<b>1.60</b>

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)

250-site results = 432-,686-site

Verification: cell-converged

$v_i$  levels match experiment

Validation of accuracy

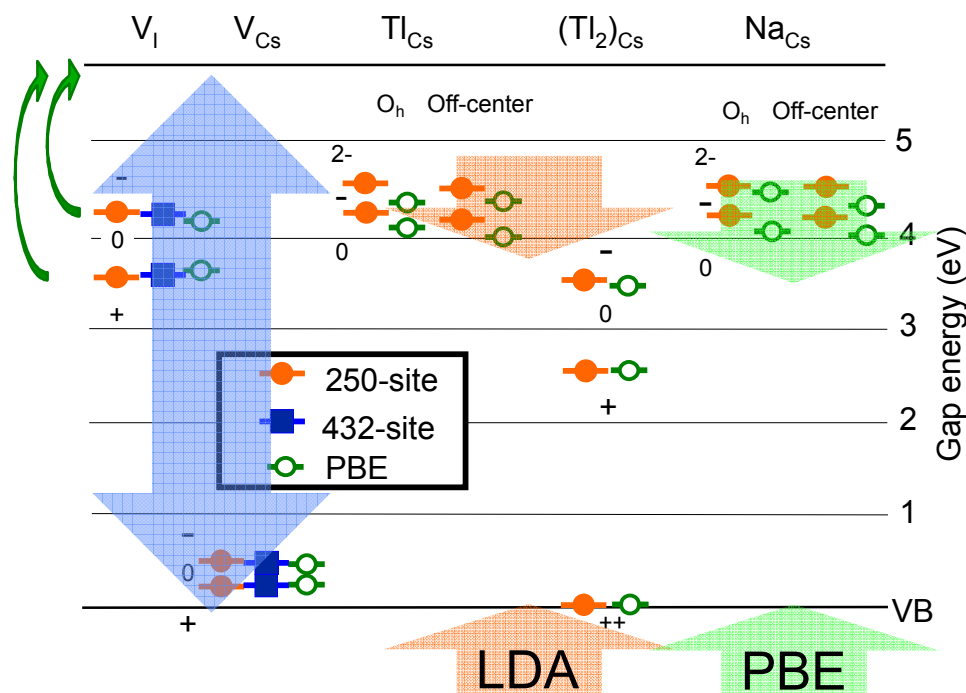
CsI band gap

KS-LDA: 3.80 eV

KS-PBE: 3.58

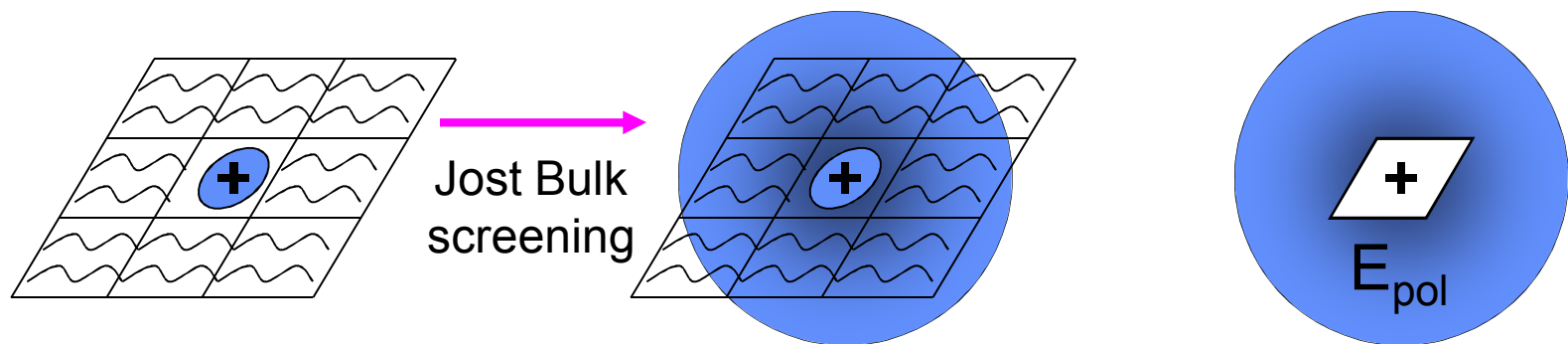
Defect span: >5.8 eV

Experiment: 6.3 eV



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

# The polarization model



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

Jost model: 
$$E_{pol} = \frac{(1 - 1/\epsilon_0) q^2}{R_{jost}}$$

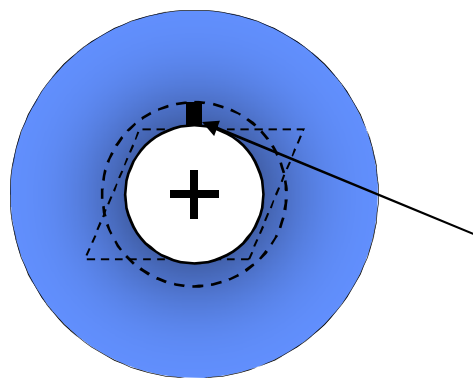
$$R_{jost} = R_{vol} - R_{skin}$$

$q$  = charge on defect

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

$R_{vol}$  = radius of volume sphere

Two parameters for any material



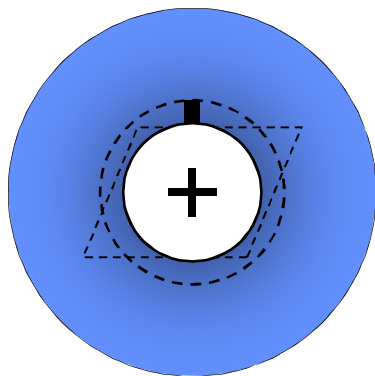
$R_{skin}$  = unscreened  
volume **inside** cell.  
fit: =1.3-1.7 Bohr

$\epsilon_0$  = static dielectric constant - expt

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



# How big is bulk screening?



$$E_{\text{pol}} = \frac{(1 - 1/\epsilon_0) q^2}{R_{\text{jost}}}$$

Defects mostly converged at 64-site cells

$E_{\text{pol}}$  mostly insensitive to  $\epsilon_0$  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

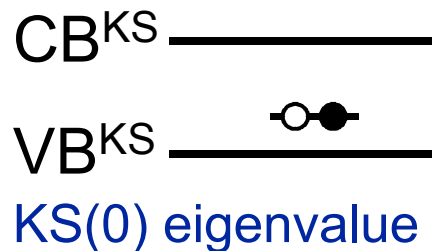
*This is lower bound on classical screening energy*

**Bulk classical screening outside defect is huge**  
**Key insight to understanding KS gap vs. defect gap**

# How is a good defect band gap possible?

Conventional picture:

Defect state depicted as eigenvalue inside KS eigenvalue gap



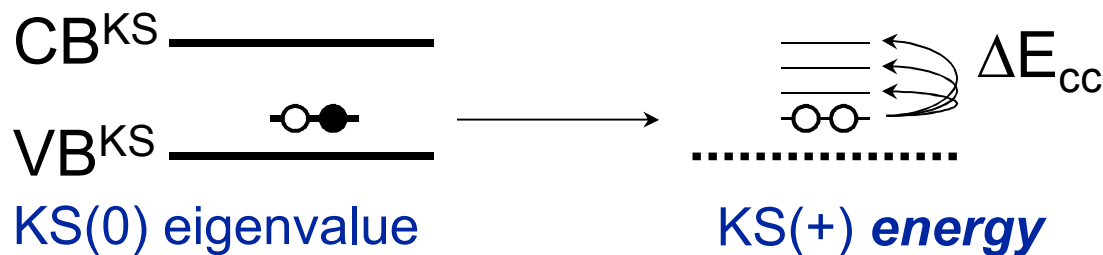
**Sham and Kohn** [Phys. Rev. **145**, 561 (1966)]

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?

What about:  
final state effects?

Effective level shift



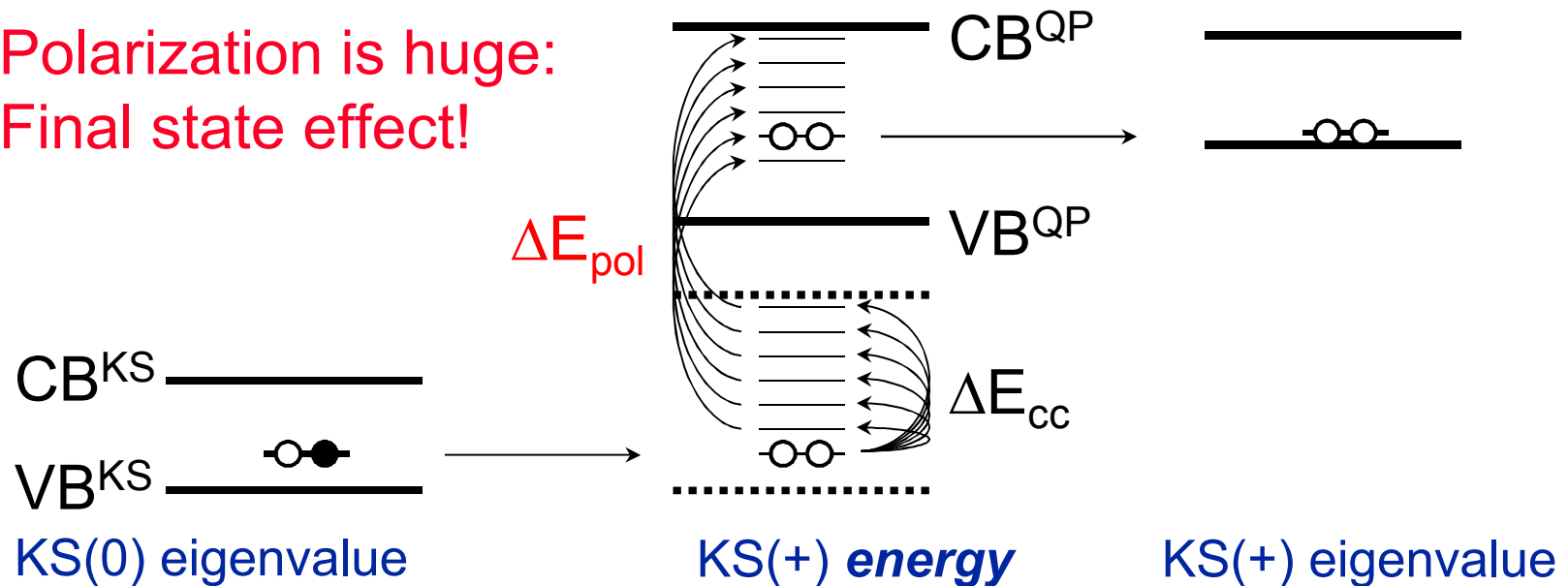
Central cell electronic relaxation (quantum):  $\Delta E_{cc}$

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.**”

# How is a good defect band gap possible?

Polarization is huge:  
Final state effect!



Central cell relaxation (quantum):  $\Delta E_{cc}$

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

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- **Total energy** DFT defect levels not constrained by KS band gap problem
- Semilocal DFT+FDSM - quantitative ( $\sim 0.1$  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)

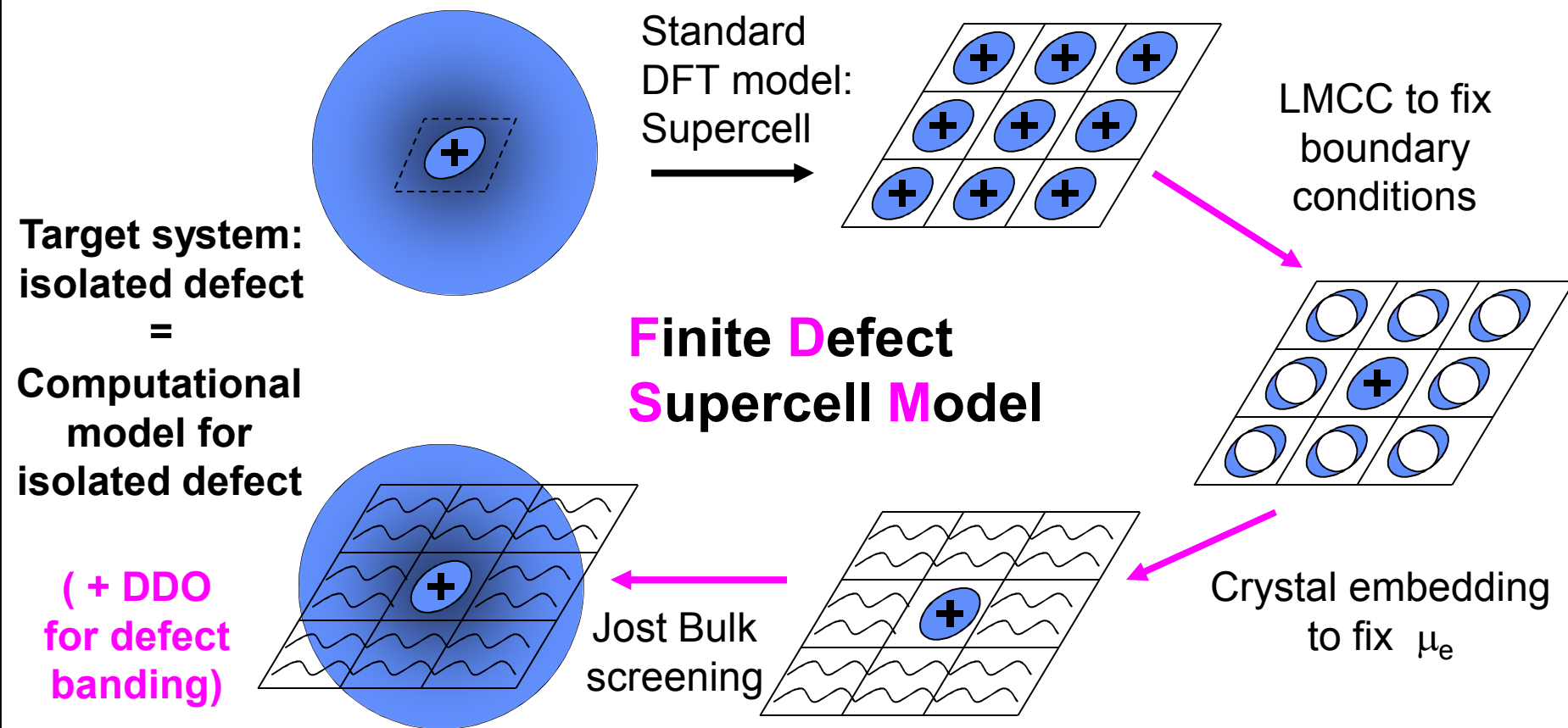
Quest DFT code information: <http://dft.sandia.gov/Quest>  
[paschul@sandia.gov](mailto:paschul@sandia.gov) <http://www.cs.sandia.gov/~paschul>

# ----- Supporting slides -----

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# A supercell theory of defect energies

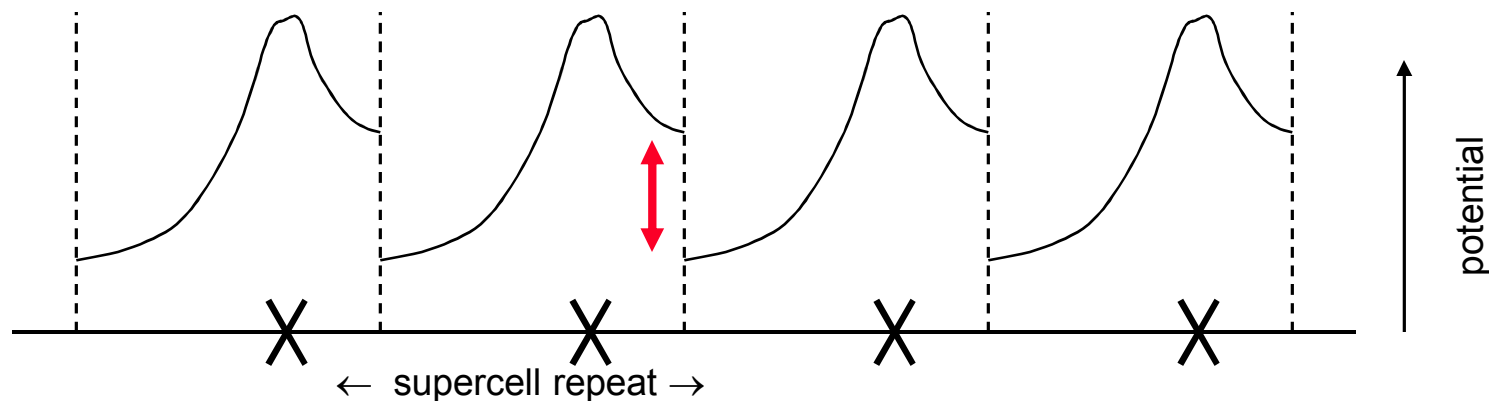
Peter A. Schultz, Phys. Rev. Lett. **96**, 246401 (2006).



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

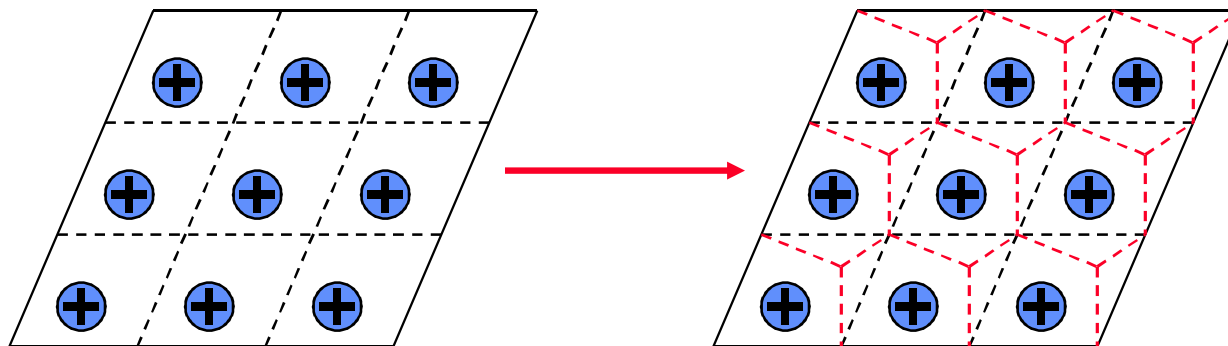
# LMCC potential in bulk systems

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 $\mu_e$

- Standard  $E_{\text{form}}$  of charged defects needs electron reservoir:

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

linked

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

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

$C_{\text{def}} = \text{fcn}\{\text{defect type, configuration, cell shape, cell size, ...}\}$

$E_{\text{defect}}(q)$  has  $qC_{\text{def}}$  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

---

## Finite Defect Supercell Model Formation Energy

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

$E_{\text{defect}}(q)$ : DFT energy with LMCC potential

-  $E_{\text{xtal}}(0) - \sum N_i \mu_i$  : match number of each type of atom

$E_{\mu 0}(q)$ : fix chemical potential  $\mu_e$  to common electron reservoir

$E_{\text{pol}}(q)$ : bulk polarization response

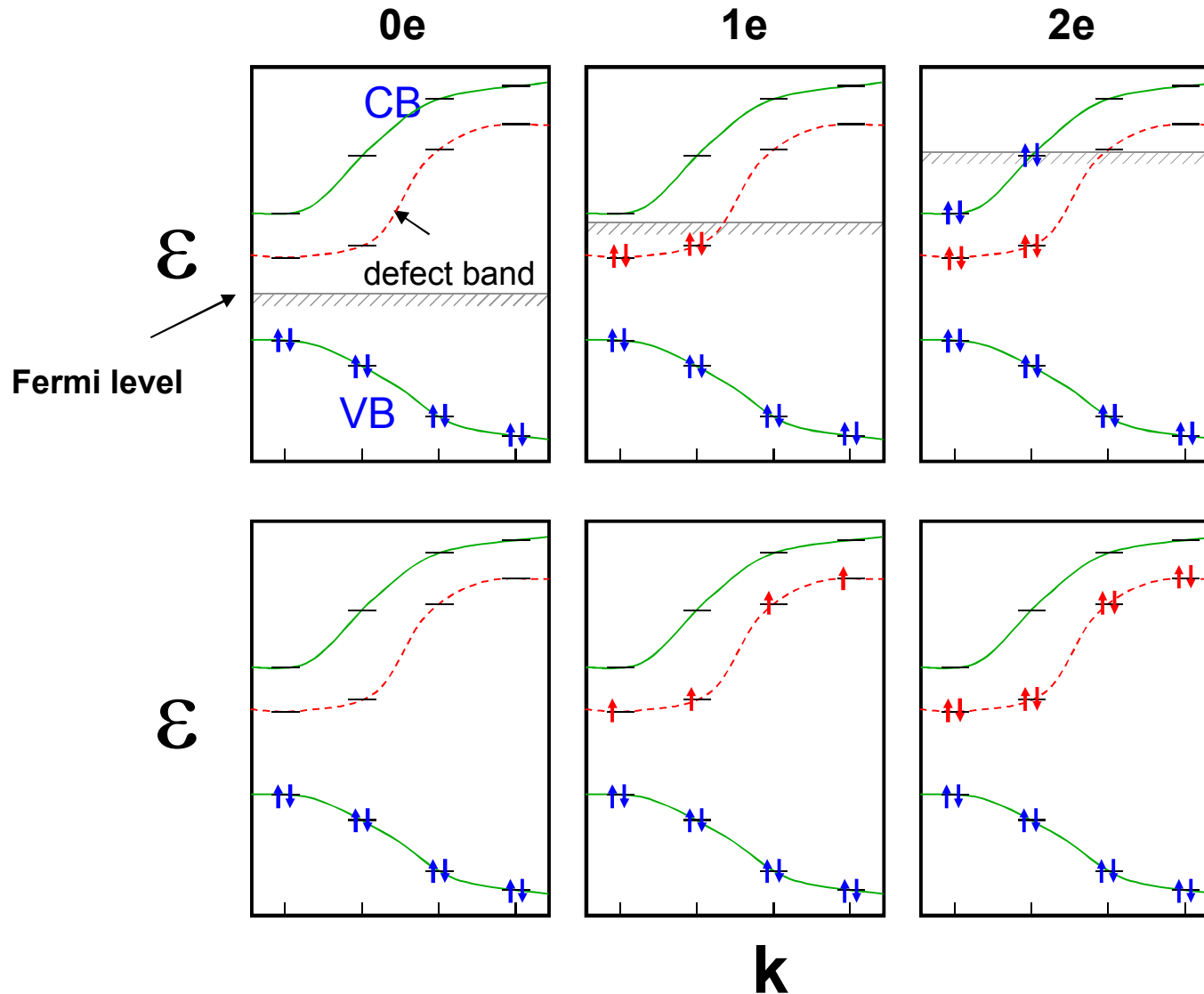
## Defect level calculation

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

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



**Standard methods:  
metallic,  
poor model  
of defect.**

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

# Charged cell convergence - Jellium

PHYSICAL REVIEW B

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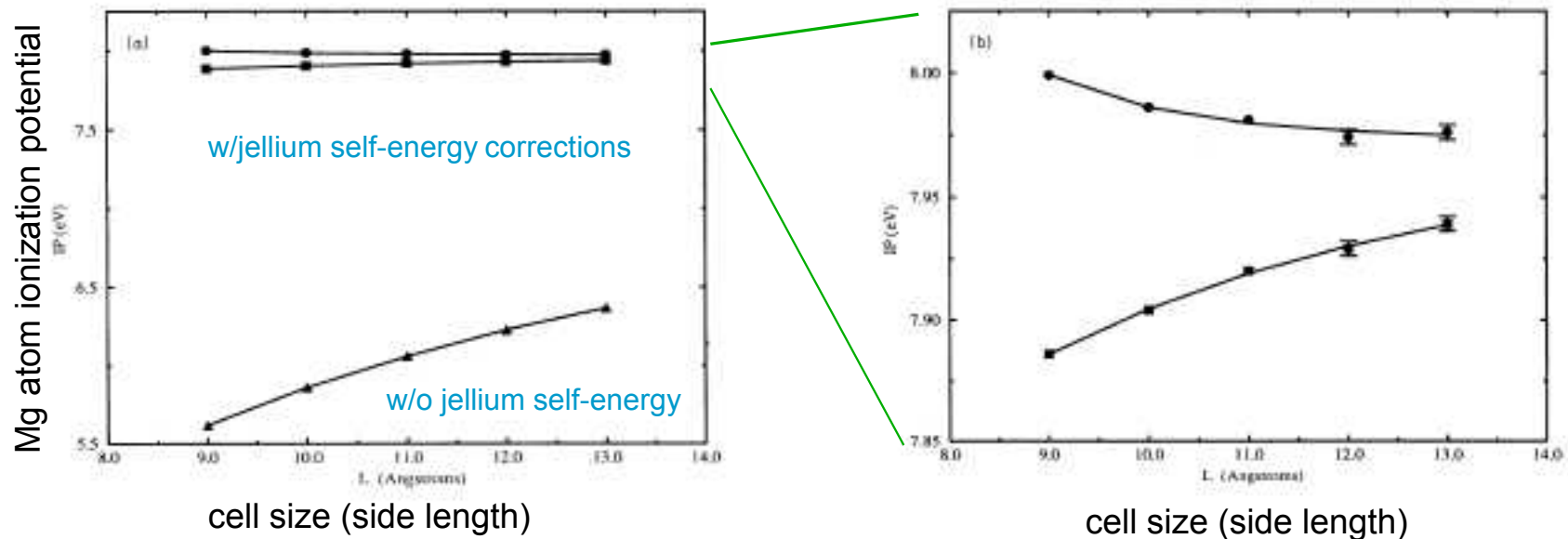
## Periodic boundary conditions in *ab initio* calculations

G. Makov and M. C. Payne

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom

(Received 19 July 1994)

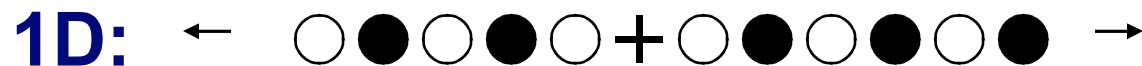
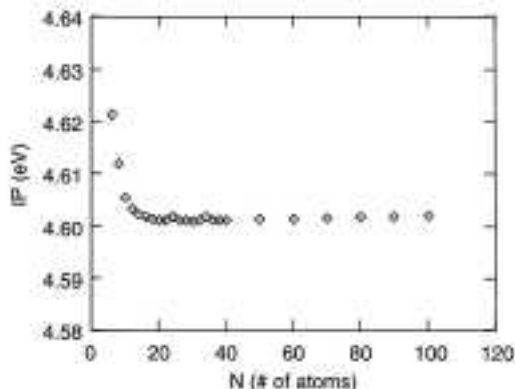
Figure 3



Variation in computed total energy due to incorrect charge potential

# LMCC: NaCl - Cl vacancy ionization

1D chain

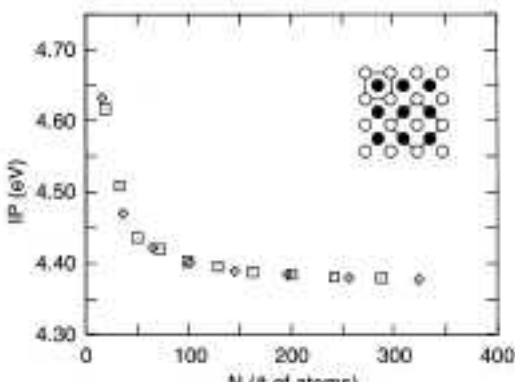


Supercell size dependence due to polarization.

Larger supercell  $\rightarrow$  more polarization

Apparent  $L^{-3}$  scaling = 1D classical dielectric screening

2D sheet

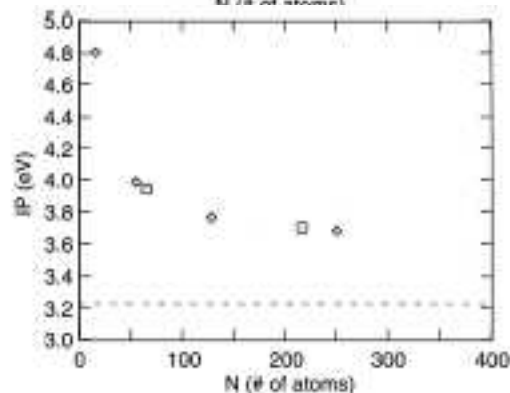


**2D:** single-layer 2D square sheet (polar&non-polar)

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

Insensitive to cell type, polar vs. non-polar

3D bulk



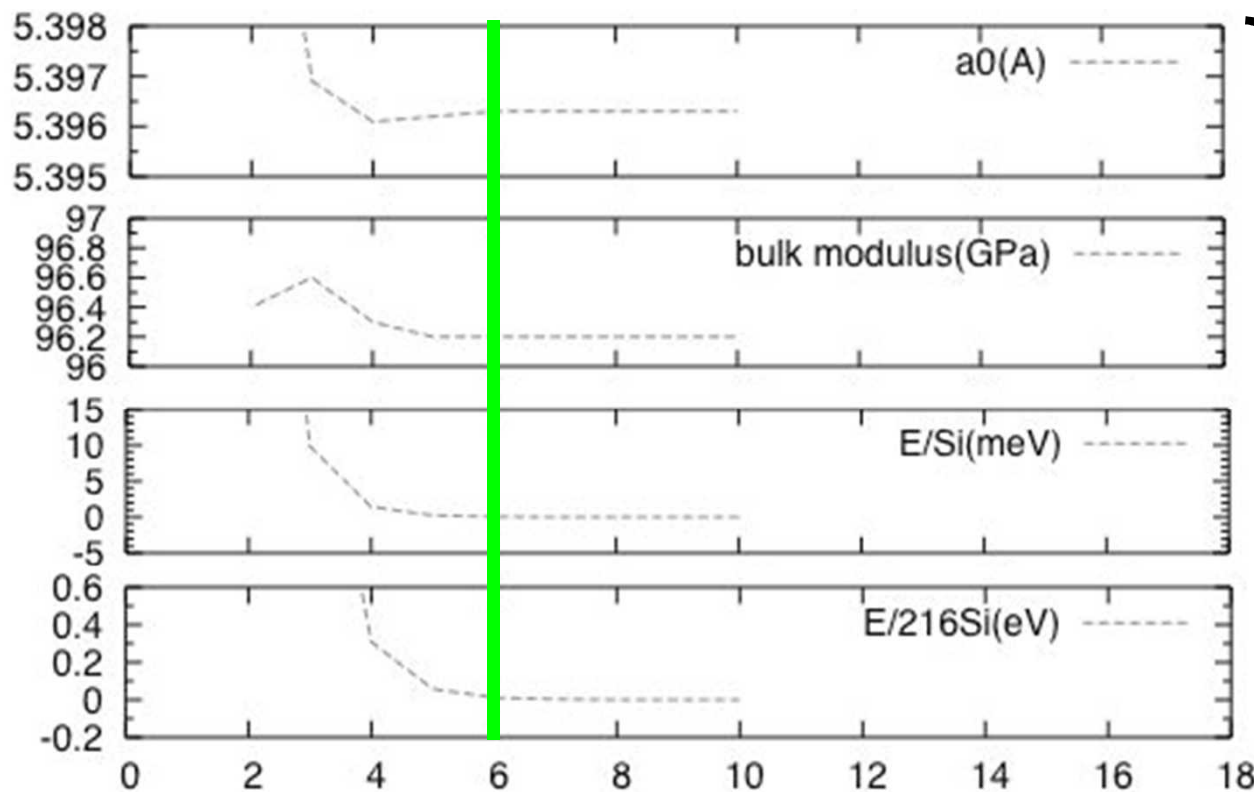
**3D:** bulk-layer 3D square sheet (fcc&sc cells)

Apparent  $L^{-1}$  scaling = 3D classical dielectric screening

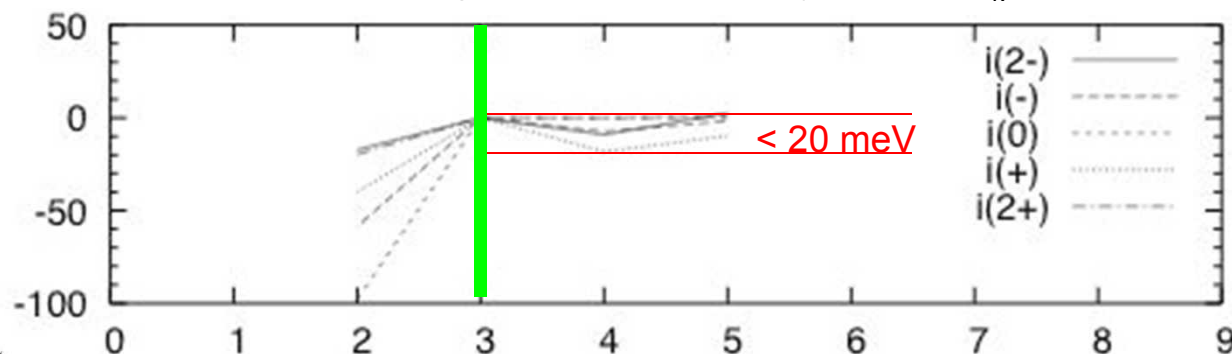
Strictly screening due to large supercell volume

Insensitive to cell shape

# BZ convergence: Si self-interstitial



K-point grid in 8-atom bulk crystal cell ( $N_k = K^3$ )



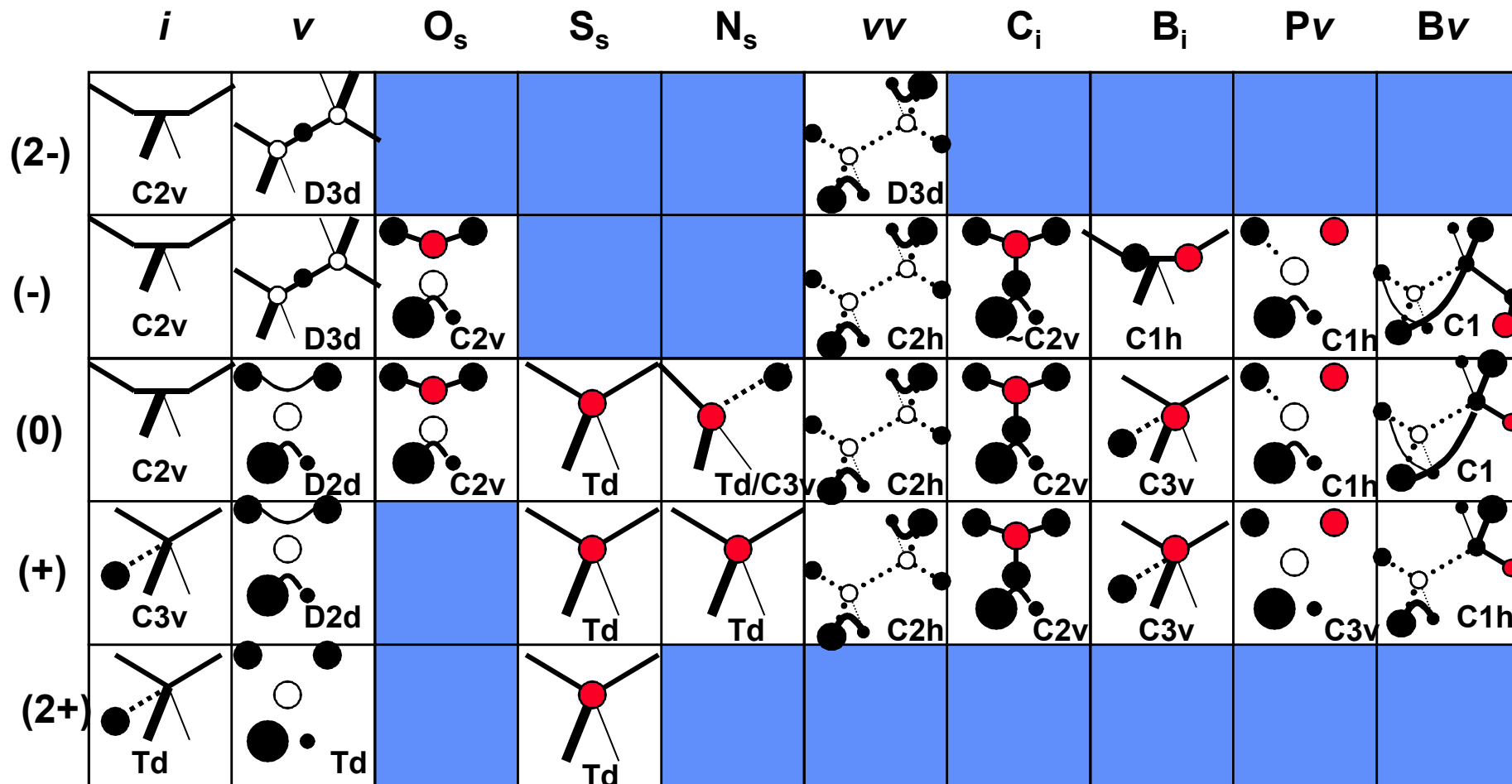
K-point grid in 64-atom defect cell ( $N_k = K^3$ )

Bulk properties  
( $a_0, B, E/\text{Si}, E_{\text{tot}}$ )  
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.

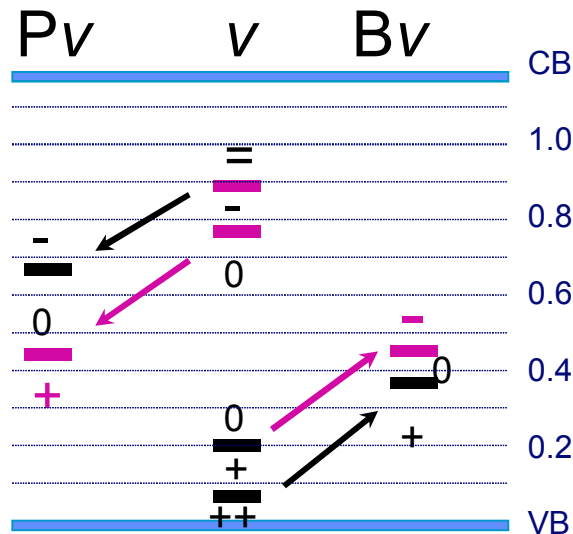
# Silicon defect structures



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

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

- Silicon level calculations - over 15 defects with levels  
 $i(= / - / 0 / + / ++)$ ,  $v(= / - / 0 / + / ++)$ ,  $vv(= / - / 0 / +)$ ,  $C_i(- / 0 / +)$ ,  $B_i(- / 0 / +)$ , **Pv**, **Bv**  
 $O_s$ (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

Pv(0/+) subsequently confirmed in experiment

[Larsen, et al PRL 97, 106402 (2006)]

**VALIDATION is key to quantitative DISCOVERY - GaAs is ALL discovery**



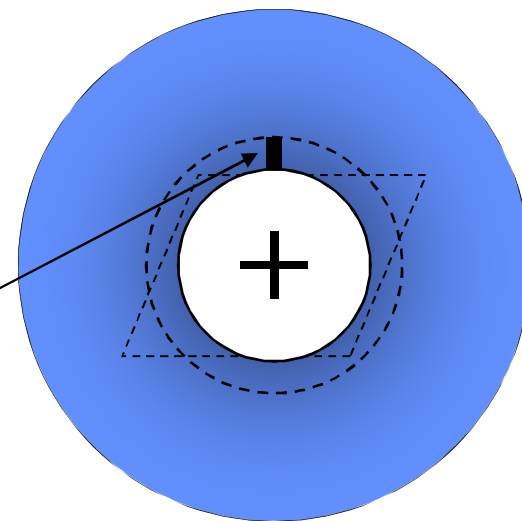
# Calibrating the polarization model: $v_{Ga}$

Jost model:

$$E_{pol} = \frac{(1 - 1/\epsilon_0) q^2}{R_j}$$

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

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



Need  $\epsilon_0$  (use 13), and  $R_{skin}$  (fit)

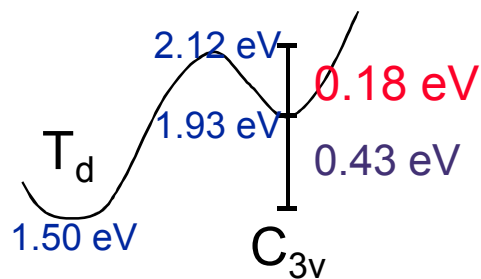
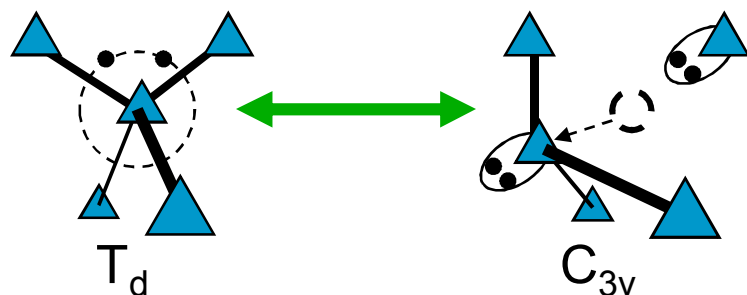
Why use  $v_{Ga}$ ?

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

EL2 = antisite  $\text{As}_{\text{Ga}}(0)$



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

EL2(0/1+)

EL2(1+/2+)

Splitting:

EL2\*

Reorientation:

## Experiment -EL2

$E_c$  -0.74 eV

$E_v$  +0.54 eV

**0.24 eV** ( $E_g=1.52$ )

no donor states

~0.3 eV

## SeqQuest/FDSM - $\text{As}_{\text{Ga}}$

$E_c$  -0.81 eV

$E_v$  +0.48 eV

**0.25 eV**

no donor states

~0.2 eV

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

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