From density functional theory to defect levels in silicon: Does the “band gap problem” matter?

Peter A. Schultz

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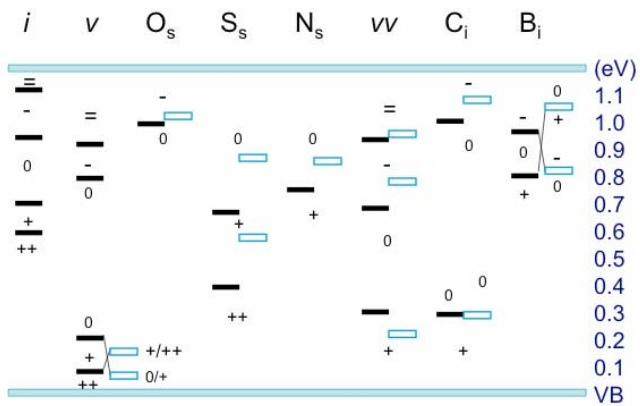
$$H\Psi = E\,\Psi$$



It is the mark of an educated mind to rest satisfied with the degree of precision which the nature of the subject admits and not to seek exactness where only an approximation is possible.

- Aristotle

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Purdue University, Thursday, August 21, 2008

SAND2008-5669P

Motivation:
Electrical effects of radiation damage

Issue: radiation effects (n,e,γ,ions) on electronics

- satellites
- weapon electronics

Historical approach: radiation testing

Radiation testing $\xleftrightarrow[\text{n,e,}\gamma\text{,ions}]{}$ **Systems response**

Renewed interest:

- long-term aging: enhanced low dose rate sensitivities
  long-term (decades) radiation damage is different
- fast transients: SPR facility decommission
  fast burst neutron test facility going away

Radiation damage: from atoms to devices

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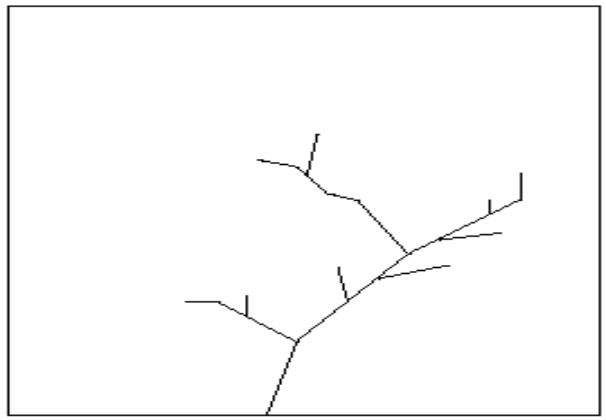
Initial defect distribution



Radiation creates displacement damage:

$$R \rightarrow V + I$$

and charge carriers (electrons and holes)

$$R \rightarrow n + p$$

Defect evolution

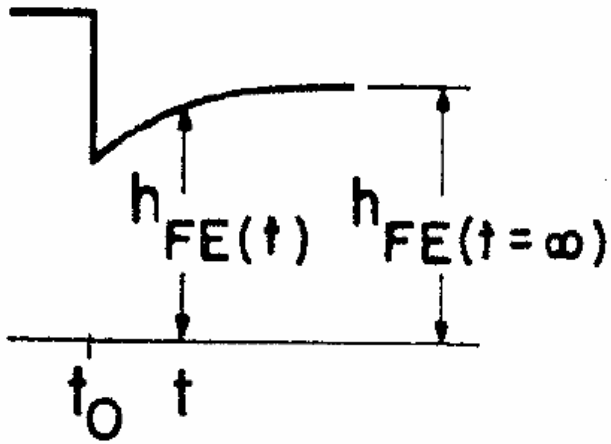
Defects react with each other, and with other dopants and impurities:

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

Defects recombine electrons and holes, modifying currents:

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

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



Radiation damage creates an evolving chemistry of defects. Those defects modify the performance of electronic devices.

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Multiscale ladder for radiation damage

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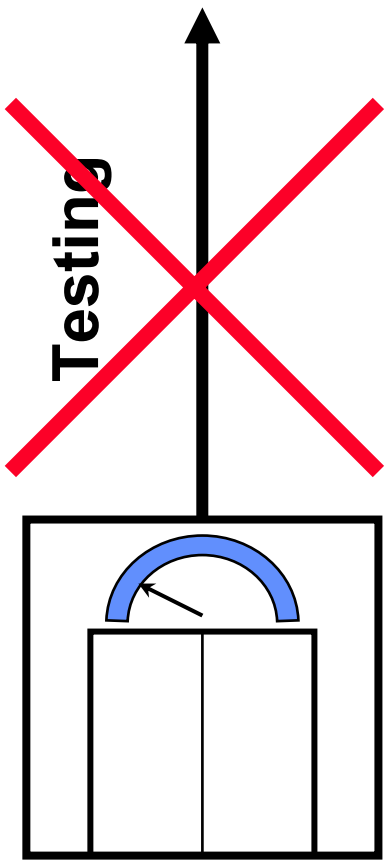
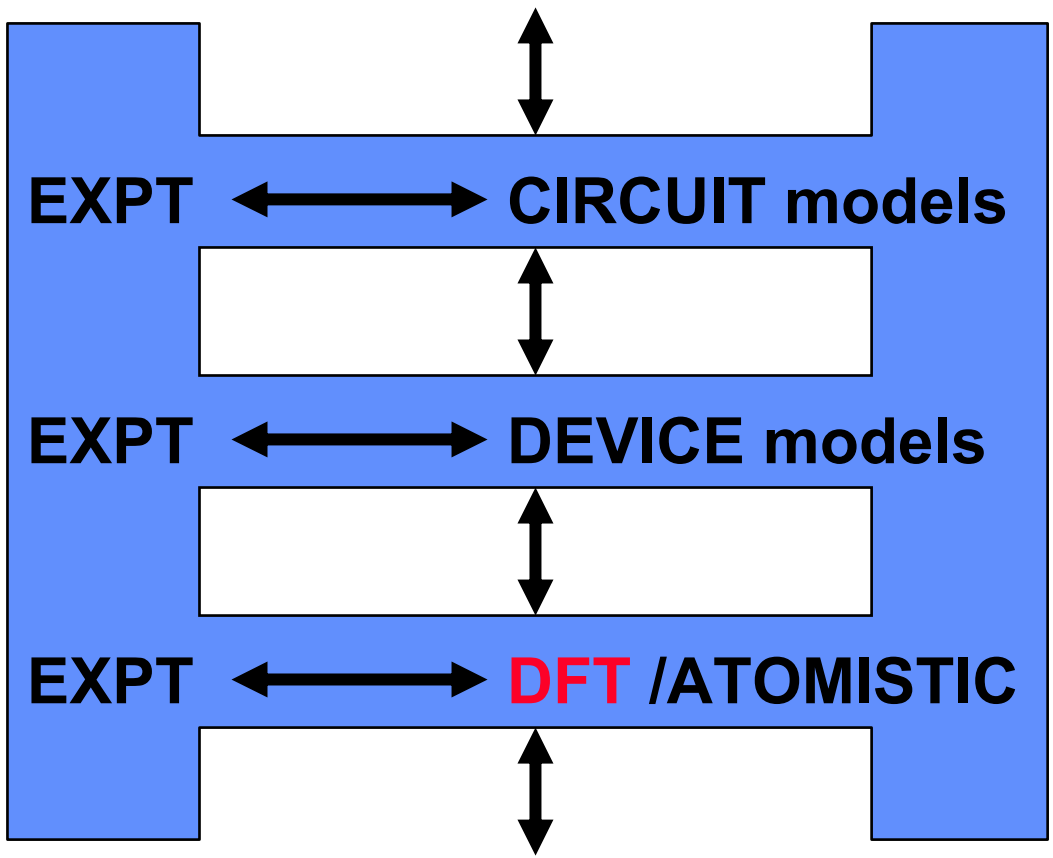
Electrical system response





Radiation damage

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The radiation defect universe

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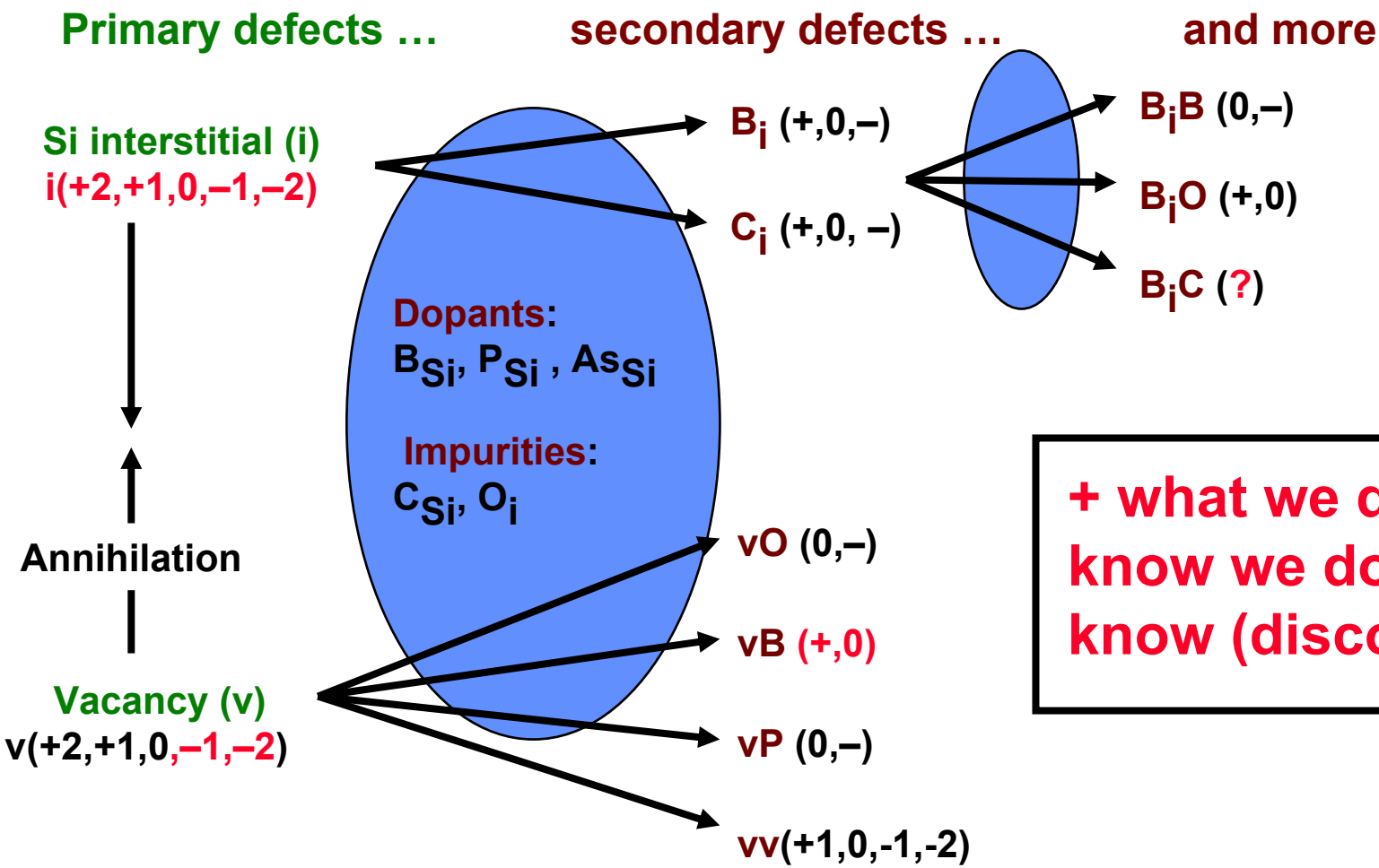

+ what we don't know we don't know (discovery)

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

What do we know, what do we need?

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•Experimental record incomplete and messy

- defect level measurements typical Uncertainty(U): ≥ kT ~ 0.03 eV
  e.g.: S(2+/+): optical CB -0.61, thermal: -0.55:-0.59
  vv(0/+): VB+0.20:+0.26, *vv*(-/0): CB-0.39:-0.44
- often larger: B_i(-/0): U=0.08, N_s(0/+): U=0.12, B*v*: a mess (U~0.10)
- U(expt) = 0.03 eV (best), ~0.1 eV (otherwise)
- incomplete knowledge (Bv, Pv, B_iX, …) … U=∞

•Density functional theory: *unproven* for levels

- DFT structural energetics accurate to no better than ~0.1-0.2 eV
- best accuracy to hope for with DFT: ~0.1-0.2 eV

•Accuracy requirement: kT=0.03 eV?, 0.1-0.2 eV?

- if 0.03 eV, then even experiment is not good enough - we're doomed
- current device (CHARON, REOS, 1D) simulations using 0.1 eV data
- apparent target requirement: 0.1 eV (device sims, and expt. record)

Radiation damage and defects

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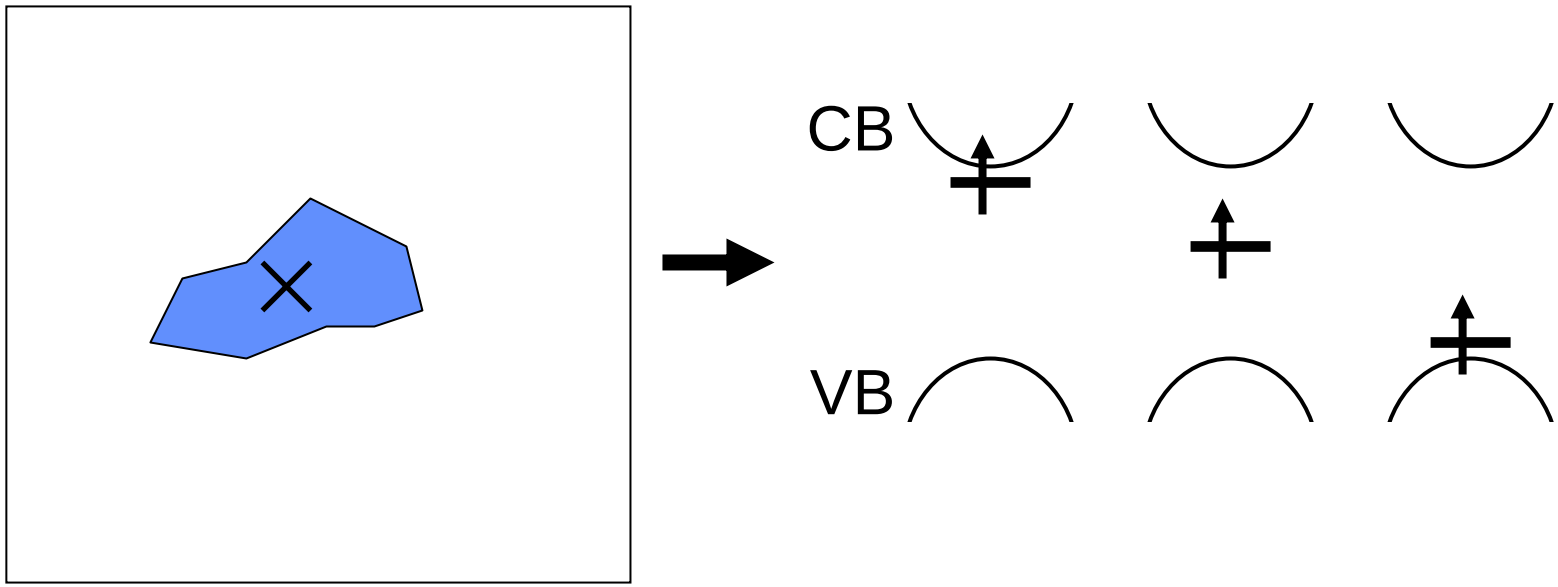
Radiation damage …



produces defects … and introduces electronic transitions

… and we would like to quantify these transitions

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The DFT band gap problem

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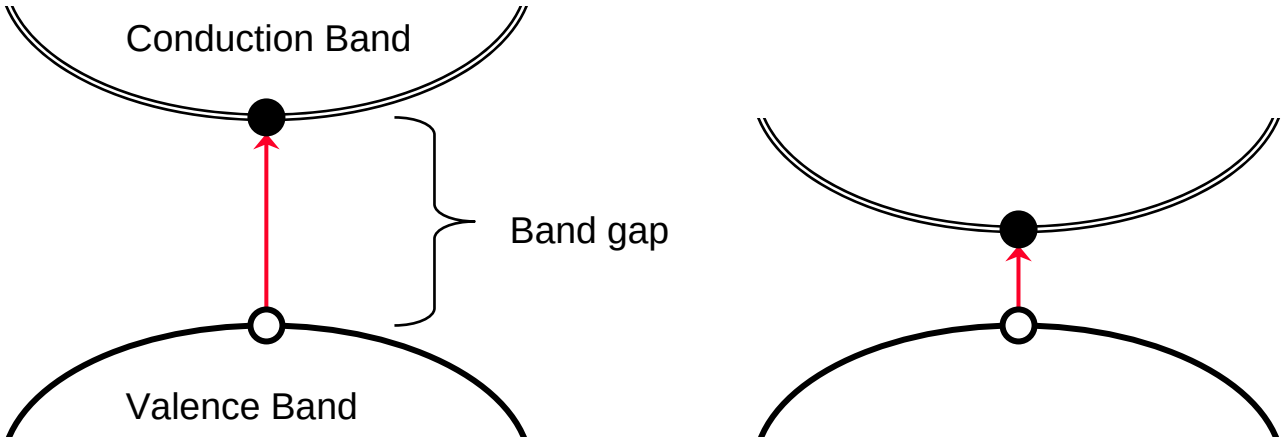

Experiment Kohn-Sham DFT eigenvalue spectrum

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

The band gap defines the energy scale for defect levels

Fundamental impediment to quantitative predictions?

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The Supercell Approximation

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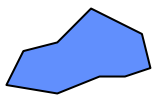
Fast Fourier Transforms are convenient means to solve 3D Poisson Equation.

DFT codes typically assume periodic boundary conditions.

However, our finite defect is not periodic …



Finite defect

The Supercell Approximation

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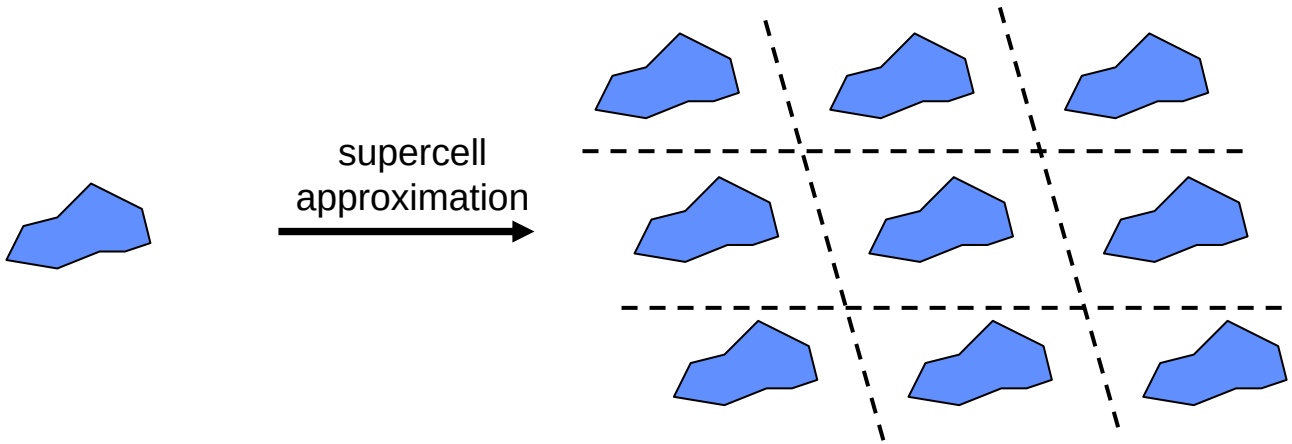

Finite defect

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.

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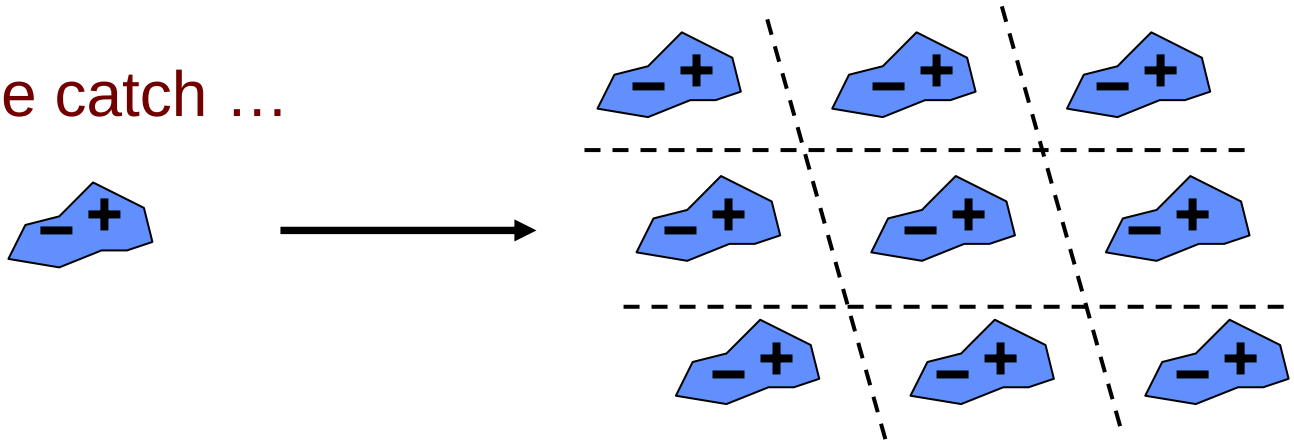
The Supercell Approximation

the catch …



DFT expense limits size of supercell - defects interact

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The Supercell Approximation

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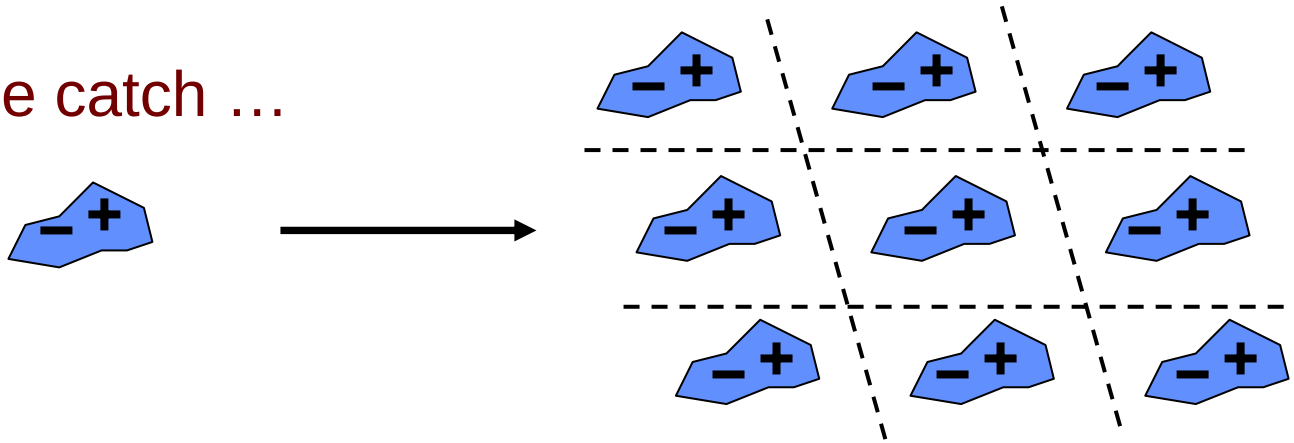
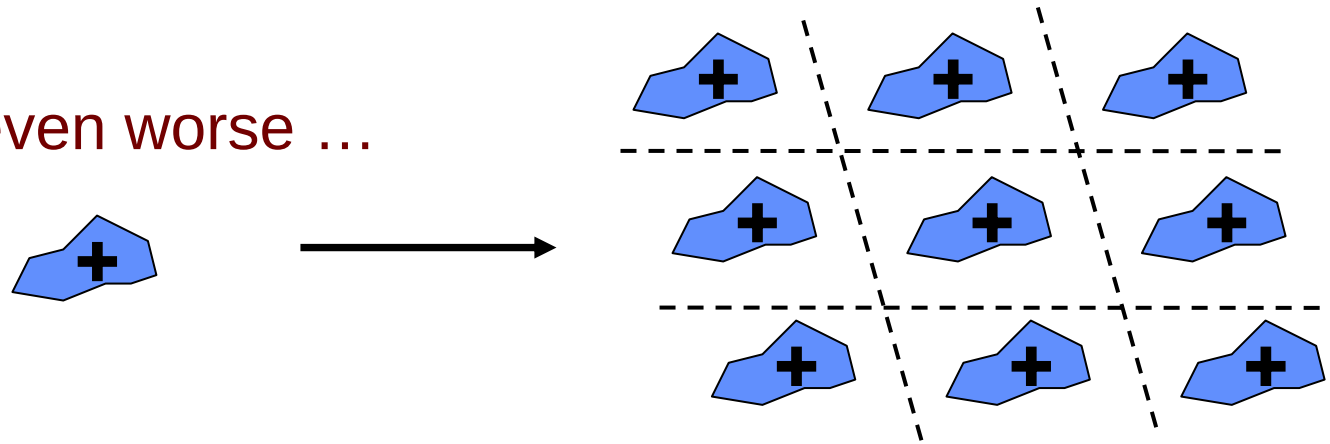
the catch …



Finite defect with dipole

Periodic (interacting) defects

even worse …



Finite charged defect

Ill-defined (Coulomb divergence)

Interactions and divergence are key issues

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Supercell issues

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- **Boundary conditions - how to handle net charge**

- need to eliminate divergence
- need to install correct long range q/r -> 0 behavior of defect charge

- **Chemical potential for electrons**

- want transition energies, (0/-), (0/+), need to fix an electron reservoir

- **Finite size effects - Bulk polarization to local charge**

- supercell has small finite volume, missing bulk dielectric response

- **Finite size effects - Defect level dispersion**

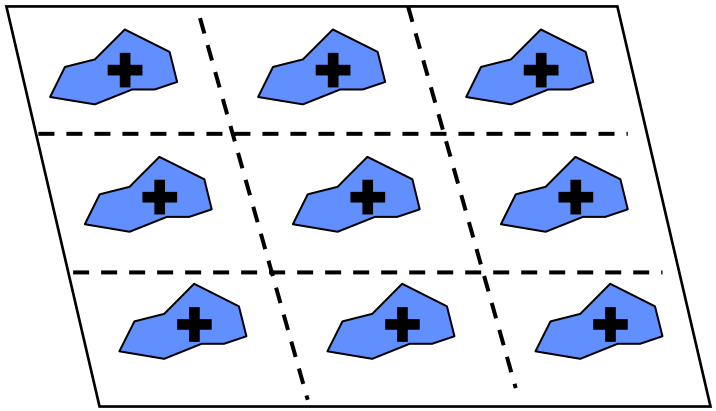
- defects interact, discrete defect states become bands, overlap CB/VB

And if you get this all right … is DFT good enough?
- e.g., is the band gap problem fatal?

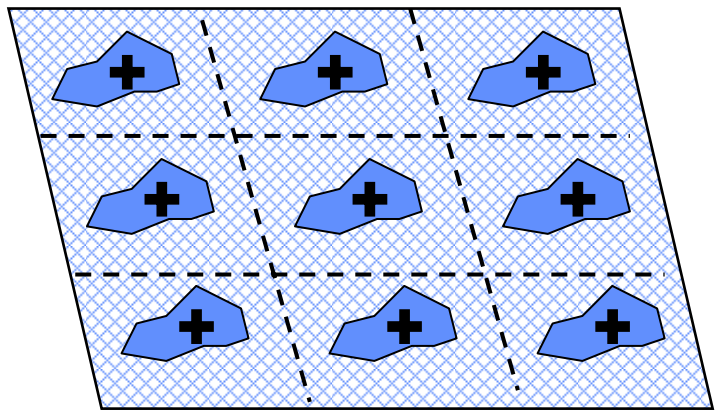
Jellium to eliminate divergence?

Isolated defect …

Apply supercell …



Neutralize with flat background charge: "jellium"



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Whence the divergence?

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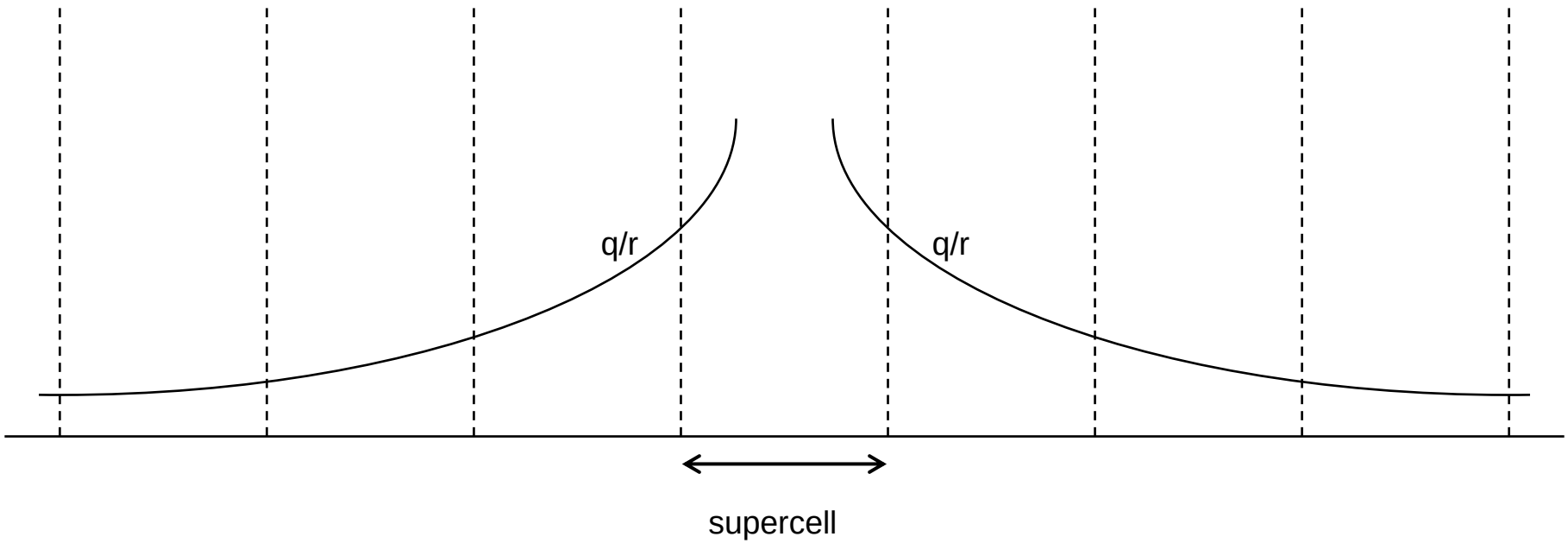

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Whence the divergence?

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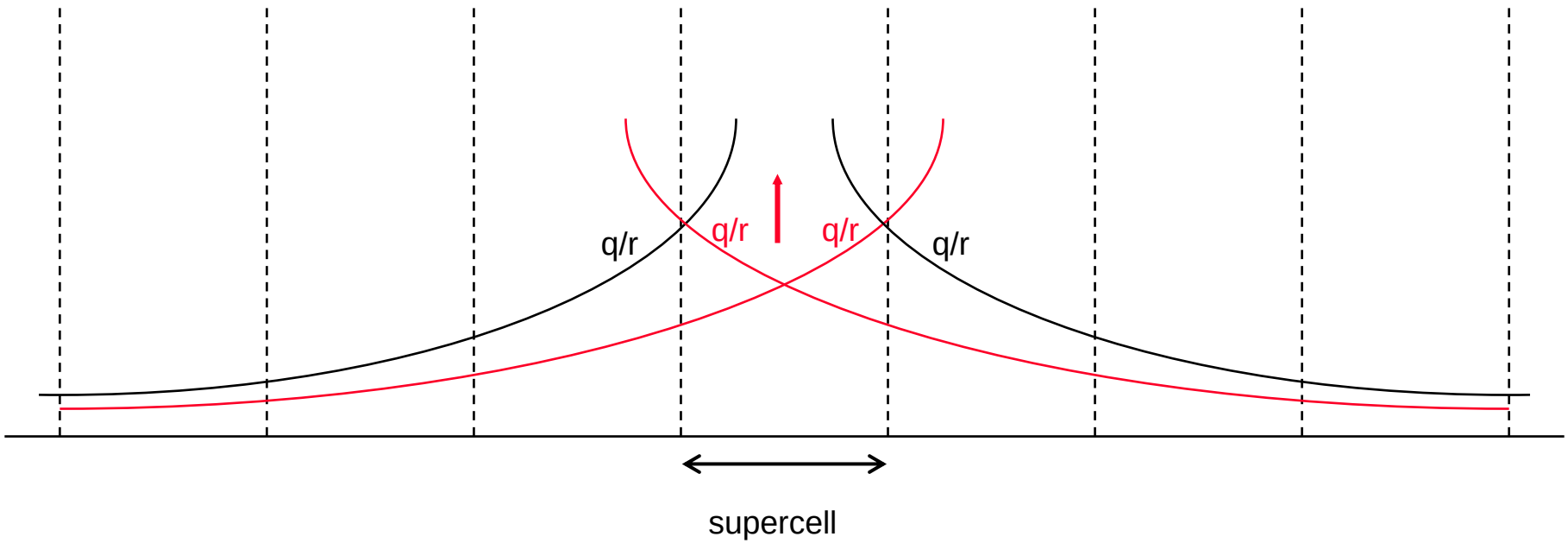

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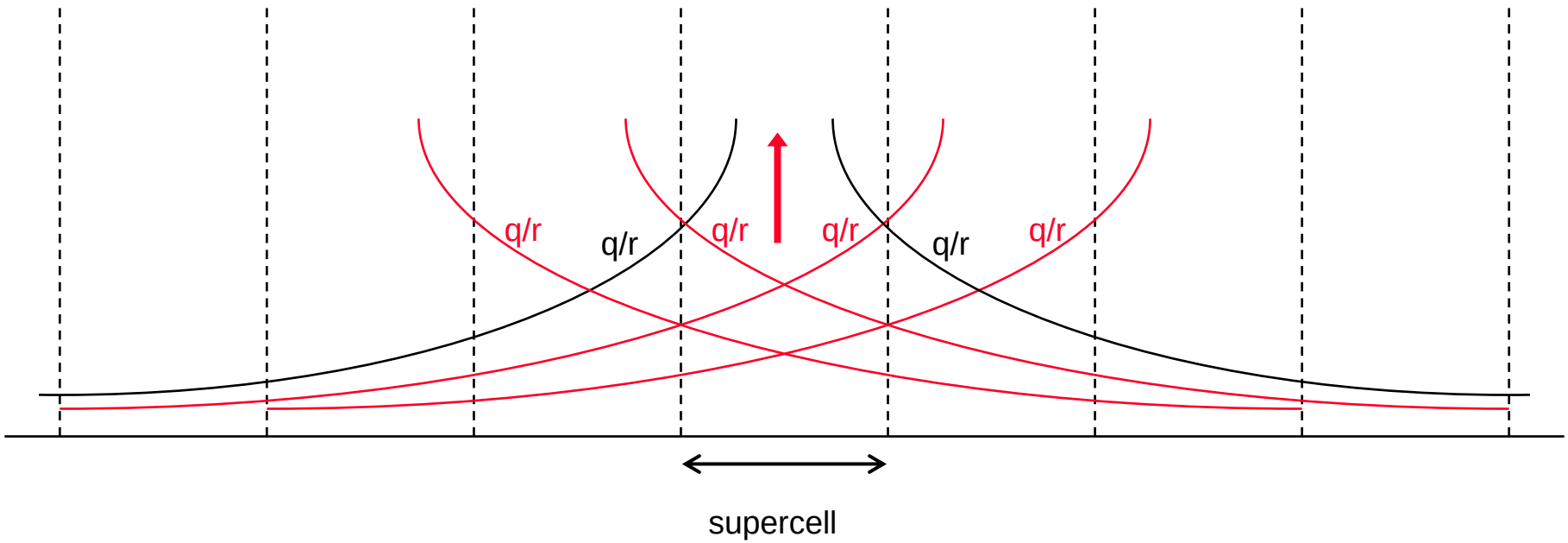

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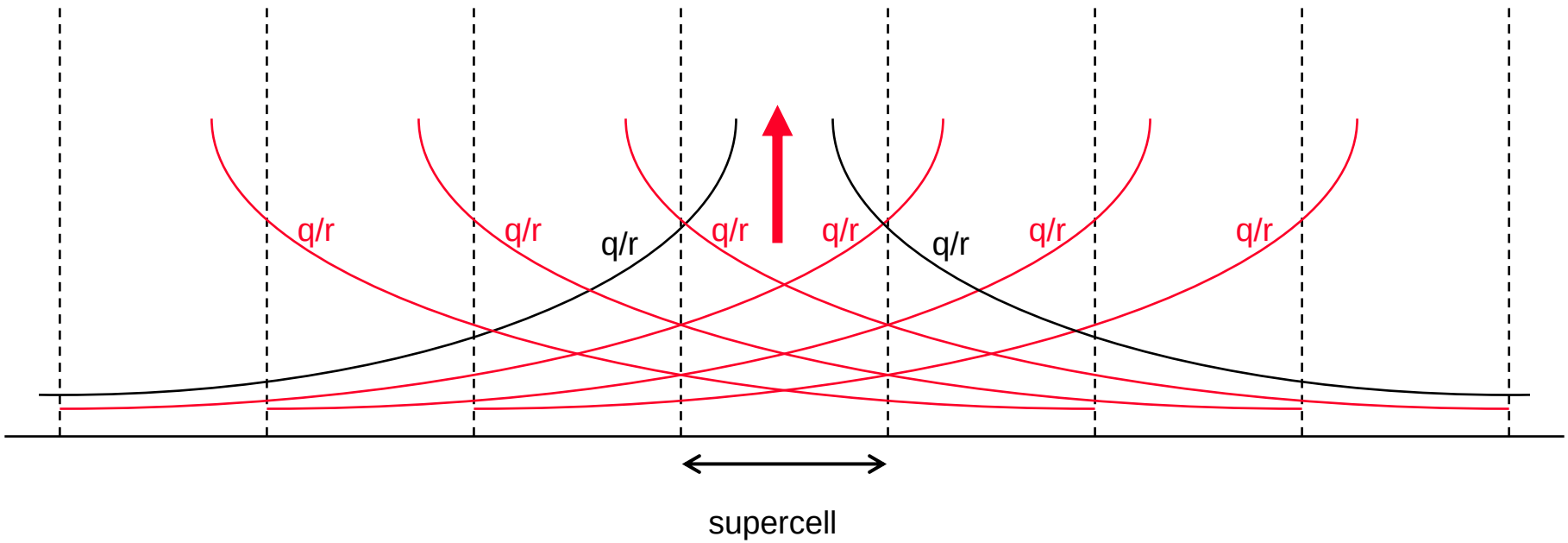

Whence the divergence?

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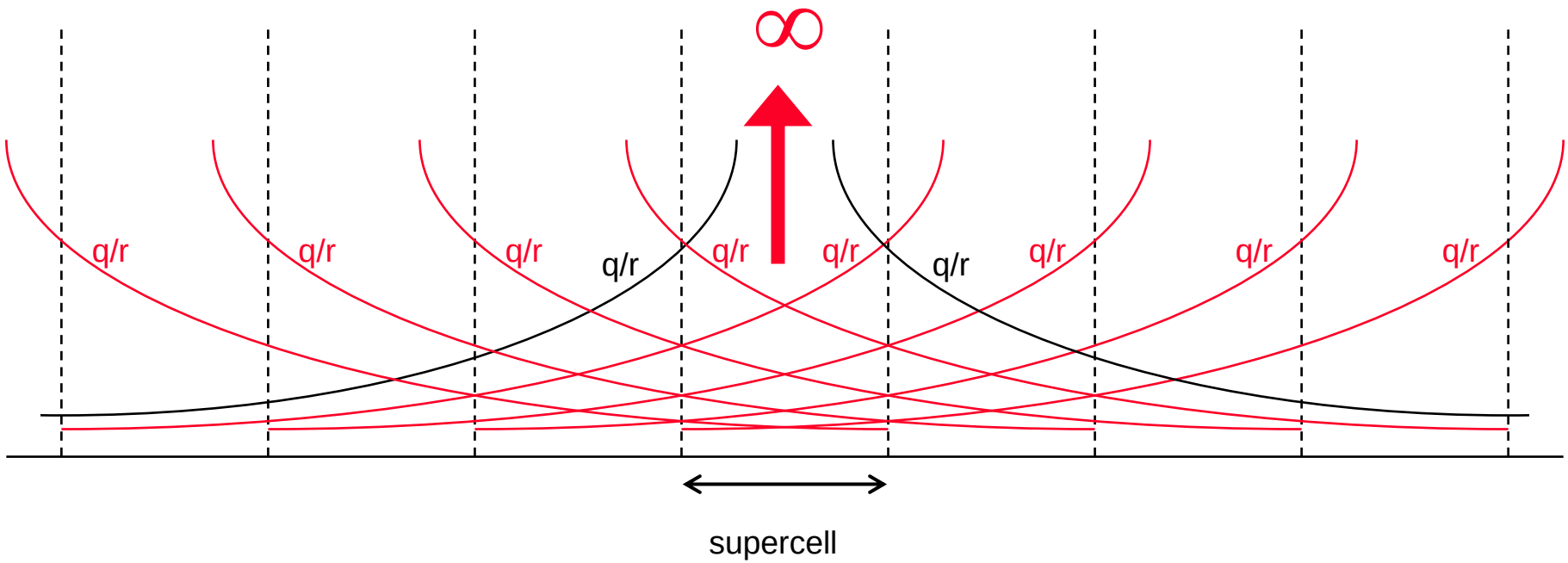

Divergence arises from infinite-ranged q/r potentials from periodic images

Divergence is not flat

Net charge boundary conditions - jellium

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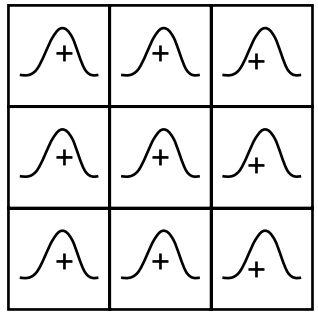
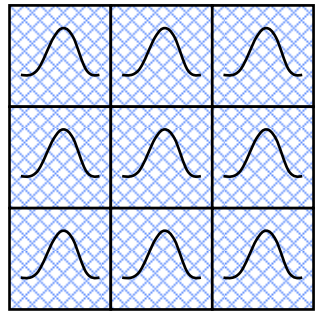
Take isolated charge density…

create cubic supercell …

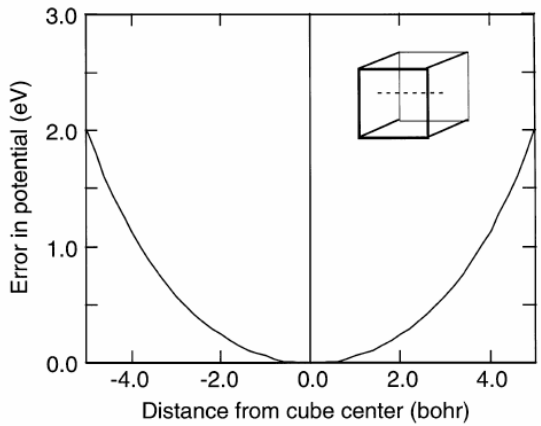


neutralize with "jellium"



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(au)	Cell size (Si)	Median Error(eV)
10.2	8	2.0 eV
20.4	64	1.0 eV
30.6	216	0.67 eV
40.8	512	0.50 eV
51.0	1000	0.40 eV

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

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

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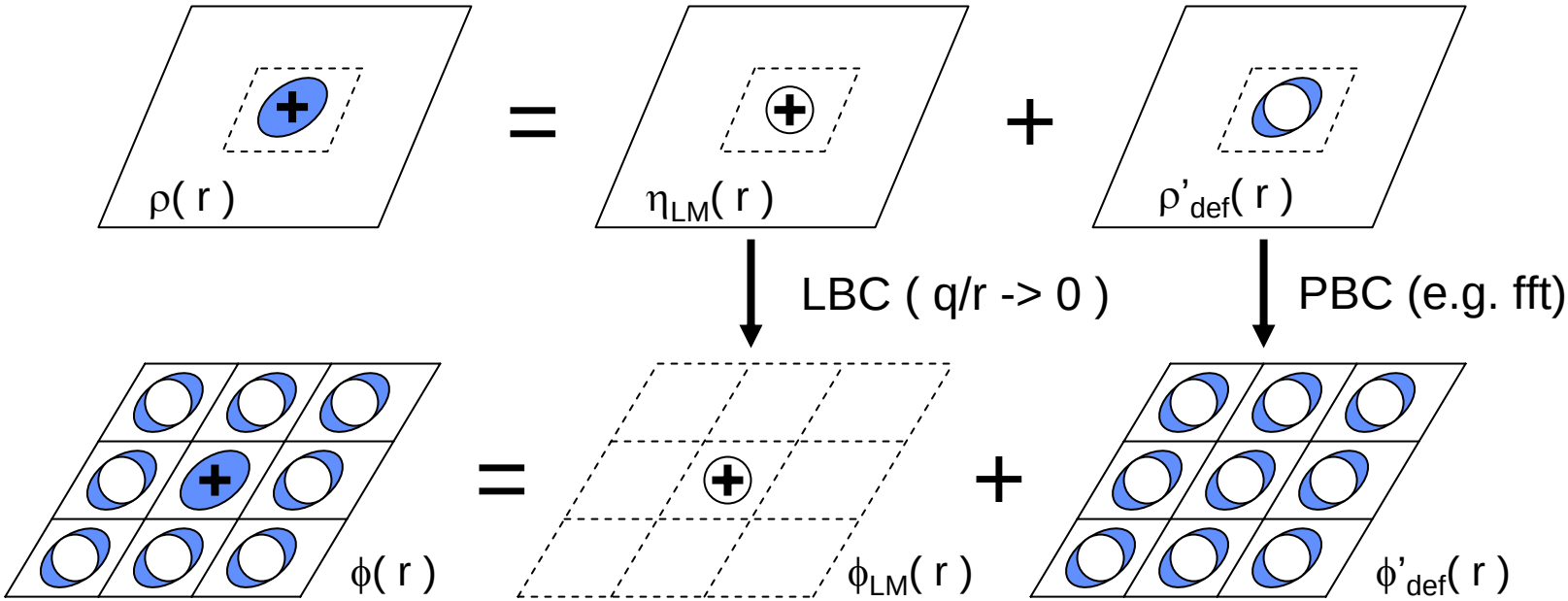
Local Moment CounterCharge (LMCC)

[P.A. Schultz, PRB **60**, 1551 (1999); PRL **84**, 1942 (2000)]

- 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 $r \to \infty$ asymptotic boundary condition
Avoids (not ignores!) Coulomb divergence

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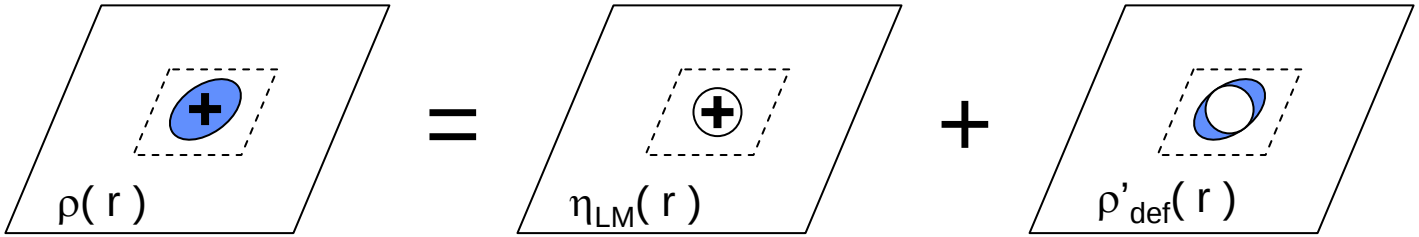
A practical method for LMCC



Requirements:

(a) $\eta_{LM}(r)$ contains the local moments(charge) to be solved
(b) $\eta_{LM}(r)$ is spatially slowly varying — fft-able
(c) $\eta_{LM}(r)$ is entirely localized within cell — define vacuum
(d) potential $\phi(r)$ associated with $\eta_{LM}(r)$ is easily evaluated

Usual suspects:

- point charges violate (b)
- Jellium (flat background) violates (a), (c), and (d)

One (not unique) solution: sum of Gaussians: $\eta_g(r) = \exp(- \alpha r^2)$

$\eta_{LM}(r) = \Sigma\, c_g\, \eta_g(r - R_g)$

For charged system: one gaussian
For dipole: pair of gaussians
Quadrupoles and above neglected (good to $O[L^{-5}]$)

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Charged cell convergence - Jellium method

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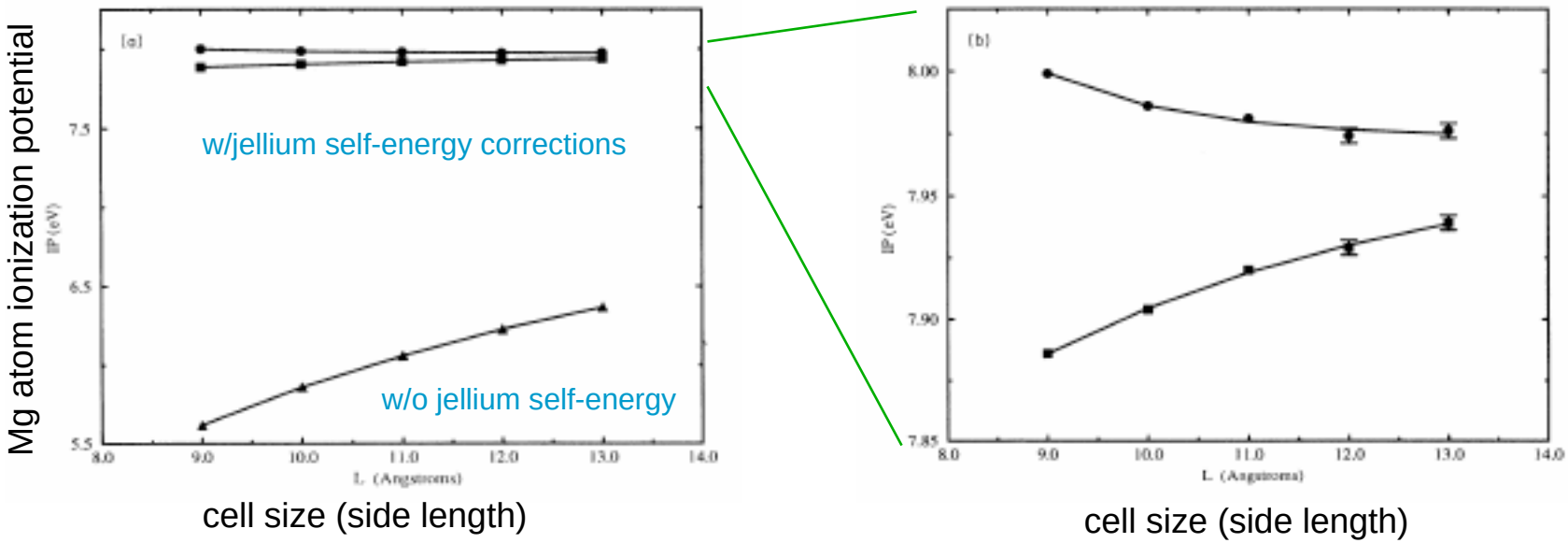
Periodic boundary conditions in *ab initio* calculations

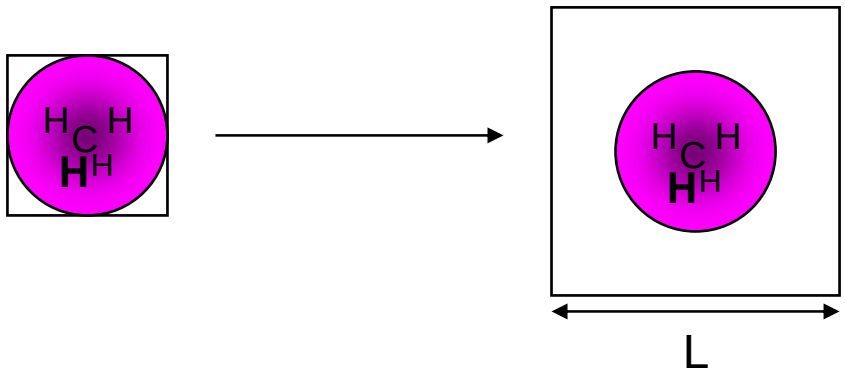
G. Makov and M. C. Payne
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom
(Received 19 July 1994)

Figure 3



Variation in computed total energy due to incorrect charge potential

Charged cell convergence - LMCC method



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: $OH \rightarrow OH[-]$ … 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
P.A. Schultz, PRB **60**, 1551 (1999)

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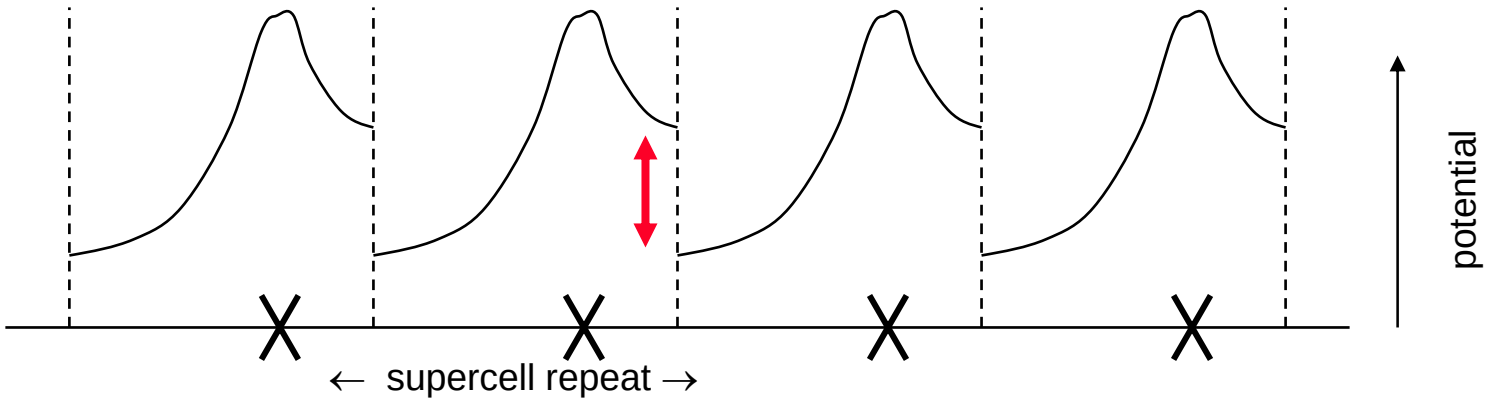
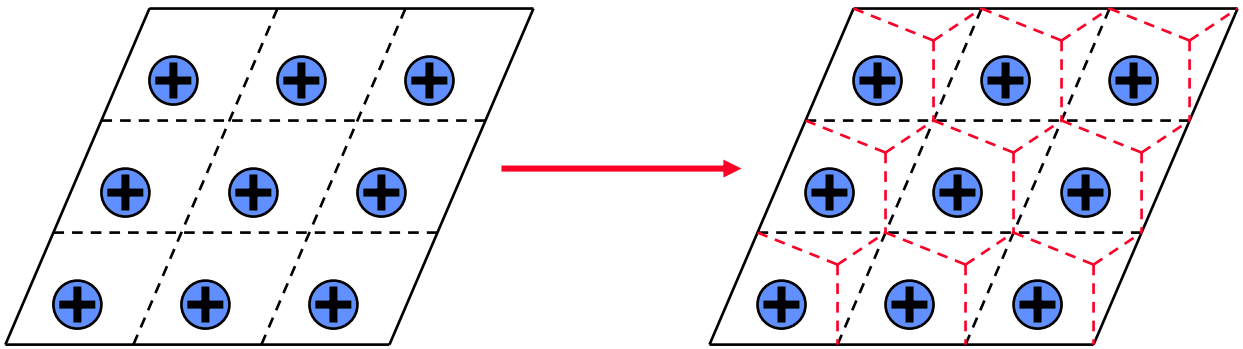
LMCC potential in bulk systems

What is the problem?



Discontinuity in potential from LMCC at supercell boundary!

The solution: Wigner-Seitz cells around LMCC positions



With WS local volume, LMCC potential is continuous

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LMCC: NaCl, Cl vacancy ionization

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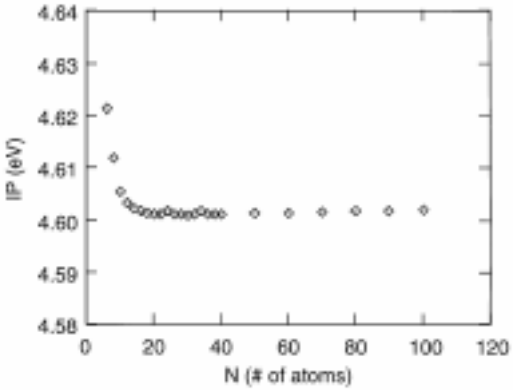
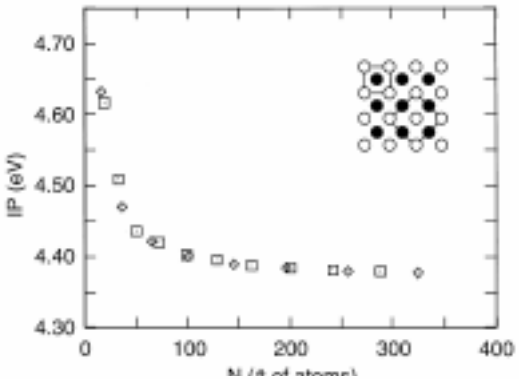
1D chain



1D: ← ○●○●○+○●○●○● →

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

2D sheet

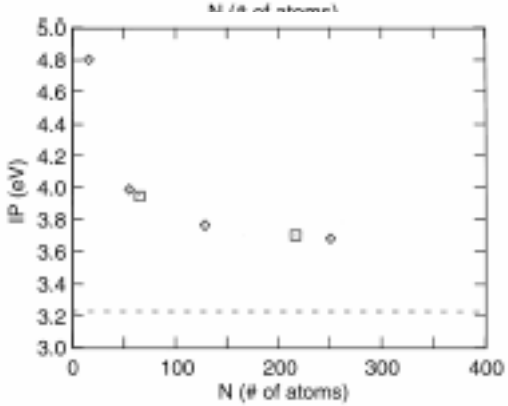


2D: single-layer 2D square sheet (polar&non-polar)

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

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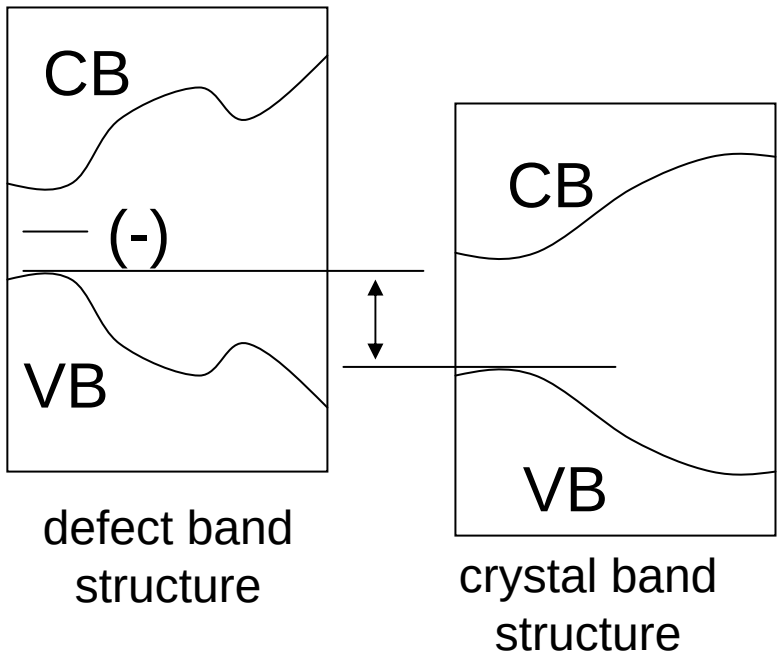
How do you set an energy zero for charge?

Kleinman [PRB **24**, 7412 (1981)]: cannot do it in bulk!

Garcia, Northrup, Van de Walle, others: empirical band alignment
- take band feature (e.g., VB, CB,) in defect calculation
and "align" with similar feature in bulk calculation



Problems with standard shifts:

1. Which feature? CB,VB top/bottom/c.m.?
2. Defect modifies bands - no clean state
3. Band gap problem: CB/VB dubious, too
4. Band bending by charge

-> unknown uncertainty

Empirically, standard scheme no better than "few tenths of eV"
Garcia,Northrup PRL **74**, 1131 (1995)

Peter A. Schultz

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**

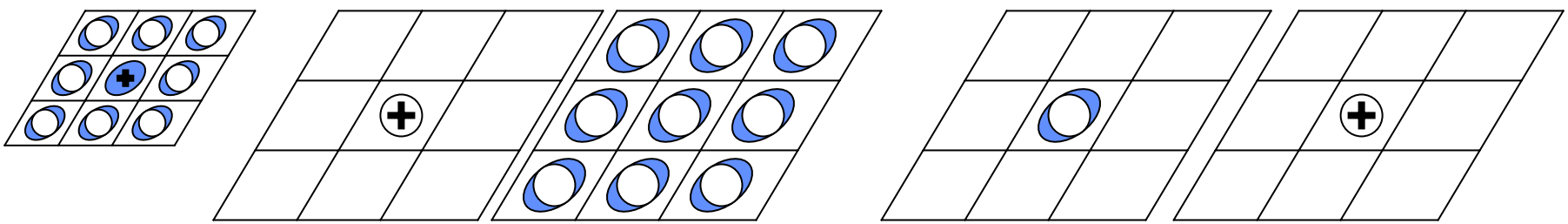
- matching VB,CB edge, band structure features, average potentials …
- Issue: renormalizing infinities, defect modified bands, band-bending, …
- calibration uncertainty of "few tenths of eV" (Garcia & Northrup) - best case

Needed a more rigorous scheme to fix electron reservoir

Chemical potential shift: Locating a fixed μ_e

Replace interaction of net charge with periodic defect potential …

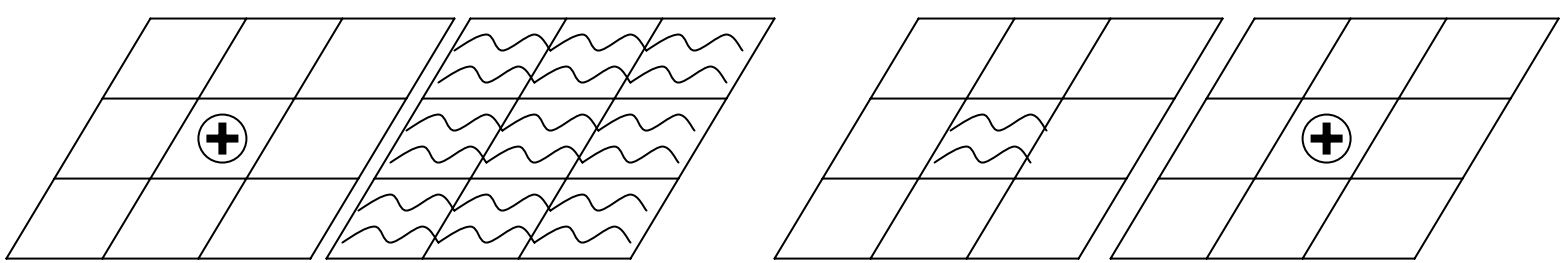
$$E_{\mu 0} = - \int dr \; \eta^{+}_{LM} \left(\phi'_{def} + C'_{def}\right) + \int_{UC} dr \; \phi^{+}_{LM} \; \rho'_{def}$$



$\eta^{+}_{LM}(r)$ $\phi'_{def}(r) + C'_{def}$ $\rho'_{def}(r)$ $\phi^{+}_{LM}(r)$ (C=0)

… with crystal:

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



$\eta^{+}_{LM}(r)$ $\phi_{xtal}(r) + C_{xtal}$ $\rho_{xtal}(r)$ $\phi^{+}_{LM}(r)$ (C=0)

Replace ***variable*** defect cell C'_{def}, with ***fixed*** crystal C_{xtal} reference
Not a rigid shift - a valid common electron reservoir for all defects

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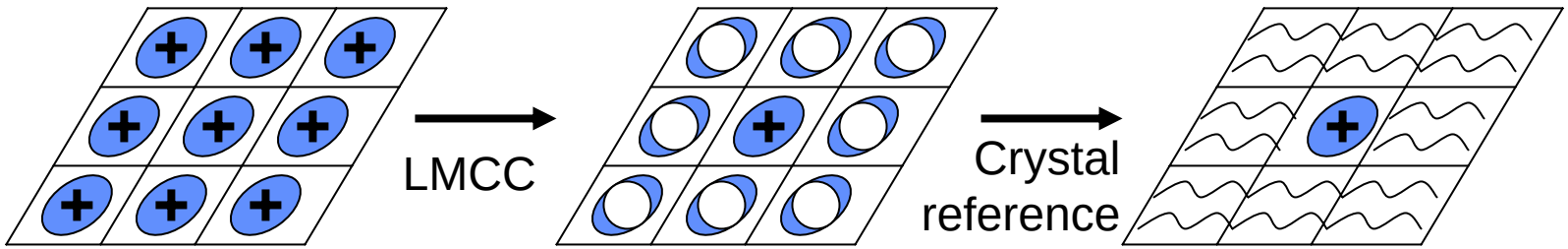
Bulk polarization in a dielectric medium



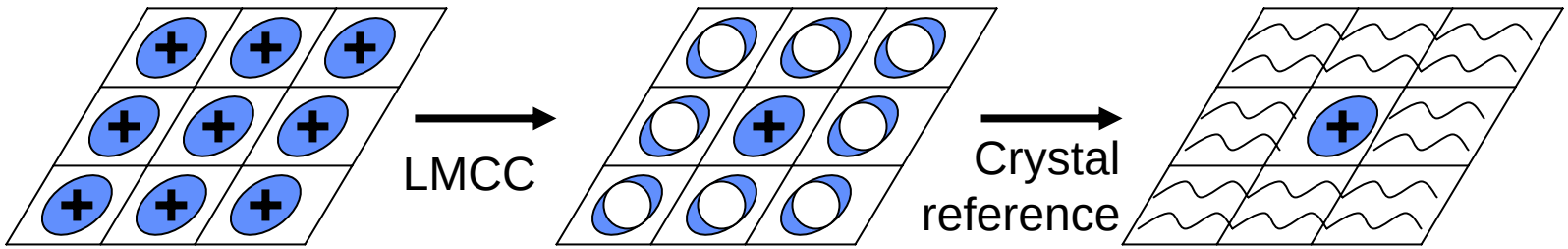
Ill-posed b.c.

Variable μ_e

Bulk polarization?

Peter A. Schultz

Bulk polarization in a dielectric medium

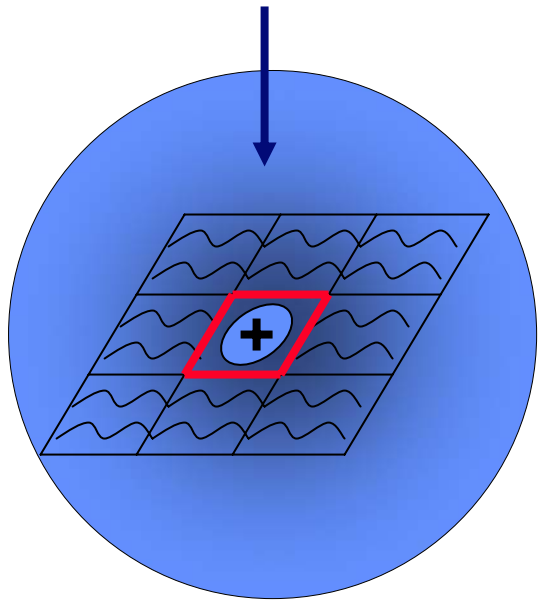


Ill-posed b.c.

Variable μ_e

Bulk polarization?

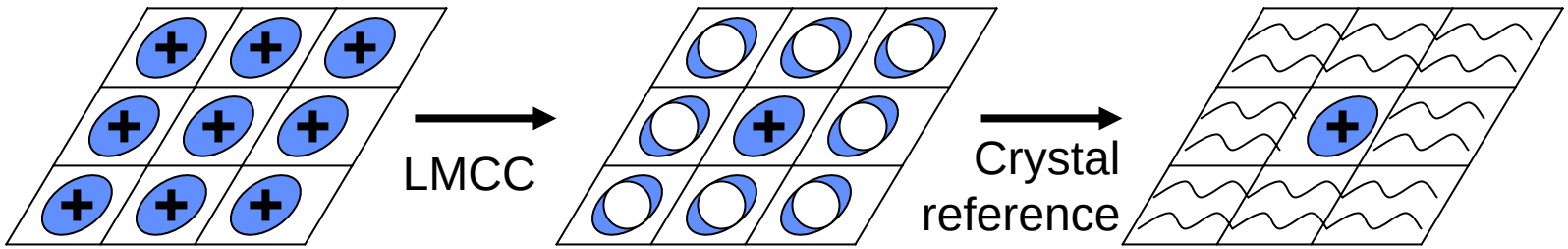
Missing polarization in bulk volume outside of supercell



Peter A. Schultz

Bulk polarization in a dielectric medium

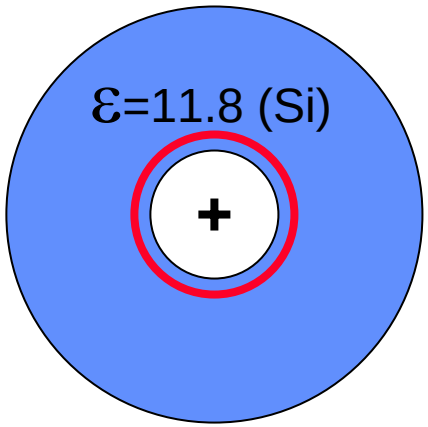
Peter A. Schultz



Ill-posed b.c.

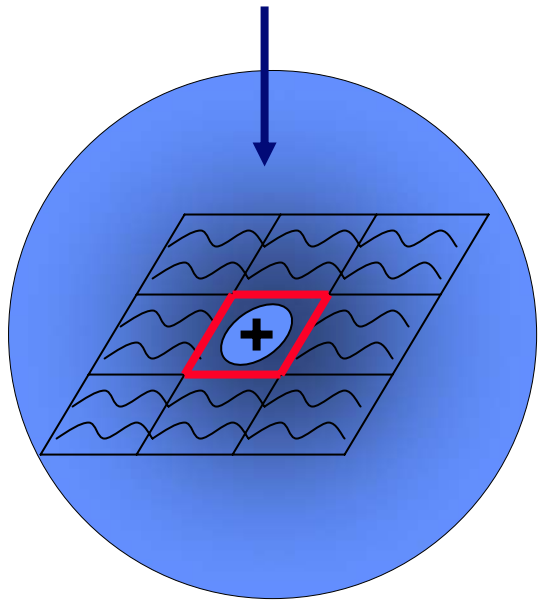
Variable μ_e

Bulk polarization?



Jost model (1934):

E_{jost} = response of dielectric to charge q in a cavity (I.e., our defect supercell)



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

Bulk polarization included through classical dielectric theory

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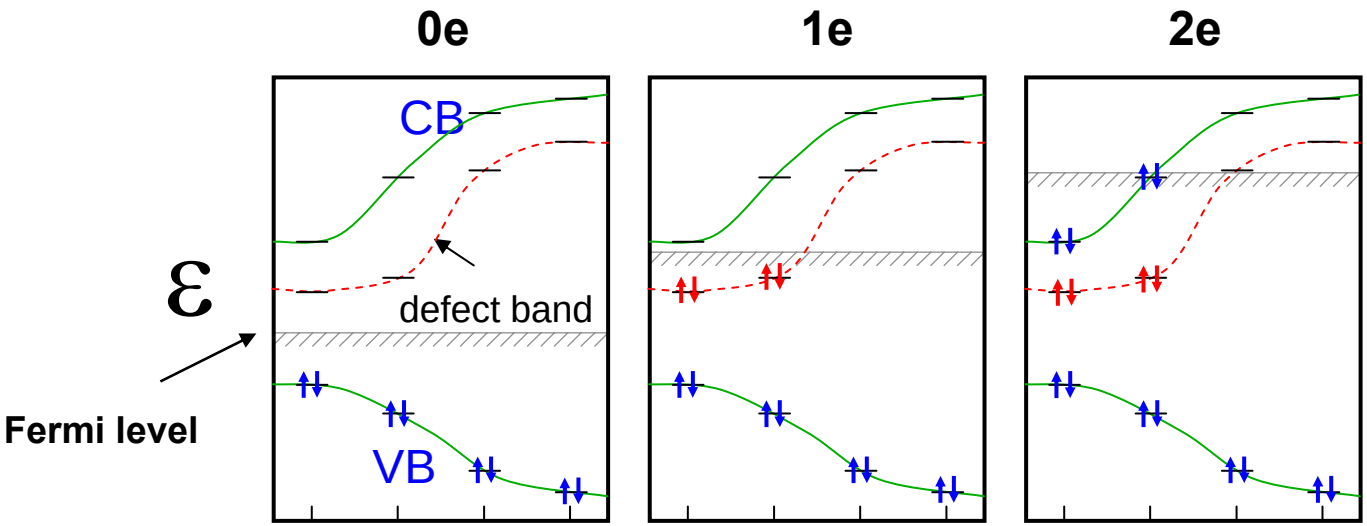
Defect banding



Standard methods: metallic, poor model of defect.

k

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Defect banding: Discrete Defect Occupation

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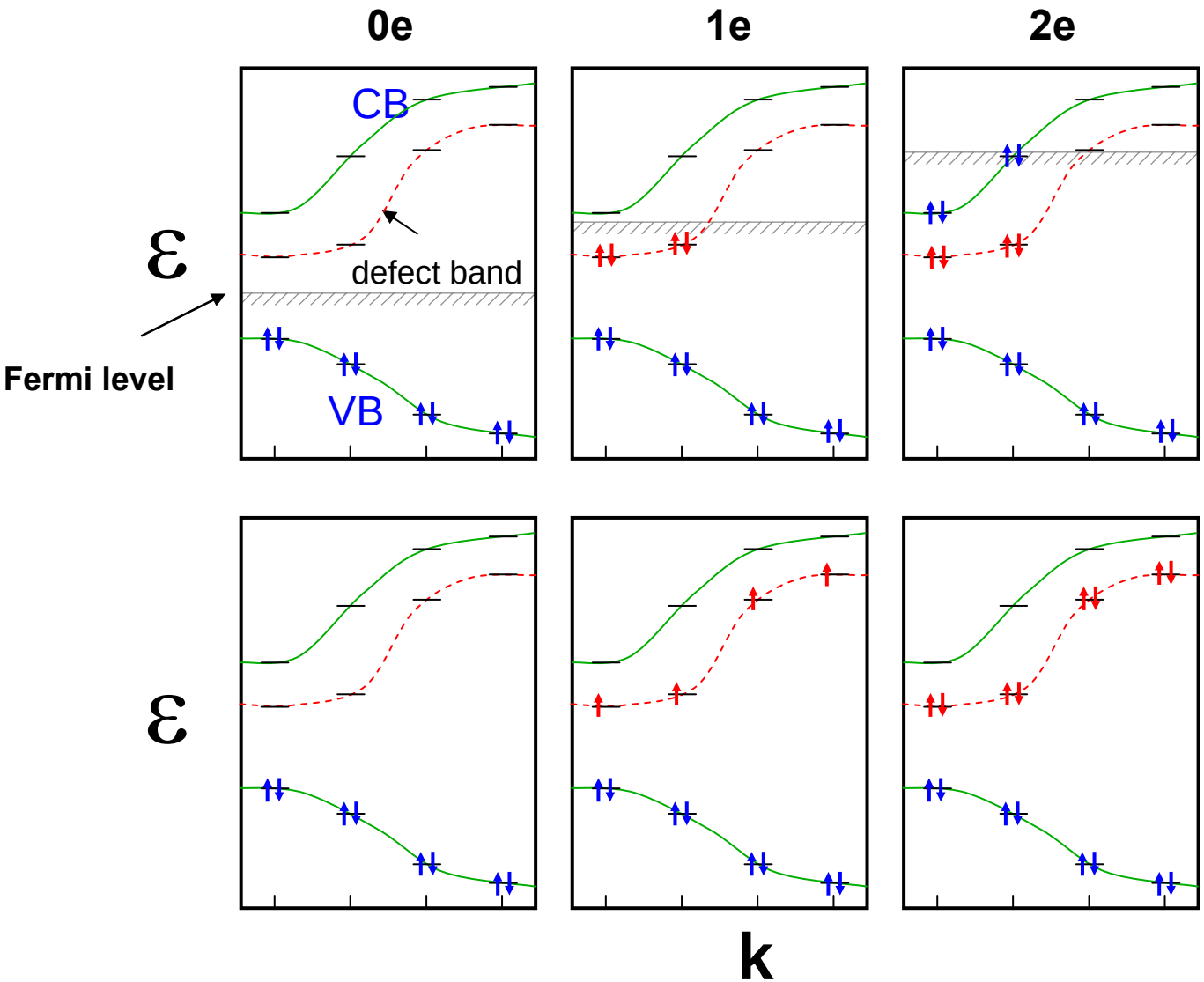

Standard methods: metallic, poor model of defect.

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

DFT Supercell issues

Peter A. Schultz

•Boundary conditions - how to handle net charge

- need to eliminate divergence, install correct q/r behavior of potential
- errors in jellium local electrostatic potential: 1.0 eV/64-site Si, fall off as 1/L
- LMCC method: Peter A. Schultz, PRL 84, 1942 (2000)

•Chemical potential for electrons

- want transition energies, (-/0), (0/+), need rigorous chemical potential
- errors in standard valence band shift schemes: "few tenths" of eV
- developed a scheme to *fix* electron reservoir for defect supercells

•Defect level dispersion

- defects interact, discrete defect states become bands, overlap CB/VB
- errors made by interacting defects - inappropriate model for defect
- Discrete Defect Occupation scheme to populate states

•Bulk response to local charge - finite size effects

- supercell has small finite volume, missing bulk polarization response
- bulk polarization is biggest number in problem - need to get it right
- modified simple Jost model (from 1934!) to model bulk polarization

And then ... what about DFT's band gap problem?

A supercell theory for defect energies

[P.A. Schultz, PRL **96**, 246401 (2006)]

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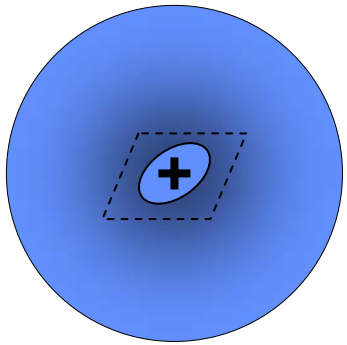
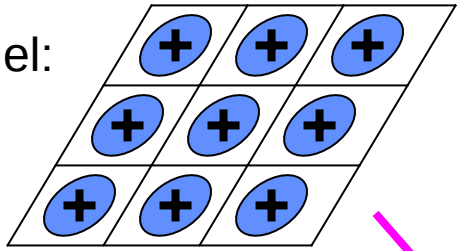
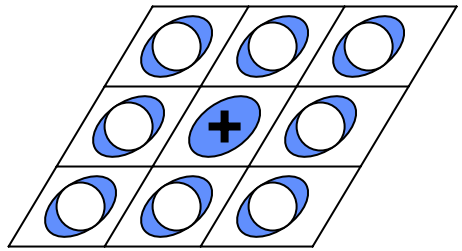
Target system: isolated defect



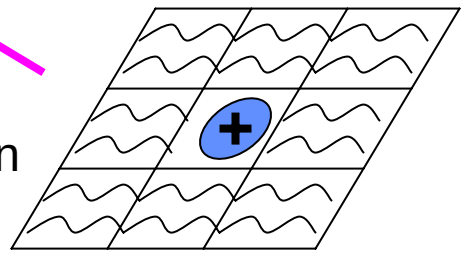
Standard DFT model: Supercell



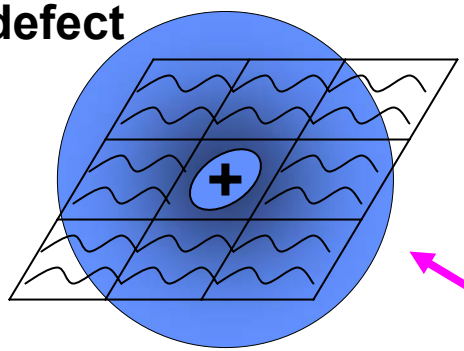
LMCC to fix boundary conditions



Crystal embedding to fix μ_e



Jost Bulk polarization



Computational model for isolated defect

Finite Defect Supercell Model

+ Discrete Defect Occupation (defect banding)

FDSM gives robust computational model for charged defect

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Charged Defect Formation Energy

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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.

The computational method: DFT/Quest

Peter A. Schultz

General purpose DFT code: SeqQuest: **http://dft.sandia.gov/Quest**

- Molecules, 1D nanowires, 2D slabs, 3D Bulk
- Metals and insulators (complex k-points)
- Multiple density functionals: LDA and GGA/PBE
- Norm-conserving pseudopotentials (“semi-local”)
- Well-converged local orbital (Gaussian-based) basis set
- Forces and stresses, with complete Pulay corrections
- Automatic geometry and cell minimization
- Fast, small, accurate, powerful --- 100’s atoms on a desktop
  - Supercomputer DFT on a desktop (plus some parallelism, too)

TDDFT under development (collaboration with Lund, AFRL)

- Non-equilibrium, electron dynamics, transport ...

Anatomy of a DFT code

(1) Create a guess density: $\rho(r) = \Sigma\, \rho_{atom}(r)$

(2) Construct a Hamiltonian, H, over a basis ϕ_i : $H_{ij} = \langle \phi_i \mid H[\rho] \mid \phi_j \rangle$

$$H = T + V_{nuc} + V_{coul}[\rho] + V_{xc}[\rho]$$

T	V_{nuc}	$V_{coul}[\rho]$	$V_{xc}[\rho]$
kinetic energy	nuclear attraction	electron-electron Coulomb repulsion	electron-electron exchange-correlation

$$V_{nuc} = \Sigma\, V_{atom}[R] \rightarrow N^3 \text{ Hamiltonian}$$

(3) Solve for wavefunctions ψ_i :

$H\, \psi_i = \varepsilon_i\, \psi_i \rightarrow N^3$ eigensolve

(4) Compute new density: $\rho(r) = \Sigma\, f_i \mid \psi_i \mid^2$

(5) Repeat (2)-(4) until self-consistent

SeqQuest:

(1) Map onto a local (Gaussian) orbital basis … small N

(2) Reformulate electrostatics … O(N) Hamiltonian

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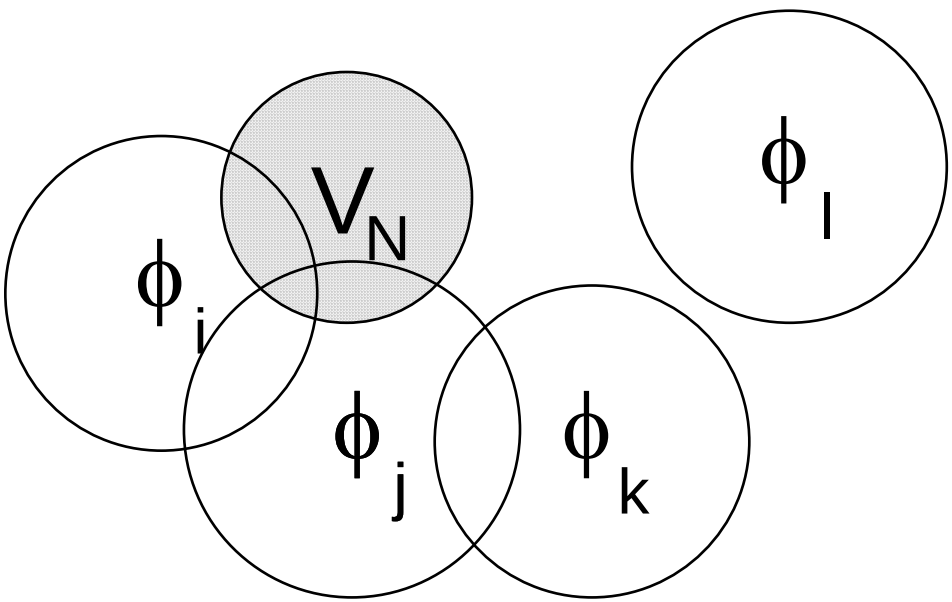
Quest: two kinds of matrix elements

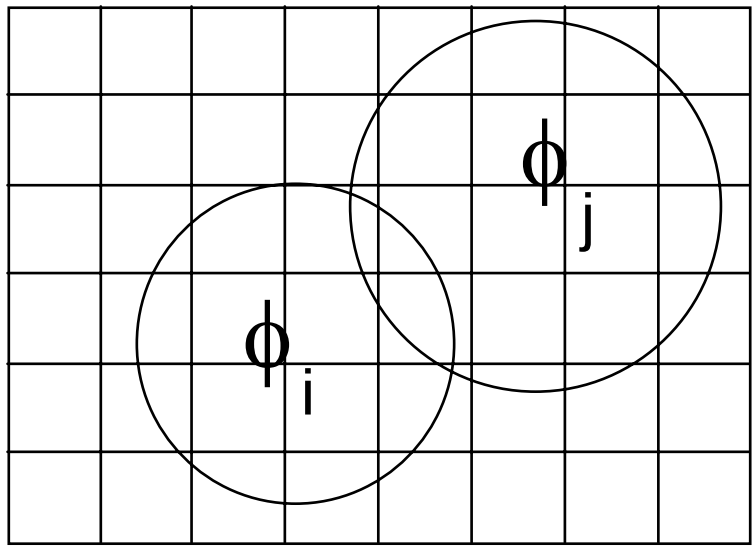
<u>Analytic local 2 or 3-center:</u>

(iteration-independent setup)



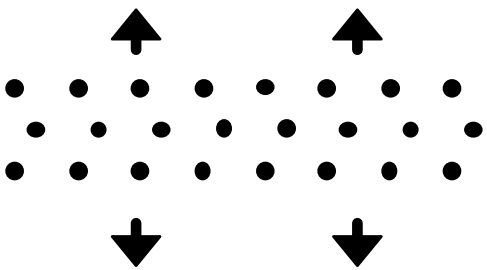
<u>Mesh-based 2-center:</u>

(iteration-dependent scf elements)

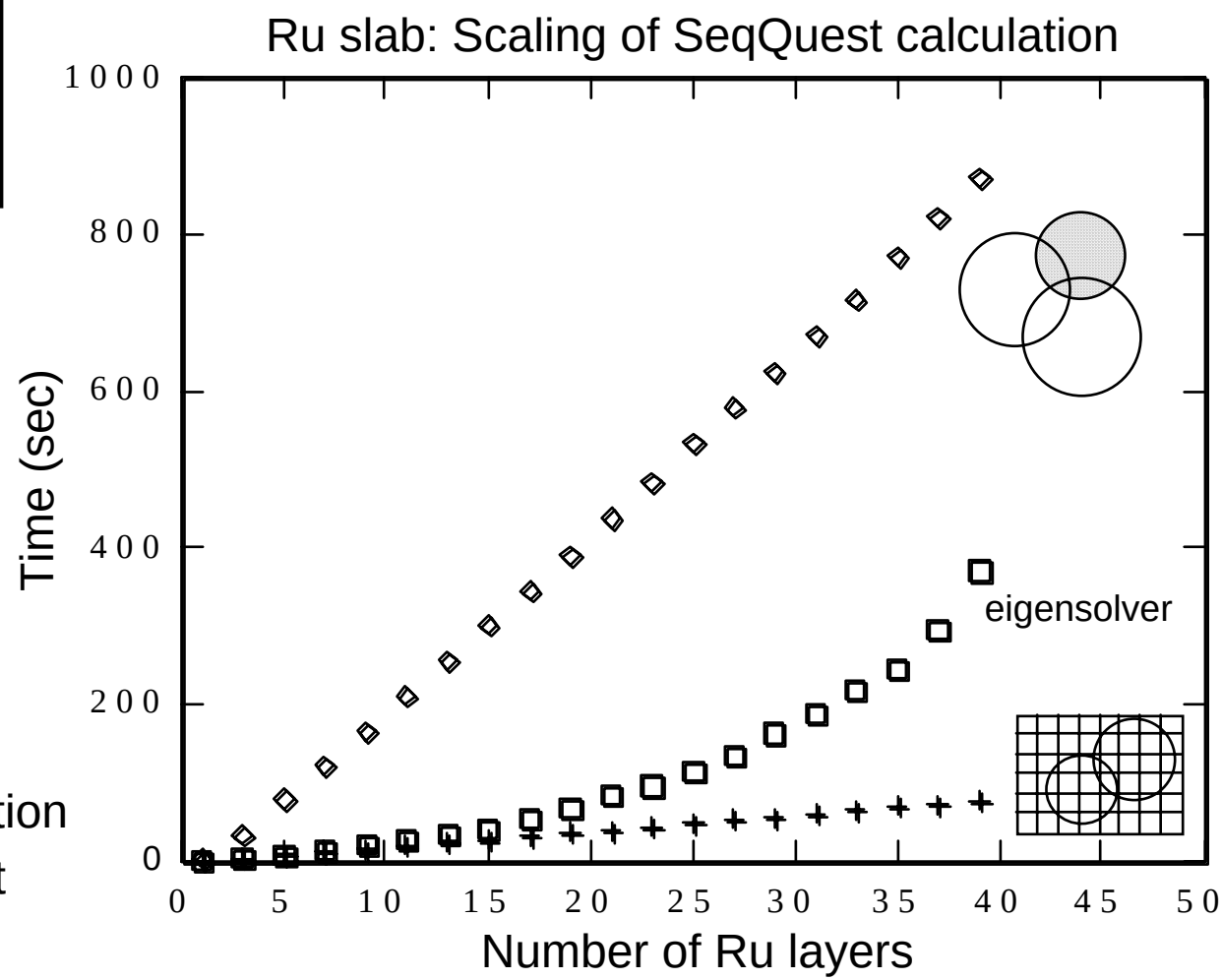


Both are O(N) !

Scaling Ru slab



(0001) 1x1 surface
vary layer thickness
a0=2.673Å, c/a=1.575
10k/IBZ, ~12Å slab separation
full DZP basis SeqQuest



Actually achieves O(N), and reaches it quickly

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Scaling: NaCl 2D slab

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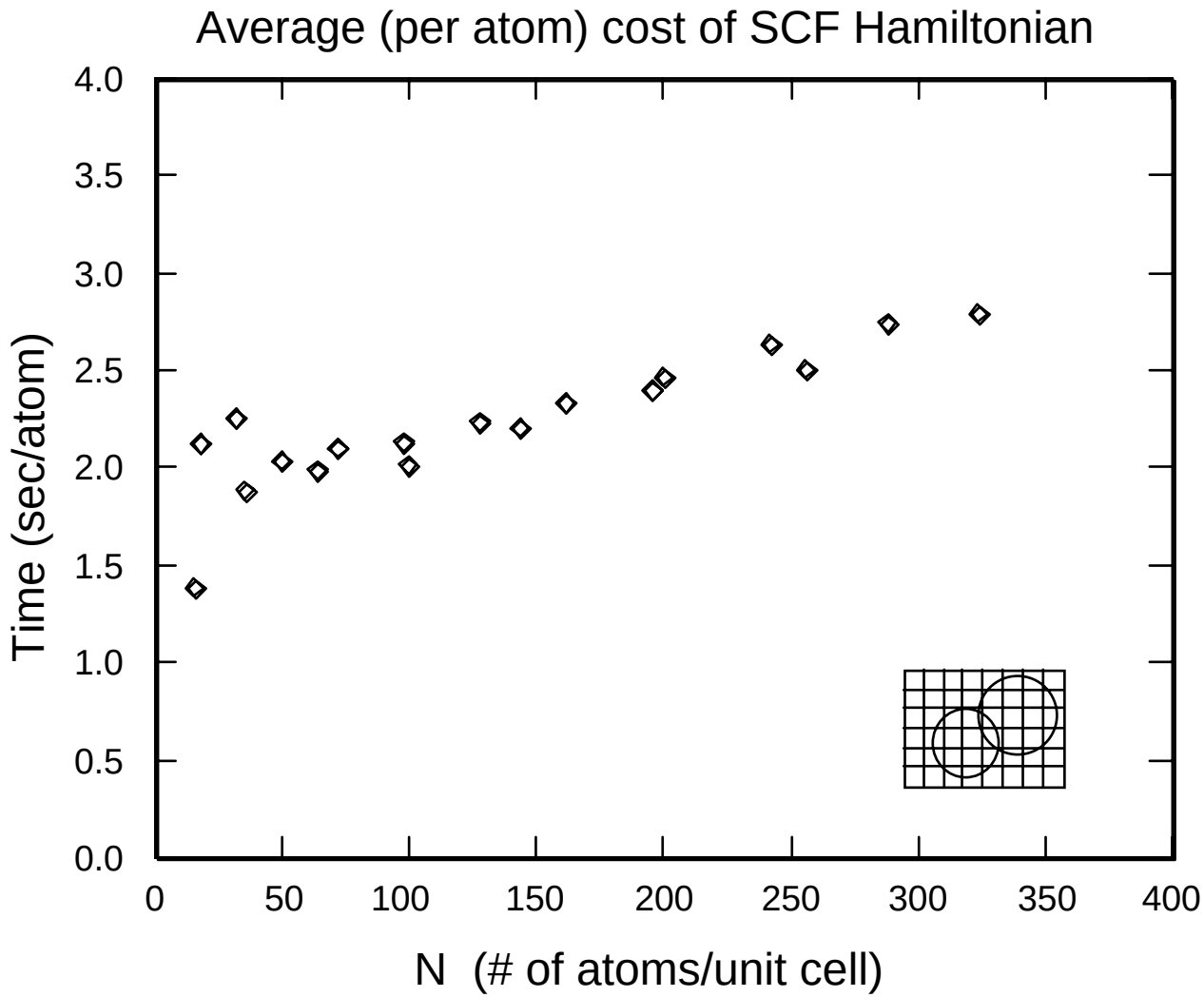

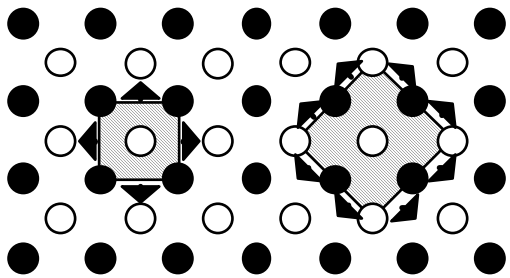

single layer slab
vary 2D extent
DZP basis, large core
non-linear partial core
a0=3.705Å, gamma point
~10.5Å slab separation

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Computational details

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Defect supercell calculations

SeqQuest code - periodic, gaussian-basis, pseudopotential code

http://dft.sandia.gov/Quest

LDA and GGA-PBE functionals

Full FDSM (LMCC, chemical potential, DDO, bulk screening)

Calculations ranging from 64-site to 512-site supercells

Converged k-point sampling

Final series: 250-site (5x5x5 fcc cell) with 2^3 *k*-points

Fully relaxed atomic positions

Lattice parameter fixed at theoretical value

LDA: 10.20 bohr (5.40 Å)

PBE: 10.34 bohr (5.47 Å)

The silicon self-interstitial

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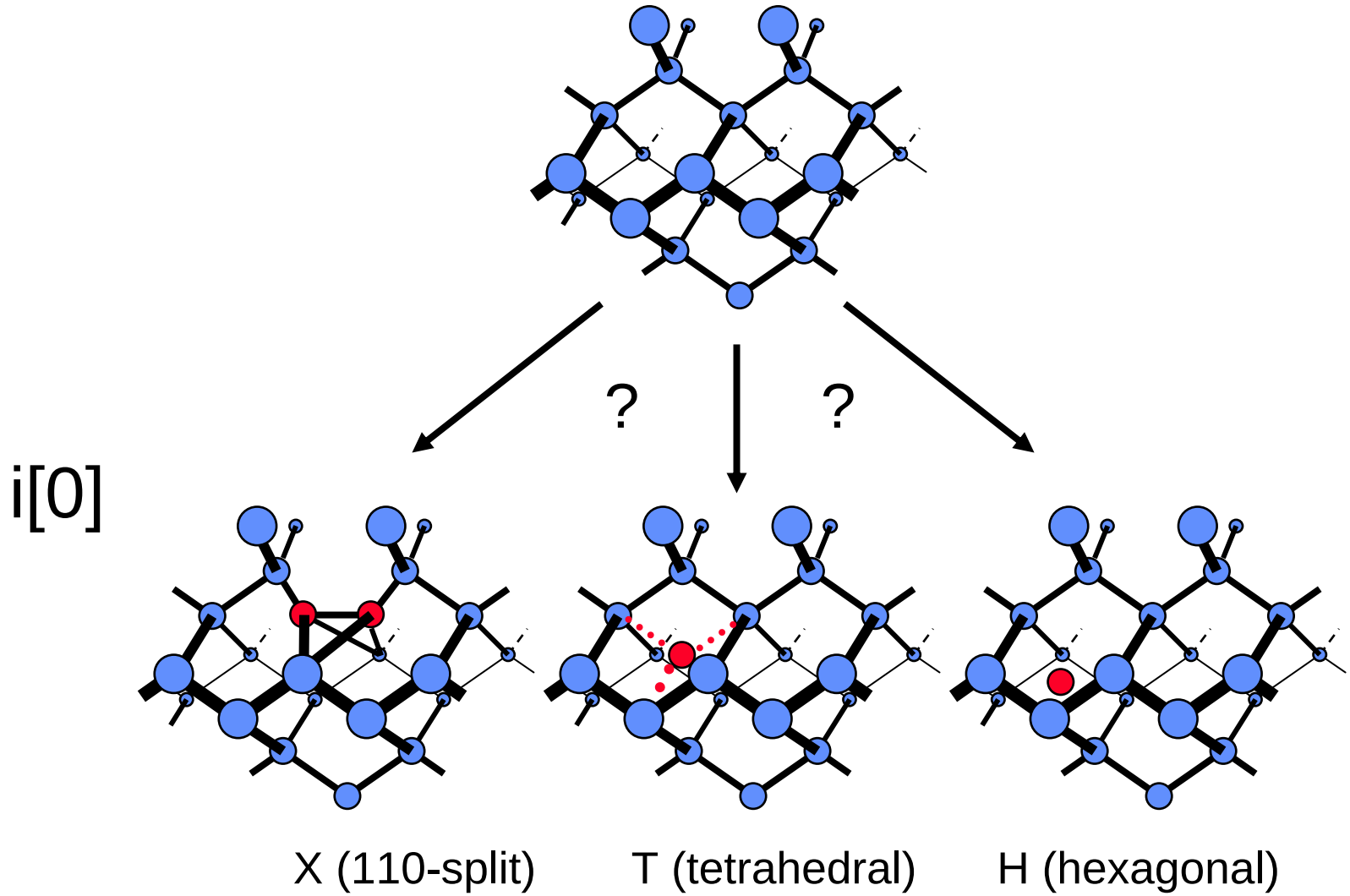

Si defect structures - DFT/LDA

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: DFT/LDA defect charge transitions

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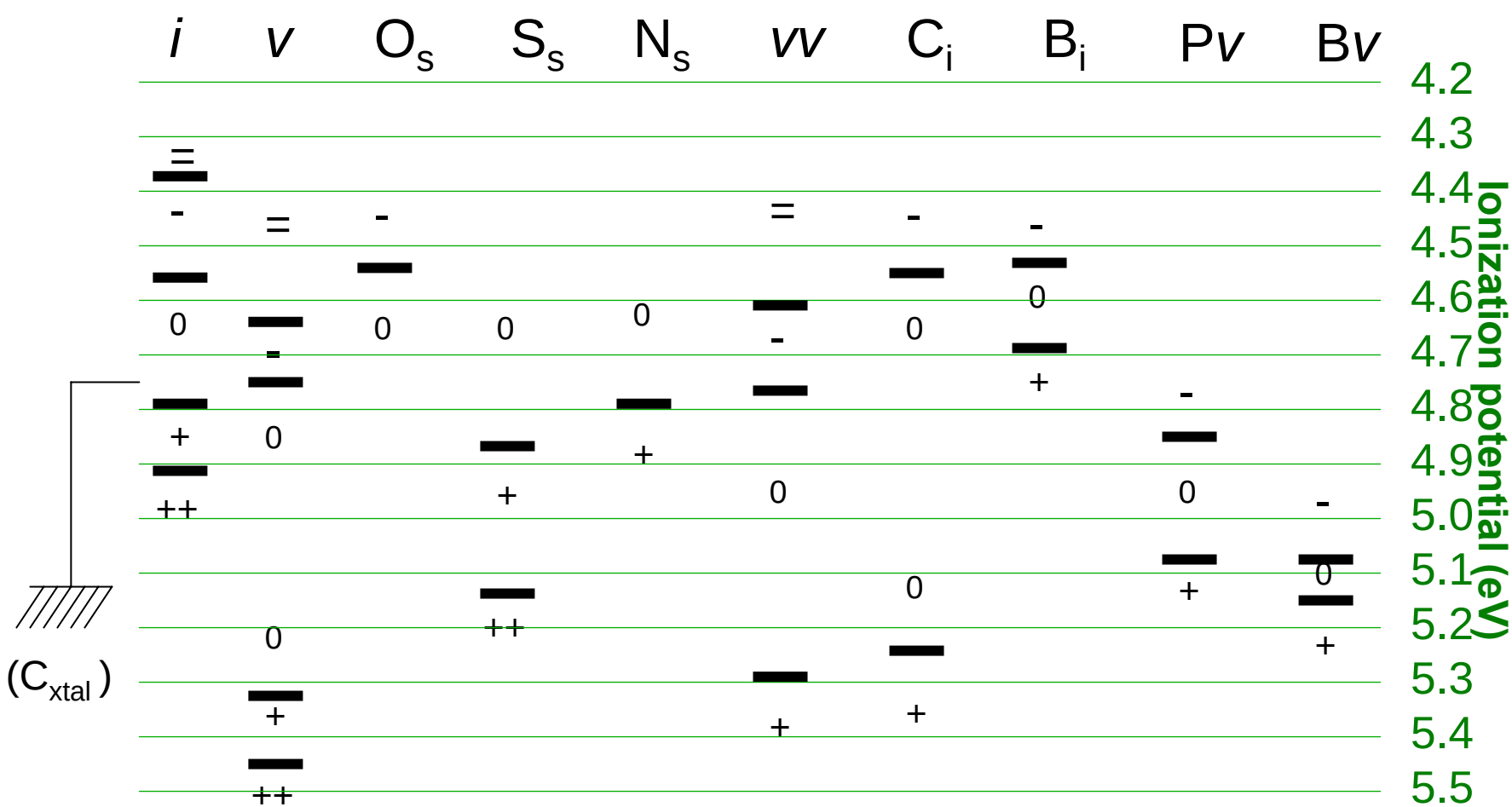
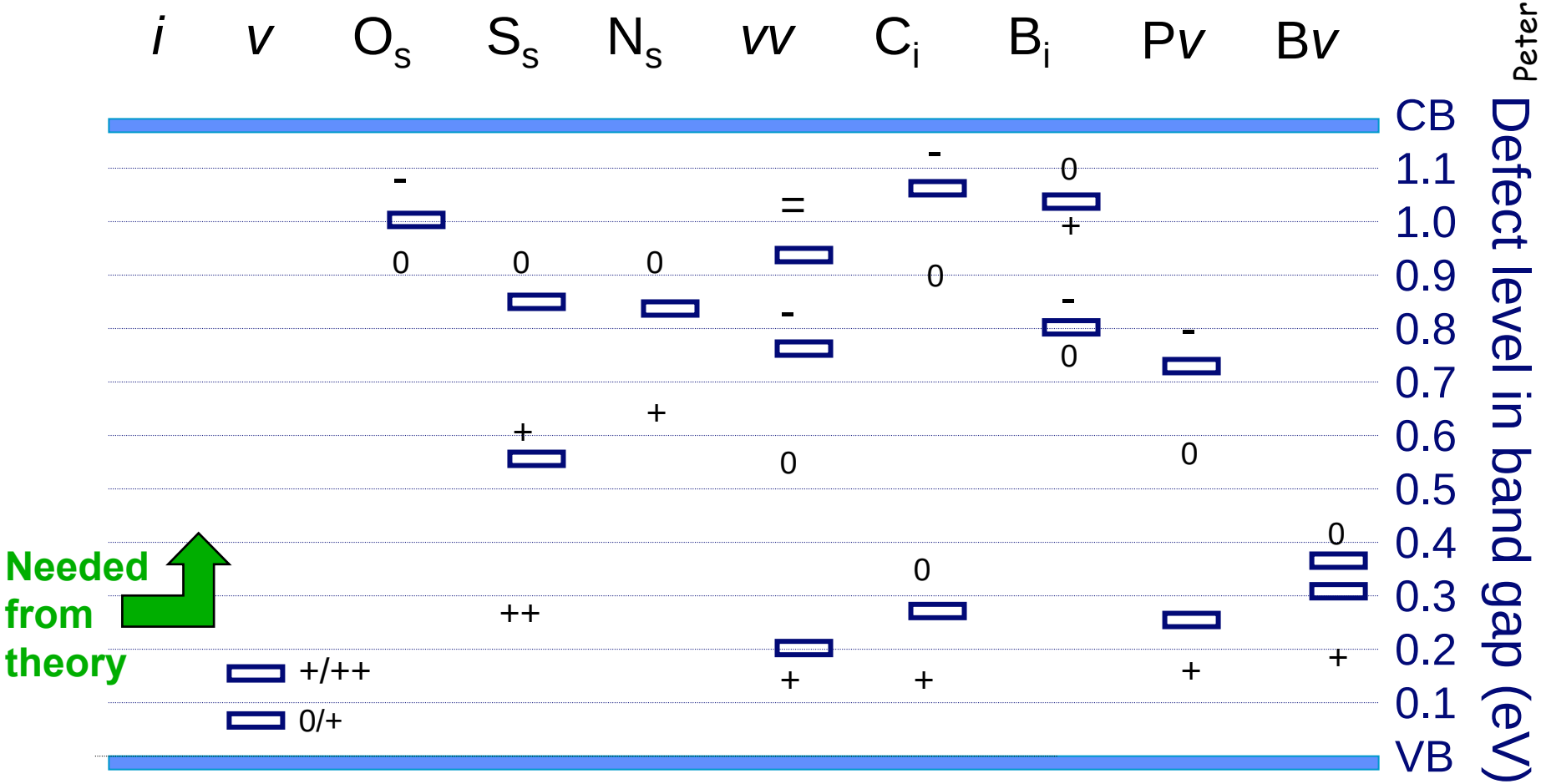


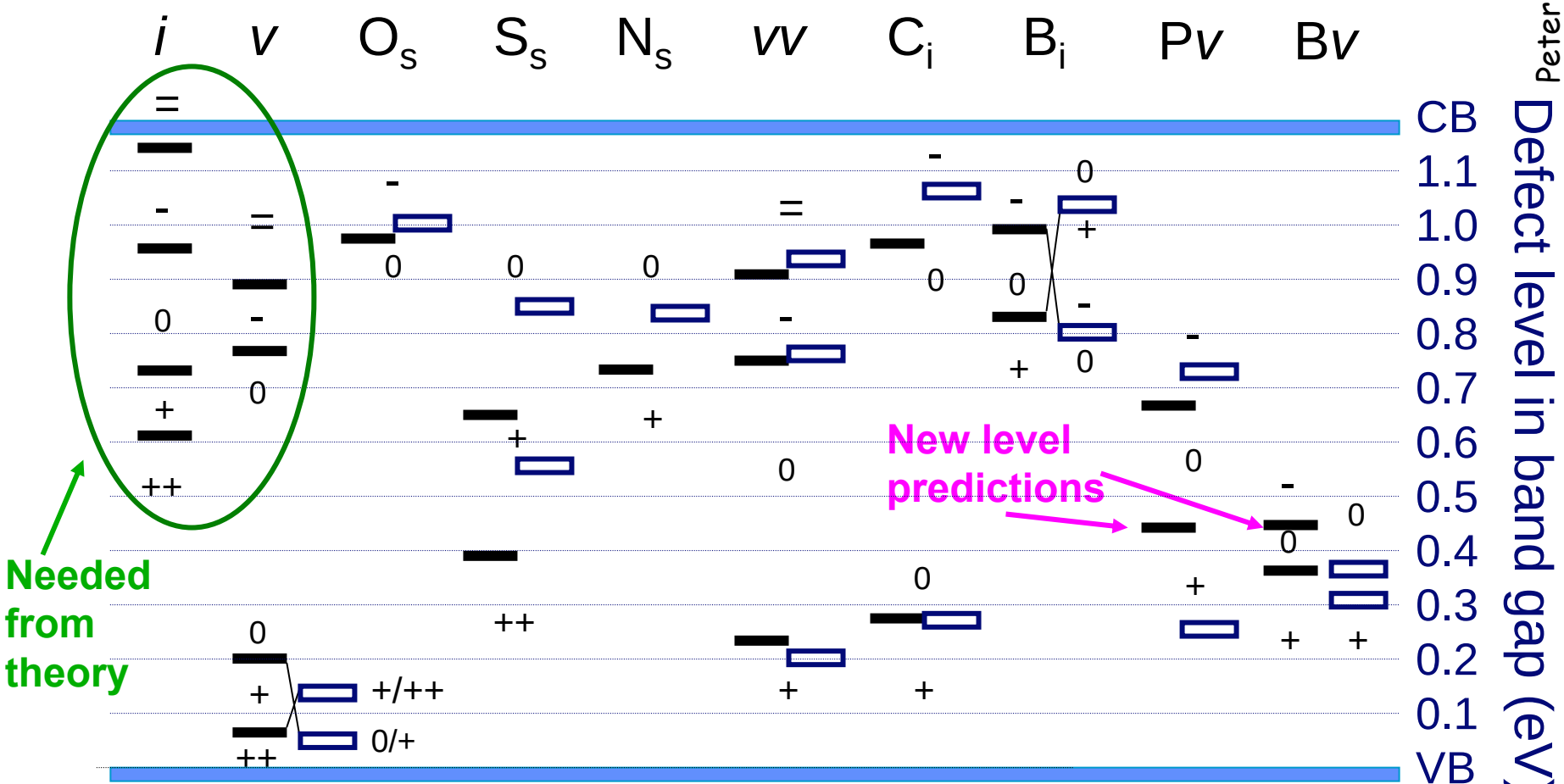
All formation energies grounded to common electron reservoir
Full width of experimental band gap seen in DFT ionization energies

Si: Experimental Levels



Experimental record is silent on most important defects!

Si: DFT/LDA vs. Experimental Levels



LDA: max error=0.25 eV, mean |error|= 0.08 eV (*v*-like: 0.04 eV)
Surprises: new charge states for P-*v* and B-*v* pair defects
Problems: Boron interstitial (negative-U), *v*acancy (0/+/2+), S(0/+/2+)

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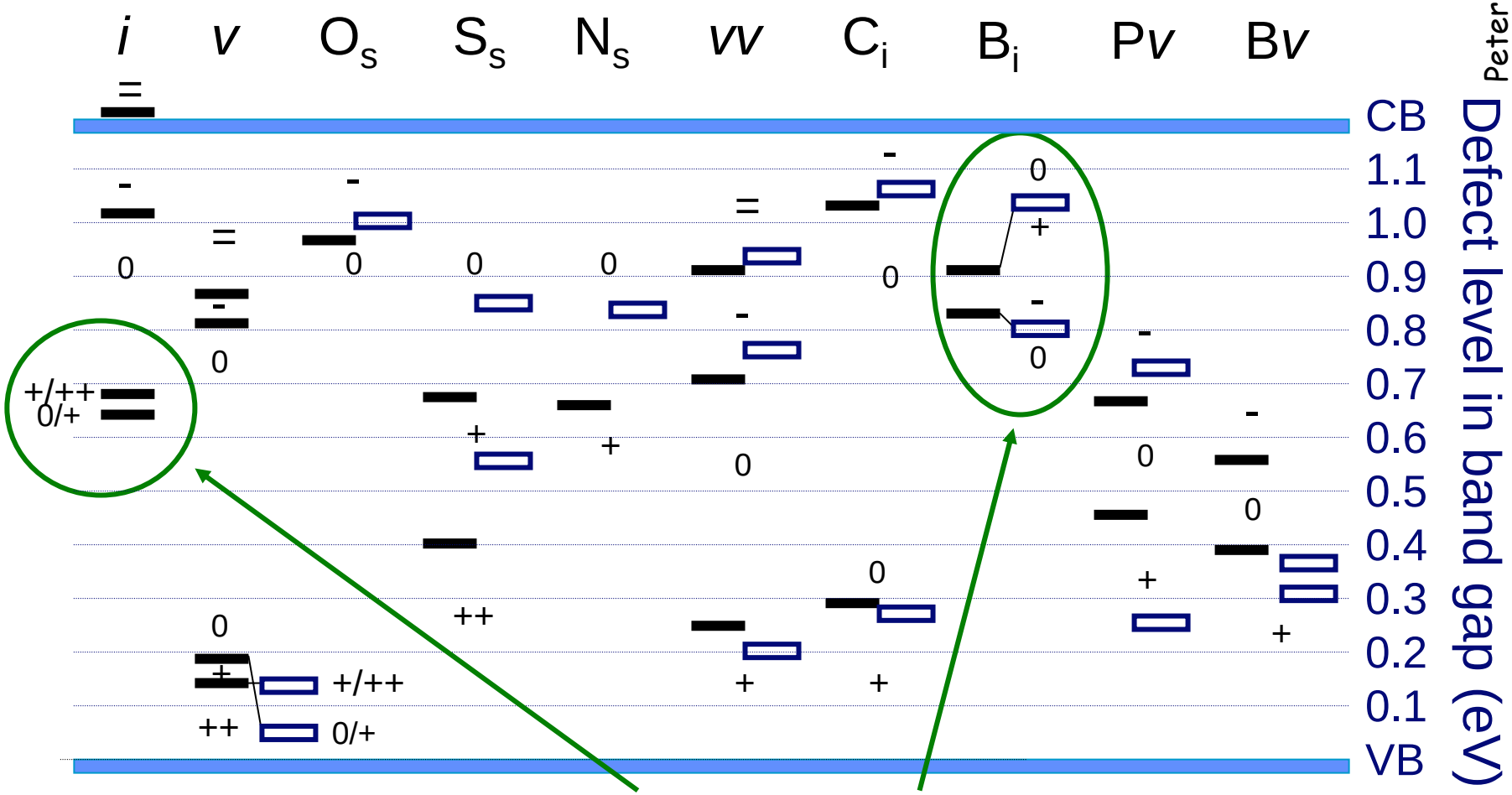
Si: GGA/PBE vs. Experimental Levels



GGA/PBE improves defect levels with bonding changes
PBE max error=0.17 eV, mean |error|=0.08 eV, (*v*-related: 0.05 eV)
New P-*v* and B-*v* levels still present

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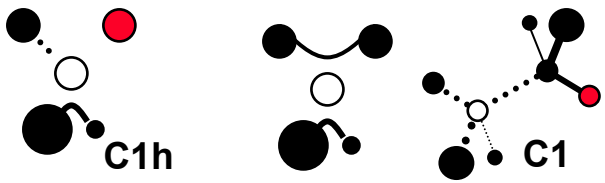
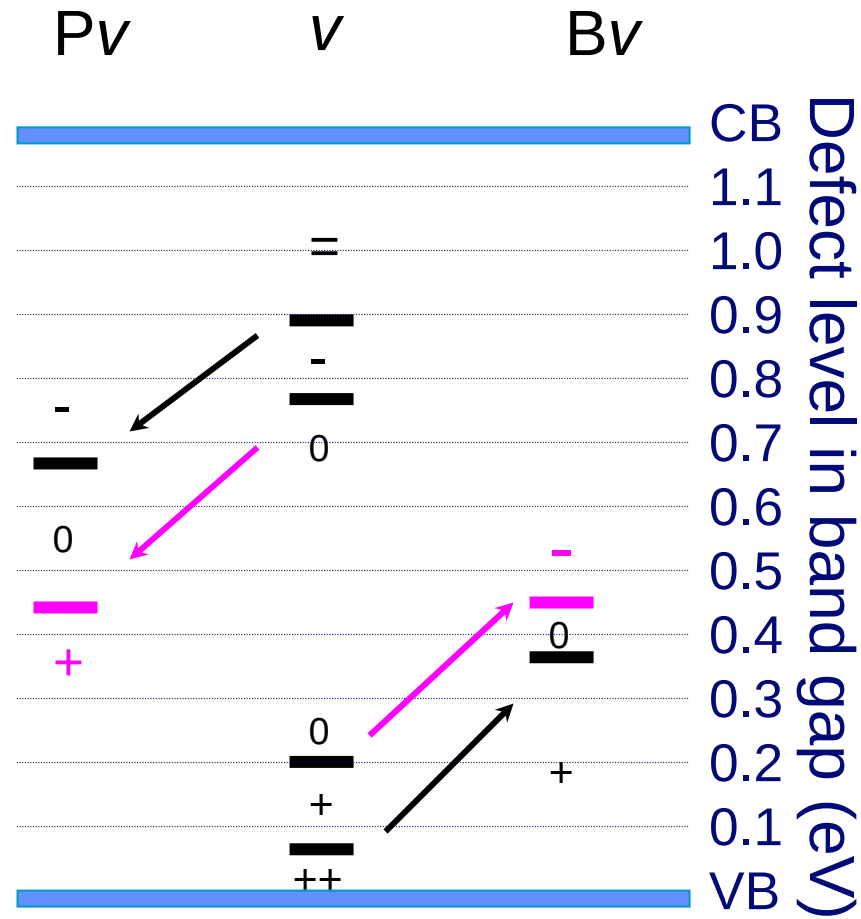
P-*v* and B-*v* charge states



6e	P*v*(-)	v(2-)	
5e	P*v*(0)	v(-)	
4e	P*v*(+)	*v*(0)	B*v*(-)
3e		*v*(+)	B*v*(0)
2e		*v*(2+)	B*v*(+)

v(0) isoelectronic with P*v*(+) and B*v*(-)



By analogy to vacancy, expect new charge states isoelectronic to v(0)
DFT finds them, they are real, I.e., >0.25 eV (max DFT error) from edge
New states at midgap -> effective recombination centers

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Summary

- Finite Defect Supercell Model - robust computational model of defect
  - fix boundary conditions (LMCC Poisson solver)
  - rigorous chemical potential (common electron reservoir)
  - bulk polarization (bulk screening through modified Jost model)
  - defect banding (discrete defect occupation scheme)
  - still needs refinement (e.g., what about strain/elastic effects?)

- Accurate DFT (LDA or PBE) Si defect levels, mean error < 0.1 eV
  - wide variety of defects - intrinsic, primary, secondary, 1st-row, 2nd-row
  - top and bottom of band gap
  - predictive despite band gap problem: new levels in P-*v* and B-*v*
  - evaluated as differences of valid ground state energies, not KS eigenvalues

- Band gap problem?
  - not in computation of localized defect states from total energy calculations!
  - However, still have issue of connecting defect level spectrum to band edges
  - Can we "fix" band gap problem (e.g., w/EXX) without screwing up energies?

Thanks to: Kevin Leung, Ann Mattsson, Art Edwards, Harry Hjalmarson, Renee Van Ginhoven

Contact information: paschul@sandia.gov, http://www.cs.sandia.gov/~paschul

Summary - II

- Beware of Black Boxes (even SeqQuest)!
  - know your assumptions, control your approximations
    "Primer", Mattsson, et al., MSMSE **13**, R1 (2005).
  - what *exactly* is your code/simulation doing?
- There is a gap between our tools (DFT codes) and reality (defects)
  - construction of valid (i.e., quantitative) computational model
- Improvements?
  - path forward to better (i.e., more accurate) functionals not clear
  - existing LDA and GGA do very well already
- Questions?

Thanks to:
Kevin Leung, Ann Mattsson, Art Edwards, Harry Hjalmarson, Renee Van Ginhoven

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

Contact information: paschul@sandia.gov, http://www.cs.sandia.gov/~paschul

Questions & Answers

Multiscale ladder for radiation damage

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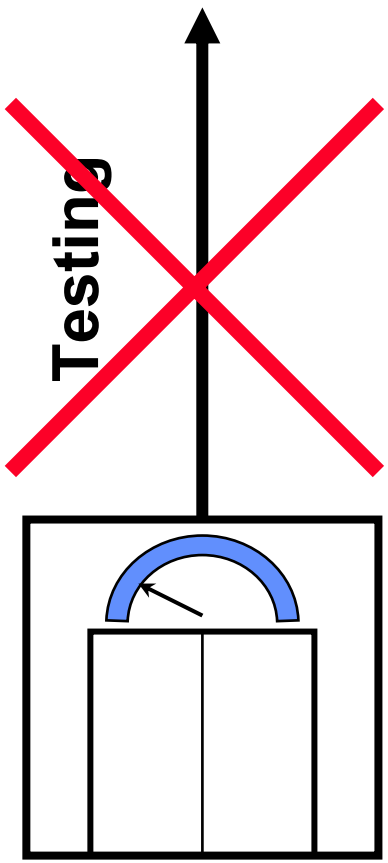
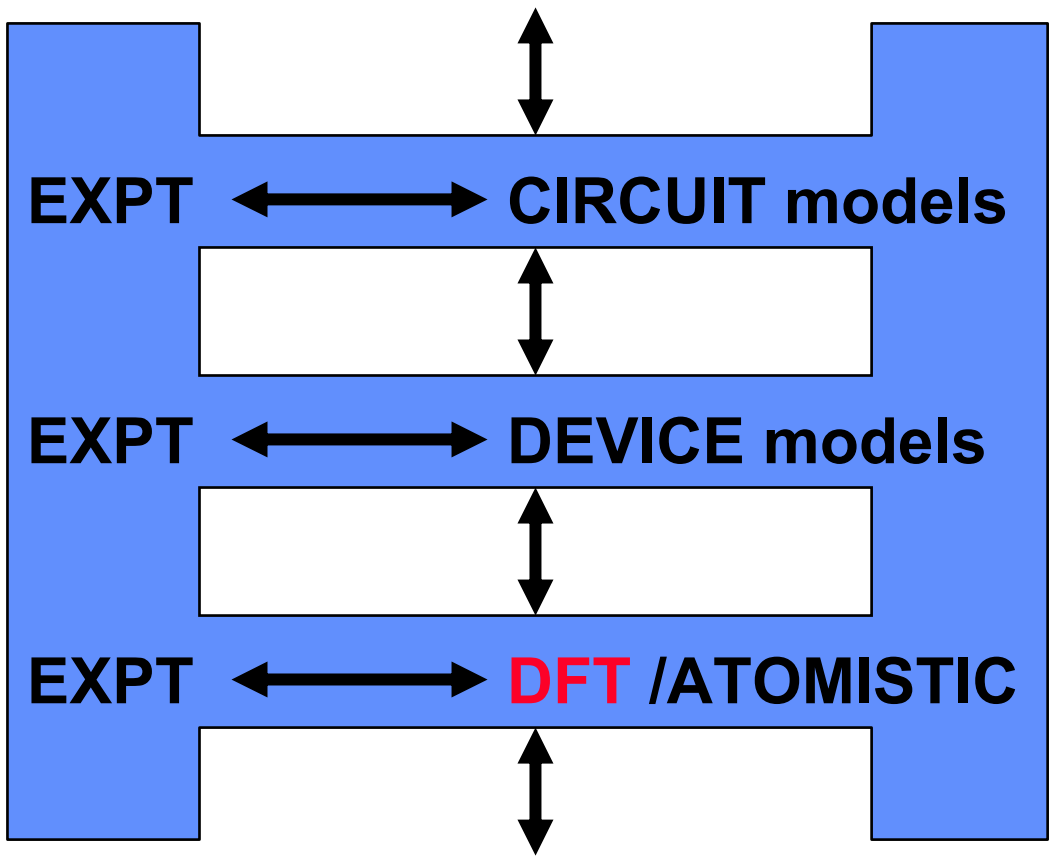
Electrical system response





Radiation damage

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Radiation damage and defects

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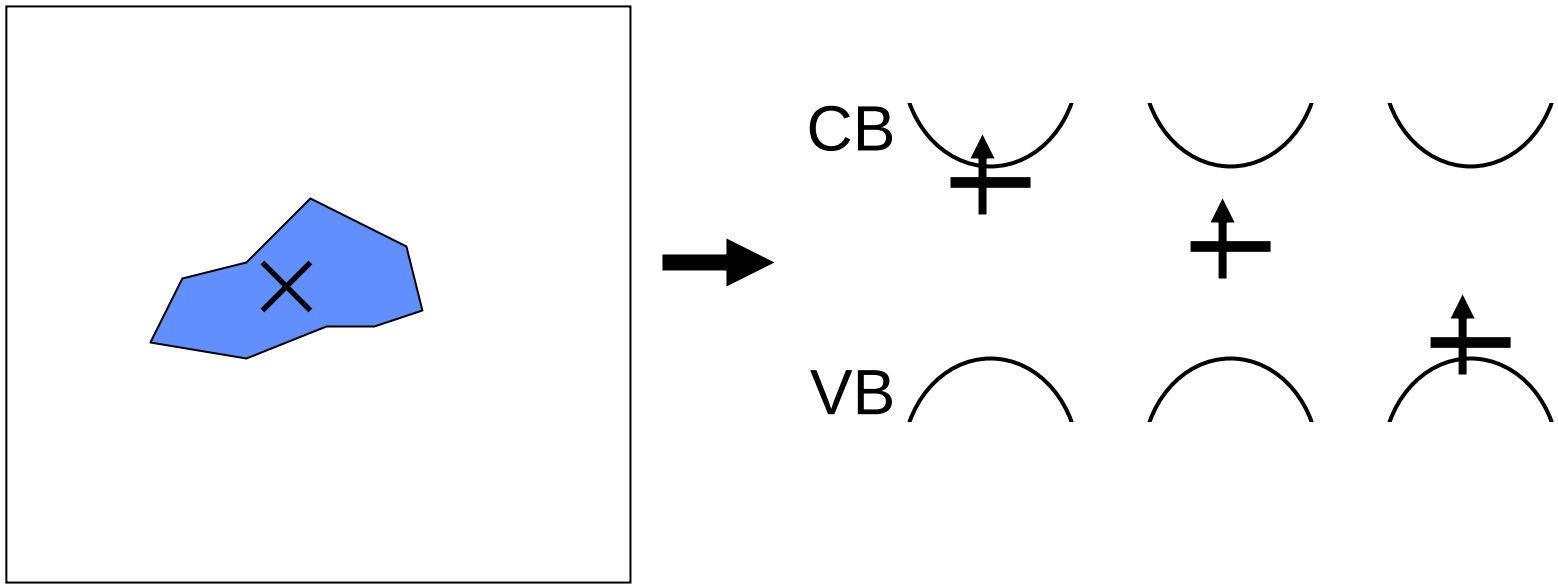
Radiation damage …



produces defects … and introduces electronic transitions

… and we would like to quantify these transitions

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