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Density-functional-theory (DFT) studies of vacancy defects in silicon using the Socorro code

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- Why Sandia cares about defects in silicon
- New DFT calculations for V, VV, and VP emphasizing:
  - convergence with respect to basis size and sampling points
  - elimination of supercell size effects
  - evaluation of exchange-correlation functionals
- Short overview of the Socorro code

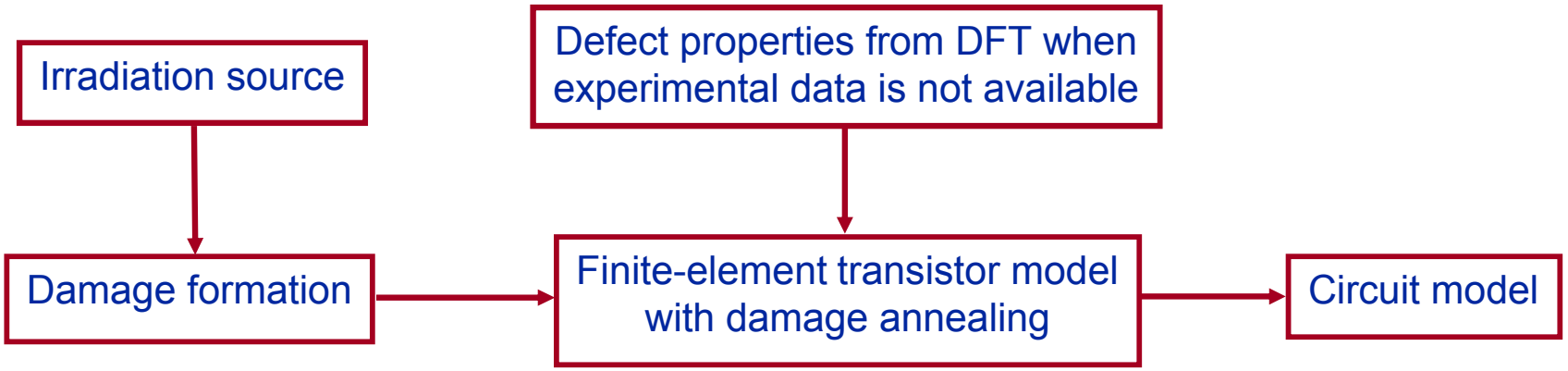
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

Why Sandia cares about defects in silicon

- Sandia is responsible for ~ 95% of the components in U.S. nuclear weapons
- Among its responsibilities, Sandia must ensure that electronic components will operate correctly during intense neutron bursts (threat environment)
- In the past, Sandia qualified electronic components using a fast-burst reactor (SPR-III) having characteristics similar to the threat environment
- In late 2006, SPR-III was shut down as a result of changes in DOE policies on Special Nuclear Materials
- In response, Sandia began the Qualification Alternatives to SPR (QASPR) program to develop a new methodology to qualify electronic components
- The three main QASPR activities are:
  - Experiments in environments not similar to the threat environment
  - Science-based computational modeling
  - Qualification protocols with quantified uncertainty

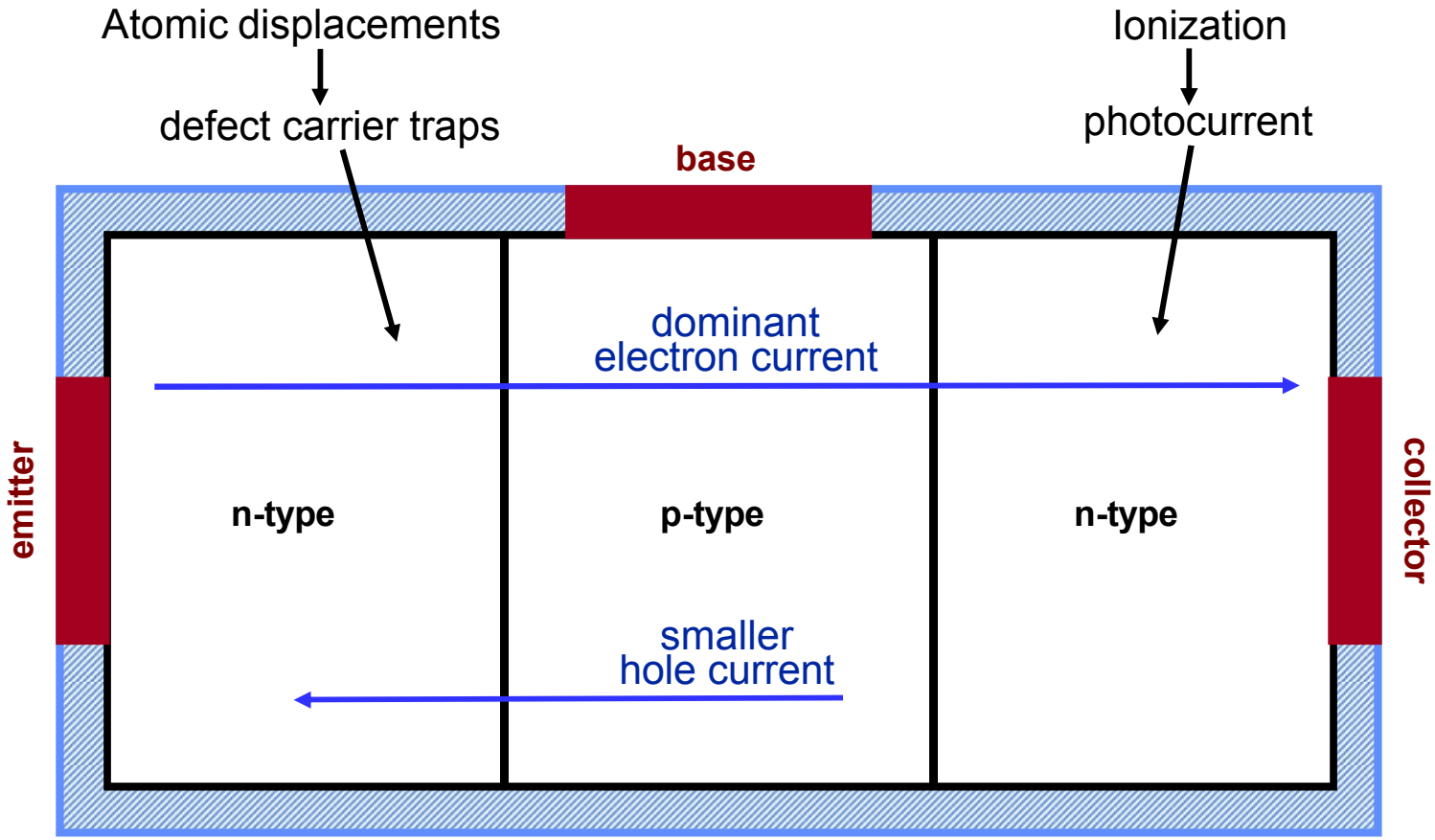
Modeling and simulation in QASPR

- Goal is to predict component performance in the threat environment with a quantified uncertainty
- Comprehensive sequence of codes extending from the irradiation source through atomic processes to device and circuit operation
- Science based rather than empirical to the greatest possible degree
- Push the envelope beyond existing methodologies to reduce uncertainties with the understanding that absolute precision is not yet attainable
- Emphasis on code verification, experimental validation, and uncertainty quantification

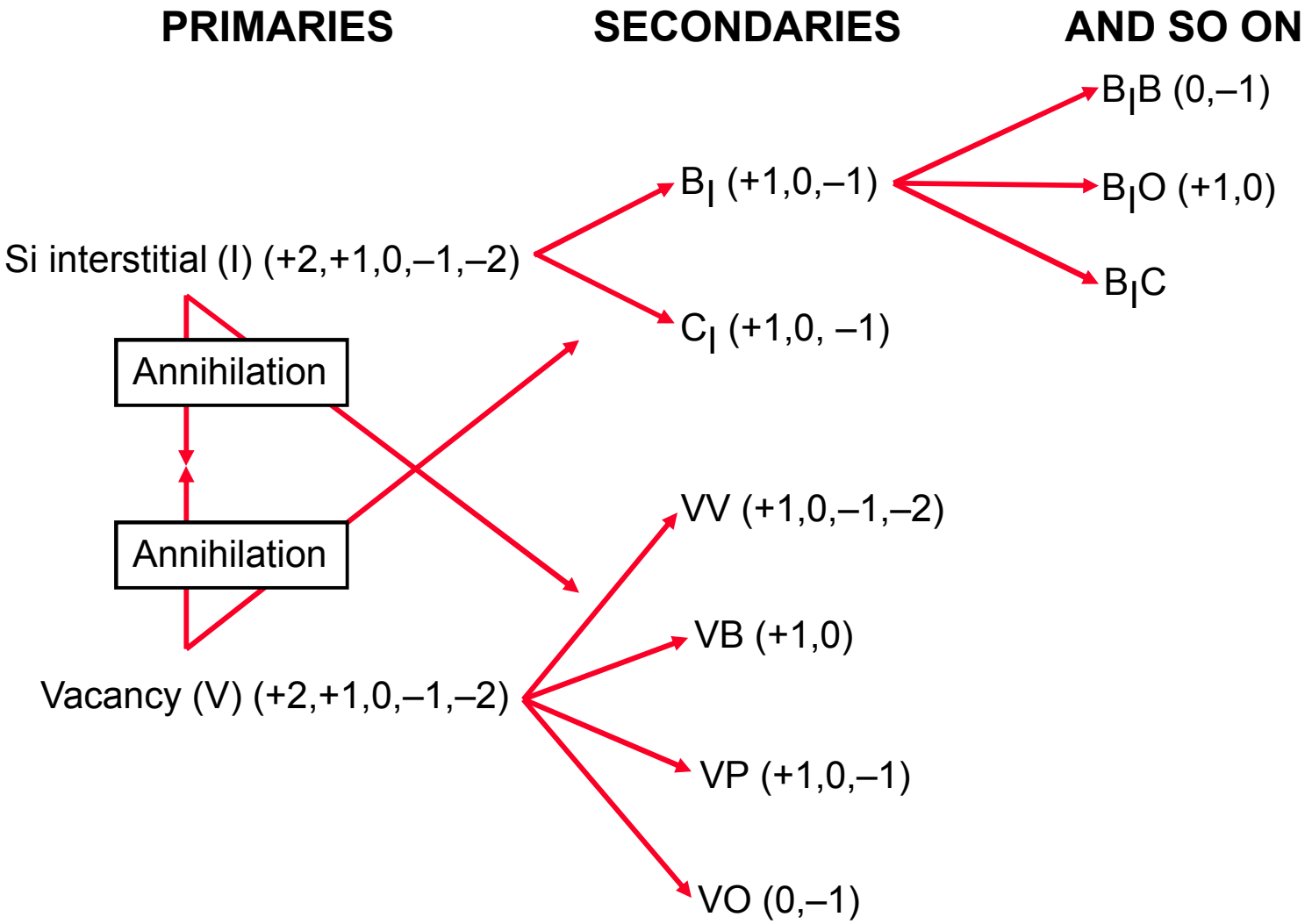


Neutron irradiation effects in a silicon bipolar transistor

Principal focus of QASPR Modeling and Simulation:
Rapid gain changes due to formation and subsequent evolution of defects that act as carrier traps: traps → carrier recombination → increased base current → reduced gain



Atomic displacements and their evolution



New DFT calculations for V, VV, and VP

DFT → *ground state* of a many-electron system

Ground state → *atomic forces* and *total energy*

Atomic forces → relax atoms to a local-energy-minimum configuration (LEMC)
→ find saddle-point configuration (SPC) of a diffusing atom

Total energy → compute the formation energy at a LEMC or SPC

- Kohn-Sham formulation of DFT with LDA and GGA exchange-correlation
- Plane wave basis (thus periodic boundary conditions)
- Norm-conserving pseudopotentials or projector-augmented wave functions
- 216-, 512-, and 1000-atom simple cubic supercells

Formation energy*: $E^{\mathrm{f}}(\mathrm{D}^q, E_{\mathrm{F}}) = E_{\mathrm{T}}(\mathrm{D}^q) - \sum_{\text{atoms}} n_{\mathrm{i}}\mu_{\mathrm{i}} + q(\varepsilon_{\mathrm{VBE}} + \Delta_{\mathrm{VBE}} + E_{\mathrm{F}})$

E_{T} : total energy of defect D in charge state q

E_{F} : Fermi level referenced to the valence-band edge (VBE)

n_i : number of type i atoms

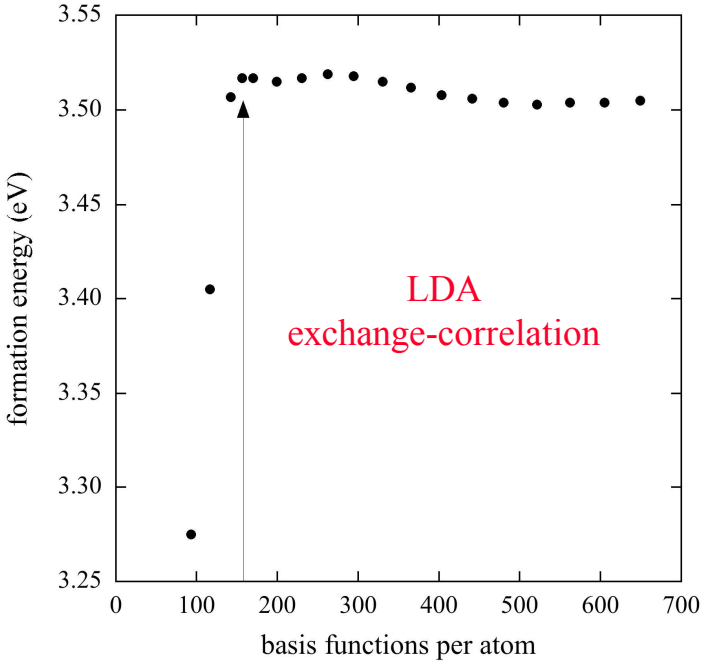
μ_i : reference chemical potential of type i atom

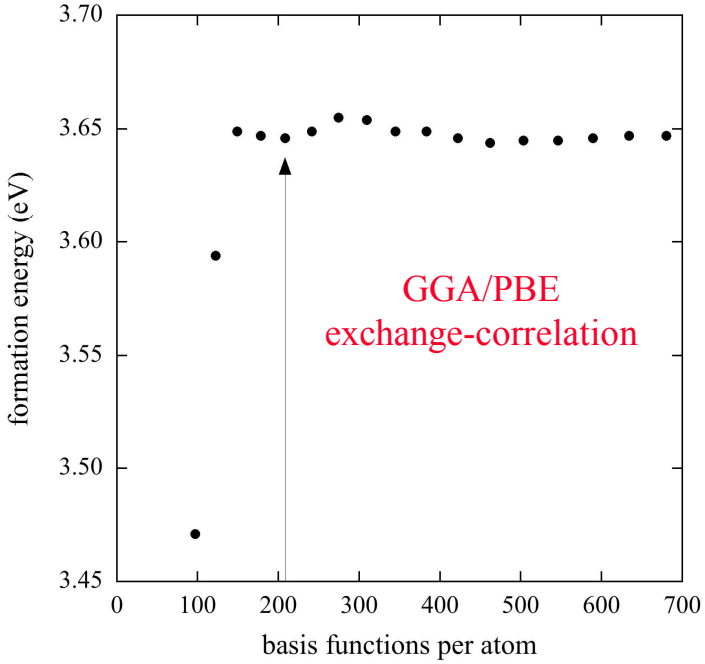
$\varepsilon_{\mathrm{VBE}}$: bulk silicon eigenvalue at the VBE

Δ_{VBE} : chosen to align computed and measured energy level

*dependences on basis size, Brillouin-zone sampling, and supercell size are not indicated

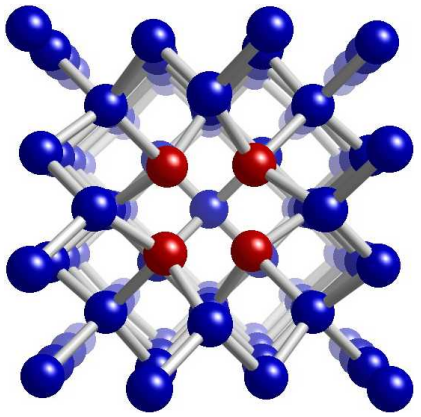
Convergence with respect to basis



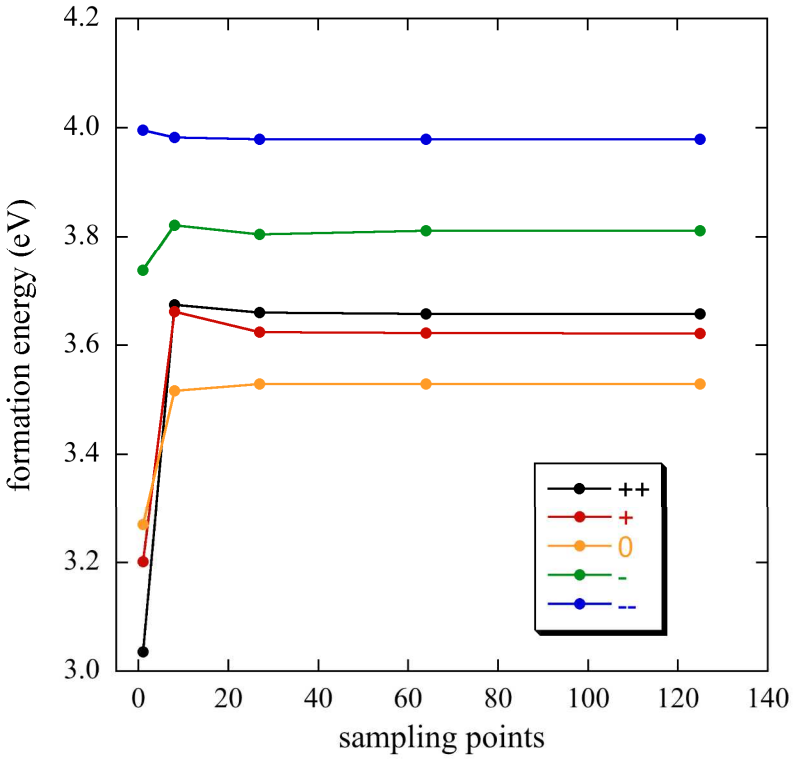


Variations in the formation energies beyond the pointers are 10 meV

Test structure: relaxed neutral vacancy in a 216-atom supercell, with {2,2,2} Monkhorst-Pack parameters used to sample the Brillouin zone

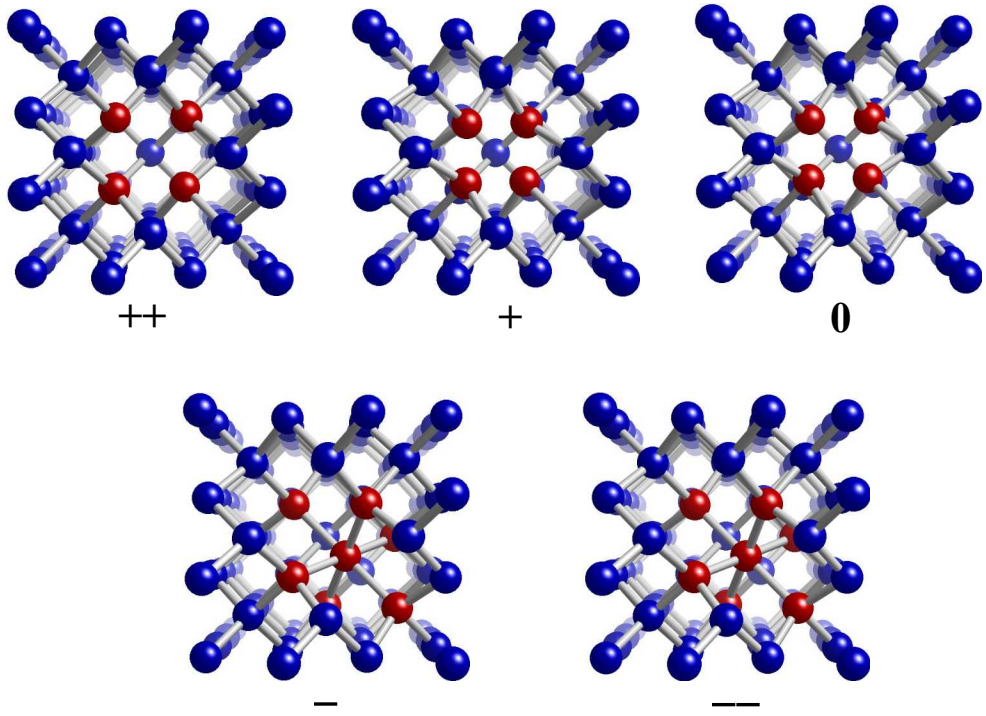


Convergence with respect to Brillouin zone sampling



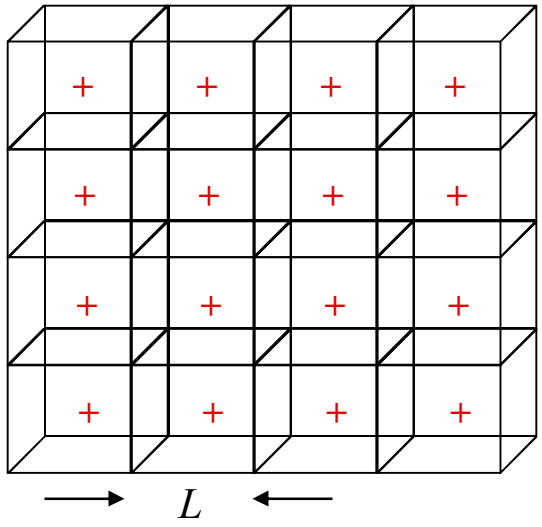
Changes in the formation energies beyond 64 sampling points are 1 meV

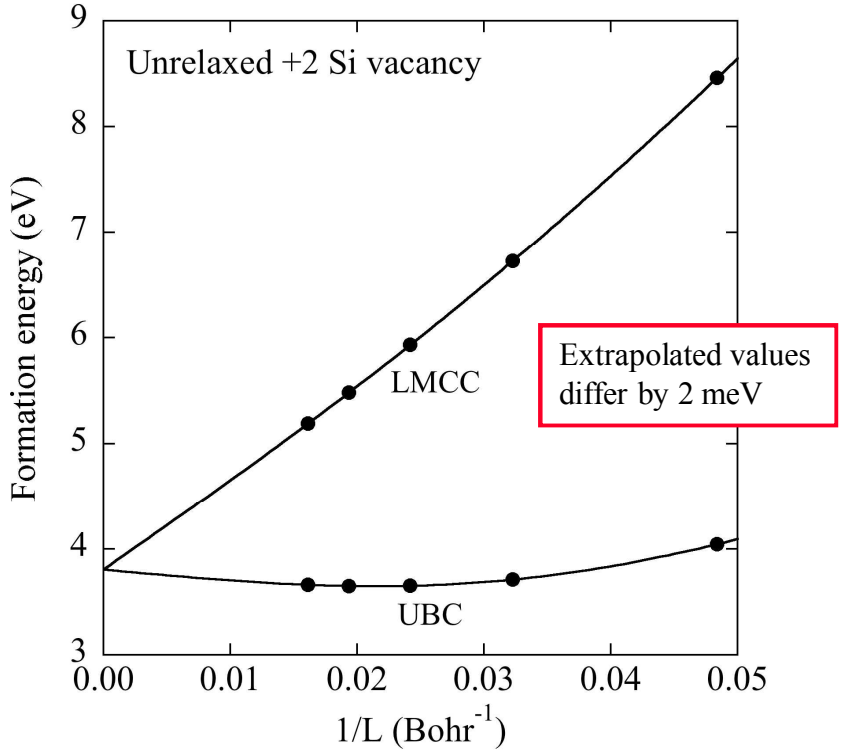
Convergence was explicitly checked for all structures. Examples shown here are relaxed vacancies in a 216-atom supercell using the LDA.



Elimination of supercell size effects

- Supercell size effects were removed by performing maximum-likelihood fits of results from a series of supercells. An example is shown below for an unrelaxed +2 vacancy in nominal 64-, 216-, 512-, 1000-, and 1728-atom supercells.
- Two methods were investigated to circumvent the divergence of the Coulomb energy: the uniform-background charge (UBC) method and the local-moment counter charge (LMCC) method.

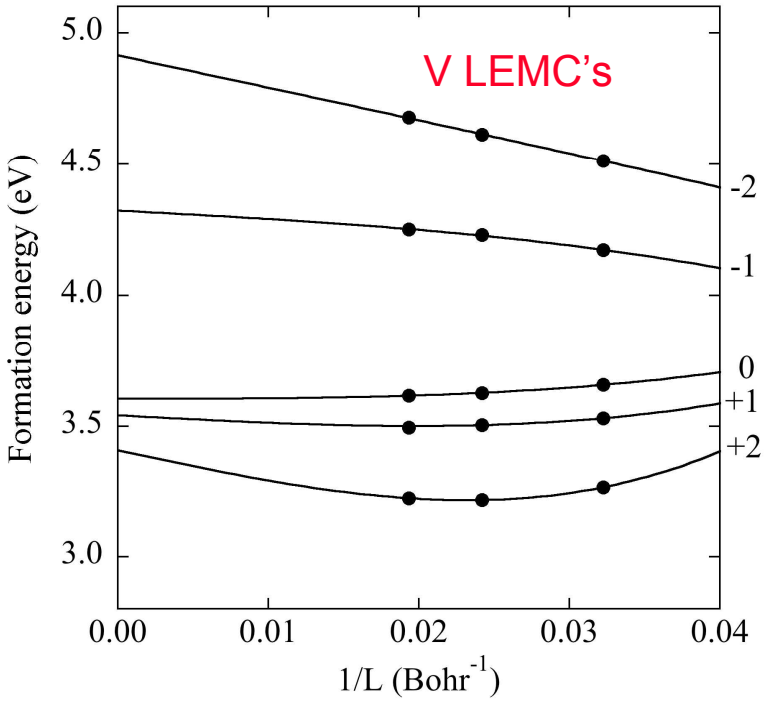


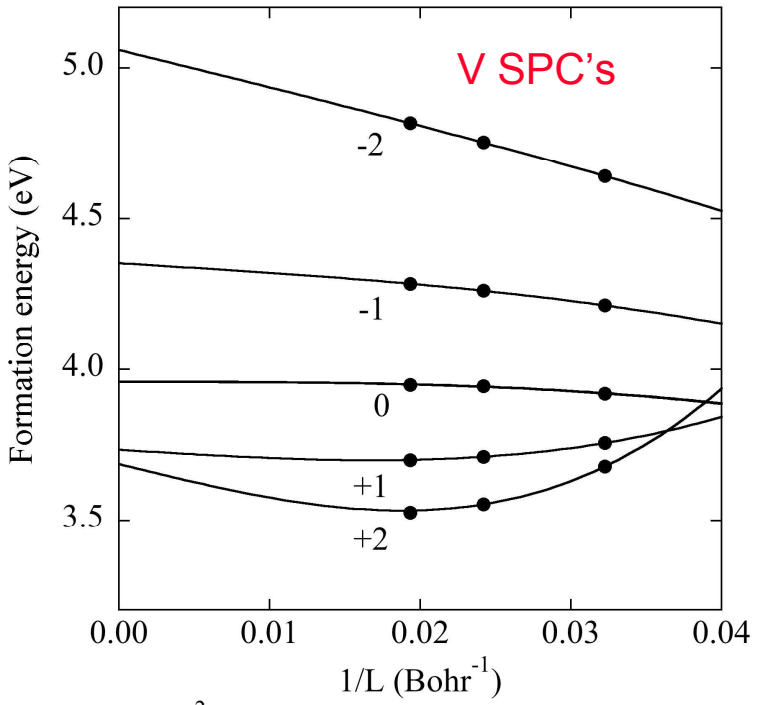


Fits are to : $E^{f}(L) = E^{f}(L \to \infty) + \frac{A_1}{L} + \frac{A_3}{L^3} + \frac{A_5}{L^5}$

Primary results from the calculations

- For the V, VV, and VP local-energy minimum configurations (LEMC's) and the V saddle-point configurations (SPC's), maximum likelihood fits were performed on formation energies from nominal 216-, 512-, and 1000-atom supercells.
- Results are shown for V LEMC's and SPC's fit to the expression below where α is the Madelung constant for a cubic lattice, q is the defect charge state, and ε is the (theoretical) static dielectric constant.

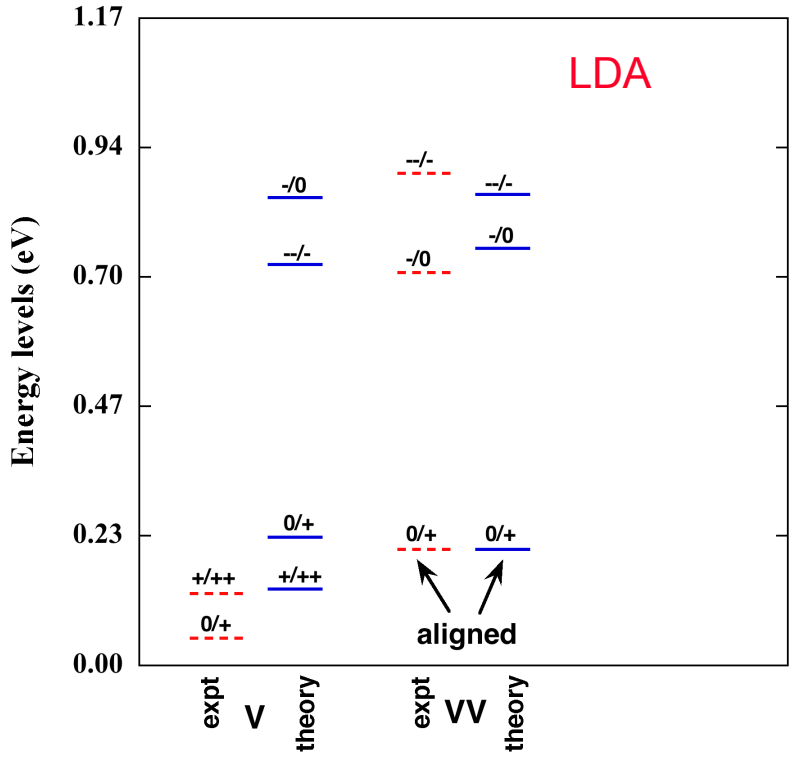


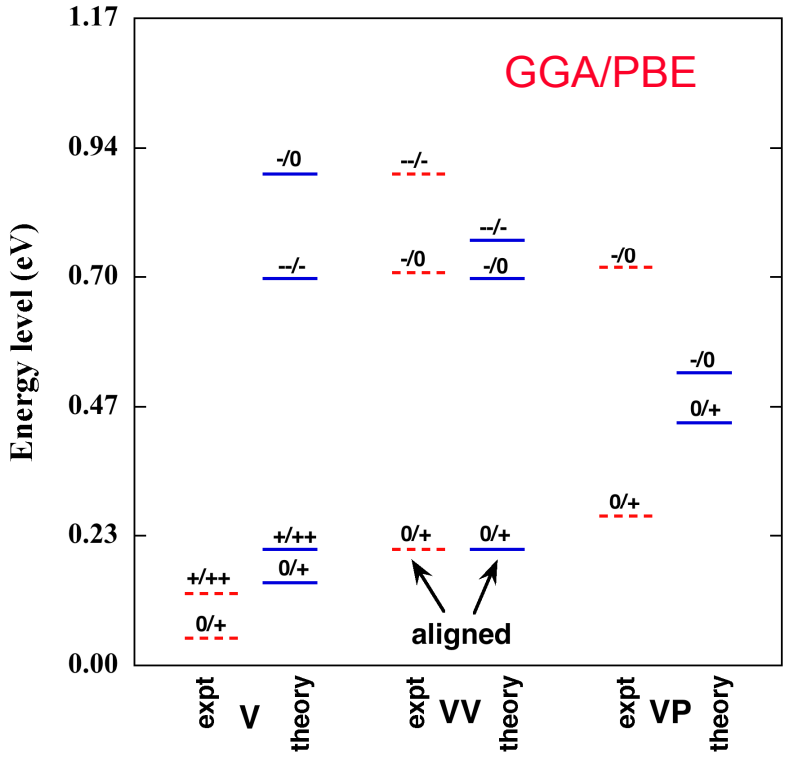


Fits are to : $E^{f}(L) = E^{f}(L \to \infty) - \frac{\alpha q^2}{\varepsilon L} + \frac{A_3}{L^3}$

Computed energy levels

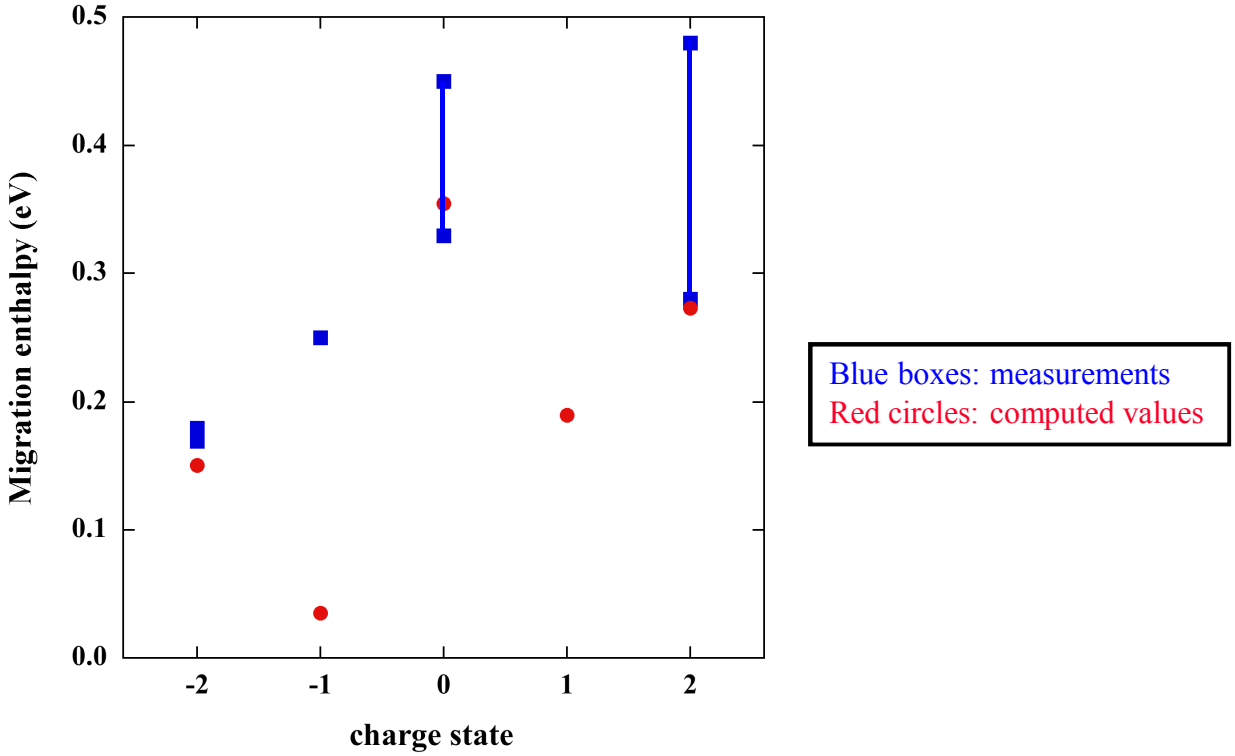
- Energy levels were obtained as differences in the extrapolated formation energies of charge states differing by 1.
- A value of Δ_{VBE} was selected to align the computed and measured 0/+ energy levels of VV.
- Note: 1) The GGA correctly displays negative-U behavior for V whereas the LDA does not.
  2) The computed and measured VP levels are quite different.





Computed V migration enthalpies

- GGA/PBE migration enthalpies were obtained as differences in the extrapolated formation energies of V SPC's and LEMC's.
- SPC's were identified using the dimer method and considering simple paths (one atom moving directly into the vacancy).
- Results for -2, 0, and +2 charge states are near or within the span of measurements.
  Result for -1 charge state is 0.21 eV from the one available measurement.
  No measurements available for +1 charge state.



Summary and collaborators

- Considerable progress was made in eliminating supercell size dependences and extending convergence, technical issues that are likely responsible for differences among previous DFT results in the literature
- Having resolved these technical issues then allows us to evaluate the underlying exchange-correlation functionals
- LDA vs. GGA/PBE:
  - The GGA energy levels of V display negative-U behavior whereas the LDA energy levels do not
  - The GGA energy levels of V and VV are within about 0.1 eV of the available measured values
  - The energy levels of VP do not agree well with measured values
- Collaborators:
  - Ryan Wixom: VV, VP, and V migration enthalpies
  - Normand Modine: removal of supercell size dependences

Basic information about Socorro

License
- Open source via a GNU General Public License
- Available free-of-charge from a publicly accessible web site

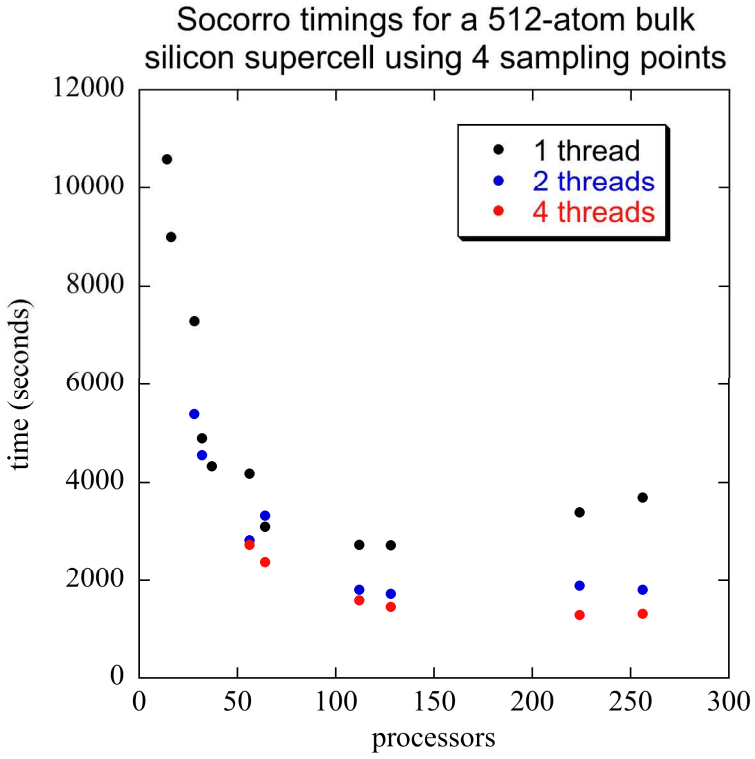
Code structure
- Written from scratch to utilize large-scale parallel computers
- Makes extensive use of Fortran 95 object-oriented capabilities
- Support for parallel communication, memory management, error reporting and polymorphic types

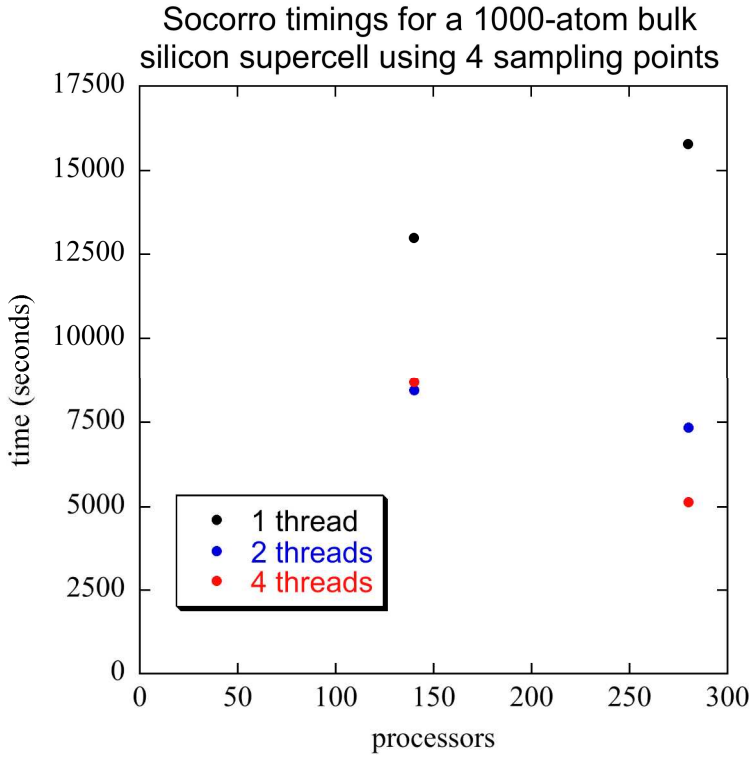
Base capabilities
- Plane wave basis
- Norm-conserving pseudopotential method
- Projector-augmented wave (PAW) method
- Multiple formulations of exchange and correlation
- Reciprocal and real-space projectors
- Atomic relaxation and molecular dynamics
- Transition-state finders

Currently configured for specific Sandia programs
- Energy levels and migration enthalpies of point defects in semiconductors
- Emphasis on high precision and formal code verification and validation

Socorro scaling on parallel computers

- We routinely perform structural relaxation in 1000-atom supercells using multiple sampling points.
- A recent addition to the code is parallelization across Brillouin-zone sampling points. The increase in speed when using this capability is shown below. (A thread is a group of processors working on one or more sampling points.)
- We expect to further improve parallelization.





Development underway or anticipated

Exact exchange DFT via an optimized effective potential

- A test-bed implementation exists for the norm-conserving pseudopotential method
- This year we will implement it in the production code and perform calculations for Sandia High Energy Density Science programs

Time-dependent DFT

- A highly capable implementation of TD-DFT exists in a non-production version
- This year we may implement it in the production code to support nanotube sensor research and development

PAW function database

- Recent upgrades to Natalie Holzwarth's atompaw code appear to give it the same capabilities as the code used to generate VASP PAW functions
- We are developing a semi-automated procedure for generating PAW functions having accurate scattering properties and requiring a modest basis size

Rubber sheeting method

- We are planning to implement the rubber sheeting method developed by Prof. Rick Matthews of Wake Forest University
- Tests by Matthews indicate that this technique can speed up atomic relaxation and molecular dynamics by a factor of about 4×

Comparison of features and capabilities

- VASP and Socorro
  - Y = yes
  - N = no
  - alpha = early stage
  - beta = middle stage
  - gamma = final stage
- Effort
  - N = none needed
  - L = 1-3 FTP-months
  - M = 5-7 FTP-months
  - H = 1-2 FTP-years
- NRL priority
  - L = low
  - M = medium
  - H = high
  - U = unknown

Feature or Capability	VASP	Socorro	Effort	NRL priority
Open source license	N	Y	N	U
User forum	Y	Y	N	H
Plane wave basis	Y	Y	N	H
Norm-conserving pseudopotential method	N	Y	N	U
Projector-augmented wave (PAW) method	Y	Y	N	H
Real-space projectors	Y	Y	N	M
Object-oriented modular structure	N	Y	N	U
k-point parallelization	N	Y	N	U
Parallel subspace diagonalization	Y	Y	N	U
PAW function database	Y	N	M-H	H
Linear response	alpha	N	H	M
Born effective charges	alpha	N	H	L
Piezoelectric tensor	alpha	N	H	L
Dielectric matrix	alpha	N	H	L
Interatomic force constants	alpha	N	H	L
Spin-polarization magnetism	Y	N	M	H
Non-collinear magnetism	Y	N	H	M
Spin-orbit coupling	Y	N	H	H
Structural relaxation	Y	Y	L	H
Transition-state finder	Y	Y	N	U
Molecular dynamics (MD)	Y	Y	N	H
Wavefunction extrapolation	Y	N	L-M	H
Non-zero charge states	Y	Y	N	U
Vibrational modes	Y	N	L	H
Stress tensor	Y	N	M	U
Electric fields	Y	N	L	M
Optical properties	beta	N	M	M
LDA+U	Y	N	M	M
Berry phase	Y	N	L	L
GW method	Y	N	H	L

Notes on selected capabilities…

PAW method: The PAW method allows a moderate plane wave basis to used for nearly all elements and allows for a systematic approach to the all electron limit. Socorro uses the formulation of PAW developed by Profs. Holzwarth and Matthews at Wake Forest University and implemented in their pwpaw code. We note that this is an aid to code verification in that results from Socorro and pwpaw can be compared.

Real-space projectors: Real-space projectors increase the speed of DFT calculations relative to reciprocal-space projectors by constraining the spatial extent of the projectors. Socorro uses the King-Smith scheme to optimize the real-space projectors whereas VASP uses a proprietary scheme that is not disclosed in the VASP manual nor is it published in a peer reviewed journal.

k-point parallelization: Socorro is able to update the wavefunctions from different Brillouin zone sampling points (k-points) in parallel. When employing this capability with large supercells, Socorro should be able to utilize on the order of 1000 processors efficiently.

PAW function database: VASP has a nearly complete database of proprietary PAW functions. Socorro does not currently have a PAW function database, but we are working to generate one using Prof. Natalie Holzwarth's atompaw code. Our approach is to try to develop an automated search routine. Results for Ga have so far been encouraging as we have developed ghost-free Ga PAW functions that have good scattering properties and require a cutoff of about 30 Ryd.

Linear Response: The implementation of linear response would be a significant extension of Socorro. Born effective charges, the piezoelectric tensor, the dielectric matrix, and interatomic force constants are applications of linear response. However, we note that linear response was implemented in an earlier code at Sandia and this implementation should be available for reference if a need for linear response arises.

Notes on selected capabilities…

Spin-polarization magnetism: Spin polarization is the key capability needed to treat magnetism and it should probably be added to Socorro in the near future. Considerable planning for its addition has already occurred and there are two major parts to the anticipated implementation: a modification of the code structure to accommodate two species of electrons (spin up and spin down), which is relatively straightforward due to the modular structure of Socorro, and coding of expressions for spin dependent exchange and correlation functionals, which could either be extracted from published papers or from another GPL code.

Non-collinear magnetism: This capability involves a major extension of a DFT code, but is relevant to only a limited set of problems. A compelling programmatic requirement and related funding would be needed to justify its implementation in Socorro. The modular structure of Socorro, however, would simplify the implementation if the need arises.

Spin-orbit coupling: There are a variety of ways to approximate spin-orbit coupling in a DFT code, ranging from simple post-processing corrections to a full solution of the Dirac equation. In VASP, the implementation of spin-orbit coupling seems to be an extension of non-collinear magnetism, and the comments given above apply.

Structural relaxation: VASP appears to have three relaxation algorithms: conjugate gradients, damped molecular dynamics, and RMM-DIIS. The last algorithm was noted by NRL staff and is a quasi-Newton relaxation algorithm that works well if the ions are initially close to their local minima, but fails badly if this is not the case. Socorro also has three relaxation algorithms implemented: steepest descents, conjugate gradients, and quenched minimization. We note that it is straightforward to add new relaxation algorithms to DFT codes since they are routines that take simple inputs (energy, forces, and perhaps history) from DFT calculations for fixed ion positions and output a new set of ion positions. In particular, published routines or routines in other GPL codes could be easily added to Socorro.

Notes on selected capabilities…

Transition-state finder: Transition-state finders search for saddle-point configurations of migrating species. Both Socorro and VASP implement the nudged elastic band and directed dimer methods. (These implementations were essentially performed by the same person: Prof. Graeme Henkelman of UT Austin.)

Molecular dynamics: VASP has three MD algorithms: NVE with a velocity Verlet algorithm, NVE with a leapfrog Verlet algorithm, and NVT with the temperature controlled using a Nosé thermostat. Socorro has four MD algorithms: NVE with a velocity Verlet algorithm, NVT with the temperature controlled through periodic rescaling of the velocities, NVT with the temperature controlled via a stochastic method due to Anderson, and NVT with the temperature controlled using the Hoover implementation of the Nosé thermostat. We note that it is straightforward to add new MD algorithms to DFT codes since they are routines that take simple inputs (energy, forces, and perhaps history) from DFT calculations for fixed ion positions and output a new set of ion positions and velocities. In particular, published routines or routines used in other GPL codes could be easily added to Socorro.

Wavefunction extrapolation: Wavefunction extrapolation refers to a transformation of the wavefunctions from one MD step to another (or one relaxation step to another) so as to reduce the number of subsequent updates needed to achieve self-consistency at the new ion positions. VASP uses a proprietary algorithm to do this. Socorro does not currently perform wavefunction extrapolation, but we are planning to implement the rubber sheeting method recently developed by Prof. Rick Matthews at Wake Forest University.

Non-zero charge states: In calculations for charged point defects using periodic boundary conditions, the Coulomb potential formally diverges. To circumvent this divergence, the charge of the point defect must be screened and the most common way to do this is to add a uniform background charge that neutralizes the defect charge. Both Socorro and VASP have this capability, however Socorro has an additional capability referred to as the local-moment counter charge method. These two techniques give very different formation energies for charged defects in a given supercell, but the same values when extrapolated to infinite supercell sizes.

Notes on selected capabilities…

Vibrational modes: This capability can be implemented either via linear response or finite displacements of all the ions in the supercell. VASP has the finite displacements implementation in version 4.6 and the linear response implementation in version 5.x (alpha stage). The finite displacements approach could be implemented fairly rapidly in Socorro since it only requires a high level routine that displaces ions and then updates the wavefunctions.

Stress tensor: VASP has the capability to compute the stress tensor in the PAW method, but Socorro does not. The derivation of the stress tensor used in VASP has not been published in a peer reviewed journal nor is it described in the VASP documentation. A derivation for the PAW method has recently become available in a preprint from a member of the ABINIT team and we have a copy of that preprint. This will serve as the starting point for the implementation of the stress tensor in Socorror.

Electric fields: A fully time dependent electric field has been implemented in Socorro as part of a time-dependent DFT implementation. If desired, it should be quite simple to add a static electric field to Socorro with an interface that avoids complexities of the time-dependent DFT implementation.

Optical properties: This post-processing capability is straightforward to implement in the approximate form used in VASP wherein local field effects are neglected.

LDA+U: A post-processing implementation of LDA+U based on the PAW occupancies, which seems to be what is implemented in VASP, would not be difficult to implement in Socorro. Although useful in some cases, this approach adds empirical corrections to DFT with questionable physical justification. We favor more systematic improvements in DFT such as the optimized effective potential formulation of the exact exchange functional. However, if a compelling programmatic need for LDA+U is identified, it could be implemented in Socorro.

Notes on selected capabilities…

Berry phase: Calculation of the Berry phase is a post-processing procedure that could be straightforwardly added to Socorro. This capability was implemented at Sandia in a code that preceded Socorro, and that implementation should be available for reference if needed.

GW method: Implementation of the GW method would be a significant extension of the Socorro codes post-processing capabilities. In general, we are more interested in improving the band gap in DFT calculations using exact exchange based approaches, which straightforwardly allow self-consistent calculations, finite electronic temperatures, and the evaluation of forces. However, we note that GW was implemented at Sandia in a code that preceded Socorro, and this implementation should be available for reference if a programmatic need for GW is identified.

Support for parallel communication

MPI calls are wrapped in overloaded functions:

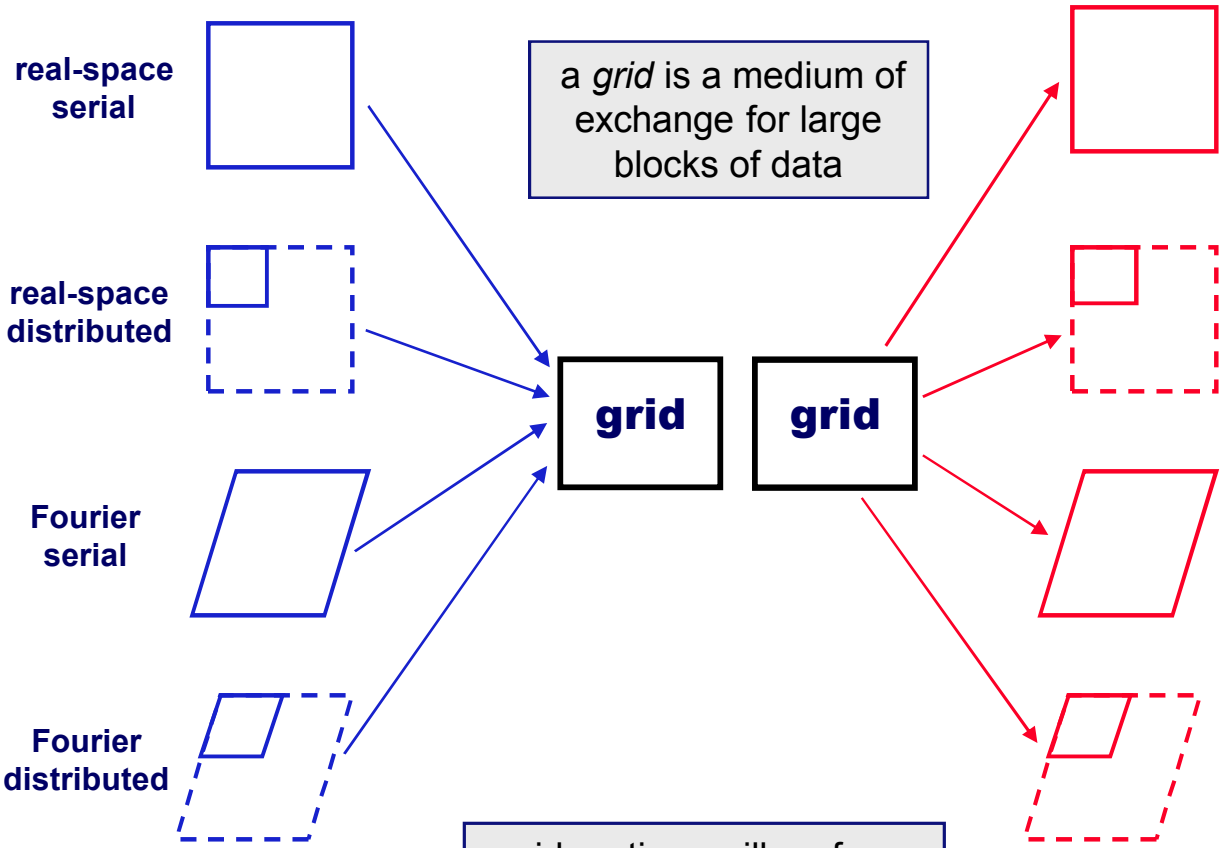
```
call broadcast(a(:))

call broadcast(b(:,:))
```

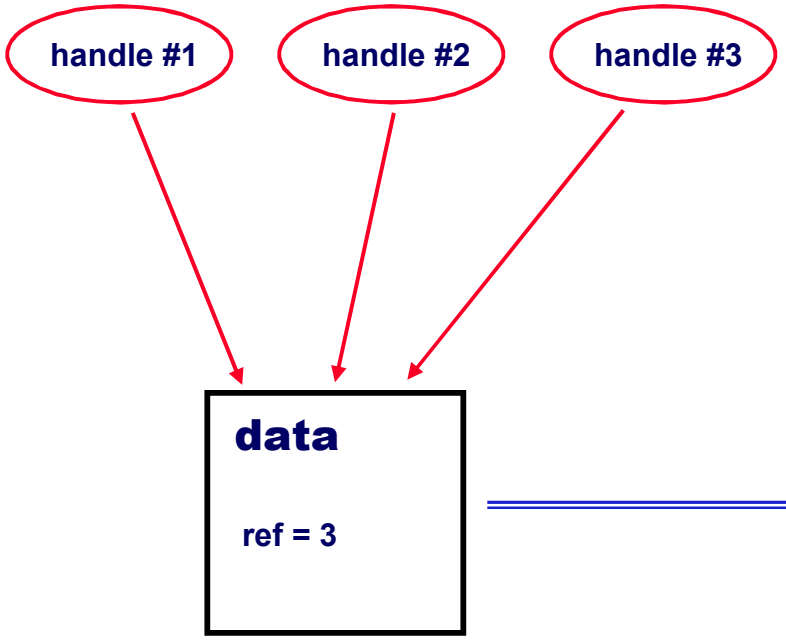
Overloading is used throughout Socorro

- **overloading means that the same name can be used for a set of related routines - the specific routine is determined from the arguments**
- **overloading has long been used in Fortran for intrinsic functions - the abs intrinsic, for example, can be called for any argument type**
- **overloading is available to programers in Fortran 90/95**
- **overloading makes higher-level programming easier by presenting a simplified interface to module routines**

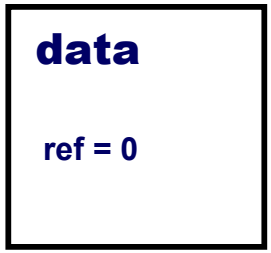
Support for parallel communication



Support for memory management



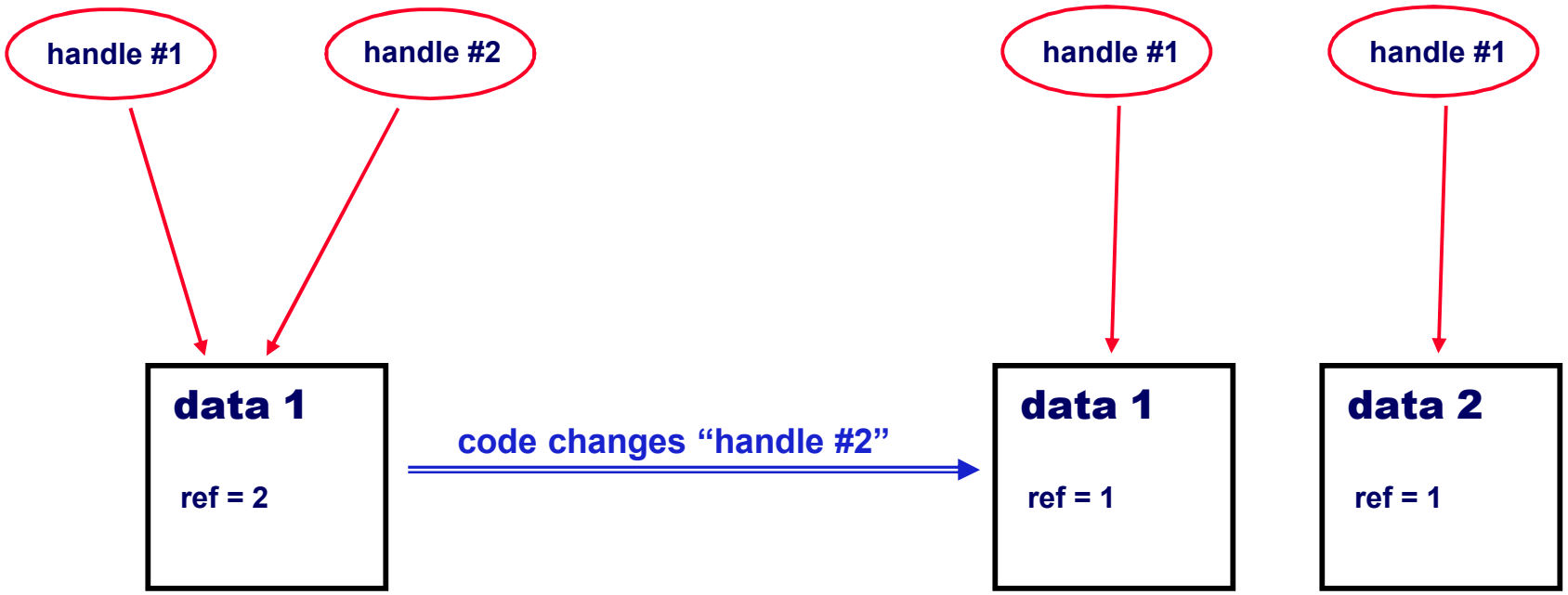
each data structure includes a set of routines that allocate memory for a new instance, manage the reference count, and deallocate memory when it's no longer needed



data is currently being used by three routines

reference count has dropped to zero, data is no longer needed and memory is therefore deallocated

Support for memory management



As long as data 1 is unchanged, routines simply get a pointer to it. A routine only gets a true copy (with separate memory) when it wants to change data 1.