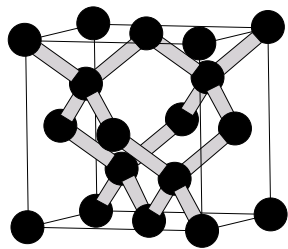


Energy Optimization of Many-Body Wave Functions: Application to Silicon Interstitial Defects

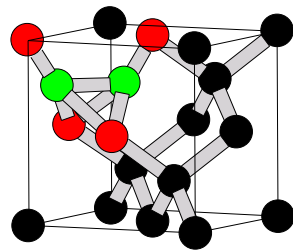
W. D. Parker, K. P. Driver, R. G. Hennig, J. W. Wilkins (Ohio State)
C. J. Umrigar (Cornell)

Support from DOE and NSF. Computing done at OSC, NERSC and NCSA.

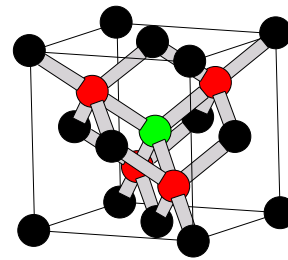
Silicon Single-Interstitial Defects



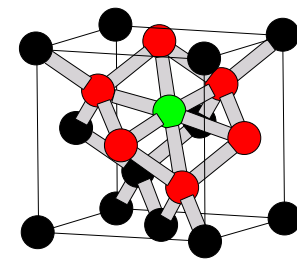
bulk



X



T



H

- Extended defects enhance dopant diffusion and limit device size.
- Single-interstitial defects nucleate extended defect precipitates.
- DFT fails for formation energies (K. Driver W46.1 room 349, 2:30pm)

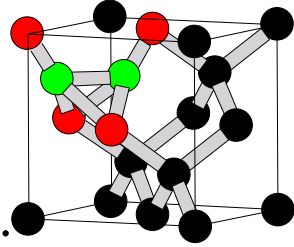
Formation Energy

$$E_{\text{form}}(\text{defect}) = E_{\text{total}}(\text{defect}) - \frac{N_{\text{atoms}}(\text{bulk}) + 1}{N_{\text{atoms}}(\text{bulk})} E_{\text{total}}(\text{bulk})$$

QMC produces accurate Si defect formation energies.

W.-K. Leung et al, Phys. Rev. Lett. **83**, 2351(1999)

Outline



In silicon single-interstitial defects,

- Covariance-based energy optimization lowers **total** energies:

$$\Delta E_{\text{total}}(\text{VMC}) \sim -0.06 \text{ eV/atom}$$

$$\Delta E_{\text{total}}(\text{DMC}) \sim -0.02 \text{ eV/atom}$$

resulting in less pseudopotential locality error

- Homogeneous 10-parameter Jastrow for $E_{\text{form}}(\text{DMC})$
accurate to $< 0.1 \text{ eV}$
- Finite size on $E_{\text{form}}(\text{DMC}) < 0.3 \text{ eV}$ for 8 atoms
 $< 0.1 \text{ eV}$ for 16 atoms
- Numerical approximation on $E_{\text{form}}(\text{DMC})$:
 $< 0.02 \text{ eV/atom}$

QMC produces accurate Si defect formation energies.

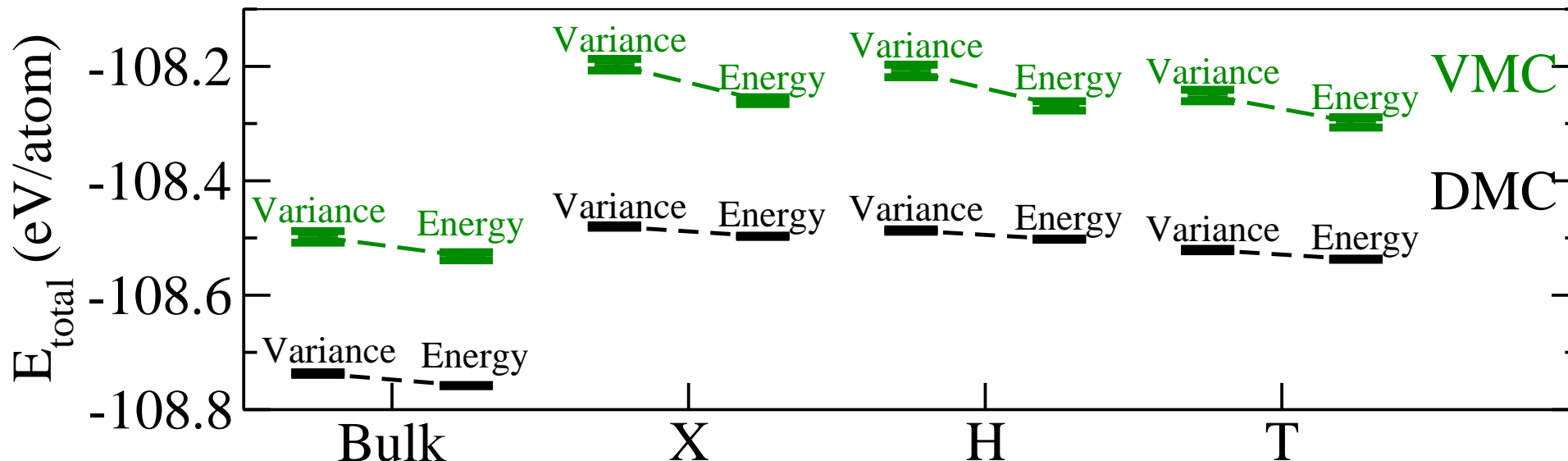
Wave Function Optimization in QMC

Variance Minimization–Fit

fit a finite set of Monte Carlo configurations to minimize the variance of the set

Energy & Variance Minimization–Newton

calculate gradient and Hessian using covariances and take Newton step



Fast convergence of covariance-based method

Lower energy for energy-minimized wave functions

Lower E_{total} (DMC) means less pseudopotential locality error

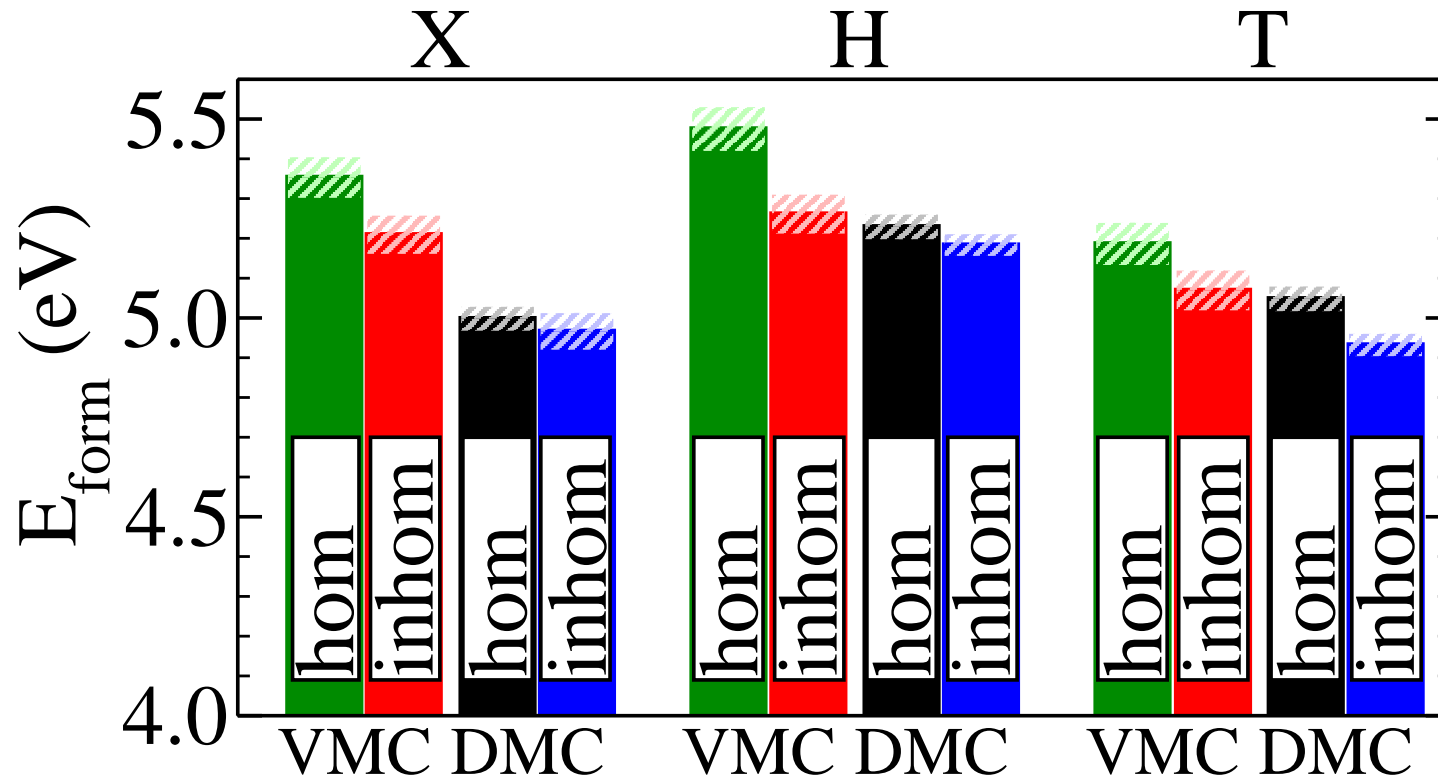
(C. Umrigar V27.2 room 324 11:27am - better optimization methods)

C.J. Umrigar and C. Filippi, Phys. Rev. Lett. **94**, 150201 (2005).

Jastrow Factor in QMC Calculations

- exponential of two 5th-order polynomials of e-e and e-n separation (9 free parameters)
- spherical cut off radius
- modify e-n Jastrow around defect atoms to test accuracy

Homogeneous vs. Inhomogeneous Electron-Nucleus Jastrow

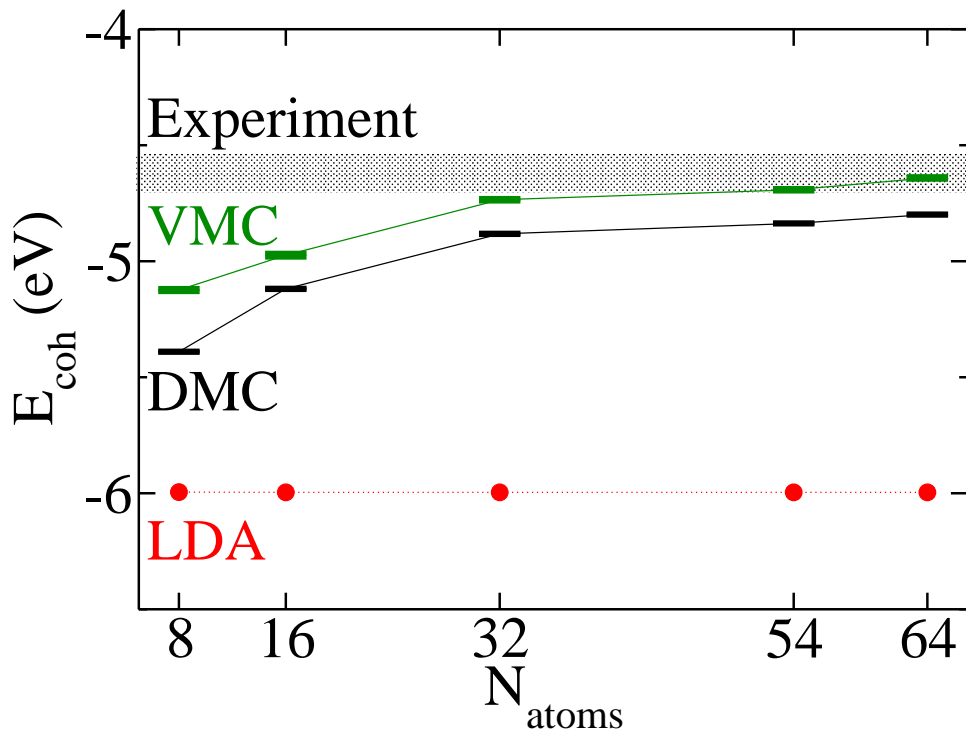


Inhomogeneous Jastrow: $\Delta E_{\text{form}}(\text{DMC}) < 0.1 \text{ eV}$

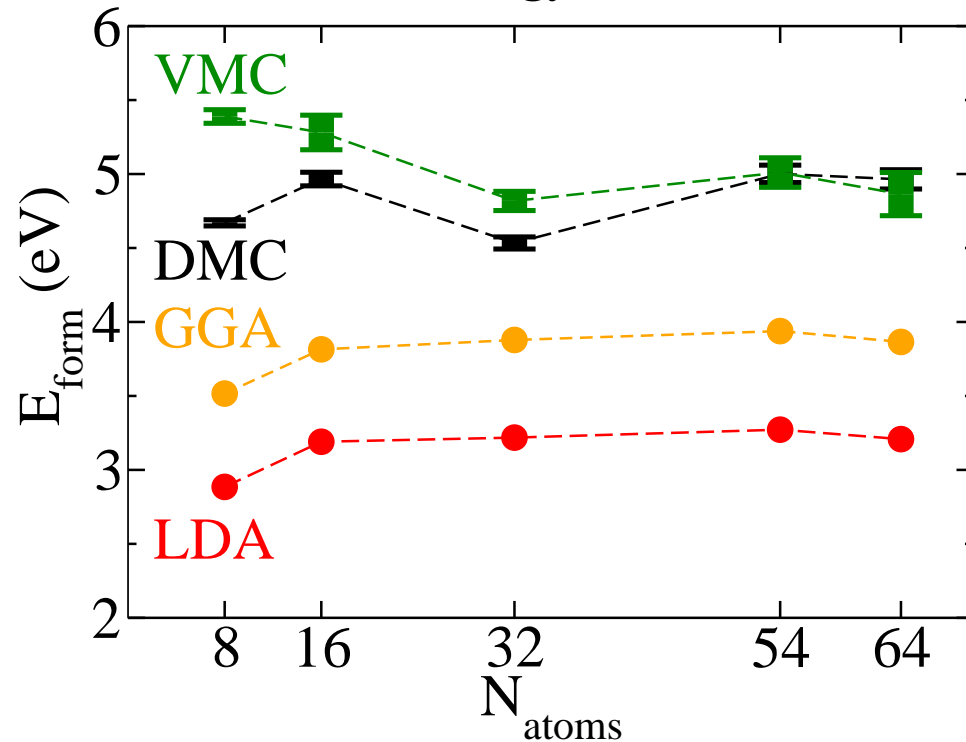
Homogeneous Jastrow: accurate for $E_{\text{form}}(\text{DMC})$ to $< 0.1 \text{ eV}$

Simulation-Cell Finite-Size Effects in QMC

Cohesive energy of silicon



Formation energy of the X defect



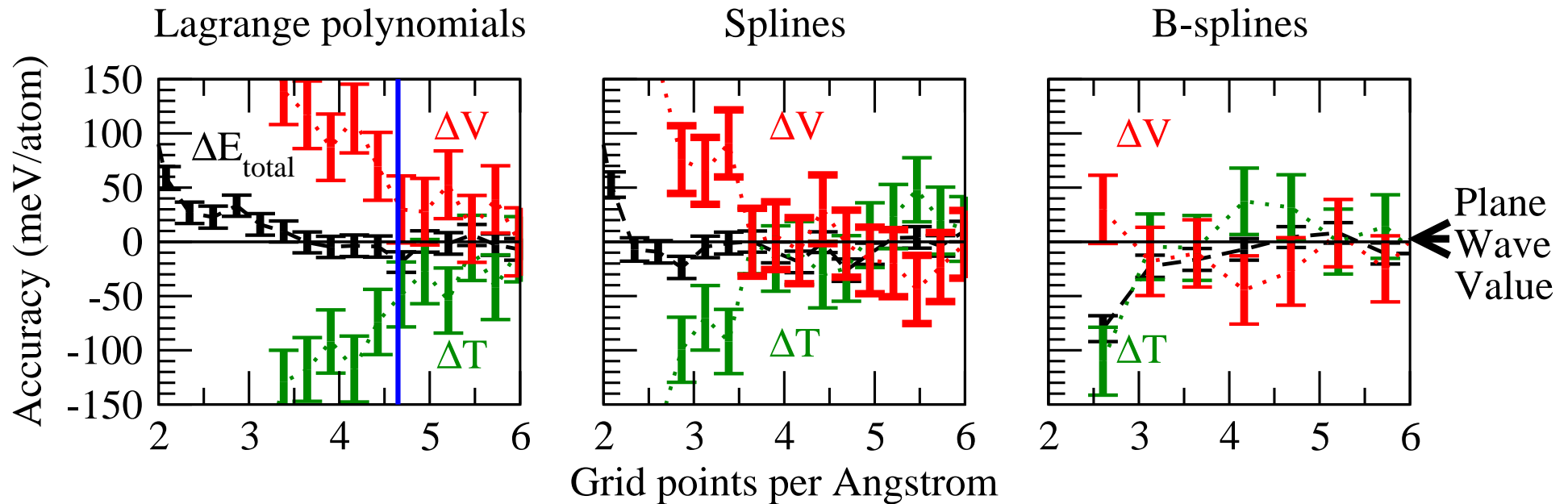
Finite-size effect < 0.3 eV for 8-atom $E_{\text{form}}(\text{DMC})$

< 0.1 eV for 16-atom $E_{\text{form}}(\text{DMC})$

Approximation of the Orbitals in the Slater Determinant

Plane-wave sums approximated piecewise by cubic polynomials

Approximation is $O(N_{\text{atoms}})$ faster than plane waves



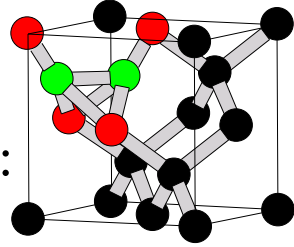
- B-splines use less memory, get T and V ($\Rightarrow \vec{\nabla}\phi$ & $\nabla^2\phi$) better than splines and Lagrange polynomials
- Splines and Lagrange polynomials run faster than B-splines

Numerical approximation on E_{total} : < 0.02 eV/atom

Williamson et al, PRL **89**, 246406 (2001).

Alfè and Gillan, PRB **70**, 161101(R) (2004).

Conclusions



In silicon single-interstitial defects,

- Covariance-based energy optimization lowers **total** energies:

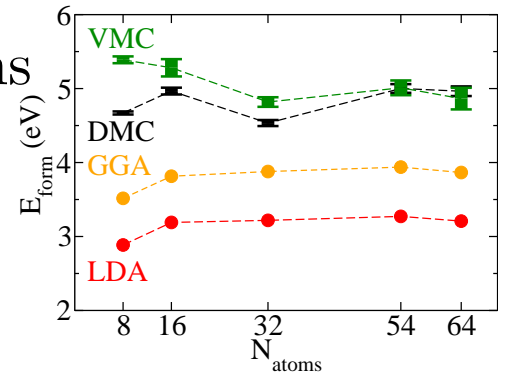
$$\Delta E_{\text{total}}(\text{VMC}) \sim -0.06 \text{ eV/atom}$$

$$\Delta E_{\text{total}}(\text{DMC}) \sim -0.02 \text{ eV/atom}$$

resulting in less pseudopotential locality error

- Homogeneous 10-parameter Jastrow for $E_{\text{form}}(\text{DMC})$
accurate to $< 0.1 \text{ eV}$

- Finite size on $E_{\text{form}}(\text{DMC}) < 0.3 \text{ eV}$ for 8 atoms
 $< 0.1 \text{ eV}$ for 16 atoms



- Numerical approximation on $E_{\text{form}}(\text{DMC})$:
 $< 0.02 \text{ eV/atom}$

QMC produces accurate Si defect formation energies.

Methods of Numerical Approximation

Lagrange polynomials

- Interpolate through control points
- Approximate ϕ , $\vec{\nabla}\phi$ & $\nabla^2\phi$ separately
- Evaluate $\phi_{\text{Lagr}}(\vec{x})$, $\vec{\nabla}\phi_{\text{Lagr}}(\vec{x})$ & $\nabla^2\phi_{\text{Lagr}}(\vec{x})$ each using 64 points

Splines

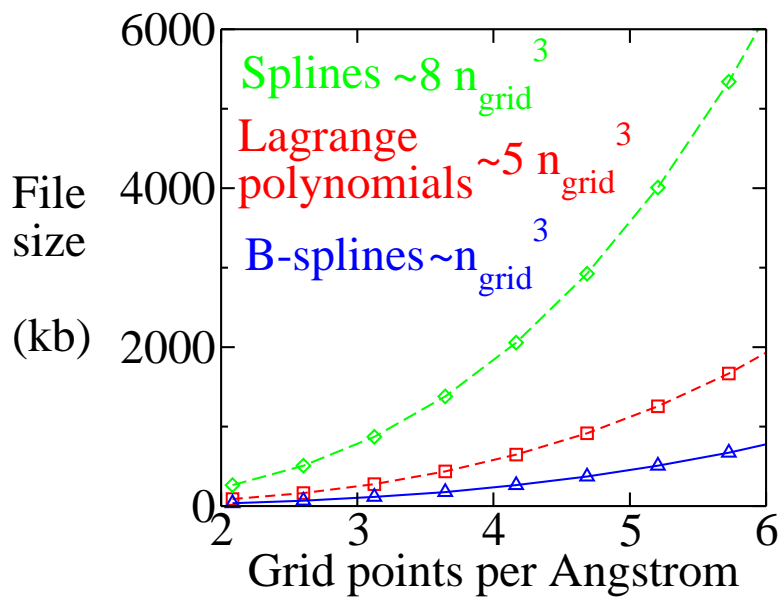
- Interpolate through control points
- Guaranteed second derivative continuity
- Evaluate $\phi_{\text{spl}}(\vec{x})$ using 8 points
- Calculate $\vec{\nabla}\phi(\vec{x})$ & $\nabla^2\phi(\vec{x})$ from $\phi_{\text{spl}}(\vec{x})$

B-splines

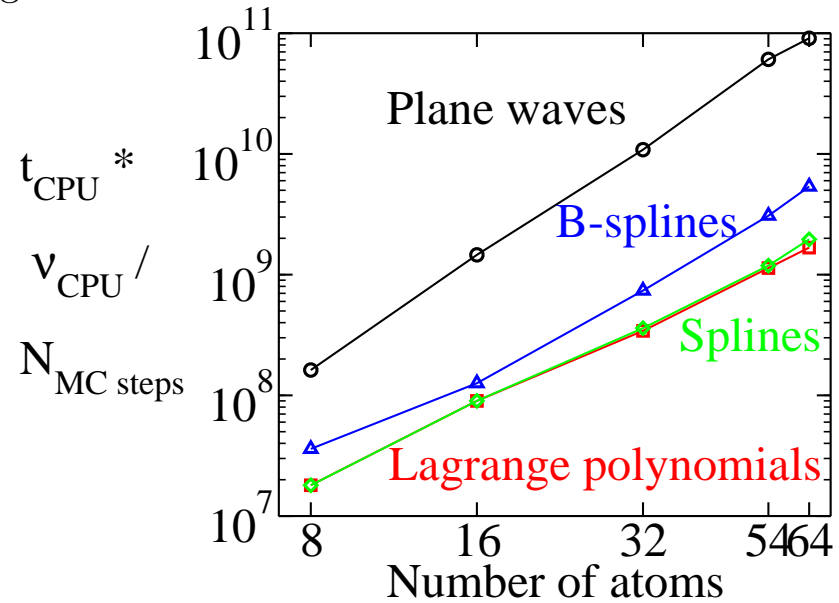
- Do **not** interpolate through control points
- Guaranteed second derivative continuity
- Evaluate $\phi_{\text{Bspl}}(\vec{x})$ using 64 points
- Calculate $\vec{\nabla}\phi(\vec{x})$ & $\nabla^2\phi(\vec{x})$ from $\phi_{\text{Bspl}}(\vec{x})$

Efficiency of Different Orbital Approximation Methods

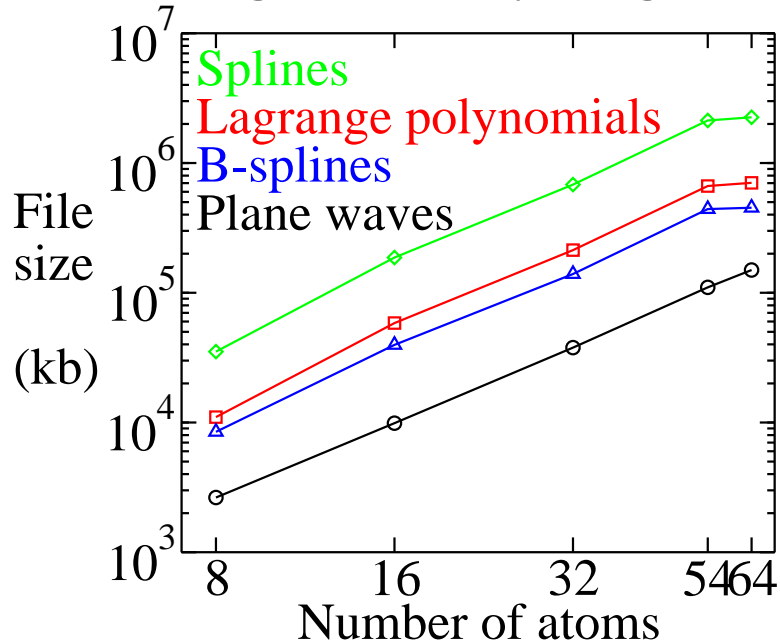
Scaling of memory usage with N_{grid}



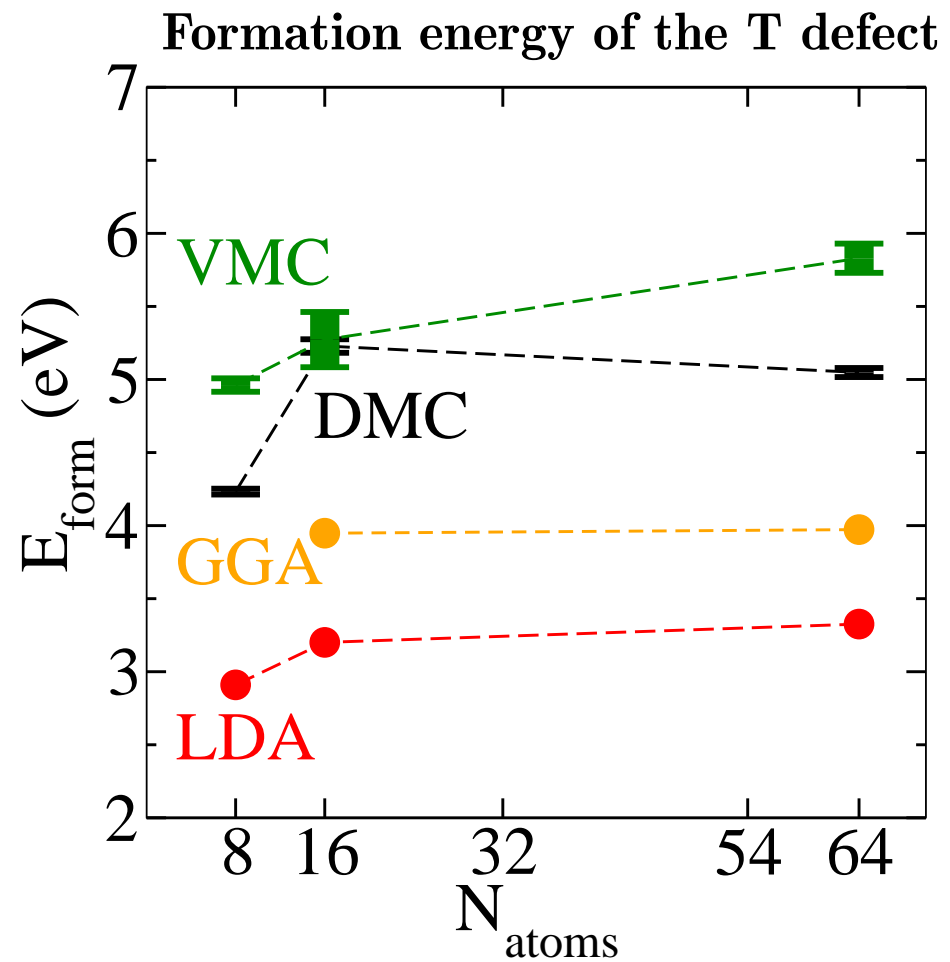
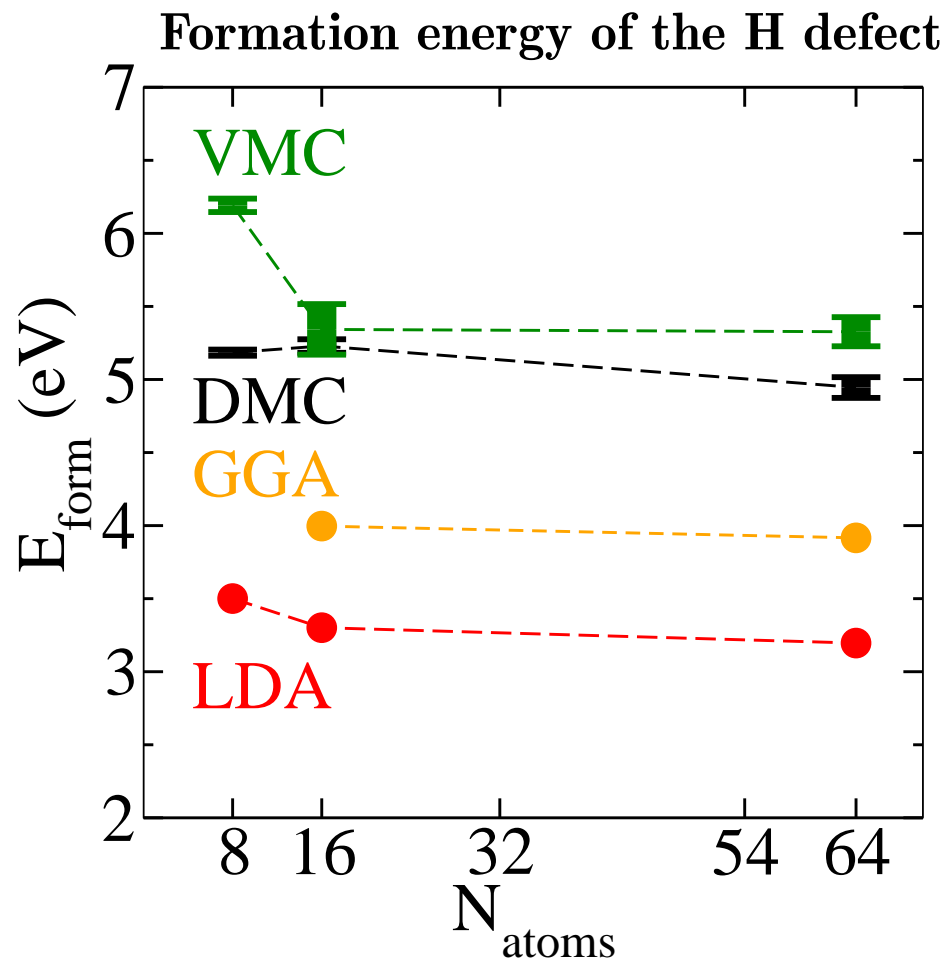
Scaling of computing time with N_{atoms}



Scaling of memory usage with N_{atoms}

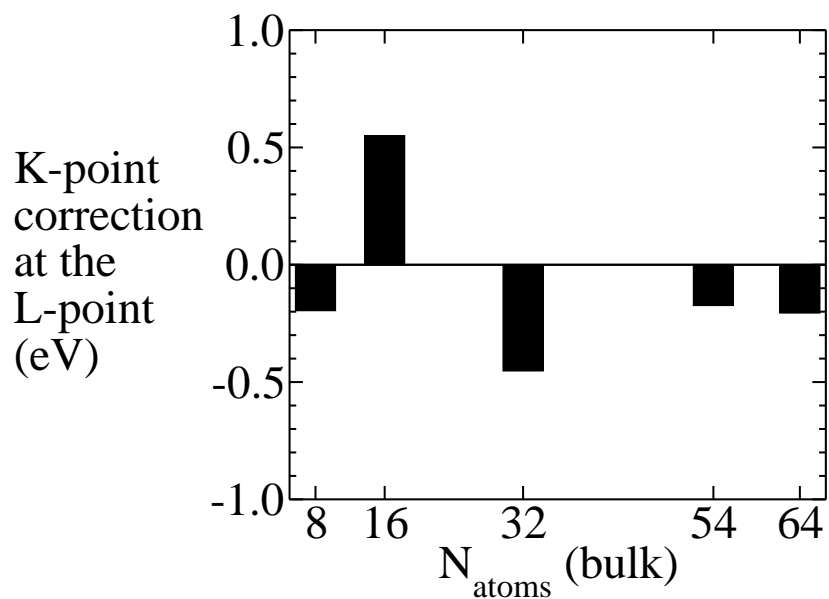


Simulation-Cell Finite-Size Effects on H and T Defects



K-point Correction to the Formation Energies

K-point correction
to the X defect formation energy



Comparison of corrected and uncorrected
X defect DMC formation energies

