

Diffusion Monte Carlo Formation Energies of Silicon Self-Interstitial Defects

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DMC and DFT: How well are they doing?

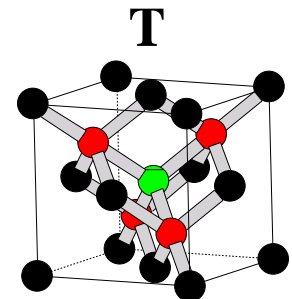
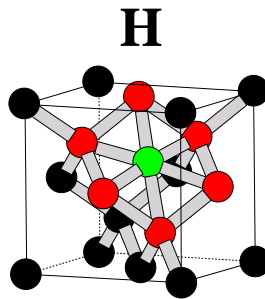
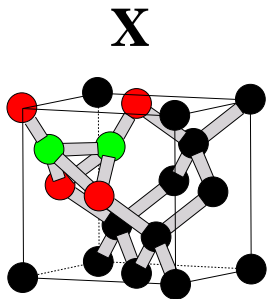
| Silicon: | Cohesive Energy* (eV) | Melting Temp. [1] |
|------------|-----------------------|-------------------|
| Experiment | 4.67 | 1685 K |
| DMC | 4.68(1) | |
| GGA (PW91) | 4.59 | 1492 K |
| LDA | 5.28 | 1300 K |

*includes 60 meV zero point energy

- DFT has room for improvement

DMC may have potential to improve on DFT

- Test Case: Silicon self-interstitial defects
- DMC and DFT calculations of single-, di-, and tri-interstitial formation energies give mixed results.



- DMC and DFT were found to disagree by 1 to 1.5 eV on single-interstitial defect energies in 1999 [2].

[1] D. Alfè and M. J. Gillan. Physical Review B 68, 205212 (2003).

[2] W. K. Leung, R. J. Needs, G. Rajagopal, S. Itoh and S. Ihara, Phys. Rev. Lett. 83, 2351 (1999).

Quantum Monte Carlo Method

Trial Wave Function and Jastrow Factor

$$\Psi_T = \underbrace{\mathcal{D}^\uparrow \mathcal{D}^\downarrow}_{\text{Slater determinant}} \times \underbrace{\mathcal{J}(r_i, r_j, r_{ij})}_{\text{Jastrow factor}}$$

Density-Functional Calculations

- Use J.L. Martin's CPW2000 and VASP

Variance Minimization

- Optimize Jastrow by variance minimization with Levenberg-Marquardt

Diffusion Monte Carlo

- Stochastic method of solving many-body Schrödinger equation
- Projection of ground state
- Defect in 64-atom cell takes 6,000 cpu hours and 4GB per processor

Approximations

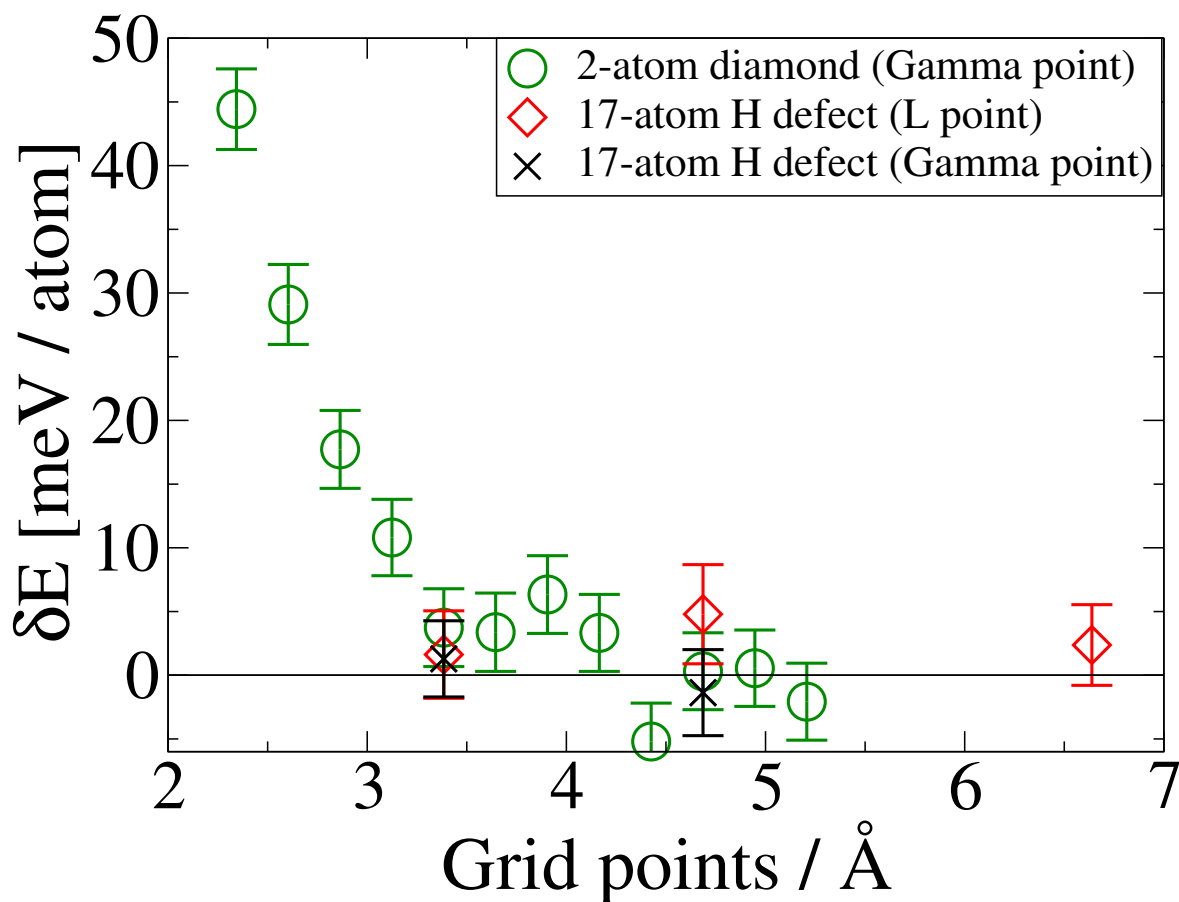
Controlled

- Statistical (increase MC steps)
- Finite-size (larger systems)
- Time-step (smaller time step)
- Population control (more walkers)
- Grid-size (decrease grid spacing)

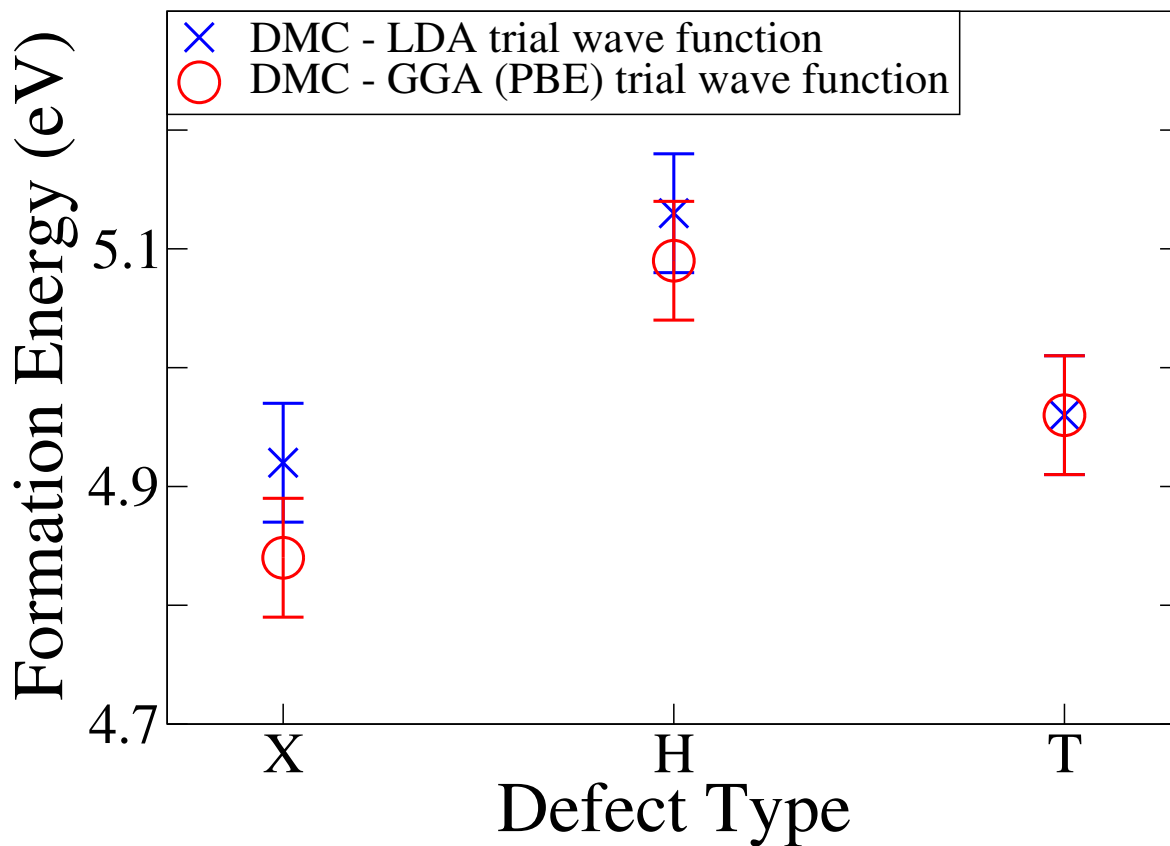
Uncontrolled

- Pseudopotential (not checked yet)
- Pseudopotential-locality (not checked yet)
- Fixed node

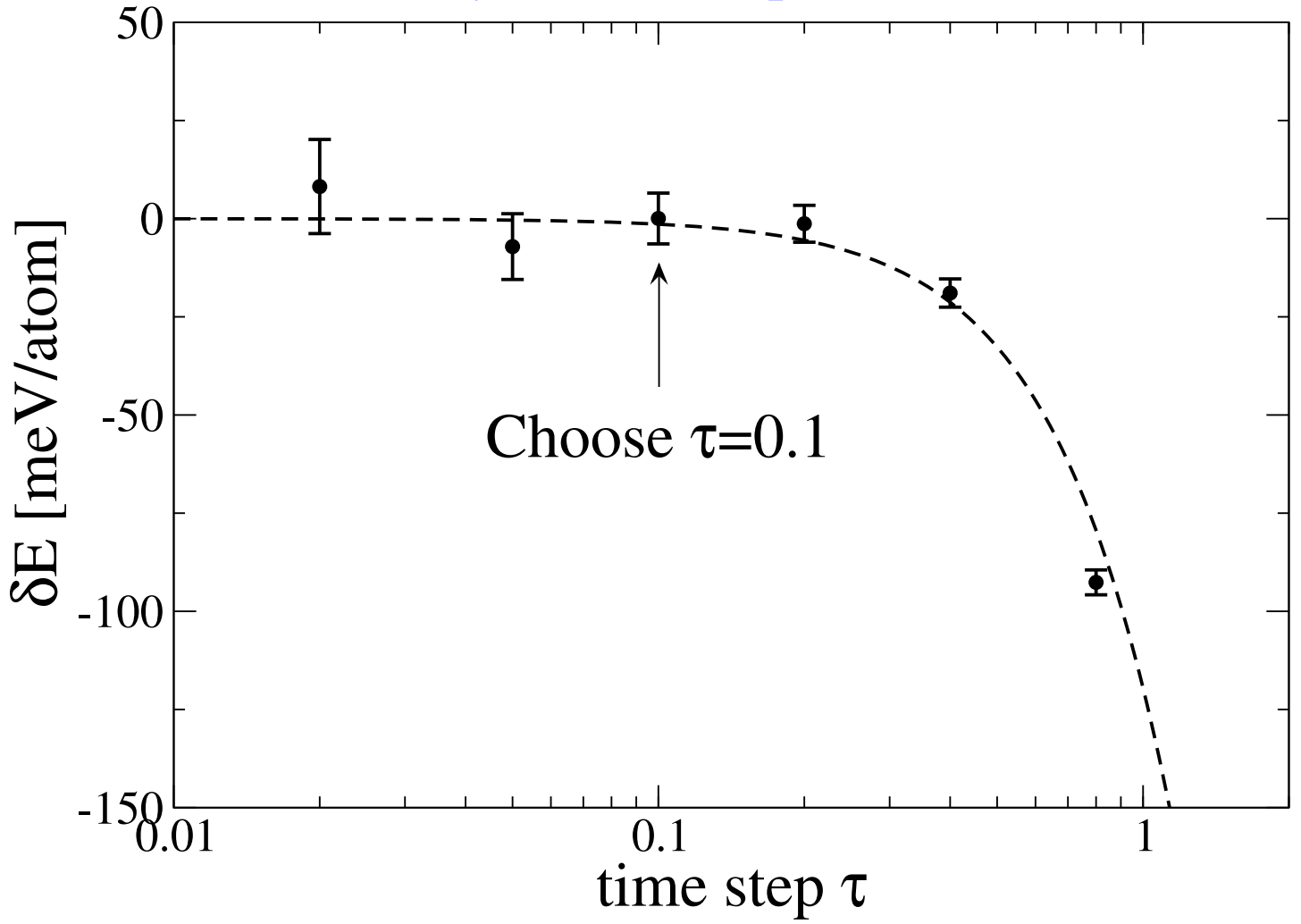
Comparison of Numerical and Analytic Orbitals in QMC



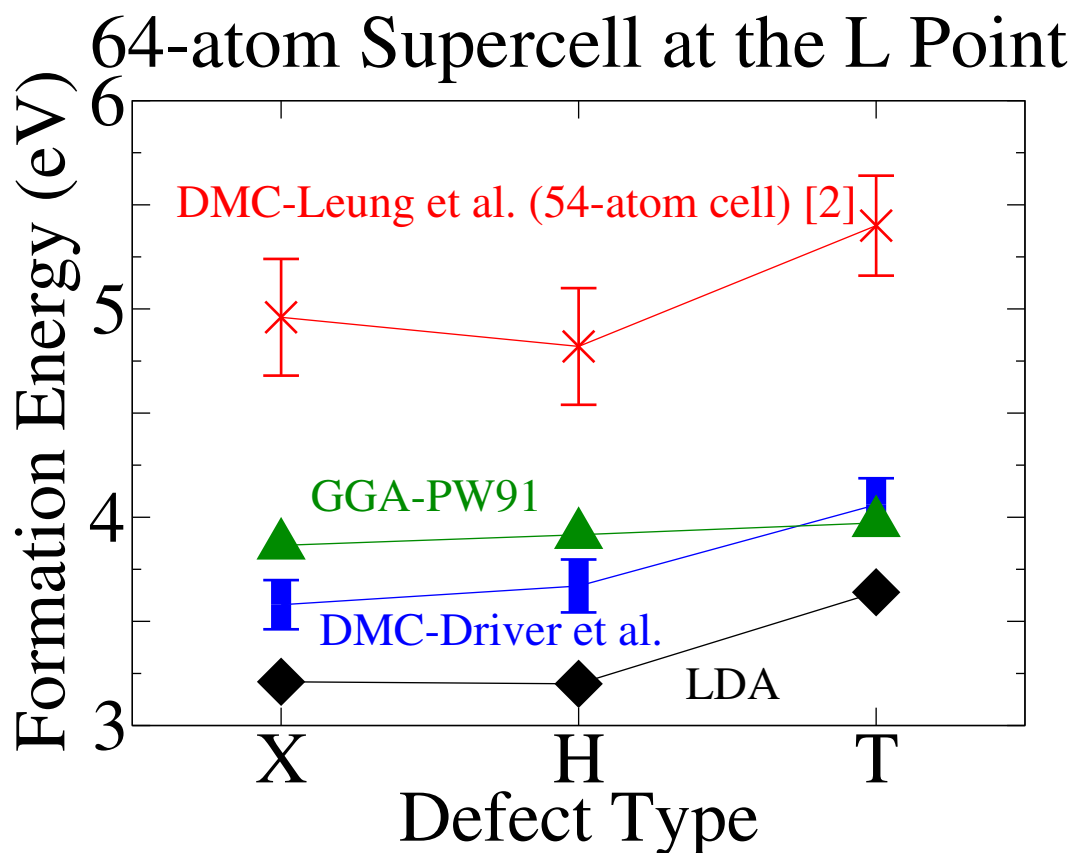
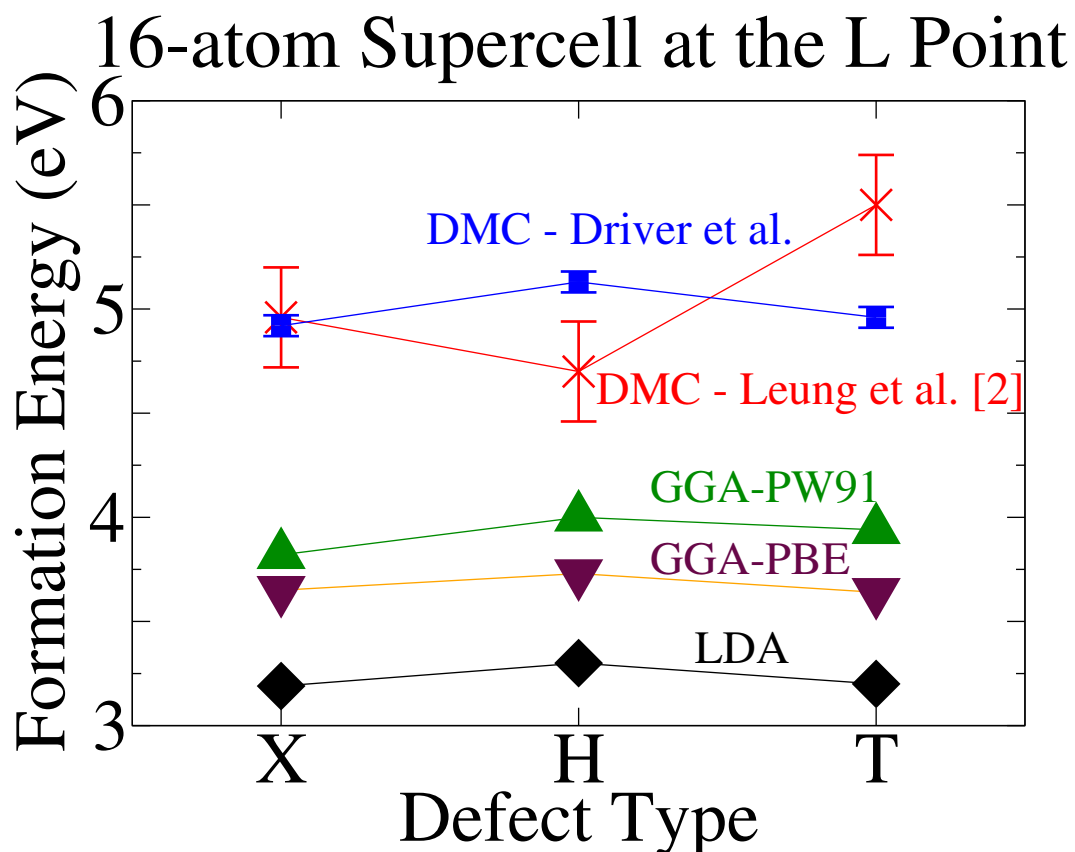
Fixed Node Error Study : LDA vs. GGA trial wave function
DMC formation energies (16-atom cell, L-point)



Study of time-step Error

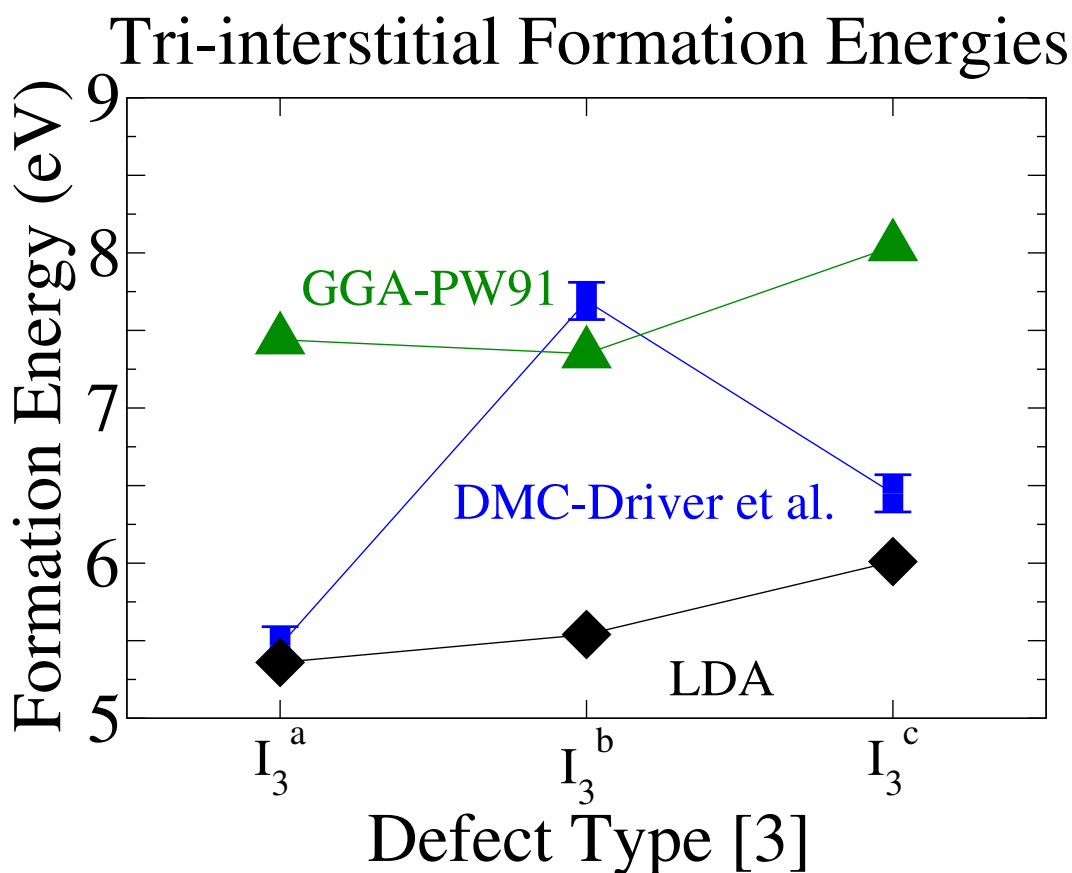
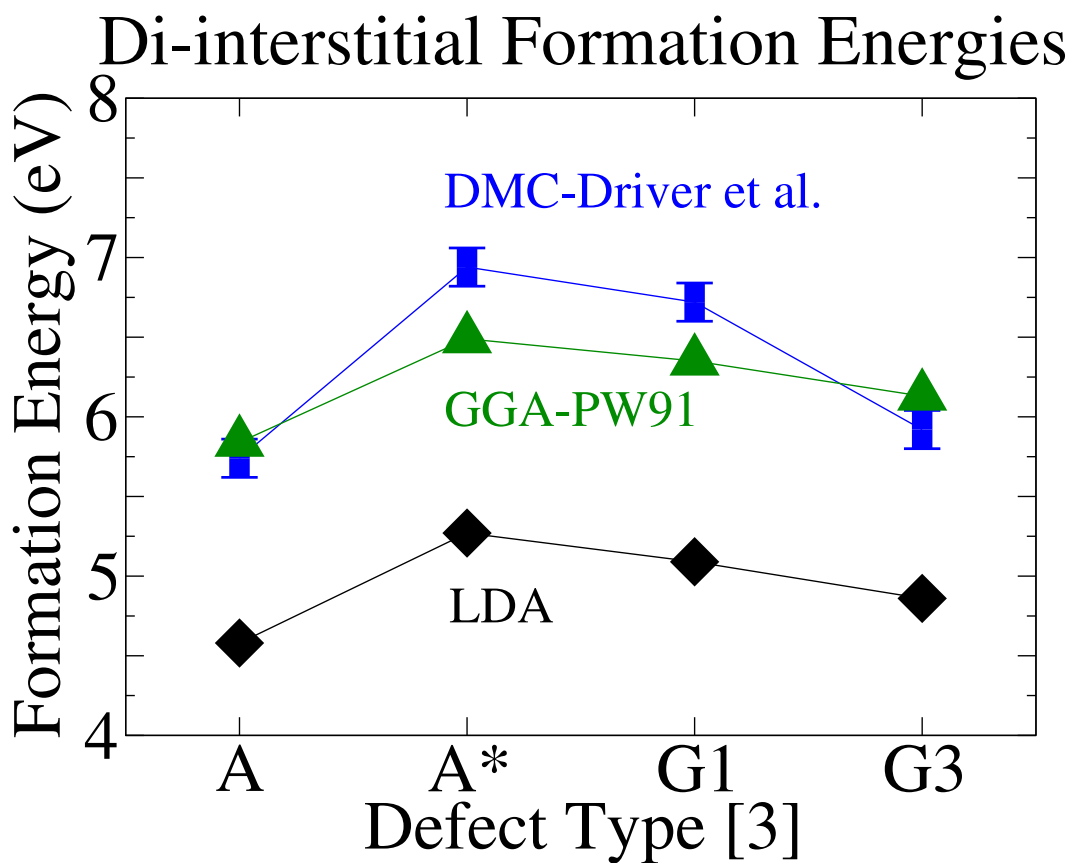


Silicon Single-interstitial Formation Energies



- 16-atom cell formation energies agree with Leung et al.
- Preliminary 64-atom cell results lie near DFT results

Di and Tri-interstitials (64-atom cells, L-point)



- Di- and Tri-interstitial formation energies also lie near DFT values.

Conclusions

- DMC energies disagree with DFT by about 1 to 1.5 eV for 16-atom cell, single-interstitial defect energies. (Agrees with results by Leung et al.)
- Our DMC energies for all larger supercell calculations are in better agreement with DFT.
- Since Leung et al. have observed the large 1-1.5eV difference between DMC and DFT in 54-atom cells, we consider our results to be in a very preliminary state until we investigate our calculations further.
- Future work: 54-atom cell, different pseudopotential, new minimization by Umrigar and Filippi [4]
- Our interests lie in trying to understand discrepancies between DMC and DFT and finding an accurate exchange-correlation functional.

[4] C. J. Umrigar and Claudia Filippi, arXiv/cond-mat/0412634 (2004).
(Cyrus discussed this work in Focus Session A32 on Monday, March 21, 2005)