

# Quantum Monte Carlo Benchmarks Density Functionals: Si Defects

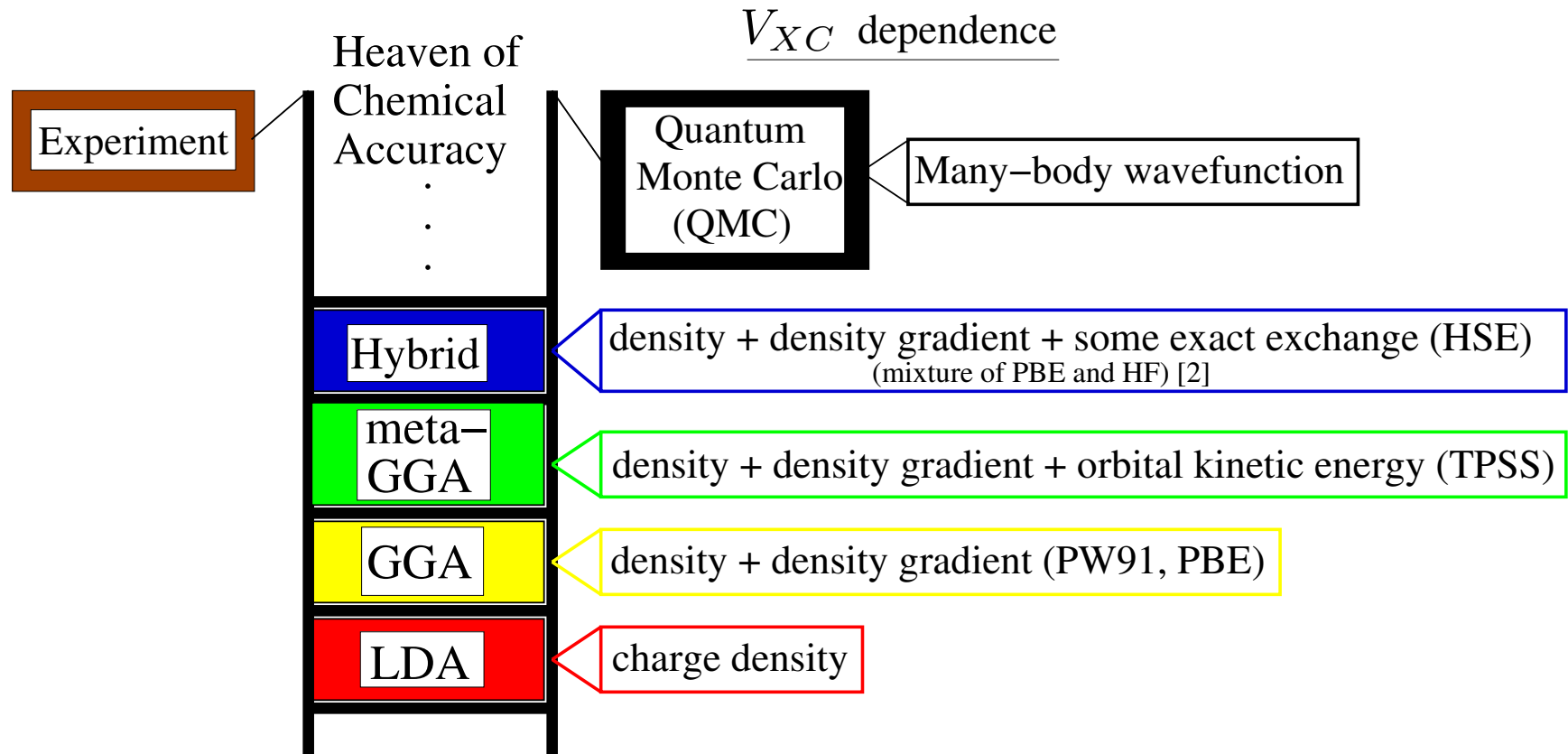
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“Jacob’s Ladder” of  $E_{XC}$  approximations in Density Functional Theory (DFT) [1]:

$$H_{DFT} = T + V_{Hartree} + V_{XC}[n, \dots]$$

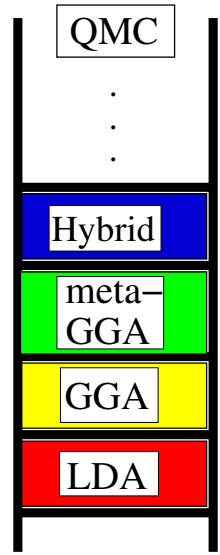


[1] J. P. Perdew *et al.* “Climbing the Density Functional Ladder.” Phys. Rev. Lett. 91, 146401 (2003).

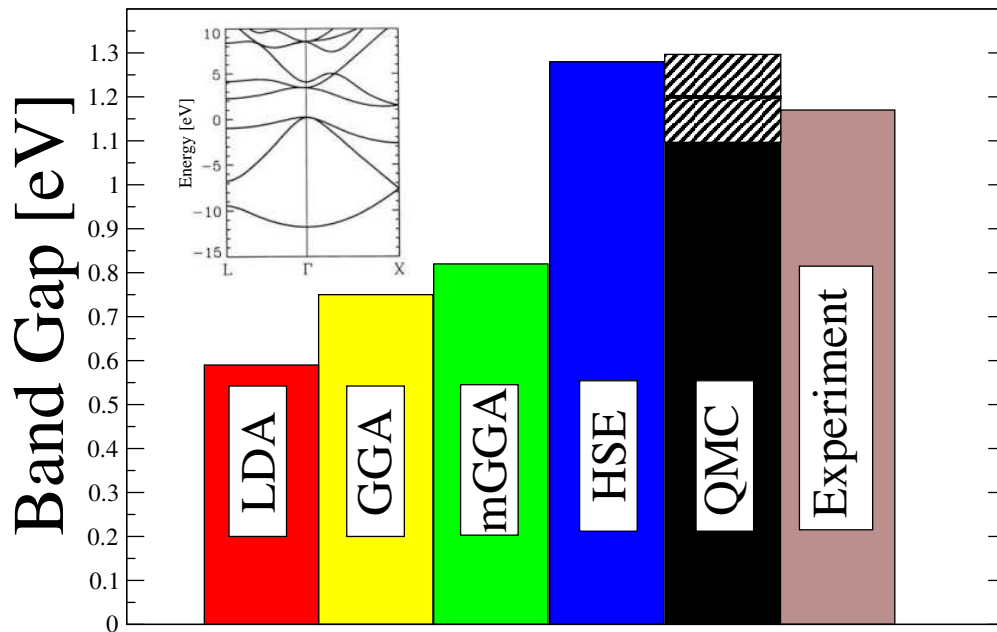
[2] J. Heyd and G. Scuseria, J. Chem. Phys. 120, 7274 (2004).

# Silicon is Important

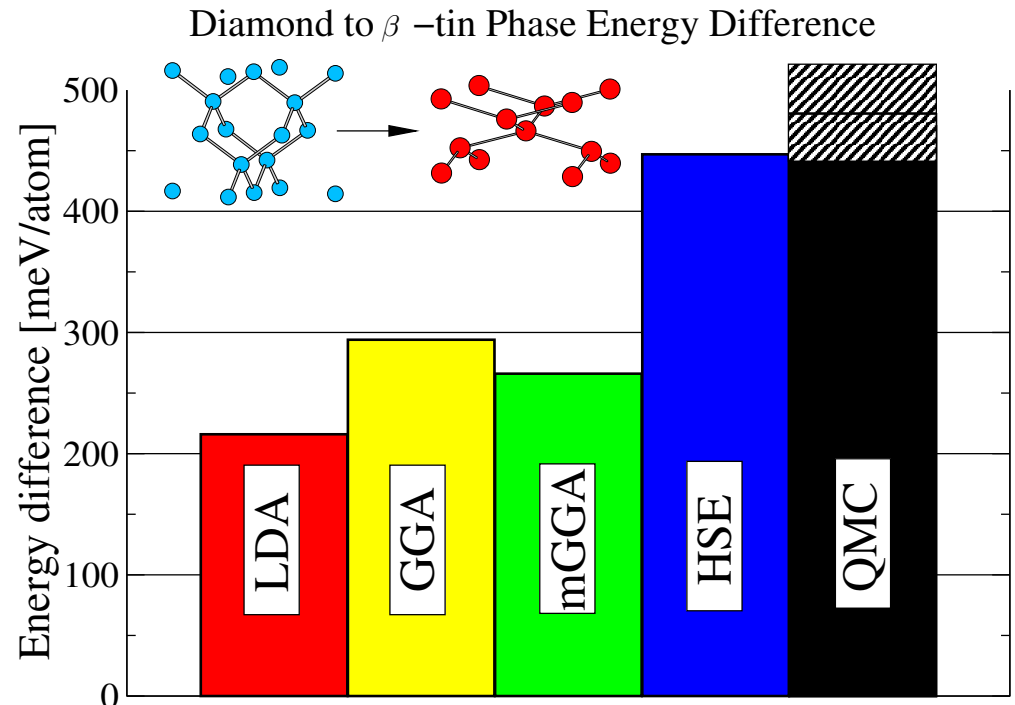
- Silicon is the cornerstone of microelectronics.
- Formation and diffusion of dopant impurities is crucial.
- Ion implantation-induced interstitials nucleate extended defects.
- Experiments do not agree on interstitial energetics.



## Bulk Silicon Band Gap



QMC: Williamson *et al.*, Phys. Rev. B, 57 (1998).



QMC: R. Hennig; See Alfe *et al.*, Phys. Rev. B, 70 (2004).

- Use QMC to identify accurate density functionals for theoretical investigations.

# Quantum Monte Carlo Method

## Trial Wave Function and Jastrow Factor

$$\Psi_T = (\text{Slater determinant}) \times (\text{Jastrow factor})$$

## Density-Functional Calculations

- J. L. Martin's CPW2000, VASP, and Gaussian

## Variational Monte Carlo

- Optimize Jastrow by “energy minimization” [3]

## Diffusion Monte Carlo

- Stochastic method of solving the many-body Schrödinger equation
- Projects out the ground state
- 64-atom cell: 6,000 cpu hours and 4 GB per processor

[3] Umrigar and Filippi, Phys. Rev. Lett. (2005).

## Approximations\*

### Controlled

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

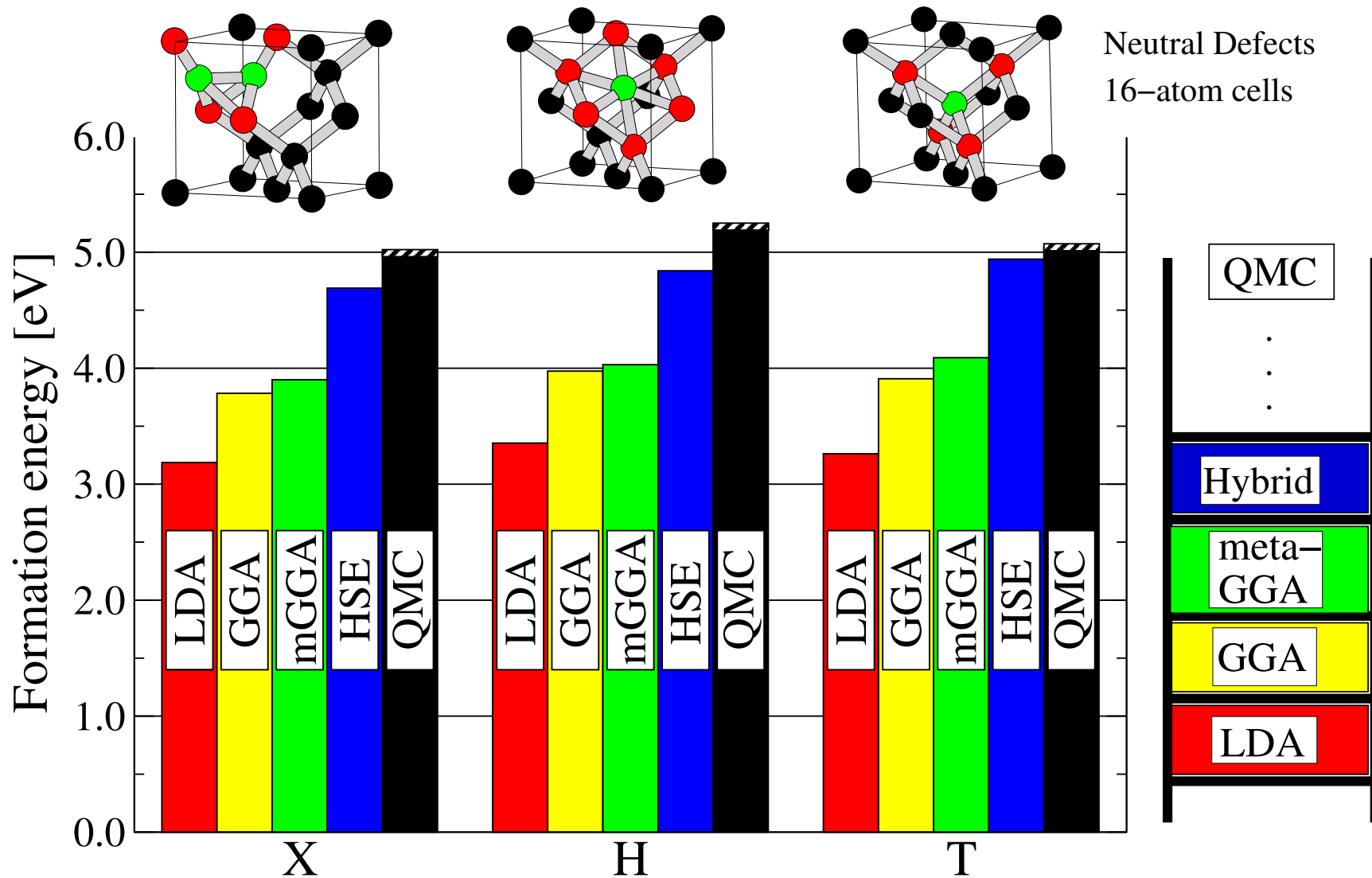
### Uncontrolled

- Pseudopotential\*\*
- Pseudopotential-locality
- Fixed node

\*See W. Parker, Session U27

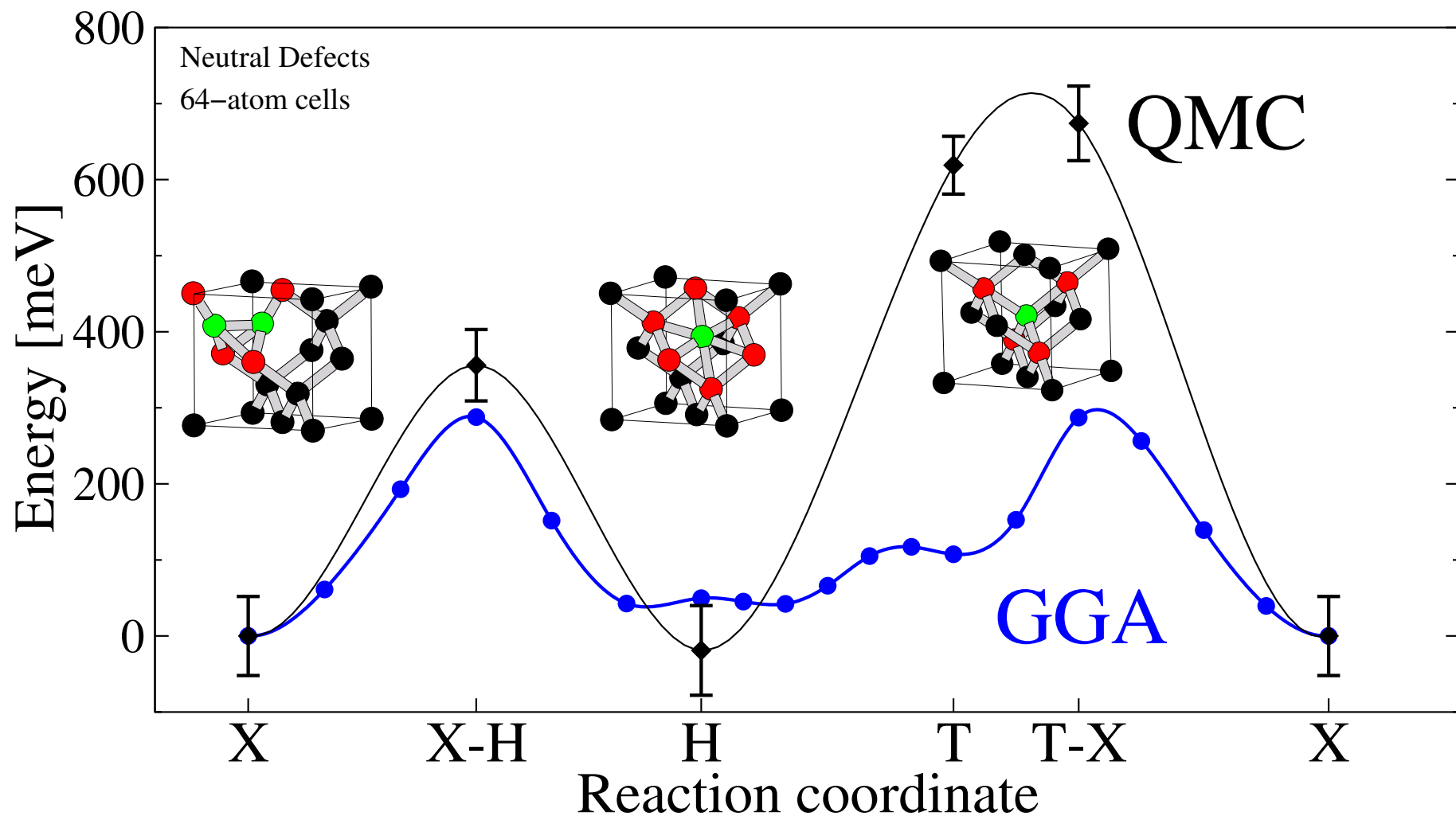
\*\*See R. Hennig, Session U27

# Accuracy of Functionals for Single Interstitials



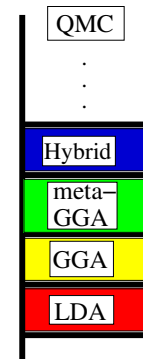
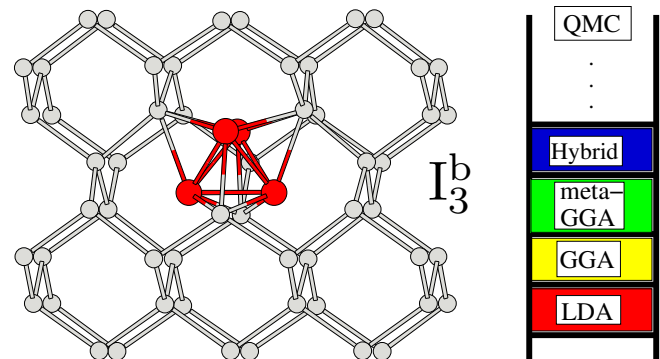
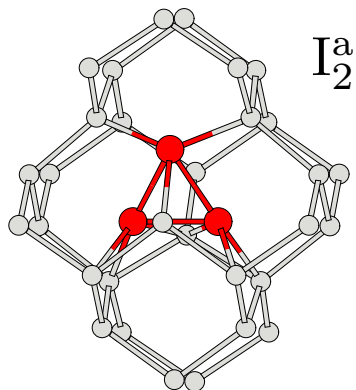
- Single interstitial results agree with earlier QMC by Leung *et al* [4].
- Observe systematic improvement of density functionals, and HSE is accurate.

# Accuracy of Functionals for Diffusion Barriers



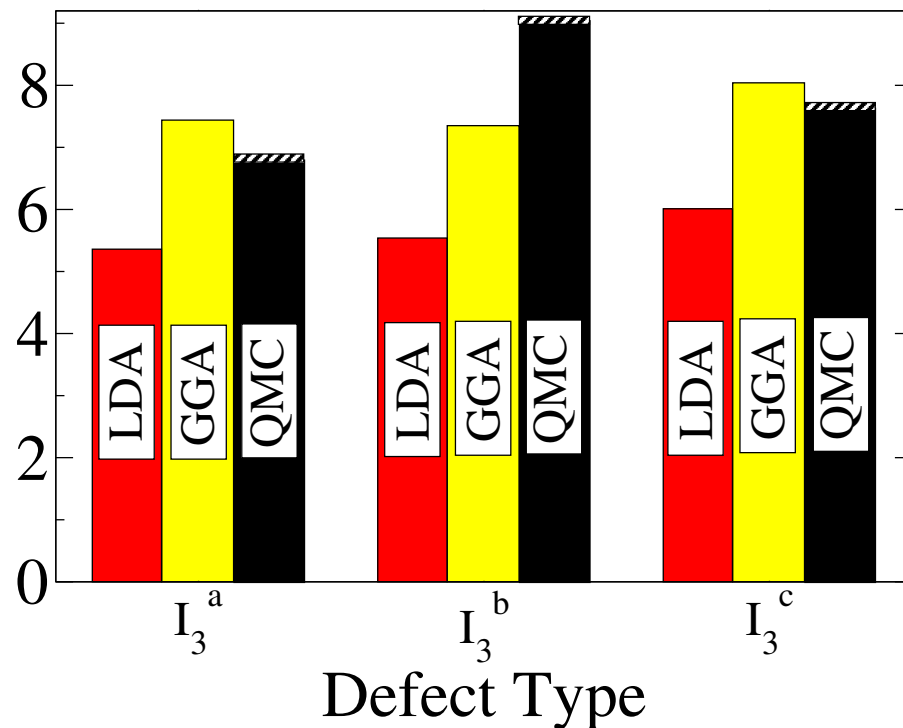
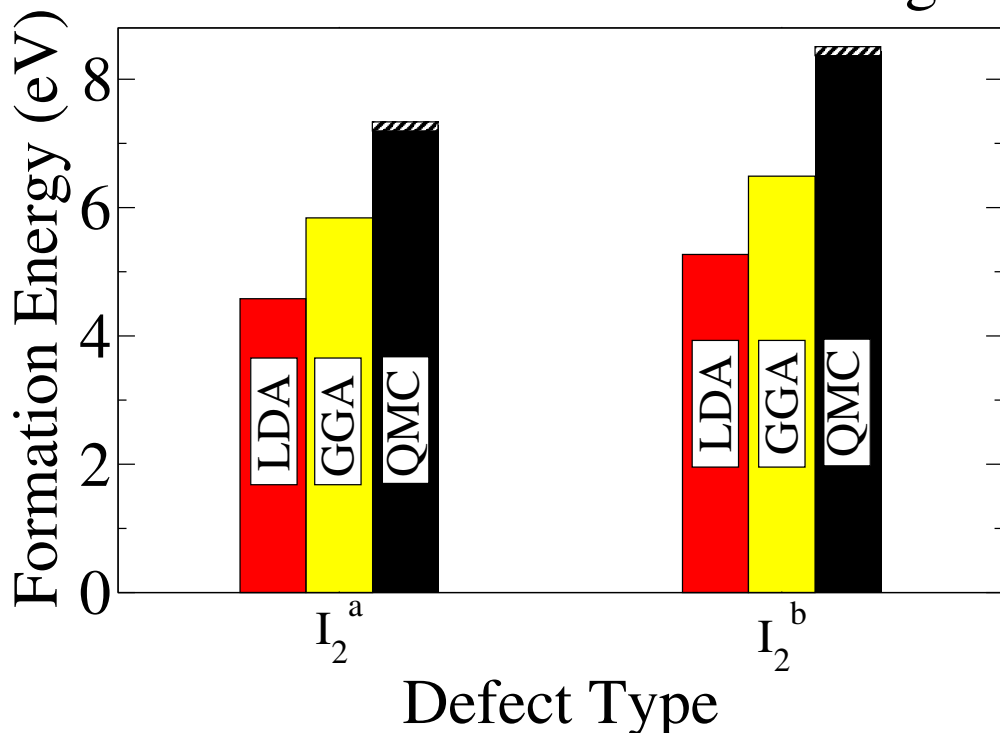
- Lowest barrier from X to H defect is similar in QMC and DFT.
- Neutral T defect formation energy and barrier are higher in QMC.

# Accuracy of Functionals for Di and Tri-Interstitials



Di-interstitial Formation Energies

Tri-interstitial Formation Energies



- In di-interstitials, LDA and GGA display ladder trend.
- In tri-interstitials, GGA improves for less distorted defects.

# Conclusions

- QMC can accurately benchmark density functionals.
- Perdew's "Jacobs Ladder" of functionals shows systematic improvement in representative silicon calculations.
- HSE hybrid functional closely reproduces QMC.
- QMC-validation of functionals allows for accurate DFT beyond QMC.  
e.g.: larger systems or dynamics

