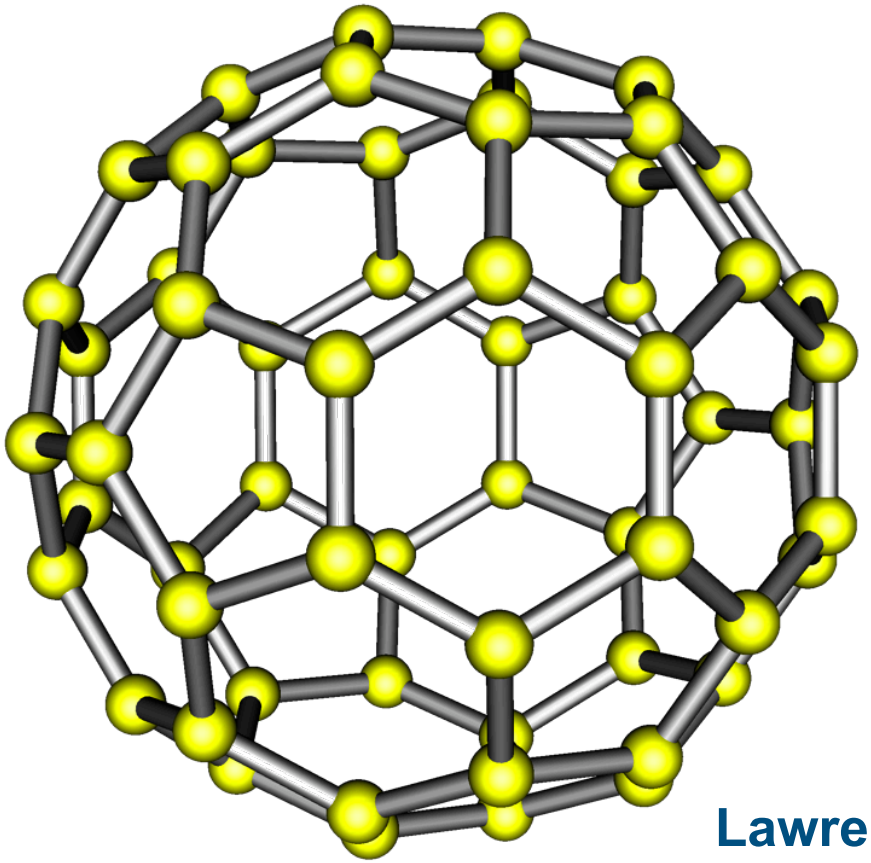
Excitations in Carbon Fullerenes calculated by GW Bethe-Salpeter and Quantum Monte Carlo



Paul R. C. Kent

Murilo L. Tiago

Fernando A. Reboredo

Oak Ridge National Laboratory

Randolph Q. Hood

Lawrence Livermore National Laboratory

OAK RIDGE National Laboratory

Acknowledgements

- **Support**
  - **DOE**
- **Codes**
  - **PARSEC & RGWBS** DFT, W-BSE, TDLDA
  - **CASINO** QMC
- **Computational support**
  - **NCCS at ORNL**
  - **NERSC**
  - **LLNL**
  - **TACC**

Questions that I will address

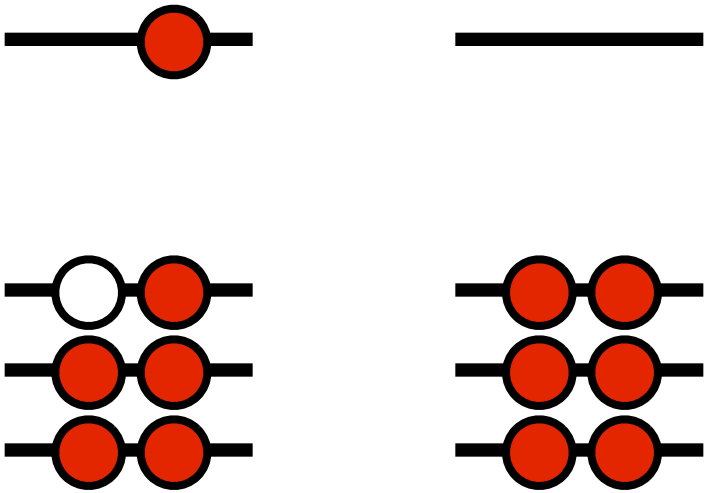
1. Do the GW-BSE and QMC correctly predict neutral and charged excitations of carbon fullerenes?

- C60 is best characterized experimentally
- We study 7 fullerenes C20-C80, including isomers

2. Where are improvements in computational methods required?

Methodology: QMC

- **Diffusion Monte Carlo is in principle exact, but fixed node approximation introduces a variational error. First excitation energies of each symmetry are also exact, but non-variational in practice**



$$\text{Triplet energy} = E_{tr} - E_{gs}$$

- **Trial wavefunction is single determinant of LDA orbitals**
  - **Costly &/or difficult to apply multi-determinants/orbital optimization/backflow approaches in large systems**
- **More challenging calculation than for e.g. cohesive energy**

Methodology: GW-BSE

- **Full absorption spectrum, excitons. Bethe-Salpeter equation for e-h interactions**
- **We have applied two different levels of approximation**

GW_0 approximation

algorithm: Hybertsen & Louie (1985)

$$\Sigma = i\,\mathbf{GW}$$

$$\mathbf{W} = \mathbf{V}_{\mathbf{coul}} + \mathbf{V}_{\mathbf{coul}}\Pi_{\mathbf{RPA}}\mathbf{V}_{\mathbf{coul}}$$

GW_f approximation

Tiago & Chelikowsky, PRB **73**, 205334 (2006)

Del Sole et al., PRB 49, 8024 (1994)

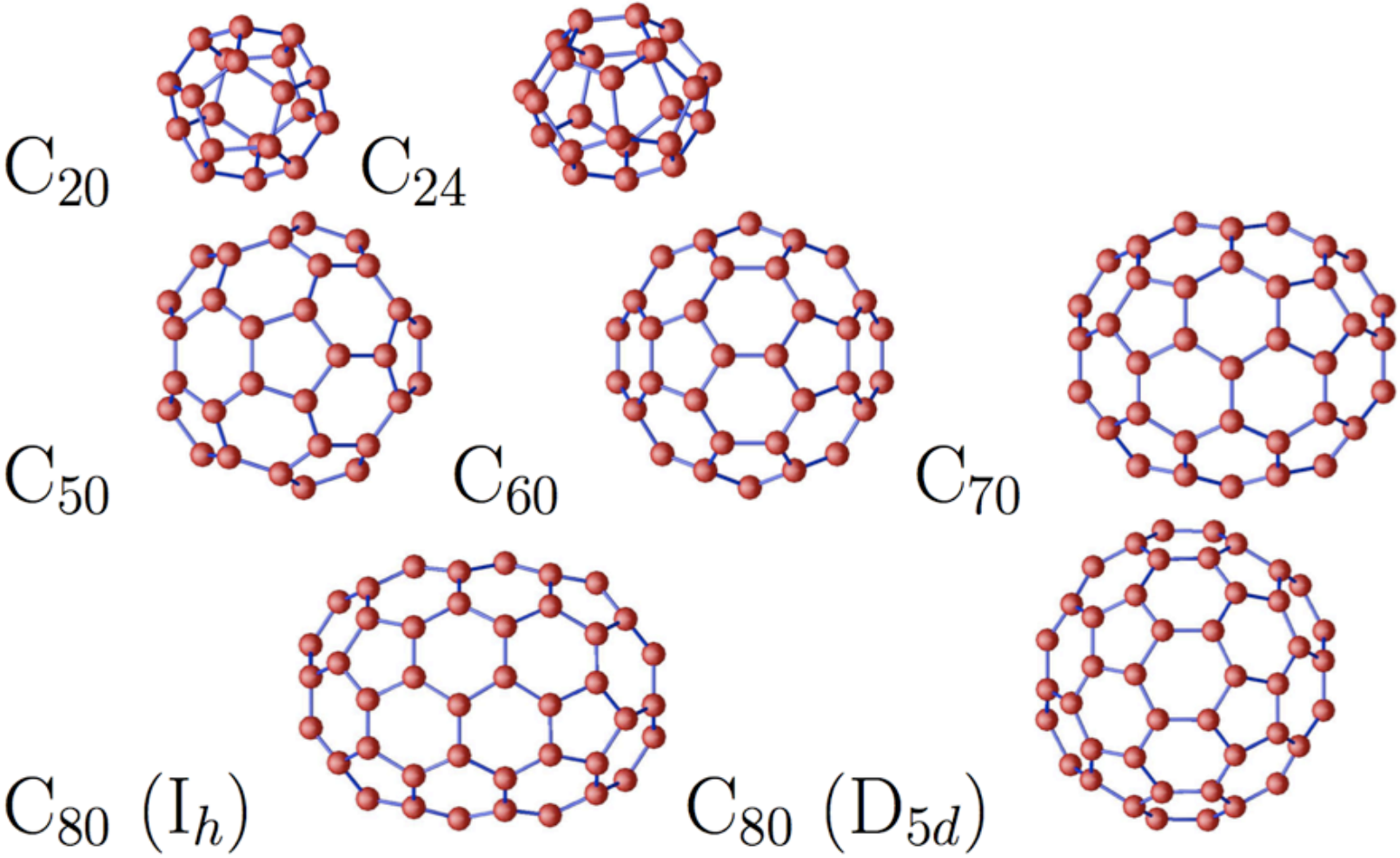
$$\Sigma = i\,\mathbf{GW}\Gamma_{\mathbf{LDA}}$$

$$\mathbf{W} = \mathbf{V}_{\mathbf{coul}} + \mathbf{V}_{\mathbf{coul}}\Pi_{\mathbf{LDA}}\mathbf{V}_{\mathbf{coul}}$$

- **GW_0 and GW_f often predict similar gaps, but differ in absolute energy levels compared to vacuum**

Fullerene geometries

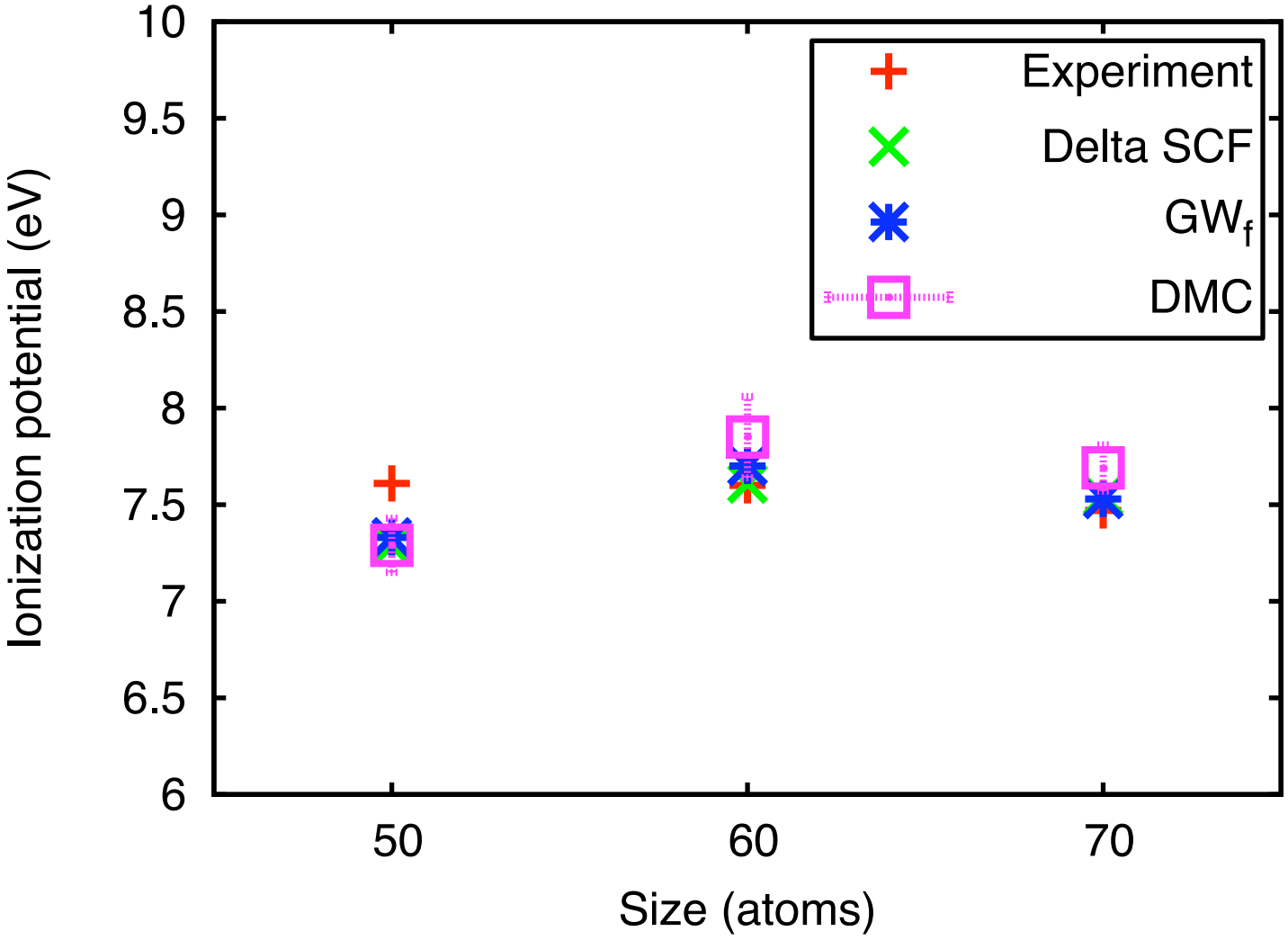
- **DFT PBE geometries obtained from real-space and plane-wave ground state calculations**



Focus on C_{50}, C_{60}, C_{70} for brevity

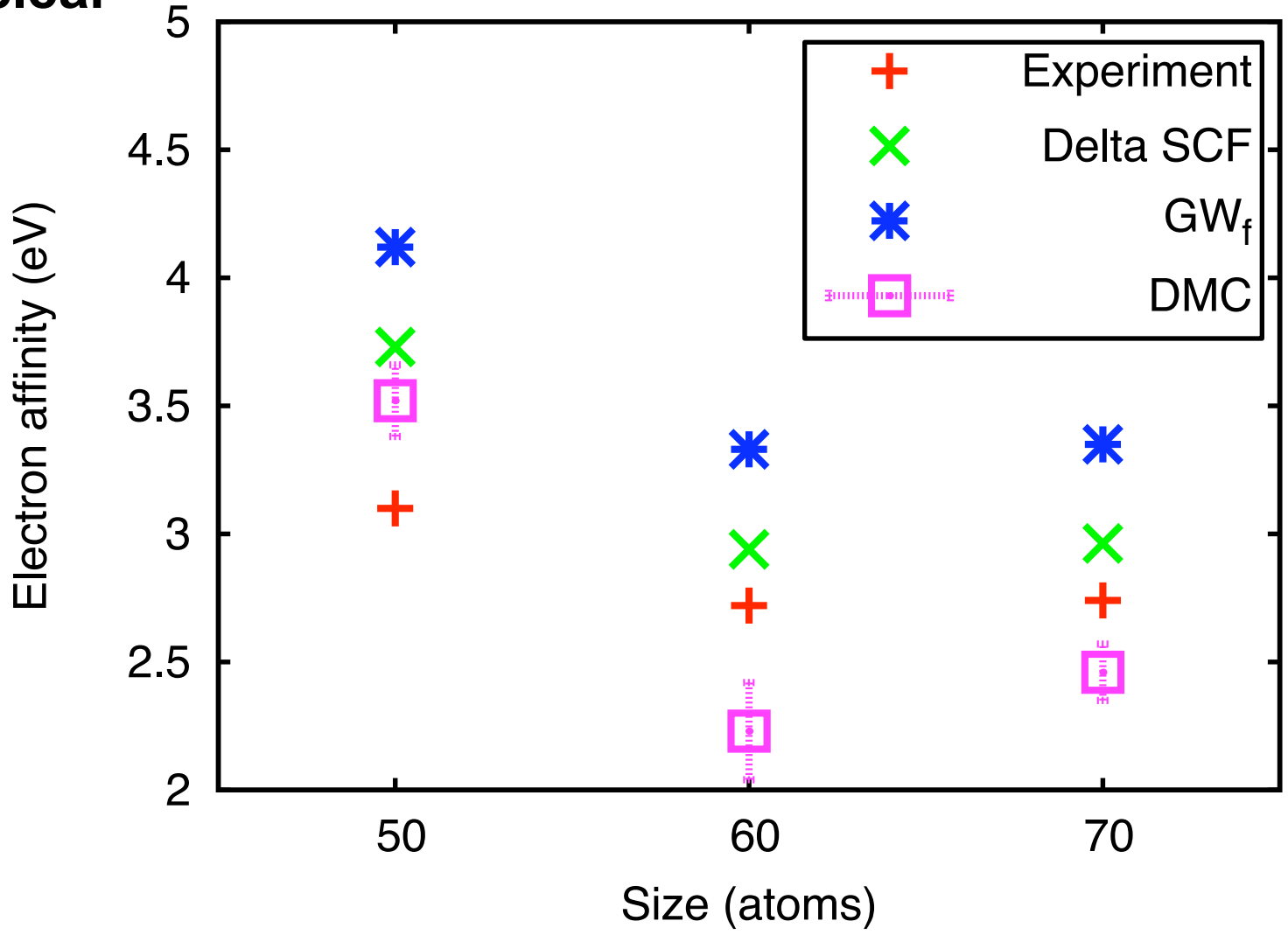
Results: Ionization Potentials

- **Good agreement for all methods**

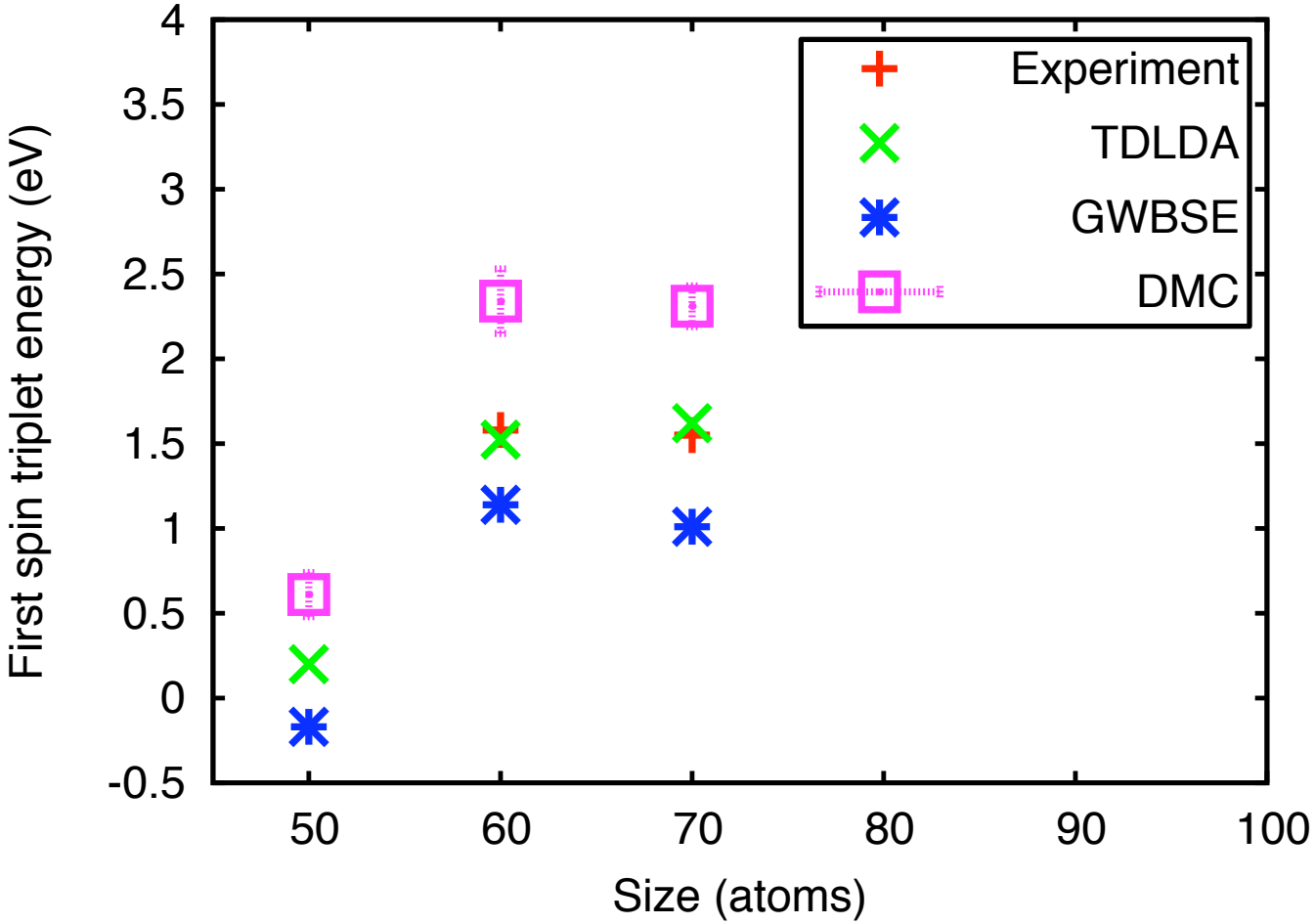


Results: Electron affinities

- **Systematic overestimation by GW, trends in DMC unclear**

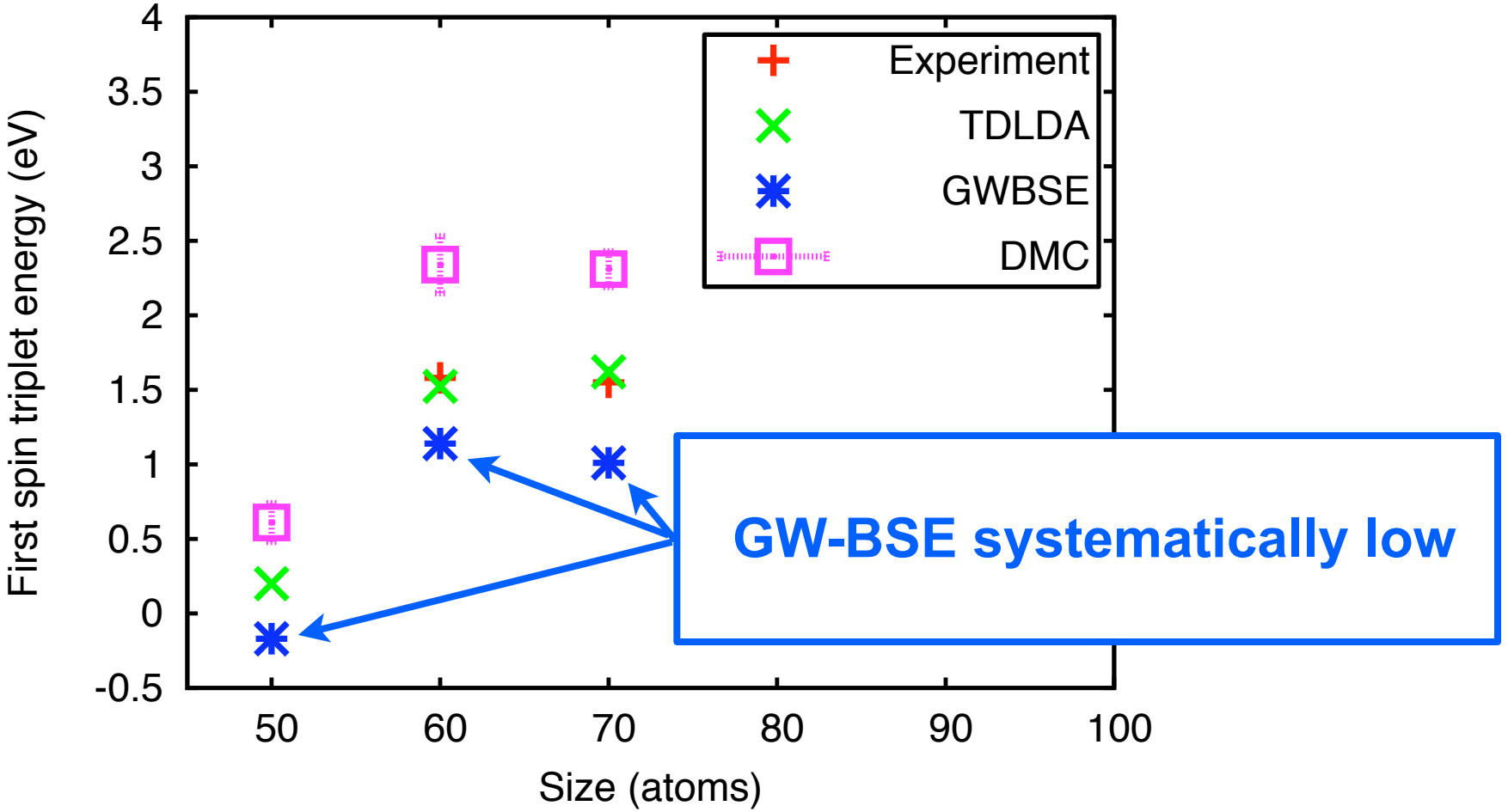


Results: First spin-triplet



- **Stoke's shifts estimated as max 0.2 eV from DFT not included in above data**

Results: First spin-triplet



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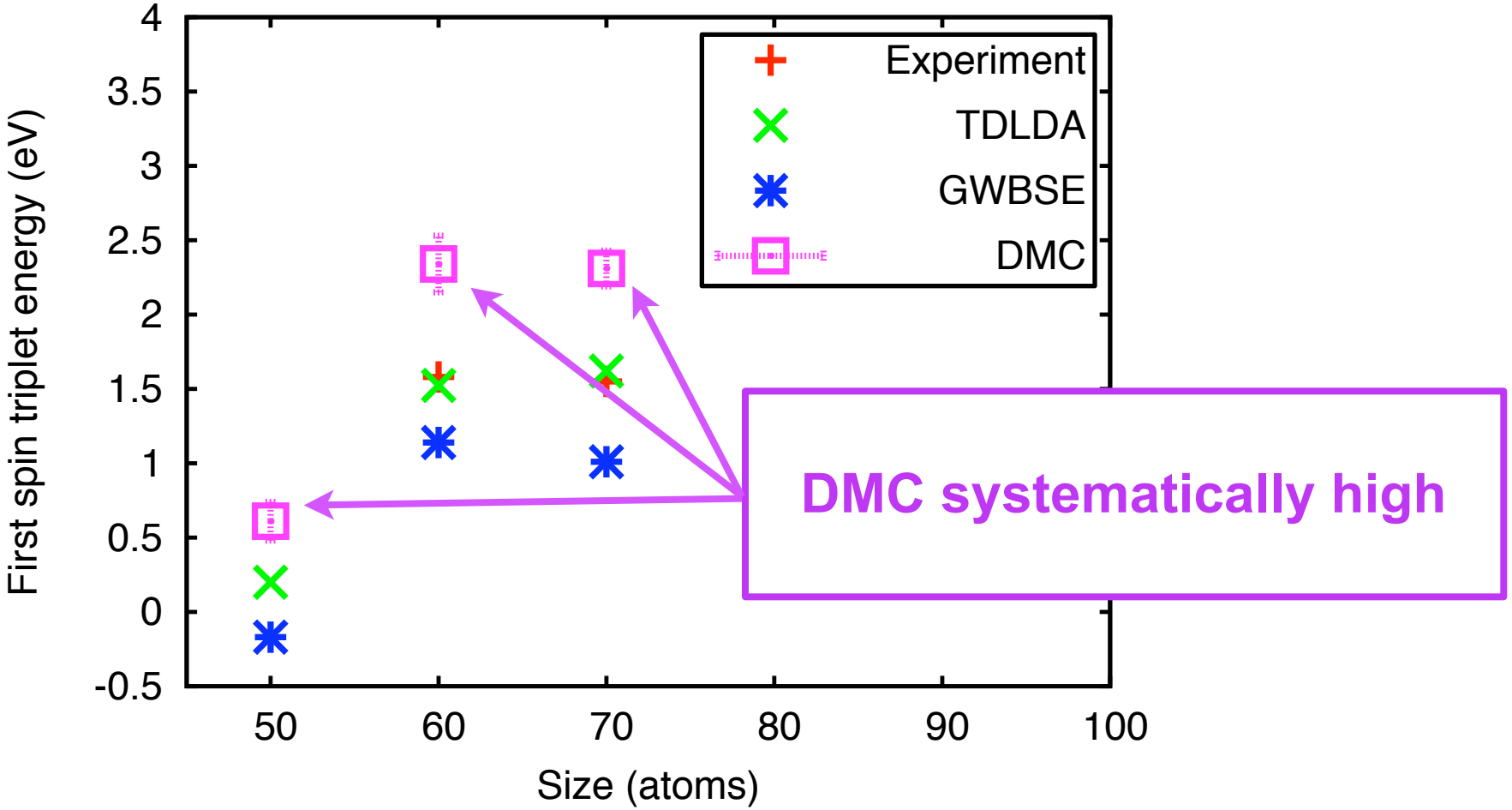

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Challenges to theory

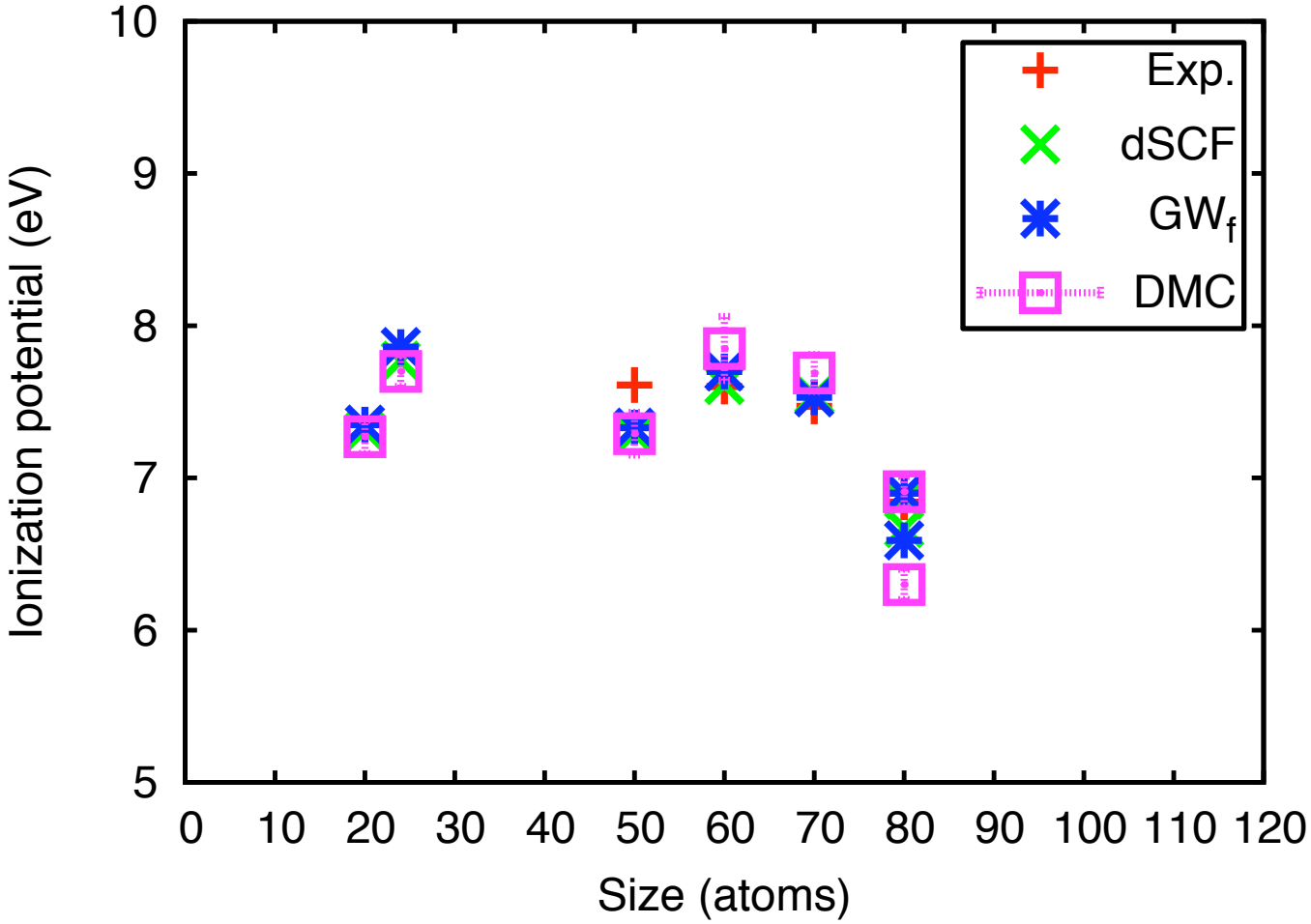
- **GW-BSE**
  - Need to improve electron affinities without worsening other quantities
  - Currently investigating self-consistent approaches
- **QMC**
  - Need improved trial wavefunctions with more optimal nodes
  - Non-systematic cancellation of nodal error is the primary error
  - Need compact multiconfigurational expansions &/or orbital optimization for large systems
  - Pseudopotential evaluation related errors are small

Summary

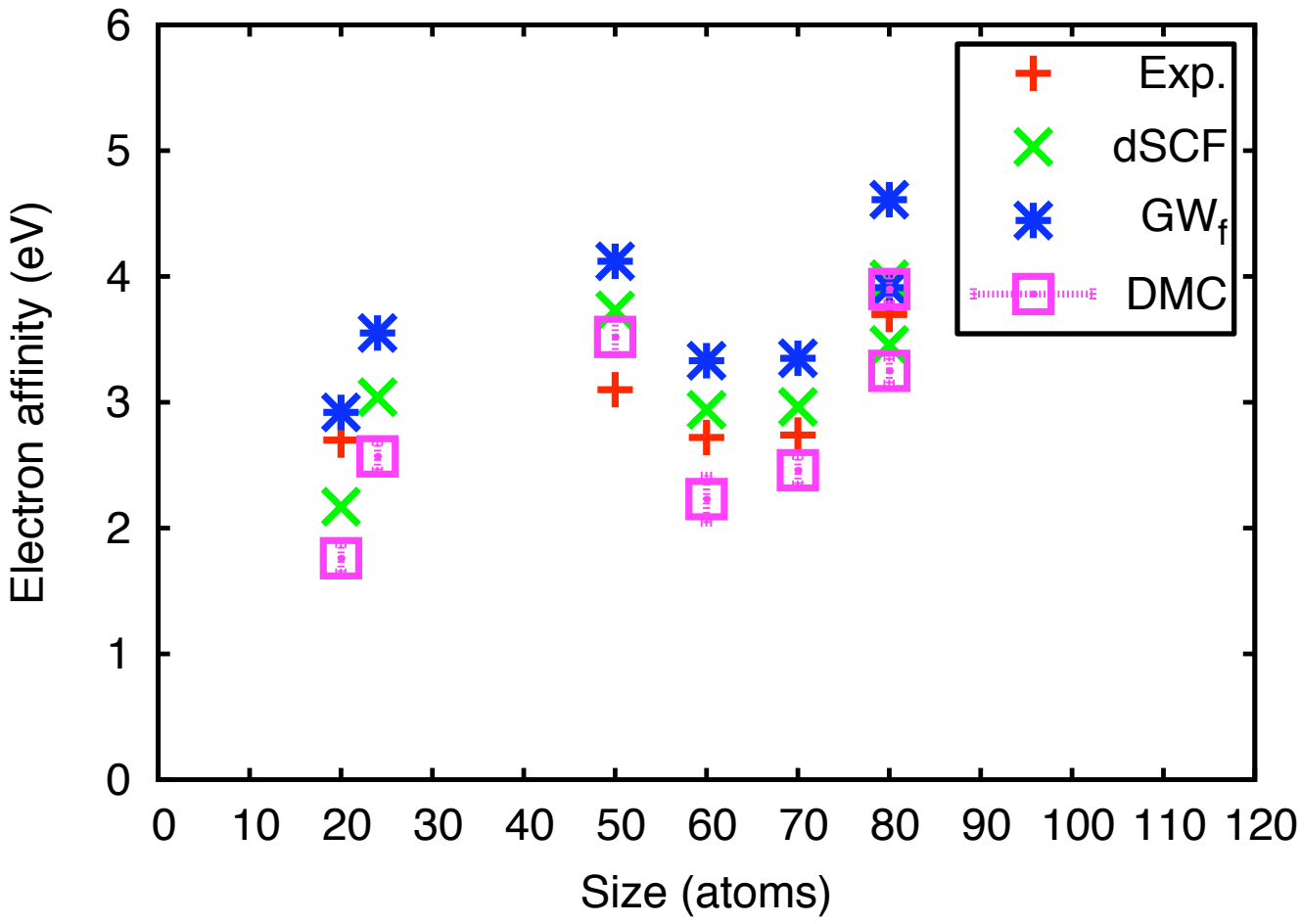
http://arxiv.org/abs/0803.0560

- **IP: well reproduced by all methods**
- **EA: systematically overestimated by GW**
- **Triplet: GW-BSE systematically low ~0.5eV (excl. Stokes)**
- **Triplet: QMC systematically high ~0.8eV (excl. Stokes)**
- **Delta SCF and TDLDA are surprisingly good, despite being poor choices in nanotubes.**

Results: Ionization Potentials



Results: Electron affinities



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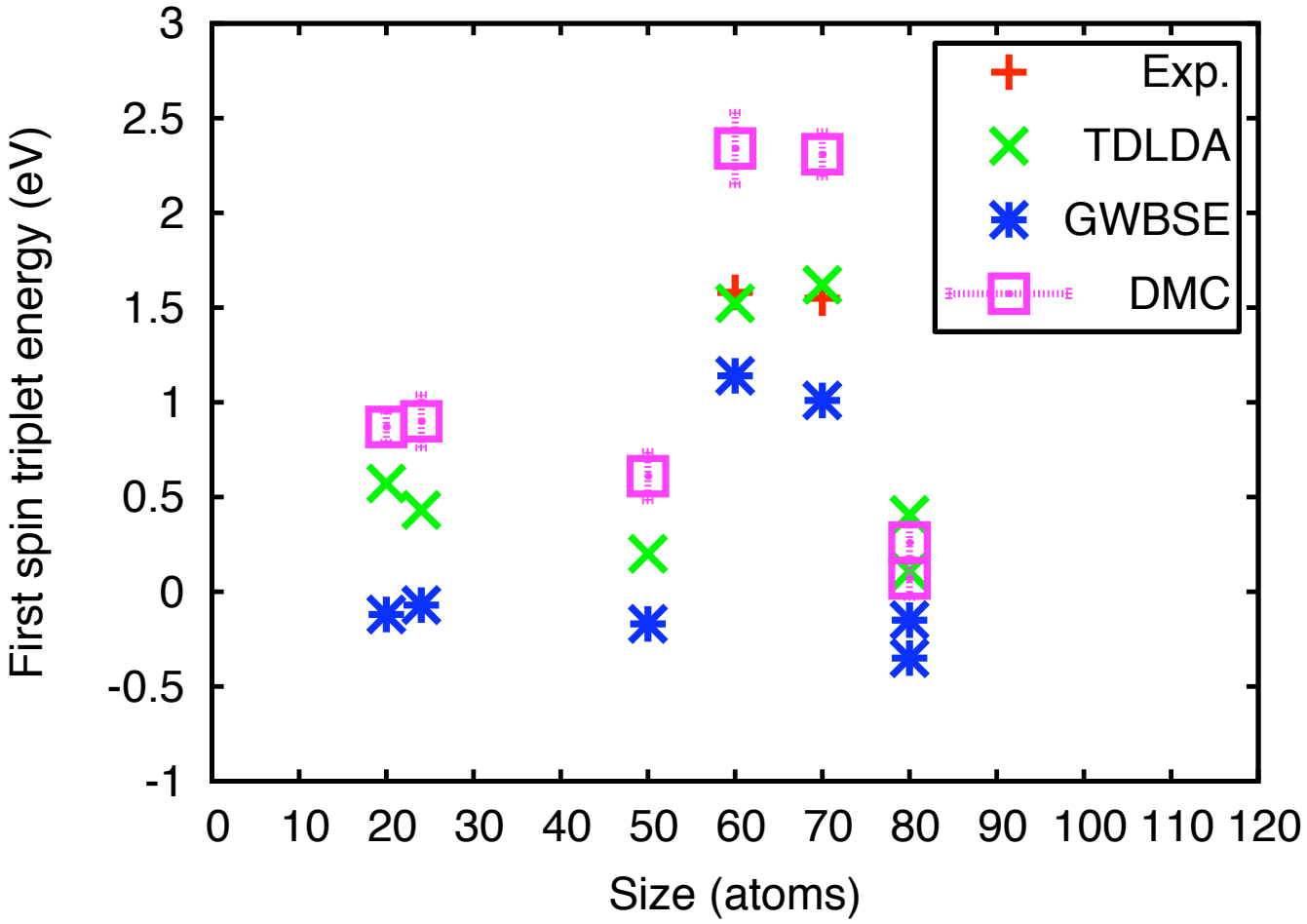

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