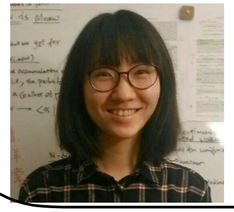
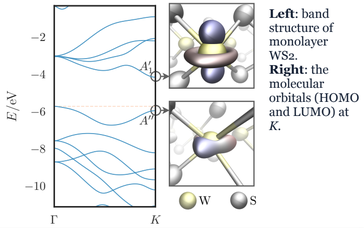
Poster advertisements

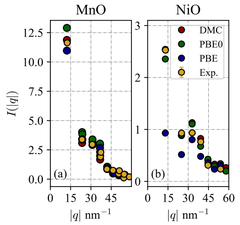


Practical spin-orbit in QMC
Yueqing Chang

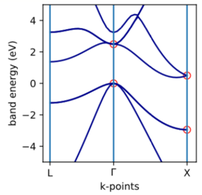


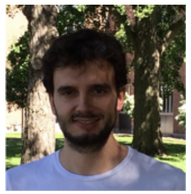
Left: band structure of monolayer WS_2. **Right**: the molecular orbitals (HOMO and LUMO) at *K*.

Neutron intensities using QMC
Alex Munoz



Band structures using QMC
William Wheeler, Shivesh Pathak





Electron-spin coupling as a predictor for “interesting” physics
Joao Rodrigues

A new prediction for spin excitations in $MgTi_2O_4$
Brian Busemeyer

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Benchmarking high accuracy methods on realistic systems

Collaboration on the many-electron problem

Presented by Lucas K. Wagner

Kiel T. Williams,[1] Li Chen,[1] Hao Shi,[2,3] Mario Motta,[4] Chunyao Niu,[3,5] Ushnish Ray,[4] Sheng Guo,[4] Robert J. Anderson,[6] Jia Li,[7] Junhao Li,[8] Lan Nguyen Tran,[7,9] Chia-Nan Yeh,[7] Bastien Mussard,[10] Sandeep Sharma,[10] Yuan Yao,[8] Mark van Schilfgaarde,[6] George H. Booth,[6] Garnet Chan,[4] Shiwei Zhang,[2,3] Emanuel Gull,[7,2] Dominika Zgid,[7,9,2] Andrew Millis,[2,11] Cyrus Umr ucas K. Wagner[1]

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[8] *Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853*

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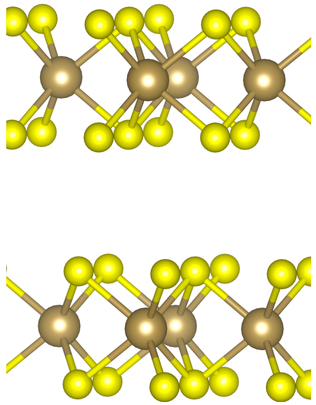
[10] *Department of Chemistry, University of Colorado, Boulder*

[11] *Department of Physics, Columbia University, New York, NY 10027*

How reliable are first principles calculations?



$$+ \quad H|\Psi\rangle = i\hbar\frac{\partial}{\partial t}|\Psi\rangle$$

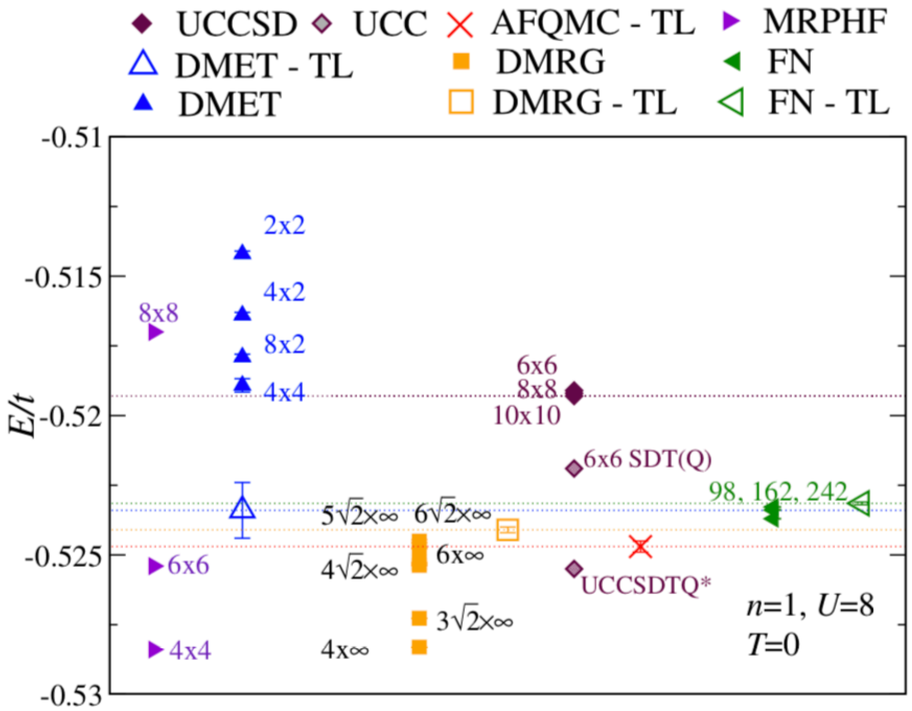
Approximation!

DFT, DMRG, QMC, GW, etc

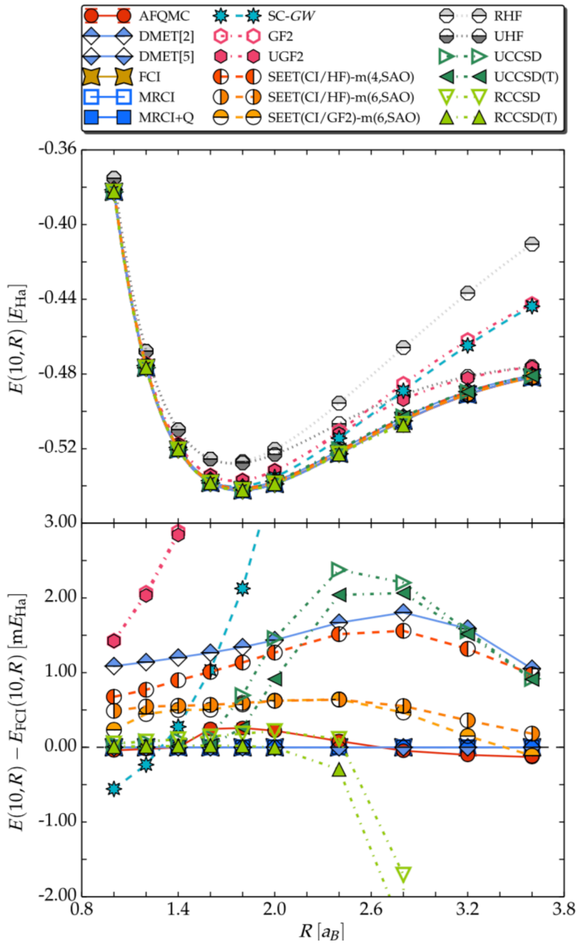
Total energy, excitations, properties

How close are these to exact solutions?

Previous work from the Collaboration



LeBlanc et al.
Agreement between high accuracy methods on the Hubbard model



Motta et al.
Chain of hydrogen atoms

Our objective

Provide total energy benchmarks for **realistic systems** on well-defined Hamiltonians.

Important systems: **transition metal compounds**, which exhibit strongly correlated behavior in materials

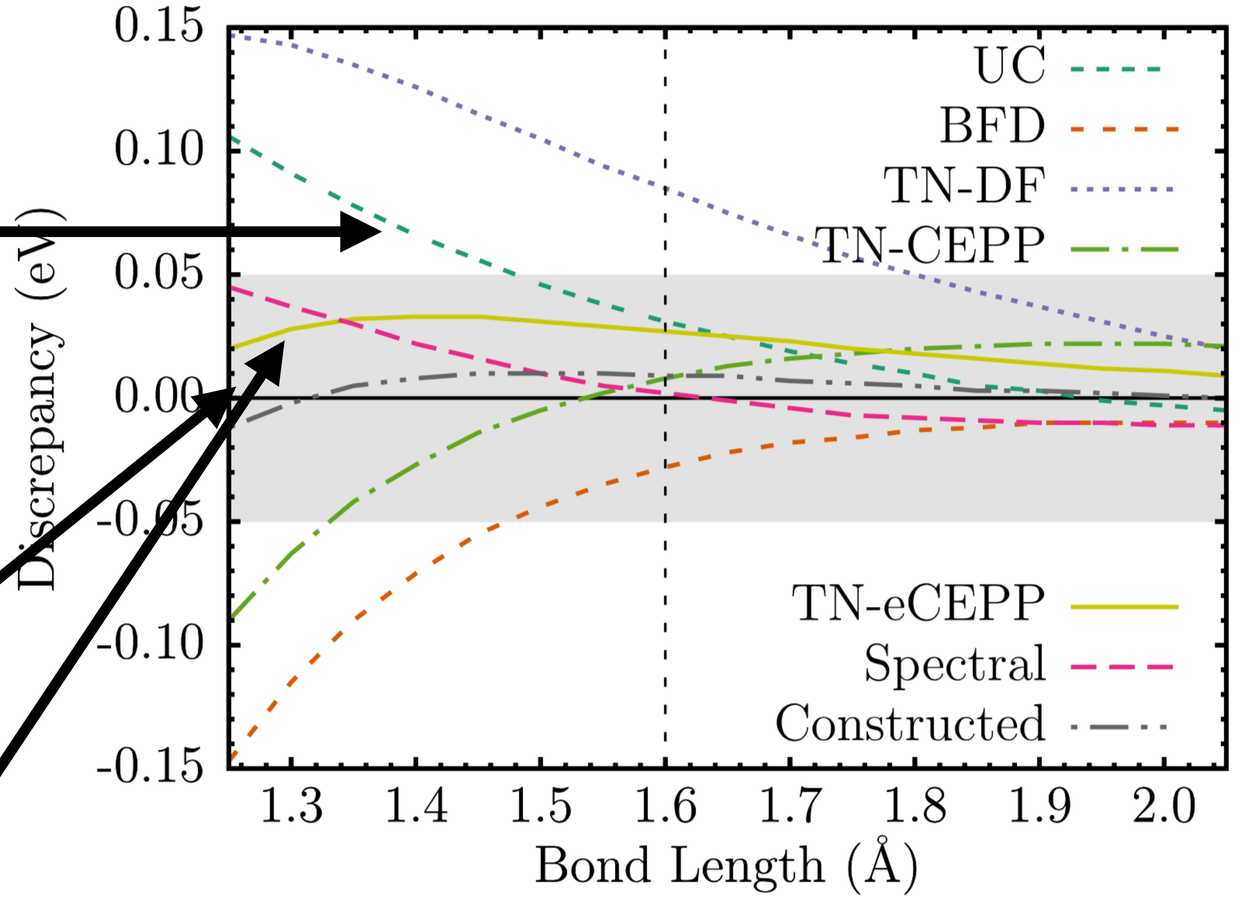
Simplify: **ground state energy**.

Choosing a Hamiltonian

Frozen core
- Complex to specify
- Not necessarily more accurate than ECPs

All electron
- Very expensive
- DMC is hard

ECPs (Trail and Needs)
- Everyone can do it
- Accurate and available



Bennett, Melton, Annaberdiyev, Wang, Shulenberger, Mitas

J. Chem. Phys. **147**, 224106 (2017)

Finite basis sets

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \hat{V}$$

Project onto discrete basis

$$H_{ij} = \langle i | \hat{H} | j \rangle$$

Sparse representation

$$\hat{H} = \sum_{ab} t_{ab} c_a^\dagger c_b + \sum_{abcd} V_{abcd} c_a^\dagger c_b^\dagger c_c c_d$$

For a single Cr atom:

	Number of one-particle orbitals	Approximate size of Hilbert space
vdz	54	10^{15}
vtz	88	10^{19}
vqz	135	10^{21}
v5z	197	10^{24}
cbs	infinite	infinite

Methods and (roughly) governing equations

Density functional theory
LDA, PBE, SCAN, HSE06

$$E = f[\rho]$$

Green's function
QSGW, SC-GW, GF2, RPA

$$G = G_0 + G_0 \Sigma G$$

Many-body wave function
AFQMC, CCSD, CCSD(T), CIC+Q, CISD,
DMC, DMRG, FCIQMC, MRLCC, SHCI

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

Embedding
SEET

Packages used

PySCF (checked Molpro)

Density functional theory
Coupled cluster
Configuration Interaction
DMRG
Integral generation

QWalk (checked CHAMP)

Fixed node diffusion QMC

MolGW (Bruneval)

QSGW (van Schilfgaard)

Home-grown codes

Self-consistent GW (Gull)

Semistochastic heat bath iteration (Umrigar)

Auxiliary field QMC (Zhang)

Multi-reference linearized coupled cluster (Sharma)

Full CI QMC (Booth)

Database

Sc, Ti, V, Cr, Mn, Fe, Cu, 0,+,M-O

18 TM systems neutral atoms, ions and oxides

×

vdz, vtz, vqz, v5z

5 basis sets

×

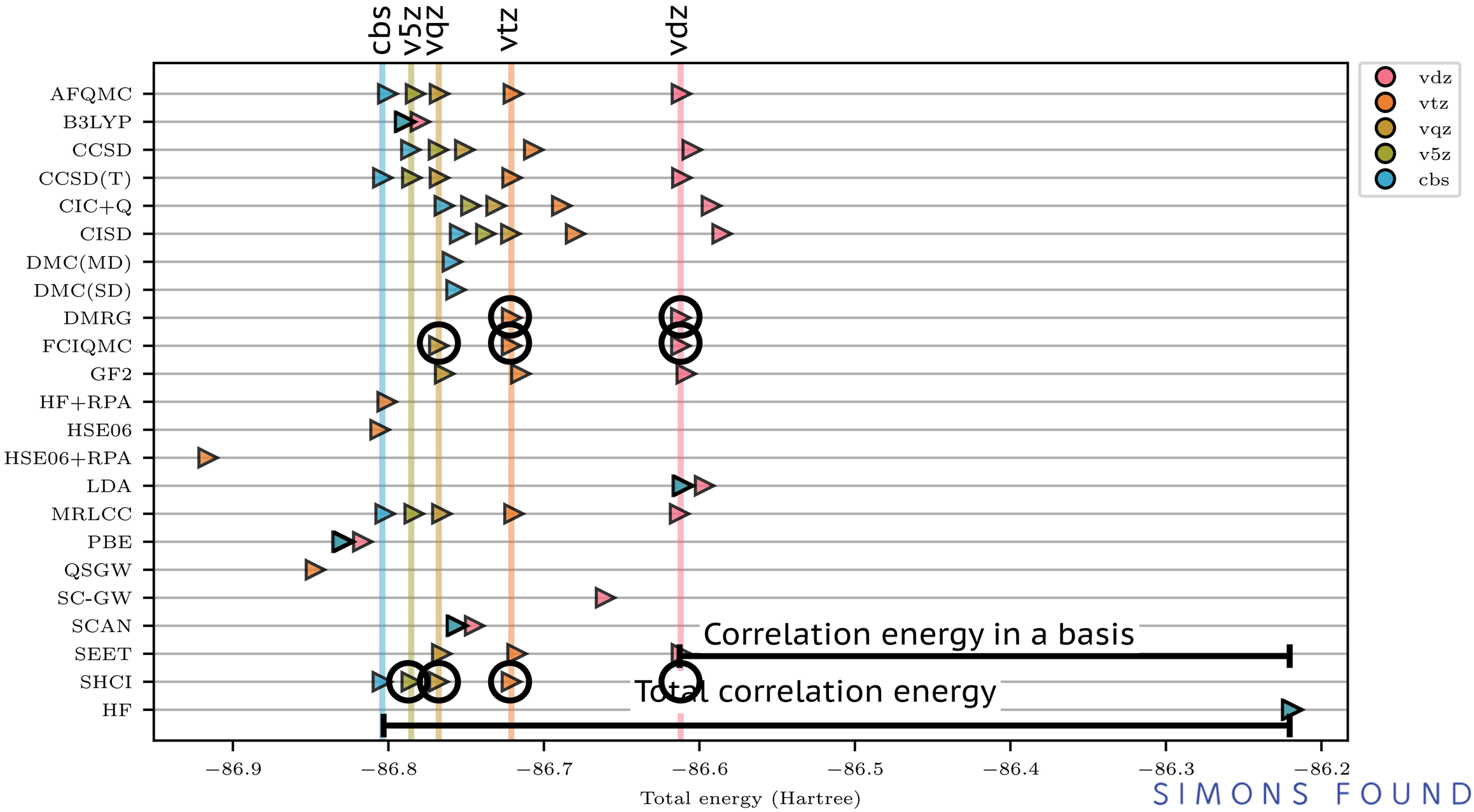
QC, QMC, GF, …

20 methods

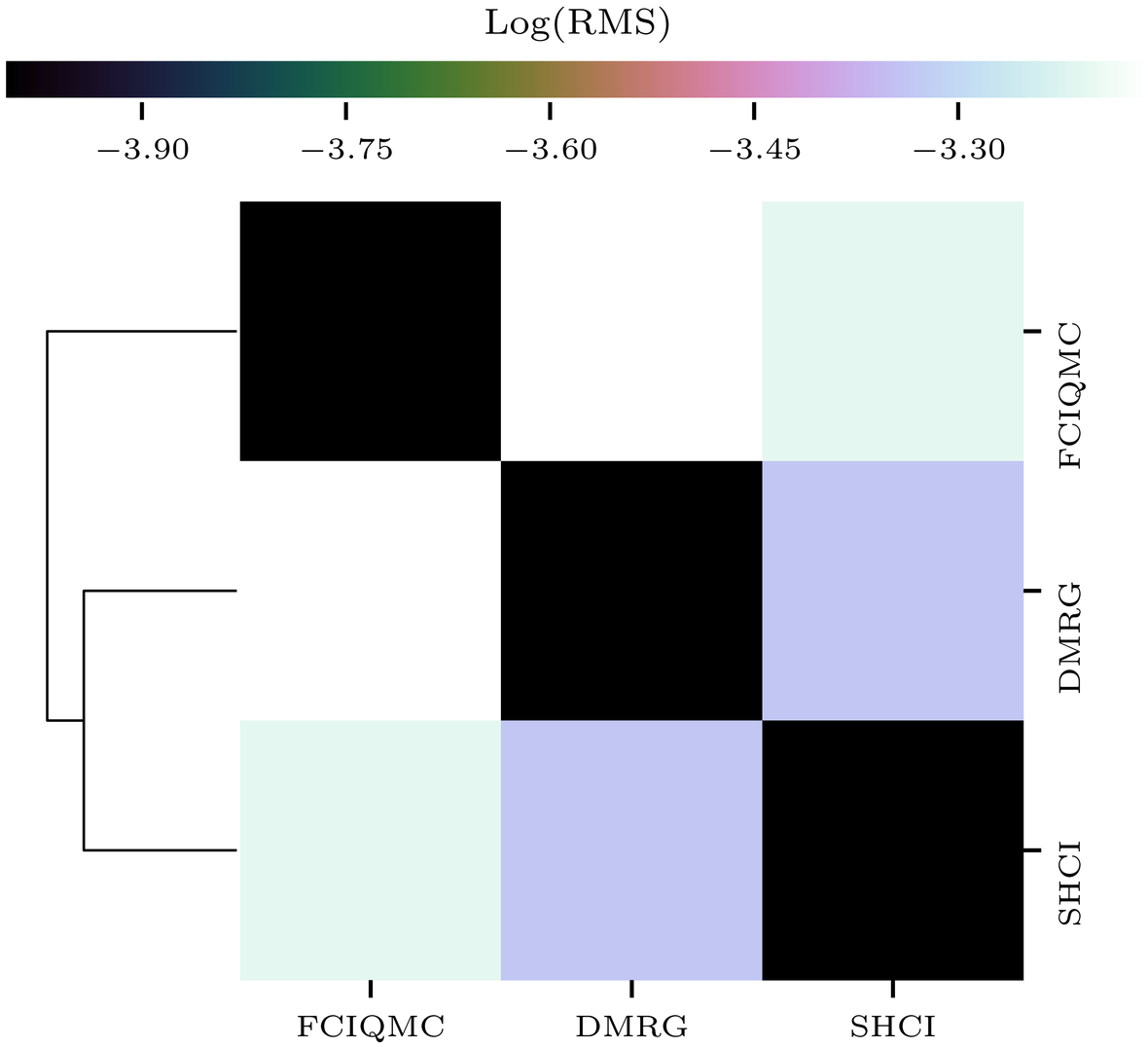
≃

4038 entries

Analysis of data (Cr atom)



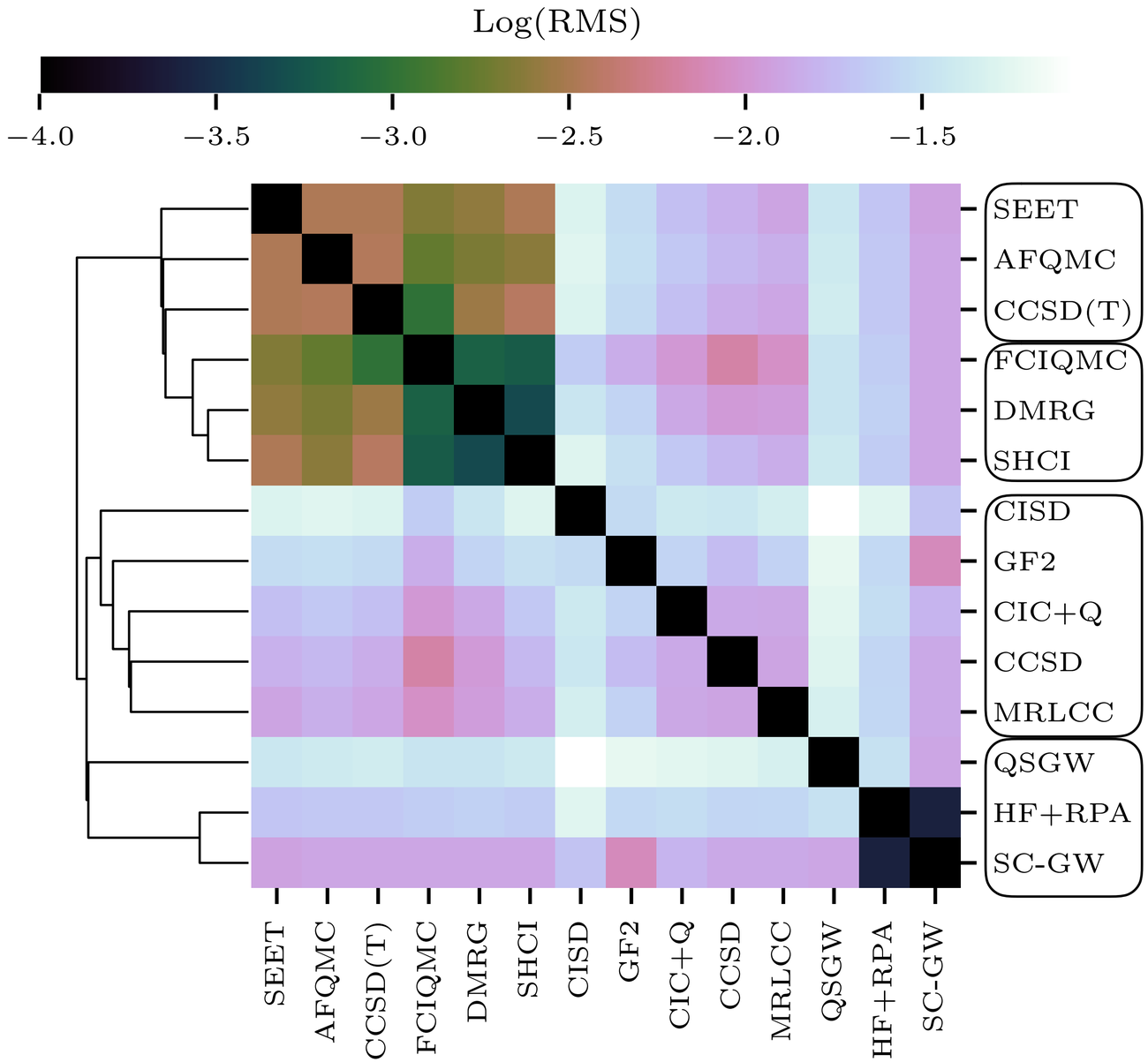
Setting a reference



3 methods that should converge to exact results **within the basis**.

RMS deviations between 3 methods are much less than 1 mHa, around chemical accuracy.

How methods agree: cluster analysis



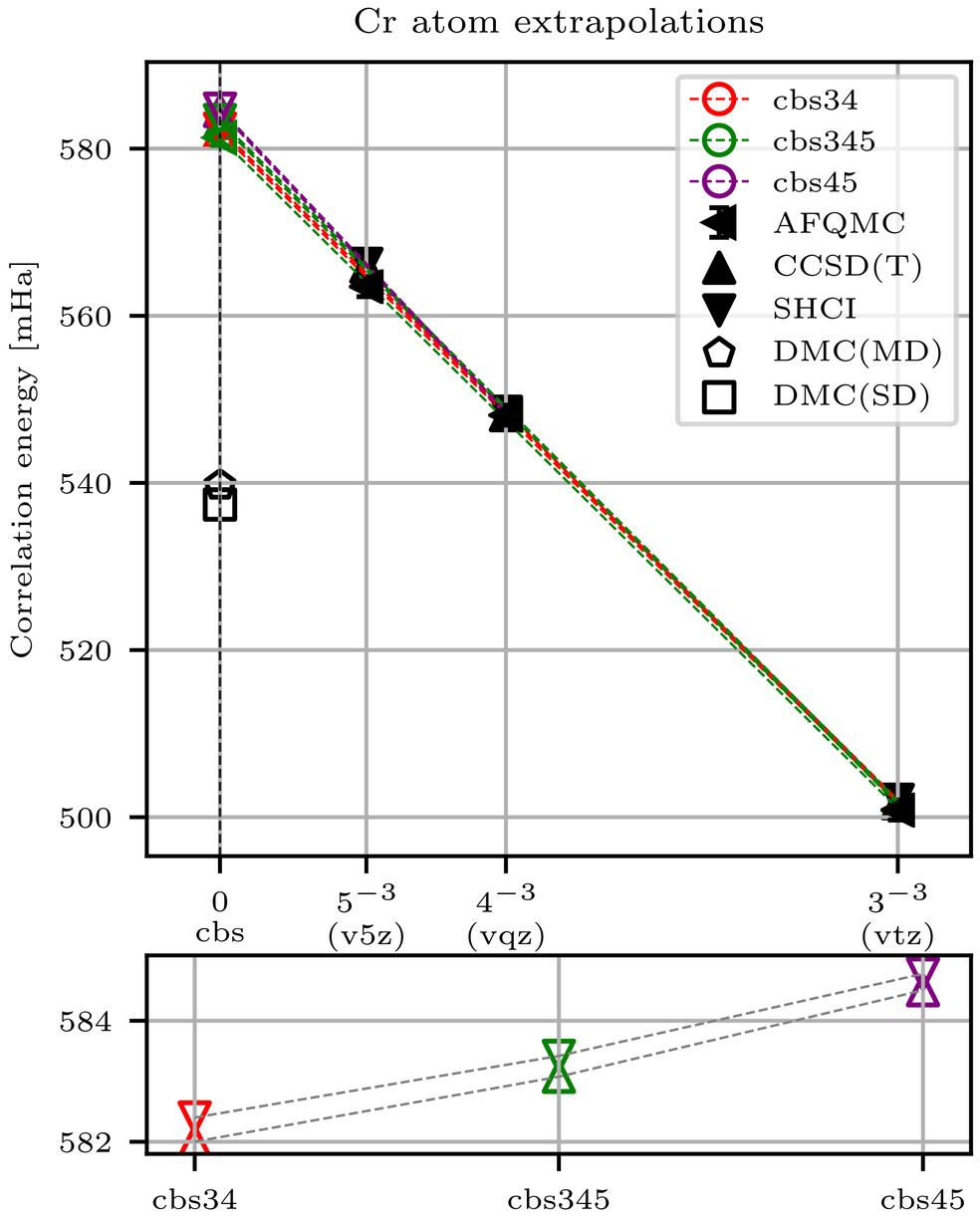
High performance quantum chemistry

“Exact” to ~1 mH

More approximate quantum chemistry

Green function

Basis set extrapolation: total energy



Basis set error scales as ~ $1/z^3$

Diffusion Monte Carlo uses the full Hamiltonian, but is approximate; separate lower bound on correlation energy.

Approximate uncertainty in extrapolated value of 2-5 mHa.

DFT results are compared only in the CBS limit.

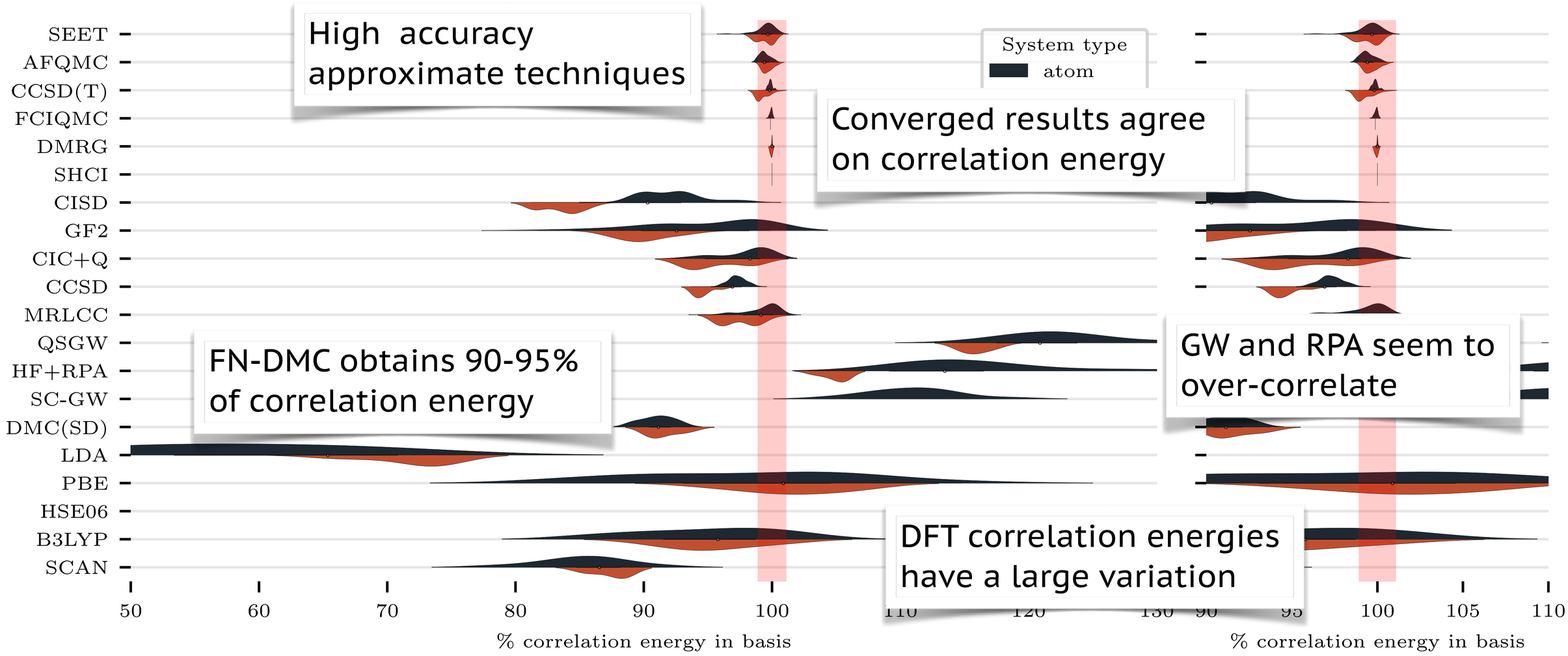
Assessing performance: correlation energy

$$100 \times \frac{E_{HF} - E_M}{E_{HF} - E_{\text{exact}}}$$

Scale-free quantity that allows us to compare different systems with different total energies

Most methods obtain consistent percentages of the correlation energy.

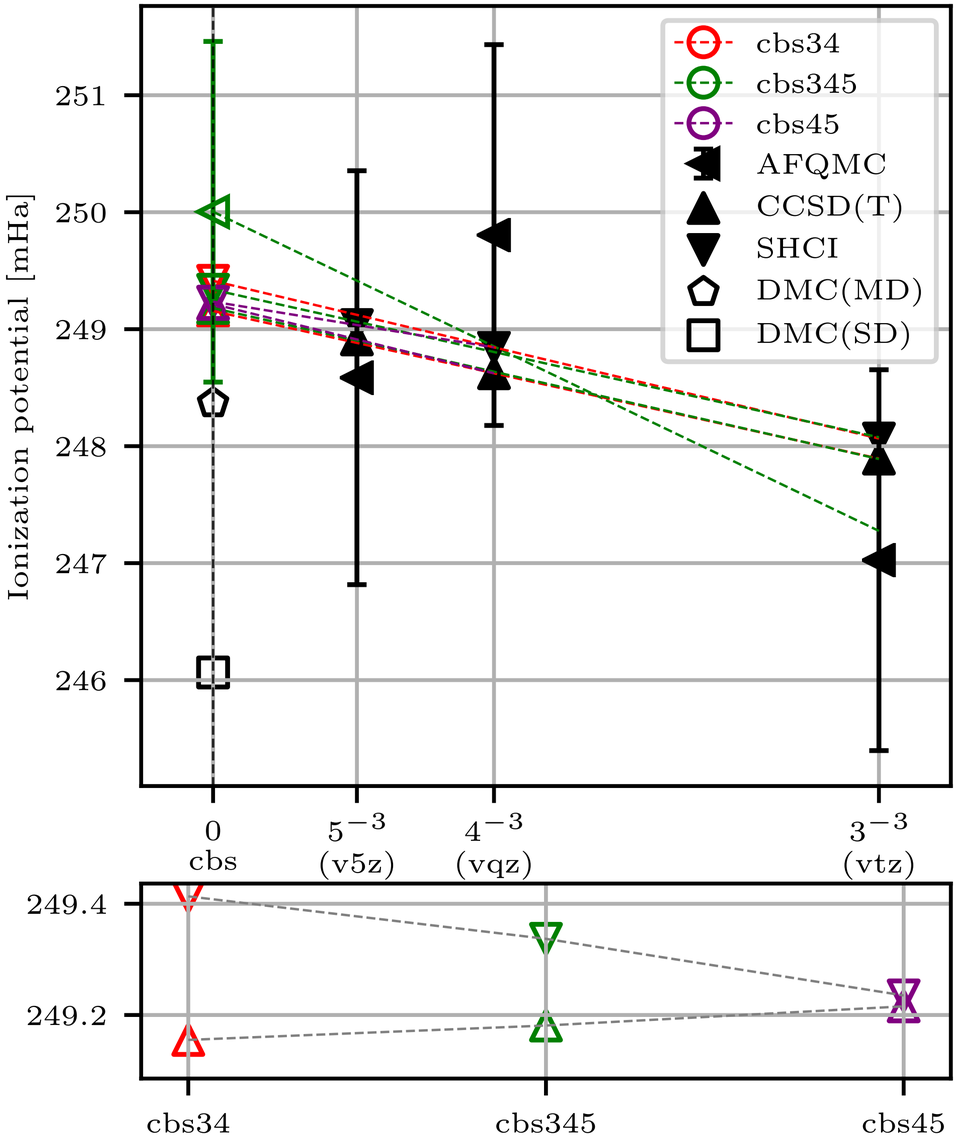
Correlation energy performance



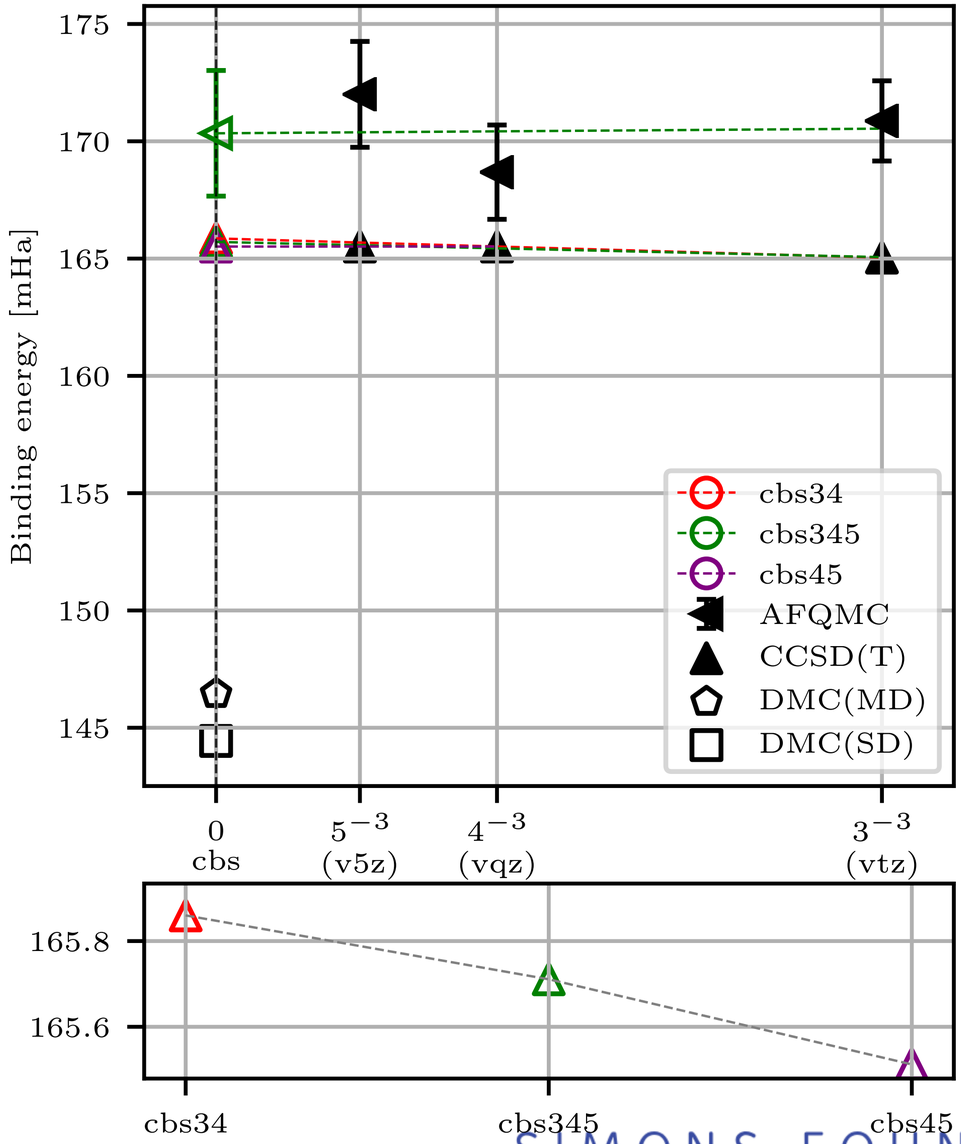
Energy differences

Basis set extrapolation: differences

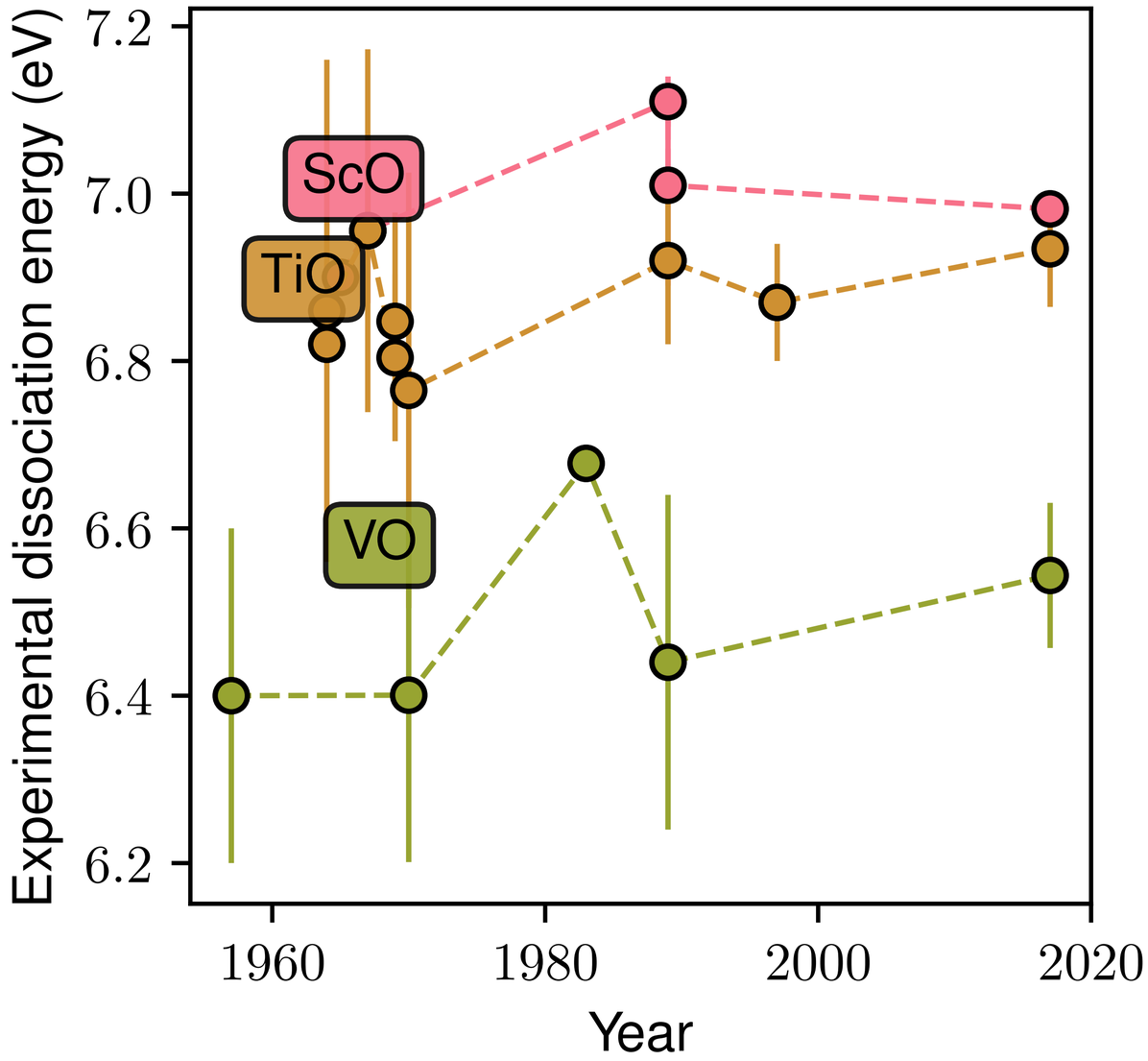
Ionization potential of Cr



Dissociation energy of CrO molecule



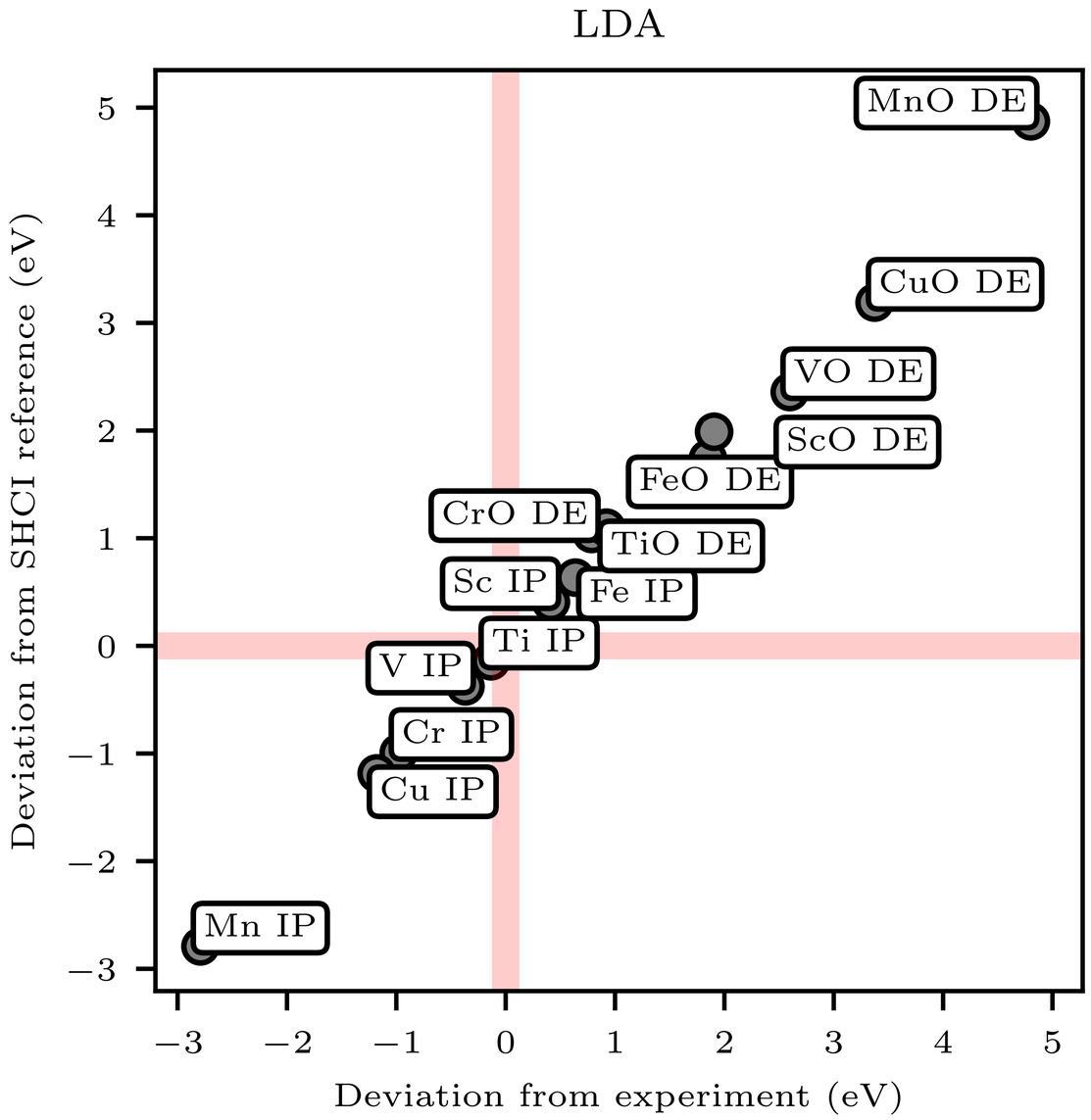
Energy differences: the difficulty with experiment

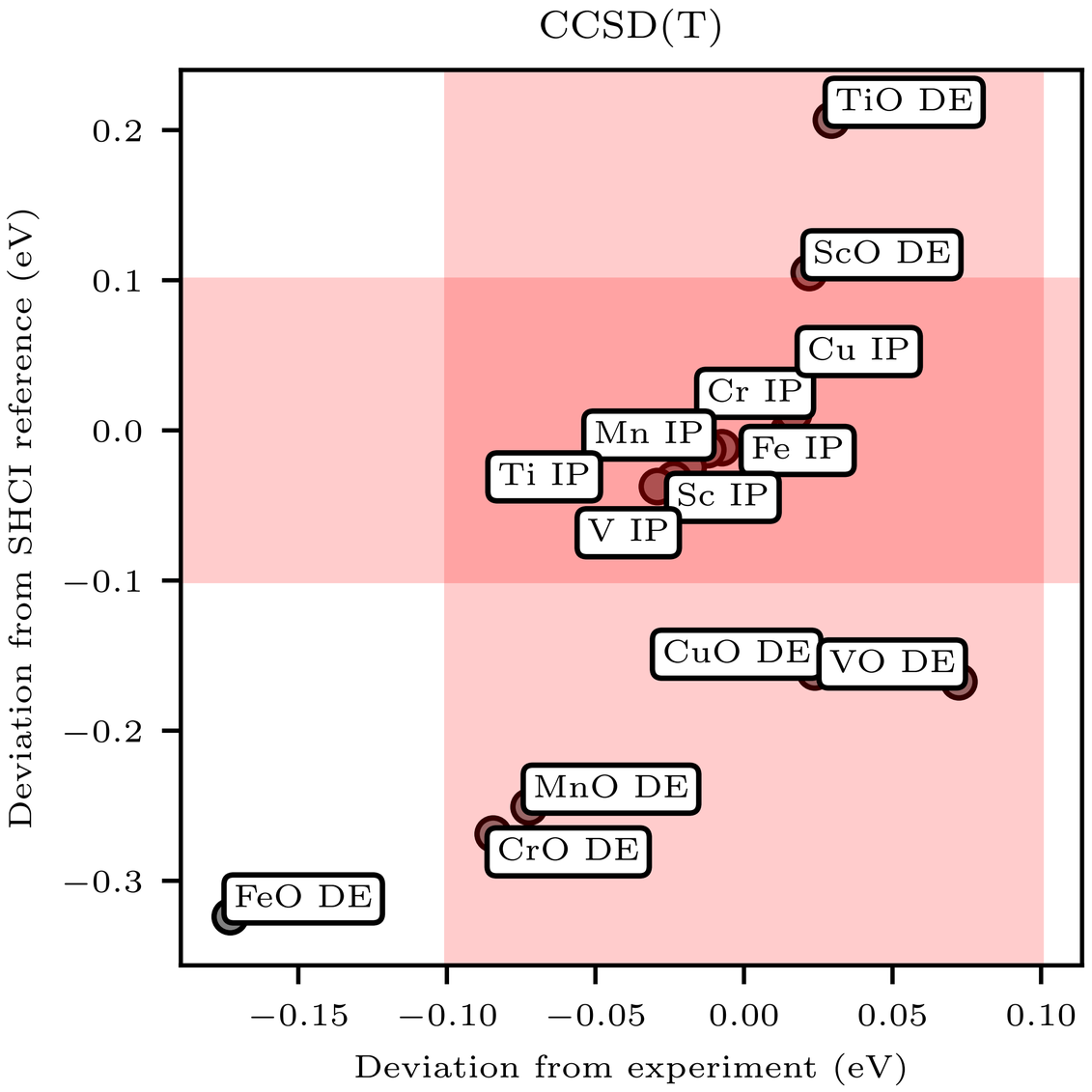


Experimental uncertainties are substantial

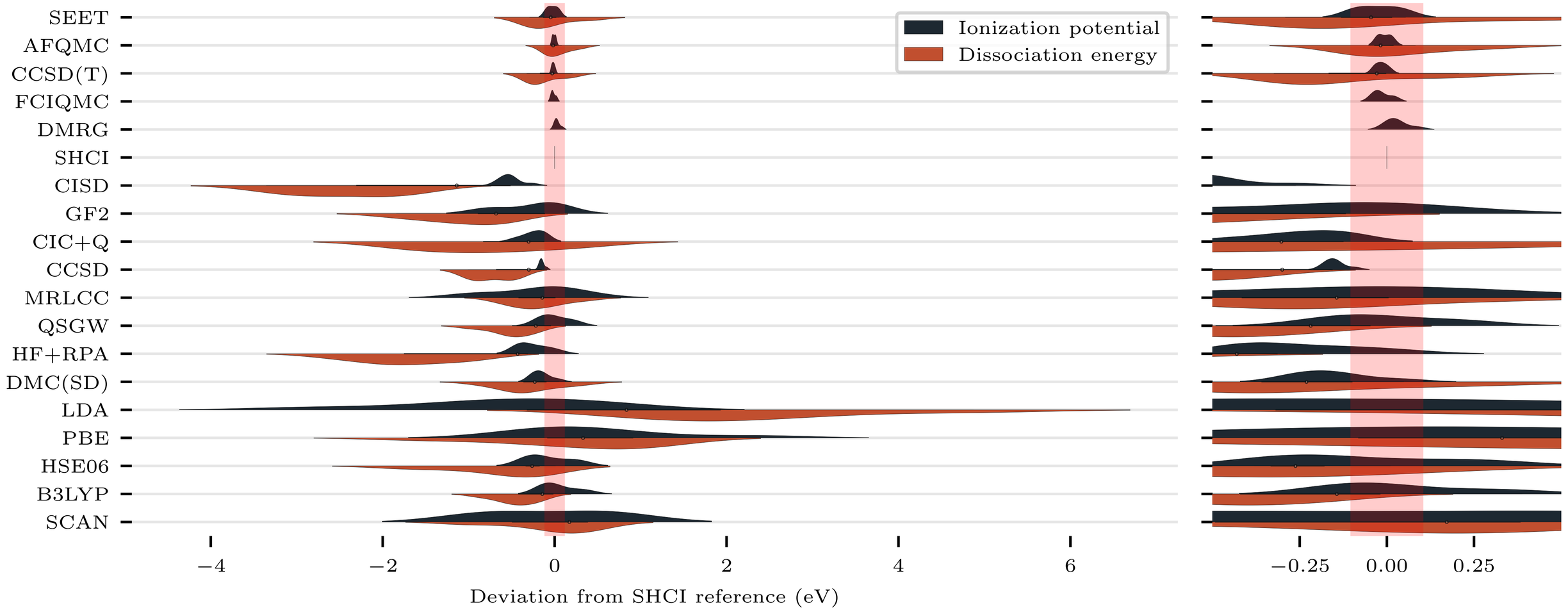
Measure the distance from the range of experimental results

Limiting factor is experiment!

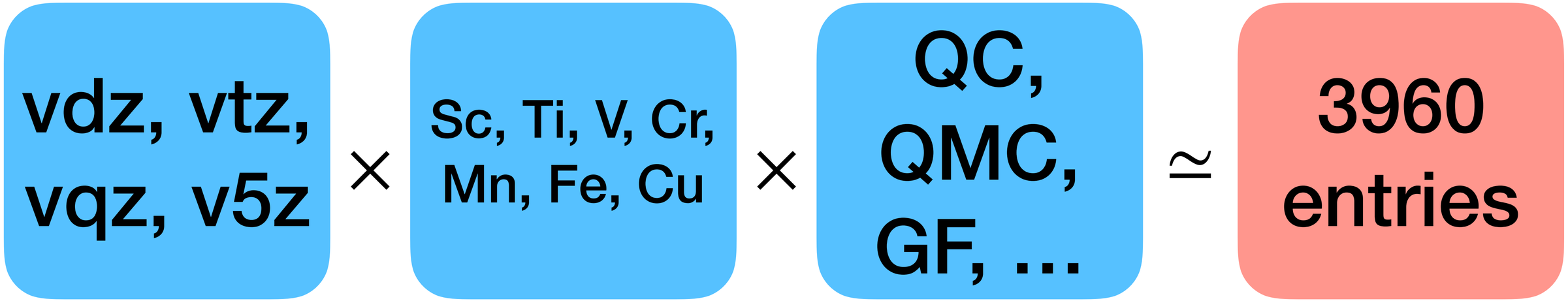




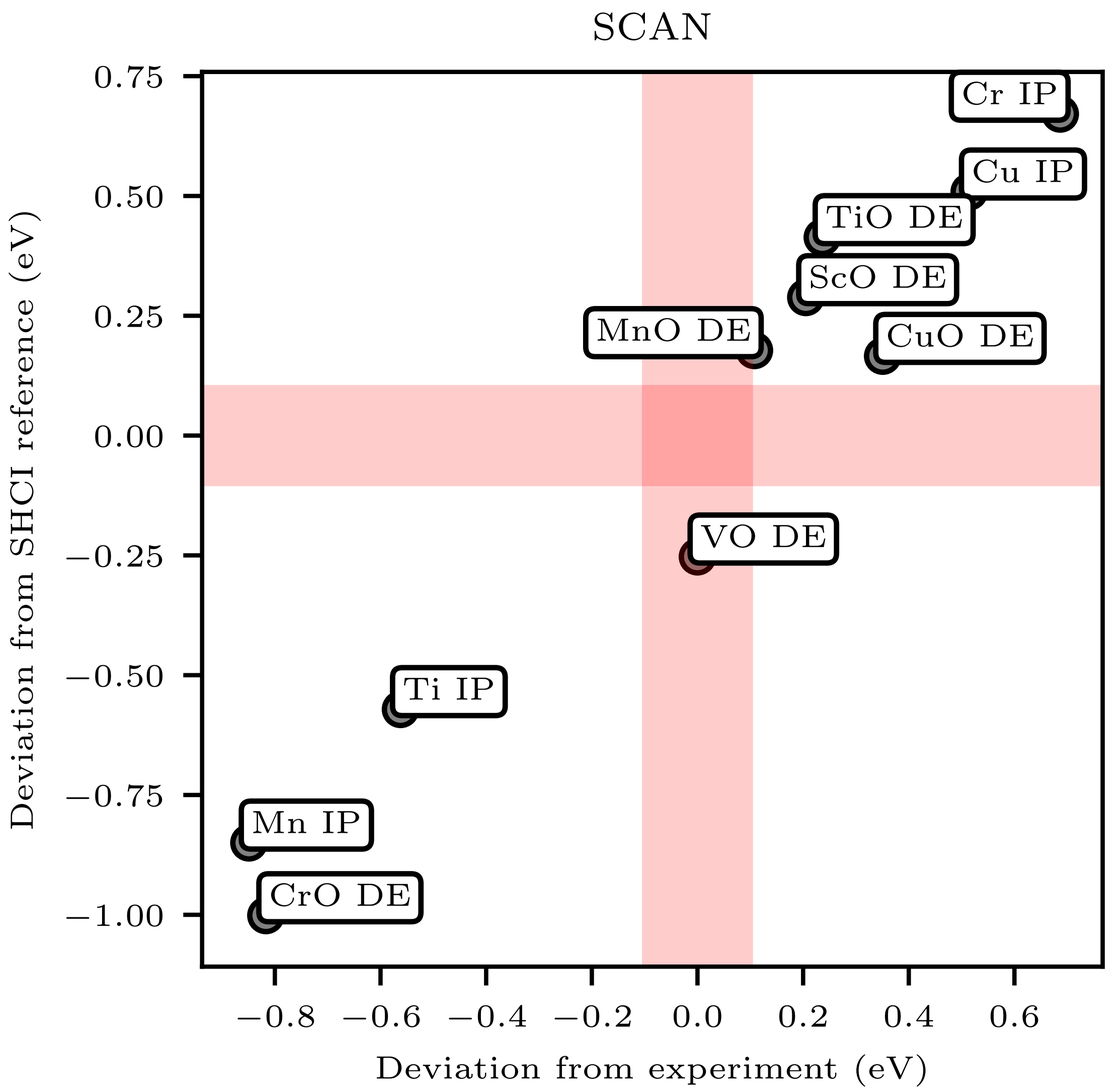
Deviation from experiment

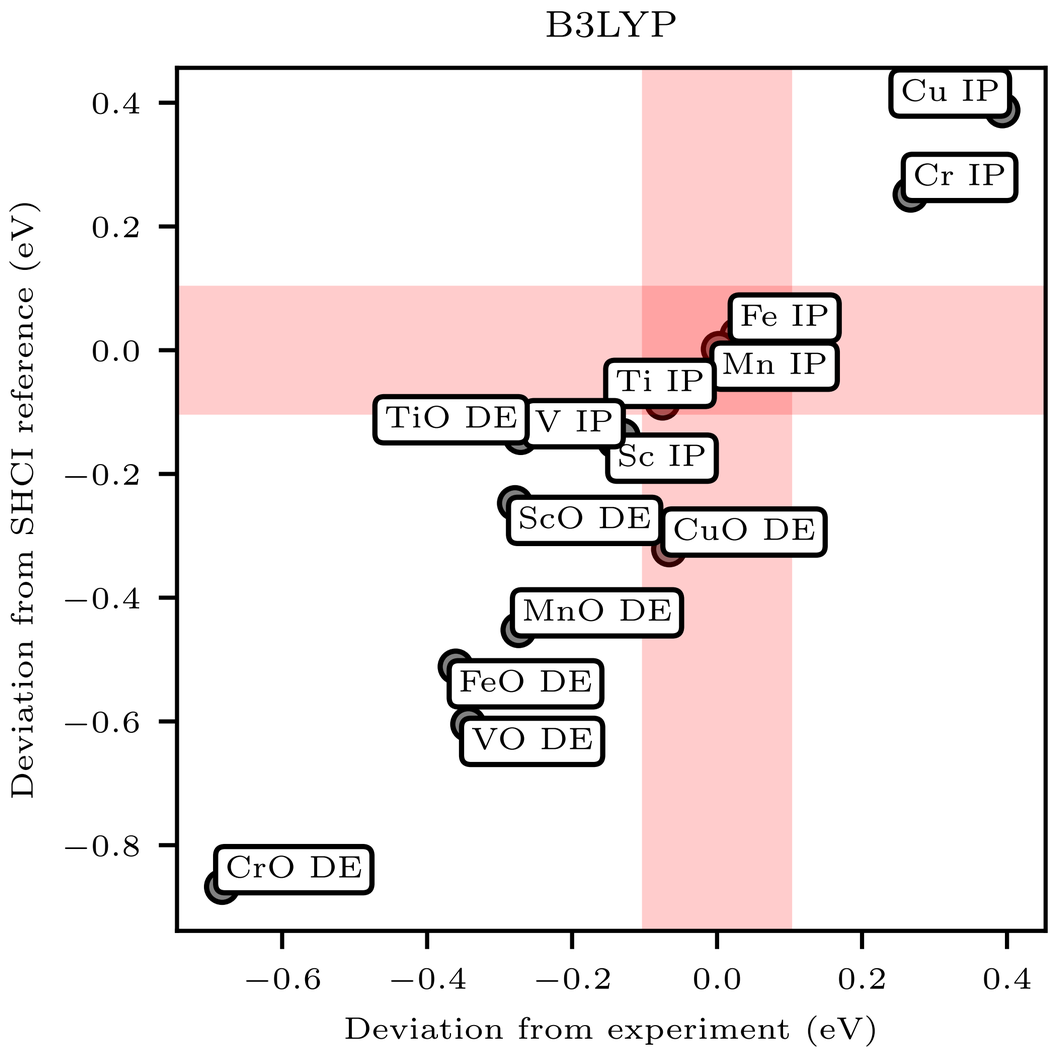


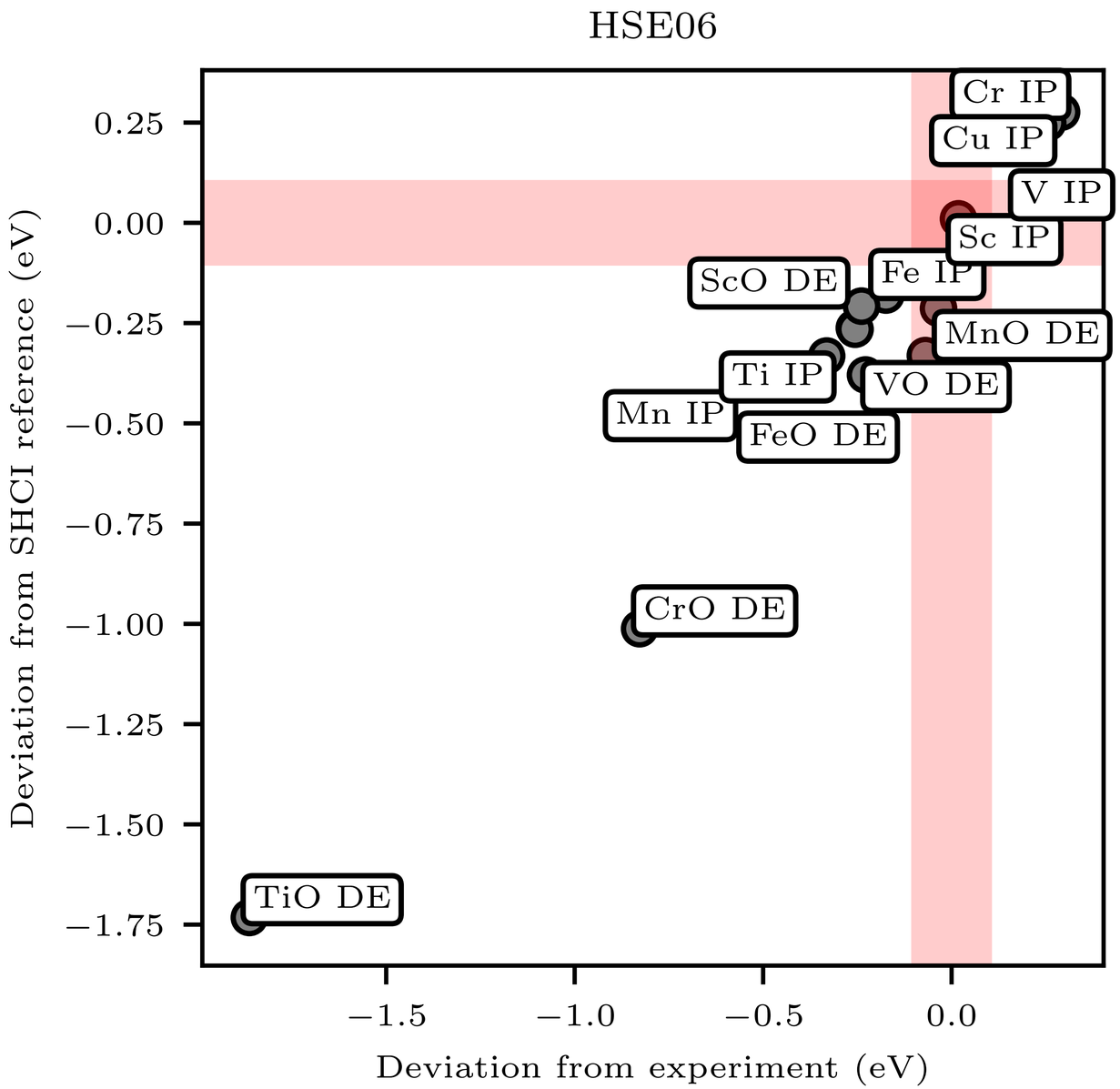
Summary

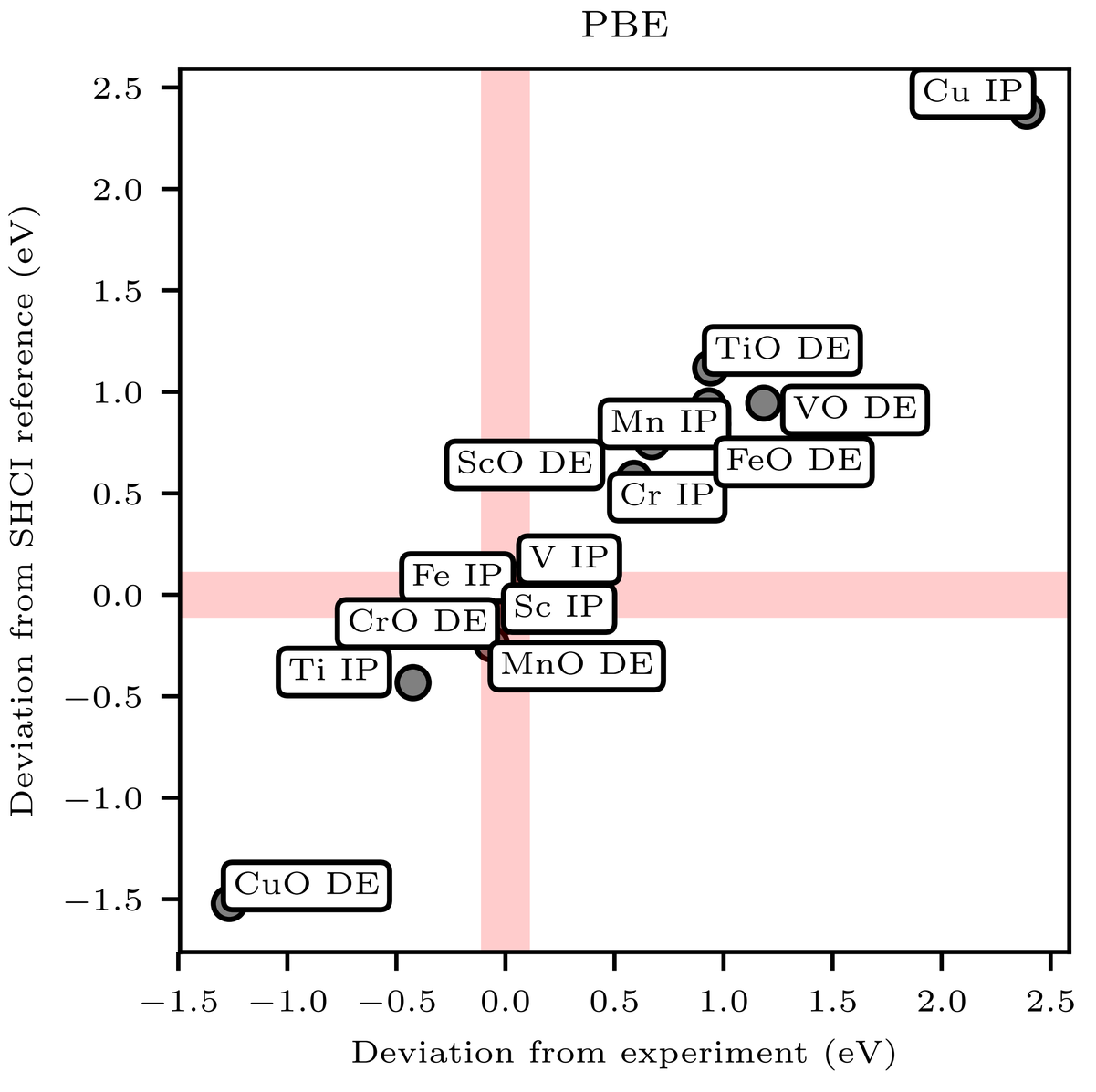


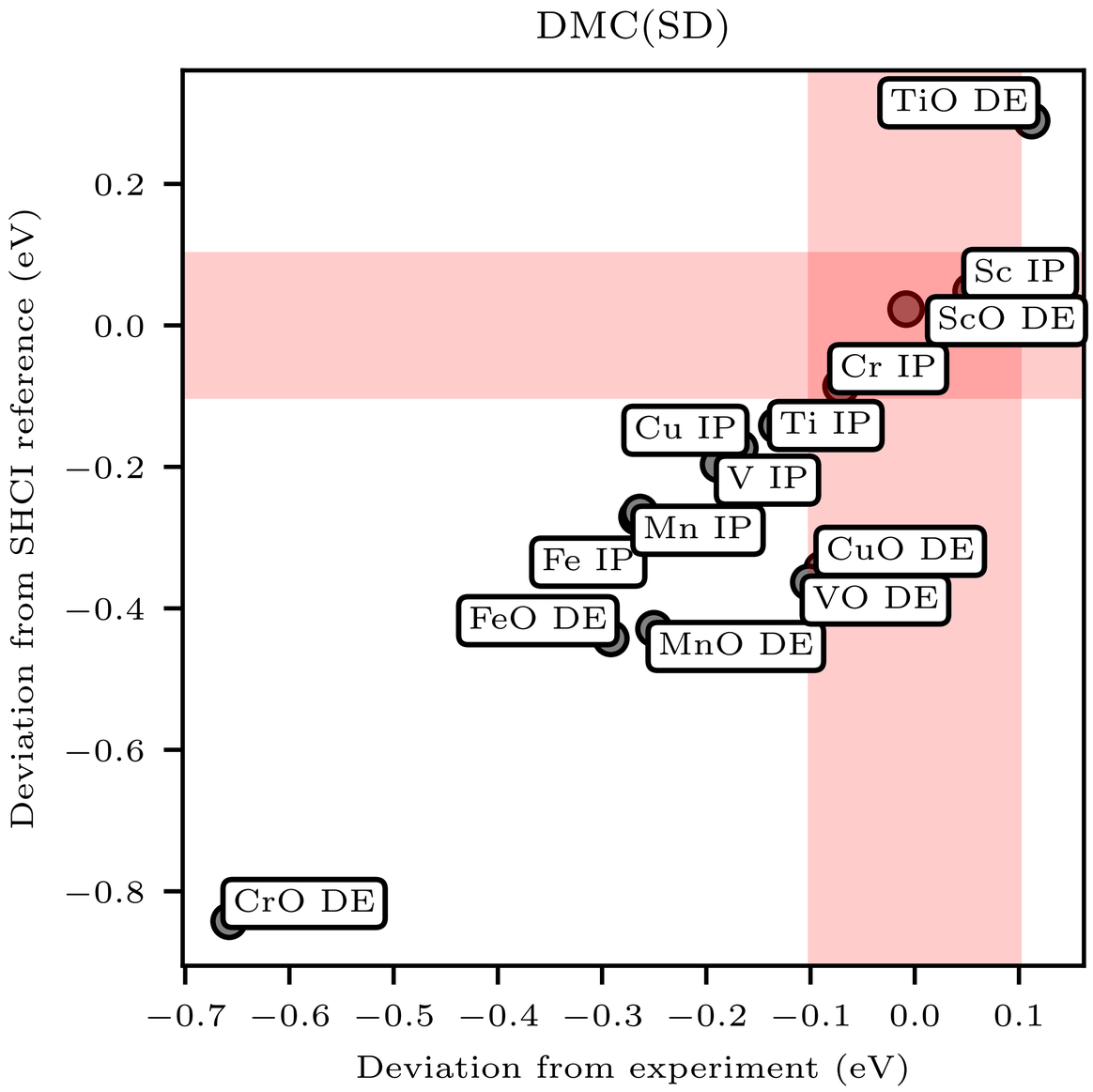
- Provenance well-defined
- Internal reference, precise results on systems containing up to 25 correlated electrons
- Enables clean method assessment
- Practical calculations rely on cancellation of error to obtain highly accurate results

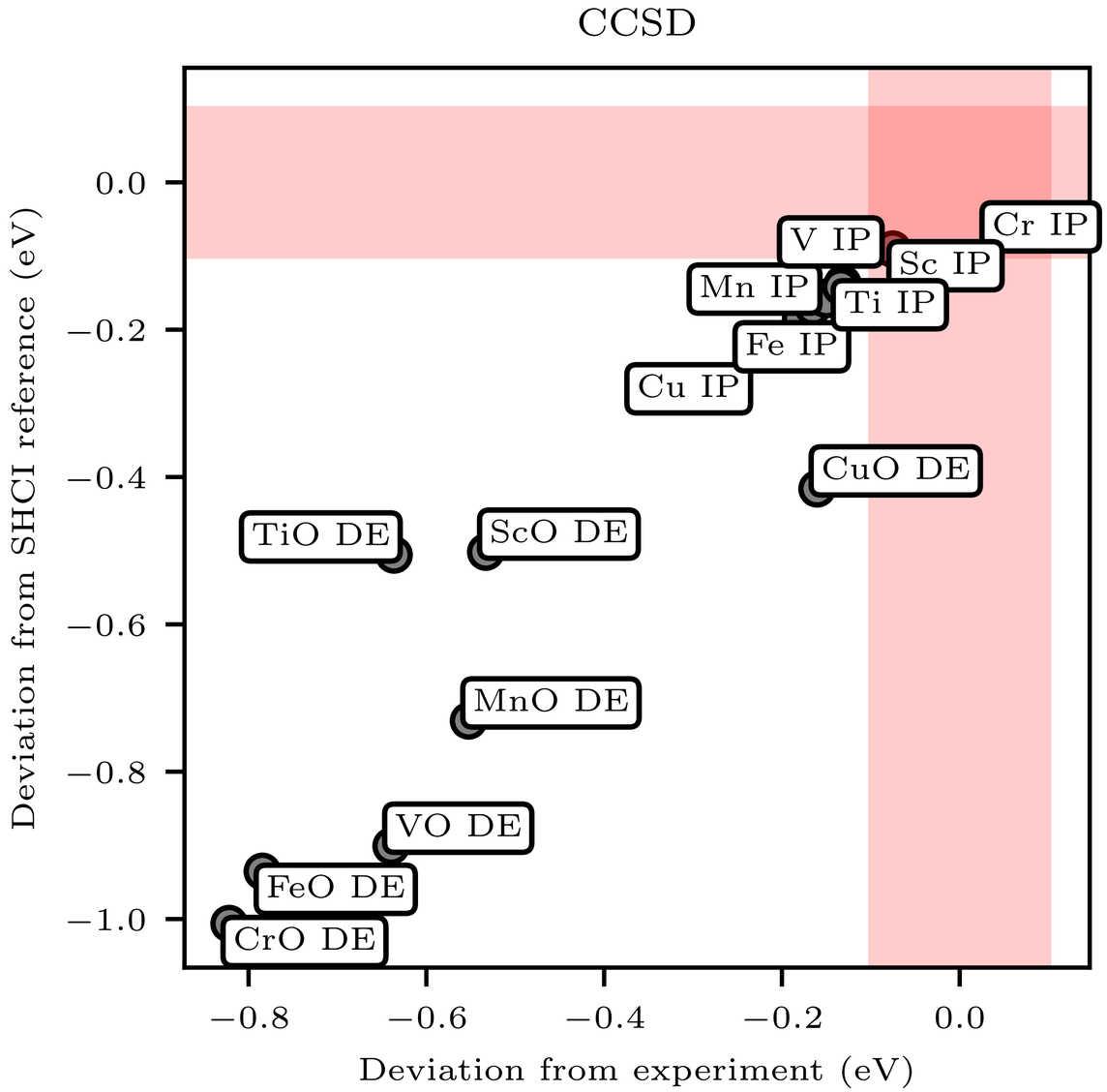


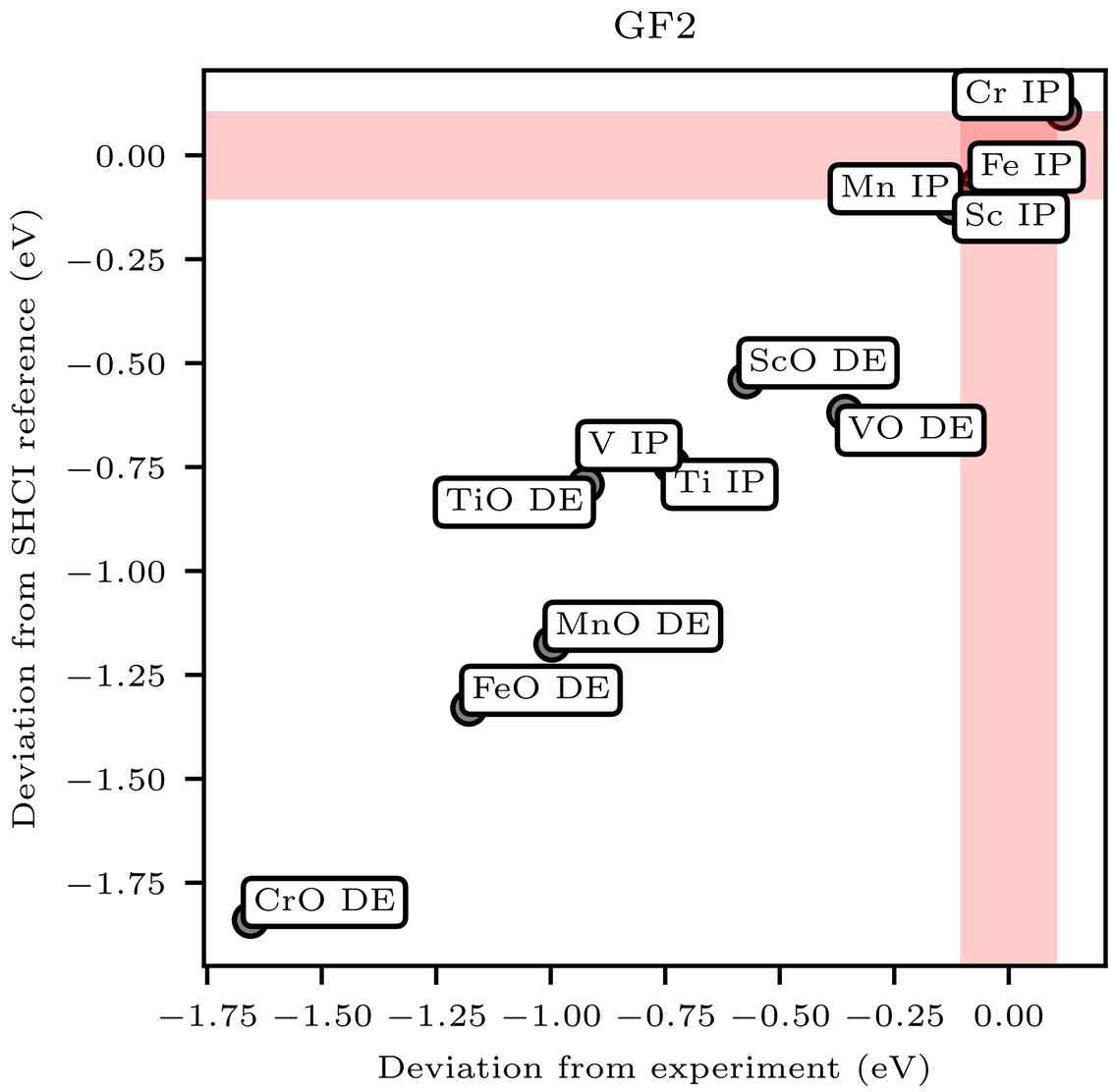


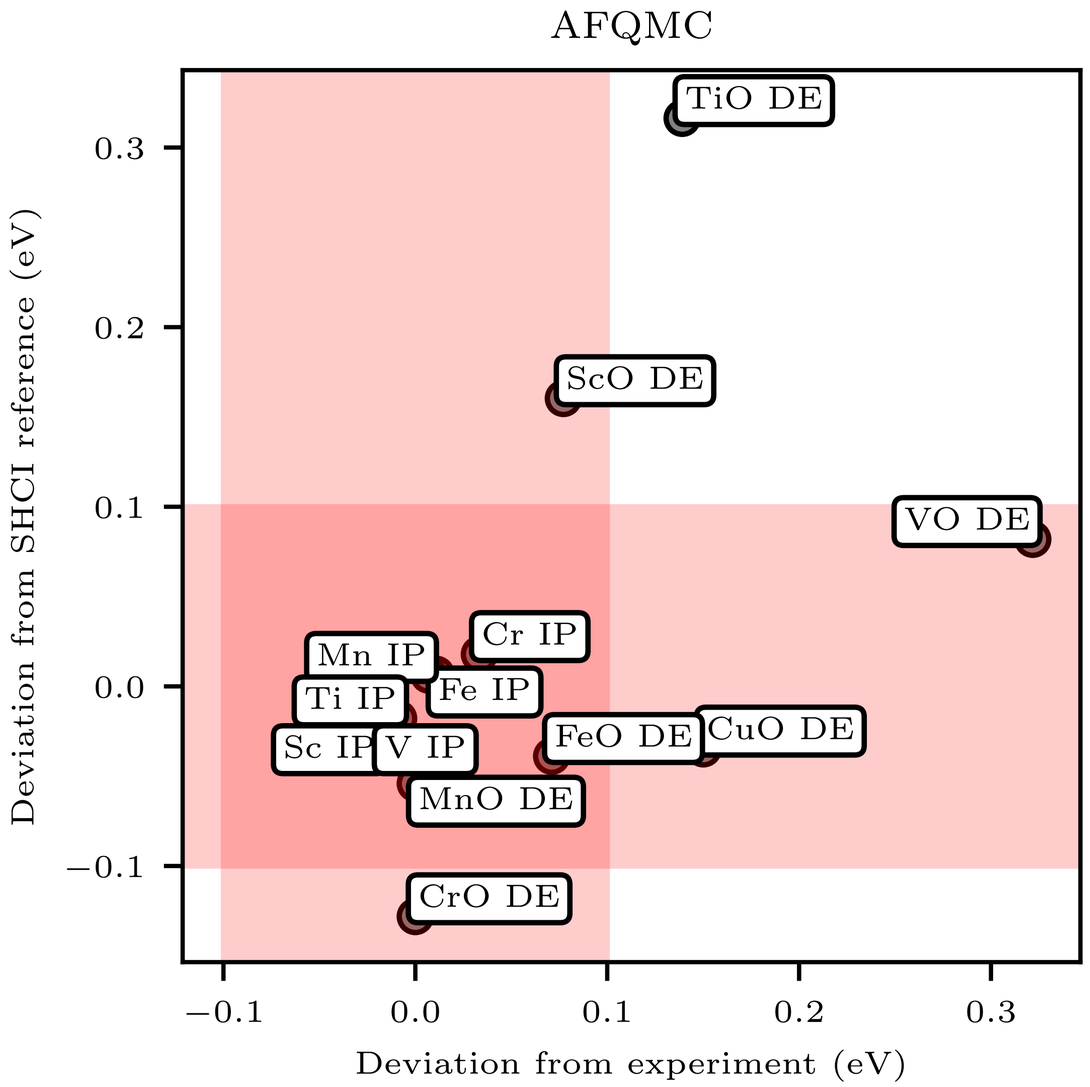




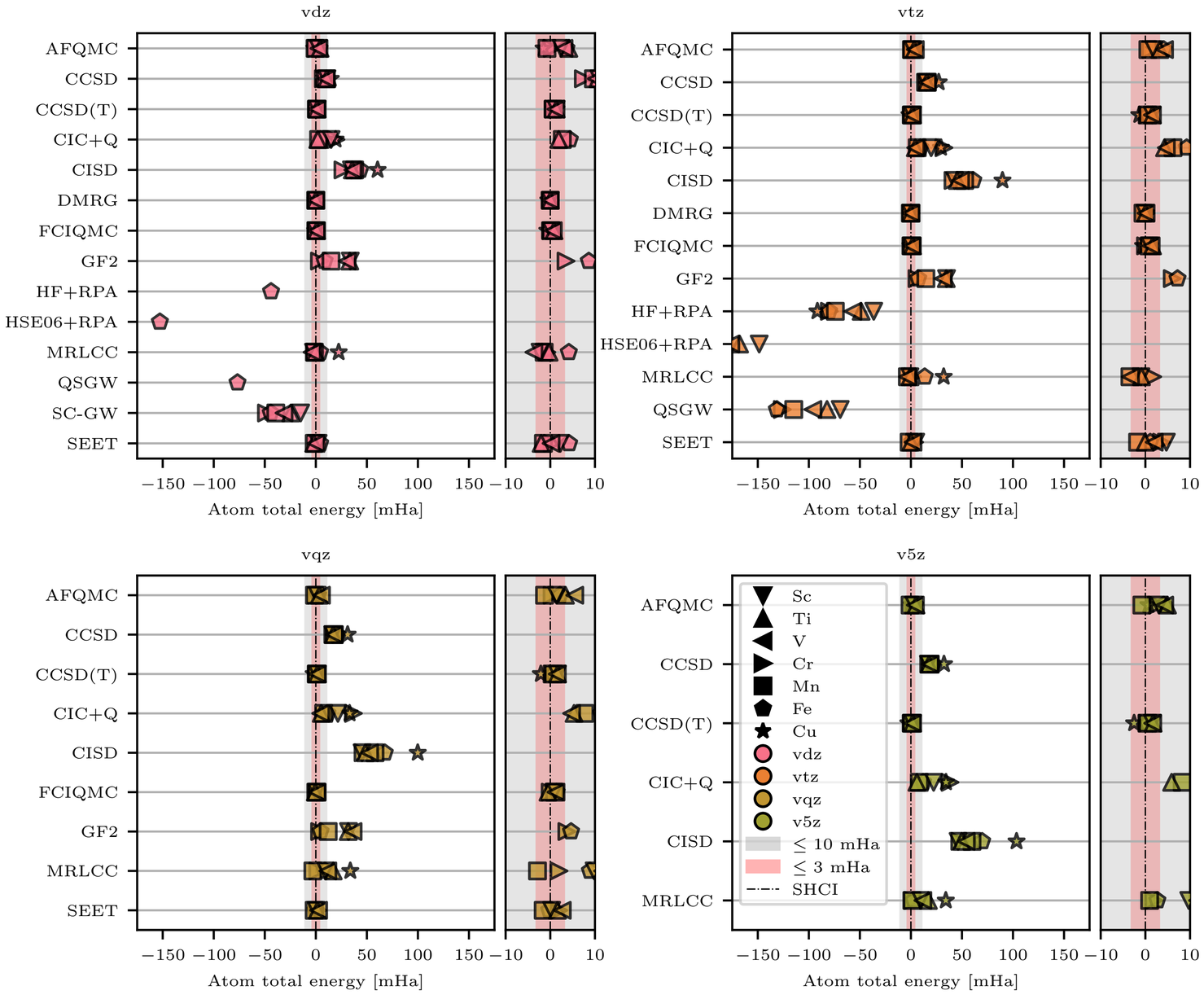








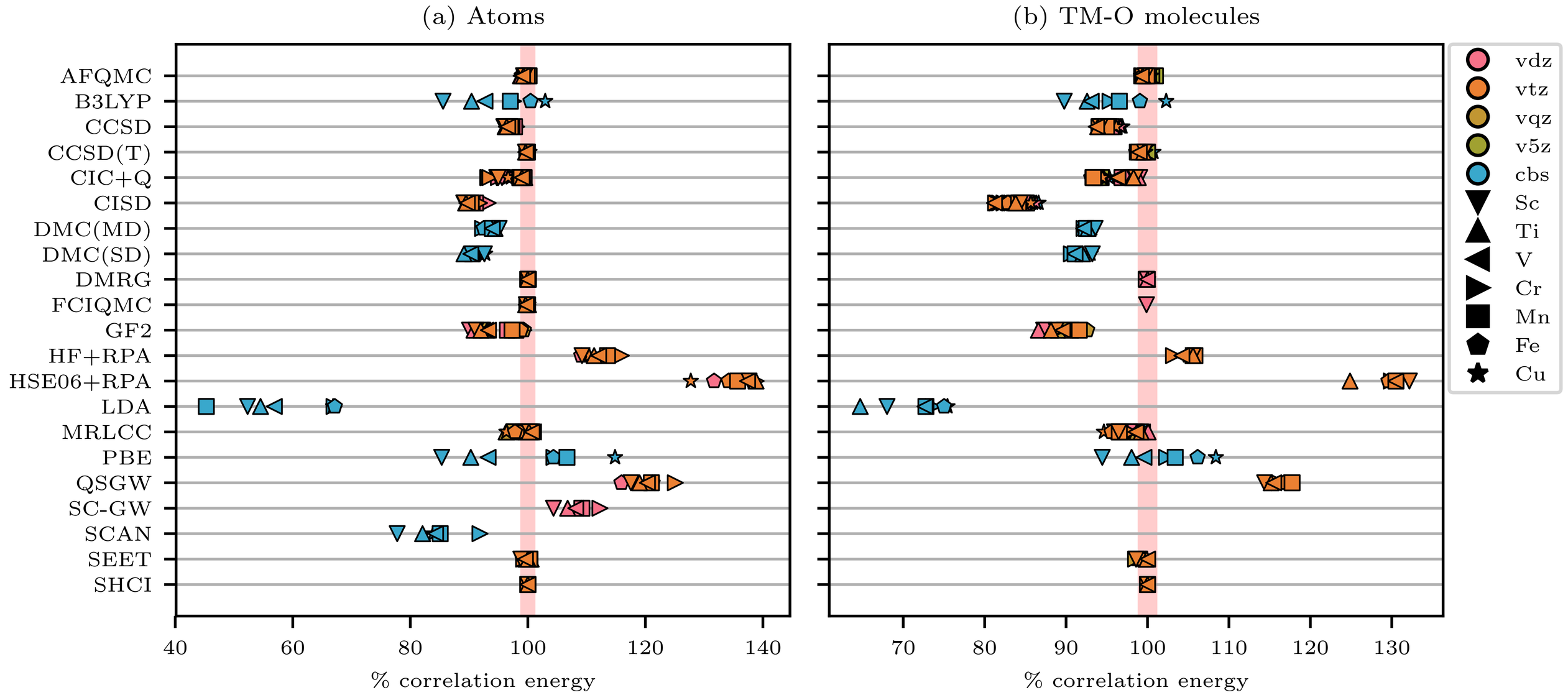
Total energy in a basis



Error is **only** the error in the solution method.

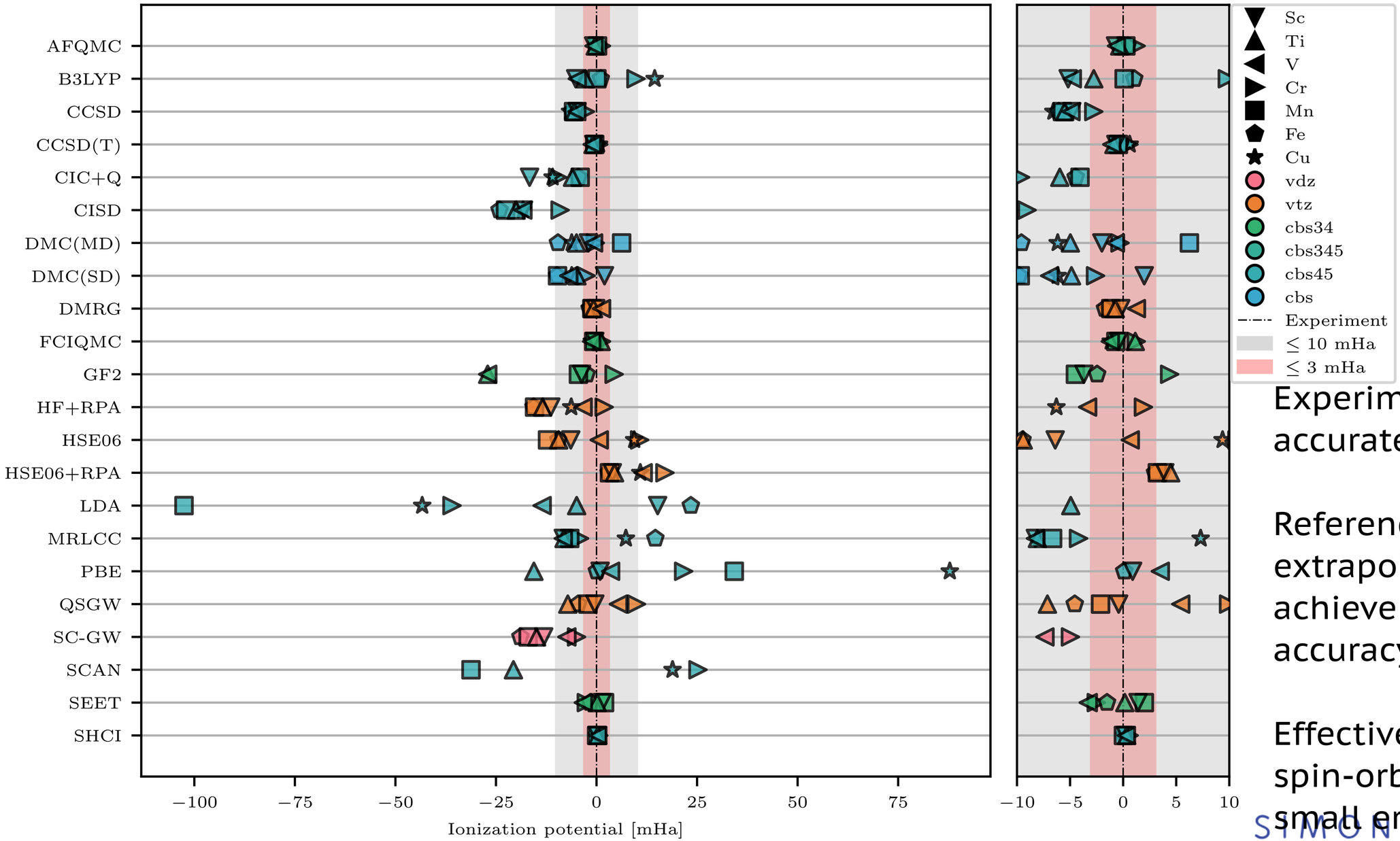
Useful for debugging and improving methods

Correlation energy



Many methods obtain very similar percentage of correlation energy across different systems and basis se

Ionization relative to experiment

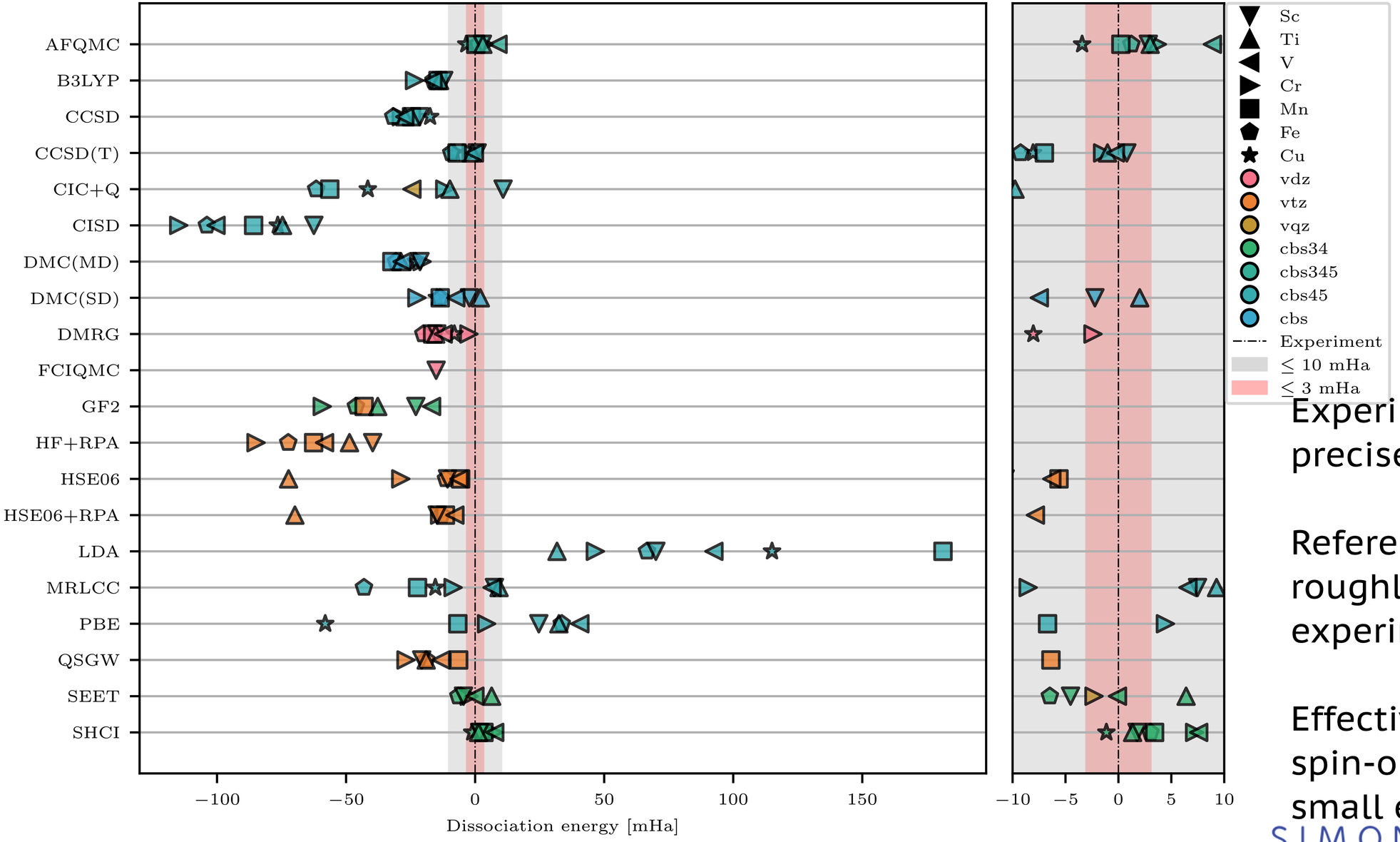


Experimental values very accurate.

Reference methods in extrapolated basis achieve “chemical accuracy” of 1 mHa.

Effective core potentials, spin-orbit effects lead to small errors.

Disocciation energy



Experimental values less precise (10 mHa spread)

Reference methods roughly as good as experiment

Effective core potentials, spin-orbit effects lead to small errors.

Did we test “strong correlation”

The systems we tested were not what chemists would call “strongly correlated.”

The 1-RDM for an accurate result is not too different from the 1-RDM of a single determinant wave function.

However, so-called “dynamic correlation” is very large in these systems.

This is why methods like CCSD(T) work very well but multi-reference methods perform worse; they have “wasted” some of their description space.

Other thoughts

One can implement correction methods based on the consistent performance of some methods (FN-DMC, for example)