High accuracy and effective models for strongly correlated electron systems

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High accuracy for real materials

A part of this SciDAC project is to evaluate new technologies for higher accuracy quantum simulations. This part is focused on using quantum Monte Carlo techniques on realistic models of materials to obtain predictive accuracy. The fundamental theory of condensed matter is the Schödinger equation for nuclei and electrons:

$$\hat{H}\Psi_s(r_1, r_2, \ldots) = E_s\Psi_s(r_1, r_2, \ldots)$$

where

$$\hat{H} = \frac{1}{2}\sum_i \nabla_i^2 + \sum_{i<j}\frac{1}{r_{ij}} + \sum_{\alpha,i}\frac{Z_\alpha}{r_{i\alpha}},$$

where for brevity we've excluded the nucleus-nucleus interactions. Our objective is to tackle this equation as directly as possible using Monte Carlo techniques to deal with the high dimensionality of Ψ. There are two main techniques we use. The first is a variational technique (VMC), which approximates the lowest eigenfunction by minimizing the expectation value of $\hat{H}$ with respect to a parameterization. Since we use Monte Carlo to evaluate the necessary integrals, we have a lot of flexibility in the functional form. The second technique is diffusion Monte Carlo (DMC), which simulates the equation

$$-\frac{d\Psi}{dt} = \hat{H}\Psi$$

stochastically. This PDE has the ground state (actually any eigenstate) as its steady state distribution. This technique, if implemented exactly, has a sign problem, which we cure by using a trial function (from the above VMC method) to approximate the values of the nodes, or zeros of the wave function.
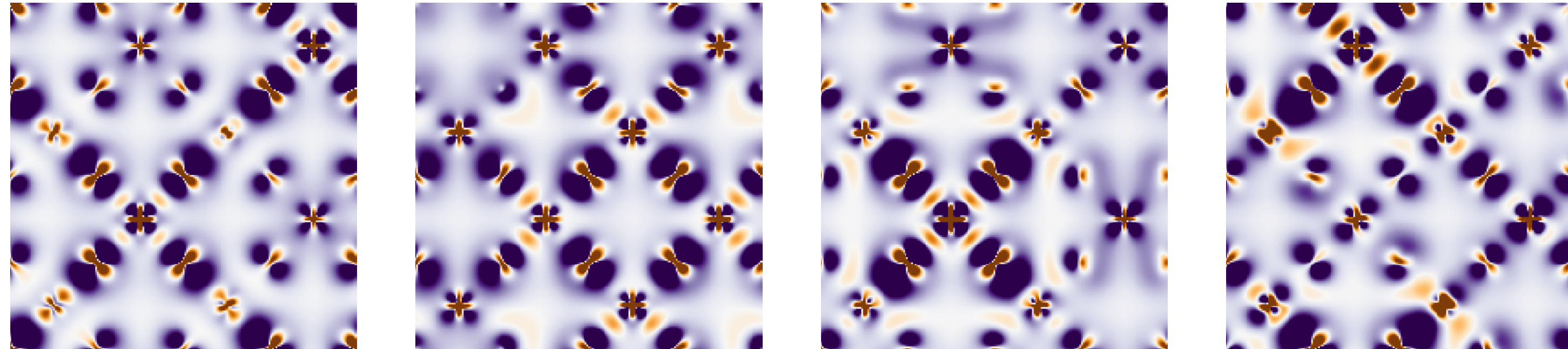
It turns out that using relatively simple trial nodal surfaces, very accurate results can be obtained for traditionally difficult systems.
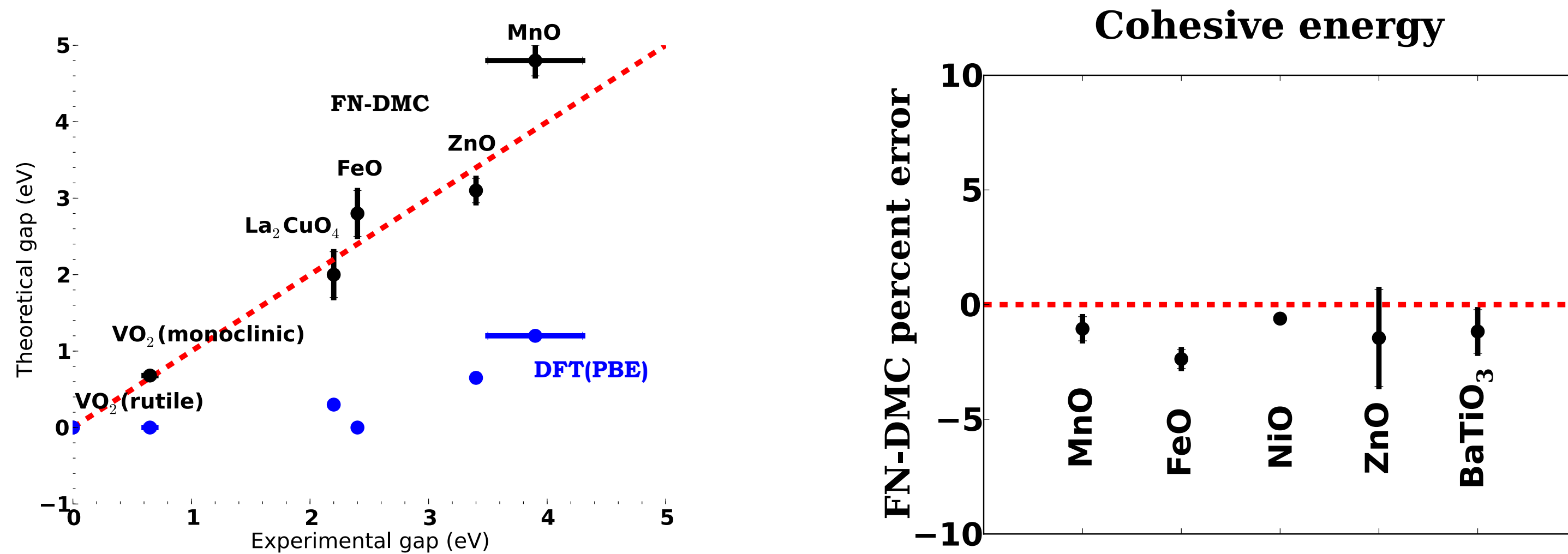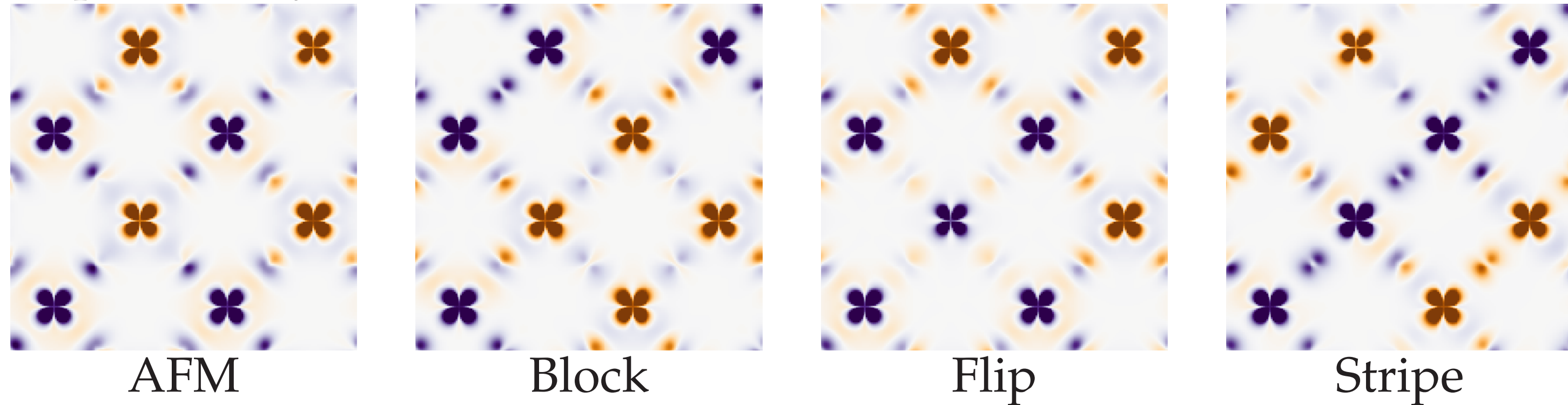

Holes in the superconducting cuprates
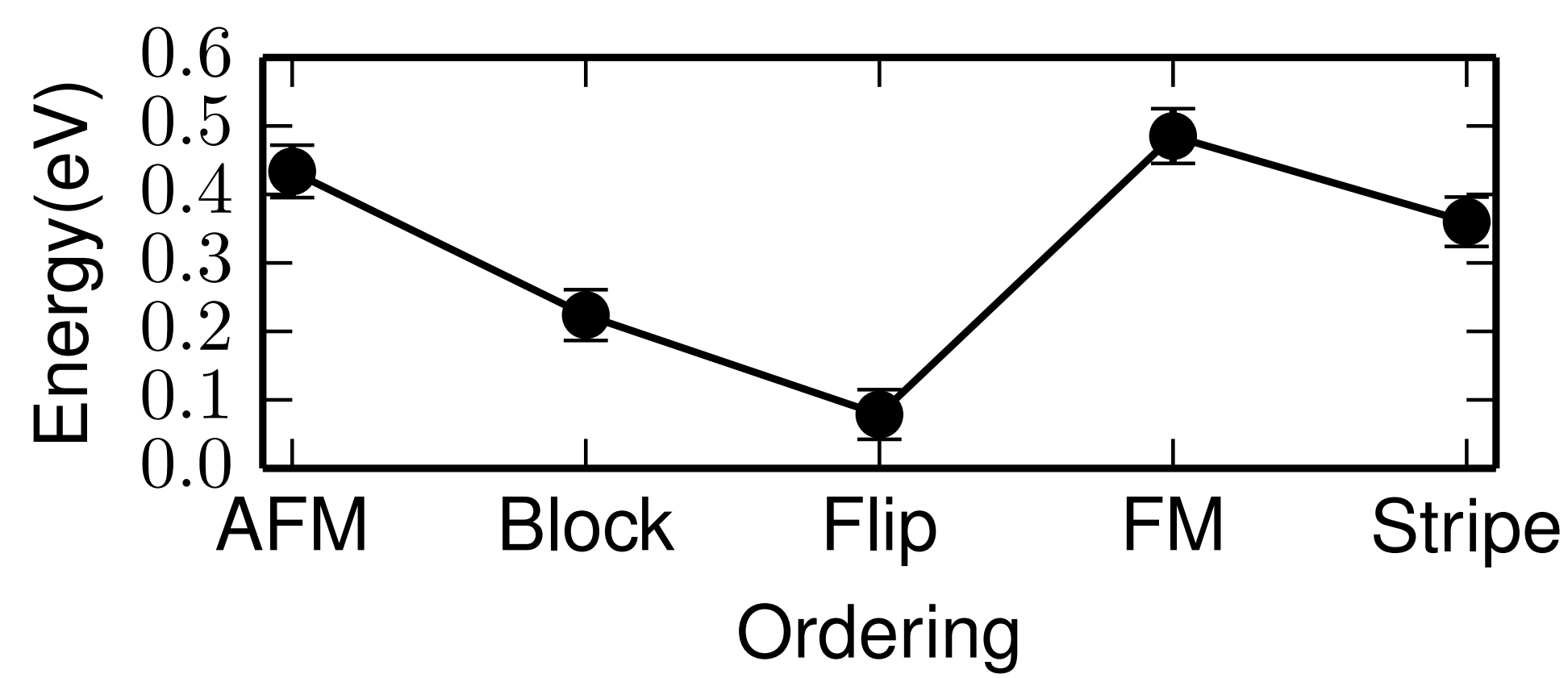
The lowest energy is a spin-polaron that appears to have zero gap–a unique structure. We have obtained the metal-insulator transition in the cuprates for the first time, provided an explanation for optical signals seen around 1eV upon doping, and provided a prediction for small peaks in X-ray and neutron experiments that have not previously been considered. More details in Ref [3]

Implementation and possible improvements

Since the method is based on Monte Carlo, it scales very well, up to 1,000,000 threads on Mira at ALCF. The technique's main disadvantage is the computational cost. While the scaling is good at $\mathcal{O}(N_e^3)$, where N_e is the number of electrons, the prefactor is about 1,000 times larger than standard density functional theory calculations. The main costs are the following:

- One-particle orbitals (3D function evaluation)
- Updating the determinant (Matrix-vector multiplication)
- Electron-electron minimum image distances
- Evaluating Jastrow correlation factors (sums of many terms)

References

[1] Burkatzki, M., C. Filippi, and M. Dolg. J. Chem. Phys. **126** 234105 (2007), *ibid* **129** 164115 (2008)

[2] H.J. Changlani, H. Zheng and LKW arXiv:1504.03704 (submitted)

[3] L.K. Wagner arXiv:1505.08091 (submitted)

Deriving effective models from first principles

Since we have an accurate method for calculating properties we'd like to use it to go from a big Hilbert space to a small Hilbert space, integrating out 'boring' things like short-range electron-electron correlations.

The Hamiltonians
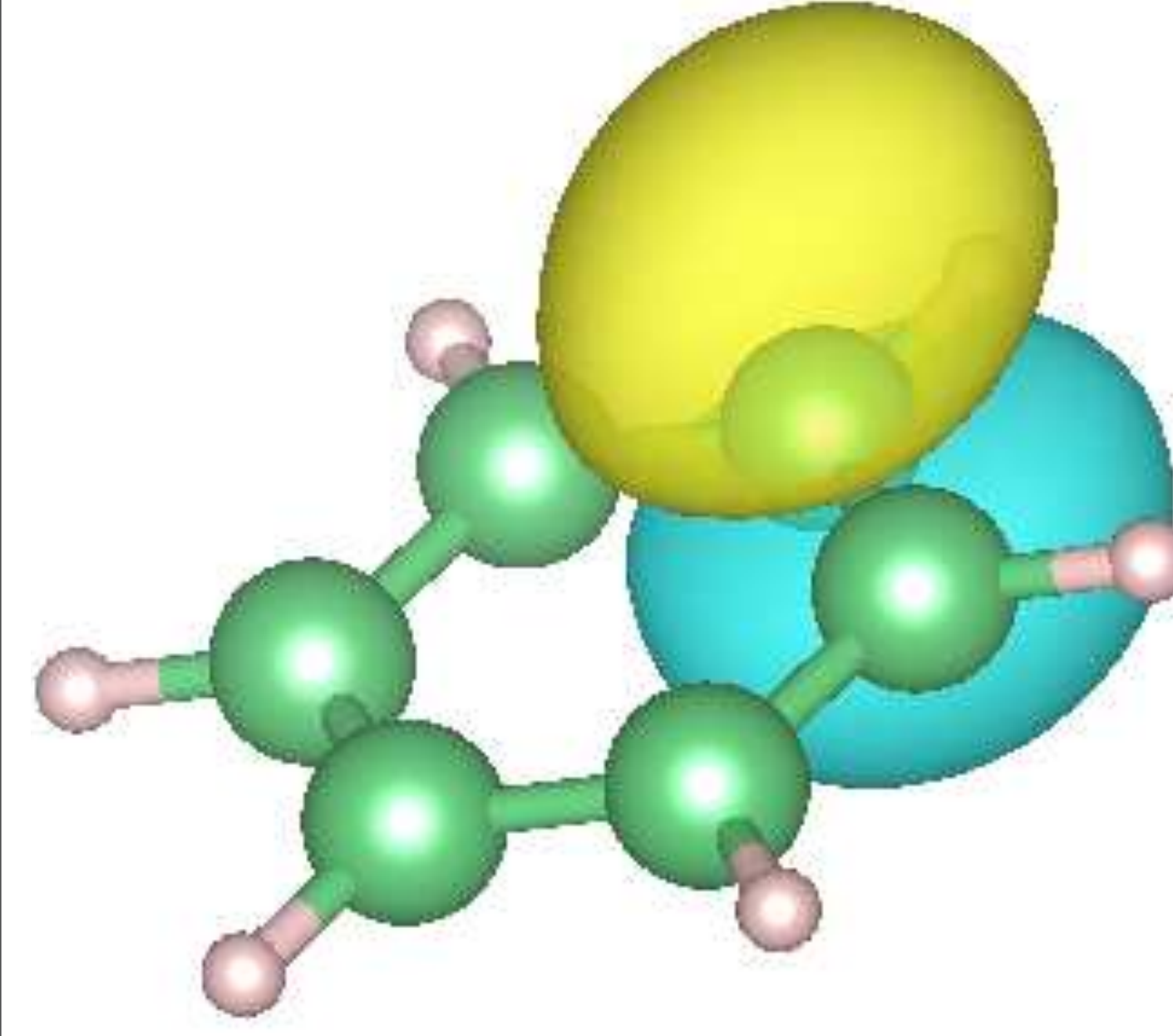
We'd like to map from a continuum Hamiltonian (large Hilbert space) to discrete lattice Hamiltonian (small Hilbert space). We do this using reduced density matrices. We will demonstrate this using a benzene ring, mapping from the continuum Hilbert space onto a 6-site lattice model. The lattice sites are the π orbitals, shown here. The Hamiltonian in the small space is then

$$\hat{H}_s = C + \sum_{ij} t_{ij}c_i^\dagger c_j + \sum_{ijkl} V_{ijkl}c_i^\dagger c_j^\dagger c_l c_k$$

if we limit ourselves to two-body interactions.

A better method

We would prefer not to solve for exact eigenvectors, since it's hard!

In the small Hilbert space, no matter the state, the expectation value of the energy is given by the expectation value of the creation/destruction operators (one- and two-body density matrix elements).

$$\tilde{E}_s \equiv \langle H\rangle_s = C + \sum_{ij} t_{ij}\langle c_i^\dagger c_j\rangle + \sum_{ijkl} V_{ijkl}\langle c_i^\dagger c_j^\dagger c_l c_k\rangle$$

This is true for **any** quantum state in the small Hilbert space.

So we can fit to *ab-initio* data by evaluating the energy expectation value $\tilde{E}_i$ and density matrix elements $\langle c_i^\dagger c_j\rangle_i$ and $\langle c_i^\dagger c_j^\dagger c_l c_k\rangle_i$ for a collection of non-eigenvalue states.

$$\begin{pmatrix} \tilde{E}_1 \\ \tilde{E}_2 \\ \ldots \\ \tilde{E}_M \end{pmatrix} = \begin{pmatrix} 1 & \langle c_i^\dagger c_j\rangle_1 & .. & \langle c_i^\dagger c_l c_k\rangle_1 & .. \\ 1 & \langle c_i^\dagger c_j\rangle_2 & .. & \langle c_i^\dagger c_l c_k\rangle_2 & .. \\ 1 & \ldots & .. & \ldots & .. \\ 1 & \langle c_i^\dagger c_j\rangle_M & .. & \langle c_i^\dagger c_l c_k\rangle_M & .. \end{pmatrix} \begin{pmatrix} C \\ t_{ij} \\ .. \\ V_{ijkl} \\ .. \end{pmatrix}$$
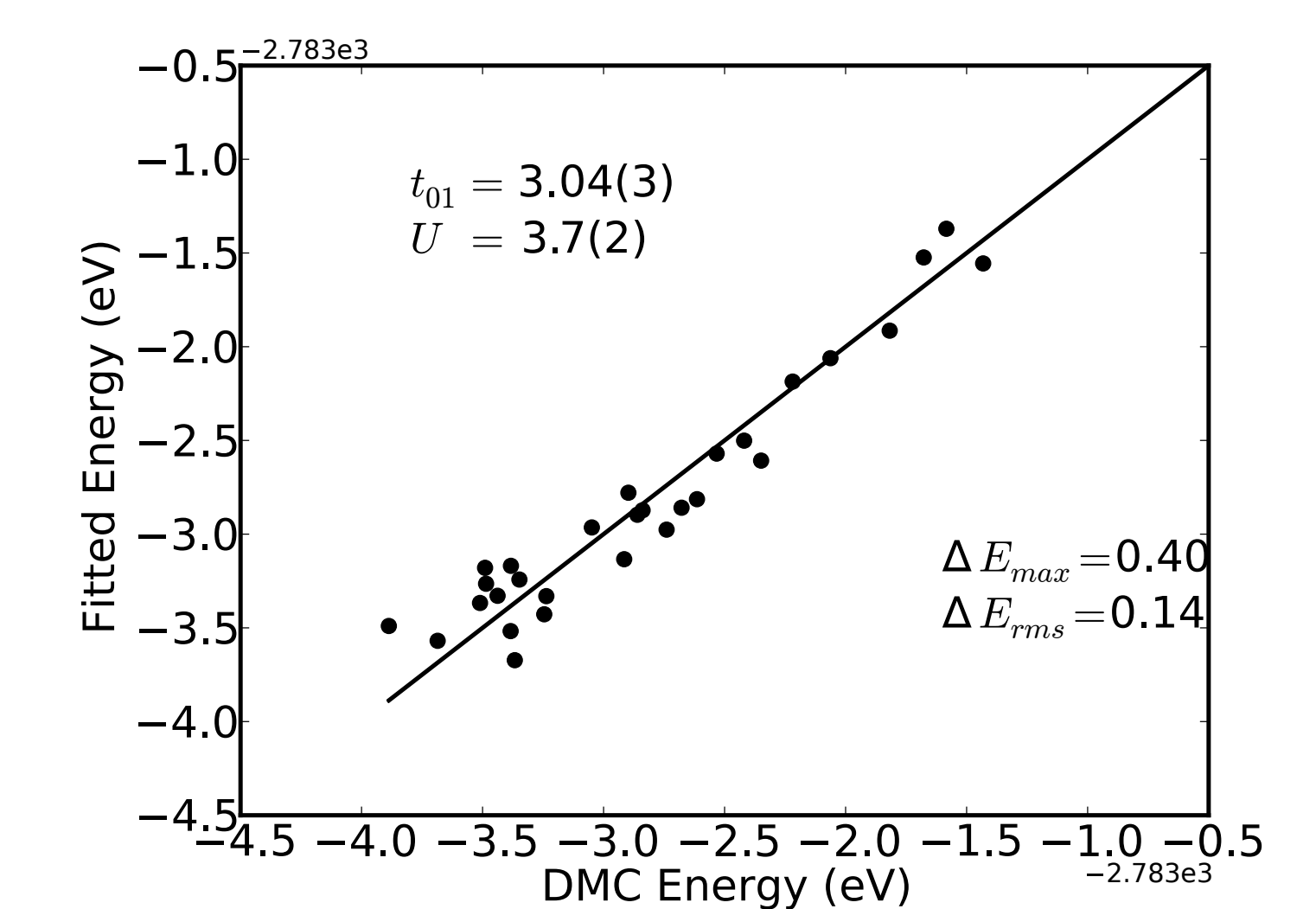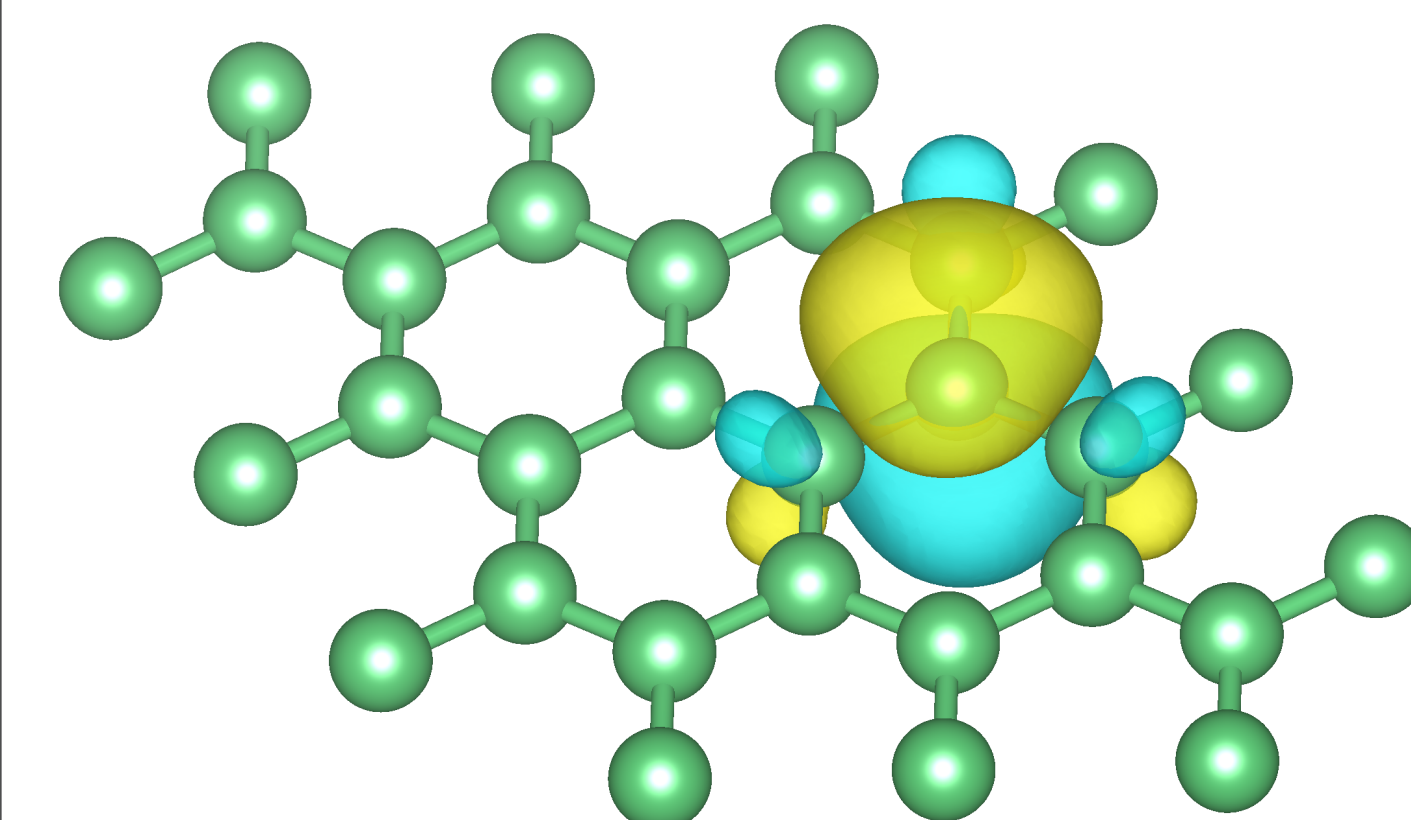
The procedure is:

- Evaluate $\tilde{E}_i$, $\langle c_i^\dagger c_j\rangle_i$, and $\langle c_i^\dagger c_j^\dagger c_l c_k\rangle_i$ in *ab-initio* QMC
- Find the best fit by least-squares. These are the model parameters.

Comparison to experiment
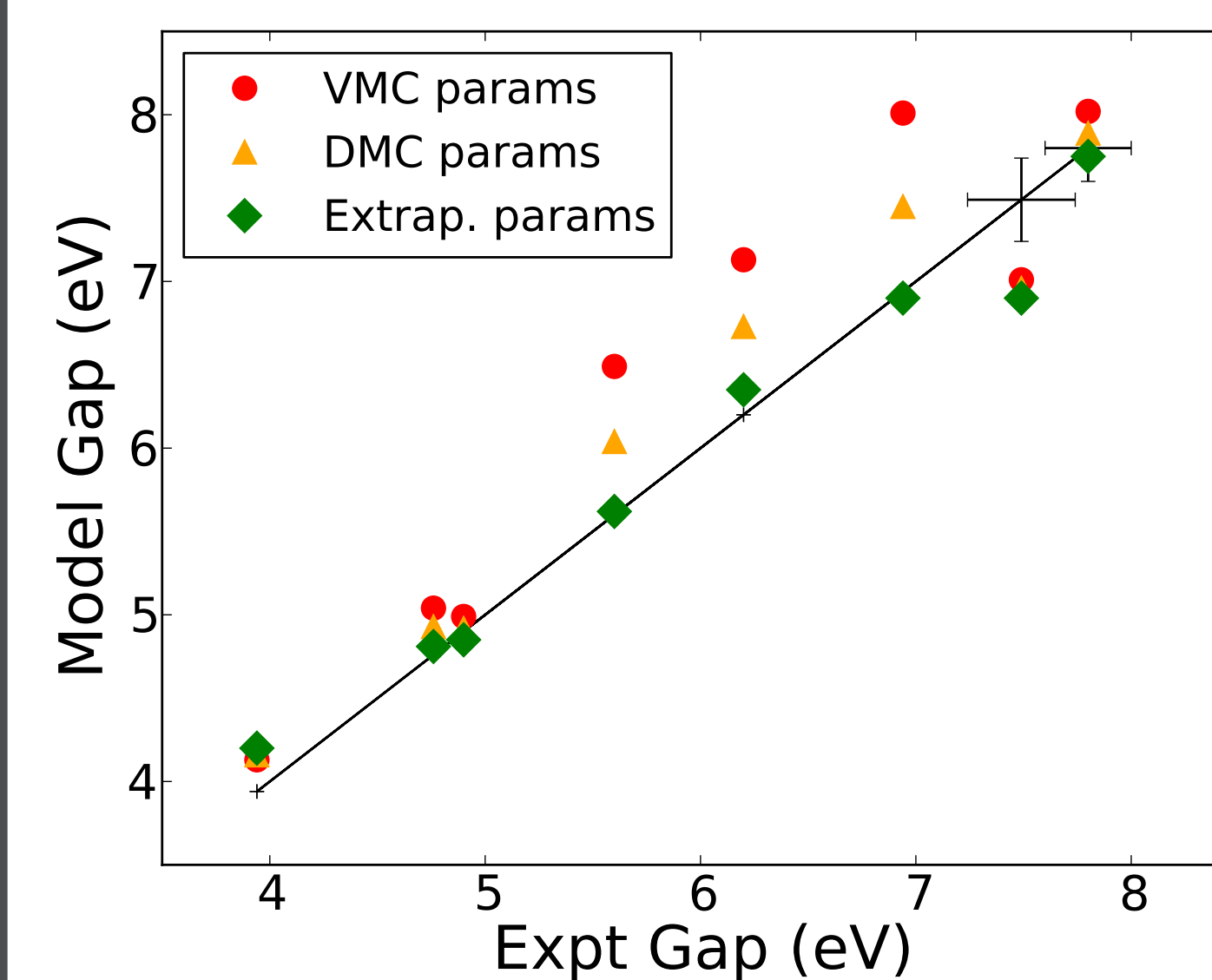
The resulting model can be solved via exact diagonalization to get excited state energies. The excitation energies are in excellent agreement with experimental ones.

Application to an extended system

We can perform the same procedure on graphene. The value of U^*/t is in good agreement with recent constrained-RPA values which reproduce the band structure.

Implementation details

The results presented here were produced using QWalk, an open-source package available at http://qwalk.org. Pseudopotentials were from BFD[1], and trial wave functions were taken from GAMESS (for molecules) or CRYSTAL (for graphene).

Acknowledgements