

Quantum Monte Carlo calculations in solids with downfolded Hamiltonians

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A systematic downfolding many-body approach for extended systems is presented [1, 2]. Many-body calculations operate on a simpler Hamiltonian which retains material-specific properties. The Hamiltonian is systematically improvable and allows one to dial, in principle, between the simplest model and the original Hamiltonian. As a by-product, pseudopotential (PSP) errors are essentially eliminated using a frozen-core (FC) treatment. The cost of the calculation is dramatically reduced without sacrificing accuracy. We use the auxiliary-field quantum Monte Carlo (AFQMC) method [3–7] to solve the downfolded Hamiltonian. This approach greatly extends the reach of general, *ab initio* many-body calculations in materials. We illustrate the approach [1] by obtaining accurate equilibrium properties in a range of solids, including semiconductors, ionic insulators, and metals. We then show that the present approach can describe BN, with an accurate EOS extending to high pressures, without resorting to all-electron calculations [8]. Finally, the spin gap in strongly correlated NiO is accurately determined and compared with experiment.

The most fundamental issue in computations of electron correlation effects is accuracy. For QMC calculations, the fermion sign problem must be controlled with an approximation. The AFQMC framework, by carrying out the random walks in non-orthogonal Slater determinant space, has shown to lead to an approximation which is more accurate and less dependent on the trial wave function (see Ref. 5 and references therein). Our approach treats downfolded Hamiltonians expressed with respect to a truncated basis set of mean-field orbitals of the target system, using AFQMC. The simplification, often with drastic reduction in computational cost, can extend the reach of *ab initio* computations to more complex materials. A large gain in statistical accuracy often results as well, because of the smaller range of energy scales (or many fewer degrees of freedom) which need to be sampled stochastically in the downfolded Hamiltonian.

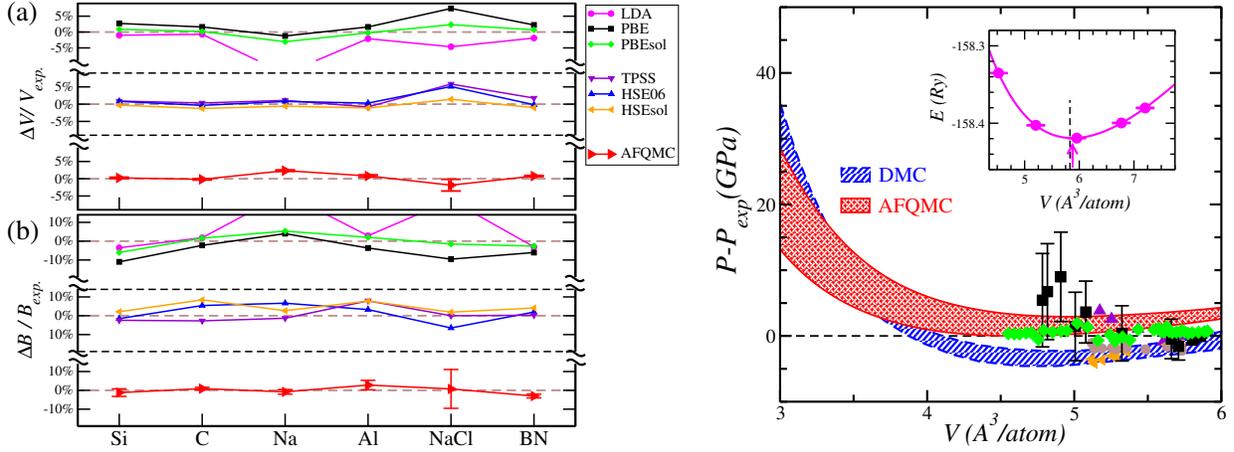


FIG. 1: Left panel: Calculated equilibrium volumes (a) and bulk moduli (b), as relative errors from experiment. Selected DFT results are also shown. Right panel: Pressure calibration and EOS in cubic BN. The main graph displays the calculated pressure vs. volume at room-temperature, using the fitted experimental curve of Datchi et al. [8] (green diamond symbols) as a pressure reference. Different symbols are from different experiments. The shading gives the overall statistical uncertainties. The all-electron DMC results are from Ref. 8. The inset shows the $T = 0$ K EOS near equilibrium from AFQMC. The calculated equilibrium position is shown by the arrow. The vertical line indicates the experimental value.

The left panel in Figure 1 summarizes the calculated equilibrium properties and compares them with experiment. Calculations for metallic bcc Na and fcc Al used twist averaging over 90 random \mathbf{k} -points. He-core PSPs were used for Na and Al, together with the FC treatment. This makes a major difference in both NaCl and Na. With a Ne-core PSP, the equilibrium volume is underestimated by $\sim 30\%$ in Na, for example. The error is eliminated by the FC approach, which allows the semi-core $2s$ and $2p$ electrons to fully relax in the *target environment of the solid* at the DFT-level, before freezing them in the corresponding KS orbitals in the many-body calculation. In a more demanding test, we apply downfolding AFQMC to obtain the EOS of cubic BN for pressures up to 900 GPa ($V \sim 0.5 V_{eq}$). This system has been identified as a promising material for an ultra-high pressure calibration scale [8]. A recent DMC study stressed the need for all-electron (AE) calculations in order to obtain reliable results at high pressures

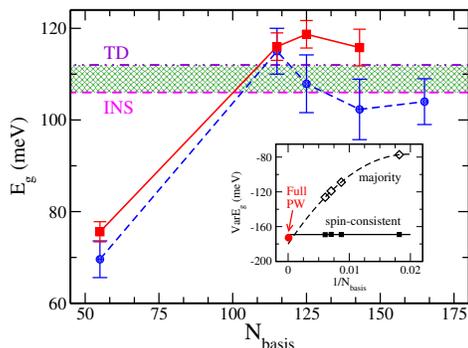


FIG. 2: AFQMC spin gap in NiO and comparison with experiment: thermodynamic measurements (TD; top line) and inelastic neutron scattering (INS; bottom line). Blue circles used averaging over only two \mathbf{k} -points and confirm convergence with respect to N_{basis} . Calculations averaging over a $4 \times 4 \times 4$ \mathbf{k} grid (red squares) are used to obtain the final results. The inset illustrates the much faster convergence enabled by using a spin-consistent basis set [1] than using the KS orbitals from the majority spin.

[8]. The difficulty underscores the PSP transferability problem and is exacerbated by the need to apply a locality approximation in DMC to treat non-local PSPs. The AE treatment would be difficult to realize for heavier atoms. Our calculations freeze the $1s$ electrons in their KS orbitals in the supercell at each volume, using extremely hard “zero-electron-core” PSPs for B and N in the downfolding procedure [1]. In most cases ~ 55 states/atom were used, but larger N_{basis} calculations were done at selected volumes to extrapolate the EOS to the complete basis set limit. As seen in the right panel Fig. 1, the calculated EOS at low pressures is in excellent agreement with experiments (see Ref. 8). At high pressures, the two QMC results are in good agreement, providing a consistent *ab initio* pressure calibration.

As a final application, we determine the spin gap between the ferromagnetic (FM) state and the antiferromagnetic (AFM-II) ground state in NiO (Fig. 2). Understanding and predicting magnetic properties of transition-metal oxides epitomizes the challenge of computations in quantum matter. NiO is a prototypical system for strong electron correlations. Many-body calculations of the spin gap have been limited, and DFT-based methods have yielded widely varying values [1]. We use Ne-core and He-core PSPs for Ni and O, respectively. The downfolded Hamiltonian treats the Ni $3s$, $3p$, $3d$, $4s$ and O $2s$, $2p$ electrons. A rhombohedral supercell with a lattice constant of 4.17 \AA containing two formula units is used. To reduce one-body finite-size effects, we used twist-averaging with a $4 \times 4 \times 4$ \mathbf{k} grid. (A recent study [9] by full configuration-interaction QMC and coupled-cluster methods, with calculations at $\mathbf{k} = \Gamma$, obtained a gap value $\sim 0.96 eV$.) One- and two-body finite-size corrections [10] are then applied to the many-body results (two-body finite-size effects are greatly reduced by cancellation, because the two phases share the same supercell). In the inset in Fig. 2, the variational gap value from the single-determinant trial wave functions is shown vs. the number of basis functions, for both the spin-consistent basis set and one which uses truncated KS orbitals of the majority spin. Both converge to the same infinite basis-set limit, as expected, but the former greatly accelerates convergence. Note that the variational gap is actually negative, i.e., the trial wave functions identify the incorrect phase for the ground state. The AFQMC calculations correctly recovers from these, and yield a final estimate of the gap of $116(3) \text{ meV}$, in good agreement with experiments [1].

The downfolding approach can be generalized to carry out excited state and many-body band structure calculations, which was recently formulated [11] in planewave AFQMC. A large number of applications are possible within the present form. Further improvements, for example by using localized virtual states or optimizing the orbitals with respect to the environments, will lead to even more general and powerful approaches.

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