Assessing the accuracy of compound formation energies with quantum Monte Carlo

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Accurately predicting the formation energy of a compound, which describes its thermodynamic stability, is a key challenge in materials physics. Here, we employ many-body quantum Monte Carlo (QMC) with single-reference trial functions to compute the formation energy of two electronically disparate compounds, the intermetallic VPt₂ and the semiconductor CuI, for which standard density functional theory (DFT) predictions using both the Perdew-Burke-Ernzerhof (PBE) and the strongly constrained and appropriately normed (SCAN) density functional approximations deviate markedly from available experimental values. For VPt₂, we find an agreement between QMC, SCAN, and PBE0 estimates, which therefore remain in disagreement with the much less exothermic experimental value. For CuI, the QMC result agrees with neither SCAN nor PBE pointing towards DFT exchange-correlation biases, likely related to the localized Cu 3d electrons. Compared to the behavior of some density functional approximations within DFT, spin-averaged QMC exhibits a smaller but still appreciable deviation when compared to experiment. The QMC result is slightly improved by incorporating spin-orbit corrections for CuI and solid I₂, so that experiment and theory are brought into imperfect but reasonable agreement within about 120 meV/atom.

I. INTRODUCTION

Achieving reliable predictions of the thermodynamic properties of solids is a critical challenge in materials physics. In particular, the formation enthalpy of a compound with respect to its constituent elements, ∆H_f, is a key quantity that encapsulates phase stability at zero temperature and strongly impacts the finite-temperature phase diagram. Given that the thermodynamic stability of inorganic crystalline compounds depends on small differences in energies of only 60 meV/atom on average,[1] highly accurate ∆H_f predictions are desirable. They may even be essential for cases without the prospect of strong error cancellation, e.g., when a compound’s competing phases include elements and/or compounds with very different electronic properties.

The challenge in predicting formation enthalpies ultimately derives from our lack of a highly accurate and computationally efficient electronic structure method, especially for solids. In the standard approach of Kohn-Sham density functional theory (DFT), the challenging many-electron nature of the problem is circumvented by (1) building the theory around a ground-state energy and electron density derived from auxiliary non-interacting electrons and (2) making non-systematically-improvable approximations to describe the exchange and correlation interactions. Despite its many successes and widespread usage,[2] the ∆H_f errors for solids using DFT with common exchange-correlation approximations provide mixed
In particular, mean absolute $\Delta H_f$ errors of 259 and 110 meV/atom were found previously for the widely-used PBE (Perdew-Burke-Ernzerhof) generalized-gradient approximation (GGA) and the newer and more sophisticated SCAN (strongly constrained and appropriately normed) meta-GGA, respectively.

In contrast to DFT, quantum Monte Carlo (QMC) is based on explicit many-electron wave functions, and it treats the exchange and correlation effects directly by solving the stationary Schr"odinger equation. In order to cope with the vastly increased computational cost, QMC employs stochastic algorithms, introducing statistical error bars, and often requires substantial supercomputer resources. The use of QMC for solids, as opposed to finite systems, is particularly computationally demanding given the need to eliminate finite-size errors via (1) employing supercells, and (2) considering multiple wave-function phases, or "twists." There are further possible biases involved that can be divided into technical ones and more fundamental ones. The technical biases involve basis sets and wave function projection parameters, and in this study we deem these issues as being under control or marginal (see Appendices for more information). We also want to mention that we employ pseudopotentials which involve technical aspects, such as valence space fidelity to all-electron ion(s) and transferability, but also deeper issues due to non-local character of corresponding operators as opposed to the local nature of the original Hamiltonian. We have focused here only on the accuracy aspect and we have found the employed pseudopotentials to be acceptable for providing the energy differences that we are interested in with sufficient accuracy.

On the fundamental side is the restriction to employ single-reference trial functions which affect the well-known fixed-node/phase bias. This aspect is significantly more challenging to control although systematic analysis and cross-comparisons between systems have proved useful in establishing quantitative bounds even for these errors. In addition, there is a significant effort underway to establish a more routine use of multi-reference trial functions for solids in future.

In this work, we employ QMC methods to compute $\Delta H_f$ and compare the results with DFT and experimental measurements for crystals that represent two classes of materials. The first system of interest is VPt$_2$, which belongs to intermetallics with weaker bonding and with a significant spin-orbit effect originating from the Pt atom. It is well-known that metals pose additional challenges to QMC methods due to the presence of the Fermi surface and possible impact of long-range electron-electron correlations. The second compound of interest is insulating CuI that involves spin-orbit effects from the iodine atoms. Since such systems have not been studied by QMC previously, our key goal has been to understand the feasibility and accuracy of such calculations. In particular, we wanted to probe for the use of single-reference trial wave functions that represents the "standard model" for QMC calculations. Furthermore, for both of these systems, DFT-predicted values for $\Delta H_f$ deviate from the experimental data quite significantly, so that another goal was to gain insights into the DFT discrepancies.

Recently, the applicability of QMC has been expanding to systems with spin-orbit (SO) interactions based on developments of the fixed-phase spin-orbital diffusion Monte Carlo (FPSODMC) method that employs many-body wave functions built with two-component spinors. In particular, atomic and molecular systems have been studied in detail, revealing the significant impact of explicit spin-orbit effects on ordering of atomic and molecular excitations and other quantities such as binding energies. Therefore, the spin-orbit effect on formation energies is another point of interest of this work.

For the intermetallic VPt$_2$, we find that QMC’s prediction is closer to SCAN’s than to PBE’s, which clearly shows the difference between these two density functional approximations (DFAs) for a metal with weak bonds. However, the difference between the theory and experiment still remains and its root cause is unclear. Experiments on these systems are notoriously difficult, while on the theory side, the single-reference QMC could be reaching its accuracy limit here. Nevertheless, this discrepancy, which is now exhibited by two independent theory approaches, should provide a motivation for revisiting this system also on the experimental side.

For our second material, CuI, the DFT formations energies using SCAN and PBE DFAs become nearly identical and they are significantly smaller in magnitude than the experimental value. Compared to DFT, QMC with averaged spin-orbit exhibits a much more exothermic formation energy prediction with reduced but still non-negligible error compared to experiment. We find that including the spin-orbit corrections for solid I$_2$ as well as CuI provides further mild improvement. After this correction, the QMC formation energy is about 120 meV/atom larger than the experiment, which is significantly better than the DFT SCAN and PBE values that underestimate the formation energy by some 210 meV/atom with the most probable reason being poor description of Cu 3d states. Indeed, our probe for this effect with the hybrid PBE0 DFA indicates correction in the right direction and confirms the overall size of the spin-orbit effect as well.

II. DESCRIPTION OF SYSTEMS

Here, we describe the systems of interest. The intermetallic VPt$_2$ crystallizes in the MoPt$_2$-type structure (orthorhombic, Immm space group), shown in Fig. 1(a), which is an ordered superstructure of the face-centered-cubic (fcc) structure (Fm3m space group). It becomes a disordered fcc solid solution above 1373 K. VPt$_2$ is found to be a non-magnetic metal in DFT. The experimental $\Delta H_f$ value for VPt$_2$ of $-386 \pm 26$ meV/atom was obtained from direct syn-
FIG. 1. Crystal structures of (a) VPt$_2$, (b) CuI, and (c) solid I$_2$. The red dashed lines indicate the conventional unit cell.

CuI is a superionic conductor with Cu sublattice melting below 642 K, it exists in the zincblende crystal structure (cubic, $F\bar{4}3m$ space group, an ordered diamond superstructure) shown in Fig. 1(b). We consider this phase, known as the $\gamma$ phase, in this work. It is a p-type transparent semiconductor with a $\sim$ 3 eV band gap.\textsuperscript{34} Wurtzite ($\beta$) and disordered-Cu$^+$ fcc ($\alpha$) phases of CuI emerge at higher temperatures.\textsuperscript{34,35} For CuI, an assessed experimental value of $-369 \pm 10$ meV/atom comes from the thermochemical database of the Russian Academy of Science and Moscow State University.\textsuperscript{36,37} This value is based on two measurements: (1) heats of solution in FeCl$_3$ and HCl with a Dewar-vessel isoperibol calorimeter at room temperature,\textsuperscript{38} and (2) an equilibrium study with elemental Cu and its amalgam.\textsuperscript{39}

Computing $\Delta H_f$ for the above compounds also requires calculations for elemental vanadium, platinum, copper, and iodine. In order to compare with experimental values, such calculations must correspond to the standard reference states,\textsuperscript{40} which are for most elements the stable phase under standard conditions. The standard reference states are the body-centered-cubic phase (bcc, $Im\bar{3}m$ space group) for V and the fcc phase for Pt and Cu, all non-magnetic metals. As these are very simple and common structures, we do not include them in Fig. 1. The standard reference state for iodine is the solid phase with an orthorhombic structure ($Cmce$ space group), a semiconductor with a band gap of 1.6 eV.\textsuperscript{41} Given that each iodine atom in this structure has a single nearest neighbor at a distance of 2.7 Å, significantly smaller than the 2nd-nearest-neighbor distance of 3.5 Å,\textsuperscript{42} solid iodine can be considered a molecular crystal (of I$_2$ molecules) and we refer to it as solid I$_2$. However, we note that there is some evidence for a covalent, rather than molecular, nature of the crystal.\textsuperscript{43}

In bonded systems, the crystal field can act to suppress or magnify spin-orbit effects, depending on the space group of the solid or point group of a molecular system. For solids with high symmetry, e.g., cubic systems, hybridization in one-particle states tends to average out a significant fraction of the spin-orbit effects. This applies even when the bonding patterns are not the same or even similar since the key point is breaking the lock of the atomic ground state symmetry and hybridizations in one-particle spinors. Unless there are some unusual symmetries that may enhance spin-orbit effects, we expect the effect of spin-orbit interactions on formation energies to be much smaller when compared to cohesive energy, since it involves the energy differences of solid energies only and the isolated atomic energies are irrelevant.

Since the phases relevant to computing the $\Delta H_f$ values of interest are all solids in our case, we ignore pressure-volume contributions and take the enthalpy to be equal to the energy. In addition, the temperature dependence of the enthalpy is neglected, as is the role of any state of partial disorder in the compounds. For example, the formation energy of the CuI solid ($s$) can then be expressed in QMC total energies:

$$\Delta H_f(\text{CuI}, s) = E_{\text{tot}}(\text{CuI}, s) - E_{\text{tot}}(\text{Cu}, s) - (1/2)E_{\text{tot}}(\text{I}_2, s)$$

with all the quantities in Eq. (1) given per chemical formula as usual.\textsuperscript{14} In what follows we further divide by the number of atoms in the formula of the target compound and therefore we report the values per atom.

## III. COMPUTATIONAL DETAILS

All calculations correspond to experimental lattice parameters and atomic positions for VPt$_2$,\textsuperscript{21} CuI\textsuperscript{22}, bcc V,\textsuperscript{21} fcc Pt,\textsuperscript{13} fcc Cu,\textsuperscript{13} and solid I$_2$.\textsuperscript{22}

We employ scalar/full-relativistic, norm-conserving pseudopotentials to describe the core electrons. For vanadium and copper, we use the neon-core, local density approximation pseudopotentials of Kroegel, Santana, and Reboredo\textsuperscript{27} with the optimized Rappe-Rabe-Kaxiras-Joannopoulos form.\textsuperscript{13} For platinum, we use a PBE
Jastrow correlation factors. Wavefunction with optimized one-, two-, and three-body 
Carlo (DMC) method were performed with 
QMCPACK 
etic energy cutoffs as above. Single-particle wavefunctions from DFT within the 
PBE exchange-correlation DFA were generated using the 
QUANTUM ESPRESSO package. 
We employ a wavefunction plane wave kinetic energy cutoff of 350 Ry for VPt, Pt, and V and 450 Ry for CuI, Cu, and solid I2. The Brillouin zone was sampled with uniform k-grids of at least 500 k-points/A^-3. Using these parameters provided one-particle orbitals with accuracy appropriate for use in QMC methods. PBE0+spin-orbit calculations were also carried out using QUANTUM ESPRESSO with the same kinetic energy cutoffs as above. 

QMCS calculations with the fixed-node diffusion Monte Carlo (DMC) method were performed with QMCPACK. 
We use the Slater-Jastrow form of the trial many-body wavefunction with optimized one-, two-, and three-body Jastrow correlation factors. 
A fixed 0.005 Ha^-1 time step was employed. We use two finite size corrections: the model periodic Coulomb interaction (MPC) and the Chiesa-Ceperley-Martin-Holzmann kinetic energy correction. 
We employ twisted averaged boundary conditions to remove one-body finite size effects and finite size extrapolation of supercell results to remove two-body finite size effects. Optimal supercells were generated via NEXUS. Further data on the QMC calculations can be found in the Appendices.

We also performed DFT calculations of the spin-orbit corrections to the I2 dimer binding energy, the CuI dimer binding energy, and solid CuI using the 
FHI-aims code with the PBE0 exchange-correlation functional and the default tight basis sets. For the CuI dimer, we first optimized the dimer bond length so that forces were less than 0.5 meV/Å. Those results did not differ in any discernible way from the results using QUANTUM ESPRESSO.

Another set of calculations was carried out using the 
DIRAC code. Specifically, we evaluated total energy shifts going from the spin-averaged case (AREP) to the full spin-orbit case (SOREP) for the I2 and CuI molecules using the aug-cc-pVTZ basis set. I2 molecular energies were calculated using the CCSD(T) method, while the COSCI (complete open-shell CI) method was used for the CuI molecule.

Considering the spin-orbit corrections, we write the formation energy as a sum of spin-averaged (AREP) contribution and the spin-orbit correction, for example, for CuI we have:

\[ \Delta H_f(CuI, s) = \Delta H_f(CuI, s)_{\text{AREP}} + \Delta^{SO}. \]  

There are only two contributions to \( \Delta^{SO} \)

\[ \Delta^{SO} = \Delta^{SO}(CuI, s) - (1/2)\Delta^{SO}(I_2, s) \]  

since we assume that the corresponding value from Cu is negligible. Further details are discussed in the next section and in the Appendices.

As explicit spin-orbit calculations using the DMC method are prohibitively expensive for very large supercell calculations used in this work, we employ the PBE0+spin-orbit contribution \( \Delta^{SO} \) for DMC values as well. We believe this is justified since PBE0 values without spin-orbit effects agree very well with DMC results as will be shown later. Note that there are significant recent efforts to evaluate spin-orbit effects using QMC in moderately large systems.

IV. RESULTS AND DISCUSSION

Due to very large total energies from semiconductors \((3s^23p^6)\) of transition elements, small to medium size supercells \((4–16\) atoms\) are employed to assess the convergence of the energy with respect to twist mesh. Let us consider the CuI case, for which we use the eight-atom conventional cell, as an example. As shown in Fig. 2(a), the energy is well converged for a twist mesh of \(8 \times 8 \times 8\).

In order to address two-body finite-size effects, we perform calculations for several supercell sizes, using twist meshes corresponding to the same converged twist density. Fig. 2(b) shows, taking CuI again as an example, the extrapolation of the energies of different supercells to the thermodynamic (bulk) limit. Notably, the data are approximately linear in the inverse number of atoms, and extrapolations of the uncorrected and corrected (i.e., using the MPC and kinetic energy corrections) data yield nearly identical values (difference of 11 meV per formula unit). We note that we find a negligible need for finite-size extrapolation for solid I2 when finite-size corrections are employed (as shown in the Appendix C). This finding that the interactions are relatively short-ranged is consistent with solid iodine’s nature as a molecular crystal; similar behavior was found previously for molecular crystals of \(\text{NH}_3\) and \(\text{CO}_2\).

Figure 3 contains the main result of this work: QMC values of \(\Delta H_f\) for VPt2 and CuI compared with other methods and experiments. The PBE and SCAN results shown for comparison are taken from past work using the projector augmented wave method in the 
VASP code. 
\(\Delta H_f\) computed from our own PBE calculations here (performed to generate trial wavefunctions) agree with the literature values to within \(\sim 30\) meV/atom, confirming the DFT-predicted \(\Delta H_f\) are not terribly sensitive to the choice of DFT code, pseudopotentials, and other computational details. PBE0 and PBE0+SO values are results from this work.

The \(\Delta H_f\) for VPt2 from QMC calculations without spin-orbit is \(-764\pm7\) meV/atom with the nominal statistical error which is very small due to the fact that it is an
FIG. 2. (a) Convergence of energy with respect to twist mesh and (b) finite size extrapolation of energies with and without finite size corrections for CuI.

FIG. 3. Computed and experimental compound formation enthalpy of VPt$_2$ (left) and CuI (right).

intensive quantity. Note however, that we do not consider this statistical uncertainty as being really representative, say, for comparisons with the DFT values. The overall error generated by the key systematic bias, which is the fixed-node approximation from the single-reference trial function, is likely much larger. Considering that energy differences involve partial fixed-node error cancellation and per atom normalization, we assume a systematic error at the level of $\approx 50$ meV/atom. In order to quantitatively ascertain this level, we would need multi-reference trial functions data with significantly lower fixed-node bias, which unfortunately are not available at present. Therefore, we use a semi-quantitative guess based on recent QMC calculations such as crystal of LaScO$_3$, solid Si with up to 216 atoms in the supercell and also estimations of exact correlation energies for 3$d$ atoms. In what follows, we therefore assume this value as an approximate error bar which includes both random uncertainties and systematic errors.
tainty and systematic biases with the caveats mentioned above.

Comparison with DFT results reveals that the formation enthalpy for VPt$_2$ calculated within the SCAN DFA ($-737$ meV/atom) is very close to the QMC value ($-764 \pm 50$ meV/atom) whereas the PBE-predicted formation enthalpy ($-555$ meV/atom) is much too small in magnitude (by 209 meV/atom). It is worth noting that the PBE0 result ($-759$ meV/atom), which completes the overall picture with a hybrid DFA, is in the same range as SCAN and QMC. In a previous larger-scale benchmark, SCAN was found to offer no improvement from PBE in predicting $\Delta H_f$ of "weakly-bound" compounds (experimental $|\Delta H_f| < 1$ eV/atom), which are mainly intermetallics like VPt$_2$. In fact, the mean absolute error compared to experiment for such compounds was found to be 20% larger for SCAN than for PBE. This observation is surprising from the perspective that intermetallics should be relatively easy to describe given they are metals with delocalized electronic states and (2) in the metallic regime (of orbital kinetic energy density), SCAN is constructed to accurately describe slowly-varying densities, just as PBE is. Although it pertains to only a single compound, which could be an exception, the VPt$_2$ result here suggests that the SCAN accuracy probably varies even if we consider just one class of compounds such as intermetallics. The $\Delta SO$ contribution to VPt$_2$ calculated using PBE0+SO is 39 meV/atom; therefore, it does not change the overall conclusion since it is only $\approx 5\%$ of the calculated formation value, see Fig. 3.

Our results raise the important question of why the experimental $\Delta H_f$ value for VPt$_2$ deviates so significantly from theory. One contributing factor may be the incomplete nature of the synthesis reaction in the measurement. As noted by Guo and Kleppa, multiple experimental probes (X-ray diffraction, scanning electron microscopy, and energy-dispersive microanalysis) showed the presence of vanadium oxide with the VPt$_2$. Although the amount observed was small (a few percent), this may contribute to an appreciable underestimation of the $\Delta H_f$ magnitude, especially due to the large $\Delta H_f$ for vanadium oxide.

We note that the case of VPt$_3$ appears to be very similar: vanadium oxide was found in experimental samples, and the measured $\Delta H_f$ value of $-284 \pm 19$ meV/atom is much smaller in magnitude than that of PBE ($-457$ meV/atom) and SCAN ($-603$ meV/atom). Interestingly, the enhancement in $\Delta H_f$ in SCAN as compared to PBE is almost the same (factor of 1.32 – 1.33) for both cases. Our results should motivate a re-investigation of the experimental $\Delta H_f$ for these compounds. More generally, we speculate that errors in experimental $\Delta H_f$ may also help explain other recent work in which experimental $\Delta H_f$ were found to differ from high-level (namely, random phase approximation) calculation results.

The CuI results stand in clear contrast to those of VPt$_2$. Here, the PBE and SCAN $\Delta H_f$ values are nearly identical ($\approx -153$ meV/atom) and are much too small in magnitude compared to the experimental value. The QMC result without including spin-orbit corrections ($-511$ meV/atom) is significantly closer to the experimental value but still is appreciably different from it. Therefore, we consider spin-orbit interactions as a possible source of the remaining discrepancy.

In order to evaluate the impact of spin-orbit on CuI, we use Eq. (4). As discussed previously, for this we use the PBE0 functional that gives the closest agreement with QMC at the AREP (averaged spin-orbit) level. Based on this, we estimate the effect of spin-orbit explicitly within the PBE0 DFA framework. The effect goes in the direction of becoming closer to the experiment, however, the correction is rather small, see, Fig. 3. We probe this correction also in an alternative way using CuI and I$_2$ molecular energy shifts that involve explicit spin-orbit COSCl. CCSD(T) calculations as well as DFT differences which gives similar results (see Appendix D). The resulting correction is given by:

$$\Delta SO = \Delta SO(CuI, s) - (1/2)\Delta SO(I_2, s) = 18 \text{ meV/atom.} \quad (4)$$

This correction reduces the QMC AREP formation energy of $-511$ meV/atom to $-493$ meV/atom which is closer to the experimental value of $-369 \pm 20$ meV/atom where we assume an effective error bar per differences between independent experiments. Therefore, incorporating spin-orbit corrections for CuI and solid I$_2$ brings theory and experiment into an imperfect but improved agreement within $\sim 120$ meV/atom.

Apart from the mild spin-orbit shift, the exchange-correlation description not only in PBE but also within the SCAN DFA appears to be of mixed quality. Given the known difficulty of describing localized 3d transition metal states, which give rise to significant self-interaction effects especially in insulators, we believe the presence of Cu 3d orbitals may be responsible for the large PBE and SCAN errors: Vanadium d states are nominally singly occupied while Cu d-states are more localized and almost fully doubly occupied with more pronounced Hubbard physics. This is also supported by the PBE0 result above that enhances the localization of 3d levels in the like-spin channel and therefore effectively increases the repulsion in the unlike-spin channel. In line with this view, we note that beyond-DFT Hubbard $U$ corrections were found to be necessary even with SCAN in describing gapped Li$_x$FePO$_4$ and Li$_x$Mn$_2$O$_4$ systems, which also contain 3d transition metal states. It is instructive to illustrate this by examining the density differences between DMC and DFT (PBE). Figure 4 shows the CuI (left panel) and VPt$_2$ density differences projected onto the (001) plane. The left panel shows that the density differences are well localized around Cu and I sites, with the difference being slightly negative (DMC density smaller than DFT) near I sites, and positive (DMC density larger than DFT) near Cu sites, indicating a difference in the description of densities arising from orbitals near the Cu sites. In contrast, the VPt$_2$ density differences are significantly smaller in magnitude and more diffuse in the
V. CONCLUSIONS

We employed QMC to calculate the formation energies for intermetallic VPt$_2$ and semiconducting CuI and compared to DFT within the PBE and SCAN DFA, hybrid PBE0 DFA DFT, and experiment. QMC calculations have been carried out with single-reference trial functions and as such, they correspond to the level of accuracy that we colloquially refer to as the QMC “standard model”. It has been applied to a plethora of systems including solids with supercells containing hundreds of valence electrons with rather consistent improvements and insights over more traditional approaches. In this study, we attempt to advance this approach for the resulting very small energy differences that are likely at the edge of its accuracy limits. We note that the computational demands are substantial, especially if we consider that the total energy of a single Cu atom with semi-core 3s$^2$3p$^6$ in valence space is above 5000 eV so an accuracy of a few tens of meV is very challenging to achieve.

For VPt$_2$, we find close agreement between QMC, SCAN, and PBE0 results. On the other hand, the difference with the experimental value is significantly larger, suggesting a need for an independent new measurement that would confirm or update the currently available data. For CuI, we find that the QMC formation energy is in a rough agreement with the experimental value within approximately 120 meV/atom, after adding corrections that take into account spin-orbit interactions in CuI and solid I$_2$. In our estimations, the spin-orbit effects from iodine appear rather small in both DFT using the PBE0 functional and in estimations using COSCI and CCSD(T) that involved CuI and I$_2$ molecules using two-component spinors. The large difference between the DFT within the PBE and SCAN DFA and QMC likely arises from difficulties in the description of localized Cu 3$d$ orbitals in CuI, consistent with large electron density differences between QMC and DFT-PBE near the Cu sites [Fig. 4 (a)]. Our results indicate that, for systems like CuI, significant exchange-correlation errors are still present even in the SCAN DFA so they likely limit its predictive power.

This study is the first attempt to address more weakly bonded intermetallics with heavy elements by QMC methods. Clearly, in order to pinpoint imperfections with higher energy resolution and to better control fixed-node bias, new developments with multi-reference trial functions and accurate pseudopotentials are highly desirable. Since not much has been known about such systems using many-body wave function methods so far, we consider our results very encouraging and promising for future studies.

VI. DATA AVAILABILITY

See Appendices for tabulated formation energies, pseudopotential tests, finite-size extrapolation plots, additional estimation of spin-orbit effect on CuI formation energy, CuI DFT band gaps, QMC variances, and other supporting data. Input and output files generated in this work are available in Materials Data Facility$^{76,77}$ and can be found at$^{78}$.

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G. Wang, B. Kincaid, H. Zhou, A. Annaberdiyev, M. C. Bennett, J. T. Krogel, and L. Mitas, arXiv:2202.04747 [cond-mat, physics:physics] (2022) arXiv: 2202.04747.

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Appendix A: Tabulated Formation Energies

Tables I and II provide the formation energies presented in the main portion of the paper.

**TABLE I.** Formation energies for CuI in units of meV/atom.

| Method      | Energy  |
|-------------|---------|
| PBE         | -156    |
| SCAN        | -151    |
| PBE0        | -419    |
| PBE0+SO     | -401    |
| DMC         | -511(50)|
| DMC+SO      | -493(50)|
| Expt.       | -369(20)|

**TABLE II.** Formation energies for VPt\textsubscript{2} in units of meV/atom.

| Method      | Energy  |
|-------------|---------|
| PBE         | -555    |
| SCAN        | -737    |
| PBE0        | -759    |
| PBE0+SO     | -720    |
| DMC         | -764(50)|
| DMC+SO      | -725(50)|
| Expt.       | -386    |

Appendix B: Validation of Iodine pseudopotential

1. Scalar Relativistic Terms

Here, we discuss atomic calculations to validate the Burkatzki-Filippi-Dolg (BFD) iodine pseudopotential\cite{Burkatzki2004}. We use a cubic simulation cell with 20 Å side length and employ the Makov-Payne finite-size correction\cite{Makov1995}. The first two ionization potentials (IPs) and the first electron affinity (EA) are tested. The atomic configurations, taken from the NIST Atomic Spectra Database\cite{NIST}, are \(^1\text{S}_0\) for the \(-1\) charge state, \(^2\text{P}_{3/2}\) for the 0 state, \(^3\text{P}_2\) for the +1 state, and \(^4\text{S}_{1/2}\) for the +2 state.

As shown in Table B.1, the computed IPs and EA agree well with past work, AE CCSD(T), and experiment, validating the use of this pseudopotential. Note that the experimental value of 3.06 eV for EA must be corrected for spin-orbit interactions for a direct comparison. The average of atomic multiplets provides a value of 3.37 eV (see Refs. \cite{Makov1995} and \cite{NIST}). A more thorough transferability tests of BFD iodine ECP can be found in Ref. \cite{Burkatzki2004}.

2. Spin-Orbit Terms

Because the BFD pseudopotential lacks the SO terms, we adopted the STU SO terms\cite{Stoermer1971} and tested the transferability with the results summarized in Table IV. We can see that almost the same quality as from STU pseudopotential is obtained, validating the direct use of STU SO terms. These tests also suggest that the STU SO terms can be adopted without changes for other elements. Analogously, STU SO terms were added to Pt pseudopotential for consistency.

Appendix C: Finite size extrapolation for solid I\textsubscript{2}

A comparison of the finite size extrapolation of solid I\textsubscript{2} with and without finite size corrections (model periodic Coulomb interaction and Chiesa-Ceperley-Martin-Holzmann kinetic energy correction) is shown in Fig. 5. Both cases lead to very similar values for the bulk limit, using linear extrapolation. We note that the energy per atom does not depend strongly on the supercell when the finite size corrections are included, as discussed in the main text.

Appendix D: Alternative estimation of SO effect in CuI

In addition to the direct PBE0+SO effects used in the paper, here we use a different way to estimate the SO effect. In order to evaluate the impact of spin-orbit interactions on CuI, we use

\[
\Delta^{SO} = \Delta^{SO}(\text{CuI}, s) - (1/2)\Delta^{SO}(\text{I}, s). \tag{D1}
\]

The first contribution is the shift for solid (s) CuI where we employ the value for the CuI molecule (m) to minimize the systematic biases. This is arranged into several differences that maximize the error cancellation as follows:

\[
\Delta^{SO}(\text{CuI}, s) = \Delta^{SO}(\text{CuI}, s) ± \Delta^{SO}(\text{CuI}, m) = [\Delta^{\text{coh}}(\text{CuI}, s) - \Delta^{\text{bind}}(\text{CuI}, m)]_{\text{DFT}} + \Delta^{SO}(\text{CuI}, m) \approx 63 - 37 - 36 = -10 \text{ meV/atom}, \tag{D2}
\]

where we use the DFT/PBE0 values of cohesion and binding while the total energy shift \(\Delta^{SO}(\text{CuI}, m)\) is found by COSCI calculations. All values above are reasonably small, suggesting a very similar impact of spin-orbit in both (s, m) systems so that the use of DFT is justifiable. Note that the spin-orbit contributions to the DFT atomic energies, which are significant and can be biased due to difficulties in imposing correct atomic symmetries, cancel out in the difference (solid cohesion – molecule binding). On the other hand, the shift in the total energy of
TABLE III. Comparison of atomic iodine ionization potential and electronic affinity (in units of eV) results. AE CCSD(T) represents scalar relativistic, fully correlated, all-electron CCSD(T) calculation results.

|      | This work DFT | This work DMC | Past DFT | Past DMC | Experiment | AE CCSD(T) |
|------|---------------|---------------|----------|----------|------------|------------|
| IP1  | 10.49         | 10.51         | 10.51    | 10.57    | 10.45      | 10.5697    |
| IP2  | 18.69         | 19.95         | –        | –        | 19.13      | 18.7665    |
| EA   | 3.24          | 3.33          | 3.25     | 3.34     | 3.06       | 3.2923     |

TABLE IV. Iodine atomic excitation errors for STU versus BFD in SOREP forms. The errors are shown for full-relativistic X2C AE gaps using COSCI. All values are in eV. STU SO terms were used for BFD calculations.

| State     | Term | AE      | STU | BFD |
|-----------|------|---------|-----|-----|
| 5s²5p³    | ²P₁/₀ | 0.000   | 0.000 | 0.000 |
| 5s²5p⁶    | ¹S₀   | -2.185  | 0.022 | 0.025 |
| 5s²5p⁴    | ³P₂   | 9.413   | 0.009 | 0.006 |
| 5s²5p³    | ⁴S₃/₂ | 27.262  | 0.097 | 0.092 |
| 5s²5p³    | ²P₁/₀ | 0.962   | 0.030 | 0.024 |
| 5s²5p⁴    | ³P₂   | 0.000   | 0.000 | 0.000 |
| ³P₀       | 0.863 | 0.046   | 0.041 |
| ³P₁       | 0.869 | -0.019 | 0.015 |
| ¹D₂       | 1.999 | -0.029 | -0.036 |
| ¹S₁       | 4.258 | -0.104 | -0.119 |
| 5s²5p³    | ⁴S₃/₂ | 0.000   | 0.000 | 0.000 |
| ²D₁/₁     | 1.959 | -0.136 | -0.142 |
| ²D₂/₂     | 2.348 | -0.101 | -0.109 |
| ²P₁/₁     | 3.765 | -0.183 | -0.195 |
| ²P₃/₁     | 4.375 | -0.116 | -0.131 |
| MAD       |       | 0.074   | 0.078 |

FIG. 5. Finite size extrapolation for solid I₂ from calculations with and without finite size corrections.
comparisons of binding \((m)\) and cohesive \((s)\) energies, reaching perhaps \(\approx 50 \text{ meV/atom}\) so that the remaining discrepancy might be possibly even smaller. In summary, correcting the QMC value based on calculations incorporating spin-orbit interactions for CuI and solid \(\text{I}_2\) brings theory and experiment into not perfect but a much improved agreement (within \(\sim 100 \text{ meV/atom}\)).

**Appendix E: QMC Variances**

Here we report the values for the variance of the local energy, which would be identically zero for the exact ground state. We find values normalized by the local energy to be similar, namely, 0.012 Ha for VPt\(_2\), 0.023 Ha for bcc V, 0.009 Ha for fcc Pt, 0.023 Ha for CuI, 0.023 Ha for fcc Cu, and 0.016 Ha for solid \(\text{I}_2\). The low variance values indicate very good consistency of optimizations for Jastrow parameters across the calculated systems.

**Appendix F: CuI DFT Gaps**

Table \(\text{V}\) provides the DFT and experimental gaps for CuI. Note the excellent agreement of PBE0+SOC and the experimental value.

| Method       | Gap [eV] |
|--------------|----------|
| PBE          | 1.25     |
| SCAN         | 3.64     |
| PBE0         | 3.38     |
| PBE0+SOC     | 3.09     |
| Expt.\([33,43]\) | 3.1     |