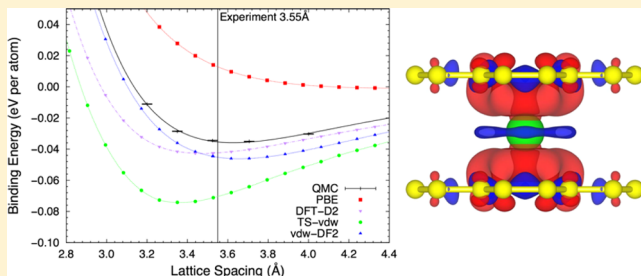


Binding and Diffusion of Lithium in Graphite: Quantum Monte Carlo Benchmarks and Validation of van der Waals Density Functional Methods

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ABSTRACT: Highly accurate diffusion quantum Monte Carlo (QMC) studies of the adsorption and diffusion of atomic lithium in AA-stacked graphite are compared with van der Waals-including density functional theory (DFT) calculations. Predicted QMC lattice constants for pure AA graphite agree with experiment. Pure AA-stacked graphite is shown to challenge many van der Waals methods even when they are accurate for conventional AB graphite. Highest overall DFT accuracy, considering pure AA-stacked graphite as well as lithium binding and diffusion, is obtained by the self-consistent van der Waals functional vdW-DF2, although errors in binding energies remain. Empirical approaches based on point charges such as DFT-D are inaccurate unless the local charge transfer is assessed. The results demonstrate that the lithium–carbon system requires a simultaneous highly accurate description of both charge transfer and van der Waals interactions, favoring self-consistent approaches.



The intercalation, diffusion, and absorption of lithium (Li) in graphite is fundamental to anode operation in nearly all deployed Li-ion batteries. The overall capacity and voltage of the electrode is determined by the structure and binding energy of Li-rich graphite, while the diffusive dynamics help determine achievable charging rates. This material remains challenging to model using density functional theory (DFT) due to the importance of accurately describing the interactions of the Li ions with the graphite lattice. These are strongly dependent on the local environment and degree of charge transfer and hence are strongly influenced by the van der Waals interaction responsible for the graphite interlayer separation. Empirical fits to the experimental data¹ resolve some of the macroscopic problems of Li binding identified in earlier works^{2,3} but can not validate the dynamics of individual ions or the contributing interactions. DFT nevertheless remains a preferred choice for models of Li-ion battery electrodes due to its balance between accuracy and cost.⁴

While DFT is in principle an exact approach, in practice it involves approximating the unknown exact density functional. We broadly denote as “DFT” the set of diverse approximations used in the field. The variety of approximations within DFT has introduced empiricism in the choice of the functional, which should be avoided to achieve predictive power. The approximation of DFT chosen is strongly dependent on the on the local environment and degree of charge transfer and, hence, are strongly influenced by the van der Waals interaction responsible for the graphite interlayer separation. van der Waals interactions are a significant challenge to DFT models since

they are either wholly missing or poorly represented within traditional density functionals.⁵ They have been added via additional empirical terms in the atomic Hamiltonian, e.g., DFT-D2 by Grimme and co-workers⁶ and by pure density functionals, e.g., vdW-DF⁷ and vdW-DF2.⁸ The empirical methods are computationally simple but must be accurately parametrized. The density functionals are more expensive to evaluate^{9,10} but are in principle more accurate because changes in bonding and charge transfer can be recognized that methods based only on atomic positions can not. The TS-vdW method¹¹ rescales the original DFT-D2 parameters according to a Hirshfeld partitioning of the charge density, thereby capturing an environment dependent van der Waals contribution at low cost.

In this article we study dilute Li in graphite using the highly accurate quantum Monte Carlo (QMC) approach. We determine (i) the binding energy of pure graphite, (ii) the binding energy of dilute lithium in graphite, and (iii) two of the diffusion barriers, all as a function of lattice separation. We use this data to assess predictions of van der Waals-including DFTs. We diagnose the errors in the different approaches, identifying a hierarchy of modeling approaches of increasing cost and accuracy. Our results provide guidance for use of these methods within the domain of energy storage and also for the design of improved van der Waals methods.

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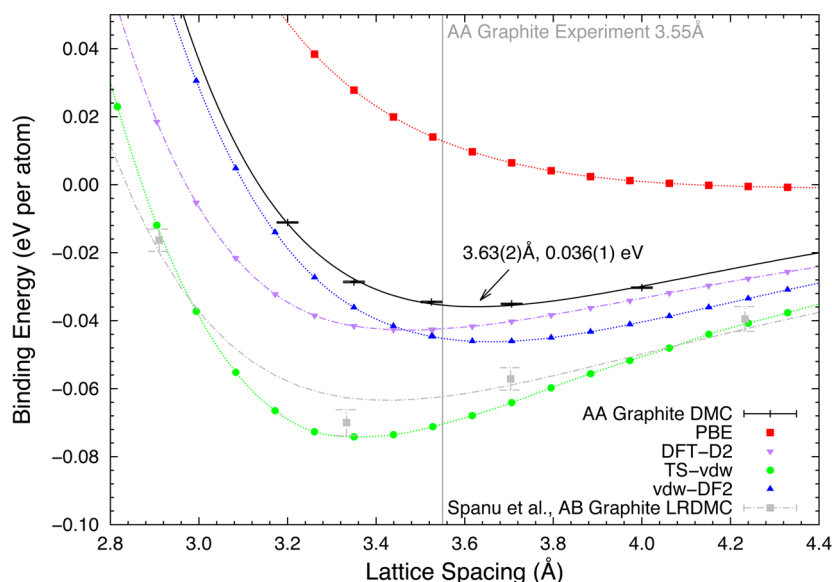


Figure 1. Calculated binding energy of AA graphite as a function of interplanar separation, for different density functionals and for DMC. A Morse fit through the DMC data is plotted, and the statistical error bars are shown. The DMC minimum is 3.63(2) Å and binding energy 36(1) meV. For other methods the lines shown are spline fits to the data. For comparison we also show the AB graphite QMC results of Spanu et al.¹⁵

QMC is a highly accurate many-body electronic structure method¹² that treats insulating and metallic systems on an equal footing, includes van der Waals interactions, and avoids the self-interaction problem of DFT.¹³ The main systematic error of the diffusion Monte Carlo (DMC) method used here is the “nodal error” (or phase error) due to the Fermion sign problem. We also use nonlocal pseudopotentials within a variational scheme¹⁴ which adds an additional systematic error. DMC has been well-validated for carbon systems, including graphite,¹⁵ bulk and defective diamond,¹⁶ and molecular crystals.¹⁷ Molecular tests^{18–21} indicate that weak interactions are well-accounted for, with sub-kcal/mol accuracy achievable. Within bulk materials, calculations on simple metals²² and metals with defects²³ give good agreement with experimental values. A survey of solids²⁴ compared structural properties for ionic, metallic, covalent, and van der Waals solids concluded that performance was consistently better than DFT. A more recent focused survey of van der Waals interaction dominated materials also considered energetics and found very good experimental agreement.²⁵ Most recently, exchange couplings for copper oxide superconductors have been found in good agreement with experimental spectroscopies,^{26,27} without the empiricism of DFT functional selection. Overall, these results indicate that the systematic errors for Li–C will be sufficiently small to assess DFT errors. While the DMC accuracy could be improved in future, e.g., via improved wave functions^{28,29} that give reduced nodal error, the current level is sufficient to examine DFT predictions.

To simplify the comparisons of different methods, we elect to study AA stacked graphite, rather than the ground-state AB stacking. First, this choice removes any ambiguity in the location of isolated lithium atoms, since by symmetry they must be midway between the centers of the carbon hexagons of adjacent graphene planes. Second, forces remain prohibitively computationally expensive in DMC for the systems we consider.

We use two supercell models, (i) containing two graphene layers each of 50 atoms and (optionally) a single Li atom, a Li concentration of $x = 0.06$ in Li_xC_6 , and (ii) a doubled height

version of supercell (i) containing 200 carbon atoms and two equispaced Li atoms, to maintain the Li concentration $x = 0.06$. These choices and methodology are similar to earlier successful studies on AB graphite,¹⁵ but much better quality statistics are required for the Li related energies, since they are not extensive. Identical supercells and structures were used for all electronic structure calculations so that differences in energies result entirely from electronic structure differences. The QMC binding energy data are reported for the larger cell, while the less sensitive diffusion barrier calculations were performed for the smaller cell. The in-plane lattice constants were held fixed at the experimental C–C bond-distance value of 1.421 Å. To assess the role of the van der Waals interaction, we varied the interplane separation over a wide range, including the experimental AB graphite lattice parameter of 3.35 Å and the fully lithiated LiC_6 lattice parameter of 3.706 Å.^{30,31}

Our QMC calculations used the Burkatzki–Filippi–Dolg set of pseudopotentials³² and single determinant with one- and two-body jastrow functions as implemented in QMCPACK.³³ Orbitals, and hence the nodal surfaces, were obtained from PBE³⁴ DFT calculations³⁵ at a 2040 eV plane wave cutoff energy. A weighted branching population of 16 000 walkers was utilized. Results are reported for a time step of 0.02 au. Tests at a smaller time step of 0.005 au determined the energies were converged to within 10 meV/C for bulk graphite. These choices are consistent with the previous applications cited above. Finite size errors were reduced with eight twists.³⁶ DFT calculations were mainly performed within the plane wave pseudopotential projector augmented wave approach,^{37–40} and also compared with all-electron numerical basis set results.⁴¹ A plane wave cutoff energy for local DFT and calculations using the empirical van der Waals approaches of Grimme et al.⁶ (DFT-D2) were 400 eV and up to 1000 eV for calculations using vdW-DF2⁸ to achieve similar convergence. To check for slow convergence, k -point sets were tested for each functional, with up to $40 \times 40 \times 8$ meshes in the bulk primitive cell and ~ 3 meV residual error.

In Figure 1 we show the computed binding energy of AA graphite. The experimental lattice constant is 3.55 Å.⁴² A Morse

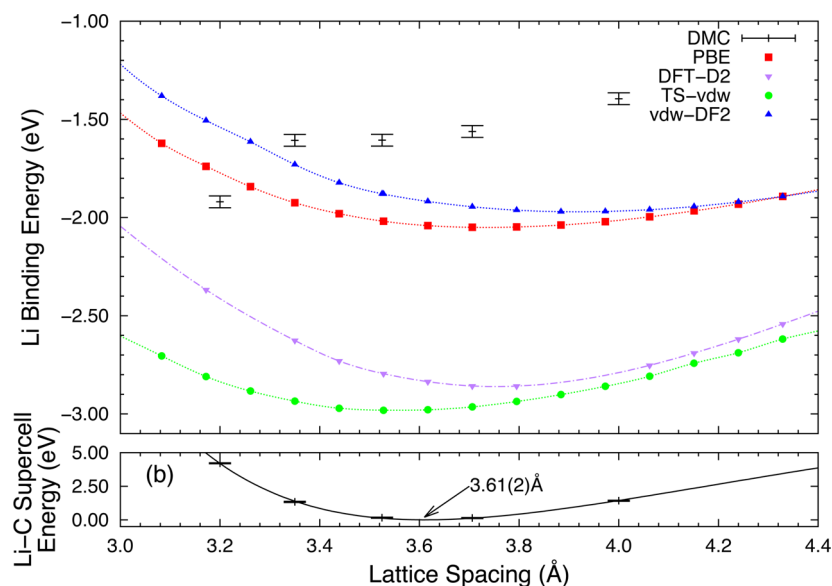


Figure 2. (a) Calculated binding energy of Li in AA graphite, for different levels of theory, as a function of interplanar separation. The lines are a guide to the eye. (b) Total energy of Li-C supercell computed using DMC, with the minimum shifted to zero energy for clarity. The line is a morse fit to the data. The minimum lattice constant $3.61(2)\text{\AA}$ is statistically indistinguishable from the bulk DMC lattice constant $3.63(2)\text{\AA}$.

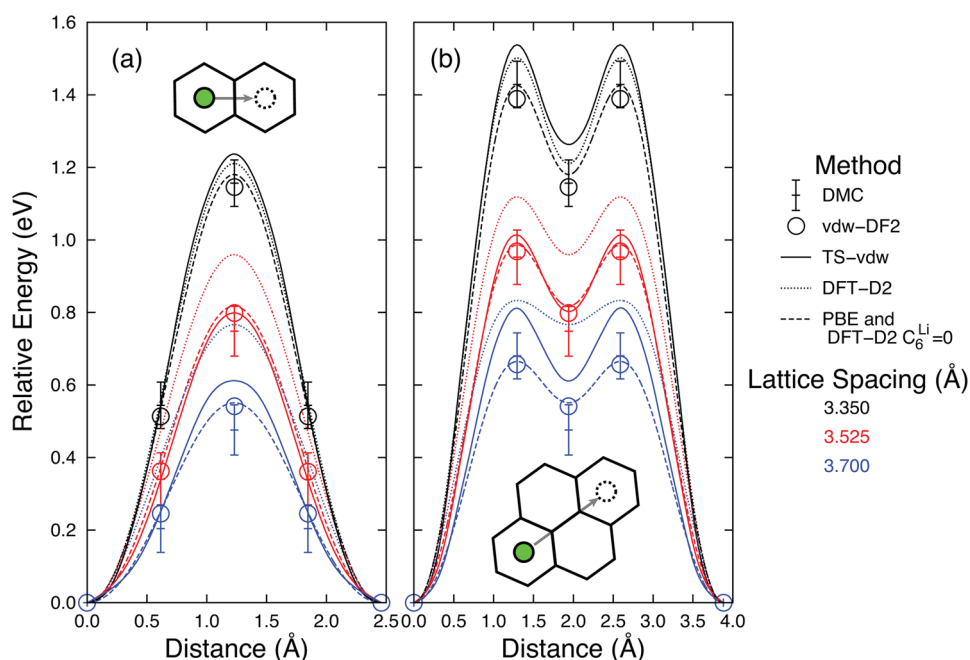


Figure 3. Calculated in-plane diffusion barrier of lithium (a) across a bond and (b) along a bond, for different levels of theory, as a function of interplanar separation with a single Li-atom at midway between graphene planes, 3.350, 3.525, and 3.700 Å apart (colors). The zero of energy is set by the energy at the initial/final positions for each method. DMC results are best matched by the self-consistent vdW-DF2 method (circles).

fit to our QMC data obtains a lattice constant $3.63(2)\text{\AA}$ and binding energy of $36(1)\text{meV}$. For comparison we also show earlier QMC data for AB graphite,¹⁵ consistent with the experimental AB lattice constant of 3.35\AA and binding energy of $\sim 62\text{ meV}$. QMC therefore correctly predicts the energetic ordering and lattice constants of AA and AB graphite, giving confidence that van der Waals interactions are well-accounted for in this system and lending support to the experimental lattice constant report.⁴² To the best of our knowledge, the binding energy of AA graphite has not been determined experimentally.

Comparing DFT results to the calculated QMC binding curve, we observe: (i) PBE does not bind due to lack of van der Waals interactions, (ii) DFT-D2 slightly overbinds at a smaller lattice constant, (iii) the TS-vdW method significantly overbinds, consistent with its behavior in AB graphite,⁴³ and (iv) the vdW-DF2 density functional obtains a near identical lattice constant to QMC but slightly overbinds by $\sim 10\text{ meV}$. This is excellent performance and indicates that the van der Waals interaction is well represented by this functional. The problems found with the van der Waals methods based on classical electromagnetics indicate that these methods should be

used with caution in layered systems, such as heterostructures of graphene and graphene analogues.

We now consider the binding energy of one Li atom in AA graphite, Figure 2a, computed with respect to the free atom and bulk AA graphite. The QMC calculated Li binding energy varies slowly with lattice constant, with a value $\sim 1.6(1)$ eV at the Li–C optimal $3.61(2)$ Å, shown in Figure 2b, except for a sharp increase toward 1.9 eV below 3.4 Å. This increase likely indicates a significant change in the predicted electronic structure under compression but could also be due to an increase in nodal error and will be studied in subsequent work. Compared to the DFT calculations the QMC binding energy is significantly smaller: (i) PBE overbinds by 0.4 eV and (ii) DFT-D2 and (iii) TS-vdW significantly overbind by 1.3 and 1.4 eV, respectively, while (iv) vdW-DF2 behaves similarly to PBE but with ~ 0.1 eV less overbinding. The difference between these results is not a uniform shift and can mainly be traced back to the differing binding energy curves of pure AA graphite. Considering the sensitivity of these calculations and the residual errors in the QMC data, we estimate that the “most accurate” DFTs are overbinding by several tenths of an eV. This error is reasonable and not an unexpected accuracy for local density functionals. Accuracy might be improved by future hybrid functionals (those including exact exchange) that also include van der Waals interactions, provided double counting is avoided. However, considering a typical Li-ion battery voltage of 3.6 V, where a 0.2 V increase signifies a worthwhile capacity improvement, errors of the magnitude identified remain highly significant for materials modeling.

Turning to the diffusivity of Li in graphite, Figure 3 shows the calculated in-plane diffusion barrier of Li using different levels of theory for two diffusion pathways, (a) across a bond, the shortest and lowest energy path in all theories, and (b) along a bond. The behavior of the different methods is broadly the same in both cases. We first examine the barriers obtained using PBE and DFT-D2, using the original parameters for Li and C.⁶ The PBE method yields very accurate barriers, indicating that they are largely determined by charge transfer, which might be expected if Li was in a purely ionic form. Inclusion of the van der Waals corrections DFT-D2 leads to a considerable overestimation of the diffusion barriers, especially at larger separations of the graphite planes, e.g., by 0.3 eV at 3.7 Å on path (a). This would lead to predictions of substantially slower diffusion, which is exponential in this activation energy. The increase in predicted diffusion barrier is slightly larger when Li is on top of a bond with four near-neighbor carbon atoms, than when it is on top of a C atom, where it is mainly interacting with two near-neighbor carbon atoms. This suggests that the Li–C interactions are not captured accurately using the original DFT-D2 parametrization. Indeed, a least-squares fit of the C_6^{Li} to the DMC barriers gave a value of zero. Using this value obtained accurate diffusion barriers for all separation distances, the relative energies being exactly equal to the PBE values, since the van der Waals correction then only contains constant carbon–carbon terms that cancel in the diffusion barrier calculation. (Note that the errors in binding energies remain.) Therefore, the main corrections to the DFT energies comes from the van der Waals interactions between graphite sheets with a redistributed $1e^-$ charge from the Li atom. It is interesting to note that use of the original DFT-D2 in this situation, motivated by the idea that the incorporation of van der Waals would increase accuracy, would actually result in a substantial reduction in accuracy: if significant charge transfer

has occurred, the C_6 parameters must be rederived⁶ for accurate results.

Interestingly, the TS-vdW method captures the barrier in excellent comparison to the DMC results at $d = 3.35$ Å and is much better than the original DFT-D2 results at the larger separation of $d = 3.7$ Å. The agreement is better when Li is on top of a bond as compared to when it is on top of an atom. Because the scheme accurately captures the reduction in the barrier to a significant fraction and agrees very well at the smaller separation of $d = 3.35$ Å, it would appear that the differences at the larger separation also result from the inadequacy of the underlying DFT to obtain accurate enough charge densities at larger separations. We expect the self-consistently screened variant of TS-vdW will further increase accuracy,⁴⁴ particularly if used with more advanced functionals. The vdW-DF2 method gives accurate barriers, potentially a little more accurate than PBE. This indicates that the vdW-DF2 captures additional charge transfer or polarization than PBE, confirmed by charge density analysis (below).

The previous results all suggest the following picture for dilute Li in graphite: the geometry is largely determined by van der Waals interactions between the graphite planes, while the Li locally donates an electron to the lattice. The resulting Li ion is barely polarizable, with very weak van der Waals interactions compared to the atom. The charge transfer gives rise to the binding energy and mostly determines the diffusivity from site to site. In Figure 4 we illustrate this by plotting the charge density difference between (a) graphite, with and without the Li atom, computed using vdW-DF2, and (b) vdW-DF2 and PBE, demonstrating that there is a small but significant greater charge transfer from Li to the lattice as well as a greater

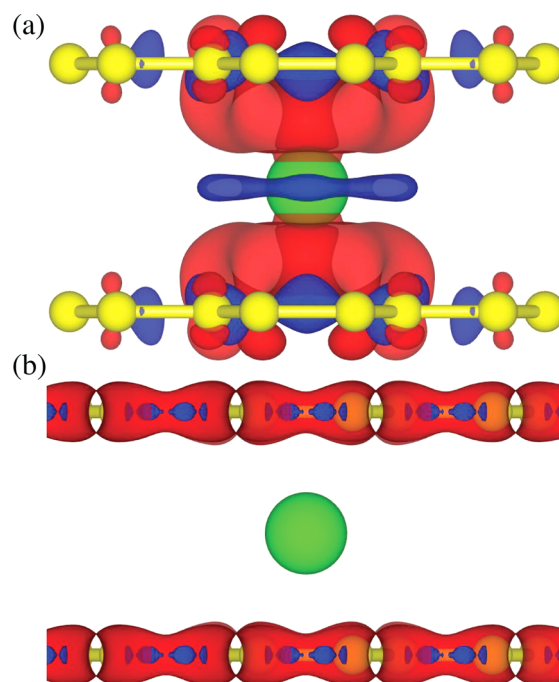


Figure 4. Charge density difference isosurfaces for interplanar separation of 3.528 Å of graphite (a) with and without lithium (green) computed using vdW-DF2 and (b) between vdW-DF2 and PBE. The isosurfaces are plotted at 0.001 electrons/Å³, with red positive and blue negative. The lithium locally donates charge to the carbon (yellow) lattice. vdW-DF2 predicts slightly more electron transfer and greater localization than PBE.

localization on the graphite. A similar picture is obtained at all examined lattice constants, including a consistently lower charge on the Li atom in vdW-DF2. This environment-dependent coupling of the van der Waals and charge-transfer effects are expected to be common to many systems and processes where metal atoms intercalate, diffuse, or adsorb, e.g., battery anode and cathode intercalation materials, pseudocapacitive materials, and membrane-like materials with pores intended for separations. As QMC calculations are beginning to be applied to these systems, their cost should be considered an upper bound to what is reasonable to spend within DFT. The graphite binding energy calculations reported here cost several hundred thousand processor hours, while the lithium binding energy calculations required 1 order of magnitude more time, which is affordable on high-end supercomputers. Less demanding DFT approximations which agree with QMC benchmarks should be preferred.

To summarize, lithium in graphite is a challenging and relevant test of van der Waals methods due to the importance of both van der Waals and charge transfer. Our accurate QMC calculations for graphite indicate that properties such as the phase diagram of carbon are within reach of these many-body methods. The self-consistent van der Waals functional vdW-DF2 gives best overall results, predicting good lattice constants, binding energies, and diffusion barriers. On addition of lithium, we observe a clear hierarchy of accuracy in the van der Waals methods, where the simplest methods can be inaccurate without proper parametrization or recognition of charge transfer (DFT-D2), while more sophisticated methods such as TS-vdW yield improved results. The self-consistent van der Waals corrected density functionals tested in this work appear to be quite accurate. Many of the residual errors are due to errors in the underlying non-van der Waals part of the density functionals.

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Notes

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