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Quantum Monte Carlo calculations of dihydrogen binding energetics on Ca cations: An assessment of errors in density functionals for weakly bonded systems

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We investigate the binding of single and quadruple hydrogen molecules on a positively charged Ca ion. By comparing with benchmark quantum Monte Carlo (QMC) calculations we demonstrate wide variability in other more approximate electronic-structure methods including common density functionals. Single determinant QMC calculations find no binding at short range by approximately 0.1 eV for the quadruple hydrogen molecule case, for a fixed hydrogen bond length of 0.77 Å. Density-functional calculations using common functionals such a local density approximation and B3LYP differ substantially from the QMC binding curve. We show that use of full Hartree-Fock exchange and Perdew-Burke-Ernzerhof (PBE) correlation (HFX+PBEC) obtains close agreement with the QMC results, both qualitatively and quantitatively. These results both motivate the use and development of improved functionals and indicate that caution is required applying electronic-structure methods to weakly bound systems such as hydrogen-storage materials based on metal-ion-decorated nanostructures.

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Our ability to accurately predict molecular adsorption energies is of widespread importance in the physical, chemical, and materials sciences. Technologically, the adsorption of small molecules on semiconductors or metals is an essential step in many catalytic or energy storage related areas. In the case of hydrogen storage, the strength of the adsorption can determine the suitability a material for practical application: if the binding is too high, release of the hydrogen will be difficult at moderate operating temperatures, while if the binding is too weak, storage of the hydrogen will be ineffective.

Calculating the energetics of hydrogen adsorption is a difficult task and requires highly accurate quantum mechanics based calculations. If the structure and eventually the dynamics of the adsorption process are to be accurately modeled, the potential-energy surface of the adsorbent and adsorbate must be accurately simulated over a length scale of at least 5 Å. Density-functional-theory- (DFT-) based methods are the most widely applied electronic structure methods for studies of hydrogen storage materials. However, in practice the DFTs are not only approximate but are also rarely benchmarked in the nonbonding and weakly bonding configurations vital for hydrogen storage.

Motivated in part by recent discussions and discrepancies for DFT predictions of hydrogen adsorption on alkaline-earth metals,[1–3] we have performed extensive quantum Monte Carlo (QMC) (Ref. 4) calculations for H_2 (dihydrogen) adsorption on the Ca^{1+} system. The ion's charge models the scenario, where the ion is absorbed on graphene.[5,6] QMC provides an accurate and unbiased reference to compare against approximate but more computationally affordable approaches. We concentrate on the interaction of hydrogens with a single ion, as opposed to a system with a substrate since the geometries are easily and unambiguously specified and the systems are already sufficient to demonstrate substantial differences in predicted binding energies and overall shape of the binding curves.

The interaction of one or many H_2 molecules with Ca^{1+} will undoubtedly involve several effects: charge transfer, polarization, and potential long-range dispersion (or van der Waals) interactions. To accurately model these systems, first-principles calculations should be able to accurately account for all these effects with little reliance on, e.g., error cancellation. For example, van der Waals interactions are naturally and accurately included within QMC approaches[7–10] but are absent from common DFTs.

In the following we: (i) describe our QMC methodology, (ii) present benchmark results for the cases of single H_2 adsorption on Ca^{1+}, and (iii) since in actual use scenarios additional hydrogen molecules will be present we also results for quadruple H_2 adsorption. These systems are constructed identically to those of Ref. 1. Finally, (iv) we summarize our findings.

I. QUANTUM MONTE CARLO

The QMC method allows for a very efficient and accurate solution of the Schrödinger equation. In contrast with many electronic-structure methods, QMC methods involve only well controlled approximations. Although their computational prefactor is often large, for small- and medium-sized molecular systems energetics close to chemical accuracy can be obtained, e.g., Refs. 11 and 12. These properties make QMC methods ideal for benchmark studies and for the assessment of computationally cheaper but more approximate methods.

QMC methods are wave function based and the most important input is the trial many-body wave function. In variational Monte Carlo (VMC) a direct variational evaluation of the energy of a trial wave function is performed using importance sampled Monte Carlo integration. VMC calculations therefore suffer from a potentially very strong dependence on the input wave function and any prior assumptions about the electronic structure but have the advantage that the actual many-body wave function is obtained and can be analyzed. In fixed-node diffusion quantum Monte Carlo (DMC), the lowest energy state consistent with the zeros (nodes) of the trial wave function is projected. This projection greatly reduces the dependence of the final energy on the input trial wave function compared to VMC. In practice, very accurate results are obtained by DMC for a wide variety of molecular and solid-state systems.[4,7–10,13,14] Due to the increased robustness we concentrate on DMC results in this study.

For our purposes, the only significant approximations in DMC calculations are (i) the use of pseudopotentials and (ii) the fixed-node approximation and consequent dependence on the nodal surface of the input trial wave function. The first approximation introduces systematic errors via the approximate treatment of core-valence interactions and via the locality approximation[15] necessary to evaluate the nonlocal pseudopotentials in DMC. We minimize these errors by using a small Ne core for the Ca pseudopotential[16] and very high-quality trial wave functions. We use the same pseudopotentials in all our calculations to ensure a fair comparison between all methods: the same Hamiltonian is solved in our QMC, DFT, and quantum chemical calculations.

To minimize the nodal errors in our DMC calculations we also use multideterminant trial wave functions obtained from configuration-interaction calculations that are subsequently reoptimized via the energy minimization method.[11] This approach is a significant advance over conventional applications of DMC, where the nodal surface of the trial wave function consists of only a single Slater determinant determined by a less accurate theory such as DFT: the nodal errors are systematically reduced to near chemical accuracy[11,12] when sufficient statistics can be obtained and the multideterminant expansion is large enough. Previous studies have shown that (i) for light molecules single determinant DMC yields results similar in accuracy coupled cluster singles doubles with perturbative triples [CCSD(T)] with the aug-cc-pVQZ basis set,[13] (ii) these errors are further reduced with multideterminant methods, e.g.,[11–13] and (iii) pseudopotential errors are small and less significant than the nodal error in these systems.[13,14]

In principle, modern trial wave-function optimization methods[11,12] can produce DMC results nearly independent of the input provided sufficiently flexible trial wave-function forms are adopted. Here we validate our single determinant nodal surface results using large configuration-interaction expansions of many determinants.

In the following calculations we use trial wave functions consisting of a weighted sum of Slater determinants multiplied by a two-body Jastrow factor. The Slater determinants consist of orbitals determined by GAMESS (Ref. 17) DFT or complete active space self-consistent-field (CASSCF) calculations expanded in the large atomic natural orbital-valence triple zeta (ANO-VTZ) Gaussian basis set.[16] The two-body Jastrow factor does not change the nodal surface but acts to enforce the electron-electron cusp condition, greatly improving the overall quality of the trial wave functions. For the QMC calculations we used the QWALK code.[18] Multideterminant QMC calculations used up to 370 determinants, where we took all CASSCF determinant of squared magnitude greater than 0.01. Energy minimization was performed starting from the truncated CASSCF results. We note that the DMC energies always lie substantially below the pure quantum chemistry results. Pseudopotentials were derived in the soft Hartree-Fock (HF) formalism.[16] An average DMC population of $\sim$30 000 walkers and a small time step of 0.005 a.u. was used. The largest DMC calculations used O(1000) processor hours per energy point.

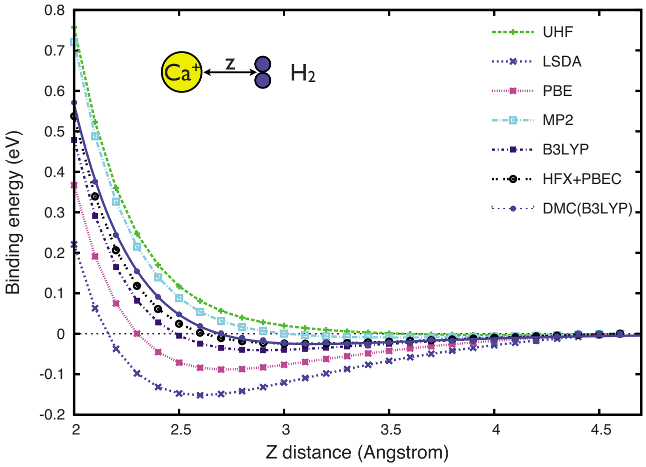

FIG. 1. (Color online) Calculated binding energy for a single hydrogen molecule (H_2) approaching Ca^{1+}. The molecule to oriented with the bond perpendicular to the line of approach (see inset). Results are shown for the UHF, the LSDA, PBE, and B3LYP density functionals, second-order MP2. We also show DMC and density-functional results calculated using exact exchange combined with PBE correlation (HFX+PBEC). The DMC calculations use a single determinant of B3LYP orbitals and a Jastrow factor for the trial wave function and nodal surface. The hydrogen molecule bond length is held fixed at 0.77 Å. The lines are a guide to the eye. Error bars are smaller than the size of the DMC symbols.

II. RESULTS FOR SINGLE H_2 ABSORPTION

Figure 1 shows our calculated binding-energy curve for the hydrogen dimer on Ca^{1+} with the molecular bond oriented perpendicularly to the line of approach. Since the calculation of forces is not well developed in QMC, for each distance from the Ca^{1+} ion we computed energies for all methods with a fixed bond length of 0.77 Å, corresponding to the value found near binding in quantum chemical calculations.[1] Only small changes in the fully relaxed value are seen over all distances, indicating that the trends in the binding at fixed bond length are representative of the relaxed case. For computational simplicity, we treat the energy of the system at $z=4.6$ Å as representing fully separated unbound system.

Our results show that while the potential-energy surface varies quantitatively between the methods, for a single dimer the general trends given are qualitatively similar for many of the methods, with a single minimum. However, unrestricted Hartree-Fock (UHF) and second-order Møller-Plesset perturbation theory (MP2) calculations show negligible binding. The DMC data show a minimum around $z=3.1$ Å and binding of $\sim$0.025 eV.

Comparing the density-functional results against the DMC energy curve we find that B3LYP (Ref. 19) functional gives a relatively good agreement with minimum at $z=<2.9$ Å. However, the local spin-density approximation (LSDA) functional[20] significantly overbinds by at least 0.1 eV while the PBE functional[21] lies midway between the B3LYP and LSDA values. None of the functionals results in false energetic minima in the binding-energy curve, however, the distance of the minimum energy varies by 0.5 Å over these functionals. Calculations using Hartree-Fock exchange combined with PBE correlation (HFX+PBEC) (similar to Refs. 22 and 23 except with 100% exchange) very closely resemble the DMC results; analysis and possible reasons for the apparent accuracy are discussed after the four dihydrogen results.

III. RESULTS FOR FOUR H_2 ABSORPTION

Figure 2 shows our calculated binding-energy curve for four hydrogen dimers on Ca^{1+}. In this system the hydrogens are pinned in a planar geometry, 90° apart in D_4 symmetry, with molecular bonds oriented perpendicularly to the line of approach (inset in Fig. 2).

The binding energies obtained with single determinant DMC display a minimum around 2.2 Å. However, comparing these energies with those over 3 Å clearly shows the minimum to be a local metastable minimum: there is no binding of four H_2 molecules in this planar geometry at short range at the single determinant DMC level. To test the accuracy of these calculations we also used multideterminant wave functions determinants, initially obtained by restricted active space restricted active space(9,37) (RAS) calculations. The binding is shifted to higher energies by ~0.1 eV indicating that the single determinant results and nodal surface are robust.

DFT-based calculations show clear energy minima around the 2.2 Å distance indicating significant binding of the H_2 molecules. Although the depth of binding varies, similar behavior is obtained for LSDA, PBE, and B3LYP. The same energetic ordering is observed as for the single hydrogen case, with LSDA displaying greatest binding. By contrast, UHF calculations display only a slight minimum around 2.3 Å. We also include quantum chemical results from RAS and CAS calculations in Fig. 2. The larger active space calculations reduce the calculated binding energy, moving the quantum chemical results toward the DMC results. Perturbative theory results also show no overall binding. A clear transition between states of A_{1g} and B_{2g} symmetries is observed[1] between 2.5 and 3.0 Å depending on the underlying theory.

Our qualitative conclusion of no binding for the four hydrogen molecule case with fixed 0.77 Å bond length is in qualitative agreement with previous quantum chemical results.[1] However, our more extensive basis sets and more rigorous DMC calculations reveal that the energy scale for any potential binding is very small, only a few tenths of an electron volt. Strikingly, even allowing a generous estimate of 0.2 eV residual systematic errors in our DMC calculations, any eventual binding will remain small (order 0.1 eV) whereas the LSDA and PBE functionals predict binding energies one order of magnitude larger.

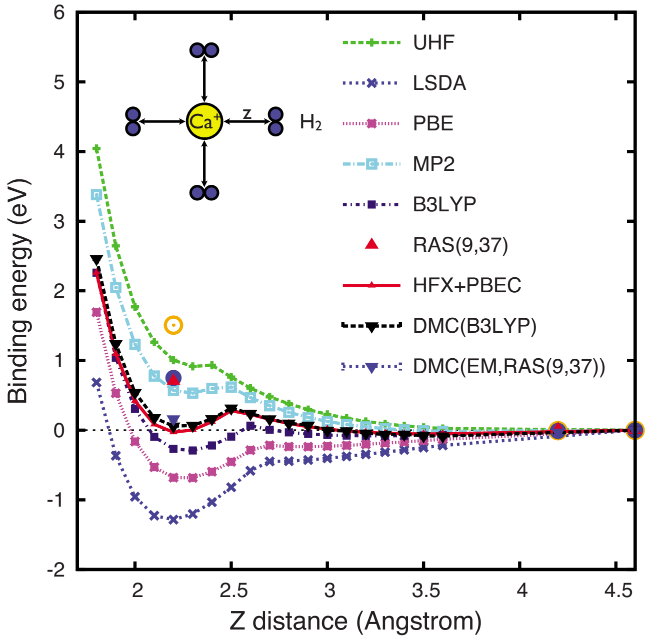

FIG. 2. (Color online) Calculated binding energy for four dihydrogen (H_2) molecules approaching Ca^{1+}. Each molecule is oriented with the bond perpendicular to the line of approach in an overall planar geometry with D4 symmetry (see inset). Results are shown for unrestricted Hartree-Fock, density-functional theory using several approximate functionals (LDA, PBE, B3LYP), and for two sets of DMC calculations. For the range of distances studied, DMC data are given for a single determinant of B3LYP orbitals and a Jastrow factor for the trial wave function and nodal surface (black triangles). At 2.2 Å separation we also compute the binding energy in DMC using energy minimized RAS multideterminant wave functions. At this distance we also show quantum chemical results for RAS(9,37) [red (gray) upwards filled triangle], RAS (9,31) [blue (dark gray) filled circle], and complete active space CAS(9,18) [orange (gray) empty circle]. HFX+PBEC indicates density-functional results calculated using exact exchange combined with PBE correlation. The hydrogen molecule bond lengths are held fixed at 0.77 Å. See text for more information. The lines drawn are a guide to the eye. DMC error bars are smaller than the symbols.

We also tested energies obtained from density-functional theory using Hartree-Fock exchange combined with PBE correlation, gradually increasing the fraction of exchange. As for the single hydrogen molecule case, the calculated binding curve accurately follows the DMC data over all distances. However, only a 100% contribution fully reproduced the DMC data; lesser contributions smoothly interpolating between the DMC and PBE results. Given the wide variation seen for other functionals, this is noteworthy, and also indicates the primary source of error in the other density-functional predictions. We argue, in accordance with Ref. 24 that the semilocal functionals provide good description of static correlation and exchange in this system. On the other hand, dynamic or long-range exchange is mostly absent in these functionals. Since our system seems not to have a strong multireference character (based on our RAS and CAS calculations) the dynamical part of exchange must play a dominant role. This last part is well described only in HF or in exact-exchange functionals such as optimized effective potential method. Therefore including full dynamical part of a exchange together with the correlation from LSDA, PBE, or B3LYP gives a good description. This observation is mostly independent from the type of the correlation used.

IV. SUMMARY

We have performed benchmark quantum Monte Carlo calculations of hydrogen molecule binding on the Ca cation. Density-functional calculations vary widely in the predicted binding energy. Density-functional calculations using Hartree-Fock exchange well reproduce the Monte Carlo results, suggesting a route—if not universal—to predictive and accurate calculations in this and related systems. We hope that our results will help further motivate the development of improved functionals. As metal ions have been proposed as hydrogen binding centers in new hydrogen-storage materials, we strongly recommend caution in applying density-functional methods to these systems. Appropriate benchmarking using quantum chemical or quantum Monte Carlo techniques is required.

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