A comparison between quantum chemistry and quantum Monte Carlo techniques for the adsorption of water on the (001) LiH surface

Theodoros Tsatsoulis, Felix Hummel, Denis Usvyat, Martin Schütz, George H. Booth, Simon S. Binnie, Michael J. Gillan, Dario Alfè, Angelos Michaelides, and Andreas Grüneis

Citation: The Journal of Chemical Physics 146, 204108 (2017); doi: 10.1063/1.4984048
View online: http://dx.doi.org/10.1063/1.4984048
View Table of Contents: http://aip.scitation.org/toc/jcp/146/20
Published by the American Institute of Physics

Articles you may be interested in

Efficient evaluation of three-center Coulomb integrals
The Journal of Chemical Physics 146, 204101 (2017); 10.1063/1.4983393

Stochastic multi-reference perturbation theory with application to the linearized coupled cluster method
The Journal of Chemical Physics 146, 044107 (2017); 10.1063/1.4974177

Quartic scaling MP2 for solids: A highly parallelized algorithm in the plane wave basis
The Journal of Chemical Physics 146, 104101 (2017); 10.1063/1.4976937

Dealing with the exponential wall in electronic structure calculations
The Journal of Chemical Physics 146, 194107 (2017); 10.1063/1.4983207

From plane waves to local Gaussians for the simulation of correlated periodic systems
The Journal of Chemical Physics 145, 084111 (2016); 10.1063/1.4961301

Perspective: Chemical reactions in ionic liquids monitored through the gas (vacuum)/liquid interface
The Journal of Chemical Physics 146, 170901 (2017); 10.1063/1.4982355
A comparison between quantum chemistry and quantum Monte Carlo techniques for the adsorption of water on the (001) LiH surface

Theodoros Tsatsoulis,1 Felix Hummel,1 Denis Usvyat,2 Martin Schütz,2 George H. Booth,3 Simon S. Binnie,4,5,6 Michael J. Gillan,4,5,6 Dario Alfe,4,5,6,7 Angelos Michaelides,4,5,6 and Andreas Grüneis1,8,a)

1Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart, Germany
2Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, D-12489 Berlin, Germany
3Department of Physics, King’s College London, Strand, London WC2R 2LS, United Kingdom
4London Centre for Nanotechnology, University College London, Gordon St., London WC1H 0AH, United Kingdom
5Thomas Young Centre, University College London, London WC1H 0AH, United Kingdom
6Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom
7Department of Earth Sciences, University College London, London WC1E 6BT, United Kingdom
8Department Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

(Received 21 February 2017; accepted 11 May 2017; published online 26 May 2017)

We present a comprehensive benchmark study of the adsorption energy of a single water molecule on the (001) LiH surface using periodic coupled cluster and quantum Monte Carlo theories. We benchmark and compare different implementations of quantum chemical wave function based theories in order to verify the reliability of the predicted adsorption energies and the employed approximations. Furthermore we compare the predicted adsorption energies to those obtained employing widely used van der Waals density-functional. Our findings show that quantum chemical approaches are becoming a robust and reliable tool for condensed phase electronic structure calculations, providing an additional tool that can also help in potentially improving currently available van der Waals density-functional. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Kohn–Sham density-functional theory (DFT) is the standard approach for the first-principles description of electronic properties in computational material science and surface chemistry. However, it is becoming clear that the limitations of the employed exchange-correlation (XC) functionals to balance off the numerous competing physical effects give rise to deficiencies in the predictive ability of the approach, generally without any systematic manner to improve upon it. One class of widely studied problems where this is particularly true is the case of molecular adsorption on periodic surfaces. Competing physical effects as well as poorly treated long-range dispersion contributions result in predicted adsorption energies and sites varying strongly with the employed XC functional (see, e.g., Refs. 1–5). This indicates fundamental shortcomings in many semi-local functionals that are difficult to remedy. Long-range dispersive interactions can be accounted for by the addition of pairwise interatomic $C_6R^{-6}$ terms to the DFT energy or by non-local functionals.6–8 In this work, we will refer to both the van der Waals corrected and van der Waals inclusive DFT methods as van der Waals density-functionals. Theoretically these corrections can be well justified and derived using quantum Drude oscillators that serve as a qualitatively correct model for electrical response properties between molecules and insulating solids. However, most van der Waals corrections also require the introduction of some adjustable parameters such as the cutoff function and cutoff radius at short distances $R$ in order to remove the attractive singularity from the $C_6R^{-6}$ terms. These parameters can be obtained by optimizing the accuracy of the dispersion corrected functionals for the description of molecular interaction energies in a given test set.

In this work, we consider an ab initio description of the true many-body wave function for a molecular adsorption problem. Two contrasting yet complementary approaches which we consider here are those from the field of quantum chemical Fock-space expansions of the wave function9 and a stochastic representation from the Diffusion Monte Carlo (DMC) technique.10 These wave function based approaches offer a thorough description of quantum many-body effects through a direct treatment of electronic correlation. Such approaches can supplement density-functional-based methods with accurate results.

DMC is a real-space quantum Monte Carlo (QMC) method, where the real-space configurations of all $N$-electrons are sampled stochastically. This stochastic distribution of electrons is evolved toward a sampling of the ground-state distribution of electrons via an imaginary-time propagator, which exponentially filters out the higher-lying eigenfunctions of the Hamiltonian from the distribution. This sampling would be exact if it were not for the “Fermion sign problem,” where the sampling collapses to the lower-energy symmetric
distribution of an $N$-particle Bosonic distribution. To avoid this, constraints are imposed whereby the correct antisymmetry is maintained by imposing a hard nodal surface for the sampling which enforces the sign of the sampled configurations. While this alleviates the Fermion sign problem, it introduces a systematic and variational error due to this nodal surface, which in practical applications is generally taken to be the nodal surface of a single Slater determinant. This represents the leading error of a DMC calculation, but it benefits from a number of appealing properties which contrast with the quantum chemical methods, such as a very minor dependence on the basis set, as well as a low-scaling with respect to the system size. DMC techniques are increasingly used to understand molecular adsorption at periodic surfaces.4,5,11,12

Quantum chemical methods constitute a hierarchy which starting from the one-particle Hartree–Fock (HF) approximation, allows for a systematic treatment of the quantum many-body effects. The simplest form of such correlated methods is the second-order Møller–Plesset (MP2) perturbation theory. Although MP2 theory provides a fair compromise between efficiency and accuracy, certain effects are not captured accurately enough or at all (e.g. three-body dispersion interactions). For systems where such effects are essential, the accuracy of the MP2 treatment is rather modest. For instance, MP2 is known to notoriously overestimate dispersion corrections in the form of an exponential of cluster operators. The CCSD(T) theory provides a compelling framework of infinite-order approximation to the electronic correlation, coupled-cluster theory that allows for an in-depth comparison of different post-mean-field methods.

Details about the structure of the system under consideration are given in Sec. II A. Computational details are presented in Secs. II B–II D for plane-wave, Gaussian basis, and DMC calculations, respectively. Section III summarizes all the results obtained from different methods. Finally, we conclude the paper in Sec. IV.

II. COMPUTATIONAL DETAILS

A. $\text{H}_2\text{O}$ on LiH geometry

The aim of this work is to compare different high-level theories for the calculation of the adsorption energy of a single water molecule on the (001) LiH surface, keeping the atomic structure of the surface fixed. The adsorption energy is defined as the difference in energy between the non-interacting fragments (water and the LiH surface) and the interacting system (water molecule on LiH),

$$E_{\text{ads}} = E_{\text{H}_2\text{O} + \text{LiH}} - E_{\text{H}_2\text{O}} - E_{\text{LiH}}.$$

An alternative definition for the adsorption energy is the difference between the energy of the system with the water molecule at its equilibrium position on the surface and that of the system in which the water molecule has been displaced vertically by 10 Å. In both definitions, the molecular structure of the water molecule has been kept the same. The latter definition is used for the DMC calculations since it allows to maximize the possible cancellation of errors.44 We stress that since we are primarily interested in benchmarking different electronic-structure methods, zero-point energy contributions or finite temperature effects are neglected. The structure of the surface with the adsorbed molecule has been obtained in the following manner. The Li and H atoms have been kept fixed to their pristine lattice sites with a lattice constant of $a = 4.084$ Å, consistent with the previous studies of the LiH crystal.19,20,40 This has the advantage of keeping the geometry consistent when supercells or fragments of different sizes are used in quantum chemical and DMC calculations. The water molecule was
relaxed on the LiH (001) surface using the Perdew–Burke–Ernzerhof (PBE) XC functional\textsuperscript{45} and a two-layer slab with the 4 \times 4 surface supercell. For these calculations, the \textit{vasp} code has been employed.\textsuperscript{46} A vacuum gap of 20.5 \text{Å} has been employed to ensure that the surface slab does not interact with its periodic image. The relaxed geometry of the water molecule adsorbed on the LiH surface is shown in Fig. 1. The DMC adsorption energy curve obtained by varying the distance between the molecule and the surface agrees well with the oxygen–surface distance of the PBE functional (2.15 \text{Å}).\textsuperscript{47} The structural coordinates of Fig. 1 are given in the supplementary material. This geometry is used throughout the paper for all density-functional and correlated calculations. The convergence of the adsorption energy with the number of layers in the slab is explored in Sec. III B.

### B. Plane-wave basis set calculations

The calculations using a plane-wave basis set presented in this work have been performed using the \textit{vasp} code employing the PAW method alongside with the Γ-point approximation to sample the first Brillouin zone. The kinetic energy cutoff that determines the size of the plane-wave basis set expansion of the one-particle states was set to 500 eV. There are numerous density-functionals that could be considered, of which we have only chosen a small selection. Thus, we assess the accuracy of one of the most widely used functionals, the PBE functional,\textsuperscript{48} as well as of several van der Waals functionals. Specifically, dispersion corrections were taken into account following the approach of Grimme\textit{ et al.}, the method of Tkatchenko and Scheffler, and the van der Waals density-functional (vdW-DF) method proposed by Dion \textit{et al.},\textsuperscript{50–53} as implemented in \textit{vasp}. In the former schemes, a correction is added to the DFT total energy after the self-consistent-field (SCF) cycle is converged, whereas the latter scheme is a non-local correlation functional that approximately accounts for dispersion interactions. In all calculations, all electronic states of the H and Li atoms were treated as valence states, whereas the 1s\textsuperscript{2} states of the O atom were kept frozen. Supercells of different sizes were used to model the LiH surface, containing 32, 64, and 128 atoms.

In the current paper, we employ psuedized Gaussian-type orbitals (PGTOs) expanded in a plane-wave basis set to span the virtual orbital manifold necessary for the quantum chemical MP2 and coupled-cluster methods. The space of the occupied orbitals from the HF calculation is projected out from the PGTOs, ensuring that they solely span the virtual space. The rediagonalization of the Fock matrix in this newly constructed virtual space allows for a canonical formulation of quantum chemical techniques. This enables considerably fewer states to be involved in many-body calculations.\textsuperscript{54} The method to obtain PGTOs invokes a pseudization procedure of the sharply peaked Gaussian basis sets, which follows the work of Kresse and Hafner.\textsuperscript{55} A more detailed explanation of PGTOs and their application to periodic systems is given in Ref. 54. PGTOs allow for a controllable and reliable extrapolation of the adsorption energies to complete basis set limit results. For the present calculations, Dunning’s contracted aug-cc-pVDZ (AVDZ), aug-cc-pVTZ (AVTZ), and aug-cc-pVQZ without g functions (AVQZ–g) basis sets\textsuperscript{56,57} were pseudized and expanded in a plane-wave basis set.\textsuperscript{54} Augmented functions were not included for the Li atom because they possess a small exponent for the radial part that introduces linear dependencies in the virtual orbital space. The AVQZ–g basis set used here does not encompass g angular momentum functions since the corresponding pseudization procedure has not yet been implemented in \textit{vasp}. Counterpoise corrections (CPs) to the basis set superposition error (BSSE)\textsuperscript{58} were included in all correlated quantum-chemical calculations with plane-waves that employ PGTOs for the virtual states.

Canonical periodic MP2 calculations using PGTOs were performed with the \textit{vasp} code.\textsuperscript{14,18} The evaluation of the two-electron-four-index integrals requires the intermediate Fourier-transformed overlap densities which are expanded into an auxiliary plane-wave basis.\textsuperscript{18} The kinetic energy cutoff $E_{k}$ defining this auxiliary basis set was set to 200 eV. All reported MP2 adsorption energies have been checked for convergence with respect to this cutoff. Table I shows the convergence of the MP2 adsorption energy with respect to the cutoff energy.

Periodic CCSD calculations were performed using the two-electron-four-index integrals calculated within the PAW method in \textit{vasp}. To further reduce the computational cost of coupled cluster methods, we first minimize the number of virtual orbitals. Pseudized Gaussian orbitals were placed only on the top-most layer of the LiH slab. In a second step, the auxiliary plane-wave basis, required for the evaluation of the Coulomb integrals, employed a kinetic energy cutoff of 100 eV.

<table>
<thead>
<tr>
<th>$E_{k}$ (eV)</th>
<th>$E_{\text{BSSE}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>242</td>
</tr>
<tr>
<td>100</td>
<td>214</td>
</tr>
<tr>
<td>150</td>
<td>211</td>
</tr>
<tr>
<td>200</td>
<td>211</td>
</tr>
<tr>
<td>250</td>
<td>211</td>
</tr>
<tr>
<td>300</td>
<td>211</td>
</tr>
</tbody>
</table>

TABLE I. MP2 adsorption energy against the cutoff energy $E_{k}$ of the auxiliary basis set. One-particle states were expanded in a plane-wave basis set with a cutoff of 500 eV, while the virtual states were constructed using an AVTZ basis set.
MP2 calculations reveal that this approximation yields adsorption energies that deviate by 3 meV from those obtained using a cutoff of 200 eV as indicated in Table I.

Ahlrichs and co-workers66,70 were used, i.e., aug-cc-pVTZ-mp2fit and cc-pVTZ-jkfit, respectively. In the periodic LMP2 and LMP2-F12 calculations, the 1s2 core states of O and Li were kept frozen. Nevertheless, the correlated core contribution of the 1s2 states of the Li atoms was computed at the MP2 level with an aug-cc-pwCVTZ basis set on the H2O + Li25H25 cluster using the molpro program package.71 The core-correlation contribution to the interaction is relatively short-range making further expansion of the cluster not necessary. Moreover, coupled-cluster calculations on finite clusters were also performed using the molpro code.

D. DMC calculations

DMC calculations have been performed with the Casino code,72 using Dirac–Fock pseudo-potentials (PP)73 and trial wave functions of the Slater–Jastrow type,

\[ \Psi_f(R) = D^{\uparrow}D^{\downarrow}\phi', \]

where \( D^{\uparrow} \) and \( D^{\downarrow} \) are Slater determinants of up- and down-spin single-electron orbitals, respectively, and \( \phi' \) is the so-called Jastrow factor, which is the exponential of a sum of one-body (electron-nucleus), two-body (electron-electron), and three-body (electron-electron-nucleus) terms. The parameters in the Jastrow factor were optimised by minimising the variance of the variational Monte Carlo energy, which for the system with one water molecule on a two-layer 3 × 3 LiH surface supercell was reduced to just over 1 Ha (740 eV2).

The imaginary time evolution of the Schrödinger equation has been performed with the usual short time approximation, using the locality approximation to treat the non-local part of the pseudopotentials.

The single particle orbitals have been obtained by DFT plane-wave calculations using the local density approximation and a plane-wave cutoff of 3400 eV, using the wscs package,75 and re-expanded in terms of B-splines,76 using the natural B-spline grid spacing given by \( a = \pi/G_{\text{max}} \), where \( G_{\text{max}} \) is the length of the largest vector employed in the plane-wave calculations.

The DMC calculations were then performed with no periodic boundary conditions in the direction perpendicular to the surface, using the Ewald interaction to model electron-electron interactions. DMC adsorption energies were computed as follows:

\[ E_{\text{ads}} = E_s - E_h, \]

where \( E_s \) is the energy of the system with the water molecule at its equilibrium position on the surface and \( E_h \) is the energy of the system in which the water molecule has been displaced vertically by 10 Å, without relaxing its structure. In the latter configuration, the residual interaction energy between the molecule and the surface is negligible, and this definition of \( E_{\text{ads}} \) maximises DMC cancellation of time step errors.44,77
Adsorption energies were calculated using time steps between 0.001 and 0.05 a.u., and we found that with a time step of 0.02 a.u., $E_{\text{ads}}$ is converged to better than 10 meV.

### III. RESULTS

In order to assess the accuracy of different theories and computational procedures, we study the adsorption of a single water molecule on the (001) surface of LiH. We present the results of DFT calculations, different periodic MP2 and coupled-cluster techniques, and compare these methods with DMC. We first discuss the convergence studies of the various theories with respect to the basis set, finite-size effects, and the number of LiH slabs, and then we compare the adsorption energies of the different methods.

#### A. Finite-size and basis set convergence

The finite-size and the basis set convergence studies summarized in this section employ a 2-layer LiH substrate as shown in Fig. 1.

We first discuss the convergence of the DFT-PBE and HF adsorption energies with respect to the system size. DFT-PBE and HF results using different implementations are summarized in Table II. The converged results are in excellent agreement with HF results using different implementations are summarized in this section employ a 2-layer LiH substrate as shown in Fig. 1.

We now turn to the discussion of the adsorption energies using different implementations of MP2 theory. LMP2-F12 is expected to provide results very close to the thermodynamic limit. On the other hand, canonical MP2 and LMP2-F12 results employing 3-layer LiH substrates with different number of atoms in the computational supercell. The LMP2-F12 result corresponds to a 1/8 extrapolation ($N \to \infty$), yielding 231 meV and 233 meV for AV(D,T)Z and AV(T,Q–g)Z extrapolated adsorption energies agree to within 2–6 meV for all studied system sizes. We note that the AV(T,Q–g)Z extrapolation is somewhat less reliable due to the presence of higher angular momentum functions in the AVQZ values. We find that the MP2 adsorption energies converge as $1/N^2$, where $N$ denotes the number of atoms in the LiH substrate. This behaviour is expected from the long-range decay of pairwise van der Waals contributions in two-dimensional systems. The convergence of the finite-size effects for the various basis set extrapolated MP2 results can be seen in Fig. 2. Using the $1/N^2$ behaviour, we can extrapolate the MP2 adsorption energies to the thermodynamic limit ($N \to \infty$), yielding 231 meV and 233 meV for AV(D,T)Z and AV(T,Q–g)Z, respectively. The 5–7 meV difference between the canonical MP2 and LMP2-F12 is likely due to the remaining basis set incompleteness in the correlation energy of the former method. Notwithstanding, the agreement of the two different schemes, which have very little in common, is impressive. The F12-based explicit correlation techniques combined with local approximation schemes accelerate the convergence of the MP2 correlation energy. Its close agreement with the periodic canonical results suggests that PGTOS provide an adequate virtual basis set for correlated calculations in plane-waves.

#### Table II. DFT-PBE and HF adsorption energies for water on 2-layer LiH substrates with different number of atoms in the supercell and different $k$-meshes. The reference 2-layer geometry with 64-atoms is shown in Fig. 1. The DFT-PBE and HF calculations have been performed with vasp and employ a 500 eV kinetic energy cutoff. The HF crystal calculations with an AVTZ-quality basis set and a $3 \times 3 \times 1 k$-mesh yield a value of 14 meV.

<table>
<thead>
<tr>
<th>$k$-mesh</th>
<th>Atoms</th>
<th>PBE</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Γ-point)</td>
<td>32</td>
<td>219</td>
<td>10</td>
</tr>
<tr>
<td>(Γ-point)</td>
<td>64</td>
<td>215</td>
<td>14</td>
</tr>
<tr>
<td>(Γ-point)</td>
<td>128</td>
<td>215</td>
<td>15</td>
</tr>
<tr>
<td>$(3 \times 3 \times 1)$</td>
<td>64</td>
<td>214</td>
<td>15</td>
</tr>
</tbody>
</table>

#### Table III. Canonical MP2 adsorption energies for water on 2-layer LiH substrates with different number of atoms in the computational supercell. The calculations were performed with vasp and employ PGTOS for the virtual orbitals alongside the Γ-point approximation. The thermodynamic limit is obtained from a $1/N^2$ extrapolation ($N$ denotes the number of atoms in the LiH substrate). The LMP2-F12 and LMP2-pF12 adsorption energies are 238 and 235 meV, respectively.

<table>
<thead>
<tr>
<th>$E_{\text{ads}}^{\text{MP2}}$ (meV)</th>
<th>Atoms</th>
<th>AVDZ</th>
<th>AVTZ</th>
<th>AVQZ–g</th>
<th>AV(D,T)Z</th>
<th>AV(T,Q–g)Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>162</td>
<td>193</td>
<td>198</td>
<td>207</td>
<td>201</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>181</td>
<td>211</td>
<td>218</td>
<td>224</td>
<td>222</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>185</td>
<td>213</td>
<td>220</td>
<td>226</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>188</td>
<td>218</td>
<td>228</td>
<td>231</td>
<td>235</td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>189</td>
<td>219</td>
<td>227</td>
<td>231</td>
<td>233</td>
<td></td>
</tr>
</tbody>
</table>

![FIG. 2. Dependence of the adsorption energy $E_{\text{ads}}$ of H$_2$O on LiH on the number of atoms of the substrate at different levels of theory and basis set extrapolations. The fitted lines correspond to 1/N$^2$ for the MP2 energies and 1/3N$^{5/4}$ for the DMC energies. MP2 results employ AV(D,T)Z and AV(T,Q)Z basis set extrapolations. The LMP2-F12 result corresponds to the thermodynamic limit. On the x-axis, $N_{\text{atoms}}$ is indicated instead of 1/N$^{\text{atoms}}$.](image-url)
TABLE IV. DMC adsorption energies for water on 2-layer LiH substrates with different number of atoms in the computational supercell.\textsuperscript{47} The thermodynamic limit is obtained from a $1/N^{5/4}$ extrapolation.\textsuperscript{78}

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$E_{\text{ads}}^{\text{DMC}}$ (meV)</th>
<th>CBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>167 (5)</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>209 (5)</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>224 (8)</td>
<td></td>
</tr>
<tr>
<td>144</td>
<td>239 (9)</td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>250 (7)</td>
<td></td>
</tr>
</tbody>
</table>

DMC adsorption energies\textsuperscript{47} against the number of atoms in the simulation supercell are provided in Table IV. The DMC adsorption energy converges more slowly with respect to the supercell size than the MP2 energy as shown in Fig. 2, due to the long ranged nature of the real-space exchange-correlation hole and reduced screening in lower dimensional materials. Drummond et al. proposed a $1/N^{5/4}$ extrapolation for the two-dimensional systems.\textsuperscript{78} Despite its statistical uncertainty, the thermodynamic limit of the DMC adsorption energy suggests that the MP2 error for this system is small but not negligible and thus a higher-order quantum chemical treatment is desirable.

Periodic coupled-cluster calculations were performed with PGTOs for the virtual orbitals. However, these Gaussian-type functions were placed only on the top-most layer of the LiH surface to reduce the computational cost. Additionally, only supercells with 32 and 64 atoms were used to model the LiH slab. AVDZ and AVTZ Gaussian basis sets were used for the construction of the PGTOs, and all results are extrapolated with respect to the basis set and the number of atoms in the supercell. MP2 results utilizing Gaussian orbitals for the full LiH surface and a finite-size extrapolation using four points verify that correlation effects are captured adequately via only top-most layer virtual states and a finite-size extrapolation using two points. The error of this simplification is about 1 meV in the MP2 energy. Consequently, it is reasonable to assume that coupled-cluster results obtained using the same simplification provide a similarly converged estimate. MP2 and coupled-cluster results are summarized in Table V and Fig. 3. The CCSD adsorption energies are close to those of MP2, differing only by 1 meV. However, the extrapolated DCSD results deviate quite significantly from the CCSD and MP2 results, yielding an adsorption energy of 243 meV in better agreement with the DMC energies. The coupled-cluster and MP2 results employ AV(D,T)Z basis set extrapolation.

Finally, a $\delta$CCSD(T) correction scheme was applied to both the canonical and the local MP2 results. In the former case, the correction $\delta$CCSD(T) was defined as

$$E_{\text{ads}}^{\delta\text{CCSD}(T)} = E_{\text{ads}}^{\text{MP2}} - E_{\text{ads}}^{\text{CCSD}(T)}$$

where canonical CCSD(T) and MP2 calculations were performed using an H$_2$O + Li$_9$H$_2$ 2-layer supercell (with an identical orientation of the water molecule as for the larger supercells) and an AVDZ basis set in a plane-wave representation. $E_{\text{ads}}^{\text{MP2}}$ is the thermodynamic limit of the MP2 adsorption energy using the AVD(T,Q–g)Z basis set extrapolation. This yields an adsorption energy of 254 meV.

The $\delta$CCSD(T) corrections to the LMP2-F12 results were computed using finite clusters. In this case, the canonical MP2 and CCSD(T) adsorption energy calculations were done on an H$_2$O + Li$_9$H$_2$ 2-layer finite cluster using the AV(D,T)Z basis sets. The water molecule geometry was taken from the periodic supercells. The correction $\delta$CCSD(T) for the periodic system was defined as

$$E_{\text{ads}}^{\delta\text{CCSD}(T)} = E_{\text{ads}}^{\text{LMP2-F12}} - E_{\text{ads}}^{\text{CCSD(T)}} = E_{\text{ads}}^{\text{MP2}} - E_{\text{ads}}^{\text{CCSD(T)}} = E_{\text{ads}}^{\text{CCSD(T0)|LCCD[S]-R}} - E_{\text{ads}}^{\text{MP2}}$$

yielding an adsorption energy of 256 meV. Incidentally we note that one cannot construct a periodic Li$_9$H$_0$ supercell and therefore a Li$_9$H$_8$ slab was used for the plane-wave based $\delta$CCSD(T). Furthermore, the finite-size error of the correction was estimated as the difference between local LCCSD(T0)LCCD(S)–R$^{-6}$ calculations\textsuperscript{81–83} on H$_2$O + Li$_9$H$_0$ and H$_2$O + Li$_{25}$H$_{25}$ clusters. This difference turned out to be negligible.

**TABLE V.** MP2 and coupled-cluster adsorption energies using LiH substrates with different number of atoms in the supercell. PGTOs were used for the virtual orbitals in the top-most layer of the LiH surface. The thermodynamic limit is obtained via a $1/N^{5/4}$ extrapolation.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$E_{\text{ads}}^{\text{MP2}}$ (meV)</th>
<th>$E_{\text{ads}}^{\text{CCSD}}$ (meV)</th>
<th>$E_{\text{ads}}^{\text{DCSD}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>157</td>
<td>192</td>
<td>207</td>
</tr>
<tr>
<td>64</td>
<td>172</td>
<td>209</td>
<td>224</td>
</tr>
<tr>
<td>$\infty$</td>
<td>216</td>
<td>230</td>
<td>230</td>
</tr>
</tbody>
</table>

![FIG. 3. Adsorption energy $E_{\text{ads}}$ of H$_2$O on LiH for different supercell sizes and levels of theory. Coupled-cluster and MP2 calculations were done using PGTOs only on the top-most layer of the LiH substrate. The fitted lines correspond to $1/N^{5/4}$ for the coupled-cluster and MP2 energies and $1/N^{7/4}$ for the DMC energies. The coupled-cluster and MP2 results employ AV(D,T)Z basis set extrapolation.\textsuperscript{80}](image)
of the order of 0.3 meV. However, we note that a $\delta$CCSD correction, defined in an analogous way as $\delta$CCSD(T), provides an adsorption energy of 219 meV, which deviates somewhat from the periodic CCSD result. In contrast, a periodic $\delta$CCSD correction, defined in an analogous way as $\delta$CCSD(T), yields an adsorption energy of 227 meV, very close to the canonical CCSD result. Thus the finite-cluster $\delta$ approach might still contain a certain error.

### B. Convergence of the adsorption energy with the number of layers

In this section, we investigate the adequacy of the chosen slab model, which consists of just two LiH layers, for studying the adsorption of water. Generally, the convergence of the adsorption energy with the number of layers in the slab is expected to be governed by long-range effects, such as electrostatics (attractive or repulsive) and dispersion (attractive). Importantly, electrostatics are already captured at the DFT or HF levels, while dispersion is not (unless the dispersion correction is added or a special DFT functional is used, which is able to describe dispersion).

Table VI demonstrates by how much the adsorption energy grows or declines if further layers are added to the slab, as computed by DFT and HF. In order to isolate the dispersion contribution, we provide the -D3 contribution separately, as well as the LMP2 correlation energy. For dispersion alone, it is actually possible to obtain convergence with the number of layers: -D3 is very inexpensive and thus can be computed for very thick slabs, while for LMP2 the inter-adsorbate-slab contribution can be extrapolated to a semi-infinite slab using the pair-specific $C_6$ coefficients fitted to the actual LMP2 pair energies (see Ref. 84 for details).

The PBE and HF results suggest that for the non-dispersive contributions, the two-layer slab is already an adequate model. Dispersion, on the contrary, is not entirely converged with just two LiH-layers. However, at the scale of the whole adsorption energy, the lack of a few meV of dispersion in the two-layer model can be tolerated.

### C. Comparison of methods

We now summarize the converged adsorption energies and compare them to a small set of widely used density functionals. All reported results employ a 2-layer LiH substrate as in Fig. 1. We believe that the mutually agreeing DMC and $\delta$CCSD(T) results can be considered as the most reliable benchmark for the present system, yielding adsorption energies between 250 (±7) meV and 256 meV. For comparison, the adsorption energy of each method is depicted in Fig. 4. A sizeable variation in the adsorption energies is evident between different van der Waals functionals (PBE-TS, 49 optB86b-vdW 53 PBE-D3 48 HSE06-D3 35 RPBE-vdW-DF 50), as well as PBE. The PBE functional underestimates the adsorption energy by roughly 45 meV, in a large part due to its lack of dispersive interactions. Grimme’s D3 correction 48 accounts for such interactions, albeit overestimating the adsorption energy for the current system, predicting a PBE-D3 adsorption energy of 350 meV, consistent with similar findings for water adsorption on ionic surfaces. 86 We note that this overestimation is less pronounced when the HSE06 87,88 hybrid functional is used in conjunction with D3, yielding a value of 306 meV. This can partly be attributed to the fact that the HSE06 functional underestimates the adsorption energy compared to PBE by as much as 85 meV. The optB86b-vdW 53 results also overbind the water molecule by roughly 45 meV, while the RPBE-vdW-DF 50 adsorption energy exhibits a similar underbinding as for the case of PBE. The best van der Waals functional estimate is provided by the Tkatchenko and Scheffler functional (PBE-TS) with iterative Hirshfeld partitioning. 89,90 The latter yields an adsorption energy of 268 meV in good agreement with $\delta$CCSD(T) results. These results illustrate the difficulties in van der Waals functionals. The PBE functional is known to provide non-electrostatic binding between closed shell systems. This attraction is rather an artifact than a real dispersive interaction. At the same time, this artificial attraction provides a quantitatively reasonable effective substitute for dispersion. However, if the physically correct dispersion is added on top, it becomes difficult to avoid double counting, leading to a deterioration of the quantitative accuracy.

Figure 4 also shows the various wave function estimates of the adsorption energy. Canonical MP2 theory underestimates the adsorption energy by 17 meV compared to DMC, while LMP2-F12 provides a slightly better estimate, partly due to the explicit correlation, leading to an improved convergence with respect to the basis set size. The LMP2-F12 adsorption energy is 238 meV, only 11 meV below the DMC result. CCSD constitutes no improvement over MP2 theory for the present case, yielding a binding energy of 229 meV only. The DCSD approximation, 59 consistent with findings in

<table>
<thead>
<tr>
<th>No. of layers</th>
<th>PBE</th>
<th>HF</th>
<th>-D3</th>
<th>LMP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-0.15</td>
<td>-1.51</td>
<td>+5.36</td>
<td>+2.44</td>
</tr>
<tr>
<td>4</td>
<td>-0.16</td>
<td>-7.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>+8.44</td>
<td></td>
<td>+4.66(+4.97)</td>
<td></td>
</tr>
</tbody>
</table>
molecular systems,59–61 considerably improves the description of water adsorption on LiH, predicting an adsorption energy of 243 meV, which is within the stochastic error of DMC but still underbinding compared to the triples corrected $\alpha$CCSD(T) results. In summary, we find excellent agreement between high-level quantum chemistry and QMC techniques as well as between different methods to compute MP2 adsorption energies. Furthermore the correlated wave function based methods yield estimates for the binding energy that lie in a relatively narrow energy window ranging from 229 meV to 256 meV.

IV. CONCLUSIONS

We have presented a comprehensive comparison between different electronic structure methods including wave function based theories and a small selection of density-functional for the prediction of the adsorption energy of a single water molecule on the (001) LiH surface.

Quantum chemical methods are systematically improvable, hence yielding increasingly accurate adsorption energies as one moves up the hierarchy to higher orders of theory. Distinguishable cluster theory and inclusion of triple excitations to CCSD theory give the best agreement with the DMC results. We find that MP2 and CCSD reach a similar level of accuracy for this system, slightly underbinding the water molecule on the LiH surface by roughly 20 meV. We also find good agreement between periodic canonical and local implementations utilizing explicit correlation techniques for improved basis set convergence. All these demonstrate that quantum chemical approaches are becoming a robust and reliable tool for condensed phase electronic structure calculations.

We have also employed van der Waals functionals for the study of the same system, finding that these functionals yield a significantly larger spread of adsorption energy estimates compared to the employed many-electron theories. The underestimation and overestimation compared to DMC and $\delta$CCSD(T) are as large as 30 meV (RPBE-vdW-DF) and 100 meV (PBE-D3), respectively. Although the PBE-TS functional achieves good agreement with the DMC and $\delta$CCSD(T) estimates for the present case, it remains difficult to achieve such a high level of accuracy for a wide class of materials using van der Waals functionals. This study contributes another benchmark system to the literature that can be used to further improve upon the currently available and computationally very efficient van der Waals functionals for cases where higher accuracy is needed.

SUPPLEMENTARY MATERIAL

See supplementary material for the structure of water adsorption on the (001) LiH surface.

ACKNOWLEDGMENTS

A.M.’s work is supported by the European Research Council under the European Union’s Seventh Framework Programme (No. FP/2007-2013)/ERC Grant Agreement No. 616121 (HeteroJect project) and the Royal Society through a Wolfson Research Merit Award. D.U. and M.S. acknowledge financial support from the Deutsche Forschungsgemeinschaft (Grant Nos. US-103/1-2 and SCHU-1456/12-1). G.H.B. is grateful for support from the Royal Society via a University Research Fellowship.
76 S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, see http://www.pwscf.org for additional information about the employed ab initio code.