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Evaluation of Density Functional with Account of van der Waals Forces by Use of Experimental H_2 Physisorption Data on Cu(111)

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Detailed experimental data for physisorption potential-energy curves of H_2 on low-indexed faces of Cu challenge theory. Recently, density-functional theory has been developed to also account for nonlocal correlation effects, including van der Waals forces. We show that one functional, denoted vdW-DF2, gives a potential-energy curve promisingly close to the experiment-derived physisorption-energy curve. The comparison also gives indications for further improvements of the functionals.

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Density-functional theory (DFT) gives in principle exact descriptions of stability and structure of electron systems, but in practice approximations have to be made to describe electron exchange and correlation (XC)[1,2]. Approximate XC functionals are commonly evaluated by comparing with results from other accurate theories or by comparing with one or two relevant experimental numbers. This Brief Report illustrates the advantages of a third approach, based on extensive experimental data, in this case a full physisorption potential derived from surface-physics measurements. Conclusions about functional development and physisorption are drawn.

In the physisorption regime, resonant elastic backscattering-diffraction experiments provide detailed quantitative knowledge. Here, data obtained for H_2 and D_2 on Cu surfaces[3–5] are used as a demanding benchmark for the performance of adsorbate potential-energy curves (PECs) calculated with a nonempirical theory for extended systems. Density functionals that aspire to account for nonlocal electron-correlation effects, including van der Waals (vdW) forces, can then be assessed. Calculations with versions of the vdW-DF method[6–9] are here shown to provide a promising description of the physisorption potential for H_2 on the Cu(111) surface, in particular the most recent one, vdW-DF2[9].

Sparse matter is abundant. Dense matter, also abundant, is since long successfully described by DFT. The recent extensions of DFT functionals to regions of low electron density, where the ubiquitous vdW forces are particularly relevant, render DFT useful also for sparse matter. The vdW-DF functional expresses the vdW interactions and correlations in the density $n(\mathbf{r})$ as a truly nonlocal six-dimensional integral[6–9]. Its key ingredients are (i) its origin in the exact adiabatic connection formula[10–12], (ii) an approximate coupling-constant integration, (iii) the use of an approximate dielectric function in a single-pole form, (iv) which is fully nonlocal and satisfies known limits, sum rules, and invariances, and (v) whose pole strength is determined by a sum rule and whose pole position is scaled to give the approximate gradient-corrected electron-gas ground-state energy locally. There are no empirical or fitted parameters, just references to general theoretical criteria.

Like composite molecules, adsorption systems have electrons in separate molecule-like regions, with exponentially decaying tails in between. Then the weakly inhomogeneous electron gas, used in the original vdW-DF method[6–8,13], might not be the most appropriate reference system for the gradient correction[14]. Although promising results have been obtained for a variety of systems, including adsorption[15,16], there is room for improvements. The recent vdW-DF2 functional uses the gradient coefficient of the B88 exchange functional[17] to determine the internal functional [Eq. (12) of Ref. 6] within the nonlocal correlation functional. This is based on application of the large-N asymptote[18,19] on appropriate molecular systems. Using this method, Elliott and Burke[20] have shown from first-principles that the correct exchange gradient coefficient β for an isolated atom (monomer) is essentially identical to the B88 value, which had been previously determined empirically[17]. Thus in the internal functional, vdW-DF2[9] replaces Z_{ab} in that equation with the value implied by the β of B88. This procedure defines the relationship between the kernels of vdW-DF and vdW-DF2 for the nonlocal correlation energy, both being transferable functionals based on physical principles and approximations and without empirical input.

The vdW-DF method also needs to choose an overall exchange functional to account for the exchange part of the interaction energy between, e.g., two monomers. The revPBE[21] exchange functional in the original vdW-DF is good at separations in typical vdW complexes[6–8]. The latter choice can be improved on[22–26]. Recent studies suggest that the PW86 exchange functional[27] most closely approximates Hartree-Fock interaction energies both for atoms[23] and molecules[24]. The vdW-DF2 functional[9] employs the PW86R functional[24], which at lower densities makes the PW86 integral form get even closer to true exchange than the original.

Evaluation of XC functionals with respect to other theoretical results is often done systematically, e.g., by benchmarking with the S22 data set[28–32]. This set contains the results from twenty-two prototypical small molecular duplexes for noncovalent interactions (hydrogen-bonded, dispersion-dominated, and mixed) in molecules and provides PECs at a very accurate level of wave-function methods, in particular the CCSD(T) method[28–32]. However, by necessity, the electron systems in such sets have finite sizes. The original vdW-DF performs well on the S22 dataset, except for hydrogen-bonded duplexes (underbinding by about 15%[9,15]). The vdW-DF2 functional reduces the mean absolute deviations of binding energy and equilibrium separation significantly[9]. PEC shapes away from the equilibrium separation are greatly improved. The long-range part of the vdW interaction, crucial for extended systems, has a weaker attraction in the vdW-DF2, which reduces the error to 8 meV at separations 1 Å away from equilibrium[9].

The ultimate assessment of XC functionals is experimental. The vdW-DF functional gives promising results in applications to a variety of systems[15], in particular for vdW bonded ones. Typical tests concern binding-energy and/or bond-length values that happen to be available. The vdW-DF2 functional has also been successfully applied to some extended systems, like graphene and graphite[9], metal-organic-frameworks systems[33], molecular crystal systems[34], physisorption systems[35,36], liquid water[37] and layered oxides[38]. Those studies also focus on comparison with just a few accessible observations.

The key step taken by the present work is to benchmark a full PEC in an extended system. Fortunately, for almost two decades, accurate experimental values for the eigenenergies of H_2 and D_2 molecules bound to Cu surfaces[3,4] have been waiting for theoretical account and assessment. The rich data bank covers results for the whole shape of the physisorption potential.

The H_2-Cu system is particularly demanding. On one hand, H_2 is a small molecule with a large HOMO-LUMO gap, far from the low-frequency polarization modes assumed in derivation of these functionals[6–9]. On the other hand, Cu is a metal, which has created particular concerns about functional development[39].

Chemically inert atoms and molecules adsorb physically on cold metal surfaces[5], characterized by low desorption temperatures ranging from a few K (He) to tens of K (say Ar and CH_4). Adsorption energies, with values from a few meV to around 100 meV, may be determined from thermal-desorption or isosteric-heat-of-adsorption measurements. For light adsorbates, like He and H_2, gas-surface-scattering experiments, involving resonance structure of the elastic backscattering, provide a more direct and elegant method, with accurate and detailed measurements of bound-level sequences in the potential well. The availability of isotopes with widely different masses (^{3}He, ^{4}He, H_2, D_2) permits a unique assignment of the levels, a determination of the well depth, and ultimately a qualified test of model potentials[40].

TABLE I: Sequences of bound-state energies for H_2 and D_2 on Cu(111). DFT eigenvalues are calculated with the vdW-DF2 potential of Fig. 1. Experimental numbers are from[3,4].

n	ϵ_n [meV]			
	H_2		D_2	
	DFT	Exper.	DFT	Exper.
0	−32.6	−23.9	−34.4	
1	−21.3	−15.5	−26.0	−19.0
2	−12.1	−8.7	−18.7	−12.9
3	−5.4	−5.0	−12.4	−8.9
4			−7.4	−5.6
5			−3.5	−3.3

The bound-level sequences from Ref. 4 (Table I) were obtained using nozzle beams of para-H_2 and normal-D_2, i.e., beams predominantly composed of $j = 0$ molecules. Thus the listed measured bound-state energies, ϵ_n, for H_2 and D_2 on Cu(111), refer to an isotropic distribution of the molecular orientation. All ϵ_n values fall accurately on a common curve when plotted versus the mass-reduced level number $\eta = (n + 1/2)/\sqrt{m}$. This implies a level assignment that is compatible with a single gas-surface potential for the two hydrogen isotopes[4]. A third-order polynomial fit to the data yields for $\eta = 0$ a potential-well depth $D = 29.5$ meV.

Analysis of the experimental energy levels in the H_2-Cu(111) PEC (Table I) within the traditional theoretical picture of the interaction between inert adsorbates and metal surfaces[41,42] gives the physisorption-energy curve of Fig. 1[3–5]. The PEC is then approximated as a superposition of a long-range vdW attraction, $V_{\rm vdW}$, and a short-range Pauli repulsion, V_R[5,41]. This results in a laterally and angularly averaged potential $V_o(z) = V_R(z) + V_{\rm vdW}(z)$, where z is the normal distance of the H_2 bond center from the jellium edge. The bound-level sequences in Table I can be accurately reproduced (< 0.3 meV) by such a PEC[3,5] (Fig. 1), having a well depth of 28.9 meV and a potential minimum located 3.52 Å outside the topmost layer of copper ion cores. From the measured intensities of the first-order diffraction beams, a very small lateral variation of the H_2-Cu(111) potential can be deduced, ~ 0.5 meV at the potential-well minimum.

A direct solution of the Schrödinger equation in $V_o(z)$ reproduces the four low-energy eigenvalues to within 3% of the measured ones. It is therefore consistent[43] to benchmark with the very accurately constructed experimental physisorption curve in Fig. 1.

Figure 1 shows our comparison of density-functional PECs against the experimental physisorption potential

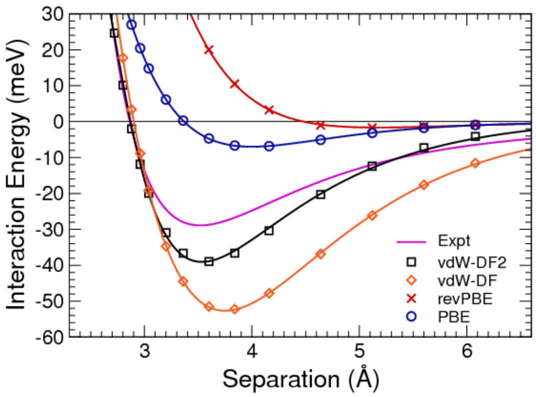

FIG. 1: Experimentally determined effective physisorption potential for H_2 on Cu(111)[3], compared with potential-energy curves for H_2 on Cu(111), calculated for the atop site in GGA-revPBE, GGA-PBE, vdW-DF2, and vdW-DF.

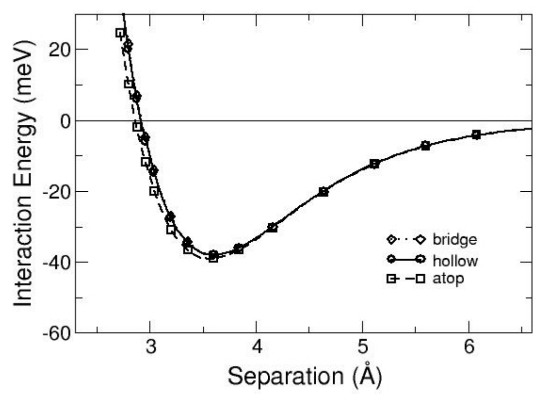

FIG. 2: Interaction potential for H_2 on Cu(111), calculated self-consistently with the vdW-DF2 functional[9] in the bridge, hollow and atop sites.

for H_2 on Cu(111). The calculations refer to H_2 adsorbed on an atop site with the molecular axis parallel to the surface plane and oriented along the ⟨100⟩ direction in this plane. The orientational dependence of the potential is known from experimental data[3] and the experimental potential, which corresponds to an isotropic distribution of the molecular orientation, will for this reason be $\sim$ 1 meV deeper than the potential calculated for the geometry specified above. Figure 1 shows PECs from vdW-DF[6] and vdW-DF2 functionals[9] as well as with two generalized-gradient approximations (GGA-PBE and GGA-revPBE). We use an efficient vdW algorithm[44] adapted from SIESTA's[45] vdW code within a modified version of the plane-wave code ABINIT[46]. The vdW interaction is treated fully self-consistently[8] (allowing also vdW forces to relax the adsorption geometry). The computational costs are the same with vdW-DF and vdW-DF2. Our choice of Troullier-Martins-type norm-conserving pseudopotentials and a high cutoff energy (70 Ry) ensures excellent convergence. We stress that there is neither a damping nor saturation function put into the vdW-DF and vdW-DF2 calculations.

The need for an account of nonlocal correlations for the description of vdW forces is illustrated by the GGA curves giving inadequate PECs. The calculated well depth in vdW-DF, 53 meV, should be compared with the measured one, 29.5 meV[4], and the one calculated from $V_o(z)$, suitably parametrized, 28.9 meV[3] (Fig. 1). We find that the vdW-DF2 PEC lies close to the experimental physisorption potential, both at the equilibrium position and at separations further away from the surface.

Calculated PECs of H_2 above bridge, atop, and hollow sites on the Cu(111) surface are shown in Fig. 2, their closeness illustrating the lack of corrugation on this surface. The experimental[3,4] and theoretical values for the corrugation roughly agree within a factor of two. The vdW-DF2 equilibrium separation is about 3.5 Å, like the value deduced from experiment (see above)[3,4].

A further refined comparison is provided by the bound-state eigenvalues for the oscillation of the hydrogen molecule in the H_2-Cu(111) physisorption-potential well (Table I). In addition to PEC shapes and eigenenergy values, there should be comparison with values for well depth and equilibrium separation, experimental ones being (29.5 meV; 3.5 Å) and those of the vdW-DF2 potential in Fig. 1 (37 meV; 3.5 Å). To place a proper perspective on the comparison we emphasize that (i) vdW-DF2 is a first-principles method, where characteristic electron energies are typically in the eV range, and (ii) the test system and results are very demanding, as other popular methods deviate significantly more from the experimental curve (for instance, application of the DFT-D3(PBE) method[47], with atom-pairwise specific dispersion coefficients and cutoff radii computed from first principles, gives (88 meV; 2.8 Å) for the PEC well depth and separation). We therefore judge that the vdW-DF2 description of well depth and equilibrium separation as very promising, and so is the relative closeness of experimental and calculated eigenenergy values in Table I.

The used benchmark shows both virtues and vices of the vdW-DF method. In the comparison with the experimental physisorption potential (Fig. 1) several qualitative similarities are found for both the vdW-DF and the vdW-DF2 functionals. The vdW-DF2 functional gives PECs in a useful qualitative and quantitative agreement with the experimental PEC, i.e., with respect to well depth, equilibrium separation, and curvature of PEC near the well bottom, and thus zero-point vibration frequency. This is very promising for applications of this nonlocal correlation functional at short and intermediate separations, relevant for the adsorption. However, the well-known small value of the vdW coefficient given by vdW-DF2[9] is seen at large separation. The discrepancies between the eigenvalues signal that the vdW-DF2 PEC might not have the right shape for H_2 on Cu(111). This is in certain contrast to the shape results of the S22 data-set[9] benchmarking. Certainly, the metallic nature of the H_2/Cu(111) system is particularly demanding for important details of the electrodynamical response. This makes the H_2/Cu(111) physisorption data challenging for electron-structure calculations, as illustrated by the mentioned DFT-D3(PBE) result.

Results, like small corrugation, binding energy, and vibrational frequency normal to the surface, in a fair agreement with experimental data show that the vdW-DF2 functional accounts for the extended nature of the surface-electron structure. However, the approximate functional cannot represent all details. The accuracy of the experimental data is high enough to stimulate a more detailed analysis of all aspects of the theoretical description. This should be valuable for the further XC-functional development.

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traction at atomic-scale separations. The function $f(z)$ lacks a rigorous prescription and this results in a level of arbitrariness to $V_{\rm vdW}(z)$. It should be noted, though, that the saturation function $f(z)$ of Refs. 3–5,42 has a formal resemblance to the damping functions introduced to adjust for double counting in semi-empirical DFT descriptions[47] of dispersive interactions. We emphasize that $f(z)$ of $V_{\rm vdW}(z)$ is likely to work across several length scales[48] because $V_{\rm vdW}(z)$ includes the effects of image planes and is consistent with the Zaremba-Kohn formulation of physisorption[41].

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