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Comment

Comment on "On the Physisorption of Water on Graphene: Sub-Chemical Accuracy from Many-Body Electronic Structure Methods"

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Comment on the Use of Finite Cluster Models in the Calculation of the Water-Graphene Binding Energy[1]

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[1]The authors of "On the Physisorption of Water on Graphene: Sub-Chemical Accuracy from Many-Body Electronic Structure Methods" (Vol. 10, iss:3 pp:358-36) agree with this comment of their work and are in agreement with the conclusions of the Comment

1.

Recent experimental work has shown that the assumed hydrophobicity of graphitic surfaces is the result of hydrocarbon contaminants and that clean graphitic surfaces are actually mildly hydrophilic.[1-4] The widespread results for the contact angle of water on the surface obtained from simulations using force field methods[5-19] has provoked studies of the water-graphene interaction potential using electronic structure calculations.[19-32] These studies can be divided into two classes, namely, those carried out on the "infinite" system using a supercell replicated through periodic boundary conditions and those involving a sequence of H_2O-$\left(C_{6n^2}H_{6n}\right)$ cluster models followed by extrapolation to the graphene limit. Due to the challenges of accurately describing the various contributions to the binding energy and in properly extrapolating long-range interactions, these calculations have resulted in a considerable spread in the values of the binding energy.

Recently, Brandenburg and co-workers[33] reported the results of periodic coupled cluster singles and doubles with perturbative triples [CCSD(T)],[34] random phase approximation[35] with GW[36] singles excitations (RPA + GWSE)[37], and fixed-node diffusion Monte Carlo (DMC)[38] calculations on the water graphene system. These calculations are the most ambitious carried out to date on this system. The DMC and RPA+GWSE calculations gave, respectively, binding energies of -99(6) and -98 meV for the most stable structure with the two H atoms of the water molecule pointing toward the surface, while the CCSD(T) calculations gave a binding energy of -87 meV. Given the various approximations involved in the CCSD(T) calculations, we consider the DMC and RPA+GWSE calculations to be more accurate and the "true" binding energy of a water molecule on the graphene surface to be -98±10 meV.

Other recent theoretical studies using cluster models combined with extrapolation to the water-graphene limit obtained values of the binding energy of -120 to -140 meV,[21-26] significantly

larger than the results of Brandenburg et al.. This disparity led these authors to conclude that extrapolation of the results of calculations of a water molecule interacting with a series of polyaromatic hydrocarbons does not lead to an accurate value of the water-graphene binding energy. We show here that such an approach yields a binding energy in close agreement with the results of Brandenburg et al. provided that one properly accounts for long-range electrostatics.

In a study from one of our groups, hereafter referred to as JKJ, density functional theory based symmetry-adapted perturbation theory (DFT-SAPT)[39-43] was used to calculate the binding energies of a water molecule interacting benzene, coronene, hexabenzocoronene, and circumcoronene sequence of molecules.[22] For weakly interacting molecules, DFT-SAPT calculations generally give interaction energies very close to large basis set CCSD(T) calculations. Moreover, the SAPT procedure provides a dissection of the net interaction energy into different physical contributions. This dissection, when applied to water interacting with the above polyaromatic molecules, revealed that the exchange and induction contributions are well converged at the water-hexabenzocoronene cluster, but that the electrostatic and dispersion interactions are not well converged at this cluster size. JKJ also decomposed the electrostatics contribution to the binding energy into a short-range term due to charge penetration and a longer-ranged contribution due to interactions between atomic multipoles of the two molecules. The former is already well converged at water-coronene.

JKJ estimated the long-range dispersion and electrostatics contributions to the water-graphene system using a H_2O-C_{216} cluster model, with the dispersion contributions being described by a sum over C_6^{ij}/R_{ij}^6 terms and the long-range electrostatic interaction being described using a point-charge model[44] for water and the Q_{20} component of the atomic quadrupole on the C atoms, with the value of Q_{20} chosen to be that of the central C atoms of circumcoronene as calculated

using a distributed multiple analysis[45] of the MP2[46] charge density. The results for the long-range dispersion and electrostatics contributions, -28 and -3 meV, respectively, were combined with the DFT-SAPT results for water-circumcoronene to obtain a value of -124 meV for the water-graphene binding energy. This value is significantly larger than that obtained by Brandenburg et al., seemingly supporting their conclusion of the inadequacy of extrapolating the results on small clusters to estimate the water-graphene binding energy.

In a recent paper, one of us revisited the calculation of long-range electrostatics interactions in the water-graphene system,[32] evaluating the multipole interaction energy using permanent moments of up to rank $\ell = 5$ on all atoms and a periodic lattice for the graphene surface together with Ewald summation. This calculation gave a value of -0.01 meV for the interaction between the multipoles of water and graphene as opposed to the -28 meV value obtained by JKJ in a more approximate treatment. When this result is combined with the other contributions from the DFT-SAPT calculations, a net binding energy of -96 meV, in excellent agreement with the result of Brandenburg, et al., is obtained (see Table 1). Thus, we conclude that a DFT-SAPT calculations on finite cluster models combined with a careful treatment of long-range multipole interactions, in fact, gives a quantitatively accurate value of the water-graphene binding energy. This is an important finding since DFT-SAPT calculations on the finite cluster models it is far less computational demanding than periodic DMC calculations with very small statistical errors or periodic RPA + GWSE calculations, especially considering the additional calculations needed to correct for finite size effects.

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Table 1. Interaction energy (meV) of the water-graphene dimer. The multipole electrostatics contribution obtained using Ewald summation.[32] Other contributions are taken from the SAPT-DFT calculations on the water-circumcoronene cluster.[22]

E_{elst}^{mult}	E_{elst}^{cp}	E_{exch}	E_{ind}	E_{disp}	E_{int}
-28.2[a]	-26.9	123.6	-33.0	-160.0	-124.4
-0.0[b]					-96.3

(E_{elst}^{mult} and E_{elst}^{cp}: multipole and charge-penetration contributions to the electrostatic interaction, E_{exch}: first-order exchange, $E_{ind} = E_{ind}^{(2)}+E_{exch-ind}^{(2)}+\delta$(HF), $E_{disp} = E_{disp}^{(2)}+E_{exch-disp}^{(2)}$, E_{int}: total interaction energy)

[a] Ref. 22: rank $\ell \leq 2$ moments, assessment for water-C_{216} cluster model

[b] Ref. 32: rank $\ell \leq 5$ moments, Ewald summation

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