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2. Project Title: Toward chemical accuracy for the description of the catalytic desulfurization process
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The goal of the project

The aim of this project is to provide a deep quantitative understanding of weak interactions relevant to the catalytic desulfurization process. Our current work is split between *benchmarking high-level theories* based on the random-phase approximation (RPA) and improving the *quantitative accuracy and universal applicability* of current van der Waals approximations such as SCAN+rVV10, putting equal weight on both the short and long-range components of the correlation.

Benchmark surface energies within Renormalized Random Phase Approximation: This work is an extension of the research that we have started in the last year. The relevance of the project is justified by the fact that all of the interactions related to the adsorption of an organic compound are occurring on metal or semiconducting surfaces. When the adsorption energy is computed, one has to rely on the clean surface energy as a contribution to the adsorption energy. In my research group we continue applying RPA to benchmark surface energies. Over the past months we have obtained surface energies of transition metals for all crystal faces.

Recently we have become aware of several factors that require further attention in our current research. A recent publication by Schmidt and Thygesen produces a discrepancy against our results, showing an underestimation of surface energies against our overestimated RPA results. The discrepancy can be traced back to the different k-meshes, energy cutoffs and vacuum region utilized in the RPA calculations. The parameters disclosed in the publication lead to underestimated surface energies by the infinite-order RPA without the kernel correction. Benchmark surface energies within RPA are scarce. On the other hand, earlier results for the jellium surface show an overestimation with the correlation component of RPA in accord with high-level DMC and ISTLS methods. The overestimation is also in accord with our results. This observation led us to do additional convergence tests regarding the applied vacuum and energy cutoffs.

Parallel to this work, we are extending our methodology to range-separated RPA. The range-separation concept in RPA was demonstrated to drastically speed up the calculations without loss of accuracy for bulk silicon. Beside the speed-up, there is another factor to be considered for the surface energies. Within density functional theory, a short-range exchange and correlation balance each other and deliver more accurate results. The standard infinite-order RPA without any kernel is constructed out of exact exchange and a long-range correlation. Kernel corrections provide more screening for the short-range and improve the balance between the exact exchange and correlation. In the range-separation scheme only the long-range component of RPA is kept, while the short-range correlation is switched to a semilocal correlation. Physically the range-separation scheme is analogous to the kernel corrections to the short-range. In addition, it can indicate how much the exact exchange balances short and long-range correlation for surfaces.

As a conclusion, our primary goal is to overcome the convergence discrepancy regarding the surface energies with infinite-order RPA, and prepare our publication with RPA and kernel-corrected RPA for transition metal surface energies.

Adsorption of organic molecules on metallic and semiconducting surfaces: The recent and computationally efficient rVV10 correlation functional for long-range van der Waals interactions has been combined with the SCAN meta-GGA and has been successfully applied to adsorption energies. Although SCAN+rVV10 delivers a generally reasonable description for various properties, it gives a disappointing treatment for some others. As a continuation of the work that we have started in the previous grant period, we are testing the SCAN and SCAN+rVV10 approximations on the adsorption of organic compound to metallic surfaces. In our assessment we are using thiophene as a representative example of aromatic compounds. We have found that, unlike for the benzene molecule, SCAN+rVV10 yields an overestimation of the adsorption energy of thiophene on coinage metal surfaces.

Our approach to improve SCAN+rVV10 is systematic. First we are utilizing a modification of the original SCAN approximation called revSCAN with more of second-order density gradient contribution to the correlation energy. A purely second-order correlation and some slight modification in the exchange component simultaneously can ensure less overbinding in SCAN+rVV10. The pure second-order behavior can be restored by removing a certain fourth-order contribution in the correlation energy. The change in the functional form requires a refitted cutoff parameter in rVV10.

The adsorption of thiophene on (111), (110) and (100) surfaces of coinage metals has been explored using SCAN, SCAN+rVV10, SCAN+D3 and revSCAN approximations. The "D3" indicates the inclusion of the "three-body" terms in the van der Waals interaction. The fitting of the rVV10 functional to revSCAN has been completed, and the cutoff parameter is determined. Our natural next step will be to include the adsorption energies with revSCAN+rVV10 in our assessment. Beside the adsorption energies we have considered all possible adsorption sites on the metal. We have found that thiophene slightly favors the rotated 45° adsorption site, however the adsorption was found stable on other sites as well. With the revSCAN+rVV10 results included, the publication is close to being prepared.

We are also investigating whether the overestimation of SCAN+rVV10 could arise from a "density-driven-error" of the semilocal SCAN itself. To test this idea, we are currently evaluating the SCAN+rVV10 energy on a self-interaction-free density from SCAN+U approximation with the empirically determined U parameter.

Figure 1. The bulk lattice constants (in Ångströms) of transition metals with SCAN, revSCAN and SCAN+rVV10. Experimental results are shown as benchmark. The lattice constant with revSCAN are larger than SCAN as an indicator that adding van der Waals interactions in rVV10 could produce a shrinking and more accuracy in the lattice constants.

Functionals Metals	SCAN	revSCAN	SCAN+rVV10	Expt.
Copper	3.56	3.57	3.54	3.62
Gold	4.09	4.11	4.07	4.07
Silver	4.08	4.11	4.06	4.08

Figure 2. The adsorption energies (in eVolts) of thiophene on the (111) crystal face of coinage metals. The revSCAN method underestimates the binding energy compared to SCAN and SCAN+rVV10 as an indication that adding the rVV10 approximation can reduce the overestimation of the SCAN+rVV10 approach.

Surface	SCAN	revSCAN	SCAN+rVV10	Experimental
Cu (111)	-0.41	-0.34	-0.74	-0.4
Ag (111)	-0.36	-0.31	-0.69	-0.52
Au (111)	-0.39	-0.32	-0.75	-0.68

<u>Impact of the research on my career and that of the students</u>

This project has largely helped me to understand the role of many-electron effects that control structures. Our first project on RPA gives me a further insight in: 1; how accurate the infinite-order RPA can be, 2; how do the kernel corrections perform for surfaces compared to bulk solids.

Our second project for the thiophene adsorption proposes a new route to balance short and long-range correlation effects for a universally applicable method for weak interactions between adsorbed compounds and surface, with chemical accuracy. This work also has provided me a better understanding how much many-body effects are relevant in this problem on the scale of the distance between interacting electrons, and to what extent the contribution of many-body interactions can be replaced by an improved semilocal approximation.

The research has involved a graduate student. The overarching research has provided an education in state-of the art electronic structure theory from semilocal to nonlocal approximations for the student. The student has gained information about the density functional theory with a focus on van der Waals interactions and meta-GGA approximations. The student has obtained extensive practice with the VASP code.

In addition, this project provided a specific research project for an undergraduate researcher in Fall 2017. This project introduced the student to the basic concepts and techniques of electronic structure calculations.