Ab initio surface chemistry from coupled cluster theory

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In this talk, I will present our recent work on the systematic application of coupled cluster with singles, doubles, and perturbative triples [CCSD(T)] to address chemical problems on solid surfaces. First-principles calculations are a cornerstone of modern surface science, but the limitations of density functional theory (DFT) with commonly used exchange-correlation functionals have been extensively documented. As the "gold standard" method of molecular quantum chemistry, CCSD(T) has been desired for surface science for decades, but its general applicability has been limited by the high computational cost due to the large number of atoms. To bridge the gap, I have developed a linear-scaling local CCSD(T) with periodic boundary conditions that extends the local natural orbital (LNO) theory, originally developed by Kállay *et al*. for molecules, to materials [1,2]. Facilitated by recent developments in periodic integrals evaluation [3–5] and correlated Gaussian basis sets [6], our LNO-CCSD(T) allows determining within chemical accuracy the potential energy surfaces for surface systems of about 100 atoms in both the thermodynamic limit and the complete basis set limit.

To demonstrate the significance of employing high-level theories in surface science, I will present results of applying correlated methods up to CCSD(T) to two surface problems [1,2]. The first problem stems from studying the binding curve and vibrational spectrum of CO molecules on the surface of MgO, and the second problem from investigating the dissociation of water molecules on the surface of Al_2O_3 and TiO_2, two prototypical and industrially important metal oxides. In both cases, the lack of quantitative accuracy by DFT, exacerbated by the sensitivity to different DFT protocols, hampers a satisfactory comparison with experiments. I will show how correlated wavefunction theory systematically improves accuracy for these surface systems by refining the treatment of electron correlation, mirroring the well-established trends in molecular quantum chemistry. In particular, CCSD(T) demonstrates exceptional predictive power by predicting the vibrational frequency shift of CO on MgO in excellent agreement with IR experiments within a few wavenumbers and the barrier heights of water dissociation on Al_2O_3 and TiO_2 within chemical accuracy. In the latter case, CCSD(T) completely alters the classical picture of fast water dissociation on defect-free Al_2O_3 surfaces established by DFT 25 years ago and helps explain recent low-temperature experiments.

[1] **H.-Z. Ye** and T. C. Berkelbach, *arXiv:2309.14651*
[2] **H.-Z. Ye** and T. C. Berkelbach, *arXiv:2309.14640*
[3] **H.-Z. Ye** and T. C. Berkelbach, *J. Chem. Phys.* **154**, 131104 (2021)
[4] **H.-Z. Ye** and T. C. Berkelbach, *J. Chem. Phys.* **155**, 124106 (2021)
[5] S. J. Bintrim, T. C. Berkelbach, and **H.-Z. Ye**, *J. Chem. Theory Comput.* **18**, 5374 (2022)
[6] **H.-Z. Ye** and T. C. Berkelbach, *J. Chem. Theory Comput.* **18**, 1595 (2022)