Some considerations on vibrational bound states at metallic surfaces

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In this contribution, I will talk about the characterization of vibrational states of small molecules adsorbed on metallic surfaces. I will first address the problem of determining dynamics-friendly potential energy surfaces using approaches such as the corrugation reduction procedure and global analytical force fields [1-3]. I will then discuss how we can compute the vibrational bound states of the adsorbates using iterative eigensolvers based on the Lanczos algorithm [4-6]. A particular emphasis will be put on the choice of the basis representation, as well as the use of symmetry projectors, spectral transformations, and polynomial acceleration techniques. If time permits, I will present how we can compute intermode relaxation between these high-dimensional vibrational states using a perturbative treatment of non-adiabatic coupling to the electrons of the metal substrate [7-9].

References

[1] R. Marquardt, F. Cuvelier, R. A. Olsen, E. J. Baerends, J.C. Tremblay and P. Saalfrank
"A new analytical potential energy surface for the adsorption system CO/Cu(100)" *J. Chem. Phys.* **132**, 074108 (2010).

[2] G. Füchsel, J.C. Tremblay, and P. Saalfrank
"A six-dimensional potential energy surface for Ru(0001)(2×2):CO", *J. Chem. Phys.* **141**, 094704 (2014)

[3] T. Serwatka, B. Paulus, and J.C. Tremblay
"A new global six-dimensional potential energy surface for NO on gold(111)" *submitted* (2018).

[4] J.C. Tremblay and T. Carrington Jr.
"Calculating vibrational energies and wave functions of vinylidene using a contracted basis with a locally reorthogonalized coupled two-term Lanczos eigensolver", *J. Chem. Phys.* **125**, 094311 (2006).

[5] G. Füchsel, J.C. Tremblay, T. Klamroth, and P. Saalfrank "Quantum dynamical simulations of the femtosecond laser induced ultrafast desorption of H_2 and D_2 from Ru(0001)" *ChemPhysChem* **14**, 1471 (2013).

[6] J.C. Tremblay, G. Füchsel, and P. Saalfrank
"Excitation, Relaxation, and Quantum Diffusion of CO on Copper", *Phys. Rev. B* **86**, 045438 (2012).

[7] J.C. Tremblay and P. Saalfrank
"Selective subsurface absorption of hydrogen in palladium using laser distillation", *J. Chem. Phys.* **131**, 084716 (2009).

[8] J.C. Tremblay, S. Monturet, and P. Saalfrank
"Electronic Damping of Adsorbate Vibrations at Metallic Surfaces", *Phys. Rev. B* **81**, 125408 (2010).

[9] J.C. Tremblay
"A unifying model for non-adiabatic coupling at metallic surfaces beyond the local harmonic approximation: from vibrational relaxation to scanning tunneling microscopy", *J. Chem. Phys.* **138**, 244106 (2013).