

Electronic excitations and energy dissipation of atoms and molecules approaching metallic surfaces

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Basic understanding of the complex physical and chemical processes that take place at the interface between gas and solids is essential to advance in the mastering and optimization of many technologies and industrial applications. Surfaces are collectors of energy via reception of electromagnetic radiation, heat, and chemical energy. Surface modification can transform the functionality of a system and thus its use. Surfaces can be active agents for atoms and molecules and help to break and create chemical bonds. Although first-principles calculations have very much helped to advance in the quantitative study of static properties, visualizing the time evolution of surface processes at the atomic and molecular level is still a tough task. The adiabatic approximation, in which electronic dissipative effects are neglected, describes reasonably well the dynamics of some of these processes. However, atoms and molecules can generate low energy electronic excitations in metal surfaces even at thermal energies. Therefore, dynamical simulations of these systems should in principle incorporate electronic non-adiabatic effects, in order to analyze how they can affect the outcome of gas-surface reactions.

Quite often, the effect of low-energy electron-hole pair excitations can be included in the theoretical description of the dynamics through an electronic friction coefficient [1]. A widely used model to calculate this friction coefficient is the local density friction approximation (LDFA) [2], which can be directly applied to perform ab initio molecular dynamics with electronic friction (AIMDEF). In this talk, I will provide the theoretical basis of the LDFA and show how it can be applied to improve over adiabatic results based on first-principles calculations. The accuracy of the LDFA approximation will be also tested by comparing its predictions with those of a non-perturbative method, namely time-dependent density functional theory (TDDFT). A jellium cluster will be used as a model system for this purpose [3]. A detailed comparison of the LDFA results and the TDDFT results at the cluster surface, a region in which the electronic density is rapidly varying, shows that a local friction approximation provides a satisfactory enough description of the force linked to the excitation of electron-hole pairs. Thus, the LDFA can be described as an efficient framework to calculate the friction coefficient introduced in multidimensional molecular dynamics simulations.

References

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