``Seeing'' the covalent bond: Simulating Atomic Force Microscopy Images

James R. Chelikowsky

Center for Computational Materials, Institute of Computational Engineering and Sciences, and the Departments of Physics and Chemical Engineering, University of Texas at Austin, Austin, Texas 78712 USA.

Advances in atomic force microscopy (AFM) have made it possible to achieve unprecedented images of covalent bonds, in some cases even to resolve the bond order in polycyclic aromatics. However, fundamental questions remain about interpreting the images and modeling the AFM tip. For example, the bright spots in non-contact AFM images can have a close correspondence to the atomic structure of a given specimen, but there can be contrast changes with tip height that cannot be interpreted directly by atomic positions. While the nature of the tip can be crucial in understanding the details of the image, the atomic structure of the tip is often unknown. This situation is compounded by the difficulty in simulating AFM images. In order to perform computational studies of AFM, one must determine the interatomic forces as a function of the tip height on a fine grid above the specimen.

I will present an efficient first-principles method [1] for simulating noncontact atomic force microscopy (nc-AFM) images using a “frozen density” embedding theory. Frozen density embedding theory enables one to efficiently compute the tip–sample interaction by considering a sample as a frozen external field. This method reduces the extensive computational load of first-principles AFM simulations by avoiding consideration of the entire tip–sample system and focusing on the tip alone. I will demonstrate that our simulation with frozen density embedding theory accurately reproduces full density functional theory simulations of freestanding hydrocarbon molecules while the computational time is significantly reduced. Our method also captures the electronic effect of a Cu(111) substrate on the AFM image of pentacene and reproduces the experimental AFM image of Cu_2N on a Cu(100) surface. This approach is applicable for theoretical imaging applications on large molecules, two-dimensional materials, and materials surfaces.

[1] Y. Sakai, A.J. Lee and J.R. Chelikowsky, Nano Lett. 16, 3242 (2016)

Email: jrc@utexas.edu