

Computational Spectroscopy and Theory of Molecular Pseudopotentials: Two Applications of Wannier Functions

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The methodology of *ab initio* molecular dynamics, wherein finite-temperature dynamical trajectories are generated using forces computed “on the fly” from electronic structure calculations, allows chemical bond breaking and forming events to be treated explicitly within a dynamical simulation. Direct access to the electronic structure also allows spectroscopic observables, such as the IR spectrum, to be determined in a relatively straightforward manner. *Ab initio* molecular dynamics has benefited substantially from its combination with maximally localized Wannier functions. The latter exploit the unitary invariance of the total energy to generate spatially localized electronic orbitals. Recently, we showed how ideas from quantum field theory can be used to reformulate the Car-Parrinello equations of motion such that these orbitals are preserved during an *ab initio* molecular dynamics calculation [1,2]. In this talk, these methods will be briefly reviewed. It will then be shown how Wannier functions can be used to compute both IR spectra and IR difference spectra with considerable efficiency. Next, the problem of QM/MM simulations will be considered, and it will be shown how Wannier functions can be used as the basis of a new theory of molecular pseudopotentials for use in such simulations. Finally, a new localized basis set approach [3,4,5,6] will be described, which, when combined with Wannier functions, could lead to a new linear-scaling approach.

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