

Extended Space Car-Parrinello Molecular Dynamics

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The first-principles molecular-dynamics approach of Car and Parrinello [1] (CP) is extended to include simultaneous “on-the-fly” evolution of occupied and unoccupied electronic states. The CP scheme is reformulated in the context of finite-temperature ensemble density-functional theory [2]; occupation numbers and unitary rotations among all states are introduced as additional variables. The evolution of these additional degrees of freedom can be governed by second-order equations of motion, in the same spirit of the original CP algorithm, or by self-consistent optimization. Both approaches will be discussed; the latter one is to be preferred in general applications. The resulting equations of motion allow for an entire space spanned by states with different fractional occupations to follow adiabatically the nuclear trajectories. This allows to treat, among others, systems where the total spin changes along a reaction pathway, where the total number of electrons fluctuates in grand-canonical equilibrium, or where the electrons have a finite-temperature distribution. Some applications to molecular reactions and to the chemisorption of small molecules on metal surfaces will be discussed.

[1] R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

[2] N. Marzari, D. Vanderbilt, and M. C. Payne, *Phys. Rev. Lett.* **79**, 1337 (1997).