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Implementation of surface hopping molecular dynamics using semiempirical methods

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Abstract

A molecular dynamics driver and surface hopping algorithm for nonadiabatic dynamics has been implemented in a development version of the MNDO semiempirical electronic structure package. The required energies, gradients and nonadiabatic couplings are efficiently evaluated on the fly using semiempirical configuration interaction methods. The choice of algorithms for the time evolution of the nuclear motion and quantum amplitudes is discussed, and different schemes for the computation of nonadiabatic couplings are analysed. The importance of molecular orbital tracking and electronic state following is underlined in the context of configuration interaction calculations. The method is applied to three case studies (ethylene, methaniminium ion, and methanimine) using the orthogonalization corrected OM2 Hamiltonian. In all three cases decay times and dynamics paths similar to high-level ab initio results are obtained.

Keywords: Surface hopping; Molecular dynamics; Potential-energy surfaces; Conical intersections; Nonadiabatic coupling terms; Semiempirical methods

1. Introduction

Molecular dynamics (MD) [1–3] is widely used for the study of equilibrium and non-equilibrium properties in physics [4,5], chemistry [6–8] and biochemistry [7,9–12]. MD simulations usually rely on the Born–Oppenheimer approximation [13], which decouples electronic and nuclear motions. The nuclei move on a single potential energy surface (PES) associated with a single electronic state which is obtained from the solution of the time-independent Schrödinger equation for a series of fixed nuclear geometries. Nuclear motion is usually described by classical equations.

The Born–Oppenheimer approximation is excellent when energy separations are large and the system is well described by a single quantum state. However, when the energy separation of different PESs becomes comparable with the magnitude of the nonadiabatic coupling (typically in the proximity of conical intersections), the Born–Oppenheimer approximation breaks down and nonadiabatic effects must be explicitly taken into account. The incorporation of nonadiabatic effects in MD is essential for describing a wide range of phenomena including photochemistry, radiationless relaxation and charge transfer reactions.

A great number of methods have been developed for the treatment of nonadiabatic effects in MD [14–44]. Among these one of the most popular is the surface hopping method of Tully [15,16,20,31,45], where the nuclei evolve on a single PES and nonadiabatic effects are included by allowing hopping from one PES to another according to the weight of the respective electronic state. This approach gives an efficient description of nonadiabatic effects, is asymptotically correct in regions of large energy separation, includes classical-quantum correlation and with a proper choice of the switching criterion guarantees microscopic reversibility [20]. On the other hand the results are not independent of the representation used for the electronic states (adiabatic or diabatic), ambiguities may arise over the choice of possible switching criteria and the total

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energy is not automatically conserved (an external constraint is needed to fix the total energy in the event of hopping). Nevertheless, surface hopping generally performs very well for molecular applications [46–49] and has therefore been widely used for the study of nonadiabatic dynamics.

In this paper, we present our implementation of the surface hopping approach in a development version of the semiempirical MNDO package [50] and a detailed analysis of technical aspects of the method. We apply the surface hopping method to three case studies using the orthogonalization corrected OM2 Hamiltonian [51,52] for the description of the PESs and show that this approach yields results comparable to ab initio methods for nonadiabatic dynamics. Section 2 describes the theory of the surface hopping method, including the fewest switches algorithm for determining when hops occur and the velocity adjustments required to maintain energy conservation. In Section 3 we discuss the implementation of the algorithm and the molecular dynamics driver used for calculating surface hopping trajectories. The implementation is applied to ethylene, the methaniminium ion and methanimine in Section 4 and conclusions are presented in Section 5.

2. Theory

The surface hopping method employs an independent trajectory approximation. A swarm of trajectories is considered, each one evolving on a single potential energy surface. At each MD timestep there is a probability that a trajectory propagating on one potential energy surface will hop to another surface. This probability is controlled by a stochastic switching algorithm, which must be designed in such a way to guarantee that at any time the fraction of all trajectories in a certain electronic state is, at least approximately, equal to the quantum population of the state.

In the surface hopping method nuclei are assumed to move along a classical trajectory $\vec{R}(t)$. The Hamiltonian describing the electron motion is

$$H(\vec{r},\vec{R}) = -\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla^2_{\vec{r}_\alpha} + V_{rR}(\vec{r},\vec{R}), \tag{1}$$

where α labels electronic degrees of freedom and V_{rR} includes nuclear-electron and electron-electron potentials. Hamiltonian (1) is time dependent through $\vec{R}(t)$. The electronic system is described by the wave function $\Phi(\vec{r},\vec{R},t)$, which is the solution of the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Phi(\vec{r},\vec{R},t)}{\partial t} = H\Phi(\vec{r},\vec{R},t). \tag{2}$$

The electronic wave function can be expanded in a basis of known orthogonal wave functions $\phi_i(\vec{r},\vec{R})$

$$\Phi(\vec{r},\vec{R},t) = \sum_i c_i(t)\phi_i(\vec{r},\vec{R}), \tag{3}$$

where $c_i(t)$ are complex-valued expansion coefficients. A common choice for the expansion is the adiabatic representation, i.e. the basis functions are solutions of the time-independent electronic Schrödinger equation

$$\left[-\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla^2_{\vec{r}_\alpha} + V_{rR}(\vec{r},\vec{R})\right]\phi_i(\vec{r},\vec{R}) = \epsilon_i\phi_i(\vec{r},\vec{R}). \tag{4}$$

Substitution of Eq. (3) into the Schrödinger equation (2), multiplication on the left by $\phi_j^*(\vec{r},\vec{R})$ and integration over $\vec{r}$ yields

$$i\hbar\frac{\mathrm{d}c_j(t)}{\mathrm{d}t} = \sum_i c_i(t)[H_{ji} - i\hbar\dot{\vec{R}}\cdot\vec{d}_{ji}], \tag{5}$$

where H_{ji} and $\vec{d}_{ji}$ are

$$H_{ji}(\vec{R}) \equiv \int\phi_j^*(\vec{r},\vec{R})\left[-\frac{\hbar^2}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla^2_{\vec{r}_\alpha} + V_{rR}(\vec{r},\vec{R})\right] \times\phi_i(\vec{r},\vec{R})\,\mathrm{d}\vec{r}, \tag{6}$$

$$\vec{d}_{ji}(\vec{R}) \equiv \int\phi_j^*(\vec{r},\vec{R})[\nabla_{\vec{R}}\phi_i(\vec{r},\vec{R})]\,\mathrm{d}\vec{r}. \tag{7}$$

and the chain rule

$$\int\phi_j^*(\vec{r},\vec{R})\frac{\partial\phi_i(\vec{r},\vec{R})}{\partial t}\mathrm{d}\vec{r} = \dot{\vec{R}}\cdot\vec{d}_{ji} \tag{8}$$

has been used. In the adiabatic representation the Hamiltonian matrix of Eq. (6) is diagonal, and Eq. (5) simplifies to

$$i\hbar\frac{\mathrm{d}c_j(t)}{\mathrm{d}t} = c_j(t)\epsilon_j - i\hbar\sum_i c_i(t)\dot{\vec{R}}\cdot\vec{d}_{ji}. \tag{9}$$

The amplitude of each quantum mechanical state at a given time is found by integrating equation (9) along the trajectory $\vec{R}(t)$. This information is used to determine whether a switch to a different classical trajectory should occur or not.

2.1. Fewest switches algorithm

The criterion for switching between states must result in a distribution of state populations over all trajectories that reflects the populations given by integrating equation (9). It is also important to achieve this result with a small number of hops, because a criterion which results in a large number of hops will give trajectories that effectively evolve on an average of the potential energy surfaces rather than on a single adiabatic surface [15]. Different choices are possible for the switching algorithm [44,53,54], but in practice the fewest switch algorithm (FSA) [15] is usually employed.

The FSA is derived by imposing that the number of switches required to reproduce the statistical distribution of state occupations is minimised. Switches between states are governed by a stochastic criterion and are usually assumed for simplicity to occur in an infinitesimal time period, although this is not a necessary condition. This causes state transitions to be discontinuous in any single trajectory, but over a swarm of trajectories this behaviour will be smoothed out as the transitions will occur at different