Efficient k-p method for the calculation of total energy and electronic density of states

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Abstract: An efficient method for calculating the electronic structure in large systems with a fully converged BZ sampling is presented. The method is based on a k.p-like approximation developed in the framework of the density functional perturbation theory. The reliability and efficiency of the method are demonstrated in test calculations on Ar and Si supercells

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Efficient Exploration of Reactive Potential Energy Surfaces
Using Car-Parrinello Molecular Dynamics

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The possibility of observing chemical reactions in \textit{ab initio} molecular dynamics runs is severely hindered by the short simulation time available. We propose a new method for accelerating the reaction process, based on the ideas of the extended Lagrangian and coarse-grained non-Markovian metadynamics. We demonstrate that by this method it is possible to simulate reactions involving complex atomic rearrangements and very large energy barriers in runs of a few picoseconds.

Moreover, they must include the relevant modes that cannot be sampled within the typical time scale of the simulation (for \textit{ab initio} MD, of the order of 10 ps). The method will not sample motions along slow modes that are not included in the collective coordinates. Examples of collective variables are distances between atoms, dihedral angles, coordination numbers, or any other function of the ionic coordinates \(R_i\).

The aim of the method is to explore the FES \(F(s)\), where \(s\) is the vector of the collective variables, denoted by \(s_a\)'s. In our approach, the collective variables are treated as new dynamical variables, and the extended system is described by a Lagrangian of the form

\[
\mathcal{L} = \mathcal{L}_0 + \frac{1}{2} \sum_a M_a s_a^2 - \frac{1}{2} \sum_a k_a [S_a(R_i) - s_a]^2 + V(t,s),
\]

where \(\mathcal{L}_0\) is the usual Lagrangian that drives the electronic and ionic dynamics, which, in our specific case, is the Car-Parrinello Lagrangian \([11]\), the second term is the (fictitious) kinetic energy of the \(s_a\)'s, the third term is a sum of harmonic potentials that restrain the value of \(S_a(R_i)\) close to the corresponding dynamic collective variable \(s_a\), and \(V(t,s)\) is a history-dependent potential whose functional form is defined below. We assume that the \(S_a(R_i)\)'s are dimensionless and rescaled so that, in a finite temperature MD run performed with \(V(t,s)\) set to zero, the amplitude of their fluctuations, \(\max(|S_a - \langle S_a \rangle|)\), is equal to 1 for all \(a\)'s. The mass \(M_a\) and the coupling constant \(k_a\) determine how fast \(s_a\) evolves in time with respect to the ionic degrees of freedom. If the masses \(M_a\) are large, the collective variables \(s_a\) are slow, so that the dynamics in the collective variables is adiabatically separated from the ionic and electronic ones \([11,15]\). The dynamics of the \(s_a\) is driven by these forces \(\dot{S}_a = k_a [S_a(R_i) - s_a] + \text{the forces coming from the history-dependent term, and the instantaneous values of} \)

\[
\text{the collective variables } S_a(R_i) \text{ fluctuate around the corresponding } s_a. \text{ One basic ingredient of the method is that,}
\]
in conditions of adiabatic separation, the $\phi_\alpha$’s provide an estimate of the derivative of the free energy with respect to the collective variables. Namely, in the limit of very large $M_\alpha$, $s_\alpha$ is approximately fixed and $\phi_\alpha$ is dynamically averaged over the electronic and ionic degrees of freedom. Hence, $s_\alpha$ efficaciously evolves with the force $\langle \phi_\alpha \rangle$ that is the derivative of the free energy with respect to $s_\alpha$ as in standard umbrella sampling and constrained dynamics [16,17].

$V(t,s)$ is constructed to fill the free energy wells and drive the system towards the lowest saddle points. If

$$V(t,s) = \int_0^t dt' |\mathbf{s}(t')| W(t') \exp \left[ -\frac{(s - s(t'))^2}{2\Delta s^2} \right] \beta \left( \frac{\mathbf{s}(t')}{|\mathbf{s}(t')|} \cdot (s - s(t')) \right)$$

that describes a $N_\alpha$-dimensional Gaussian tube, with axis along the trajectory. $V(t,s)$ results from the accumulation of tube slices of infinitesimal thickness $d\mathbf{s}(t')$ in the direction of the trajectory, whereas, in the orthogonal direction, their size is given by $\Delta s^\perp$. For an optimally efficient filling, $\Delta s^\perp$ is taken to be comparable to the estimated well size [14]. The prefactor $W(t)$ has the dimensions of an energy, and it is chosen so as to adapt the time-dependent potential to the free energy landscape, as we show in the following.

$$V(t,s) = \sum_{i < k} W_i \exp \left[ -\frac{(s - s_i)^2}{2(\Delta s_i^\perp)^2} \right] \exp \left[ -\frac{[\mathbf{s}^\perp - s_i \cdot (s - s_i^\perp)]^2}{2(\Delta s_i^\perp)^2} \right]$$

where $s_i = \{s_\alpha(t_i)\}$ and $\Delta s_i^\perp = |s_i^\perp - s_i|$. The adaptive prefactor $W_i$ is given by $W_i = \lambda \sum_\alpha (s_i^\perp - s_i^\alpha)(k_\alpha[S_\alpha(R_i) - s_i^\alpha])$, where $\lambda < 1$ and the average is taken over the time interval $\Delta t$. This form amounts to estimating $W_i \approx \int_{t_i}^{t_i+\Delta t} dt' \mathbf{s}(t') \frac{d\mathbf{s}}{dt}$, in order to balance the force coming from the underlying FES. All the parameters described above are system dependent and they strongly affect the efficiency in escaping from the local minima, as well as the resolution in reconstructing the underlying FES. Although the trajectories generated by the algorithm discussed describe the most probable mechanisms of the process, we remark that they are not true dynamical trajectories, not even in the neighborhood of the transition state [7], nor can the relation between the underlying FES and realistic trajectories be easily expressed.

We apply this method to two examples. The first one is the well-known and much studied electrocyclic reaction in the C$_2$H$_6$ system [18]. This molecule has three stable configurations, the cyclobutene (cycle), the s-cis-buta-1,3-diene (cis), and the most stable s-trans-buta-1,3-diene (trans) [18]. Starting from the cycle, the reaction involves the breaking of the C1-C4 bond (see Fig. 1) and the rotation of the two groups CH$_2$ in order to form the planar cis or trans geometries, with a barrier of ~30 kcal/mol [19]. The two events can be simultaneous or slightly separated in time, but according to orbital symmetry considerations, the electrocyclic reaction occurs in a concerted corotatory fashion on the electronic ground state surface [19]. As reaction coordinates we choose the carbon-carbon distances C1-C2, C3-C4, and C1-C4. Obviously this choice is not unique, but we checked that different sets of variables, such as, e.g., dihedral angles,

FIG. 1. C1-C4 distance during the MD run. The masses are set to 50 amu and the $k_\alpha$’s to 0.3. $V(t,s)$ is updated every 0.012 ps, $\Delta s^\perp$ is 0.15, $s_i^\perp$ fluctuates in the interval [0.07:0.1], and $W$ between 1.0 and 8.0 kcal/mol. The arrows indicate which configuration the system is in: (a) is the cycle, (b) the trans, and (c) the cis configuration. With larger Gaussians [$\Delta s^\perp = 0.2$, and consequently larger $s_i^\perp$ and $W (= 6.5$ kcal/mol)] and smaller $M_\alpha$ (1 amu), the transition is observed within 1 ps, at a cost of a more coarse evaluation of the energy profile.
lead to quantitatively similar results. We run a Car-Parrinello MD [20] at \( T = 300\) K driven by the Lagrangian in Eq. (1), with the additional history-dependent term in Eq. (3). The \( M_{\alpha}'s \) and the coupling constants \( k_{\alpha}'s \) are chosen so that the variables complete 3–5 fluctuations per picosecond, and the maximum value of \( k_{\alpha}[S_{\alpha}(R_{i}) - s_{\alpha}]^{2} \) is not larger than a few kcal/mol, assuming that this allows a sufficient adiabatic separation. In the first 6 ps, the system remains in the initial configuration, as shown by the plot of the C1-C4 distance in Fig. 1. While the well is filled with more and more Gaussians, the total energy increases and the oscillations of the collective variables become wider. After about 6.5 ps a transition state is reached and the system moves fast toward the new minimum, transforming into the trans configuration. The transition is indicated by the large change in the C1-C4 distance (from 1.6 to 4 Å), while both the C1-C2 and the C3-C4 (not shown in the figure) are contracted, due to the formation of the double bond. Analysis of the trajectory along the transition path shows that the corotatory movement of the CH\(_{2}\) and the C1-C4 bond breaking take place simultaneously. After the first transition at 6.5 ps, the system crosses the energy barrier separating the trans from the cis configurations several times. After about 27 ps a recrossing of the first transition state occurs, and the system transforms back into the cycle configuration. Once the overall topology of the FES is known, we can adapt the resolution in order to determine more precisely the geometry and the energy of the stationary points, by tuning opportunely the size of the Gaussians and the separation time \( t_{i+1} - t_{i} \). Since at 300 K the entropic contribution to the FES is negligible with respect to the barrier height, for large \( t \ V(t,s) \) is a measure of the FES. It is reassuring that the differences in energy among the three minima and the height of the energy barrier, estimated through \( V(t_{\text{final}},s) \), are in agreement, within 2 kcal/mol, with those calculated by the standard methods of geometry optimization and eigenvalue following [1,3,4]. Note that even if during the simulation the exact transition state geometry is not reached, the trajectory passes very close to it, providing a very good guess for the transition state geometry. From this guess any standard optimization method finds the exact geometry in very few iterations.

This simple example has been used to validate our approach in a case where the standard methods are capable of finding the transition state. The situation is different for more complex systems, where there are many and nontrivial transition states and minima. One such example is the dehydrogenation of clusters of the type Si\(_{n}\)H\(_{x}\), the structure of which evolves as a function of \( n \) and \( x \). Different methods have been applied to the study of this problem [21–24]. More recently Miyazaki et al. [25] have studied the \( n = 6 \) case and its hydrogenated derivatives. For each stoichiometry studied, possible equilibrium structures have been proposed, which usually show high symmetry and an even distribution of the H atoms. Starting from the Si\(_{6}\)H\(_{8}\) stoichiometry. (a) is the structure reported in Ref. [25], while (b) and (c) are encountered in the MD run performed with \( \Delta s^{+} = 0.3 \) and \( M_{\alpha} = 1 \) amu, where \( V(t,s) \) is updated with a new Gaussian every 0.003 ps. (b) and (c) are, respectively, 12.2 and 8.5 kcal/mol lower in energy than (a).

![Figure 2](image)

**FIG. 2.** Examples of minimum energy structures in the Si\(_{6}\)H\(_{8}\) stoichiometry. (a) is the structure reported in Ref. [25], while (b) and (c) are encountered in the MD run performed with \( \Delta s^{+} = 0.3 \) and \( M_{\alpha} = 1 \) amu, where \( V(t,s) \) is updated with a new Gaussian every 0.003 ps. (b) and (c) are, respectively, 12.2 and 8.5 kcal/mol lower in energy than (a).
which the lowest in energy are (d) and (e), although they are higher than the structures of Refs. [25,27].

In conclusion, the method presented here allows the PES of complex systems to be explored efficiently in a very short time and slow chemical reactions to be simulated with a minimum amount of chemical insight into the problem. We believe that this new method greatly expands the scope of \textit{ab initio} molecular dynamics.

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[26] The MD run is performed in the canonical ensemble at 300 K, with a time step of 5 a.u. The electronic part is again described by the Martins-Troullier PP (cutoff 30 Ry) and the BLYP exchange-correlation functional.
[27] In other runs of a similar length, we have found different pathways and different structures, so that also for Si$_6$H$_4$ we were able to discover structures more stable than the corresponding one in Ref. [25].