Ab Initio Molecular Dynamics with Born-Oppenheimer and Extended Lagrangian Methods Using Atom Centered Basis Functions

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Received February 25, 2003

In *ab initio* molecular dynamics, whenever information about the potential energy surface is needed for integrating the equations of motion, it is computed "on the fly" using electronic structure calculations. For Born-Oppenheimer methods, the electronic structure calculations are converged, whereas in the extended Lagrangian approach the electronic structure is propagated along with the nuclei. Some recent advances for both approaches are discussed.

Key Words : *Ab initio* molecular dynamics, Direct classical trajectory calculations, Born-Oppenheimer dynamics, Extended Lagrangian dynamics, ADMP

Introduction

As discussed in numerous chapters and monographs,[1-16] classical trajectories of molecules moving on potential energy surfaces provide a wealth of information about reactivity and dynamics. Because molecular dynamics calculations may involve extensive sampling of initial conditions and / or long simulation times, the molecular energy and its derivatives need to be computed frequently during the integration of the equations of motion. Traditionally, such studies have used analytic potential energy surfaces fitted to experimental and computational data. Potential energy surfaces obtained from well parameterized molecular mechanics calculations can be quite satisfactory for simulations near equilibrium. However, for reactive systems, specific potential energy surfaces must be devised for each unique system. Constructing potential energy surfaces by fitting to experimental data and / or *ab initio* molecular orbital energies can be both tedious and full of pitfalls.[17,18] Alternatively, *ab initio* or semi-empirical molecular orbital calculations can be used directly to obtain the energies and derivatives as they are needed, thus avoiding the fitting process.[19] This approach has been termed *ab initio* molecular dynamics (AIMD). The calculation of trajectories by AIMD methods is a comparatively new area[19] and is expanding rapidly as affordability of computer power increases and more efficient software is developed.

Direct classical trajectory calculations can be grouped into two major categories: Born-Oppenheimer (BO) methods and extended Lagrangian (EL) methods. For the former, the electronic structure calculation is fully converged in the Born-Oppenheimer (clamped nuclei) approximation, each time that information about the potential energy surface is needed for a given nuclear configuration. In the extended Lagrangian approach, both the wavefunction and the nuclei are treated as dynamic variables. With an appropriate adjustment of the time scales for the dynamics of the wavefunction, both can be propagated satisfactorily with Lagrangian equations of motion, without the extra work of converging the wavefunction at each step. The resulting dynamics of the nuclei are comparable to that obtained with the Born-Oppenheimer approximation but at lower cost. The Car-Parrinello method is the archetypical example of this approach.[20] The present overview is not intended to be a thorough review of the field, but is concerned only with some highlights of recent contributions to the development of AIMD methods from a chemical perspective.

Results and Discussion

Born-Oppenheimer methods. The simplest approach for Born-Oppenheimer dynamics uses electronic structure methods to calculate the energy and gradients directly. Methods such as velocity Verlet, fourth order Runge-Kutta, sixth order Adams-Moulton-Bashforth and related predictor-corrector algorithms[21] are typical gradient-based methods used to integrate the equations of motion. Because this class of integrators requires fairly small time steps to determine the trajectories accurately, many thousands of electronic structure calculations may be needed, even for fairly fast reactions. Code for calculating classical trajectories has been incorporated into a number of widely distributed electronic structure packages (Dalton, DMol, Gamess, Gaussian, HyperChem, NWChem, etc.). Alternatively, a standard electronic structure package can be called as a subroutine from a classical trajectory code.

Analytic second derivatives of the energy (Hessians) can be calculated readily for a number of electronic structure methods, including Hartree-Fock (HF), multi-configuration SCF (MCSCF), density functional theory (DFT) and second order Møller-Plesset perturbation theory (MP2). The gradient and Hessian provide a local quadratic approximation to the potential energy surface and the equations of motion can be integrated on this local surface in closed form, allowing significantly larger steps between electronic structure calculations than for gradient-based methods. This approach was pioneered by Helgaker, Uggerud and Jensen in their studies of $H_2 + H$ and $CH_2OH \rightarrow HCO^+ + H_2$ at the MCSCF level of theory.[22,23] Numerous systems have now been studied by
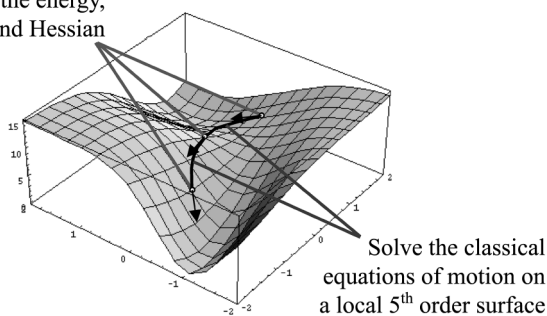
Calculate the energy, gradient and Hessian

Solve the classical equations of motion on a local 5th order surface

Figure 1. Hessian-based predictor-corrector algorithm for integrating trajectories on the Born-Oppenheimer surface.

Figure 3. Comparison of the error in the conservation of energy versus step size for trajectories integrated with the second order Hessian-based method (squares) and the Hessian-based predictor-corrector method with a fifth order polynomial (circles) or a rational function (triangles) for the corrector step (slopes of the least squares fits in parenthesis).

Figure 4. Relative cpu times as a function of the number of updates for Hessian-based Born-Oppenheimer trajectory calculations.

these authors with the second order Hessian-based trajectory integration method, including $C_2H_6^+$, $H_3O^+ + NH_3$, $CH_2NH_2^+$, $NHNH_2^+$, $NH_2NH_3^+$ and $HNO + HNO$.[24-30]

Figure 1 illustrates a Hessian-based predictor-corrector method that we developed a few years ago.[31-33] Given a Hessian from an electronic structure calculation, a predictor step is taken on the local quadratic surface. The Hessian is then recalculated and a fifth order polynomial or a rational function is fitted to the energies, gradients and Hessians at the beginning and end points of this predictor step. The Bulrisch-Stoer algorithm[21] is used to re-integrate the trajectory on the fitted surface to yield a corrector step (see Figure 2). The process is repeated for each step. Since the Hessian at the end of the last step is used for the next predictor step, the electronic structure work is the same as for the second order Hessian-based method (*i.e.* one Hessian calculation per step). As shown in Figure 3, the error in the conservation of energy for the Hessian-based predictor-corrector method is three orders of magnitude lower than for the second order Hessian-based method, permitting a ten-fold increase in the step size without loss of accuracy in the energy conservation. This means an order of magnitude increase in the efficiency of the AIMD calculation, since the number of electronic structure calculations for a given trajectory is reduced by a factor of ten.

Algorithms for geometry optimization use updating formulas to maintain and improve an estimated Hessian during an optimization.[34,35] This approach can be applied to our Hessian-based predictor-corrector method for integrating trajectories. We have found that Bofill's formula[36] can be used to update the Hessian for 5-10 steps before it needs to be recalculated. As shown in Figure 4, this speeds up the trajectory integration by a factor of 3 or more for systems containing 4 to 6 heavy atoms. With updating, the step size needs to be only slightly smaller to maintain the same energy conservation as without updating. We have used the
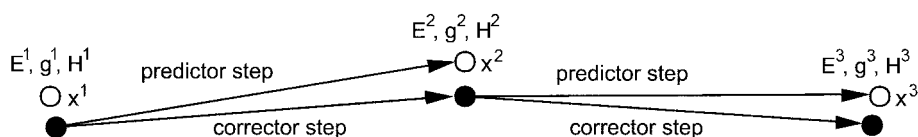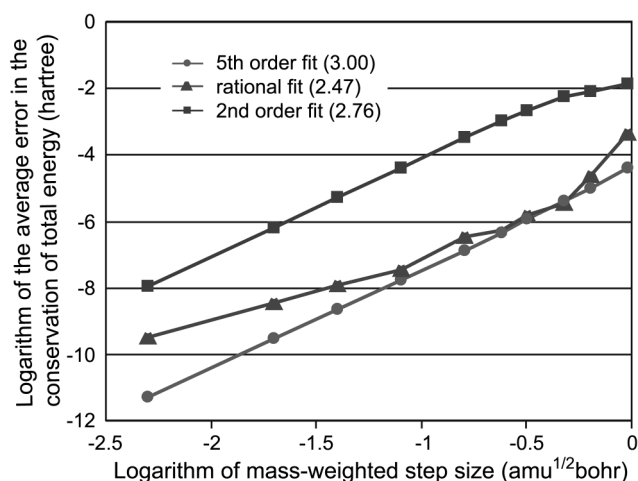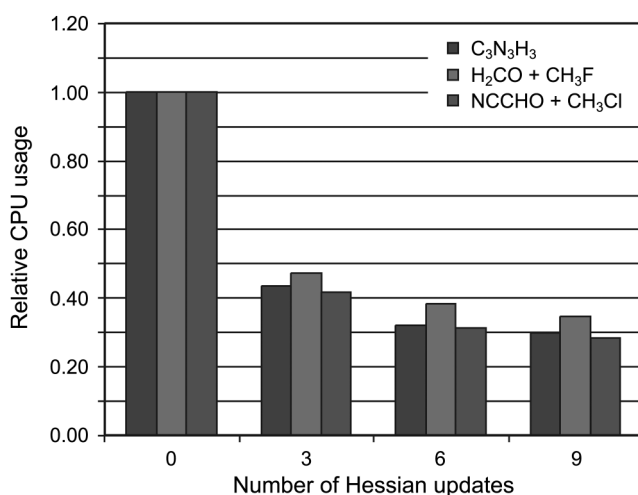
Hessian-based predictor-corrector method (with and without updating) in studies of $H_2CO \rightarrow H_2 + CO$, $F + C_2H_4 \rightarrow C_2H_3F$, $C_2H_2O_2$ (glyoxal) $\rightarrow H_2 + 2\ CO$ & $H_2CO + CO$, $C_2N_4H_2$ (s-tetrazine) $\rightarrow N_2 + 2\ HCN$ and $HXCO \rightarrow HX + CO$.[31,37-46]

Collins has developed a novel method for growing potential energy surfaces for dynamics by using trajectories to determine where additional electronic structure calculations are needed.[47-53] An initial approximation to the potential energy surface is constructed with a modest number of

E^1, g^1, H^1
$\bigcirc x^1$ predictor step E^2, g^2, H^2 $\bigcirc x^2$ predictor step E^3, g^3, H^3 $\bigcirc x^3$
corrector step   corrector step

Figure 2. Details of the Hessian-based predictor-corrector algorithm for integrating classical trajectories.

energy, gradient and Hessian calculations along the reaction path. This local information is linked with distance weighted interpolants to yield a global surface. As more trajectories are run, some explore regions of the surface farther away from the existing data points. Additional electronic structure calculations are performed in these regions to improve the accuracy of the interpolated surface. The process continues until the desired dynamical properties become stable with respect to improvements in the surface. This approach has been used by Collins and co-workers to study a number of systems, including OH + H_2, N + H_3^+, BH^+ + H_2 and triazine dissociation.[54-60]

Extended Lagrangian methods. Converging wavefunctions for every time step in a trajectory calculation can be costly. Since relatively small time steps are used, the change in the wavefunction may be small enough so that it can be treated by suitable equations of motion. In 1985 Car and Parrinello[20] outlined such an approach for *ab initio* molecular dynamics (for reviews, see Ref. 61-63). Use of the time dependent Schrödinger equation was impractical, since it would necessitate very small time steps. Instead, they constructed an extended Lagrangian to obtain classical-like equations of motion for the wavefunction:

$$L = 1/2 Tr[\mathbf{V}^T \mathbf{M} \mathbf{V}] + \mu \Sigma \int |\partial \phi_i/\partial t|^2 d\mathbf{r} - E(\mathbf{R}, \phi_i)$$
$$- \Sigma \Lambda_{ij} (\int \phi_i^* \phi_j d\mathbf{r} - \delta_{ij}) \tag{1}$$

where $\mathbf{R}$, $\mathbf{V}$ and $\mathbf{M}$ are the nuclear positions, velocities and masses, μ is the fictitious electronic mass, $\mathbf{r}$ are the electronic coordinates and Λ_{ij} are Lagrangian multipliers to ensure that the orbitals remain orthonormal. The coefficients of the molecular orbitals, ϕ_i, are expanded in a plane wave basis.[64,65] This simplifies many of the integrals and facilitates applications to condensed matter. However, a very large number of plane waves is needed and the types of density functionals that can be used easily is limited (*e.g.* hybrid functionals are expensive since the Hartree-Fock exchange is difficult to calculate). Furthermore, pseudopotentials must be used to replace core electrons, since these cannot be describe well by reasonable sized plane wave basis sets. Even with these limitations, the Car-Parrinello approach and its variants have seen extensive usage in the physics community.[66]

Molecular electronic structure calculations in chemistry are usually carried out with atom centered basis functions (*e.g.* gaussians) rather than plane waves.[67-70] Since atom centered basis functions are automatically positioned where the density is the greatest, far fewer functions are needed than plane waves. Fast integral packages are available for gaussian basis functions and hybrid density functionals are handled readily. Because the density matrix becomes sparse for large molecules, Hartree-Fock and density functional calculations can be made to scale linearly with molecular size.[71-73] These features, coupled with the extensive experience that the chemistry community has with levels of theory and basis sets, lead us to develop the atom-centered

density matrix propagation (ADMP) method for molecular dynamics.[74-76]

The equations for propagation of the density matrix are simplest in an orthonormal basis. In many ways, this is similar to density matrix search methods for calculating electronic energies.[77] In the ADMP approach, the extended Lagrangian for the system is

$$L = 1/2 Tr[\mathbf{V}^T \mathbf{M} \mathbf{V}] + 1/2 Tr[(\mu^{1/4} \mathbf{W} \mu^{1/4})^2]$$
$$- E(\mathbf{R}, \mathbf{P}) - Tr[\Lambda(\mathbf{PP} - \mathbf{P})] \tag{2}$$

where $\mathbf{P}$, $\mathbf{W}$ and μ are the density matrix, the density matrix velocity and the fictitious mass matrix for the electronic degrees of freedom. Constraints on the total number of electrons and the idempotency are imposed using the Lagrangian multiplier matrix Λ. The energy is calculated using the McWeeny purification of the density,[78] $\tilde{\mathbf{P}} = 3\,\mathbf{P}^2 - 2\,\mathbf{P}^3$. The Euler-Lagrange equations of motion are

$$\mathbf{M}\, d^2\mathbf{R}/dt^2 = -\,\partial E/\partial \mathbf{R}|_{\mathbf{P}};$$
$$\mu\, d^2\mathbf{P}/dt^2 = -\,[\partial E/\partial \mathbf{P}|_{\mathbf{R}} + \Lambda \mathbf{P} + \mathbf{P}\Lambda - \Lambda] \tag{3}$$

These can be integrated using the velocity Verlet algorithm,[64,79]

$$\mathbf{P}_{i+1} = \mathbf{P}_i + \mathbf{W}_i \Delta t - \mu^{-1/2}\,[\partial E(\mathbf{R}_i, \mathbf{P}_i)/\partial \mathbf{P}|_{\mathbf{R}} + \Lambda_i \mathbf{P}_i + \mathbf{P}_i \Lambda_i - \Lambda_i]$$
$$\times \mu^{-1/2} \Delta t^2/2$$
$$\mathbf{W}_{i+1/2} = \mathbf{W}_i - \mu^{-1/2}\,[\partial E(\mathbf{R}_i, \mathbf{P}_i)/\partial \mathbf{P}|_{\mathbf{R}} + \Lambda_i \mathbf{P}_i + \mathbf{P}_i \Lambda_i - \Lambda_i]$$
$$\times \mu^{-1/2} \Delta t/2 = [\mathbf{P}_{i+1} - \mathbf{P}_i]/\Delta t$$
$$\mathbf{W}_{i+1} = \mathbf{W}_{i+1/2} - \mu^{-1/2}\,[\partial E(\mathbf{R}_{i+1}, \mathbf{P}_{i+1})/\partial \mathbf{P}|_{\mathbf{R}} + \Lambda_{i+1} \mathbf{P}_{i+1}$$
$$+ \mathbf{P}_{i+1} \Lambda_{i+1} - \Lambda_{i+1}]\, \mu^{-1/2} \Delta t/2 \tag{4}$$

A simple iterative scheme is used to determine the Lagrangian multipliers so that $\mathbf{P}_{i+1}$ and $\mathbf{W}_{i+1}$ satisfy the idempotency constraints.[74,75]

$$\mathbf{P}_{i+1} \leftarrow \mathbf{P}_{i+1} + \mu^{-1/2}\,[\mathbf{P}_i\, \mathbf{T}\mathbf{P}_i + (\mathbf{I} - \mathbf{P}_i)\mathbf{T}(\mathbf{I} - \mathbf{P}_i)]\, \mu^{-1/2}\, \mathbf{T}$$
$$= \mu^{1/2}\,[\tilde{\mathbf{P}}_{i+1} - \mathbf{P}_{i+1}]\, \mu^{1/2}$$
$$\mathbf{W}_{i+1} \leftarrow \mathbf{W}_{i+1} + \mu^{-1/2}\,[\mathbf{P}_{i+1}\mathbf{T}\mathbf{P}_{i+1} + (\mathbf{I} - \mathbf{P}_{i+1})\mathbf{T}(\mathbf{I} - \mathbf{P}_{i+1})]\, \mu^{-1/2}\, \mathbf{T}$$
$$= \mu^{1/2}\,[\tilde{\mathbf{W}}_{i+1} - \mathbf{W}_{i+1}]\, \mu^{1/2} \tag{5}$$

where $\tilde{\mathbf{W}}_{i+1} = \mathbf{P}_{i+1}\mathbf{W}_{i+1}(\mathbf{I} - \mathbf{P}_{i+1}) + \mathbf{P}_{i+1}\mathbf{W}_{i+1}(\mathbf{I} - \mathbf{P}_{i+1})$. In calculating $\partial E/\partial \mathbf{R}|_{\mathbf{P}}$ we need to take into account that $\mathbf{P}$ is not converged and that $\mathbf{U}$, the transformation between the non-orthogonal atomic orbital basis and the orthonormal basis, depends on $\mathbf{R}$. This leads to a somewhat more complicated expression than used for gradients of converged SCF energies.

$$\partial E/\partial \mathbf{R}|_{\mathbf{P}} = Tr[\mathbf{U}^{-t}\, \partial \mathbf{h'}/\partial \mathbf{R}|_{\mathbf{P}}\, \mathbf{U}^{-1}\, \tilde{\mathbf{P}} + \mathbf{U}^{-t}\, \partial \mathbf{G'}(\tilde{\mathbf{P}})/\partial \mathbf{R}|_{\mathbf{P}}\, \mathbf{U}^{-1}\, \tilde{\mathbf{P}}]$$
$$- Tr[\mathbf{F}\, \partial \mathbf{U}/\partial \mathbf{R}\, \mathbf{U}^{-1}\, \tilde{\mathbf{P}} + \tilde{\mathbf{P}}\, \mathbf{U}^{-t}\, \partial \mathbf{U}^t/\partial \mathbf{R}\, \mathbf{F}] + dV_{NN}/d\mathbf{R}$$
$$= Tr[\partial \mathbf{h'}/\partial \mathbf{R}|_{\mathbf{P}}\, \tilde{\mathbf{P}}' + \partial \mathbf{G'}(\tilde{\mathbf{P}}')/\partial \mathbf{R}|_{\mathbf{P}}\, \tilde{\mathbf{P}}']$$
$$- Tr[\mathbf{F'}\, \mathbf{U}^{-1}\, \partial \mathbf{U}/\partial \mathbf{R}\, \tilde{\mathbf{P}}' + \tilde{\mathbf{P}}'\, \partial \mathbf{U}^t/\partial \mathbf{R}\, \mathbf{U}^{-t}\, \mathbf{F'}] + dV_{NN}/d\mathbf{R} \tag{6}$$
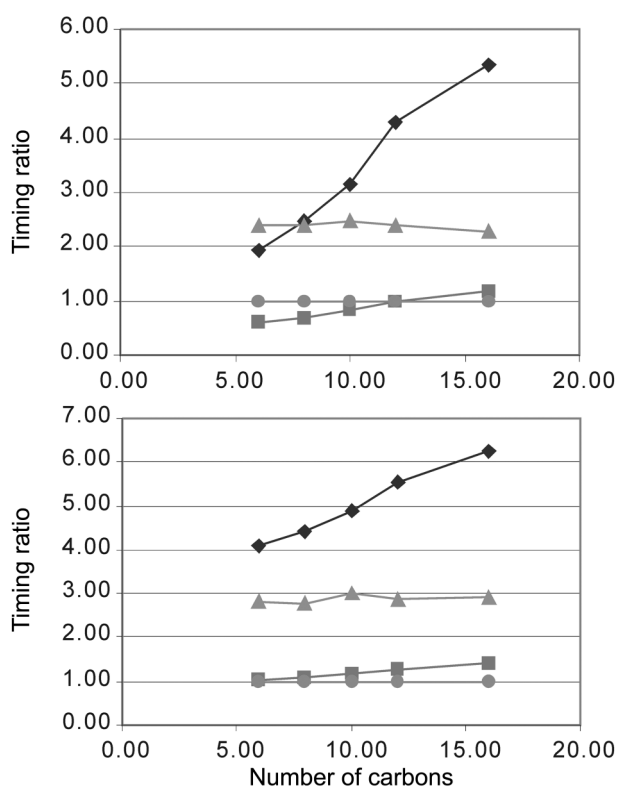
Figure 5. Ratios of estimated timings for Born-Oppenheimer versus ADMP trajectory calculations on linear hydrocarbons, C_nH_{2n+2}, computed at HF/6-31G(d) (top) and B3LYP/6-31G(d) (bottom) with the Hessian-based predictor-corrector method (diamonds), Hessian-based predictor-corrector with updating (squares), gradient based velocity Verlet (triangles) and ADMP (diamonds).

where the primed quantities are integrals in the atomic orbital basis and $\mathbf{U}^t\,\mathbf{U} = \mathbf{S'}$. An important factor in the viability of this approach is that we have been able to obtain the derivative of the transformation matrix in closed form for Cholesky orthonormalization.[74]

$$(\partial\mathbf{U}/\partial\mathbf{R}\,\mathbf{U}^{-1})_{\mu\nu} = (\mathbf{U}^{-t}\,\partial\mathbf{S'}/\partial\mathbf{R}\,\mathbf{U}^{-1})_{\mu\nu} \text{ for } \mu < \nu,$$
$$= 1/2\,(\mathbf{U}^{-t}\,\partial\mathbf{S'}/\partial\mathbf{R}\,\mathbf{U}^{-1})_{\mu\nu} \text{ for } \mu = \nu,$$
$$= 0 \text{ for } \mu > \nu. \quad (7)$$

Unlike earlier approaches to propagating Hartree-Fock and generalized valence bond wavefunctions[80-83] the ADMP method shows excellent energy conservation without thermostats and does not require periodic re-convergence of the electronic structure.

To estimate the relative timing of the BO and ADMP methods for molecular dynamics, we considered a series of linear hydrocarbons (see Figure 5). One Fock matrix and one gradient evaluation per time step are needed in the ADMP approach. This is used as the reference for all the other methods. BO method with velocity Verlet uses approximately the same time step as ADMP but needs an average of 10 Fock matrix evaluations to converge the wavefunction. The Hessian-based trajectory integration methods can employ much larger time steps and still maintain the same level of

energy conservation or better. When updating is used, the cost of calculating the Hessian is spread out over a number of steps thereby reducing the average cost per step. As seen in Figure 5, this approach is most efficient for small molecules and for cases that require more accurate dynamics. The ADMP approach wins for larger systems and shows its advantage even earlier for hybrid DFT methods.[76]

The ADMP method has some of the specific advantages and greater flexibility when compared to the Car-Parrinello approach. All electrons can be treated explicitly and pseudo-potentials are not required. Any density functional, including hybrid functionals, can be employed. Smaller fictitious masses can be used and good adiabaticity can be maintained without thermostats.[74-76] For ionic systems, vibrational frequencies calculated by the plane-wave Car-Parrinello method show a disturbing dependence on the fictitious electronic mass;[84] however, the ADMP method is free from this problem.[76] The ADMP trajectories compare very well with those computed by BO methods.[74] Specifically, for $CH_2O \rightarrow H_2 + CO$ and $C_2H_2O_2 \rightarrow H_2 + 2\ CO$, the ADMP trajectories give product translational, rotational and vibrational energy distributions that are very close to the BO results.[76] The ADMP is being extended to QM/MM treatments for biological systems, and has been used to study the solvation of excess protons in water clusters and hydroxyl-stretch red shifts in chloride water clusters.[76]

Summary

Recent advances in computer hardware and software are making the applications of *ab initio* molecular dynamic increasingly more practical. Born-Oppenheimer methods offer the advantage of propagating molecules on well defined potential energy surfaces. Extended Lagrangian methods yield very similar dynamics at a reduced cost. The coming years will bring a rapid increase in the number and types of systems that are studied with these approaches.

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