Molecular Dynamics and Monte Carlo Simulations

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Chapter 1

From Quantum Mechanics to Classical Mechanics

Adapted from:
“Ab Initio Molecular Dynamics
Basic Theory and Advanced Methods”
Dominique Marx and Jürg Hutter
Cambridge University Press (2009)
Chapter 2 (pp. 11-20)

1. Deriving classical molecular dynamics from quantum mechanics

In this course, we will treat computational methods that are able to describe the properties of thermodynamic ensembles of molecules. These properties are either determined via stochastic sampling methods (*Monte Carlo Simulations*) or by following the time evolution of a molecular system for a sufficient amount of time (*Molecular Dynamics Simulations*). We will see in Chapter 2, that these two different ways of sampling are actually equivalent. In both methods however, the atoms are treated purely as classical point particles. At first sight, this seems to be at variance with all what you have learned from your courses in *Quantum Mechanics* and *Introduction to Electronic Structure Methods*. Since the properties of chemical systems are largely determined by their electronic structure, and electrons are light particles, we usually have to describe such systems using *Quantum Mechanics*. However, under certain circumstances, *Classical Mechanics* can bring us a long way even for atomistic systems! In this Chapter, we will look in detail into the approximations that are needed to derive classical point particle dynamics from the quantum mechanical time-dependent Schrodinger equation.

The starting point of all what follows is non-relativistic quantum mechanics as formalized via the time-dependent Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) = \mathcal{H}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) \tag{1.1}$$

in conjunction with the combined electronic-nuclear Hamiltonian

$$\begin{aligned}\mathcal{H} &= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_\mathrm{e}}\nabla_i^2 \\ &+ \frac{1}{4\pi\varepsilon_0}\sum_{i<j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} - \frac{1}{4\pi\varepsilon_0}\sum_{I,i}\frac{e^2 Z_I}{|\mathbf{R}_I-\mathbf{r}_i|} + \frac{1}{4\pi\varepsilon_0}\sum_{I<J}\frac{e^2 Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} \\ &= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_\mathrm{e}}\nabla_i^2 + V_{\mathrm{n-e}}(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) \\ &= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \mathcal{H}_\mathrm{e}(\{\mathbf{r}_i\},\{\mathbf{R}_I\})\end{aligned} \tag{1.2}$$

for the electronic $\{r_i\}$ and nuclear $\{\mathcal{R}_I\}$ degrees of freedom taking the electron-electron, electron-nuclear, and nuclear-nuclear Coulomb interactions into account. Here, $\mathcal{M}_I$ and $\mathcal{Z}_I$ are mass and atomic number of the Ith nucleus, the electron mass and charge are denoted by m_e and $-e$, and ε_o is the vacuum permittivity. In order to keep the current derivation as transparent as possible, we will introduce the more convenient atomic units (a.u.) only at a later stage.

The goal of this section is to derive molecular dynamics of classical point particles, that is essentially classical mechanics for the nuclear motion, starting from Schrodinger's quantum-mechanical wave equation Eq. (1.1) for both electrons and nuclei.

The starting point of the derivation we will follow here is to consider the

electronic part of the Hamiltonian for fixed nuclei, i.e. the so-called clamped-nuclei part $\mathcal{H}_e$ of the full Hamiltonian, Eq. (1.2). Next, it is supposed that the exact solution of the corresponding time-independent (stationary) electronic Schrodinger equation,

$$\mathcal{H}_{\mathrm{e}}(\{\mathbf{r}_i\};\{\mathbf{R}_I\})\Psi_k = E_k(\{\mathbf{R}_I\})\Psi_k(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) \tag{1.3}$$

is known for clamped nuclei at positions $\{\mathcal{R}_I\}$. Here, the spectrum of $\mathcal{H}_e$ is assumed to be discrete and the eigenfunctions to be orthonormalized

$$\int \Psi_k^\star(\{\mathbf{r}_i\};\{\mathbf{R}_I\})\Psi_l(\{\mathbf{r}_i\};\{\mathbf{R}_I\})\, d\mathbf{r} = \delta_{kl} \tag{1.4}$$

at all possible positions of the nuclei; $\int \cdots d\mathbf{r}$ refers to integration over all $i = 1, ...n$ electronic position variables $r = \{r_i\}$. Knowing all these adiabatic eigenfunctions at all possible nuclear configurations, the total wave function in Eq. (1.1) can be expanded

$$\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) = \sum_{l=0}^{\infty} \Psi_l(\{\mathbf{r}_i\};\{\mathbf{R}_I\})\chi_l(\{\mathbf{R}_I\};t) \tag{1.5}$$

in terms of the complete set of eigenfunctions $\{\Psi_l\}$ of $\mathcal{H}_e$ where the nuclear wave functions $\{\chi_l\}$ can be viewed to be time-dependent expansion coefficients. This is an ansatz of the total wave function, introduced by Born in 1951 for the time-independent problem, in order to separate systematically the light electrons from the heavy nuclei.

Insertion of this Ansatz Eq. (1.5) into the time-dependent coupled Schrodinger equation Eq. (1.1) followed by multiplication from the left by $\Psi_k^\star(\{\mathbf{r}_i\};\{\mathbf{R}_I\})$ and integration over all electronic coordinates r leads to a set of coupled differential equations

$$\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(\{\mathbf{R}_I\})\right]\chi_k + \sum_l \mathcal{C}_{kl}\chi_l = i\hbar\frac{\partial}{\partial t}\chi_k \tag{1.6}$$

where

$$\mathcal{C}_{kl} = \int \Psi_k^\star \left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\right]\Psi_l\, d\mathbf{r} \quad + \sum_I \frac{1}{M_I}\int \psi_k^*\,(-i\hbar\nabla_I)\psi_l\; dr(-i\hbar\nabla_I) \tag{1.7}$$

is the exact nonadiabatic coupling operator that mediates coupling between different electronic states k and l.

$$C_{kl} = -\sum_I \frac{\hbar^2}{2M_I} D_{kl}^I(R) + \sum_I \frac{\hbar^2}{M_I} d_{kl}^I(R)\nabla_I \tag{1.7a}$$

$$D_{kl}^{I}(R) = \int \psi_k^* \, \nabla_I^2 \psi_l \; dr \tag{1.7b}$$

$$d_{kl}^{I}(R) = \int \psi_k^* \, \nabla_I \; \psi_l \; dr \tag{1.7c}$$

$\mathcal{D}_{kl}^{I}(\mathcal{R})$ are the second-order nonadiabatic coupling elements and $\mathcal{d}_{kl}^{I}(\mathcal{R})$ are the first-order nonadiabatic coupling vectors. Both coupling terms depend inversely on the nuclear mass, so that C_{kl} -> 0 for $\mathcal{M}_I$ -> ∞, i.e. there is no coupling with other electronic states, the dynamics evolves on a single electronic state (adiabatic dynamics) and the Born-Oppenheimer approximation (i.e. the separation between electronic and nuclear degrees of freedom) is fully valid.

An alternative expression for the nonadiabatic coupling vectors $\mathcal{d}_{kl}^{I}$ is (see exercises)

$$d_{kl}^{I} = \frac{\int \Psi_k^* \, \nabla_I \mathrm{H}_e \Psi_l \; dr}{E_l - E_k} \tag{1.7d}$$

Eq. (1.7d) shows that the first-order coupling between different electronic states is inversely proportional to the energy difference between them. This means that for the case that the nuclear masses are large (Eqs. 1.7b and c) and/or the different electronic states are well separated in energy (Eq. 1.7d), the off-diagonal nonadiabatic coupling elements can be neglected.

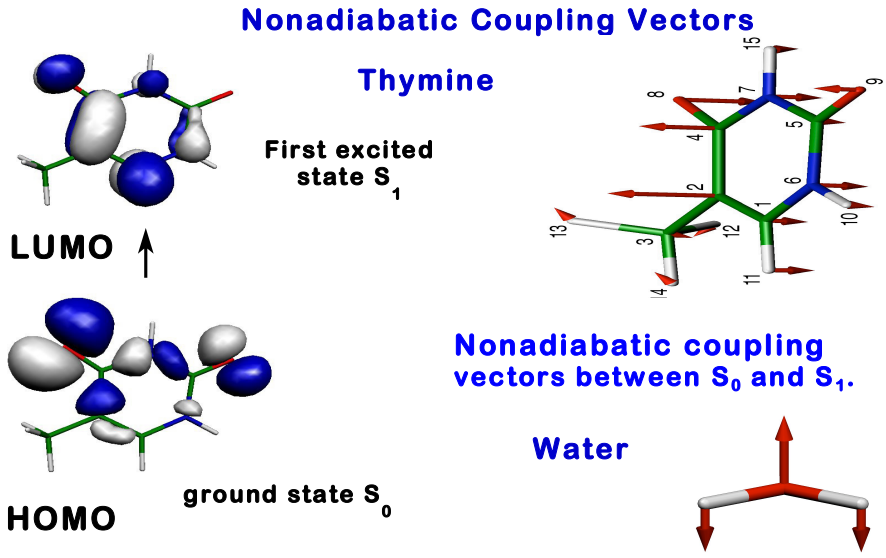

Fig.1.1 Nonadiabatic coupling vectors between the ground and the first excited state for thymine and water.

The diagonal contribution C_{kk} depends only on a single adiabatic wave function Ψ_k and as such represents a correction to the adiabatic eigenvalue $\mathcal{E}_k$ of the electronic Schrodinger equation Eq. (1.3) in the kth state. As a result, the "adiabatic approximation" to the fully nonadiabatic problem Eq. (1.6) is obtained by considering only these diagonal terms,

$$C_{kk} = -\sum_I \frac{\hbar^2}{2M_I} \int \Psi_k^\star \ \nabla_I^2 \ \Psi_k \, d\mathbf{r} \tag{1.8}$$

the second term of Eq. (1.7) being zero when the electronic wave function is real, which leads to complete decoupling

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_I\}) + C_{kk}(\{\mathbf{R}_I\}) \right] \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k \tag{1.9}$$

of the fully coupled original set of differential equations Eq. (1.6). This, in turn, implies that the motion of the nuclei proceeds without changing the quantum state, k, of the electronic subsystem during time evolution. Correspondingly, the coupled wave function in Eq. (1.1) can be decoupled simply

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \approx \Psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \chi_k(\{\mathbf{R}_I\}; t) \tag{1.10}$$

into a direct product of an electronic and a nuclear wave function. Note that this amounts to taking into account only a single term in the general expansion Eq. (1.5).

The ultimate simplification consists in neglecting also the diagonal coupling terms

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_I\}) \right] \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k \tag{1.11}$$

which defines the famous "Born-Oppenheimer approximation". Thus, both the adiabatic approximation and the Born-Oppenheimer approximation are readily derived as special cases based on the particular functional Ansatz Eq. (1.5) of the total wave function.

The next step in the derivation of classical molecular dynamics is the task of approximating the nuclei as classical point particles. How can this be achieved in the framework where a full quantum-mechanical wave equation, χ_k describes the motion of all nuclei in a selected electronic state Ψ_k? In order to proceed, it is first noted that for a great number of physical situations the Born-Oppenheimer approximation can safely be applied, but there are problems where this is not the case. Examples for such break-downs of the Born-Oppenheimer approximations are for instance systems in electronically excited states where the energy separation between different electronic states becomes small (e.g. during photochemical events), systems in strong laser fields, in which electronic and nuclear degrees of freedom are evolving on similar characteristic time scales or Jahn-Teller systems, in which electronic and nuclear degrees of freedom are strongly coupled.

However for a majority of cases in which the system is in the electronic ground state, the Born-Oppenheimer approximation is valid. Based on this

assumption, the following derivation will be built on Eq. (1.11) being the Born-Oppenheimer approximation to the fully coupled solution, Eq. (1.6).
A well-known route to extract semiclassical mechanics from quantum mechanics in general starts with rewriting the corresponding wave function

$$\chi_k(\{\mathbf{R}_I\};t) = A_k(\{\mathbf{R}_I\};t)\ \exp\left[iS_k(\{\mathbf{R}_I\};t)/\hbar\right] \tag{1.12}$$

in terms of an amplitude factor $\mathcal{A}_k$ and a phase S_k which are both considered to be real and $\mathcal{A}_k > 0$ in this polar representation.

Polar Representation of the Nuclear Wavefunction

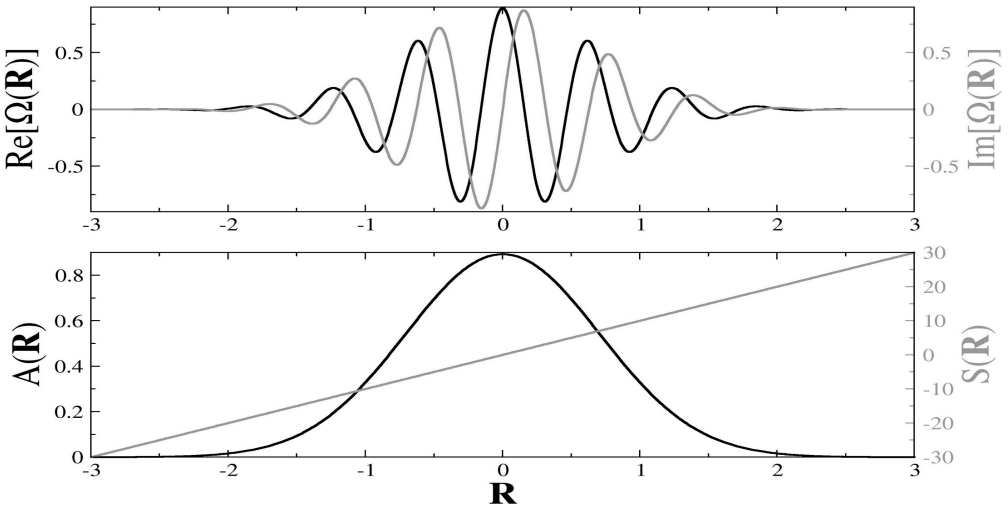

Fig. 1.2 Illustration of a complex nuclear wavefunction χ(R), represented in terms of real and imaginary part (χ(R) = Re[χ(R)] + i Im[χ(R)]; upper panel) and in terms of the two real functions A(R) and S(R) (χ(R) = A(R)exp[iS(R)/ $\hbar$]; lower panel).

After transforming the nuclear wave function in Eq. (1.11) for a chosen electronic state k accordingly and after separating the real and imaginary parts, the equations for the nuclei

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I}\left(\nabla_I S_k\right)^2 + E_k = \hbar^2 \sum_I \frac{1}{2M_I}\frac{\nabla_I^2 A_k}{A_k} \tag{1.13}$$

$$\frac{\partial A_k}{\partial t} + \sum_I \frac{1}{M_I}\left(\nabla_I A_k\right)\left(\nabla_I S_k\right) + \sum_I \frac{1}{2M_I} A_k\left(\nabla_I^2 S_k\right) = 0 \tag{1.14}$$

are re-expressed (exactly) in terms of the new variables S_k and $\mathcal{A}_k$ instead of using Reχ_k and Imχ_k. It is noted in passing that this quantum fluid dynamic (or hydrodynamic, Bohmian) representation. Eqs. (1.13)-(1.14), can actually be used to solve the time-dependent Schrodinger equation.
The relation for the amplitude, Eq. (1.14), may be rewritten after multiplying by $2\mathcal{A}_k$ from the left as a continuity equation

$$\frac{\partial A_k^2}{\partial t} + \sum_I \frac{1}{M_I} \nabla_I \left(A_k^2 \nabla_I S_k \right) = 0 \tag{1.15}$$

$$\frac{\partial \rho_k}{\partial t} + \sum_I \nabla_I \mathbf{J}_{k,I} = 0 \tag{1.16}$$

with the help of the identification of the nuclear probability density $\rho_k = |\chi_k|^2 = \mathcal{A}_k^2$, obtained directly from the definition Eq. (1.12) , and with the associated current density defined as $\mathbf{J}_{k,I} = A_k^2 (\nabla_I S_k)/M_I$.

This continuity equation Eq. (1.16) is independent of ħ and ensures locally the conservation of the particle probability density $|\chi_k|^2$ of the nuclei in the presence of a flux.
More important for the present purpose is a detailed discussion of the relation for the phase S_k, Eq. (1.13), of the nuclear wave function that is associated with the kth electronic state. This equation contains one term that depends explicitly on ħ, a contribution that vanishes

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} \left(\nabla_I S_k \right)^2 + E_k = 0 \tag{1.17}$$

if the classical limit is taken as ħ -> 0. Note that a systematic expansion in terms of ħ would, instead, lead to a hierarchy of semiclassical methods. The resulting equation Eq. (1.17) is now isomorphic to the equation of motion in the Hamilton- Jacobi formulation of classical mechanics

$$\frac{\partial S_k}{\partial t} + H_k \left(\{\mathbf{R}_I\}, \{\nabla_I S_k\} \right) = 0 \tag{1.18}$$

with the classical Hamilton function

$$H_k(\{\mathbf{R}_I\}, \{\mathbf{P}_I\}) = T(\{\mathbf{P}_I\}) + V_k(\{\mathbf{R}_I\}) \tag{1.19}$$

for a given conserved energy $dE_k^{tot} / dt = 0$ and hence

$$\frac{\partial S_k}{\partial t} = -\left(T + E_k \right) = -E_k^{\mathrm{tot}} = \mathrm{const} \tag{1.20}$$

defined in terms of (generalized) coordinates $\{\mathcal{R}_j\}$ and their conjugate canonical momenta $\{\mathcal{P}_j\}$. With the help of the connecting transformation

$$\mathbf{P}_I \equiv \nabla_I S_k \quad \left[= M_I \frac{\mathbf{J}_{k.I}}{\rho_k} \right] \tag{1.21}$$

the Newtonian equations of motion, $\dot{\mathbf{P}}_I = -\nabla_I V_k(\{\mathbf{R}_I\})$, corresponding to

the Hamilton-Jacobi form Eq. (1.17) can be read off

$$\frac{d\mathbf{P}_I}{dt} = -\nabla_I E_k \quad \text{or}$$

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_k^{\mathrm{BO}}(\{\mathbf{R}_I(t)\}) \tag{1.22}$$

separately for each decoupled electronic state k. Thus, the nuclei move according to *classical* mechanics in an effective potential, $\mathcal{V}_k^{BO}$, which is given by the Born-Oppenheimer potential energy surface $\mathcal{E}_k$ obtained by solving simultaneously the *time-independent* electronic Schrodinger equation for the kth state, Eq. (1.3), at the given nuclear configuration $\{\mathcal{R}_I(t)\}$. In other words, this time-local many-body interaction potential due to the quantum electrons is a function of the set of all classical nuclear positions at time t. Since the Born-Oppenheimer total energies in a specific adiabatic electronic state yield directly the forces used in this variant of *ab initio* molecular dynamics, this particular approach is often called "Born-Oppenheimer molecular dynamics".

It is conceivable to fully decouple the task of generating the classical nuclear dynamics from the task of computing the quantum potential energy surface. In a first step, the global potential energy surface $\mathcal{E}_o$, which depends on all nuclear degrees of freedom $\{\mathcal{R}_I\}$, is computed for many different nuclear configurations by solving the stationary Schrodinger equation separately for all these situations. In a second step, these data points are fitted to an analytical functional form to yield a global potential energy surface, from which the gradients can be obtained analytically. In a third step, the Newtonian equations of motion are solved on this surface for many different initial conditions, producing a "swarm" of classical trajectories $\{\mathcal{R}_I(t)\}$. This is, in a nutshell, the basis of classical trajectory calculations on global potential energy surfaces as used very successfully to understand scattering and chemical reaction dynamics of small systems in vacuum.
Such approaches suffer severely from the "dimensionality bottleneck" as the number of active nuclear degrees of freedom increases. One traditional way out of this dilemma, making possible calculations of large systems, is to approximate the global potential energy surface

$$V_{\mathrm{e}}^{\mathrm{E}} \approx V_{\mathrm{e}}^{\mathrm{FF}}(\{\mathbf{R}_I\}) = \sum_{I=1}^{N} v_1(\mathbf{R}_I) + \sum_{I<J}^{N} v_2(\mathbf{R}_I, \mathbf{R}_J) \quad + \sum_{I<J<K}^{N} v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots \tag{1.36}$$

in terms of a truncated expansion of many-body contributions, which is sometimes called a "force field". At this stage, the electronic degrees of freedom are replaced approximately by a set of interaction potentials $\{v_n\}$ and are no longer included as explicit degrees of freedom when the nuclei are propagated. Thus, the mixed quantum/ classical problem is reduced to purely classical mechanics, once the $\{v_n\}$ are determined.
“Standard" molecular dynamics

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{FF}(\{\mathbf{R}_I(t)\}) \quad (1.37)$$

relies crucially on such a force field idea as opposed to *ab initio* molecular dynamics, where the key feature is that the potential and thus the forces are obtained from solving the electronic structure problem concurrently to generating the trajectory $\{\mathcal{R}_I(t)\}$.

In force field-based molecular dynamics, typically only two-body v_2 or three-body v_3 interactions are taken into account, although very sophisticated models exist that include nonadditive many-body interactions. This amounts to a dramatic simplification and removes, in particular, the dimensionality bottleneck since the global potential surface is reconstructed from a manageable sum of additive few-body contributions.

The flipside of the medal is the introduction of the drastic approximation embodied in Eq. (1.36), which basically excludes the study of chemical reactions from the realm of computer simulation.

As a result of the derivation presented above, the essential assumptions underlying standard force field-based molecular dynamics become very transparent.

The electrons follow adiabatically the classical nuclear motion and can be integrated out so that the nuclei evolve on a single Born-Oppenheimer potential energy surface (typically, but not necessarily, given by the electronic ground state), which is generally approximated in terms of few-body interactions.

Actually, force field-based molecular dynamics for many-body systems is only made possible by somehow decomposing the global potential energy.

In order to illustrate this point, consider the simulation of N = 500 argon atoms in the liquid phase where the interactions can be described faithfully by additive two-body terms, i.e. $V_e^{FF}(\{\mathbf{R}_I\}) \approx \sum_{I<J}^{N} v_2(|\mathbf{R}_I - \mathbf{R}_J|)$.

Thus, the determination of the pair potential v_2 from *ab initio* electronic structure calculations consists in computing and fitting a one-dimensional function only. The corresponding task of determining a global potential energy surface, however, amounts to doing that in about 10^{1500} dimensions, which is simply impossible. In the case of neat argon this is obviously not necessary, but this assessment changes drastically if the 500 atoms are not all identical and, for instance, are those that form a small enzyme catalyzing a particular biochemical reaction.