

Background for Research in the Welborn Group

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Potential energy surfaces are a precious tool to understand any chemical reactions (including charge transfer reactions) at the molecular level. It allows the identification of (i) minimum energy wells where reactants and products sit at equilibrium and (ii) the most likely path from one well to another. It is the shape of this path on the surface that defines the reaction kinetics at the macroscopic scale. Due to the easy visualization of the reactant and product states, potential energy surfaces are favored by many for the study of chemical reactions. However, the mapping of a molecular assembly electronic state onto a two (usually) dimensional surface is naturally based on many approximations. A meaningful understanding of how potential energy surfaces are built and drawn is required to be able to use them for a detailed kinetic analysis.

1 Potential energy surfaces

Leaving the spin aside, let \vec{R} and \vec{r} be the coordinate vectors for the nuclei (n) and electrons (e), respectively. The stationary Schrödinger equation of the coupled nuclear-electronic problem reads:

$$\left[T_n(\vec{R}) + T_e(\vec{r}) + V_{en}(\vec{R}, \vec{r}) + V_{ee}(\vec{r}) + V_{nn}(\vec{R}) \right] \Psi(\vec{R}, \vec{r}) = E_{\text{tot}} \Psi(\vec{R}, \vec{r}), \quad (1)$$

where E_{tot} is the total energy of the system. T_n (T_e) is the kinetic energy operator of the nuclei (electrons). V_{en} , V_{ee} and V_{nn} are the operators describing the electro-nuclear, electronic and nuclear electrostatic interactions, respectively. The total wavefunction $\Psi(\vec{R}, \vec{r})$ is an Hilbert space function and can be written as a linear combination of basis functions. Providing that the set of basis functions completely describes the whole of Hilbert space, the expansion is an exact reformulation of $\Psi(\vec{R}, \vec{r})$. Taking the electronic wavefunctions $\{\Psi_{\vec{R}}^i(\vec{r})\}$ as a (complete) basis set, one can write:

$$\Psi(\vec{R}, \vec{r}) = \sum_i \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) \quad (2)$$

where the summation is over the electronic states i and the expansion coefficients $\{\chi_{i\nu}\}$ are the nuclear wavefunctions with quantum number ν . The existence of such functions entails that nuclear and electronic degrees of freedom can be separated. This is justified by the fact that nuclei and electrons move on different time scales due to their substantial

mass difference. Equation 2 is often called the Born-Oppenheimer (or adiabatic) separation. Note that the separation is not “total” in the sense that the electronic wavefunction still depends parametrically upon the nuclear coordinates. Here, we make the difference between the Born-Oppenheimer separation (Equation 2) and the Born-Oppenheimer approximation as defined later. Both originate from the observation that nuclei are effectively immobile compared with electrons. However, it leads to different results and the two terms are not interchangeable.

Substituting Equation 2 into Equation 1 gives:

$$\left[T_n(\vec{R}) + T_e(\vec{r}) + V_{en}(\vec{R}, \vec{r}) + V_{ee}(\vec{r}) + V_{nn}(\vec{R}) \right] \sum_i \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) = E_{\text{tot}} \sum_i \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}). \quad (3)$$

Given that the hamiltonian operators are identical for any electronic state i , we can write:

$$\sum_i \left[T_n(\vec{R}) + T_e(\vec{r}) + V_{en}(\vec{R}, \vec{r}) + V_{ee}(\vec{r}) + V_{nn}(\vec{R}) \right] \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) = \sum_i E_{\text{tot}} \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}). \quad (4)$$

We rearrange the expression to follow the separation of the variables of the wavefunction:

$$\begin{aligned} \sum_i \left[\left(T_n(\vec{R}) + V_{nn}(\vec{R}) \right) \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) + \chi_{i\nu}(\vec{R}) \left(T_e(\vec{r}) + V_{en}(\vec{R}, \vec{r}) + V_{ee}(\vec{r}) \right) \Phi_i(\vec{r}; \vec{R}) \right] \\ = \sum_i E_{\text{tot}} \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}). \end{aligned} \quad (5)$$

Since the electronic wavefunctions Φ_i are eigenstates of the electronic hamiltonian $H_e = T_e + V_{en} + V_{ee}$ with eigenvalue E_i , it yields:

$$\sum_i \underbrace{\left[\left(T_n(\vec{R}) + V_{nn}(\vec{R}) \right) \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) + \chi_{i\nu}(\vec{R}) E_i \Phi_i(\vec{r}; \vec{R}) \right]}_{(T_n(\vec{R}) + V_{nn}(\vec{R}) + E_i) \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R})} = \sum_i E_{\text{tot}} \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}), \quad (6)$$

The action of the kinetic operator for the nuclei, T_n (second order derivative operator in the nuclear configurational space) requires more attention because the electronic wavefunctions depend parametrically on the nuclear coordinates. We rearrange the previous equation as:

$$\sum_i \left[\Phi_i(\vec{r}; \vec{R}) \left(V_{nn}(\vec{R}) + E_i \right) \chi_{i\nu}(\vec{R}) + T_n(\vec{R}) \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) \right] = \sum_i E_{\text{tot}} \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}), \quad (7)$$

and apply the chain rule for differentiating the product of the nuclear and electronic wavefunctions:

$$\begin{aligned} T_n(\vec{R}) \chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) &\propto \vec{\nabla}_{\vec{R}}^2 \left[\chi_{i\nu}(\vec{R}) \Phi_i(\vec{r}; \vec{R}) \right] \\ &\propto \vec{\nabla}_{\vec{R}} \left[\left(\vec{\nabla}_{\vec{R}} \chi_{i\nu}(\vec{R}) \right) \Phi_i(\vec{r}; \vec{R}) + \chi_{i\nu}(\vec{R}) \left(\vec{\nabla}_{\vec{R}} \Phi_i(\vec{r}; \vec{R}) \right) \right] \\ &\propto \underbrace{\left(\vec{\nabla}_{\vec{R}}^2 \chi_{i\nu}(\vec{R}) \right)}_{T_n(\vec{R}) \chi_{i\nu}(\vec{R})} \Phi_i(\vec{r}; \vec{R}) + 2 \left(\vec{\nabla}_{\vec{R}} \chi_{i\nu}(\vec{R}) \right) \left(\vec{\nabla}_{\vec{R}} \Phi_i(\vec{r}; \vec{R}) \right) + \chi_{i\nu}(\vec{R}) \left(\vec{\nabla}_{\vec{R}}^2 \Phi_i(\vec{r}; \vec{R}) \right). \end{aligned} \quad (8)$$

Equation 8 shows that the nuclear and electronic degrees of freedom are not completely decoupled. Physically, this means that the motion of the nuclei can cause a transition between electronic states, which goes against the idea behind the adiabatic separation previously stated. Mathematically, we can describe the deviation to the adiabatic separation by grouping all terms where nuclear and electronic degrees of freedom are not separable as follows:

$$T_n(\vec{R})\chi_{i\nu}(\vec{R})\Phi_i(\vec{r}; \vec{R}) = \Phi_i(\vec{r}; \vec{R})T_n(\vec{R})\chi_{i\nu}(\vec{R}) + \sum_k \Theta_{ik}\chi_{k\nu}(\vec{R})\Phi_i(\vec{r}; \vec{R}), \quad (9)$$

where Θ_{ij} is the nonadiabaticity operator. Two assumptions can now be made, more commonly known as the Born-Oppenheimer approximation. First, we neglect all electronic excitations and the expansion in Equation 2 is truncated to the ground state ($\{i\} = 0$). Therefore, the wavefunction considered - let it be named $\Psi_0(\vec{R}, \vec{r})$ - is not the exact wavefunction. Second, we assume that the heavy nuclei are more localized in space than the electrons and $\vec{\nabla}_{\vec{R}}\Phi_i(\vec{r}; \vec{R})$ becomes negligible in front of $\vec{\nabla}_{\vec{R}}^2\chi_{i\nu}(\vec{R})$. This effectively removes the contribution from the nonadiabaticity operator and, upon the Born-Oppenheimer approximation, Equation 10 becomes

$$T_n(\vec{R})\chi_{0\nu}(\vec{R})\Phi_0(\vec{r}; \vec{R}) \stackrel{\text{BO}}{=} \Phi_0(\vec{r}; \vec{R})T_n(\vec{R})\chi_{0\nu}(\vec{R}). \quad (10)$$

Equation 7 is rewritten accordingly:

$$\Phi_0(\vec{r}; \vec{R}) \left(V_{nn}(\vec{R}) + E_0 \right) \chi_{0\nu}(\vec{R}) + \Phi_0(\vec{r}; \vec{R})T_n(\vec{R})\chi_{0\nu}(\vec{R}) = E_{\text{tot}}\chi_{0\nu}(\vec{R})\Phi_0(\vec{r}; \vec{R}), \quad (11)$$

where E_0 is the ground state energy of the system. Finally, factorizing out the electronic wavefunction, we obtain an expression governing the motion of the nuclei:

$$\left(\underbrace{V_{nn}(\vec{R}) + E_0}_{U_0(\vec{R})} + T_n(\vec{R}) \right) \chi_{0\nu}(\vec{R}) = E_{\text{tot}}\chi_{0\nu}(\vec{R}), \quad (12)$$

where the nuclei are subject to $U_0(\vec{R})$, the ground state electronic potential energy. Since the nuclear coordinate vector has as many dimensions as the triple of the number of atoms in the system, $U_0(\vec{R})$ is an hypersurface. Strictly speaking, it is a surface only for molecular assemblies whose atomic positions can be described by exactly two variables. Nevertheless, we commonly refer to the electronic potential energy in the nuclear configuration space of polyatomic molecules as Potential Energy Surface (PES). Within this formalism, the electronic states are termed adiabatic states.

2 Transitions between potential energy surfaces: crossing, avoided crossing and attempted crossing

In the previous section we saw how PES are the ground state electronic potential energy, including the nuclear repulsion, of a given molecular assembly in the nuclear configuration

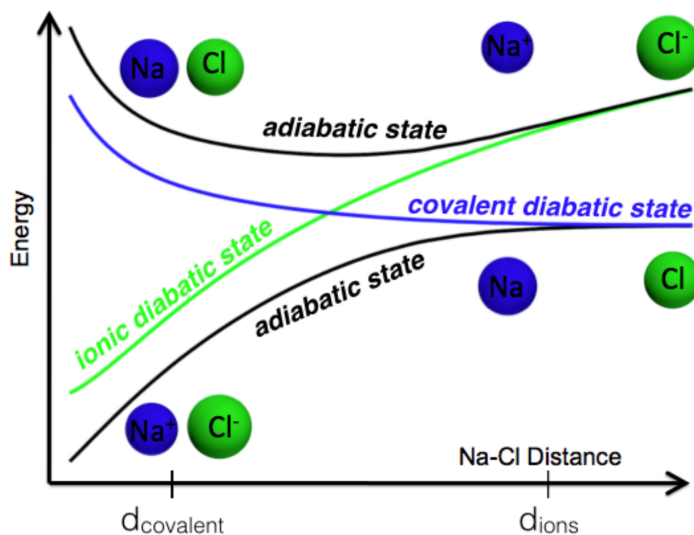


Figure 1: Diabatic and adiabatic electronic potential energy curves for the dissociation of NaCl.

space. At fixed position of the nuclei, the PES provides information about the ground state energy of the molecules involved in a chemical reaction. It is the transition from the reactant PES to the product PES that allows to follow the dynamics of a reaction. Here, we will qualitatively describe how two PES intersect (or do not!). Quantitatively, we often use diabatic states to approximate the true adiabatic states of the system to compute the reaction rate.

Conceptually it is easier to start with the case where the PES reduces to a curve, that is when a single nuclear coordinate is enough to describe the configurational space. A classic example is the dissociation of the sodium chloride molecule, NaCl, where the position of one of the atom, say Cl can be expressed with respect to the position of the other, say Na, through the interatomic distance, d_{NaCl} .

Here, the PES is a curve describing the variation of the potential energy of the salt dissociation reactants or products as a function of the unique variable d_{NaCl} (Figure 2). The dissociation reaction is the transformation upon which the diatomic neutral molecule NaCl splits into its constitutive ions: $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$.

As the reaction progresses d_{NaCl} increases from $d_{\text{NaCl}} = d_{\text{covalent}}$ to $d_{\text{NaCl}} = d_{\text{ions}}$. In such a simple case, we consider that the main contribution to the energy of the system comes from the energy stored in the bond between the sodium and chlorine atoms. In the diabatic picture of the dissociation reaction, the system moves from the PES associated with the energy of the covalent bond onto the PES associated with the energy of the ionic bond. At $d_{\text{NaCl}} = d_{\text{covalent}}$ the energy of the ionic bond is lower than the energy of the covalent bond. The reverse applies at $d_{\text{NaCl}} = d_{\text{ions}}$. Therefore there is a specific value of d_{NaCl} at which the energy of the covalent and ionic bonds are the same. This is the point where the two diabatic PES cross, allowing the transition from reactant to product states. In the adiabatic picture of the reaction one considers the system as a mixed state, linear combination of covalent and ionic states. Therefore, through the range of d_{NaCl} the PES gives neither the

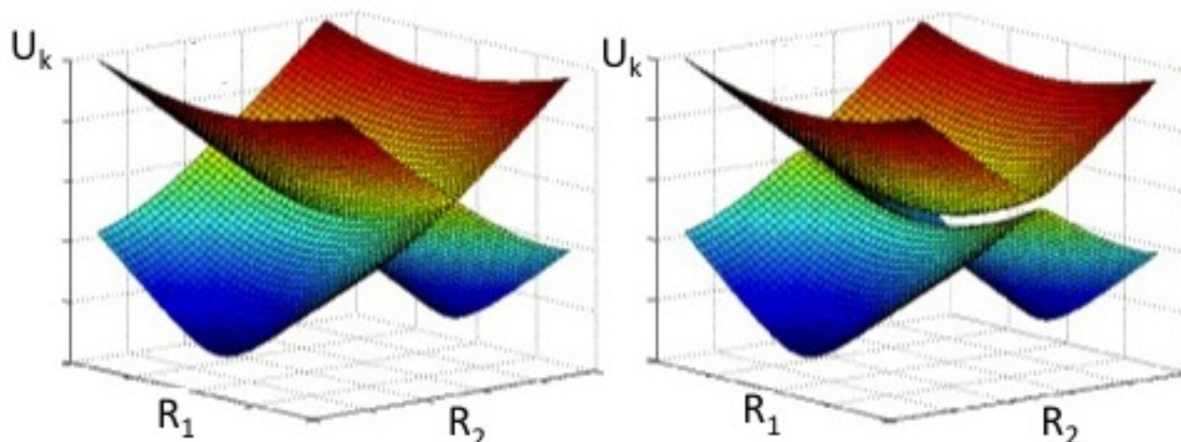


Figure 2: Hypothetical electronic diabatic (left) and adiabatic (right) potential energy surfaces (U_k) as a function of two nuclear coordinates, R_1 and R_2 , while the remaining coordinates are kept fixed under the assumption that it does not affect the potential energy surface for the reaction under study.

energy of the covalent nor ionic bond but the sum of the contribution of each one to the state. The reactants (products) can be seen as the limiting scenario where one has 100 % (0 %) of covalent state and 0 % (100 %) of ionic state. At these points the adiabatic meets the diabatic description of the reaction. In between however the adiabatic PES never cross as opposed to the diabatic ones. This is because energy degeneracy is forbidden between adiabatic states which will adapt upon a change in nuclear configuration as to remain the eigenstates of the molecular hamiltonian. Because of its effect on PES this concept is often referred to as the "non-crossing" or "avoided-crossing" rule. This means that the adiabatic description of a chemical reaction cannot be strictly applied to charge transfer reactions as it cannot account for the transition from one state to another. Naturally these concepts extend to polyatomic molecular assembly where PES are hypersurfaces of the nuclear configuration space. Figure 2.3 provides an illustration of the crossing (a) and avoided crossing (b) of two hypothetical two dimensional PES.

If the gap between two adiabatic PES is narrow enough, as in Figure 2, there will be a finite probability for a transition to happen. In other words, the system will attempt to cross to the product PES and will eventually succeed. Two mechanisms can lead to this "attempted crossing" scenario. First, the charge can directly tunnel through the energy barrier from the reactant to the product equilibrium states. The second mechanism finds its origin in the contribution of the coupling terms in the nonadiabaticity operator (see Equation 10) in the region of avoided crossing. Intuitively the size of the gap between two PES is proportional to the strength of the coupling between the adiabatic states. A small gap is then associated to a weak coupling. In such a case, we can apply the Born-Oppenheimer approximation (which ignores the effect of the nonadiabaticity operator) everywhere but near the avoided crossing. There, the coupling terms, which originate from the action of the nuclear kinetic operator on the nuclear and electronic wavefunctions, cannot be neglected

anymore. It gives the fast moving nuclei the ability to ignore the gap and cross over to the other adiabatic surface. Since it requires that the nuclei have sufficient kinetic energy, it is a thermally activated transition. The crossing between two adiabatic PES in the weak coupling regime is called nonadiabatic transition in reference to the diabatic nature of such an eventuality. The nonadiabatic description is well suited to intermolecular charge transfer because the weak coupling condition is verified. Indeed, in molecular systems, the transferred charge is strongly localized on either the donor (reactant state) or acceptor (product state). Therefore, at first approximation the adiabatic states will mostly be one state or the other, following the diabatic states, and the true mixed nature being only revealed for a narrow range of nuclear configuration. Approximating a charge transfer event as a nonadiabatic transition enables the rate at which the reaction occurs to be calculated. The frequency at which an attempted crossing will be successful is the microscopic phenomenon governing the kinetics of charge transfer reactions. Calculating the rate of charge transfer is quantifying this frequency.

3 Classical approximation of nuclear motion

In the Born-Oppenheimer approximation, the quantum mechanical motion of the nuclei is given by the following time-dependent Schrödinger Equation:

$$i\hbar \frac{\partial \chi_{0\nu}(\vec{R}, t)}{\partial t} = \left(U_0(\vec{R}) + T_n(\vec{R}) \right) \chi_{0\nu}(\vec{R}, t), \quad (13)$$

which can be solved numerically only for a few degrees of freedom. In the high temperature limit and/or heavy nuclei limit, it is sufficient to treat the nuclei as classical degrees of freedom. Classical dynamics can be formally derived from Equation 13. Writing $\chi_{0\nu}(\vec{R}, t)$ in polar representation,

$$\chi_{0\nu}(\vec{R}, t) = A(\vec{R}, t) \exp(iS(\vec{R}, t)/\hbar), \quad (14)$$

where $A(\vec{R}, t) \in R > 0$ and $S(\vec{R}, t) \in R$ and inserting into Equation 13, we get (after separation of real and imaginary parts):

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I S)^2 + U_0(\vec{R}) - \sum_I \frac{\hbar^2}{2M_I} \frac{\nabla_I^2 A}{A} = 0 \quad (15)$$

$$\frac{\partial A}{\partial t} + \sum_I \frac{1}{M_I} (\nabla_I S)(\nabla_I A) + \sum_I \frac{1}{2M_I} A \nabla_I^2 S = 0 \quad (16)$$

Taking the limit $\hbar \rightarrow 0$ (classical limit) in Equation 15 yields an expression for S that is isomorph to the Hamiltonian-Jacobi Equation of classical mechanics:

$$\frac{\partial S^{\text{cl}}}{\partial t} + \sum_I \frac{\vec{p}_I^2}{2M_I} + U_0(\vec{R}) = 0 \quad (17)$$

where S^{cl} is the classical action and \vec{p}_I the classical momentum of particle I . We obtain the classical equations of motions from the derivatives of the Hamiltonian function $H = \sum_I \vec{p}_I^2/(2M_I) + U_0(\vec{R})$:

$$\frac{d\vec{R}_I}{dt} = \frac{\partial H}{\partial \vec{p}_I} \quad (18)$$

and

$$\frac{d\vec{p}_I}{dt} = -\frac{\partial H}{\partial \vec{R}_I} \quad (19)$$

The latter equation is Newton's second law of motion:

$$\vec{f}_I = M_I \frac{d^2 \vec{R}_I}{dt^2} = -\nabla U_0(\vec{R}) \quad (20)$$

4 Molecular dynamics

Assuming classical nuclear motion on a potential energy surface E_R^0 , the time evolution or trajectory of the nuclei can be solved using Newton's equation of motion:

$$\vec{f}_I = M_I \frac{d^2 \vec{R}_I}{dt^2} \quad (21)$$

$$\vec{f}_I = -\frac{\partial U_0(\vec{R})}{\partial \vec{R}_I}, \quad (22)$$

where $\vec{f}_I = d\vec{p}_I/dt$ is the force on atom I . Solving the coupled equation for all atoms I in the system is generally referred to as molecular dynamics (MD) calculation.

If the potential energy $U_0(\vec{R})$ is given by an empirical function of the nuclear coordinates (i.e. force fields), it is termed classical molecular dynamics. If $U_0(\vec{R})$ is obtained from *ab initio* or density functional theory (DFT) the calculations are termed *ab initio* molecular dynamics (AIMD) or density functional based molecular dynamics (DFTMD). There are two ways of carrying out AIMD or DFTMD simulations in practice. One option is to carry out *ab initio* or DFT energy calculations for many different configurations of the system followed by a fit of the points to an analytic representation of $U_0(\vec{R})$ prior to the MD simulation. Once $U_0(\vec{R})$ is obtained Equations 21-22 are solved. The other option is to solve the electronic structure problem and Equations 21-22 simultaneously. This latter option is termed on the fly AIMD or DFTMD, which is nowadays the standard.

5 Time stepping algorithms

The classical dynamics of interacting many-particle systems as given by Equations 21-22 cannot be solved analytically. Iterative numerical schemes have to be used.

The first step is a discretization of time in terms of small increments called time steps which we assume to be of equal length δt . Counting the successive equidistant points on the

time axis by the index m , $t_m = m\delta t$ with $t_0 = 0$, the evolution of the system is described by a series of the coordinate values:

$$\begin{aligned}\vec{R}(t_0) &= \vec{R}(0) \\ \dots \\ \vec{R}(t_{m-1}) &= \vec{R}(t_m - \delta t) \\ \vec{R}(t_m) & \\ \vec{R}(t_{m+1}) &= \vec{R}(t_m + \delta t)\end{aligned}\tag{23}$$

plus a similar series for the velocities $\frac{d\vec{R}}{dt}$. In the following we will discuss three popular algorithms for computation of the discrete series of positions and velocities, the Verlet, Velocity Verlet and leap-frog algorithms.

5.1 The Verlet algorithm

The algorithm is based on a Taylor expansion of the coordinates around t forward and backward in time.

$$\vec{R}_I(t + \delta t) = \vec{R}_I(t) + \frac{d\vec{R}_I}{dt}(t)\delta t + \frac{\vec{f}_I(t)}{2M_I}\delta t^2 + \frac{1}{6}\frac{d^3\vec{R}_I}{dt^3}(t)\delta t^3 + \mathcal{O}(\delta t^4)\tag{24}$$

$$\vec{R}_I(t - \delta t) = \vec{R}_I(t) - \frac{d\vec{R}_I}{dt}(t)\delta t + \frac{\vec{f}_I(t)}{2M_I}\delta t^2 - \frac{1}{6}\frac{d^3\vec{R}_I}{dt^3}(t)\delta t^3 + \mathcal{O}(\delta t^4)\tag{25}$$

Adding these two equations gives

$$\vec{R}_I(t + \delta t) = 2\vec{R}_I(t) - \vec{R}_I(t - \delta t) + \frac{\vec{f}_I(t)}{M_I}\delta t^2 + \mathcal{O}(\delta t^4),\tag{26}$$

meaning that we need to know the positions at time t and $t - \delta t$ to know the positions at time $t + \delta t$. Note that the velocity does not enter this equation (the force is independent of the velocity).

The velocities are obtained by subtracting Equation 25 from Equation 24:

$$\frac{d\vec{R}_I}{dt}(t) = \frac{1}{2\delta t} \left[\vec{R}_I(t + \delta t) - \vec{R}_I(t - \delta t) \right] + \mathcal{O}(\delta t^3).\tag{27}$$

Since we need to know the positions at time $t + \delta t$ and $t - \delta t$ to know the velocity at time t , the velocity update is one step behind the position update. This is an issue to calculate system properties that depend on the velocity such as the kinetic energy for example. This lead to a modification of the algorithm, called the Velocity Verlet algorithm.

5.2 The Velocity Verlet algorithm

Here, the update of the positions and the velocities occur at the same time step. The positions are given by Equation 24 neglecting terms higher than second order.

$$\vec{R}_I(t + \delta t) = \vec{R}_I(t) + \frac{d\vec{R}_I}{dt}(t)\delta t + \frac{\vec{f}_I(t)}{2M_I}\delta t^2 + \mathcal{O}(\delta t^3)\tag{28}$$

We can then calculate the force at the updated positions:

$$\vec{f}_I(t + \delta t) = \vec{f}_I(\vec{R}_I(t + \delta t)). \quad (29)$$

Considering Equation 25 for going back in time from $t + \delta t$ to t , we can write:

$$\vec{R}_I(t) = \vec{R}_I(t + \delta t) - \frac{d\vec{R}_I}{dt}(t + \delta t)\delta t + \frac{\vec{f}_I(t + \delta t)}{2M_I}\delta t^2 + \mathcal{O}(\delta t^3). \quad (30)$$

Adding Equation 30 to the forward expansion Equation 28, we get:

$$\frac{d\vec{R}_I}{dt}(t + \delta t) = \frac{d\vec{R}_I}{dt}(t) + \frac{1}{2M_I} \left[\vec{f}_I(t) + \vec{f}_I(t + \delta t) \right] \delta t + \mathcal{O}(\delta t^3), \quad (31)$$

to update the velocities. Note that the Verlet and Velocity Verlet algorithms are equivalent and produce exactly the same trajectory.

5.3 The leap-frog algorithm

The leap-frog algorithm is another modification of the Verlet algorithm. In this scheme, the positions and velocities are half a time step out of step:

$$\frac{d\vec{R}_I}{dt}(t - \delta t/2) = \frac{1}{\delta t} \left[\vec{R}_I(t) - \vec{R}_I(t - \delta t) \right] \quad (32)$$

$$\frac{d\vec{R}_I}{dt}(t + \delta t/2) = \frac{1}{\delta t} \left[\vec{R}_I(t + \delta t) - \vec{R}_I(t) \right] \quad (33)$$

The forces at time t are used to advance the velocities of a full time step (the velocities leap-frog over the current time step t):

$$\frac{d\vec{R}_I}{dt}(t + \delta t/2) = \frac{d\vec{R}_I}{dt}(t - \delta t/2) + \frac{\vec{f}_I(t)}{M_I}\delta t, \quad (34)$$

which allows us to update the positions:

$$\vec{R}_I(t + \delta t) = \vec{R}_I(t) + \frac{d\vec{R}_I}{dt}(t + \delta t/2)\delta t. \quad (35)$$

Finally, the velocities at time t are obtained with:

$$\frac{d\vec{R}_I}{dt}(t) = \frac{1}{2} \left[\frac{d\vec{R}_I}{dt}(t - \delta t/2) + \frac{d\vec{R}_I}{dt}(t + \delta t/2) \right] \quad (36)$$

The leap-frog algorithm is more efficient as it only requires to store one set of positions and one set of velocities.

5.4 The Beeman algorithm

The Beeman algorithm is closely related to the Verlet algorithm and provides a more accurate expression for the velocities and better energy conservation. This is the algorithm we use in the group when running MD in Tinker.

$$\vec{R}_I(t + \delta t) = \vec{R}(t) + \frac{d\vec{R}_I}{dt}(t)\delta t + \frac{1}{6} \left[4 \frac{\vec{f}_I(t)}{M_I} - \frac{\vec{f}_I(t - \delta t)}{M_I} \right] \delta t^2 \quad (37)$$

$$\frac{d\vec{R}_I}{dt}(t + \delta t) = \frac{d\vec{R}_I}{dt}(t) + \frac{1}{6} \left[2 \frac{\vec{f}_I(t + \delta t)}{M_I} + 5 \frac{\vec{f}_I(t)}{M_I} - \frac{\vec{f}_I(t - \delta t)}{M_I} \right] \quad (38)$$

Note that the more complex expressions make the calculation more expensive.

6 Metropolis Monte Carlo methods

Given a system at constant number N , volume V and temperature T , the probability p_i of finding it in a microstate i with total energy E_i is proportional to

$$p_i = \frac{\exp(-\beta E_i)}{Q(N, V, T)}, \quad (39)$$

where $\beta = 1/(k_B T)$ and k_B is Boltzmann's constant. The partition function $Q(N, V, T)$ is defined as:

$$Q(N, V, T) = \sum_i \exp(\beta E_i), \quad (40)$$

and the average of an operator A is given by:

$$\langle A \rangle = \sum_i p_i A_i = \frac{1}{Q} \sum_i \exp\left(-\frac{E_i}{k_B T}\right) A_i, \quad (41)$$

where A_i is the physical value of A for state i . The simplest way to calculate this average with Monte Carlo would be to choose M states at random and average:

$$A_M = \frac{\sum_i^M A_i \exp(-\beta E_i)}{\sum_i^M \exp(-\beta E_i)}. \quad (42)$$

In theory the limit of an infinite number of sampling points ($M \rightarrow \infty$) gives $A_M \rightarrow \langle A \rangle$. However, in practice there are two major issues: (i) the number of state points in a statistical mechanical system usually grows exponentially with system size and (ii) averages like Equation 42 are typically dominated by a small fraction of these states, which are very unlikely to be found via random uniform sampling.

To address this issue, we will use importance sampling with the Boltzmann distribution. The most popular technique to do this in atomic and molecular simulations is based on a biased random walk through configuration space as follows:

- Start with a given configuration o for which the Boltzmann factor is $\exp(-\beta E_o)$

- Choose and accept a new configuration n , with energy E_n , with transition probability $\pi(o \rightarrow n)$
- Calculate the value of the operator you are interested in and add it to your average
- Repeat to create a Monte Carlo trajectory through phase space

Note that transition probabilities summed over all states must add up to unity. This helps define the probability that we stay at the same state o in a Monte Carlo step:

$$\pi(o \rightarrow o) = 1 - \sum_{n \neq o} \pi(o \rightarrow n) \quad (43)$$

These stochastic Monte Carlo trajectories are different from the deterministic trajectories you will encounter in molecular dynamics techniques. They don't need to resemble the realistic dynamics of a physical system at all. In fact, it is exactly this property of "non-realism" that makes the Monte Carlo technique so useful: we can invent clever methods that sample phase space much more efficiently than a realistic dynamics would.

Detailed balance

At any given time in a Monte Carlo simulation, we can measure the probability of sampling state o , $P(o)$ by counting what fraction of walkers are in state o . Once the system has reached equilibrium, $P(o)$ should be stationary: the average population of walkers in any state o should not change with time (i.e. Monte Carlo steps). This implies that the number of systems making a transition to a given state is equal to the number of systems leaving that state. In mathematical form, it yields:

$$P(o) \sum_i \pi(o \rightarrow i) = \sum_j P(j) \pi(j \rightarrow o). \quad (44)$$

In practice, a more stringent condition is usually imposed:

$$P(o) \pi(o \rightarrow n) = P(n) \pi(n \rightarrow o), \quad (45)$$

which is called detailed balance. In equilibrium, the average number of accepted moves from a state o to any other state n is exactly cancelled by the number of reverse moves from n to o . Detailed balance guarantees that, once equilibrium is established, the ensemble of random walkers populates the state o with the correct distribution $P(o)$.

In the Metropolis Monte Carlo method, we impose a Boltzmann distribution: $P(i) \propto \exp(\beta E_i)$. To choose a transition probability that satisfies detailed balance, it is useful to split up the determination of $\pi(o \rightarrow n)$ into two steps: (i) choose a new configuration n with a transition matrix probability $\alpha(o \rightarrow n)$ (ii) accept or reject this new configuration with an acceptance probability $\text{acc}(o \rightarrow n)$. In other words, the transition probability is rewritten as:

$$\pi(o \rightarrow n) = \alpha(o \rightarrow n) \text{acc}(o \rightarrow n). \quad (46)$$

Many Monte Carlo methods take α to be symmetric, i.e. $\alpha(o \rightarrow n) = \alpha(n \rightarrow o)$. The detailed balance condition therefore implies that:

$$\frac{\pi(o \rightarrow n)}{\pi(n \rightarrow o)} = \frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{P(n)}{P(o)} = \exp(-\beta(E_n - E_o)). \quad (47)$$

By choosing transition probabilities $\pi(o \rightarrow n)$ in this way, which conserves detailed balance, the equilibrium population of Monte Carlo trajectories will populate the states with the desired Boltzmann distribution.

There are many possible choices of $\text{acc}(o \rightarrow n)$ that would satisfy detailed balance and condition 47. The metropolis algorithm, by far the most popular recipe, states:

$$\begin{aligned} \text{acc}(o \rightarrow n) &= P(n)/P(o) = \exp(-\beta(E_n - E_o)) && \text{if } P(n) < P(o) \\ &= 1 && \text{if } P(n) \geq P(o), \end{aligned} \quad (48)$$

which means that if the energy decreases we always accept the trial move whereas if the energy increases we accept the move with probability proportional to the Boltzmann factor of the energy difference.