

Density functional theory based MD

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1 Introduction

In order to improve computer simulations, an accurate treatment of microscopic interactions is an essential requirement. A quantum mechanical description of a system contains all information on interactions, however, a straightforward solution of the Schrödinger equation is accompanied by an exceeding computational cost [1]. Therefore, approximations must be made. In this handout, density functional theory is introduced as a quantum mechanical method to simplify a system and compute the ground state properties. Density functional theory (DFT)-based molecular dynamics combines quantum mechanical calculations with molecular dynamic simulations and represents one possible choice of quantum mechanical calculation methods in the framework of *ab initio* molecular dynamics (AIMD) [2]. Since AIMD simulations acquire knowledge of a physical system without including experimental data, nowadays, AIMD is an indispensable tool for many body systems in physics, chemistry and biology [2, 3, 4].

2 The Potential energy surface

In order to describe the states and dynamic evolution of a many body system quantum mechanically, the potential energy surface (PES) is introduced. Here, we use a single water molecule as a paradigm. Considering symmetry and assuming the O-H bonds to have the same length, the nuclear positions of the H_2O molecule can be described by two degrees of freedom [5]: The bond length between the O-H atoms q_1 and the H-O-H angle q_2 . For the following, we assume that the potential energy of the molecule can be calculated for a certain state of q_1 and q_2 . The potential energy surface E_{PES} is introduced as the surface of potential energies, resulting from all possible values of q_1 and q_2 , and can be seen in figure 1. The minimum of the PES is the equilibrium state of the system, which in figure 1 is denoted

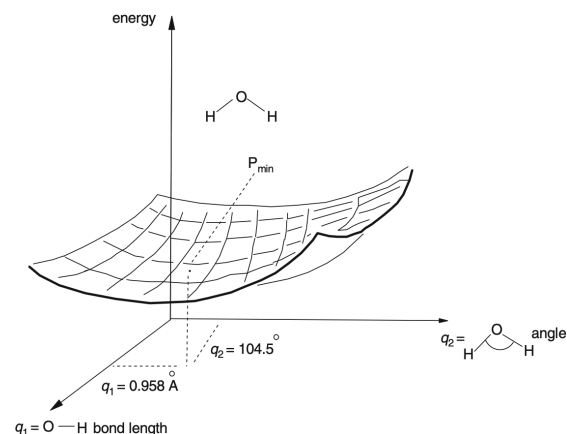


Figure 1: Schematic potential energy surface of a H_2O molecule [5].

by P_{\min} . The concept of the potential energy surface can be expanded to more complex many body systems.

Considering dynamic systems, points on the PES can be explored over time, however, the Born-Oppenheimer approximation must be taken into account, since it decouples electronic and nuclear motion. Due to the differences in mass, time scales of electronic and nuclear motions are of different order of magnitude. Electronic response seems almost sudden on nuclear timescales, whereas on electronic timescales nuclear motion seems almost static. In Born-Oppenheimer approximated systems, a change in nuclear configuration causes an instantaneous rearrangement of the electronic ground state configuration [1, 2].

Moreover, forces can be calculated from the negative gradient of the potential energy $\mathbf{F} = -\nabla E_{\text{PES}}(\mathbf{R})$, where \mathbf{R} denotes the set of degrees of freedom of a system [6]. Further derivatives provide a classifications of points on the PES. Knowing the PES would result in a complete knowledge of all possible nuclear states, which the system can occupy, provided by the assumption of electronic ground state configuration.

The concept of the PES allows us to treat nuclei as classical particles and involve quantum mechanical interactions of electrons simultaneously. The system's states are described in a classical sense, however, the interactions are treated accurately. In the framework of the PES, density functional theory (DFT) will be introduced as a method to calculate the potential energy and other ground state properties.

3 The density functional theory

3.1 The many body problem

An isolated, non-relativistic system of N nuclei and N_e electrons can be described by the time-independent Schrödinger equation

$$H\Psi = E\Psi, \quad (1)$$

$$(T_N + T_e + V_{ee}(\mathbf{r}) + V_{Ne}(\mathbf{R}, \mathbf{r}) + V_{NN}(\mathbf{R}))\Psi(\mathbf{R}, \mathbf{x}) = E\Psi(\mathbf{R}, \mathbf{x}), \quad (2)$$

where T represents the kinetic operators of nuclei (index N) and electrons (index e) [1]. The potential operators V_{ij} label the interaction between the particles denoted in the indices $i, j \in \{e, N\}$. All nuclei positions are labeled with \mathbf{R} and all electronic positions (\mathbf{r}) and spins (s) with $\mathbf{x} = (\mathbf{r}, s)$. The time-independent Schrödinger equation is the system's energy eigenvalue equation with eigenvalue E and eigenstates Ψ .

Since for sufficiently large many body systems equation 2 is highly complex, approximations are required to provide numerical solutions. Considering the timescales of dynamic evolution, the Born-Oppenheimer approximation represents a useful approach, that factorizes the total wave function Ψ into an electronic Φ and nuclear wave function χ , i.e. $\Psi = \chi \cdot \Phi$. As a consequence, the eigenvalue equation splits into an electronic and nuclear part [1]:

$$(T_N + \varepsilon_0(\mathbf{R}) + V_{NN}(\mathbf{R}))\chi(\mathbf{R}) = E\chi(\mathbf{R}), \quad (3)$$

$$(T_e + V_{ee}(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}))\Phi_0(\mathbf{x}, \mathbf{R}) = \varepsilon_0(\mathbf{R})\Phi_0(\mathbf{x}, \mathbf{R}), \quad (4)$$

where ε_0 is the energy eigenvalue of the electronic Schrödinger equation. Moreover, electronic excitation can be neglected by assuming the adiabatic approximation, wherefore electrons will always occupy the ground state Φ_0 . The eigenvalue equations show that the system energy E in equation 3 depends on the eigenvalue ε_0 of the electronic Schrödinger equation (equation 4).

Therefore, the electronic ground state is necessary to determine the nuclear behavior. Further approximations on nuclear behavior are discussed in section 4.

In order to obtain a higher accuracy, the electronic ground state needs to be calculated quantum mechanically [1]. In equation 4, the ionic positions \mathbf{R} induce an external potential $v(\mathbf{r})$. The electronic Schrödinger equation becomes

$$(T_e + V_{ee} + V_{\text{ext}})\Phi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \varepsilon_0 \Phi_0(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (5)$$

with the external potential operator $V_{\text{ext}} = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i)$.

So far, this handout followed an approach simplifying a many body system. In order to continue breaking down the system to become numerically solvable, the density functional theory (DFT) is introduced. It represents one of several approximation methods to solve equation 5. DFT enables numerical calculations of the quantum mechanical ground state in an affordable computational expense.

3.2 Hohenberg-Kohn DFT

Density functional theory is based on the electronic density $n(\mathbf{r})$ rather than wave functions $\Phi(\mathbf{r})$. Physical properties as the energy $E[n(\mathbf{r})]$ will depend on the density and become functionals, since the density is a function of space.

The density is defined by

$$n(\mathbf{r}) = N_e \sum_{\sigma} \int d\mathbf{x}_2 \dots \int d\mathbf{x}_N |\underbrace{\Phi(\mathbf{r}, \sigma, \mathbf{x}_2, \dots, \mathbf{x}_N)}_{\mathbf{x}_1}|^2, \quad (6)$$

$$N_e = \int d\mathbf{r} n(\mathbf{r}) \quad (7)$$

and normalized to the number of electrons N_e [7].

In 1964, Hohenberg and Kohn established two theorems, that represent the basis of DFT. The first theorem proves that "... $v(\mathbf{r})$ is a unique functional of $n(\mathbf{r})$, apart from a trivial additive constant." [8], i.e. the ground state density determines all properties of the system uniquely. Since all properties can be expressed in terms of the density $n(\mathbf{r})$, the dependencies of the ground state description reduce, from $3N_e$ variables in the wave function image, to three variables. The second Hohenberg-Kohn theorem states that the ground state density uniquely minimizes the energy functional $\varepsilon[n(\mathbf{r})] = \varepsilon_0$ [8]. Thus, the variational principle can still be applied.

Even though Hohenberg-Kohn equations reduce the dimensions, the system does not appear to be simplified yet. The theorems further state the possibility to obtain the ground state using the density, however, the density still remains unknown. A solution for this issue is provided by the Kohn-Sham construction.

3.3 Kohn-Sham equations

The Kohn-Sham construction transfers the image of interacting electrons constrained by an external potential, into an image of non-interacting quasiparticles experiencing an effective (external) potential $v_{\text{eff}}[n]$. Both images return the ground state density. The Hohenberg-Kohn theorems, therefore, allow us to use both images to obtain the ground state properties by minimizing the energy functional.

The time-independent Schrödinger equation decouples for the Kohn-Sham single particle wave

functions (orbitals) $\phi_i(\mathbf{r})$ and are called the Kohn-Sham single particle equations

$$\left(-\frac{1}{2}\Delta_i + v_{\text{eff}}[n]\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \quad (8)$$

where Hartree atomic units are used ($\hbar = m_e = e = 1$) [9]. The density also simplifies to [9]

$$n(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2. \quad (9)$$

The effective potential (equation 10) is expressed in terms of the external potential $v(\mathbf{r})$, the Coulomb repulsion and the exchange-correlation functional E_{XC} [7]

$$v_{\text{eff}}[n] = v(\mathbf{r}) + \underbrace{\int d(\mathbf{r}') \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}}_{v_{\text{H}}} + \underbrace{\frac{\delta E_{\text{XC}}}{\delta n(\mathbf{r})}}_{v_{\text{XC}}[n]}. \quad (10)$$

The second term, which describes the Coulomb repulsion, is called the Hartree potential v_{H} and is well defined if the density is known [10]. The third potential $v_{\text{XC}}[n] = \frac{\delta E_{\text{XC}}}{\delta n(\mathbf{r})}$ describes exchange and correlation contributions and is the functional derivative of the exchange correlation functional in terms of the density. The concept behind the exchange correlation functional is further discussed in section 3.4. Since all fictitious particles in equation 8 are equally affected by the effective potential, the Kohn-Sham construction transform the system in terms of a mean-field approach. The single particle equations and the energy functional become

$$\left(-\frac{1}{2}\Delta_i + v(\mathbf{r}) + v_{\text{H}}[n] + v_{\text{XC}}[n]\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \quad (11)$$

$$\varepsilon[n] = T_{\text{s}}[n] + \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + U[n] + E_{\text{XC}}[n], \quad (12)$$

where $T_{\text{s}}[n]$ is the single particle kinetic energy and $U[n]$ the coulomb repulsion [8, 11]. In order to calculate the energy in equation 12, the Kohn-Sham equations (equation 11) need to be solved for the single particle wave functions, which requires the density. Consequently, the energy (as a functional of the electron density) could be calculated if the exchange-correlation energy E_{XC} would be known. This statement could be exemplified by rewriting the energy into a known and unknown part [10]

$$\varepsilon[n(\mathbf{r})] = E_{\text{known}}[n(\mathbf{r})] + E_{\text{XC}}[n(\mathbf{r})]. \quad (13)$$

The ground state energy could be calculated exactly, if the exchange-correlation functional would be known exactly [12]. The form of the exchange-correlation functional turns out to be an essential part in DFT.

In summary, the Kohn-Sham single particle image describes the system in terms of a mean field approach. Interactions between electrons are included in the exchange correlation functional and create an effective potential for the non-interacting fictitious particles.

3.4 Exchange-correlation functional

Before transforming into the Kohn-Sham image, electrons interact via correlation (spin independent) and exchange interaction governed by the Pauli exclusion principle (spin dependent). Transforming into the Kohn-Sham single particle image, both interactions are included in the exchange-correlation functional $E_{XC}[n] = E_X[n] + E_C[n]$, which can be split in terms of an exchange $E_X[n]$ and correlation part $E_C[n]$ [7]. DFT is an exact theory, however, approximations must be made for a practical use, since the exchange-correlation functional is not exactly known. According to the Hohenberg-Kohn theorems, this functional has a uniform solution and was further titled as "...holy grail of electronic structure theory..."[12], as the solution cannot be derived analytically.

Approximations reach different levels of complexity and can be classified into local density approximations (LDA), generalized gradient approximations (GGA), non-local approximations etc. Since there are also hybrid functionals, a strict classification is not applicable, but in order to provide a rough overview, the following will expand on the LDA, GGA and non-local functionals.

As the name suggests, LDA only involves the local density. The exchange-correlation energy can be formulated as $E_{XC}^{LDA}[n] = \int d\mathbf{r} f(n(\mathbf{r}))$. The LDA is the exact solution for the homogeneous electron gas, hence the explicit analytic function $f(n(\mathbf{r}))$ can be deduced from this example [12]. For non-neutral spin systems, LDA can be expanded to the local spin density approximation (LSDA) [4]. LDA provides good results for systems with slowly varying densities, whereas for strong variations in the density, the approximation needs to be enhanced [11]. Besides local information of the density, semi-local contributions, i.e. gradient approximations $\nabla n(\mathbf{r})$, improve the density approximation and are known as GGA. The general form can be written as $E_{XC}^{GGA}[n] = \int d\mathbf{r} f_{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \nabla^2 n(\mathbf{r}))$, with f_{GGA} being the explicit function of the GGA [1]. Local and semi-local functionals can be combined in versatile ways, however, non-local effects like long-range Coulomb interaction can only be approximated by non-local functionals $E_{XC}^{nonloc}[n] = \int d\mathbf{r} f_{nonloc}(n(\mathbf{r}, \mathbf{r}'))$ [12, 13, 14]. Different exchange correlation functionals provide different advantages in regard to physical interactions. Therefore, the choice of the exchange correlation functional is based on the complexity of the interactions. Depending on the physical system, it is selected in a way to provide a minimum of computational overhead and maximum accuracy.

3.5 Basis sets and pseudopotentials

In order to solve equation 11 for the ground state density, an analytical description of the orbitals (eigenstates $|\phi_i\rangle$ of the Kohn-Sham single particle equations) is necessary. This is done by projecting them onto an arbitrary basis $|n\rangle$

$$|\phi_i\rangle = \sum_{n=1}^{\infty} \langle n|\phi_i\rangle |n\rangle . \quad (14)$$

Since infinite basis sets are practically impossible to realize, all numerically applied quantum mechanical calculations approach the projection onto a finite basis set. In order to minimize the loss of the finite projection, the basis set should represent the underlying physics of the system. Further, the approximation accuracy increases with increasing length of the basis set, however, the same holds for the computational effort [4]. In regard to computational implementation, a balance between both accuracy and computational cost is necessary.

Basis sets can be distinguished in spatially localized (atomic-like orbitals) and extended types

(plane-wave basis sets). The plane-wave basis set is evolved in a Fourier expansion up to a certain cutoff energy and extends over position space. It is mostly used for periodic systems [1]. For isolated systems, spatially localized basis functions like Gaussian functions are more appropriate.

Electronic interactions mostly are due to valence electrons, rather than core electrons. In order to improve performances, ionic and core-electronic potentials are approximated together by pseudopotentials, in a so-called "frozen core" calculation, rather than an "all electron" calculation. Regarding the cutoff, they are classified into *soft* and *hard* pseudopotentials [10].

3.6 The Self consistent solution

In order to perform numerical calculations, the variational principle is applied using the self consistent field (SCF) method. Combining equations 11 and 12, they show a recursive behaviour, i.e. an initial density leads to another density, that can be applied again to calculate a further density [15]. Due to the self consistency of the system, this process can converge, i.e. the process will be finished if the new density $n(\mathbf{r})_{n+1}$ (energy) lies within a certain criterion regarding the old density $n(\mathbf{r})_n$ (energy). The converged density is the result for the ground state density. Based on the obtained ground state density, all electronic ground state properties can be calculated [16]. The convergence is not guaranteed, but it can be improved by enhanced iteration methods [15]. Also a clever guess of the initial density reduces the number SCF iterations.

4 *Ab initio* MD

4.1 Molecular dynamics

In classical molecular dynamics, N particles are interacting via mutual forces. Each state is described by spatial and momentum coordinates $(\mathbf{R}_I, \mathbf{P}_I)$, where I iterates over all particles. The state of the system is described by a set of all particle coordinates $(\mathbf{R}, \mathbf{P}) := (\{\mathbf{R}_I\}, \{\mathbf{P}_I\})$. Knowing forces due to the mutual interaction, the particle motion can be simulated by integrating the Newtonian equations of motion over time, however, the forces need to be updated after each integration step. Since the time step can not be infinitely small, MD simulation will never be perfectly precise, but can be an accurate approximation. A requirement for accurate simulations is an accurate description of the forces.

In molecular simulations of sufficiently large system, ergodicity is assumed, i.e. time and ensemble averages of observables are equal $\bar{A} = \langle A \rangle$. Information on the positions and velocities of nuclei during their motion allows us to calculate observables, e.g. the radial distribution function $g(r)$ (RDF)

$$g(r) = \frac{K}{r^2} \left\langle \sum_{I \neq J} \delta(|\mathbf{R}_I - \mathbf{R}_J| - r) \right\rangle, \quad (15)$$

where K is a normalization constant and r the radial distance [1].

4.2 AIMD

In order to adapt equation 3 into a classical scheme, nuclear motion can be derived mathematically by considering the classical limit of quantum mechanics [2]. Particle I at location \mathbf{R}_I with momentum \mathbf{P}_I will follow the Newtonian equation of motion

$$\mathbf{F}_I = \frac{d\mathbf{P}_I}{dt} = -\nabla_I E_{\text{PES}}(\mathbf{R}) = -\nabla_I (V_{\text{NN}}(\mathbf{R}) + \varepsilon_0(\mathbf{R})) \quad (16)$$

where \mathbf{F}_I is the force acting on the i -th particle and $\nabla_I E_{\text{PES}}(\mathbf{R})$ can further be seen as slope of the PES [2]. The PES is composed of the potential $V_{\text{NN}}(\mathbf{R})$, that is mutually induced by the nuclei and an electronic part $\varepsilon_0(\mathbf{R})$ [1]. The calculation of $\nabla_I V_{\text{NN}}(\mathbf{R})$ is comparatively straightforward, whereas $\nabla_I \varepsilon_0(\mathbf{R})$ is the demanding part of the force calculation in AIMD simulations. In *ab initio* molecular dynamics (AIMD) simulations, the gradients of the PES are calculated by electronic structure methods as DFT, which solve the electronic Schrödinger equation numerically [1, 4]. AIMD enables MD simulations of many body systems without using pre-formulated potentials describing the interactions. By avoiding those explicitly formulated potentials, the system is simulated "from scratch" i.e. with a minimum of external input. In AIMD simulations, values and gradients of the PES are calculated quantum mechanically "on the fly" [4]. Comparing AIMD results to experimental data can yield insight into electronic properties and mechanisms. *Ab initio* molecular dynamics can further predict properties, which have not been verified with experimental measurements yet [10]. AIMD therefore represents an interface between macroscopic observables and microscopic properties on quantum mechanical scales.

4.3 Examples of AIMD methods

Modern AIMD simulations have versatile applications, however, there are basic concepts classifying AIMD simulations. In the following, two fundamental methods will be presented [17].

Born-Oppenheimer MD The first method is characterized by performing DFT calculations at each time step in order to obtain the forces. The computational overhead of many successive SCF loops can be reduced by cleverly choosing the initial density. The initial wave functions (i.e. base of the density) are propagated in a time-reversible way to generate the following initial wave functions [17]. Nuclei are evolving directly on the PES, since each point on the surface is calculated explicitly. This method is commonly known as Born-Oppenheimer molecular dynamics (BOMD) [10].

Car-Parrinello MD Besides BOMD, an alternative time evolution method of AIMD was proposed in 1985 by Car and Parrinello in order to reduce the computational time [18]. In Car-Parrinello molecular dynamics (CPMD), the ground state energy is solved via DFT as an initial condition, however, the MD is generated by extending the equations of classical dynamics. Additional fictitious electronic degrees of freedom are added to the classical nuclear equations of motion. These additional degrees of freedom enable an approximation of electronic state evolution. The resulting electronic behaviour is controlled by a fictitious mass. Instead of exploring the energy surface directly (like BOMD), nuclear motion is approximated based on the initially calculated energy through DFT [1, 10, 17].

Regarding computational power that currently is available, CPMD and BOMD are almost equally efficient, however, CPMD can further be applied for time-dependent DFT e.g. for excited state calculations [2].

4.4 Applications

Within various applications from solid state physics, phase transitions, surface structures, molecules and many more [2], the application of DFT-based AIMD allows us to investigate complex systems like liquid water [19]. The simulation of liquid water is very sensitive to the used exchange correlation functional, wherefore the effects of different functionals can be demonstrated easily [20]. Here, a Car-Parinello simulation of 64 water molecules in a cubic cell is presented in order to show the comparison of simulated to experimental data.

In figure 2 the Perdew-Burke-Ernzshof (PBE) and the strongly constrained and appropriately normed (SCAN) meta-GGA functional are compared to experimental data from X-Ray and neutron diffraction experiments.

The peak in figure 2 B at around $r = 1 \text{ \AA}$ arises from the intramolecular, covalent bond in each molecule, whereas all other peaks stem from intermolecular interactions between different molecules. The RDFs show the various interacting forces, e.g. H-bonded molecules produce the first peak in figure 2 A and the second in figure 2 B.

It can be concluded that SCAN better agrees with the experimental results, than the PBE functional. Since SCAN was more recently introduced than PBE, this shows that even in DFT-based MD, progress is still made.

Besides accessible observables, that classical MD simulations offer (as RDF), access to further observables arises from the electronic structure calculations. One example is the infrared absorption coefficient $\alpha(\omega)$, that depends on the electric dipole moment. Since the dipole moment can be calculated from the electronic density, AIMD enable the calculation of the infrared absorption coefficient [1, 21]. Another example can be found in NMR, as AIMD can be used to compute the response of chemical shifts and magnetic susceptibilities [22]. Moreover, DFT and AIMD provide the possibility to obtain angles and bond lengths, which can be used to develop force field sets [5].

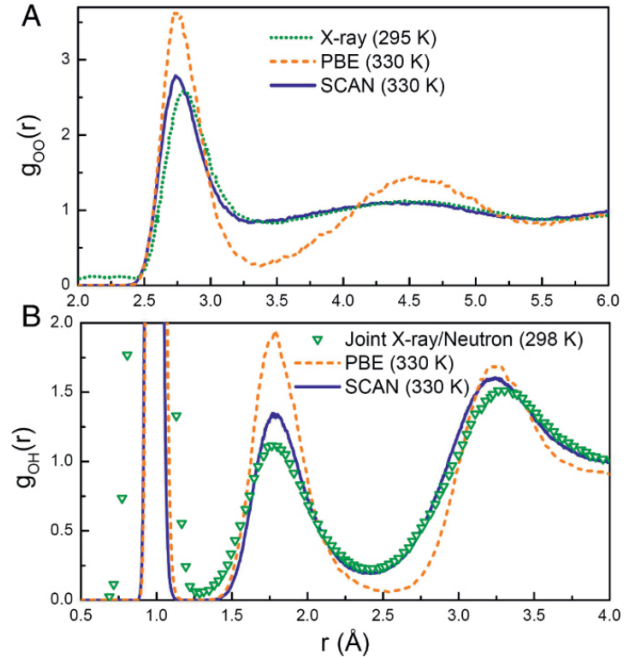


Figure 2: RDFs of liquid water predicted by SCAN and PBE compared to diffraction experiments [20].

5 Conclusion

This handout introduced density functional theory based molecular dynamics. Within the theoretical description of a quantum mechanical many body system, DFT is one electronic structure method to compute energies and gradients on the potential energy surface and can be used in AIMD. Since quantum mechanical calculations provide highly accurate information on the system properties, AIMD provides certain advantages compared to force field methods. The following sections answer the questions why and for which systems it is reasonable to use DFT-based MD.

Strength In comparison to force field MD, AIMD provides access to more observables, like the infrared absorption coefficient. These observables can directly be compared to NMR, IR and Raman spectroscopy measurements [1]. AIMD enables the simulation of proton transfer in chemical reactions, since the process of breaking and forming bonds is described by overcoming potential barriers on the PES [23]. This enables the simulation of chemical reactions. In order to perform force field-based MD simulations, potentials have to be developed in advance, for which information on the PES is required [2]. In AIMD simulation, such knowledge is not required and system properties can be obtained by performing the simulation. Since a potential approximation is not required, phenomena as phase transitions can be analyzed. The access to the electronic structure can yield insight into the origin of even unexpected events [2].

Limitations Since DFT-based AIMD is assumed to calculate accurate points and slopes of the PES, it is important to mention the limitations arising from DFT in the first place. DFT, as one of many methods calculating electronic structure, is still an approximation, since the exact expression of the exchange correlation functional is unknown and the basis set is finite [5]. Regarding the choice between AIMD and a force field approach, the system size needs to be taken into account. Force field MD in principle scales squared in the number of system particles $\mathcal{O}(N^2)$ [24], whereas AIMD scales cubic in the particle number (or number of basis sets) $\mathcal{O}(N^3)$ [1]. Intuitively, the additional computational expense of AIMD could also be seen within the force calculation, since in force field approaches no electronic structure needs to be solved and forces are pre-constructed. Therefore, AIMD simulations offer times of 10-100 picoseconds for systems up to around 100-1000 particles [19]. In the framework of MD simulations, these are comparatively small time and size scales, since force field MD can achieve larger system sizes, up to a factor of 100 [19]. However, with increasing computational power, the realm of affordable AIMD simulations grows [19]. The time step of AIMD simulations generally is smaller than 1 fs, as e.g. vibrational frequencies should be covered. In addition, a lower boundary occurs from uncertainties of the electronic structure method (e.g DFT) [11]. The event, that wants to be covered with the simulation, should in general be situated in the accessible time scale.

Within these restrictions, DFT-based AIMD offers great possibilities and since structure calculations are based on fundamental quantum mechanics, AIMD is even in an aesthetically sense quite satisfying. To sum it up, DFT-based MD is the method of choice for complex but comparatively small MD systems.

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