Auf den folgenden Seiten finden Sie die für den Car-Parrinello Versuch relevanten Teile aus einem umfangreichen Übersichtsartikel. Wenn Sie mehr wissen möchten oder z.B. Referenzen nachschlagen wollen, so können Sie dies online anhand des vollständigen Artikels unter http://www.theochem.ruhr-uni-bochum.de/go/cprev.html tun.

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Hinweise zu den Abschnitten:

- Kapitel 2.1:
  Sie müssen die Herleitung nicht im Detail nachvollziehen. Lernziel ist es, ihnen einen Eindruck zu vermitteln, welche Näherungen gemacht werden müssen, um die Molekulardynamik mit klassischen Kernfreiheitsgraden aus der gekoppelten, zeitabhängigen Schrödingergleichung für Elektronen und Kerne herzuleiten.

- Kapitel 2.4:
  wenn Sie dieses Kapitel **verstanden** haben, so haben Sie auch die Car-Parrinello Idee als solche verstanden!

- Kapitel 2.7:
  dies ist eine Auffrischung der Grundlagen von wichtigen Elektronenstrukturmethoden in einer konsistenten Schreibweise. Wichtig für Sie ist besonders das Kapitel 2.8.2, in dem ebene Wellen als Basissatz eingeführt werden, die lokalisierten Basisfunktionen aus Kapitel 2.8.1. kennen Sie ja bereits.

- Kapitel 4.2.3:
  hier lernen Sie die Weiterentwicklung der Nosé--Hoover Thermostaten kennen; dieses Kapitel können Sie bei Zeitknappheit auslassen.

Ab initio molecular dynamics: Theory and Implementation

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AB INITIO MOLECULAR DYNAMICS:
THEORY AND IMPLEMENTATION

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The rapidly growing field of *ab initio* molecular dynamics is reviewed in the spirit of a series of lectures given at the Winterschool 2000 at the *John von Neumann Institute for Computing, Jülich*. Several such molecular dynamics schemes are compared which arise from following various approximations to the fully coupled Schrödinger equation for electrons and nuclei. Special focus is given to the Car–Parrinello method with discussion of both strengths and weaknesses in addition to its range of applicability. To shed light upon why the Car–Parrinello approach works several alternate perspectives of the underlying ideas are presented. The implementation of *ab initio* molecular dynamics within the framework of plane wave–pseudopotential density functional theory is given in detail, including diagonalization and minimization techniques as required for the Born–Oppenheimer variant. Efficient algorithms for the most important computational kernel routines are presented. The adaptation of these routines to distributed memory parallel computers is discussed using the implementation within the computer code `CPMD` as an example. Several advanced techniques from the field of molecular dynamics, (constant temperature dynamics, constant pressure dynamics) and electronic structure theory (free energy functional, excited states) are introduced. The combination of the path integral method with *ab initio* molecular dynamics is presented in detail, showing its limitations and possible extensions. Finally, a wide range of applications from materials science to biochemistry is listed, which shows the enormous potential of *ab initio* molecular dynamics for both explaining and predicting properties of molecules and materials on an atomic scale.

1   Setting the Stage: Why *Ab Initio* Molecular Dynamics ?

Classical molecular dynamics using "predefined potentials", either based on empirical data or on independent electronic structure calculations, is well established as a powerful tool to investigate many–body condensed matter systems. The broadness, diversity, and level of sophistication of this technique is documented in several monographs as well as proceedings of conferences and scientific schools [12,135,270,217,69,59,177]. At the very heart of any molecular dynamics scheme is the question of how to describe – that is in practice how to approximate – the interatomic interactions. The traditional route followed in molecular dynamics is to determine these potentials in advance. Typically, the full interaction is broken up into two–body, three–body and many–body contributions, long–range and short–range terms etc., which have to be represented by suitable functional forms, see Sect. 2 of Ref. [253] for a detailed account. After decades of intense research, very elaborate interaction models including the non–trivial aspect to represent them

analytically were devised [253,539,584].

Despite overwhelming success – which will however not be praised in this review – the need to devise a "fixed model potential" implies serious drawbacks, see the introduction sections of several earlier reviews [513,472] for a more complete digression on these aspects. Among the most delicate ones are systems where (i) many different atom or molecule types give rise to a myriad of different interatomic interactions that have to be parameterized and / or (ii) the electronic structure and thus the bonding pattern changes qualitatively in the course of the simulation. These systems can be called "chemically complex".

The reign of traditional molecular dynamics *and* electronic structure methods was greatly extended by the family of techniques that is called here "*ab initio* molecular dynamics". Other names that are currently in use are for instance Car–Parrinello, Hellmann–Feynman, first principles, quantum chemical, on–the–fly, direct, potential–free, quantum, etc. molecular dynamics. The basic idea underlying every *ab initio* molecular dynamics method is to compute the forces acting on the nuclei from electronic structure calculations that are performed "on–the–fly" as the molecular dynamics trajectory is generated. In this way, the electronic variables are not integrated out beforehand, but are considered as active degrees of freedom. This implies that, given a suitable approximate solution of the many–electron problem, also "chemically complex" systems can be handled by molecular dynamics. But this also implies that the approximation is shifted from the level of selecting the model potential to the level of selecting a particular approximation for solving the Schrödinger equation.

Applications of *ab initio* molecular dynamics are particularly widespread in materials science and chemistry, where the aforementioned difficulties (i) and (ii) are particularly severe. A collection of problems that were already tackled by *ab initio* molecular dynamics including the pertinent references can be found in Sect. 5. The power of this novel technique lead to an explosion of the activity in this field in terms of the number of published papers. The locus can be located in the late–eighties, see the squares in Fig. 1 that can be interpreted as a measure of the activity in the area of *ab initio* molecular dynamics. As a matter of fact the time evolution of the number of citations of a particular paper, the one by Car and Parrinello from 1985 entitled "Unified Approach for Molecular Dynamics and Density–Functional Theory" [108], parallels the trend in the entire field, see the circles in Fig. 1. Thus, the resonance that the Car and Parrinello paper evoked and the popularity of the entire field go hand in hand in the last decade. Incidentally, the 1985 paper by Car and Parrinello is the last one included in the section "Trends and Prospects" in the reprint collection of "key papers" from the field of atomistic computer simulations [135]. That the entire field of *ab initio* molecular dynamics has grown mature is also evidenced by a separate PACS classification number (71.15.Pd "Electronic Structure: Molecular dynamics calculations (Car–Parrinello) and other numerical simulations") that was introduced in 1996 into the *Physics and Astronomy Classification Scheme* [486].

Despite its obvious advantages, it is evident that a price has to be payed for putting molecular dynamics on *ab initio* grounds: the correlation lengths and relaxation times that are accessible are much smaller than what is affordable via
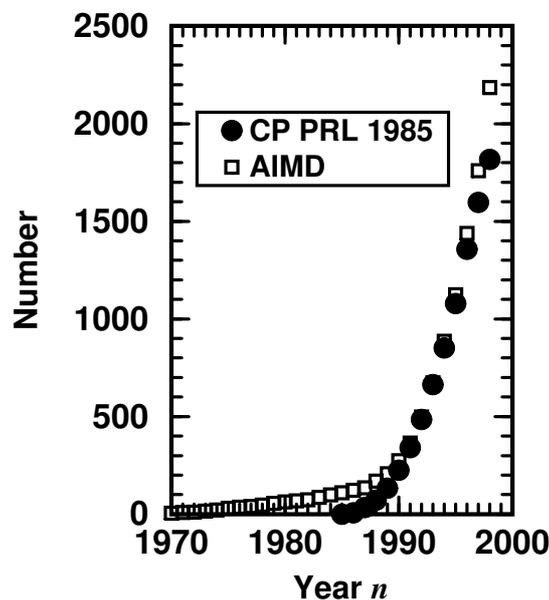
Figure 1. Publication and citation analysis. Squares: number of publications which appeared up to the year n that contain the keyword "*ab initio* molecular dynamics" (or synonyma such as "first principles MD", "Car–Parrinello simulations" etc.) in title, abstract or keyword list. Circles: number of publications which appeared up to the year n that cite the 1985 paper by Car and Parrinello [108] (including misspellings of the bibliographic reference). Self–citations and self–papers are excluded, i.e. citations of Ref. [108] in their own papers and papers coauthored by R. Car and / or M. Parrinello are *not* considered in the respective statistics. The analysis is based on the CAPLUS ("Chemical Abstracts Plus"), INSPEC ("Physics Abstracts"), and SCI ("Science Citation Index") data bases at STN International. Updated statistics from Ref. [405].

standard molecular dynamics. Another appealing feature of standard molecular dynamics is less evident, namely the "experimental aspect of playing with the potential". Thus, tracing back the properties of a given system to a simple physical picture or mechanism is much harder in *ab initio* molecular dynamics. The bright side is that new phenomena, which were not forseen before starting the simulation, can simply happen if necessary. This gives *ab initio* molecular dynamics a truly predictive power.

Ab initio molecular dynamics can also be viewed from another corner, namely from the field of classical trajectory calculations [649,541]. In this approach, which has its origin in gas phase molecular dynamics, a *global* potential energy surface is constructed in a first step either empirically or based on electronic structure calculations. In a second step, the dynamical evolution of the nuclei is generated by using classical mechanics, quantum mechanics or semi / quasiclassical approximations of various sorts. In the case of using classical mechanics to describe the dynamics – the focus of the present overview – the limiting step for large systems is

3

the first one, why so? There are $3N - 6$ internal degrees of freedom that span the global potential energy surface of an unconstrained N–body system. Using for simplicity 10 discretization points per coordinate implies that of the order of 10^{3N-6} electronic structure calculations are needed in order to map such a global potential energy surface. Thus, the computational workload for the first step grows roughly like $\sim 10^N$ with increasing system size. This is what might be called the "dimensionality bottleneck" of calculations that rely on *global* potential energy surfaces, see for instance the discussion on p. 420 in Ref. [254].

What is needed in *ab initio* molecular dynamics instead? Suppose that a useful trajectory consists of about 10^M molecular dynamics steps, i.e. 10^M electronic structure calculations are needed to generate one trajectory. Furthermore, it is assumed that 10^n independent trajectories are necessary in order to average over different initial conditions so that 10^{M+n} *ab initio* molecular dynamics steps are required in total. Finally, it is assumed that each single–point electronic structure calculation needed to devise the global potential energy surface and one *ab initio* molecular dynamics time step requires roughly the same amount of CPU time. Based on this truly simplistic order of magnitude estimate, the advantage of *ab initio* molecular dynamics vs. calculations relying on the computation of a global potential energy surface amounts to about $10^{3N-6-M-n}$. The crucial point is that for a given statistical accuracy (that is for M and n fixed and independent on N) and for a given electronic structure method, the computational advantage of "on–the–fly" approaches grows like $\sim 10^N$ with system size.

Of course, considerable progress has been achieved in trajectory calculations by carefully selecting the discretization points and reducing their number, choosing sophisticated representations and internal coordinates, exploiting symmetry etc. but basically the scaling $\sim 10^N$ with the number of nuclei remains a problem. Other strategies consist for instance in reducing the number of active degrees of freedom by constraining certain internal coordinates, representing less important ones by a (harmonic) bath or friction, or building up the global potential energy surface in terms of few–body fragments. All these approaches, however, invoke approximations beyond the ones of the electronic structure method itself. Finally, it is evident that the computational advantage of the "on–the–fly" approaches diminish as more and more trajectories are needed for a given (small) system. For instance extensive averaging over many different initial conditions is required in order to calculate quantitatively scattering or reactive cross sections. Summarizing this discussion, it can be concluded that *ab initio* molecular dynamics is the method of choice to investigate large and "chemically complex" systems.

Quite a few review articles dealing with *ab initio* molecular dynamics appeared in the nineties [513,223,472,457,224,158,643,234,463,538,405] and the interested reader is referred to them for various complementary viewpoints. In the present overview article, emphasis is put on both broadness of the approaches and depth of the presentation. Concerning the broadness, the discussion starts from the Schrödinger equation. Classical, Ehrenfest, Born–Oppenheimer, and Car–Parrinello molecular dynamics are "derived" from the time–dependent mean–field approach that is obtained after separating the nuclear and electronic degrees of freedom. The most extensive discussion is related to the features of the basic Car–Parrinello approach

but all three *ab initio* approaches to molecular dynamics are contrasted and partly compared. The important issue of how to obtain the correct forces in these schemes is discussed in some depth. The most popular electronic structure theories implemented within *ab initio* molecular dynamics, density functional theory in the first place but also the Hartree–Fock approach, are sketched. Some attention is also given to another important ingredient in *ab initio* molecular dynamics, the choice of the basis set.

Concerning the depth, the focus of the present discussion is clearly the implementation of both the basic Car–Parrinello and Born–Oppenheimer molecular dynamics schemes in the `CPMD` package [142]. The electronic structure approach in `CPMD` is Hohenberg–Kohn–Sham density functional theory within a plane wave / pseudopotential implementation and the Generalized Gradient Approximation. The formulae for energies, forces, stress, pseudopotentials, boundary conditions, optimization procedures, parallelization etc. are given for this particular choice to solve the electronic structure problem. One should, however, keep in mind that a variety of other powerful *ab initio* molecular dynamics codes are available (for instance `CASTEP` [116], `CP-PAW` [143], `fhi98md` [189], `NWChem` [446], `VASP` [663]) which are partly based on very similar techniques. The classic Car–Parrinello approach [108] is then extended to other ensembles than the microcanonical one, other electronic states than the ground state, and to a fully quantum–mechanical representation of the nuclei. Finally, the wealth of problems that can be addressed using *ab initio* molecular dynamics is briefly sketched at the end, which also serves implicitly as the "Summary and Conclusions" section.

2 Basic Techniques: Theory

2.1 Deriving Classical Molecular Dynamics

The starting point of the following discussion is non–relativistic quantum mechanics as formalized via the time–dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = \mathcal{H} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \tag{1}$$

in its position representation in conjunction with the standard Hamiltonian

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

for the electronic $\{\mathbf{r}_i\}$ and nuclear $\{\mathbf{R}_I\}$ degrees of freedom. The more convenient atomic units (a.u.) will be introduced at a later stage for reasons that will soon become clear. Thus, only the bare electron–electron, electron–nuclear, and nuclear–nuclear Coulomb interactions are taken into account.

The goal of this section is to derive classical molecular dynamics [12,270,217] starting from Schrödinger's wave equation and following the elegant route of Tully [650,651]. To this end, the nuclear and electronic contributions to the total wavefunction $\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$, which depends on *both* the nuclear and electronic coordinates, *have* to be separated. The simplest possible form is a product ansatz

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \approx \Psi(\{\mathbf{r}_i\}; t) \, \chi(\{\mathbf{R}_I\}; t) \, \exp\left[\frac{i}{\hbar}\int_{t_0}^t dt' \tilde{E}_{\mathrm{e}}(t')\right] \;, \qquad (3)$$

where the nuclear and electronic wavefunctions are separately normalized to unity at every instant of time, i.e. $\langle\chi; t|\chi; t\rangle = 1$ and $\langle\Psi; t|\Psi; t\rangle = 1$, respectively. In addition, a convenient phase factor

$$\tilde{E}_{\mathrm{e}} = \int d\mathbf{r}d\mathbf{R} \; \Psi^\star(\{\mathbf{r}_i\}; t) \, \chi^\star(\{\mathbf{R}_I\}; t) \, \mathcal{H}_{\mathrm{e}} \, \Psi(\{\mathbf{r}_i\}; t) \, \chi(\{\mathbf{R}_I\}; t) \qquad (4)$$

was introduced at this stage such that the final equations will look nice; $\int d\mathbf{r}d\mathbf{R}$ refers to the integration over all $i = 1, \dots$ and $I = 1, \dots$ variables $\{\mathbf{r}_i\}$ and $\{\mathbf{R}_I\}$, respectively. It is mentioned in passing that this approximation is called a one–determinant or single–configuration ansatz for the *total* wavefunction, which at the end must lead to a mean–field description of the coupled dynamics. Note also that this product ansatz (excluding the phase factor) differs from the Born–Oppenheimer ansatz [340,350] for separating the fast and slow variables

$$\Phi_{\mathrm{BO}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = \sum_{k=0}^\infty \tilde{\Psi}_k(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})\tilde{\chi}_k(\{\mathbf{R}_I\}; t) \qquad (5)$$

even in its one–determinant limit, where only a single electronic state k (evaluated for the nuclear configuration $\{\mathbf{R}_I\}$) is included in the expansion.

Inserting the separation ansatz Eq. (3) into Eqs. (1)–(2) yields (after multiplying from the left by $\langle\Psi|$ and $\langle\chi|$ and imposing energy conservation $d\langle\mathcal{H}\rangle/dt \equiv 0$) the following relations

$$i\hbar\frac{\partial\Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_{\mathrm{e}}}\nabla_i^2\Psi + \left\{\int d\mathbf{R} \, \chi^\star(\{\mathbf{R}_I\}; t)V_{\mathrm{n-e}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})\chi(\{\mathbf{R}_I\}; t)\right\}\Psi \quad (6)$$

$$i\hbar\frac{\partial\chi}{\partial t} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\chi + \left\{\int d\mathbf{r} \, \Psi^\star(\{\mathbf{r}_i\}; t)\mathcal{H}_{\mathrm{e}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})\Psi(\{\mathbf{r}_i\}; t)\right\}\chi \;. \quad (7)$$

This set of coupled equations defines the basis of the time–dependent self–consistent field (TDSCF) method introduced as early as 1930 by Dirac [162], see also Ref. [158]. Both electrons and nuclei move quantum–mechanically in time–dependent effective potentials (or self–consistently obtained average fields) obtained from appropriate averages (quantum mechanical expectation values $\langle\dots\rangle$) over the other class of degrees of freedom (by using the nuclear and electronic wavefunctions, respectively). Thus, the single–determinant ansatz Eq. (3) produces, as already anticipated, a mean–field description of the coupled nuclear–electronic quantum dynamics. This is the price to pay for the simplest possible separation of electronic and nuclear variables.

The next step in the derivation of classical molecular dynamics is the task to approximate the nuclei as classical point particles. How can this be achieved in the framework of the TDSCF approach, given one quantum–mechanical wave equation describing all nuclei? A well–known route to extract classical mechanics from quantum mechanics in general starts with rewriting the corresponding wavefunction

$$\chi(\{\mathbf{R}_I\};t) = A(\{\mathbf{R}_I\};t) \, \exp\left[iS(\{\mathbf{R}_I\};t)/\hbar\right] \tag{8}$$

in terms of an amplitude factor A and a phase S which are both considered to be real and $A > 0$ in this polar representation, see for instance Refs. [163,425,535]. After transforming the nuclear wavefunction in Eq. (7) accordingly and after separating the real and imaginary parts, the TDSCF equation for the nuclei

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I S)^2 + \int d\mathbf{r} \, \Psi^\star \mathcal{H}_e \Psi = \hbar^2 \sum_I \frac{1}{2M_I} \frac{\nabla_I^2 A}{A} \tag{9}$$

$$\frac{\partial A}{\partial t} + \sum_I \frac{1}{M_I} (\nabla_I A)(\nabla_I S) + \sum_I \frac{1}{2M_I} A \left(\nabla_I^2 S\right) = 0 \tag{10}$$

is (exactly) re–expressed in terms of the new variables A and S. This so–called "quantum fluid dynamical representation" Eqs. (9)–(10) can actually be used to solve the time–dependent Schrödinger equation [160]. The relation for A, Eq. (10), can be rewritten as a continuity equation [163,425,535] with the help of the identification of the nuclear density $|\chi|^2 \equiv A^2$ as directly obtained from the definition Eq. (8). This continuity equation is independent of $\hbar$ and ensures locally the conservation of the particle probability $|\chi|^2$ associated to the nuclei in the presence of a flux.

More important for the present purpose is a more detailed discussion of the relation for S, Eq. (9). This equation contains one term that depends on $\hbar$, a contribution that vanishes if the classical limit

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I S)^2 + \int d\mathbf{r} \, \Psi^\star \mathcal{H}_e \Psi = 0 \tag{11}$$

is taken as $\hbar \to 0$; an expansion in terms of $\hbar$ would lead to a hierarchy of semi-classical methods [425,259]. The resulting equation is now isomorphic to equations of motion in the Hamilton–Jacobi formulation [244,540]

$$\frac{\partial S}{\partial t} + \mathcal{H}\left(\{\mathbf{R}_I\}, \{\nabla_I S\}\right) = 0 \tag{12}$$

of classical mechanics with the classical Hamilton function

$$\mathcal{H}(\{\mathbf{R}_I\}, \{\mathbf{P}_I\}) = T(\{\mathbf{P}_I\}) + V(\{\mathbf{R}_I\}) \tag{13}$$

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

$$\mathbf{P}_I \equiv \nabla_I S \tag{14}$$

the Newtonian equation of motion $\dot{\mathbf{P}}_I = -\nabla_I V(\{\mathbf{R}_I\})$ corresponding to Eq. (11)

$$\frac{d\mathbf{P}_I}{dt} = -\nabla_I \int d\mathbf{r} \; \Psi^\star \mathcal{H}_e \Psi \qquad \text{or}$$

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \int d\mathbf{r} \; \Psi^\star \mathcal{H}_e \Psi \tag{15}$$

$$= -\nabla_I V_e^E(\{\mathbf{R}_I(t)\}) \tag{16}$$

can be read off. Thus, the nuclei move according to classical mechanics in an effective potential V_e^E due to the electrons. This potential is a function of only the nuclear positions at time t as a result of averaging $\mathcal{H}_e$ over the electronic degrees of freedom, i.e. computing its quantum expectation value $\langle \Psi | \mathcal{H}_e | \Psi \rangle$, while keeping the nuclear positions fixed at their instantaneous values $\{\mathbf{R}_I(t)\}$.

However, the nuclear wavefunction still occurs in the TDSCF equation for the electronic degrees of freedom and has to be replaced by the positions of the nuclei for consistency. In this case the classical reduction can be achieved simply by replacing the nuclear density $|\chi(\{\mathbf{R}_I\};t)|^2$ in Eq. (6) in the limit $\hbar \to 0$ by a product of delta functions $\prod_I \delta(\mathbf{R}_I - \mathbf{R}_I(t))$ centered at the instantaneous positions $\{\mathbf{R}_I(t)\}$ of the classical nuclei as given by Eq. (15). This yields e.g. for the position operator

$$\int d\mathbf{R} \; \chi^\star(\{\mathbf{R}_I\};t) \, \mathbf{R}_I \, \chi(\{\mathbf{R}_I\};t) \; \overset{\hbar \to 0}{\longrightarrow} \; \mathbf{R}_I(t) \tag{17}$$

the required expectation value. This classical limit leads to a time–dependent wave equation for the electrons

$$i\hbar \frac{\partial \Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_{n-e}(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\}) \Psi$$

$$= \mathcal{H}_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\}) \; \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\};t) \tag{18}$$

which evolve self–consistently as the classical nuclei are propagated via Eq. (15). Note that now $\mathcal{H}_e$ and thus Ψ depend *parametrically* on the classical nuclear *positions* $\{\mathbf{R}_I(t)\}$ at time t through $V_{n-e}(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\})$. This means that feedback between the classical and quantum degrees of freedom is incorporated in both directions (at variance with the "classical path" or Mott non–SCF approach to dynamics [650,651]).

The approach relying on solving Eq. (15) together with Eq. (18) is sometimes called "Ehrenfest molecular dynamics" in honor of Ehrenfest who was the first to address the question [a] of how Newtonian classical dynamics can be derived from Schrödinger's wave equation [174]. In the present case this leads to a hybrid or mixed approach because only the nuclei are forced to behave like classical particles, whereas the electrons are still treated as quantum objects.

Although the TDSCF approach underlying Ehrenfest molecular dynamics clearly is a mean–field theory, transitions between electronic states are included

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[a] The opening statement of Ehrenfest's famous 1927 paper [174] reads:

"Es ist wünschenswert, die folgende Frage möglichst elementar beantworten zu können: *Welcher Rückblick ergibt sich vom Standpunkt der Quantenmechanik auf die Newtonschen Grundgleichungen der klassischen Mechanik?*"

in this scheme. This can be made evident by expanding the *electronic* wavefunction Ψ (as opposed to the *total* wavefunction Φ according to Eq. (5)) in terms of many electronic states or determinants Ψ_k

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = \sum_{k=0}^{\infty} c_k(t)\Psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \tag{19}$$

with complex coefficients $\{c_k(t)\}$. In this case, the coefficients $\{|c_k(t)|^2\}$ (with $\sum_k |c_k(t)|^2 \equiv 1$) describe explicitly the time evolution of the populations (occupations) of the different states $\{k\}$ whereas interferences are included via the $\{c_k^\star c_{l\neq k}\}$ contributions. One possible choice for the basis functions $\{\Psi_k\}$ is the adiabatic basis obtained from solving the time–independent electronic Schrödinger equation

$$\mathcal{H}_e(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})\Psi_k = E_k(\{\mathbf{R}_I\})\Psi_k(\{\mathbf{r}_i\}; \{\mathbf{R}_I\}) \ , \tag{20}$$

where $\{\mathbf{R}_I\}$ are the instantaneous nuclear positions at time t according to Eq. (15). The actual equations of motion in terms of the expansion coefficients $\{c_k\}$ are presented in Sect. 2.2.

At this stage a further simplification can be invoked by restricting the total electronic wave function Ψ to be the ground state wave function Ψ_0 of $\mathcal{H}_e$ at each instant of time according to Eq. (20) and $|c_0(t)|^2 \equiv 1$ in Eq. (19). This should be a good approximation if the energy difference between Ψ_0 and the first excited state Ψ_1 is everywhere large compared to the thermal energy $k_B T$, roughly speaking. In this limit the nuclei move according to Eq. (15) on a single potential energy surface

$$V_e^E = \int d\mathbf{r} \ \Psi_0^\star \mathcal{H}_e \Psi_0 \equiv E_0(\{\mathbf{R}_I\}) \tag{21}$$

that can be computed by solving the *time–independent* electronic Schrödinger equation Eq. (20)

$$\mathcal{H}_e \Psi_0 = E_0 \Psi_0 \ , \tag{22}$$

for the ground state only. This leads to the identification $V_e^E \equiv E_0$ via Eq. (21), i.e. in this limit the Ehrenfest potential is identical to the ground–state Born–Oppenheimer potential.

As a consequence of this observation, it is conceivable to decouple the task of generating the nuclear dynamics from the task of computing the potential energy surface. In a first step E_0 is computed for many nuclear configurations by solving Eq. (22). In a second step, these data points are fitted to an analytical functional form to yield a global potential energy surface [539], from which the gradients can be obtained analytically. In a third step, the Newtonian equation of motion Eq. (16) is solved on this surface for many different initial conditions, producing a "swarm" of classical trajectories. This is, in a nutshell, the basis of *classical trajectory calculations* on global potential energy surfaces [649,541].

As already alluded to in the general introduction, 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 is to approximate the

global potential energy surface

$$V_e^E \approx V_e^{\text{approx}}(\{\mathbf{R}_I\}) = \sum_{I=1}^N v_1(\mathbf{R}_I) + \sum_{I<J}^N v_2(\mathbf{R}_I, \mathbf{R}_J)$$
$$+ \sum_{I<J<K}^N v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots \qquad (23)$$

in terms of a truncated expansion of many–body contributions [253,12,270]. At this stage, the electronic degrees of freedom are replaced by interaction potentials $\{v_n\}$ and are not featured as explicit degrees of freedom in the equations of motion. Thus, the mixed quantum / classical problem is reduced to purely classical mechanics, once the $\{v_n\}$ are determined. *Classical molecular dynamics*

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{\text{approx}}(\{\mathbf{R}_I(t)\}) \qquad (24)$$

relies crucially on this idea, where typically only two–body v_2 or three–body v_3 interactions are taken into account [12,270], although more sophisticated models to include non–additive interactions such as polarization exist. This amounts to a dramatic simplification and removes the dimensionality bottleneck as the global potential surface is constructed from a manageable sum of additive few–body contributions — at the price of introducing a drastic approximation and of basically excluding chemical transformations from the realm of simulations.

As a result of this derivation, the essential assumptions underlying classical molecular dynamics become 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 in general approximated in terms of few–body interactions.

Actually, classical 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 [175] where the interactions can faithfully be described by additive two–body terms, i.e. $V_e^{\text{approx}}(\{\mathbf{R}_I\}) \approx \sum_{I<J}^N v_2(|\mathbf{R}_I - \mathbf{R}_J|)$. Thus, the determination of the pair potential v_2 from *ab initio* electronic structure calculations amounts to computing and fitting a one–dimensional function. The corresponding task to determine a global potential energy surface amounts to doing that in about 10^{1500} dimensions, which is simply impossible (and on top of that not necessary for Nobel gases!).

2.2 Ehrenfest Molecular Dynamics

A way out of the dimensionality bottleneck other than to approximate the global potential energy surface Eq. (23) or to reduce the number of active degrees of freedom is to take seriously the classical nuclei approximation to the TDSCF equations, Eq. (15) and (18). This amounts to computing the Ehrenfest force by actually solv-

ing numerically

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \int d\mathbf{r} \, \Psi^\star \mathcal{H}_e \Psi$$
$$= -\nabla_I \langle \Psi \, | \mathcal{H}_e | \, \Psi \rangle \qquad (25)$$
$$= -\nabla_I \langle \mathcal{H}_e \rangle$$
$$= -\nabla_I V_e^{\mathrm{E}}$$
$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\mathrm{n-e}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\}) \right] \Psi$$
$$= \mathcal{H}_e \Psi \qquad (26)$$

the coupled set of equations simultaneously. Thereby, the *a priori* construction of any type of potential energy surface is avoided from the outset by solving the time–dependent electronic Schrödinger equation "on–the–fly". This allows one to compute the force from $\nabla_I \langle \mathcal{H}_e \rangle$ for each configuration $\{\mathbf{R}_I(t)\}$ generated by molecular dynamics; see Sect. 2.5 for the issue of using the so–called "Hellmann–Feynman forces" instead.

The corresponding equations of motion in terms of the adiabatic basis Eq. (20) and the time–dependent expansion coefficients Eq. (19) read [650,651]

$$M_I \ddot{\mathbf{R}}_I(t) = -\sum_k |c_k(t)|^2 \nabla_I E_k - \sum_{k,l} c_k^\star c_l \left(E_k - E_l \right) \mathbf{d}_I^{kl} \qquad (27)$$

$$i\hbar \dot{c}_k(t) = c_k(t) E_k - i\hbar \sum_{I,l} c_l(t) \dot{\mathbf{R}}_I \mathbf{d}_I^{kl} \quad , \qquad (28)$$

where the coupling terms are given by

$$\mathbf{d}_I^{kl}(\{\mathbf{R}_I(t)\}) = \int d\mathbf{r} \, \Psi_k^\star \nabla_I \Psi_l \qquad (29)$$

with the property $\mathbf{d}_I^{kk} \equiv \mathbf{0}$. The Ehrenfest approach is thus seen to include rigorously non–adiabatic transitions between different electronic states Ψ_k and Ψ_l within the framework of classical nuclear motion and the *mean–field* (TDSCF) approximation to the electronic structure, see e.g. Refs. [650,651] for reviews and for instance Ref. [532] for an implementation in terms of time–dependent density functional theory.

The restriction to one electronic state in the expansion Eq. (19), which is in most cases the ground state Ψ_0, leads to

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \langle \Psi_0 \, | \mathcal{H}_e | \, \Psi_0 \rangle \qquad (30)$$

$$i\hbar \frac{\partial \Psi_0}{\partial t} = \mathcal{H}_e \Psi_0 \qquad (31)$$

as a special case of Eqs. (25)–(26); note that $\mathcal{H}_e$ is time–dependent via the nuclear coordinates $\{\mathbf{R}_I(t)\}$. A point worth mentioning here is that the propagation of the wavefunction is unitary, i.e. the wavefunction preserves its norm and the set of orbitals used to build up the wavefunction will stay orthonormal, see Sect. 2.6.

Ehrenfest molecular dynamics is certainly the oldest approach to "on–the–fly" molecular dynamics and is typically used for collision– and scattering–type problems [154,649,426,532]. However, it was never in widespread use for systems with many active degrees of freedom typical for condensed matter problems for reasons that will be outlined in Sec. 2.6 (although a few exceptions exist [553,34,203,617] but here the number of explicitly treated electrons is fairly limited with the exception of Ref. [617]).

2.3 Born–Oppenheimer Molecular Dynamics

An alternative approach to include the electronic structure in molecular dynamics simulations consists in straightforwardly solving the *static* electronic structure problem in each molecular dynamics step given the set of *fixed* nuclear positions at that instance of time. Thus, the electronic structure part is reduced to solving a *time–independent* quantum problem, e.g. by solving the time–independent Schrödinger equation, concurrently to propagating the nuclei via classical molecular dynamics. Thus, the time–dependence of the electronic structure is a consequence of nuclear motion, and not intrinsic as in Ehrenfest molecular dynamics. The resulting Born–Oppenheimer molecular dynamics method is defined by

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \{ \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle \} \tag{32}$$

$$E_0 \Psi_0 = \mathcal{H}_e \Psi_0 \tag{33}$$

for the electronic ground state. A deep difference with respect to Ehrenfest dynamics concerning the nuclear equation of motion is that the minimum of $\langle \mathcal{H}_e \rangle$ has to be reached in each Born–Oppenheimer molecular dynamics step according to Eq. (32). In Ehrenfest dynamics, on the other hand, a wavefunction that minimized $\langle \mathcal{H}_e \rangle$ initially will also stay in its respective minimum as the nuclei move according to Eq. (30)!

A natural and straightforward extension [281] of ground–state Born–Oppenheimer dynamics is to apply the same scheme to any excited electronic state Ψ_k without considering any interferences. In particular, this means that also the "diagonal correction terms" [340]

$$D_I^{kk}(\{\mathbf{R}_I(t)\}) = -\int d\mathbf{r}\, \Psi_k^\star \nabla_I^2 \Psi_k \tag{34}$$

are *always* neglected; the inclusion of such terms is discussed for instance in Refs. [650,651]. These terms renormalize the Born–Oppenheimer or "clamped nuclei" potential energy surface E_k of a given state Ψ_k (which might also be the ground state Ψ_0) and lead to the so–called "adiabatic potential energy surface" of that state [340]. Whence, Born–Oppenheimer molecular dynamics should not be called "adiabatic molecular dynamics", as is sometime done.

It is useful for the sake of later reference to formulate the Born–Oppenheimer equations of motion for the special case of effective one–particle Hamiltonians. This might be the Hartree–Fock approximation defined to be the variational minimum of the energy expectation value $\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle$ given a single Slater determinant $\Psi_0 = \det\{\psi_i\}$ subject to the constraint that the one–particle orbitals ψ_i are orthonormal

$\langle \psi_i | \psi_j \rangle = \delta_{ij}$. The corresponding constraint minimization of the total energy with respect to the orbitals

$$\min_{\{\psi_i\}} \left\{ \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle \right\} \Bigg|_{\{\langle \psi_i | \psi_j \rangle = \delta_{ij}\}} \tag{35}$$

can be cast into Lagrange's formalism

$$\mathcal{L} = - \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \sum_{i,j} \Lambda_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right) \tag{36}$$

where Λ_{ij} are the associated Lagrangian multipliers. Unconstrained variation of this Lagrangian with respect to the orbitals

$$\frac{\delta \mathcal{L}}{\delta \psi_i^\star} \overset{!}{=} 0 \tag{37}$$

leads to the well–known Hartree–Fock equations

$$\mathcal{H}_e^{\mathrm{HF}} \psi_i = \sum_j \Lambda_{ij} \psi_j \tag{38}$$

as derived in standard text books [604,418]; the diagonal canonical form $\mathcal{H}_e^{\mathrm{HF}} \psi_i = \epsilon_i \psi_i$ is obtained after a unitary transformation and $\mathcal{H}_e^{\mathrm{HF}}$ denotes the effective one–particle Hamiltonian, see Sect. 2.7 for more details. The equations of motion corresponding to Eqs. (32)–(33) read

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\{\psi_i\}} \left\{ \langle \Psi_0 | \mathcal{H}_e^{\mathrm{HF}} | \Psi_0 \rangle \right\} \tag{39}$$

$$0 = -\mathcal{H}_e^{\mathrm{HF}} \psi_i + \sum_j \Lambda_{ij} \psi_j \tag{40}$$

for the Hartree–Fock case. A similar set of equations is obtained if Hohenberg–Kohn–Sham density functional theory [458,168] is used, where $\mathcal{H}_e^{\mathrm{HF}}$ has to be replaced by the Kohn–Sham effective one–particle Hamiltonian H_e^{KS}, see Sect. 2.7 for more details. Instead of diagonalizing the one–particle Hamiltonian an alternative but equivalent approach consists in directly performing the constraint minimization according to Eq. (35) via nonlinear optimization techniques.

Early applications of Born–Oppenheimer molecular dynamics were performed in the framework of a semiempirical approximation to the electronic structure problem [669,671]. But only a few years later an *ab initio* approach was implemented within the Hartree–Fock approximation [365]. Born–Oppenheimer dynamics started to become popular in the early nineties with the availability of more efficient electronic structure codes in conjunction with sufficient computer power to solve "interesting problems", see for instance the compilation of such studies in Table 1 in a recent overview article [82].

Undoubtedly, the breakthrough of Hohenberg–Kohn–Sham density functional theory in the realm of chemistry – which took place around the same time – also helped a lot by greatly improving the "price / performance ratio" of the electronic structure part, see e.g. Refs. [694,590]. A third and possibly the crucial reason that boosted the field of *ab initio* molecular dynamics was the pioneering introduction of

the Car–Parrinello approach [108], see also Fig. 1. This technique opened novel avenues to treat large–scale problems via *ab initio* molecular dynamics and catalyzed the entire field by making "interesting calculations" possible, see also the closing section on applications.

2.4 Car–Parrinello Molecular Dynamics

2.4.1 Motivation

A non–obvious approach to cut down the computational expenses of molecular dynamics which includes the electrons in a single state was proposed by Car and Parrinello in 1985 [108]. In retrospect it can be considered to combine the advantages of both Ehrenfest and Born–Oppenheimer molecular dynamics. In Ehrenfest dynamics the time scale and thus the time step to integrate Eqs. (30) and (31) simultaneously is dictated by the intrinsic dynamics of the electrons. Since electronic motion is much faster than nuclear motion, the largest possible time step is that which allows to integrate the electronic equations of motion. Contrary to that, there is no electron dynamics whatsoever involved in solving the Born–Oppenheimer Eqs. (32)–(33), i.e. they can be integrated on the time scale given by nuclear motion. However, this means that the electronic structure problem has to be solved self–consistently at each molecular dynamics step, whereas this is avoided in Ehrenfest dynamics due to the possibility to propagate the wavefunction by applying the Hamiltonian to an initial wavefunction (obtained e.g. by one self–consistent diagonalization).

From an algorithmic point of view the main task achieved in ground–state Ehrenfest dynamics is simply to keep the wavefunction automatically minimized as the nuclei are propagated. This, however, might be achieved – in principle – by another sort of deterministic dynamics than first–order Schrödinger dynamics. In summary, the "Best of all Worlds Method" should (i) integrate the equations of motion on the (long) time scale set by the nuclear motion but nevertheless (ii) take intrinsically advantage of the smooth time–evolution of the dynamically evolving electronic subsystem as much as possible. The second point allows to circumvent explicit diagonalization or minimization to solve the electronic structure problem for the next molecular dynamics step. Car–Parrinello molecular dynamics is an efficient method to satisfy requirement (ii) in a numerically stable fashion and makes an acceptable compromise concerning the length of the time step (i).

2.4.2 Car–Parrinello Lagrangian and Equations of Motion

The basic idea of the Car–Parrinello approach can be viewed to exploit the quantum–mechanical adiabatic time–scale separation of fast electronic and slow nuclear motion by transforming that into classical–mechanical adiabatic energy–scale separation in the framework of dynamical systems theory. In order to achieve this goal the two–component quantum / classical problem is mapped onto a two–component purely classical problem with two separate energy scales at the expense of loosing the explicit time–dependence of the quantum subsystem dynamics. Furthermore, the central quantity, the energy of the electronic subsystem $\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle$

evaluated with some wavefunction Ψ_0, is certainly a function of the nuclear positions $\{\mathbf{R}_I\}$. But at the same time it *can* be considered to be a functional of the wavefunction Ψ_0 and thus of a set of one–particle orbitals $\{\psi_i\}$ (or in general of other functions such as two–particle geminals) used to build up this wavefunction (being for instance a Slater determinant $\Psi_0 = \det\{\psi_i\}$ or a combination thereof). Now, in classical mechanics the force on the nuclei is obtained from the derivative of a Lagrangian with respect to the nuclear positions. This suggests that a functional derivative with respect to the orbitals, which are interpreted as classical fields, might yield the force on the orbitals, given a suitable Lagrangian. In addition, possible constraints within the set of orbitals have to be imposed, such as e.g. orthonormality (or generalized orthonormality conditions that include an overlap matrix).

Car and Parrinello postulated the following class of Lagrangians [108]

$$\mathcal{L}_{\mathrm{CP}} = \underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \,\middle|\, \dot{\psi}_i \right\rangle}_{\text{kinetic energy}} - \underbrace{\left\langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \right\rangle}_{\text{potential energy}} + \underbrace{constraints}_{\text{orthonormality}} \quad (41)$$

to serve this purpose. The corresponding Newtonian equations of motion are obtained from the associated Euler–Lagrange equations

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad (42)$$

$$\frac{d}{dt}\frac{\delta \mathcal{L}}{\delta \dot{\psi}_i^\star} = \frac{\delta \mathcal{L}}{\delta \psi_i^\star} \quad (43)$$

like in classical mechanics, but here for both the nuclear positions and the orbitals; note $\psi_i^\star = \langle \psi_i |$ and that the constraints are holonomic [244]. Following this route of ideas, generic Car–Parrinello equations of motion are found to be of the form

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} \left\langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \right\rangle + \frac{\partial}{\partial \mathbf{R}_I} \{constraints\} \quad (44)$$

$$\mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^\star} \left\langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \right\rangle + \frac{\delta}{\delta \psi_i^\star} \{constraints\} \quad (45)$$

where μ_i ($= \mu$) are the "fictitious masses" or inertia parameters assigned to the orbital degrees of freedom; the units of the mass parameter μ are energy times a squared time for reasons of dimensionality. Note that the constraints within the total wavefunction lead to "constraint forces" in the equations of motion. Note also that these constraints

$$constraints = constraints \ (\{\psi_i\}, \{\mathbf{R}_I\}) \quad (46)$$

might be a function of both the set of orbitals $\{\psi_i\}$ and the nuclear positions $\{\mathbf{R}_I\}$. These dependencies have to be taken into account properly in deriving the Car–Parrinello equations following from Eq. (41) using Eqs. (42)–(43), see Sect. 2.5 for a general discussion and see e.g. Ref. [351] for a case with an additional dependence of the wavefunction constraint on nuclear positions.

According to the Car–Parrinello equations of motion, the nuclei evolve in time at a certain (instantaneous) physical temperature $\propto \sum_I M_I \dot{\mathbf{R}}_I^2$, whereas a "fictitious temperature" $\propto \sum_i \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle$ is associated to the electronic degrees of freedom. In this terminology, "low electronic temperature" or "cold electrons" means that the electronic subsystem is close to its instantaneous minimum energy $\min_{\{\psi_i\}} \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle$, i.e. close to the exact Born–Oppenheimer surface. Thus, a ground–state wavefunction optimized for the initial configuration of the nuclei will stay close to its ground state also during time evolution if it is kept at a sufficiently low temperature.

The remaining task is to separate in practice nuclear and electronic motion such that the fast electronic subsystem stays cold also for long times but still follows the slow nuclear motion adiabatically (or instantaneously). Simultaneously, the nuclei are nevertheless kept at a much higher temperature. This can be achieved in nonlinear classical dynamics via decoupling of the two subsystems and (quasi–) adiabatic time evolution. This is possible if the power spectra stemming from both dynamics do not have substantial overlap in the frequency domain so that energy transfer from the "hot nuclei" to the "cold electrons" becomes practically impossible on the relevant time scales. This amounts in other words to imposing and maintaining a metastability condition in a complex dynamical system for sufficiently long times. How and to which extend this is possible in practice was investigated in detail in an important investigation based on well–controlled model systems [467,468] (see also Sects. 3.2 and 3.3 in Ref. [513]), with more mathematical rigor in Ref. [86], and in terms of a generalization to a second level of adiabaticity in Ref. [411].

2.4.3 Why Does the Car–Parrinello Method Work ?

In order to shed light on the title question, the dynamics generated by the Car–Parrinello Lagrangian Eq. (41) is analyzed [467] in more detail invoking a "classical dynamics perspective" of a simple model system (eight silicon atoms forming a periodic diamond lattice, local density approximation to density functional theory, normconserving pseudopotentials for core electrons, plane wave basis for valence orbitals, 0.3 fs time step with $\mu = 300$ a.u., in total 20 000 time steps or 6.3 ps), for full details see Ref. [467]); a concise presentation of similar ideas can be found in Ref. [110]. For this system the vibrational density of states or power spectrum of the electronic degrees of freedom, i.e. the Fourier transform of the statistically averaged velocity autocorrelation function of the classical fields

$$f(\omega) = \int_0^\infty dt \cos(\omega t) \sum_i \left\langle \dot{\psi}_i; t \,\middle|\, \dot{\psi}_i; 0 \right\rangle \tag{47}$$

is compared to the highest–frequency phonon mode $\omega_n^{\max}$ of the nuclear subsystem in Fig. 2. From this figure it is evident that for the chosen parameters the nuclear and electronic subsystems are dynamically separated: their power spectra do not overlap so that energy transfer from the hot to the cold subsystem is expected to be prohibitively slow, see Sect. 3.3 in Ref. [513] for a similar argument.

This is indeed the case as can be verified in Fig. 3 where the conserved energy E_{cons}, physical total energy E_{phys}, electronic energy V_e, and fictitious kinetic energy
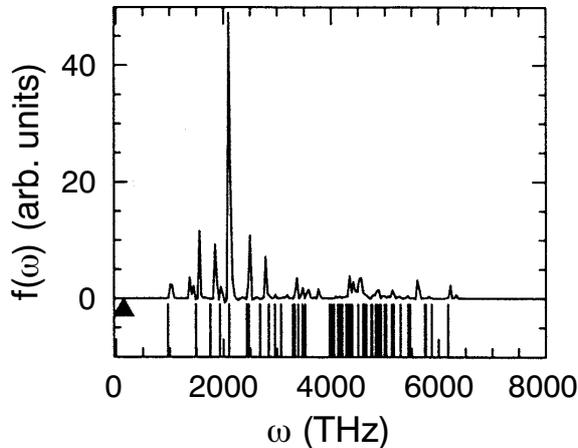
Figure 2. Vibrational density of states Eq. (47) (continuous spectrum in upper part) and harmonic approximation thereof Eq. (52) (stick spectrum in lower part) of the electronic degrees of freedom compared to the highest–frequency phonon mode $\omega_{\mathrm{n}}^{\mathrm{max}}$ (triangle) for a model system; for further details see text. Adapted from Ref. [467].

of the electrons T_{e}

$$E_{\mathrm{cons}} = \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \left| \dot{\psi}_i \right. \right\rangle + \sum_I \frac{1}{2}M_I \dot{\mathbf{R}}_I^2 + \langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle \tag{48}$$

$$E_{\mathrm{phys}} = \sum_I \frac{1}{2}M_I \dot{\mathbf{R}}_I^2 + \langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle = E_{\mathrm{cons}} - T_{\mathrm{e}} \tag{49}$$

$$V_{\mathrm{e}} = \langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle \tag{50}$$

$$T_{\mathrm{e}} = \sum_i \frac{1}{2}\mu_i \left\langle \dot{\psi}_i \left| \dot{\psi}_i \right. \right\rangle \tag{51}$$

are shown for the same system as a function of time. First of all, there should be a conserved energy quantity according to classical dynamics since the constraints are holonomic [244]. Indeed "the Hamiltonian" or conserved energy E_{cons} is a constant of motion (with relative variations smaller than 10^{-6} and with no drift), which serves as an extremely sensitive check of the molecular dynamics algorithm. Contrary to that the electronic energy V_{e} displays a simple oscillation pattern due to the simplicity of the phonon modes.

Most importantly, the fictitious kinetic energy of the electrons T_{e} is found to perform *bound* oscillations around a *constant*, i.e. the electrons "do not heat up" systematically in the presence of the hot nuclei; note that T_{e} is a measure for deviations from the exact Born–Oppenheimer surface. Closer inspection shows actually two time scales of oscillations: the one visible in Fig. 3 stems from the drag exerted by the moving nuclei on the electrons and is the mirror image of the V_{e} fluctuations. Superimposed on top of that (not shown, but see Fig. 4(b)) are small–amplitude high frequency oscillations intrinsic to the fictitious electron dynamics with a period of only a fraction of the visible mode. These oscillations are actually instrumental
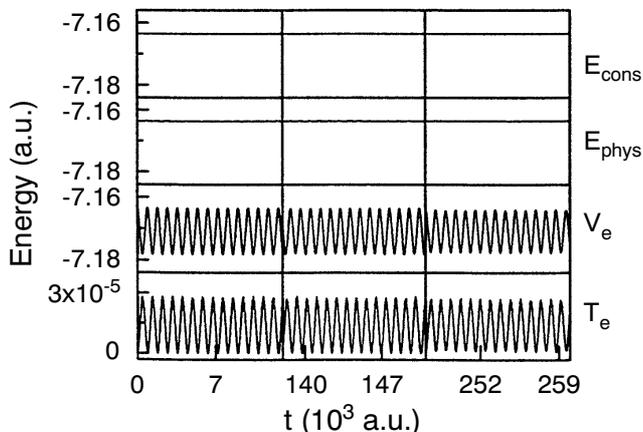
Figure 3. Various energies Eqs. (48)–(51) for a model system propagated via Car–Parrinello molecular dynamics for at short (up to 300 fs), intermediate, and long times (up to 6.3 ps); for further details see text. Adapted from Ref. [467].

for the stability of the Car–Parrinello dynamics, vide infra. But already the visible variations are three orders of magnitude smaller than the physically meaningful oscillations of V_e. As a result, E_{phys} defined as $E_{cons} - T_e$ or equivalently as the sum of the nuclear kinetic energy and the electronic total energy (which serves as the potential energy for the nuclei) is essentially constant on the relevant energy and time scales. Thus, it behaves approximately like the strictly conserved total energy in classical molecular dynamics (with only nuclei as dynamical degrees of freedom) or in Born–Oppenheimer molecular dynamics (with fully optimized electronic degrees of freedom) and is therefore often denoted as the "physical total energy". This implies that the resulting physically significant dynamics of the nuclei yields an excellent approximation to microcanonical dynamics (and assuming ergodicity to the microcanonical ensemble). Note that a different explanation was advocated in Ref. [470] (see also Ref. [472], in particular Sect. VIII.B and C), which was however revised in Ref. [110]. A discussion similar in spirit to the one outlined here [467] is provided in Ref. [513], see in particular Sect. 3.2 and 3.3.

Given the adiabatic separation and the stability of the propagation, the central question remains if the forces acting on the nuclei are actually the "correct" ones in Car–Parrinello molecular dynamics. As a reference serve the forces obtained from full self–consistent minimizations of the electronic energy $\min_{\{\psi_i\}} \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle$ at each time step, i.e. Born–Oppenheimer molecular dynamics with extremely well converged wavefunctions. This is indeed the case as demonstrated in Fig. 4(a): the physically meaningful dynamics of the x–component of the force acting on one silicon atom in the model system obtained from stable Car–Parrinello fictitious dynamics propagation of the electrons and from iterative minimizations of the electronic energy are extremely close.

Better resolution of one oscillation period in (b) reveals that the gross deviations are also oscillatory but that they are four orders of magnitudes smaller than

18
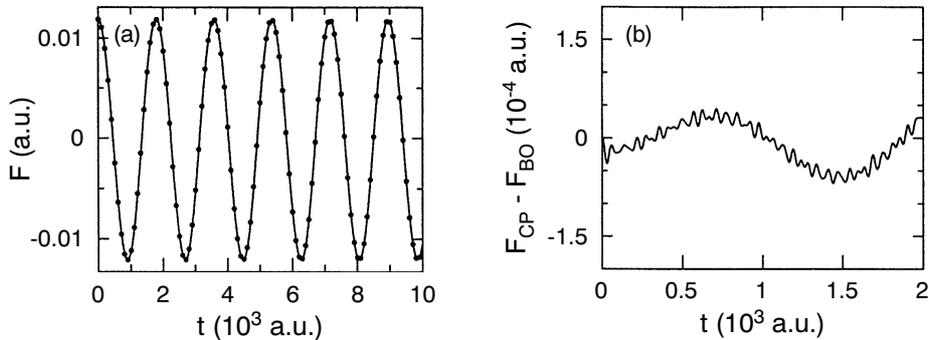
Figure 4. (a) Comparison of the x–component of the force acting on one atom of a model system obtained from Car–Parrinello (solid line) and well–converged Born–Oppenheimer (dots) molecular dynamics. (b) Enlarged view of the difference between Car–Parrinello and Born–Oppenheimer forces; for further details see text. Adapted from Ref. [467].

the physical variations of the force resolved in Fig. 4(a). These correspond to the "large–amplitude" oscillations of T_e visible in Fig. 3 due to the drag of the nuclei exerted on the quasi–adiabatically following electrons having a *finite* dynamical mass μ. Note that the inertia of the electrons also dampens artificially the nuclear motion (typically on a few–percent scale, see Sect. V.C.2 in Ref. [75] for an analysis and a renormalization correction of M_I) but decreases as the fictitious mass approaches the adiabatic limit $\mu \to 0$. Superimposed on the gross variation in (b) are again high–frequency *bound oscillatory small–amplitude* fluctuations like for T_e. They lead *on physically relevant time scales* (i.e. those visible in Fig. 4(a)) to "averaged forces" that are very close to the exact ground–state Born–Oppenheimer forces. This feature is an important ingredient in the derivation of adiabatic dynamics [467,411].

In conclusion, the Car–Parrinello force can be said to deviate at most instants of time from the exact Born–Oppenheimer force. However, this does not disturb the physical time evolution due to (i) the smallness and boundedness of this difference *and* (ii) the intrinsic averaging effect of small–amplitude high–frequency oscillations within a few molecular dynamics time steps, i.e. on the sub–femtosecond time scale which is irrelevant for *nuclear* dynamics.

2.4.4 How to Control Adiabaticity ?

An important question is under which circumstances the adiabatic separation can be achieved, and how it can be controlled. A simple harmonic analysis of the frequency spectrum of the orbital classical fields close to the minimum defining the ground state yields [467]

$$\omega_{ij} = \left(\frac{2(\epsilon_i - \epsilon_j)}{\mu} \right)^{1/2} \, , \tag{52}$$

19

where ϵ_j and ϵ_i are the eigenvalues of occupied and unoccupied orbitals, respectively; see Eq. (26) in Ref. [467] for the case where both orbitals are occupied ones. It can be seen from Fig. 2 that the harmonic approximation works faithfully as compared to the exact spectrum; see Ref. [471] and Sect. IV.A in Ref. [472] for a more general analysis of the associated equations of motion. Since this is in particular true for the lowest frequency $\omega_e^{\min}$, the handy analytic estimate for the lowest possible electronic frequency

$$\omega_e^{\min} \propto \left(\frac{E_{\text{gap}}}{\mu} \right)^{1/2} \quad , \tag{53}$$

shows that this frequency increases like the square root of the electronic energy difference E_{gap} between the lowest unoccupied and the highest occupied orbital. On the other hand it increases similarly for a decreasing fictitious mass parameter μ.

In order to guarantee the adiabatic separation, the frequency difference $\omega_e^{\min} - \omega_n^{\max}$ should be large, see Sect. 3.3 in Ref. [513] for a similar argument. But both the highest phonon frequency $\omega_n^{\max}$ and the energy gap E_{gap} are quantities that a dictated by the physics of the system. Whence, the only parameter in our hands to control adiabatic separation is the fictitious mass, which is therefore also called "adiabaticity parameter". However, decreasing μ not only shifts the electronic spectrum upwards on the frequency scale, but also stretches the entire frequency spectrum according to Eq. (52). This leads to an increase of the maximum frequency according to

$$\omega_e^{\max} \propto \left(\frac{E_{\text{cut}}}{\mu} \right)^{1/2} \quad , \tag{54}$$

where E_{cut} is the largest kinetic energy in an expansion of the wavefunction in terms of a plane wave basis set, see Sect. 3.1.3.

At this place a limitation to decrease μ arbitrarily kicks in due to the maximum length of the molecular dynamics time step $\Delta t^{\max}$ that can be used. The time step is inversely proportional to the highest frequency in the system, which is $\omega_e^{\max}$ and thus the relation

$$\Delta t^{\max} \propto \left(\frac{\mu}{E_{\text{cut}}} \right)^{1/2} \tag{55}$$

governs the largest time step that is possible. As a consequence, Car–Parrinello simulators have to find their way between Scylla and Charybdis and have to make a compromise on the control parameter μ; typical values for large–gap systems are $\mu = 500$–1500 a.u. together with a time step of about 5–10 a.u. (0.12–0.24 fs). Recently, an algorithm was devised that optimizes μ during a particular simulation given a fixed accuracy criterion [87]. Note that a poor man's way to keep the time step large and still increase μ in order to satisfy adiabaticity is to choose heavier nuclear masses. That depresses the largest phonon or vibrational frequency $\omega_n^{\max}$ of the nuclei (at the cost of renormalizing all *dynamical* quantities in the sense of classical isotope effects).

Up to this point the entire discussion of the stability and adiabaticity issues was based on model systems, approximate and mostly qualitative in nature. But recently it was actually proven [86] that the deviation or the absolute error Δ_μ of the Car–Parrinello trajectory relative to the trajectory obtained on the exact Born–Oppenheimer potential energy surface is controlled by μ:

Theorem 1 iv.): There are constants $C > 0$ and $\mu^\star > 0$ such that

$$\Delta_\mu = \left| \mathbf{R}^\mu(t) - \mathbf{R}^0(t) \right| + \left| \left| \psi^\mu; t \right\rangle - \left| \psi^0; t \right\rangle \right| \leq C\mu^{1/2} \quad , \quad 0 \leq t \leq T \qquad (56)$$

and the fictitious kinetic energy satisfies

$$T_{\mathrm{e}} = \frac{1}{2}\mu \left\langle \dot\psi^\mu; t \middle| \dot\psi^\mu; t \right\rangle \leq C\mu \quad , \quad 0 \leq t \leq T \qquad (57)$$

for all values of the parameter μ satisfying $0 < \mu \leq \mu^\star$, where up to time $T > 0$ there exists a unique nuclear trajectory on the exact Born–Oppenheimer surface with $\omega_{\mathrm{e}}^{\min} > 0$ for $0 \leq t \leq T$, i.e. there is "always" a finite electronic excitation gap. Here, the superscript μ or 0 indicates that the trajectory was obtained via Car–Parrinello molecular dynamics using a finite mass μ or via dynamics on the exact Born–Oppenheimer surface, respectively. Note that not only the nuclear trajectory is shown to be close to the correct one, but also the wavefunction is proven to stay close to the fully converged one up to time T. Furthermore, it was also investigated what happens if the initial wavefunction at $t = 0$ is not the minimum of the electronic energy $\langle \mathcal{H}_{\mathrm{e}} \rangle$ but trapped in an excited state. In this case it is found that the propagated wavefunction will keep on oscillating at $t > 0$ also for $\mu \to 0$ and not even time averages converge to any of the eigenstates. Note that this does not preclude Car–Parrinello molecular dynamics in excited states, which is possible given a properly "minimizable" expression for the electronic energy, see e.g. Refs. [281,214]. However, this finding might have crucial implications for electronic level–crossing situations.

What happens if the electronic gap is very small or even vanishes $E_{\mathrm{gap}} \to 0$ as is the case for metallic systems? In this limit, all the above–given arguments break down due to the occurrence of zero–frequency electronic modes in the power spectrum according to Eq. (53), which necessarily overlap with the phonon spectrum. Following an idea of Sprik [583] applied in a classical context it was shown that the coupling of separate Nosé–Hoover thermostats [12,270,217] to the nuclear and electronic subsystem can maintain adiabaticity by counterbalancing the energy flow from ions to electrons so that the electrons stay "cool" [74]; see Ref. [204] for a similar idea to restore adiabaticity. Although this method is demonstrated to work in practice [464], this *ad hoc* cure is not entirely satisfactory from both a theoretical and practical point of view so that the well–controlled Born–Oppenheimer approach is recommended for strongly metallic systems. An additional advantage for metallic systems is that the latter is also better suited to sample many $\mathbf{k}$–points (see Sect. 3.1.3), allows easily for fractional occupation numbers [458,168], and can handle efficiently the so–called charge sloshing problem [472].

2.4.5 The Quantum Chemistry Viewpoint

In order to understand Car–Parrinello molecular dynamics also from the "quantum chemistry perspective", it is useful to formulate it for the special case of the Hartree–Fock approximation using

$$\mathcal{L}_{\text{CP}} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2} \mu_i \left\langle \dot{\psi}_i \,\middle|\, \dot{\psi}_i \right\rangle$$
$$- \left\langle \Psi_0 | \mathcal{H}_{\text{e}}^{\text{HF}} | \Psi_0 \right\rangle + \sum_{i,j} \Lambda_{ij} \left(\left\langle \psi_i \,\middle|\, \psi_j \right\rangle - \delta_{ij} \right) \quad . \tag{58}$$

The resulting equations of motion

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \left\langle \Psi_0 \,\middle|\, \mathcal{H}_{\text{e}}^{\text{HF}} \,\middle|\, \Psi_0 \right\rangle \tag{59}$$

$$\mu_i \ddot{\psi}_i(t) = -\mathcal{H}_{\text{e}}^{\text{HF}} \psi_i + \sum_j \Lambda_{ij} \psi_j \tag{60}$$

are very close to those obtained for Born–Oppenheimer molecular dynamics Eqs. (39)–(40) except for (i) no need to minimize the electronic total energy expression and (ii) featuring the additional fictitious kinetic energy term associated to the orbital degrees of freedom. It is suggestive to argue that both sets of equations become identical if the term $|\mu_i \ddot{\psi}_i(t)|$ is small at any time t compared to the physically relevant forces on the right–hand–side of both Eq. (59) and Eq. (60). This term being zero (or small) means that one is at (or close to) the minimum of the electronic energy $\langle \Psi_0 | \mathcal{H}_{\text{e}}^{\text{HF}} | \Psi_0 \rangle$ since time derivatives of the orbitals $\{\psi_i\}$ can be considered as variations of Ψ_0 and thus of the expectation value $\langle \mathcal{H}_{\text{e}}^{\text{HF}} \rangle$ itself. In other words, no forces act on the wavefunction if $\mu_i \ddot{\psi}_i \equiv 0$. In conclusion, the Car–Parrinello equations are expected to produce the correct dynamics and thus physical trajectories in the microcanonical ensemble in this idealized limit. But if $|\mu_i \ddot{\psi}_i(t)|$ is small for all i, this also implies that the associated kinetic energy $T_{\text{e}} = \sum_i \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle / 2$ is small, which connects these more qualitative arguments with the previous discussion [467].

At this stage, it is also interesting to compare the structure of the Lagrangian Eq. (58) and the Euler–Lagrange equation Eq. (43) for Car–Parrinello dynamics to the analogues equations (36) and (37), respectively, used to derive "Hartree–Fock statics". The former reduce to the latter if the dynamical aspect and the associated time evolution is neglected, that is in the limit that the nuclear and electronic momenta are absent or constant. Thus, the Car–Parrinello ansatz, namely Eq. (41) together with Eqs. (42)–(43), can also be viewed as a prescription to derive a new class of "dynamical *ab initio* methods" in very general terms.

2.4.6 The Simulated Annealing and Optimization Viewpoints

In the discussion given above, Car–Parrinello molecular dynamics was motivated by "combining" the positive features of both Ehrenfest and Born–Oppenheimer molecular dynamics as much as possible. Looked at from another side, the Car–Parrinello method can also be considered as an ingenious way to perform *global* optimizations (minimizations) of nonlinear functions, here $\langle \Psi_0 | \mathcal{H}_{\text{e}} | \Psi_0 \rangle$, in a high–dimensional parameter space including complicated constraints. The optimization

parameters are those used to represent the total wavefunction Ψ_0 in terms of simpler functions, for instance expansion coefficients of the orbitals in terms of Gaussians or plane waves, see e.g. Refs. [583,375,693,608] for applications of the same idea in other fields.

Keeping the nuclei frozen for a moment, one could start this optimization procedure from a "random wavefunction" which certainly does not minimize the electronic energy. Thus, its fictitious kinetic energy is high, the electronic degrees of freedom are "hot". This energy, however, can be extracted from the system by systematically cooling it to lower and lower temperatures. This can be achieved in an elegant way by adding a non–conservative damping term to the electronic Car–Parrinello equation of motion Eq. (45)

$$\mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^\star} \langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle + \frac{\delta}{\delta \psi_i^\star} \{constraints\} - \gamma_{\mathrm{e}} \mu_i \psi_i \ , \qquad (61)$$

where $\gamma_{\mathrm{e}} \geq 0$ is a friction constant that governs the rate of energy dissipation [610]; alternatively, dissipation can be enforced in a discrete fashion by reducing the velocities by multiplying them with a constant factor < 1. Note that this deterministic and dynamical method is very similar in spirit to simulated annealing [332] invented in the framework of the stochastic Monte Carlo approach in the canonical ensemble. If the energy dissipation is done slowly, the wavefunction will find its way down to the minimum of the energy. At the end, an intricate global optimization has been performed!

If the nuclei are allowed to move according to Eq. (44) in the presence of another damping term a combined or simultaneous optimization of both electrons and nuclei can be achieved, which amounts to a "global geometry optimization". This perspective is stressed in more detail in the review Ref. [223] and an implementation of such ideas within the CADPAC quantum chemistry code is described in Ref. [692]. This operational mode of Car–Parrinello molecular dynamics is related to other optimization techniques where it is aimed to optimize simultaneously both the structure of the nuclear skeleton and the electronic structure. This is achieved by considering the nuclear coordinates and the expansion coefficients of the orbitals as variation parameters on the same footing [49,290,608]. But Car–Parrinello molecular dynamics is more than that because even if the nuclei continuously move according to Newtonian dynamics at finite temperature an initially optimized wavefunction will stay optimal along the nuclear trajectory.

2.4.7 The Extended Lagrangian Viewpoint

There is still another way to look at the Car–Parrinello method, namely in the light of so–called "extended Lagrangians" or "extended system dynamics" [14], see e.g. Refs. [136,12,270,585,217] for introductions. The basic idea is to couple additional degrees of freedom to the Lagrangian of interest, thereby "extending" it by increasing the dimensionality of phase space. These degrees of freedom are treated like classical particle coordinates, i.e. they are in general characterized by "positions", "momenta", "masses", "interactions" and a "coupling term" to the particle's positions and momenta. In order to distinguish them from the physical degrees of freedom, they are often called "fictitious degrees of freedom".

The corresponding equations of motion follow from the Euler–Lagrange equations and yield a microcanonical ensemble in the extended phase space where the Hamiltonian of the extended system is strictly conserved. In other words, the Hamiltonian of the physical (sub–) system is no more (strictly) conserved, and the produced ensemble is no more the microcanonical one. Any extended system dynamics is constructed such that time–averages taken in that part of phase space that is associated to the physical degrees of freedom (obtained from a partial trace over the fictitious degrees of freedom) are physically meaningful. Of course, dynamics and thermodynamics of the system are affected by adding fictitious degrees of freedom, the classic examples being temperature and pressure control by thermostats and barostats, see Sect. 4.2.

In the case of Car–Parrinello molecular dynamics, the basic Lagrangian for Newtonian dynamics of the nuclei is actually extended by classical *fields* $\{\psi_i(\mathbf{r})\}$, i.e. functions instead of coordinates, which represent the quantum wavefunction. Thus, vector products or absolute values have to be generalized to scalar products and norms of the fields. In addition, the "positions" of these fields $\{\psi_i\}$ actually have a physical meaning, contrary to their momenta $\{\dot{\psi}_i\}$.

2.5 What about Hellmann–Feynman Forces ?

An important ingredient in all dynamics methods is the efficient calculation of the forces acting on the nuclei, see Eqs. (30), (32), and (44). The straightforward numerical evaluation of the derivative

$$\mathbf{F}_I = -\nabla_I \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle \tag{62}$$

in terms of a finite–difference approximation of the total electronic energy is both too costly and too inaccurate for dynamical simulations. What happens if the gradients are evaluated analytically? In addition to the derivative of the Hamiltonian itself

$$\nabla_I \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle = \langle \Psi_0 | \nabla_I \mathcal{H}_e | \Psi_0 \rangle \\ + \langle \nabla_I \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \langle \Psi_0 | \mathcal{H}_e | \nabla_I \Psi_0 \rangle \tag{63}$$

there are in general also contributions from variations of the wavefunction $\sim \nabla_I \Psi_0$. In general means here that these contributions vanish exactly

$$\mathbf{F}_I^{\text{HFT}} = - \langle \Psi_0 | \nabla_I \mathcal{H}_e | \Psi_0 \rangle \tag{64}$$

if the wavefunction is an exact eigenfunction (or stationary state wavefunction) of the particular Hamiltonian under consideration. This is the content of the often–cited Hellmann–Feynman Theorem [295,186,368], which is also valid for many variational wavefunctions (e.g. the Hartree–Fock wavefunction) provided that *complete basis sets* are used. If this is not the case, which has to be assumed for numerical calculations, the additional terms have to be evaluated explicitly.

In order to proceed a Slater determinant $\Psi_0 = \det\{\psi_i\}$ of one–particle orbitals ψ_i, which themselves are expanded

$$\psi_i = \sum_\nu c_{i\nu} \, f_\nu(\mathbf{r}; \{\mathbf{R}_I\}) \tag{65}$$

stressed that the energy conservation seen in Fig. 5(top) is routinely achieved in Car–Parrinello molecular dynamics simulations.

2.7 Electronic Structure Methods

2.7.1 Introduction

Up to this point, the electronic structure method to calculate the *ab initio* forces $\nabla_I \langle \Psi | \mathcal{H}_e | \Psi \rangle$ was not specified in detail. It is immediately clear that *ab initio* molecular dynamics is not tied to any particular approach, although very accurate techniques are of course prohibitively expensive. It is also evident that the strength or weakness of a particular *ab initio* molecular dynamics scheme is intimately connected to the strength or weakness of the chosen electronic structure method. Over the years a variety of different approaches such as density functional [108,679,35,472,343,36], Hartree–Fock [365,254,191,379,281,284,316,293], generalized valence bond (GVB) [282,283,228,229,230], complete active space SCF (CASSCF) [566,567], full configuration interaction (FCI) [372], semiempirical [669,671,91,?,114,666,280] or other approximate [473,454,551,455,170,171,26] methods were combined with molecular dynamics, and this list is certainly incomplete.

The focus of the present review clearly is Car–Parrinello molecular dynamics in conjunction with Hohenberg–Kohn–Sham density functional theory [301,338]. In the following, only those parts of density functional theory are presented that impact directly on *ab initio* molecular dynamics. For a deeper presentation and in particular for a discussion of the assumptions and limitations of this approach (both conceptually and in practice) the reader is referred to the existing excellent literature [591,320,458,168]. For simplicity, the formulae are presented for the spin–unpolarized or restricted special case.

Following the exposition of density functional theory, the fundamentals of Hartree–Fock theory, which is often considered to be the basis of quantum chemistry, are introduced for the same special case. Finally, a glimpse is given at post Hartree–Fock methods. Again, an extensive text–book literature exists for these wavefunction–based approaches to electronic structure calculations [604,418]. The very useful connection between the density–based and wavefunction–based methods goes back to Löwdin's work in the mid fifties and is e.g. worked out in Chapt. 2.5 of Ref. [458], where Hartree–Fock theory is formulated in density–matrix language.

2.7.2 Density Functional Theory

The total ground–state energy of the interacting system of electrons with classical nuclei fixed at positions $\{\mathbf{R}_I\}$ can be obtained

$$\min_{\Psi_0} \{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle\} = \min_{\{\phi_i\}} E^{\text{KS}}[\{\phi_i\}]$$

as the minimum of the Kohn–Sham energy [301,338]

$$E^{\text{KS}}[\{\phi_i\}] = T_s[\{\phi_i\}] + \int d\mathbf{r} \ V_{\text{ext}}(\mathbf{r}) \ n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \ V_{\text{H}}(\mathbf{r}) \ n(\mathbf{r}) + E_{\text{xc}}[n] \ , \quad (75)$$

which is an explicit functional of the set of auxiliary functions $\{\phi_i(\mathbf{r})\}$ that satisfy the orthonormality relation $\langle \phi_i \mid \phi_j \rangle = \delta_{ij}$. This is a dramatic simplification since the minimization with respect to all possible *many–body* wavefunctions $\{\Psi\}$ is replaced by a minimization with respect to a set of orthonormal one–particle functions, the Kohn–Sham orbitals $\{\phi_i\}$. The associated electronic one–body density or charge density

$$n(\mathbf{r}) = \sum_i^{\mathrm{occ}} f_i \mid \phi_i(\mathbf{r}) \mid^2 \tag{76}$$

is obtained from a single Slater determinant built from the occupied orbitals, where $\{f_i\}$ are integer occupation numbers.

The first term in the Kohn–Sham functional Eq. (75) is the kinetic energy of a non–interacting reference system

$$T_{\mathrm{s}}[\{\phi_i\}] = \sum_i^{\mathrm{occ}} f_i \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle \tag{77}$$

consisting of the same number of electrons exposed to the same external potential as in the fully interacting system. The second term comes from the fixed external potential

$$V_{\mathrm{ext}}(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}|} + \sum_{I<J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{78}$$

in which the electrons move, which comprises the Coulomb interactions between electrons and nuclei and in the definition used here also the internuclear Coulomb interactions; this term changes in the first place if core electrons are replaced by pseudopotentials, see Sect. 3.1.5 for further details. The third term is the Hartree energy, i.e. the classical electrostatic energy of two charge clouds which stem from the electronic density and is obtained from the Hartree potential

$$V_{\mathrm{H}}(\mathbf{r}) = \int d\mathbf{r}' \ \frac{n(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} \ , \tag{79}$$

which in turn is related to the density via

$$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi n(\mathbf{r}) \tag{80}$$

Poisson's equation. The last contribution in the Kohn–Sham functional, the exchange–correlation functional $E_{\mathrm{xc}}[n]$, is the most intricate contribution to the total electronic energy. The electronic exchange and correlation effects are lumped together and basically define this functional as the remainder between the exact energy and its Kohn–Sham decomposition in terms of the three previous contributions.

The minimum of the Kohn–Sham functional is obtained by varying the energy functional Eq. (75) for a fixed number of electrons with respect to the density Eq. (76) or with respect to the orbitals subject to the orthonormality constraint,

see e.g. the discussion following Eq. (35) for a similar variational procedure. This leads to the Kohn–Sham equations

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \right\} \phi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\phi_j(\mathbf{r}) \qquad (81)$$

$$\left\{ -\frac{1}{2}\nabla^2 + V^{\text{KS}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\phi_j(\mathbf{r}) \qquad (82)$$

$$H_{\text{e}}^{\text{KS}}\phi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\phi_j(\mathbf{r}) \ , \qquad (83)$$

which are one–electron equations involving an effective *one–particle* Hamiltonian H_{e}^{KS} with the local potential V^{KS}. Note that H_{e}^{KS} nevertheless embodies the electronic *many–body* effects by virtue of the exchange–correlation potential

$$\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} = V_{\text{xc}}(\mathbf{r}) \ . \qquad (84)$$

A unitary transformation within the space of the occupied orbitals leads to the canonical form

$$H_{\text{e}}^{\text{KS}}\phi_i = \epsilon_i\phi_i \qquad (85)$$

of the Kohn–Sham equations, where $\{\epsilon_i\}$ are the eigenvalues. In conventional static density functional or "band structure" calculations this set of equations has to be solved self–consistently in order to yield the density, the orbitals and the Kohn–Sham potential for the electronic ground state [487]. The corresponding total energy Eq. (75) can be written as

$$E^{\text{KS}} = \sum_i \epsilon_i - \frac{1}{2}\int d\mathbf{r} \ V_{\text{H}}(\mathbf{r}) \ n(\mathbf{r}) + E_{\text{xc}}[n] - \int d\mathbf{r} \ \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \ n(\mathbf{r}) \ , \qquad (86)$$

where the sum over Kohn–Sham eigenvalues is the so–called "band–structure energy".

Thus, Eqs. (81)–(83) together with Eqs. (39)–(40) define Born–Oppenheimer molecular dynamics within Kohn–Sham density functional theory, see e.g. Refs. [232,616,594,35,679,472,36,343,344] for such implementations. The functional derivative of the Kohn–Sham functional with respect to the orbitals, the Kohn–Sham force acting on the orbitals, can be expressed as

$$\frac{\delta E^{\text{KS}}}{\delta \phi_i^\star} = f_i H_{\text{e}}^{\text{KS}}\phi_i \ , \qquad (87)$$

which makes clear the connection to Car–Parrinello molecular dynamics, see Eq. (45). Thus, Eqs. (59)–(60) have to be solved with the effective one–particle Hamiltonian in the Kohn–Sham formulation Eqs. (81)–(83). In the case of Ehrenfest dynamics presented in Sect. 2.2, which will not be discussed in further detail at this stage, the Runge–Gross time–dependent generalization of density functional theory [258] has to be invoked instead, see e.g. Refs. [203,617,532].

Crucial to any application of density functional theory is the approximation of the unknown exchange and correlation functional. A discussion focussed on the

utilization of such functionals in the framework of *ab initio* molecular dynamics is for instance given in Ref. [588]. Those exchange–correlation functionals that will be considered in the implementation part, Sect. 3.3, belong to the class of the "Generalized Gradient Approximation"

$$E_{xc}^{GGA}[n] = \int d\mathbf{r} \ n(\mathbf{r}) \ \varepsilon_{xc}^{GGA}(n(\mathbf{r}); \nabla n(\mathbf{r})) \ , \tag{88}$$

where the unknown functional is approximated by an integral over a function that depends only on the density and its gradient at a given point in space, see Ref. [477] and references therein. The combined exchange–correlation function is typically split up into two additive terms ε_x and ε_c for exchange and correlation, respectively. In the simplest case it is the exchange and correlation energy density $\varepsilon_{xc}^{LDA}(n)$ of an interacting but homogeneous electron gas at the density given by the "local" density $n(\mathbf{r})$ at space–point $\mathbf{r}$ in the inhomogeneous system. This simple but astonishingly powerful approximation [320] is the famous local density approximation LDA [338] (or local spin density LSD in the spin–polarized case [40]), and a host of different parameterizations exist in the literature [458,168]. The self–interaction correction [475] SIC as applied to LDA was critically assessed for molecules in Ref. [240] with a disappointing outcome.

A significant improvement of the accuracy was achieved by introducing the gradient of the density as indicated in Eq. (88) beyond the well–known straightforward gradient expansions. These so–called GGAs (also denoted as "gradient corrected" or "semilocal" functionals) extended the applicability of density functional calculation to the realm of chemistry, see e.g. Refs. [476,42,362,477,478,479] for a few "popular functionals" and Refs. [318,176,577,322] for extensive tests on molecules, complexes, and solids, respectively.

Another considerable advance was the successful introduction of "hybrid functionals" [43,44] that include to some extent "exact exchange" [249] in addition to a standard GGA. Although such functionals can certainly be implemented within a plane wave approach [262,128], they are prohibitively time–consuming as outlined at the end of Sect. 3.3. A more promising route in this respect are those functionals that include higher–order powers of the gradient (or the local kinetic energy density) in the sense of a generalized gradient expansion beyond the first term. Promising results could be achieved by including Laplacian or local kinetic energy terms [493,192,194,662], but at this stage a sound judgment concerning their "prize / performance ratio" has to await further scrutinizing tests. The "optimized potential method" (OPM) or "optimized effective potentials" (OEP) are another route to include "exact exchange" within density functional theory, see e.g. Sect. 13.6 in Ref. [588] or Ref. [251] for overviews. Here, the exchange–correlation functional $E_{xc}^{OPM} = E_{xc}[\{\phi_i\}]$ depends on the individual orbitals instead of only on the density or its derivatives.

2.7.3 Hartree–Fock Theory

Hartree–Fock theory is derived by invoking the variational principle in a restricted space of wavefunctions. The antisymmetric ground–state electronic wavefunction is approximated by a single Slater determinant $\Psi_0 = \det\{\psi_i\}$ which is constructed

from a set of one–particle spin orbitals $\{\psi_i\}$ required to be mutually orthonormal $\langle\psi_i|\psi_j\rangle = \delta_{ij}$. The corresponding variational minimum of the total electronic energy $\mathcal{H}_e$ defined in Eq. (2)

$$
\begin{aligned}
E^{\mathrm{HF}}[\{\psi_i\}] = &\sum_i \int d\mathbf{r}\, \psi_i^\star(\mathbf{r}) \left[-\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) \\
&+ \frac{1}{2} \sum_{ij} \int\int d\mathbf{r}\, d\mathbf{r}'\, \psi_i^\star(\mathbf{r})\psi_j^\star(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_i(\mathbf{r})\psi_j(\mathbf{r}') \\
&+ \frac{1}{2} \sum_{ij} \int\int d\mathbf{r}\, d\mathbf{r}'\, \psi_i^\star(\mathbf{r})\psi_j^\star(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_j(\mathbf{r})\psi_i(\mathbf{r}') \quad (89)
\end{aligned}
$$

yields the lowest energy and the "best" wavefunction within a one–determinant ansatz; the external Coulomb potential V_{ext} was already defined in Eq. (78). Carrying out the constraint minimization within this ansatz (see Eq. (36) in Sect. 2.3 for a sketch) leads to

$$
\left\{ -\frac{1}{2}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + \sum_j \mathcal{J}_j(\mathbf{r}) - \sum_j \mathcal{K}_j(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\psi_j(\mathbf{r}) \quad (90)
$$

$$
\left\{ -\frac{1}{2}\nabla^2 + V^{\mathrm{HF}}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\psi_j(\mathbf{r}) \quad (91)
$$

$$
H_e^{\mathrm{HF}}\psi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\psi_j(\mathbf{r}) \quad (92)
$$

the Hartree–Fock integro–differential equations. In analogy to the Kohn–Sham equations Eqs. (81)–(83) these are effective one–particle equations that involve an effective one–particle Hamiltonian H_e^{HF}, the (Hartree–) Fock operator. The set of canonical orbitals

$$
H_e^{\mathrm{HF}}\psi_i = \epsilon_i\psi_i \quad (93)
$$

is obtained similarly to Eq. (85). The Coulomb operator

$$
\mathcal{J}_j(\mathbf{r})\, \psi_i(\mathbf{r}) = \left[\int d\mathbf{r}'\, \psi_j^\star(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_j(\mathbf{r}') \right] \psi_i(\mathbf{r}) \quad (94)
$$

and the exchange operator

$$
\mathcal{K}_j(\mathbf{r})\, \psi_i(\mathbf{r}) = \left[\int d\mathbf{r}'\, \psi_j^\star(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_i(\mathbf{r}') \right] \psi_j(\mathbf{r}) \quad (95)
$$

are most easily defined via their action on a particular orbital ψ_i. It is found that upon acting on orbital $\psi_i(\mathbf{r})$ the exchange operator for the j–th state "exchanges" $\psi_j(\mathbf{r}') \rightarrow \psi_i(\mathbf{r}')$ in the kernel as well as replaces $\psi_i(\mathbf{r}) \rightarrow \psi_j(\mathbf{r})$ in its argument, compare to the Coulomb operator. Thus, $\mathcal{K}$ is a non–local operator as its action on a function ψ_i at point $\mathbf{r}$ in space requires the evaluation and thus the knowledge of that function throughout all space by virtue of $\int d\mathbf{r}'\, \psi_i(\mathbf{r}')\dots$ the required integration. In this sense the exchange operator does not possess a simple classical interpretation like the Coulomb operator $\mathcal{C}$, which is the counterpart of

the Hartree potential V_H in Kohn–Sham theory. The exchange operator vanishes exactly if the antisymmetrization requirement of the wavefunction is relaxed, i.e. only the Coulomb contribution survives if a Hartree product is used to represent the wavefunction.

The force acting on the orbitals is defined

$$\frac{\delta E^{HF}}{\delta \psi_i^\star} = H_e^{HF} \psi_i \qquad (96)$$

similarly to Eq. (87). At this stage, the various *ab initio* molecular dynamics schemes based on Hartree–Fock theory are defined, see Eqs. (39)–(40) for Born–Oppenheimer molecular dynamics and Eqs. (59)–(60) for Car–Parrinello molecular dynamics. In the case of Ehrenfest molecular dynamics the time–dependent Hartree–Fock formalism [162] has to be invoked instead.

2.7.4 Post Hartree–Fock Theories

Although post Hartree–Fock methods have a very unfavorable scaling of the computational cost as the number of electrons increases, a few case studies were performed with such correlated quantum chemistry techniques. For instance *ab initio* molecular dynamics was combined with GVB [282,283,228,229,230], CASSCF [566,567], as well as FCI [372] approaches, see also references therein. It is noted in passing that Car–Parrinello molecular dynamics can only be implemented straightforwardly if energy and wavefunction are "consistent". This is not the case in perturbation theories such as e.g. the widely used Møller–Plesset approach [292]: within standard MP2 the energy is correct to second order, whereas the wavefunction is the one given by the uncorrelated HF reference. As a result, the derivative of the MP2 energy with respect to the wavefunction Eq. (96) does not yield the correct force on the HF wavefunction in the sense of fictitious dynamics. Such problems are of course absent from the Born–Oppenheimer approach to sample configuration space, see e.g. Ref. [328,317,33] for MP2, density functional, and multireference CI *ab initio* Monte Carlo schemes.

It should be kept in mind that the rapidly growing workload of post HF calculations, although extremely powerful in principle, limits the number of explicitly treated electrons to only a few. The rapid development of correlated electronic structure methods that scale linearly with the number of electrons will certainly broaden the range of applicability of this class of techniques in the near future.

2.8 Basis Sets

2.8.1 Gaussians and Slater Functions

Having selected a specific electronic structure method the next choice is related to which basis set to use in order to represent the orbitals ψ_i in terms of simple analytic functions f_ν with well–known properties. In general a *linear* combination of such basis functions

$$\psi_i(\mathbf{r}) = \sum_\nu c_{i\nu} f_\nu(\mathbf{r}; \{\mathbf{R}_I\}) \qquad (97)$$

is used, which represents exactly any reasonable function in the limit of using a complete set of basis functions. In quantum chemistry, Slater–type basis functions (STOs)

$$f_{\mathbf{m}}^{\mathrm{S}}(\mathbf{r}) = N_{\mathbf{m}}^{\mathrm{S}}\, r_x^{m_x} r_y^{m_y} r_z^{m_z}\ \exp\left[-\zeta_{\mathbf{m}}|\mathbf{r}|\right] \tag{98}$$

with an exponentially decaying radial part and Gaussian–type basis functions (GTOs)

$$f_{\mathbf{m}}^{\mathrm{G}}(\mathbf{r}) = N_{\mathbf{m}}^{\mathrm{G}}\, r_x^{m_x} r_y^{m_y} r_z^{m_z}\ \exp\left[-\alpha_{\mathbf{m}} r^2\right] \tag{99}$$

have received widespread use, see e.g. Ref. [292] for a concise overview–type presentation. Here, $N_{\mathbf{m}}$, $\zeta_{\mathbf{m}}$ and $\alpha_{\mathbf{m}}$ are constants that are typically kept fixed during a molecular electronic structure calculation so that only the orbital expansion coefficients $c_{i\nu}$ need to be optimized. In addition, fixed linear combinations of the above–given "primitive" basis functions can be used for a given angular momentum channel $\mathbf{m}$, which defines the "contracted" basis sets.

The Slater or Gaussian basis functions are in general centered at the positions of the nuclei, i.e. $\mathbf{r} \to \mathbf{r} - \mathbf{R}_I$ in Eq. (98)–(99), which leads to the linear combination of *atomic orbitals* (LCAO) ansatz to solve differential equations algebraically. Furthermore, their derivatives as well as the resulting matrix elements are efficiently obtained by differentiation and integration in real–space. However, Pulay forces (see Sect. 2.5) will result for such basis functions that are fixed at atoms (or bonds) if the atoms are allowed to move, either in geometry optimization or molecular dynamics schemes. This disadvantage can be circumvented by using *freely* floating Gaussians that are distributed in space [582], which form an originless basis set since it is localized but not atom–fixed.

2.8.2 Plane Waves

A vastly different approach has its roots in solid–state theory. Here, the ubiquitous periodicity of the underlying lattice produces a periodic potential and thus imposes the same periodicity on the density (implying Bloch's Theorem, Born–von Karman periodic boundary conditions etc., see e.g. Chapt. 8 in Ref. [27]). This heavily suggests to use plane waves as the generic basis set in order to expand the periodic part of the orbitals, see Sect. 3.1.2. Plane waves are defined as

$$f_{\mathbf{G}}^{\mathrm{PW}}(\mathbf{r}) = N \exp\left[i\mathbf{G}\mathbf{r}\right]\ , \tag{100}$$

where the normalization is simply given by $N = 1/\sqrt{\Omega}$; Ω is the volume of the periodic (super–) cell. Since plane waves form a complete and orthonormal set of functions they can be used to expand orbitals according to Eq. (97), where the labeling ν is simply given by the vector $\mathbf{G}$ in reciprocal space / G–space (including only those $\mathbf{G}$–vectors that satisfy the particular periodic boundary conditions). The total electronic energy is found to have a particularly simple form when expressed in plane waves [312].

It is important to observe that plane waves are originless functions, i.e. they do *not* depend on the positions of the nuclei $\{\mathbf{R}_I\}$. This implies that the Pulay forces Eq. (67) vanish exactly even within a *finite* basis (and using a fixed number

of plane waves, see the discussion related to "Pulay stress" in Sect. 2.5), which tremendously facilitates force calculations. This also implies that plane waves are a very unbiased basis set in that they are "delocalized" in space and do not "favor" certain atoms or regions over others, i.e. they can be considered as an ultimately "balanced basis set" in the language of quantum chemistry. Thus, the only way to improve the quality of the basis is to increase the "energy cutoff" E_{cut}, i.e. to increase the largest $|\mathbf{G}|$–vector that is included in the finite expansion Eq. (97). This blind approach is vastly different from the traditional procedures in quantum chemistry that are needed in order to produce reliable basis sets [292]. Another appealing feature is that derivatives in real–space are simply multiplications in G– space, and both spaces can be efficiently connected via Fast Fourier Transforms (FFTs). Thus, one can easily evaluate operators in that space in which they are diagonal, see for instance the flow charts in Fig. 6 or Fig. 7.

According to the well–known "No Free Lunch Theorem" there cannot be only advantages connected to using plane waves. The first point is that the pseudopotential approximation is intimately connected to using plane waves, why so? A plane wave basis is basically a lattice–symmetry–adapted three–dimensional Fourier decomposition of the orbitals. This means that increasingly large Fourier components are needed in order to resolve structures in real space on decreasingly small distance scales. But already orbitals of first row atoms feature quite strong and rapid oscillations close to the nuclei due to the Pauli principle, which enforces a nodal structure onto the wavefunction by imposing orthogonality of the orbitals. However, most of chemistry is ruled by the valence electrons, whereas the core electrons are essentially inert. In practice, this means that the innermost electrons can be taken out of explicit calculations. Instead they are represented by a smooth and nodeless effective potential, the so–called pseudopotential [296,297,484,485,139], see for instance Refs. [487,578,221] for reviews in the context of "solid state theory" and Refs. [145,166] for pseudopotentials as used in "quantum chemistry". The resulting pseudo wavefunction is made as smooth as possible close to the nuclear core region. This also means that properties that depend crucially on the wavefunction close to the core cannot be obtained straightforwardly from such calculations. In the field of plane wave calculations the introduction of "soft" norm–conserving *ab initio* pseudopotentials was a breakthrough both conceptually [274] and in practice [28]. Another important contribution, especially for transition metals, was the introduction of the so–called ultrasoft pseudopotentials by Vanderbilt [661]. This approaches lead to the powerful technique of plane wave–pseudopotential electronic structure calculations in the framework of density functional theory [312,487]. Within this particular framework the issue of pseudopotentials is elaborated in more detail in Sect. 3.1.5.

Another severe shortcoming of plane waves is the backside of the medal of being an unbiased basis set: there is no way to shuffle more basis functions into regions in space where they are more needed than in other regions. This is particularly bad for systems with strong inhomogeneities. Such examples are all–electron calculations or the inclusion of semi–core states, a few heavy atoms in a sea of light atoms, and (semi–) finite systems such as surfaces or molecules with a large vacuum region in order to allow the long–range Coulomb interactions to decay. This is often referred to as the multiple length scale deficiency of plane wave calculations.
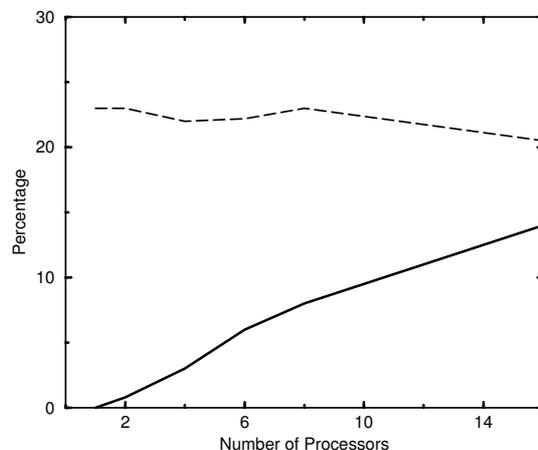
Figure 14. Percentage of total CPU time spend in global communication routines (solid line) and in Fourier transform routines (dashed line) for a system of 64 silicon atoms on a Cray T3E/600 computer.

addition to the adaptation of the overlap routine, also the matrix multiply routines needed for the orthogonalization step have to be done in parallel. Although there are libraries for these tasks available the complexity of the code is considerably increased.

3.9.5 Summary

Efficient parallel algorithms for the plane wave–pseudopotential density functional theory method exist. Implementations of these algorithms are available and were used in most of the large scale applications presented at the end of this paper (Sect. 5). Depending on the size of the problem, excellent speedups can be achieved even on computers with several hundreds of processors. The limitations presented in the last paragraph are of importance for high–end applications. Together with the extensions presented, existing plane wave codes are well suited also for the next generation of supercomputers.

4 Advanced Techniques: Beyond ...

4.1 Introduction

The discussion up to this point revolved essentially around the "basic" *ab initio* molecular dynamics methodologies. This means in particular that *classical* nuclei evolve in the electronic *ground state* in the *microcanonical* ensemble. This combination allows already a multitude of applications, but many circumstances exist where the underlying approximations are unsatisfactory. Among these cases are

situations where

- it is necessary to keep temperature and /or pressure constant (such as during journeys in phase diagrams or in the investigation of solid–state phase transitions),

- there is a sufficient population of excited electronic states (such as in materials with a small or vanishing electronic gap) or dynamical motion occurs in a single excited states (such as after photoexcitation events),

- light nuclei are involved in crucial steps of a process (such as in studies of proton transfer or muonium impurities).

In the following subsections techniques are introduced which transcede these limitations. Thus, the realm of *ab initio* molecular dynamics is considerably increased beyond the basic setup as discussed in general terms in Sect. 2 and concerning its implementation in Sect. 3. The presented "advanced techniques" are selected because they are available in the current version of the CPMD package [142], but their implementation is not discussed in detail here.

4.2 Beyond Microcanonics

4.2.1 Introduction

In the framework of statistical mechanics all ensembles can be formally obtained from the microcanonical or NVE ensemble – where particle number, volume and energy are the external thermodynamic control variables – by suitable Laplace transforms of its partition function; note that V is used for volume when it comes to labeling the various ensembles in Sect. 4 and its subsections. Thermodynamically this corresponds to Legendre transforms of the associated thermodynamic potentials where intensive and extensive conjugate variables are interchanged. In thermodynamics, this task is achieved by a "sufficiently weak" coupling of the original system to an appropriate infinitely large bath or reservoir via a link that establishes thermodynamic equilibrium. The same basic idea is instrumental in generating distribution functions of such ensembles by computer simulation [98,250]. Here, two important special cases are discussed: thermostats and barostats, which are used to impose temperature instead of energy and / or pressure instead of volume as external control parameters [12,445,270,585,217].

4.2.2 Imposing Temperature: Thermostats

In the limit of ergodic sampling the ensemble created by standard molecular dynamics is the microcanonical or NVE ensemble where in addition the total momentum is conserved [12,270,217]. Thus, the temperature is not a control variable in the Newtonian approach to molecular dynamics and whence it cannot be preselected and fixed. But it is evident that also within molecular dynamics the possibility to control the average temperature (as obtained from the average kinetic energy of the nuclei and the energy equipartition theorem) is welcome for physical reasons. A *deterministic* algorithm of achieving temperature control in the spirit of extended

system dynamics [14] by a sort of dynamical friction mechanism was devised by Nosé and Hoover [442,443,444,307], see e.g. Refs. [12,445,270,585,217] for reviews of this well–established technique. Thereby, the canonical or NVT ensemble is generated in the case of ergodic dynamics.

As discussed in depth in Sect. 2.4, the Car–Parrinello approach to *ab initio* molecular dynamics works due to a dynamical separation between the physical and fictitious temperatures of the nuclear and electronic subsystems, respectively. This separability and thus the associated metastability condition breaks down if the electronic excitation gap becomes comparable to the thermal energy or smaller, that is in particular for metallic systems. In order to satisfy nevertheless adiabaticity in the sense of Car and Parrinello it was proposed to couple separate thermostats [583] to the classical fields that stem from the electronic degrees of freedom [74,204]. Finally, the (long–term) stability of the molecular dynamics propagation can be increased due to the same mechanism, which enables one to increase the time step that still allows for adiabatic time evolution [638]. Note that these technical reasons to include additional thermostats are by construction absent from any Born–Oppenheimer molecular dynamics scheme.

It is well–known that the standard Nosé–Hoover thermostat method suffers from non–ergodicity problems for certain classes of Hamiltonians, such as the harmonic oscillator [307]. A closely related technique, the so–called Nosé–Hoover–chain thermostat [388], cures that problem and assures ergodic sampling of phase space even for the pathological harmonic oscillator. This is achieved by thermostatting the original thermostat by another thermostat, which in turn is thermostatted and so on. In addition to restoring ergodicity even with only a few thermostats in the chain, this technique is found to be much more efficient in imposing the desired temperature.

Nosé–Hoover–chain thermostatted Car–Parrinello molecular dynamics was introduced in Ref. [638]. The underlying equations of motion read

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E^{\mathrm{KS}} - M_I \dot{\xi}_1 \dot{\mathbf{R}}_I \tag{268}$$

$$Q_1^{\mathrm{n}} \ddot{\xi}_1 = \left[\sum_I M_I \dot{\mathbf{R}}_I^2 - g k_{\mathrm{B}} T \right] - Q_1^{\mathrm{n}} \dot{\xi}_1 \dot{\xi}_2$$

$$Q_k^{\mathrm{n}} \ddot{\xi}_k = \left[Q_{k-1}^{\mathrm{n}} \dot{\xi}_{k-1}^2 - k_{\mathrm{B}} T \right] - Q_k^{\mathrm{n}} \dot{\xi}_k \dot{\xi}_{k+1} \left(1 - \delta_{kK} \right) \quad \text{where } k = 2, \ldots, K$$

for the nuclear part and

$$\mu \ddot{\phi}_i = -H_{\mathrm{e}}^{\mathrm{KS}} \phi_i + \sum_{ij} \Lambda_{ij} \phi_j - \mu \dot{\eta}_1 \dot{\phi}_i \tag{269}$$

$$Q_1^{\mathrm{e}} \ddot{\eta}_1 = 2 \left[\sum_i^{\mathrm{occ}} \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - T_{\mathrm{e}}^0 \right] - Q_1^{\mathrm{e}} \dot{\eta}_1 \dot{\eta}_2$$

$$Q_l^{\mathrm{e}} \ddot{\eta}_l = \left[Q_{l-1}^{\mathrm{e}} \dot{\eta}_{l-1}^2 - \frac{1}{\beta_{\mathrm{e}}} \right] - Q_l^{\mathrm{e}} \dot{\eta}_l \dot{\eta}_{l+1} \left(1 - \delta_{lL} \right) \quad \text{where } l = 2, \ldots, L$$

for the electronic contribution. These equations are written down in density functional language (see Eq. (75) and Eq. (81) for the definitions of E^{KS} and $H_{\mathrm{e}}^{\mathrm{KS}}$,

respectively), but completely analogues expressions are operational if other electronic structure approaches are used instead. Using separate thermostatting baths $\{\xi_k\}$ and $\{\eta_l\}$, chains composed of K and L coupled thermostats are attached to the nuclear and electronic equations of motion, respectively.

By inspection of Eq. (268) it becomes intuitively clear how the thermostat works: $\dot{\xi}_1$ can be considered as a *dynamical* friction coefficient. The resulting "dissipative dynamics" leads to non–Hamiltonian flow, but the friction term can aquire positive or negative sign according to its equation of motion. This leads to damping or acceleration of the nuclei and thus to cooling or heating if the instantaneous kinetic energy of the nuclei is higher or lower than $k_{\mathrm{B}}T$ which is preset. As a result, this extended system dynamics can be shown to produce a canonical ensemble in the subspace of the nuclear coordinates and momenta. In spite of being non–Hamiltonian, Nosé–Hoover (–chain) dynamics is also distinguished by conserving an energy quantity of the extended system, see Eq. (272).

The desired average physical temperature is given by T and g denotes the number of dynamical degrees of freedom to which the nuclear thermostat chain is coupled (i.e. constraints imposed on the nuclei have to be subtracted). Similarly, T_{e}^0 is the desired fictitious kinetic energy of the electrons and $1/\beta_{\mathrm{e}}$ is the associated temperature. In principle, β_{e} should be chosen such that $1/\beta_{\mathrm{e}} = 2T_{\mathrm{e}}^0/N_{\mathrm{e}}$ where N_{e} is the number of dynamical degrees of freedom needed to parameterize the wavefunction minus the number of constraint conditions. It is found that this choice requires a very accurate integration of the resulting equations of motion (for instance by using a high–order Suzuki–Yoshida integrator, see Sect. VI.A in Ref. [638]). However, relevant quantities are rather insensitive to the particular value so that N_{e} can be replaced heuristically by N_{e}' which is the number of orbitals ϕ_i used to expand the wavefunction [638].

The choice of the "mass parameters" assigned to the thermostat degrees of freedom should be made such that the overlap of their power spectra and the ones the thermostatted subsystems is maximal [74,638]. The relations

$$Q_1^{\mathrm{n}} = \frac{g k_{\mathrm{B}} T}{\omega_{\mathrm{n}}^2} \; , \qquad Q_k^{\mathrm{n}} = \frac{k_{\mathrm{B}} T}{\omega_{\mathrm{n}}^2} \tag{270}$$

$$Q_1^{\mathrm{e}} = \frac{2 T_{\mathrm{e}}^0}{\omega_{\mathrm{e}}^2} \; , \qquad Q_l^{\mathrm{e}} = \frac{1}{\beta_{\mathrm{e}} \omega_{\mathrm{e}}^2} \tag{271}$$

assures this if ω_{n} is a typical phonon or vibrational frequency of the nuclear subsystem (say of the order of 2000 to 4000 cm^{-1}) and ω_{e} is sufficiently large compared to the maximum frequency $\omega_{\mathrm{n}}^{\mathrm{max}}$ of the nuclear power spectrum (say 10 000 cm^{-1} or larger). The integration of these equations of motion is discussed in detail in Ref. [638] using the velocity Verlet / RATTLE algorithm.

In some instances, for example during equilibration runs, it is advantageous to go one step further and to actually couple one chain of Nosé–Hoover thermostats to every individual nuclear degree of freedom akin to what is done in path integral molecular dynamics simulations [637,644,646], see also Sect. 4.4. This so–called "massive thermostatting approach" is found to accelerate considerably the expensive equilibration periods within *ab initio* molecular dynamics, which is useful for both Car–Parrinello and Born–Oppenheimer dynamics.

In classical molecular dynamics two quantities are conserved during a simulation, the total energy and the total momentum. The same constants of motion apply to (exact) microcanonical Born–Oppenheimer molecular dynamics because the only *dynamical* variables are the nuclear positions and momenta as in classical molecular dynamics. In microcanonical Car–Parrinello molecular dynamics the total energy of the *extended* dynamical system composed of nuclear and electronic positions and momenta, that is E_{cons} as defined in Eq. (48), is also conserved, see e.g. Fig. 3 in Sect. 2.4. There is also a conserved energy quantity in the case of thermostatted molecular dynamics according to Eq. (268)–(269). Instead of Eq. (48) this constant of motion reads

$$
\begin{aligned}
E_{\mathrm{cons}}^{\mathrm{NVT}} = {} & \sum_i^{\mathrm{occ}} \mu \left\langle \dot{\phi}_i \middle| \dot{\phi}_i \right\rangle + \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + E^{\mathrm{KS}} \left[\{\phi_i\}, \{\mathbf{R}_I\} \right] \\
& + \sum_{l=1}^{L} \frac{1}{2} Q_l^{\mathrm{e}} \dot{\eta}_l^2 + \sum_{l=2}^{L} \frac{\eta_l}{\beta_{\mathrm{e}}} + 2T_{\mathrm{e}}^0 \eta_1 \\
& + \sum_{k=1}^{K} \frac{1}{2} Q_k^{\mathrm{n}} \dot{\xi}_k^2 + \sum_{k=2}^{K} k_{\mathrm{B}} T \xi_k + g k_{\mathrm{B}} T \xi_1
\end{aligned} \tag{272}
$$

for Nosé–Hoover–chain thermostatted canonical Car–Parrinello molecular dynamics [638].

In microcanonical Car–Parrinello molecular dynamics the total nuclear momentum $\mathbf{P}_{\mathrm{n}}$ is no more a constant of motion as a result of the fictitious dynamics of the wavefunction; this quantity as well as other symmetries and associated invariants are discussed in Ref. [467]. However, a generalized linear momentum which embraces the electronic degrees of freedom

$$
\mathbf{P}_{\mathrm{CP}} = \mathbf{P}_{\mathrm{n}} + \mathbf{P}_{\mathrm{e}} = \sum_I \mathbf{P}_I + \sum_i^{\mathrm{occ}} \mu \left\langle \dot{\phi}_i \middle| - \nabla_{\mathbf{r}} \middle| \phi_i \right\rangle + \mathrm{c.c.} \tag{273}
$$

can be defined [467,436]; $\mathbf{P}_I = M_I \dot{\mathbf{R}}_I$. This quantity is a constant of motion in unthermostatted Car–Parrinello molecular dynamics due to an exact cancellation of the nuclear and electronic contributions [467,436]. As a result, the nuclear momentum $\mathbf{P}_{\mathrm{n}}$ fluctuates during such a run, but in practice $\mathbf{P}_{\mathrm{n}}$ is conserved *on the average* as shown in Fig. 1 of Ref. [436]. This is analogues to the behavior of the physical total energy E_{phys} Eq. (49), which fluctuates slightly due to the presence of the fictitious kinetic energy of the electrons T_{e} Eq. (51).

As recently outlined in detail it is clear that the coupling of more than one thermostat to a dynamical system, such as done in Eq. (268)–(269), destroys the conservation of momentum [436], i.e. $\mathbf{P}_{\mathrm{CP}}$ is no more an invariant. In unfavorable cases, in particular in small–gap or metallic regimes where there is a substantial coupling of the nuclear and electronic subsystems, momentum can be transferred to the nuclear subsystem such that $\mathbf{P}_{\mathrm{n}}$ grows in the course of a simulation. This problem can be cured by controlling the nuclear momentum (using e.g. scaling or constraint methods) so that the total nuclear momentum $\mathbf{P}_{\mathrm{n}}$ remains small [436].