

2 From the Schrödinger Equation to Molecular Dynamics

In particle methods, the laws of classical mechanics [48, 371] are used, in particular Newton's second law. In this chapter we will pursue the question why it makes sense to apply the laws of classical mechanics, even though one should use the laws of quantum mechanics. Readers that are more interested in the algorithmic details or in the implementation of algorithms in molecular dynamics can skip this chapter.

In quantum mechanics, the Schrödinger equation is taking the place of Newton's equations. But the Schrödinger equation is so complex that it can be solved analytically only for a few simple cases. Also the direct numerical solution on computers is limited to very simple systems and very small numbers of particles because of the high dimension of the space in which the Schrödinger equation is posed. Therefore, approximation procedures are used to simplify the problem. These procedures are based on the fact that the electron mass is much smaller than the mass of the nuclei. The idea is to split the Schrödinger equation, which describes the state of both the electrons and nuclei, with a separation approach into two coupled equations. The influence of the electrons on the interaction between the nuclei is then described by an effective potential. This potential results from the solution of the so-called electronic Schrödinger equation. As a further approximation the nuclei are moved according to the classical Newton's equations using either effective potentials which result from quantum mechanical computations (which include the effects of the electrons) or empirical potentials that have been fitted to the results of quantum mechanical computations or to the results of experiments.

All in all, this approach is a classical example for a hierarchy of approximation procedures and an example for the use of effective quantities. In the following, the derivation of the molecular dynamics method from the laws of quantum mechanics is presented. For further details see the large body of available literature, for example [372, 427, 554], [381, 514], and [417, 626, 627].

2.1 The Schrödinger Equation

Up to the end of the nineteenth century, classical physics could answer the most important questions using Newton's equations of motion. The Lagrange formalism and the Hamilton formalism both lead to generalized classical

equations of motion that are essentially equivalent. These equations furnish how the change in time of the position of particles depends on the forces acting on them. If initial positions and initial velocities are given, the positions of the particles are determined uniquely for all later points in time. Observable quantities such as angular momentum or kinetic energy can then be represented as functions of the positions and the impulses of the particles.

In the beginning of the twentieth century the theory of quantum mechanics was developed. There, the dynamics of the particles is described by a new equation of motion, the Schrödinger equation. In contrast to Newton's equations its solution no longer provides unique trajectories, meaning uniquely determined positions and impulses of the particles, but only probabilistic statements about the positions and impulses of the particles. Furthermore, position and impulse of a single particle can no longer be measured arbitrarily accurately at the same time (Heisenberg's uncertainty principle) and certain observables, as for example the energies of bound electrons, can only assume certain discrete values. All statements that can be made about a quantum mechanical system can be derived from the state function (or wave function) Ψ which is given as the solution of the Schrödinger equation. Let us consider as an example a system consisting of N nuclei and K electrons. The time-dependent state function of such a system can be written in general as

$$\Psi = \Psi(\mathbf{R}_1, \dots, \mathbf{R}_N, \mathbf{r}_1, \dots, \mathbf{r}_K, t),$$

where \mathbf{R}_i and \mathbf{r}_i denote positions in three-dimensional space \mathbb{R}^3 associated to the i th nucleus and the i th electron, respectively. The variable t denotes the time-dependency of the state function. The vector space (space of configurations) in which the coordinates of the particles are given is therefore of dimension $3(N + K)$. In the following we will abbreviate $(\mathbf{R}_1, \dots, \mathbf{R}_N)$ and $(\mathbf{r}_1, \dots, \mathbf{r}_K)$ with the shorter notation \mathbf{R} and \mathbf{r} , respectively.

According to the statistical interpretation of the state function, the expression

$$\Psi^*(\mathbf{R}, \mathbf{r}, t) \Psi(\mathbf{R}, \mathbf{r}, t) dV_1 \cdots dV_{N+K} \quad (2.1)$$

describes the probability to find the system under consideration at time t in the volume element $dV_1 \cdots dV_{N+K}$ of the configuration space centered at the point (\mathbf{R}, \mathbf{r}) . By integrating over a volume element of the configuration space one determines the probability to find the system in this domain.

We assume in the following that nuclei and electrons are charged particles. The electrostatic potential (Coulomb potential) of a point charge (with elementary charge $+e$) is $\frac{e}{4\pi\epsilon_0} \frac{1}{r}$, where r is the distance from the position of the charged particle and ϵ_0 is the dielectric constant. $1/(4\pi\epsilon_0)$ is also called Coulomb constant. An electron moving in this potential has the potential energy $V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$. Neglecting spin and relativistic interactions and assuming that no external forces act on the system, the Hamilton operator associated to the system of nuclei and electrons is given as the sum over the operators for the kinetic energy and the Coulomb potentials,

$$\begin{aligned}
\mathcal{H}(\mathbf{R}, \mathbf{r}) := & -\frac{\hbar^2}{2m_e} \sum_{k=1}^K \Delta_{\mathbf{r}_k} + \frac{e^2}{4\pi\epsilon_0} \sum_{k < j}^K \frac{1}{\|\mathbf{r}_k - \mathbf{r}_j\|} - \frac{e^2}{4\pi\epsilon_0} \sum_{k=1}^K \sum_{j=1}^N \frac{Z_j}{\|\mathbf{r}_k - \mathbf{R}_j\|} \\
& + \frac{e^2}{4\pi\epsilon_0} \sum_{k < j}^N \frac{Z_k Z_j}{\|\mathbf{R}_k - \mathbf{R}_j\|} - \frac{\hbar^2}{2} \sum_{k=1}^N \frac{1}{M_k} \Delta_{\mathbf{R}_k}.
\end{aligned} \tag{2.2}$$

Here, M_j and Z_j denote the mass and the atomic number of the j th nucleus, m_e is the mass of an electron and $\hbar = h/2\pi$ with h being Planck's constant. $\|\mathbf{r}_k - \mathbf{r}_j\|$ are the distances between electrons, $\|\mathbf{r}_k - \mathbf{R}_j\|$ are distances between electrons and nuclei and $\|\mathbf{R}_k - \mathbf{R}_j\|$ are distances between nuclei. The operators $\Delta_{\mathbf{R}_k}$ and $\Delta_{\mathbf{r}_k}$ stand here for the Laplace operator with respect to the nuclear coordinates \mathbf{R}_k and with respect to the electronic coordinates \mathbf{r}_k .¹ In the following we will denote the separate parts of (2.2) in abbreviated form (written in the same order) with

$$\mathcal{H} = T_e + V_{ee} + V_{eK} + V_{KK} + T_K. \tag{2.3}$$

The meanings of the individual parts are the following: T_e and T_K are the operators of the kinetic energy of the electrons and of the nuclei, respectively. V_{ee} , V_{KK} and V_{eK} refer to the operators of the potential energy of the interactions (thus the Coulomb energy) between only the electrons, between only the nuclei, and between the electrons and the nuclei, respectively.

The state function Ψ is now given as the solution of the Schrödinger equation

$$i\hbar \frac{\partial \Psi(\mathbf{R}, \mathbf{r}, t)}{\partial t} = \mathcal{H} \Psi(\mathbf{R}, \mathbf{r}, t) \tag{2.4}$$

where i denotes the imaginary unit. The expression $\Delta_{\mathbf{R}_k} \Psi(\mathbf{R}, \mathbf{r}, t)$, which occurs in $\mathcal{H} \Psi$, stands there for $\Delta_{\mathbf{Y}} \Psi(\mathbf{R}_1, \dots, \mathbf{R}_{k-1}, \mathbf{Y}, \mathbf{R}_{k+1}, \dots, \mathbf{R}_N, \mathbf{r}, t)|_{\mathbf{R}_k}$, that is, the application of the Laplace operator to Ψ seen as a function of \mathbf{Y} (the k th vector of coordinates) and the evaluation of the resulting function at the point $\mathbf{Y} = \mathbf{R}_k$. The operators $\Delta_{\mathbf{r}_k}$ and later $\nabla_{\mathbf{R}_k}$ and others are to be understood in an analogous way.

In the following we consider the case that the Hamilton operator \mathcal{H} is not explicitly time-dependent, as we already assumed in (2.2).² Then, the separation approach

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \psi(\mathbf{R}, \mathbf{r}) \cdot f(t) \tag{2.5}$$

of Ψ with a function $\psi = \psi(\mathbf{R}, \mathbf{r})$ that does not depend on time and a function $f = f(t)$ that depends on time when substituted into (2.4) gives rise to

¹ If we denote the three components of \mathbf{R}_k by $(\mathbf{R}_k)_1, (\mathbf{R}_k)_2$ and $(\mathbf{R}_k)_3$, then we obtain $\Delta_{\mathbf{R}_k} = \frac{\partial^2}{\partial (\mathbf{R}_k)_1^2} + \frac{\partial^2}{\partial (\mathbf{R}_k)_2^2} + \frac{\partial^2}{\partial (\mathbf{R}_k)_3^2}$.

² Since the Hamilton operator \mathcal{H} depends on the coordinates and impulses of the particles, it depends implicitly on time this way. If time-dependent external forces act on the system, the Hamilton operator could also explicitly depend on time. Then, one would write $\mathcal{H}(\mathbf{R}, \mathbf{r}, t)$ to reflect this dependency.

$$i\hbar \frac{df(t)}{dt} \psi(\mathbf{R}, \mathbf{r}) = f(t) \mathcal{H} \psi(\mathbf{R}, \mathbf{r}), \quad (2.6)$$

since \mathcal{H} does not act on $f(t)$.³ A formal division of both sides by the term $\psi(\mathbf{R}, \mathbf{r}) \cdot f(t) \neq 0$ yields

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = \frac{1}{\psi(\mathbf{R}, \mathbf{r})} \mathcal{H} \psi(\mathbf{R}, \mathbf{r}). \quad (2.7)$$

The left hand side contains only the time coordinate t , the right hand side only the coordinates in space. Therefore, both sides have to be equal to a common constant E and (2.7) can be separated. We obtain the two equations

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = E \quad (2.8)$$

and

$$\mathcal{H} \psi(\mathbf{R}, \mathbf{r}) = E \psi(\mathbf{R}, \mathbf{r}). \quad (2.9)$$

The differential equation (2.8) describes the evolution over time of the wave function. Its general solution reads

$$f(t) = ce^{-iEt/\hbar}. \quad (2.10)$$

Equation (2.9) is an eigenvalue problem for the Hamilton operator \mathcal{H} with the energy eigenvalue E . This equation is called time-independent (or stationary) Schrödinger equation. To every energy eigenvalue E_n there is one (or, in the case of degenerated states, several) associated energy eigenfunctions ψ_n . Also, for every energy eigenvalue E_n , (2.10) yields a time-dependent term f_n . The solution of the time-dependent Schrödinger equation (2.4) is then given as a linear combination of the energy eigenfunctions ψ_n and the associated time-dependent terms f_n of the form

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \sum_n c_n e^{-iE_n t/\hbar} \psi_n(\mathbf{R}, \mathbf{r}) \quad (2.11)$$

with the weights $c_n = \int \psi_n^*(\mathbf{R}, \mathbf{r}) \Psi(\mathbf{R}, \mathbf{r}, 0) d\mathbf{R} d\mathbf{r}$.

Similar to the time-dependent Schrödinger equation, (2.9) is so complex that analytical solutions can only be given for a few very simple systems. The development of approximation procedures is therefore a fundamental area of research in quantum mechanics. There exists an entire hierarchy of approximations that exploit the different physical properties of nuclei and electrons [417, 626, 627]. We will consider these approximations in the following in more detail.

³ One then also calls ψ state or wave function.

2.2 A Derivation of Classical Molecular Dynamics

In the following we will derive, starting from the time-dependent Schrödinger equation (2.4), the equations of classical molecular dynamics by a series of approximations. We follow [417] and [626, 627].

2.2.1 The TDSCF Approach and Ehrenfest's Molecular Dynamics

First, we decompose the Hamilton operator (2.3) as follows: We set

$$\mathcal{H} = \mathcal{H}_e + T_K \quad (2.12)$$

with the electronic Hamilton operator

$$\mathcal{H}_e := T_e + V_{ee} + V_{eK} + V_{KK}. \quad (2.13)$$

We decompose \mathcal{H}_e further into its kinetic and potential part

$$\mathcal{H}_e := T_e + V_e$$

where now

$$V_e := V_{ee} + V_{eK} + V_{KK}$$

is just the operator for the potential energy of the entire system.

The wave function $\Psi(\mathbf{R}, \mathbf{r}, t)$ depends on the coordinates of the electrons and of the nuclei as well as on time. First, we separate the wave function into a simple product form⁴

$$\Psi(\mathbf{R}, \mathbf{r}, t) \approx \tilde{\Psi}(\mathbf{R}, \mathbf{r}, t) := \chi(\mathbf{R}, t) \phi(\mathbf{r}, t) \exp \left[\frac{i}{\hbar} \int_{t_0}^t \tilde{E}_e(t') dt' \right] \quad (2.14)$$

of the contribution of the nuclei and electrons to the full wave function Ψ . It is assumed that the nuclear wave function $\chi(\mathbf{R}, t)$ and the electronic wave function $\phi(\mathbf{r}, t)$ are normalized for any point in time t , that means that both $\int \chi^*(\mathbf{R}, t) \chi(\mathbf{R}, t) d\mathbf{R} = 1$ and $\int \phi^*(\mathbf{r}, t) \phi(\mathbf{r}, t) d\mathbf{r} = 1$ hold. The phase factor \tilde{E}_e is chosen in the form

$$\tilde{E}_e(t) = \int \phi^*(\mathbf{r}, t) \chi^*(\mathbf{R}, t) \mathcal{H}_e \phi(\mathbf{r}, t) \chi(\mathbf{R}, t) d\mathbf{R} d\mathbf{r} \quad (2.15)$$

which is convenient for the following derivation of a coupled system of equations.

Now, we insert (2.14) into the time-dependent Schrödinger equation (2.4) with Hamilton operator \mathcal{H} , multiply from the left with $\phi^*(\mathbf{r}, t)$ and $\chi^*(\mathbf{R}, t)$

⁴ This approximation is a so-called single determinant or single configuration ansatz for the full wave function. It can only result in a mean field description of the coupled dynamics.

and integrate over \mathbf{R} and \mathbf{r} . Finally, we require conservation of energy, that is,

$$\frac{d}{dt} \int \tilde{\Psi}^* \mathcal{H} \tilde{\Psi} d\mathbf{R} d\mathbf{r} = 0,$$

and obtain thereby the coupled system of equations

$$i \hbar \frac{\partial \phi}{\partial t} = - \sum_k \frac{\hbar^2}{2m_e} \Delta_{\mathbf{r}_k} \phi + \left(\int \chi^*(\mathbf{R}, t) V_e(\mathbf{R}, \mathbf{r}) \chi(\mathbf{R}, t) d\mathbf{R} \right) \phi, \quad (2.16)$$

$$i \hbar \frac{\partial \chi}{\partial t} = - \sum_k \frac{\hbar^2}{2M_k} \Delta_{\mathbf{R}_k} \chi + \left(\int \phi^*(\mathbf{r}, t) \mathcal{H}_e(\mathbf{R}, \mathbf{r}) \phi(\mathbf{r}, t) d\mathbf{r} \right) \chi. \quad (2.17)$$

These equations constitute the foundation for the TDSCF approach (*time-dependent self-consistent field*) introduced by Dirac in 1930, see [181, 186]. Both unknowns again obey a Schrödinger equation, but now with a time-dependent effective operator for the potential energy which arises as an appropriate average of the other unknown. These averages can also be interpreted as quantum mechanical expectation values with respect to the operators V_e and \mathcal{H}_e and give a mean field description of the coupled dynamics.

As a next step the nuclear wave function χ is to be approximated by classical point particles. For this, we first write the wave function χ as

$$\chi(\mathbf{R}, t) = A(\mathbf{R}, t) \exp \left[\frac{i}{\hbar} S(\mathbf{R}, t) \right] \quad (2.18)$$

with an amplitude $A > 0$ and a phase factor S , both real [187, 427, 536]. Substitution into the equation for the nuclei in the TDSCF system (2.17) and separating real and imaginary parts leads to the coupled system of equations

$$\frac{\partial S}{\partial t} + \sum_k^N \frac{1}{2M_k} (\nabla_{\mathbf{R}_k} S)^2 + \int \phi^* \mathcal{H}_e \phi d\mathbf{r} = \hbar^2 \sum_k^N \frac{1}{2M_k} \frac{\Delta_{\mathbf{R}_k} A}{A}, \quad (2.19)$$

$$\frac{\partial A}{\partial t} + \sum_k^N \frac{1}{M_k} (\nabla_{\mathbf{R}_k} A) (\nabla_{\mathbf{R}_k} S) + \sum_k^N \frac{1}{2M_k} A (\Delta_{\mathbf{R}_k} S) = 0. \quad (2.20)$$

Here, $\nabla_{\mathbf{R}_k} = \left(\frac{\partial}{\partial(\mathbf{R}_k)_1}, \frac{\partial}{\partial(\mathbf{R}_k)_2}, \frac{\partial}{\partial(\mathbf{R}_k)_3} \right)^T$. The abbreviation $(\nabla_{\mathbf{R}_k} S)^2$ denotes the scalar product of $\nabla_{\mathbf{R}_k} S$ with itself and $(\nabla_{\mathbf{R}_k} A) (\nabla_{\mathbf{R}_k} S)$ denotes the scalar product of the vectors $\nabla_{\mathbf{R}_k} A$ and $\nabla_{\mathbf{R}_k} S$. This system corresponds exactly to the second equation in the TDSCF system (2.17) in the new variables A and S .⁵ The only term that directly depends on \hbar is the right hand side of

⁵ This is the so-called quantum fluid dynamics representation [182, 187, 427, 536, 668] which opens up another possibility to treat the time-dependent Schrödinger equation. (2.20) can be written with $|\chi|^2 \equiv A^2$ as continuity equation that locally conserves the probability density $|\chi|^2$ of the nuclei under a flow.

equation (2.19). In the limit $\hbar \rightarrow 0$ equation (2.19) gives⁶

$$\frac{\partial S}{\partial t} + \sum_k^N \frac{1}{2M_k} (\nabla_{\mathbf{R}_k} S)^2 + \int \phi^* \mathcal{H}_e \phi d\mathbf{r} = 0.^7 \quad (2.21)$$

Setting $\nabla_{\mathbf{R}} S = (\nabla_{\mathbf{R}_1} S, \dots, \nabla_{\mathbf{R}_N} S)$, this is isomorphic to the Hamilton-Jacobi form

$$\frac{\partial S}{\partial t} + H(\mathbf{R}, \nabla_{\mathbf{R}} S) = 0 \quad (2.22)$$

of the equations of motion of classical mechanics with the classical Hamilton function⁸

$$H(\mathbf{R}, \mathbf{P}) = T(\mathbf{P}) + V(\mathbf{R}) \quad (2.23)$$

with $\mathbf{P} = (\mathbf{P}_1, \dots, \mathbf{P}_N)$, where one puts

$$\mathbf{P}_k(t) \equiv \nabla_{\mathbf{R}_k} S(\mathbf{R}(t), t).$$

Here, \mathbf{R} corresponds to generalized coordinates and \mathbf{P} to their conjugated moments. Newton's equations of motion $\dot{\mathbf{P}}_k = -\nabla_{\mathbf{R}_k} V(\mathbf{R})$ associated to equation (2.22) are then

$$\frac{d\mathbf{P}_k}{dt} = -\nabla_{\mathbf{R}_k} \int \phi^* \mathcal{H}_e \phi d\mathbf{r} \quad \text{or} \quad (2.24)$$

$$M_k \ddot{\mathbf{R}}_k(t) = -\nabla_{\mathbf{R}_k} \int \phi^* \mathcal{H}_e \phi d\mathbf{r} \quad (2.25)$$

$$=: -\nabla_{\mathbf{R}_k} V_e^{Ehr}(\mathbf{R}(t)). \quad (2.26)$$

The nuclei move now according to the laws of classical mechanics in an effective potential given by the electrons. This so-called *Ehrenfest potential* V_e^{Ehr} is a function of the nuclear coordinates \mathbf{R} at time t . It results from an averaging over the degrees of freedom of the electrons, weighted by \mathcal{H}_e , where the nuclear coordinates are kept constant at their current positions $\mathbf{R}(t)$.

There is still the wave function χ of the nuclei in the equation for the electrons in the system for the TDSCF approach (2.16). Consistency requires it to be replaced by the position of the nuclei. Thus, if one replaces the probability density of the nuclei $|\chi(\mathbf{R}, t)|^2$ by the product of delta functions

⁶ Because of this approximation step, the function ϕ is only an approximation of the original wave function ϕ in (2.16) and (2.17). To keep the notation simple we denote this approximation again by the symbol ϕ .

⁷ An expansion of the right hand side of equation (2.19) with respect to \hbar leads to a hierarchy of semi-classical methods [427].

⁸ In the literature often the notation \mathbf{Q} is found instead of \mathbf{R} for the generalized classical coordinates. For the sake of simplicity, we will continue using the notation \mathbf{R} in this chapter.

$\Pi_k \delta(\mathbf{R}_k - \mathbf{R}_k(t))$ in the limit $\hbar \rightarrow 0$ in (2.16), then one obtains for example for the position operator \mathbf{R}_k with

$$\int \chi^*(\mathbf{R}, t) \mathbf{R}_k \chi(\mathbf{R}, t) d\mathbf{R} \xrightarrow{\hbar \rightarrow 0} \mathbf{R}_k(t) \quad (2.27)$$

the classical position $\mathbf{R}_k(t)$ as limit of the quantum mechanical expectations. Here, the delta functions are centered in the instantaneous positions $\mathbf{R}(t)$ of the nuclei given by (2.25). For (2.16), this classical limit process⁹ leads to a time-dependent wave equation for the electrons

$$i \hbar \frac{\partial \phi_{\mathbf{R}(t)}(\mathbf{r}, t)}{\partial t} = - \sum_k \frac{\hbar^2}{2m_e} \Delta_{\mathbf{r}_k} \phi_{\mathbf{R}(t)}(\mathbf{r}, t) + V_e(\mathbf{R}(t), \mathbf{r}) \phi_{\mathbf{R}(t)}(\mathbf{r}, t) \quad (2.28)$$

$$= \mathcal{H}_e(\mathbf{R}(t), \mathbf{r}) \phi_{\mathbf{R}(t)}(\mathbf{r}, t), \quad (2.29)$$

that move in a self-consistent way with the nuclei, if the classical nuclei are propagated by (2.25). Note that now \mathcal{H}_e and therefore the wave function ϕ of the electrons depend parametrically via V_e on the positions $\mathbf{R}(t)$ of the nuclei. The nuclei are thus treated as classical particles, whereas the electrons are still treated using quantum mechanics. In honor of Ehrenfest, who first posed the question how Newton's classical dynamics could be derived from Schrödinger's equation, one often calls approaches that are based on the equations

$$M_k \ddot{\mathbf{R}}_k(t) = -\nabla_{\mathbf{R}_k} V_e^{Ehr}(\mathbf{R}(t)), \quad (2.30)$$

$$i \hbar \frac{\partial \phi_{\mathbf{R}(t)}(\mathbf{r}, t)}{\partial t} = \mathcal{H}_e(\mathbf{R}(t), \mathbf{r}) \phi_{\mathbf{R}(t)}(\mathbf{r}, t) \quad (2.31)$$

Ehrenfest molecular dynamics. Alternatively, one finds such approaches in the literature under the name QCMD (quantum-classical molecular dynamics model) [104, 204, 447]. Note again that the wave function $\phi_{\mathbf{R}(t)}$ of the electrons is here not equal to the wave function ϕ in (2.16), since an approximation was introduced by the limit process for the positions of the nuclei. The wave function of the electrons depends implicitly on \mathbf{R} via the coupling in the system, which we expressed by the parametric notation $\phi_{\mathbf{R}(t)}$. In the following we will omit this parametrization for the sake of simplicity and will denote, if clear from the context, the electronic wave function just by ϕ .

2.2.2 Expansion in the Adiabatic Basis

The TDSCF approach leads to a mean field theory. One should keep in mind that transitions between different electronic states are still possible in this

⁹ A justification of the transition from the Schrödinger equation to Newton's equation of motion of the nuclei is given by the theorem of Ehrenfest [381, 554] which describes the time evolution of averages of observables.

setting. This can be seen as follows: We expand the electronic wave function ϕ from (2.31) for fixed t in an appropriate basis $\{\phi_j\}$ of the electronic states

$$\phi_{\mathbf{R}(t)}(\mathbf{r}, t) = \sum_{j=0}^{\infty} c_j(t) \phi_j(\mathbf{R}(t), \mathbf{r}) \quad (2.32)$$

with complex coefficients $\{c_j(t)\}$ and $\sum_j |c_j(t)|^2 \equiv 1$. The $\{|c_j(t)|^2\}$ describe explicitly how the occupancy of the different states j evolves over time. A possible orthonormal basis, called *adiabatic* basis, results from the solution of the time-independent electronic Schrödinger equation

$$\mathcal{H}_e(\mathbf{R}, \mathbf{r}) \phi_j(\mathbf{R}, \mathbf{r}) = E_j(\mathbf{R}) \phi_j(\mathbf{R}, \mathbf{r}), \quad (2.33)$$

where \mathbf{R} denotes the nuclear coordinates from equation (2.25) at the chosen time t . The values $\{E_j\}$ are here the energy eigenvalues of the electronic Hamilton operator $\mathcal{H}_e(\mathbf{R}, \mathbf{r})$, and the $\{\phi_j\}$ are the associated energy eigenfunctions.

For (2.30) and (2.31) one obtains with the expansion (2.32) the equations of motion in the adiabatic basis (2.33) as [447, 626, 627]

$$M_k \ddot{\mathbf{R}}_k(t) = - \sum_j |c_j(t)|^2 \nabla_{\mathbf{R}_k} E_j - \sum_{j,l} c_j^*(t) c_l(t) (E_j - E_l) d_k^{jl}, \quad (2.34)$$

$$i \hbar \dot{c}_j(t) = c_j(t) E_j - i \hbar \sum_{k,l} c_l(t) \dot{\mathbf{R}}_k(t) d_k^{jl}, \quad (2.35)$$

with the coupling terms given as

$$d_k^{jl} = \int \phi_j^* \nabla_{\mathbf{R}_k} \phi_l d\mathbf{r}, \quad (2.36)$$

$$d_k^{jj} \equiv 0. \quad (2.37)$$

Here, we used the properties

$$\begin{aligned} \int \phi_j^*(\mathbf{R}, \mathbf{r}) \nabla_{\mathbf{R}_k} \mathcal{H}_e \phi_l(\mathbf{R}, \mathbf{r}) d\mathbf{r} &= (E_l(\mathbf{R}) - E_j(\mathbf{R})) \int \phi_j^*(\mathbf{R}, \mathbf{r}) \nabla_{\mathbf{R}_k} \phi_l(\mathbf{R}, \mathbf{r}) d\mathbf{r}, \\ \int \phi_j^*(\mathbf{R}, \mathbf{r}) \dot{\phi}_l(\mathbf{R}, \mathbf{r}) d\mathbf{r} &= \sum_{k=1}^N \dot{\mathbf{R}}_k(t) \int \phi_j^*(\mathbf{R}, \mathbf{r}) \nabla_{\mathbf{R}_k} \phi_l(\mathbf{R}, \mathbf{r}) d\mathbf{r}, \quad \forall j \neq l, \end{aligned}$$

of the adiabatic basis and used furthermore that ϕ and \mathbf{R} in $V_e^{Ehr}(\mathbf{R}(t))$ can be treated as independent variables. This implies that the time-dependent wave function can be represented by a linear combination of adiabatic states and that its evolution in time is described by the Schrödinger equation (2.31). Here, $|c_j(t)|^2$ is the probability density that the system is in state ϕ_j at time point t .¹⁰

¹⁰ This model can be modified by the assumption that the system remains in an adiabatic state until it jumps instantaneously to another adiabatic state. The coefficients $c_j(t)$ and the coupling terms d_k^{jl} serve as a criterion for such a jump. This assumption is made in the so-called *surface-hopping* method [300, 625].

2.2.3 Restriction to the Ground State

As a further simplification we will restrict the whole electronic wave function ϕ to a single state, typically the ground state ϕ_0 of \mathcal{H}_e according to the stationary equation (2.33) with $|c_0(t)|^2 \equiv 1$ as in (2.32). We thus assume that the system remains in the state ϕ_0 , and truncate the expansion (2.32) after the first term. This approximation is justified as long as the difference in energy between ϕ_0 and the first excited state ϕ_1 is everywhere large enough compared to the thermal energy $k_B T$ so that transitions to excited states¹¹ do not play a significant role.¹² The nuclei are then moved according to the equation of motion (2.25) on a single hypersurface of the potential energy

$$V_e^{Ehr}(\mathbf{R}) = \int \phi_0^*(\mathbf{R}, \mathbf{r}) \mathcal{H}_e(\mathbf{R}, \mathbf{r}) \phi_0(\mathbf{R}, \mathbf{r}) d\mathbf{r} \equiv E_0(\mathbf{R}). \quad (2.38)$$

To compute this surface, the time-independent electronic Schrödinger equation (2.33)

$$\mathcal{H}_e(\mathbf{R}, \mathbf{r}) \phi_0(\mathbf{R}, \mathbf{r}) = E_0(\mathbf{R}) \phi_0(\mathbf{R}, \mathbf{r}) \quad (2.39)$$

has to be solved for its ground state. Hence, we identified the Ehrenfest potential function V_e^{Ehr} just as the potential E_0 of the stationary electronic Schrödinger equation for the ground state. Note that E_0 is here a function of the nuclear coordinates \mathbf{R} .

2.2.4 Approximation of the Potential Energy Hypersurface and Classical Molecular Dynamics

As a consequence of (2.38), the computation of the dynamics of the nuclei can now be *separated* from the computation of the hypersurface for the potential energy. If we assume at first that we can solve the stationary electronic Schrödinger equation (2.33) for a given nuclear configuration, then we could derive an entirely classical approach by the following steps: First, the energy of the ground state $E_0(\mathbf{R})$ is determined for as many representative nuclear configurations \mathbf{R}^j as possible from the stationary electronic Schrödinger equation (2.39). In this way, we evaluate the function $V_e^{Ehr}(\mathbf{R})$ at a number of points and gain a number of data points $(\mathbf{R}^j, V_e^{Ehr}(\mathbf{R}^j))$. From these discrete data points we then approximately reconstruct the global potential energy hypersurface for V_e^{Ehr} . For this, we compute an approximate potential surface by an expansion of many-body potentials in analytical form

¹¹ In the case of bound atoms the spectrum is discrete. The ground state is an eigenstate with the smallest energy level. The first excited state is an eigenstate with the second smallest energy level.

¹² So-called branching processes cannot be described this way in a satisfactory manner.

$$V_e^{Ehr} \approx V_e^{appr}(\mathbf{R}) = \sum_{k=1}^N V_1(\mathbf{R}_k) + \sum_{k<l}^N V_2(\mathbf{R}_k, \mathbf{R}_l) + \sum_{k<l<m}^N V_3(\mathbf{R}_k, \mathbf{R}_l, \mathbf{R}_m) + \dots, \quad (2.40)$$

which is appropriately truncated. With such an expansion the electronic degrees of freedom are replaced with interaction potentials V_n and are therefore no longer explicit degrees of freedom of the equations of motion. After the V_n are specified, the mixed quantum-mechanical and classical problem (2.30), (2.31) is reduced to a completely classical problem. We obtain Newton's equations of motion of classical molecular dynamics

$$M_k \ddot{\mathbf{R}}_k(t) = -\nabla_{\mathbf{R}_k} V_e^{appr}(\mathbf{R}(t)). \quad (2.41)$$

Here, the gradients can be computed analytically.

This method of classical molecular dynamics is feasible for many-body systems because the global potential energy gets decomposed according to (2.40). Here, in practice, the same form of the potential is used for the same kind of particles. For instance, if only a two-body potential function

$$V_e^{appr} \approx \sum_{k<l}^N V_2(\|\mathbf{R}_k - \mathbf{R}_l\|)$$

of the distance is used, only *one* one-dimensional function V_2 has to be determined.

This is certainly a drastic approximation that has to be justified in many respects and that brings a number of problems with it. It is not obvious how many and which typical nuclear configurations have to be considered to reconstruct the potential function from the potentials of these configurations with an error which is not too large. In addition, the error caused by the truncation of the expansion (2.40) plays certainly a substantial role. The precise form of the analytic potential functions V_n and the subsequent fitting of their parameters also have a decisive influence on the size of the approximation error. The assumption that the global potential function is represented well by a sum of simple potentials of a few generic forms and the transferability of a potential function to other nuclear configurations are further critical issues. Altogether, not all approximation errors can be controlled rigorously in this approach. Furthermore, quantum mechanical effects and therefore chemical reactions are excluded by construction. Nevertheless, the method has been proven successful, in particular in the computation of macroscopic properties.

The methods used in practice to determine the interactions in real systems are either based on the approximate solution of the stationary electronic Schrödinger equation (ab initio methods) and subsequent force-matching [208] or on the fitting (that is, parametrization) of given analytic potentials to experimental or quantum mechanical results. In the first approach, the potential is constructed implicitly using ab initio methods. There, the

electronic energy E_0 and the corresponding forces are computed approximately¹³ for a number of chosen example configurations of the nuclei. By extrapolation/interpolation to other configurations an approximate potential energy hypersurface can be constructed that can in turn be approximated by simple analytic functions. In the second, more empirical approach, one directly chooses an analytic form of the potential which contains certain form functions that depend on geometric quantities such as distances, angles or coordinates of particles. Subsequently, this form is fitted by an appropriate determination of its parameters to available results from quantum mechanical computations or from actual experiments. In this way one can model interactions that incorporate different kinds of bond forces, possible constraints, conditions on angles, etc. If the results of the simulation are not satisfactory, the potentials have to be improved by the choice of better parameters or by the selection of better forms of the potential functions with other or even extended sets of parameters. The construction of good potentials is still a form of art and requires much skill, work, and intuition. Programs such as GULP [5, 244] or THBFIT [6] can help in the creation of new forms of potentials and in the fitting of parameters for solids and crystals.

Some Simple Potentials. The simplest interactions are those between two particles. Potentials that only depend on the distance $r_{ij} := \|\mathbf{R}_j - \mathbf{R}_i\|$ between any pair of particles are called pair potentials. Here, we use $(\mathbf{R}_1, \dots, \mathbf{R}_N)$ as a notation for the classical coordinates $\mathbf{R}(t)$. The associated potential energy V has the form

$$V(\mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_{i=1}^N \sum_{j=i+1}^N U_{ij}(r_{ij}),$$

where U_{ij} denotes the potential acting between the particles i and j . Examples for such pair potentials U_{ij} between two particles are:

– **The Gravitational Potential**

$$U(r_{ij}) = -G_{\text{Grav}} \frac{m_i m_j}{r_{ij}}. \quad (2.42)$$

¹³ The wave function in the electronic Schrödinger equation is still defined in a high-dimensional space. The coordinates of the electrons are in \mathbb{R}^{3K} . An analytic solution or an approximation by a conventional numerical discretization method is impossible in general. Therefore, approximation methods have to be used that substantially reduce the dimension of the problem. Over the years, many variants of such approximation methods have been proposed and used, such as the Hartree-Fock method, the density functional theory, configuration interaction methods, coupled-cluster methods, generalized valence bond techniques, the tight-binding approach, or the Harris functional method. An overview of the different approaches can be found for example in [526, 528].

– **The Coulomb Potential**

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}. \quad (2.43)$$

– **The van der Waals Potential**

$$U(r_{ij}) = -a \left(\frac{1}{r_{ij}} \right)^6.$$

– **The Lennard-Jones Potential**

$$U(r_{ij}) = \alpha\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^n - \left(\frac{\sigma}{r_{ij}} \right)^m \right], \quad m < n. \quad (2.44)$$

Here, α is given as $\alpha = \frac{1}{n-m} \left(\frac{n^n}{m^m} \right)^{\frac{1}{n-m}}$. This potential is parametrized by σ and ϵ . The value ϵ describes the depth of the potential and thereby the strength of the repulsive and attractive forces. Materials of different strength can be simulated in this way. Increasing ϵ leads to stronger bonds and therefore harder materials. The value σ parametrizes the zero crossing of the potential. With $m = 6$ (as in the van der Waals force) and $n = 12$ the Lennard-Jones potential – as well as the resulting force – decreases very rapidly with increasing distance. Here, the choice $n = 12$ does not stem from physical considerations but merely from mathematical simplicity.

For $(m, n) = (10, 12)$ we obtain the related potential function

$$U(r_{ij}) = A/r_{ij}^{12} - B/r_{ij}^{10},$$

which allows the empirical modeling of hydrogen bonds. The parameters A and B depend on the kind of the particular hydrogen bond and are in general fitted to experimental data.

– **The Morse Potential**

$$U(r_{ij}) = D(1 - e^{-a(r_{ij}-r_0)})^2. \quad (2.45)$$

D is the dissociation energy of the bond, a is an appropriately chosen parameter which depends on the frequency of the bond vibrations, and r_0 is a reference length.

– **Hooke's Law** (Harmonic Potential)

$$U(r_{ij}) = \frac{k}{2}(r_{ij} - r_0)^2.$$

Note that we omitted the indices i, j in the notation for the potentials U .

These simple potentials are certainly limited in their applications. However, noble gases can be represented well this way since their atoms are only attracted to each other by the van der Waals force. These simple potentials

are also used outside of molecular dynamics, as for instance in the simulation of fluids on the microscale. However, more complex kinds of interactions, such as the ones that occur in metals or molecules, can not be simulated with such potentials in a realistic manner [209]. For this, other kinds of potential functions are needed that include interactions between several atoms of a molecule.

Since the eighties such many-body interactions have been introduced as potential functions. The various approaches involve density and coordination number, respectively, and exploit the idea that bonds are the weaker the higher the local density of the particles is. This led to the development of potentials with additional terms that most often consist of two components, a two-body part and a part which takes the coordination number (that is, the local density of particles) into account. Examples of such potentials are the glue model [209], the embedded atom method [174], the Finnis-Sinclair potential [232] and also the so-called effective-medium theory [336]. All these approaches differ strongly in the way how the coordination number is used in the construction of the potential. Sometimes different parametrizations are obtained even for the same material because of the different constructions. Special many-body potentials have been developed specifically for the study of crack propagation in materials [593].

Still more complex potentials are needed for instance for the modeling of semiconductors such as silicon. The potentials developed for these materials also use the concept of coordination number and bond order, that means that the strength of the bond depends on the local neighborhood. These potentials share a strong connection with the glue models. Stillinger and Weber [584] use a two-body and an additional three-body term in their potential. The family of potentials developed by Tersoff [603] was modified slightly by Brenner [122] and used in a similar form also in the modeling of hydrocarbons.

2.3 An Outlook on the Methods of Ab Initio Molecular Dynamics

Until now we have employed approximation methods for the approximate solution of the electronic Schrödinger equation only to obtain data for the specification and fitting of analytical potential function for the methods of classical molecular dynamics. But they can also be used in each time step of Newton's equation to directly compute the potential energy hypersurface for the actual nuclear coordinates. This is the basic idea of the so-called ab initio molecular dynamics. One solves the electronic Schrödinger equation approximately to determine the effective potential energy of the nuclei. From it one can compute the forces on the nuclei and move the nuclei according to Newton's equation of motion given these forces. This principle in its different variants forms the basis of the Ehrenfest molecular dynamics, the Born-Oppenheimer molecular dynamics and the Car-Parinello method.

Ehrenfest Molecular Dynamics. We consider again equations (2.30), (2.31) and assume that the system remains in a single adiabatic state, typically the ground state ϕ_0 . Then, one obtains

$$M_k \ddot{\mathbf{R}}_k(t) = -\nabla_{\mathbf{R}_k} \int \phi_0^*(\mathbf{R}(t), \mathbf{r}) \mathcal{H}_e(\mathbf{R}(t), \mathbf{r}) \phi_0(\mathbf{R}(t), \mathbf{r}) d\mathbf{r} \quad (2.46)$$

$$= -\nabla_{\mathbf{R}_k} V_e^{Ehr}(\mathbf{R}(t)),$$

$$i \hbar \frac{\partial \phi_0(\mathbf{R}(t), \mathbf{r})}{\partial t} = \mathcal{H}_e \phi_0(\mathbf{R}(t), \mathbf{r}), \quad (2.47)$$

where $\phi_{\mathbf{R}(t)}(\mathbf{r}, t) = c_0(t) \phi_0(\mathbf{R}(t), \mathbf{r})$ was assumed with $|c_0(t)|^2 \equiv 1$, compare (2.32).

Born-Oppenheimer Molecular Dynamics. In the derivation of the so-called Born-Oppenheimer molecular dynamics one uses the large difference in masses between electrons and atomic nuclei. The ratio¹⁴ of the velocity v_K of a nucleus to the velocity of an electron v_e is in general smaller than 10^{-2} . Therefore, one assumes that the electrons adapt instantaneously to the changed nuclear configuration and so are always in the quantum mechanical ground state associated to the actual position of the nuclei. The movement of the nuclei during the adaptation of the electron movement is negligibly small in the sense of classical dynamics. This justifies to set

$$\Psi(\mathbf{R}, \mathbf{r}, t) \approx \Psi^{BO}(\mathbf{R}, \mathbf{r}, t) := \sum_{j=0}^{\infty} \chi_j(\mathbf{R}, t) \phi_j(\mathbf{R}, \mathbf{r}), \quad (2.48)$$

which allows to separate the fast from the slow variables. In contrast to (2.14) the electronic wave functions $\phi_j(\mathbf{R}, \mathbf{r})$ depend no longer on time but depend on the nuclear coordinates \mathbf{R} . Using a Taylor expansion of the stationary Schrödinger equation and several approximations that rely on the difference in masses between electrons and nuclei, see for example Chapter 8.4 in [546], the stationary Schrödinger equation can be separated into two equations, the electronic Schrödinger equation and an equation for the nuclei. The first equation describes how the electrons behave when the position of the nuclei is fixed. Its solution leads to an effective potential that appears in the equation for the nuclei and describes the effect of the electrons on the interaction between the nuclei. After restriction to the ground state and further approximations, the Born-Oppenheimer molecular dynamics results which is given by the equations

$$M_k \ddot{\mathbf{R}}_k(t) = -\nabla_{\mathbf{R}_k} \min_{\phi_0} \left\{ \int \phi_0^*(\mathbf{R}(t), \mathbf{r}) \mathcal{H}_e(\mathbf{R}(t), \mathbf{r}) \phi_0(\mathbf{R}(t), \mathbf{r}) d\mathbf{r} \right\}$$

$$=: -\nabla_{\mathbf{R}_k} V_e^{BO}(\mathbf{R}(t)), \quad (2.49)$$

¹⁴ The ratio of the mass m_e of an electron and the mass M_K of a nucleus is – except for hydrogen and helium – smaller than 10^{-4} . Furthermore, according to classical kinetic gas theory, the energy per degree of freedom of non-interacting particles is the same, thus it holds $m_e v_e^2 = M_K v_K^2$.

$$\mathcal{H}_e(\mathbf{R}(t), \mathbf{r})\phi_0(\mathbf{R}(t), \mathbf{r}) = E_0(\mathbf{R}(t))\phi_0(\mathbf{R}(t), \mathbf{r}).$$

With the forces $\mathbf{F}_k(t) = M_k \ddot{\mathbf{R}}_k(t)$ acting on the nuclei, their positions can be moved according to the laws of classical mechanics.¹⁵

In our case, in which we consider the ground state and neglect all coupling terms, the Ehrenfest potential V_e^{Ehr} agrees, according to equation (2.38), with the Born-Oppenheimer potential V_e^{BO} . However, the dynamics is fundamentally different. In the Born-Oppenheimer method, the computation of the electron structure is reduced to the solution of the stationary Schrödinger equation, which then is used to compute the forces acting at that time on the nuclei so that the nuclei can be moved according to the laws of classical molecular dynamics. The time-dependency of the state of the electrons is here exclusively a consequence of the classical motion of the nuclei and not, as in the case of the Ehrenfest molecular dynamics, determined from the time-dependent Schrödinger equation in the coupled system of equations (2.46). In particular the time evolution of the state of the electrons in the Ehrenfest method corresponds to a unitary propagation [360, 361, 375]. If the initial state is minimal, its norm and minimality are maintained [218, 605]. This is not true for the Born-Oppenheimer dynamics in which a minimization is needed in every time step.

A further difference of the two methods is the following: Let us assume that particle functions ψ_{α_i} are given from which, as for instance in the Hartree-Fock method,¹⁶ with $\mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_K)$ product functions $\psi_{\alpha_1 \dots \alpha_K}^{SD}$, the so-called Slater determinants,¹⁷ are formed by

$$\psi_{\alpha_1 \dots \alpha_K}^{SD}(\mathbf{r}, t) = \frac{1}{\sqrt{K!}} \det \begin{vmatrix} \psi_{\alpha_1}(\mathbf{r}_1, t) & \psi_{\alpha_1}(\mathbf{r}_2, t) & \dots & \psi_{\alpha_1}(\mathbf{r}_K, t) \\ \psi_{\alpha_2}(\mathbf{r}_1, t) & \psi_{\alpha_2}(\mathbf{r}_2, t) & \dots & \psi_{\alpha_2}(\mathbf{r}_K, t) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{\alpha_K}(\mathbf{r}_1, t) & \psi_{\alpha_K}(\mathbf{r}_2, t) & \dots & \psi_{\alpha_K}(\mathbf{r}_K, t) \end{vmatrix}. \quad (2.50)$$

For an approximate solution of the electronic Schrödinger equation one now expands the ground state $\phi_0(\mathbf{R}(t), \mathbf{r})$ with help of these products of particle functions as

$$\phi_0(\mathbf{R}(t), \mathbf{r}) = \sum_{\alpha_1, \dots, \alpha_K} \gamma_{\alpha_1, \dots, \alpha_K}(t) \psi_{\alpha_1 \dots \alpha_K}^{SD}(\mathbf{r}, t) \quad (2.51)$$

with the coefficients

¹⁵ There is also the approach to apply this method to every excited state ϕ_j without taking interferences into account, i.e., to proceed analogously to (2.33-2.36) and to neglect all or only certain coupling terms [304, 359].

¹⁶ In density functional theory one uses a different kind of function for the particles, but the principle is the same.

¹⁷ This means that the spin of the particles is neglected here.

$$\gamma_{\alpha_1, \dots, \alpha_K}(t) := \int \psi_{\alpha_1 \dots \alpha_K}^{*SD}(\mathbf{r}, t) \phi_0(\mathbf{R}(t), \mathbf{r}) d\mathbf{r}. \quad (2.52)$$

Then, one has to minimize in equation (2.49) under the constraint that the particle functions are orthonormal, $\int \psi_{\alpha_i}^* \psi_{\alpha_j} d\mathbf{r} = \delta_{\alpha_i \alpha_j}$, since this is a necessary requirement for the expansion (2.51). Since the time evolution of the electrons under the Ehrenfest dynamics is a unitary propagation, the particle functions remain orthonormal if they were orthonormal at the initial time.

Car-Parrinello Molecular Dynamics. The advantage of the Ehrenfest dynamics is that the wave function stays minimal with respect to the current position of the nuclei. The disadvantage is that the size of the time step is determined by the motion of the electrons and is therefore “small”. The size of the time step in the Born-Oppenheimer dynamics is determined by the motion of the nuclei, on the other hand, and is therefore certainly “larger”. The disadvantage however is that a minimization is required in each time step. The Car-Parrinello molecular dynamics [137, 469] attempts to combine the advantages of both methods and to avoid their disadvantages. The fundamental idea is to transform the quantum mechanical separation of the time scales of the “fast” electrons and the “slow” nuclei into a classical adiabatic separation of energy scales within the theory of dynamical systems and to neglect the explicit time-dependency of the motion of the electrons [106, 465, 466, 515].

To understand the idea, we consider at first again the Ehrenfest and Born-Oppenheimer dynamics. If restricted to the ground state $\phi_0(\mathbf{R}, \mathbf{r})$, the central quantity

$$V_{El}(\mathbf{R}) := \int \phi_0^*(\mathbf{R}, \mathbf{r}) \mathcal{H}_e(\mathbf{R}, \mathbf{r}) \phi_0(\mathbf{R}, \mathbf{r}) d\mathbf{r} = E_0(\mathbf{R})$$

is a function of the position of the nuclei \mathbf{R} . From the Lagrange function of classical mechanics for the motion of the nuclei

$$L(\mathbf{R}, \dot{\mathbf{R}}) = \sum_k^N \frac{1}{2} M_k \dot{\mathbf{R}}_k^2 - V_{El}(\mathbf{R}), \quad (2.53)$$

we obtain, using the appropriate Euler-Lagrange equations $\frac{d}{dt} \frac{\partial L}{\partial \dot{\mathbf{R}}_k} = \frac{\partial L}{\partial \mathbf{R}_k}$, the equation of motion (2.49)

$$M_k \ddot{\mathbf{R}}_k(t) = -\nabla_{\mathbf{R}_k} E_0(\mathbf{R}(t)). \quad (2.54)$$

One can regard the energy of the ground state $E_0 = V_{El}$ also as a functional of the wave function ϕ_0 . If the wave function ϕ_0 has an expansion with now time-dependent particle functions $\{\psi_i(\mathbf{r}, t)\}$, analog to the expansion (2.51) in (one or several) Slater determinants (2.50), V_{El} can also be seen as a functional of the orbitals $\{\psi_i(\mathbf{r}, t)\}$. The force acting on the nuclei is obtained

in classical mechanics as the derivative of a Lagrange function with respect to the positions of the nuclei. If one now also views the orbitals as “classical particles”,¹⁸ one can determine the forces acting on the orbitals as the functional derivative of an appropriate Lagrange function with respect to the orbitals. Then, a purely classical approach results in a Lagrange function of the form [137]

$$L_{CP}(\mathbf{R}, \dot{\mathbf{R}}, \{\psi_i\}, \{\dot{\psi}_i\}) = \sum_k \frac{1}{2} M_k \dot{\mathbf{R}}_k^2 + \sum_i \frac{1}{2} \mu_i \int \dot{\psi}_i^* \dot{\psi}_i d\mathbf{r} - V_{El}(\mathbf{R}, \{\psi_i\}) + \varphi(\mathbf{R}, \{\psi_i\}) \quad (2.55)$$

with the “fictitious masses” μ_i of the orbitals $\{\psi_i\}$ and a general, appropriately chosen constraint φ . A simple example for such a constraint is the orthonormality of the orbitals. This yields

$$\varphi(\mathbf{R}, \{\psi_i\}) = \sum_{i,j} \lambda_{ij} \left(\int \psi_i^* \psi_j d\mathbf{r} - \delta_{ij} \right)$$

with the Lagrange multipliers λ_{ij} . In this simple case φ does not depend (plane wave basis) or does only implicitly depend (Gaussian basis) on $\mathbf{R}(\mathbf{t})$. The respective Euler-Lagrange equations

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\mathbf{R}}_k} = \frac{\partial L}{\partial \mathbf{R}_k}, \quad \frac{d}{dt} \frac{\delta L}{\delta \dot{\psi}_i^*} = \frac{\delta L}{\delta \psi_i^*} \quad (2.56)$$

give Newton’s equations of motion¹⁹

$$M_k \ddot{\mathbf{R}}_k(t) = -\nabla_{\mathbf{R}_k} \int \phi_0^* \mathcal{H}_e \phi_0 d\mathbf{r} + \nabla_{\mathbf{R}_k} \varphi(\mathbf{R}, \{\psi_i\}), \quad (2.57)$$

$$\mu_i \ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta}{\delta \psi_i^*} \int \phi_0^* \mathcal{H}_e \phi_0 d\mathbf{r} + \frac{\delta}{\delta \psi_i^*} \varphi(\mathbf{R}, \{\psi_i\}). \quad (2.58)$$

The nuclei move according to a physical temperature proportional to the kinetic energy $\sum_k M_k \dot{\mathbf{R}}_k^2$ of the nuclei. In contrast, the electrons move according to a “fictitious temperature” proportional to the fictitious kinetic energy $\sum_i \mu_i \int \dot{\psi}_i^* \dot{\psi}_i d\mathbf{r}$ of the orbitals.²⁰

Let the initial state ϕ_0 at time t_0 be exactly the ground state. For a “low temperature of the electrons” the electrons move almost exactly on the Born-Oppenheimer surface. But the “temperature of the electrons” has to be “high” enough so that the electrons can adjust to the motion of the nuclei. The problem in practice is the “right temperature control”. The subsystem of the physical motion of the nuclei described by equation (2.57) and the

¹⁸ For this, one treats the orbitals in the context of a classical field theory.

¹⁹ $\psi_i^*(\mathbf{r}, t)$ and $\psi_i(\mathbf{r}, t)$ are linearly independent for complex variations.

²⁰ The physical kinetic energy of the electrons is included in E_0 .

subsystem of the fictitious orbital motions described by equation (2.58) have to be separated in such a way that the fast electronic subsystem stays “cold” for a long time and nevertheless immediately adjusts to the slow motion of the nuclei, while keeping the nuclei at the same time at their physical temperature (which is much higher). In particular, there is no transfer of energy allowed between the physical subsystem of the (“hot”) nuclei and the fictitious subsystem of the (“cold”) electrons. It is possible to satisfy these requirements if the force spectrum of the degrees of freedom of the electrons $f(\omega) = \int_0^\infty \cos(\omega t) \left(\sum_i \int \dot{\psi}_i^*(\mathbf{r}, t) \dot{\psi}_i(\mathbf{r}, 0) d\mathbf{r} \right) dt$ and that of the nuclei do not overlap in any range of frequencies [515]. In [106] it could be shown that the absolute error of the Car-Parrinello trajectory can be controlled relative to the trajectory determined by the exact Born-Oppenheimer surface by using the parameters μ_i .

The Hellmann-Feynman Theorem. In the molecular dynamics methods described above the force acting on a nucleus has to be determined according to the equations (2.46), (2.49) and (2.57). A direct numerical evaluation of the derivative

$$\mathbf{F}_k(\mathbf{R}) = -\nabla_{\mathbf{R}_k} \int \phi_0^* \mathcal{H}_e \phi_0 d\mathbf{r},$$

for instance using a finite difference approximation, is too expensive on the one hand and too inaccurate for dynamical simulations on the other hand. It is therefore desirable to evaluate the derivative analytically and to apply it directly to the different parts of \mathcal{H}_e . This is made possible by the following approach: Let q be any coordinate $(\mathbf{R}_k)_i, i \in \{1, 2, 3\}$ of any component \mathbf{R}_k of \mathbf{R} . Keep now all other components of \mathbf{R} and the other two coordinates of \mathbf{R}_k fixed and only allow q to vary. Then, the electronic Hamilton operator $\mathcal{H}_e(\mathbf{R}, \mathbf{r}) = \mathcal{H}(q)$ depends on q (besides \mathbf{r}) according to equation (2.13) via the operators $V_{eK}(\mathbf{R}, \mathbf{r})$ and $V_{KK}(\mathbf{R})$. By the stationary electronic Schrödinger equation

$$\mathcal{H}(q)\phi_0(q) = E_0(q)\phi_0(q) \quad (2.59)$$

therefore also the state of the electrons ϕ_0 (beside \mathbf{r}) and the energy E_0 depend on q . If the electronic state is assumed to be normalized, that is, it satisfies $\int \phi_0^* \phi_0 d\mathbf{r} = 1$, then a translation by q results in a force $F(q)$ of²¹

$$-F(q) = \frac{dE_0(q)}{dq} = \int \phi_0^*(q) \frac{d\mathcal{H}(q)}{dq} \phi_0(q) d\mathbf{r}. \quad (2.60)$$

The justification for this result is provided by the **Hellmann-Feynman Theorem**:²² Let $\phi_j(q)$ be the normalized eigenfunction of a self-adjoint op-

²¹ An analogous results holds for the excited states ϕ_j with the associated eigenvalues $E_j(q)$ and the associated Schrödinger equation $\mathcal{H}(q)\phi_j(q) = E_j(q)\phi_j(q)$.

²² The so-called Hellmann-Feynman theorem for quantum mechanical forces was proven originally in 1927 by Ehrenfest [204], it was discussed later by Hellman [311] and was rediscovered independently by Feynmann [225] in 1939.

erator $\mathcal{H}(q)$ associated to the eigenvalue $E_j(q)$ and q a real parameter, then it holds that

$$\frac{dE_j(q)}{dq} = \int \phi_j^*(q) \frac{d\mathcal{H}(q)}{dq} \phi_j(q) d\mathbf{r}. \quad (2.61)$$

This can be shown as follows: Using the product rule one obtains

$$\begin{aligned} \frac{dE_j(q)}{dq} &= \int \phi_j^*(q) \frac{d\mathcal{H}(q)}{dq} \phi_j(q) d\mathbf{r} + \\ &\quad \int \frac{d\phi_j^*(q)}{dq} \mathcal{H}(q) \phi_j(q) d\mathbf{r} + \int \phi_j^*(q) \mathcal{H}(q) \frac{d\phi_j(q)}{dq} d\mathbf{r}. \end{aligned}$$

The $\phi_j(q)$ are eigenfunctions associated to the eigenvalue $E_j(q)$, therefore it holds that

$$\begin{aligned} \frac{dE_j(q)}{dq} &= \int \phi_j^*(q) \frac{d\mathcal{H}(q)}{dq} \phi_j(q) d\mathbf{r} + \\ &\quad E_j(q) \int \frac{d\phi_j^*(q)}{dq} \phi_j(q) d\mathbf{r} + E_j(q) \int \phi_j^*(q) \frac{d\phi_j(q)}{dq} d\mathbf{r} \\ &= \int \phi_j^*(q) \frac{d\mathcal{H}(q)}{dq} \phi_j(q) d\mathbf{r} + E_j(q) \frac{d}{dq} \int \phi_j^*(q) \phi_j(q) d\mathbf{r} \end{aligned}$$

and now the normalization condition for ϕ_j implies the theorem.

This allows a simple numerical computation of the forces between different bound atoms. Because of

$$\mathbf{F}_k(\mathbf{R}) = -\nabla_{\mathbf{R}_k} \int \phi_0^* \mathcal{H}_e \phi_0 d\mathbf{r} = -\int \phi_0^* \nabla_{\mathbf{R}_k} \mathcal{H}_e \phi_0 d\mathbf{r} \quad (2.62)$$

and

$$\nabla_{\mathbf{R}_k} \mathcal{H}_e = \nabla_{\mathbf{R}_k} (V_{ee} + V_{eK} + V_{KK}) = \nabla_{\mathbf{R}_k} (V_{eK} + V_{KK})$$

one obtains the force on the k th nucleus as

$$\begin{aligned} \mathbf{F}_k(\mathbf{R}) &= -\int \phi_0^* \nabla_{\mathbf{R}_k} (V_{eK} + V_{KK}) \phi_0 d\mathbf{r} \\ &= -\int \phi_0^* \nabla_{\mathbf{R}_k} V_{eK} \phi_0 d\mathbf{r} - \nabla_{\mathbf{R}_k} V_{KK} \\ &= \frac{e^2}{4\pi\epsilon_0} \left(\int \phi_0^* \phi_0 \sum_{i=1}^K \sum_{j=1}^N \nabla_{\mathbf{R}_k} \frac{Z_j}{\|\mathbf{R}_j - \mathbf{r}_i\|} d\mathbf{r} - \nabla_{\mathbf{R}_k} \sum_{i<j}^N \frac{Z_i Z_j}{\|\mathbf{R}_i - \mathbf{R}_j\|} \right). \end{aligned} \quad (2.63)$$

The derivatives now act directly on the potential functions V_{KK} and V_{eK} and can be computed analytically. The force $\mathbf{F}_k = \mathbf{F}_k(\mathbf{R})$ on the k th nucleus therefore results from the Coulomb forces (from the potential V_{KK}) acting between the nuclei and an additional effective force caused by the electrons. This effective force has the form of a Coulomb force induced by a hypothetical electron cloud with a density given by the solution of the electronic Schrödinger equation. In this way, the influence of the electrons on the nuclei is taken into account.