Second-generation wave-function thermostat for *ab initio* molecular dynamics

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A rigorous two-thermostat formulation for *ab initio* molecular dynamics using the fictitious Lagrangian approach is presented. It integrates the concepts of mass renormalization and temperature control for the wave functions. The new thermostat adapts to the instantaneous kinetic energy of the nuclei and thus minimizes its influence on the dynamics. Deviations from the canonical ensemble, which are possible in the previous two-thermostat formulation, are avoided. The method uses a model for the effective mass of the wave functions, which is open to systematic improvement.

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I. INTRODUCTION

Ab initio molecular dynamics,[1] also called the Car-Parrinello method, allows to study the dynamical and finite-temperature behavior of molecules, surfaces and solids with forces from highly accurate first-principles density-functional simulations.[2,3] This approach has revolutionized the way electronic structure calculations are done to date. Two main variants of this approach have established themselves. The original approach of Car and Parrinello[1] uses a fictitious Lagrangian to deduce a dynamical equation of motion for the wave functions, while the so-called ''exact'' Born-Oppenheimer dynamics[4] performs self-consistency loops for each set of atomic positions.

The underlying idea of the fictitious Lagrangian approach is to treat the electronic wave functions as dynamical fields that obey a Newton-type equation of motion. If the temperature attributed to the motion of the wave functions is sufficiently low, the wave functions propagate close to the Born-Oppenheimer surface (i.e., the instantaneous electronic ground state). Thus, the electronic wave functions can be propagated with relatively minor computational effort while the nuclei are moving. Self-consistency loops for each step of the trajectory are avoided.

A difficulty arises from the requirement that the wave functions should remain sufficiently close to the Born-Oppenheimer surface so that physically correct forces on the nuclei are produced. This implies that the wave functions must remain ''cold,'' while at the same time the nuclei are at a relatively high physical temperature. Hence *ab initio* molecular-dynamics simulations are in principle nonequilibrium simulations.

In most cases, the heat transfer between the electronic and the atomic subsystems is sufficiently slow as a result of the separation between electronic and nuclear frequency spectra.[5] For long simulations, however, one has to bear in mind that the nuclear and electronic variables will eventually, even though very slowly, approach thermal equilibrium, where the wave functions deviate from the Born-Oppenheimer surface and the forces acting on the atoms are nonphysical. In order to rigorously maintain a stable simulation, two thermostats[6,7] are introduced.[8] One thermostat keeps the nuclei at their physical temperature and the other one adsorbs the additional heat transfer to the wave functions. The optimum temperature for the wave-function dynamics, which is required so that the wave functions can follow the nuclei adiabatically, has been discussed earlier.[8]

However, the previous two-thermostat formulation has three deficiencies.

(1) For systems consisting of parts that are only in weak thermal contact, the thermostats do not guarantee that the canonical ensemble is correctly sampled. The heat transfer from the nuclei to the wave functions is larger for some atoms than for others, which may result in different effective temperatures for different parts of the system.

(2) The target kinetic energy for the wave-function dynamics is constant over time and is determined according to the target temperature of the atoms. For small systems the fluctuations in the atomic kinetic energy can be sizable. In that case the wave-function thermostat will heat the wave functions when the atomic kinetic energy is low and cool more than necessary if the atoms have a high kinetic energy. This has an adverse effect on the nuclear trajectories.

(3) The goal of the wave-function thermostat is to keep the wave functions cold. The thermostat, however, induces fluctuations in the wave-function kinetic energy and thus introduces undesired heating sequences.

In this paper, I analyze the trajectories of the nuclei and propose a formulation of the two-thermostat method, which overcomes these deficiencies. The proposed method links the target temperature for the electronic wave-functions directly to the instantaneous motion of the atoms. Thus the wave function thermostat adapts to the temperature fluctuations of the nuclei, and minimizes its influence on the atomic trajectories. Second, the indirect influence of the wave-function thermostat on the atomic trajectories is compensated using an additional, opposing friction term in the equations of motion for the atoms.

A detailed numerical analysis of the errors in the forces resulting from the deviations from the Born-Oppenheimer surface and due to the previous two-thermostat formulation has been performed.[9]

In Sec. II, the previous two-thermostat formulation is restated, which allows me to introduce my notation. In Sec. III, effective equations of motion for the nuclei under the influence of the wave function dynamics are derived. Section IV discusses a potential thermodynamical instability in the previous two-thermostat formulation of Car-Parrinello dynam-

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ics. Section V describes the two-thermostat formulation. An approximate scheme for deriving the parameters of the theory and technicalities of the present implementation are given in Sec. VI. Test calculations are presented in Sec. VII.

II. EQUATIONS OF MOTION WITH TWO THERMOSTATS

Let me first describe my notation. The electrons are described by one-particle wave functions $|\Psi_n\rangle$. The wave functions $|\Psi_n\rangle$ are related by a linear transformation $|\Psi_n\rangle = T|\tilde{\Psi}_n\rangle$ to the variational parameters $|\tilde{\Psi}_n\rangle$. Often the variational parameters are vectors and the transformation is defined by a basis set $|\chi_k\rangle$ in the form $|\Psi_n\rangle = \Sigma_k |\chi_k\rangle \tilde{\Psi}_{k,n}$. Here, I have in mind the projector-augmented wave (PAW) method,[10] where the variational parameters are themselves fields, namely, the so-called pseudo wave functions $|\tilde{\Psi}\rangle$. The pseudo wave functions are expanded in a basis set, a detail that does not concern here. The pseudo wave functions of the PAW method are conceptionally identical to the wave functions of the pseudopotential formalism.

In the *ab initio* molecular-dynamics method with the previous two-thermostat formulation, the following coupled system of equations of motion is solved.

$$m_\Psi |\ddot{\tilde{\Psi}}_n\rangle = -\tilde{H}|\tilde{\Psi}_n\rangle + \sum_m \tilde{O}|\tilde{\Psi}_m\rangle \Lambda_{m,n} - m_\Psi |\dot{\tilde{\Psi}}_n\rangle \dot{x}_\Psi ,$$

$$M_i \ddot{R}_i = F_i - M_i \dot{R}_i \dot{x}_R ,$$

$$Q_\Psi \ddot{x}_\Psi = 2\left(\sum_n \langle \dot{\tilde{\Psi}}_n | m_\Psi | \dot{\tilde{\Psi}}_n \rangle - E_{kin,0} \right),$$

$$Q_R \ddot{x}_R = 2\left(\sum_i \frac{1}{2} M_i \dot{R}_i^2 - \frac{1}{2} g k_B T \right). \tag{1}$$

If $E[R,|\Psi\rangle]$ is the Kohn-Sham total energy functional, the pseudo Hamiltonian $\tilde{H}$ is defined such that $dE/d\langle\tilde{\Psi}_n| = \tilde{H}|\tilde{\Psi}_n\rangle$ and the forces F_i are the partial derivatives of the Kohn-Sham total-energy functional with respect to the atomic positions. The pseudo-overlap operator $\tilde{O} = T^\dagger T$ is obtained from the transformation between the true wave functions $|\Psi\rangle$ and the pseudo wave functions $|\tilde{\Psi}\rangle$. The overlap between two wave functions is $\langle\Psi_n|\Psi_m\rangle = \langle\tilde{\Psi}_n|\tilde{O}|\tilde{\Psi}_m\rangle$. The Lagrange parameters introduced to keep the wave functions orthogonal are denoted as $\Lambda_{m,n}$. The mass of the wave functions is m_Ψ. In practice, an operator diagonal in a plane-wave representation is used. The nuclear masses are denoted as M_i, where i is the index of the corresponding atom. Q_Ψ and Q_E are the "masses" of the thermostat variables x_Ψ and x_R for wave functions and nuclei, respectively. These masses determine the reponse time and the dominant frequency of the thermostats. g is the number of nuclear degrees of freedom and k_B is the Boltzmann constant. $E_{kin,0}$ is a parameter that determines the target kinetic energy of the wave functions in the simulations. Its value is chosen according to an estimate of the Born-Oppenheimer kinetic energy of the wave functions. In the entire paper Hartree atomic units ($\hbar = e = m_e = 4\pi\epsilon_0 = 1$) are used. The present formulation of the thermostat differs from Hoover's: the thermostat variable used by Hoover corresponds to the *time derivatives* of the thermostat variables x_R and x_Ψ used here. This choice has the advantage that the thermostats obey second-order differential equations just as the nuclear position and the wave functions.

Even though the equations of motion given above cannot be derived from a Lagrangian formalism, they have a conserved energy

$$E_c = \sum_n \langle \dot{\tilde{\Psi}}_n | m_\Psi | \dot{\tilde{\Psi}}_n \rangle + \sum_i \frac{1}{2} M_i \dot{R}_i^2 + E[|\Psi_n\rangle, R_i] + \frac{1}{2} Q_\Psi \dot{x}_\Psi^2 + 2E_{kin,0} x_\Psi + \frac{1}{2} Q_R \dot{x}_R^2 + g k_B T x_R . \tag{2}$$

The first two terms are the kinetic energies of wave functions and nuclei, the third is the potential energy, i.e., the density-functional total energy. The remaining terms are kinetic and potential energies of the two thermostats for wave functions and nuclei.

Simulations with the two thermostats reach a stationary state in which the wave-function thermostat variable x_Ψ exhibits an approximately constant drift to larger values, which freezes out the deviations from the Born-Oppenheimer approximation. As a consequence of energy conservation[11] the atom thermostat variable decreases at an average rate

$$\langle \dot{x}_R \rangle = -\frac{E_{kin_0}}{\frac{1}{2} g k_B T} \langle \dot{x}_\Psi \rangle, \tag{3}$$

which restores the energy absorbed by the wave-function thermostat.

III. EFFECTIVE EQUATIONS OF MOTION FOR THE NUCLEI

In order to understand the motion of the nuclei with the wave functions and thermostats tied to them, let me derive effective equations of motions for the nuclei. It is useful to consider the atoms as quasiparticles, each of which consists of a nucleus and a wave-function cloud, i.e. the distortion of the surrounding electron gas. Just as an electron distorts a surrounding crystal lattice to form a polaron, here a nucleus distorts the electron gas to form a quasiparticle called an atom. The distortion of the electron gas and its wave functions, will be called wave function cloud. The effective equations of motion are obtained from the equations of motion in Eq. (1) by constraining the wave functions to be identical to the exact Born-Oppenheimer wave function. The details of the derivation are given in Appendix A. Here, only the result is shown,

$$\sum_j [M_i\delta_{i,j}+K_{i,j}]\ddot{R}_j=F_i-M_i\dot{R}_i\dot{x}_R-\sum_j K_{i,j}\dot{R}_j\dot{x}_\Psi -\sum_{j,k}\left(\frac{\partial K_{i,j}}{\partial R_k}-\frac{1}{2}\frac{\partial K_{j,k}}{\partial R_i}\right)\dot{R}_j\dot{R}_k. \tag{4}$$

$K_{i,j}$ is the effective-mass tensor as function of the nuclear positions

$$K_{i,j}=2\sum_n \left\langle \frac{\partial\tilde{\Psi}_n^{BO}}{\partial R_i}\middle| m_\Psi \middle|\frac{\partial\tilde{\Psi}_n^{BO}}{\partial R_j}\right\rangle, \tag{5}$$

where $|\tilde{\Psi}_n^{BO}\rangle$ are the Born-Oppenheimer wave functions.

Let me discuss this equation:

The nuclei obtain an effective mass $M_i\delta_{i,j}+K_{i,j}$. The atoms appear to be heavier than the nuclei alone, because the wave functions also need to be accelerated, whenever the nuclei accelerate. This effect has been realized before[12,10] and corrections are in common use today.

The third term on the right-hand side of Eq. (4) is related to the friction imposed by the wave-function thermostat on the wave functions. As the thermostat removes kinetic energy from the wave functions, the atoms are also cooled down. In particular, for two loosely coupled subsystems, where one subsystem has a different average effective wave-function mass than the other, a drift of the thermostat variables cools one subsystem at the cost of the other. This may cause deviations from the canonical ensemble as discussed in more detail in the following section.

The last term in Eq. (4) describes the effect of the changes of the effective mass as the atoms are moving around. This term will not be discussed in more detail, because in this paper an approximation with the effective masses, independent of the atomic positions will be employed, where this term vanishes.

IV. DEVIATIONS FROM THE CANONICAL ENSEMBLE

Here, the deviations from the canonical ensemble mentioned above are investigated. The rate of energy change of a subsystem A imposed by the thermostats is according to Eq. (4)

$$\dot{E}_A=-\sum_{i\in A} M_i\dot{R}_i^2\dot{x}_R-\sum_{i,j\in A} K_{i,j}\dot{R}_i\dot{R}_j\dot{x}_\Psi. \tag{6}$$

Assuming that subsystem A is in thermal equilibrium at a temperature T_A, the thermal average of $\dot{R}_i\dot{R}_j$ is $\langle\dot{R}_i\dot{R}_j\rangle_T=\delta_{i,j}k_BT_A/M_i$. Furthermore, the drifts of the two-thermostat variables are related by Eq. (3).[13] Thus, Eq. (6) can be transformed to

$$\langle\dot{E}_A\rangle_T=g_Ak_BT_A\langle\dot{x}_\Psi\rangle\left[\frac{E_{kin,0}}{gk_BT/2}-\frac{1}{g_A}\sum_{i\in A}\frac{K_{i,i}}{M_i}\right], \tag{7}$$

where g and g_A are the number of degrees of freedom of the total system and subsystem A.

If the thermal average of the Born-Oppenheimer wave-function kinetic energy,

$$\sum_{i,j}\frac{1}{2}\langle\dot{R}_iK_{i,j}\dot{R}_j\rangle=\frac{1}{2}k_BT\left[\sum_{i\in A}\frac{K_{i,i}}{M_i}+\sum_{i\in B}\frac{K_{i,i}}{M_i}\right], \tag{8}$$

is chosen for $E_{kin,0}$, one obtains

$$\langle\dot{E}_A\rangle_T=\frac{g_Ag_B}{g_A+g_B}k_BT_A\dot{x}_\Psi\left[\frac{1}{g_B}\sum_{i\in B}\frac{K_{i,i}}{M_i}-\frac{1}{g_A}\sum_{i\in A}\frac{K_{i,i}}{M_i}\right], \tag{9}$$

where $g_B=g-g_A$, is the number of degrees of freedom in the subsystem B, which together with subsystem A makes up the complete system.

Hence, the effect of the thermostats can be described as a heat flow from one system to the other, with a heat-transport coefficient

$$\lambda_x=-\frac{\langle\dot{E}_A\rangle_T-\langle\dot{E}_B\rangle_T}{T_A-T_B} =-\frac{g_Ag_B}{g_A+g_B}k_B\dot{x}_\Psi\left[\frac{1}{g_B}\sum_{i\in B}\frac{K_{i,i}}{M_i}-\frac{1}{g_A}\sum_{i\in A}\frac{K_{i,i}}{M_i}\right]. \tag{10}$$

Note that λ_x is negative. Thermal equilibrium is only reached when total heat-transport coefficient among subsystems is positive. This clearly shows that there is a thermodynamical instability when the physical thermal coupling is smaller (in absolute values) than the implicit coupling via the thermostats.

The conditions for this thermodynamic instability are that (1) the drift in the wave-function thermostat is sufficiently rapid, (2) $K_{i,i}/M_i$ is very different for the atoms of one subsystem as compared to the other, and (3) the thermal coupling between the systems is sufficiently small, so that the effect of the thermostats is appreciable compared to the physical thermal coupling. While these conditions rarely corroborate, already the fluctuations, which result from a nearby instability, can render the results of a simulation inaccurate.

V. EQUATIONS OF MOTION WITH CONTROLLED HEAT BACK FEEDING

To cure the problems of the two-thermostat formulation, terms are added to the equations of motion that compensate the effect of the finite effective mass of the wave functions in the downfolded equations of motion for the atoms. I proceed with the assumption that the effective mass tensor of the wave functions is known. Later, I will discuss an approximate expression to be used in practice.

I propose a new set of equations of motion, which is the main result of this paper,

$$m_\Psi|\ddot{\tilde{\Psi}}_n\rangle=-\tilde{H}|\tilde{\Psi}_n\rangle+\sum_m \tilde{O}|\tilde{\Psi}_m\rangle\Lambda_{m,n}-m_\Psi|\dot{\tilde{\Psi}}_n\rangle\dot{x}_\Psi,$$

$$\sum_j (M_i\delta_{i,j}-K_{i,j})\ddot{R}_j=F_i-M_i\dot{R}_i\dot{x}_R+\sum_j K_{i,j}\dot{R}_j\dot{x}_\Psi+\sum_{i,j}\left(\frac{\partial K_{i,j}}{\partial R_k}-\frac{1}{2}\frac{\partial K_{j,k}}{\partial R_i}\right)\dot{R}_j\dot{R}_k,$$

$$Q_\Psi\ddot{x}_\Psi=2\,\theta(\dot{x}_\Psi)\left[\sum_n \langle\dot{\tilde{\Psi}}_n|m_\Psi|\dot{\tilde{\Psi}}_n\rangle-\sum_{i,j}\frac{1}{2}K_{i,j}\dot{R}_i\dot{R}_j\right]$$

$$Q_R\ddot{x}_R=2\left(\sum_i \frac{1}{2}M_i\dot{R}_i^2-\frac{1}{2}gk_BT\right). \tag{11}$$

The step function $\theta(\dot{x})$ in the equation of motion for the wave-function thermostat will be discussed in detail below. Even if the step function is removed, these equations create a stable and energy-conserving dynamics. Its role is to shut the thermostat down for those periods of time where the thermostat would otherwise heat the wave functions.

The system of equations (11) has a conserved energy

$$E_c=+\sum_i \frac{1}{2}M_i\dot{R}_i^2+E[|\Psi_n\rangle,R_i]+\sum_n \langle\dot{\tilde{\Psi}}_n|m_\Psi|\dot{\tilde{\Psi}}_n\rangle-\sum_{i,j}\frac{1}{2}K_{i,j}\dot{R}_i\dot{R}_j+\frac{1}{2}Q_\Psi\dot{x}_\Psi^2+\frac{1}{2}Q_R\dot{x}_R^2+gk_BTx_R. \tag{12}$$

The second line of Eq. (12) is the kinetic energy of the *free* motion of the wave functions representing deviations from the Born-Oppenheimer surface.

The new system of equations of motion differs in four points from the ones used previously.

(1) The nuclear mass is reduced by the effective wave-function mass, so that the effective mass of atoms, namely, the sum of the reduced mass of the nuclei and mass of the wave-function cloud add up to the true nuclear mass. This correction has been previously suggested[12,10] and is a common practice in state-of-the-art *ab initio* molecular-dynamics simulations.

(2) A friction force $\Sigma_j K_{i,j}\dot{R}_j\dot{x}_\Psi$ acting on the atoms has been added. This term is controlled by the wave-function thermostat and opposes the drag from the wave-functions, which themselves are slowed down by the wave function thermostat. The rate of energy added to or removed from the physical system by the wave-function thermostat is $[\Sigma_n\langle\dot{\tilde{\Psi}}_n|m_\psi|\dot{\tilde{\Psi}}_n\rangle-\Sigma_{i,j}K_{i,j}\dot{R}_i\dot{R}_j]\dot{x}_\Psi$. This energy transfer is proportional to the deviation of the wave functions from the Born-Oppenheimer surface. Hence the thermostat acts only on the *free* oscillations of the wave functions.

(3) The estimate $\frac{1}{2}\Sigma_{i,j}K_{i,j}\dot{R}_i\dot{R}_j$ for the instantaneous Born-Oppenheimer kinetic energy has been introduced into the feedback equations for the wave-function thermostat instead of a constant target energy used previously. This modification was necessary in order to obtain a conserved energy. Besides restoring energy conservation, this term has another beneficial role, which is most important for systems with large kinetic-energy fluctuations. The wave-function thermostat adapts to the instantaneous kinetic energy of the nuclei and acts only on the deviations of the wave functions from the Born-Oppenheimer surface. The wave-function thermostat would remain inactive for Born-Oppenheimer wave functions.

(4) The wave-function thermostat shuts down in an energy-conserving fashion when it would otherwise heat the wave functions. This is discussed in the following.

Despite the more complex equations of motion the conserved energy has one term less. There is no potential-energy term related to the wave functions, which has important implications. The thermostat variable oscillates repeatedly between cooling and heating the wave functions. Heating the wave functions is not desirable, as one would like to keep them at their lowest temperature compatible with the dynamics.

A better strategy is to couple the wave-function thermostat to the system only when cooling is required. This can be done in an energy-conserving way, since the contribution of the wave-function thermostat to the conserved energy vanishes whenever $\dot{x}_\Psi$ vanishes. Thus, the equation of motion for the wave-function thermostat in Eq. (11) has been modified by introducing a step function $\theta(\dot{x}_\Psi)$. $\theta(x)$ is the Heaviside step function defined as $\theta(x\geqslant 0)=1$, $\theta(0)=\frac{1}{2}$, and $\theta(x<0)=0$. The discretization of the equation of motion for the wave-function thermostat including the step function is not straightforward. This equation means the following. The thermostat dynamics is switched on with zero velocity when the wave-function kinetic energy grows larger than the target. $\dot{x}_\Psi$ grows and transfers energy from the wave-function dynamics into the nuclear subsystem until the velocity of the thermostat variable vanishes again. At this point, the wave-function kinetic energy is below its target. Instead of allowing the thermostat to heat the system, the thermostat variable x_Ψ is instead kept constant, implying that the thermostat is effectively switched off. If the equation of motion is solved continuously, the velocity of the thermostat vanishes exactly, when the thermostat shuts down. The velocity will remain zero, until the wave function kinetic energy grows above its target, and thus does not affect the dynamics for that period of time. The thermostat switches on again, when the kinetic energy grows above the target. Thus the trajectories proceed without any perturbation, as long the wave-function kinetic energy remains below its target value. In a discretized equation of motion the velocity of the thermostat must be explicitly reset to zero, whenever it would otherwise turn negative.

To summarize, the thermostat resets the kinetic energy to a lower value if the wave functions become too hot, while transfering the energy into the nuclear dynamics. Note that even when the wave-function thermostat is on, the atomic trajectories are affected only if the effective-mass tensor is inaccurate. Hence the thermostat can operate more strongly before affecting the atomic dynamics.

The thermostat variable of the atom thermostat does not experience any longer a steady drift in the present formulation. This can be deduced from the conserved-energy expression as follows. A drift of the thermostat variables is possible in principle, because a fixed translation of a thermostat vari-

able does not affect the dynamics and is, therefore, not observable. The time-averaged drift of x_R vanishes, because the potential energy of the atom thermostat is the only term in the conserved energy that depends on the thermostat variable. All other terms in the conserved energy are observable and, therefore, stationary.

A drift of the wave-function thermostat variable does not affect the conserved energy. Hence, a drift of x_Ψ is possible. This drift counterbalances the heat flow from the nuclei to the wave functions but does not add to the conserved energy.

In the remainder of this section, I will discuss a possible dynamical instability and how it can be avoided. The Born-Oppenheimer kinetic energy enters with a negative sign, which may point to a possible instability of the wave functions, when the bare mass tensor with elements $M_i\delta_{i,j} - K_{i,j}$ does not turn not to be positive definite. A particle with negative mass accelerates in the opposite direction of the forces, and runs away from a minimum. The condition for the bare mass tensor to be positive definite poses a strict upper bound on the wave-function mass m_Ψ.

In practice one needs to be even more restrictive. There is an internal excitation of the quasiparticle "atom," where the nucleus oscillates with high frequency about the wave-function cloud. This mode can be identified clearly when the wave functions are frozen and only the bare nuclei are allowed to move. If the bare mass of the nuclei is small, these oscillations may have high frequency that require a small time step in the discretization. While this mode falls into the class of deviations from the Born-Oppenheimer surface, the thermostat does not cure the problem since the wave-function kinetic energy is smaller than its target $\frac{1}{2}\Sigma_{i,j}K_{i,j}\dot{R}_i\dot{R}_j$. To avoid that problem I suggest to keep the wave-function mass m_Ψ sufficiently small, so that $K_{i,i} < \frac{1}{2}M_i$.

VI. IMPLEMENTATION

A. The model of an infinitely dilute gas

The new equations of motion require an analytic expression that approximates the effective-mass tensor. As a start, I adopt the model of an infinitely dilute gas of atoms, which has been used in the context of the previous wave-function thermostat and mass renormalization. The model of an infinitely dilute gas assumes that the Born-Oppenheimer wave functions can be divided into purely atomic contributions, and that those are identical to the wave functions of the corresponding isolated atoms.

The rationale for the model of an infinitely dilute gas is that the most rapid variations of the wave function occur near the nucleus, and are little affected by the bonding environment. Thus, already the isolated atom will capture most of the relevant contributions. One can envisage better approximations for the effective mass of the wave functions, which depend explicitly on the atomic positions, and which may be derived from a tight-binding-like description.

I insert the atomic wave function into the expression given in Eq. (5) for the effective-mass tensor of a given atom and obtain

$$K_{i,j} = -2\sum_n \langle \tilde{\Psi}_n | \nabla_i m_\Psi \nabla_j | \tilde{\Psi}_n \rangle. \tag{13}$$

It can be shown that in this approximation $K_{i,j}$ is diagonal for each atom with three identical matrix elements on its main diagonal. For symmetry reasons, the acceleration of an isotropic atom is parallel to the force, that is, $F = \lambda \ddot{R}$ with some parameter λ. Hence, the acceleration is an eigenvector of the effective-mass tensor $(M\delta_{i,j} + K_{i,j})\ddot{R}_j = \lambda \ddot{R}_j$. Since λ is independent of the direction of the applied force, K has three identical eigenvalues. Therefore, $K_{i,j}$ has the form of a unity matrix times a constant and the identity $K_{i,j} = \delta_{i,j}\frac{1}{3}\mathrm{Tr}\,K$ holds.

Thus one can obtain a more simple form of our model effective mass as,

$$K_{i,j} = \frac{2}{3}\delta_{i,j}\sum_n \langle \tilde{\Psi}_n | -\sum_i \nabla_i m_\Psi \nabla_i | \tilde{\Psi}_n \rangle. \tag{14}$$

In the special case of a G-independent mass,[14] the weight of the wave-function cloud is directly related to the kinetic energy of the pseudo wave functions, as reported previously,[8]

$$K_{i,j} = \frac{4m_\Psi}{3}\delta_{i,j}\sum_n \left\langle \tilde{\Psi}_n \middle| -\frac{1}{2}\nabla^2 \middle| \tilde{\Psi}_n \right\rangle. \tag{15}$$

A G-dependent wave-function mass, usually a mass-tensor diagonal in reciprocal space with elements depending on the reciprocal space vector of the augmented plane waves, is nowadays common practice. It allows to control the rapid oscillations of plane waves with large wave vectors[15] and avoids instabilities that occur otherwise when the basis set is increased. There are several choices for the G-dependence of the wave-function mass. I use an expression for the effective mass

$$m_\Psi(G,G') = m_\Psi^0(1 + cG^2)\delta_{G,G'}. \tag{16}$$

In order to obtain the effective-mass tensor, I determine the pseudo wave functions of the atom and transform them into G space via a Bessel transform. Then I evaluate

$$A = \sum_n f_n \int dG G^2 |\tilde{\Psi}_n(G)|^2, \tag{17}$$

$$B = \sum_n f_n \int dG G^4 |\tilde{\Psi}_n(G)|^2, \tag{18}$$

which are combined with the chosen parameters for the wave-function mass to the effective-mass tensor of the wave functions

$$K_{i,j} = \delta_{i,j}\frac{2}{3}m_\Psi^0(A_i + cB_i). \tag{19}$$

The variables f_n are the occupation numbers of the one-particle states. Typical values for A_i and B_i are given in Table I. Note, that these values depend on the choice of pseudo wave functions and are not transferable. They are

TABLE I. Coefficients A and B for Eq. (19) for different elements and their values relative to the nuclear masses. These values are not transferable.

Atom	A	B	$10^4(A/M)$	$10^4(B/M)$
H	0.830	2.830	4.518	15.403
He	3.505	17.128	4.803	23.475
C	5.837	22.292	2.666	10.181
O	14.569	86.109	4.995	29.525
F	20.304	143.785	5.863	41.518
Si	3.327	6.320	0.650	1.234
Cl	12.821	41.841	1.984	6.474
Fe	10.950	71.366	1.075	7.010
Ru	17.606	95.952	0.956	5.208
Os	16.874	86.002	0.848	4.320

listed here solely to provide the reader with a feeling of the order of magnitudes involved.

The effective wave-function mass must be substantially smaller than the nuclear masses, i.e., $\frac{2}{3}m_\Psi(A+cB)<M$, in order to obtain a stable dynamics. If this requirement is violated the reduced mass of the atom is negative, and atoms accelerate in the opposite direction of the force acting on them.

B. Discretized equations of motion

All equations of motion are implemented using the Verlet algorithm. An equation of motion for a general coordinate x has the form

$$m\ddot{x}=F-m\dot{x}f, \tag{20}$$

where f is a friction coefficient, which may be constant or imposed by a thermostat. The thermostat x creates a canonical ensemble by tuning the friction via $f=\dot{x}$ with time.

The equations of motion discretized with a time step Δ are obtained by replacing derivatives by the differential quotients $\dot{x}=[x(t+\Delta)-x(t-\Delta)]/(2\Delta)+O(\Delta^2)$ and $\ddot{x}=[x(t+\Delta)-2x(t)+x(t-\Delta)]/\Delta^2+O(\Delta^2)$ as,

$$x(t+\Delta)=\frac{2}{1+a}x(t)-\frac{1-a}{1+a}x(t-\Delta)+F(t)\frac{\Delta^2}{m}\frac{1}{1+a}, \tag{21}$$

where $a=f\Delta/2$.

The choice $a=0$ yields energy-conserving trajectories and $a=1$ results in steepest-descent dynamics. Intermediate values of a are the regime of friction dynamics.

Because the thermostat can be propagated only with the knowledge of the instantaneous kinetic energy, which in turn depends on the propagated value of the thermostat, I extrapolate the thermostat variable for $t+\Delta$ from the present and the previous two-thermostat values,

$$x(t+\Delta)=4x(t)-6x(t-\Delta)+4x(t-2\Delta)-x(t-3\Delta)+O(\Delta^4). \tag{22}$$

This expression introduces errors of the forces of order Δ^2, which is consistent with the overall accuracy of the Verlet algorithm.

The step function for the thermostat is implemented by resetting $\dot{x}_\Psi$ to zero for the propagation of wave function and nuclear positions, whenever it has a negative value otherwise, and by setting $x_\Psi(t-n\Delta)=x(t)$, whenever the velocity $\dot{x}_\Psi(t)$ would become negative during the propagation of the thermostat variable.

VII. TESTS

In order to test stability and accuracy of the method, I investigated two systems. A simulation of carbon monoxide shall illustrate how the thermostats adapt to large fluctuations of the nuclear kinetic energy. This test case allows also a test of the accuracy. Iron has been used as example for a metal and shows the stability of the trajectories against frequent band crossings.

The simulations described in the following have been performed with the Perdew-Burke-Ernzerhof density functional.[16,17] The plane-wave cutoff for the wave functions has been set at 30 Ry and the one for the density at 60 Ry. A time step of $\Delta=10$ a.u.$=0.12$ fs has been used together with a G-independent wave-function mass of $1000m_e$. The frequency of the thermostat for the nuclei has been chosen to 10 THz, which is unusually large. The frequency of the wave-function thermostat has been set to 100 THz.

A. Carbon Monoxide

The unit cell size is a 13 Å fcc unit cell. The electrostatic interaction between periodic images has been subtracted.[18] A $1\times s+1\times p+1\times d$ projector set has been used, that is one projector for every relevant set of angular momentum quantum numbers. The one-center density has been expanded into spherical harmonics up to angular momentum of $\ell=2$. Parameter $A=5.87$ for carbon and 15.42 for oxygen have been used, resulting in an effective mass of the wave-function cloud amounts to 17% and 35% of the physical nuclear mass for carbon and oxygen, respectively. Rotations and translations have been frozen out by constraints so that a truely one-dimensional system is studied. The simulation has been performed at 1000 K.

The experimental value for the CO stretch vibration is 2170 cm^{-1}.[19] The experimental bond length is 1.1283 Å.[20] Fixed point calculation predict a bond length of 1.138 Å and a stretch frequency of 2125 cm^{-1}. These deviations are in the range of errors expected for the density functional used.

Simulations lasting several picoseconds have been performed.[21] A sequence of 0.3 ps is shown in Fig. 1. The deviation of the wave-function kinetic energy from the Born-Oppenheimer surface is -0.05 times the variation of the potential energy and overall smaller than 5 meV. This indicates that the dilute-atomic-gas model overestimates the effective masses by about 10%. On the other hand, 90% of the error has been removed.

The reduced mass of atoms with the wave-function cloud is 25% of the true reduced mass, which, without correction,

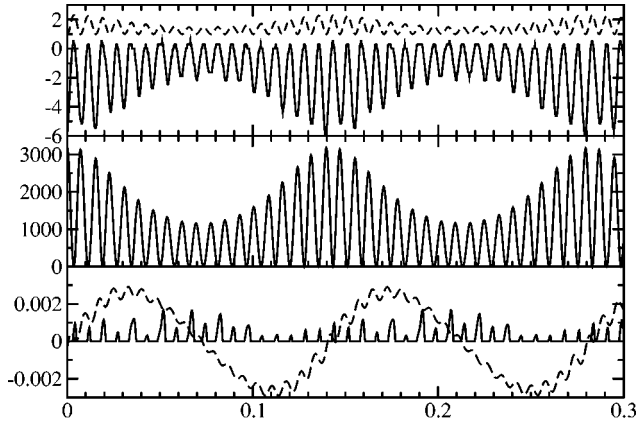

FIG. 1. Energies of carbon monoxide versus time in picoseconds. Top, non-Born-Oppenheimer kinetic energy of the wave functions in meV (full line) and total energy in units of 0.1 eV (dashed line) displaced vertically. Middle, instantaneous ''temperature'' in kelvin. Bottom, friction imposed by the thermostats in units of $2/\Delta$ for wave functions (full line) and nuclei (dashed line).

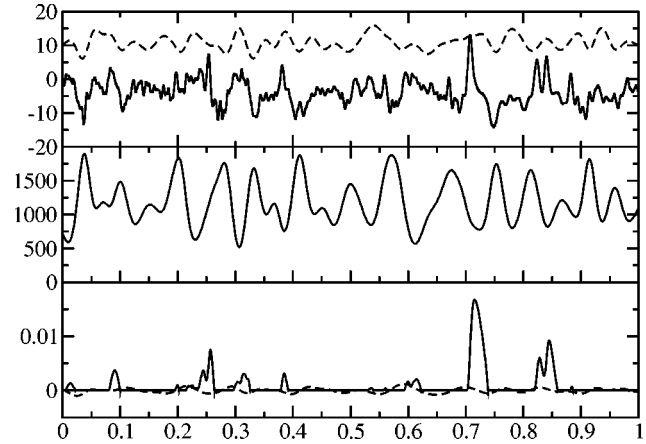

FIG. 2. Energies of austenite (fcc Iron) in an eight-atom supercell versus time in picoseconds. Top, total non-Born-Oppenheimer kinetic energy of the wave functions in meV (full line) and total energy in units of 0.1 eV (dashed). Middle, instantaneous ''temperature'' in kelvin. Bottom, friction imposed by the thermostats in units of $2/\Delta$ for wave functions (full line) and nuclei (dashed line).

would result in an overestimate of 10% in the frequencies. Given the error in the effective masses one can expect frequencies that overestimate the frequency derived from static calculation by 1%, which is in good agreement with the value of 2148 cm^{-1} obtained from averaging vibrational periods during 5 ps.

The friction measured in units of $\Delta/2$ remains below $4\times10^{-3}(2/\Delta)$, which is very small indicating that the heat transfer from wave functions to the nuclei is small in this system. The total energy is conserved to within 5 meV/ps and scales down with the size of the time step.

B. Iron

As a test of a metallic system I have chosen γ iron. An eight-atom fcc unit cell has been used. Since only the Γ point was included in the *k*-point sampling, I do not expect the simulation to be a realistic description of the material. The simulation temperature is 1185 K, at the martensitic phase-transformation temperature. The parameter A was about 12% larger than the kinetic energy per atom, in order to account for the promotion of *s*- to *d*-electrons as one goes from an atom to the solid. The effective mass of the wave function per atom is 4.75 amu [$\mathrm{amu}=M(^{12}\mathrm{C})/12$], about 9% of the nuclear mass. The atom thermostat had a period of 0.1 ps, and the wave-function thermostat had a period of 0.01 fs. The band gap due to finite *k*-point sampling is typically about 0.1–0.2 eV.

The results for the simulation of one picosecond is shown in Fig. 2. The total-energy variation is of order 1 eV. The mean average kinetic energy related to the non-Born-Oppenheimer motion is 3 meV. The total energy drifts with 0.47 meV/ps. The typical energy deviation from the Born-Oppenheimer surface is 10–15 meV.

Most of the time the thermostat is switched off as the kinetic energy remains below the target defined by the effective masses. The most pronounced quenching sequence occurs at 0.7 ps. Here the sharp increase of the wave-function kinetic energy indicates a band crossing. A band crossing results in a randomization of the wave functions as the occupied state changes its character into that of the formerly unoccupied state, and would otherwise render the remainder of the simulation useless. The wave-function thermostat brings the wave functions back to the Born-Oppenheimer surface, while the perturbation of the nuclear dynamics during this rather strong quench is minimized by the opposing force acting on the nuclei.

VIII. CONCLUSION

In summary, a refined formulation of the two-thermostat approach for *ab initio* molecular dynamics has been presented. The approach aims at controlling only the deviations from the Born-Oppenheimer wave functions. The influence on the Born-Oppenheimer motion of the wave functions and the nuclear motion is minimized by additional forces opposing the indirect friction of the atoms. Furthermore, the thermostat is active only if the wave-function kinetic energy grows beyond its estimated Born-Oppenheimer value. The two-thermostat formulation can be applied to small systems with large fluctuations of the nuclear kinetic energy and the fictitious Born-Oppenheimer wave-function kinetic energy.

The approach rests on an expression for the effective-mass tensor of the wave functions. A simple formula has been derived from the previously employed model of an infinitely dilute gas. Systematic improvements of effective-mass tensor, which will improve the quality of the simulation, can be envisaged.

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APPENDIX: DOWNFOLDING THE WAVE-FUNCTION DYNAMICS

Here, the effective equations of motion, Eq. (4), for the nuclei are derived, which include the forces of the wave functions acting on the nuclei.

The starting point is the following set of equations:

$$m_\Psi|\ddot{\tilde{\Psi}}_n\rangle = -\tilde{H}|\tilde{\Psi}_n\rangle + \sum_m \tilde{O}|\tilde{\Psi}_m\rangle - m_\Psi|\dot{\tilde{\Psi}}_n\rangle\dot{x}_\Psi,$$

$$M\ddot{R}_i = F_i. \tag{A1}$$

The wave functions are constrained to remain exactly on the Born-Oppenheimer surface,

$$\tilde{\Psi}_n(r,t) = \tilde{\Psi}_n^{BO}(r,R(t)). \tag{A2}$$

The Born-Oppenheimer wave functions $\tilde{\Psi}_n^{BO}(r,R_i)$ are the ground-state wave function for a given set of atomic positions R_i.

Because the Born-Oppenheimer wave functions depend on the nuclear positions, the forces acting on the wave functions translate into additional forces acting on the nuclei. Thus, effective equations of motion for the atoms are obtained. The atoms are now ''quasiparticles'' consisting of nuclei and the wave-function clouds following them.

The constraints are enforced by the method of Lagrange multipliers: The constraint forces, which describe the effect of the wave-function cloud, are the derivatives of a ''constraint energy''

$$E^c = \sum_n (\langle\tilde{\Psi}_n - \tilde{\Psi}_n^{BO}|\Phi_n\rangle + \langle\Phi_n|\tilde{\Psi}_n - \tilde{\Psi}_n^{BO}\rangle), \tag{A3}$$

with the auxiliary fields Φ_n acting as Lagrange parameters. The resulting constraint forces are

$$F^c_{|\Psi_n\rangle} = -\frac{\partial E^c}{\partial\langle\tilde{\Psi}_n|} = |\Phi_n\rangle, \tag{A4}$$

$$F^c_{\langle\Psi_n|} = -\frac{\partial E^c}{\partial|\tilde{\Psi}_n\rangle} = \langle\Phi_n|, \tag{A5}$$

$$F^c_{R_i} = -\frac{\partial E^c}{\partial R_i} = \sum_n \left(\left\langle\frac{\partial\tilde{\Psi}_n^{BO}}{\partial R_i}\middle|\Phi_n\right\rangle + \left\langle\Phi_n\middle|\frac{\partial\tilde{\Psi}_n^{BO}}{\partial R_i}\right\rangle\right). \tag{A6}$$

The constraint forces are inserted in the equation of motion for the wave functions

$$m_\Psi|\ddot{\tilde{\Psi}}_n\rangle = -\tilde{H}|\tilde{\Psi}_n\rangle + \sum_m \tilde{O}|\tilde{\Psi}_m\rangle\Lambda_{m,n} - m_\Psi|\dot{\tilde{\Psi}}_n\rangle\dot{x}_\Psi - |\Phi_n\rangle. \tag{A7}$$

With the help of the constraint condition $|\tilde{\Psi}(t)\rangle = |\tilde{\Psi}_n^{BO}(R(t))\rangle$ and the fact that $\tilde{H}|\tilde{\Psi}_n^{BO}\rangle = \Sigma_m\tilde{O}|\tilde{\Psi}_m^{BO}\rangle\Lambda_{m,n}$ the auxiliary fields $|\Phi_n\rangle$ are related to the Born-Oppenheimer wave functions via Eq. (A7) as

$$\begin{aligned}|\Phi_n\rangle &= -m_\Psi|\ddot{\Psi}_n^{BO}\rangle - m_\Psi|\dot{\Psi}_n^{BO}\rangle\dot{x}_\Psi \\ &= -\sum_{i,j} m_\Psi\left|\frac{\partial^2\Psi_n^{BO}}{\partial R_i\partial R_j}\right\rangle\dot{R}_i\dot{R}_j - \sum_i m_\Psi\left|\frac{\partial\Psi_n^{BO}}{\partial R_i}\right\rangle\ddot{R}_i \\ &\quad -\sum_i m_\Psi\left|\frac{\partial\Psi_n^{BO}}{\partial R_i}\right\rangle\dot{R}_i\dot{x}_\Psi.\end{aligned} \tag{A8}$$

The auxiliary fields are inserted into the expression for the constraint forces acting on the atoms, Eq. (A6), and after a few transformations the additional forces of the wave-function cloud acting on the atoms are obtained,

$$\begin{aligned}F^c_{R_i} &= -\sum_n\left[\left\langle\frac{\partial\tilde{\Psi}_n^{BO}}{\partial R_i}\right| m_\Psi(|\ddot{\tilde{\Psi}}_n^{BO}\rangle + |\dot{\tilde{\Psi}}_n^{BO}\rangle\dot{x}_\Psi)\right. \\ &\quad \left. + (\langle\ddot{\tilde{\Psi}}_n^{BO}| + \dot{x}_\Psi\langle\dot{\tilde{\Psi}}_n^{BO}|)m_\Psi\left|\frac{\partial\tilde{\Psi}_n^{BO}}{\partial R_i}\right\rangle\right] \\ &= -\sum_j K_{i,j}\ddot{R}_j - \sum_{j,k}\left(\frac{\partial K_{i,j}}{\partial R_k} - \frac{1}{2}\frac{\partial K_{j,k}}{\partial R_i}\right)\dot{R}_j\dot{R}_k \\ &\quad -\sum_j K_{i,j}\dot{R}_j\dot{x}_\Psi.\end{aligned} \tag{A9}$$

The effective equation of motion given in Eq. (4) for the nuclei is obtained by adding the corresponding constraint forces to the equations of motion for the nuclei.

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