

How well do Car–Parrinello simulations reproduce the Born–Oppenheimer surface? Theory and examples

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We derive an analytic expression for the average difference between the forces on the ions in a Car–Parrinello simulation and the forces obtained at the same ionic positions when the electrons are at their ground state. We show that for common values of the fictitious electron mass, a systematic bias may affect the Car–Parrinello forces in systems where the electron–ion coupling is large. We show that in the limit where the electronic orbitals are rigidly dragged by the ions the difference between the two dynamics amounts to a rescaling of the ionic masses, thereby leaving the thermodynamics intact. We study the examples of crystalline magnesium oxide and crystalline and molten silicon. We find that for crystalline silicon the errors are very small. For crystalline MgO the errors are very large but the dynamics can be quite well corrected within the rigid-ion model. We conclude that it is important to control the effect of the electron mass parameter on the quantities extracted from Car–Parrinello simulations. © 2002 American Institute of Physics.

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I. INTRODUCTION

Since its introduction in 1985 the Car–Parrinello (CP) method¹ has increasingly been used to study an ever wider range of problems in the dynamics and thermodynamics of solids and liquids under various conditions and in studying the dynamics of chemical reactions. CP is an efficient method to solve the Kohn–Sham equations of density functional theory² “on the fly,” as the electronic ground state evolves due to changing ionic positions. It is based on the introduction of an additional inertia associated with the electronic orbitals, which are evolved as classical degrees of freedom along the ionic molecular dynamics (MD) trajectory. Its popularity stems from its efficiency relative to full Born–Oppenheimer (BO) dynamical methods, where the electronic orbitals are forced to be in the ground state for each ionic configuration, and from the observation that apart from small fluctuations which average out on a femtosecond time scale the physical quantities which are extracted from it are indistinguishable from BO dynamics.³

It is known that the introduction into the electronic system of a fictitious inertia introduces differences into the dynamics relative to the BO dynamics. However these differences have never been fully quantified or analyzed in the context of the appropriate theoretical framework. In this paper we carefully examine the relationship between CP and BO dynamics and show how the difference between them scales with the value of the fictitious mass parameter, μ . We derive analytic expressions for such differences in the limit

of the fictitious kinetic energy associated with electronic orbitals being a minimum. As has been proposed previously,⁴ we show how these errors may be corrected in the ideal case where the electron–ion coupling can be modeled as a rigid dragging of localized atomic orbitals and show its application to specific examples. We suggest that quantities extracted from CP simulations should always be checked against their possible dependence on the value of μ .

The central issue is the following: the classical motion of the electronic orbitals in CP can be thought of as being made up of two components.⁵ One component consists of fast oscillations with period equal to or faster than $\tau_e \sim 2\pi\sqrt{\mu/E_g}$, E_g being the lowest electronic excitation energy and μ the fictitious electronic mass.³ The second component is the unavoidable but “adiabatic” response of the electronic orbitals to the ionic dynamics, whose shortest characteristic time we denote by τ_i ($\tau_e \ll \tau_i$). It is generally thought that keeping the time scales (or frequency spectra) of the two components well separated (i.e., by reducing μ) ensures a correct adiabatic decoupling and guarantees that the CP dynamics is a faithful representation of the BO dynamics. We show here that the adiabatic decoupling is a necessary but not sufficient condition for the accuracy of CP dynamics. In particular, the fictitious inertia also causes the slow component of the electronic dynamics to exchange momentum and energy with the ions, yielding a departure of the CP forces on the ions from the BO ones for large values of μ .

We begin by outlining the relevant theory and deriving an expression for the difference between CP forces and BO forces in the limit of minimum fictitious electronic kinetic energy. We then consider the simplified model of rigid ions and derive the error in the forces for this system. We show how the thermodynamics and the dynamics can be corrected for systems in which the rigid-ion model provides a good

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description of the electronic structure. We illustrate these theoretical considerations by studying the examples of magnesium oxide and silicon.

II. THEORY

The Car–Parrinello method makes use of the following classical Lagrangian:

$$L_{\text{CP}} = \sum_i \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i\}, \{\mathbf{R}_I\}] \quad (1)$$

to generate trajectories for the ionic and electronic degrees of freedom via the coupled set of equations of motion

$$M_I \ddot{\mathbf{R}}_I^\alpha = - \frac{\partial E[\{\psi_i\}, \{\mathbf{R}_I\}]}{\partial R_I^\alpha} = F_{\text{CP}_I}^\alpha, \quad (2)$$

$$\mu_i |\ddot{\psi}_i\rangle = - \frac{\delta E[\{\psi_i\}, \{\mathbf{R}_I\}]}{\delta \langle \psi_i |}, \quad (3)$$

where M_I and \mathbf{R}_I are the mass and position, respectively, of atom I , $|\psi_i\rangle$ are the Kohn–Sham orbitals which are allowed to evolve as classical degrees of freedom with inertial parameters μ_i , and $E[\{\psi_i\}, \{\mathbf{R}_I\}]$ is the Kohn–Sham energy functional evaluated for the set of ionic positions $\{\mathbf{R}_I\}$ and the set of orbitals $\{\psi_i\}$. The functional derivative of the Kohn–Sham energy in Eq. (3) is implicitly restricted to variations of $\{\psi_i\}$ that preserve orthonormality.

We wish to compare the dynamics of ions evolved with this method with the true BO dynamics. For this purpose, we decompose the CP orbitals as

$$|\psi_i\rangle = |\psi_i^{(0)}\rangle + |\delta\psi_i\rangle, \quad (4)$$

where $|\psi_i^{(0)}\rangle$ are the ground state (BO) orbitals which are uniquely defined for given ionic coordinates as those that minimize $E[\{\psi_i\}, \{\mathbf{R}_I\}]$. This allows us to consider separately the evolution of the instantaneous electronic ground state and the deviations of the CP orbitals from that ground state.

A preliminary interesting observation follows from such a decomposition: strictly speaking, the CP equations do not reduce to the BO equations in the limit of vanishing $\delta\psi_i$, for any finite value of μ . In fact, because of the dependence of the ionic coordinates on time, the BO orbitals have a nonvanishing “acceleration” given by

$$|\ddot{\psi}_i^{(0)}\rangle = \sum_I \ddot{R}_I^\alpha \frac{\partial |\psi_i^{(0)}\rangle}{\partial R_I^\alpha} + \sum_{I,J} \dot{R}_I^\alpha \dot{R}_J^\beta \frac{\partial^2 |\psi_i^{(0)}\rangle}{\partial R_J^\beta \partial R_I^\alpha}, \quad (5)$$

where we have used the fact that

$$|\dot{\psi}_i^{(0)}\rangle = \sum_I \dot{R}_I^\alpha \frac{\partial |\psi_i^{(0)}\rangle}{\partial R_I^\alpha}. \quad (6)$$

It now becomes clear that Eq. (3) is not compatible with a vanishing departure of the CP orbitals from the BO orbitals, since the right-hand side of Eq. (3) would vanish if $\{\psi_i\} = \{\psi_i^{(0)}\}$, while the left-hand side would not, by virtue of Eq. (5). So the CP orbitals cannot take their ground state values unless μ vanishes too. As a consequence of this, the ionic

dynamics is affected by a bias proportional to μ and, as we will see, to the strength of the electron–ion interaction.

We now wish to explore the consequences that such a departure from the ground state has on the instantaneous CP forces F_{CP} . We thus calculate how CP forces deviate from the BO forces F_{BO} at a given point in phase space along the CP trajectory. We may write, for the α th Cartesian component of the force on atom I :

$$\begin{aligned} -F_{\text{CP}_I}^\alpha &= \frac{\partial E[\{\mathbf{R}_I\}; \{\psi_i\}]}{\partial R_I^\alpha} \\ &= \frac{dE[\{\mathbf{R}_I\}; \{\psi_i\}]}{dR_I^\alpha} - \sum_i \left(\frac{\delta E[\{\mathbf{R}_I\}; \{\psi_i\}]}{\delta |\psi_i\rangle} \right. \\ &\quad \left. \times \frac{\partial |\psi_i^{(0)}\rangle}{\partial R_I^\alpha} + \frac{\partial \langle \psi_i^{(0)} |}{\partial R_I^\alpha} \frac{\delta E[\{\mathbf{R}_I\}; \{\psi_i\}]}{\delta \langle \psi_i |} \right). \end{aligned} \quad (7)$$

Substitution of Eq. (3) yields

$$\begin{aligned} -F_{\text{CP}_I}^\alpha &= \frac{dE[\{\mathbf{R}_I\}; \{\psi_i\}]}{dR_I^\alpha} \\ &\quad - \sum_i \mu_i \left(\langle \dot{\psi}_i | \frac{\partial |\psi_i^{(0)}\rangle}{\partial R_I^\alpha} + \frac{\partial \langle \psi_i^{(0)} |}{\partial R_I^\alpha} | \dot{\psi}_i \rangle \right). \end{aligned} \quad (8)$$

Using the expansion

$$\begin{aligned} \frac{dE[\{\mathbf{R}_I\}; \{\psi_i\}]}{dR_I^\alpha} &= \frac{d}{dR_I^\alpha} \left\{ E[\{\mathbf{R}_I\}; \{\psi_i\}]_{|\psi_i^{(0)}\rangle} \right. \\ &\quad + \sum_i \left(\left. \frac{\delta E[\{\mathbf{R}_I\}; \{\psi_i\}]}{\delta |\psi_i\rangle} \right)_{|\psi_i^{(0)}\rangle} |\delta\psi_i\rangle \right. \\ &\quad \left. + \langle \delta\psi_i | \frac{\delta E[\{\mathbf{R}_I\}; \{\psi_i\}]}{\delta \langle \psi_i |} \right)_{|\psi_i^{(0)}\rangle} \right\} \\ &= -F_{\text{BO}_I}^\alpha + 0 + \text{order}(\delta\psi_i^2) \end{aligned} \quad (9)$$

we can write the error in the CP force as

$$\begin{aligned} \Delta F_I^\alpha &= F_{\text{CP}_I}^\alpha - F_{\text{BO}_I}^\alpha = \sum_i \mu_i \left(\langle \dot{\psi}_i | \frac{\partial |\psi_i^{(0)}\rangle}{\partial R_I^\alpha} + \frac{\partial \langle \psi_i^{(0)} |}{\partial R_I^\alpha} | \dot{\psi}_i \rangle \right) \\ &\quad + \text{order}(\delta\psi_i^2). \end{aligned} \quad (10)$$

Having established the connection, to first order in $\delta\psi_i$, between the CP and the BO forces, we assume adiabatic decoupling and look for contributions to this difference that do not vanish when averaged over time scales longer than the fictitious dynamics of the electrons (τ_e) but shorter than the time scales of the ionic dynamics (τ_i). Only these contributions are expected to contribute significantly to the ionic dynamics.³ To this end we rewrite Eq. (3), using Eq. (4), as

$$\begin{aligned}
|\dot{\psi}_i\rangle &= |\delta\dot{\psi}_i\rangle + \sum_I \dot{R}_I^\alpha \frac{\partial|\psi_i^{(0)}\rangle}{\partial R_I^\alpha} + \sum_{I,J} \dot{R}_I^\alpha \dot{R}_J^\beta \frac{\partial^2|\psi_i^{(0)}\rangle}{\partial R_J^\beta \partial R_I^\alpha} \\
&= -\frac{1}{\mu_i} \frac{\delta E[\{\psi_i\}, \{\mathbf{R}_I\}]}{\delta\langle\psi_i|} \\
&= -\frac{1}{\mu_i} \left(\frac{\delta^2 E[\{\mathbf{R}_I\}, \{\psi_i\}]}{\delta|\psi_i\rangle \delta\langle\psi_i|} \Big|_{\{\psi_i^{(0)}\}} |\delta\psi_i\rangle \right. \\
&\quad \left. + \text{order}(\delta\psi_i^2) \right) \quad (11)
\end{aligned}$$

and we show that when Eq. (11) is averaged over a time scale shorter than τ_i but longer than τ_e , then $\delta\psi_i$ vanishes. In order to prove it, we re-express Eq. (11) as

$$\langle\varphi_j|\delta\dot{\psi}_i\rangle + \langle\varphi_j|\chi^{(i)}\rangle \approx -\frac{k_j^{(i)}}{\mu_i} \langle\varphi_j|\delta\psi_i\rangle, \quad (12)$$

where

$$\begin{aligned}
|\chi^{(i)}(\{\mathbf{R}_I(t), \dot{\mathbf{R}}_I(t), \ddot{\mathbf{R}}_I(t)\})\rangle \\
= \sum_I \ddot{R}_I^\alpha \frac{\partial|\psi_i^{(0)}\rangle}{\partial R_I^\alpha} + \sum_{I,J} \dot{R}_I^\alpha \dot{R}_J^\beta \frac{\partial^2|\psi_i^{(0)}\rangle}{\partial R_J^\beta \partial R_I^\alpha}, \quad (13)
\end{aligned}$$

$$\hat{K}^{(i)}(\{\mathbf{R}_I(t)\}) = \frac{\delta^2 E[\{\mathbf{R}_I\}, \{\psi_i\}]}{\delta|\psi_i\rangle \delta\langle\psi_i|} \Big|_{\{\psi_i^{(0)}\}} \quad (14)$$

and $|\varphi_j^{(i)}\rangle$ is an eigenvector of $\hat{K}^{(i)}$ with eigenvalue $k_j^{(i)} \cdot |\chi^{(i)}\rangle$ and $\hat{K}^{(i)}$, by definition, vary on the time scale of ionic motion. We consider time scales much smaller than $\tau_i = 2\pi/\omega_i$ such that $|\chi^{(i)}\rangle, \hat{K}^{(i)}$ and $|\varphi_j\rangle$ are approximately constant. In this case a solution of Eq. (12) is of the form

$$\langle\varphi_j|\delta\psi_i\rangle = B e^{i\omega_j^{(i)}t} - \frac{\langle\varphi_j|\chi^{(i)}\rangle}{(\omega_j^{(i)})^2}, \quad (15)$$

where $\omega_j^{(i)} = \sqrt{k_j^{(i)}/\mu_i}$ and B is a complex constant. If we assume that $\omega_j^{(i)}$ is very large relative to ω_i then the average value of $\langle\varphi_j|\delta\psi_i(t)\rangle$ over time scales much greater than $2\pi/\omega_j^{(i)}$ is

$$\begin{aligned}
\overline{\langle\varphi_j(\tau)|\delta\psi_i\rangle} &= \frac{1}{\Delta\tau} \int_{\tau-\Delta\tau/2}^{\tau+\Delta\tau/2} \langle\varphi_j(\tau)|\delta\psi_i(t)\rangle dt \\
&\approx -\frac{\langle\varphi_j(\tau)|\chi^{(i)}(\tau)\rangle}{(\omega_j^{(i)})^2} \quad \text{for } \frac{2\pi}{\omega_j^{(i)}} \ll \Delta\tau \ll \frac{2\pi}{\omega_i} \quad (16)
\end{aligned}$$

$$\Rightarrow \overline{\langle\varphi_j(\tau)|\delta\dot{\psi}_i\rangle} \approx 0. \quad (17)$$

Since

$$|\delta\dot{\psi}_i\rangle = \sum_j \langle\varphi_j|\delta\dot{\psi}_i\rangle |\varphi_j\rangle \quad (18)$$

this means that for time scales which are intermediate between typical time scales of ionic and CP orbital motion $|\dot{\psi}_i\rangle \approx |0\rangle$.

To summarize: If we consider the dynamics of the electronic orbitals to consist of an adiabatic response of the electronic orbitals to the ionic dynamics and an independent fast

oscillating part then, under the assumption that the time scales of the fast component are much shorter than the shortest time period in the ionic system, i.e., assuming adiabatic decoupling, the average error in the Car–Parrinello forces is given by [using Eqs. (10), (11), and (17)]

$$\begin{aligned}
\Delta F_I^\alpha &= 2 \sum_I \mu_i \Re \left\{ \sum_J \ddot{R}_J^\beta \frac{\partial\langle\psi_i^{(0)}|}{\partial R_I^\alpha} \frac{\partial|\psi_i^{(0)}\rangle}{\partial R_J^\beta} \right. \\
&\quad \left. + \sum_{J,K} \dot{R}_J^\beta \dot{R}_K^\gamma \frac{\partial\langle\psi_i^{(0)}|}{\partial R_I^\alpha} \frac{\partial^2|\psi_i^{(0)}\rangle}{\partial R_K^\gamma \partial R_J^\beta} \right\} + \text{order}(\delta\psi_i^2). \quad (19)
\end{aligned}$$

This correction varies on ionic time scales and therefore does not necessarily average out as the usual “fast” component does. However, its value depends linearly on the electronic mass. This implies that a simple way to ensure that its contribution in a CP simulation is negligible consists of reducing systematically the electronic mass. Although a smaller μ implies a smaller time step for the integration of the CP equations of motion, the time step scales as $\Delta t \sim \mu^{1/2}$, which means that reducing μ by an order of magnitude brings about a computational overhead of only a factor of 3. A more quantitative discussion is presented in Secs. IV and V.

We also notice that if the term proportional to $\dot{R}\dot{R}$ on the right-hand side of Eq. (19) vanishes (e.g., by symmetry, see the following), and the tensor in the term proportional to \ddot{R} is constant, then the correction (19) reduces to a rescaling of the atomic masses, which is known to leave thermodynamics intact. This is discussed in more detail in Sec. III.

III. THE RIGID ION APPROXIMATION

In order to gain insight into the scale of this problem with the CP forces we consider the simple example of rigid ions. We assume that each electron is localized around an ion and that there is no distortion of a particular ion’s charge distribution as it moves in the field of the other ions. We can refer each wave function ψ_i to a particular ion as follows:

$$\psi_i(\mathbf{r}) = \phi_{I\eta}(\mathbf{r} - \mathbf{R}_I), \quad (20)$$

where the electronic states are labeled by an ion index, I , and the index η labeling the electronic state of the ion. The rigidity of the ionic charge distribution means that

$$\begin{aligned}
\frac{\partial\phi_{I\eta}(\mathbf{r} - \mathbf{R}_I)}{\partial \mathbf{R}_I} &= -\frac{\partial\phi_{I\eta}(\mathbf{r} - \mathbf{R}_I)}{\partial \mathbf{r}}, \\
\frac{\partial\phi_{I\eta}(\mathbf{r} - \mathbf{R}_I)}{\partial \mathbf{R}_J} &= 0, \quad \forall J \neq I. \quad (21)
\end{aligned}$$

Equation (19) becomes

$$\begin{aligned}
\Delta F_I^\alpha &= 2 \sum_\eta \mu_\eta \Re \left\{ \ddot{R}_I^\beta \int \frac{\partial\phi_{I\eta}^*(\mathbf{r} - \mathbf{R}_I)}{\partial r^\alpha} \frac{\partial\phi_{I\eta}(\mathbf{r} - \mathbf{R}_I)}{\partial r^\beta} d\mathbf{r} \right. \\
&\quad \left. + \dot{R}_I^\beta \dot{R}_I^\gamma \int \frac{\partial\phi_{I\eta}^*(\mathbf{r} - \mathbf{R}_I)}{\partial r^\alpha} \frac{\partial^2\phi_{I\eta}(\mathbf{r} - \mathbf{R}_I)}{\partial r^\gamma \partial r^\beta} d\mathbf{r} \right\}. \quad (22)
\end{aligned}$$

The second term in Eq. (22) vanishes due to symmetry, at least assuming an atomic charge density with spherical symmetry. The first term may be written in terms of $E_k^{I\eta}$ the quantum electronic kinetic energy of an electron in state η of atom I as

$$2 \sum_{\eta} \mu_{\eta} \Re \left\{ \ddot{R}_I^{\beta} \int \frac{\partial \phi_{I\eta}^*(\mathbf{r}-\mathbf{R}_I)}{\partial r^{\alpha}} \frac{\partial \phi_{I\eta}(\mathbf{r}-\mathbf{R}_I)}{\partial r^{\beta}} d\mathbf{r} \right\} = -\frac{2m_e}{3\hbar^2} \ddot{R}_I^{\alpha} \sum_{\eta} \mu_{\eta} E_k^{I\eta}, \quad (23)$$

where m_e is the (real) mass of an electron. Since the ions are rigid the quantum kinetic energy associated with each one is a constant and Eq. (22) becomes

$$\Delta F_I^{\alpha} = -\Delta M_I \ddot{R}_I^{\alpha} \quad (24)$$

with

$$\Delta M_I = \frac{2m_e}{3\hbar^2} \sum_{\eta} \mu_{\eta} E_k^{I\eta}. \quad (25)$$

In this case the ionic positions and velocities are updated during a Car–Parrinello simulation according to

$$(M_I + \Delta M_I) \ddot{R}_I^{\alpha} = F_{\text{BO}}^{\alpha}. \quad (26)$$

In other words, for systems where the rigid ion approximation is valid, the CP approximation amounts simply to a rescaling of the ionic masses. Since the classical partition function depends only on the interaction potential, the thermodynamics of the system as calculated with a CP dynamics is identical to the thermodynamics of the BO system. The definition of temperature will however be affected, because if the actual ionic dynamics in CP is given by Eq. (26), then the real temperature at which the system equilibrates, at least in the case of a microcanonical dynamics for the ions, is given by

$$k_B T = \frac{1}{3N} \sum_{I,\alpha} (M_I + \Delta M_I) \langle (v_I^{\alpha})^2 \rangle, \quad (27)$$

where $\langle \rangle$ signifies the average over time and N is the number of atoms. This differs from the standard definition by the addition of a term proportional to ΔM_I . The additional term in Eq. (27) can be readily traced to the additional inertia caused by the rigid dragging of the electronic orbitals. In fact, using Eqs. (6) and (21), we can show that this term coincides, within the rigid ion model, with the fictitious electronic kinetic energy, when the contribution from the dynamics of the $\delta\psi_i$ is negligible, i.e.,

$$T_{\text{el}} = \sum_i \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle = \frac{1}{2} \sum_{I,\alpha} \Delta M_I \langle (v_I^{\alpha})^2 \rangle. \quad (28)$$

In other words if the electronic orbitals move rigidly with the ions the actual inertia of the ions in a CP simulation can be obtained by adding to the “bare” ionic inertia the inertia carried by the electronic orbitals. This result has been pointed out previously⁴ and ionic masses are commonly renormalized when dynamical quantities are being investigated.

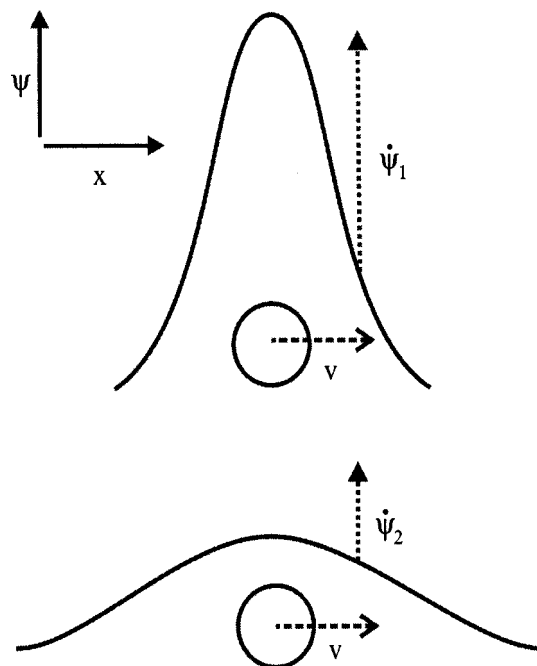


FIG. 1. The mechanism by which the effective ionic inertia is related to the quantum kinetic energy of the localized electronic wave functions within the rigid-ion approximation: For two ions of the same species which are moving with the same velocity \mathbf{v} , the one carrying the more localized electronic wave function (top) has a higher effective mass. The more localized electronic wave function $\psi_1(x)$ has, on average, a greater slope $d\psi(x)/dx$ (and hence kinetic energy) than the more extended wave function (bottom) $\psi_2(x)$. Since for a given ionic velocity \mathbf{v} a greater slope implies a greater rate of change with respect to time ($\dot{\psi}_1 > \dot{\psi}_2$), the localized wave function changes more per unit time than the extended wave function. In order to increase the ion's velocity one also needs to increase the rate of change of the massive wave function localized on it. The total inertia associated with this required change of the rate of change of the wave function is related to the quantum kinetic energy via Eq. (25) and this quantity must be added to the bare ionic mass in order to obtain its effective mass.

Figure 1 illustrates how, within the simplified rigid-ion model, the ionic inertia depends on the kinetic energy of the electrons. For a given ionic velocity, the wave function at a point in space has to change more quickly when it is highly localized (and therefore with a high quantum kinetic energy) than when it is extended. To accelerate an ion one also needs to increase the rate of change of the wave function localized on it. Since the wave function carries an inertia (μ) the effective inertia of the ion is greater than the bare ionic mass. In more general (nonrigid-ion) situations, the collective movement of the ions is affected by the requirement that the “heavy” electronic wave functions are rearranged as the system evolves.

We now explore the consequences that such a modification of the ionic inertia has on typical observables extracted from CP simulations. First, as already mentioned, the correct definition of temperature in a microcanonical CP simulation is given by Eq. (27). Similarly, in a simulation where temperature is controlled, e.g., through a Nosé thermostat,⁶ the quantity to be monitored corresponds to the instantaneous value of Eq. (27). Dynamical observables will also be affected by the additional inertia, as already noted in the case of phonons extracted from CP-MD in carbon systems.^{7,8} In the case of homogeneous systems (a single atomic species in

TABLE I. Technical details of the simulations.

Simulation No.	System	Temperature (K)	μ_0 (a.u.)	E_p (Ry)	E_{cut} (Ry)	Δt (a.u.)	$\sum_i \mu_i \langle \psi_i \psi_i \rangle$ (a.u. $\times 10^4$)	L (a.u.)
1	Si	330	270	1.0	12.0	5.0	4.36	20.42
2	Si	330	270	1.0	12.0	5.0	4.36	20.42
3	Si(liquid)	2000	270	1.0	12.0	10.0	4.35	19.8
4	MgO	2800	400	2.7	90.0	8.0	66.3	14.5
5	Si	330	200	1.0	12.0	5.0	3.23	20.42
6	Si	330	800	1.0	12.0	10.0	12.92	20.42
7	MgO (M_O rescaled)	2800	100	2.7	90.0	4.0	16.55	14.5
8	MgO (M_O rescaled)	2800	400	2.7	90.0	8.0	66.4	14.5
9	MgO	2800	200	2.7	90.0	5.65	33.1	14.5
10	MgO	2800	100	2.7	90.0	4.0	16.55	14.5

which all the atoms are in similar local chemical environments) all dynamical quantities can be simply rescaled using the mass correction of Eq. (26). However, for heterogeneous systems the correction is not always trivial, as different mass corrections apply to different atomic species due to different atomic kinetic energies. In practice, we found that a convenient and more general way to express the mass correction of ion I is given by

$$\Delta M_I = f_I \frac{2m_e E_k^{\text{total}}}{3N\hbar^2}, \quad (29)$$

where f_I is a dimensionless constant which takes into account the relative contribution of species I to the total quantum kinetic energy E_k^{total} .

IV. SIMULATIONS

In order to gain more insight into the theory put forward in the previous sections, we have performed CP simulations on pressurized magnesium oxide and on silicon. Among the insulators (we restrict our analysis to insulators as adiabatic decoupling is less obvious in metallic systems and this would complicate considerably our analysis), MgO and silicon are extremal cases: MgO is a highly ionic system with large quantum kinetic energy associated with the strongly localized charge distribution; Silicon on the other hand is a covalent system where electron states are much more delocalized. Within our pseudopotential description of MgO,⁹ the $1s$, $2s$, and $2p$ states are frozen into the core of Mg whereas only the $1s$ states are frozen into the core of O. Since there is very nearly complete transfer of the two $3s$ electrons from Mg to O (inspection of charge density contour plots reveal no evidence of any valence charge anywhere except surrounding O sites) the electron quantum kinetic energy may to a first approximation be attributed to electronic states localized on oxygen ions. This makes MgO an ideal system to study within the rigid ion model since only the oxygen mass will be rescaled. As mentioned in Sec. III, additional problems arise if one deals with more than one electron-carrying species as the quantum kinetic energy must be divided between these species. The large quantum kinetic energy of MgO means that the error in the CP forces should be large relative to many materials. The simulations of MgO were performed at a high pressure (~ 900 kbar) as this enhanced its ionicity.

Silicon on the other hand is a covalent/metallic system with relatively low quantum kinetic energy. As such it should be one of the systems most favorable to the Car–Parrinello approximation but least favorable to description in terms of rigid ions.

A. Technical details

We have performed ten different simulations. The technical details are summarized in Table I.

All simulations were performed with a cubic simulation cell of side L (see Table I) under periodic boundary conditions and with 64 atoms in the unit cell. We used a plane wave basis set with an energy cut off for the wave functions of E_{cut} . The Brillouin zone was sampled using only the Γ point. In each simulation we have used the mass preconditioning scheme of Tassone *et al.*,¹⁰ and the parameters μ_0 and E_p in Table I are defined as in Ref. 10. With the use of a preconditioning scheme, whereby the electronic mass is scaled with the kinetic energy of the plane wave, the time step can be increased by a factor of 2–3 with respect to the non-preconditioned case.¹⁰ The use of a preconditioning scheme worsens considerably the agreement of the CP forces with the BO ones. In particular, we have checked that using the parameters μ_0 and E_p that optimize the time step causes an increase by about a factor of 3 in the correction term (19). However, in order to bring this error to its non-preconditioned value, a value of μ_0 three times smaller would be required, with a consequent reduction of the time step of only $\sqrt{3}$. Considering that the preconditioning scheme allows a 2–3 increase of the time step, a reduction of $\sqrt{3}$ still makes the preconditioning scheme marginally superior.

Liquid silicon is metallic and so, as suggested by Blöchl and Parrinello,¹¹ two Nosé thermostats were used to counteract the effects of energy transfer between the ions and the $|\delta\psi_i\rangle$ due to overlap of their frequency spectra. The values of the parameters used were $Q_e = 21.3$ a.u./atom, $E_{\text{kin},0} = 1.65 \times 10^{-4}$ a.u./atom and $Q_R = 244400$ a.u. These were chosen for compatibility with those of Ref. 16 by taking into account the slight increase in temperature and scaling accordingly.

In all simulations, with the exception of simulation 2, the system was first allowed to evolve for at least 1 ps and this trajectory was discarded. For simulation 2, this initial equilibration time was 0.5 ps. All results reported are taken from

the continuations of these equilibration trajectories.

In all simulations, the total quantum kinetic energy of the system, and hence the average mass correction (29), varied during the simulation by less than 0.3%. It was therefore taken as a constant in further analysis.

The total energy of all the degrees of freedom (including the thermostats in simulation 3) was conserved in all simulations *at least* to within one part in 10^5 .

B. Results

In order to check the predictions of the theory developed in Secs. II and III, we have taken segments of CP trajectories and calculated the true BO forces along these segments by putting the electronic orbitals to their ground state with a steepest descent method. We look at the instantaneous error in the α th Cartesian component of the CP force on atom I relative to the r.m.s. BO force component, i.e.,

$$\delta F_I^\alpha(t) = \frac{\Delta F_I^\alpha(t)}{\sqrt{\frac{\sum_c \sum_{J,\beta} (F_{BOJ}^\beta)^2}{3NN_c}}} \quad (30)$$

and the instantaneous relative error minus the relative error predicted by the rigid-ion model:

$$[\delta F_I^\alpha(t)]_{\text{corr}} = \frac{\Delta F_I^\alpha(t) + \Delta M_I \ddot{R}_I^\alpha}{\sqrt{\frac{\sum_c \sum_{J,\beta} (F_{BOJ}^\beta)^2}{3NN_c}}}, \quad (31)$$

where N_c is the number of ionic configurations at which the error in the CP forces was calculated and \sum_c is the sum over all such configurations. The value of ΔM_I in Eq. (31) is determined using the rigid-ion-model expression (29), and E_k^{total} was given its average value during the simulation. The scaling parameters which were found to give best results for silicon and oxygen were $f_{\text{Si}} = 1.0$ and $f_{\text{O}} = 1.92$, respectively.

We also look at $\langle \delta F_I^\alpha \rangle$ and $\langle \delta F_I^\alpha \rangle_{\text{corr}}$ the rms values of $[\delta F_I^\alpha]$ and $[\delta F_I^\alpha]_{\text{corr}}$ over all the ions, Cartesian components, and configurations tested.

Since the CP forces are affected by a “fast” component whose effect on the ionic dynamics is believed to average out on the time scale of the ionic motion, we introduce the quantity $\Gamma(\tau)$, defined as

$$\Gamma(\tau) = \int_0^\tau \frac{1}{3N} \sum_{I,\alpha} \left| \frac{\int_{t_0}^{t_0+\tau} \Delta F_I^\alpha(t) dt}{\int_{t_0}^{t_0+\tau} |\Delta F_I^\alpha(t)| dt} \right| d\tau, \quad (32)$$

If we begin our comparison between CP and BO forces at some instant t_0 along the trajectory then inspection of $\Gamma(\tau)$ gives a feeling for how large the fast component is. If the errors in all the forces of the system oscillate rapidly with an average of zero then $\Gamma(\tau)$ decreases very quickly from the value of one at $\tau=0$ to zero at $\tau \sim \tau_e$. For systematic errors $\Gamma(\tau)$ should decrease gradually from one to zero on a time scale of the order of the period of τ_i . In realistic cases $\Gamma(\tau)$ drops from one and levels off to a smaller value for $\tau \sim \tau_e$, and then decreases gradually to zero for τ exceeding τ_i . The

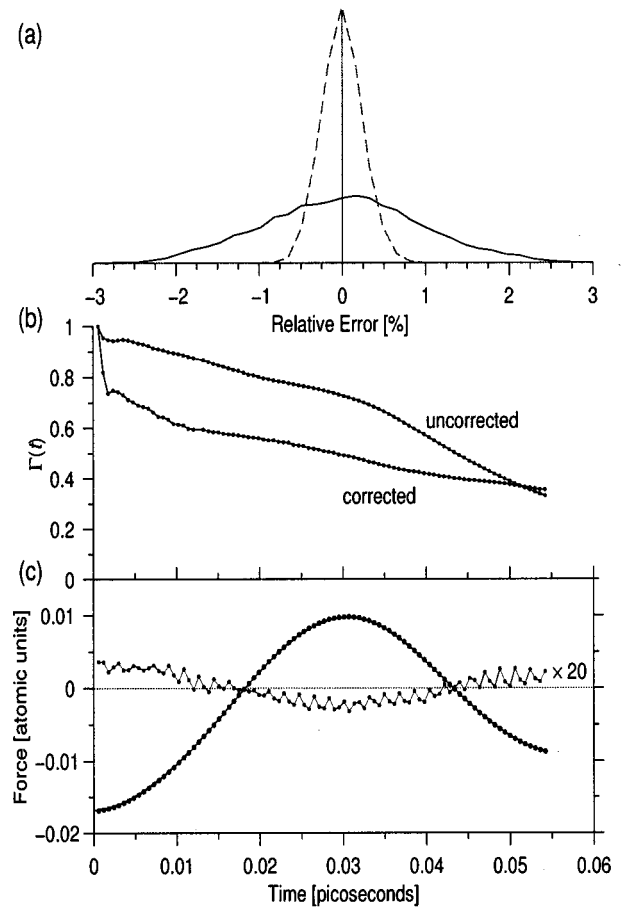


FIG. 2. Simulation 1. (a) Distribution among all atoms I and all Cartesian components α of the percentage errors in the CP forces relative to the BO forces at the same ionic positions, $100 \times \delta F_I^\alpha(t)$ (full line) and these errors when the forces have been partially corrected according to a rigid-ion model, $100 \times [\delta F_I^\alpha(t)]_{\text{corr}}$ (dashed line). (b) $\Gamma(\tau)$ as defined by Eq. (32) for the full error in the forces and those as partially corrected according to the rigid-ion model (c) $F_{BO_i}^\alpha$, $F_{CP_i}^\alpha$ and $(F_{CP_i}^\alpha - F_{BO_i}^\alpha)$ (multiplied by a factor of 20 for visibility) for a typical force component. Dots indicate the points at which the BO force was calculated (every 5 time steps).

value of $\Gamma(\tau)$ on the plateau between τ_e and τ_i provides a measure of how much of the errors calculated in Eqs. (30) and (31) are attributable to a systematic (i.e., “slow”) departure from the BO surface.

We begin by looking at the forces in silicon in both the solid at 330 K and the liquid at 2000 K (simulations 1, 2, and 3). Simulation 1 was preceded by a short run where the temperature was set to about 1000 K. Electrons were then relaxed in their ground state and the ionic velocities set to zero. This allows the electrons to smoothly accelerate with the ions. A microcanonical simulation followed where the ionic temperature reached, after a short equilibration, the value of 330 K. This procedure was followed in all the simulations reported here, except where discussed.

In solid Si at 330 K (Fig. 2) we find that the standard deviation of the error in the Car–Parrinello forces is 0.94%. However, most of this error can be attributed to a rigid dragging of the Si atomic orbitals. The standard deviation of the error is in fact reduced to 0.24% after the rigid-ion correction (26) is subtracted. The $\sim 30\%$ drop of $\Gamma(t)$ (corrected)

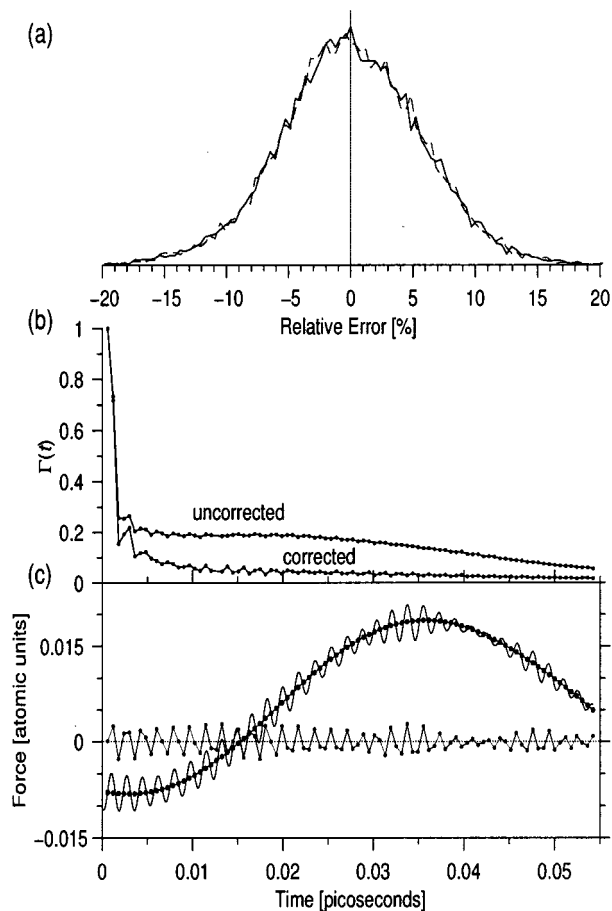


FIG. 3. Simulation 2, Crystalline Si at 330 K when the electrons receive a “kick” at the beginning of the simulation. See caption of Fig. 1 for an explanation. $(F_{CP_i}^\alpha - F_{BO_i}^\alpha)$ has not been scaled for visibility.

shown in Fig. 2(b) indicates that $\sim 30\%$ of the residual 0.24% error can be attributed to “fast” oscillations, so that the overall average error introduced by the CP approximation, once corrected for the rigid dragging and under the assumption that the fast component is not relevant, is less than 0.2%.

As has been pointed out previously by Remler and Madden,¹² it is important to begin the dynamics with electrons and ions moving in a consistent way as we have done here in all simulations except the one we now discuss (simulation 2) and in the case of liquid Si (simulation 3). We found that the error in the forces increases substantially if the simulation is not started from zero ionic velocities, a procedure that would otherwise have the advantage of shortening considerably the time needed to reach thermal equilibrium. Simulation 2 started from the end of simulation 1, but electrons have been put in the ground state before restarting (ionic velocities and positions were instead kept unchanged). Forces were tested after 0.5 ps from the electron quenching.

The standard deviation of the error in forces is now 5.7% and the error in the forces as corrected according to the rigid ion approximation at 5.68% is not significantly improved. However clearly from inspection of $\Gamma(t)$ in Fig. 3(b) and the sample force component in Fig. 3(c) most of this error can be attributed to the high frequency oscillations of the electronic orbitals. If we assume that these oscillations do not influence

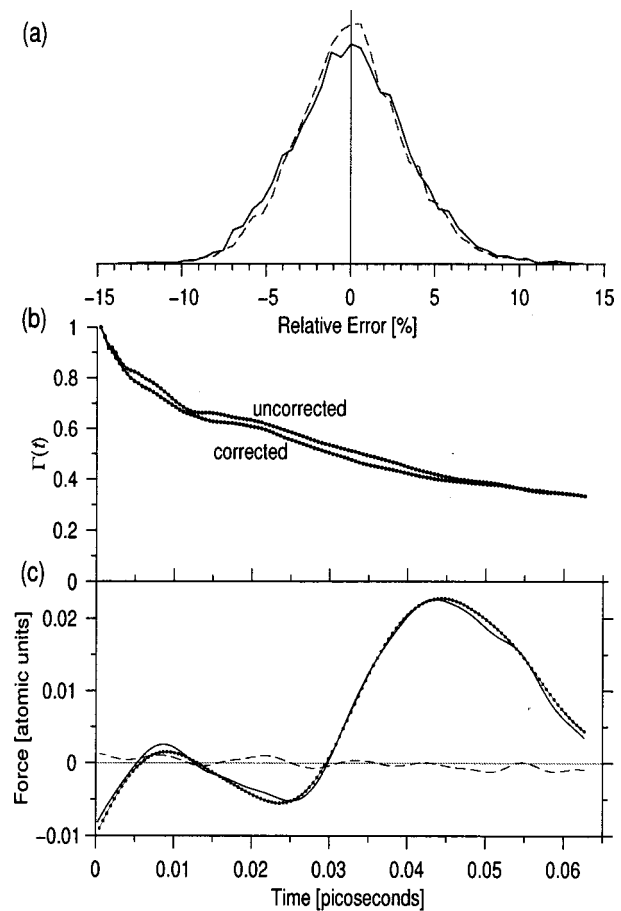


FIG. 4. Simulation 3. Liquid Si at 2000 K. See the caption of Fig. 1 for an explanation. $(F_{CP_i}^\alpha - F_{BO_i}^\alpha)$ has not been scaled for visibility.

the ionic dynamics, the error reduces to about 1.2% for the uncorrected forces and to less than 0.5% for the corrected forces. The amplitudes of these oscillations are nevertheless significant and may affect the thermodynamics in a way that is not easy to predict. These oscillations clearly originate from the initial jerk experienced by the electrons in their ground state and survive for a long time due to the adiabatic decoupling.

In the liquid the situation is considerably worse than in the crystal. The standard deviation of the error in the forces is 3.4%, which improves only to 3.1% with the rigid-ion correction. There do not seem to be high frequency, high amplitude oscillations here despite the simulation being started with finite ionic velocities. However, there are oscillations of a lower frequency (although still quite high relative to ionic time scales) which are probably due to the presence of the Nosé thermostat (Fig. 4). It may be that the Nosé thermostat has the effect of damping out the kinds of oscillations seen in Fig. 3 but the presence of these other oscillations is hardly an improvement. This highlights the need for careful choice of parameters for the Nosé thermostat, particularly the value of $E_{kin,0}$. It is not clear how one should choose this parameter in general. For example, here we have used a value of $E_{kin,0}$ compatible with Ref. 16, however we note that this is considerably smaller than the value recommended in Ref. 11, which was obtained according to a rigid-

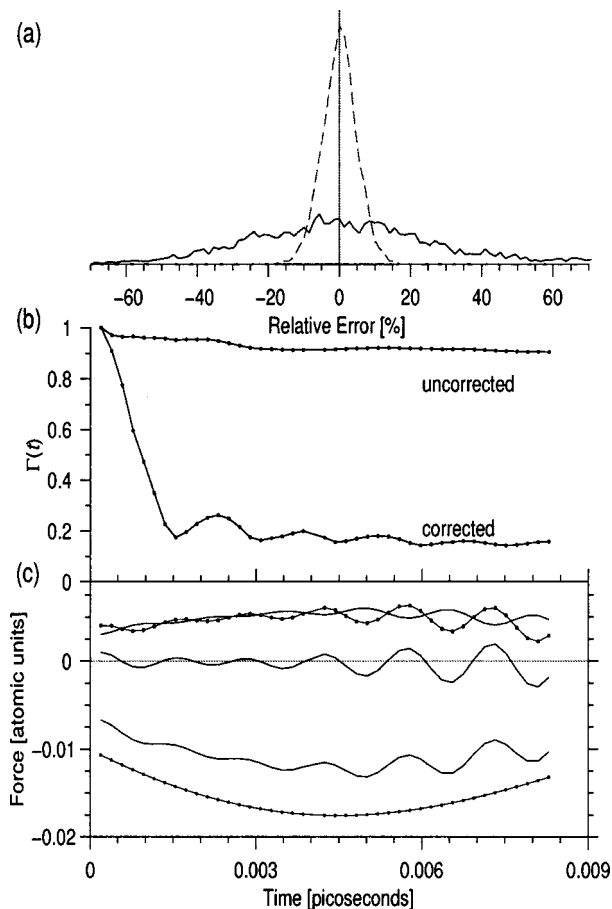


FIG. 5. Simulation 4. Forces on the oxygen ions in crystalline MgO at 2800 K. (a) and (b) are as in Fig. 1(c). From top to bottom: the error in the CP forces ($F_{\text{CP}_i}^\alpha - F_{\text{BO}_i}^\alpha$), the error in the CP forces as predicted by the rigid-ion model $-\Delta M_O \ddot{R}_i^\alpha$ (dotted line), the difference between the true error in the CP forces and the predicted error ($F_{\text{CP}_i}^\alpha - F_{\text{BO}_i}^\alpha + \Delta M_O \ddot{R}_i^\alpha$), the CP force $F_{\text{CP}_i}^\alpha$ and the BO force at the same ionic positions $F_{\text{BO}_i}^\alpha$ for a typical force component. Dots indicate the points at which the BO force was calculated (every time step).

ion model. We have also done simulations using higher values of $E_{\text{kin},0}$ and in all cases the errors in the forces have been greater. Therefore, it is likely that by decreasing $E_{\text{kin},0}$ further we might further improve the forces. However, this has not been attempted here. The issue of thermostating a system in a way which minimizes the kinds of errors seen here while accounting for the evolution of the electronic ground state in a more general way than is allowed by the rigid-ion approximation has recently been tackled by Blöchl.¹³

We now look at the forces in crystalline MgO with $\mu_0 = 400$ a.u. (Fig. 5). The relatively high quantum kinetic energy associated with states attached to the O ions means that, according to Eq. (23), the errors in the forces are considerably larger for the O ions than we have seen for Si. The errors in the CP forces have in fact a standard deviation as large as 32%. However, when this is corrected as in Eq. (26) by attributing all the quantum kinetic energy to states rigidly following the O ions the standard deviation of the error reduces to 4.8%. Furthermore, the corrected value of $\Gamma(t)$ indicates that about 80% of the error on the O forces cancels

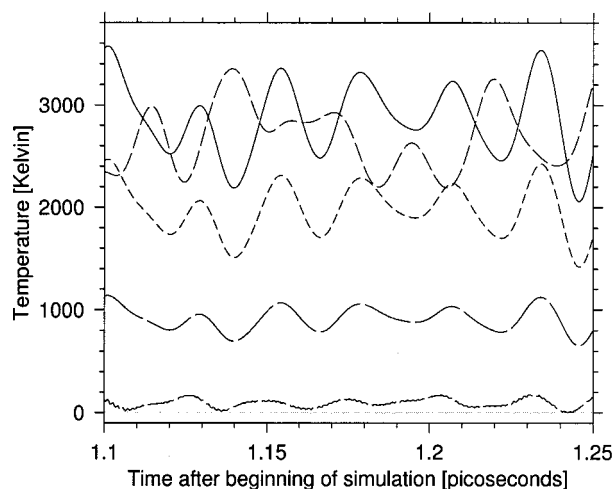


FIG. 6. Simulation 4. Dashed lines from top to bottom are: Mg temperature, O temperature, T_{el} , and $10 \times (T_{\text{el}} - T_{\Delta M_O})$. The full line is the oxygen temperature when it is calculated with a mass which is increased by A_O .

out after account is taken for the high frequency oscillations, suggesting that a more appropriate estimate of the error is $\sim 0.4\%$. The amplitude of the fast oscillations is a cause for concern however and since the simulation was begun at zero ionic velocity it is not clear how it may be reduced further.

1. Temperature

We focus here only on MgO, as the effects of the electronic dragging are enhanced. According to the results of Sec. III, we should expect a difference between the naive definition of temperature and the definition corrected by the electronic dragging, Eq. (27). In the case of MgO, as noted previously, this correction affects only the oxygen atoms, as only a minor amount of electronic charge is carried by the Mg^{2+} ion. In Fig. 6 we show the behavior of the instantaneous values of the naive and corrected temperatures. The corrected temperature exceeds the naive definition by about 500 K. More interestingly, in Fig. 6 we also report the contributions to the temperature of the two atomic species. It is clear that the naive definition would imply that the two species are not at thermal equilibrium. On the other hand, use of the corrected definition for the oxygen temperature brings the temperature of the two species into much better agreement, supporting the conclusion, based on the rigid-ion model, that thermodynamics can be restored by a simple rescaling of the oxygen mass. The mass rescaling, as calculated with Eq. (22), amounts to $\Delta M_O \sim 7.5$ u ($M_O = 16$ u). We also report in Fig. 6 the instantaneous value of the fictitious electronic kinetic energy, the left-hand side of Eq. (28), and the difference between this quantity and the right-hand side of Eq. (28), which represents the contribution due to the rigid dragging of the electronic orbitals. The difference is very small, implying that residual contributions due, for example, to the fast electronic oscillations are negligible in MgO compared to the slow dragging of the orbitals.

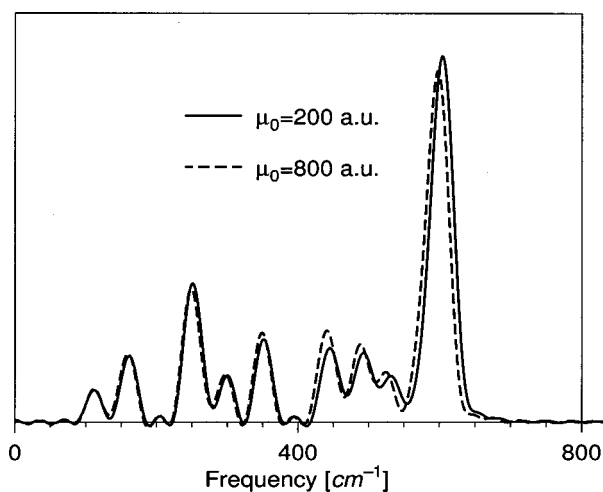


FIG. 7. Phonon density of states of crystalline silicon for $\mu_0=200$ a.u. (simulation 5) and for $\mu_0=800$ a.u. (simulation 6).

2. Phonon spectra

We have calculated the phonon densities of states of crystalline Si and MgO by Fourier transforming the velocity autocorrelation function. In all cases, the first picosecond of the simulation was discarded and results obtained by averaging over at least one subsequent picosecond. For silicon the velocity autocorrelation function was calculated on a time domain of length 1.2 ps and for MgO on a time domain of length 0.5 ps.

In silicon (Fig. 7) the difference is reasonably small. According to the rigid-ion model the frequencies should be corrected using

$$\omega_{\text{corrected}} = \omega_{\text{CP}} \sqrt{1 + \Delta M/M}, \quad (33)$$

where ω_{CP} is the frequency as extracted directly from the CP simulation. We find that for silicon this overestimates by about a factor of 2 the amount of the correction. This small discrepancy may be due to the length of simulation used for calculating the frequency spectra or due to a breakdown of the rigid-ion description when $\mu_0=800$ a.u. It may also be that neglecting the effect of the fast oscillations is not completely appropriate when the dragging contribution is small.

In MgO, as expected, the difference is much larger. We calculate the phonon spectra for $\mu_0=400$ a.u. and for $\mu_0=100$ a.u. and find large differences between them (see Fig. 8) highlighting again how the dynamics depends on the value of μ . The fact that two species are involved complicates matters as the mass correction is different for the two species (it actually vanishes for Mg). Therefore we should not expect simply a rigid shift of the frequencies. However, if the rigid-ion approximation is valid, one may conceive to rescale the oxygen mass *a priori* in Eq. (2) as $\tilde{M}_O = M_O - \Delta M_O$, so that the actual CP dynamics expressed in terms of the BO forces, Eq. (26), becomes identical to the BO dynamics if the rigid ion approximation holds. We have done this for MgO, again for $\mu_0=400$ a.u. and $\mu_0=100$ a.u. and we see that the results are much improved. There are only small differences in the positions of the peaks and the overall shapes of the curves

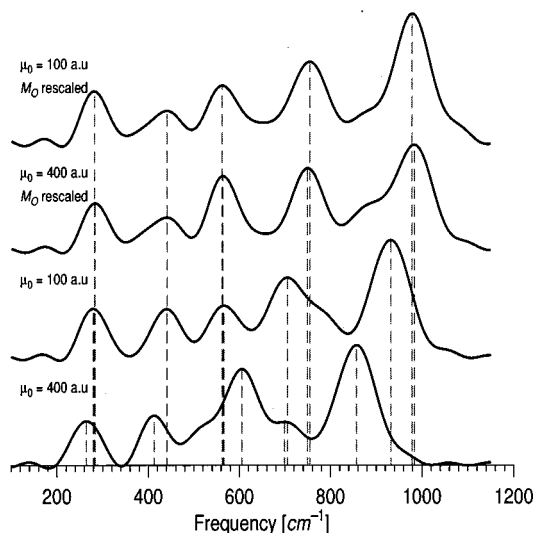


FIG. 8. Phonon density of states of crystalline MgO for $\mu_0=100$ a.u. and for $\mu_0=400$ a.u. with rescaled (simulations 7 and 8) and unrescaled (simulations 10 and 4) oxygen masses.

are very similar. We notice that with $\mu_0=100$ a.u. (and no mass correction) frequencies are within 8% of the correct ones. This implies that in order to obtain a phonon spectrum of MgO with a 4% accuracy in the peak positions (4% is the typical uncertainty of a pseudopotential density functional theory approach¹⁵) the value of μ_0 should be about 50 a.u., which implies a $\Delta t \sim 2.8$ a.u., or about 1.5×10^4 time steps/ps.

3. Dependence of error on μ

We now try to address the question of how the error in the CP forces depends on the fictitious electron mass. According to Eq. (19) the error should scale approximately linearly with the mass. However this is based on the simplifying assumptions that the oscillations in $|\delta\psi_i\rangle$ have a small amplitude and that the $|\delta\psi_i\rangle$ do not on average exchange energy with the ions, i.e., full adiabatic decoupling is achieved. Figure 9 shows $\langle \delta F_i^\alpha \rangle$ and $\langle \delta F_i^\alpha \rangle_{\text{corr}}$ for the oxy-

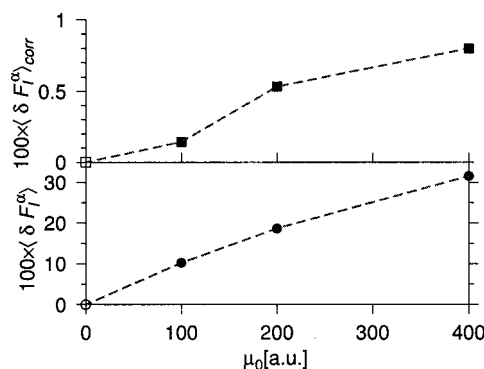


FIG. 9. Scaling of the standard deviation of the errors in the forces on the oxygen ions with μ_0 (Simulations 4, 9, and 10). $\langle \delta F_i^\alpha \rangle_{\text{corr}}$ has been reduced to eliminate canceling high frequency oscillations by inspection of $\Gamma(t)$.

gen ion for three different values of μ_0 , where $\langle \delta F_I^\alpha \rangle_{\text{corr}}$ has been scaled to eliminate the contribution of errors from high frequency oscillations by inspection of $\Gamma(t)$.

Since the uncorrected error is dominated by the effect of the displacement of the equilibrium positions of the orbitals from the ground state, this scales approximately linearly with μ_0 . The small error which remains after the rigid-ion correction has been applied could have contributions from many different sources including deviations from the rigid-ion description and interactions between the ions and the $|\delta\psi_i\rangle$. It is also of the order of the fluctuations in E_k^{total} during the simulation.

V. DISCUSSION

The various cases studied in this work have been explicitly chosen because of their “extremal” behavior. The oxygen ions in MgO have a very strong electron–ion coupling as shown by the large quantum kinetic energy. However, oxygen seems to be well described within the rigid-ion approximation and so the thermodynamics are probably quite close to those of a BO system. Crystalline silicon is less well described in terms of rigid ions (although still remarkably well) but it has a much lower electron–ion coupling so the errors in the forces are very small. If we “measure” the departure of the CP dynamics from the BO dynamics in terms of $\Delta M/M$, with ΔM defined as in Eq. (26), then it appears that the elements where the departure is expected to be larger are located on the upper right-hand side of the periodic table, because they combine a low atomic mass with a large binding energy of the valence electrons (and thus a large quantum kinetic energy). Transition metals may also be strongly affected, because of the large number and strong localization of the d electrons. However, the higher the localization of the orbitals, the higher the chances that the description of the electronic dynamics in terms of rigid orbitals is correct. The large departure observed in the case of MgO suggests that a proper assessment of how much the CP forces differ from the BO ones is mandatory in most systems. This can be achieved by either calculating the BO forces for selected ionic configurations, or by performing simulations for different (smaller) values of μ , and checking how the results scale with decreasing μ . If the departure is large then it is likely that in many cases the CP forces can be brought into good agreement with the BO ones by simply rescaling the ionic masses.

Additional complications may arise when the dynamics lead to fundamental changes in the electronic structure. The first and second derivatives of the electronic orbitals with respect to the positions of the ions, which appear in Eq. (19), may become relevant in regions of phase space where the electrons play a significant role. For example, if charge transfer between ions occurs, or if a substantial rearrangement of the electronic orbitals takes place, as in a chemical reaction, then the simple method of rescaling the ionic masses will no longer work. In some of these cases the Born–Oppenheimer approximation itself may become invalid. In all other cases a

check of the dependence of the CP results on the electronic mass is strongly suggested.

If one is to judge the quality of a CP simulation by the errors in the forces as we have largely done here, then a question which needs to be addressed is to what extent these errors manifest themselves as errors in the properties of interest in the simulation. It is likely that random high frequency oscillations in the forces such as those due to the dynamics of the $\delta\psi_i$ have no discernible effect on the thermodynamics of the system if such oscillations are small. The magnitude of the oscillations seen here in the case of MgO may be a cause for concern. However, we have checked that structural properties are not strongly affected by these errors. Ionic pair-correlation functions are only marginally affected by the electronic mass. A rough estimate of the error in the thermal expansion can be obtained by considering that, in the case of MgO, the average pressures during the $\mu = 100$ and 400 a.u. simulations differ by about 2 GPa. Because the bulk modulus of MgO at those conditions is ~ 700 GPa,¹⁴ a 2 GPa pressure difference would cause a 0.3% volume difference at isobaric conditions. The volume expansion in MgO at 2800 K and 100 GPa is about 3%¹⁵ with respect to 0 K and 100 GPa, implying that the uncertainty in the thermal expansion is about 10%.

All of the effects discussed in this paper are dependent on the choice of the fictitious mass parameter, μ , and by reducing this parameter all thermodynamic and dynamic properties of a simulation may be brought arbitrarily close to those in a Born–Oppenheimer system. A reduction of μ has the drawback that the time step required to integrate the equation of motion for the electronic orbitals is reduced thereby decreasing the computational efficiency of the method. However, the time step scales as $\Delta t \sim \mu^{1/2}$. This means that reducing μ by an order of magnitude increases the simulation time by only a factor of 3. By checking how the property of interest in a simulation scales with μ one can control the level of approximation with which it is calculated.^{16,17}

VI. CONCLUSIONS

Under the assumption that high frequency electronic oscillations (i.e., the dynamics of the $|\delta\psi_i\rangle$) are small and independent of ionic motion, we have shown that Car–Parrinello simulations amount to solving the equation of motion for the ions

$$M_I \ddot{R}_I^\alpha = F_{\text{BO}_I}^\alpha + 2 \sum_i \mu_i \Re \left\{ \sum_J \ddot{R}_J^\beta \frac{\partial \langle \psi_i^{(0)} |}{\partial R_I^\alpha} \frac{\partial |\psi_i^{(0)}\rangle}{\partial R_J^\beta} + \sum_{J,K} \dot{R}_J^\beta \dot{R}_K^\gamma \frac{\partial \langle \psi_i^{(0)} |}{\partial R_I^\alpha} \frac{\partial^2 |\psi_i^{(0)}\rangle}{\partial R_K^\gamma \partial R_J^\beta} \right\}. \quad (34)$$

We have compared the forces in simulations of Si and MgO for a number of different values of μ to the BO forces and found that in the case of Si the errors are small and change very slightly the phonon spectrum of the crystal. In MgO we observe very large systematic errors in the forces which are however mostly attributable to a rescaling of the

mass of the oxygen ion, thereby preserving the thermodynamics. When corrected for this effect the errors are slightly higher than those in crystalline Si but still quite small. The phonon densities of states further confirm both the inadequacy of CP at these values of μ without the rigid-ion correction to describe dynamics and the ability of the rigid-ion model to correct the dynamics in MgO.

We have demonstrated the necessity for checking the dependence of results of CP simulations on the value of the fictitious mass parameter μ .

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