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Theory of *ab initio* molecular-dynamics calculations

G. Pastore* and E. Smargiassi†
Scuola Internazionale Superiore di Studi Avanzati, Via Beirut 4, 34014 Trieste, Italy

F. Buda
Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210

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The theoretical basis of the first-principles molecular dynamics introduced by Car and Parrinello [Phys. Rev. Lett. **55**, 2471 (1985)] is investigated. We elucidate how the classical dynamics generated by the Car-Parrinello Lagrangian approximates efficiently the quantum adiabatic evolution of a system and discuss the role played by the spectrum of the eigenvalues of the Hamiltonian of Kohn and Sham [Phys. Rev. **140**, A1133 (1965)]. A detailed characterization of the statistical ensemble sampled in the numerical simulation is given. By combining theoretical arguments and numerical results we demonstrate that the motion of the electronic variables is a superposition of a direct drag due to the ions and of high-frequency normal modes. By making a connection with the averaging methods of classical mechanics, we argue that whenever it is possible to get a large separation between the time scales of these modes and the ionic frequencies, the dynamics of the ions closely approximates that resulting from the adiabatic approximation. We introduce simple n-level models, easily amenable to analytic treatment, to add clarity and study the possible mechanisms of broken adiabaticity encountered in the actual calculations.

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I. INTRODUCTION

The study of the dynamics of the ions using interparticle forces evaluated from electronic quantum-mechanical calculations has been beyond computational possibility for many years. For this reason, computer simulations of realistic systems have until recently only been performed by modeling the ionic interactions with empirical potentials. While reliable potentials for many physically interesting systems have been derived so far, their limited transferability and the lack of systematic techniques for their derivation have caused a continuing desire for a true "first-principles" simulation method.

In a seminal paper, Car and Parrinello [1] demonstrated the feasibility of an *ab initio* molecular-dynamics (AIMD) calculation. By that we mean the numerical integration of the Newton equations of motion for a given number of ions with forces derived, at each time step, from the instantaneous electronic configuration.

The Car-Parrinello (CP) approach to the AIMD provides an algorithm that is very efficient from the computational point of view because the updating of the electronic degrees of freedom for each ionic configuration does not involve explicit minimization of the electronic density functional. The basic idea is to introduce a fictitious *Newtonian* dynamics for the electronic variables. For a subset of the possible initial conditions, the coupled set of equations of motion for the ionic and electronic variables generates an ion dynamics that closely approximates a microcanonical evolution, and the ions interact through forces indistinguishable from those derived from the Born-Oppenheimer energy surface. So far, a number of investigations have been performed, or are in progress, on very different materials as semiconductors (in crystalline, amorphous, or liquid phases), *s*-*p* bonded metals, alloys, microclusters, and for different properties, such as defect properties, grain boundaries, and surface properties.

While considerable progress has been made on many computational aspects of the method, little attention has yet been given to developing the underlying theory. Consequently there have been some misunderstandings about the justification for the method. Furthermore, practitioners in the field of AIMD lack a theoretical framework to organize empirical observations about the numerical results and to investigate possible improvements of the original method. We think that the time is ripe for a first attempt to closely examine the theoretical issues underlying the Car-Parrinello method.

In this paper we pursue a twofold task: first, we give a brief review of the method from a purely classical mechanics perspective. In this context, we discuss the characterization of the statistical ensemble sampled by the CP dynamics by working out the first integrals of this dynamical system. Second, we study the relations between the spectral properties of the electronic Hamiltonian and the *classical* adiabatic evolution of the electronic degrees of freedom in the CP simulation system.

In particular, we show that the CP dynamics of the electronic variables consists of small oscillations whose eigenfrequencies are approximately given by the differences between eigenvalues of the effective Schrödinger equation. By making connection with the "averaging" method of classical mechanics [2, 3], we argue that precisely this oscillating dynamics makes it possible to approximate the desired Born-Oppenheimer dynamics of the ionic system. Furthermore, we relate the possibility of maintaining the ionic subsystem as close as possible to a microcanonical system to the well-known existence of adiabatic invariants in a system of fast oscillators. Finally, by using simplified models which have only a few electronic levels, we investigate in greater detail the possible mechanisms of the adiabaticity breakdown in the CP dynamics.

The paper is organized as follows. In Sec. II we briefly summarize the CP formalism and describe how it is used in actual calculations. The constants of motion related to the symmetries of the CP Lagrangian are discussed. We also give some typical examples of the results of actual calculations, and illustrate the empirical relations between the spectrum of the Hamiltonian and the numerical behavior of the simulation. In Sec. III we analyze the theoretical justification of the CP method from a purely classical point of view. In Sec. IV we introduce a class of simple few-level systems that can be used to model the cases of broken adiabaticity in the CP method. In the same section we discuss, with numerical examples, the similarities and differences of the few-level models and the actual calculations. Final conclusions are collected in Sec. V.

II. *AB INITIO* MOLECULAR-DYNAMICS SIMULATION

A. Electronic quantum adiabatic evolution and classical ionic dynamics

The existing methods of calculating the interionic forces from first principles require the validity of the quantum adiabatic approximation. As a consequence of the large mass difference between ions and electrons, the time scales of their motions are usually well separated and the (fast) electrons have enough time to readjust and thus follow the (slow) ionic movement. Within a time-dependent quantum description, departures of the electronic wave functions from the instantaneous ground state during the ionic evolution are always present but, in many cases, remain very small. The quantum adiabatic approximation amounts to a reduction in the original dynamical problem to that of the parametric evolution of the ground state.

Deviations from the quantum adiabatic approximation are expected whenever the gap in the electronic-excitation spectrum is such that the electronic-transition frequencies become comparable to, or smaller than, the typical frequencies of the ionic motion. However, even in the case of metallic systems, the effect of such deviations on many physical properties is not dramatic (a detailed discussion of the physical justification of the adiabatic approximation in metals is summarized in Ref. [4]).

The quantum adiabatic approximation allows us to separate the electronic and the ionic degrees of freedom in such a way that a partial average of the electronic variables and the classical limit on the ionic degrees of freedom is equivalent to introducing an effective classical ionic system. The effective Hamiltonian is

$$H_I = H_I^0(\{\mathbf{R}_I, \dot{\mathbf{R}}_I\}) + F(\{\mathbf{R}_I\}), \tag{1}$$

where H_I^0 contains the ionic kinetic energy and the bare ion-ion interaction ($\{\mathbf{R}_I\}$ are the ionic positions and $\{\dot{\mathbf{R}}_I\}$ the ionic velocities). $F(\{\mathbf{R}_I\})$ is the free energy of an inhomogeneous electron gas in the presence of fixed ions at positions $\{\mathbf{R}_I\}$.

The free energy $F(\{\mathbf{R}_I\})$ can be evaluated using density-functional theory (DFT) [5]. Within DFT the electronic ground state is described in terms of the density $\rho(r)$ that is obtained by minimizing $F(\{\mathbf{R}_I\})$ considered as a functional of $\rho(r)$. We will indicate the functional dependence by square brackets.

Many existing implementations of the DFT are based on the Kohn and Sham (KS) formulation for the electronic density functional $F([\rho(\mathbf{r})], \{\mathbf{R}_I\})$ within the local-density approximation (LDA) [6]. This is one of the most accurate and commonly used approaches for present-day electronic structure calculations in condensed-matter physics. For temperatures much smaller than the Fermi temperature the electronic free energy is well approximated by the ground-state energy $U(\{\mathbf{R}_I\})$. Thus the technology developed for total-energy calculations [7, 8] can be used to derive the effective interaction.

The forces on the ions due to the electrons in the ground state can be obtained from the Born-Oppenheimer (BO) potential energy surface:

$$U_{\mathrm{BO}}(\{\mathbf{R}_I\}) = \min_{\rho(r)} E([\rho(\mathbf{r})], \{\mathbf{R}_I\}) \tag{2}$$

as

$$\mathbf{F}_I = -\frac{\partial U_{BO}(\{\mathbf{R}_I\})}{\partial \mathbf{R}_I}. \tag{3}$$

Thus, a straightforward numerical simulation of the ionic motion with the electrons lying on the BO surface would require that at each time step the electronic degrees of freedom are quenched in their ground state. This procedure would require the solution of a self-consistent electronic-structure problem at each time step in typical simulation runs of about 10^4 – 10^5 time steps. Even with a very small time step for the ionic evolution, present state-of-the-art minimization algorithms require of the order of 10 iterations to converge to the BO forces. Moreover, it is not safe to reduce the accuracy of each minimization. With a poorly converged electronic minimization, a systematic damping of the ionic motion occurs [9]. In the next part of this section we shall describe the alternative approach proposed by Car and Parrinello.

B. The Born-Oppenheimer evolution and the Car-Parrinello Lagrangian

We shall concentrate on the CP method to perform an AIMD within the framework of the LDA-KS functional using norm-conserving pseudopotentials to replace ionic cores and a plane-wave basis set [8]. However, we stress that most of our conclusions have more general validity and can be easily adapted to the case of different functionals.

Within the pseudopotential implementation of the LDA in the KS scheme, the ionic potential energy corresponding to the electrons in the ground state can be found by minimizing the KS total-energy functional $E_{\mathrm{KS}}\left[\{\psi_i(\mathbf{r})\},\{\mathbf{R}_I\}\right]$ with respect to the one-particle wave functions $\psi_i(\mathbf{r})$ describing the valence-electron density (here i represents any set of suitable quantum numbers), subject to orthonormalization constraint. The explicit expression of E_{KS} in terms of orthonormal one-particle orbitals $\psi_i(\mathbf{r})$ is

$$E_{\mathrm{KS}}\left[\{\psi_i(\mathbf{r})\},\{\mathbf{R}_I\}\right]=\sum_i f_i\int\psi_i^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\psi_i(\mathbf{r})d\mathbf{r}+\frac{1}{2}\int\int\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2$$
$$+\int\epsilon_{\mathrm{XC}}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}+E_{eI}(\,[\psi_i(\mathbf{r})]\,,\{\mathbf{R}_I\})+U_I^0(\{\mathbf{R}_I\}). \qquad (4)$$

The terms on the right-hand side of the previous equation are, respectively, the electronic kinetic energy, the electrostatic Hartree term, the integral of the LDA exchange and correlation energy density ϵ_{XC}, the electron-ion pseudopotential interaction, and the ion-ion interaction potential energy. The electronic density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r})=\sum_i f_i|\psi_i(\mathbf{r})|^2, \qquad (5)$$

where the f_i are the occupation numbers. The electron-ion coupling term generally includes local and nonlocal components of the atomic pseudopotentials [8].

The gradient of the functional E_{KS} with respect to the electronic coordinates can be written as

$$\frac{\delta E_{\mathrm{KS}}}{\delta\psi_i^*(\mathbf{r})}=f_iH_{\mathrm{KS}}\psi_i(\mathbf{r}). \qquad (6)$$

This equation defines H_{KS}—the KS Hamiltonian operator.

Consistent with the quantum adiabatic approximation, the time evolution of the electronic variables — $\psi_i(\mathbf{r},t)$ — would be given by the solution of

$$H_{\mathrm{KS}}(t)\psi_i^{\mathrm{KS}}(\mathbf{r};t)=\epsilon_i(t)\psi_i^{\mathrm{KS}}(\mathbf{r};t), \qquad (7)$$

where the time dependence of H_{KS} comes from the slow ionic evolution given by Newton's equations:

$$M_I\ddot{\mathbf{R}}_I=\mathbf{F}_I=-\frac{\partial U_{\mathrm{KS}}}{\partial\mathbf{R}_I}. \qquad (8)$$

Here, U_{KS} is the minimum of E_{KS} with respect to ψ_i.

The Car-Parrinello dynamics, instead, aims to approximate this *parametric* evolution through the classical *dynamical* evolution of the electronic and ionic variables generated by the Lagrangian

$$\mathcal{L}_{\mathrm{CP}}=\mu\sum_i\int|\dot{\psi}_i(\mathbf{r})|^2d\mathbf{r}+\tfrac{1}{2}\sum_I M_I\dot{\mathbf{R}}_I^2-E_{\mathrm{KS}}\left[\{\psi_i\},\mathbf{R}_I\right]$$
$$+\sum_{i,j}\Lambda_{ij}\left(\int\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r}-\delta_{ij}\right), \qquad (9)$$

where the ψ_i are regarded as classical fields, M_I are the ionic masses, E_{KS} is the LDA-KS functional, μ is a masslike parameter with dimensions of an energy times a squared time, and the last term ensures orthonormality of the wave functions. In this paper, we express all quantities in atomic units, unless explicitly stated. In particular, we will express the fictitious mass μ in a.u., meaning that the natural atomic unit for μ is 1 hartree $\times 1$ atu^2 (atomic time units; 1 atu= 2.42×10^{-17} s).

The constraints ($\int\psi_i^*\psi_j=\delta_{ij}$) on the KS orbitals are clearly holonomic and stationary, and are completely equivalent to the well-known rigid constraints of classical mechanics. These constraints do not do any work on the system and no dissipation occurs due to their presence.

In systems with few degrees of freedom it is customary to eliminate these kinds of constraints by a transformation to a suitable system of independent coordinates (Lagrangian coordinates) that automatically satisfy the constraints. However, when the number of the degrees of freedom is large, such a procedure is not practical and one is forced to account for them by introducing in the Lagrangian a term containing the constraint equations multiplied by suitable unknown Lagrange multipliers Λ_{ij}. The matrix Λ is Hermitian if the Lagrangian has real values.

The equations of motion resulting from the Lagrangian Eq. (9) are

$$\mu\ddot{\psi}_i(\mathbf{r},t)=-f_iH_{KS}\psi_i(\mathbf{r},t)+\sum_j\Lambda_{ij}\psi_j(\mathbf{r}), \qquad (10)$$

$$M_I\ddot{\mathbf{R}}_I=-\left.\frac{\partial E_{KS}}{\partial\mathbf{R}_I}\right|_\rho, \qquad (11)$$

and

$$N_{ij}(t)=\int\psi_i^*(\mathbf{r},t)\psi_j(\mathbf{r},t)d\mathbf{r}=\delta_{ij} \qquad (12)$$

from which the unknowns $\psi_i(\mathbf{r},t),\mathbf{R}_I(t)$ and $\Lambda_{ij}(t)$ can be obtained for any choice of the initial conditions $\mathbf{R}_I(0),\dot{\mathbf{R}}_I(0),\psi_i(\mathbf{r},0),\dot{\psi}_i(\mathbf{r},0)$ such that $N_{ij}(0)=\delta_{ij}$ and $\dot{N}_{ij}(0)=0$. A couple of comments are in order.

(1) The dynamics generated by Eqs. (10) and (12) for the KS orbitals is generally different from the adiabatic evolution on the BO surface [Eq. (7)] and so the forces on the ions in Eq. (11) are generally different from the BO forces [Eq. (8)]. Only if the wave functions remain close to the solutions of Eq. (7) can we expect the ionic trajectories to be good approximations to the evolution obtained from the true BO energy surface.

(2) An explicit, formal expression for $\Lambda_{ij}(t)$ can be obtained from Eqs. (10) and (12):

$$\Lambda_{ij}=\frac{f_i+f_j}{2}\int\psi_j^*H_{\mathrm{KS}}\psi_id\mathbf{r}-\mu\int\dot{\psi}_j^*\dot{\psi}_id\mathbf{r}. \qquad (13)$$

This expression is not suitable for numerical integration of the equations of motion, as discussed by Car and Parrinello [10]. Here, we stress that this is the *only* form of the Lagrange multiplier matrix compatible with the equations of motion. In particular, the term depending on $\dot\psi$ cannot be ignored without destroying the conservative character of the system [(10)–(12)] over long times. Details of the practical solution of the equations of motion can be found in some recent overviews of the method [9, 10].

C. Constants of motion

The knowledge of the constants of motion is an obvious starting point to study the dynamics of complex systems. Moreover, if the dynamics is used to sample configurations in a numerical simulation, information on such constants is essential to characterize the relevant statistical ensemble. In addition, it can provide exact results that can be used as a test of the numerical accuracy of the integration scheme.

Since the CP Lagrangian is time independent, a first obvious constant of motion is the total energy of the whole system defined as

$$H = K_f + H_I, \tag{14}$$

where $K_f = \mu \sum_i \int |\dot\psi_i|^2 d\mathbf{r}$ is the classical kinetic energy of the KS orbitals. This quantity has no relation to the physical quantum kinetic energy and, to stress this point we follow Remler and Madden [9] by referring to it as the "fake" kinetic energy. H_I is the physical Hamiltonian of the electron-ion system. The constance of H has no direct physical interpretation. However, as long as the fake kinetic energy remains negligible with respect to the other terms ($K_f \ll |H_I|$) the total energy $H_I = K_I + E_{\rm KS}$, where K_I is the ionic kinetic energy, is almost constant. From the statistical-mechanical point of view, this dynamics can be used to sample the ionic microcanonical ensemble (H_I =const), provided that the ergodic hypothesis is satisfied. This approximate microcanonical dynamics is effective in simulating the quantum adiabatic behavior if the forces on the ions in Eq. (11) closely approximate the correct forces [Eq. (8)]. In addition to the total energy, the system described by the CP Lagrangian may have additional constants of motion corresponding to other symmetries.

In the case of a complex representation of the KS orbitals $\psi_i(r)$, an almost trivial symmetry is related to the invariance of the Lagrangian with respect to multiplication of the orbitals by a (constant) phase factor.

As a consequence of this invariance, in the case of a complex representation we have the constants of motion

$$J_{ii} = \int (\dot\psi_i^* \psi_i - \psi_i^* \dot\psi_i) d\mathbf{r}. \tag{15}$$

Another obvious but more interesting conservation law is the generalization of conservation of the linear momentum of the center of mass in isolated classical systems.

It is evident that, in the absence of external forces, $\mathcal{L}_{\rm CP}$ is invariant under a global displacement of the ionic coordinates by an arbitrary vector $\mathbf{a}$:

$$\mathbf{R}'_I = \mathbf{R}_I + \mathbf{a}, \tag{16}$$

if the electronic terms in Eq. (9) are invariant under a change of the KS orbitals

$$\psi'_i(\mathbf{r}) = \psi_i(\mathbf{r} - \mathbf{a}), \tag{17}$$

$$\dot\psi'_i(\mathbf{r}) = \dot\psi_i(\mathbf{r} - \mathbf{a}). \tag{18}$$

Within a plane-wave-expansion scheme this is equivalent to a phase change of the Fourier coefficients $c^i_{\mathbf{G}}$ of the ψ_i:

$$c'^i_{\mathbf{G}} = \mathrm{e}^{\mathrm{i}\mathbf{a}\cdot\mathbf{G}} c^i_{\mathbf{G}} \tag{19}$$

and of the conjugate momenta

$$\mu \dot c'^{i*}_{\mathbf{G}} = \mathrm{e}^{-\mathrm{i}\mathbf{a}\cdot\mathbf{G}} \mu \dot c^{i*}_{\mathbf{G}}, \tag{20}$$

with the induced change

$$\rho'_{\mathbf{G}} = \rho_{\mathbf{G}} \mathrm{e}^{\mathrm{i}\mathbf{a}\cdot\mathbf{G}} \tag{21}$$

in the Fourier transform of the charge density. Then, in the absence of external forces, the CP Lagrangian is invariant with respect to this transformation whose infinitesimal generators are constants of motion. It is straightforward to verify that the following expression for the ℓth component of the (vector) generator induces the infinitesimal global translation of the system along the ℓ spatial direction:

$$\mathcal{P}^\ell = \sum_I M_I \dot R^\ell_I + \mu \sum_{\mathbf{G},n} \mathrm{i} G^\ell \dot c^{n*}_{\mathbf{G}} c^n_{\mathbf{G}}. \tag{22}$$

In general, as a consequence of the conservation of $\mathcal{P}^\ell$, the sum of the forces on the ionic center of mass is not zero at each time step. However, we can on average recover the usual conservation of the total ionic momentum. Due to the periodic-boundary conditions, the CP Lagrangian is not invariant under rotations.

Finally, there is another set of constants of motion whenever a subset of the KS orbitals has the same occupation numbers. It is easy to show that every group of unitary transformations (orthogonal for a real representation) of a set of occupied orbitals with the same occupation numbers f_i is a (continuous) symmetry group for the LDA-KS functional. Moreover, the fake kinetic-energy term is also invariant, provided the unitary transformation is time independent.

This symmetry is reflected in the presence of additional constants of motion only referring to the occupied orbitals. The explicit expressions of such constants are the off-diagonal elements of the anti-Hermitian (antisymmetric in the case of real ψ_i) matrix

$$J_{ij} = \int (\dot\psi_i^* \psi_j - \psi_i^* \dot\psi_j) d\mathbf{r}. \tag{23}$$

Their constancy over the trajectories when $f_i = f_j$ can be checked by differentiating J_{ij} with respect to time and using the equations of motion as well as the fact that Λ is Hermitian.

We explicitly note that, if the initial conditions for the electronic variables are such that not all the J_{ij} are zero, there will be a "rotation" of the KS orbitals superimposed on the coupled ionic and electronic dynamics, and *completely decoupled from the ionic dynamics* as can be checked by the invariance of the forces on the ions [Eq. (11)] with respect to the previously mentioned transformation of the occupied states.

D. Molecular dynamics

The practical way of performing AIMD with the CP Lagrangian is as follows.

(1) For a given initial ionic configuration, the electronic system is put, as closely as possible, in its ground state.

(2) With these starting conditions for $\mathbf{R}_I(0)$ and $\psi_i(\mathbf{r},0)$ and suitable initial conditions on the velocities, one starts to integrate numerically the equations of motion. The simplest choice for the initial velocities is $\dot{\mathbf{R}}_I(0) = 0$ and $\dot{\psi}_i(\mathbf{r},0) = 0$ for a nonequilibrium ionic position but other choices may be more efficient, provided that the compatibility condition $\dot{N}_{ij}(0) = 0$ is fulfilled and that the initial fake kinetic energy is small.

(3) If μ is small enough and as long as K_f remains very small, one empirically finds that the resulting ionic trajectories approximate the true adiabatic ionic motion and allow one to evaluate suitable statistical averages as in the usual microcanonical molecular dynamics (MD).

Thus, AIMD is a conventional MD for an enlarged system (ionic and electronic degrees of freedom) with the additional requirement that the electrons have to follow the evolution of their instantaneous ground state as driven by the ionic dynamics and that their kinetic energy must remain very small. In other words, the system has to stay in a metastable state corresponding to a very low temperature of the electronic variables regardless of the ionic temperature.

As an example of the typical behavior of different quantities during a successful simulation with the CP method, in Fig. 1 we show the behavior of some dynamical variables for a typical simulation of a crystalline semiconductor. The example uses a very simplified model of bulk crystalline silicon. We have used an fcc elementary cell of side 10.26 a.u. with the diamondlike basis of two Si atoms. The electron-ion interaction has been described by the pseudopotential of Bachelet, Hamann, and Schlüter [11], used in a separable form [12] and including only the s and p components of the pseudopotential. The fictitious electronic mass μ was 300 a.u. The small cutoff in the plane-wave expansion (6 Ry) and the use of only the Γ point to sample the Brillouin zone make this system a caricature of real silicon. For example, it turns out that the diamond structure for this system is only a *local* minimum. The direct gap at Γ for the diamond lattice we obtain is 2.24 eV.

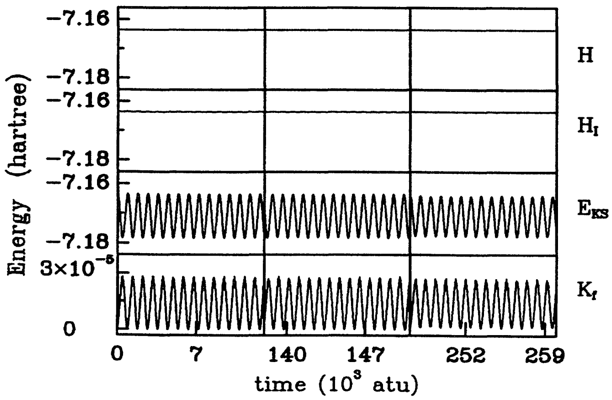

FIG. 1. Typical behavior of some dynamical quantities during the CP dynamics for a system with large gap (see text). From top to bottom: CP Hamiltonian (H); ionic Hamiltonian (H_I); electroionic total energy (E_{KS}); fake electronic kinetic energy (K_f).

However, for the purpose of illustration of the behavior of the CP method, the accuracy of the representation of the experimental data is irrelevant and this silicon-toy model has the advantage of showing the typical behavior of realistic simulations for semiconductors with a small number of electronic degrees of freedom (only 33 independent plane waves for each of the four states, resulting in a computational cost of about 0.04 s per step on a CRAY-YMP computer) and an easily controllable ionic dynamics [12].

In Fig. 1 we show three time intervals of about 3.15×10^{-13} s each, corresponding to the first, the middle, and the last thousand time steps out of a run of 20 000 time steps ($\Delta t = 13$ atu). The equations of motion were integrated using Verlet's algorithm [13]. From the top to the bottom the displayed quantities are H, H_I, E_{KS} and K_f in hartrees.

The almost constant behavior of H gives a check of the numerical accuracy in the integration of the equations of motion. Actually, very small fluctuations, due to the discretization of the time evolution, are present but not visible on the scale of the figure since they correspond to relative variations of energy less than 10^{-6} and there is no systematic drift around the average value, as guaranteed by Verlet's algorithm.

Due to the boundedness and to the small value of the oscillations of K_f, the ionic Hamiltonian $H_I = H - K_f$ also has very small fluctuations around its average value. These fluctuations are two or three times larger than the fluctuations of H. Nevertheless their size remains of the same order of magnitude as the numerical fluctuations due to the discretization of the time. Thus, for all practical purposes, the ionic dynamics keeps H_I constant like in the conventional MD. The total energy (E_{KS}), which acts like the potential energy in a classical MD, shows a trivial oscillating behavior due to the simplicity of the possible ionic modes in this system. A minimization performed at the end of this series of 20 000 time steps showed explicitly that the departure from the BO surface was less than 10^{-5} hartree.

Finally, the bottom part of Fig. 1 shows the fake kinetic energy K_f on a scale enlarged by five orders of magnitude with respect to the other. First of all we note that this function steadily oscillates with a maximum value of about 2.5×10^{-5} hartree. This is far from the estimated equipartition value of 9.5×10^{-3} hartree and there is no indication of a systematic gain of kinetic energy of the electronic variables over the time interval covered by 20 000 time steps.

We also notice that the motion of the electronic orbitals as shown by K_f contains two main components. The first component, the slowest, corresponds to a "dragging" by the ions with their own frequency. A second component has a higher frequency than the first and is more visible upon further magnification of Fig. 2. It is due to the intrinsic dynamics of the KS orbitals. As we will argue it is just the presence of this high frequency component of small amplitude which makes the CP dynamics able to follow the slowly changing ground state.

The example shown here is representative of systems well suited to AIMD. These can be empirically characterized by the presence of a large gap which separates the occupied electronic energy levels from the empty ones.

In some other cases, the numerical behavior shows that the equilibration between ionic and electronic degrees of freedom is faster and systematic transfer of energy is clearly visible over a scale of few hundreds or even tens of time steps. For example, in Fig. 3 we show the behavior of K_f and of the average ionic temperature (T) for a crystalline sample of 63 silicon atoms in the presence of a vacancy. The electronic mass μ is 400 a.u., the integration time step is 7 atu, and the plane-wave cutoff is 12 Ry. The fake kinetic energy steadily increases as a consequence of an irreversible transfer of energy from the ionic to the electronic component. Correspondingly, the value of H_I decreases and the average ionic temperature lowers. In this system, due to the presence of the vacancy, there is a small electronic excitation energy. The behavior shown in Fig. 3 is typical of many systems with a small slowly varying gap.

In other cases, the transfer of energy to the electronic components is faster. In Fig. 4 we show data for the first few oscillations of a tin dimer on the lowest-energy-singlet surface. An fcc cell with a lattice parameter of 30 a.u. was used in connection with a cutoff of 6 Ry. Only s and p components of the pseudopotential were used. The fictitious mass of the electronic degrees of freedom was 2400 a.u. and the time step was 12 atu. There is an evident correlation between the phase of the ionic motion and that of the gain of kinetic energy of the electronic degrees of freedom. A direct calculation of the KS energy levels for this case showed that a degeneracy of the lowest unoccupied level and the highest occupied one, which occurs at distances smaller than the equilibrium distance (about 5.0 a.u.), is removed at larger distances by the opening of a small gap (about 0.3 eV, at the interatomic distance of 5.2 a.u.) between these two levels. Thus, in this system the gap is periodically opened and nearly closed as a consequence of the ionic motion.

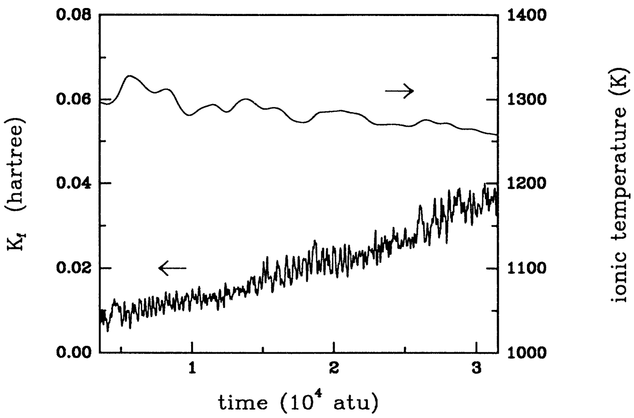

FIG. 3. Fake kinetic energy (lower curve) and averaged ionic temperature (upper curve) in a simulation of a vacancy in a hot bulk-silicon crystal.

In Fig. 5, we show the less systematic but even more catastrophic transfer of energy from the ionic to the electronic components in a sample of 16 sodium atoms starting in a bcc structure at the initial ionic temperature close to 200 K. The cutoff used was 9 Ry and the integration time step was 7 atu, in connection with an electronic mass of 300 a.u. Once again, this behavior can be related to peculiar features of the KS eigenvalues. In the present case, the starting configuration is the ideal bcc structure, then the highest orbital is a member of a degenerate multiplet of six levels. During the ionic evolution, just before the jump in K_f, one of these empty levels becomes lower in energy than the highest occupied one. This behavior of K_f is also reflected in a jump in

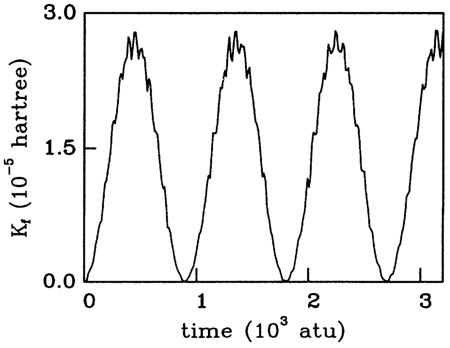

FIG. 2. Same system as in Fig. 1. Fake kinetic energy on an enlarged scale. Note the high-frequency oscillations.

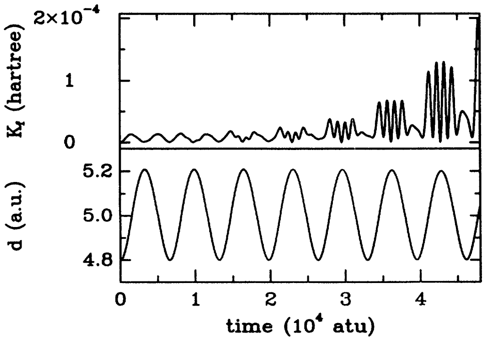

FIG. 4. Time evolution of the fake kinetic energy and interatomic distance of a vibrating tin dimer in its lowest singlet state.

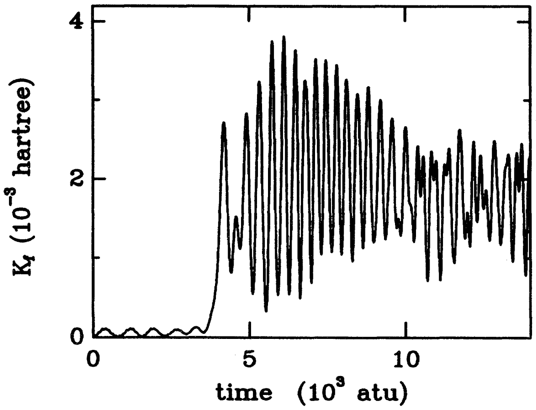

FIG. 5. Evolution of the fake kinetic energy of 16 sodium atoms in a bcc bulk crystal at low temperature.

the ionic total energy H_I. Depending on the temperature of the sample, the jump in the fake kinetic energy displayed in Fig. 5 can be followed by others, each one increasing the average value of K_f.

The previous observations are quite general: every time some *classical* nonadiabatic effect is detected, one can empirically relate it to characteristic features of the energy gap between the occupied and unoccupied KS states.

On physical grounds, one might suspect a correlation between the energy spectrum and the validity of the classical adiabatic approximation, since in such situations the quantum adiabatic approximation itself is expected to be poor. However, while physical intuition can provide useful hints in analyzing this kind of situation, it is not completely evident how to fill the gap between physical arguments based on the *quantum*-mechanical nature of real systems and the purely *classical* nature of the CP Lagrangian. Moreover, the exact nature of the process of energy transfer is left unidentified by this analogy. In the following section we present a natural explanation for this phenomenology.

III. CP DYNAMICS, THE SPECTRUM OF THE KS HAMILTONIAN, AND ADIABATIC BEHAVIOR

A. Oscillatory motion of the electronic variables

The metastable two-temperature regime set up in the CP dynamics is extremely efficient at approximating the constraint of maintaining the electronic energy functional at the minimum *without explicit minimization*. The origin of this behavior can be traced back to the classical adiabatic nature of the dynamics of the electronic degrees of freedom. At the beginning of a numerical simulation, the electronic subsystem is in an initial state which is very close to the minimum of the energy surface. When the ions start moving, their motion causes a change in the instantaneous position of the minimum in the electronic parameter space. The electrons experience restoring forces and start moving. If they start from a neighborhood of a stable equilibrium position, there will be a range of initial velocities such that a regime of small oscillations is originated. As we show in Appendix A, for small perturbations of the LDA-KS ground state, the instantaneous force on orbital ψ_i is

$$F_i = -\sum_{l=m+1}^{\infty} f_i(\varepsilon_l - \varepsilon_i)\delta\alpha_l^i \chi_l(r) - \sum_{l=1}^{m} \frac{(f_l - f_i)}{2}(\varepsilon_i - \varepsilon_l)\delta\alpha_l^i \chi_l(r), \tag{24}$$

where m is the number of occupied states, ε_i are the eigenvalues of the KS Hamiltonian, and $\delta\alpha_k^i$ are the variation of the coefficients of an expansion of the state ψ_i [initially in the eigenstate $\chi_i(r)$] over an orthonormal set of eigenstates—$\chi_k(r)$—of the instantaneous Hamiltonian. If the KS Hamiltonian were a linear operator, from this result one could immediately derive that the intrinsic dynamics of the orbitals consists, for small oscillations, of harmonic modes with frequencies equal to

$$\omega_{ij}^{(1)} = [f_j(\varepsilon_i^* - \varepsilon_j)/\mu]^{1/2} \tag{25}$$

and

$$\omega_{ij}^{(2)} = [(f_j - f_i)(\varepsilon_i - \varepsilon_j)/2\mu]^{1/2}, \tag{26}$$

where ε_i^* indicates the eigenvalue of the ith unoccupied and ε_j the jth occupied level. As one could expect, in the case of the actual KS Hamiltonian, the nonlinearities quantitatively modify this result, although in many cases a semiquantitative agreement holds between the ideal linear case and the real normal-mode spectrum.

If we neglect the dependencies of the eigenvalues on $\delta\alpha$ we can conclude that the system will be stable (pure real frequencies) if the occupied states correspond to the lowest m one-particle eigenvalues and, in the case of unequal occupation numbers (f_i) of these occupied states, if states with increasing eigenvalues have decreasing occupation.

If the occupation numbers are equal ($f_i = f_j$ for all i and j), there will be no component of the first-order force in the subspace of the occupied orbitals and the second summation in Eq. (24) will be missing. According to the discussion about the constants of motion in Sec. II, this result remains valid also after including the dependency of the KS eigenvalues on the state.

As an illustration, in Fig. 6 we show the vibrational density of states (VDOS) of the electronic degrees of freedom of the two-atom silicon system previously discussed. This spectral function is the Fourier transform of the temporal velocity autocorrelation function of the Fourier coefficients of the KS orbitals

$$\gamma(\omega) = \int_0^{\infty} \sum_{i,\mathbf{G}} \langle \dot{c}_{\mathbf{G}}^{i*}(t)\dot{c}_{\mathbf{G}}^{i}(0)\rangle \cos(\omega t)dt, \tag{27}$$

where the time average is performed over 3000 time steps ($\Delta t = 5$ atu). The ions were taken at fixed positions (corresponding to the ideal crystal). The electronic variables

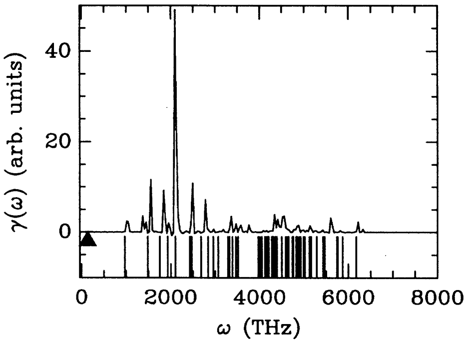

FIG. 6. Vibrational spectrum of the normal modes of the electronic degrees of freedom (continuous curve) for the same system as Fig. 1. The solid triangle indicates the position of the highest ionic frequency. The vertical bars below the spectrum represent the frequencies obtained from Eq. (25).

started the dynamics with zero velocity and with a maximum random displacement of 4% from the configuration corresponding to the minimum energy. Checks with smaller maximum displacements proved that the oscillations are in the linear regime. Additional averaging over four independent initial conditions have been used. A Gaussian cutoff function was used to allow the Fourier transform of this nondecaying correlation function.

With the present choice of μ and the parameters reported above, the frequency spectrum spans about 5000 THz in ω starting from 1010 THz and with a maximum frequency of about 6700 THz. Due to the cutoff function, we cannot attribute absolute meaning to the height of the peaks. Notice however that, since there are 254 independent electronic degrees of freedom, there should be a large number of quasidegenerate modes. For comparison we have reported as vertical segments under $\gamma(\omega)$ the positions of the frequencies resulting from Eq. (25) (i.e. assuming a non-self-consistent KS Hamiltonian). It can be seen that the position of the minimum frequency and the bandwidth resulting from the simple linear approximation are in reasonable agreement with that from the calculated VDOS.

The VDOS obviously scales with $\mu^{1/2}$. As a guide a triangular mark shows the position of the highest ionic frequency Ω (about 140 THz). As we will argue, the important parameter which makes the CP method work is the ratio between Ω and the lower edge of the electronic VDOS at fixed ionic positions: to ensure a good separation of the intrinsic ionic and electronic time scales, provided that the smallest eigenfrequency in the VDOS is not zero, it is enough to decrease the value of the fictitious mass μ to scale the whole spectrum toward higher frequencies. However in choosing the optimal value for μ one has to reach a compromise between this requirement of having the largest minimum frequency in the VDOS and the competing observation that the highest frequency is inversely proportional to the maximum integration time step. If, for the moment, we assume that the relevant character of a dynamics which has to generate a good approximation to an adiabatic evolution is a good separation between Ω and the smallest electronic frequency ($\omega_{\min}$, say), we see that, for comparable ratio $\omega_{\min}/\Omega$, the dynamic evolution generating the VDOS with the smallest bandwidth will allow the largest integration step.

In the previous analysis of the electronic VDOS we neglected the ionic motion. In the cases studied here, we have found that the only observable effect due to its inclusion was a small (less than 1%) decrease of the ionic frequencies. However, we think that the general behavior of the total (ionic and electronic) dynamical matrix could deserve a more thorough investigation, in particular in the presence of a very strong electron-ion interaction.

B. Classical adiabaticity in the CP system

Now, coming to the justification of the CP method, we notice that the intrinsic high-frequency motion of the electronic variables has two main consequences: (1) It allows the electronic degrees of freedom to follow the slow evolution of the ionic variables; (2) it makes the irreversible exchanges of energy between fast and slow variables very small.

These statements can be put on a sounder basis by making connection with the general theory of asymptotic perturbation of Hamiltonian systems [3, 14, 15]. Let us recall in an informal way two major results of classical mechanics relevant to our case.

The first is the so called "averaging method" [2,3] that gives a justification for the fact that the Hamiltonian of a system containing fast and slow variables can be approximated very closely by an "averaged" Hamiltonian obtained by performing an average of the fast coordinates in the original one.

The second related result is the existence of high-order adiabatic invariants in almost integrable systems [3, 16]. This implies the existence of quantities which remain almost constant over times very rapidly increasing with the rate of change in the Hamiltonian.

The formal statements of the previous results as well as the extension of conditions of validity and the range of applicability to the broadest class of system are the subject of contemporary research in the field of dynamical systems [16]. We do not claim that they are applicable without qualification to the behavior of the CP system. Rather, we take a more empirical attitude and refer to these two principles to explain qualitatively the behavior of the CP system in actual simulations.

The averaging method can naturally explain the previous point (1). According to this principle, a system of rapidly oscillating variables perturbed by a slow variation of the parameters (at a rate ν) can be approximated by the system obtained by averaging over the fast motion. If this motion consists of oscillations around the minimum of the electronic density functional, the averaged position of the electronic coordinates will remain very close to the position of the minimum. Then, the trajectory of the real system remains close, within order ν, to that of the "average system" over times proportional to some inverse power of ν. Notice [3] that the nontrivial part of this result is related to the nondivergence of the two trajectories over times inversely increasing with ν. As a result of the continuous dependence of the interatomic forces on the KS orbitals [Eq. (11)], the oscillations of the CP electronic variables around the BO surface will also induce oscillations in the forces on the ions close to the exact forces.

In Fig. 7 we illustrate the way the averaging method works for the forces on the ions as obtained from the CP Lagrangian. We show as a continuous curve one component of the force on one silicon atom in the same system as Fig. 1. Dots correspond to a straightforward implementation of an AIMD by fully minimizing the energy functional at each ionic time step.

On the scale of this figure, it is evident that the forces in the CP system closely follow the BO forces. In Fig. 8 we can see the difference of the CP and BO forces over the first period of the ionic motion. On this enlarged scale it is possible to see that the instantaneous forces in the CP dynamics may differ from the BO value, but the absolute differences are small. The difference shows two main frequencies. The fastest one is due to the intrinsic fast electronic dynamics. The slowest one comes from a small component of the electronic motion with the ionic frequency. This is due to the (weak) coupling between purely electronic and purely ionic modes. The important point to notice is that all these deviations from the BO forces are very small and oscillatory.

The existence of adiabatic invariants, again a consequence of the fast dynamics of the electronic variables, accounts for the quasimicrocanonical behavior of the CP system [i.e., the previous point (2)]. In a regime of small oscillations, for each normal mode the quantity E_i/ω_i— where E_i is the energy of the mode and ω_i its frequency— is an adiabatic invariant. This means that

$$\left|\frac{E_i(T)}{\omega_i(T)} - \frac{E_i(0)}{\omega_i(0)}\right| < \nu \tag{28}$$

for every time T less than ν^{-r}. The value of r depends on the spectrum of the eigenfrequencies and, in any case, is not less than $\frac{1}{2}$ [15]. We believe that in many cases of the CP dynamics, the effective value of r is larger than this lower bound.

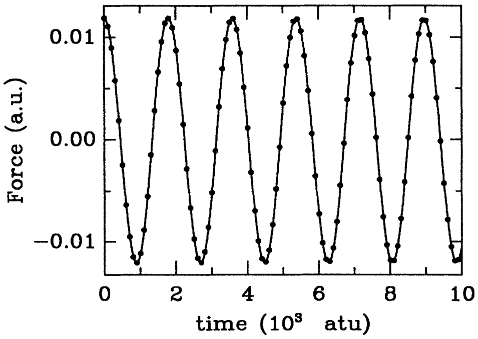

FIG. 7. Component x of the force on one silicon atom of the system of Fig. 1 as a function of time. Solid line: force from CP dynamics (F_{CP}). Dots: force from a well-converged electronic minimization performed at each ionic step (F_{BO}). Not all the data for F_{BO} were plotted.

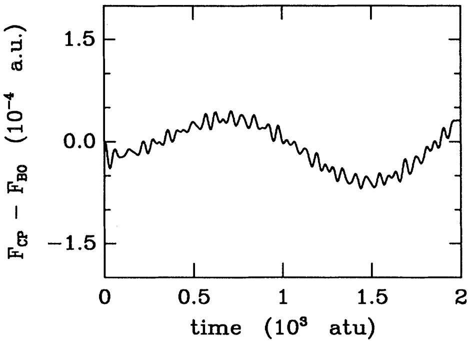

FIG. 8. Difference between F_{CP} and F_{BO} from Fig. 7 on an enlarged scale.

Equation (28) can be interpreted as the condition of an approximate reversibility of the unavoidable exchanges of energy between the ith mode and the rest of the system. Indeed, every time a quasiperiodic evolution of the frequencies makes $\omega_i(T)$ close to the initial value $\omega_i(0)$, $E_i(T)$ will take values close to the initial one. Since for linear oscillators E_i is proportional to the average kinetic energy of that mode, we can maintain the metastable two-temperature regime over times of the order ν^{-r}.

If the electronic frequencies become comparable with the ionic frequencies, there will be no adiabatic invariant and we can expect a "disordered" transfer of energy from the ionic to electronic degrees of freedom with the following rapid equilibration of the whole system. The effectiveness of this energy transfer depends, of course, on the strength of the electron-ion interaction: the weaker the latter, the smaller the former can be.

IV. THE n-LEVEL MODELS

The previous discussion has elucidated the role played by the gap between the energies of the occupied and empty orbitals to establish the fast oscillations of the electronic variables and the importance of having the largest possible separation between electronic and ionic frequencies. It is clear that if the gap of the system always remains larger than some positive nonzero value, it is possible to choose a value of the effective mass μ that pushes the lowest electronic frequency towards higher values.

However, in some cases it is impossible to predict in advance what the evolution of the spectrum of the electronic eigenfrequencies will be. The ionic evolution itself may cause some initially empty level to become lower in energy than an occupied one. In these cases it is not possible to find a fictitious mass μ such that the conditions for the applicability of the adiabatic and the averaging principles will be satisfied.

Thus, it seems necessary to investigate in more detail the nonlinear dynamics of the electronic oscillations to understand the possible mechanisms of the broken classical adiabaticity. A direct analysis of the nonlinearized dynamics of the electronic degrees of freedom of the full CP Lagrangian would be necessary, but, due to the complexity of the KS Hamiltonian and to the large number of electronic variables which requires the use of Lagrange multipliers, it is not easy to go beyond perturbative results. To simplify the problem we shall study the model problem of the CP dynamics generated by a linear (non-self-consistent) Hamiltonian for a system with a finite dimensional state space. We claim that this simplified model contains most of the relevant physics of the real case and we shall show numerically that, under normal conditions, the effect of nonlinearities does not change the qualitative picture very much.

Let H be a Hamiltonian matrix defined on a finite dimensional, n-state, Hilbert space. The matrix elements H_{ij} slowly depend on time. In addition, at variance with the KS case, H is a linear operator. The functions $\{\Phi_i(\mathbf{r}), i = 1, \ldots, n\}$ belong to an orthonormal set of basis functions which, for simplicity, may be taken as eigenfunctions of H at the time $t = 0$:

$$H(0)\Phi_i(\mathbf{r}) = \varepsilon_i \Phi_i(\mathbf{r}). \tag{29}$$

Let the first m ($m < n$) levels be occupied with occupation numbers $0 \le f_i \le f_{\max}$. The ground state at $t = 0$ will be described by the determinant made of the first m eigenstates of $H(0)$. We investigate the behavior of the classical system obtained by writing the CP Lagrangian at fixed ionic positions (without loss of generality we can assume that the states are represented by real functions):

$$\mathcal{L}'_{\rm CP}(\psi, \dot\psi) = \tfrac{1}{2}\mu \sum_i f_i \int \dot\psi_i^2 d\mathbf{r} - \tfrac{1}{2} \sum_i f_i \int \psi_i H \psi_i d\mathbf{r} - \sum_{i,j} \Lambda_{ij} \left(\int \psi_i \psi_j \, d\mathbf{r} - \delta_{ij} \right). \tag{30}$$

Notice the factor $\frac{1}{2}$ for real degrees of freedom and the definition of the fictitious mass μ, different from that originally introduced by Car and Parrinello [1], which makes the occupation f_i explicitly appear in the kinetic term. In the case of equal occupation ($f_i = f_{\max}$ for all i), this choice makes the eigenfrequencies of the electronic variables independent of the occupation.

We can exploit the possibility offered by the small number of variables to reduce explicitly the electronic degrees of freedom to the independent ones by a change of variables. In terms of suitable Lagrangian coordinates, the Lagrange multipliers are redundant and the last term of Eq. (30) disappears. The equations of motion of the electronic degrees of freedom, at fixed ionic configuration, follow from the usual Euler-Lagrange equations. The explicit form can be obtained as soon as an explicit representation of ψ_i is found.

In Appendix B we discuss a general way to represent the electronic variables of a finite dimensional space in terms of special unitary (or special orthogonal, for real representations) matrices. The derivation of the explicit form of the Lagrangian and of the equations of motion is straightforward but quickly becomes cumbersome with increasing dimensionality of the space (n) and the number of occupied one-particle orbitals (m). We have worked out in detail some cases corresponding to small values of n and m. Here, we discuss the cases $n = 2, m = 1$ and $n = 3$ with $m = 2$. Despite their simplicity, we believe that these cases are typical enough to represent the full class of models.

A. The case $n = 3$, $m = 2$

We can express the occupied states ψ_1 and ψ_2 as functions of the Lagrangian coordinates θ, φ, and ξ as

$$\psi_1 = (\cos\theta\cos\varphi)\Phi_1 + (\cos\theta\sin\varphi\sin\xi + \sin\theta\cos\xi)\Phi_2 + (-\sin\varphi\cos\xi\cos\theta + \sin\xi\sin\theta)\Phi_3, \tag{31}$$

$$\psi_2 = (-\sin\theta\cos\varphi)\Phi_1 + (-\sin\theta\sin\varphi\sin\xi + \cos\theta\cos\xi)\Phi_2 + (\sin\varphi\cos\xi\sin\theta + \sin\xi\cos\theta)\Phi_3. \tag{32}$$

The full expression of $\mathcal{L}''_{\rm CP}$ in terms of these Lagrangian coordinates is given in Appendix C.

By linearizing the equations of motion, we arrive at the following simple expressions consistent with Eqs. (25) and (26):

$$\mu(f_1 + f_2)\ddot\theta + (f_1 - f_2)(\varepsilon_2 - \varepsilon_1)\theta = 0, \tag{33}$$

$$\mu\ddot\varphi + (\varepsilon_3 - \varepsilon_1)\varphi = 0, \tag{34}$$

$$\mu\ddot\xi + (\varepsilon_3 - \varepsilon_2)\xi = 0. \tag{35}$$

We see that the coordinates used in Eqs. (31) and (32) reduce naturally to the normal coordinates for the linearized system.

The physics behind these equations is clear. We have chosen the phases in such a way that, when the independent variables are zero, ψ_1 corresponds to the lowest eigenstate Φ_1 and ψ_2 to the next Φ_2. A perturbation will make ψ_1 and ψ_2 acquire components of all the other states. The restoring forces induce oscillations with frequencies proportional to the square root of the differences of eigenvalues.

For equally occupied states ($f_1 = f_2$) Eq. (33) gives zero frequency for the restoring force. Correspondingly, the nonlinear equation of motion for θ resulting from the full Lagrangian (Appendix C) can be integrated immediately to give the following constant of motion:

$$\dot\theta + \dot\xi \sin\varphi = \text{const}. \tag{36}$$

One can easily check that it corresponds to a free "rotation" in the two-dimensional space of the occupied states (see Sec. II) and that Eq. (36) can be derived from formula (23) for the constant of motion J_{12}.

If, as a consequence of a broken adiabaticity, the amplitude of the electronic oscillations increases the linearized equations of motion will not be able to describe the real evolution of the system. The nonlinear equations in the case $n = 3$ are quite complicated. However, we note that while three is the minimum number of levels which allows us to represent the whole phenomenology of the real case, if the main interest is in the instabilities originating from the dynamics of the energy gap it is possible to get the correct qualitative picture by analyzing the simpler case $n = 2$. We think that the relevance of this very simplified model to the analysis of the full KS dynamics close to instability points is due to the fact that in most of the practical cases the subspace involved in the instability is just one-dimensional. More complex instabilities involving higher-dimensional subspaces seem to have a very small probability.

B. The case $n = 2$, $m = 1$

In this case, we have only one Lagrangian coordinate — $\theta(t)$ — in terms of which we express the wave function as

$$\psi = \left(\cos\frac{\theta}{2}\right)\Phi_1 + \left(\sin\frac{\theta}{2}\right)\Phi_2 \tag{37}$$

and the exact equation of motion is

$$\ddot{\theta}(t) = \frac{\Delta E}{\mu}\sin[\theta(t) - \theta_0] \tag{38}$$

which is the equation of motion of the nonlinear oscillator (pendulum). The gap $\Delta E = \varepsilon_2 - \varepsilon_1$ and the equilibrium angle θ_0 appearing in Eq. (38) can be expressed in terms of the matrix elements of H. In particular, they are independent parameters.

Now, let us consider the effect of the ionic motion. For slow variations of the matrix elements, the electronic variables will be able to readjust themselves to follow the instantaneous values. However, when ΔE decreases we can expect two regimes where, at different levels of severity, the classical adiabatic behavior of the system will be destroyed.

The first regime corresponds to the case of a system where the energy gap becomes so small that the electronic frequencies are comparable to or smaller than the ionic ones. In such a situation the flux of energy between the ionic and the electronic component may find efficient channels.

In the second regime, as soon as ΔE becomes negative (at the crossing of the two levels) a real dynamical instability appears in the electronic subsystem. In the analogy with the physical pendulum, this occurrence corresponds to a change of the equilibrium angle from θ_0 to $\theta_0 + \pi$. It is as if the gravitational force changes from pointing downwards to upwards. The effect is the appearance of an instability in the oscillating motion and a rapid increase of electronic kinetic energy.

The simple Eq. (38) can be exactly integrated in terms of elliptic functions if the parameters ΔE and θ_0 are constant. For a specific choice of a periodic time dependence on time of the gap, the linearized equation would reduce to the Mathieu's equation. However, as far as the present authors know, analytical studies relevant to the case of instability in the nonlinear case (ΔE which becomes negative) are lacking. For this reason, in the present paper we have limited the study of the dynamics of the two-level model to numerical investigations. More analytical investigations are planned.

In order to use the two-level model to numerically study the mechanism of broken adiabaticity in the CP system, we have added a term for the additional ionic-like variables to the electronic Lagrangian [Eq. (30)]. By considering the ionic role in the determination of the electronic gap and ground state, it seems a natural choice to treat ΔE and θ_0 as independent degrees of freedom.

A very simple choice for the intrinsic dynamics of $G(t) = \Delta E(t)$ and $\theta_0(t)$ — hereafter referred to as ionic degrees of freedom — is a harmonic dynamics with natural frequencies significantly smaller than the electronic one.

A possible Lagrangian is the following:

$$\begin{aligned}\mathcal{L} = {}& \tfrac{1}{2}\mu\dot{\theta}^2 + \tfrac{1}{2}M_g\dot{G}^2 + \tfrac{1}{2}M_0\dot{\theta}_0^2 + G\cos(\theta - \theta_0)\\ & -\tfrac{1}{2}\Omega_1^2 M_g(G - G_0)^2 - \tfrac{1}{2}\Omega_2^2 M_0\theta_0^2,\end{aligned} \tag{39}$$

where

$$G(t) = G_0 g(t) = [\varepsilon_2(0) - \varepsilon_1(0)]g(t). \tag{40}$$

The potential energy has always a global minimum at $G = 1/\Omega_1^2 + G_0$, $\theta = 0$ and $\theta_0 = 0$. The resulting equations of motion are

$$\mu\ddot{\theta}(t) = -G_0 g(t)\sin[\theta(t) - \theta_0(t)], \tag{41}$$

$$\ddot{\theta}_0(t) = \frac{G_0}{M_0}g(t)\sin[\theta(t) - \theta_0(t)] + \Omega_2^2\theta_0, \tag{42}$$

$$\ddot{g}(t) = -\Omega_1^2\,[g(t) - 1] + \frac{1}{M_g G_0}\cos[\theta(t) - \theta_0(t)]. \tag{43}$$

The form of this Lagrangian has been chosen to give an ionic motion that, for suitable choices of the parameters, would correspond to slightly perturbed harmonic oscillations at frequencies Ω_1 and Ω_2.

In the following we present results of a numerical integration of the previous equations of motion for three cases that have strong connections with the behavior of the real numerical experiments with the CP method discussed at the end of Sec. II. We have, respectively, (a) the case of a system with a large gap, (b) the case of a system which periodically becomes gapless, and (c) the case of a real level crossing.

In case (a) we have not considered the gap as dynamical variable. We have fixed its value to $\Delta E = 0.12$ hartree. By using atomic units, the parameters of the model are the mass of the "electronic" degree of freedom (μ) is 300 and that of the "ionic" degree of freedom (M_0) is 1.5×10^5. The intrinsic frequency of θ_0 (Ω_2) is 1.445×10^{-3} to ensure a separation of the two scales of time similar to that realized in the system of Fig. 1. The initial conditions are $\theta(0) = 1.01$, $\theta_0(0) = 1$, and $\dot{\theta}(0) = \dot{\theta}_0(0) = 0$. In Fig. 9, we have reported results for the "fake" kinetic energy K_f, the "electronic" variable θ and its difference with respect to the instantaneous ground state ($\theta = \theta_0$). The plot of K_f is very similar to that of Fig. 2. The high-frequency mode is superimposed to the slow mode that can be regarded as a drag by the ionic degrees of freedom. Notice that these two components both contribute to K_f. The result for $\theta - \theta_0$ nicely illustrates the averaging principle. Here, in analogy with the situation depicted in Fig. 8 for the forces in the CP system, the deviations from the BO surface show high-frequency components as well as contributions at the ionic frequency due to the finite coupling between the two subsystems.

Case (b) is illustrated in Fig. 10. It has to be com-

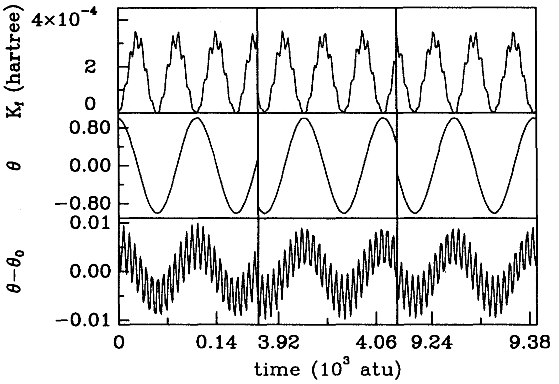

FIG. 9. Two-level model: the case of a large constant gap. From top to bottom: fake kinetic energy (K_f); electronic degree of freedom (θ); deviation from the instantaneous ground state ($\theta - \theta_0$).

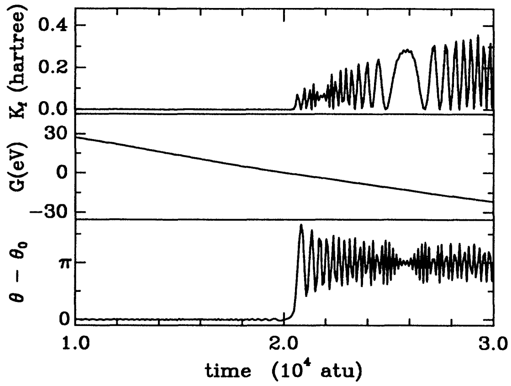

FIG. 11. Two-level model: behavior around a level crossing. From top to bottom: fake kinetic energy (K_f); energy gap (G); deviation from the instantaneous ground state ($\theta - \theta_0$).

pared with Fig. 4 (tin dimer). In that case, the energy gap between highest occupied and lowest unoccupied orbitals was periodically opening and closing. Here, to simulate such a variation within our model system, we have suitably chosen the parameters and the initial conditions. The parameters were $\mu = 300$, $M_0 = 6.0 \times 10^4$, $\Omega_1 = 1.13 \times 10^{-3}$, $\Omega_2 = 4.2 \times 10^{-4}$, and $G_0 = 2 \times 10^{-3}$. We set the initial conditions to $\theta(0) = 1.02$, $\theta_0(0) = 1$, $g(0) = 7$, and all the starting velocities were zero. Only the behaviour around the crossing is shown. In the real case of the tin dimer and in the two-level model we find the same characteristic transfer of energy from the ionic to the electronic degrees of freedom.

Finally, in Fig. 11 we show case (c). The parameters were $\mu = 300$, $M_0 = 6.0 \times 10^4$, $M_g = 1.5 \times 10^8$, $\Omega_1 = 1.095 \times 10^{-4}$, $\Omega_2 = 4.2 \times 10^{-4}$, and $G_0 = 8 \times 10^{-3}$. We set the initial conditions to $\theta(0) = 1.02$, $\theta_0(0) = 1$, $g(0) = 190$, and all the starting velocities were zero. With these parameters, an empty state goes below an occupied one during the CP dynamics. With a small delay, the system responds to the creation of the instability by increasing K_f. Then, the adiabatic invariance is lost and the larger amplitude of the oscillations around the new ground state ($\theta_0 = \pi$) increases making the averaging principle less effective. Such a behavior of the nonlinear oscillator model shows that the level crossing is actually a catastrophic event in the CP dynamics. After crossing, the highest occupied orbital acquires a large velocity of mixing between the two crossed levels with subsequent increased inaccuracies in the evaluation of the forces and in the ionic dynamics.

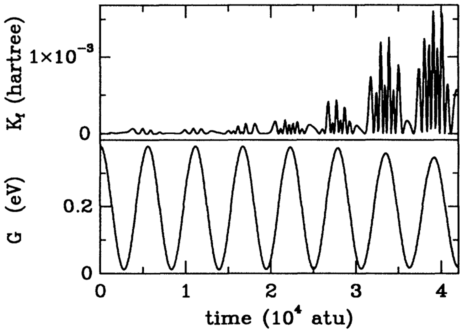

FIG. 10. Two-level model: time evolution of the fake kinetic energy and the energy gap in the case of a periodically closing gap.

V. DISCUSSION AND CONCLUSIONS

In this paper we have analyzed the dynamics generated by the CP Lagrangian from the point of view of classical mechanics. We have given a characterization of the statistical ensemble relevant for the CP-AIMD in terms of the first integrals of the system. From our analysis it follows that, for all practical purposes, the sampling of the ionic configurations in the "CP-ensemble" is equivalent to that of a microcanonical ensemble at fixed value of total ionic momentum, as in the ordinary MD.

We have studied how the regime of small oscillations around the electronic ground state is approximately connected to the spectrum of the energy levels of the KS Hamiltonian. From our discussion it is straightforward to derive a criterion to choose an optimal value of the free parameter — μ — of the CP Lagrangian.

We have sketched how to put the theoretical justification of the method on a sounder basis by making contact with contemporary research on asymptotic methods in Hamiltonian systems [16]. As we have noticed, we need such methods, more powerful than the usual perturbation theory, to account for stability over a long-time scale.

We are aware that our rather informal discussion on the justification of the method remains at the level of qualitative arguments. However, we think that it allows analysis of actual numerical experiments within a unified conceptual framework. A substantial amount of future work seems to be necessary to get more formal and quantitative results. In this respect we hope that our presentation of the problem will stimulate further work.

We have introduced simplified two- and three-level models to make the analysis of the CP dynamics easier. With the help of these models we have studied two main mechanisms driving nonadiabaticity in the CP system. In both cases, as a consequence of a reduced gap, the time scale of the electronic motion becomes comparable with the ionic one.

In the first case, an "effective" resonance between the ionic and electronic frequencies may open a channel to transfer energy from the ions to the electronic variables in a continuous irreversible way. In the second case, a level crossing between occupied and empty levels drives a true structural instability of the potential surface that affects the electronic degrees of freedom.

Further quantitative study of the relative efficiency of these two mechanisms is desirable to get realistic estimates of the actual equilibration times of the CP system. In any case, from the point of view of performing an AIMD, if the electronic dynamics is not faster than the ionic one, the almost exact error cancellation of the forces on the ions is not valid. However, from our analysis we can also argue that not all the electronic variables will be affected equally but only the — possibly small — subset of the highest occupied orbitals.

In conclusion, from our analysis it is clear that physical systems with a well-defined and stable energy gap are the most suitable for simulation using the CP method. While the occurrence of adiabaticity breaking is a slow or rare event it is possible to use the standard CP dynamics by periodically correcting the deviation from the BO surface with electronic minimizations. However, as soon as this deviation rate becomes comparable with the ionic velocities, different approaches are required to efficiently perform an AIMD.

So far, the practical solution [17] of these nonadiabaticity problems is to partially recover the direct approach to the AIMD by performing explicit electronic minimizations when the departure from the BO surface becomes substantial, and to give up a microcanonical ionic evolution in favor of a canonical one. Although such a method works pretty well in practice, we believe that there is room for improvement and our analysis can provide a useful guideline to such an aim. We are currently investigating possible alternative methods to deal with metallic systems within a microcanonical scheme.

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APPENDIX A: PERTURBATIVE ANALYSIS OF THE FORCE ON THE ELECTRONIC DEGREES OF FREEDOM

The generic state $|\psi_i\rangle$ in the infinite dimensional Hilbert space $\mathcal{H}$ can always be expanded as

$$|\psi_i\rangle = \sum_k^{\infty} \alpha_k^i |\chi_k\rangle \tag{A1}$$

where $|\chi_k\rangle$ is an orthonormal basis. If we choose it to be made by eigenstates of the KS Hamiltonian $H_{\rm KS}$ (in the following briefly referred as H), the canonic ground state orbital $|\psi_i^0\rangle$ of a system with m occupied states can be written as in Eq. (A1) with coefficients

$$\alpha_k^{0i} = \begin{cases} \delta_{ik}, & k \le m \\ 0, & k > m. \end{cases}$$

A state $|\psi_i\rangle$ close but not equal to $|\psi_i^0\rangle$ will have coefficients

$$\alpha_k^i = \alpha_k^{0i} + \delta\alpha_k^i. \tag{A2}$$

Notice that, due to the orthonormalization of the states, for each pair of states i and j we have, at the first order in $\delta\alpha$,

$$\delta\alpha_i^{j*} + \delta\alpha_j^i = 0. \tag{A3}$$

The matrix elements

$$H_{li} = \langle\psi_l|H|\psi_i\rangle \tag{A4}$$

between two occupied orbitals can be written as

$$H_{li} = \sum_k^{\infty} (\delta_{lk} + \delta\alpha_k^{l*})(\delta_{ik} + \delta\alpha_k^i)\varepsilon_k. \tag{A5}$$

At the first order, the force on the perturbed orbital $|\psi_i\rangle$ will be

$$\begin{aligned}
F_i &= -f_i H|\psi_i\rangle + \sum_l^m \Lambda_{il}|\psi_l\rangle = -f_i H|\psi_i\rangle + \sum_l^m \frac{(f_i+f_l)}{2} H_{li}|\psi_l\rangle \\
&= -f_i \sum_k^{\infty} (\alpha_k^{0i} + \delta\alpha_k^i)\varepsilon_k|\chi_k\rangle \\
&\quad + \sum_l^m \frac{(f_i+f_l)}{2} \sum_k^{\infty} (\alpha_k^{0l*} + \delta\alpha_k^{l*})(\alpha_k^{0i} + \delta\alpha_k^i)\varepsilon_k \sum_{k'}^{\infty} (\alpha_{k'}^{0l} + \delta\alpha_{k'}^l)|\chi_{k'}\rangle \\
&= -\sum_{k=m+1}^{\infty} f_i(\varepsilon_k - \varepsilon_i)\delta\alpha_k^i|\chi_k\rangle \\
&\quad + \sum_{l=1}^{m} \left(-f_i\varepsilon_l\delta\alpha_l^i + f_i\varepsilon_i\delta\alpha_l^i + \varepsilon_l\delta\alpha_l^i + \frac{(f_i+f_l)}{2}\varepsilon_l\delta\alpha_l^i + \frac{(f_i+f_l)}{2}\varepsilon_i\delta\alpha_i^{l*} \right) |\chi_l\rangle + O((\delta\alpha)^2) \\
&= -\sum_{k=m+1}^{\infty} f_i(\varepsilon_k - \varepsilon_i)\delta\alpha_k^i|\chi_k\rangle - \sum_{l=1}^{m} \frac{(f_l-f_i)}{2}(\varepsilon_i - \varepsilon_l)\delta\alpha_l^i|\chi_l\rangle + O((\delta\alpha)^2).
\end{aligned}$$

In simplifying the last term Eq. (A3) has been used.

APPENDIX B: THE LAGRANGIAN COORDINATES FOR ORTHONORMAL ORBITALS

If S is a suitable special orthogonal matrix (special unitary in the complex case) belonging to some irreducible representation of the SO(n) group [SU(n) in the complex case], we can represent the general occupied state ψ_i at the time t as

$$\psi_i(t) = \sum_{j=1}^{n} S_{ij}(t)\Phi_i, \quad i = 1, \ldots, m. \tag{B1}$$

Due to the orthogonality of the matrix S and of the base functions Φ_i, the first m rows are orthonormal vectors. Then, if we use a set of $m[n-m(m+1)/2]$ generators of the representation of the group—$\{\alpha_i(t)\}$—as independent variables to describe the electronic degrees of freedom we have a representation of the electrons through a system of coordinates that satisfy the constraint by construction (Lagrangian coordinates). Notice that the configuration space of our system is exactly isomorphic to that of an m-dimensional rigid body with a fixed point in an n-dimensional space.

APPENDIX C: THE CP LAGRANGIAN OF THE THREE-LEVEL MODEL

With the expression of ψ_1 and ψ_2 given in Eqs. (31) and (32) the explicit form of the Lagrangian in terms of the independent variables ξ, φ and θ is

$$\begin{aligned}\mathcal{L}_3 = {} & +\tfrac{1}{2}\mu\{\dot{\varphi}^2(f_1\cos^2\theta + f_2\sin^2\theta) + \dot{\xi}^2\left[f_1 + f_2 - \cos^2\varphi(f_1\cos^2\theta + f_2\sin^2\theta)\right] \\ & \qquad + \dot{\theta}^2(f_1+f_2) + 2(f_1+f_2)\dot{\xi}\dot{\theta}\sin\varphi + 2(f_2 - f_1)\dot{\xi}\dot{\varphi}\sin\theta\cos\theta\cos\varphi\} \\ & + \frac{f_2}{2}(\varepsilon_{21} + \varepsilon_{32}\cos^2\xi)\cos^2\varphi \\ & + \frac{(f_1 - f_2)}{2}\{\varepsilon_{32}\cos^2\xi + 2\varepsilon_{32}\sin\xi\cos\xi\sin\theta\cos\theta\sin\varphi \\ & \qquad\qquad + \cos^2\theta\left[\varepsilon_{32}(1 - 2\cos^2\xi) + (\varepsilon_{21} + \varepsilon_{32}\cos^2\xi)\cos^2\varphi\right]\},\end{aligned}$$

where $\varepsilon_{ij} = \varepsilon_i - \varepsilon_j$.

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[*] Present address: Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, 34014 Trieste, Italy.

[†] Present address: Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom.

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