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CANONICAL STATISTICAL AVERAGES OF COUPLED QUANTUM-CLASSICAL SYSTEMS

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Abstract

We study the thermal equilibrium distribution generated by a Nosé-Hoover thermostat coupled to a mixed quantum-classical system, whose time evolution is taken to be either Ehrenfest (E), or Car-Parrinello (CP) type. It is found that neither E or CP dynamics lead to the correct averages for the quantum subsystem. A new classical modified CP dynamics is introduced, and explicitly shown by theory and model simulation, to yield the correct averages.

Contents

Chapter 1

Introduction

Mixed quantum-classical systems are of wide interest in several areas of physics and chemistry. For instance, in condensed matter physics, nuclei or ions can often be considered as classical particles, while electrons require a quantum treatment. The dynamics of these systems has received much attention recently, particularly in connection with developments in computer simulations[1,2,3].

It is well known that a clearcut separation between quantum and classical behaviour exists only in the adiabatic Born-Oppenheimer (BO) regime, in which the electrons remain in a single energy eigenstate. In this case the temporal evolution of the system can be found by solving Newton's equations for the nuclei coupled to time-dependent Schrödinger's equations for the electrons. The resulting dynamics is often called Ehrenfest (E) dynamics[4,5,1]. If the electrons are in the ground-state rather than in a generic eigenstate, one can use an alternative and often computationally more efficient scheme in which Newton's equations are used also for the electronic degrees of freedom, as shown by Car and Parrinello (CP)[6,2]. However, both CP and E dynamics are incorrect in presence of non-adiabatic transitions, which originate characteristic quantum effects in the 'slow' nuclear dynamics as well. In this case, practical algorithms fully based on differential equations are not available and *ad hoc* stochastic procedures, such as the surface hopping model,[7,4,3] have been used to compute the temporal evolution of the mixed quantum-classical system. In view of their intrinsic complexity, applications of such schemes have been mostly limited to the case of a single quantum particle immersed in a classical bath.

Under the assumption of ergodicity time averages are equivalent to ensemble averages. Then the following question arises: can we compute canonical averages for a mixed quantum-classical system by averaging over trajectories generated by any appropriate dynamics? For classical systems, for example, schemes like the Nosé or the Nosé-Hoover thermostat have been proposed which achieve precisely this goal[8]. It would be interesting to investigate if suitable generalizations of the E or the CP dynamics allow to achieve this goal also for quantum systems. Indeed a generalization of the Nosé theorem to quantum systems was recently discussed in a paper[9], in which it was additionally suggested that a simple E-type dynamics could yield the correct canonical distribution. This is an intriguing possibility since the thermalization of a quantum sub-system among different energy eigenstates necessarily implies a breakdown of adiabaticity. However one can not exclude that an improper dynamics of non-adiabatic processes, like E or CP, might still be able to yield correct equilibrium distributions. More generally it is not clear what are the conditions that a continuous dynamics of non-adiabatic processes should satisfy in order to yield the correct quantum canonical distribution.

In this work we present a general formulation of the thermal equilibrium properties of mixed quantum-classical systems whose dynamics is governed by E or CP equations, in which a classical Nosé-Hoover thermostat is coupled to quantum degrees of freedom. Our analysis is based on a generalized Liouville equation. We show that an important requirement must be obeyed by any chosen dynamics in order to reproduce the exact canonical distribution of the mixed system. As it turns out, neither ordinary E nor ordinary

CP dynamics satisfy this requirement: they in fact lead to a different distribution. This implies that extensions of the Nosé theorem to the mixed quantum-classical case cannot be realized by simple E dynamics, contrary to what was assumed in calculations presented in Ref. [9]. In this work, in addition we explicitly suggest that a novel dynamics of a modified CP type would yield the correct distribution. We corroborate our theory with numerical simulations on a simple two-level quantum system coupled to a Nosé-Hoover thermostat via a chain of classical anharmonic oscillators. We find perfect agreement between the results of the simulations and the analytical distribution functions corresponding to E, CP and modified CP dynamics, respectively.

Chapter 2

Canonical Ensembles

2.1 Ehrenfest dynamics

We begin by considering n classical particles with coordinates q_i, momenta p_i and masses m_i, coupled to a (discrete) quantum system with normalized wave-function $|\Psi>$. In E dynamics the wave-function evolution is governed by a time-dependent Schroedinger equation while the classical particles are moved by a force averaged on the quantum state. The resulting equations for the mixed system are:

$$\dot{\mathrm{q}}_i = \mathrm{p}_i/m_i \tag{2.1}$$

$$\dot{\mathrm{p}}_i = - < \Psi|\frac{\partial}{\partial \mathrm{q}_i}H(\mathrm{q})|\Psi > - \frac{\partial V(\mathrm{q})}{\partial \mathrm{q}_i} \tag{2.2}$$

$$i\hbar|\dot{\Psi} >= H(\mathrm{q})|\Psi > \tag{2.3}$$

where the dot indicates time derivative, $H(\mathrm{q})$ is the quantum Hamiltonian with the classical q coordinates as parameters, $V(\mathrm{q})$ is an extra potential acting strictly on classical variables. For this motion the conservation of energy:

$$E_{Ehr} =< \Psi|H(\mathrm{q})|\Psi > +V(\mathrm{q}) + \sum_i \frac{1}{2}\frac{\mathrm{p}_i^2}{m_i} \tag{2.4}$$

is easily verified. To ensure thermal equilibrium at temperature T we couple a Nosé-Hoover thermostat ξ to the classical particles. Eq. (2.2) is replaced by:

$$\dot{\mathrm{p}}_i = - < \Psi | \frac{\partial}{\partial \mathrm{q}_i} H(\mathrm{q}) | \Psi > - \frac{\partial V(\mathrm{q})}{\partial \mathrm{q}_i} - \xi \mathrm{p}_i \tag{2.5}$$

and the time evolution of ξ is given by:

$$\dot{\xi} = (\sum_i \frac{\mathrm{p}_i^2}{m_i} - n\,kT)/Q \tag{2.6}$$

where k is the Boltzmann constant and Q is the effective mass of the thermostat. Under ergodic conditions, the Nosè-Hoover thermostat coupled to the *classical* sub-system is completely equivalent for equilibrium properties to a large external bath. In order to find the equilibrium distribution generated in the mixed quantum- classical system by Eqs. (2.1,2.3,2.5,2.6) we follow an approach which is commonly used for purely classical system[10,8]. First we notice that if $|\Psi >= \sum_j (a_j + i b_j) |j>$ in terms of N orthogonal basis vectors $(|j>)_{j=1,\ldots,N}$, with a_j, b_j real coefficients, then the quantum state is uniquely specified by the vector $\mathbf{X} = (a_j, b_j)_j$. Then a distribution function $\rho(\mathbf{\Gamma}, t)$ can be defined in the generalized phase space $\mathbf{\Gamma} = (\mathrm{q}, \mathrm{p}, \mathbf{X}, \xi)$. From probability conservation we get:

$$\frac{d}{dt}\rho = - \left(\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} \right) \rho \tag{2.7}$$

where the divergence of the extended generalized velocity,

$$\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} = \sum_i^n \frac{\partial}{\partial \mathrm{q}_i} \cdot \dot{\mathrm{q}}_i + \sum_i^n \frac{\partial}{\partial \mathrm{p}_i} \cdot \dot{\mathrm{p}}_i + \sum_j^N \frac{\partial \dot{a}_j}{\partial a_j} + \sum_j^N \frac{\partial \dot{b}_j}{\partial b_j} + \frac{\partial \dot{\xi}}{\partial \xi} \tag{2.8}$$

can be evaluated using the equations of motion (2.1,2.3,2.5,2.6) obtaining:

$$\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} = -n\xi \tag{2.9}$$

Only the Nosé-Hoover friction term in the equation (2.5) for $\dot{\mathrm{p}}_i$ contributes to this divergence. In particular no contributions arise from the quantum motion, since $H(\mathbf{q})$ is an Hermitian operator. Thus, upon removing the thermostat the divergence vanishes and under ergodic condition the space $(\mathbf{q}, \mathbf{p}, \mathbf{X})$ is uniformly covered by the motion, as is the phase space $(\mathbf{q}, \mathbf{p})$ in ordinary classical microcanonical dynamics.

In analogy with the purely classical case we can define an effective 'energy'

$$E_e(\Gamma) = E_{Ehr} + \frac{1}{2}Q\xi^2 = < \Psi|H(\mathbf{q})|\Psi > + V(\mathbf{q}) + \sum_i \frac{1}{2}\frac{\mathbf{p}_i^2}{m_i} + \frac{1}{2}Q\xi^2 \quad (2.10)$$

whose time derivative can be calculated using the equations of motion obtaining:

$$\frac{dE_e}{dt} = -nkT\xi \quad (2.11)$$

This allows rewriting Eq. (2.7) as:

$$\frac{d\rho}{dt} = -\frac{1}{kT}\frac{dH_e}{dt}\rho \quad (2.12)$$

A stationary solution to this equation is given by:

$$\rho_s(\Gamma) = \exp[-H_e(\Gamma)/kT]\delta(< \Psi|\Psi > -1) \quad (2.13)$$

where the delta function expresses the additional condition of norm conservation of the wave-function. Thus under ergodic conditions the time average of a generic quantum observable $O(\mathbf{q})$ within E dynamics is equal to:

$$< O >_{Ehr} = \frac{\int_{<\Psi|\Psi>=1} d^nq\ d^Na\ d^Nb < \Psi|O(\mathbf{q})|\Psi > \exp[-(< \Psi|H(\mathbf{q})|\Psi > + V(\mathbf{q}))/kT]}{\int_{<\Psi|\Psi>=1} d^nq\ d^Na\ d^Nb \exp[-(< \Psi|H(\mathbf{q})|\Psi > + V(\mathbf{q}))/kT]} \quad (2.14)$$

2.2 Car-Parrinello dynamics

In CP dynamics the wave-function is treated as a classical field moved accordingly to the classical Lagrangian:

$$\mathcal{L} = \mu < \dot{\Psi}|\dot{\Psi} > -U_{CP} + \lambda(< \Psi|\Psi > -1) \quad (2.15)$$

with

$$U_{CP} =< \Psi|H(\mathbf{q})|\Psi > +V(\mathbf{q}) + \sum_i \frac{1}{2}\frac{\mathbf{p}_i^2}{m_i} \tag{2.16}$$

where the fictitious mass μ characterizes the response of the wave-function to an applied force and the Lagrangian multiplier λ represents the (holonomic) constraint of normalization. From this Lagrangian we obtain again Eqs. (2.1) and (2.2) for the motion of canonical $\mathbf{q}_i$ and $\mathbf{p}_i$ coordinates whereas the Schroedinger equation (2.3) is replaced with:

$$\mu|\ddot{\Psi} >= -H(\mathbf{q})|\Psi > +\lambda|\Psi > \tag{2.17}$$

The conserved energy in this dynamics is:

$$E_{CP} = \mu < \dot{\Psi}|\dot{\Psi} > + < \Psi|H(\mathbf{q})|\Psi > +V(\mathbf{q}) + \sum_i \frac{1}{2}\frac{\mathbf{p}_i^2}{m_i} \tag{2.18}$$

In CP system the wave-function can be considered real, thus, being $(|j>)_{j=1,\ldots,N}$ a real basis, the state of the *'quantum'* subsystem is uniquely specified by the vector $\mathbf{Y} = (a_j, p_{a_j})_j$, where $p_{a_j} = 2\mu\dot{a}_j$ are the classical canonical momenta associated to the variables a_j. All degrees of freedom are classical and the the classical canonical $\rho(\mathbf{q},\mathbf{p},\mathbf{Y}) = -exp(-E_{CP}/kT)$, defined on the space $(\mathbf{q},\mathbf{p},\mathbf{Y})$, can be used directly to calculate the averages. Thus the average of a quantum observable $O(\mathbf{q})$ with no dependence on $\mathbf{p}$ and on $\mathbf{p_a}$, is given by

$$< O >_{CP}= \frac{\int_{<\Psi|\Psi>=1} d^nq\, d^Na \; < \Psi|O(\mathbf{q})|\Psi > \exp[-(< \Psi|H(\mathbf{q})|\Psi > +V(\mathbf{q}))/kT]}{\int_{<\Psi|\Psi>=1} d^nq\; d^Na \exp[-(< \Psi|H(\mathbf{q})|\Psi > +V(\mathbf{q}))/kT]} \tag{2.19}$$

This expression is identical to the (2.14), however, since in this case the wave-function is real, the integration is restricted to the $\mathbf{a}$ variables only. Also in this case to get this canonical distribution in a finite system we can apply a thermostat on the classical $(\mathbf{p},\mathbf{q})$ subsystem. Following the treatment of the previous section it is easy to recover expression (2.19).

2.3 Correct quantum-classical averages

To get the correct expression for mixed quantum-classical system we start treating all the degrees of freedom quantum-mechanically, obtaining for the average of quantum observable $O(\mathbf{q})$:

$$< O >_{full-quantum} = \frac{Tr_{\{|j>\}\otimes\{|\mathbf{q}>\}}[O(\mathbf{q})\exp[-(H(\mathbf{q})+V(\mathbf{q}))/kT]]}{Tr_{\{|j>\}\otimes\{|\mathbf{q}>\}}[\exp[-(H(\mathbf{q})+V(\mathbf{q}))/kT]]} \tag{2.20}$$

where the trace is performed on product of Hilbert spaces $\{|j>\}$ and $\{|\mathbf{q}>\}$. Under the assumption that the classical limit $[\mathbf{p}_i, \mathbf{q}_i] = 0$ applies Eq. (2.20) becomes:

$$< O >_{exa} = \frac{\int d^n q\, Tr[O(\mathbf{q})\exp[-(H(\mathbf{q})+V(\mathbf{q}))/kT]]}{\int d^n q\, Tr[\exp[-(H(\mathbf{q})+V(\mathbf{q}))/kT]]} \tag{2.21}$$

where the trace is performed on the $\{|j>\}$ space only. The canonical averages in both E and CP dynamics are different from this correct expectation value. In CP and E averages the wave-function appears in the exponent and the trace of Eq. (2.21) is replaced by a continuous integration, which misses the discreteness of quantum subspace. It is thus no surprise that a quantum subsystem described by Eqs. (2.14) and (2.19) actually behaves as a classical one. For instance, for T going to zero, the quadratic form in the exponent of E and CP canonical averages originates a behavior equivalent to $(2N-2)$ or to $(N-1)$ *classical* linear oscillators, respectively.

We now observe that it is the form of the conserved energy E_{Ehr}, E_{CP} in microcanonical dynamics which produces a wrong statistical behavior of a quantum sub-system. In Eqs. (2.4), (2.18), when $|\Psi>$ is given by a linear superposition of eigenstates $|\phi_j(\mathbf{q})>$ corresponding to the eigenenergies $E_j(\mathbf{q})$, the energy is conserved only on average and the mixed motion does not explore the correct microcanonical ensemble, where *energy has to be conserved exactly as in a full quantum treatment.*

2.4 Modified CP dynamics

Eqs. (2.14) (2.19) would yield the correct statistical distribution, if the wavefunction $|\Psi>$ *could be constrained to visit only the discrete set of eigenvectors of the Hamiltonian instead of running continuously over all their possible linear combinations.* This suggests that a possible way of obtaining the correct distribution, without performing a full quantum treatment, consists in adding a fictitious constraining potential U_f to the potential U_{CP} in CP dynamics, which favorites the configuration corresponding to the quantum Hamiltonian eigenstates. For instance such a potential can be of the form:

$$U_f(\mathrm{q},\mathrm{X}) = \eta[<\Psi|H^2(\mathrm{q})|\Psi> - <\Psi|H(\mathrm{q})|\Psi>^2] \qquad (2.22)$$

where η is a positive coupling constant. This potential has the property of being a positive definite quantity which vanishes only at eigenstates. In the limit of large η the resulting modified CP dynamics mimics the level quantization of the true quantum spectrum in terms of a classical motion consisting of a succession of activated jumps between the valleys of the total potential $U_{CP}+U_f$. To get the canonical average of this modified CP dynamics we add in the exponents of Eq. (2.19) the fictitious potential U_f. In the limit of large η we can expand quadratically the potential around the Hamiltonian eigenstate and perform the gaussian integrations. The resulting average takes the form of a sum over independent 'valleys' E_i yielding:

$$<O>_{modCP} = \frac{\int d^n q \sum_i <\phi_i(\mathrm{q})|O(\mathrm{q})|\phi_i(\mathrm{q})> \exp[-(E_i(\mathrm{q})+V(\mathrm{q}))/kT]|Det_{\phi_i}|^{-1}}{\int d^n q \sum_i \exp[-(E_i(\mathrm{q})+V(\mathrm{q}))/kT]|Det_{\phi_i}|^{-1}} \qquad (2.23)$$

where $|\phi_i(\mathrm{q})>$ are the eigenstates of $H(\mathrm{q})$, with eigenvalues $E_i(\mathrm{q})$, and Det_{ϕ_i} is the determinant of the operator $H - <\phi_i|H|\phi_i> = H - E_i$ in the space orthogonal to $|\phi_i>$. The determinant accounts for the difference between distinct valleys caused by the unequal spacing of the energy levels. Eq. (2.23) recovers the discreteness of the quantum spectrum but the *Det* factors modify the weight of the different eigenstates. It follows that an *exact* expression for the average can be obtained from the weighted average $< O|Det_{\Psi}| >_{modCP} \; / < |Det_{\Psi}| >_{modCP}$. Although exact in principle, this average may not be easy to implement, since knowledge of the determinant implies knowledge of the spectrum of H. However, it is a nontrivial result, since any a-priori information and/or reasonable approximation for this determinant will automatically produce a valuable approximation to the exact quantum average.

Chapter 3

Simulation on model system

3.1 The model system

In order to verify the results of the previous chapter we have applied the above theory to a simple mixed system consisting of a two-level quantum Hamiltonian coupled to a chain of n classical one-dimensional anharmonic oscillators with masses $m_i = 1$ and potential

$$V(\mathbf{q}) = c(1)q_1^4 + \sum_{i=2}^{n} c(i)(q_i - q_{i-1})^4 \tag{3.1}$$

The quantum Hamiltonian is given by:

$$H(\mathbf{q}) = \Delta|\phi(\mathbf{q}) >< \phi(\mathbf{q})| \tag{3.2}$$

where Δ is a constant energy gap and

$$|\phi(\mathbf{q}) >= \sin(q_n - q_{n-1})|1 > + \cos(q_n - q_{n-1})|2 > \tag{3.3}$$

To enforce thermal equilibration the classical oscillators are coupled to a Nosé thermostat of mass Q. We have considered three different dynamics for the mixed system, namely E, CP, and modified CP dynamics, respectively. If the system is ergodic the time averages will coincide with the canonical averages calculated in the previous chapter. The non linearity of the classical potential and the different coefficients $c(i)$ guarantee ergodicity also in a small system. Thus the number n of classical non-linear oscillators was taken equal to 5 after numerically verifying that in this case the system is sufficiently ergodic. To ensure rapid thermalization the frequencies of the wave-function dynamics, of the classical oscillators and of the thermostat must be comparable. This was achieved in E and CP dynamics by choosing $m_i = \Delta = \mu = 1$, $c(i)$ randomly distributed between .5 and 1.5, and $Q = nkT$. In the case of modified CP dynamics we used $\eta = 50$ and scaled by this value the $c(i)$ coefficients and all the masses, i.e. m_i, Q,μ. The potential U_f was cutoff at the value $5kT$ in order to allow the system to cross the barrier separating the two valleys of $U_f + U_{CP}$ for a sufficient number of times during a numerical dynamical simulation.

3.2 Results of the simulations

In our model system the canonical averages deduced in the previous chapter are easily evaluated, either analytically or in terms of simple one-dimensional integrals. For instance, the exact average energy of the two-level quantum system is given by:

$$< H(\mathrm{q}) >_{exa} = \frac{\Delta \exp(-\Delta/kT)}{1 + \exp(-\Delta/kT)} \tag{3.4}$$

while for E and CP dynamics we get:

$$< H(\mathrm{q}) >_{Ehr} = kT - \frac{\Delta \exp(-\Delta/kT)}{1 - \exp(-\Delta/kT)} \tag{3.5}$$

$$< H(\mathrm{q}) >_{CP} = \frac{\int_0^{2\pi} d\theta \sin^2\theta \, \Delta \exp(-\sin^2\theta \, \Delta/kT)}{\int_0^{2\pi} d\theta \exp(-\sin^2\theta \, \Delta/kT)} \tag{3.6}$$

Notice that for a two-level quantum system with fixed gap Δ the determinant Det_{ϕ_i} is just a constant that factorizes out. Thus in this case the averages in the modified CP dynamics with $\eta \to \infty$ coincide with the exact results also without the determinant corrections. In the case of finite η and a cutoff potential the canonical distribution deviates slightly from the correct one, and can be calculated using eq. (2.19) with U_f added to the energy.

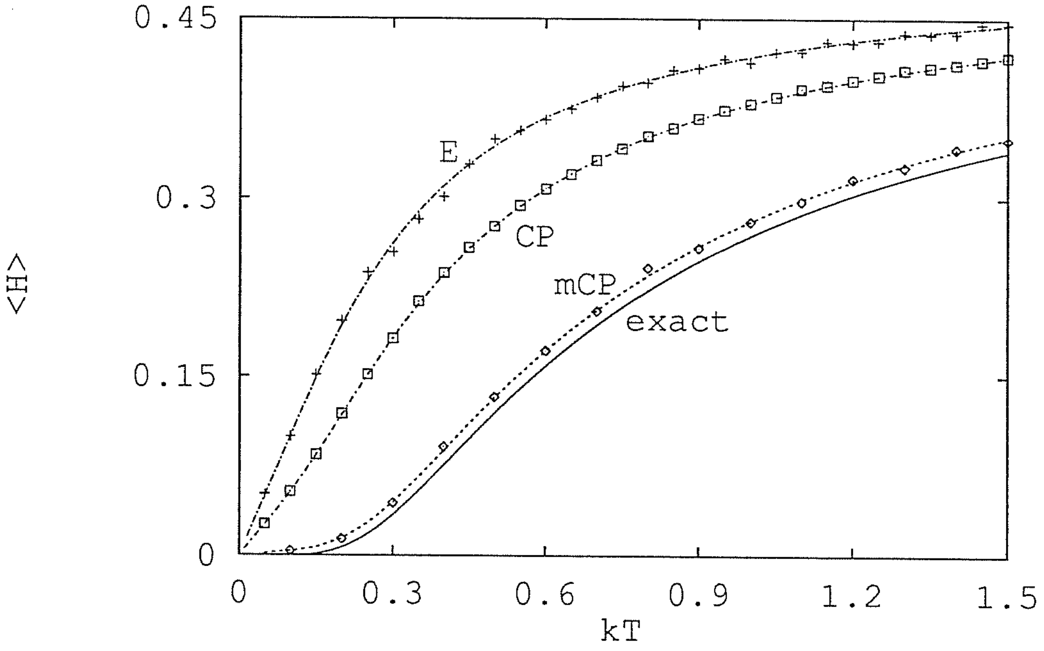

Figure 3.1: Average energy of the quantum two-level system vs. temperature. The curves have been calculated using the analytical distribution formulae. The dots refer to time averages using E, CP and modified CP equations of motions.

The canonical averages for energy vs. T corresponding to the four cases discussed above are reported as lines in Fig. (3.1). We observe that the thermal distribution within E or CP dynamics is very different from the exact one, particularly at low T where the characteristic quantum exponential behaviour is replaced by a classical linear behaviour in both the E and the CP cases. On the contrary, the modified CP dynamics originates a thermal distribution which is very close to the exact one already with the finite U_f potential used in the present calculation[11].

We now perform 'molecular dynamics' simulations to compute average energies by means of time averages using the E, CP, and modified CP equations of motion. The results are again reported in Fig. (3.1) as points. Firstly, we notice that the results of the time averages agree perfectly with those obtained directly from the canonical distribution formulae. This provides a striking demonstration of the validity of the Nosé-Hoover procedure to compute canonical averages also in the present rather unconventional situation. Secondly, it might seem that, when considering systems more complex than the present one, the large η values, that are required to recover the correct quantum equilibrium distribution in terms of classical modified CP dynamics, would necessitate prohibitively long simulation times to achieve thermal equilibration. Luckily this is not the case since, in realistic systems, the gap between different eigenstates depends on the instantaneous configuration, and transitions between different BO surfaces basically occur at level crossings, where the barrier separating different valleys is very small

3.3 Conclusion

In summary, we have presented an analysis of the thermal equilibrium properties of mixed quantum-classical systems described by different dynamics. In particular, we have found that it is possible to reproduce the thermal equilibrium distribution of a *quantum* subsystem by an appropriate *classical* dynamics, which exploits the notion of a fictitious constraining potential to mimic the discrete character of a quantum spectrum. This idea is now being pursued in applications to more realistic systems. It would be very interesting if modified CP dynamics could also serve to simulate non-adiabatic dynamic processes. This would be possible if the classical hopping probability between different valleys within modified CP dynamics could reproduce the quantum transition probability between different eigenstates.

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