

### 1. Basis sets, energy, superpositions, and transformations

$$|\Psi\rangle = |\psi_{adi}\rangle C_{adi} = |\psi_{dia}\rangle C_{dia}, \quad (1.1)$$

Where the coefficients  $C_{adi}$  and  $C_{dia}$  are the amplitudes. They represent the (time- or representation-dependent) “populations”.

In the following derivations, we assume a vector-matrix notation, so that  $|\psi\rangle = (\psi_1, \psi_2, \dots, \psi_N)$ .

Likewise, the amplitudes are the column-vectors:  $C = (c_1, c_2, \dots, c_N)^T$ , so that  $|\psi_{adi}\rangle C_{adi}$  is essentially a scalar product:  $|\psi_{adi}\rangle C_{adi} = \sum_i \psi_i C_{adi,i}$ .

Let us also assume that the diabatic basis is not orthonormal, so:

$$\langle \psi_{dia} | \psi_{dia} \rangle = S. \quad (1.2)$$

Denote the transformation between the two basis sets by the transformation matrix  $U$  (not necessarily a unitary one):

$$|\psi_{adi}\rangle = |\psi_{dia}\rangle U \quad (1.3)$$

To satisfy Eq. 1.1, the amplitudes should relate to each other correspondingly:

$$C_{dia} = U C_{adi} \leftrightarrow C_{adi} = U^{-1} C_{dia}. \quad (1.4)$$

We also assume that the adiabatic basis is orthonormal:

$$\langle \psi_{adi} | \psi_{adi} \rangle = U^+ \langle \psi_{dia} | \psi_{dia} \rangle U = U^+ S U = I \quad (1.5)$$

The total electronic energy (Ehrenfest) of the system is given by the Hamiltonian expectation value on the superposition Eq. 1.1. In the adiabatic basis, it will be:

$$E_{tot} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{C_{adi}^+ H_{adi} C_{adi}}{C_{adi}^+ C_{adi}} = \frac{C_{dia}^+ H_{dia} C_{dia}}{C_{dia}^+ S C_{dia}}, \quad (1.6)$$

Here, we introduced the matrix elements of the electronic Hamiltonian operator in the two bases:

$$H_{adi} = \langle \psi_{adi} | H | \psi_{adi} \rangle. \quad (1.7)$$

$$H_{dia} = \langle \psi_{dia} | H | \psi_{dia} \rangle. \quad (1.8)$$

Using, Eqs. 1.3, 1.7, and 1.8, we can see that:

$$H_{adi} = U^+ H_{dia} U = \tilde{H}_{dia}. \quad (1.9)$$

Here, the tilde-notation is used to represent a similarity transformation:

$$\tilde{X} = U^+ X U. \quad (1.10)$$

## 2. The stationary (time-independent) variational principle and stationary Schrodinger equation

To determine the adiabatic eigenfunctions, one minimizes the total energy with respect to the variations of the diabatic-to-adiabatic transformation matrix:

$$\delta E_{tot} = \delta \left[ \frac{C_{adi}^+ U^+ H_{dia} U C_{adi}}{C_{adi}^+ U^+ S U C_{adi}} \right] = \frac{(C_{adi}^+ \delta U^+ H_{dia} U C_{adi} + C_{adi}^+ U^+ H_{dia} \delta U C_{adi})(C_{adi}^+ U^+ S U C_{adi}) - (C_{adi}^+ U^+ H_{dia} U C_{adi})(C_{adi}^+ \delta U^+ S U C_{adi} + C_{adi}^+ U^+ S \delta U C_{adi})}{|C_{adi}^+ U^+ S U C_{adi}|^2} = 0 \quad (2.1)$$

Which leads to:

$$H_{dia} U = S U H_{adi}. \quad (2.2)$$

Or, equivalently, to:

$$H |\psi_{adi}\rangle = |\psi_{adi}\rangle H_{adi}. \quad (2.3)$$

Indeed, projecting Eq. 2.3 onto the diabatic basis yields:

$$\langle \psi_{dia} | H | \psi_{adi} \rangle = \langle \psi_{dia} | \psi_{adi} \rangle H_{adi}. \quad (2.4a)$$

$$\langle \psi_{dia} | H | \psi_{dia} \rangle U = \langle \psi_{dia} | \psi_{dia} \rangle U H_{adi}. \quad (2.4b)$$

$$H_{dia} U = S U H_{adi}. \quad (2.4c)$$

## 3. Adiabatic and diabatic derivative couplings

Define the derivative couplings:

$$D_{adi} \equiv \langle \psi_{adi} | \nabla \psi_{adi} \rangle, \quad (3.1)$$

$$D_{dia} \equiv \langle \psi_{dia} | \nabla \psi_{dia} \rangle \quad (3.2)$$

The two are related by:

$$D_{adi} = U^+ \langle \psi_{dia} | \nabla \psi_{dia} \rangle U + U^+ \langle \psi_{dia} | \psi_{dia} \rangle \nabla U = U^+ D_{dia} U + U^+ S \nabla U. \quad (3.3a)$$

Or using the transformation Eq. 1.10:

$$D_{adi} = \tilde{D}_{dia} + U^+ S \nabla U. \quad (3.3b)$$

Note the symmetries:

$$D_{adi} + D_{adi}^+ = 0 \rightarrow D_{adi}^+ = -D_{adi} \quad (3.4)$$

which comes from the orthogonality of the adiabatic states, Eq. 1.5.

$$D_{dia}^+ + D_{adi} = \nabla S. \quad (3.5)$$

Which originates, analogously, from Eq. 1.2

#### 4. General relationship between the derivatives of the adiabatic and diabatic properties

Lets differentiate Eqs. 2.2:

$$\nabla H_{dia} U + H_{dia} \nabla U = \nabla S U H_{adi} + S \nabla U H_{adi} + S U \nabla H_{adi}, \quad (4.1)$$

Multiply both sides by  $U^+$ :

$$U^+ \nabla H_{dia} U = -U^+ H_{dia} \nabla U + U^+ \nabla S U H_{adi} + U^+ S \nabla U H_{adi} + U^+ S U \nabla H_{adi}, \quad (4.2a)$$

Using Eq. 1.5:

$$U^+ \nabla H_{dia} U = -U^+ H_{dia} \nabla U + U^+ \nabla S U H_{adi} + U^+ S \nabla U H_{adi} + \nabla H_{adi}, \quad (4.2b)$$

Using Eq. 2.4c:

$$U^+ \nabla H_{dia} U = -H_{adi} U^+ S \nabla U + U^+ \nabla S U H_{adi} + U^+ S \nabla U H_{adi} + \nabla H_{adi}, \quad (4.2c)$$

Or

$$U^+ \nabla H_{dia} U - (U^+ \nabla S U) H_{adi} = \nabla H_{adi} + (U^+ S \nabla U) H_{adi} - H_{adi} (U^+ S \nabla U), \quad (4.3d)$$

Using Eq. 3.3b:

$$U^+ \nabla H_{dia} U - (U^+ \nabla S U) H_{adi} = \nabla H_{adi} + (D_{adi} - U^+ D_{dia} U) H_{adi} - H_{adi} (D_{adi} - U^+ D_{dia} U), \quad (4.4a)$$

Rearranging terms:

$$U^+ \nabla H_{dia} U - (U^+ \nabla S U) H_{adi} + (U^+ D_{dia} U H_{adi} - H_{adi} U^+ D_{dia} U) = \nabla H_{adi} + (D_{adi} H_{adi} - H_{adi} D_{adi}). \quad (4.4b)$$

Using the condition, Eq. 3.5, we can simplify a part of the left-hand side:

$$\begin{aligned} -(U^+ \nabla S U) H_{adi} + (U^+ D_{dia} U H_{adi} - H_{adi} U^+ D_{dia} U) &= -U^+ D_{dia} U H_{adi} - U^+ D_{dia}^+ U H_{adi} + \\ (U^+ D_{dia} U H_{adi} - H_{adi} U^+ D_{dia} U) &= -U^+ D_{dia}^+ U H_{adi} - H_{adi} U^+ D_{dia} U. \end{aligned} \quad (4.5)$$

Then, keeping in mind the property Eq. 3.4 and the transformation Eq. 1.10, we arrive at:

$$U^+ \nabla H_{dia} U - (\tilde{D}_{dia}^+ H_{adi} + H_{adi} \tilde{D}_{dia}) = \nabla H_{adi} - (D_{adi}^+ H_{adi} + H_{adi} D_{adi}). \quad (4.6)$$

This equation can be written in a more compact and symmetric form:

$$\widetilde{\nabla H_{dia}} - (\tilde{D}_{dia}^+ \tilde{H}_{dia} + \tilde{H}_{dia} \tilde{D}_{dia}) = \nabla H_{adi} - (D_{adi}^+ H_{adi} + H_{adi} D_{adi}). \quad (4.7)$$

It makes much sense, because if the two bases are the same (the eigenvectors are trivial:  $U = I$ ), Eq. 4.7 becomes an identity.

These equations can be derived in another way. Lets differentiate Eq. 1.7:

$$\nabla \langle \psi_{adi} | H | \psi_{adi} \rangle = \nabla H_{adi} = \langle \nabla \psi_{adi} | H | \psi_{adi} \rangle + \langle \psi_{adi} | \nabla H | \psi_{adi} \rangle + \langle \psi_{adi} | H | \nabla \psi_{adi} \rangle, \quad (4.8a)$$

Using Eq. 2.3 and the definition Eq. 3.1:

$$\nabla H_{adi} = D_{adi}^+ H_{adi} + \langle \psi_{adi} | \nabla H | \psi_{adi} \rangle + H_{adi} D_{adi}, \quad (4.8b)$$

In other words, the right-hand side of Eq. 4.7 is nothing but:

$$\langle \psi_{adi} | \nabla H | \psi_{adi} \rangle = \nabla H_{adi} - (D_{adi}^+ H_{adi} + H_{adi} D_{adi}). \quad (4.9)$$

Likewise, lets differentiate Eq. 1.8:

$$\nabla \langle \psi_{dia} | H | \psi_{dia} \rangle = \nabla H_{dia} = \langle \nabla \psi_{dia} | H | \psi_{dia} \rangle + \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle + \langle \psi_{dia} | H | \nabla \psi_{dia} \rangle, \quad (4.10)$$

Lets apply the transformation Eq. 1.10 to both sides of Eq. 4.9a:

$$U^+ \nabla H_{dia} U = U^+ \langle \nabla \psi_{dia} | H | \psi_{dia} \rangle U + U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U + U^+ \langle \psi_{dia} | H | \nabla \psi_{dia} \rangle U, \quad (4.11)$$

By Eq. 1.3:

$$U^+ \nabla H_{dia} U = U^+ \langle \nabla \psi_{dia} | H | \psi_{adi} \rangle + U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U + \langle \psi_{adi} | H | \nabla \psi_{dia} \rangle U, \quad (4.12a)$$

So:

$$U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U = U^+ \nabla H_{dia} U - (U^+ \langle \nabla \psi_{dia} | H | \psi_{adi} \rangle + \langle \psi_{adi} | H | \nabla \psi_{dia} \rangle U), \quad (4.12b)$$

$$U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U = U^+ \nabla H_{dia} U - (U^+ \langle \nabla \psi_{dia} | \psi_{adi} \rangle H_{adi} + H_{adi} \langle \psi_{adi} | \nabla \psi_{dia} \rangle U), \quad (4.12c)$$

$$U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U = U^+ \nabla H_{dia} U - (U^+ D_{dia}^+ U H_{adi} + H_{adi} U^+ D_{dia} U), \quad (4.12e)$$

By Eq. 1.9 and 1.10:

$$U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U = \widetilde{\nabla H_{dia}} - (\widetilde{D}_{dia}^+ \widetilde{H}_{dia} + \widetilde{H}_{dia} \widetilde{D}_{dia}), \quad (4.12f)$$

Thus, the left-hand side of Eq. 4.7 is nothing but:

$$U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U = \langle \psi_{adi} | \nabla H | \psi_{adi} \rangle. \quad (4.13)$$

Comparing Eqs. 4.12f and 4.9, one arrives at Eqs. 4.6 and 4.7

## 5. Derivatives of the total electronic energy

Lets' compute the derivatives of the expectation value of the Hamiltonian on the arbitrary (not necessarily normalized) wavefunction, Eq. 1.1:

$$F = -\nabla E_{tot} = -\nabla \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = -\frac{\langle \Psi | \Psi \rangle \nabla [\langle \Psi | H | \Psi \rangle] - \langle \Psi | H | \Psi \rangle \nabla [\langle \Psi | \Psi \rangle]}{|\langle \Psi | \Psi \rangle|^2} \quad (5.1)$$

To proceed further, we'll need to make an assumption regarding the nature of the amplitudes that enter the basis-set expansion Eq. 1.1. In section 1, we have stated that these coefficients depend on time. But, they may also depend on the spatial coordinate. In fact, since the basis transformation matrix,  $U$ , generally depends on coordinates, Eq. 1.4 forces one of the sets of coefficients to be position-dependent. In practice, one may assume that once the representation (basis) is chosen, the corresponding wavefunction amplitudes of each basis function depend on time only. Indeed, this appear quite reasonable. However, such a construction makes sense only until one is not concerned with representation-invariance of the results.

Lets see how the difference in the dynamics arises from a (postulative) choice of whether to treat one of the coefficients position-dependent on position-independent. In both cases, we will assume the adiabatic coefficients (amplitudes) depend on time only (although, this is already one of the points of postulative formulation of the dynamics). Then, the force in the adiabatic basis is given by:

$$F = -C_{adi}^+ \frac{\nabla \langle \psi_{adi} | H | \psi_{adi} \rangle - E_{tot} \nabla \langle \psi_{adi} | \psi_{adi} \rangle}{\langle \Psi | \Psi \rangle} C_{adi} = -C_{adi}^+ \frac{\nabla \langle \psi_{adi} | H | \psi_{adi} \rangle}{\langle \Psi | \Psi \rangle} C_{adi} = C_{adi}^+ f_{adi} C_{adi}. \quad (5.2)$$

where:

$$f_{adi} \equiv -\frac{\nabla \langle \psi_{adi} | H | \psi_{adi} \rangle}{\langle \Psi | \Psi \rangle} = -\frac{1}{\langle \Psi | \Psi \rangle} \nabla H_{adi}. \quad (5.3)$$

### Case 1: Diabatic coefficients are position-independent

In the diabatic basis, the derivatives take the form:

$$F = -C_{dia}^+ \frac{\nabla [\langle \psi_{dia} | H | \psi_{dia} \rangle] - E_{tot} \nabla [\langle \psi_{dia} | \psi_{dia} \rangle]}{\langle \Psi | \Psi \rangle} C_{dia} = C_{dia}^+ f_{dia} C_{dia}, \quad (5.4)$$

with:

$$f_{dia} \equiv -\frac{1}{\langle \Psi | \Psi \rangle} [\nabla H_{dia} - E_{tot} \nabla S]. \quad (5.5)$$

Keeping in mind, Eq. 1.4, the following relationship should hold:

$$f_{adi} = U^+ f_{dia} U. \quad (5.6)$$

Keeping Eqs. 4.6, 4.7 in mind, Eq. 5.6 holds if the following condition is true:

$$-U^+ \nabla H_{dia} U + (\tilde{D}_{dia}^+ H_{adi} + H_{adi} \tilde{D}_{dia}) - (D_{adi}^+ H_{adi} + H_{adi} D_{adi}) = -U^+ [\nabla H_{dia} - E_{tot} \nabla S] U. \quad (5.7a)$$

$$(\tilde{D}_{dia}^+ H_{adi} + H_{adi} \tilde{D}_{dia}) - (D_{adi}^+ H_{adi} + H_{adi} D_{adi}) = U^+ E_{tot} \nabla S U. \quad (5.7b)$$

Using Eq. 3.3:

$$-(U^+ S \nabla U)^+ H_{adi} - H_{adi} (U^+ S \nabla U) = U^+ E_{tot} \nabla S U, \quad (5.7c)$$

This equation is not bound to be true.

### Case 2: Diabatic coefficients are position-dependent

The dependence is introduced via the transformation matrix  $U$ , according to Eq. 1.4.

So Eq. 5.2 becomes:

$$F = C_{dia}^+ f_{dia} C_{dia} - \frac{1}{\langle \Psi | \Psi \rangle} [\nabla C_{dia}^+ [H_{dia} - E_{tot} S] C_{dia} - C_{dia}^+ [H_{dia} - E_{tot} S] \nabla C_{dia}], \quad (5.8)$$

Using Eq. 1.4:

$$F = C_{dia}^+ f_{dia} C_{dia} - \frac{1}{\langle \Psi | \Psi \rangle} C_{dia}^+ (U^+)^{-1} \nabla U^+ [H_{dia} - E_{tot} S] C_{dia} - \frac{1}{\langle \Psi | \Psi \rangle} C_{dia}^+ [H_{dia} - E_{tot} S] \nabla U U^{-1} C_{dia}, \quad (5.9a)$$

$$F = C_{dia}^+ \left( f_{dia} - \frac{1}{\langle \Psi | \Psi \rangle} [(U^+)^{-1} \nabla U^+ [H_{dia} - E_{tot} S] - [H_{dia} - E_{tot} S] \nabla U U^{-1}] \right) C_{dia}. \quad (5.9b)$$

Introducing:

$$f'_{dia} \equiv \frac{1}{\langle \Psi | \Psi \rangle} [-\nabla H_{dia} + E_{tot} \nabla S - (U^+)^{-1} \nabla U^+ [H_{dia} - E_{tot} S] - [H_{dia} - E_{tot} S] \nabla U U^{-1}]. \quad (5.10)$$

Now we want to prove that:

$$f_{adi} = U^+ f'_{dia} U, \quad (5.11)$$

Indeed, the right-hand side of Eq. 5.11 becomes:

$$U^+ [-\nabla H_{dia} + E_{tot} \nabla S - (U^+)^{-1} \nabla U^+ [H_{dia} - E_{tot} S] - [H_{dia} - E_{tot} S] \nabla U U^{-1}] U, \quad (5.12a)$$

$$-U^+ \nabla H_{dia} U + E_{tot} U^+ \nabla S U - \nabla U^+ [H_{dia} - E_{tot} S] U - U^+ [H_{dia} - E_{tot} S] \nabla U, \quad (5.12b)$$

$$-U^+ \nabla H_{dia} U + E_{tot} (U^+ \nabla S U + \nabla U^+ S U + U^+ S \nabla U) - \nabla U^+ H_{dia} U - U^+ H_{dia} \nabla U, \quad (5.12c)$$

$$-U^+ \nabla H_{dia} U - \nabla U^+ H_{dia} U - U^+ H_{dia} \nabla U, \quad (5.12d)$$

$$-U^+ \nabla H_{dia} U - \nabla U^+ S U H_{adi} - H_{adi} U^+ S \nabla U, \quad (5.12e)$$

$$-U^+ \nabla H_{dia} U - \left[ (D_{adi} - \tilde{D}_{dia})^+ H_{adi} + H_{adi} (D_{adi} - \tilde{D}_{dia}) \right] = -\nabla H_{adi}, \quad (5.12f)$$

The last result originates from Eq. 4.6, 4.7. Thus, Eq. 5.11 holds and the dynamics is invariant with respect to the choice of representation.

## 6. Ehrenfest dynamics in adiabatic representation

Consider a quantum-classical Hamiltonian:

$$H_{qc} = T + E_{tot} = \sum_n \frac{p_n^2}{2m_n} + E_{tot}. \quad (6.1)$$

With the potential energy given by Eq. 1.6. Applying the Hamiltonian equations of motion, we obtain:

$$\dot{q}_n = \frac{\partial H_{qc}}{\partial p_n} = \frac{p_n}{m_n}, \quad (6.2)$$

$$\dot{p}_n = -\frac{\partial H_{qc}}{\partial q_n} = F_n = -C_{adi}^+ f_{adi} C_{adi}, \quad (6.3)$$

With the adiabatic force given by Eqs. 5.3.

The evolution of the electronic degrees of freedom is given by the TD-SE:

$$i\hbar \frac{\partial |\Psi\rangle}{\partial t} = H |\Psi\rangle. \quad (6.4)$$

Because  $\frac{\partial}{\partial t} = \sum_n \left[ \dot{q}_n \frac{\partial}{\partial q_n} + \dot{p}_n \frac{\partial}{\partial p_n} \right]$  and the basis wavefunctions do not depend on momentum, we obtain after the projection on the adiabatic states:

$$i\hbar \frac{\partial C_{adi}}{\partial t} = H_{adi} C_{adi} - i\hbar \sum_n D_{adi,n} \frac{p_n}{m_n} C_{adi}, \quad (6.5)$$

Which means:

$$\dot{C}_{adi} = -\frac{i}{\hbar} H_{adi} C_{adi} - \sum_n D_{adi,n} \frac{p_n}{m_n} C_{adi}, \quad (6.6)$$

$$\dot{C}_{adi}^+ = \frac{i}{\hbar} C_{adi}^+ H_{adi} + C_{adi}^+ \sum_n D_{adi,n} \frac{p_n}{m_n}. \quad (6.7)$$

Now, consider the time-derivative of the quantum-classical Hamiltonian, Eq. 6.1:

$$\frac{dH_{qc}}{dt} = \sum_n \left( \frac{\partial H_{qc}}{\partial q_n} \dot{q}_n + \frac{\partial H_{qc}}{\partial p_n} \dot{p}_n \right) + \dot{C}_{adi}^+ H_{adi} C_{adi} + C_{adi}^+ H_{adi} \dot{C}_{adi}, \quad (6.8a)$$

$$\begin{aligned} \frac{dH_{qc}}{dt} = \sum_n \left( \frac{\partial H_{qc}}{\partial q_n} \frac{p_n}{m_n} + \frac{\partial H_{qc}}{\partial p_n} \dot{p}_n \right) + \left[ \frac{i}{\hbar} C_{adi}^+ H_{adi} + C_{adi}^+ \sum_n D_{adi,n} \frac{p_n}{m_n} \right] H_{adi} C_{adi} + C_{adi}^+ H_{adi} \left[ -\frac{i}{\hbar} H_{adi} C_{adi} - \sum_n D_{adi,n} \frac{p_n}{m_n} C_{adi} \right], \end{aligned} \quad (6.8b)$$

$$\frac{dH_{qc}}{dt} = \sum_n C_{adi}^+ \frac{p_n}{m_n} (\nabla_{q_n} H_{adi} + \dot{p}_n) C_{adi} + C_{adi}^+ \sum_n (D_{adi,n} H_{adi} - H_{adi} D_{adi,n}) \frac{p_n}{m_n} C_{adi}, \quad (6.8c)$$

$$\frac{dH_{qc}}{dt} = \sum_n C_{adi}^+ \frac{p_n}{m_n} \left( \dot{p}_n + \nabla_{q_n} H_{adi} - (D_{adi,n}^+ H_{adi} + H_{adi} D_{adi,n}) \right) C_{adi}. \quad (6.8d)$$

If one assumes the nuclear dynamics is driven by Eqs. 6.2, 6.3, one arrives at:

$$\frac{dH_{qc}}{dt} = -C_{adi}^+ \sum_n \frac{p_n}{m_n} (D_{adi,n}^+ H_{adi} + H_{adi} D_{adi,n}) C_{adi}, \quad (6.9)$$

which implies the total energy, Eq. 6.1 is not conserved! It would be, provided the electronic coefficients do not change.

Instead, if one assumes that:

$$\dot{p}_n = f_n^{MF,adi} \equiv -\nabla_{q_n} H_{adi} + (D_{adi,n}^+ H_{adi} + H_{adi} D_{adi,n}) = -\langle \psi_{adi} | \nabla H | \psi_{adi} \rangle, \quad (6.10)$$

then the quantity, Eq. 5.1 is conserved.

Here, we have introduced a mean-field (Ehrenfest) force in the adiabatic representation.

Equation 6.10 is not derived from Eq. 6.1 using the classical Hamiltonian EOMs, Eqs. 6.2-6.3. Thus, the quantity Eq. 6.1 is NOT a Hamiltonian, but is just a CONSERVED QUANTITY, an INTEGRAL OF MOTION. It is naturally associated with a quantum-classical energy. As a consequence, the dynamics driven by Eqs. 6.2 and 6.10 (Ehrenfest dynamics in the adiabatic representation) is an example of non-Hamiltonian dynamics. The term in the parentheses in Eq. 6.10 is essentially an electronic friction.

Note, that the Ehrenfest forces do not originate from the Hellman-Feynman theorem directly.

## 7. Ehrenfest dynamics in diabatic representation

We start with the quantum-classical Hamiltonian, Eq. 6.1 and derive the Hamiltonian EOMs. Assuming the time-dependence of the diabatic coefficients, we have:

$$\dot{q}_n = \frac{\partial H_{qc}}{\partial p_n} = \frac{p_n}{m_n}, \quad (7.1)$$

$$\dot{p}_n = -\frac{\partial H_{qc}}{\partial q_n} = F_n = -C_{dia}^+ f'_{dia} C_{dia}, \quad (7.2)$$

Where  $f'_{dia}$  can be computed by inverting Eq. 5.6:

$$f'_{dia} = U S f_{adi} S U^+. \quad (7.3)$$

The TD-SE in the diabatic basis will be:

$$i\hbar S \frac{\partial C_{dia}}{\partial t} = H_{dia} C_{dia} - i\hbar \sum_n D_{dia,n} \frac{p_n}{m_n} C_{dia}, \quad (7.4)$$

Which means:

$$\dot{C}_{dia} = -\frac{i}{\hbar} S^{-1} H_{dia} C_{dia} - \sum_n S^{-1} D_{dia,n} \frac{p_n}{m_n} C_{dia}, \quad (7.5)$$

$$\dot{C}_{dia}^+ = \frac{i}{\hbar} C_{dia}^+ H_{dia} S^{-1} - C_{dia}^+ \sum_n D_{dia,n}^+ S^{-1} \frac{p_n}{m_n}. \quad (7.6)$$

Now, consider the time-derivative of the quantum-classical Hamiltonian, Eq. 6.1:

$$\frac{dH_{qc}}{dt} = \sum_n \left( \frac{\partial H_{qc}}{\partial q_n} \dot{q}_n + \frac{\partial H_{qc}}{\partial p_n} \dot{p}_n \right) + \dot{C}_{dia}^+ H_{dia} C_{dia} + C_{dia}^+ H_{dia} \dot{C}_{dia}, \quad (7.7a)$$

$$\begin{aligned} \frac{dH_{qc}}{dt} = \sum_n \left( \frac{\partial H_{qc}}{\partial q_n} \frac{p_n}{m_n} + \frac{\partial H_{qc}}{\partial p_n} \dot{p}_n \right) + \left[ \frac{i}{\hbar} C_{dia}^+ H_{dia} S^{-1} - C_{dia}^+ \sum_n D_{dia,n}^+ S^{-1} \frac{p_n}{m_n} \right] H_{dia} C_{dia} + \\ C_{dia}^+ H_{dia} \left[ -\frac{i}{\hbar} S^{-1} H_{dia} C_{dia} - \sum_n S^{-1} D_{dia,n} \frac{p_n}{m_n} C_{dia} \right], \end{aligned} \quad (7.7b)$$



$$\frac{dH_{qc}}{dt} = \sum_n \left( \frac{\partial H_{qc}}{\partial q_n} \frac{p_n}{m_n} + \frac{\partial H_{qc}}{\partial p_n} \dot{p}_n \right) - C_{dia}^+ \left[ \sum_n (D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n}) \frac{p_n}{m_n} \right] C_{dia}, \quad (7.7c)$$

If one assumes the dynamics driven by Eqs. 7.1, 7.2, one arrives at:

$$\frac{dH_{qc}}{dt} = \sum_n \left( C_{dia}^+ (f'_{dia,n} + \dot{p}_n) C_{dia} \frac{p_n}{m_n} \right) - C_{dia}^+ \left[ \sum_n (D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n}) \frac{p_n}{m_n} \right] C_{dia} \quad (7.7d)$$

and

$$\frac{dH_{qc}}{dt} = -C_{dia}^+ \left[ \sum_n (D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n}) \frac{p_n}{m_n} \right] C_{dia}. \quad (7.7e)$$

which implies the total energy, Eq. 6.1 will not be conserved!

Instead, if one assumes that:

$$\dot{p}_n = f_n^{MF,dia} \equiv f'_{dia,n} + (D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n}), \quad (7.8)$$

then the quantum-classical energy, Eq. 6.1, is conserved.

Lets look at  $U^+ f_{dia}^{MF} U$ . Using Eq. 5.11:

$$U^+ f_{dia}^{MF} U = f_{adi} + (U^+ D_{dia}^+ S^{-1} H_{dia} U + U^+ H_{dia} S^{-1} D_{dia} U), \quad (7.9a)$$

Using Eq. 2.2:

$$U^+ f_{dia}^{MF} U = f_{adi} + (U^+ D_{dia}^+ S^{-1} S U H_{adi} + H_{adi} U^+ S S^{-1} D_{dia} U), \quad (7.9b)$$

Simplifies to:

$$U^+ f_{dia}^{MF} U = f_{adi} + (U^+ D_{dia}^+ U H_{adi} + H_{adi} U^+ D_{dia} U), \quad (7.9c)$$

With the transformation Eq. 1.10:

$$U^+ f_{dia}^{MF} U = f_{adi} + (\tilde{D}_{dia}^+ \tilde{H}_{dia} + \tilde{H}_{dia} \tilde{D}_{dia}). \quad (7.10)$$