1. Basis sets, energy, superpositions, and transformations

$$|\Psi\rangle = |\psi_{adi}\rangle C_{adi} = |\psi_{dia}\rangle C_{dia}, \tag{1.1}$$

Where the coefficients C_{adi} and C_{dia} depend only on time (the amplitudes).

In the following derivations, we assume the 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.

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

$$\langle \psi_{dia}|\psi_{dia}\rangle = S. \tag{1.2}$$

The transformation between the basis functions is realized via the unitary matrix U:

$$|\psi_{adi}\rangle = |\psi_{dia}\rangle U \tag{1.3}$$

So in the adiabatic basis, the overlap matrix is the identity matrix:

$$\langle \psi_{adi}|\psi_{adi}\rangle = U^+\langle \psi_{dia}|\psi_{dia}\rangle U = U^+ S U = I \tag{1.4}$$

Note that there are many possible choices for the basis transformation matrix (e.g. $U = S^{-\frac{1}{2}}$ is the trivial choice). They all would diagonalize the overlap matrix. However, not all of them would diagonalize the electronic Hamiltonian.

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:

$$E_{tot} = \frac{\langle \Psi|H|\Psi\rangle}{\langle \Psi|\Psi\rangle} = \frac{C_{adi}^+\langle \psi_{adi}|H|\psi_{adi}\rangle C_{adi}}{C_{adi}^+\langle \psi_{adi}|\psi_{adi}\rangle C_{adi}} = \frac{C_{adi}^+ H_{adi} C_{adi}}{C_{adi}^+ C_{adi}}, \tag{1.5}$$

whereas in the diabatic basis, it is:

$$E_{tot} = \frac{\langle \Psi|H|\Psi\rangle}{\langle \Psi|\Psi\rangle} = \frac{C_{dia}^+\langle \psi_{dia}|H|\psi_{dia}\rangle C_{dia}}{C_{dia}^+\langle \psi_{dia}|\psi_{dia}\rangle C_{dia}} = \frac{C_{dia}^+ H_{dia} C_{dia}}{C_{dia}^+ S C_{dia}}. \tag{1.6}$$

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

$$H_{adi} = \langle \psi_{adi}|H|\psi_{adi}\rangle. \tag{1.7}$$

$$H_{dia} = \langle \psi_{dia}|H|\psi_{dia}\rangle. \tag{1.8}$$

One can relate the two equations Eq. 1.5 and 1.6 by:

$$E_{tot} = \frac{C_{adi}^+ U^+ H_{dia} U C_{adi}}{C_{adi}^+ U^+ S U C_{adi}} = \frac{C_{dia}^+ H_{dia} C_{dia}}{C_{dia}^+ S C_{dia}}, \tag{1.9}$$

From where, it follows that:

$$C_{dia} = U C_{adi} \leftrightarrow C_{adi} = U^{-1} C_{dia}. \tag{1.10}$$

2. The stationary (time-independent) variational principle

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

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

$$(2.1)$$

Which leads to:

$$H_{dia} U = S U H_{adi}. \tag{2.2}$$

Or, equivalently, to:

$$H |\psi_{adi}\rangle = |\psi_{adi}\rangle H_{adi}. \tag{2.3}$$

That is the adiabatic basis is composed of the eigenfunctions of the time-independent Hamiltonian. Projecting the right and left hand sides of Eq. 2.3 onto the adiabatic basis and keeping in mind Eq. 1.4, and the definition Eq. 1.5, one obtains:

$$\langle \psi_{adi} | H | \psi_{adi} \rangle = \langle \psi_{adi} | \psi_{adi} \rangle H_{adi}. \tag{2.4}$$

Projecting Eq. 2.3 to the diabatic basis, leads to Eq. 2.2.

We can also introduce a unitary transformation of the diabatic Hamiltonian. Using Eq. 1.4, one can show that it converts the diabatic Hamiltonian into the adiabatic:

$$U^+ H_{dia} U = U^+ S U H_{adi} = H_{adi}, \tag{2.5}$$

This is also consistent with the definitions Eq. 1.3, 1.7, and 1.8:

$$U^+ H_{dia} U = U^+ \langle \psi_{dia} | H | \psi_{dia} \rangle U = \langle \psi_{adi} | H | \psi_{adi} \rangle = H_{adi}. \tag{2.6}$$

TO DO: To go beyond Ehrenfest, one would need to consider a variation of the basis amplitudes, alongside the states themselves. One also would need to apply the time-dependent variational principle (different quantity being varied).

3. The Ehrenfest forces, derivative couplings

Lets' compute the Ehrenfest (also known as the mean field, MF) forces, which are defined as the derivatives of the expectation value of the Hamiltonian on the normalized wavefunction:

$$F = -\nabla E_{tot} = -\nabla \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = -\frac{\langle \Psi | \Psi \rangle \nabla [\langle \Psi | H | \Psi \rangle] - \langle \Psi | H | \Psi \rangle \nabla [\langle \Psi | \Psi \rangle]}{|\langle \Psi | \Psi \rangle|^2} \tag{3.1}$$

For our purposes, we will assume the overall wavefunction normalized for all time, so:

$$F = -[\nabla \langle \Psi | H | \Psi \rangle - H_{adi} \nabla \langle \Psi | \Psi \rangle] = -[\langle \nabla \Psi | H | \Psi \rangle + \langle \Psi | \nabla H | \Psi \rangle + \langle \Psi | H | \nabla \Psi \rangle] + H_{adi} \nabla \langle \Psi | \Psi \rangle = C_{adi}^+ f_{adi} C_{adi} = C_{dia}^+ f_{dia} C_{dia}. \tag{3.2}$$

Here, we introduced the forces in the two bases:

$$f_{adi} = -\nabla H_{adi} = -[\langle \nabla \psi_{adi} | H | \psi_{adi} \rangle + \langle \psi_{adi} | \nabla H | \psi_{adi} \rangle + \langle \psi_{adi} | H | \nabla \psi_{adi} \rangle]. \tag{3.3}$$

$$f_{dia} = -[\nabla H_{dia} - H_{adi} \nabla S] = -[\langle \nabla \psi_{dia} | H | \psi_{dia} \rangle + \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle + \langle \psi_{dia} | H | \nabla \psi_{dia} \rangle - H_{adi} \nabla S]. \tag{3.4}$$

The definitions Eqs. 3.3 and 3.3 come from the assumption in Eq. 1.1.

Define the derivative couplings:

$$D_{adi} \equiv \langle \psi_{adi} | \nabla \psi_{adi} \rangle, \tag{3.5}$$

$$D_{dia} \equiv \langle \psi_{dia} | \nabla \psi_{dia} \rangle \tag{3.6}$$

Note the symmetries:

$$D_{adi} + D_{adi}^+ = 0 \rightarrow D_{adi}^+ = -D_{adi} \tag{3.7}$$

which comes from the orthogonality of the adiabatic states, Eq. 1.4.

$$D_{dia}^+ + D_{adi} = \nabla S. \tag{3.8}$$

Using Eq. 2.3, we can simplify Eq. 3.3:

$$f_{adi} = -[\langle \psi_{adi} | \nabla H | \psi_{adi} \rangle + (D_{adi}^+ H_{adi} + H_{adi} D_{adi})] = -\langle \psi_{adi} | \nabla H | \psi_{adi} \rangle + (D_{adi} H_{adi} - H_{adi} D_{adi}) = -\nabla H_{adi} \tag{3.9}$$

Recall that the matrix H_{adi} is diagonal (containing the adiabatic energies). Thus, the matrices f_{adi} are also diagonal – these are essentially the state-specific adiabatic forces.

Rearranging the terms in Eq. 3.9, we obtain:

$$\nabla H_{adi} + (D_{adi} E - E D_{adi}) = \langle \psi_{adi} | \nabla H | \psi_{adi} \rangle = U^+ \langle \psi_{dia} | \nabla H | \psi_{dia} \rangle U. \tag{3.10}$$

Which determines the computational scheme for computing the adiabatic forces and nonadiabatic couplings. It is important to note that the ∇H_{adi} constitutes only the diagonal terms of $\langle \psi_{adi}|\nabla H|\psi_{adi}\rangle$ whereas the matrix $DE - ED$ has zeroes on its diagonal, so it corresponds to the off-diagonal elements of the $\langle \psi_{adi}|\nabla H|\psi_{adi}\rangle$ matrix.

4. Relationship between adiabatic and diabatic derivative couplings and forces

Lets first look at the relationship between the derivative couplings in the two representations, Eqs. 3.5, 3.6:

$$D_{adi} \equiv \langle \psi_{adi}|\nabla \psi_{adi}\rangle = U^+\langle \psi_{dia}|\nabla \psi_{dia}\rangle U + U^+\langle \psi_{dia}|\psi_{dia}\rangle \nabla U = U^+ D_{dia}U + U^+ S\nabla U. \qquad (4.1)$$

Lets differentiate Eqs. 2.2:

$$\nabla H_{dia}U + H_{dia}\nabla U = \nabla SUH_{adi} + S\nabla UH_{adi} + SU\nabla H_{adi}, \qquad (4.2)$$

Multiply both sides by U^+:

$$U^+\nabla H_{dia}U = -U^+ H_{dia}\nabla U + U^+\nabla SUH_{adi} + U^+ S\nabla UH_{adi} + U^+ SU\nabla H_{adi}, \qquad (4.3a)$$
$$U^+\nabla H_{dia}U = -U^+ H_{dia}\nabla U + (U^+\nabla SU + U^+ S\nabla U)H_{adi} + \nabla H_{adi}, \qquad (4.3b)$$

$$U^+\nabla H_{dia}U = -H_{adi}U^+ S\nabla U + (U^+\nabla SU + U^+ S\nabla U)H_{adi} + \nabla H_{adi}, \qquad (4.3c)$$

Or

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

Now, using Eq. 4.1:

$$U^+\nabla H_{dia}U - (U^+\nabla SU)H_{adi} = \nabla H_{adi} + (D_{adi} - U^+ D_{dia}U)H_{adi} - H_{adi}(D_{adi} - U^+ D_{dia}U), \qquad (4.4)$$

Or, finally:

$$U^+\nabla H_{dia}U - (U^+\nabla SU)H_{adi} + (U^+ D_{dia}UH_{adi} - H_{adi}U^+ D_{dia}U) = \nabla H_{adi} + (D_{adi}H_{adi} - H_{adi}D_{adi}). \qquad (4.5)$$

Using the condition, Eq. 3.8, we can simplify the left-hand side:

$$-(U^+\nabla SU)H_{adi} + (U^+ D_{dia}UH_{adi} - H_{adi}U^+ D_{dia}U) = -U^+ D_{dia}UH_{adi} - U^+ D_{dia}^+ UH_{adi} +$$
$$(U^+ D_{dia}UH_{adi} - H_{adi}U^+ D_{dia}U) = -U^+ D_{dia}^+ UH_{adi} - H_{adi}U^+ D_{dia}U. \qquad (4.6)$$

Considering Eq. 4.6 and Eq. 3.7, Eq. 4.5 can be brought to a symmetric form:

$$U^+\nabla H_{dia}U - \left(\tilde{D}_{dia}^+ H_{adi} + H_{adi}\tilde{D}_{dia}\right) = \nabla H_{adi} - \left(D_{adi}^+ H_{adi} + H_{adi}D_{adi}\right). \qquad (4.7)$$

Here, we introduced the variables carrying tildas. They represent the similarity transform of the underlying matrix, e.g.:

$$\tilde{D}_{dia}^+ = U^+ D_{dia}^+ U. \tag{4.8}$$

Considering Eq. 2.6, this equation can be further transformed into:

$$\widetilde{\nabla H_{dia}} - \left(\tilde{D}_{dia}^+ \tilde{H}_{dia} + \tilde{H}_{dia}\tilde{D}_{dia}\right) = \nabla H_{adi} - \left(D_{adi}^+ H_{adi} + H_{adi}D_{adi}\right). \tag{4.9}$$

Or:

$$\nabla H_{adi} = \widetilde{\nabla H_{dia}} + \left(D_{adi}^+ H_{adi} + H_{adi}D_{adi}\right) - \left(\tilde{D}_{dia}^+ \tilde{H}_{dia} + \tilde{H}_{dia}\tilde{D}_{dia}\right). \tag{4.10}$$

From Eq. 3.9 and 4.10, we conclude that:

$$\tilde{D}_{dia}^+ \tilde{H}_{dia} + \tilde{H}_{dia}\tilde{D}_{dia} = 0. \tag{4.11}$$

Now, lets relate the adiabatic and diabatic forces:

$$f_{adi} = -\nabla H_{adi} = -[U^+ \langle \nabla\psi_{dia}|H|\psi_{dia}\rangle U + \nabla U^+ \langle \psi_{dia}|H|\psi_{dia}\rangle U + U^+ \langle \psi_{dia}|\nabla H|\psi_{dia}\rangle U +$$
$$U^+ \langle \psi_{dia}|H|\nabla\psi_{dia}\rangle U + U^+ \langle \psi_{dia}|H|\psi_{dia}\rangle \nabla U], \tag{4.12a}$$

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(\nabla U^+ H_{dia} U + U^+ H_{dia}\nabla U\right). \tag{4.12b}$$

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(\nabla U^+ S U H_{adi} + H_{adi}U^+ S\nabla U\right). \tag{4.12c}$$

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left((D_{adi}^+ - U^+ D_{dia}^+ U)H_{adi} + H_{adi}(D_{adi} - U^+ D_{dia}U)\right). \tag{4.12d}$$

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(D_{adi}^+ H_{adi} + H_{adi}D_{adi}\right) + \left(U^+ D_{dia}^+ U H_{adi} + H_{adi}U^+ D_{dia}U\right). \tag{4.12e}$$

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(D_{adi}^+ H_{adi} + H_{adi}D_{adi}\right). \tag{4.12f}$$

Which is equivalent to Eq. 4.10, just with an opposite sign.

But we can go further:

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(\left(\tilde{D}_{dia}^+ + \nabla U^+ S U\right)\tilde{H}_{dia} + \tilde{H}_{dia}\left(\tilde{D}_{dia} + U^+ S\nabla U\right)\right). \tag{4.13}$$

Using Eq. 4.11:

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(\nabla U^+ S U \tilde{H}_{dia} + \tilde{H}_{dia}U^+ S\nabla U\right). \tag{4.14a}$$

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(\nabla U^+ S U H_{adi} + H_{adi}U^+ S\nabla U\right). \tag{4.14b}$$

$$f_{adi} = -\widetilde{\nabla H_{dia}} - \left(\nabla U^+ H_{dia} U + U^+ H_{dia}\nabla U\right) = -\nabla H_{dia}. \tag{4.14c}$$

Which is essentially the definition.

Lets look at the similarity transform of the adiabatic force:

$$U^+ f_{dia} U = -\widetilde{\nabla H_{dia}} + U^+ H_{adi} \nabla S U, \tag{4.15a}$$

$$U^+ f_{dia} U = f_{adi} + (\nabla U^+ H_{dia} U + U^+ H_{dia} \nabla U) + U^+ H_{adi} \nabla S U, \tag{4.15b}$$

$$U^+ f_{dia} U = f_{adi} + \left((D_{adi}^+ - \tilde{D}_{dia}^+) H_{adi} + H_{adi} (D_{adi} - \tilde{D}_{dia}) \right) + U^+ H_{adi} \nabla S U, \tag{4.15c}$$

$$U^+ f_{dia} U = f_{adi} + (D_{adi}^+ H_{adi} + H_{adi} D_{adi}) + U^+ H_{adi} \nabla S U, \tag{4.16c}$$

Vide infra:

$$U^+ (f_{dia} - H_{adi} \nabla S) U = f_{adi} + (D_{adi}^+ H_{adi} + H_{adi} D_{adi}) = f_{adi}^{MF}, \tag{4.17}$$

Note that, in general, f_{adi} is not the same as $\tilde{f}_{dia} = U^+ f_{dia} U$.

5. Forces in Ehrenfest dynamics (adiabatic representation)

Consider a quantum-classical Hamiltonian:

$$H_{qc} = T + E_{tot} = \sum_n \frac{p_n^2}{2m_n} + E_{tot}. \tag{5.1}$$

With the potential given by Eq. 1.5. Applying the Hamiltonian equations of motion, we obtain:

$$\dot{q}_n = \frac{\partial H_{qc}}{\partial p_n} = \frac{p_n}{m_n}, \tag{5.2}$$

$$\dot{p}_n = -\frac{\partial H_{qc}}{\partial q_n} = F_n = -C_{adi}^+ \nabla_{q_n} H_{adi} C_{adi}, \tag{5.3}$$

With the force given by Eqs. 3.2, 3.3.

The evolution of the time-dependent coefficients is given by the TD-SE:

$$i\hbar \frac{\partial |\Psi\rangle}{\partial t} = H |\Psi\rangle. \tag{5.4}$$

Because $\frac{\partial}{\partial t} = (\dot{q})^+ \nabla_q + (\dot{p})^+ \nabla_p$ and the basis wavefunctions do not depend on momentum, we obtain after the projection on the adiabatic states:

$$i\hbar \frac{\partial C_{adi}}{\partial t} = H_{adi} C_{adi} - i\hbar \sum_n D_{adi,n} \frac{p_n}{m_n} C_{adi}, \tag{5.5}$$

Which means:

$$\dot{C}_{adi} = -\frac{i}{\hbar} H_{adi} C_{adi} - \sum_n D_{adi,n} \frac{p_n}{m_n} C_{adi}, \tag{5.6}$$

$$\dot{C}^+_{adi} = \frac{i}{\hbar} C^+_{adi} H_{adi} + C^+_{adi} \sum_n D_{adi,n} \frac{p_n}{m_n}. \tag{5.7}$$

Now, consider the time-derivative of the quantum-classical Hamiltonian, Eq. 5.1:

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

$$\left[\frac{i}{\hbar} C^+_{adi} H_{adi} + C^+_{adi} \sum_n D_{adi,n} \frac{p_n}{m_n} \right] H_{adi} C_{adi} + C^+_{adi} H_{adi} \left[-\frac{i}{\hbar} H_{adi} C_{adi} - \sum_n D_{adi,n} \frac{p_n}{m_n} C_{adi} \right] =$$

$$\sum_n C^+_{adi} \frac{p_n}{m_n} \left(\nabla_{q_n} H_{adi} + \dot{p}_n \right) C_{adi} + C^+_{adi} \sum_n (D_{adi,n} H_{adi} - H_{adi} D_{adi,n}) \frac{p_n}{m_n} C_{adi} = \sum_n C^+_{adi} \frac{p_n}{m_n} \left(\nabla_{q_n} H_{adi} + \right.$$

$$\dot{p}_n + \left(D_{adi,n} H_{adi} - H_{adi} D_{adi,n} \right) \right) C_{adi}, \tag{5.8}$$

If one assumes the dynamics driven by Eqs. 5.2, 5.3, one arrives at:

$$\frac{dH_{qc}}{dt} = C^+_{adi} \sum_n \frac{p_n}{m_n} \left(D_{adi,n} H_{adi} - H_{adi} D_{adi,n} \right) C_{adi}, \tag{5.9}$$

which implies the total energy, Eq. 5.1 will not be conserved!

Instead, if one assumes that:

$$\dot{p}_n = f_n^{MF} \equiv -\nabla_{q_n} H_{adi} - \left(D_{adi,n} H_{adi} - H_{adi} D_{adi,n} \right), \tag{5.10}$$

then the quantity, Eq. 5.1 is conserved.

Comparing, Eq. 5.10 with Eq. 3.9, one finds that

$$f_{adi}^{MF} = f_{adi} - (D_{adi} H_{adi} - H_{adi} D_{adi}) = -\langle \psi_{adi} | \nabla H | \psi_{adi} \rangle. \tag{5.11}$$

Equation 5.10 is not derived from Eq. 5.1 using the classical Hamiltonian EOMs, Eqs. 5.2-5.3. Thus, the quantity Eq. 5.1 is NOT a Hamiltonian, but is just a CONSERVED QUANTITY, an INTEGRAL OF MOTION. It can still be associated with the energy. As a consequence, the dynamics driven by Eqs. 5.2 and 5.10 (Ehrenfest dynamics) is an example of non-Hamiltonian dynamics. The term in the parentheses in Eq. 5.10 is essentially an electronic friction.

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

6. Forces in Ehrenfest dynamics (diabatic representation)

Consider a quantum-classical Hamiltonian:

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

With the potential given by Eq. 1.5. Applying the Hamiltonian equations of motion, we obtain:

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

$$\dot{p}_n = -\frac{\partial H_{qc}}{\partial q_n} = F_n = -C_{dia}^+ \left(\nabla_{q_n} H_{dia} - H_{adi} \nabla_{q_n} S \right) C_{dia}, \tag{6.3}$$

With the force given by Eqs. 3.2, 3.3.

The evolution of the time-dependent coefficients is given by the TD-SE:

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

Because $\frac{\partial}{\partial t} = (\dot{q})^+ \nabla_q + (\dot{p})^+ \nabla_p$ and the basis wavefunctions do not depend on momentum, we obtain after the projection on the adiabatic states:

$$i\hbar S \frac{\partial C_{dia}}{\partial t} = H_{dia} C_{dia} - i\hbar \sum_n D_{dia,n} \frac{p_n}{m_n} C_{dia}, \tag{6.5}$$

Which means:

$$\dot{C}_{dia} = -\frac{i}{\hbar} S^{-1} H_{dia} C_{dia} - \sum_n S^{-1} D_{dia,n} \frac{p_n}{m_n} C_{dia}, \tag{6.6}$$

$$\dot{C}_{dia}^+ = \frac{i}{\hbar} C_{dia}^+ H_{dia} S^{-1} - C_{dia}^+ \sum_n D_{dia,n}^+ S^{-1} \frac{p_n}{m_n}. \tag{6.7}$$

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

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

$$\frac{dH_{qc}}{dt} = \sum_n \left(\frac{\partial H_{qc}}{\partial q_n} \frac{p_n}{m_n} + \frac{\partial H_{qc}}{\partial p_n} \dot{p}_n \right) + \left[\frac{i}{\hbar} C_{dia}^+ H_{dia} S^{-1} - C_{dia}^+ \sum_n D_{dia,n}^+ S^{-1} \frac{p_n}{m_n} \right] H_{dia} C_{dia} +$$
$$C_{dia}^+ H_{dia} \left[-\frac{i}{\hbar} S^{-1} H_{dia} C_{dia} - \sum_n S^{-1} D_{dia,n} \frac{p_n}{m_n} C_{dia} \right], \tag{6.8b}$$

$$\frac{dH_{qc}}{dt} = \sum_n \left(\frac{\partial H_{qc}}{\partial q_n} \frac{p_n}{m_n} + \frac{\partial H_{qc}}{\partial p_n} \dot{p}_n \right) - C_{dia}^+ \left[\sum_n \left(D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n} \right) \frac{p_n}{m_n} \right] C_{dia}, \tag{6.8c}$$

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

$$\frac{dH_{qc}}{dt} = \sum_n \left(C_{dia}^+ \left((\nabla_{q_n} H_{dia} - H_{adi} \nabla_{q_n} S) + \dot{p}_n \right) C_{dia} \frac{p_n}{m_n} \right) - C_{dia}^+ \left[\sum_n (D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n}) \frac{p_n}{m_n} \right] C_{dia} \tag{6.9}$$

So, if we assume:

$$\dot{p}_n = f_{dia} = -\nabla_{q_n} H_{dia} + H_{adi} \nabla_{q_n} S, \tag{6.10}$$

then:

$$\frac{dH_{qc}}{dt} = -C_{dia}^+ \left[\sum_n (D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n}) \frac{p_n}{m_n} \right] C_{dia}. \tag{6.11}$$

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

Instead, if one assumes that:

$$\dot{p}_n = f_n^{MF,dia} \equiv -\nabla_{q_n} H_{dia} + H_{adi} \nabla_{q_n} S + (D_{dia,n}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia,n}), \tag{6.11}$$

then the quantity, Eq. 6.1 is conserved.

$$f_n^{MF,dia} = f_{dia} + (D_{dia}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia}), \tag{6.12a}$$

$$U^+ f_n^{MF,dia} U = U^+ f_{dia} U + U^+ (D_{dia}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia}) U, \tag{6.12b}$$

$$U^+ f_n^{MF,dia} U = f_{adi}^{MF} + U^+ H_{adi} \nabla S U + U^+ (D_{dia}^+ S^{-1} H_{dia} + H_{dia} S^{-1} D_{dia}) U, \tag{6.12c}$$

Simplifying the expressions on the right-hand side, we obtain:

$$U^+ H_{adi} \nabla S U + U^+ D_{dia}^+ S^{-1} H_{dia} U + U^+ H_{dia} S^{-1} D_{dia} U, \tag{6.13a}$$

$$U^+ H_{adi} \nabla S U + U^+ D_{dia}^+ S^{-1} S U H_{adi} + H_{adi} U^+ S S^{-1} D_{dia} U, \tag{6.13b}$$

$$U^+ H_{adi} \nabla S U + U^+ D_{dia}^+ U H_{adi} + H_{adi} U^+ D_{dia} U, \tag{6.13c}$$

$$U^+ H_{adi} \nabla S U + \widetilde{D}_{dia}^+ \widetilde{H}_{dia} + \widetilde{H}_{dia} \widetilde{D}_{dia}, \tag{6.13d}$$

$$U^+ H_{adi} \nabla S U. \tag{6.13e}$$

That is:

$$U^+ f_n^{MF,dia} U = f_{adi}^{MF} + U^+ H_{adi} \nabla S U, \tag{6.14a}$$

$$U^+ \left(f_n^{MF,dia} - H_{adi} \nabla S \right) U = f_{adi}^{MF}. \tag{6.14b}$$