Alexey V. Akimov, Initial version: 12/25/2015; latest revision: 12/25/2015

Meyer-Miller-Thoss-Stock (MMTS) formulation revised

1. Statement 1

In variables $q_i = \mathrm{Re}(c_i)$ and $p_i = \mathrm{Im}(c_i)$, the TD-SE:

$$i\hbar \frac{\partial c_i(t)}{\partial t} = \sum_j H_{ij} c_j(t), \tag{1.1}$$

can be written as:

$$\begin{aligned} \frac{dq_k}{dt} &= \sum_j \left[\mathrm{Re}(\Omega_{kj}) p_j + \mathrm{Im}(\Omega_{kj}) q_j\right] = \frac{\partial H_{eff}}{\partial p_k} \\ \frac{dp_k}{dt} &= -\sum_j \left[\mathrm{Re}(\Omega_{kj}) q_j - \mathrm{Im}(\Omega_{kj}) p_j\right] = -\frac{\partial H_{eff}}{\partial q_k} \end{aligned}, \tag{1.2}$$

with

$$\Omega = \frac{H}{\hbar}. \tag{1.3}$$

Proof:

$$\begin{aligned} & i\hbar \frac{d\,\mathrm{Re}(c_k) + i\,\mathrm{Im}(c_k)}{dt} = \sum_j H_{kj}\left[\mathrm{Re}(c_j) + i\,\mathrm{Im}(c_j)\right] = \sum_j \left[\mathrm{Re}(H_{kj}) + i\,\mathrm{Im}(H_{kj})\right]\left[\mathrm{Re}(c_j) + i\,\mathrm{Im}(c_j)\right] = \\ & = \sum_j \left[\mathrm{Re}(H_{kj})\mathrm{Re}(c_j) - \mathrm{Im}(H_{kj})\mathrm{Im}(c_j)\right] + i\left[\mathrm{Re}(H_{kj})\mathrm{Im}(c_j) + \mathrm{Im}(H_{kj})\mathrm{Re}(c_j)\right] \Leftrightarrow \\ & \frac{d\,\mathrm{Re}(c_k)}{dt} = \sum_j \left[\mathrm{Re}(\Omega_{kj})\mathrm{Im}(c_j) + \mathrm{Im}(\Omega_{kj})\mathrm{Re}(c_j)\right] \\ & \frac{d\,\mathrm{Im}(c_k)}{dt} = -\sum_j \left[\mathrm{Re}(\Omega_{kj})\mathrm{Re}(c_j) - \mathrm{Im}(\Omega_{kj})\mathrm{Im}(c_j)\right] \end{aligned} \tag{1.4}$$

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Note that the leftmost equalities in Eqs. 1.2 are exact and true for a general Hamiltonian, Hermitian or non-Hermitian. The rightmost equalities in Eq. 1.2 are desired, but are not always possible – they are only possible if the Hamiltonian H is Hermitian (classical analog: Hamiltonian dynamics). If H is non-Hermitian, the rightmost equalities can not be met, additional terms are needed (classical analog: non-Hamiltonian dynamics).

2. Statement 2

For a Hermitian Hamiltonian, $H_{ij} = H^*_{ji}$, Eqs. 1.2 are Hamiltonian (proof of the rightmost equalities), with the effective Hamiltonian, H_{eff} , given by:

$$H_{eff} = \sum_{i,j} \mathrm{Re}\left(\frac{H_{ij}}{2\hbar}\right)\left(q_i q_j + p_i p_j\right) + \sum_{i,j} \mathrm{Im}\left(\frac{H_{ij}}{\hbar}\right) p_i q_j \ . \tag{2.1}$$

Proof:

First, assume a very general quadratic form of the effective Hamiltonian:

$$H_{eff} = \sum_{i,j} B_{ij} q_i q_j + \sum_{i,j} C_{ij} p_i p_j + \sum_{i,j} D_{ij} p_i q_j \ . \tag{2.2}$$

Then

$$\begin{aligned} \frac{\partial H_{eff}}{\partial p_k} &= \sum_j \left(C_{kj} + C_{jk}\right) p_j + \sum_j D_{kj} q_j \\ \frac{\partial H_{eff}}{\partial q_k} &= \sum_j \left(B_{kj} + B_{jk}\right) q_j + \sum_j D_{jk} p_j \end{aligned} , \tag{2.3}$$

and

$$\begin{aligned} \frac{dq_k}{dt} &= \sum_j \left[\mathrm{Re}\left(\Omega_{kj}\right) p_j + \mathrm{Im}\left(\Omega_{kj}\right) q_j\right] = \frac{\partial H_{eff}}{\partial p_k} \\ \frac{dp_k}{dt} &= -\sum_j \left[\mathrm{Re}\left(\Omega_{kj}\right) q_j - \mathrm{Im}\left(\Omega_{kj}\right) p_j\right] = -\frac{\partial H_{eff}}{\partial q_k} \end{aligned} . \tag{2.4}$$

We want the rightmost sides of Eq. 2.4 be satisfied:

$$\begin{aligned} \frac{\partial H_{eff}}{\partial p_k} &= \sum_j \left(C_{kj} + C_{jk}\right) p_j + \sum_j D_{kj} q_j = \dot{q}_k = \sum_j \mathrm{Re}\left(\Omega_{kj}\right) p_j + \sum_j \mathrm{Im}\left(\Omega_{kj}\right) q_j \\ -\frac{\partial H_{eff}}{\partial q_k} &= \sum_j \left(-B_{kj} - B_{jk}\right) q_j + \sum_j -D_{jk} p_j = \dot{p}_k = -\sum_j \mathrm{Re}\left(\Omega_{kj}\right) q_j + \sum_j \mathrm{Im}\left(\Omega_{kj}\right) p_j \end{aligned} . \tag{2.5}$$

These equations are equivalent to:

$$\mathrm{Im}(\Omega_{kj}) = D_{kj}, \tag{2.6a}$$

$$\mathrm{Im}(\Omega_{kj}) = -D_{jk}. \tag{2.6b}$$

Equations 2.6a and 2.6b imply:

$$\mathrm{Im}(\Omega_{jk}) = -D_{kj} = -\mathrm{Im}(\Omega_{kj}). \tag{2.7c}$$

From Eq. 2.5, we find that:

$$\mathrm{Re}(\Omega_{kj}) = (C_{kj} + C_{jk}), \tag{2.8a}$$

$$\mathrm{Re}(\Omega_{kj}) = (B_{kj} + B_{jk}). \tag{2.8b}$$

Equations 2.8a and 2.9b imply:

$$\mathrm{Re}(\Omega_{kj}) = \mathrm{Re}(\Omega_{jk}). \tag{2.8c}$$

To see that:

$$\mathrm{Re}(\Omega_{kj}) = (C_{kj} + C_{jk}) = (C_{jk} + C_{kj}) = \mathrm{Re}(\Omega_{jk}). \tag{2.9}$$

The matrices C and B can be related to each other as $C = B$ or $C = B^T$. These two conditions can be satisfied simultaneously, if the matrices are symmetric. There is little physical meaning in requiring either of matrices C or B to be non-symmetric, so this condition is met practically always.

In summary, we have shown that:

$$\mathrm{Re}(\Omega_{kj}) = \mathrm{Re}(\Omega_{jk}), \tag{2.10a}$$

$$\mathrm{Im}(\Omega_{jk}) = -\mathrm{Im}(\Omega_{kj}). \tag{2.10b}$$

In other words, the Hamiltonian equations of motion, Eq. 2.4, are held only when the quantum Hamiltonian, H, is Hermitian. The form of the effective Hamiltonian can be derived as follows.

Using the relationship, $C = B$, we can simplify Eq. 2.2 to:

$$H_{eff} = \sum_{i,j} B_{ij}\left(q_i q_j + p_i p_j\right) + \sum_{i,j} D_{ij} p_i q_j \,. \tag{2.11}$$

Using the fact that $\mathrm{Re}\left(\Omega_{kj}\right) = \left(B_{kj} + B_{jk}\right)$, and $B = B^T$, we obtain:

$$B = \frac{1}{2}\mathrm{Re}\left(\Omega\right) = \mathrm{Re}\left(\frac{H}{2\hbar}\right). \tag{2.12}$$

From the above definitions, it follows that:

$$D = \mathrm{Im}\left(\Omega\right) = \mathrm{Im}\left(\frac{H}{\hbar}\right). \tag{2.13}$$

Combining Eqs. 2.11-2.13, we finally obtain:

$$H_{eff} = \sum_{i,j} \mathrm{Re}\left(\frac{H_{ij}}{2\hbar}\right)\left(q_i q_j + p_i p_j\right) + \sum_{i,j} \mathrm{Im}\left(\frac{H_{ij}}{\hbar}\right) p_i q_j \,. \tag{2.14}$$

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3. Statement 3

If the electronic Hamiltonian is Hermitian, then the total electronic energy, E, is related to the effective mapped Hamiltonian, H_{eff}, as:

$$E = 2\hbar H_{eff} \,. \tag{3.1}$$

Proof:

$$\begin{aligned} E &= \langle \Psi | H | \Psi \rangle = \sum_{i,j} c_i^* c_j H_{ij} = \sum_{i,j} H_{ij}\left[\left(q_i q_j + p_i p_j\right) + i\left(q_i p_j - p_i q_j\right)\right] = \\ &= \sum_{i,j}\left[\mathrm{Re}\left(H_{ij}\right) + i\,\mathrm{Im}\left(H_{ij}\right)\right]\left[\left(q_i q_j + p_i p_j\right) + i\left(q_i p_j - p_i q_j\right)\right] = \\ &= \sum_{i,j}\left[\mathrm{Re}\left(H_{ij}\right)\left(q_i q_j + p_i p_j\right) - \mathrm{Im}\left(H_{ij}\right)\left(q_i p_j - p_i q_j\right)\right] + \\ &+ i\sum_{i,j}\mathrm{Re}\left(H_{ij}\right)\left(q_i p_j - p_i q_j\right) + i\sum_{i,j}\mathrm{Im}\left(H_{ij}\right)\left(q_i q_j + p_i p_j\right) \end{aligned} \,. \tag{3.2}$$

Then, using the hermiticity of the vibronic Hamiltonian, H:

$$\mathrm{Re}(H_{ij}) = \mathrm{Re}(H_{ji}), \tag{3.2a}$$

$$\mathrm{Im}(H_{ij}) = -\mathrm{Im}(H_{ji}), \tag{3.2b}$$

and re-summing the resulting terms, we obtain:

$$\begin{aligned}\sum_{i,j} \mathrm{Re}(H_{ij})(q_i p_j - p_i q_j) = \sum_{i<j} \mathrm{Re}(H_{ij})(q_i p_j - p_i q_j) + \sum_{i>j} \mathrm{Re}(H_{ij})(q_i p_j - p_i q_j) = \\ = \sum_{i<j} \mathrm{Re}(H_{ij})(q_i p_j - p_i q_j) + \sum_{i<j} \mathrm{Re}(H_{ji})(q_j p_i - p_j q_i) = 0\end{aligned}. \tag{3.3}$$

and

$$\begin{aligned}\sum_{i,j} \mathrm{Im}(H_{ij})(q_i q_j + p_i p_j) = \sum_{i<j} \mathrm{Im}(H_{ij})(q_i q_j + p_i p_j) + \sum_{i>j} \mathrm{Im}(H_{ij})(q_i q_j + p_i p_j) = \\ = \sum_{i<j} \mathrm{Im}(H_{ij})(q_i q_j + p_i p_j) + \sum_{i<j} \mathrm{Im}(H_{ji})(q_j q_i + p_j p_i) = 0\end{aligned}. \tag{3.4}$$

So, the imaginary term is zero, as it should be, and the energy is:

$$E = \sum_{i,j} \left[\mathrm{Re}(H_{ij})(q_i q_j + p_i p_j) - \mathrm{Im}(H_{ij})(q_i p_j - p_i q_j) \right]. \tag{3.5}$$

The last term is:

$$\begin{aligned}\sum_{i,j} \left[-\mathrm{Im}(H_{ij})(q_i p_j - p_i q_j) \right] = \sum_{i,j} \mathrm{Im}(H_{ij})(p_i q_j - q_i p_j) = \sum_{i,j} \mathrm{Im}(H_{ij}) p_i q_j - \sum_{i,j} \mathrm{Im}(H_{ij}) q_i p_j = \\ = \sum_{i,j} \mathrm{Im}(H_{ij}) p_i q_j + \sum_{i,j} \mathrm{Im}(H_{ji}) q_i p_j = \sum_{i,j} \mathrm{Im}(H_{ij}) p_i q_j + \sum_{i,j} \mathrm{Im}(H_{ij}) q_j p_i = 2\sum_{i,j} \mathrm{Im}(H_{ij}) p_i q_j\end{aligned}. \tag{3.6}$$

Thus, the energy is:

$$E = \sum_{i,j} \mathrm{Re}(H_{ij})(q_i q_j + p_i p_j) + 2\sum_{i,j} \mathrm{Im}(H_{ij}) p_i q_j = 2\hbar H_{eff}. \tag{3.7}$$

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