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*J. Chem. Phys.* 147, 064112 (2017)

<https://doi.org/10.1063/1.4995301>



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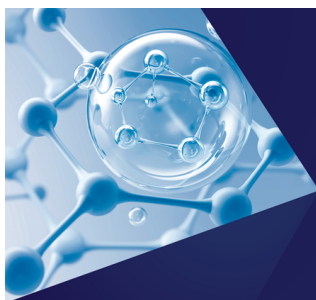
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# On the adiabatic representation of Meyer-Miller electronic-nuclear dynamics

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(Received 9 May 2017; accepted 10 July 2017; published online 11 August 2017)

The Meyer-Miller (MM) classical vibronic (electronic + nuclear) Hamiltonian for electronically non-adiabatic dynamics—as used, for example, with the recently developed symmetrical quasiclassical (SQC) windowing model—can be written in either a diabatic or an adiabatic representation of the electronic degrees of freedom, the two being a canonical transformation of each other, thus giving the same dynamics. Although most recent applications of this SQC/MM approach have been carried out in the diabatic representation—because most of the benchmark model problems that have exact quantum results available for comparison are typically defined in a diabatic representation—it will typically be much more convenient to work in the adiabatic representation, e.g., when using Born-Oppenheimer potential energy surfaces (PESs) and derivative couplings that come from electronic structure calculations. The canonical equations of motion (EOMs) (i.e., Hamilton's equations) that come from the adiabatic MM Hamiltonian, however, in addition to the common first-derivative couplings, also involve second-derivative non-adiabatic coupling terms (as does the quantum Schrödinger equation), and the latter are considerably more difficult to calculate. This paper thus revisits the adiabatic version of the MM Hamiltonian and describes a modification of the classical adiabatic EOMs that are entirely equivalent to Hamilton's equations but that do not involve the second-derivative couplings. The second-derivative coupling terms have not been neglected; they simply do not appear in these modified adiabatic EOMs. This means that SQC/MM calculations can be carried out in the adiabatic representation, without approximation, needing only the PESs and the first-derivative coupling elements. The results of example SQC/MM calculations are presented, which illustrate this point, and also the fact that simply neglecting the second-derivative couplings in Hamilton's equations (and presumably also in the Schrödinger equation) can cause very significant errors. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4995301>]

## I. INTRODUCTION

Over the last few years, we have been exploring how well the classical Meyer-Miller (MM) model for electronic-nuclear dynamics<sup>1,2</sup>—together with new symmetrical quasi-classical (SQC) models<sup>3</sup> for “quantizing” the electronic degrees of freedom (DOFs) initially and finally—can describe electronically non-adiabatic processes in molecular systems. This SQC/MM approach has been seen to perform quite well for a variety of applications, describing both large and small coupling regimes as well as coherence/de-coherence phenomena in the electronic DOFs, all the more surprising as it is essentially standard classical molecular dynamics (MD) (with each electronic state being characterized as a classical harmonic oscillator, together with the usual classical treatment of all the nuclear DOFs). For a recent review of this work, see Ref. 4.

Most applications of the SQC/MM methodology to date have used the diabatic version of the classical MM electronic-nuclear Hamiltonian since most of the model systems for

which accurate quantum mechanical results are available for comparison (e.g., various spin-boson problems) are defined in a diabatic representation of the electronic DOFs. For applications to “real” molecular systems, however—i.e., those with electronic potential energy surfaces (PESs) and their non-adiabatic couplings obtained from *ab initio* electronic structure calculations (i.e., “quantum chemistry”), possibly done “on the fly”—it will typically be more convenient to use the adiabatic representation of the electronic DOFs since the relevant quantities (Born-Oppenheimer PESs and their derivative couplings) are the direct output of such electronic structure calculations.

There is an adiabatic version of the MM Hamiltonian, developed in the original paper,<sup>1</sup> which is formally equivalent to the diabatic version, one being a classical canonical transformation of the other. Like the diabatic MM Hamiltonian, the adiabatic version is also an “exact” Hamiltonian in the sense that it would be the exact quantum mechanical Hamiltonian *operator* were all the classical electronic and nuclear coordinates and momenta treated as operators in the usual quantum fashion. The classical equations of motion (EOMs) (i.e., Hamilton's equations) generated by the adiabatic version of the MM Hamiltonian, however, involve second-derivative non-adiabatic coupling terms (see Sec. II B) in

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addition to the more common first-derivative couplings, in precisely the same way that the quantum Schrödinger equation in the adiabatic electronic representation involves first- and second-derivative non-adiabatic coupling terms. Having to compute these second-derivative couplings is a significant increase in difficulty for electronic structure calculations, so they are often neglected, which is clearly an approximation (e.g., when the first-derivative coupling is large, the second-derivative coupling is typically larger); examples presented in Sec. III show that serious errors can result by simply discarding the second-derivative couplings.

The purpose of this paper, therefore, is to revisit the adiabatic representation of the MM Hamiltonian and most importantly to show that the classical EOMs (i.e., Hamilton's equations generated from the adiabatic MM Hamiltonian) can be rewritten in a form that involves only the first-derivative non-adiabatic couplings but which nevertheless *exactly* reproduce the full MM dynamics in the adiabatic representation. That is, these modified EOMs do not correspond to neglecting the second derivative couplings; they simply do not appear. One thus has the somewhat ironic situation that the modified EOMs (that *do not* involve second derivative coupling terms) cannot be written as Hamilton's equations that come from any classical Hamiltonian, yet they are exactly equivalent to Hamilton's EOMs that come from the adiabatic MM Hamiltonian (and that *do* involve second-derivative coupling terms)! Realizing this has been a welcome surprise to us, for it means that one can implement MM classical electronic-nuclear dynamics in the adiabatic electronic representation, without approximation, needing only the first-derivative non-adiabatic coupling terms.

This paper is organized as follows: In Sec. II A, we present a concise but comprehensive summary of the adiabatic version of the MM Hamiltonian, and in Sec. II B, we present the modified EOMs that are free from second-derivative couplings and which we recommend for use in all situations. Example SQC/MM calculations presented in Sec. III illustrate the importance of these second-order effects in standard spin-boson benchmark applications and, furthermore, that the effects are captured in calculations using the modified EOMs. Our conclusions are summarized in Sec. IV.

## II. SUMMARY OF THE THEORY

### A. Review of the MM Hamiltonian in the adiabatic representation

The Meyer-Miller (MM) Hamiltonian maps the dynamics of a set of electronic states onto a set of classical harmonic oscillators whose excitations represent the electronic occupation/configuration. Starting with the diabatic version, in Cartesian harmonic oscillator coordinates  $\{x_i\}$  and momenta  $\{p_i\}$  corresponding to a set of, say  $F$ , diabatic electronic states, the MM Hamiltonian is given by

$$H(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}) = \frac{1}{2\mu} \mathbf{P}^2 + \sum_i^F \left( \frac{1}{2} p_i^2 + \frac{1}{2} x_i^2 - \gamma \right) H_{ii}(\mathbf{R}) + \sum_{i<j}^F (p_i p_j + x_i x_j) H_{ij}(\mathbf{R}), \quad (1)$$

where  $(\mathbf{R}, \mathbf{P})$  are the coordinates and momenta of the (perhaps very many) nuclear DOFs,  $\{H_{ij}(\mathbf{R})\}$  is an  $F \times F$  diabatic electronic Hamiltonian matrix dependent on the nuclear coordinates, and  $\gamma$  is a zero point energy (ZPE) parameter that we have found to be optimally set to about  $\frac{1}{3}$ .

In the adiabatic representation, the MM Hamiltonian takes the form

$$H(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}) = \frac{1}{2\mu} (\mathbf{P} + \Delta \mathbf{P})^2 + \sum_i^F \left( \frac{1}{2} p_i^2 + \frac{1}{2} x_i^2 - \gamma \right) E_i(\mathbf{R}) \quad (2)$$

where the diabatic electronic matrix  $\{H_{ij}(\mathbf{R})\}$  of Eq. (1) has been replaced by its eigenvalues  $\{E_i(\mathbf{R})\}$ , the Born-Oppenheimer PESs corresponding to the  $F$  electronic states, and where the expression for the kinetic energy now contains the term

$$\Delta \mathbf{P}(\mathbf{x}, \mathbf{p}, \mathbf{R}) = \sum_{ij}^F x_i p_j \mathbf{d}_{ij}(\mathbf{R}), \quad (3a)$$

where  $\mathbf{d}_{ij}(\mathbf{R}) \equiv \left\langle \phi_i \left| \frac{\partial \phi_j}{\partial \mathbf{R}} \right. \right\rangle$  is the standard first-derivative non-adiabatic coupling vector/element between electronic states  $i$  and  $j$ , which is skew-symmetric ( $\mathbf{d}_{ij} = -\mathbf{d}_{ji}$ ), so that Eq. (3a) can also be written equivalently as

$$\Delta \mathbf{P}(\mathbf{x}, \mathbf{p}, \mathbf{R}) = \sum_{i<j}^F (x_i p_j - x_j p_i) \mathbf{d}_{ij}(\mathbf{R}). \quad (3b)$$

$\Delta \mathbf{P}$  is a vector potential that modifies the canonical momentum in the kinetic energy term similar to the magnetic vector potential appearing in the classical Hamiltonian for a charged particle in an electromagnetic field (see, e.g., Ref. 5 at p. 130). Here, the vector potential  $\Delta \mathbf{P}$  gives rise to non-adiabatic transitions in the adiabatic picture (the potential energy terms being diagonal), and it also contributes to the force on the nuclear DOFs, as will be apparent below.

It is interesting to note that Eq. (2) has the same form as the quantum mechanical (QM) vibronic Hamiltonian operator in the adiabatic representation, which is given (as a matrix in the electronic basis and operators  $\hat{\mathbf{P}}$  and  $\hat{\mathbf{R}}$  of the nuclear DOFs) by

$$\hat{H}_{ij} = -\frac{\hbar^2}{2\mu} \left( \delta_{ij} \frac{\partial^2}{\partial \mathbf{R}^2} + 2 \underbrace{\left\langle \phi_i \left| \frac{\partial \phi_j}{\partial \mathbf{R}} \right. \right\rangle}_{\mathbf{d}_{ij}} \frac{\partial}{\partial \mathbf{R}} + \underbrace{\left\langle \phi_i \left| \frac{\partial^2 \phi_j}{\partial \mathbf{R}^2} \right. \right\rangle}_{\mathbf{D}_{ij}} \right) + \delta_{ij} E_i(\mathbf{R}), \quad (4)$$

where the second-derivative coupling  $\mathbf{D}_{ij}$  arises in the kinetic energy operator in addition to the first-derivative coupling  $\mathbf{d}_{ij}$ . However, Eq. (4) can also be written<sup>6,7</sup> as

$$\hat{H}_{ij} = \frac{1}{2\mu} (\hat{\mathbf{P}} - i\hbar \mathbf{d}(\mathbf{R}))_{ij}^2 + \delta_{ij} E_i(\mathbf{R}), \quad (5)$$

where  $\mathbf{d}(\mathbf{R})$  is the *matrix* of first derivative coupling vectors (and  $\hat{\mathbf{P}}_{ij} = -i\hbar \delta_{ij} \partial / \partial \mathbf{R}$ ); here the second-derivative coupling does not appear explicitly, but arises through the non-commutivity of  $\hat{\mathbf{P}}$  and  $\mathbf{d}(\mathbf{R})$ , i.e., because of the latter's  $\mathbf{R}$ -dependence. [As will be seen below, it is also the  $\mathbf{R}$ -dependence of  $\mathbf{d}_{ij}(\mathbf{R})$  that gives rise to the second-derivative coupling terms in the classical adiabatic representation.] The

MM classical adiabatic Hamiltonian [Eq. (2)] can be obtained directly from the above QM Hamiltonian [Eq. (5)] by using the general classical analog relation of Ref. 1, whereby the classical analog (CA) of a QM hermitian operator/matrix  $\hat{A}$  is given by

$$\hat{A} \xrightarrow{\text{CA}} \sum_i \left( \frac{1}{2} p_i^2 + \frac{1}{2} x_i^2 - \gamma \right) A_{ii} + \sum_{i \neq j} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) \text{Re}[A_{ij}] - \sum_{i \neq j} x_i p_j \text{Im}[A_{ij}], \quad (6)$$

where we have used a variable zero point energy (ZPE)  $\gamma$ -parameter in the diagonal terms in accord with the standard SQC protocol. (The QM ZPE parameter is  $\gamma = \frac{1}{2}$ .) This was in fact the procedure used in Ref. 1 to obtain the classical vibronic Hamiltonian in a diabatic representation.

Equation (6) can also be used to generalize to the case of an electronic basis  $\{|\phi_i(\mathbf{R})\rangle\}$  that is neither diabatic nor (fully) adiabatic, i.e., one that depends on nuclear coordinates  $\mathbf{R}$  but in which the electronic Hamiltonian matrix is not diagonal. Assuming that the electronic matrix in this basis  $\{H_{ij}\}$  is real-symmetric, the general classical vibronic Hamiltonian encompassing Eqs. (1) and (2) is

$$H(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}) = \frac{1}{2\mu} \left( \mathbf{P} + \sum_{i \neq j} x_i p_j \mathbf{d}_{ij}(\mathbf{R}) \right)^2 + \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j - \gamma \delta_{ij} \right) H_{ij}(\mathbf{R}), \quad (7)$$

where the definition of  $\Delta \mathbf{P}$  has been inserted explicitly. Equation (7) could be used in situations where one desires to work in an electronic basis that depends on the nuclear coordinates but which is not fully adiabatic (e.g., when the adiabatic PESs are degenerate or nearly so, when a partial diabaticization may be desirable, etc.).

Finally, although the classical adiabatic Hamiltonian [Eq. (2)] was obtained in Ref. 1 via a canonical transformation from the diabatic version [Eq. (1)] using a classical generating function to carry out the transformation, for completeness, Appendix A shows an alternate (but equivalent) approach for doing this (based on the symplectic character of such transformations). This also validates the classical vibronic Hamiltonian of Eq. (7) for a general electronic representation.

## B. Equations of motion

As discussed in the Introduction, the chief contribution of this paper is a modified form of the classical equations of motion (EOMs) generated from the adiabatic version of the MM Hamiltonian [Eq. (2)] [and also its generalization Eq. (7)]. The canonical EOMs (i.e., Hamilton's equations, see below) involve second-derivative couplings  $\mathbf{D}_{ij}$ , in addition to the more common first-derivative couplings  $\mathbf{d}_{ij}$ , for the same reason that they appear in the adiabatic representation of the quantum Hamiltonian operator [Eq. (4)] (i.e., from the  $\mathbf{R}$ -dependence of  $\mathbf{d}_{ij}$ ). Because computing these second-derivative couplings constitutes a significant increase in the difficulty of *ab initio* electronic structure calculations, they are often neglected, which is clearly an approximation (sometimes very severe, as illustrated by some of the examples treated in

Sec. III). The goal, therefore, is to derive EOMs that avoid  $\mathbf{D}_{ij}$  without introducing any approximation.

The canonical classical adiabatic EOMs are given by Hamilton's equations

$$\dot{x}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial x_i}, \quad \dot{\mathbf{R}} = \frac{\partial H}{\partial \mathbf{P}}, \quad \dot{\mathbf{P}} = -\frac{\partial H}{\partial \mathbf{R}}$$

applied to the adiabatic MM Hamiltonian of Eq. (2). If the effective potential term in Eq. (2),

$$V_{\text{eff}}(\mathbf{x}, \mathbf{p}, \mathbf{R}) \equiv \sum_i \left( \frac{1}{2} p_i^2 + \frac{1}{2} x_i^2 - \gamma \right) E_i(\mathbf{R}), \quad (8)$$

is replaced with a symmetrized form<sup>8</sup> (which is almost always employed),

$$V_{\text{eff}}(\mathbf{x}, \mathbf{p}, \mathbf{R}) \equiv \frac{1}{F} \sum_i E_i(\mathbf{R}) + \frac{1}{F} \sum_{ij} \frac{1}{4} (p_i^2 - p_j^2 + x_i^2 - x_j^2) (E_i(\mathbf{R}) - E_j(\mathbf{R})), \quad (8')$$

then the canonical EOMs are given explicitly as follows:

$$\dot{x}_i = p_i \frac{1}{F} \sum_j (E_i(\mathbf{R}) - E_j(\mathbf{R})) + \sum_j x_j \mathbf{d}_{ji}(\mathbf{R}) \cdot \frac{\mathbf{P} + \Delta \mathbf{P}}{\mu}, \quad (9a)$$

$$\dot{p}_i = -x_i \frac{1}{F} \sum_j (E_i(\mathbf{R}) - E_j(\mathbf{R})) + \sum_j p_j \mathbf{d}_{ji}(\mathbf{R}) \cdot \frac{\mathbf{P} + \Delta \mathbf{P}}{\mu}, \quad (9b)$$

$$\dot{\mathbf{R}} = \frac{\mathbf{P} + \Delta \mathbf{P}}{\mu}, \quad (9c)$$

$$\dot{\mathbf{P}} = -\frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} - \sum_{ij} x_i p_j \frac{\partial}{\partial \mathbf{R}} \mathbf{d}_{ij} \cdot \frac{\mathbf{P} + \Delta \mathbf{P}}{\mu}. \quad (9d)$$

One sees that Eqs. (9a)–(9c) involve only the first derivative coupling term  $\mathbf{d}_{ij}(\mathbf{R})$  but that Eq. (9d)—which is related to the force on the nuclear DOFs—involves its derivative, and thus the usual second-derivative coupling  $\mathbf{D}_{ij}$ . If these second-derivative coupling terms are ignored, as is often done (because their calculation is considerably more difficult than the first-derivative couplings), then Eq. (9d) is replaced by Eq. (9d'),

$$\dot{\mathbf{P}} \approx -\frac{\partial V_{\text{eff}}}{\partial \mathbf{R}}, \quad (9d')$$

which is an approximation that is sometimes not a problem, but that sometimes is (see the examples in Sec. III). Also, the total energy will not be conserved if this approximation is made.

However, it has been discovered that this problem may be completely eliminated—i.e., the exact dynamics of the adiabatic Meyer-Miller Hamiltonian of Eq. (2) [or Eq. (7)] may be computed without any knowledge of the second-derivative couplings—by working in terms of the *kinematic* momentum  $\mathbf{P}_{\text{kin}}$  (see Ref. 5 at p. 135) rather than the canonical momentum  $\mathbf{P}$ , which is defined by

$$\mathbf{P}_{\text{kin}} \equiv \mathbf{P} + \Delta \mathbf{P}. \quad (10a)$$



In terms of  $\mathbf{P}_{\text{kin}}$ , Eq. (9c) thus becomes

$$\dot{\mathbf{R}} = \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (10b)$$

and to obtain a closed set of EOMs, one needs an expression for  $\dot{\mathbf{P}}_{\text{kin}}$  in terms of the other variables. From its definition by Eq. (10a), one has

$$\dot{\mathbf{P}}_{\text{kin}} = \dot{\mathbf{P}} + \frac{d}{dt} \Delta \mathbf{P}, \quad (10c)$$

and by using Eq. (9d) for the first term on the RHS of Eq. (10c), and the chain rule to obtain  $\frac{d}{dt} \Delta \mathbf{P}(\mathbf{x}(t), \mathbf{p}(t), \mathbf{R}(t))$ , one finds

$$\begin{aligned} \dot{\mathbf{P}}_{\text{kin}} = & -\frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} - \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{R}} \cdot \dot{\mathbf{R}} \\ & + \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{R}} \cdot \dot{\mathbf{R}} + \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{x}} \cdot \dot{\mathbf{x}} + \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{p}} \cdot \dot{\mathbf{p}}, \end{aligned} \quad (11)$$

where the terms involving  $\frac{\partial}{\partial \mathbf{R}} \mathbf{d}_{ij}$  are seen to cancel, leaving

$$\dot{\mathbf{P}}_{\text{kin}} = \sum_{ij} (\dot{x}_i p_j + x_i \dot{p}_j) \mathbf{d}_{ij} - \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}}.$$

Using Eqs. (9a) and (9b) for  $\dot{x}_i$  and  $\dot{p}_j$  then gives the desired expression for  $\dot{\mathbf{P}}_{\text{kin}}$  so that the modified EOMs re-expressed in terms of  $\mathbf{P}_{\text{kin}}$ , which we refer to as the kinematic EOMs, are given by

$$\dot{x}_i = p_i \frac{1}{F} \sum_j (E_i(\mathbf{R}) - E_j(\mathbf{R})) + \sum_j x_j \mathbf{d}_{ji}(\mathbf{R}) \cdot \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (12a)$$

$$\dot{p}_i = -x_i \frac{1}{F} \sum_j (E_i(\mathbf{R}) - E_j(\mathbf{R})) + \sum_j p_j \mathbf{d}_{ji}(\mathbf{R}) \cdot \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (12b)$$

$$\dot{\mathbf{R}} = \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (12c)$$

$$\dot{\mathbf{P}}_{\text{kin}} = -\frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} - \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) (E_j(\mathbf{R}) - E_i(\mathbf{R})) \mathbf{d}_{ij}(\mathbf{R}), \quad (12d)$$

which do not involve the second-derivative coupling term  $\mathbf{D}_{ij}(\mathbf{R})$ . [Appendix B shows that this same procedure can also be carried through for the generalized MM Hamiltonian of Eq. (7), i.e., to produce EOMs that are independent of second-derivative couplings]. It should also be noted that in addition to causing electronic transitions [Eqs. (12a) and (12b)], the first-derivative coupling vector  $\mathbf{d}_{ij}(\mathbf{R})$  also contributes to the force on the nuclear DOFs [i.e., in Eq. (12d)] in addition to that from  $V_{\text{eff}}$ .

An important aspect of the kinematic adiabatic EOMs<sup>9</sup> of Eq. (12), which we emphasize again, is that they are entirely equivalent to the original canonical adiabatic EOMs of Eq. (9)—i.e., when they are integrated, they give exactly the same dynamics—because all that has been done is a straightforward change of variables without any approximation. The practical advantage of Eq. (12), of course, is that these kinematic EOMs do not involve the second-derivative couplings that are involved in the original canonical EOMs, yet they have not been neglected; they simply do not appear in the modified EOMs.

It is also clear that the conserved energy is still given by the MM Hamiltonian of Eq. (2). Rewritten in terms of  $\mathbf{P}_{\text{kin}}$ , this is simply

$$E(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}_{\text{kin}}) = \frac{\mathbf{P}_{\text{kin}}^2}{2\mu} + V_{\text{eff}}(\mathbf{x}, \mathbf{p}, \mathbf{R}). \quad (13)$$

However, it must be emphasized that while Eq. (13) is a correct expression for the total energy (nuclear + electronic) that is conserved along a trajectory generated by integrating the kinematic EOMs [Eq. (12)], it is labeled “*E*” not “*H*” because it is not a Hamiltonian function since the change of variables  $\mathbf{P} \rightarrow \mathbf{P}_{\text{kin}}$  is not a canonical transformation (i.e.,  $\mathbf{P}_{\text{kin}}$  is not the momentum canonically conjugate to the coordinate  $\mathbf{R}$ ). For example, if one assumed that  $\mathbf{R}$  and  $\mathbf{P}_{\text{kin}}$  were canonically conjugate variables and Eq. (13) was a classical Hamiltonian, Hamilton’s equations would give no electronic transitions since it does not involve any non-adiabatic coupling!

Because the kinematic EOMs [Eq. (12)] are not Hamilton’s equations for *any* classical Hamiltonian, Appendix C explores the question of whether there is any classical formulation from which they emerge. A possibility for this is Lagrange’s equations (at least for the nuclear DOFs) since it is the coordinates and their time derivatives (i.e., the velocities) that are the fundamental variables of a Lagrangian (rather than the coordinates and their canonically conjugate momenta that are the variables of a Hamiltonian). It is shown in Appendix C that a hybrid formulation—Lagrangian for the nuclear DOFs and Hamiltonian for the electronic DOFs—does indeed accomplish this [i.e., generates the kinematic EOMs, Eq. (12)].

The EOMs given by Eq. (12) also emerge from the forward-backward linearization approximation to a mixed quantum-classical Liouville formulation used by Kapral *et al.*<sup>10</sup> in the adiabatic representation. This approach utilizes the MM oscillator (“mapping”) representation for the electronic DOFs and makes a linearization approximation<sup>11–14</sup> to the difference of the forward and backward trajectories in a Heisenberg time-evolved operator. The development presented here in Sec. II B shows that the EOMs in Eq. (12) are exactly equivalent to the canonical EOMs (Hamilton’s equations) in Eq. (9) that result from the adiabatic version of the MM classical vibronic Hamiltonian.

Finally, it is interesting to note that Eq. (12d) is closely related to the Ehrenfest force on the nuclear DOFs in the adiabatic representation (as, has been noted before,<sup>1</sup> it is also in the diabatic representation of the MM Hamiltonian). This follows from the general version of the Hellman-Feynman theorem (i.e., for the diagonal and off-diagonal matrix elements of the force): the adiabatic eigenfunctions are defined as the eigenfunctions of the electronic Hamiltonian operator at nuclear coordinates  $\mathbf{R}$ ,

$$\hat{H}_{\text{el}}(\mathbf{R})|\phi_j(\mathbf{R})\rangle = E_j(\mathbf{R})|\phi_j(\mathbf{R})\rangle, \quad (14)$$

and if one differentiates this with respect to  $\mathbf{R}$  and projects onto the eigenstate  $|\phi_i(\mathbf{R})\rangle$ , one obtains

$$\begin{aligned} \langle \phi_i(\mathbf{R}) | \frac{\partial H_{\text{el}}(\mathbf{R})}{\partial \mathbf{R}} | \phi_j(\mathbf{R}) \rangle \\ = \frac{\partial E_i(\mathbf{R})}{\partial \mathbf{R}} \delta_{ij} + (E_j(\mathbf{R}) - E_i(\mathbf{R})) \mathbf{d}_{ij}(\mathbf{R}). \end{aligned} \quad (15)$$

Using this, one sees that Eq. (12d) for  $\dot{\mathbf{P}}_{\text{kin}}(t)$  can be written [ignoring the ZPE term  $\gamma$  and the symmetrization in going from Eq. (8) to Eq. (8')] as

$$\begin{aligned}\dot{\mathbf{P}}_{\text{kin}} &= - \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) \left( (E_j - E_i) \mathbf{d}_{ij} + \delta_{ij} \frac{\partial E_i}{\partial \mathbf{R}} \right) \\ &= - \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) \langle \phi_i | \frac{\partial \hat{H}_{\text{el}}}{\partial \mathbf{R}} | \phi_j \rangle \\ &= - \sum_{ij} c_i^* c_j \langle \phi_i | \frac{\partial \hat{H}_{\text{el}}}{\partial \mathbf{R}} | \phi_j \rangle \\ &\equiv - \langle \psi | \frac{\partial \hat{H}_{\text{el}}}{\partial \mathbf{R}} | \psi \rangle,\end{aligned}\quad (16)$$

i.e., as the Ehrenfest force (where the time-dependent electronic state is  $|\psi\rangle \equiv \sum_i c_i |\phi_i\rangle$ , and MM's definition of  $c_i = \frac{1}{\sqrt{2}}(x_i + i p_i)$  has been used). We note further, as shown in Appendix B, that the generalized version of the MM Hamiltonian given in Eq. (7) and its EOMs also yield this same result. Thus, the force on the nuclear DOFs in all representations of the MM classical electronic-nuclear Hamiltonian is basically the Ehrenfest force; although as we have discussed in detail several times, the overall SQC/MM model is not the Ehrenfest *method* because of the way the SQC model defines initial and final electronic states (which is essentially an approximate version of Bohr-Sommerfeld quantization, a semiclassical concept).

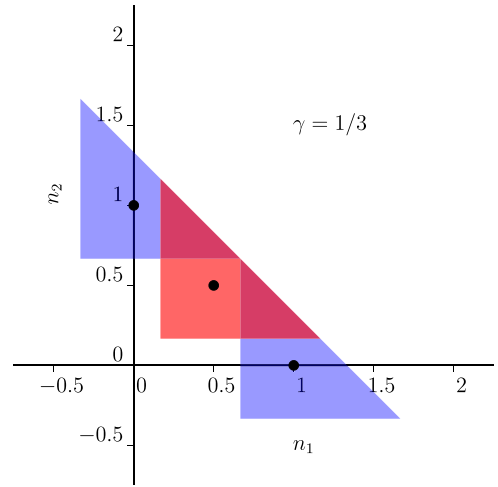


FIG. 1. Triangle SQC windowing scheme: quantum state windows centered at  $(n_1, n_2) = (1, 0)$  and  $(n_1, n_2) = (0, 1)$ ,  $n_i = \frac{1}{2} p_i + \frac{1}{2} x_i - \gamma$  [see Eqs. (1) and (2)]; off-diagonal density matrix element represented by the window centered at  $(n_1, n_2) = (\frac{1}{2}, \frac{1}{2})$  (not used here, but see Ref. 17 for details); this triangle windowing scheme is used for all SQC calculations herein, as it is important to properly treat the weak-coupling regime (see Ref. 16), which is considered in Fig. 3. (See any of Refs. 4, 15, 16, 18, and 19 for a detailed description of the SQC/MM methodology.)

### III. EXAMPLE APPLICATIONS

The following applications illustrate two important points:  
(i) the equivalence of the adiabatic and diabatic MM

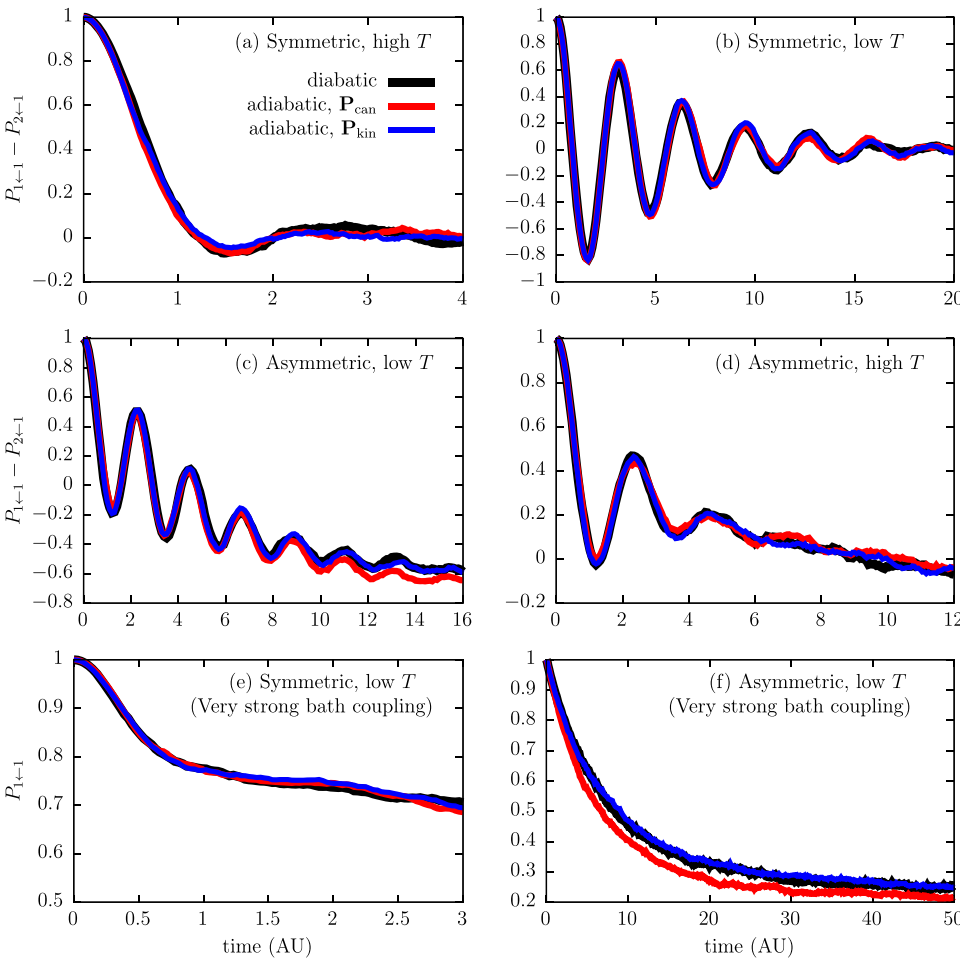


FIG. 2. Adiabatic SQC/MM calculations using (i) the EOMs of Eq. (9) in terms of  $\mathbf{P}_{\text{can}}$  [neglecting  $\mathbf{D}_{ij}$  terms in Eq. (9d)], and (ii) using the modified EOMs of Eq. (12) in terms of  $\mathbf{P}_{\text{kin}}$ , both compared with previous diabatic SQC/MM calculations for the following six versions of the SB problem at temperature  $T = ((k_B\beta)^{-1})$  and with non-adiabatic coupling constant  $\Delta = 1$  [in Eq. (17)]: (a)  $\epsilon = 0$ ,  $\beta\Delta = 0.1$ ,  $\omega_c = 2.5\Delta$ ,  $\alpha = 0.09$ ; (b)  $\epsilon = 0$ ,  $\beta\Delta = 5$ ,  $\omega_c = 2.5\Delta$ ,  $\alpha = 0.09$ ; (c)  $\epsilon = 1$ ,  $\beta\Delta = 5$ ,  $\omega_c = 2.5\Delta$ ,  $\alpha = 0.1$ ; (d)  $\epsilon = 1$ ,  $\beta\Delta = 0.25$ ,  $\omega_c = \Delta$ ,  $\alpha = 0.1$ ; (e)  $\epsilon = 0$ ,  $\beta\Delta = 1$ ,  $\omega_c = \Delta$ ,  $\alpha = 2$ ; (f)  $\epsilon = 5$ ,  $\beta\Delta = 0.1$ ,  $\omega_c = 2\Delta$ ,  $\alpha = 4$ , where  $\omega_c$  is the bath's characteristic frequency;  $\alpha$  is a bath "friction" parameter that gives the coupling constants  $\{c_k\}$  as a function of the frequencies  $\{\omega_k\}$  (see Refs. 4, 15, and 16);  $\alpha$  is significantly stronger for versions (e) and (f) (see Ref. 20). (Each calculation runs for a 10 000 trajectory ensemble.)

Hamiltonians so long as the first- and second-derivative non-adiabatic coupling elements are properly incorporated in the adiabatic calculations, and (ii) that sometimes neglecting the second-derivative coupling terms in the adiabatic representation leads to minimal error, but other times it is an extremely poor approximation, demonstrating the importance of the “kinematic” adiabatic EOMs [Eq. (12)]—i.e., written in terms of  $\mathbf{P}_{\text{kin}}$ —which properly include the effects of both first- and second-derivative couplings (even though the latter do not appear explicitly in the EOMs). For the purpose of illustrating these two points, we use the popular spin-boson (SB) model of a 2-state electronically non-adiabatic process in a condensed phase environment, specifically a standard suite of benchmark versions (see below) that we have used before.

The details of the spin-boson (SB) model may be found in Refs. 4, 15, and 16. Briefly, it is given by a diabatic electronic Hamiltonian matrix of the form

$$\mathbf{H}(\mathbf{Q}) = \begin{bmatrix} V_0(\mathbf{Q}) + V_1(\mathbf{Q}) + \epsilon & \Delta \\ \Delta & V_0(\mathbf{Q}) - V_1(\mathbf{Q}) - \epsilon \end{bmatrix}, \quad (17)$$

where the off-diagonal electronic coupling  $\Delta$  is taken to be a constant independent of nuclear coordinates, and the diagonal elements are shifted multidimensional harmonic potentials given by

$$V_0(\mathbf{Q}) = \sum_{k=1}^G \frac{1}{2} \omega_k^2 Q_k^2 \quad \text{and} \quad V_1(\mathbf{Q}) = \sum_{k=1}^G c_k Q_k,$$

which are energetically biased in Eq. (17) by  $2\epsilon$ . The frequencies  $\{\omega_k\}$  and coupling strengths  $\{c_k\}$  are chosen to characterize a condensed phase environment; here,  $G = 100$  frequencies are selected from an “Ohmic” distribution with exponential cutoff and sampled thermally according to the standard Wigner distribution function. (See Refs. 4, 15, and 16 for the details of selecting  $\{\omega_k\}$  and  $\{c_k\}$  for these models.)

We consider a suite of six SB models: the four versions originally used<sup>15</sup> and two additional versions recently suggested and treated using exact methods by Walters and Makri.<sup>20</sup> In Ref. 16, we recently treated all six versions using our new SQC triangle windowing methodology—see Fig. 1—and in all cases, we found excellent agreement with the exact QM results. We thus take these diabatic SQC/MM calculations as the benchmark results to which are compared the corresponding adiabatic calculations<sup>21</sup> using two versions of the adiabatic EOMs: (i) the approximate canonical EOMs [i.e., using Eq. (9d’)] that neglect the second-derivative couplings (as is often done since they are more difficult to obtain from *ab initio* quantum chemistry), and (ii) the kinematic EOMs [Eq. (12)] written in terms of the kinematic nuclear momenta  $\mathbf{P}_{\text{kin}}$ , which, even though they do not involve second-derivative coupling terms, are exactly equivalent to the canonical EOMs [Eq. (9)] if second- as well as first-derivative couplings are included in the latter. Figure 2 is for the case of relatively strong electronic coupling ( $\Delta = 1$ ) in the diabatic Hamiltonian, and Fig. 3 for weak electronic coupling ( $\Delta = 0.1$ ), with

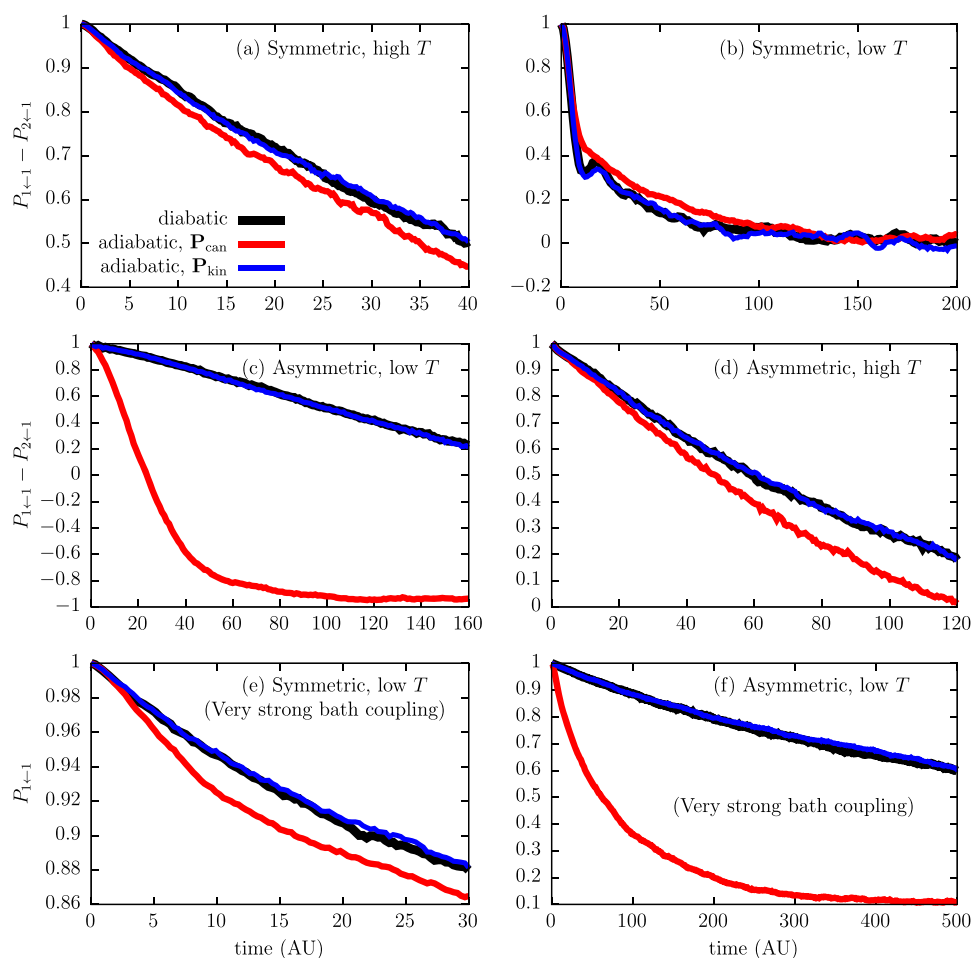


FIG. 3. Same as Fig. 2 but for weak non-adiabatic coupling  $\Delta = 0.1$  and  $10\times$  time scale (and again using 10 000 trajectory ensembles).

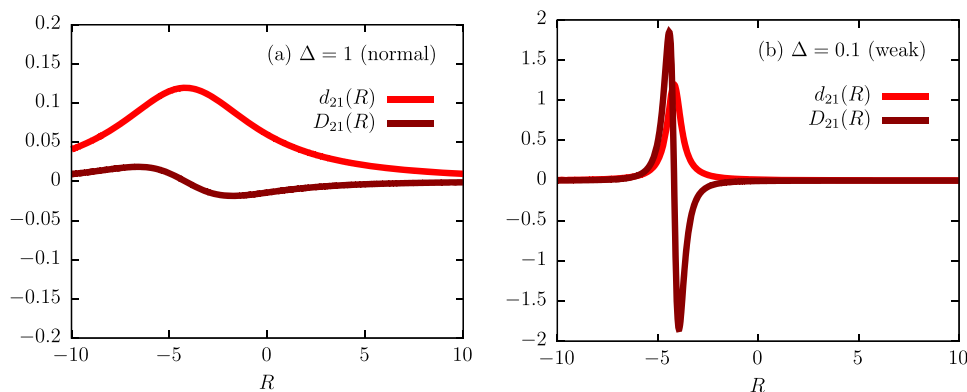


FIG. 4. Sample first- and second-derivative couplings corresponding to SB version (c) shown in Figs. 2 and 3; the chosen  $R$  coordinate is the harmonic bath mode closest to  $\omega_c$ .

all other parameters in the various cases given in the figure captions.

The SQC/MM results shown in Figs. 2 and 3 may be summarized very succinctly. In all cases, the results given by the kinematic adiabatic EOMs [Eq. (12)] agree essentially exactly with those of the diabatic calculations (which are the “benchmark” results). This *must* be the case (unless there is a mistake in the theory or the numerics) because the kinematic adiabatic EOMs are equivalent to the full/unaltered canonical adiabatic dynamics/EOMs (that includes first- and second-derivative couplings) that are equivalent to the diabatic dynamics/EOMs (since these two are related by a canonical transformation).

Having verified that this first point is true, the test is whether or not neglecting the second-derivative coupling in the canonical adiabatic dynamics [i.e., using Eq. (9d') rather than Eq. (9d)] causes much error. For the case of strong diabatic electronic coupling (Fig. 2), one sees that these approximate adiabatic results show some error [e.g., Figs. 2(c) and 2(f)], but not much. Thus, neglecting the second-derivative coupling in these cases is a reasonable approximation. For weak diabatic electronic coupling (Fig. 3), however, one sees that the neglect of second-derivative coupling causes very noticeable error, and in some of these examples [e.g., Figs. 3(c) and 3(f)], quite a disastrous error.

This behavior in Figs. 2 and 3 is actually quite easy to understand. When the diabatic electronic coupling is large (Fig. 2), the splitting between the adiabatic potentials is large and the derivative coupling spread out, but not large. See, e.g., Fig. 4(a). In the opposite limit, when the diabatic electronic coupling is small (Fig. 3), the derivative coupling is strongly peaked at avoided crossings (or near conical intersections) where it becomes large and the second-derivative coupling is also large (or often larger). See, e.g., Fig. 4(b). Neglecting the second derivative coupling is thus not a major approximation in the former case, while it is in the latter.

#### IV. SUMMARY AND CONCLUSION

This paper has focused on the adiabatic version of the Meyer-Miller classical vibronic (electronic + nuclear) Hamiltonian for describing electronically non-adiabatic processes in molecular systems. Hamilton's equations that result from this Hamiltonian, the canonical classical equations of motion (EOMs), give the correct vibronic dynamics; however, they involve second-derivative non-adiabatic coupling terms

(in addition to the usual first-derivative couplings), which adds considerable extra difficulty when generating the adiabatic (Born-Oppenheimer) potential energy surfaces and their derivative couplings from *ab initio* electronic structure calculations. This is completely analogous to the first- and second-derivative coupling terms that appear in the corresponding quantum mechanical Schrödinger equation. It is thus common to neglect the second-derivative coupling terms.

It has been shown here, however, that a modified version of the classical EOMs in the adiabatic representation can be obtained—by using the kinematic momentum variable for the nuclear DOFs rather than the canonical momentum—which involve only the first-derivative non-adiabatic coupling terms but are nevertheless completely equivalent to the canonical EOMs (i.e., Hamilton's equations), which involve second- as well as first-derivative coupling elements; the second-derivative terms have not been neglected in these “kinematic” EOMs, they simply do not appear in them. Application to a suite of spin-boson model problems verifies that the kinematic adiabatic EOMs do indeed produce the same results as the canonical EOMs (that involve second- as well as first-derivative coupling terms), and also that very significant errors can result if second-derivative couplings are neglected in the canonical EOMs.

These kinematic adiabatic EOMs are expected to be most significant for carrying out classical simulations using the adiabatic version of SQC/MM model for “real” molecular systems that use *ab initio* electronic structure calculations to obtain the PESs and first-derivative couplings, for these are the quantities that are the direct “output” of such calculations.

#### ACKNOWLEDGMENTS

We thank Professor Eran Rabani for a useful discussion regarding the Heisenberg EOMs for the kinematic momentum.

This work was supported by the National Science Foundation under Grant No. CHE-1464647 and by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

In addition, this research utilized computation resources provided by the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.



## APPENDIX A: RIGOROUS DERIVATION OF THE ADIABATIC AND GENERALIZED REPRESENTATIONS

The adiabatic version of the MM Hamiltonian [Eq. (2)] is rigorously derived from the diabatic one [Eq. (1)] by making a canonical transformation from the old set of diabatic canonical variables to a new canonical adiabatic set in terms of which the new Hamiltonian is expressed. One way to do this is by the “generating function” technique (see Ref. 22 at p. 378 *et seq.*) used in the original MM paper. Another way (equivalent and equally rigorous) is through the “symplectic approach” (see Ref. 22 at p. 391 *et seq.*), namely, that for a transformation to be canonical<sup>23</sup> from a set of old variables ( $\mathbf{q}, \mathbf{p}$ ) to a set of new variables ( $\tilde{\mathbf{q}}, \tilde{\mathbf{p}}$ ), the transformation equations  $\tilde{\mathbf{q}}(\mathbf{q}, \mathbf{p})$ ,  $\tilde{\mathbf{p}}(\mathbf{q}, \mathbf{p})$  and their inverses  $\mathbf{q}(\tilde{\mathbf{q}}, \tilde{\mathbf{p}})$ ,  $\mathbf{p}(\tilde{\mathbf{q}}, \tilde{\mathbf{p}})$  must satisfy the following relations (enforcing conservation of phase space volume):

$$\begin{bmatrix} \frac{\partial \tilde{q}_i}{\partial q_j} & \frac{\partial \tilde{q}_i}{\partial p_j} \\ \frac{\partial \tilde{p}_i}{\partial q_j} & \frac{\partial \tilde{p}_i}{\partial p_j} \end{bmatrix} = \begin{bmatrix} \frac{\partial p_i}{\partial \tilde{p}_j} & -\frac{\partial q_i}{\partial \tilde{p}_j} \\ -\frac{\partial p_i}{\partial \tilde{q}_j} & \frac{\partial q_i}{\partial \tilde{q}_j} \end{bmatrix}. \quad (\text{A1})$$

For the case of converting the diabatic MM Hamiltonian [Eq. (1)] to the adiabatic version [Eq. (2)], most of the transformation relationships are predetermined: The new/adiabatic electronic variables ( $\tilde{\mathbf{x}}, \tilde{\mathbf{p}}$ ) are related to the old/diabatic ones ( $\mathbf{x}, \mathbf{p}$ ) by

$$\begin{aligned} \tilde{\mathbf{x}} &= \mathbf{U}(\mathbf{R}) \cdot \mathbf{x}, \\ \tilde{\mathbf{p}} &= \mathbf{U}(\mathbf{R}) \cdot \mathbf{p}, \end{aligned} \quad (\text{A2})$$

where  $\mathbf{U}$  is the unitary matrix that diagonalizes the diabatic electronic matrix  $\mathbf{H}(\mathbf{R})$ .<sup>24</sup> Furthermore (as a practical matter), the nuclear coordinates are required to be the same in both representations, i.e.,  $\tilde{\mathbf{R}} \equiv \mathbf{R}$ .

This leaves the sole task to identify the new canonical momentum  $\tilde{\mathbf{P}}$ . From the diagonal relations in Eq. (A1),  $\tilde{\mathbf{R}} = \mathbf{R}$  implies

$$\frac{\partial \mathbf{P}(\tilde{\mathbf{R}}, \tilde{\mathbf{P}}, \tilde{\mathbf{x}}, \tilde{\mathbf{p}})}{\partial \tilde{\mathbf{P}}} = 1, \quad (\text{A3})$$

i.e., that  $\mathbf{P}$  is  $\tilde{\mathbf{P}}$  plus some function of the other variables,

$$\mathbf{P} = \tilde{\mathbf{P}} + \Delta \mathbf{P}(\tilde{\mathbf{R}}, \tilde{\mathbf{x}}, \tilde{\mathbf{p}}). \quad (\text{A4})$$

To determine this  $\Delta \mathbf{P}$  function, the diagonal relations in Eq. (A1) between different classes of DOFs are useful,

$$\frac{\partial \tilde{x}_i}{\partial \mathbf{R}} = \frac{\partial \mathbf{P}}{\partial \tilde{p}_i}, \quad \frac{\partial \tilde{p}_i}{\partial \mathbf{R}} = -\frac{\partial \mathbf{P}}{\partial \tilde{x}_i}, \quad (\text{A5})$$

which, in combination with Eq. (A2) (and its inverse), when applied to Eq. (A4) require

$$\begin{aligned} \frac{\partial \Delta \mathbf{P}}{\partial \tilde{p}_i} &= \sum_{jk} \frac{\partial U_{ik}}{\partial \mathbf{R}} U_{kj}^\dagger \tilde{x}_j = -\sum_j \mathbf{d}_{ij} \tilde{x}_j, \\ \frac{\partial \Delta \mathbf{P}}{\partial \tilde{x}_i} &= -\sum_{jk} \frac{\partial U_{ik}}{\partial \mathbf{R}} U_{kj}^\dagger \tilde{p}_j = \sum_j \mathbf{d}_{ij} \tilde{p}_j \end{aligned} \quad (\text{A6})$$

[recognizing  $\mathbf{d}_{ij}$  since  $U_{ik} \equiv \langle \phi_i(\mathbf{R}) | k \rangle$  is the transformation from diabatic state  $k$ ]. These relations are clearly satisfied for each of the  $i$ th electronic DOFs by

$$\Delta \mathbf{P} = \sum_{i < j} (\tilde{x}_i \tilde{p}_j - \tilde{p}_i \tilde{x}_j) \mathbf{d}_{ij}(\mathbf{R}) \quad (\text{A7})$$

which (removing the tildes) is the expression for  $\Delta \mathbf{P}$  given in Eq. (3b). Making the change  $\mathbf{P} \rightarrow \mathbf{P} + \Delta \mathbf{P}$  in the diabatic MM Hamiltonian of Eq. (1) and applying Eq. (A2) to transform the potential energy term<sup>25</sup> immediately gives the adiabatic MM Hamiltonian of Eq. (2).

Note that the only consequence of assuming an adiabatic coordinate-dependent basis transformation  $U(\mathbf{R})$  was the diagonal form of  $\{E_i(\mathbf{R})\}$ . Relaxing the assumption that the coordinate-dependent basis set is adiabatic gives the generalized MM Hamiltonian of Eq. (7) that applies for any electronic basis—adiabatic, diabatic, or anything in between.

## APPENDIX B: GENERALIZED REPRESENTATION AND EQUATIONS OF MOTION

Equation (7) from Sec. II A is a generalized version of the MM Hamiltonian for which the electronic basis states  $\{|\phi_i(\mathbf{R})\rangle\}$  depend parametrically on nuclear coordinates  $\mathbf{R}$  but are not the adiabatic eigenfunctions of the electronic Hamiltonian; the electronic Hamiltonian matrix in this basis is thus not diagonal, but there is still some residual derivative coupling (because the basis varies with  $\mathbf{R}$ ).

For example, the basis could be the result of approximately “diabatizing” the adiabatic electronic states from an *ab initio* electronic structure calculation (in order to minimize the derivative coupling and then make the approximation of neglecting it). A fully diabatic Hamiltonian has electronic coupling only via the electronic matrix  $\{H_{ij}(\mathbf{R})\}$ , and the adiabatic Hamiltonian has it only via the derivative coupling  $\mathbf{d}_{ij}(\mathbf{R})$ , while the generalized version of Eq. (7) allows it to be distributed between both sources. Thus, with Eq. (7), one could perform an approximate diabaticization—and benefit from the improved numerics—but then, rather than simply neglecting the residual derivative coupling term, include it in the EOMs generated from Eq. (7), without approximation—i.e., the vibronic dynamics would still be exact, even if the diabaticization is not.

As was done with Eq. (2), modified EOMs can be derived for the generalized Hamiltonian of Eq. (7) in which no second-order derivative coupling terms appear by rewriting the canonical EOMs (i.e., Hamilton’s equations) in terms of the kinematic momentum  $\mathbf{P}_{\text{kin}}$  (as opposed to the standard canonical momentum). Thus, if Eq. (7) is symmetrized in the usual way [e.g., see Eq. (8’) and Refs. 15 and 19] to give

$$H = \frac{1}{2\mu} (\mathbf{P} + \Delta \mathbf{P})^2 + V_{\text{eff}}, \quad (\text{B1})$$

where now

$$\begin{aligned} V_{\text{eff}} &\equiv \frac{1}{F} \sum_i^F H_{ii}(\mathbf{R}) \\ &+ \frac{1}{F} \sum_{ij}^F \frac{1}{4} (p_i^2 - p_j^2 + x_i^2 - x_j^2) (H_{ii} - H_{jj})(\mathbf{R}) \\ &+ \sum_{i \neq j}^F \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) H_{ij}(\mathbf{R}), \end{aligned} \quad (\text{B2})$$

then these new kinematic EOMs in terms of  $\mathbf{P}_{\text{kin}}$ , analogous to Eq. (12) but for this more general Hamiltonian, are

$$\dot{x}_i = p_i \frac{1}{F} \sum_{j \neq i}^F (H_{ii} - H_{jj}) (\mathbf{R}) + \sum_{j \neq i}^F \left( x_j \mathbf{d}_{ji}(\mathbf{R}) \cdot \frac{\mathbf{P}_{\text{kin}}}{\mu} + p_j H_{ji}(\mathbf{R}) \right), \quad (\text{B3a})$$

$$\dot{p}_i = -x_i \frac{1}{F} \sum_{j \neq i}^F (H_{ii} - H_{jj}) (\mathbf{R}) + \sum_{j \neq i}^F \left( p_j \mathbf{d}_{ji}(\mathbf{R}) \cdot \frac{\mathbf{P}_{\text{kin}}}{\mu} - x_j H_{ji}(\mathbf{R}) \right), \quad (\text{B3b})$$

$$\dot{\mathbf{R}} = \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (\text{B3c})$$

$$\dot{\mathbf{P}}_{\text{kin}} = \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) [\mathbf{H}, \mathbf{d}]_{ij}(\mathbf{R}) - \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}}, \quad (\text{B3d})$$

where Eq. (B3d) involves the commutator of the  $F \times F$  electronic Hamiltonian matrix  $\{H_{ij}\}$  with the  $F \times F$  matrix of derivative coupling vectors  $\{\mathbf{d}_{ij}\}$  [cf. Eq. (12d)]. Again, these EOMs are seen to be free of second-order derivative coupling terms.

Likewise, for these generalized EOMs, the conserved energy is still given by the MM Hamiltonian substituted with  $\mathbf{P} + \Delta \mathbf{P} = \mathbf{P}_{\text{kin}}$ , i.e.,

$$E(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}_{\text{kin}}) = \frac{\mathbf{P}_{\text{kin}}^2}{2\mu} + V_{\text{eff}}(\mathbf{x}, \mathbf{p}, \mathbf{R}), \quad (\text{B4})$$

and the “generator” of these EOMs [because Eq. (B4) is not a Hamiltonian] may be found by taking the partial Legendre transform of Eq. (B1) (as explained in Appendix C) yielding

$$\mathcal{H}(\mathbf{x}, \mathbf{p}, \mathcal{L}(\mathbf{R}, \dot{\mathbf{R}})) \equiv V_{\text{eff}}(\mathbf{x}, \mathbf{p}, \mathbf{R}) - \frac{1}{2} \mu \dot{\mathbf{R}}^2 + \Delta \mathbf{P}(\mathbf{x}, \mathbf{p}, \mathbf{R}) \cdot \dot{\mathbf{R}}, \quad (\text{B5})$$

which gives Eqs. (B3a) and (B3b) upon application of Hamilton’s equations and Eq. (B3d) when the Euler-Lagrange equation is applied to it. Equations (B4) and (B5) are thus the same as Eqs. (13) and (C6), but with  $V_{\text{eff}}$  given by Eq. (B2).

Finally, the relation to the Ehrenfest force—discussed above with respect to Eq. (2)—carries over in almost the same way for the general case of Eq. (7). Without the symmetrization applied to Eq. (7) and leaving out the ZPE term (i.e., setting  $\gamma = 0$ ), one has

$$V_{\text{eff}} = \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) H_{ij}(\mathbf{R}), \quad (\text{B6})$$

and the equation for the force on the nuclei ( $= \dot{\mathbf{P}}_{\text{kin}}$ ) due to the electronic configuration can be shown to be

$$\dot{\mathbf{P}}_{\text{kin}} = \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) \left( [\mathbf{H}, \mathbf{d}]_{ij} - \frac{\partial H_{ij}}{\partial \mathbf{R}} \right), \quad (\text{B7})$$

which now involves the commutator of the  $F \times F$  electronic Hamiltonian matrix  $\{H_{ij}\}$  with the  $F \times F$  matrix of derivative

coupling vectors  $\{\mathbf{d}_{ij}\}$  [cf. the first line of Eq. (16)]. However, applying the derivative product rule to  $\frac{\partial}{\partial \mathbf{R}} \langle \phi_i | \hat{H}_{\text{el}} | \phi_j \rangle$  for states  $\{|\phi_i(\mathbf{R})\rangle\}$  that are not necessarily adiabatic gives

$$\frac{\partial H_{ij}}{\partial \mathbf{R}} = [\mathbf{H}, \mathbf{d}]_{ij} + \langle \phi_i(\mathbf{R}) | \frac{\partial \hat{H}_{\text{el}}}{\partial \mathbf{R}} | \phi_j(\mathbf{R}) \rangle. \quad (\text{B8})$$

Using this more general Hellman-Feynman type expression, Eq. (B7) simplifies to

$$\begin{aligned} \dot{\mathbf{P}}_{\text{kin}} &= - \sum_{ij} \left( \frac{1}{2} x_i x_j + \frac{1}{2} p_i p_j \right) \langle \phi_i(\mathbf{R}) | \frac{\partial \hat{H}_{\text{el}}}{\partial \mathbf{R}} | \phi_j(\mathbf{R}) \rangle \\ &\equiv - \langle \psi | \frac{\partial \hat{H}_{\text{el}}}{\partial \mathbf{R}} | \psi \rangle, \end{aligned} \quad (\text{B9})$$

assuming  $\left[ \frac{\partial \hat{H}_{\text{el}}}{\partial \mathbf{R}} \right]_{ij}$  is real, which is (again) the Ehrenfest force on the nuclei due to electronic configuration  $|\psi\rangle = \sum_i c_i |\phi_i\rangle$  [where  $c_i \equiv \frac{1}{\sqrt{2}}(x_i + ip_i)$ ].

## APPENDIX C: PARTIAL LEGENDRE TRANSFORM

The Hamiltonian is a function of pairs of coordinates and canonically conjugate momenta  $(R_i, P_i)$ , but the standard way in classical mechanics to instead work in terms of pairs of coordinates and their corresponding velocities  $(R_i, \dot{R}_i)$  is through the classical Lagrangian,

$$\mathcal{L}(\mathbf{R}, \dot{\mathbf{R}}) = \sum_i \frac{1}{2} \mu \dot{R}_i^2 - V(\mathbf{R}, \dot{\mathbf{R}}), \quad (\text{C1})$$

from which EOMs are generated by the Euler-Lagrange equations,

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{R}_i} = \frac{\partial \mathcal{L}}{\partial R_i}, \quad (\text{C2})$$

which gives an expression for  $\dot{\mathbf{R}} = f(\mathbf{R}, \dot{\mathbf{R}})$  that can be converted to two first order equations in the usual way by identifying  $\mathbf{P}_{\text{kin}} \equiv \mu \dot{\mathbf{R}}$  and therefore  $\dot{\mathbf{P}}_{\text{kin}} = \mu f'(\mathbf{R}, \dot{\mathbf{R}})$ . The relationship between the Hamiltonian and Lagrangian functions themselves is through the Legendre transform,

$$H(\mathbf{R}, \mathbf{P}) + \mathcal{L}(\mathbf{R}, \dot{\mathbf{R}}) = \sum_i P_i \dot{R}_i, \quad (\text{C3})$$

which provides a prescription for obtaining one generator,  $\mathcal{L}$  or  $H$ , from the other.

We are interested, however, in finding a simple generator for the EOMs in Eqs. (12) and (B3), which, although written in terms of the kinematic momentum  $\mathbf{P}_{\text{kin}} \equiv \mu \dot{\mathbf{R}}$  for the nuclear DOFs, are in terms of the canonical momenta  $\{p_i\}$  for the electronic variables. We therefore only seek to exchange  $\mathbf{P}$  for  $\dot{\mathbf{R}}$  and this may be accomplished by subtracting from  $H$  the product  $\mathbf{P} \cdot \dot{\mathbf{R}}$  (i.e., performing a partial Legendre transform),

$$H(\mathbf{x}, \mathbf{p}, \mathbf{R}, \mathbf{P}) - \mathbf{P} \cdot \dot{\mathbf{R}} = \frac{1}{2\mu} (\mathbf{P} + \Delta \mathbf{P})^2 + V_{\text{eff}} - \mathbf{P} \cdot \dot{\mathbf{R}}. \quad (\text{C4})$$

After eliminating  $\mathbf{P}$  by using Hamilton’s equation,

$$\dot{\mathbf{R}} = \frac{\partial H}{\partial \mathbf{P}} = \frac{1}{\mu} (\mathbf{P} + \Delta \mathbf{P}), \quad (\text{C5})$$

Equation (C4) becomes

$$\mathcal{H}(\mathbf{x}, \mathbf{p}, \mathcal{L}(\mathbf{R}, \dot{\mathbf{R}})) \equiv V_{\text{eff}}(\mathbf{x}, \mathbf{p}, \mathbf{R}) - \frac{1}{2} \mu \dot{\mathbf{R}}^2 + \Delta \mathbf{P}(\mathbf{x}, \mathbf{p}, \mathbf{R}) \cdot \dot{\mathbf{R}}, \quad (\text{C6})$$

a function  $\mathcal{H}$  that remains “Hamiltonian-like” with respect to the electronic variables  $\{x_i, p_i\}$  but, as indicated by the dependency on  $\mathcal{L}(\mathbf{R}, \dot{\mathbf{R}})$ , is “Lagrangian-like” with respect to the nuclear coordinates and velocities.<sup>26</sup>

Thus, with  $V_{\text{eff}}$  corresponding to the generalized and symmetrized MM Hamiltonian of Appendix B [Eqs. (B1) and (B2)], Hamilton’s equations applied to Eq. (C6) give Eqs. (B3a) and (B3b) for the evolution of the electronic DOFs, but the Euler-Lagrange equation [Eq. (C2)] gives the evolution of the nuclear DOFs,

$$\begin{aligned} \frac{d}{dt} \frac{\partial \mathcal{H}}{\partial \dot{\mathbf{R}}} &= \frac{\partial \mathcal{H}}{\partial \mathbf{R}} \\ \frac{d}{dt} (-\mu \dot{\mathbf{R}} + \Delta \mathbf{P}) &= \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{R}} \cdot \dot{\mathbf{R}} + \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} \end{aligned}$$

or [as with Eq. (11)]

$$\begin{aligned} \mu \ddot{\mathbf{R}} &= \frac{d}{dt} \Delta \mathbf{P} - \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{R}} \cdot \dot{\mathbf{R}} - \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} \\ &= \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{x}} \cdot \dot{\mathbf{x}} + \frac{\partial \Delta \mathbf{P}}{\partial \mathbf{p}} \cdot \dot{\mathbf{p}} - \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} \\ &= \sum_{ij} (\dot{x}_i p_j + x_i \dot{p}_j) \mathbf{d}_{ij} - \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}}, \end{aligned}$$

which, after substituting in expressions for  $\dot{\mathbf{x}}$  and  $\dot{\mathbf{p}}$  (and some algebra), yields

$$\mu \ddot{\mathbf{R}} = \sum_{ij} \left( \frac{1}{2} p_i p_j + \frac{1}{2} x_i x_j \right) [\mathbf{H}, \mathbf{d}]_{ij}(\mathbf{R}) - \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}}.$$

Identifying  $\mathbf{P}_{\text{kin}} \equiv \mu \dot{\mathbf{R}}$ , this is the same EOMs for  $\mathbf{P}_{\text{kin}}$  as Eq. (B3d).

<sup>1</sup>H.-D. Meyer and W. H. Miller, *J. Chem. Phys.* **70**, 3214 (1979).

<sup>2</sup>G. Stock and M. Thoss, *Phys. Rev. Lett.* **78**, 578 (1997), which provides an alternate, more rigorous way to obtain the MM classical vibronic Hamiltonian via the Schwinger bosonization procedure.

<sup>3</sup>S. J. Cotton and W. H. Miller, *J. Phys. Chem. A* **117**, 7190 (2013).

<sup>4</sup>W. H. Miller and S. J. Cotton, *Faraday Discuss.* **195**, 9 (2016).

<sup>5</sup>J. J. Sakurai, *Modern Quantum Mechanics*, Revised ed. (Addison-Wesley, 1995).

<sup>6</sup>C. A. Mead and D. G. Truhlar, *J. Chem. Phys.* **70**, 2284 (1979).

<sup>7</sup>D. R. Yarkony, *Rev. Mod. Phys.* **68**, 985 (1996).

<sup>8</sup>The symmetrized  $V_{\text{eff}}$  of Eq. (8')—a result of re-writing Eq. (8) relative to the average of the diagonal electronic matrix elements (see Refs. 15 and 19)—gives electronic EOMs [Eqs. (9a) and (9b)] expressed in terms of the differences between the PESs, which can have numerical advantages.

<sup>9</sup>It is perhaps not surprising that the (QM) Heisenberg EOMs for the kinematic momentum operator, defined analogous to Eq. (10a), has the same form as Eq. (12d), where all the electronic and nuclear variables are the corresponding Heisenberg operators in the full space of electronic and nuclear DOFs. The Heisenberg EOMs thus involves only the first-derivative operator but are unfortunately much less feasible for QM calculations than the Schrödinger equation.

<sup>10</sup>C.-Y. Hsieh, J. Schofield, and R. Kapral, *Mol. Phys.* **111**, 3546 (2013).

<sup>11</sup>H. Wang, X. Sun, and W. H. Miller, *J. Chem. Phys.* **108**, 9726 (1998).

<sup>12</sup>X. Sun, H. Wang, and W. H. Miller, *J. Chem. Phys.* **109**, 7064 (1998).

<sup>13</sup>X. Sun, H. Wang, and W. H. Miller, *J. Chem. Phys.* **109**, 4190 (1998).

<sup>14</sup>Q. Shi and E. Geva, *J. Phys. Chem. A* **108**, 6109 (2004).

<sup>15</sup>S. J. Cotton and W. H. Miller, *J. Chem. Phys.* **139**, 234112 (2013).

<sup>16</sup>S. J. Cotton and W. H. Miller, *J. Chem. Phys.* **145**, 144108 (2016).

<sup>17</sup>W. H. Miller and S. J. Cotton, *J. Chem. Phys.* **145**, 081102 (2016).

<sup>18</sup>S. J. Cotton and W. H. Miller, *J. Phys. Chem. A* **119**, 12138 (2015).

<sup>19</sup>S. J. Cotton and W. H. Miller, *J. Chem. Theory Comput.* **12**, 983 (2016).

<sup>20</sup>P. L. Walters and N. Makri, *J. Chem. Phys.* **144**, 044108 (2016).

<sup>21</sup>To recast the standard diabatic spin-boson (SB) problem into the adiabatic representation, we simply diagonalize Eq. (17) to find the adiabatic (Born-Oppenheimer) PESs  $\{E_i(\mathbf{R})\}$  and calculate first-derivative non-adiabatic coupling element vectors  $\mathbf{d}_{ij}$  via the standard expression,

$$\mathbf{d}_{ij} = \frac{1}{E_j - E_i} \sum_k U_{ik} \frac{\partial H_{kk}}{\partial \mathbf{R}} U_{jk},$$

(note,  $\partial H_{k \neq k'} / \partial \mathbf{R} = 0$ ) where  $\mathbf{U}(\mathbf{R})$  is the unitary/rotation matrix which diagonalizes  $\mathbf{H}(\mathbf{R})$ . {The second-derivative coupling element matrices  $\mathbf{D}_{ij}$  are not required as we neglect them in Eq. (9) [i.e., by using Eq. (9d')] and they do not appear in Eq. (12).}

<sup>22</sup>H. Goldstein, *Classical Mechanics*, 2nd ed. (Addison-Wesley, 1980).

<sup>23</sup>Technically, here a “restricted” canonical transformation, i.e., one which does not depend on time.

<sup>24</sup>The diagonal relations from Eq. (A1) are satisfied with respect to the electronic variables because of  $\mathbf{U}$ ’s symmetry.

<sup>25</sup>Note:  $\gamma \sum_i H_{ii} = \gamma \sum_i E_i$  (i.e., traces are invariant to unitary transform).

<sup>26</sup>Note that  $\mathcal{L} = V[\text{potential}] - T[\text{kinetic}]$  appears in Eq. (C6), but that sign change has no effect on the Euler-Lagrange equation [Eq. (C2)]. Also note that one can “determine” the canonical momenta corresponding to this “Lagrangian”  $\mathcal{H}$  in the standard way except with a sign change, i.e., by using  $\mathbf{P} \equiv -\frac{\partial \mathcal{H}}{\partial \dot{\mathbf{R}}}$ , which gives  $\mathbf{P} = \mu \dot{\mathbf{R}} - \Delta \mathbf{P}$ , as it must for consistency.