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A multi-trajectory theory of inelastic collisions

Ralph Eric Turner[†] and John S Dahler[‡]

[†] Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

[‡] Departments of Chemistry and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455, USA

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Abstract. A systematic approximation scheme is presented for introducing multi-classical trajectories into the theory of inelastic collisions. In general, the translational and internal degrees of freedom are coupled through an interaction picture potential which is non-local in translational space and which has no diagonal elements in the internal space. For each different pair of internal states this potential has a unique classical trajectory generated by the Hamiltonian which is the arithmetic mean of the two appropriate (internal state) diagonal elements of the full system Hamiltonian. Localisation of this potential in translational position space produces a multi-trajectory eikonal theory. Finally, replacing the unique classical trajectories with fully parametrised trajectories gives a multi-trajectory version of the standard impact parameter approximation. Results for both atomic and molecular (adiabatic and diabatic) bases are presented.

1. Introduction

The use of classical trajectories in inelastic scattering theory has received much attention over the years. In one standard approach, the impact parameter approximation (Mott and Massey 1965, Child 1974, Levine 1969, Bransden 1970, Bates and McCarroll 1958, 1962, Willets and Gallaher 1966, Delos *et al* 1972, Delos and Thorson 1972), attention is focused on the changes of internal state that occur when the relative motion of the two colliding heavy particles is confined to a single, classical trajectory. This trajectory may be a rectilinear, constant-velocity path or a curved path associated with some reference potential. In either case the relative motion of the centres of mass is treated as if changes of internal state did not occur. The shortcomings of this approximation include its reliance on a single trajectory and the lack of dependence of that trajectory on the internal states of the system. In cases where only two internal states are involved (Marchi and Smith 1965, Olson and Smith 1971) a way of dealing with the latter of these deficiencies is to use the classical trajectory generated by a Hamiltonian which includes the arithmetic mean of the initial and final state diagonal elements of the coupling interaction between the internal and translational degrees of freedom. The forced-common-turning-point method of Bates and Crothers (1970) provides a related but distinct way of dealing with this two-state problem. Finally, a many-state theory has been suggested by McCann and Flannery (1975) who propose the use of a single trajectory based on a potential function that is determined along with the internal-state wavefunction in a self-consistent manner.

The alternative considered here is a theory which assigns a different, classical trajectory to each pair of internal states. According to this theory the amplitudes $\mathbf{c}(t) = (c_1, c_2, \dots, c_N)$ of the internal states are governed by a set of equations

$$\dot{\mathbf{c}}(t) = \mathbf{bc} \quad (1.1)$$

involving a matrix $\mathbf{b} = \{b_{jk}; j \neq k\}$, each element of which is associated with a trajectory that depends on the average of two diagonal elements of the coupling interaction between the internal and translational degrees of freedom. Thus, the solutions of these N coupled equations are dependent on $\frac{1}{2}N(N-1)$ two-state interactions and the corresponding set of $\frac{1}{2}N(N-1)$ classical trajectories. The present paper provides a formal development of this multi-trajectory (MT) theory, including a systematic procedure for introducing the classical trajectories and a prescription for computing the coupling matrix \mathbf{b} . It is reasonable to expect that the numerical predictions of this theory will be more realistic than those based on theories using single-trajectory approximations to the heavy-particle motion.

The approach which will be used to construct the multi-trajectory theory parallels Turner and Dahler's (1980) systematic development of the standard, single-trajectory impact parameter approximation. The first step is to cast the theory in terms of the interaction picture and quantal Liouville superoperators which are descriptive of the heavy-particle motions. Classical trajectories are then introduced by replacing the phase-space representatives of these quantal superoperators with their classical limits (analogues). This leads to an interaction picture potential operator which is non-local in the space of the translational degrees of freedom. Localisation of this potential operator results in a multi-trajectory eikonal approximation. Replacement of the eikonal trajectories with fully parametrised classical trajectories then generates a MT impact parameter approximation to the scattering problem. Although the general structure of the theory is independent of which representation has been chosen for the internal degrees of freedom, many details are not. Therefore, § 2 is devoted to the MT approximation using an atomic basis. The result obtained is a generalisation of Marchi and Smith's (1965) theory for a two-state system. The MT formalism specific to the molecular (adiabatic or diabatic) basis is then presented in § 3.

2. Atomic basis, multi-trajectory theory

The system to be considered consists of two composite particles. The corresponding Hamiltonian, H , can be decomposed into three parts, H_0 , H_{int} and V . The first of these is itself the sum of two terms: K , the relative kinetic energy of the centres of mass of the two composite particles and V_0 , a potential which operates only on the distance separating these two centres. Associated with the isolated particles is an internal state Hamiltonian, H_{int} , which is assumed to admit N discrete eigenstates with kets $|n\rangle$ and energies E_n (notation: $(H_{\text{int}} - E_n)|n\rangle = 0$). H_0 and H_{int} are associated with different degrees of freedom and so commute with one another. Coupling between the internal and translational motions is provided by the potential V .

Associated with the total Hamiltonian is the Schrödinger picture state vector $|\Psi(t)\rangle$, governed by the equation

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = H |\Psi(t)\rangle \quad (2.1)$$

and subject to the precollisional, initial ($t' \rightarrow -\infty$) condition

$$|\Psi(t')\rangle = |\Psi_{\text{tr}}(t')\rangle \otimes |\Psi_{\text{int}}(t')\rangle \quad (2.2)$$

which here is taken to be the product of a translational factor $|\Psi_{\text{tr}}(t')\rangle$ and the internal state $|\Psi_{\text{int}}(t')\rangle = |1\rangle$. It is assumed that the initial translational state is an incoming free wavepacket with average impact parameter \mathbf{B}'' and average momentum \mathbf{P}'' ($\mathbf{P}'' \cdot \mathbf{B}'' = 0$).

In the atomic basis the Schrödinger picture state vector becomes the sum

$$|\Psi(t)\rangle = \sum_{n=1}^N \int d\mathbf{R} |\mathbf{R}, n\rangle \psi_n(\mathbf{R}, t) \quad (2.3)$$

of wavefunctions, $\psi_n(\mathbf{R}, t) = \langle \mathbf{R}, n | \Psi(t) \rangle$, which satisfy the differential equations

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi_n(\mathbf{R}, t) &= \sum_{m=1}^N \int d\mathbf{R}' \langle \mathbf{R}, n | H | \mathbf{R}', m \rangle \psi_m(\mathbf{R}', t) \\ &= \left(-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 + V_0(\mathbf{R}) + E_n \right) \psi_n(\mathbf{R}, t) + \sum_{m=1}^N V_{nm}(\mathbf{R}) \psi_m(\mathbf{R}, t). \end{aligned} \quad (2.4)$$

Here μ is the reduced mass associated with the translational motion and $V_{nm}(\mathbf{R}) \equiv \langle \mathbf{R}, n | V | \mathbf{R}, m \rangle$.

2.1. Classical trajectory approximation (CTA)

The procedure which will be used to introduce classical trajectories requires that the theory be recast in an interaction picture specific to the internal state basis which has been selected and that the heavy-particle dynamics then be expressed in terms of the phase-space representatives of the corresponding quantal (Liouville) superoperators. The first step in this procedure is to rewrite the total Hamiltonian as

$$\begin{aligned} H &= H_0 + H_{\text{int}} + V \\ &= \sum_{n=1}^N |n\rangle (H_n + E_n) \langle n| + \sum_{n \neq m}^N \sum_{m=1}^N |n\rangle V_{nm} \langle m| \end{aligned} \quad (2.5)$$

with $H_n \equiv H_0 + V_{nn}$. The interaction picture (I) state vector, specific to the atomic basis, is then defined by

$$\begin{aligned} |\Psi_I(t)\rangle &= \exp\left(\frac{i}{\hbar}(t-t') \sum_{n=1}^N |n\rangle (H_n + E_n) \langle n|\right) |\Psi(t)\rangle \\ &= \sum_{n=1}^N \left[|n\rangle \exp\left(\frac{i}{\hbar}(H_n + E_n)(t-t')\right) \langle n| \right] |\Psi(t)\rangle. \end{aligned} \quad (2.6)$$

The evolution of this vector is governed by the equation

$$i \frac{d}{dt} |\Psi_I(t)\rangle = b_{\text{op}}(t) |\Psi_I(t)\rangle \quad (2.7)$$

which contains the (self-adjoint) interaction picture potential operator

$$b_{\text{op}}(t) = \hbar^{-1} \sum_{n \neq m}^N \sum_{m=1}^N |n\rangle V_{nm}(t) \exp[i\omega_{nm}(t-t')] \langle m|. \quad (2.8)$$

Here, $\omega_{nm} \equiv \hbar^{-1}(E_n - E_m)$ and

$$V_{nm}(t) \equiv \exp[(i/\hbar)H_n(t-t')]V_{nm} \exp[-(i/\hbar)H_m(t-t')] \quad (2.9)$$

is a translational interaction picture potential operator whose time development is generated by the two different Hamiltonian operators, H_n and H_m . The atomic basis wavefunctions associated with the interaction picture state vector $|\Psi_I(t)\rangle$ are defined by

$$\begin{aligned} \psi_n^I(\mathbf{R}, t) &= \langle \mathbf{R}, n | \Psi_I(t) \rangle \\ &= \int d\mathbf{R}' \langle \mathbf{R} | \exp\left(\frac{i}{\hbar}(H_n + E_n)(t-t')\right) | \mathbf{R}' \rangle \psi_n(\mathbf{R}', t) \end{aligned} \quad (2.10)$$

and satisfy wave equations

$$i\hbar \frac{\partial}{\partial t} \psi_n^I(\mathbf{R}, t) = \sum_{m \neq n} \int d\mathbf{R}' \langle \mathbf{R} | V_{nm}(t) | \mathbf{R}' \rangle \exp[(i/\hbar)\omega_{nm}(t-t')] \psi_m^I(\mathbf{R}', t) \quad (2.11)$$

containing the non-local interactions $\langle \mathbf{R} | V_{nm}(t) | \mathbf{R}' \rangle$.

The next step in the development is to express the time dependence of the translational potential operators $V_{nm}(t)$ in terms of superoperators. This can be done by examining the differential equations

$$\begin{aligned} dV_{nm}(t)/dt &= (i/\hbar)(H_n V_{nm}(t) - V_{nm}(t)H_m) \\ &= (\mathcal{L}_{nm} + \hbar^{-1}\mathcal{U}_{nm})V_{nm}(t) \end{aligned} \quad (2.12)$$

satisfied by these potentials. Here, \mathcal{L}_{nm} is the Liouville superoperator

$$\mathcal{L}_{nm} = \hbar^{-1}[\frac{1}{2}(H_n + H_m),]_- \equiv \hbar^{-1}[H_{nm},]_- \quad (2.13)$$

associated with the two-state average Hamiltonian, $H_{nm} = H_0 + \frac{1}{2}(V_{nn} + V_{mm})$, and \mathcal{U}_{nm} is the anticommutator

$$\mathcal{U}_{nm} = [\frac{1}{2}(H_n - H_m),]_+ \equiv \frac{1}{2}[U_{nm},]_+ \quad (2.14)$$

connected with the difference of potential operators, $U_{nm} = V_{nn} - V_{mm}$.

The solution of equation (2.12) is given by the formula

$$V_{nm}(t) = \exp[i\mathcal{L}_{nm}(t-t')] \mathcal{G}(t, t') V_{nm} \quad (2.15)$$

where

$$\mathcal{G}(t, t') = T \exp\left(\frac{i}{\hbar} \int_{t'}^t ds \mathcal{U}_{nm}(s)\right) \quad (2.16)$$

(with T denoting the Dyson chronological operator) is a member of the time-ordered group of operators generated by

$$\mathcal{U}_{nm}(t) = \exp[-i\mathcal{L}_{nm}(t-t')] \mathcal{U}_{nm} \exp[i\mathcal{L}_{nm}(t-t')]. \quad (2.17)$$

The time dependence of $V_{nm}(t)$, given by equation (2.15), is determined by the translational superoperator \mathcal{L}_{nm} and by the potential difference superoperator \mathcal{U}_{nm} . The classical motion (CM) approximation is obtained when these two superoperators are replaced with their classical limits ($\hbar \rightarrow 0$). These limits are easily computed using the phase-space representation (Weyl 1927, Wigner 1932). Thus, \mathcal{L}_{nm} is replaced with the classical Poisson bracket associated with the average Hamiltonian H_{nm} and,

from (see appendix for notation)

$$\begin{aligned}
 \sigma \langle \langle \mathbf{R}, \mathbf{P} | \mathcal{U}_{nm} | \mathbf{R}', \mathbf{P}' \rangle \rangle_{\mathcal{S}} &= h^{-3} \text{Tr} \Delta(\mathbf{R}, \mathbf{P}) \mathcal{U}_{nm} \Delta(\mathbf{R}', \mathbf{P}') \\
 &= 2\delta(\mathbf{R} - \mathbf{R}') \cos\left(\frac{1}{2}\hbar \nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{P}}\right) \frac{1}{2} \mathcal{U}_{nm}(\mathbf{R}) \delta(\mathbf{P} - \mathbf{P}') \\
 &\underset{h \rightarrow 0}{\sim} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{P} - \mathbf{P}') \mathcal{U}_{nm}(\mathbf{R}) \\
 &= \sigma \langle \langle \mathbf{R}, \mathbf{P} | \mathcal{U}_{nm}^{\text{CM}} | \mathbf{R}', \mathbf{P}' \rangle \rangle_{\mathcal{S}} \tag{2.18}
 \end{aligned}$$

it can be seen that the CM approximation to the phase-space representative of \mathcal{U}_{nm} is simply multiplication by the potential difference $\mathcal{U}_{nn}(\mathbf{R}) = V_{nm}(\mathbf{R}) - V_{mm}(\mathbf{R})$. Consequently, the phase-space function associated with $V_{nm}(t)$, but with a time dependence generated by classical instead of quantum mechanics, is given by

$$\begin{aligned}
 V_{nm}(\mathbf{R}, \mathbf{P} | t)^{\text{CTA}} &= \left\langle \left\langle \mathbf{R}, \mathbf{P} \left| \exp[i\mathcal{L}_{nm}^{\text{CM}}(t-t')] T \right. \right. \right. \\
 &\quad \times \exp\left(\frac{i}{\hbar} \int_{t'}^t ds \exp[-i\mathcal{L}_{nm}^{\text{CM}}(s-t')] \mathcal{U}_{nm}^{\text{CM}} \exp[i\mathcal{L}_{nm}^{\text{CM}}(s-t')]\right) \left. \left. \right| V_{nm} \right\rangle \right\rangle_{\mathcal{C}} \\
 &= \exp\left(\frac{i}{\hbar} \int_{t'}^t ds \mathcal{U}_{nm}[\mathbf{R}_{nm}(s | \mathbf{R}, \mathbf{P})]\right) V_{nm}[\mathbf{R}_{nm}(t | \mathbf{R}, \mathbf{P})]. \tag{2.19}
 \end{aligned}$$

The factor $\mathbf{R}_{nm}(s | \mathbf{R}, \mathbf{P})$ appearing in the last of these expressions is the solution of Hamilton's equations based on the average Hamiltonian H_{nm} , for which the initial ($t = t' \rightarrow -\infty$) values of position and momentum are equal to \mathbf{R} and \mathbf{P} , respectively.

The classical-trajectory quantal operator associated with the exact translational potential, $V_{nm}(t)$ of equation (2.9), is given by the formula

$$\begin{aligned}
 V_{nm}(t)^{\text{CTA}} &= h^{-3} \int d\mathbf{R} d\mathbf{q} d\mathbf{P} \exp\left(-\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{q}\right) |\mathbf{R} - \frac{1}{2}\mathbf{q}\rangle \\
 &\quad \times \exp\left(\frac{i}{\hbar} \int_{t'}^t ds \mathcal{U}_{nm}[\mathbf{R}_{nm}(s | \mathbf{R}, \mathbf{P})]\right) V_{nm}[\mathbf{R}_{nm}(t | \mathbf{R}, \mathbf{P})] \langle \mathbf{R} + \frac{1}{2}\mathbf{q} |. \tag{2.20}
 \end{aligned}$$

This has been obtained by using $V_{nm}(\mathbf{R}, \mathbf{P} | t)^{\text{CTA}}$, defined according to equation (2.19), in the Weyl correspondence (Weyl 1927) for the interaction picture potential operator. With $V_{nm}(t)^{\text{CTA}}$ in place of $V_{nm}(t)$, the operator $b_{\text{op}}(t)$ of equation (2.8) becomes

$$\begin{aligned}
 b_{\text{op}}(t)^{\text{CTA}} &= \sum_{n \neq m}^N \sum_{n \neq m}^N h^{-3} \int d\mathbf{R} d\mathbf{q} d\mathbf{P} |\mathbf{R} - \frac{1}{2}\mathbf{q}, n\rangle \exp\left(-\frac{i}{\hbar} \mathbf{P} \cdot \mathbf{q}\right) \\
 &\quad \times b_{nm}(\mathbf{R}, \mathbf{P} | t) \langle \mathbf{R} + \frac{1}{2}\mathbf{q}, m | \tag{2.21}
 \end{aligned}$$

where $b_{nm}(\mathbf{R}, \mathbf{P} | t)$ denotes the function

$$b_{nm}(\mathbf{R}, \mathbf{P} | t) = \hbar^{-1} V_{nm}[\mathbf{R}_{nm}(t | \mathbf{R}, \mathbf{P})] \exp[i\tau_{nm}(\mathbf{R}, \mathbf{P} | t)] \tag{2.22}$$

and

$$\tau_{nm}(\mathbf{R}, \mathbf{P} | t) = \omega_{nm}(t - t') + \hbar^{-1} \int_{t'}^t ds \mathcal{U}_{nm}[\mathbf{R}_{nm}(s | \mathbf{R}, \mathbf{P})]. \tag{2.23}$$

$b_{\text{op}}(t)^{\text{CTA}}$, the interaction picture potential operator of the classical multi-trajectory theory, is non-local in the space of translational degrees of freedom and is off-diagonal in the space of internal states. Connected to each pair of internal states, n and m , is

a unique classical trajectory, generated by the average Hamiltonian, H_{nm} . The operator $b_{op}(t)^{CTA}$ determines the evolution of the state vector $|\Psi_I(t)^{CTA}\rangle$ according to the equation

$$i \frac{d}{dt} |\Psi_I(t)^{CTA}\rangle = b_{op}(t)^{CTA} |\Psi_I(t)^{CTA}\rangle. \quad (2.24)$$

Consequently, the atomic basis wavefunctions, $\psi_n^I(\mathbf{R}, t)^{CTA} \equiv \langle \mathbf{R}, n | \Psi_I(t)^{CTA} \rangle$, associated with this CTA state vector satisfy the wave equations

$$i \frac{\partial}{\partial t} \psi_n^I(\mathbf{R}, t)^{CTA} = \sum_{m \neq n}^N \sum_n^N \hbar^{-3} \int d\mathbf{R}' d\mathbf{P}' \exp\left(-\frac{i}{\hbar} \mathbf{P}' \cdot (\mathbf{R}' - \mathbf{R})\right) \times b_{nm}[\frac{1}{2}(\mathbf{R} + \mathbf{R}'), \mathbf{P}' | t] \psi_m^I(\mathbf{R}' | t)^{CTA}. \quad (2.25)$$

These equations and their molecular-basis counterparts (cf equation (3.26) of the following section) are the most general of the classical multi-trajectory equations which will be derived in this paper. They are the formally exact consequences of inserting the classical limit of the heavy-particle dynamics into the operators which determine the collisional alterations of the internal state. The coupling elements b_{nm} which appear in the wave equations (2.25) are completely determined by the *classical* heavy-particle trajectories $\mathbf{R}_{nm}(t | \mathbf{R}, \mathbf{P})$.

2.2. Eikonal approximation (EA)

The complexity of the wave equations (2.25) is due principally to the non-locality of the CTA interaction representation potential operator $b_{op}(t)^{CTA}$ and of the associated potential functions $b_{nm}(\mathbf{R}, \mathbf{P} | t)$. The result of removing this non-locality is a multi-trajectory generalisation of the eikonal theory which has previously been reported by Turner (1980). The interaction picture potentials are localised by replacing the classical trajectories $\mathbf{R}_{nm}(t | \mathbf{R}, \mathbf{P})$ with trajectories $\mathbf{R}_{nm}(t | \mathbf{R}, \mathbf{P}'')$, to each of which has been assigned a common value, $\mathbf{P}'' = \text{avg } \mathbf{P}$, of the initial relative momentum. This approximation produces an eikonal state vector $|\Psi_I(t)^{EA}\rangle$ whose equation of motion

$$i \frac{d}{dt} |\Psi_I(t)^{EA}\rangle = b_{op}(t | \mathbf{P}'')^{EA} |\Psi_I(t)^{EA}\rangle \quad (2.26)$$

involves the eikonal potential operator

$$b_{op}(t | \mathbf{P}'')^{EA} = \sum_{n \neq m}^N \sum_n^N \int d\mathbf{R} |\mathbf{R}, n\rangle b_{nm}(\mathbf{R}, \mathbf{P}'' | t) \langle \mathbf{R}, m|. \quad (2.27)$$

This operator is local in translational space and depends parametrically on the average momentum \mathbf{P}'' . The wavefunctions associated with $|\Psi_I(t)^{EA}\rangle$ satisfy the wave equations

$$i \frac{\partial}{\partial t} \psi_n^I(\mathbf{R}, t)^{EA} = \sum_{m \neq n}^N \sum_n^N b_{nm}(\mathbf{R}, \mathbf{P}'' | t) \psi_m^I(\mathbf{R}, t). \quad (2.28)$$

2.3. Decoupled motions (DC) or impact parameter approximation

In the multi-trajectory eikonal approximation the relative translational motion of the two colliding composite particles remains coupled to the internal degrees of freedom. However, when the position variable \mathbf{R} is replaced with a single fixed parameter, \mathbf{B}'' ,

this coupling is eliminated and the interaction picture potential reduces to the operator

$$b_{\text{op}}(t|\mathbf{B}'', \mathbf{P}'')^{\text{DC}} = 1_{\text{tr}} \sum_{n \neq m}^N \sum_{m \neq n}^N |n\rangle b_{nm}(t|\mathbf{B}'', \mathbf{P}'') \langle m|, \quad (2.29)$$

each element of which depends parametrically on the average initial relative momentum, \mathbf{P}'' , and on the impact parameter, \mathbf{B}'' , associated with the initial wave packet.

The interaction picture state vector of this DC approximation satisfies the equation of motion

$$i \frac{d}{dt} |\Psi_I(t)^{\text{DC}}\rangle = \left(\sum_{n \neq m}^N \sum_{m \neq n}^N |n\rangle b_{nm}(t|\mathbf{B}'', \mathbf{P}'') \langle m| \right) |\Psi_I(t)^{\text{DC}}\rangle \quad (2.30)$$

and the corresponding wavefunctions, $C_n(t) \equiv \langle n | \Psi_I(t)^{\text{DC}} \rangle$, satisfy the coupled equations

$$i \frac{d}{dt} C_n(t) = \sum_{m \neq n} b_{nm}(t|\mathbf{B}'', \mathbf{P}'') C_m(t) \quad C_k(t') = \delta_{kl} \quad (2.31)$$

which are identical in form to those of the standard impact parameter approximation. Here, however, each element of the coupling matrix \mathbf{b} is determined by a different classical trajectory. The Schrödinger picture state vector of this approximate theory (cf equation (2.2) for comparison) is given by the sum

$$\begin{aligned} |\Psi(t)^{\text{DC}}\rangle &= \sum_{n=1}^N \{ \exp[-(i/\hbar)H_n(t-t')] |\Psi_{\text{tr}}(t')\rangle \} \otimes \{ |n\rangle \langle n| \exp[-(i/\hbar)H_{\text{int}}(t-t')] |\Psi_I(t)^{\text{DC}}\rangle \} \\ &= \sum_{n=1}^N \int d\mathbf{R} |\mathbf{R}, n\rangle \psi_n(\mathbf{R}, t)^{\text{DC}} \end{aligned} \quad (2.32)$$

of wavefunctions

$$\psi_n(\mathbf{R}, t)^{\text{DC}} = C_n(t) \exp[-(i/\hbar)E_n(t-t')] \int d\mathbf{R}' \langle \mathbf{R} | \exp[-(i/\hbar)H_n(t-t')] | \mathbf{R}' \rangle \psi_{\text{tr}}(\mathbf{R}') \quad (2.33)$$

with $\psi_{\text{tr}}(\mathbf{R}) \equiv \langle \mathbf{R} | \Psi_{\text{tr}}(t') \rangle$. Each of these is the product of a translational function with quantal motion generated by the single-channel Hamiltonian operator $H_n = H_0 + V_{nn}$ and an internal state amplitude, $C_n(t)$, with motion determined by the entire set of $\frac{1}{2}N(N-1)$ classical trajectories. Thus, the translational motion associated with a particular internal state is unaffected by changes of internal state that occur during a collision. (Indeed, if V had no off-diagonal internal state matrix elements, then $|\Psi(t)^{\text{DC}}\rangle$ given by (2.32) would be exact.) On the other hand, the internal degrees of freedom respond to the translational motion as if each pair of internal states were experiencing a collision whose translational trajectory is generated by an average Hamiltonian specific to that pair. This multi-trajectory impact parameter theory is a generalisation of Marchi and Smith's (1965) two-state theory.

3. Molecular basis, multi-trajectory theory

The objective here is to construct the counterpart for a molecular adiabatic or diabatic basis (Tully 1976, O'Malley 1971) of the atomic-basis, multi-trajectory theory

developed in the preceding section. To accomplish this the total Hamiltonian of a two-atom system is written as the sum

$$H = K_N + H_e \quad (3.1)$$

of the relative (translational) kinetic energy of the atomic nuclei (reduced mass μ_N) and the internal state, electronic Hamiltonian

$$H_e = K_e + V_{ee} + V_{eN} + V_{NN}. \quad (3.2)$$

Here, K_e is the electronic kinetic energy, V_{ee} the sum of all electron–electron interactions, V_{eN} the electronic–nuclear interactions and V_{NN} the internuclear, coulombic potential energy.

The unit operator for this system can be written as

$$\begin{aligned} 1_{\text{op}} &= 1_N \otimes 1_e = \left(\int d\mathbf{R} |\mathbf{R}\rangle \langle \mathbf{R}| \right) \otimes \left(\sum_{n=1}^N |\phi_n(\mathbf{R}_{\text{op}})\rangle \langle \phi_n(\mathbf{R}_{\text{op}})| \right) \\ &= \sum_{n=1}^N \int d\mathbf{R} |\mathbf{R}, \phi_n(\mathbf{R})\rangle \langle \mathbf{R}, \phi_n(\mathbf{R})| \end{aligned} \quad (3.3)$$

where $\{\phi_n(\mathbf{R}); n = 1, 2, \dots, N\}$ denotes a complete orthonormal set for the electronic degrees of freedom, specific to the internuclear separation \mathbf{R} . For large values of $|\mathbf{R}|$ this set becomes equal to the atomic basis $\{|n\rangle; n = 1, 2, \dots, N\}$. In the ‘molecular representation’ the Hamiltonian takes the form

$$H = \sum_n \sum_m |\phi_n(\mathbf{R}_{\text{op}})\rangle H_{nm,\text{op}} \langle \phi_m(\mathbf{R}_{\text{op}})|. \quad (3.4)$$

Here $H_{nm,\text{op}}$ is the operator (on the nuclear, translational degrees of freedom)

$$\begin{aligned} H_{nm,\text{op}} &= \langle \phi_n(\mathbf{R}_{\text{op}}) | H | \phi_m(\mathbf{R}_{\text{op}}) \rangle \\ &= \int d\mathbf{R}' \int d\mathbf{R} |\mathbf{R}'\rangle \langle \mathbf{R}, \phi_n(\mathbf{R}) | H | \mathbf{R}', \phi_m(\mathbf{R}') \rangle \langle \mathbf{R}' | \\ &= \delta_{nm} K_{\text{op}} + V_{nm,\text{op}} + V_{nm,\text{op}}^{\text{BO}} + W_{nm,\text{op}}^{\text{BO}} \end{aligned} \quad (3.5)$$

with $K_{\text{op}} = (2\mu_N)^{-1} \mathbf{P}_{\text{op}}^2$ and where \mathbf{P}_{op} is the translational momentum operator. The Born–Oppenheimer coupling terms V^{BO} and W^{BO} are given by the formulae

$$V_{nm,\text{op}}^{\text{BO}} = \mu_N^{-1} \mathbf{p}_{nm,\text{op}}^{\text{BO}} \cdot \mathbf{P}_{\text{op}} \quad (3.6)$$

with

$$\begin{aligned} \mathbf{p}_{nm,\text{op}}^{\text{BO}} &= \int d\mathbf{R} |\mathbf{R}\rangle \mathbf{p}_{nm}^{\text{BO}}(\mathbf{R}) \langle \mathbf{R}| \\ \mathbf{p}_{nm}^{\text{BO}}(\mathbf{R}) &= -i\hbar \int d\mathbf{r} \phi_n^*(\mathbf{r}|\mathbf{R}) \nabla_{\mathbf{R}} \phi_m(\mathbf{r}|\mathbf{R}) \end{aligned} \quad (3.7)$$

and

$$\begin{aligned} W_{nm,\text{op}}^{\text{BO}} &= \int d\mathbf{R} |\mathbf{R}\rangle W_{nm}^{\text{BO}}(\mathbf{R}) \langle \mathbf{R}| \\ W_{nm}^{\text{BO}}(\mathbf{R}) &= -(\hbar^2/2\mu_N) \int d\mathbf{r} \phi_n^*(\mathbf{r}|\mathbf{R}) \nabla_{\mathbf{R}}^2 \phi_m(\mathbf{r}|\mathbf{R}). \end{aligned} \quad (3.8)$$

Here \mathbf{r} denotes the composite of all electronic coordinates and $\phi_n(\mathbf{r}|\mathbf{R}) = \langle \mathbf{r} | \phi_n(\mathbf{R}) \rangle$ is the coordinate representative of the molecular state $|\phi_n(\mathbf{R})\rangle$. Finally, the electronic potential operator is defined by

$$V_{nm,op} = \int d\mathbf{R}' |\mathbf{R}'\rangle V_{nm}(\mathbf{R}') \langle \mathbf{R}'| \tag{3.9}$$

$$V_{nm}(\mathbf{R}) = \int d\mathbf{r} \phi_n^*(\mathbf{r}|\mathbf{R}) H_e(\mathbf{r}, \mathbf{R}) \phi_m(\mathbf{r}|\mathbf{R}).$$

The Schrödinger picture state vector descriptive of a collision between the two atoms satisfies the equation (cf (2.1))

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = H |\Psi(t)\rangle \tag{3.10}$$

and is subject to the initial ($t' \rightarrow -\infty$) condition (cf (2.2))

$$|\Psi(t')\rangle = |\Psi_N(t')\rangle \otimes |\Psi_e(t')\rangle. \tag{3.11}$$

Here, the initial electronic state is selected to be

$$|\Psi_e(t')\rangle = \lim_{|\mathbf{R}'| \rightarrow \infty} |\phi_1(\mathbf{R}')\rangle = |1\rangle.$$

The molecular representation of $|\Psi(t)\rangle$ is given by

$$\begin{aligned} |\Psi(t)\rangle &= \sum_{n=1}^N |\phi_n(\mathbf{R}_{op})\rangle \langle \phi_n(\mathbf{R}_{op}) | \Psi(t) \rangle \\ &= \sum_{n=1}^N \int d\mathbf{R} |\mathbf{R}, \phi_n(\mathbf{R})\rangle \chi_n(\mathbf{R}, t) \\ &= \sum_{n=1}^N \int d\mathbf{R} d\mathbf{r} |\mathbf{R}, \mathbf{r}\rangle \phi_n(\mathbf{r}|\mathbf{R}) \chi_n(\mathbf{R}, t) \end{aligned} \tag{3.12}$$

and it follows from (3.10) that the Schrödinger wavefunctions $\chi_n(\mathbf{R}, t) = \langle \mathbf{R}, \phi_n(\mathbf{R}) | \Psi(t) \rangle$ satisfy the familiar set of coupled differential equations

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \chi_n(\mathbf{R}, t) &= \sum_{m=1}^N \int d\mathbf{R}' \langle \mathbf{R}, \phi_n(\mathbf{R}) | H | \mathbf{R}', \phi_m(\mathbf{R}') \rangle \chi_m(\mathbf{R}', t) \\ &= \sum_{m=1}^N \left[\delta_{nm} \left(-\frac{\hbar^2}{2\mu_N} \nabla_{\mathbf{R}}^2 \right) - i\hbar \mathbf{p}_{nm}^{BO}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} + W_{nm}^{BO}(\mathbf{R}) + V_{nm}(\mathbf{R}) \right] \chi_m(\mathbf{R}, t) \end{aligned} \tag{3.13}$$

appropriate to the adiabatic/diabatic molecular representation.

3.1. Classical trajectory approximation

Here, as in the previous theory based on the atomic representation (§ 2.1), the first step toward introducing classical trajectories is a decomposition of the total Hamiltonian into the sum ($H = H_1 + H_2$) of diagonal and off-diagonal parts

$$H_1 = \sum_{n=1}^N |\phi_n(\mathbf{R}_{op})\rangle H_{nn,op} \langle \phi_n(\mathbf{R}_{op})| \quad \text{and} \quad H_2 = \sum_{n \neq m}^N \sum_{m=1}^N |\phi_n(\mathbf{R}_{op})\rangle H_{nm,op} \langle \phi_m(\mathbf{R}_{op})| \tag{3.14}$$

respectively. Following standard practice, all diagonal Born–Oppenheimer couplings will be neglected as well as the off-diagonal elements of $W_{nm,op}^{BO}$. Consequently, the symbols $H_{nn,op}$ and $H_{nm,op}$ are henceforth to be identified with the two operators

$$H_{nn,op} = K_{op} + V_{nn,op} \quad \text{and} \quad H_{nm,op} = V_{nm,op}^{BO} + V_{nm,op} \quad (n \neq m). \quad (3.15)$$

If the molecular basis is adiabatic, $V_{nm,op}$ vanishes identically and $V_{nm,op}^{BO}$ is the only source of coupling among the electronic states. However, when the basis is diabatic, the couplings $V_{nm,op}$ will generally be of far greater importance than the relatively negligible BO operators, $V_{nm,op}^{BO}$.

The interaction picture state vector

$$\begin{aligned} |\Psi_I(t)\rangle &= \exp[(i/\hbar)H_1(t-t')]\Psi(t) \\ &= \left(\sum_{n=1}^N |\phi_n(\mathbf{R}_{op})\rangle \exp[(i/\hbar)H_{nn,op}(t-t')\langle\phi_n(\mathbf{R}_{op})| \right) |\Psi(t)\rangle \end{aligned} \quad (3.16)$$

satisfies equation (2.7) but with $b_{op}(t)$ given by

$$\begin{aligned} b_{op}(t) &= \hbar^{-1} \exp[(i/\hbar)H_1(t-t')]H_2 \exp[-(i/\hbar)H_1(t-t')] \\ &= \hbar^{-1} \sum_{n \neq m}^N \sum_{m=1}^N |\phi_n(\mathbf{R}_{op})\rangle H_{nm,op}(t) \langle\phi_m(\mathbf{R}_{op})| \end{aligned} \quad (3.17)$$

$$\begin{aligned} H_{nm,op}(t) &= \exp[(i/\hbar)H_{nn,op}(t-t')]H_{nm,op} \exp[-(i/\hbar)H_{mm,op}(t-t')] \\ &= V_{nm,op}(t) + V_{nm,op}^{BO}(t) \end{aligned} \quad (3.18)$$

instead of by equation (2.8). The interaction picture wavefunctions ψ_n^I are related to the Schrödinger picture functions χ_n in the manner

$$\begin{aligned} \psi_n^I(\mathbf{R}, t) &\equiv \langle\mathbf{R}, \phi_n(\mathbf{R})|\Psi_I(t)\rangle \\ &= \int d\mathbf{R}' \langle\mathbf{R}|\exp[(i/\hbar)H_{nn,op}(t-t')|\mathbf{R}'\rangle\chi_n(\mathbf{R}', t) \end{aligned} \quad (3.19)$$

and satisfy the wave equations

$$i\hbar \frac{\partial}{\partial t} \psi_n^I(\mathbf{R}, t) = \sum_{m \neq n}^N \int d\mathbf{R}' \langle\mathbf{R}|H_{nm,op}(t)|\mathbf{R}'\rangle \psi_m^I(\mathbf{R}', t). \quad (3.20)$$

Were it not for the BO couplings which have been discarded, these equations would be exact and equivalent to equation (3.13).

Classical trajectories can be introduced using the procedure described in § 2.1. In particular, the phase-space function associated with the operator $V_{nm,op}(t)$, but with classical instead of quantal translational dynamics, is (cf equation (2.19))

$$V_{nm}(\mathbf{R}, \mathbf{P}|t)^{CTA} = \exp\left(\frac{i}{\hbar} \int_{t'}^t ds \mathcal{U}_{nm}[\mathbf{R}_{nm}(s|\mathbf{R}, \mathbf{P})]\right) V_{nm}[\mathbf{R}_{nm}(t|\mathbf{R}, \mathbf{P})]. \quad (3.21)$$

The objects \mathcal{U}_{nm} and $\mathbf{R}_{nm}(t|\mathbf{R}, \mathbf{P})$ occurring here are defined as before, but with subscripts referring to molecular instead of atomic basis states. The average Hamiltonian associated with the two states n and m is $K_N + \frac{1}{2}(V_{nn} + V_{mm})$.

The phase-space representation of the Born–Oppenheimer operator $V_{nm,op}^{BO}$ is

$$\begin{aligned} V_{nm}^{BO}(\mathbf{R}, \mathbf{P}) &= \mathcal{S} \langle \langle \mathbf{R}, \mathbf{P} | V_{nm,op}^{BO} \rangle \rangle_{\mathcal{C}} \\ &= \mu_N^{-1} \mathbf{p}_{nm}^{BO}(\mathbf{R}) \cdot \mathbf{P} + (i\hbar/2\mu_N) \nabla_{\mathbf{R}} \cdot \mathbf{p}_{nm}^{BO}(\mathbf{R}) \\ &\simeq \mu_N^{-1} \mathbf{p}_{nm}^{BO}(\mathbf{R}) \cdot \mathbf{P}. \end{aligned} \quad (3.22)$$

The term proportional to the gradient of $\mathbf{p}_{nm}^{BO}(\mathbf{R})$ has been discarded because it is of the same order as $W_{nm}^{BO}(\mathbf{R}, \mathbf{P})$. The phase-space function associated with $V_{nm,op}^{BO}(t)$, but with classical instead of quantal translational motion, is given by the formula

$$\begin{aligned} V_{nm}^{BO}(\mathbf{R}, \mathbf{P}|t)^{CTA} &= \mu_N^{-1} \exp\left(\frac{i}{\hbar} \int_{t'}^t ds \mathcal{U}_{nm}[\mathbf{R}_{nm}(s|\mathbf{R}, \mathbf{P})]\right) \\ &\quad \times \mathbf{p}_{nm}^{BO}[\mathbf{R}_{nm}(t|\mathbf{R}, \mathbf{P})] \cdot \mathbf{P}_{nm}(t|\mathbf{R}, \mathbf{P}) \end{aligned} \quad (3.23)$$

where $\mathbf{P}_{nm}(t|\mathbf{R}, \mathbf{P})$ denotes the momentum part of the classical trajectory generated by the average Hamiltonian $K_N + \frac{1}{2}(V_{nn} + V_{mm})$.

The quantal operator corresponding to the phase-space function

$$H_{nm}(\mathbf{R}, \mathbf{P}|t)^{CTA} = V_{nm}(\mathbf{R}, \mathbf{P}|t)^{CTA} + V_{nm}^{BO}(\mathbf{R}, \mathbf{P}|t)^{CTA}$$

is

$$\begin{aligned} H_{nm,op}(t)^{CTA} &= h^{-3} \int d\mathbf{R} d\mathbf{q} d\mathbf{P} \exp[-(i/\hbar)\mathbf{P} \cdot \mathbf{q}] |\mathbf{R} - \frac{1}{2}\mathbf{q}\rangle \\ &\quad \times H_{nm}(\mathbf{R}, \mathbf{P}|t)^{CTA} \langle \mathbf{R} + \frac{1}{2}\mathbf{q} |. \end{aligned} \quad (3.24)$$

The classical trajectory approximation to the interaction picture state vector satisfies equation (2.24) with $b_{op}(t)^{CTA}$ given by

$$\begin{aligned} b_{op}(t)^{CTA} &= h^{-1} \sum_{n \neq m}^N \sum_{m \neq n}^N h^{-3} \int d\mathbf{R} d\mathbf{q} d\mathbf{P} |\mathbf{R} - \frac{1}{2}\mathbf{q}, \phi_n(\mathbf{R} - \frac{1}{2}\mathbf{q})\rangle \exp[-(i/\hbar)\mathbf{P} \cdot \mathbf{q}] \\ &\quad \times H_{nm}(\mathbf{R}, \mathbf{P}|t)^{CTA} \langle \mathbf{R} + \frac{1}{2}\mathbf{q}, \phi_m(\mathbf{R} + \frac{1}{2}\mathbf{q}) | \end{aligned} \quad (3.25)$$

and the corresponding interaction picture wavefunctions are solutions of the wave equations

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi_n^I(\mathbf{R}, t)^{CTA} &= \sum_{m \neq n}^N h^{-3} \int d\mathbf{R}' d\mathbf{P}' \exp[-(i/\hbar)\mathbf{P}' \cdot (\mathbf{R} - \mathbf{R}')] \\ &\quad \times H_{nm}[\frac{1}{2}(\mathbf{R} + \mathbf{R}'), \mathbf{P}'|t]^{CTA} \psi_m^I(\mathbf{R}', t)^{CTA}. \end{aligned} \quad (3.26)$$

These are the molecular-basis counterparts of the atomic-basis wave equations (2.25).

3.2. Eikonal approximation

The multi-trajectory eikonal approximation is obtained by assigning to each classical trajectory the same initial value of momentum and identifying this common value with the average momentum, \mathbf{P}'' , of the incident wavepacket. Thus, $\mathbf{R}_{nm}(t|\mathbf{R}, \mathbf{P})$ and $\mathbf{P}_{nm}(t|\mathbf{R}, \mathbf{P})$ are replaced by $\mathbf{R}_{nm}(t|\mathbf{R}, \mathbf{P}'')$ and $\mathbf{P}_{nm}(t|\mathbf{R}, \mathbf{P}'')$, respectively. The resulting eikonal approximation to the interaction picture state vector satisfies equation (2.26)

with $b_{\text{op}}(t|\mathbf{P}'')^{\text{EA}}$ given by the operator

$$b_{\text{op}}(t|\mathbf{P}'')^{\text{EA}} = \hbar^{-1} \sum_{n \neq m}^N \sum_{m \neq n}^N \int d\mathbf{R} |\mathbf{R}, \phi_n(\mathbf{R})\rangle H_{nm}(\mathbf{R}, \mathbf{P}''|t)^{\text{CTA}} \langle \mathbf{R}, \phi_m(\mathbf{R})| \quad (3.27)$$

which is local in translational configuration space. The wavefunctions of this approximate theory satisfy the equations

$$i\hbar \frac{\partial}{\partial t} \psi_n^{\text{I}}(\mathbf{R}, t)^{\text{EA}} = \sum_{m \neq n}^N H_{nm}(\mathbf{R}, \mathbf{P}''|t)^{\text{CTA}} \psi_m(\mathbf{R}, t)^{\text{EA}}. \quad (3.28)$$

3.3. Decoupled motions approximation

Finally, the molecular state representation of the multi-trajectory impact parameter theory is obtained by replacing the initial state variable \mathbf{R} in $H_{nm}(\mathbf{R}, \mathbf{P}''|t)^{\text{CTA}}$ with the impact parameter \mathbf{B}'' of the incident wavepacket. This approximation decouples the translational and internal state dynamics. Its effect is to replace the Schrödinger wavefunction $\chi_n(\mathbf{R}, t)$ of equation (3.12) by the decoupled motions approximation

$$\chi_n(\mathbf{R}, t)^{\text{DC}} = A_n(t) \int d\mathbf{R}' |\mathbf{R}'\rangle \exp[-(i/\hbar)H_{nn,\text{op}}(t-t')] \psi_{\text{tr}}(\mathbf{R}') \quad (3.29)$$

with $\psi_{\text{tr}}(\mathbf{R}) \equiv \langle \mathbf{R} | \Psi_N(t') \rangle$. The electronic state amplitudes $\{A_n(t)\}$ are solutions of the coupled impact parameter equations

$$i \frac{d}{dt} A_n(t) = \sum_{m \neq n}^N \hbar^{-1} H_{nm}(\mathbf{B}'', \mathbf{P}''|t)^{\text{CTA}} A_m(t) \quad A_k(t') = \delta_{k1} \quad (3.30)$$

specific to the molecular basis. The structure and interpretation of these equations are completely analogous to those of their atomic-basis counterparts, equation (2.31).

4. Summary

A systematic approximation scheme has been presented by which a multiplicity of classical, heavy-particle trajectories can be introduced into the quantum theory of inelastic collisions. This scheme used the part of the total Hamiltonian which was diagonal in the internal-state representation to define an interaction picture. The Weyl correspondence was then invoked as a means of inserting classical heavy-particle dynamics into the interaction picture potential. Three levels of treatment were considered, namely (i) a non-local classical trajectory approximation, (ii) a localised, eikonal theory and (iii) a decoupled motions or impact parameter approximation. Both the second and third of these involved a definite but non-unique momentum parameter, \mathbf{P}'' . The impact parameter theory involved a position parameter, \mathbf{B}'' , as well. The proper choices for these parameters depend upon the specifics of the collision problem being considered. However, the most obvious thing to do was to identify \mathbf{P}'' and \mathbf{B}'' with the average momentum and impact parameter of the incident, freely moving wavepacket.

The theory has been developed using both atomic and molecular (adiabatic or diabatic) representations of the internal states.

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Appendix. Phase-space representation

The Weyl correspondence or Wigner equivalence representation has been used in §§ 2.1 and 3.1 to construct *quantal* potential operators with time dependences (Heisenberg picture) generated by *classical* dynamics. The purpose of this appendix is not to present the theory of the Weyl correspondence, which can be found elsewhere (Weyl 1927, Wigner 1932, Leaf 1968), but simply to identify symbols associated with it which appear in this paper. The formalism involves the two so-called ideal elements, $|\mathbf{R}, \mathbf{P}\rangle_{\mathcal{O}} \equiv \hbar^{-3} \Delta(\mathbf{R}, \mathbf{P})$ and $|\mathbf{R}, \mathbf{P}\rangle_{\mathcal{S}} \equiv \Delta(\mathbf{R}, \mathbf{P})$, the first associated with the space of observables (\mathcal{O}) and the second with the space of statistical states (\mathcal{S}). Here Δ is a self-adjoint operator with the phase-space (\mathbf{R}, \mathbf{P}) representations

$$\begin{aligned} \Delta(\mathbf{R}, \mathbf{P}) &= \int d\mathbf{R}' \exp[-(i/\hbar)\mathbf{R}' \cdot \mathbf{P}] |\mathbf{R} - \frac{1}{2}\mathbf{R}'\rangle \langle \mathbf{R} + \frac{1}{2}\mathbf{R}'| \\ &= \int d\mathbf{P}' \exp[(i/\hbar)\mathbf{R} \cdot \mathbf{P}'] |\mathbf{P} - \frac{1}{2}\mathbf{P}'\rangle \langle \mathbf{P} + \frac{1}{2}\mathbf{P}'|. \end{aligned} \quad (\text{A1})$$

The ideal elements form the bases of a complete bi-orthonormal representation (Srinivas and Wolf 1975, Turner and Snider 1980). Thus, the unit operator on the space of observables has the resolution

$$1_{\mathcal{O}} = \int d\mathbf{R} d\mathbf{P} |\mathbf{R}, \mathbf{P}\rangle_{\mathcal{O}} \langle \langle \mathbf{R}, \mathbf{P} | \quad (\text{A2})$$

and

$$\begin{aligned} \langle \langle \mathbf{R}, \mathbf{P} | \mathbf{R}', \mathbf{P}' \rangle \rangle_{\mathcal{S}} &\equiv \hbar^{-3} \text{Tr} \Delta(\mathbf{R}, \mathbf{P})^{\dagger} \Delta(\mathbf{R}', \mathbf{P}') \\ &= \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{P} - \mathbf{P}'). \end{aligned} \quad (\text{A3})$$

A quantal operator A_{op} and its phase-space representative $A(\mathbf{R}, \mathbf{P})$ are connected through the relations

$$A_{\text{op}} = \int d\mathbf{R} d\mathbf{P} |\mathbf{R}, \mathbf{P}\rangle_{\mathcal{O}} A(\mathbf{R}, \mathbf{P}) \quad (\text{A4})$$

$$A(\mathbf{R}, \mathbf{P}) = \langle \langle \mathbf{R}, \mathbf{P} | A_{\text{op}} \rangle \rangle_{\mathcal{O}} = \text{Tr} \Delta(\mathbf{R}, \mathbf{P}) A_{\text{op}}. \quad (\text{A5})$$

The quantal Liouville superoperator associated with a Hamiltonian operator $H = K + V$ is the generator of operator motion (Heisenberg picture) defined by

$$A_{\text{op}}(t) = \exp[(i/\hbar)Ht] A_{\text{op}} \exp[-(i/\hbar)Ht] = \exp(i\mathcal{L}t) A_{\text{op}}. \quad (\text{A6})$$

This superoperator can be written as the commutator $\mathcal{L} = \hbar^{-1}[H,]_-$. Its phase-space representation is

$$\begin{aligned} \mathcal{S}\langle\langle \mathbf{R}, \mathbf{P} | \mathcal{L} | \mathbf{R}', \mathbf{P}' \rangle\rangle_{\mathcal{C}} &= \hbar^{-3} \text{Tr} \Delta(\mathbf{R}, \mathbf{P})^\dagger \mathcal{L} \Delta(\mathbf{R}', \mathbf{P}') \\ &= -i \frac{\mathbf{P}}{\mu} \cdot \nabla_{\mathbf{R}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{P} - \mathbf{P}') + \frac{2i}{\hbar} \delta(\mathbf{R} - \mathbf{R}') \\ &\quad \times [\sin \frac{1}{2} \hbar \nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{P}}] V(\mathbf{R}) \delta(\mathbf{P} - \mathbf{P}'). \end{aligned} \quad (\text{A7})$$

The first term of this expression, due to $\mathcal{K} = \hbar^{-1}[K,]_-$, is independent of \hbar . It is the generator of rectilinear, unaccelerated motion in quantum and classical mechanics alike. The second term, due to $\mathcal{V} = \hbar^{-1}[V,]_-$, depends explicitly on the value of Planck's constant and so distinguishes between classical and quantal dynamics. In the small- \hbar limit of classical motion (CM), (A7) becomes

$$\begin{aligned} \mathcal{S}\langle\langle \mathbf{R}, \mathbf{P} | \mathcal{L} | \mathbf{R}', \mathbf{P}' \rangle\rangle_{\mathcal{C}} &\underset{\hbar \rightarrow 0}{\sim} -i \frac{\mathbf{P}}{\mu} \cdot \nabla_{\mathbf{R}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{P} - \mathbf{P}') + i \nabla_{\mathbf{R}} V(\mathbf{R}) \cdot \nabla_{\mathbf{P}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{P} - \mathbf{P}') \\ &\equiv \mathcal{S}\langle\langle \mathbf{R}, \mathbf{P} | \mathcal{L}^{\text{CM}} | \mathbf{R}', \mathbf{P}' \rangle\rangle_{\mathcal{C}} \end{aligned} \quad (\text{A8})$$

and so it follows that the classical limit of \mathcal{L} is the multiple $i[H,]_{\text{PB}}$ of the Poisson bracket.

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