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Quantum transition state theory: featuring ensemble pre-equilibrium approximation

Juan R. Jenniton

Abstract   In this article, we use an ensemble pre-equilibrium approximation to vindicate the use of Heisenberg Equation of Motion and some other approximation for the rate of the change of quasi-equilibrium state in order to derive, based on the most precise and accurate existing theory of reaction rates to date, a rate law for any given elementary step of a chemical reaction that applies even to the condensed phase. The necessity of such a theory arises because first of all, quantum mechanics must be taken into account, and secondly, other molecules and especially the solvent may play an important role in the transition state of any elementary reaction, and we have devised a theory for doing so. Also, the correct theory for reaction rates critically depends on a complete set of wavefunctions of the transition state representing initially the products and finally the reactants, and we show a simple way for deriving it. We also show that several prevailing formulas in the literature for the cumulative reaction rate within the range of applicability of non-relativistic mechanics to the electrons and nuclei of the reacting systems within the reactor are exactly equivalent to each other, even in the condensed phase, and therefore the present theory is exact within the laws of quantum non-relativistic mechanics.

Keywords   Transition state theory · Ensemble pre-equilibrium approximation · Scattering theory · Reaction rate

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Introduction

The simplest prevailing theory for predicting rate constants based on the set of all available quantum states of the reacting molecules is transition state theory. It assumes rather simplistically that reactants form an intermediate "activated complex" that is in chemical equilibrium with reactants and that if the reactants had sufficient energy to begin with, then once they reach the saddle point of their common potential energy surface, they can never return back to reactants, but go on to form products. This assumption is completely untenable in quantum mechanics, for the reason that quantum mechanical tunneling may be involved, and the Heisenberg uncertainty principle places a fundamental limitation on how well both position and momentum can be measured simultaneously.

The most accurate and precise prevailing theory to date uses scattering theory to calculate reaction rates. This theory is exact, subject to some hidden assumptions that shall be made clear later. We shall show that this *exact* reactive scattering theory can be adapted in a way that holds irrespective of these hidden assumptions.

What is needed in order to correct transition state theory is a complete set of wavefunctions that initially represents reactants and finally products. Furthermore, we need a method of evaluating this exact rate in a way that is valid even for the condensed phase.

1 Derivation of ehrenfest theorm for the pre-equilibrium approximation

In chemical kinetics, when one is confronted with a reaction mechanism that consists first of a fast reversible step, followed by a slow one, a convenient approximation is that of a pre-equilibrium of the first step. See for example the reaction scheme 1.1:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$
$$C + F \overset{k_2}{\rightarrow} G \tag{1.1}$$

We can find the rate of production of G as

$$\frac{dn_G}{dt} = k_2 n_D n_F \tag{1.2}$$

However, since the second step is rate-determining, Eq. 1.3 gives us a pre-equilibrium condition.

$$\frac{n_C n_D}{n_A n_B} = K_1 \tag{1.3}$$

Therefore we derive Eq. 1.4 for the intermediate D.

$$n_D = \frac{K_1 n_A n_B}{n_C} \tag{1.4}$$

Then, the rate of production of G is given by Eq. 1.5.

$$\frac{dn_G}{dt} = \frac{K_1 k_2 n_{AN} n_B n_F}{n_C} = \frac{k n_{AN} n_B n_F}{n_C} \tag{1.5}$$

However in quantum mechanics, we may have the following scenario: $\hat{\rho}_0 \underset{W_{1\to0}}{\overset{W_{0\to1}}{\rightleftarrows}}$ $\hat{\rho}_1 \underset{W_{2\to1}}{\overset{W_{1\to2}}{\rightleftarrows}} \hat{\rho}_2 \ldots \underset{W_{\alpha\to\alpha-1}}{\overset{W_{\alpha-1\to\alpha}}{\rightleftarrows}} \hat{\rho}_\alpha \ldots$ where a non-unitary process may induce reversible transitions from one mixed state to another at random. If there are M systems in the ensemble, then the density matrix of a hypothetical system, identical in nature and constitution to each of the systems in the ensemble {by transitivity all the systems are identical to each other in this manner}, representative of the entire ensemble, is given by 1.6;

$$\hat{\rho} = \frac{1}{M} \sum_\alpha m_\alpha \hat{\rho}_\alpha, \tag{1.6}$$

In Eq. 1.6, m_α is the number of systems in state $\hat{\rho}_\alpha$. Then we can find the rate of change of the thermodynamic state in 1.7.

$$\dot{\hat{\rho}} = \frac{1}{M} \sum_\alpha \dot{m}_\alpha \hat{\rho}_\alpha + \frac{1}{M} \sum_\alpha m_\alpha \dot{\hat{\rho}}_\alpha \tag{1.7}$$

The assumption that we will make is that each $\hat{\rho}_\alpha$ undergoes unitary evolution, but that this unitary evolution is the rate determining step. And so therefore we shall assume that $\dot{m}_\alpha \approx 0$. In fact, the rate is: $\dot{m}_\alpha = \sum_\beta \{W_{\beta\to\alpha} m_\beta - W_{\alpha\to\beta} m_\alpha\}$. We can now make a so-called detailed-balance approximation: $W_{\beta\to\alpha} m_\beta = W_{\alpha\to\beta} m_\alpha$, where the $W_{\beta\to\alpha}$'s depend on the local quasi-equilibrium state of the system. The law of unitary evolution is expressed by 1.8:

$$\dot{\hat{\rho}}_\alpha = \frac{1}{i\hbar}\left[\hat{H}, \hat{\rho}_\alpha\right] \tag{1.8}$$

Therefore

$$\dot{\hat{\rho}} \approx \frac{1}{i\hbar}\left[\hat{H}, \hat{\rho}\right] \tag{1.9}$$

Then it follows that the rate of change of *any* property is given by 1.10:

$$\frac{\delta\langle\hat{A}\rangle}{\delta t} \approx \frac{1}{i\hbar}\langle[\hat{A}, \hat{H}]\rangle \tag{1.10}$$
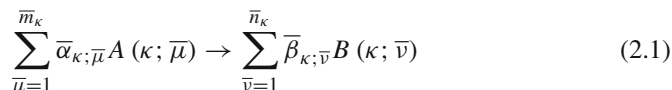
This is known as the ***Heisenberg Equation of Motion.*** The operator $\hat{H}$ is known as the Hamiltonian of the system {it is just the energy of the system}. We shall also make the ansatz (1.11) under the pre-equilibrium approximation that

$$\frac{\delta \langle \hat{n}_X \rangle}{\delta t} = n_X{}^\circ + \sum_\kappa \left\{ \overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa} \right\} \frac{\delta \left(\left\langle \hat{n}_{\kappa+} \hat{\xi}_{\kappa+} \right\rangle - \left\langle \hat{n}_{\kappa-} \hat{\xi}_{\kappa-} \right\rangle \right)}{\delta t} \qquad (1.11)$$

What we are saying is that $\hat{n}'_X = \hat{n}^\circ_X + \sum_\kappa \left\{ \overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa} \right\} \cdot \left(\hat{n}_{\kappa+} \hat{\xi}_{\kappa+} - \hat{n}_{\kappa-} \hat{\xi}_{\kappa-} \right)$, where $\hat{n}^\circ_X \hat{H} = \hat{H} \hat{n}^\circ_X$, and that $\langle \hat{n}_X \rangle (t) = \langle \hat{n}_X \rangle (t_0) + \int_{t_0}^{t} \left\langle \hat{n}'_X \right\rangle (t') \, dt'$, where we use $\hat{n}'_X = \frac{1}{i\hbar} \left[\hat{n}'_X, \hat{H} \right]$. There is a simple solution: $\frac{d}{dt} \langle \hat{n}_X \rangle (t) = \left\langle \hat{n}'_X \right\rangle (t)$. This gives a nonlinear first order differential equation.

2 Discussion of reaction mechanism and constraints incumbent on the system

A chemical reaction consists of a series of elementary reactions. Now each reaction step can be written as 2.1:

$$\sum_{\overline{\mu}=1}^{\overline{m}_\kappa} \overline{\alpha}_{\kappa;\overline{\mu}} A \left(\kappa; \overline{\mu} \right) \rightarrow \sum_{\overline{\nu}=1}^{\overline{n}_\kappa} \overline{\beta}_{\kappa;\overline{\nu}} B \left(\kappa; \overline{\nu} \right) \qquad (2.1)$$

Here we take into account the reversibility of every individual reaction step. The system is subject therefore to the following constraints in 2.2:

$$\begin{aligned}
& \hat{n}_X + \overline{\alpha}_{X;\kappa} \hat{n}_{\kappa+} = N_X, \forall \kappa \forall X \in \left\{ A^{(\kappa;\overline{\mu})}; \forall \overline{\mu} \right\} \\
& \hat{n}_Y + \overline{\beta}_{Y;\kappa} \hat{n}_{\kappa-} = N_Y, \forall \kappa \forall Y \in \left\{ B^{(\kappa;\overline{\nu})}; \forall \overline{\nu} \right\} \\
& \hat{n}_{\kappa+} + \hat{n}_{\kappa-} + \hat{n}_{\mathscr{s}_\kappa} = N_{\mathscr{s}_\kappa} = 1, \forall \kappa \\
& \mathrm{Tr}\, \hat{\rho} = 1 \\
& \mathrm{Tr} \hat{\rho} \hat{H}^{\%} = E \\
& \mathrm{Tr} \hat{\rho} \hat{N}_X = N_X, \forall \kappa \forall X \\
& \mathrm{Tr} \hat{\rho} \left\{ \hat{n}_{\kappa+} + \hat{n}_{\kappa-} + \hat{n}_{\mathscr{s}_\kappa} \right\} = N_{\mathscr{s}_\kappa} = 1
\end{aligned} \qquad (2.2)$$

The quantity $\hat{N}_X$ is the operator for the number of molecules of type X. The formula for the Hamiltonian is given by (2.3)

$$\hat{H}^{\%} = \hat{H}^\circ + \sum_\kappa \left(\hat{\Omega}^{(\hat{n}_{\kappa+})}_{\kappa+} + \hat{\Omega}^{(\hat{n}_{\kappa-})}_{\kappa-} \right) \hat{H}_{\kappa\pm} + \sum_\kappa \left(\hat{\Omega}^{(\hat{n}_{\mathscr{s}_\kappa})}_{\mathscr{s}_\kappa} - 1 \right) \hat{H}_{\mathscr{s}_\kappa}, \qquad (2.3)$$

where $\hat{\Omega}^{(\hat{n}_A)}_A \hat{x} = \sum_{j=1}^{\hat{n}_A} \hat{\Omega}_{(A;j)} \hat{x} \hat{\Omega}^\dagger_{(A;j)}, \forall \hat{x}; \hat{\Omega}_{(A;j)} = \sum_\sigma \left| \psi^{(j)}_\sigma \right\rangle \langle \psi_\sigma |$, and $\hat{H}^\circ$ is the Hamiltonian when the reactants, products, and surroundings are all free and not

participating in any reaction. In Appendix A2, we shall show you how we derived the following result expressed by 2.3:

$$\frac{\delta n_X}{\delta t} = \sum_{\kappa} \{\overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa}\} \left\{ k_{\kappa+} \prod_{\overline{\mu}=1}^{\overline{m}} n_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}} - k_{\kappa-} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} n_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}} \right\}. \quad (2.3)$$

The functions $k_{\kappa+}$ & $k_{\kappa-}$ are the forward and backward rate constants of any given elementary step in a reaction mechanism. Formula A2.5 gives their exact values:

$$k_{\kappa+} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\mu}=1}^{\overline{m}_\kappa} Q_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}} \mathrm{Tr}_{\$_\kappa} \mathrm{Tr}_{\varphi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{E}_{\Phi_{\kappa+}} \right] e^{-\beta \hat{E}_{\Phi_{\kappa+}}}$$

$$k_{\kappa-} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} Q_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}} \mathrm{Tr}_{\$_\kappa} \mathrm{Tr}_{\varphi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{E}_{\Phi_{\kappa+}} \right] e^{-\beta \hat{E}_{\Phi_{\kappa+}}}. \quad (2.4)$$

We can also write this in another way:

$$k_{\kappa+} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\mu}=1}^{\overline{m}_\kappa} Q_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}} \mathrm{Tr}_{\$_\kappa} \mathrm{Tr}_{\varphi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}} \right] e^{-\beta \hat{H}_{\Phi_{\kappa+}}}$$

$$k_{\kappa-} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} Q_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}} \mathrm{Tr}_{\$_\kappa} \mathrm{Tr}_{\varphi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}} \right] e^{-\beta \hat{H}_{\Phi_{\kappa+}}}. \quad (2.5)$$

Because of invariance of a trace to unitary transformations, we find that

$$Z_{\Phi_{\kappa+}} = Z_{\Phi_{\kappa-}}$$
$$\mathrm{Tr}_{\Phi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}} \right] Z_{\Phi_{\kappa+}}^{-1} e^{-\beta \hat{H}_{\Phi_{\kappa+}}}$$
$$= \mathrm{Tr}_{\Phi_{\kappa-}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa-}, \hat{H}_{\Phi_{\kappa-}} \right] Z_{\Phi_{\kappa-}}^{-1} e^{-\beta \hat{H}_{\Phi_{\kappa-}}}. \quad (2.6)$$

The same formulas can also be written:

$$k_{\kappa+} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\mu}=1}^{\overline{m}_\kappa} Q_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}} \mathrm{Tr}_{\$_\kappa} \mathrm{Tr}_{\varphi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}} \right] e^{-\beta \hat{H}_{\Phi_{\kappa+}}}$$

$$k_{\kappa-} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} Q_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}} \mathrm{Tr}_{\$_\kappa} \mathrm{Tr}_{\varphi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}} \right] e^{-\beta \hat{H}_{\Phi_{\kappa+}}}. \quad (2.7)$$

We also find that

$$
k_{\kappa+} = \frac{\overline{Q}^{\ddagger}_{\varphi_{\kappa+}}}{\prod_{\overline{\mu}=1}^{\overline{m}_\kappa} \overline{Q}^{\overline{\alpha}_{\kappa;\overline{\mu}}}_{A(\kappa;\overline{\mu})}} \mathrm{Tr}_{\varphi_{\kappa+}}\, (i\hbar)^{-1} \overline{\left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \overline{Q}^{\ddagger-1}_{\varphi_{\kappa+}} e^{-\beta\hat{\varepsilon}_{\varphi_{\kappa+}}}}
$$

$$
k_{\kappa-} = \frac{\overline{Q}^{\ddagger}_{\varphi_{\kappa+}}}{\prod_{\overline{\nu}=1}^{\overline{n}_\kappa} \overline{Q}^{\overline{\beta}_{\kappa;\overline{\nu}}}_{B(\kappa;\overline{\nu})}} \mathrm{Tr}_{\varphi_{\kappa+}}\, (i\hbar)^{-1} \overline{\left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \overline{Q}^{\ddagger-1}_{\varphi_{\kappa+}} e^{-\beta\hat{\varepsilon}_{\varphi_{\kappa+}}}}.
$$

(2.8)

We therefore find that:

$$
k_{\kappa+} = \frac{\overline{Q}^{\ddagger}_{\varphi_{\kappa+}}}{\prod_{\overline{\mu}=1}^{\overline{m}_\kappa} \overline{Q}^{\overline{\alpha}_{\kappa;\overline{\mu}}}_{A(\kappa;\overline{\mu})}} \left\langle (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \right\rangle_{\varphi_{\kappa+}}
$$

$$
k_{\kappa-} = \frac{\overline{Q}^{\ddagger}_{\varphi_{\kappa+}}}{\prod_{\overline{\nu}=1}^{\overline{n}_\kappa} \overline{Q}^{\overline{\beta}_{\kappa;\overline{\nu}}}_{B(\kappa;\overline{\nu})}} \left\langle (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \right\rangle_{\varphi_{\kappa+}},
$$

(2.9)

where $\overline{Q}^{\ddagger}_{\varphi_{\kappa+}} = \mathrm{Tr}_{\varphi_{\kappa+}} \overline{e^{-\beta\hat{\varepsilon}_{\varphi_{\kappa+}}}}$, and

$$
\left\langle (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{E}_{\Phi_{\kappa+}}\right] \right\rangle_{\varphi_{\kappa+}} = \mathrm{Tr}_{\varphi_{\kappa+}}\, (i\hbar)^{-1} \overline{\left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \overline{Q}^{\ddagger-1}_{\varphi_{\kappa+}} e^{-\beta\hat{\varepsilon}_{\varphi_{\kappa+}}}}
$$

$$
= \frac{\mathrm{Tr}_{\mathfrak{s}_\kappa} \mathrm{Tr}_{\varphi_{\kappa+}}\, (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] e^{-\beta\hat{E}_{\Phi_{\kappa+}}}}{Z_{\mathfrak{s}} \overline{Q}^{\ddagger}_{\varphi_{\kappa+}}}
$$

$$
= \frac{\mathrm{Tr}_{\Phi_{\kappa+}}\, (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] e^{-\beta\hat{E}_{\Phi_{\kappa+}}}}{Z_{\mathfrak{s}} \overline{Q}^{\ddagger}_{\varphi_{\kappa+}}}
$$

$$
= \frac{Z_{\Phi_{\kappa+}}}{Z_{\mathfrak{s}} \overline{Q}^{\ddagger}_{\varphi_{\kappa+}}} \left\langle (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \right\rangle_{\Phi_{\kappa+}}.
$$

(2.10)

Now we can find that $\left\langle (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \right\rangle_{\Phi_{\kappa+}} = \left(2\pi\hbar Z_{\Phi_{\kappa+}}\right)^{-1} \int_0^\infty N_{\kappa+}(E) e^{-\beta E}$
dE. The function $N_{\kappa+}(E) = h \mathrm{Tr}_{\Phi_{\kappa+}} (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_{\kappa+}}\right] \delta\left(E - \hat{H}_{\Phi_{\kappa+}}\right)$, is known
as **Cumulative Reaction Probability**. One can easily show that the cumulative reaction probability for the backward reaction = cumulative reaction probability for the forward reaction.

In classical transition state theory, the reaction is successful if and only if given enough time the activated complex will **permanently** end up in products. We shall use the identity

$$x = \{2\wp(x) - 1\}|x|, \quad \wp(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases}$$

$$\frac{x}{|x|} = 2\wp(x) - 1 \rightarrow \therefore \wp(x) = \frac{1}{2}\left\{\frac{x}{|x|} + 1\right\}. \tag{2.11}$$

Basically, we are using $\wp(x) = \frac{1}{2}\left\{\frac{x}{|x|} + 1\right\}$ as the definition of the Heaviside function, using $\lim\limits_{x<0, x\to 0}\frac{x}{|x|} = -1$, $\lim\limits_{x>0, x\to 0}\frac{x}{|x|} = +1$. Thus the only possible eigenvalues of the Heaviside of any Hermitian observable are 0 and 1, and the absolute value function of any Hermitian observable must be positive semi-definite. Now the "transition state" complex of any elementary reaction must have a set of coordinates and for every coordinate there must exist a unique canonically conjugate momentum, and furthermore no two different coordinates can have the same canonically conjugate momentum. So in the low velocity approximation where non-relativistic mechanics applies, we can use:

$$E = \frac{1}{2}\dot{\boldsymbol{x}}^* \overset{\leftrightarrow}{\boldsymbol{M}}_0 \dot{\boldsymbol{x}} + \widehat{V}(\boldsymbol{x}). \tag{2.12}$$

Relativistic corrections can also be added if necessary. We know that the operator for the velocity is: $\dot{\hat{\boldsymbol{x}}} = \frac{1}{i\hbar}\left[\hat{\boldsymbol{x}}, \hat{H}\right]$. $\overset{\leftrightarrow}{\boldsymbol{M}}_0$ is a symmetric positive definite matrix. We will now define: $\hat{H}_0 = \frac{1}{2}\dot{\hat{\boldsymbol{x}}}^* \overset{\leftrightarrow}{\boldsymbol{M}}_0 \dot{\hat{\boldsymbol{x}}}$. This is the interaction free Hamiltonian, or kinetic energy, of a nonrelativistic noninteracting system. An interesting property is that for $\lim\limits_{\tau\to\pm\infty} e^{-i\hat{H}\tau/\hbar}e^{i\hat{H}_0\tau/\hbar} = \hat{\Omega}^{(\pm)}$, we shall now use time dependent scattering theory. We find that

$$\hat{\Omega}^{(\pm)}|E,\varphi\rangle = |E,\varphi\rangle + \frac{1}{E - \hat{H}_0 \pm i\varepsilon}\hat{V}\hat{\Omega}^{(\pm)}|E,\varphi\rangle$$

$$\hat{H}_0|E,\varphi\rangle = E|E,\varphi\rangle \tag{2.13}$$

We find that $\hat{H}\hat{\Omega}^{(\pm)}|E,\varphi\rangle = E\hat{\Omega}^{(\pm)}|E,\varphi\rangle = \hat{\Omega}^{(\pm)}E|E,\varphi\rangle = \hat{\Omega}^{(\pm)}\hat{H}_0|E,\varphi\rangle$.

We therefore find out that

$$\hat{H}\hat{\Omega}^{(\pm)} = \hat{\Omega}^{(\pm)}\hat{H}_0$$

$$\hat{\Omega}^{(\pm)\dagger}\hat{H} = \hat{H}_0\hat{\Omega}^{(\pm)\dagger} \tag{2.14}$$

We find that $\left|\varphi^{(\pm)}\right\rangle = \hat{\Omega}^{(\pm)}|\varphi\rangle = \lim\limits_{\tau\to\pm\infty} e^{-i\hat{H}\tau/\hbar}e^{i\hat{H}_0\tau/\hbar}|\varphi\rangle$. We also find out that if $\hat{A}\hat{H}_0 = \hat{H}_0\hat{A}$, then $\hat{\Omega}^{(-)}\hat{A}\hat{\Omega}^{(-)\dagger} = \lim\limits_{\tau\to+\infty} e^{i\hat{H}\tau/\hbar}e^{-i\hat{H}_0\tau/\hbar}\hat{A}e^{i\hat{H}_0\tau/\hbar}e^{-i\hat{H}\tau/\hbar} = \lim\limits_{\tau\to+\infty} e^{i\hat{H}\tau/\hbar}\hat{A}e^{-i\hat{H}\tau/\hbar} = \lim\limits_{\tau\to+\infty} \hat{A}_{(Heisenberg)}(\tau)$. We also find out that $\hat{\Omega}^{(-)}\hat{A}\hat{\Omega}^{(-)\dagger}$ $\hat{H} = \hat{\Omega}^{(-)}\hat{A}\hat{H}_0\hat{\Omega}^{(\pm)\dagger} = \hat{\Omega}^{(-)}\hat{H}_0\hat{A}\hat{\Omega}^{(-)\dagger} = \hat{H}\hat{\Omega}^{(-)}\hat{A}\hat{\Omega}^{(-)\dagger}$. We know however that

$\hat{x}\hat{H}_0 = \hat{H}_0\hat{x}$. Therefore

$$\hat{\Omega}^{(-)}\hat{x}\hat{\Omega}^{(-)\dagger}\hat{H} = \hat{H}\hat{\Omega}^{(-)}\hat{x}\hat{\Omega}^{(-)\dagger}$$
$$\lim_{\tau \to +\infty} e^{i\hat{H}\tau/\hbar}\hat{x}e^{-i\hat{H}\tau/\hbar}\hat{H} = \hat{H}e^{i\hat{H}\tau/\hbar}\hat{x}e^{-i\hat{H}\tau/\hbar} \qquad (2.15)$$

so we find that $\lim_{\tau \to +\infty} \hat{x}_{(Heisenberg)}(\tau) = \hat{v}^{-}$, is a constant of motion. As we shall see, it is this constant of motion that determines the asymptotic future destiny of the system.

We find that in classical *Newtonian* mechanics that we can use a Hamiltonian of the form:

$$H \equiv \widehat{H}\left(\ldots, x_\mu, \ldots, \Pi_\mu, \ldots\right) \qquad (2.16)$$

We can also write this as:

$$H \equiv \widehat{H}\left(\ldots, x_\mu, \ldots, \Pi_\mu, \ldots\right) = \sum_{j=1}^{n^\diamond} \frac{\mathbf{p}^{(j)2}}{2m_0^{(j)}} + \sum_{j=1}^{n^\diamond} m_0^{(j)}c^2 + \widehat{V}\left(\ldots, \mathbf{r}^{(j)}, \ldots\right) \qquad (2.17)$$

We can also write:

$$H \equiv \widehat{H}\left(\ldots, x_\mu, \ldots, \Pi_\mu, \ldots\right) = \sum_{\mu=1}^{3}\sum_{j=1}^{n^\diamond} \frac{\Pi_\mu^{(j)2}}{2m_0^{(j)}} + \sum_{j=1}^{n^\diamond} m_0^{(j)}c^2 + \widehat{V}\left(\ldots, x_\mu^{(j)}, \ldots\right) \qquad (2.18)$$

Now let $\Pi_\mu^{'(j)} = \frac{\Pi_\mu^{(j)}}{\sqrt{m_0^{(j)}}}$ and $x_\mu^{'(j)} = x_\mu^{(j)}\sqrt{m_0^{(j)}}$. Then

$$H \equiv \widehat{H}\left(\ldots, x_\mu, \ldots, \Pi_\mu, \ldots\right) = \sum_{\mu=1}^{3}\sum_{j=1}^{n^\diamond} \frac{1}{2}\Pi_\mu^{'(j)2} + \sum_{j=1}^{n^\diamond} m_0^{(j)}c^2 + \widehat{V}\left(\ldots, x_\mu^{'(j)}, \ldots\right) \qquad (2.19)$$

The amazing thing is that $\Pi_\mu^{'(j)} = \frac{\Pi_\mu^{(j)}}{\sqrt{m_0^{(j)}}} = \frac{m_0^{(j)}v_\mu^{(j)}}{\sqrt{m_0^{(j)}}} = v_\mu^{(j)}\sqrt{m_0^{(j)}} = \frac{dx_\mu^{'(j)}}{dt} = v_\mu^{'(j)}$.

Then by a further transformation, we can take $H \equiv \widehat{H}\left(\ldots, x_\mu, \ldots, \Pi_\mu, \ldots\right) = \sum_{\mu=1}^{3}$ $\sum_{j=1}^{n^\diamond} \frac{1}{2}\Pi_\mu^{''(j)2} + \sum_{j=1}^{n^\diamond} m_0^{(j)}c^2 + \widehat{V}\left(\ldots, x_\mu^{''(j)}, \ldots\right)$ so that one of the new coordinates is the reaction coordinate. Then we can write a Hamiltonian of this form: $\hat{H} = \sum_{\mu'=1}^{3n^\diamond} \frac{1}{2}\hat{\Pi}_{\mu'}^{''2} + \sum_{j=1}^{n^\diamond} m_0^{(j)}c^2 + \widehat{V}\left(\ldots, \hat{x}_{\mu'}'', \ldots\right) + \text{Relativistic Corrections.}$

It is sufficient to define an unperturbed Hamiltonian $\hat{H}_0 = \sum_{\mu'=1}^{3n^\diamond} \frac{1}{2} \hat{v}''^2_{\mu'} + \sum_{j=1}^{n^\diamond} m_0^{(j)} c^2$,

where $\hat{x}''_{\mu'} = \hat{s}^\ddagger \delta_{\mu',1} + \sum_{v'=2}^{3n^\diamond} \hat{x}''_{v'} \delta_{\mu',1}$, $\hat{v}''_{\mu'} = \frac{1}{i\hbar} \left[\hat{x}''_{\mu'}, \hat{H} \right]$. Notice that $\hat{v}^\ddagger \hat{H}_0 = \hat{H}_0 \hat{v}^\ddagger$. We can also define: $\hat{V}^\diamond = \hat{H} - \hat{H}_0$. Substituting this potential into 2.13, 2.14, we find that $\lim_{\tau \to +\infty} e^{i\hat{H}\tau/\hbar} \hat{v}^\ddagger e^{-i\hat{H}\tau/\hbar} \hat{H} = \hat{H} e^{i\hat{H}\tau/\hbar} \hat{v}^\ddagger e^{-i\hat{H}\tau/\hbar}$. However, $\hat{v}^{\ddagger-} = \lim_{\tau \to +\infty} e^{i\hat{H}\tau/\hbar} e^{-i\hat{H}_0\tau/\hbar} \hat{v}^\ddagger e^{-i\hat{H}_0\tau/\hbar} e^{-i\hat{H}\tau/\hbar} = \lim_{\tau \to +\infty} e^{i\hat{H}\tau/\hbar} \hat{v}^\ddagger e^{-i\hat{H}\tau/\hbar}$, is the reaction coordinate velocity (RCV) in the infinite future. This infinite future RCV is a constant of motion. Therefore $\lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \hat{s}^\ddagger_{(Heisenberg)} (\tau' + \tau) = \lim_{\tau \to +\infty} \hat{s}^\ddagger_{(Heisenberg)} (\tau) + \lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \int_\tau^{\tau+\tau'} \hat{v}^\ddagger_{(Heisenberg)} (t) \, dt$. However, $\tau \le t \le \tau + \tau' \& \tau \to +\infty, \tau' \to +\infty \Rightarrow \hat{v}^\ddagger_{(Heisenberg)} (t) = e^{i\hat{H}t/\hbar} \hat{v}^\ddagger e^{-i\hat{H}t/\hbar} = \hat{v}^{\ddagger-}$. Therefore $\lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \hat{s}^\ddagger_{(Heisenberg)} (\tau' + \tau) = \lim_{\tau \to +\infty} \hat{s}^\ddagger_{(Heisenberg)} (\tau) + \lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \hat{v}^{\ddagger-} \tau'$. Furthermore: $\lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \left\{ \hat{s}^\ddagger_{(Heisenberg)} (\tau' + \tau) - s_0^\ddagger \right\} = \lim_{\tau \to +\infty} \left\{ \hat{s}^\ddagger_{(Heisenberg)} (\tau) - s_0^\ddagger \right\} + \lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \hat{v}^{\ddagger-} \tau'$. Now we shall form:

$$\wp\left(\hat{s}^\ddagger_{(Heisenberg)} (\tau' + \tau) - s_0^\ddagger \right) = \frac{1}{2} \left\{ \frac{\hat{s}^\ddagger_{(Heisenberg)} (\tau' + \tau) - s_0^\ddagger}{\left| \hat{s}^\ddagger_{(Heisenberg)} (\tau' + \tau) - s_0^\ddagger \right|} + 1 \right\}$$

$$= \frac{1}{2} \left\{ \frac{\hat{s}^\ddagger_{(Heisenberg)} (\tau) - s_0^\ddagger + \hat{v}^{\ddagger-} \tau'}{\left| \hat{s}^\ddagger_{(Heisenberg)} (\tau) - s_0^\ddagger + \hat{v}^{\ddagger-} \tau' \right|} + 1 \right\}$$

$$(2.20)$$

However, it turns out that $\hat{s}^\ddagger_{(Heisenberg)} (\tau) \& s_0^\ddagger$ can be temporarily considered to be bounded: $-\frac{X}{2} \le \hat{s}^\ddagger_{(Heisenberg)} (\tau) \le +\frac{X}{2} \& -\frac{X}{2} \le s_0^\ddagger \le +\frac{X}{2}$. Therefore we can let $\hat{s}^\ddagger_{(Heisenberg)} (\tau) - s_0^\ddagger = X \hat{q}^\ddagger_{(Heisenberg)} (\tau)$. Then $-1 \le \hat{q}^\ddagger_{(Heisenberg)} (\tau) \le +1$. Then

$$\wp\left(\hat{s}^\ddagger_{(Heisenberg)} (\tau' + \tau) - s_0^\ddagger \right) = \frac{1}{2} \left\{ \frac{X \hat{q}^\ddagger_{(Heisenberg)} (\tau) + \hat{v}^{\ddagger-} \tau'}{\left| X \hat{q}^\ddagger_{(Heisenberg)} (\tau) + \hat{v}^{\ddagger-} \tau' \right|} + 1 \right\}$$

$$= \frac{1}{2} \left\{ \frac{X \tau'^{-1} \hat{q}^\ddagger_{(Heisenberg)} (\tau) + \hat{v}^{\ddagger-}}{\left| X \tau'^{-1} \hat{q}^\ddagger_{(Heisenberg)} (\tau) + \hat{v}^{\ddagger-} \right|} + 1 \right\}$$

$$= \frac{1}{2} \left\{ \frac{\hat{v}^{\ddagger-}}{\left| \hat{v}^{\ddagger-} \right|} + 1 \right\} = \wp\left(\hat{v}^{\ddagger-} \right) \quad (2.21)$$

Ergo: $\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}e^{i\hat{H}\{\tau+\tau'\}/\hbar}\wp\left(\hat{s}^{\ddagger}-s_0^{\ddagger}\right)e^{-i\hat{H}\{\tau+\tau'\}/\hbar}\equiv\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}\wp$ $\left(\hat{s}^{\ddagger}_{(Heisenberg)}\left(\tau'+\tau\right)-s_0^{\ddagger}\right)=\wp(\hat{v}^{\ddagger-})$. We shall now define: $\hat{P}^{-}_{\Phi}=\lim\limits_{X\to+\infty}$ $\lim\limits_{\tau'X^{-1}\to+\infty}\lim\limits_{\tau\to+\infty}e^{i\hat{H}\{\tau+\tau'\}/\hbar}\wp\left(\hat{s}^{\ddagger}-s_0^{\ddagger}\right)e^{-i\hat{H}\{\tau+\tau'\}/\hbar}=\wp(\hat{v}^{\ddagger-})$, which is in fact the projection operator for all the eigenstates of the full Hamiltonian such that constitute *forward moving* products in the infinite future.

A similar argument shows that: $\lim\limits_{\tau\to\infty}e^{-i\hat{H}\tau/\hbar}\hat{v}^{\ddagger}e^{i\hat{H}\tau/\hbar}\hat{H}=\hat{H}e^{-i\hat{H}\tau/\hbar}\hat{v}^{\ddagger}e^{i\hat{H}\tau/\hbar}$. However, $\hat{v}^{\ddagger+}=\lim\limits_{\tau\to+\infty}e^{-i\hat{H}\tau/\hbar}e^{i\hat{H}_0\tau/\hbar}\hat{v}^{\ddagger}e^{-i\hat{H}_0\tau/\hbar}e^{i\hat{H}\tau/\hbar}=\lim\limits_{\tau\to+\infty}e^{-i\hat{H}\tau/\hbar}\hat{v}^{\ddagger}e^{i\hat{H}\tau/\hbar}$, is the reaction coordinate velocity (RCV) in the infinite past. This infinite past RCV is also a constant of the motion. Therefore $\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}\hat{s}^{\ddagger}_{(Heisenberg)}\left(-\tau'-\tau\right)=$ $\lim\limits_{\tau\to+\infty}\hat{s}^{\ddagger}_{(Heisenberg)}\left(-\tau\right)+\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}\int_{-\tau}^{-\tau-\tau'}\hat{v}^{\ddagger}_{(Heisenberg)}(t)\,dt$. Then $-\tau\geq t\geq$ $-\tau-\tau'\&\tau\to+\infty,\tau'\to+\infty\Rightarrow\hat{v}^{\ddagger}_{(Heisenberg)}(-t)=e^{-i\hat{H}t/\hbar}\hat{v}^{\ddagger}e^{i\hat{H}t/\hbar}=$ $\hat{v}^{\ddagger+}$. Now here comes the tricky part: $\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}\hat{s}^{\ddagger}_{(Heisenberg)}\left(-\tau'-\tau\right)=$ $\lim\limits_{\tau\to+\infty}\hat{s}^{\ddagger}_{(Heisenberg)}\left(-\tau\right)-\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}\hat{v}^{\ddagger-}\tau'$. Then $\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}\left\{s_0^{\ddagger}-\right.$ $\left.\hat{s}^{\ddagger}_{(Heisenberg)}\left(-\tau'-\tau\right)\right\}=\lim\limits_{\tau\to+\infty}\left\{s_0^{\ddagger}-\hat{s}^{\ddagger}_{(Heisenberg)}\left(-\tau\right)\right\}+\lim\limits_{\tau\to+\infty}\lim\limits_{\tau'\to+\infty}\hat{v}^{\ddagger+}\tau'$. Then

$$\wp\left(s_0^{\ddagger}-\hat{s}^{\ddagger}_{(Heisenberg)}\left(-\tau'-\tau\right)\right)=\frac{1}{2}\left\{\frac{-X\hat{q}^{\ddagger}_{(Heisenberg)}\left(-\tau\right)+\hat{v}^{\ddagger+}\tau'}{\left|-X\hat{q}^{\ddagger}_{(Heisenberg)}\left(-\tau\right)+\hat{v}^{\ddagger+}\tau'\right|}+1\right\}$$

$$=\frac{1}{2}\left\{\frac{-X\tau'^{-1}\hat{q}^{\ddagger}_{(Heisenberg)}\left(-\tau\right)+\hat{v}^{\ddagger+}}{\left|-X\tau'^{-1}\hat{q}^{\ddagger}_{(Heisenberg)}\left(-\tau\right)+\hat{v}^{\ddagger+}\right|}+1\right\}$$

$$=\frac{1}{2}\left\{\frac{\hat{v}^{\ddagger+}}{\left|\hat{v}^{\ddagger+}\right|}+1\right\}=\wp\left(\hat{v}^{\ddagger+}\right)\qquad(2.22)$$

Ergo: we derive another projection $\hat{P}^{+}_{\Psi}=\lim\limits_{X\to+\infty}\lim\limits_{\tau'X^{-1}\to+\infty}\lim\limits_{\tau\to+\infty}e^{-i\hat{H}\{\tau+\tau'\}/\hbar}\wp$ $\left(s_0^{\ddagger}-\hat{s}^{\ddagger}\right)e^{i\hat{H}\{\tau+\tau'\}/\hbar}=\wp(\hat{v}^{\ddagger+})$ which is in fact the projection operator for all the eigenstates of the full Hamiltonian such that constitute *forward moving* reactants in the infinite past. In fact, all reactants in the infinite past must move forwards, and all products in the infinite future must move forwards.

We can also define another unperturbed Hamiltonian: $\hat{H}_0'=\sum\limits_{\mu'=1}^{3n^{\diamond}}\frac{1}{2}\hat{\Pi}''^2_{\mu'}+\sum\limits_{j=1}^{n^{\diamond}}$ $m_0^{(j)}c^2$, which we shall use later. Then define a new potential $\hat{V}'^{\diamond}=\hat{H}-\hat{H}_0'$ and substitute into 2.12 and 2.13 as before. Then we find that $\lim\limits_{\tau\to\pm\infty}e^{i\hat{H}\tau/\hbar}\hat{\Pi}''_{\mu'}e^{-i\hat{H}\tau/\hbar}$

$\hat{H} = \hat{H}e^{i\hat{H}\tau/\hbar}\hat{\Pi}''_{\mu'}e^{-i\hat{H}\tau/\hbar}$, so that $\lim_{\tau\to\pm\infty} e^{-i\hat{H}\tau/\hbar}\hat{\Pi}''_{\mu'}e^{i\hat{H}\tau/\hbar} = \hat{\Pi}''^{(\pm)'}_{\mu'}$ constitutes

a conserved quantity in its own right. If that is done, then $\lim_{\tau\to\pm\infty} \frac{1}{i\hbar}\left[e^{-i\hat{H}\tau/\hbar}\hat{x}''_{\mu'}e^{i\hat{H}\tau/\hbar},\right.$

$\left.\hat{H}\right] = \lim_{\tau\to\pm\infty} e^{-i\hat{H}\tau/\hbar}\hat{v}''_{\mu'}e^{i\hat{H}\tau/\hbar}$, as we have seen before. However, we can prove that

$\lim_{\tau\to\pm\infty} e^{-i\hat{H}\tau/\hbar}e^{i\hat{H}'_0\tau/\hbar}\hat{H}_0 e^{-i\hat{H}_0\tau/\hbar}e^{i\hat{H}\tau/\hbar} = \hat{H} = \sum_{\mu'=1}^{3n^\diamond} \frac{1}{2}\hat{\Pi}''^{(\pm)'2}_{\mu'} + \sum_{j=1}^{n^\diamond} m_0^{(j)}c^2$. How-

ever, $\hat{H}\hat{\Pi}''^{(\pm)'}_{\mu'} = \hat{\Pi}''^{(\pm)'}_{\mu'}\hat{H}$. This means that $\hat{\Pi}''^{(\pm)'}_{\mu'} = \lim_{\tau\to\pm\infty} e^{-i\hat{H}\tau/\hbar}\hat{\Pi}''^{(\pm)}_{\mu'}e^{i\hat{H}\tau/\hbar}$

is a constant of motion. Then we see that $\hat{H}\hat{\Pi}''^{(\pm)'}_{\mu'} = \hat{\Pi}''^{(\pm)'}_{\mu'}\hat{H}$.

This means that

$$\hat{\Omega}^{(\pm)\dagger}\left\{\frac{e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{H} - \hat{H}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}}{i\hbar}\right\}\hat{\Omega}^{(\pm)}$$

$$= \hat{\Omega}^{(\pm)\dagger}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{v}''_{\mu'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{\Omega}^{(\pm)}$$

$$= \frac{\hat{\Omega}^{(\pm)\dagger}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{H}\hat{\Omega}^{(\pm)} - \hat{\Omega}^{(\pm)\dagger}\hat{H}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{\Omega}^{(\pm)}}{i\hbar}$$

$$= \frac{\hat{\Omega}^{(\pm)\dagger}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{\Omega}^{(\pm)}\hat{H}'_0 - \hat{H}'_0\hat{\Omega}^{(\pm)\dagger}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{\Omega}^{(\pm)}}{i\hbar}$$

$$= \hat{\Omega}^{(\pm)\dagger}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{v}''_{\mu'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{\Omega}^{(\pm)}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{v}''_{\mu'}e^{i\hat{H}\bar{\tau}/\hbar}$$

$$= \hat{\Omega}^{(\pm)}\cdot\frac{\hat{\Omega}^{(\pm)\dagger}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{\Omega}^{(\pm)}\hat{H}'_0 - \hat{H}'_0\hat{\Omega}^{(\pm)\dagger}e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}\hat{\Omega}^{(\pm)}}{i\hbar}\cdot\hat{\Omega}^{(\pm)\dagger}$$

$$= \frac{1}{i\hbar}\left[e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}, \hat{\Omega}^{(\pm)}\hat{H}'_0\hat{\Omega}^{(\pm)\dagger}\right]$$

where we have used $\hat{\Omega}^{(\pm)}\hat{\Omega}^{(\pm)\dagger} = \hat{\Omega}^{(\pm)\dagger}\hat{\Omega}^{(\pm)} = \sum_\sigma\int_{-\infty}^\infty |E,\sigma\rangle\langle E,\sigma|\,dE$. The next

step is this: $e^{-i\hat{H}\bar{\tau}/\hbar}\hat{v}''_{\mu'}e^{i\hat{H}\bar{\tau}/\hbar} = \frac{1}{i\hbar}\left[e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}, \hat{\Omega}^{(\pm)}\hat{H}'_0\hat{\Omega}^{(\pm)\dagger}\right]$. Then

$$e^{-i\hat{H}\bar{\tau}/\hbar}\hat{v}''_{\mu'}e^{i\hat{H}\bar{\tau}/\hbar} = \lim_{\tau\to\pm\infty}\frac{1}{i\hbar}\left[e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}, e^{-i\hat{H}\tau/\hbar}e^{i\hat{H}'_0\tau/\hbar}\hat{H}'_0 e^{-i\hat{H}'_0\tau/\hbar}e^{i\hat{H}\tau/\hbar}\right]$$

$$= \lim_{\tau\to\pm\infty}\frac{1}{i\hbar}\left[e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}, e^{-i\hat{H}\tau/\hbar}e^{i\hat{H}'_0\tau/\hbar}\sum_{\mu'=1}^{3n^\diamond}\frac{1}{2}\hat{\Pi}''^2_{\mu'}e^{-i\hat{H}'_0\tau/\hbar}e^{i\hat{H}\tau/\hbar}\right]$$

$$= \lim_{\tau\to\pm\infty}\frac{1}{i\hbar}\left[e^{-i\hat{H}\bar{\tau}/\hbar}\hat{x}''_{v'}e^{i\hat{H}\bar{\tau}/\hbar}, e^{-i\hat{H}\tau/\hbar}\sum_{\mu'=1}^{3n^\diamond}\frac{1}{2}\hat{\Pi}''^2_{\mu'}e^{i\hat{H}\tau/\hbar}\right].$$

In fact, one can see that

$$\lim_{\tau\to\pm\infty}\frac{1}{i\hbar}\left[e^{-i\hat{H}\tau/\hbar}\hat{x}''_{v'}e^{i\hat{H}\tau/\hbar}, e^{-i\hat{H}\tau/\hbar}\sum_{\mu'=1}^{3n^\diamond}\frac{1}{2}\hat{\Pi}''^2_{\mu'}e^{i\hat{H}\tau/\hbar}\right]$$

$$= \lim_{\tau \to \pm\infty} e^{-i\hat{H}\tau/\hbar} \hat{v}''_{\mu'} e^{i\hat{H}\tau/\hbar}$$

$$= \lim_{\tau \to \pm\infty} \frac{1}{i\hbar} e^{-i\hat{H}\tau/\hbar} \left[\hat{x}''_{\nu'}, \sum_{\mu'=1}^{3n^\diamond} \frac{1}{2} \hat{\Pi}''^2_{\mu'} \right] e^{i\hat{H}\tau/\hbar} = \lim_{\tau \to \pm\infty} e^{-i\hat{H}\tau/\hbar} \hat{\Pi}''_{\mu'} e^{i\hat{H}\tau/\hbar}$$

$$= \lim_{\tau \to \pm\infty} e^{-i\hat{H}\tau/\hbar} e^{i\hat{H}\tau_0/\hbar} \hat{\Pi}''_{\mu'} e^{-i\hat{H}\tau_0/\hbar} e^{i\hat{H}\tau/\hbar} = \hat{\Pi}''^{(\pm)'}_{\mu'}.$$

Ergo, we find that $\lim_{\tau \to \pm\infty} e^{-i\hat{H}\tau/\hbar} \hat{v}''_{\mu'} e^{i\hat{H}\tau/\hbar} = \hat{\Pi}''^{(\pm)'}_{\mu'}$ is a constant of the motion.

Therefore: $\lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \left\{ \hat{s}^{\ddagger}_{(Heisenberg)} (\tau' + \tau) - s^{\ddagger}_0 \right\}$

$= \lim_{\tau \to +\infty} \left\{ \hat{s}^{\ddagger}_{(Heisenberg)} (\tau) - s^{\ddagger}_0 \right\} + \lim_{\tau \to +\infty} \lim_{\tau' \to +\infty} \hat{\Pi}''^{\ddagger(-)'} \tau'$. By the same methods we used before,

$$\varphi\left(\hat{s}^{\ddagger}_{(Heisenberg)} (\tau' + \tau) - s^{\ddagger}_0 \right) = \frac{1}{2} \left\{ \frac{X\hat{q}^{\ddagger}_{(Heisenberg)} (\tau) + \hat{\Pi}''^{\ddagger(-)'} \tau'}{\left| X\hat{q}^{\ddagger}_{(Heisenberg)} (\tau) + \hat{\Pi}''^{\ddagger(-)'} \tau' \right|} + 1 \right\}$$

$$= \frac{1}{2} \left\{ \frac{X\tau'^{-1} \hat{q}^{\ddagger}_{(Heisenberg)} (\tau) + \hat{\Pi}''^{\ddagger(-)'}}{\left| X\tau'^{-1} \hat{q}^{\ddagger}_{(Heisenberg)} (\tau) + \hat{\Pi}''^{\ddagger(-)'} \right|} + 1 \right\}$$

$$= \frac{1}{2} \left\{ \frac{\hat{\Pi}''^{\ddagger(-)'}}{\left| \hat{\Pi}''^{\ddagger(-)'} \right|} + 1 \right\} = \varphi\left(\hat{\Pi}''^{\ddagger(-)'} \right).$$

And

$$\varphi\left(s^{\ddagger}_0 - \hat{s}^{\ddagger}_{(Heisenberg)} (-\tau' - \tau) \right) = \frac{1}{2} \left\{ \frac{-X\hat{q}^{\ddagger}_{(Heisenberg)} (-\tau) + \hat{\Pi}''^{\ddagger(+)'} \tau'}{\left| -X\hat{q}^{\ddagger}_{(Heisenberg)} (-\tau) + \hat{\Pi}''^{(+)'}_{\mu'} \tau' \right|} + 1 \right\}$$

$$= \frac{1}{2} \left\{ \frac{-X\tau'^{-1} \hat{q}^{\ddagger}_{(Heisenberg)} (-\tau) + \hat{\Pi}''^{\ddagger(+)'}}{\left| -X\tau'^{-1} \hat{q}^{\ddagger}_{(Heisenberg)} (-\tau) + \hat{\Pi}''^{\ddagger(+)'} \right|} + 1 \right\}$$

$$= \frac{1}{2} \left\{ \frac{\hat{\Pi}''^{\ddagger(+)'}}{\left| \hat{\Pi}''^{\ddagger(+)'} \right|} + 1 \right\} = \varphi\left(\hat{\Pi}''^{\ddagger(+)'} \right).$$

We have successfully shown that

$$\hat{P}^-_\Phi = \lim_{X \to +\infty} \lim_{\tau' X^{-1} \to +\infty} \lim_{\tau \to +\infty} e^{i\hat{H}\{\tau+\tau'\}/\hbar} \varphi\left(\hat{s}^{\ddagger} - s^{\ddagger}_0 \right) e^{-i\hat{H}\{\tau+\tau'\}/\hbar}$$

$$= \varphi\left(\hat{v}^{\ddagger-}\right) = \varphi\left(\hat{\Pi}''^{\ddagger(-)'}\right)$$

$$\hat{P}_\Psi^+ = \lim_{X\to+\infty}\lim_{\tau'X^{-1}\to+\infty}\lim_{\tau\to+\infty} e^{-i\hat{H}\{\tau+\tau'\}/\hbar}\,\varphi\left(s_0^\ddagger - \hat{s}^\ddagger\right) e^{i\hat{H}\{\tau+\tau'\}/\hbar}$$

$$= \varphi\left(\hat{v}^{\ddagger+}\right) = \varphi\left(\hat{\Pi}''^{\ddagger(+)'}\right)$$

(2.23)

We can also prove that

$$\hat{P}_\Psi^- = \lim_{X\to+\infty}\lim_{\tau'X^{-1}\to+\infty}\lim_{\tau\to+\infty} e^{i\hat{H}\{\tau+\tau'\}/\hbar}\,\varphi\left(s_0^\ddagger - \hat{s}^\ddagger\right) e^{-i\hat{H}\{\tau+\tau'\}/\hbar}$$

$$= \varphi\left(-\hat{v}^{\ddagger-}\right) = \varphi\left(-\hat{\Pi}''^{\ddagger(-)'}\right)$$

$$\hat{P}_\Phi^+ = \lim_{X\to+\infty}\lim_{\tau'X^{-1}\to+\infty}\lim_{\tau\to+\infty} e^{-i\hat{H}\{\tau+\tau'\}/\hbar}\,\varphi\left(s_0^\ddagger - \hat{s}^\ddagger\right) e^{i\hat{H}\{\tau+\tau'\}/\hbar}$$

$$= \varphi\left(-\hat{v}^{\ddagger+}\right) = \varphi\left(-\hat{\Pi}''^{\ddagger(+)'}\right)$$

(2.24)

All reactants in the infinite past go forwards and all products in the infinite future go forwards. Likewise, all reactants in the infinite future have negative reaction coordinate momentum, and so do all products in the infinite past.

3 Derivation of scattering theory reaction rates

According to Levine [1], the rate of change of a variable in the infinite future is given by the following formula:

$$\lim_{t\to+\infty}\frac{d}{dt}\langle\psi_{E,\mu}|\,e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}\,|\psi_{E,\mu}\rangle$$

$$= \lim_{t\to+\infty}\frac{d}{dt}\langle\psi_{E,\mu}|\,e^{-i\hat{H}_0t/\hbar}e^{i\hat{H}t/\hbar}\hat{A}e^{-i\hat{H}t/\hbar}e^{i\hat{H}_0t/\hbar}\,|\psi_{E,\mu}\rangle$$

$$= \frac{1}{i\hbar}\langle\psi_{E,\mu}|\,e^{-i\hat{H}_0t/\hbar}e^{i\hat{H}t/\hbar}\left[\hat{A},\hat{H}\right]e^{-i\hat{H}t/\hbar}e^{i\hat{H}_0t/\hbar}\,|\psi_{E,\mu}\rangle$$

$$= \frac{1}{i\hbar}\left\langle\psi_{E,\mu}^{(+)}\right|\left[\hat{A},\hat{H}\right]\left|\psi_{E,\mu}^{(+)}\right\rangle$$

$$= \sum_\nu\int_{-\infty}^{\infty}\frac{2\pi}{\hbar}\left|\langle\psi_{E',\nu}|\,\hat{V}\,\left|\psi_{E,\mu}^{(+)}\right\rangle\right|^2\delta\left(E'-E\right)\left\{A_\nu - A_\mu\right\}dE' \quad (3.1)$$

we do not intend to derive this. For the derivation, see [1]. In Formula 3.1, we used the assumption that $\hat{A}\hat{H}_0 = \hat{H}_0\hat{A}$ {in fact $\hat{A} = \sum_\mu\int_{-\infty}^{\infty}A_\mu\,|\psi_{E,\mu}\rangle\langle\psi_{E,\mu}|\,dE$}

and the fact that $\hat{H}_0\,|\psi_{E,\mu}\rangle = E\,|\psi_{E,\mu}\rangle$, and $e^{i\hat{H}_0t/\hbar}\,|\psi_{E,\mu}\rangle = e^{iEt/\hbar}\,|\psi_{E,\mu}\rangle$. However, $\left\langle\psi_{E',\nu}|\,\hat{V}\,\left|\psi_{E,\mu}^{(+)}\right\rangle = \langle\psi_{E',\nu}|\,\hat{V}\hat{\Omega}^{(+)}\,|\psi_{E',\nu}\rangle = \langle\psi_{E',\nu}|\,\hat{T}^{(+)}\,|\psi_{E',\nu}\rangle\right.$, where now

we define: $\hat{T}^{(+)} = \hat{V}\hat{\Omega}^{(+)}$. We intend to prove that $\left|\psi_{E,\mu}^{(+)}\right\rangle$ satisfies the Lippmann–Schwinger equation. By reading chapters 7 and 8 of [2], one can show that $\left|\psi_{E,\mu}^{(+)}\right\rangle$ actually satisfies the Lippmann–Schwinger equation, but the proof of this is rather complicated and involves Green's functions. According to the same work [2], we can write the matrix elements of the S-matrix as $\left\langle\psi_{E',\nu}^{(-)}|\psi_{E,\mu}^{(+)}\right\rangle = \delta\left(E'-E\right)\delta_{\nu,\mu} - 2\pi i \left\langle\psi_{E',\nu}\right|\hat{T}\left|\psi_{E,\mu}\right\rangle\delta\left(E'-E\right) = S_{\nu\leftarrow\mu}(E)\delta\left(E'-E\right)$, where we define: $S_{\nu\leftarrow\mu}(E) = \delta_{\nu,\mu} - 2\pi i \left\langle\psi_{E,\nu}\right|\hat{T}\left|\psi_{E,\mu}\right\rangle$. Then one can show that the reaction "rate" for a given initial state is:

$$\frac{1}{i\hbar}\left\langle\Psi_{E,\mu}^{(+)}\right|\left[\hat{A},\hat{H}\right]\left|\Psi_{E,\mu}^{(+)}\right\rangle$$

$$= \sum_\nu \int_{-\infty}^{\infty} \frac{2\pi}{\hbar}\left|\left\langle\psi_{E',\nu}\right|\hat{V}\left|\psi_{E,\mu}^{(+)}\right\rangle\right|^2 \delta\left(E'-E\right)\left\{A_\nu - A_\mu\right\}dE' \quad (3.2)$$

where $A_\nu = \delta_{\psi_\nu \in \Phi}$. Then we find that

$$\frac{1}{i\hbar}\left\langle\Psi_{E,\mu}^{(+)}\right|\left[\hat{A},\hat{H}\right]\left|\Psi_{E,\mu}^{(+)}\right\rangle$$

$$= \sum_\nu \int_{-\infty}^{\infty} \frac{2\pi}{\hbar}\left|\left\langle\psi_{E',\nu}|\hat{V}|\psi_{E,\mu}^{(+)}\right\rangle\right|^2 \delta\left(E'-E\right)\left\{\delta_{\psi_\nu \in \Phi} - \delta_{\psi_\mu \in \Phi}\right\}dE'$$

$$\sum_{\nu,\tilde{\nu}}\int_{-\infty}^{\infty} \frac{2\pi}{\hbar}\left|\left\langle\psi_{E,\nu}|\hat{V}|\psi_{E,\mu}^{(+)}\right\rangle\right|^2 \left\{\delta_{\psi_\nu = \Phi_{\tilde{\nu}}} - \delta_{\psi_\mu = \Phi_{\tilde{\nu}}}\right\}dE'$$

$$= \sum_{\tilde{\nu}} \frac{2\pi}{\hbar}\left|\left\langle\Phi_{E,\tilde{\nu}}\right|\hat{T}\left|\Psi_{E,\mu}\right\rangle\right|^2 \quad (3.3)$$

We can now write: $\left\langle\Phi_{E,\tilde{\nu}}\right|\hat{T}\left|\Psi_{E,\mu}\right\rangle = \frac{S_{\Phi_\nu \leftarrow \Psi_\mu}(E) - \delta_{\Phi_\nu,\Psi_\mu}}{-2\pi i}$. However $\delta_{\Phi_\nu,\Psi_\mu} = 0$ because reactants and products are distinct from one another. Therefore $\frac{2\pi}{\hbar}\left|\left\langle\Phi_{E,\tilde{\nu}}\right|\hat{T}\left|\Psi_{E,\mu}\right\rangle\right|^2 = \frac{2\pi}{\hbar}\left|\frac{S_{\Phi_\nu \leftarrow \Psi_\mu}(E)}{-2\pi i}\right|^2 = \frac{2\pi}{(2\pi)^2\hbar}\left|S_{\Phi_\nu \leftarrow \Psi_\mu}(E)\right|^2 = \frac{1}{h}\left|S_{\Phi_\nu \leftarrow \Psi_\mu}(E)\right|^2$. But we know for a fact that we can take a canonical ensemble density matrix: $\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Z}$ and find the rate as

$$\mathrm{Tr}\hat{\rho}.\frac{1}{i\hbar}\hat{P}_\Psi^{(+)}\left[\hat{A},\hat{H}\right]\hat{P}_\Psi^{(+)} = \int_{-\infty}^{\infty} Z^{-1}e^{-\beta E}\sum_\mu \frac{1}{i\hbar}\left\langle\Psi_{E,\mu}^{(+)}\right|\left[\hat{A},\hat{H}\right]\left|\Psi_{E,\mu}^{(+)}\right\rangle dE$$

$$= \int_{-\infty}^{\infty} Z^{-1}e^{-\beta E}\sum_{\mu\tilde{\nu}} \frac{1}{h}\left|S_{\Phi_\nu \leftarrow \Psi_\mu}(E)\right|^2 dE$$

$$= (2\pi\hbar Z)^{-1} \int_{-\infty}^{\infty} e^{-\beta E} N(E) dE \qquad (3.4)$$

Actually, this is not quite right. We interpret the density matrix as: $\hat{\rho} = \lim_{\tau\to+\infty}$
$e^{-i\hat{H}\tau/\hbar} e^{i\hat{H}_0\tau/\hbar} \wp\left(\hat{\Pi}^{\ddagger}\right) Z^{-1} e^{-\beta\hat{H}_0} \wp\left(\hat{\Pi}^{\ddagger}\right) e^{-i\hat{H}_0\tau/\hbar} e^{i\hat{H}\tau/\hbar}$, where $Z = \text{Tr}\wp\left(\hat{\Pi}^{\ddagger}\right)$
$e^{-\beta\hat{H}_0}\wp\left(\hat{\Pi}^{\ddagger}\right)$. By the way, $\lim_{\tau\to+\infty} e^{-i\hat{H}\tau/\hbar} e^{i\hat{H}_0\tau/\hbar} \wp\left(\hat{\Pi}^{\ddagger}\right) e^{-i\hat{H}_0\tau/\hbar} e^{i\hat{H}\tau/\hbar} = \hat{P}_{\Psi}^{+}$.
However, we know that

$$\left|\Psi_{E,\mu}^{(+)}\right\rangle = \int_{-\infty}^{\infty} \sum_{\nu} \left|\psi_{E',\nu}^{(-)}\right\rangle\left\langle\psi_{E',\nu}^{(-)}|\Psi_{E,\mu}^{(+)}\right\rangle dE' = \int_{-\infty}^{\infty} \sum_{\nu} \left|\psi_{E',\nu}^{(-)}\right\rangle\left\langle\psi_{E',\nu}^{(-)}|\Psi_{E,\mu}^{(+)}\right\rangle dE'$$

$$\qquad (3.5)$$

$$\int_{-\infty}^{\infty} \sum_{\nu} \left|\psi_{E',\nu}^{(-)}\right\rangle S_{\psi_\nu\leftarrow\Psi_\mu}\left(E'\right) \delta\left(E'-E\right) dE' = \sum_{\nu} \left|\psi_{E,\nu}^{(-)}\right\rangle S_{\psi_\nu\leftarrow\Psi_\mu}(E)$$

However, we will add an additional projection operator for products in the infinite future: $\hat{P}_{\Phi}^{-}\left|\Psi_{E,\mu}^{(+)}\right\rangle = \sum_{\nu} \hat{P}_{\Phi}^{-}\left|\psi_{E,\nu}^{(-)}\right\rangle S_{\psi_\nu\leftarrow\Psi_\mu}(E) = \sum_{\nu} \delta_{\psi_\nu\in\Phi}\left|\psi_{E,\nu}^{(-)}\right\rangle S_{\psi_\nu\leftarrow\Psi_\mu}(E)$.
We also know that $\left\langle(s^{\ddagger},s''')^{(-)}|\psi_{E,\nu}^{(-)}\right\rangle = \varphi_\nu(s''')\, p_\nu^{\ddagger-1/2}\left\langle s^{\ddagger}|p_\nu^{\ddagger}\right\rangle$. However, it is well
known in quantum mechanics that $\left\langle s^{\ddagger}|p_\nu^{\ddagger}\right\rangle = \frac{e^{ip_\nu^{\ddagger}s^{\ddagger}/\hbar}}{(2\pi\hbar)^{1/2}}$. Therefore: $\left\langle(s^{\ddagger},s''')^{(-)}|\psi_{E,\nu}^{(-)}\right\rangle$
$= \varphi_\nu(s''')\, p_\nu^{\ddagger-1/2}\left\langle s^{\ddagger}|p_\nu^{\ddagger}\right\rangle = \frac{\varphi_\nu(s''')e^{ip_\nu^{\ddagger}s^{\ddagger}/\hbar}}{\left(2\pi\hbar v_\nu^{\ddagger}\right)^{1/2}}$. What we need to remind ourselves is:
$\left|\psi_{E,\nu}^{(-)}\right\rangle = p_\nu^{\ddagger-1/2}\left|\tilde{\psi}_{\varphi_\nu,p_\nu^{\ddagger}}\right\rangle \lim_{\tau\to\infty} e^{-iE\tau/\hbar} = \left|\hat{\Pi}^{\ddagger(-)}\right|^{-1/2}\left|\tilde{\psi}_{\varphi_\nu,p_\nu^{\ddagger}}^{(-)}\right\rangle$. It therefore follows
that

$$\left\langle\Psi_{E,\mu}^{(+)}\right|\hat{P}_{\Phi}^{-}\hat{v}^{\ddagger(-)}\hat{P}_{\Phi}^{-}\left|\Psi_{E,\mu}^{(+)}\right\rangle = \sum_{\tilde{\nu},\tilde{\nu}'} \left(S_{\Phi_{\tilde{\nu}'}\leftarrow\Psi_\mu}(E)\right)^{*}\left\langle\Phi_{E,\tilde{\nu}'}^{(-)}\right|\hat{v}^{\ddagger(-)}\left|\Phi_{E,\tilde{\nu}}^{(-)}\right\rangle S_{\Phi_{\tilde{\nu}}\leftarrow\Psi_\mu}(E)$$

$$= \sum_{\tilde{\nu},\tilde{\nu}'} \left(S_{\Phi_{\tilde{\nu}'}\leftarrow\Psi_\mu}(E)\right)^{*}\left\langle\tilde{\psi}_{\Phi_{\tilde{\nu}'},p_{\tilde{\nu}'}^{\ddagger}}^{(-)}\right|\left|\hat{\Pi}^{\ddagger(-)}\right|^{-1/2}\hat{v}^{\ddagger(-)}\left|\hat{\Pi}^{\ddagger(-)}\right|^{-1/2}\left|\tilde{\psi}_{\Phi_{\tilde{\nu}},p_{\tilde{\nu}}^{\ddagger}(-)}\right\rangle S_{\Phi_{\tilde{\nu}}\leftarrow\Psi_\mu}(E)$$

$$= \sum_{\tilde{\nu},\tilde{\nu}'} \left(S_{\Phi_{\tilde{\nu}'}\leftarrow\Psi_\mu}(E)\right)^{*}\left\langle\tilde{\psi}_{\Phi_{\tilde{\nu}'},p_{\tilde{\nu}'}^{\ddagger}(-)}\right|v_{\tilde{\nu}'}^{\ddagger-1/2}v_{\tilde{\nu}}^{\ddagger+1/2}\left|\tilde{\psi}_{\Phi_{\tilde{\nu}},p_{\tilde{\nu}}^{\ddagger}(-)}\right\rangle S_{\Phi_{\tilde{\nu}}\leftarrow\Psi_\mu}(E) \qquad (3.6)$$

However,

$$\left\langle\tilde{\psi}_{\Phi_{\tilde{\nu}'},p_{\tilde{\nu}'}^{\ddagger}}^{(-)}\right|\left|\tilde{\psi}_{\Phi_{\tilde{\nu}},p_{\tilde{\nu}}^{\ddagger}}^{(-)}\right\rangle = \int_{-X/2}^{X/2} \int \left\langle\tilde{\psi}_{\Phi_{\tilde{\nu}'},p_{\tilde{\nu}'}^{\ddagger}}^{(-)}\right|\left|s^{\ddagger},s'''\right\rangle\left\langle s^{\ddagger},s'''\right|\left|\tilde{\psi}_{\Phi_{\tilde{\nu}},p_{\tilde{\nu}}^{\ddagger}}^{(-)}\right\rangle ds^{\ddagger} d\left\langle\left\langle s'''\right\rangle\right\rangle$$

$$= \left\langle \varphi_{\Phi_{\tilde{v}'}} | \varphi_{\Phi_{\tilde{v}}} \right\rangle \int_{-X/2}^{X/2} \left\langle p_{v'}^{\ddagger} \Big| \Big| s^{\ddagger} \right\rangle \left\langle s^{\ddagger} \Big| \Big| p_{v'}^{\ddagger} \right\rangle ds^{\ddagger}$$

$$= \left\langle \varphi_{\Phi_{\tilde{v}'}} | \varphi_{\Phi_{\tilde{v}}} \right\rangle \int_{-X/2}^{X/2} \frac{e^{-ip_v^{\ddagger}s^{\ddagger} - ip_v^{\ddagger}s^{\ddagger}}}{(2\pi\hbar)^{1/2}} \cdot \frac{e^{ip_v^{\ddagger}s^{\ddagger}}}{(2\pi\hbar)^{1/2}} ds^{\ddagger} = \frac{X}{h} \delta_{\tilde{v}',\tilde{v}} \quad (3.7)$$

Therefore: $\left\langle \Psi_{E,\mu}^{(+)} \Big| \hat{P}_{\Phi}^{-} \hat{v}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \Big| \Psi_{E,\mu}^{(+)} \right\rangle = \frac{X}{h} \sum_{\tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2$. We find that

$\sum_{\tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2 = \frac{1}{X} \left\langle \Psi_{E,\mu}^{(+)} \Big| \hat{P}_{\Phi}^{-} \hat{v}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \Big| \Psi_{E,\mu}^{(+)} \right\rangle$. Then

$$N(E) = \sum_{\mu\tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2 = \frac{1}{X} \sum_{\mu} \left\langle \Psi_{E,\mu}^{(+)} \Big| \hat{P}_{\Phi}^{-} \hat{v}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \Big| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= \frac{1}{X} \text{Tr} \hat{P}_{\Psi}^{+} \delta \left(\hat{H} - E \right) \hat{P}_{\Phi}^{-} \hat{v}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \hat{P}_{\Psi}^{+} = \text{Tr} \hat{P}_{\Psi}^{+} \delta \left(\hat{H} - E \right) \hat{P}_{\Phi}^{-} \hat{F}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \hat{P}_{\Psi}^{+}$$

$$(3.8)$$

where $\hat{F}^{\ddagger(-)} = \frac{\hat{v}^{\ddagger(-)}}{X}$ is the operator for the average flux along the reaction coordinate. In fact,

$$\left\langle \Psi_{E,\mu}^{(+)} \Big| \hat{P}_{\Phi}^{-} \cdot \frac{\hat{v}^{\ddagger(-)} \delta \left(\hat{s}^{\ddagger(-)} - s^{\ddagger} \right) + \delta \left(\hat{s}^{\ddagger(-)} - s^{\ddagger} \right) \hat{v}^{\ddagger(-)}}{2} \cdot \hat{P}_{\Phi}^{-} \Big| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= \text{Re} \int \left\langle \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \Big| \cdot \Big| (s^{\ddagger}, s''')^{(-)} \right\rangle \left\langle (s^{\ddagger}, s''')^{(-)} \Big| \hat{v}^{\ddagger(-)} \Big| \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \right\rangle d \langle\!\langle s''' \rangle\!\rangle$$

$$= \text{Re} \int \left\langle \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \Big| \Big| (s^{\ddagger}, s''')^{(-)} \right\rangle \overset{\ddagger}{\underset{\frown}{\hat{v}}} \left\langle (s^{\ddagger}, s''')^{(-)} \Big| \Big| \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \right\rangle d \langle\!\langle s''' \rangle\!\rangle$$

$$= \text{Re} \int \left\langle \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} | (s^{\ddagger}, s''')^{(-)} \right\rangle \overset{\ddagger}{\underset{\frown}{\hat{v}}} \left\langle (s^{\ddagger}, s''')^{(-)} | \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \right\rangle d \langle\!\langle s''' \rangle\!\rangle$$

$$= \text{Re} \sum_{\tilde{v},\tilde{v}'} \int \left(S_{\Phi_{\tilde{v}'} \leftarrow \Psi_{\mu}}(E) \right)^* \cdot \frac{\varphi_{\tilde{v}'}^{*}(s''') e^{-ip_v^{\ddagger}s^{\ddagger}/}}{\left(2\pi v_{\tilde{v}'}^{\ddagger}\right)^{1/2}} \overset{\ddagger}{\underset{\frown}{\hat{v}}} \cdot \frac{\varphi_{\tilde{v}}(s''') e^{ip_v^{\ddagger}s^{\ddagger}/}}{\left(2\pi v_{\tilde{v}'}^{\ddagger}\right)^{1/2}} S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) d \langle\!\langle s''' \rangle\!\rangle$$

$$= \text{Re} \frac{1}{h} \sum_{\tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2 = \frac{1}{h} \sum_{\tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2 \quad (3.9)$$

So if we let $\frac{\hat{v}^{\ddagger(-)} \delta \left(\hat{s}^{\ddagger(-)} - s^{\ddagger} \right) + \delta \left(\hat{s}^{\ddagger(-)} - s^{\ddagger} \right) \hat{v}^{\ddagger(-)}}{2} = \hat{F}^{\ddagger(-)}$, be the outgoing-state flux through the dividing surface between reactants and products, we find that

$$\frac{\hat{v}^{\ddagger(-)} \delta \left(\hat{s}^{\ddagger(-)} - s^{\ddagger} \right) + \delta \left(\hat{s}^{\ddagger(-)} - s^{\ddagger} \right) \hat{v}^{\ddagger(-)}}{2} = \hat{F}^{\ddagger(-)} = \frac{1}{i\hbar} \left[\varphi \left(\hat{s}^{\ddagger(-)} - s^{\ddagger} \right), \hat{H} \right]$$

$$= \frac{1}{i\hbar} \hat{\Omega}^{(-)} \left[\varphi \left(\hat{s}^{\ddagger} - s^{\ddagger} \right), \hat{H}_0' \right] \hat{\Omega}^{(-)\dagger}$$

$$(3.10)$$

because $\hat{H}_0' = \sum_{\mu'=1}^{3n^\diamond} \frac{1}{2}\hat{\Pi}''^2_{\mu'} + \sum_{j=1}^{n^\diamond} m_0^{(j)} c^2$. So putting it all together,

$$N(E) = \sum_{\mu\tilde{\nu}} \left| S_{\Phi_{\tilde{\nu}} \leftarrow \Psi_\mu}(E) \right|^2 = h \sum_\mu \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{P}_\Phi^- \hat{F}^{\ddagger(-)} \hat{P}_\Phi^- \right| \Psi_{E,\mu}^{(+)} \right\rangle = h \, \mathrm{Tr} \, \hat{P}_\Psi^+ \delta$$

$$\left(\hat{H} - E \right) \hat{P}_\Phi^- \hat{F}^{\ddagger(-)} \hat{P}_\Phi^- \hat{P}_\Psi^+ \equiv h \, \mathrm{Tr} \, \hat{P}_\Psi^+ \delta \left(\hat{H} - E \right) \hat{P}_\Phi^- \hat{F}^{\ddagger(-)} \hat{P}_\Phi^- \hat{P}_\Psi^+ \qquad (3.11)$$

Prevailing methods fail to take these projection operators into account. But assume that $s^\ddagger > s_0^\ddagger$. Then it follows that

$$\left\langle \Psi_{E,\mu}^{(+)} \left| \frac{\hat{v}^{\ddagger(-)} \delta \left(\hat{s}^{\ddagger(-)} - s^\ddagger \right) + \delta \left(\hat{s}^{\ddagger(-)} - s^\ddagger \right) \hat{v}^{\ddagger(-)}}{2} \cdot \right| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= \mathrm{Re} \int \left\langle \Psi_{E,\mu}^{(+)} \right| \cdot \left| \left(s^\ddagger, s''' \right)^{(-)} \right\rangle \left\langle \left(s^\ddagger, s''' \right)^{(-)} \left| \hat{v}^{\ddagger(-)} \right| \Psi_{E,\mu}^{(+)} \right\rangle d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$$

$$= \mathrm{Re} \int \left\langle \Psi_{E,\mu}^{(+)} \right| \left| \left(s^\ddagger, s''' \right)^{(-)} \right\rangle \underset{\sim}{\hat{v}}^{\ddagger} \left\langle \left(s^\ddagger, s''' \right)^{(-)} \right| \left| \Psi_{E,\mu}^{(+)} \right\rangle d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$$

$$= \mathrm{Re} \int \left\langle \Psi_{E,\mu}^{(+)} \left| \left(s^\ddagger, s''' \right)^{(-)} \right\rangle \underset{\sim}{\hat{v}}^{\ddagger} \left\langle \left(s^\ddagger, s''' \right)^{(-)} \right| \Psi_{E,\mu}^{(+)} \right\rangle d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$$

$$= \mathrm{Re} \sum_{\tilde{\nu},\tilde{\nu}'} \int \left(S_{\Phi_{\tilde{\nu}'} \leftarrow \Psi_\mu}(E) \right)^* \cdot \frac{\varphi_{\tilde{\nu}'}^* \left(s''' \right) e^{-ip_{\tilde{\nu}'}^\ddagger s^\ddagger / \hbar}}{\left(2\pi v_{\tilde{\nu}'}^\ddagger \right)^{1/2}} \underset{\sim}{\hat{v}}^\ddagger$$

$$\cdot \frac{\varphi_{\tilde{\nu}} \left(s''' \right) e^{ip_{\tilde{\nu}}^\ddagger s^\ddagger / \hbar}}{\left(2\pi v_{\tilde{\nu}'}^\ddagger \right)^{1/2}} S_{\Phi_{\tilde{\nu}} \leftarrow \Psi_\mu}(E) d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$$

$$= \mathrm{Re} \frac{1}{h} \sum_{\tilde{\nu}} \left| S_{\Phi_{\tilde{\nu}} \leftarrow \Psi_\mu}(E) \right|^2 = \frac{1}{h} \sum_{\tilde{\nu}} \left| S_{\Phi_{\tilde{\nu}} \leftarrow \Psi_\mu}(E) \right|^2 \qquad (3.12)$$

because we can guess that $\left\langle \left(s^\ddagger, s''' \right)^{(-)} | \psi_{E,\nu}^{(-)} \right\rangle = \varphi_\nu \left(s''' \right) p_\nu^{\ddagger-1/2} \left\langle s^\ddagger | p_\nu^\ddagger \right\rangle$, and $\left| \Psi_{E,\mu}^{(+)} \right\rangle = \sum_\nu \left| \psi_{E,\nu}^{(-)} \right\rangle S_{\psi_\nu \leftarrow \Psi_\mu}(E) = \sum_\nu \left| \psi_{E,\nu}^{(-)} \right\rangle S_{\psi_\nu \leftarrow \Psi_\mu}(E)$. Then at $s^\ddagger$, one would naturally expect $\left| \psi_{E,\nu}^{(-)} \right\rangle$ to be a product instead of a reactant, in fact, $\left\langle \left(s^\ddagger, s''' \right)^{(-)} | \psi_{E,\nu}^{(-)} \right\rangle = \left\langle \left(s^\ddagger, s''' \right)^{(-)} | \Phi_{E,\nu}^{(-)} \right\rangle = \varphi_\nu \left(s''' \right) p_\nu^{\ddagger-1/2} \left\langle s^\ddagger | p_\nu^\ddagger \right\rangle = \frac{\varphi_\nu(s''') e^{ip_\nu^\ddagger s^\ddagger / \hbar}}{\left(2\pi\hbar v_\nu^\ddagger \right)^{1/2}}$, as $s^\ddagger \to +\frac{X}{2}$. Therefore we get:

$$N(E) = \sum_{\mu\tilde{\nu}} \left| S_{\Phi_{\tilde{\nu}} \leftarrow \Psi_\mu}(E) \right|^2 = \sum_\mu \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{F}^{\ddagger(-)} \right| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= h \mathrm{Tr} \hat{P}_\Psi^+ \delta \left(\hat{H} - E \right) \hat{F}^{\ddagger(-)} \hat{P}_\Psi^+ \equiv h \mathrm{Tr} \delta \left(\hat{H} - E \right) \hat{F}^{\ddagger(-)} \hat{P}_\Psi^+ \qquad (3.13)$$

However, if we use $\left\langle s^{\ddagger}, s''' | \psi_{E,\nu}^{(-)} \right\rangle = \lim\limits_{t \to \infty} \dfrac{\varphi_{\nu}(s''') e^{i p_{\nu s}^{\ddagger} s^{\ddagger}/\hbar}}{\left(2\pi\hbar v_{\nu}^{\ddagger}\right)^{1/2}} e^{-iEt/\hbar}$, we can write

$$N(E) = \sum_{\mu\tilde{\nu}} \left| S_{\Phi_{\tilde{\nu}} \leftarrow \Psi_{\mu}}(E) \right|^2 = \sum_{\mu} \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{F}^{\ddagger} \right| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= h\mathrm{Tr}\, \hat{P}_{\Psi}^{+} \delta\left(\hat{H} - E\right) \hat{F}^{\ddagger} \hat{P}_{\Psi}^{+} \equiv h\mathrm{Tr}\, \delta\left(\hat{H} - E\right) \hat{F}^{\ddagger} \hat{P}_{\Psi}^{+} \qquad (3.14)$$

This is also reminiscent of a formula that Miller [3] had derived. We can also make a simplifying approximation: electrons in molecules move and thereby generate magnetic fields that can be represented by a vector potential. But the vector potential induced by a moving electron is directly proportional to its scalar potential and its velocity, and inversely proportional to the square of the speed of light in vacuum, which is so large, that it is sufficient for our purposes to ignore the vector potentials. Then the Hamiltonian will take on this form: $\hat{H} = \sum\limits_{\mu=1}^{3} \sum\limits_{j=1}^{n^{\diamond}} \dfrac{\hat{\mathbf{p}}_{\mu}^{(j)2}}{2m_0^{(j)}} +$ $\sum\limits_{j'=1}^{n_{e^-}} \left(c\hat{\boldsymbol{\alpha}}_{j'} \cdot \hat{\mathbf{p}}_{j'} + \hat{\beta}_{j'} m_{e^-} c^2 \right) + \sum\limits_{j=1}^{n^{\diamond}} m_0^{(j)} c^2 + \widehat{V}\left(\ldots, \hat{x}_{\mu}^{(j)}, \ldots, \hat{\mathbf{r}}_{j'}, \ldots\right)$, where we have used special relativity in the form of the Dirac Equation for the electrons. Then $\left[f(x_{\nu}), c\{\hat{\alpha}_{j'}\}_{\mu} \{p_{j'}\}_{\mu} \right] = c\{\hat{\alpha}_{j'}\}_{\mu} \left[f(x_{\nu}), \{p_{j'}\}_{\mu} \right]$, then we shall see that $\left[f(x_{\nu}), \{p_{j'}\}_{\mu} \right] = ih\left\{ \partial_{\{x_{j'}\}_{\mu}} f \right\}(x_{\nu})$. Then we see that $\frac{1}{i\hbar}\left[f(\hat{x}_{\nu}), \hat{H} \right] =$ $\sum\limits_{\mu} \dfrac{\hat{v}_{\mu} \cdot \{\partial_{x_{\mu}} f\}(\hat{x}_{\nu}) + \{\partial_{x_{\mu}} f\}(\hat{x}_{\nu}) \cdot \hat{v}_{\mu}}{2}$, even in the case of the electrons, because $c\hat{\alpha}_{j'}$ commutes with $f(\hat{x}_{\nu})$. But most of the time, it is atoms that get exchanged instead of electrons. In such a case, the reaction coordinate depends only on the configurations of the atoms. In all cases however, the scattering theory formula for $N(E)$ is exact.

Except possibly in the case of electrons, the prevailing conventional wisdom that holds that atoms move at speeds within the range of applicability of non-relativistic mechanics is an excellent approximation at low or ordinary temperatures. When the reaction coordinate depends on charge distribution, a more accurate calculation can be made by using the full explicit scattering theory. It turns out that in atoms, the electrons are moving at about 0.6 % of the speed of light, and numerical calculations show that non-relativistic mechanics will reproduce the expected results of special relativity for the kinetic energy accurate to 4 decimal places. Within this margin of error, the non-relativistic quantum theory is quantum mechanically exact even for electrons.

We shall also attempt to derive the same CRP in another case:

$$\mathrm{Re}\left\langle \Psi_{E,\mu}^{(+)} \left| \dfrac{\hat{v}^{\ddagger(-)} \delta\left(\hat{s}^{\ddagger(-)} - s_0\right) + \delta\left(\hat{s}^{\ddagger(-)} - s_0\right) \hat{v}^{\ddagger(-)}}{2} \cdot \hat{P}_{\Phi}^{-} \right| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= \mathrm{Re} \int \left\langle \Psi_{E,\mu}^{(+)} \right| \cdot \left| (s_0, s''')^{(-)} \right\rangle \left\langle (s_0, s''')^{(-)} \left| \hat{v}^{\ddagger(-)} \right| \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \right\rangle d\left(\!\left(s'''\right)\!\right)$$

$$= \text{Re} \int \left\langle \Psi_{E,\mu}^{(+)} \middle| \middle| (s_0, s''')^{(-)} \right\rangle \overset{\ddagger}{\underset{\frown}{\hat{v}}} \left\langle (s_0, s''')^{(-)} \middle| \middle| \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \right\rangle d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$$

$$= \text{Re} \int \left\langle \Psi_{E,\mu}^{(+)} \middle| (s_0, s''')^{(-)} \right\rangle \overset{\ddagger}{\underset{\frown}{\hat{v}}} \left\langle (s_0, s''')^{(-)} \middle| \hat{P}_{\Phi}^{-} \Psi_{E,\mu}^{(+)} \right\rangle d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$$

$$= \text{Re} \sum_{\tilde{v}, \tilde{v}'} \int \left(S_{\overline{\Phi}_{\tilde{v}'} \leftarrow \Psi_{\mu}}(E) \right)^* \cdot \frac{\overline{\varphi}_{\tilde{v}'}^*(s''') e^{-i p_{\tilde{v}'}^{\ddagger} s_0 / \hbar}}{\left(2\pi \hbar v_{\tilde{v}'}^{\ddagger} \right)^{1/2}} \overset{\ddagger}{\underset{\frown}{\hat{v}}} \cdot \frac{\varphi_{\tilde{v}}(s''') e^{i p_{\tilde{v}}^{\ddagger} s_0 / \hbar}}{\left(2\pi \hbar v_{\tilde{v}'}^{\ddagger} \right)^{1/2}} S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$$

$$= \text{Re} \frac{1}{h} \sum_{\tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2 = \frac{1}{h} \sum_{\tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2 \tag{3.15}$$

We therefore find:

$$N(E) = \sum_{\mu \tilde{v}} \left| S_{\Phi_{\tilde{v}} \leftarrow \Psi_{\mu}}(E) \right|^2 = Re \sum_{\mu} \left\langle \Psi_{E,\mu}^{(+)} \middle| \hat{F}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \middle| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= h\,Re\,\text{Tr}\, \delta \left(\hat{H} - E \right) \hat{F}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \hat{P}_{\Psi}^{+}$$

$$= h\,\text{Tr}\, \frac{\hat{F}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \hat{P}_{\Psi}^{+} + \hat{P}_{\Psi}^{+} \hat{P}_{\Phi}^{-} \hat{F}^{\ddagger(-)}}{2} \delta \left(\hat{H} - E \right) \tag{3.16}$$

Now using 2.23, 2.24, we now have $N(E) = h\,Re\,\text{Tr}\, \delta \left(\hat{H} - E \right) \hat{F}^{\ddagger(-)} \varphi \left(\hat{\Pi}''^{\ddagger(-)'} \right)$ $\varphi \left(\hat{\Pi}''^{\ddagger(+)'} \right)$. Unfortunately, $\varphi \left(\hat{\Pi}''^{\ddagger(+)'} \right)$ does not contain the entire complete set of wavefunctions. The projection operator $\varphi \left(\hat{\Pi}''^{\ddagger(+)'} \right)$, only contains the wavefunctions $\left| \Psi_{E,\mu}^{(+)} \right\rangle$. According to Garshchuk and Tannor [4], there also exists another set of wavefunctions with the same energy orthogonal to $\left| \Psi_{E,\mu}^{(+)} \right\rangle$. But laying this aside for a moment, it is commonly stated that $\left\langle s^{\ddagger}, s''' | \Phi_{E,\nu}^{(-)} \right\rangle = \varphi_{\nu}(s''') p_{\nu}^{\ddagger-1/2} \left\langle s^{\ddagger} | p_{\nu}^{\ddagger} \right\rangle = \frac{\varphi_{\nu}(s''') e^{i p_{\nu}^{\ddagger} s^{\ddagger} / \hbar}}{\left(2\pi \hbar v_{\nu}^{\ddagger} \right)^{1/2}}$ is the wave-mechanics wavefunction of a product in a given outgoing microstate. In most cases, especially the cases we would expect to be using transition state theory, it is atoms that get exchanged, and non-relativistic mechanics is applicable under ordinary thermodynamic conditions. Therefore we shall use a purely Newtonian Hamiltonian over these atoms, and the flux will be: $\hat{F} = \frac{1}{i\hbar} \left[\varphi \left(\hat{s}^{\ddagger} - s_0 \right), \hat{H} \right] = \frac{\hat{v}^{\ddagger} \delta \left(\hat{s}^{\ddagger} - s_0 \right) + \delta \left(\hat{s}^{\ddagger} - s_0 \right) \hat{v}^{\ddagger}}{2}$. Then $N(E) = h\,Re\,\text{Tr}\, \delta \left(\hat{H} - E \right) \hat{F} \varphi \left(\hat{\Pi}''^{\ddagger(-)'} \right) \varphi \left(\hat{\Pi}''^{\ddagger(+)'} \right)$.

We shall now evaluate: $\left\langle \Psi_{E,\mu}^{(+)} \middle| \hat{F}^{\ddagger} \hat{P}_{\Phi}^{-} \middle| \Psi_{E,\mu}^{(+)} \right\rangle$. Using the fact that $\hat{P}_{\Phi}^{+} \left| \Psi_{E,\mu}^{(+)} \right\rangle = 0$, we can write:

$$\left\langle \Psi_{E,\mu}^{(+)} \middle| \hat{F} \hat{P}_{\Phi}^{-} \middle| \Psi_{E,\mu}^{(+)} \right\rangle = \left\langle \Psi_{E,\mu}^{(+)} \middle| \hat{F} \left\{ \hat{P}_{\Phi}^{-} - \hat{P}_{\Phi}^{+} \right\} \middle| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= \left\langle \Psi_{E,\mu}^{(+)} \left| \int_{-\infty}^{\infty} \hat{F} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar} dt \right| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= \left\langle \Psi_{E,\mu}^{(+)} \left| \int_{-\infty}^{\infty} \hat{F} e^{i[\hat{H}-E]t/\hbar} \hat{F} dt \right| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= h \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{F} \delta\left(\hat{H}-E\right) \hat{F} \right| \Psi_{E,\mu}^{(+)} \right\rangle \qquad (3.17)$$

Because $\hat{F}\delta\left(\hat{H}-E\right)\hat{F}$ is Hermitian, it follows that $h\left\langle \Psi_{E,\mu}^{(+)} \left| \hat{F}\delta\left(\hat{H}-E\right) \hat{F} \right| \Psi_{E,\mu}^{(+)} \right\rangle$ is real. We find that

$$N(E) = h\,Re\,\mathrm{Tr}\,\delta\left(\hat{H}-E\right) \hat{F}^{\ddagger}\hat{P}_{\Phi}^{-}\hat{P}_{\Psi}^{+}$$

$$= h\,Re\,\sum_{\mu} \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{F}^{\ddagger}\hat{P}_{\Phi}^{-} \right| \Psi_{E,\mu}^{(+)} \right\rangle = h^2 \sum_{\mu} \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{F}\delta\left(\hat{H}-E\right) \hat{F} \right| \Psi_{E,\mu}^{(+)} \right\rangle$$

$$= h^2 \sum_{\mu} \int_{-\infty}^{\infty} \delta\left(E'-E\right) \left\langle \Psi_{E',\mu}^{(+)} \left| \hat{F}\delta\left(\hat{H}-E\right) \hat{F} \right| \Psi_{E',\mu}^{(+)} \right\rangle dE'$$

$$= h^2 \sum_{\mu} \int_{-\infty}^{\infty} \left\langle \Psi_{E',\mu}^{(+)} \left| \delta\left(\hat{H}-E\right) \hat{F}\delta\left(\hat{H}-E\right) \hat{F} \right| \Psi_{E',\mu}^{(+)} \right\rangle dE'$$

$$= h^2\,\mathrm{Tr}\,\delta\left(\hat{H}-E\right) \hat{F}\delta\left(\hat{H}-E\right) \hat{F}\hat{P}_{\Psi}^{+} \qquad (3.18)$$

We can choose some other set, $\left|\Phi_{E,\mu}^{(+)}\right\rangle$. But notice that $\hat{P}_{\Psi}^{+}=\sum_{\mu}\int_{-\infty}^{\infty}\left|\Psi_{E,\mu}^{(+)}\right\rangle\left\langle\Psi_{E,\mu}^{(+)}\right| dE$, and that $\sum_{\mu}\int_{-\infty}^{\infty}\left|\Phi_{E,\mu}^{(+)}\right\rangle\left\langle\Phi_{E,\mu}^{(+)}\right| dE = \hat{P}_{\Phi}^{+}$, and

$$\hat{P}_{\Psi}^{+} = \lim_{X\to+\infty}\lim_{\tau'X^{-1}\to+\infty}\lim_{\tau\to+\infty} e^{-i\hat{H}\{\tau+\tau'\}/\hbar}\,\wp\left(s_0^{\ddagger}-\hat{s}^{\ddagger}\right) e^{i\hat{H}\{\tau+\tau'\}/\hbar}$$

$$= \wp\left(\hat{v}^{\ddagger+}\right) = \wp\left(\hat{\Pi}''^{\ddagger(+)'}\right)$$

$$\hat{P}_{\Phi}^{+} = \lim_{X\to+\infty}\lim_{\tau'X^{-1}\to+\infty}\lim_{\tau\to+\infty} e^{-i\hat{H}\{\tau+\tau'\}/\hbar}\,\wp\left(s_0^{\ddagger}-\hat{s}^{\ddagger}\right) e^{i\hat{H}\{\tau+\tau'\}/\hbar}$$

$$= \wp\left(-\hat{v}^{\ddagger+}\right) = \wp\left(-\hat{\Pi}''^{\ddagger(+)'}\right) \qquad (3.19)$$

Now we shall prove that $\mathrm{Tr}\,\delta\left(\hat{H}-E\right) \hat{F}\delta\left(\hat{H}-E\right) \hat{F}\hat{P}_{\Psi}^{+} = \mathrm{Tr}\,\delta\left(\hat{H}-E\right)$ $\hat{F}\delta\left(\hat{H}-E\right) \hat{F}\hat{P}_{\Phi}^{+}$. Simple! There exists a unitary transformation $\hat{U}_{\Psi\to\Phi} = \sum_{\mu}\int_{-\infty}^{\infty}\left|\Phi_{E,\mu}^{(+)}\right\rangle\left\langle\Psi_{E,\mu}^{(+)}\right| dE + \sum_{\mu}\int_{-\infty}^{\infty}\left|\Psi_{E,\mu}^{(+)}\right\rangle\left\langle\Phi_{E,\mu}^{(+)}\right| dE$ that interchanges

the reactants and the products. There also exists another unitary transformation of this sort: $\hat{Y} = \int_{-\infty}^{\infty} \left| -p^{\ddagger} \right\rangle \left\langle p^{\ddagger} \right| dp^{\ddagger}$ that changes the sign of the momentum. Yet there exists also another unitary transformation: $\hat{\mathcal{K}} = \int \ldots \int_{-\infty}^{\infty} \left| s_0 - s'^{\ddagger}, s''' \right\rangle \left\langle s^{\ddagger} + s'^{\ddagger}, s''' \right| ds'^{\ddagger} d \left\langle\!\left\langle s''' \right\rangle\!\right\rangle$ that changes *incident* reactants into *incident* products and *incident* products into *incident* reactants. Proof: $\hat{\mathcal{K}} \hat{s}^{\ddagger} \hat{\mathcal{K}}^{\dagger} = -\hat{s}^{\ddagger}$, and $\hat{\mathcal{K}} \wp \left(\hat{s}^{\ddagger} - s_0^{\ddagger} \right) \hat{\mathcal{K}}^{\dagger} = \wp \left(s_0^{\ddagger} - \hat{s}^{\ddagger} \right)$. And because $\hat{\mathcal{K}} \hat{H} \hat{\mathcal{K}}^{\dagger} = \hat{H}$, it follows from 2.23 and 2.24 that $\hat{\mathcal{K}} \hat{P}_{\Psi}^{+} \hat{\mathcal{K}}^{\dagger} = \hat{P}_{\Phi}^{+}$ and $\hat{\mathcal{K}} \hat{F} \hat{\mathcal{K}}^{\dagger} = -\hat{F}$. In fact, this is not quite right. It turns out that the correct operator is $\hat{\mathcal{K}} = \int \ldots \int_{-\infty}^{\infty} \left| s_0 - s'^{\ddagger}, s_0''' - s'''^{\ddagger} \right\rangle \left\langle s^{\ddagger} + s'^{\ddagger}, s_0''' + s'''^{\ddagger} \right| ds'^{\ddagger} d \left\langle\!\left\langle s'''^{\ddagger} \right\rangle\!\right\rangle$. But traces of matrices are independent of the unitary transformations applied. Therefore $h \, \mathrm{Tr} \, \hat{F} \delta \left(\hat{H} - E \right) \hat{F} \hat{P}_{\Psi}^{+} = h \, \mathrm{Tr} \, \hat{F} \delta \left(\hat{H} - E \right) \hat{F} \hat{P}_{\Phi}^{+}$, in agreement with the time-reversal symmetry of quantum mechanics. But

$$
\begin{aligned}
N(E) &= h \, Re \mathrm{Tr} \, \delta \left(\hat{H} - E \right) \hat{F}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \hat{P}_{\Psi}^{+} \\
&= h^2 \, \mathrm{Tr} \, \delta \left(\hat{H} - E \right) \hat{F} \delta \left(\hat{H} - E \right) \hat{F} \hat{P}_{\Psi}^{+} = h^2 \, \mathrm{Tr} \, \delta \left(\hat{H} - E \right) \hat{F} \delta \left(\hat{H} - E \right) \hat{F} \hat{P}_{\Phi}^{+} \\
&= \frac{1}{2} h^2 \, \mathrm{Tr} \, \delta \left(\hat{H} - E \right) \hat{F} \delta \left(\hat{H} - E \right) \hat{F} \left\{ \hat{P}_{\Phi}^{+} + \hat{P}_{\Psi}^{+} \right\} \\
&= \frac{1}{2} \cdot (2\pi\hbar)^2 \, \mathrm{Tr} \, \delta \left(\hat{H} - E \right) \hat{F} \delta \left(\hat{H} - E \right) \hat{F}
\end{aligned}
\tag{3.20}
$$

using the fact that $\hat{P}_{\Phi}^{+} + \hat{P}_{\Psi}^{+} = \wp \left(\hat{\Pi}''^{\ddagger(+)'} \right) + \wp \left(-\hat{\Pi}''^{\ddagger(+)'} \right) = 1$. QUOD ERAT DEMONSTRANDUM. One can explicitly see the microscopic reversibility of the cumulative reaction probability by a unitary transformation. This is exactly the same formula that Miller, Schwartz and Tromp [5] have derived.

There is also another built in assumption to using $\left\langle s^{\ddagger}, s''' \middle| \Phi_{E,v}^{(-)} \right\rangle = \varphi_v \left(s''' \right) p_v^{\ddagger-1/2}$ $\left\langle s^{\ddagger} \middle| p_v^{\ddagger} \right\rangle = \frac{\varphi_v(s''') e^{i p_v^{\ddagger} s^{\ddagger}/\hbar}}{\left(2\pi\hbar v_v^{\ddagger} \right)^{1/2}}$. It is assumed that in the asymptotic region of the reactants and the products, the scattering potential approaches zero. This may be true in gases, but not in condensed phase. In solution, there are always sources of scattering with the solvent. However, we could assume that in solution, asymptotic reactants and asymptotic products both have some common background potential $\widehat{V_0}$ that becomes independent of the reaction coordinate in these asymptotic limits. But notice that the average flux is independent of which side you choose to place the dividing surface on. That is because the transition state is in a steady-state: the probability of finding the system between two different dividing surfaces is time-independent for a stationary state.

For a quantum mechanically exact version of transition state theory, we now have:

$$
N(E) = h \, Re \mathrm{Tr} \, \delta \left(\hat{H} - E \right) \hat{F} \wp \left(\hat{\Pi}''^{\ddagger(-)'} \right) \wp \left(\hat{\Pi}''^{\ddagger(+)'} \right)
$$

$$= h \mathrm{Tr}\, \delta\left(\hat{H} - E\right) . \frac{\hat{F} \wp\left(\hat{\Pi}''^{\ddagger(-)'}\right) + \wp\left(\hat{\Pi}''^{\ddagger(-)'}\right) \hat{F}}{2} . \wp\left(\hat{\Pi}''^{\ddagger(+)'}\right)$$

$$= \frac{h}{2} \sum_{\mu} \left\{ \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{F} \wp\left(\hat{\Pi}''^{\ddagger(-)'}\right) \right| \Psi_{E,\mu}^{(+)} \right\rangle + \left\langle \Psi_{E,\mu}^{(+)} \left| \wp\left(\hat{\Pi}''^{\ddagger(-)'}\right) \hat{F} \right| \Psi_{E,\mu}^{(+)} \right\rangle \right\}$$

$$= \frac{h}{2} \sum_{\mu} \left\{ \left\langle \Psi_{E,\mu,Incident}^{(+)} \left| \hat{F} \right| \Psi_{E,\mu,Transmitted}^{(+)} \right\rangle \right.$$

$$\left. + \left\langle \Psi_{E,\mu,Transmitted}^{(+)} \left| \hat{F} \right| \Psi_{E,\mu,Incident}^{(+)} \right\rangle \right\} \tag{3.21}$$

This tells us that the CRP comes from a transition from being incident on the side of reactants to being transmitted to the side of products. The other version of the CRP is this: $N(E) = h \sum_{\mu} \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{P}_{\Phi}^{-} \hat{F}^{\ddagger(-)} \hat{P}_{\Phi}^{-} \right| \Psi_{E,\mu}^{(+)} \right\rangle$. In this case where non-relativistic mechanics is applicable and the reaction is entirely due to the exchange of atoms, and in the asymptotic regions of reactants and products, the background potential becomes locally independent of the reaction coordinate, we can replace $\hat{F}^{\ddagger(-)}$ with $\hat{F}$ and write $N(E) = h \sum_{\mu} \left\langle \Psi_{E,\mu}^{(+)} \left| \hat{P}_{\Phi}^{-} \hat{F} \hat{P}_{\Phi}^{-} \right| \Psi_{E,\mu}^{(+)} \right\rangle = h \sum_{\mu} \left\langle \Psi_{E,\mu,Transmitted}^{(+)} \left| \hat{F} \right| \Psi_{E,\mu,Transmitted}^{(+)} \right\rangle$. This is the idea behind a quantum mechanically exact transition state theory: the CRP is due entirely to the *transmissive* flux at the products side of the potential energy surface of incident reactants.

The wavefunctions $\left| \Psi_{E,\mu,Transmitted}^{(+)} \right\rangle$ will give us a complete set of states that initially represent incident reactants and finally transmitted products. The prevailing literature has therefore given us everything necessary to solve this problem as a quantum tunneling problem, in a way that is also consistent with the results of scattering theory.

Furthermore, we would like to prove that this "exact" transition state theory also works for condensed phase.

4 Proof that this theory also applies in condensed phase

In solution phase, when a group of reactants get together to make a trial attempt to react, the solvent can randomly affect the outcome of the reaction.

In a local quasi-equilibrium state, the probability of finding a system in a given state equals the probability of finding the system in its time-reversed image. Or else we could find a process whereby a system can make transitions between a given stage and its time-reversed dual and cause a finite rate of change of state. And microscopic reversibility says that if A & A* are time-reversed duals of each other, then the transition probability from A* to A = the transition probability from A to A*. Therefore there will be a zero rate of change of state if and only if the probability of A* = the probability of A.

In fact, if the system is a liquid and you have two mutually miscible pure liquids reacting with each other, the concentration of molecules is so high, that interactions of

a given reactant complex with all of the other molecules in the system must be taken into account. We have devised a novel heuristic method to do exactly that. First of all, consider the reactant complex and the surroundings. The surroundings is either non-participating or participating in the reaction. If the surroundings is non-participating, then the reaction complex cannot form, and this means that the reaction cannot occur.

Different surroundings in the same system are mutually coextensive and immoveable with respect to each other. That is, they can be treated as a microcanonical or a canonical ensemble of identical immoveable coextensive systems.

The total number of surroundings must be in all cases equal to 1.

The relevant observable that changes is $\hat{n}'_X = \hat{n}^\circ_X + \sum_\kappa \{\overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa}\} \cdot \left(\hat{n}_{\kappa+}\hat{\xi}_{\kappa+}\right.$ $\left. -\hat{n}_{\kappa-}\hat{\xi}_{\kappa-}\right)$, just as before. Then just as before, we find that $\frac{\delta n_X}{\delta t} = \sum_\kappa \{\overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa}\}$ $\left\{ k_{\kappa+} \prod_{\overline{\mu}=1}^{\overline{m}} n_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}} - k_{\kappa-} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} n_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}} \right\}$, and

$$k_{\kappa+} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\mu}=1}^{\overline{m}_\kappa} Q_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}} \mathrm{Tr}\, \hat{P}_{\psi_\kappa}^{(+)} \cdot (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_\kappa}\right] e^{-\beta \hat{H}_{\Phi_\kappa}}$$

$$k_{\kappa-} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} Q_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}} \mathrm{Tr}\, \hat{P}_{\psi_\kappa}^{(+)} \cdot (i\hbar)^{-1} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_\kappa}\right] e^{-\beta \hat{H}_{\Phi_\kappa}} \qquad (4.1.\mathrm{A})$$

where $\hat{P}_{\psi_\kappa}^{(+)}$ is a projection operator for initial incident reactants. We also have another way of writing this that we shall derive shortly. However scattering theory shows us that

$$e^{-\beta \hat{H}_{\Phi_\kappa}} = \lim_{\tau \to \infty} e^{-i\hat{H}_{\Phi_\kappa}\{t+\tau\}/\hbar} e^{i\{\hat{H}_0\}_{\Phi_\kappa}\{t+\tau\}/\hbar} e^{-\beta\{\hat{H}_0\}_{\Phi_\kappa}} e^{-i\{\hat{H}_0\}_{\Phi_\kappa}\{t+\tau\}/\hbar} e^{i\hat{H}_{\Phi_\kappa}\{t+\tau\}/\hbar}$$

$$= \hat{\Omega}_{\Phi_\kappa}^{(+)} e^{-\beta\{\hat{H}_0\}_{\Phi_\kappa}} \hat{\Omega}_{\Phi_\kappa}^{(+)\dagger} \qquad (4.1.\mathrm{B})$$

The formulas in Chapter II are not quite *exactly* correct. We should write:

$$k_{\kappa+} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\mu}=1}^{\overline{m}_\kappa} Q_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}} \mathrm{Tr}\, \hat{P}_{\psi_\kappa}^{(0)} \cdot (i\hbar)^{-1} \hat{\Omega}_{\Phi_\kappa}^{(+)\dagger} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_\kappa}\right] \hat{\Omega}_{\Phi_\kappa}^{(+)} e^{-\beta\{\hat{H}_0\}_{\Phi_\kappa}}$$

$$k_{\kappa-} = \frac{1}{Z_{\$_\kappa} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} Q_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}} \mathrm{Tr}\, \hat{P}_{\psi_\kappa}^{(0)} \cdot (i\hbar)^{-1} \hat{\Omega}_{\Phi_\kappa}^{(+)\dagger} \left[\hat{\xi}_{\kappa+}, \hat{H}_{\Phi_\kappa}\right] \hat{\Omega}_{\Phi_\kappa}^{(+)} e^{-\beta\{\hat{H}_0\}_{\Phi_\kappa}}$$

$$(4.1.\mathrm{C})$$

where $\hat{P}_{\psi_\kappa}^{(0)}$ is for any given elementary step, the projection operator for reactants in the non-interacting system.

But $\hat{\xi}_{\kappa+}\left\{\hat{H}_0\right\}_{\Phi_\kappa} = \left\{\hat{H}_0\right\}_{\Phi_\kappa}\hat{\xi}_{\kappa+}$. We also find that for step κ, $e^{-\beta\left\{\hat{H}_0\right\}_{\Phi_\kappa}} = \sum_\mu \int_{-\infty}^{\infty} e^{-\beta E}\left|\psi_{E,\mu}^{(0)}\right\rangle\left\langle\psi_{E,\mu}^{(0)}\right| dE$, where $\hat{H}^\ddagger \equiv \hat{H}_{\Phi_\kappa}$ and $\hat{H}_0^\ddagger \equiv \left\{\hat{H}_0\right\}_{\Phi_\kappa}$. Then $e^{-\beta\hat{H}_0^\ddagger} = \sum_\mu \int_{-\infty}^{\infty} e^{-\beta E}\left|\psi_{E,\mu}^{(0)}\right\rangle\left\langle\psi_{E,\mu}^{(0)}\right| dE$. We therefore find that

$$\mathrm{Tr}\,\hat{P}_\Psi^{(0)}\cdot(i\hbar)^{-1}\,\hat{\Omega}_\Phi^{(+)\dagger}\left[\hat{\xi}^\ddagger,\hat{H}^\ddagger\right]\hat{\Omega}_\Phi^{(+)}e^{-\beta\hat{H}_0^\ddagger}$$

$$= (i\hbar)^{-1}\sum_\mu\int_{-\infty}^{\infty} e^{-\beta E}\left\langle\Psi_{E,\mu}^{(0)}\right|\hat{\Omega}_\Phi^{(+)\dagger}\left[\hat{\xi}^\ddagger,\hat{H}^\ddagger\right]\hat{\Omega}_\Phi^{(+)}\left|\Psi_{E,\mu}^{(0)}\right\rangle dE \quad (4.1.D)$$

Over here we use $\hat{\Omega}_\Phi^{(+)} = \lim_{\tau\to\infty} e^{-i\hat{H}^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}$. Then we find that

$$\mathrm{Tr}\,\hat{P}_\Psi^{(0)}\cdot(i\hbar)^{-1}\,\hat{\Omega}_\Phi^{(+)\dagger}\left[\hat{\xi}^\ddagger,\hat{H}^\ddagger\right]\hat{\Omega}_\Phi^{(+)}e^{-\beta\hat{H}_0^\ddagger}$$

$$= (i\hbar)^{-1}\sum_\mu\int_{-\infty}^{\infty} e^{-\beta E}\left\langle\Psi_{E,\mu}^{(0)}\right|\hat{\Omega}_\Phi^{(+)\dagger}\left[\hat{\xi}^\ddagger,\hat{H}^\ddagger\right]\hat{\Omega}_\Phi^{(+)}\left|\Psi_{E,\mu}^{(0)}\right\rangle dE$$

$$= \lim_{\tau\to\infty}\frac{d}{dt}\sum_\mu\int_{-\infty}^{\infty} e^{-\beta E}\left\langle\Psi_{E,\mu}^{(0)}\right|e^{-i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}^\ddagger\{t+\tau\}/\hbar}\hat{\xi}^\ddagger e^{-i\hat{H}^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}\left|\Psi_{E,\mu}^{(0)}\right\rangle dE$$

$$(4.1.E)$$

and also $\hat{\xi}^\ddagger\hat{H}_0^\ddagger = \hat{H}_0^\ddagger\hat{\xi}^\ddagger$. The relevant observable is $\hat{A}^\ddagger = \hat{\xi}^\ddagger$.

However, we showed precisely how to evaluate $\lim_{\tau\to\infty}\frac{d}{dt}\left\langle\psi_{E^\ddagger,\mu}^{(0)}\right|e^{-i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}$ $e^{i\hat{H}^\ddagger\{t+\tau\}/\hbar}\hat{A}^\ddagger e^{-i\hat{H}^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}\left|\psi_{E^\ddagger,\mu}^{(0)}\right\rangle$. We find that

$$\lim_{\tau\to\infty}\frac{d}{dt}\left\langle\psi_{E,\mu}^{(0)}\right|e^{-i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}^\ddagger\{t+\tau\}/\hbar}\hat{A}^\ddagger e^{-i\hat{H}^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}\left|\psi_{E,\mu}^{(0)}\right\rangle$$

$$= \sum_\nu\frac{2\pi}{\hbar}\left|\left\langle\psi_{E^\ddagger,\nu}^{(0)}\right|\hat{T}^\ddagger\left|\psi_{E^\ddagger,\mu}^{(0)}\right\rangle\right|^2\left\{A_\nu^\ddagger - A_\mu^\ddagger\right\}, \quad (4.2)$$

just as before. The first person who ever discovered this master equation is Lippmann [6–8]. However, $A_\nu^\ddagger = \delta_{\psi_\nu\in\Phi} = \{1$ if $\psi_\nu\in\Phi;\ 0$ if $\psi_\nu\notin\Phi\,\}$. Therefore the specific initial state rate of reaction is $\sum_{\tilde{\nu}}\frac{2\pi}{\hbar}\left|\left\langle\Phi_{E^\ddagger,\tilde{\nu}}^{(0)}\right|\hat{T}^\ddagger\left|\Psi_{E^\ddagger,\mu}^{(0)}\right\rangle\right|^2$. In fact, we can now write:

$$\lim_{\tau\to\infty}\frac{d}{dt}\left\langle\psi_{E^\ddagger,\mu}^{(0)}\right|e^{-i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}^\ddagger\{t+\tau\}/\hbar}\hat{A}^\ddagger e^{-i\hat{H}^\ddagger\{t+\tau\}/\hbar}e^{i\hat{H}_0^\ddagger\{t+\tau\}/\hbar}\left|\psi_{E^\ddagger,\mu}^{(0)}\right\rangle$$

$$= \sum_\nu\widehat{W}_{\nu\leftarrow\mu}^\ddagger\left(E^\ddagger\right)\left\{A_\nu^\ddagger - A_\mu^\ddagger\right\}, \quad (4.3)$$

where $\widehat{W}^{\ddagger}_{\nu \leftarrow \mu}\left(E^{\ddagger}\right) = \frac{2\pi}{\hbar}\left|\left\langle \Phi^{(0)}_{E^{\ddagger},\nu}\left|\hat{T}^{\ddagger}\right|\Psi^{(0)}_{E^{\ddagger},\mu}\right\rangle\right|^2 = \frac{1}{2\pi\hbar}\left|\mathcal{S}^{\ddagger}_{\Phi^{(0)}_{\nu} \leftarrow \Psi^{(0)}_{\mu}}\left(E^{\ddagger}\right)\right|^2$. Then

we find that $\mathrm{Tr}\hat{P}^{(0)}_{\Psi}.(i\hbar)^{-1}\hat{\Omega}^{(+)\dagger}_{\Phi}\left[\hat{\xi}^{\ddagger}, \hat{H}^{\ddagger}\right]\hat{\Omega}^{(+)}_{\Phi}e^{-\beta\hat{H}^{\ddagger}_0} = \frac{1}{2\pi\hbar}\int^{\infty}_{-\infty} N(E)e^{-\beta E}dE$. But within the domain of validity of non-relativistic mechanics, we showed that all the former Cumulative Reaction Probability formulas are equivalent the one we derived.

5 How to numerically implement this theory

Our novel contribution is to take into account the role of the solvent in the course of a reaction. The solvent interacts with the reactants in many ways, including ion-dipole forces, dipole-dipole, dipole-induced dipole, and polarization and repulsive forces from collisions. The solvent may also act as a reactant, product, catalyst, or inhibitor. Once we incorporate the solvent into the Hamiltonian of the reaction complex, we can solve the Lippmann–Schwinger Equation for its eigenstates, and calculate the S-matrix.

The flux method that we derived requires a flux operator, but that is easy to find. Once we have solved the Lippmann–Schwinger Equation, we can incorporate this into the average transmissive flux, using $N(E) = h \sum_{\mu}\left\langle\Psi^{(+)}_{E,\mu}\left|\hat{P}^{-}_{\Phi}\hat{F}^{\ddagger(-)}\hat{P}^{-}_{\Phi}\right|\Psi^{(+)}_{E,\mu}\right\rangle$. If non-relativistic mechanics is applicable, and the asymptotic scattering potential becomes independent of the reaction coordinate for infinite values of the reaction coordinate position variable, then we can replace $\hat{F}^{\ddagger(-)}$ with $\hat{F}$.

This problem is much simpler in gas phase because you do not need to worry about the role of the solvent. For example take the simplistic reaction $H + D_2$. The expected products are HD and D. One would expect non-relativistic mechanics to apply here, as it does in almost every case involving chemical reactions. All you need to do is form the complete set $\hat{P}^{-}_{\Phi}\left|\Psi^{(+)}_{E,\mu}\right\rangle$ of wavefunctions representing initially reactants and finally products, and calculate the trace using this set of wavefunctions.

6 Conclusion

The latest theory of reaction dynamics is exact and can be proven by the generalized Ehrenfest theorem of Lippmann. We also showed how the scattering theory formula for the cumulative reaction probability can be converted in order to derive an "exact" transition state theory and how this same exact transition state theory is equivalent to several other formulas for cumulative reaction probability that have already been derived in the accepted literature. We even showed how, deriving a master equation for the rate of change of probabilities of the eigenstates of the Hamiltonian based on the generalized Ehrenfest theorem of Lippmann, one can derive the rate laws for elementary chemical reactions (and show that it obeys microscopic reversibility).

Appendix

Derivation of thermodynamic alpha parameters

The thermodynamic alpha parameters can be determined either canonically or micro-canonically. First we shall do the microcanonical version. Then

$$
\Omega(E) e^{\sum_\varsigma \alpha_\varsigma N_\varsigma} e^{-\beta E}
$$

$$
= \sum_{(\ldots,n_{\varsigma,\sigma},\ldots)} \delta_{E(\ldots,n_{\varsigma,\sigma},\ldots)=E} \delta_{(\ldots,n_{\varsigma,\sigma},\ldots)\in\tilde{\mathscr{D}}\left(\ldots,n_{\overline{\varsigma}}^{(0)},\ldots\right)} e^{\sum_{\varsigma,\sigma}\alpha_\varsigma n_{\varsigma,\sigma}} e^{-\beta E(\ldots,n_{\varsigma,\sigma},\ldots)} \Omega^{(\ldots,n_{\varsigma,\sigma},\ldots)}
$$

$$\tag{A1.1}$$

where $\Omega^{(\ldots,n_{\varsigma,\sigma},\ldots)} = \frac{1}{\prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!} \prod_\varsigma \prod_\sigma \gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})}$, where $\gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})}$ is 1 if $n_{\varsigma,\sigma} = 0, 1$ and 0 if $n_{\varsigma,\sigma} \geq 2$ if ς is a fermion, $\gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})} = n_{\varsigma,\sigma}!$ if ς is a boson. Then

$$
N_{\varsigma'} \Omega(E) e^{\sum_\varsigma \alpha_\varsigma N_\varsigma} e^{-\beta E}
$$

$$
= \sum_{(\ldots,n_{\varsigma,\sigma},\ldots)} \left\{ \sum_{\sigma'} n_{\varsigma',\sigma'} \right\} \delta_{E(\ldots,n_{\varsigma,\sigma},\ldots)=E} \delta_{(\ldots,n_{\varsigma,\sigma},\ldots)\in\tilde{\mathscr{D}}\left(\ldots,n_{\overline{\varsigma}}^{(0)},\ldots\right)} e^{\sum_{\varsigma,\sigma}\alpha_\varsigma n_{\varsigma,\sigma}} e^{-\beta E(\ldots,n_{\varsigma,\sigma},\ldots)} \Omega^{(\ldots,n_{\varsigma,\sigma},\ldots)}
$$

$$\tag{A1.2}$$

However we can prove that

$$
n_{\varsigma',\sigma'} \Omega^{(\ldots,n_{\varsigma,\sigma},\ldots)} = \frac{n_{\varsigma',\sigma'}}{\prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!} \prod_\varsigma \prod_\sigma \gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})} = \gamma_{\varsigma',\sigma'} \Omega^{\left(\ldots,n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'},\ldots\right)}
$$

$$\tag{A1.3}$$

Then

$$
N_{\varsigma'} \Omega(E) e^{\sum_\varsigma \alpha_\varsigma N_\varsigma} e^{-\beta E}
$$

$$
= \sum_{\sigma'} \left\{ \sum_{(\ldots,n_{\varsigma,\sigma},\ldots)} \gamma_{\varsigma',\sigma'} \delta_{E(\ldots,n_{\varsigma,\sigma},\ldots)=E} \delta_{(\ldots,n_{\varsigma,\sigma},\ldots)\in\tilde{\mathscr{D}}\left(\ldots,n_{\overline{\varsigma}}^{(0)},\ldots\right)} e^{\sum_{\varsigma,\sigma}\alpha_\varsigma n_{\varsigma,\sigma}} e^{-\beta E(\ldots,n_{\varsigma,\sigma},\ldots)} \Omega^{\left(\ldots,n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'},\ldots\right)} \right\}
$$

$$
= \sum_{\sigma'} \left\{ \sum_{(\ldots,n'_{\varsigma,\sigma},\ldots)} \gamma_{\varsigma',\sigma'} \delta_{E(\ldots,n_{\varsigma,\sigma},\ldots)=E} \delta_{(\ldots,n'_{\varsigma,\sigma},\ldots)\in\tilde{\mathscr{D}}\left(\ldots,n_{\overline{\varsigma}}^{'(0)},\ldots\right)} \right.
$$

$$
\left. \times e^{\sum_\varsigma \alpha_\varsigma \left\{n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'}\right\}} e^{\alpha_\varsigma - \beta \varepsilon_{\varsigma',\sigma'}} e^{-\beta E\left(\ldots,n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'},\ldots\right)} \Omega^{(\ldots,n'_{\varsigma,\sigma},\ldots)} \right\}
$$

$$
= \Omega(E) e^{\sum_\varsigma \alpha_\varsigma N_\varsigma} e^{-\beta E} \sum_{\sigma'} \left\langle \gamma_{\varsigma',\sigma'} e^{\alpha_\varsigma - \beta \varepsilon_{\varsigma',\sigma'}} \right\rangle_{\left(N_{\varsigma'}+\delta_{\varsigma',\varsigma}\right)\to\left(N_{\varsigma'}\right)}
$$

$$\tag{A1.4}$$

And thus we can define: $e^{\alpha_{\varsigma'}}\mathrm{Tr}_{(\varsigma')}\left\langle\hat{\gamma}_{\varsigma'}e^{-\beta\hat{\varepsilon}_{\varsigma'}}\right\rangle_{\left(N_{\varsigma'}+\delta_{\varsigma',\varsigma}\right)\to\left(N_{\varsigma'}\right)} = e^{\alpha_{\varsigma'}}\overline{Q}_{\varsigma'}$, where

$$
\left\langle\hat{A}\right\rangle_{\left(N_{\varsigma'}+\delta_{\varsigma',\varsigma}\right)\to\left(N_{\varsigma'}\right)}\Omega(E)e^{\sum_{\varsigma}\alpha_{\varsigma}N_{\varsigma}}e^{-\beta E}
$$

$$
=\sum_{\sigma'}\left\{\sum_{(...,n_{\varsigma,\sigma},...)}\gamma_{\varsigma',\sigma'}\delta_{E(...,n_{\varsigma,\sigma},...)=E}\delta_{(...,n_{\varsigma,\sigma},...)\in\tilde{\mathscr{L}}\left(...,n_{\overline{\varsigma}}^{(0)},...\right)}\right.
$$

$$
\left.\times e^{\sum_{\varsigma,\sigma}\alpha_{\varsigma}\left\{n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'}\right\}}\left\langle\hat{A}\right\rangle(...,n_{\varsigma,\sigma},...)e^{-\beta E\left(...,n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'},...\right)}\Omega\left(...,n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'},...\right)\right\}
$$

$$\tag{A1.5}$$

We therefore find that $N_{\varsigma'} = e^{\alpha_{\varsigma'}}\overline{Q}_{\varsigma'}$. Therefore $\ln\frac{N_{\varsigma'}}{Q_{\varsigma'}} = \alpha_{\varsigma'}$, QUOD ERAT DE-MONSTRANDUM.

In the canonical ensemble we find:
$Z(\beta) = \sum_{(...,n_{\varsigma,\sigma},...)}\delta_{(...,n_{\varsigma,\sigma},...)\in\tilde{\mathscr{L}}\left(...,n_{\overline{\varsigma}}^{(0)},...\right)}e^{-\beta E(...,n_{\varsigma,\sigma},...)}\Omega(...,n_{\varsigma,\sigma},...)$. Then

$$
N_{\varsigma'}Z^{(...,N_{\varsigma},...)}(\beta)
$$

$$
=\sum_{(...,n_{\varsigma,\sigma},...)}\left\{\sum_{\sigma'}n_{\varsigma',\sigma'}\right\}\delta_{(...,n_{\varsigma,\sigma},...)\in\tilde{\mathscr{L}}\left(...,n_{\overline{\varsigma}}^{(0)},...\right)}e^{-\beta E(...,n_{\varsigma,\sigma},...)}\Omega(...,n_{\varsigma,\sigma},...)
$$

$$
=\sum_{\sigma'}\left\{\sum_{(...,n_{\varsigma,\sigma},...)}\gamma_{\varsigma',\sigma'}\delta_{(...,n_{\varsigma,\sigma},...)\in\tilde{\mathscr{L}}(...,N_{\varsigma},...)}e^{-\beta E(...,n_{\varsigma,\sigma},...)}\Omega\left(...,n_{\varsigma,\sigma}-\delta_{(\varsigma,\sigma)=\varsigma',\sigma'},...\right)\right\}
$$

$$
=\sum_{\sigma'}\left\{\sum_{(...,n_{\varsigma,\sigma},...)}\gamma_{\varsigma',\sigma'}\delta_{(...,n'_{\varsigma,\sigma},...)\in\tilde{\mathscr{L}}\left(...,N_{\varsigma}-\delta_{\varsigma,\varsigma'},...\right)}e^{-\beta\varepsilon_{\varsigma',\sigma'}}e^{-\beta E\left(...,n'_{\varsigma,\sigma},...\right)}\Omega\left(...,n'_{\varsigma,\sigma},...\right)\right\}
$$

$$
= Tr_{(\varsigma')}\left\langle\hat{\gamma}_{\varsigma'}e^{-\beta\hat{\varepsilon}_{\varsigma'}}\right\rangle\times Z^{\left(...,N_{\varsigma}-\delta_{\varsigma,\varsigma'},...\right)}(\beta) = e^{\alpha_{\varsigma'}}Tr_{(\varsigma')}\left\langle\hat{\gamma}_{\varsigma'}e^{-\beta\hat{\varepsilon}_{\varsigma'}}\right\rangle\times Z^{(...,N_{\varsigma},...)}(\beta)
$$

$$\tag{A1.6}$$

Therefore: $e^{\alpha_{\varsigma'}}\mathrm{Tr}_{(\varsigma')}\left\langle\hat{\gamma}_{\varsigma'}e^{-\beta\hat{\varepsilon}_{\varsigma'}}\right\rangle = e^{\alpha_{\varsigma'}}\overline{Q}_{\varsigma'}$, leading to the same results as before. The net result is that the rate of any given step of a reaction is:

$$
\dot{\xi}_{\kappa}^{\pm} = \left\{\frac{Q_{(\psi)}^{\ddagger\ddagger}}{\prod_{\varsigma\pm}\overline{Q}_{\varsigma\pm}^{n_{\kappa,\varsigma\pm}}}\prod_{\varsigma\pm}N_{\varsigma\pm}^{n_{\kappa,\varsigma\pm}}\right\}\times k_{\kappa}^{\ddagger\ddagger}
$$

$$
k_{\kappa}^{\ddagger\ddagger} = (2\pi\hbar Z)^{-1}\int_{-\infty}^{\infty}e^{-\beta E}N_{\kappa}(E)dE \triangleleft\text{Canonical ensemble}
$$

$$
k_{\kappa}^{\ddagger\ddagger} = \left(2\pi\hbar\,\widehat{\omega}(E)\right)^{-1}N_{\kappa}(E)\triangleleft\text{Microcanonical ensemble}\tag{A1.7}
$$

and $\frac{d\langle n_X \rangle}{dt} = \sum_\kappa \{\dot{\xi}_\kappa^+ - \dot{\xi}_\kappa^-\} \{n_{X,\kappa}^- - n_{X,\kappa}^+\}$. Each elementary step has the following

form: $\sum_{\varsigma^+} n_{\kappa,\varsigma^+} X_{\varsigma^+} \rightleftarrows \sum_{\varsigma^-} n_{\kappa,\varsigma^-} X_{\varsigma^-}$. This is the simpler form, but the more complex form used in Chapter II can be derived this way, by considering the surroundings as both a reactant and a product in each step of the reaction, provided that identical "surroundings" in the same system are distinguishable {because they are not free to move about the system} but identical reactant complexes {+surroundings} in the same system are free to move, and are therefore indistinguishable.

Then the form of the rate law is: $\dot{\xi}_\kappa^\pm = \left\{ \dfrac{Z_{(\psi)}^{\ddagger\ddagger}}{Z_{S_\kappa} \prod_{\varsigma^\pm} \overline{Q}_{\varsigma^\pm}^{n_{\kappa,\varsigma^\pm}}} \prod_{\varsigma^\pm} N_{\varsigma^\pm}^{n_{\kappa,\varsigma^\pm}} \right\} \times k_\kappa^{\ddagger\ddagger}$, where

$Z_{(\psi)}^{\ddagger\ddagger}$ is the partition function of reactant complex + surroundings treated as one single complex. As can be proven, the necessary and sufficient condition for chemical

equilibrium is that for every step of the reaction, $\dfrac{\prod_{\varsigma^-} N_{\varsigma^-}^{n_{\kappa,\varsigma^-}}}{\prod_{\varsigma^+} N_{\varsigma^+}^{n_{\kappa,\varsigma^+}}} = \dfrac{\prod_{\varsigma^-} \overline{Q}_{\varsigma^-}^{n_{\kappa,\varsigma^-}}}{\prod_{\varsigma^+} \overline{Q}_{\varsigma^+}^{n_{\kappa,\varsigma^+}}}$.

Derivation of rate law

We now have $\frac{d\langle n_X \rangle}{dt} = \frac{d\langle n_X' \rangle}{dt} = \sum_\kappa \{\overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa}\} \cdot \left(\frac{d}{dt}\left\langle \hat{n}_{\kappa+}^{(+)} \hat{\xi}_{\kappa+} \right\rangle - \frac{d}{dt}\left\langle \hat{n}_{\kappa-}^{(+)} \hat{\xi}_{\kappa-} \right\rangle \right)$.

But we now have to find $\frac{d}{dt}\left\langle \hat{n}_{\kappa\pm}^{(+)} \hat{\xi}_{\kappa\pm} \right\rangle$. We find that

$$
\begin{aligned}
\frac{d}{dt}\left\langle \hat{n}_{\kappa\pm}^{(+)} \hat{\xi}_{\kappa\pm} \right\rangle &= \frac{1}{i\hbar}\left\langle \left[\hat{n}_{\kappa\pm}^{(+)} \hat{\xi}_{\kappa\pm}, \hat{H} \right] \right\rangle = \frac{1}{i\hbar}\left\langle \hat{n}_{\kappa\pm}^{(+)}\left[\hat{\xi}_{\kappa\pm}, \hat{H} \right] \right\rangle \\
&= \frac{1}{i\hbar}\,\mathrm{Tr}\,\hat{\rho}\left[\hat{\xi}_{\kappa\pm}, \hat{H} \right] = \frac{1}{i\hbar}\,\mathrm{Tr}\hat{\rho}_\kappa^{(0)}\hat{\Omega}_\kappa^{(0)\dagger}\left[\hat{\xi}_{\kappa\pm}, \hat{H} \right]\hat{\Omega}_\kappa^{(0)} \quad (\mathrm{A2.1})
\end{aligned}
$$

We shall now use $\hat{H} = \hat{H}_\kappa^{(0)} + \hat{V}_\kappa^{\ddagger} \equiv \hat{H}_{\$_\kappa}^{(0)} + \hat{H}_{\phi_\kappa}^{(0)} + \hat{V}_\kappa^{\ddagger}$. But by 2.3, we can write

$$
\begin{aligned}
\hat{H}^\% &= \hat{H}^\circ + \sum_\kappa \left(\hat{\hat{\Omega}}_{\kappa+}^{(\hat{n}_{\kappa+})} + \hat{\hat{\Omega}}_{\kappa-}^{(\hat{n}_{\kappa-})} \right)\hat{H}_{\kappa\pm} + \sum_\kappa \left(\hat{\hat{\Omega}}_{\$_\kappa}^{(\hat{n}_{\$_\kappa})} - 1 \right)\hat{H}_{\$_\kappa} \\
&= \hat{H}^\circ + \sum_{\kappa' \neq \kappa} \left(\hat{\hat{\Omega}}_{\kappa'+}^{(\hat{n}_{\kappa'+})} + \hat{\hat{\Omega}}_{\kappa'-}^{(\hat{n}_{\kappa'-})} \right)\hat{H}_{\kappa'\pm} \\
&\quad + \left(\hat{\hat{\Omega}}_{\kappa+}^{(\hat{n}_{\kappa+})} + \hat{\hat{\Omega}}_{\kappa-}^{(\hat{n}_{\kappa-})} \right)\hat{H}_{\kappa\pm} + \sum_\kappa \left(\hat{\hat{\Omega}}_{\$_\kappa}^{(\hat{n}_{\$_\kappa})} - 1 \right)\hat{H}_{S_\kappa} \quad (\mathrm{A2.2})
\end{aligned}
$$

Then

$$
\left(\hat{\hat{\Omega}}_{\kappa+}^{(\hat{n}_{\kappa+})} + \hat{\hat{\Omega}}_{\kappa-}^{(\hat{n}_{\kappa-})} \right)\hat{H}_{\kappa\pm} = \sum_{j=1}^{\hat{n}_{\kappa+}} \hat{\Omega}_{(\kappa+;j)} \hat{H}_{\kappa\pm} \hat{\Omega}_{(\kappa+;j)}^\dagger + \sum_{j=1}^{\hat{n}_{\kappa-}} \hat{\Omega}_{(\kappa-;j)} \hat{H}_{\kappa\pm} \hat{\Omega}_{(\kappa-;j)}^\dagger
$$

$$= \sum_{j=1}^{\hat{n}_{\Phi_\kappa}} \hat{\Omega}_{(\phi_\kappa;j)} \hat{H}_{\Phi_\kappa} \hat{\Omega}^\dagger_{(\phi_\kappa;j)} = \hat{H}_{\Phi_\kappa} + \sum_{j=2}^{\hat{n}_{\Phi_\kappa}} \hat{\Omega}_{(\phi_\kappa;j)} \hat{H}_{\Phi_\kappa} \hat{\Omega}^\dagger_{(\phi_\kappa;j)} \qquad (A2.3)$$

Therefore $\hat{H}^\% = \hat{H}^\circ + \sum_{j=2}^{\hat{n}_{\Phi_\kappa}} \hat{\Omega}_{(\phi_\kappa;j)} \hat{H}_{\Phi_\kappa} \hat{\Omega}^\dagger_{(\phi_\kappa;j)} + \sum_\kappa \left(\hat{\hat{\Omega}}^{(\hat{n}_{S_\kappa})}_{S_\kappa} - 1 \right) \hat{H}_{S_\kappa} + \hat{H}_{\Phi_\kappa}$. But $\hat{H}_{\Phi_\kappa} \equiv \hat{H}^{(0)}_{\Phi_\kappa} + \hat{V}^{\ddagger}_{\Phi_\kappa}$. Then we can use $\hat{H}^\% = \hat{H}^{\%(0)}_{(\kappa)} + \hat{V}^{\ddagger}_\kappa$, where $\hat{V}^{\ddagger}_\kappa \equiv \hat{V}^{\ddagger}_{\Phi_\kappa}$, and $\hat{H}^{\%(0)}_{(\kappa)} = \hat{H}^\circ + \sum_{j=2}^{\hat{n}_{\Phi_\kappa}} \hat{\Omega}_{(\phi_\kappa;j)} \hat{H}_{\Phi_\kappa} \hat{\Omega}^\dagger_{(\phi_\kappa;j)} + \sum_\kappa \left(\hat{\hat{\Omega}}^{(\hat{n}_{S_\kappa})}_{S_\kappa} - 1 \right) \hat{H}_{S_\kappa} + \hat{H}^{(0)}_{\Phi_\kappa}$. We now find that $\hat{H}^\circ + \sum_{j=2}^{\hat{n}_{\Phi_\kappa}} \hat{\Omega}_{(\phi_\kappa;j)} \hat{H}_{\Phi_\kappa} \hat{\Omega}^\dagger_{(\phi_\kappa;j)} + \sum_\kappa \left(\hat{\hat{\Omega}}^{(\hat{n}_{S_\kappa})}_{S_\kappa} - 1 \right) \hat{H}_{S_\kappa} = \hat{H}'^\%$ commutes with $\hat{\xi}_{\kappa\pm}$ and $\hat{n}^{(+)}_{\kappa\pm}$ because these operators $\hat{\xi}_{\kappa\pm}$ only refers to the specific reactant complex in question, and $\hat{n}^{(+)}_{\kappa\pm}$ is an operator in Fock Space of populations of states and species of particles in the system, as opposed to the Hilbert Space unique to any one given particular species. The operators $\hat{\xi}_{\kappa\pm}$ and $\hat{H}_{\Phi_\kappa}, \hat{H}^{(0)}_{\Phi_\kappa}, \hat{V}^{\ddagger}_{\Phi_\kappa}$, are all operators unique to the Hilbert Space of the specific reactant complex in question. **We now find that for any observable $\hat{A}^{\ddagger}_{\Phi_\kappa}$ unique to the Hilbert Space of the specific reactant complex in question, that observable must evolve *independently* of all other species in the system**. We also find that $\hat{H}'^\%$ commutes with $\hat{H}_{\Phi_\kappa}, \hat{H}^{(0)}_{\Phi_\kappa}, \hat{V}^{\ddagger}_{\Phi_\kappa}$ and $\hat{A}^{\ddagger}_{\Phi_\kappa}$. It also commutes with $\hat{H}_{\Phi_\kappa} \equiv \hat{H}^{(0)}_{\Phi_\kappa} + \hat{V}^{\ddagger}_{\Phi_\kappa}$. Ergo: $e^{i\hat{H}^\% t/\hbar} \hat{A}^{\ddagger}_{\Phi_\kappa} e^{-i\hat{H}^\% t/\hbar} = e^{i\hat{H}_{\Phi_\kappa} t/\hbar} \hat{A}^{\ddagger}_{\Phi_\kappa} e^{-i\hat{H}_{\Phi_\kappa} t/\hbar}$. We also find that $e^{i\hat{H}^{\%(0)}_{\Phi_\kappa} t/\hbar} \hat{A}^{\ddagger}_{\Phi_\kappa} e^{-i\hat{H}^{\%(0)}_{\Phi_\kappa} t/\hbar} = e^{i\hat{H}^{(0)}_{\Phi_\kappa} t/\hbar} \hat{A}^{\ddagger}_{\Phi_\kappa} e^{-i\hat{H}^{(0)}_{\Phi_\kappa} t/\hbar}$. Therefore:

$$
\begin{aligned}
\frac{d}{dt} \left\langle \hat{n}^{(+)}_{\kappa\pm} \hat{\xi}_{\kappa\pm} \right\rangle &= \frac{1}{i\hbar} \left\langle \left[\hat{n}^{(+)}_{\kappa\pm} \hat{\xi}_{\kappa\pm}, \hat{H}_{\Phi_\kappa} \right] \right\rangle = \frac{1}{i\hbar} \left\langle \hat{n}^{(+)}_{\kappa\pm} \left[\hat{\xi}_{\kappa\pm}, \hat{H}_{\Phi_\kappa} \right] \right\rangle \\
&= \frac{1}{i\hbar} \operatorname{Tr} \hat{\rho} \hat{n}^{(0)}_{\kappa\pm} \left[\hat{\xi}_{\kappa\pm}, \hat{H}_{\Phi_\kappa} \right] = \frac{1}{i\hbar} \operatorname{Tr} \hat{\rho}^{(0)}_\kappa \hat{n}^{(0)}_{\kappa\pm} \left[\hat{\xi}_{\kappa\pm}, \hat{H}_{\Phi_\kappa} \right] \hat{\Omega}^{\%(0)}_\kappa \\
&= \frac{1}{i\hbar} \operatorname{Tr} \hat{\rho}^{(0)}_\kappa \hat{n}^{(0)}_{\kappa\pm} \hat{\Omega}^{(0)\dagger}_\kappa \left[\hat{\xi}_{\kappa\pm}, \hat{H}_{\Phi_\kappa} \right] \hat{\Omega}^{(0)}_\kappa = \frac{1}{i\hbar} \left\langle \hat{n}^{(0)}_{\kappa\pm} \hat{\Omega}^{(0)\dagger}_\kappa \left[\hat{\xi}_{\kappa\pm}, \hat{H}_{\Phi_\kappa} \right] \hat{\Omega}^{(0)}_\kappa \right\rangle^{(0)}_\kappa
\end{aligned}
$$
$$(A2.1)$$

The step before last part arises because **observables unique to the Hilbert Space of the specific reactant complex in question, that observable must evolve *independently* of all other species in the system**.

Now we must evaluate $\operatorname{Tr} \hat{\rho}^{(0)}_\kappa \hat{n}^{(0)}_{\kappa\pm} \hat{X}_{\Phi_\kappa}$. For a canonical ensemble, we have $\hat{\rho}^{(0)}_\kappa = \frac{e^{-\beta \hat{H}^{\%(0)}_{(\kappa)}}}{Z^{\%(0)}_{(\kappa)}}$. Then $Z^{\%(0)}_{(\kappa)} \operatorname{Tr} \hat{\rho}^{(0)}_\kappa \hat{n}^{(0)}_{\kappa\pm} \hat{X}_{\Phi_\kappa} = \operatorname{Tr} e^{-\beta \hat{H}^{\%(0)}_{(\kappa)}} \hat{n}^{(0)}_{\kappa\pm} \hat{X}_{\Phi_\kappa}$. Furthermore, there *is* a way to derive this. It will require the use of the formula for the trace of a matrix: $\operatorname{Tr} A = \sum_{(\dots, n_{\varsigma,\sigma}, \dots)} \frac{1}{\prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!} \left\{ \left[\prod_{\varsigma,\sigma} \gamma^{(n_{\varsigma,\sigma})}_{\varsigma,\sigma} \right] \dots \operatorname{Tr}_{\varsigma,\sigma;1} \dots \operatorname{Tr}_{\varsigma,\sigma;n_{\varsigma,\sigma}} \dots A \right\}$. Now if species ς, is a fermion {spin = 1/2 an odd integer}, then $\gamma^{(n_{\varsigma,\sigma})}_{\varsigma,\sigma} = 1$ if $n_{\varsigma,\sigma} = 0, 1$; $\gamma^{(n_{\varsigma,\sigma})}_{\varsigma,\sigma} = 0$ if $n_{\varsigma,\sigma} \geq 2$. If species ς is a boson {spin is a whole number}, then $\gamma^{(n_{\varsigma,\sigma})}_{\varsigma,\sigma} = n_{\varsigma,\sigma}!$

If species ς is a corrected boltzon {i.e., the number of states is much larger than the number of particles}, then a good approximation is $\gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})} = 1$. In Eq. A2.2, the formula for $\left\langle \hat{n}_\chi \hat{X} \right\rangle$ is derived:

$$\mathrm{Tr}\left\{\hat{n}_\chi \hat{X} e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma\right)-\beta\hat{H}}\right\}$$

$$= \sum_{(\dots,n_{\varsigma,\sigma},\dots)} \frac{1}{\prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!} \left\{\left[\prod_{\varsigma,\sigma}\gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})}\right]\dots \mathrm{Tr}_{\varsigma,\sigma;1}\dots \mathrm{Tr}_{\varsigma,\sigma;n_{\varsigma,\sigma}}\dots \sum_{\sigma'} n_{\chi,\sigma'}\hat{X}e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\}$$

$$= \sum_{(\dots,n'_{\varsigma,\sigma},\dots)} \frac{1}{\prod_{\varsigma,\sigma} n'_{\varsigma,\sigma}!} \left\{\left[\prod_{\varsigma,\sigma}\gamma_{\varsigma,\sigma}^{(n'_{\varsigma,\sigma})}\right]\dots \mathrm{Tr}_{\varsigma,\sigma;1}\dots \mathrm{Tr}_{\varsigma,\sigma;n_{\varsigma,\sigma}}\dots e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}} \mathrm{Tr}_\chi\hat{\gamma}_\chi e^{\alpha_\chi-\beta\hat{\varepsilon}_\chi}\hat{X}\right\}$$

$$= \mathrm{Tr}'\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta_\varepsilon\hat{H}}\right\}\times \mathrm{Tr}_\chi\overline{\hat{\gamma}_\chi e^{\alpha_\chi-\beta\hat{\varepsilon}_\chi}\hat{X}} \qquad (A2.2)$$

And therefore: $\left\langle\hat{n}_\chi\hat{X}\right\rangle = \mathrm{Tr}_\chi\overline{\hat{\gamma}_\chi e^{\alpha_\chi-\beta\hat{\varepsilon}_\chi}\hat{X}}$. And also, it turns out that $\mathrm{Tr}\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\} = \mathrm{Tr}'\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\}$. The formula $\mathrm{Tr}\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\}$ is the

original grand canonical partition function and the formula $\mathrm{Tr}'\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\}$, is the grand canonical partition function when the number of particles of type χ is reduced by exactly 1 without a corresponding change in any of the other variables independent of χ. A calculation of standard statistical mechanics will readily tell you that it is possible to adjust the values of α_ς so that $\mathrm{Tr}\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\} = \mathrm{Tr}'\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\}$, or equivalently $\left(\frac{\partial}{\partial N_\chi}\ln\mathrm{Tr}\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\}\right)_{\dots,\alpha_\varsigma,\dots,\beta,\dots} = 0$, and thus follows A2.2. However, $\mathrm{Tr}\left\{e^{\left(\sum_\varsigma\alpha_\varsigma\hat{n}_\varsigma\right)-\beta\hat{H}}\right\} = e^{\left(\sum_\varsigma\alpha_\varsigma N_\varsigma\right)}\mathrm{Tr}\,e^{-\beta\hat{H}}$ because we have used petit canonical ensemble constraints.

This gives us: $\frac{d}{dt}\left\langle\hat{n}_{\kappa\pm}^{(+)}\hat{\xi}_{\kappa\pm}\right\rangle = e^{\alpha\phi_{\kappa\pm}}\mathrm{Tr}\,\hat{P}_{\kappa\pm}^{(0)}e^{-\beta\hat{H}_{\phi_\kappa}^{(0)}}\hat{\Omega}_\kappa^{(0)\dagger}\left[\hat{\xi}_{\kappa\pm},\hat{H}_{\phi_\kappa}\right]\hat{\Omega}_\kappa^{(0)}$. But the constraints incumbent on the system give us:

$$e^{\alpha\phi_{\kappa+}} = e^{\alpha S_\kappa}\prod_{\overline{\mu}=1}^{\overline{m}} e^{\overline{\alpha}_{\kappa;\overline{\mu}}\alpha_{A(\kappa;\overline{\mu})}}$$

$$e^{\alpha \phi_{\kappa -}} = e^{\alpha s_\kappa} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} e^{\overline{\beta}_{\kappa;\overline{\nu}} \alpha B(\kappa;\overline{\nu})}$$

(A2.3)

We can now evaluate $e^{\alpha s_\kappa}$: Given that the number of "surroundings" which is either 0 or 1, and the same is true for the number of transition states of any kind formed from reactants + surroundings, we now suppose that different "surroundings" in the same state are distinguishable—they are not free to move or exchange places with one another in its native state. But different transition states of the same kind and in the same state are indistinguishable {in their native state they are free to move and exchange places with one another}, but they are corrected boltzons because the number of accessible states is much larger than the total number of transition states.

We find:

$$N_\$ = \mathrm{Tr}\left\{ \hat{n}_\$ e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma\right) - \beta_\varepsilon \hat{H}} \right\} \sum_{(\dots,n_{\varsigma,\sigma},\dots)} \frac{1}{\prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!}$$

$$\left\{ \left\{ \prod_{\varsigma,\sigma} \gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})} \right\} \dots \mathrm{Tr}_{\varsigma,\sigma;1} \dots \mathrm{Tr}_{\varsigma,\sigma;n_{\varsigma,\sigma}} \dots \sum_{\sigma'} n_{\$,\sigma'} e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma\right) - \beta_\varepsilon \hat{H}} \right\}$$

$$= \sum_{(\dots,n_{\varsigma,\sigma},\dots)} \frac{N_\$!}{\prod_{\sigma'} n_{\$,\sigma'}! \cdot \prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!}$$

$$\left\{ \left\{ \prod_{\varsigma,\sigma} \gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})} \right\} \dots \mathrm{Tr}_{\varsigma,\sigma;1} \dots \mathrm{Tr}_{\varsigma,\sigma;n_{\varsigma,\sigma}} \dots e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma\right) - \beta \hat{H}} \sum_{\sigma'} n_{\$,\sigma'} e^{\alpha_\$ - \beta \hat{E}_\$} \right\}$$

$$= \sum_{\sigma'} \sum_{(\dots,n_{\varsigma,\sigma},\dots)} \frac{n_{\$,\sigma'} \cdot N_\$!}{\prod_{\sigma'} n_{\$,\sigma'}! \cdot \prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!}$$

$$\left\{ \left\{ \prod_{\varsigma,\sigma} \gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})} \right\} \dots \mathrm{Tr}_{\varsigma,\sigma;1} \dots \mathrm{Tr}_{\varsigma,\sigma;n_{\varsigma,\sigma}} \dots e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma\right) - \beta \hat{H}} e^{\alpha_\$ - \beta \hat{E}_\$} \right\}$$

$$= N_\$ \sum_{\sigma'} \sum_{(\dots,n_{\varsigma,\sigma},\dots)} \frac{\{N_\$ - 1\}!}{\prod_{\sigma'} n_{\$,\sigma'}! \prod_{\varsigma,\sigma} n_{\varsigma,\sigma}!}$$

$$\left\{ \left\{ \prod_{\varsigma,\sigma} \gamma_{\varsigma,\sigma}^{(n_{\varsigma,\sigma})} \right\} \dots \mathrm{Tr}_{\varsigma,\sigma;1} \dots \mathrm{Tr}_{\varsigma,\sigma;n_{\varsigma,\sigma}} \dots e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma\right) - \beta \hat{H}} e^{\alpha_\$ - \beta \hat{E}_\$} \right\}$$

$$= N_\$ \mathrm{Tr}' \left\{ e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma\right) - \beta_\varepsilon \hat{H}} \right\} \times \mathrm{Tr}_\$ e^{\alpha_\$ - \beta \hat{E}_\$}$$

(A2.4)

But this time, $\text{Tr}'\left\{ e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma \right) - \beta_\varepsilon \hat{H}} \right\}$ is the grand canonical partition function when the number of "surroundings" in the system is reduced by exactly 1. As always, it is possible to adjust the values of α_ς so that $\text{Tr}'\left\{ e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma \right) - \beta_\varepsilon \hat{H}} \right\} = \text{Tr}\left\{ e^{\left(\sum_\varsigma \alpha_\varsigma \hat{n}_\varsigma \right) - \beta_\varepsilon \hat{H}} \right\}$. We therefore find that $\text{Tr}_\varsigma e^{\alpha_\varsigma - \beta \hat{E}_\varsigma} = 1$, so that $e^{\alpha_\varsigma} = \dfrac{1}{\text{Tr}_\varsigma e^{-\beta \hat{E}_\varsigma}} = \dfrac{1}{Z_\varsigma}$. And as for the reactants and products, we find that $e^{\alpha_X} = \dfrac{N_X}{\text{Tr}_X \hat{\gamma}_X e^{-\beta \hat{\varepsilon}_X}} = \dfrac{N_X}{Q_X}$.

By definition, $\hat{\Omega}_\kappa^{(0)} = \lim\limits_{\tau \to \infty} e^{-i\hat{H}_{\varPhi_\kappa}\{t+\tau\}/\hbar} e^{i\hat{H}_{\varPhi_\kappa}^{(0)}\{t+\tau\}/\hbar}$. Since both Hamiltonians in this Moller Wave Operator are invariant to the interchange, $\hat{\mathcal{K}}_\kappa^{(0)} = \int \dots \int_{-\infty}^{\infty} \left| s_0 - s'^{\ddagger}, s''' \right\rangle \left\langle s^{\ddagger} + s'^{\ddagger}, s''' \right| ds'^{\ddagger} d\langle\!\langle s''' \rangle\!\rangle$ that changes *incident* reactants into *incident* products and *incident* products into *incident* reactants, it follows that the Moller Wave Operators must have the same property: $\hat{\mathcal{K}}_\kappa^{(0)} \hat{\Omega}_\kappa^{(0)} = \hat{\Omega}_\kappa^{(0)} \hat{\mathcal{K}}_\kappa^{(0)}$. Also the same is true when $\hat{\mathcal{K}}_\kappa^{(0)} = \int \dots \int_{-\infty}^{\infty} \left| s_0 - s'^{\ddagger}, s'''_0 - s'''^{\ddagger} \right\rangle \left\langle s^{\ddagger} + s'^{\ddagger}, s'''_0 + s'''^{\ddagger} \right| ds'^{\ddagger} d\langle\!\langle s'''^{\ddagger} \rangle\!\rangle$. Thus we have two different operators that can change *incident* reactants into *incident* products and *incident* products into *incident* reactants. Both of these interchange operators are unitary over the Hilbert Space unique to the reactant complex of interest: $\hat{\mathcal{K}}_\kappa^{(0)} \hat{\mathcal{K}}_\kappa^{(0)\dagger} = \hat{\mathcal{K}}_\kappa^{(0)\dagger} \hat{\mathcal{K}}_\kappa^{(0)} = 1$.

Therefore:

$$
\begin{aligned}
\frac{\delta n_X}{\delta t} &= \sum_\kappa \{ \overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa} \} \left\{ \frac{\prod_{\overline{\mu}=1}^{\overline{m}} n_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}}{\prod_{\overline{\mu}=1}^{\overline{m}_\kappa} Q_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}} - \frac{\prod_{\overline{\nu}=1}^{\overline{n}_\kappa} n_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}}{\prod_{\overline{\nu}=1}^{\overline{n}_\kappa} Q_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}} \right\} \\
&\quad \times \frac{\text{Tr} \hat{P}_{\varPhi_{\kappa+}}^{(0)} \cdot (i\hbar)^{-1} \hat{\Omega}_\kappa^{(0)\dagger} \left[\hat{\xi}_{\kappa \pm}, \hat{H}_{\varPhi_\kappa} \right] \hat{\Omega}_\kappa^{(0)} e^{-\beta \hat{H}_{\varPhi_\kappa}^{(0)}}}{Z_\varsigma} \\
&= \sum_\kappa \{ \overline{\beta}_{X;\kappa} - \overline{\alpha}_{X;\kappa} \} \left\{ k_{\kappa+} \prod_{\overline{\mu}=1}^{\overline{m}} n_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}} - k_{\kappa-} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} n_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}} \right\}. \quad (A2.5)
\end{aligned}
$$

where

$$
\begin{aligned}
k_{\kappa+} &= \frac{Z_{\varPhi_\kappa}}{Z_{\varsigma_\kappa} \prod_{\overline{\mu}=1}^{\overline{m}_\kappa} Q_{A(\kappa;\overline{\mu})}^{\overline{\alpha}_{\kappa;\overline{\mu}}}} \text{Tr}\, \hat{P}_{\varPhi_{\kappa+}}^{(0)} (i\hbar)^{-1} \hat{\Omega}_\kappa^{(0)\dagger} \left[\hat{\xi}_{\kappa \pm}, \hat{H}_{\varPhi_\kappa} \right] \hat{\Omega}_\kappa^{(0)} Z_{\varPhi_\kappa}^{-1} e^{-\beta \hat{H}_{\varPhi_\kappa}^{(0)}} \\
k_{\kappa-} &= \frac{Z_{\varPhi_\kappa}}{Z_{\varsigma_\kappa} \prod_{\overline{\nu}=1}^{\overline{n}_\kappa} Q_{B(\kappa;\overline{\nu})}^{\overline{\beta}_{\kappa;\overline{\nu}}}} \text{Tr}\, \hat{P}_{\varPhi_{\kappa+}}^{(0)} (i\hbar)^{-1} \hat{\Omega}_\kappa^{(0)\dagger} \left[\hat{\xi}_{\kappa \pm}, \hat{H}_{\varPhi_\kappa} \right] \hat{\Omega}_\kappa^{(0)} Z_{\varPhi_\kappa}^{-1} e^{-\beta \hat{H}_{\varPhi_\kappa}^{(0)}}.
\end{aligned}
$$

$$(A2.6)$$

Because of invariance of a trace to unitary transformations, we find that

$$\text{Tr}\ \hat{P}^{(0)}_{\Phi_{\kappa+}}\,(i\hbar)^{-1}\,\hat{\Omega}^{(0)\dagger}_{\kappa}\left[\hat{\xi}_{\kappa+},\,\hat{H}_{\Phi_{\kappa}}\right]\hat{\Omega}^{(0)}_{\kappa}e^{-\beta\hat{H}^{(0)}_{\Phi_{\kappa}}}$$

$$=\text{Tr}\ \hat{P}^{(0)}_{\Psi_{\kappa+}}\,(i\hbar)^{-1}\,\hat{\Omega}^{(0)\dagger}_{\kappa}\left[\hat{\xi}_{\kappa-},\,\hat{H}_{\Phi_{\kappa}}\right]\hat{\Omega}^{(0)}_{\kappa}e^{-\beta\hat{H}^{(0)}_{\Phi_{\kappa}}}. \qquad (A2.7)$$

It would also be interesting to note that $\text{Tr}\ \hat{P}^{(0)}_{\Phi_{\kappa}}e^{-\beta\hat{H}^{(0)}_{\Phi_{\kappa}}}=\text{Tr}\ \hat{P}^{(0)}_{\Psi_{\kappa}}e^{-\beta\hat{H}^{(0)}_{\Phi_{\kappa}}}=Z_{\Phi_{\kappa}}=Z_{\Psi_{\kappa}}$ for the same reason: these traces are interconvertible by a unitary transform.

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