

## CONCERNING THE SCALING BEHAVIOR IN THE CLASSICAL MECHANICS OF NON-REACTIVE COLLISIONS: AN ANALYTIC INVESTIGATION

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The classical mechanical treatment of non-reactive scattering processes is cast into a convenient formalism for describing the changes in the internal linear momentum affected by a collision. The dependence of these changes on the initial internal linear momentum and coordinate is shown to be weak. Combining this result with the classical virial theorem leads to a classical scaling theory for internal energy changes. In its simplest form, this theory explicitly exhibits the dependence of the internal energy transfer on four factors: (1) the initial internal energy; (2) the initial internal coordinate; (3) the bound state potential; and (4) the average momentum transfer. At a given initial kinetic energy, these four quantities suffice to characterize the systematic variation of the internal energy transfer with initial internal energy and coordinate. The combination of the classical scaling theory with the quasiclassical histogram quantization method is determination of all other transition probabilities  $P_{n \rightarrow n-\Delta}$ ,  $\Delta = 1, 2, \dots, n$ . This includes classically forbidden processes for which the scaling theory yields an exact value of zero.

### 1. Introduction

Although quantum mechanics provides a correct description of collision processes involving atomic and molecular systems, implementation of the quantum scattering formalism is extremely difficult for systems with more than a few internal states. Development of approximation methods such as exponential distorted wave and dimensionality reduction schemes has extended the range of quantal dynamics [1, 2]. Of course, the most well-known approximation involves replacing the quantum mechanical description with the classical mechanical one. Such an approach is asymptotically correct in the limit of large quantum numbers, and has been implemented for systems much too large for study by quantal methods [3].

Classical trajectory techniques do suffer from serious difficulties. One of major interest for chemical systems is the extraction of state-to-state information from continuous classical variables. Various direct approaches have been

developed, including the histogram binning method [3-5], a geometrical or continuous mapping technique [6] and classical *S*-matrix theory [7, 8]. Indirect approaches have utilized classical energy transfer moments combined with either an inversion procedure [4, 9] or a correspondence between the classical and quantum forced oscillator [10]. All of these methods have been applied to a variety of systems and the results are often quite reasonable.

Another more subtle difficulty involves the interrelationship among classical quantities such as energy transfer moments and state-to-state transition probabilities. All methods which utilize the moments always incorporate additional assumptions about the appropriate relationship (e.g. an information theoretic form). A few simple questions can be posed to further illustrate this problem: (1) Do classical energy loss moments directly imply a certain set of state-to-state transition probabilities within a particular quantization scheme, and vice versa? (2) Are

all the state-to-state transition probabilities essentially independent (except for the restriction of probability conservation)? Such questions probe our understanding of the systematics of classical dynamics, and its relationship to quantum mechanics. The answers are of both fundamental and practical interest.

In this article, we present the initial development of an approximate *fully classical scaling theory* for internal molecular variables. This theory provides a general relationship for changes in the internal linear momentum and internal energy, resulting from a bimolecular non-reactive collision, in terms of the isolated molecules' properties and the impulse in the collision. Utilizing this theory, one can investigate some of the previously mentioned problems. As an initial illustration, the internal energy scaling relationship is combined with the histogram quantization method to yield the quantum number scaling theory for transition probabilities which is appropriate to this quasi-classical theory. Testing against exact histogram transition probabilities shows the scaling theory to describe accurately the quantum number variation. In another article, we derive the scaling for energy loss moments and show how these can provide directly all the state-to-state transition probabilities within various classical quantization procedures.

This paper is divided into four parts. Section 2 consists of an exposition of classical dynamics within the perturbative and sudden limits<sup>‡</sup>; these dynamical approximations [1] are used to investigate the appropriate scaling relationships for linear momentum and internal energy changes. General expressions are given in section 3 for the scaling of vibrational transition probabilities  $P_{n \rightarrow n'}$  within the histogram quantization procedure. Section 3 also contains examples for the harmonic and Morse oscillator cases. A discussion of quantum versus classical histogram relative quantities and a brief conclusion follow in section 4.

<sup>‡</sup> The perturbative limit in quantum mechanics also leads to a scaling relationship [11] identical to that previously derived within the energy correct sudden scaling theory [12].

## 2. Classical scattering theory

We consider a system described by one internal coordinate and momentum,  $(r, p)$  and center-of-momentum translational coordinates and momenta  $(\mathbf{R}, \mathbf{P}) = (R_1, R_2, R_3, P_1, P_2, P_3)$ . This separation of the internal and relative degrees of freedom is assumed to hold throughout the collision, which restricts our treatment to non-reactive processes. The hamiltonian is defined by

$$H = (2\mu)^{-1}P^2 + V(\mathbf{R}, r) + h(p, r), \quad (2.1)$$

where  $\mu$  is the collision reduced mass and  $V(\mathbf{R}, r)$  is the intermolecular potential which vanishes as  $R \equiv |\mathbf{R}|$  approaches infinity. The internal molecular hamiltonian is given as

$$h(p, r) = (2m)^{-1}p^2 + v(r), \quad (2.2)$$

where  $m$  is the internal reduced mass and  $v(r)$  is the potential for the (bound) molecule. We emphasize that more internal degrees of freedom can be included provided that  $h$  remains separable in  $r$  and  $p$ . Further discussion of this point occurs at the end of section 2.2.

The dynamical evolution of the collision is governed by Hamilton's equations which become

$$\dot{P}_i = -\frac{\partial V(\mathbf{R}, r)}{\partial R_i}, \quad \dot{R}_i = P_i/\mu, \quad i = 1, 2, 3, \quad (2.3a)$$

$$\dot{p} = -\frac{\partial v(r)}{\partial r} - \frac{\partial V(\mathbf{R}, r)}{\partial r}, \quad \dot{r} = p/m. \quad (2.3b)$$

Specification of the initial conditions at a total energy,  $E$ , as  $t \rightarrow -\infty$ :

$$r = r_0, \quad p = p_0, \quad (2.3c)$$

$$|\mathbf{R}| = \text{large}, \quad \hat{\mathbf{R}} = \hat{\mathbf{R}}_0, \quad (2.3d)$$

$$\mathbf{R}_0 \times \mathbf{P}_0 = \mathbf{L}_0, \quad P_0 = \{2\mu[E - h(p_0, r_0)]\}^{1/2}, \quad (2.3e)$$

suffices to yield the final values which are evaluated when  $|\mathbf{R}|$  is large once again. Specifically, the internal momentum change is generally a function of all the initial conditions,

$$p(t) = p_0(t) + F(P_0, \mathbf{L}_0, r_0, p_0, t), \quad (2.4)$$

where  $p_0(t)$  is the time-dependent internal momentum in the absence of the collision and  $F$  is an unknown function. Eqs. (2.3a)–(2.3e) can be integrated numerically once  $v(r)$ ,  $m$ ,  $\mu$  and  $V(\mathbf{R}, r)$  are specified and  $F$  can be determined. We do not take this approach since the *variation of the internal variable changes* with initial values  $p_0$  and  $r_0$  is of main interest. Therefore, we study the dynamical solutions within the context of two standard but generally complementary approximations, namely those defined by the sudden and perturbation assumptions. Generalizations beyond these limits<sup>‡</sup> are discussed in section 2.3.

### 2.1. Sudden approximation

The fundamental assumption is that one (or more) of the internal coordinates remains unchanged during the course of the collision. This occurs when the time duration of the collision is short compared to the characteristic period of the motion of the appropriate internal coordinate. Suppress all reference to other internal degrees of freedom and denote the sudden coordinate by  $r$ . Eqs. (2.3a) and (2.3b) then apply in the form,

$$\dot{P}_i = -\frac{\partial V(\mathbf{R}, r_0)}{\partial R_i}, \quad R_i = P_i/\mu \quad (2.5a)$$

and

$$\dot{p} = -\frac{\partial V(\mathbf{R}, r)}{\partial r} \Big|_{r=r_0}, \quad \dot{r} = 0. \quad (2.5b)$$

The factor  $\partial v_0(r)/\partial r$  is dropped for consistency in eq. (2.5b), since in the absence of a collision  $\dot{r} = 0$  would imply  $\dot{p} = 0$ . The critical feature of the approximation involves the separation of  $\dot{r}$  and  $\dot{p}$ ; the time-dependence of  $p$  is trivially determined from eq. (2.5b) when  $\dot{r} = 0$  but it should not be assumed that  $\dot{p} = 0$ . This separation is analogous to the quantum mechanical sudden approximation where the state-to-state  $S$ -matrix elements are generated by taking matrix elements of a fixed-coordinate representation sudden  $S$ -matrix [1b, 12, 13].

<sup>‡</sup> See ref. [17] and the note added in proof.

Eq. (2.5b) can be solved formally to yield

$$p(t') = p_0 - \int_{-\infty}^{t'} \frac{\partial V(\mathbf{R}, r)}{\partial r} \Big|_{r=r_0} dt, \quad (2.6)$$

where  $p_0$  is the initial internal momentum. From eqs. (2.3) and (2.5a), the translational coordinate is a function of time,  $\mathbf{P}_0$ ,  $\mathbf{L}_0$  and  $r_0$ , i.e.  $\mathbf{R} \equiv \mathbf{R}(t, \mathbf{P}_0, \mathbf{L}_0, r_0)$ . Defining the impulse of the force in the  $r$ -coordinate as

$$f(\mathbf{P}_0, \mathbf{L}_0, r_0) \equiv - \int_{-\infty}^{\infty} \frac{\partial V(\mathbf{R}, r)}{\partial r} \Big|_{r=r_0} dt, \quad (2.7)$$

yields a functional relationship for the change in the internal momentum,

$$p - p_0 = f(\mathbf{P}_0, \mathbf{L}_0, r_0), \quad (2.8)$$

where

$$p \equiv p(t' \rightarrow \infty) \quad (2.9)$$

is the final internal momentum. Eq. (2.8) is the desired result of the form in eq. (2.4) which allows one to correlate changes in the internal momentum with variations in  $r_0$  at a given  $\mathbf{P}_0$ ,  $\mathbf{L}_0$ . For example, at a specified kinetic energy and impact parameter, the momentum *change* depends only upon the initial internal coordinate value. We emphasize two important points about eq. (2.8):

- (i) the internal momentum  $p_0$  does not appear in  $f$ , which implies that action-angle variables or any new coordinates such that  $r' = g(r, p)$  cannot be used; and,
- (ii) the relationship cannot be used to quantify classical results without further manipulation, since from (i) the momentum  $p$  is a linear momentum variable.

The solution of the difficulty in (ii) is presented in section 2.3 after we first derive eq. (2.8) from another viewpoint.

### 2.2. Perturbation approximation

The fundamental assumption is that one (or more) of the internal coordinates is only weakly affected by the collision. As before we suppress all indication of other degrees of freedom, and

let the appropriate coordinate be  $r$ . Define the collision-free values as  $\bar{r}(t)$  and  $\bar{p}(t)$ , which satisfy the equations

$$\dot{\bar{p}}(t) = -\left. \frac{\partial v(r)}{\partial r} \right|_{r=\bar{r}(t)}, \quad \dot{\bar{r}}(t) = \bar{p}(t)/m, \quad (2.10)$$

and let the additional time-dependences be included as

$$r(t) = \bar{r}(t) + r^+(t), \quad (2.11a)$$

$$p(t) = \bar{p}(t) + p^+(t). \quad (2.11b)$$

Substitution of eq. (2.11) into eq. (2.3) and use of eq. (2.10) yields

$$\dot{P}_i = -\frac{\partial V(\mathbf{R}, r(t))}{\partial R_i}, \quad \dot{R}_i = P_i/\mu \quad (2.12a)$$

and

$$\dot{p}^+(t) = \left. \frac{\partial v(r)}{\partial r} \right|_{r=\bar{r}(t)} - \left. \frac{\partial v(r)}{\partial r} \right|_{r=r(t)} - \left. \frac{\partial V(\mathbf{R}, r)}{\partial r} \right|_{r=r(t)},$$

$$\dot{r}^+ = \dot{p}^+/m. \quad (2.12b)$$

These exact equations are simply the classical analog of the quantum interaction representation.

The perturbative assumption implies that the right hand sides of eqs. (2.12a) and (2.12b) can be evaluated at  $r(t) = \bar{r}(t)$ . The equation for  $r^+$  becomes trivial and will be neglected in the following developments. The dynamics is then governed by the approximate equations,

$$\dot{P}_i = -\frac{\partial V(\mathbf{R}, \bar{r}(t))}{\partial R_i}, \quad \dot{R}_i = P_i/\mu, \quad (2.13a)$$

$$\dot{p}^+(t) = \left. \frac{\partial V(\mathbf{R}, r)}{\partial r} \right|_{r=\bar{r}(t)}. \quad (2.13b)$$

Integrating eq. (2.13b) and using the fact that  $p^+(t \rightarrow -\infty) = 0$  leads to

$$p(t') = \bar{p}(t') - \int_{-\infty}^{t'} \left. \frac{\partial V(\mathbf{R}, r)}{\partial r} \right|_{r=\bar{r}(t)} dt. \quad (2.14)$$

This result is very similar to eq. (2.6) except that the derivative is evaluated at a time-dependent  $r = \bar{r}(t)$ . Since the amplitude and

time-dependence of  $\bar{r}(t)$  will generally depend upon the initial internal energy, eqs. (2.13) and (2.14) must be further simplified before a functional relationship like eq. (2.8) obtains.

For the problems which we are primarily concerned with, namely vibrational transitions, the time-variation of  $\bar{r}(t)$  is fast compared to that of  $\mathbf{R}(t)$ . (Note that this separation of time scales is exactly the reverse of the sudden approximation presented in section 2.1.) Since  $\bar{r}(t)$  varies quickly compared to  $\mathbf{R}(t)$ , the  $\bar{r}(t)$  dependence in eq. (2.13a) can be assumed to "average-out". The translational dynamics is then governed by

$$\dot{P}_i = -\frac{\partial V(\mathbf{R}, \langle \bar{r} \rangle)}{\partial R_i}, \quad \dot{R}_i = P_i/\mu, \quad (2.15)$$

where

$$\langle \bar{r} \rangle = T^{-1} \int_0^T \bar{r}(t) dt \quad (2.16)$$

is the average of  $\bar{r}(t)$  over a vibrational period. Similarly, we can evaluate the derivative in eq. (2.14) at  $r = \langle \bar{r} \rangle$  since only the change of  $p(t')$  on the collision time-scale is required; in other words, the time-dependence of  $\bar{r}(t)$  affects the short-time variation of  $p(t')$  but not the long-time collisional behavior. In addition, since  $\bar{p}(t')$  displays periodic motion, we can choose a value of  $t' = T'$  sufficiently large to ensure convergence of the integral in eq. (2.14) and such that  $\bar{p}(T') = \bar{p}_0(t' \rightarrow -\infty) = p_0$ . Eq. (2.14) becomes

$$p - p_0 = f(P_0, \mathbf{L}_0, \langle \bar{r} \rangle), \quad (2.17)$$

where  $f$  is given by eq. (2.7) with  $r_0$  replaced by  $\langle \bar{r} \rangle$  and  $p = p(T')$  is the final momentum. Eq. (2.17) is of the same form as eq. (2.4) with  $\langle \bar{r} \rangle$  replacing  $r_0$ .

The functional relationship between changes in internal momentum and the other system variables is identical within either the sudden approximation, eq. (2.8), or the perturbation theory, eq. (2.17). An analogous situation holds in quantum mechanics where the quantum number scaling theory derived within the energy corrected sudden, ECS, approximation [12] also

results from the distorted wave Born approximation [11]. In their details, the two classical eqs. (2.8) and (2.17) are different, since in the sudden approximation a constant  $p(t)$  obtains at large  $t$ , while in the perturbative result  $p(t)$  retains a time-dependence in this limit. This feature is another implication of the fact that changes in *linear momenta* do not correspond directly to quantum state-to-state transitions. We consider this problem in section 2.3.

One feature common to both equations is the appearance of only a single internal variable in  $f$ . For a system with more internal degrees of freedom, the function  $f$  would depend upon all the other coordinates and momenta, provided the internal hamiltonian is separable in the particular  $r$  and  $p$ .

We note that previous work along these lines has been presented by Marcus and co-workers [15] and Cross [16], who used eqs. (2.8) and (2.17) to simplify dynamical calculations. By contrast, the present investigation focuses on the derivation of the scaling properties of classical dynamics as implied by these equations.

### 2.3. Classical scaling theory

The previous derivations apply to the change in internal linear momentum during the collision process. The internal energy  $\epsilon$ , and action  $I$  play a more fundamental role in characterizing the isolated molecule, and in connecting classical to quantum mechanics [7]. These are related by

$$I(\epsilon) \equiv \int p \, dr = \int [2m(\epsilon - v(r))]^{1/2} \, dr, \quad (2.18)$$

and knowledge of one then implies the other. The classical scaling relationship for internal energy changes is derived in the following pages.

We consider the final internal energy momentum and potential ( $\epsilon$ ,  $p(t)$  and  $v(t)$  respectively) and the corresponding initial values ( $\epsilon_0$ ,  $p_0(t)$  and  $v_0(t)$ ) all at the same time  $t$ . The starting point is the equation

$$\begin{aligned} p(t) &= (2m)^{1/2} [\epsilon - v(t)]^{1/2} \\ &= (2m)^{1/2} [\epsilon_0 - v_0(t) + \Delta(t)]^{1/2}, \end{aligned} \quad (2.19)$$

where

$$\Delta(t) = \epsilon - v(t) - [\epsilon_0 - v_0(t)]. \quad (2.20)$$

Expanding eq. (2.19) in  $\Delta(t)$ , we find to lowest order in  $\Delta(t)$ ,

$$p(t) - p_0(t) = (2m)^{1/2} \Delta(t) / 2[\epsilon_0 - v_0(t)]^{1/2}. \quad (2.21)$$

This equation can be connected to the previous scaling of linear momentum in eqs. (2.8) and (2.17) (or even the general equation (2.4)). The connection is not identical in both cases due to the different time-dependences in the sudden and perturbative limits, but the resulting scaling theory is identical.

In the sudden limit,  $v(t)$  and  $v_0(t)$  are the same since the coordinate does not change. Evaluation of eq. (2.21) at long times and use of eq. (2.8) leads to

$$f(P_0, L_0, r_0) = (2m)^{1/2} \frac{\epsilon - \epsilon_0}{2[\epsilon_0 - v(r_0)]^{1/2}}. \quad (2.22)$$

In the perturbative limit, we evaluate eq. (2.21) at some long time which is an integral number of periods of the initial motion. However,  $\Delta(t)$  does not become simply  $\epsilon - \epsilon_0$  in this limit since changes in the coordinate do occur in the perturbation theory description. In fact, any change in internal energy should be distributed between the kinetic and potential energy terms. Since the internal motion is nearly free on a collision time scale, the classical virial theorem [14] determines the partitioning. Then,

$$f(P_0, L_0, \langle \bar{r} \rangle) = (2m)^{1/2} \frac{\bar{T} - \bar{T}_0}{2[\epsilon_0 - v(r_0)]^{1/2}}, \quad (2.23a)$$

where the average internal kinetic energy is given by

$$\bar{T} = \frac{1}{2} \overline{dv(r)/dr}. \quad (2.23b)$$

Eqs. (2.22) and (2.23) are similar in form, and correspond to different internal energy partitioning. For the harmonic oscillator where  $\bar{T} = \epsilon/2$  this reduces to a simple scale change, and the functional dependence of the energy transfer on the initial internal energy and coordinate is identical. In general this will not be the

case and we expect eq. (2.23) to more accurately describe vibrationally inelastic processes. For this reason, the specific analysis and examples will be based upon eq. (2.23). However, we emphasize the most important physical ramification of both equations is that the energy transfer is not independent of the initial internal energy. A similar statement holds for the change in the action.

All the variables in eq. (2.23) pertain solely to the molecular system except  $f$ , which depends upon both translational and internal variables. This unknown dependence of  $f$  on  $\langle \bar{r} \rangle$  does not rigorously allow for a scaling relationship to be derived based upon eq. (2.23). If  $f$  is weakly dependent on or even independent of  $\langle \bar{r} \rangle$ , then a classical scaling theory results. Such an assumption will hold in two typical situations. First, when a first-order Taylor series of the intermolecular potential, i.e.

$$V(\mathbf{R}, r) \approx V(\mathbf{R}, r_c) + (r - r_c) \left. \frac{\partial V(\mathbf{R}, r)}{\partial r} \right|_{r=r_c},$$

is accurate, then  $f$  depends upon  $\langle \bar{r} \rangle$  only through the variation of the trajectory with  $\langle \bar{r} \rangle$  in eq. (2.15). Second, when the potential is locally exponential around the turning point, i.e.

$$V(\mathbf{R}, r) = L^2/2\mu R^2 + V(\mathbf{R}, r) \\ \approx V_0 \exp[\alpha(R - R_T)] \exp(\alpha' r),$$

then the trajectory is modified such that  $V_0 \exp(\alpha' r)$  becomes the translational kinetic energy and  $f$  is just  $\alpha'$  times the potential. These two cases should adequately characterize vibrational transitions.

Making the simplest assumption that  $f$  is independent of  $\langle \bar{r} \rangle$  leads to a zeroth order classical scaling theory. After suppression of the translation coordinate variables in  $f$ , we find

$$g^{(0)} = (\bar{T}_0 - \bar{T})/[\varepsilon_0 - v(r_0)]^{1/2}, \quad (2.24)$$

where the definition  $f(P_0, \mathbf{L}_0) = -(2m)^{1/2} g^{(0)}/2$  has been made. The generalization of eq. (2.24) to the situation where the  $\langle \bar{r} \rangle$  and  $p_0$  dependence is weak but non-zero is quite straightforward and simply consists of replacing the left

hand side of eq. (2.24) by the first order Taylor series in  $\langle \bar{r} \rangle$  and  $p_0$ , i.e. make the transformation  $g^{(0)} \rightarrow g^{(0)} + \langle \bar{r} \rangle g^{(1)} + p_0 g^{(2)}$ . We expect that these generalizations will be more important than the inclusion of higher order factors in  $\bar{T}_0 - \bar{T}$  in eq. (2.24); the results in the next section indicate that the quadratic factor never makes more than a few percent contribution. It is clear that the  $g^{(i)}$  are functions of both the translational and angular momenta. Most importantly,  $g^{(i)}$ ,  $i = 1, 2, 3$ , are all constant for a specific initial kinetic energy and impact parameter. This fact combined with the sudden approximation derivation indicates that only *deexcitation processes* should be considered – with excitations treated using time-reversal symmetry. (See the note added in proof and ref. [17] for the lifting of this restriction.)

Eq. (2.24) and its generalizations are the central results of this article since they constitute a classical scaling relationship for the internal energy changes. For example, using eqs. (2.24) and (2.23b) and given  $g^{(0)}$ , we can determine all the energy changes for every initial energy and coordinate. Conversely, any non-zero energy change in one initial configuration, i.e.  $\varepsilon_0$  and  $r_0$ , suffices to determine  $g^{(0)}$ , and thus all other internal energy changes for the same kinetic energy and impact parameter. Furthermore, eq. (2.24) can be combined with any quasiclassical theory (based upon internal energy or action variations) in order to provide a quantum number scaling theory appropriate to the particular theory. We emphasize that although eq. (2.24) will lead to such individual classical scaling theories, particular theories and types of classical information may be less sensitive to the assumptions in the derivation. Thus, testing of each scaling relationship will generally be necessary.

An initial example of the utility and accuracy of the scaling relationship in eq. (2.24) is presented in the next section for the commonly used histogram quantization procedure. In another article [17], we show how such scaling relationships lead to a detailed solution to the extraction of state-to-state vibrational transition probabilities from classical energy moments.

### 3. Quasiclassical histogram scaling

The transition probability from an initial quantum state  $n$  to a final state  $n'$  is defined for each initial coordinate  $r_0$  (and implicitly for each direction + or - of the momentum) as [3-5]

$$P_{n \rightarrow n'}(r_0) = 1, \quad E(n' - 1/2) \leq \varepsilon \leq E(n' + 1/2), \\ = 0, \quad \text{otherwise.} \quad (3.1)$$

Throughout this section we use the notation that  $E(y)$  is the internal energy for any value of  $y$  and  $\varepsilon$  is the final classical internal energy. The physically meaningful transition probability is simply a phase space average of  $P_{n \rightarrow n'}(r_0)$  over the distribution of  $r_0$ -values. Thus,

$$P_{n \rightarrow n'} = N_n^{-1} \int_{r_<}^{r_>} P_{n \rightarrow n'}(r_0) W_n(r_0) dr_0, \quad (3.2)$$

where the unnormalized classical position distribution function is [18]

$$W_n(r_0) = [E(n) - v(r_0)]^{-1/2}, \quad (3.3)$$

and, due to the two momentum directions,

$$N_n = 2 \int_{r_<}^{r_>} W_n(r_0) dr_0. \quad (3.4)$$

Here,  $r_>$  and  $r_<$  are the inner and outer classical turning points for the quantum state  $n$ .

The value of  $P_{n \rightarrow n'}(r_0)$  in eq. (3.2) will be unity only over a certain set of ranges of  $r_0$ -values. Letting these be symbolized by  $[r_1, r_2]$ ,  $[r_3, r_4], \dots, [r_{2m-1}, r_{2m}]$ , we rewrite eq. (3.2) in the equivalent form

$$P_{n \rightarrow n'} = N_n^{-1} \sum_{i=1}^m \int_{r_{2i-1}}^{r_{2i}} W_n(r_0) dr_0. \quad (3.5)$$

Eq. (3.5) clearly shows that the determination of the number and range of the  $r_i$  is "all" that is necessary to implement the histogram quantization procedure. These are provided by the classical internal energy scaling theory in eqs. (2.23b) and (2.24) as explained in the following sections.

To simplify the discussion, we make the following transformation of variables

$$v(r_0) = E(n) \sin^2 \theta, \quad (3.6)$$

which ensures that the range of contributing values is symmetric through the  $\theta = 0$  minimum. Substitution of eq. (3.6) into eq. (2.24) yields

$$g^{(0)} = [\bar{T}(E(n)) - \bar{T}(\varepsilon)]/E(n)^{1/2} \cos \theta, \quad (3.7a)$$

where the dependence of  $\bar{T}$  on the total internal energy is shown explicitly. Eq. (3.7a) can be solved for  $T(\varepsilon)$  to give

$$\bar{T}(\varepsilon) = \bar{T}(E(n)) - g^{(0)} E(n)^{1/2} \cos \theta. \quad (3.7b)$$

For deexcitation processes, the inequality  $E(n' + 1/2) \geq \varepsilon$  implies a maximum value  $\theta_{\max} < \pi/2$ , and the inequality  $E(n' - 1/2) \leq \varepsilon$  implies a minimum value  $\theta_{\min} \geq 0$ . More precisely,

$$\bar{T}(E(n' + 1/2)) = \bar{T}(E(n)) - g^{(0)} E(n)^{1/2} \cos \theta_{\max} \quad (3.8a)$$

and

$$\bar{T}(E(n' - 1/2)) = \bar{T}(E(n)) - g^{(0)} E(n)^{1/2} \cos \theta_{\min}, \quad (3.8b)$$

with the restrictions

$$n' < n \quad (3.8c)$$

and

$$0 \leq \theta_{\min} \leq \theta_{\max} \leq \pi/2. \quad (3.8d)$$

Eqs. (3.8a)–(3.8d) show that the ranges  $[\theta_{\min}, \theta_{\max}]$  and  $[-\theta_{\max}, -\theta_{\min}]$  contribute to the histogram transition probability  $P_{n \rightarrow n'}$ . Since only one momentum direction enters (with the other leading to excitations), the integral in eq. (3.5) becomes

$$P_{n \rightarrow n'} = N_n^{-1} 2E(n)^{1/2} \int_{\theta_{\min}}^{\theta_{\max}} \sin \theta \left( \frac{dv(r_0)}{dr_0} \right)^{-1} d\theta. \quad (3.9)$$

This equation and eqs. (3.8a)–(3.8d) provide the quantum number variation of  $P_{n \rightarrow n'}$  for deexcitation processes at the *same initial kinetic energy*. One simply utilizes a very restricted set of input  $P_{n_1 \rightarrow n'_1}$  to determine  $g^{(0)}$  which then generates all other  $P_{n \rightarrow n'}$ . Some of these may be zero, i.e. classically forbidden, if  $g^{(0)}$  is so small that  $\theta_{\max} = 0 = \theta_{\min}$ .

The simplest input set is any single non-zero  $P_{n \rightarrow 0}$ , since  $\theta_{\min} = 0$  when  $n' = 0$  as the final

energy cannot be less than  $E(-1/2) = 0$ ; then only  $\theta_{\max}$  needs to be found from eq. (3.9) and this generates  $g^{(0)}$  through eq. (3.7a) with  $n = \bar{n}$  and  $\varepsilon = E(1/2)$ . A more complicated input set is  $P_{n \rightarrow n-\Delta}$ ,  $\Delta = 1, 2, \dots, l$ , where  $l$  is the largest value for which the probability is non-zero; then  $\theta_{\min}$  for  $P_{n \rightarrow n-1}$  becomes  $\theta_{\max}$  for  $P_{n \rightarrow n-2}$  etc., and this suffices to determine the appropriate  $\theta_{\max}$  and  $\theta_{\min}$ , which then yield  $g^{(0)}$ . Combinations of these input sets are also feasible, but it is important to emphasize that the basic problem is finding a set of consistent  $\theta_{\min}$  and  $\theta_{\max}$  values. By contrast, higher order scaling relationships based upon  $g^{(0)} + \langle \bar{r} \rangle g^{(1)} + p_0 g^{(2)}$  require more than one input probability to determine  $g^{(0)}$ ,  $g^{(1)}$  and  $g^{(2)}$ . We will not pursue this further since the analysis of energy transfer moments will be shown to provide more direct solutions for the higher order scaling theories.

For the initial application of the scaling theory, we consider the harmonic oscillator-atom collision system. With all energies in units of  $\hbar\omega$ , the necessary formulas are

$$v(r_0) = \frac{1}{2} \hbar^{-1} m \omega (r_0 - r_c)^2, \quad (3.10a)$$

$$E(y) = y + \frac{1}{2} \quad (3.10b)$$

and

$$\bar{T}(E(y)) = E(y)/2, \quad (3.10c)$$

where  $r_c$  is the potential minimum. Using eqs. (3.6) and (3.10), the integral in eq. (3.9) can be evaluated with the result

$$P_{n \rightarrow n}^{(\text{HO})} = \pi^{-1} (\theta_{\max} - \theta_{\min}), \quad (3.11)$$

where  $\theta_{\max}$  and  $\theta_{\min}$  still satisfy eqs. (3.8) with eqs. (3.10b) and (3.10c) providing the internal energies. Clearly, input of  $P_{n \rightarrow 0}^{(\text{HO})}$  at a single impact parameter and at a given kinetic energy determines  $\theta_{\max}$  which then determines  $g^{(0)}$ . If the transition probability  $P_{n \rightarrow n-\Delta}$  is sufficiently small so that  $\theta_{\min} = 0$ , then eqs. (3.11) and (3.8a) yield the extremely simple scaling relationship,

$$(n_1 + 1/2)^{1/2} \cos(\pi P_{n_1 \rightarrow n_1 - \Delta}^{(\text{HO})}) \\ = (n_2 + 1/2)^{1/2} \cos(\pi P_{n_2 \rightarrow n_2 - \Delta}^{(\text{HO})}). \quad (3.12)$$

The transition probabilities for the collinear  $\text{H}_2\text{-(Br}_2\text{)}$  system [19] are shown in table 1. The

Table 1

Quasiclassical histogram transition probabilities: scaling analysis for the collinear atom-harmonic oscillator system,  $(\text{H}_2\text{)-Br}_2^a)$

$E_k$ <sup>b)</sup>	Transition	QCH <sup>c)</sup>	Scaling prediction <sup>d)</sup>	Exact quantum <sup>e)</sup>
1.5	1-0	cf <sup>f)</sup>	cf	3.45-2
	2-1	1.07-1	(input) <sup>g)</sup>	6.81-2
	3-2	2.15-1	2.06-1	9.86-2
	4-3	2.76-1	2.52-1	1.27-1
	5-4	3.23-1	2.80-1	- <sup>h)</sup>
2.5	1-0	9.23-2	(input)	5.77-2
	2-1	2.46-1	2.34-1	1.09-1
	3-2	3.01-1	2.84-1	1.54-1
	4-3	3.38-1	3.13-1	-
	5-4	3.53-1	3.48-1	2.26-1
3.5	1-0	2.00-1	(input)	7.92-2
	2-1	2.76-1	2.84-1	1.46-1
	3-2	3.23-1	3.22-1	-
	4-3	3.53-1	3.45-1	2.44-1
	5-4	3.69-1	3.61-1	3.05-1

<sup>a)</sup> The system parameters for the dynamical calculations are given in ref. [16].

<sup>b)</sup> Kinetic energy in units of  $\hbar\omega$  in the initial state.

<sup>c)</sup> Quasiclassical histogram transition probability generated from trajectory calculations utilizing 64 trajectories.

<sup>d)</sup> Scaling predictions based upon eqs. (3.9), (3.10b), (3.10c) and (3.11). The scaling solution reduces to eq. (3.12) for the  $\Delta = 1$  transitions. The scaling theory predicts that *all quanta changes of more than one are classically forbidden* for all the initial states and energies presented here; this agrees perfectly with the dynamical calculations.

<sup>e)</sup> Exact quantum result from ref. [19].

<sup>f)</sup> Classically forbidden.

<sup>g)</sup> The QCH transition probability is used as input to the scaling.

<sup>h)</sup> Transition not reported in ref. [19].

single quanta deexcitation probabilities are sufficiently small so that  $\theta_{\min} = 0$  for all initial states. The scaling relationship in eq. (3.8) reduces to eq. (3.12) for  $\Delta = 1$ , while the multiquanta transitions are predicted to be classically forbidden for all the kinetic energies and initial states in table 1. The quantitative agreement for the  $P_{n \rightarrow n-1}$  is very good, and the predictions of classically forbidden transitions are perfect. The latter feature is especially interesting since there is no a priori reason to believe that  $P_{n \rightarrow n-1}$  alone implies anything



about  $P_{n \rightarrow n-2}$  etc.; the classical scaling analysis provides the intimate relationship. The exact quantal  $P_{n \rightarrow n-1}$  are shown in table 1 to illustrate the different quantum number variation of quantum and quasiclassical histogram transition probabilities. Finally, we note that the quadratic expansion term of eq. (2.19),  $-\Delta(r)^2/[\epsilon_0 - v(r_0)]^2$ , was included in order to investigate the importance of such higher order contributions to the scaling; the resulting more complex scaling theory leads to the same results to five significant figures as those based upon eq. (3.8).

The transition probabilities for the collinear  $H_2$ -He system [19] are shown in table 2. The results are not as quantitatively accurate as for the  $Br_2$ -( $H_2$ ) system, and some differences between the first order and second order scaling theories do appear. However, all the qualitative trends are correctly described including the increase and then decrease of  $P_{n \rightarrow n-1}$  as  $n$  increases, the particular classically forbidden processes and especially the classically allowed  $P_{4 \rightarrow 2}$  transition at  $E_k = 2.5$ . Closer inspection shows that the scaling results decrease in accuracy as the collision energy increases and that the first order scaling is usually better than second order scaling. Both these features are related to the fact that the  $H_2$ -He system is non-perturbative but also non-sudden; in other words, the time-scales for the collision and the internal vibrational motion are comparable. Thus, a more complex scaling theory (see ref. [17] and the note added in proof) should be utilized, and the better accuracy of the first order solution for the simple scaling using only  $g^{(0)}$  is not meaningful. Lastly, note the exact quantal values do not follow the same trend as the classical ones, but the difference between the magnitudes of the QCH and exact quantal transition probabilities is smaller for this system than for the  $Br_2$ -( $H_2$ ) system.

A more complex illustration involves the atom-Morse oscillator collision system defined, in units of  $\hbar\omega$ , by the formulas

$$v(r_0) = D\{1 - \exp[\alpha(r_0 - r_e)]\}^2 \quad (3.13a)$$

and

$$E(y) = (y + 1/2) - (y + 1/2)^2/4D, \quad (3.13b)$$

where  $r_e$  is the potential minimum. The virial theorem in eq. (2.23b) is slightly more difficult to implement, but the result is still analytic:

$$\begin{aligned} \bar{T}(E(y)) &= D[1 - E(y)/D]^{1/2} \\ &\times \{1 - [1 - E(y)/D]^{1/2}\}. \end{aligned} \quad (3.13c)$$

Using eqs. (3.6) and (3.13) the integral in eq. (3.9) can be evaluated with the result

$$\begin{aligned} P_{n \rightarrow n}^{(MO)} &= 2\pi^{-1} \{ \arctan [(\tan(\theta_{\max}/2) - \alpha_n)/\beta_n] \\ &\quad - \arctan [(\tan(\theta_{\min}/2) - \alpha_n)/\beta_n] \}, \end{aligned} \quad (3.14a)$$

where

$$\alpha_n = [E(n)/D]^{1/2} \quad (3.14b)$$

and

$$\beta_n = (1 - \alpha_n^2)^{1/2} = 1 - (n + 1/2)/2D. \quad (3.14c)$$

Here,  $\theta_{\max}$  and  $\theta_{\min}$  satisfy eq. (3.8) with eqs. (3.13b) and (3.13c) providing the internal energies.

The transition probabilities for the collinear He- $H_2$  Morse oscillator system [19] are shown in table 3. The scaling predictions, using the Morse oscillator eqs. (3.13b) and (3.14), are generally accurate to better than 20% and predict all the qualitative features correctly. In contrast, the approximate treatment of this system by the harmonic oscillator scaling eqs. (3.10b) and (3.11) leads to considerably less accurate qualitative and quantitative results. This is an important point since it clearly implies that the Morse oscillator system does not simply correspond to the harmonic system with reduced transition probabilities. Furthermore, even the approximation of the Morse oscillator virial result in eq. (3.13c) by the harmonic oscillator eq. (3.10c), retaining all other variables appropriate to the Morse system, leads to a worsening of the scaling predictions; most evident are the predictions that  $P_{4 \rightarrow 3}$  is classically allowed at  $E_k = 1.560$  and that  $P_{5 \rightarrow 3}$  is classically forbidden at  $E_k = 3.560$ . This indicates that even the partitioning of internal energy between the kinetic and potential energies strongly influences the dynamics. Finally, we should emphasize that as in the harmonic  $H_2$ -He system, the quantitative

Table 2  
 Quasiclassical histogram transition probabilities: scaling analysis for the collinear atom-harmonic oscillator system, He-H<sub>2</sub><sup>a)</sup>

$E_k$ <sup>b)</sup>	Transition	QCH <sup>c)</sup>	Scaling predictions		
			first order <sup>d)</sup>	second order <sup>e)</sup>	exact quantum <sup>f)</sup>
1.5	1-0	cf <sup>a)</sup>	cf	cf	2.95-2
	2-1	cf	cf	cf	5.50-2
	2-0	cf	cf	cf	2.04-3
	3-2	cf	cf	cf	7.70-2
	3-1	cf	cf	cf	5.39-3
	4-3	1.40-1	(input) <sup>h)</sup>	(input)	9.60-2
	4-2	cf	cf	cf	9.55-3
	5-4	2.31-1	1.95-1	1.95-1	- <sup>i)</sup>
	5-3	cf	cf	cf	-
2.5	1-0	3.10-1	(input)	(input)	1.33-1
	2-1	3.90-1	3.57-1	3.57-1	2.17-1
	2-0	cf	cf	cf	2.25-2
	3-2	4.40-1	3.80-1	3.80-1	2.68-1
	3-1	cf	cf	cf	5.24-2
	4-3	3.23-1	3.21-1	2.54-1	-
	4-2	1.38-1	7.30-2	1.41-1	-
	5-4	2.50-1	2.48-1	2.10-1	3.12-1
	5-3	2.50-1	1.57-1	1.95-1	1.09-1
3.5	1-0	3.90-1	(input)	(input)	2.94-1
	2-1	3.10-1	2.04-1	1.51-1	3.69-1
	2-0	1.70-1	2.11-1	2.65-1	9.13-2
	3-2	2.15-1	1.61-1	1.21-1	-
	3-1	3.08-1	2.68-1	1.66-1	-
	4-3	1.70-1	1.37-1	1.05-1	3.04-1
	4-2	2.50-1	2.33-1	1.25-1	2.21-1
	5-4	1.38-1	1.21-1	9.30-1	-
	5-3	1.85-1	1.67-1	1.06-1	-

<sup>a)-c)</sup> See table 1.

<sup>d)</sup> Scaling predictions based upon eqs. (3.9), (3.10b), (3.10c) and (3.11).

<sup>e)</sup> Scaling predictions including the quadratic term,  $[E(n) = \epsilon]^2/8 E(n)^{3/2} \cos^3 \theta$ , in eqs. (3.7) and (3.8), which follows from eq. (2.19). <sup>f)</sup> Exact quantum result from ref. [19]. <sup>g)</sup> Classically forbidden.

<sup>h)</sup> The QCH transition probability is used as input to the scaling. <sup>i)</sup> Transition probability not reported in ref. [19].

accuracy of the Morse scaling decreases at the higher energies due to the comparable time scale for the collisional and internal motion.

#### 4. Summary and conclusion

The general results of this article pertain to the change in the classical internal molecular variables,  $p$  and  $r$ , during a collision. These can be summarized in two statements. First, the internal momentum *transfer* is a weak function

of the initial internal momentum and coordinate. Second, and following from the first, the internal energy transfer is a known strong function of the initial internal energy and coordinate but only a weak function of the initial momentum. The preponderance of the development in section 2 was designed to show that these statements follow from Hamilton's equations when the time-scales for internal motion and collisional interactions differ substantially. In addition, these statements were cast into a simple mathematical formalism,

Table 3  
Quasiclassical histogram transition probabilities: scaling analysis for the collinear atom-Morse oscillator system, He-H<sub>2</sub> <sup>a)</sup>

$E_k$ <sup>b)</sup>	Transition	QCH <sup>c)</sup>	Scaling predictions		
			Morse <sup>d)</sup>	harmonic virial <sup>e)</sup>	harmonic <sup>f)</sup>
1.560	1-0	cf <sup>g)</sup>	cf	cf	cf
	2-1	cf	cf	cf	cf
	3-2	cf	cf	cf	cf
	4-3	cf	cf	1.14-1	1.48-1
	5-4	2.00-1	(input) <sup>h)</sup>	(input)	(input)
2.560	1-0	cf	cf	cf	cf
	2-1	1.38-1	(input)	(input)	(input)
	3-2	2.77-1	2.92-1	2.53-1	2.22-1
	4-3	3.54-1	3.92-1	3.21-1	2.64-1
	5-4	4.00-1	4.77-1	3.71-1	2.90-1
3.560	1-0	1.69-1	(input)	(input)	(input)
	2-1	3.23-1	3.35-1	3.08-1	2.67-1
	3-2	3.69-1	4.28-1	3.81-1	3.09-1
	4-3	4.00-1	5.01-1	4.32-1	3.34-1
	4-2	cf	cf	cf	cf
	5-4	2.31-1	3.87-1	4.73-1	3.51-1
	5-3	1.85-1	1.79-1	cf	cf

<sup>a)-c)</sup> See table 1.

<sup>d)</sup> Scaling predictions based upon the full Morse scaling in eqs. (3.8), (3.13b), (3.13c) and (3.14). The Morse parameter  $D = 9.3$ .

<sup>e)</sup> Scaling predictions based upon replacement of the Morse virial relationship eq. (3.13c) by the harmonic virial eq. (3.10c). All energies and the probability integral are given by the Morse eqs. (3.13b) and (3.14) respectively.

<sup>f)</sup> Scaling prediction based upon replacing the Morse oscillator by a harmonic oscillator and using eqs. (3.8), (3.10b), (3.10c) and (3.11). <sup>g)</sup> Classically forbidden. <sup>h)</sup> The QCH transition probability is used as input to the scaling.

which to a good approximation characterizes the systematics of classical dynamics.

A detailed illustration of the use of this formalism was presented for the commonly applied quasiclassical histogram technique. The results for both Morse and harmonic oscillators showed that any *single* non-zero transition probability  $P_{n \rightarrow n'}$  contains essentially all information necessary to generate the entire remaining probabilities, at the same initial translational kinetic energy. This predictive ability extended even to the determination of those transitions which were classically forbidden.

That the systematics of classical trajectory calculations can be described by any scaling formalism is quite surprising. This is especially true because of the fact that there exist dynamically forbidden but energetically allowed transitions; hence, any analysis based upon dis-

tribution functions which are constrained only by energetics must fail. Another difficulty involves the local nature of classical mechanics which implies that different regions in phase space can be sampled by different initial states. The results of this article clearly indicate that such difficulties are not insurmountable, and that even an extremely simple classical scaling theory accurately describes the classical dynamics of non-reactive collisions for systems with one internal degree of freedom.

The scaling of quasiclassical histogram vibrational transition probabilities in section 3 can be utilized to reduce the effort in trajectory calculations. The combination of the energy scaling equation with other quasiclassical procedures can provide similar reductions. More interesting from a fundamental standpoint would be the investigation of the various quantum number scaling theories implied by the different

quantization procedures [3–8]; comparisons among the different theories and to the known quantal scaling theory [12] (within its range of validity) may indicate a particular theory or extension thereof which most accurately describes the qualitative trends of quantum mechanical calculations. Extensions of the present energy scaling to systems with more than a single internal degree of freedom also need to be considered. Perhaps it is worthwhile

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### Note added in proof

A general derivation of classical scaling relationships has been discovered based upon replacement of functional derivatives by ordinary derivatives. This work [17] lifts essentially all of the restrictions on the present scaling relationship except that reactive processes are still excluded. In addition, the more general relationship reduces to eq. (2.24) of the present article when the first *total* moment of the average kinetic energy change, i.e.  $\langle \bar{T} - \bar{T}_0 \rangle$ , is small.

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