to discuss the present results any further.

Acknowledgment. This research has been supported by the Department of Energy (Office of Basic Energy Sciences) Contract EY-76-S-03-0034 Project Agreement No. 217.

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Semiclassical Comparison of Quasi-Classical and Quantum Moments of Distribution of States in Molecular Collisions

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(Received October 10, 1978)

Publication costs assisted by the California Institute of Technology

State-to-state transition probabilities for molecular collisions are often computed from classical trajectories by equating quasi-classical and quantum moments of the final energy distributions and using some functional form to relate the transition probabilities to the quantum moments. The equality between quantum and quasi-classical moments in examined using semiclassical theory.

Introduction

The semiclassical theory of inelastic and reactive collisions[1,2] has been used both qualitatively, providing insight into the validity of classical trajectories for treating such collisions, and quantitatively. In the latter, transition probabilities have been calculated. The computation involves (1) the evaluation of integrals, (2) multidimensional root searches, or (3), via the added approximation of partial averaging,[3] one-dimensional root searches. In cases (2) and (3) the search is for classical trajectories leading from the initial to the desired final quantum number(s). In applications to real systems thus far, the third method has apparently been the one principally used.[3,4]

Another method of using classical trajectories first selects the trajectories in a quasi-classical manner, the initial action variables chosen in a discrete way and the initial conjugate angle variables (phases) chosen in a uniform way, in conformity with WKB (semiclassical) theory. One next assumes that the quasi-classical and quantum moments of a distribution of final averages (of energies of each degree of freedom, usually) are equal, an assumption which has been tested in some cases where exact results are available.[5] Some functional form or model is then used for the transition probabilities to evaluate the parameters from the moments. Typically, the number of moments used is small (one to three).[6] When the number of importantly contributing transitions is comparable to the number of moments, the method can be reasonably accurate. Its usefulness for the remaining transitions then depends on the correctness of the assumed functional form. In the present article semiclassical theory is used to compare quasi-classical and quantum moments of quantum numbers and their classical analogues. (These numbers are more precisely defined than "energies of the individual degrees of freedom"; the latter assume additivity of such "energies".) In some cases averages of absolute values rather than moments have been equated. We do not consider this procedure here. The justification given below for approximately equating the moments is based on analytic functions of operators and so does not treat absolute values. Application of the moment method is made elsewhere to vibrational–vibrational transfer.[7,8]

† Contribution No. 5898.

Semiclassical Calculation of Moments

The collisional cross section is given by (1) for transition from quantum numbers whose totality is denoted by n to final values n', regardless of any changes in the remaining quantum numbers, collectively denoted by m:

$$\sigma_{n'n} = \frac{\pi}{k^2}\sum_m p_{n'n}(m)\rho_m \tag{1}$$

where k is the wave number associated with the initial relative velocity $v(k = \mu v/\hbar)$; $p_{n'n}(m)$ is the probability of the $n \rightarrow n'$ transition for given values of the other quantum numbers m, summed over all final values m'; $p_{n'n}(m)$ depends on k; and ρ_m is the probability of being in the state m.

The corresponding state-to-state rate constant $k_{n'n}$ is

$$k_{n'n} = \int_0^\infty v\sigma_{n'n}\, 4\pi k^2\rho_k\, \mathrm{d}k \tag{2}$$

where $4\pi k^2\rho_k\, \mathrm{d}k$ is the Maxwell–Boltzmann probability of finding the system in $(k, k + \mathrm{d}k)$.

The probability $p_{n'n}(m)$ is given by

$$p_{n'n}(m) = \sum_{m'}|S_{n'm'nm}|^2 \tag{3}$$

where $S_{n'm'nm}$ is an S-matrix element. Part of the sum over m in (1) yields a degeneracy $2l + 1$, since the value of

0022-3654/79/2083-0944$01.00/0

$\sum_{m'}|S_{n'm'nm}|^2$ is independent of the m_l present in the "totality" m (l is the orbital quantum number for relative motion, m_l is its z projection, and ρ_m is the same for each m_l in $-l \leq m_l \leq l$.) The sum over m includes also a sum over l from 0 to ∞. $S_{n'm'nm}$ is given semiclassically by[1,2]

$$S_{n'm'nm} = \int \Phi^{0*}_{n'm'}(\bar{w})\ \Psi^{(+)}_{nm}(\bar{w})\ \mathrm{d}\bar{w} \tag{4}$$

where $\Psi^{(+)}_{nm}(\bar{w})$ is a semiclassical wave function for the collision, expressed in terms of reduced angle coordinates whose totality is denoted by $\bar{w}$. There are $N-1$ such coordinates in a collision involving N coordinates, the Nth coordinate being time.[1] $\Phi^0_{n'm'(\bar{w})}$ is the unperturbed function in these $N-1$ coordinates for a system in final state $n'm'$. (The usual variables are the $N-1$ angle variables w and the radial coordinate R, but a canonical transformation[1] converts these to $\bar{w}$ (conjugate to final classical quantum numbers $\bar{n}$) and time t and to $\bar{w}^0$ (conjugate to initial classical quantum numbers n) and time t. $\mathrm{d}\bar{w}$ denotes a product $\Pi_i \mathrm{d}\bar{w}_i$, $i = 1$ to $N-1$. $\Psi^+_{nm}(\bar{w})$ and $\Phi^0_{n'm}(\bar{w})$ have the following form, semiclassically

$$\Phi^0_{n'm}(\bar{w}) = \exp(2\pi i n'\bar{w} + 2\pi i m'\bar{w}) \tag{5}$$

$$\Psi^+_{nm}(\bar{w}) = (\det \partial\bar{w}/\partial\bar{w}^0)^{-1/2} \exp(i\varphi) \tag{6}$$

where $n'\bar{w}$ and $m'\bar{w}$ denote $\sum_i n_i'\bar{w}_i$ and $\sum_j m_j'\bar{w}_j$, respectively (i.e., sums over the relevant coordinates), the determinant is $N-1 \times N-1$, and the phase φ of the semiclassical wave function has the property that

$$(1/2\pi)\partial\varphi/\partial\bar{w} = \bar{n}\varphi \tag{7}$$

$\bar{n}$ is the final value of the classical analogue of a quantum number (an actionlike variable) for the trajectory which begins at (n,m) and ends at $\bar{w}$.

The quantum mechanical average value of any function of n', $\mathrm{f}(n')$ for thermally averaged collisions for a given initial state n, is

$$\langle \mathrm{f} \rangle = \sum_{n'} \int_0^\infty \mathrm{f}(n')\ v\sigma_{n'n} 4\pi k^2 \rho_k\ \mathrm{d}k / \sum_{n'} k_{n'n} \tag{8}$$

where $k_{n'n}$ is given by (2).

In the semiclassical $\bar{w}$ representation, an actionlike operator $\mathbf{n}$ canonically conjugate to $\bar{w}$ is $(1/2\pi i)\partial/\partial\bar{w}$,[9] i.e.

$$\mathbf{n} \equiv (1/2\pi i)\partial/\partial\bar{w} \tag{9}$$

Thereby, from (5) and (9) we have

$$\mathrm{f}(\mathbf{n})\ \Phi^0_{n'm}(\bar{w}) = \mathrm{f}(n')\ \Phi^0_{n'm}(\bar{w}) \tag{10}$$

From (1), (3), (4), (8), and (10), we have

$$\langle \mathrm{f} \rangle = \sum_{n'm'm} \int \langle \Psi^+_{nm} | \Phi^0_{n'm'} \rangle \times \langle \mathrm{f}(\mathbf{n})\ \Phi^0_{n'm} | \Psi^+_{nm} \rangle \rho_m v 4\pi k^2 \rho_k\ \mathrm{d}k / \sum_{n'} k_{n'n} \tag{11}$$

The Hermitian operator $\mathrm{f}(\mathbf{n})$ may be transposed in (6) so as to act on the last Ψ^+_{nm}. Using the closure relation (discussed below) for $\Phi^0_{n'm'}$ one then obtains

$$\langle \mathrm{f} \rangle = \sum_m \int \langle \mathrm{f}(\mathbf{n}) \rangle_{mk} \rho_m v 4\pi k^2 \rho_k\ \mathrm{d}k / \sum_{n'} k_{n'n} \tag{12}$$

where

$$\langle \mathrm{f}(\mathbf{n}) \rangle_{mk} = \langle \Psi^+_{nm} | \mathrm{f}(\mathbf{n}) | \Psi^+_{nm} \rangle \tag{13}$$

The dependence of $\langle \mathrm{f} \rangle_{mk}$ on n is suppressed in the notation.

When n' and m' belong to the set of positive and negative integers, the eigenfunctions $\exp(2\pi i n'\bar{w} + 2\pi i m'\bar{w})$ form a complete set on the unit interval of the $\bar{w}'$ so one can see from (4)–(6) and (15) below that the semiclassical $\sum|S_{m'n'mn}|^2$ summed over m' and n' equals unity. In some cases one or more of the n' and m' is restricted to nonnegative values (e.g., n' for vibrations or total angular momenta), and then this $\sum|S_{m'n'mn}|^2$ is only approximately unity. Since the trajectories begin in some initial state n (and m), then provided the action variables J for such degrees of freedom do not come too close to zero, the corresponding matrix element $S_{m'n'mn}$ in (4) for negative n' (and m') has stationary phase points only at complex values of the $\bar{w}$'s; the transition is thereby "classically forbidden", the resulting matrix element is exponentially small, and the deviation of the $S_{n'm'nm}$'s from unitarity is correspondingly small. Indeed, it is precisely for those degrees of freedom having positive and negative quantum numbers that the semiclassical description in action-angle variables is exact (no classical turning points), while for the others the quantum action operator $\mathbf{J}$ was made to correspond to $(\mathbf{n} + \sigma)h$, where δ (zero in the case where n is unrestricted) was chosen to yield agreement with WKB eigenvalues.[1,9] A consequence of this approximation is seen later. Similarly, the closure relation used for the semiclassical $\Phi_{n'm'}(\bar{w})$ in obtaining (12)–(13) from (11) is exactly fulfilled when n' and m' are not restricted to positive integers. It is approximately fulfilled, when applied to (11), when they are restricted, since the $\langle \Psi^+_{nm} | \Phi^0_{n'm'} \rangle$ are exponentially small for negative integers n' or m'.

We shall write the wave function (6) as

$$\Psi^+_{nm}(\bar{w}) = A \exp(i\varphi) \tag{14}$$

On noting that

$$A^2\ \mathrm{d}\bar{w} = (\det \partial\bar{w}^0/\partial\bar{w})\mathrm{d}\bar{w} = \mathrm{d}\bar{w}^0 \tag{15}$$

one finds[10]

$$\langle \mathbf{n} \rangle_{mk} = \int_0^1 \bar{n}\ \mathrm{d}\bar{w}^0 \equiv \langle \bar{n} \rangle_c \tag{16}$$

$$\langle (\mathbf{n} - \langle \mathbf{n} \rangle_{mk})^2 \rangle_{mk} = \langle (\bar{n} - \langle \bar{n} \rangle_c)^3 \rangle_c \tag{17}$$

$$\langle (\mathbf{n} - \langle \mathbf{n} \rangle_{mk})^3 \rangle_{mk} = \langle (\bar{n} - \langle \bar{n} \rangle_c)^3 \rangle_c \tag{18}$$

where $\langle \mathrm{f} \rangle_c$ denotes the integral $\int \mathrm{f}\ \mathrm{d}\bar{w}^0$ over the unit interval and is actually a quasi-classical average (an average of the trajectory results over the initial phases $\bar{w}^0$ for given initial quantum numbers (n,m) and k). Terms of order h^2, relative to the classical terms, were neglected from the right-hand sides of (17) and (18); none were neglected in (16).[10]

Within the stated approximations one sees semiclassically from (16)–(18) that the quantum and quasi-classical average are equal. In using (15) it was also assumed that $\det \partial\bar{w}^0/\partial\bar{w}$ is nonsingular. Singularities in the preexponential factor A of semiclassical wave functions sometimes occur. They reflect a breakdown in semiclassical theory, but not necessarily in the approximate equality of quasi-classical and quantum moments.

In virtue of (16)–(18) it is useful to examine the results for an exactly soluble problem, namely, the forced oscillator problem. Here, $\bar{n}$ depends on $\bar{w}^0$ as[11]

$$\bar{n} = n + \alpha[(2n+1)/h]^{1/2} \cos 2\pi\bar{w}^0 + (\alpha^2/2h) \tag{19}$$

where α depends on the strength of the interaction of the oscillator with the time-dependent force and involves a Fourier integral of that force. The exact quantum and classical averages of n' and $\bar{n}$, respectively, have been given,[12] from which one obtains the following relations between the moments:

$$\langle n' \rangle_q = \langle \bar{n} \rangle_c \tag{20}$$

$$\langle (n' - \langle n' \rangle_q)^2 \rangle_q = \langle (\bar{n} - \langle \bar{n} \rangle_c)^2 \rangle_c \tag{21}$$

$$\langle (n' - \langle n' \rangle_q)^3 \rangle_q = \langle (\bar{n} - \langle \bar{n} \rangle_c)^3 \rangle_c + \alpha^2/2h \quad (22)$$

where $\langle f(n') \rangle_q$ denotes $\sum f(n') p^q_{n'n}$, the sum being over all n', $p^q_{n'n}$ being the quantum mechanical probability for the transition $n \rightarrow n'$. Comparison shows that eq 16–18 are in error only in the case of the third moment result (18), and that the error is of the order of $\alpha^2/2h$. Equation 22 suggests, since $\langle \bar{n} - n \rangle_c$ for this problem is $\alpha^2/2h$ (as one can see directly from (19)) that instead of equating quantum third moments $\langle \bar{n} - n \rangle_c$ be added to the quasi-classical one. It will be useful to have further comparison of exact classical trajectory and quantum results for other problems to test this possibility. The results in (20)–(22) are also interesting in that they apply even in the presence of a singularity of $d\bar{w}^0/d\bar{w}$. For example, trigonometric arguments for the forced oscillator problem yield[11]

$$\sin 2\pi(\bar{w}^0 - \bar{w}) = [\alpha/\{(2n + 1)h\}^{1/2}] \sin 2\pi\bar{w} \quad (23)$$

Thus, when $\alpha/[(2n + 1)h]^{1/2}$ exceeds unity $\sin 2\pi\bar{w}$ cannot reach the value of unity. In fact, as $\bar{w}^0$ increases 0 to 1, $\bar{w}$ under such conditions no longer rises from 0 to 1 but instead rises to a some value, falls back to zero, then becomes negative, and at $\bar{w}^0 = 1$ becomes zero again. Thereby, $d\bar{w}/d\bar{w}^0$ is zero at two points inside the interval (0, 1) and so $d\bar{w}/d\bar{w}^0$ is singular. This singularity does not, fortunately, affect the relations (20)–(22) between the moments.

In the semiclassical treatment of this problem, one can handle the singularity as follows. The semiclassical wave function is now the sum of two terms each of the form (6) for each value of $\bar{w}$, one drawn from the $\bar{w}^0$ region of positive $d\bar{w}/d\bar{w}^0$, the other from $\bar{w}^0$ region of negative $d\bar{w}/d\bar{w}^0$ (using terminology appropriate to the above one-dimensional problem). When the moments are calculated, and when the cross terms are neglected (they are highly oscillatory), the term arising from $\Psi^{+*}f\Psi$ then corresponds [via (15)] to one $\bar{w}^0$ interval and the other corresponds to the other $\bar{w}^0$ interval. One again obtains (16)–(18).

Until now, we have considered moments at a given m and k, via the averages $\langle \rangle_{mk}$ in (16)–(18). One then integrates over k, multiples by ρ_m, and sums over m (the latter provides the "quasi-classical" treatment for the m quantum numbers). The new averages yield overall averages for the various moments. The foregoing remarks about $\langle \rangle_{mk}$, based on (15)–(22), then apply also to the averages given by (12). Finally, in practice some of the quantum numbers in m, such as l, are quite large, and their part of the multiple sum over m is typically replaced by integrals.

In summary, we have seen that according to semiclassical theory, subject to the approximations indicated, the quasi-classical and quantum moments for changes in quantum numbers, weighted as in (12), are equal, as are those in (13). [A deviation from this equality was seen to exist, as for example in the third moment for the forced oscillator problem.[12]] Since the quasi-classical moments of the changes in quantum numbers can be evaluated from classical trajectories when one uses action-angle variables to define the initial and final states, one then has values for the quantum moments of these changes. When a particular functional form[6] is assumed for the quantum mechanical state-to-state transition probabilities or state-to-state cross sections, the quantum moments can be expressed in terms of the parameters appearing in the functional form and one can then evaluate those parameters by equating the quantum moment to the known quasi-classical ones. One thus obtains, indirectly, values for the state-to-state transition probabilities[5] and cross sections using classical trajectories.

Acknowledgment. It is a pleasure to acknowledge research support by the National Science Foundation.

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(10) For completeness, we note that integration by parts was extensively used and that the neglected term on the right side of (17) is $\int A'^2\, d\bar{w}^0$ and that on the right side of (18) is $\int 3(\bar{n} - \langle \bar{n} \rangle_c)A'^2\, d\bar{w} - \int \bar{n}''\, d\bar{w}^0$, where primes denote $d/d2\pi\bar{w}$. If one multiplies (17) by h^2, since $\langle (n - \langle n \rangle_c)^2 h^2$ is a classical quantity, $(n + \delta)h$ being a classical action variable, the added but neglected term is seen to be of order h^2. If one multiples (18) by h^3 for the same reason, then since $3(\bar{n} - \langle \bar{n} \rangle_c)h$ is a classical quantity, and $\bar{n}''h$ is also a classical quantity one sees that the neglected terms in (18) are of the order of h^2. The last term in (22), when (22) is multiplied by h^3 to obtain a classical quantity for the first term on the right side of (22), is of the order of h^2.
(11) In writing eq 19 and 23 we use Figure 1 and related text of P. Pechukas and M. S. Child, *Mol. Phys.*, **31**, 973 (1976), with somewhat different notation: our $(2\bar{n} + 1)^{1/2}$ and $(2n + 1)^{1/2}$ are their $(2n + 1)^{1/2}$ and $(2m + 1)^{1/2}$, respectively, our $2\pi\bar{w}^0$ and $2\pi\bar{w}$ are their θ and θ'. (θ' is the angle between the segments α and $(2n + 1)^{1/2}$ in Figure 1). The radius of the circle described by the phase angle θ is (in their notation) $(2m + 1)^{1/2}$. Equations 19 and 23 follow by standard trigonometry. They worked in units of $h = 1$, and in (19) and (23) we have reintroduced the h.
(12) G. Schatz, F. J. McLafferty, and J. Ross, ref 5, Table I.