Semiclassical collision theory. Multidimensional integral method*

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Numerical results on the integral expression for the semiclassical S matrix are compared with exact quantum results for a multidimensional problem. The collision of a rigid rotor with an atom is treated. The integral method proves to be easy to apply. Within its range of maximum validity (no sign changes in the pre-exponential factor of the semiclassical wavefunction) the agreement was typically within 20%. When sign changes occurred, the agreement was about a factor of 2 or better. Conditions affecting sign changes are described.

I. INTRODUCTION

There has been considerable interest in the "exact" semiclassical theory[1,2] of inelastic and reactive collisions in the past several years.[1-8] An expression has been obtained for the S matrix of the collisions in the form of a primitive semiclassical (PSC) uniform approximation (several kinds of) and an integral approximation. The latter, when it can be used, is convenient in that it avoids the search for the stationary phase points of its integrand, needed for the other two.

The use of the integral expression[1e,1j,2c] has been examined numerically for the case of one internal coordinate,[1d,2b] namely for the inelastic collinear collision of an atom and a diatomic molecule. The results were in good agreement with the exact quantum results provided the transition probability was not too low ($>10^{-3}$). It has not been examined for the case of higher dimensions, and we do so in this paper.

An integral expression can be obtained from the expression[1e,1j]

$$S_{mn}\delta(E-E') = \langle \psi^{(-)}_{mE'} \mid \psi^{(+)}_{nE} \rangle \tag{1.1}$$

by introducing appropriate semiclassical values for $\psi^{(+)}_{nE}$ and $\psi^{(-)}_{mE'}$.

Use of a primitive semiclassical expression for these ψ's in (1.1) in terms of conventional coordinates yields ψ's which "blow up" at classical turning points ("caustics"), i.e., at boundaries between classically allowed and nonallowed regions.[9] The integral would then be inaccurate. The use of a suitable canonical transformation, either from action-angle[1e] or from conventional[1j] coordinates, to new coordinates reduces and in some cases eliminates these turning points.[1d,1j] In the new coordinates all but one are constants of the motion (they are the "reduced angle variables" $\bar{w}_i$) and the remaining one is time. Such turning points as remain are caused by significant distortions in the internal and translational motions.

We examine the accuracy of the integral for (a) the case where the cited canonical transformation to $\bar{w}$ and time has eliminated the turning points, and (b) for the case where the transformation has only reduced the number of such points. In case (b) one could still seek a newer canonical transformation to eliminate the turning points.

Uniform approximations for evaluating some of these integrals are described in a later paper.[1k]

II. INTEGRAL EXPRESSION

The integral is given by[1e,1j,2c]

$$S_{mn} = \int_0^1 \cdots \int_0^1 \left| \frac{\partial \bar{w}_i}{\partial \bar{w}_j^0} \right|^{-1/2} (\exp i\Delta) \prod_{i=1}^{r} d\bar{w}_i \,, \tag{2.1}$$

where the $\bar{w}_i$ are related to the final angle variables w_i of the internal coordinates and to the final value of the radial coordinate R, and the $\bar{w}_i^0$ are related to the initial angle variables w_i^0, and to the initial R by

$$\bar{w}_i = w_i - \mu R_2 \nu_2^i / p_{R_2} \,, \quad \bar{w}_i^0 = w_i^0 - \mu R_1 \nu_{i_1}^i / p_{R_1} \,, \tag{2.2}$$

and Δ is given by

$$\Delta = 2\pi \sum_{i=1}^{r} \left[(n_i^f - m_i)\bar{w}_i - \int_{n_i}^{n_i^f} w_i(t)\, dn_i(t) \right] - \int_{p_{R_1}}^{p_{R_2}} R(t)\, dp_R(t) + \tfrac{1}{2}\pi(l_1 + l_2 + 1) \,. \tag{2.3}$$

Here $(m_1, \cdots, m_r)$ is denoted by m in (2.1). $n_i(t)$, $w_i(t)$, $p_R(t)$, and $R(t)$ vary continuously along a classical trajectory leading from their initial values denoted by n_i, w_i^0, p_{R_1}, and R_1, to their final values n_i^f, w_i, p_{R_2}, and R_2. The ν^i in (2.2) are the frequencies $\partial H_0/\partial(2\pi n_i)$, where H_0 is the Hamiltonian at large R. $2\pi n_i^f$ is (with the choice of $\hbar = 1$) canonically conjugate to w_i, and the initial value $2\pi n_i$ is canonically conjugate to w_i^0.[1h] The n_i are the quantum numbers; l_1 and l_2 are initial and final values of the orbital angular momentum quantum number l. The sum over i in (2.3) is over all the r internal coordinates, of which the angle canonically conjugate to l is one. The determinant in (2.1) is an $r \times r$ signed determinant.

A measure of the accuracy of the simple exponential expressions[8] for $\psi^{(+)}$ and $\psi^{(-)}$ introduced into (1.1) to obtain (2.1) is reflected in the fraction of the integration points which involves sign changes in the Jacobian $|\partial \bar{w}_i/\partial \bar{w}_j^0|^{-1/2}$ in the domain of integration. The greater the fraction of such sign changes the more the simple exponential expressions for $\psi^{(+)}$ and $\psi^{(-)}$ are a poor approximation to the exact wavefunctions (in the region of the sign changes), and the poorer should be the accuracy of the integral. In contrast, the uniform and PSC expressions,[1,2] for S_{mn} require accuracy of the integrand (and hence of wavefunctions) only in small regions of the domain of integration, namely in the neighborhoods of the stationary phase points. The errors that we are discussing here lead typically to errors of only a factor of 2 or so in $|S_{mn}|^2$ (for the integral but not for the uniform approximation).

We examine in the present paper the accuracy of (2.1) for a problem with two internal coordinates and draw some comparison with the number of sign changes in the integrand. There are exact quantum mechanical results available on rotational–translational energy transfer in collisions between an atom and a rigid homonuclear rotor,[10] as well as some at larger quantum numbers prompted by the present semiclassical study.[11] This problem has $\gamma=2$ in Eq. (2.1).

III. NUMERICAL RESULTS

The quantum[10,11] or classical[1k,2c] Hamiltonian which will be used here for the atom–homonuclear rigid rotor problem is well known, together with the classical equations of motion which follow from it. Quantum treatments[10,11] have yielded probabilities for transitions from initial orbital and rotational angular momenta, $\hat{l}_1$ and $\hat{j}_1$, respectively, to final momenta, $\hat{l}_2$ and $\hat{j}_2$, for a given total angular momentum $\hat{J}$. With mass measured in units of the reduced mass μ of the collision partners, energy in units of the Lennard-Jones well depth parameter ϵ, and distance in terms of the radial distance R_m at the minimum of the Lennard-Jones interaction potential, the Hamiltonian of the system used in Refs. 1(k) and 10 is

$$H=\frac{1}{2}p_R^2+\frac{\hat{l}^2}{2R^2}+\frac{\hat{j}_2}{2I}+(R^{-12}-2R^{-6})[1+aP_2(\cos\gamma)]\,, \qquad (3.1)$$

where I is the moment of inertia of the rigid rotor in units of μR_m^2, a is the asymmetry parameter, and R is the separation distance in units of R_m. p_R is the momentum of relative motion of the atom and the center of mass of the rotor (in units of $\sqrt{\mu\epsilon}$). $\hat{l}$ and $\hat{j}$ are the angular momenta of the orbital motion and of the rotor, respectively, in units of $R_m\sqrt{\mu\epsilon}$. γ is the angle between the line of centers and the axis of the rotor, and is[11]

$$\cos\gamma=-\cos q_l\cos q_j+\frac{\hat{l}^2+\hat{j}^2-\hat{J}^2}{2\hat{l}\hat{j}}\sin q_l\sin q_j\,. \qquad (3.2)$$

The derivation of (3.1)–(3.2) and definition of the angles have been taken from Pars.[12] q_l and q_j are the variables canonically conjugate to $\hat{l}$ and $\hat{j}$,[13] and equal to $2\pi w_l$ and $2\pi w_j$, respectively. (w_l and w_j are canonically conjugate to $2\pi l$ and $2\pi j$.)[14] The w's vary over a unit interval. In the present units, the instantaneous values of the angular momenta are related to those of the quantum numbers by a semiclassical relation,

$$\hat{l}\equiv(l+\tfrac{1}{2})\hbar_0,\quad \hat{j}\equiv(j+\tfrac{1}{2})\hbar_0,\quad \hat{J}=(J+\tfrac{1}{2})\hbar_0, \qquad (3.3)$$

where l, j, and J are quantum numbers. The dimensionless constant $\hbar_0$ is $\hbar/(R_m\sqrt{\mu\epsilon})$, because of the present units of $\hat{l}$. In Eq. (3.2) $P_2(\cos\gamma)$ is a Legendre polynomial[15] and the potential energy is that of a homonuclear diatomic rigid rotor. The system parameters considered[10,11] are $I=0.4$, $a=0.25$, and $\hbar_0^2=1/500$.

With the use of Eqs. (3.1) and (3.2) and Hamilton's equations,

$$\begin{aligned} dR/dt&=\partial H/\partial p_R\,, & dp_R/dt&=-\partial H/\partial R\,,\\ dq_l/dt&=\partial H/\partial\hat{l} & d\hat{l}/dt&=-\partial H/\partial q_l\,,\\ dq_j/dt&=\partial H/\partial\hat{j} & d\hat{j}/dt&=-\partial H/\partial q_j\,, \end{aligned} \qquad (3.4)$$

trajectories were computed to generate data for the S-matrix elements.

Changing from the $\bar{w}_j$ to the $\bar{w}_j^0$ as independent variables in (2.1), the Jacobian is $|\partial\bar{w}_i/\partial\bar{w}_j^0|$. Rewriting the result in terms of the $\bar{q}$'s and $\bar{q}^0$'s we have, in the present case,[16]

$$S^J_{i_2,j_2;i_1,j_1}=(2\pi)^{-2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\left|\frac{\partial(\bar{q}_i,\bar{q}_j)}{\partial(\bar{q}_i^0,\bar{q}_j^0)}\right|^{1/2}e^{i\Delta}\,d\bar{q}_i^0\,d\bar{q}_j^0\,, \qquad (3.5)$$

where the pre-exponential factor is again a signed determinant and where

$$\Delta=(l'-l_2)\bar{q}_l-\int_{l_1}^{l'}q_l\,dl+(j'-j_2)\bar{q}_j-\int_{j_1}^{j'}q_j\,dj-\int_{p_{R_1}}^{p'_R}R\,dP_R/\hbar_0 +\tfrac{1}{2}\pi(l_1+l_2+1)\,. \qquad (3.6)$$

All the quantities in the three integrands denote instantaneous values along a trajectory beginning at some initial values $\bar{q}_j^0$, $\bar{q}_l^0$, j_1, and l_1 and leading to final values of l, j, and p_R denoted by a subscript f. (The (t)'s in (2.3) are omitted for brevity.) From (2.2), $\bar{q}_j$, $\bar{q}_l$, $\bar{q}_j^0$, and $\bar{q}_l^0$ are related to the initial and final q's by

$$q_l=\bar{q}_l+(\hat{l}/R^fp'_R)\,,\quad q_j=\bar{q}_j+(\hat{j}R^f/Ip'_R)\,, \qquad (3.7)$$

$$q_l^0=\bar{q}_l^0+(\hat{l}/R_1p_{R_1}),\quad q_j^0=\bar{q}_j^0+(\hat{j}_1R_1/Ip_{R_1})\,. \qquad (3.8)$$

The $\bar{q}$ variables in (3.7)–(3.8) are calculated by definition only at the start and end of each trajectory of a given $\bar{q}_j^0$, $\bar{q}_l^0$, j_1, l_1, and p_{R_1}. Each trajectory yields a particular $\bar{q}_j$, $\bar{q}_l$, j', l', and p'_R.

In the present problem the integration domain can be chosen to be $0\le\bar{q}_i^0\le\pi$ $(i=1,2)$, instead of $(0,2\pi)$, because of the symmetry of the homonuclear diatomic rotor, and the integral for S_{mn} can then be multiplied by a factor of 4. The integration points in (3.5) were chosen to be evenly spaced, namely $k\pi/(N-1)$, with $k=0,1,\cdots,N-1$; there are N^2 points in a π^2 domain. The phase Δ needed in (3.5) was obtained by integrating, along with the necessary (six) equations of motion, a seventh equation for a quantity ϕ.

$$\frac{d\phi}{dt}=-q_l\frac{d\hat{l}}{dt}-q_j\frac{d\hat{j}}{dt}-\frac{R\,dp_R}{dt}\,, \qquad (3.9)$$

from its initial value of zero, and noting that Δ equals ϕ plus $\frac{1}{2}\pi(l_1+l_2+1)$. The seven coupled differential equations were integrated using a Hamming predictor-corrector numerical integration routine.[17] The final numerical evaluation of the integral was done with a two-dimensional trapezoidal rule.

To calculate the values of the constants of each trajectory $\bar{q}_i^0$ and $\bar{q}_i$ from (q_i^0,R_1) and (q_i,R_2), respectively, $(i=j,l)$ one may use the expressions, valid at $R_1=R_2=\infty$,

$$\bar{q}_i^0=q_i^0-R_1\nu_i/p_{R1}\,,\quad \bar{q}_i=q_i-R_2\nu_i/p_{R2}\,, \qquad (3.10)$$

where p_{R1} and p_{R2} are the asymptotic values at $R=\infty$ and where the ν_i are the unperturbed frequencies $\partial H_0/\partial(2\pi n_i)$. Use of this equation requires that the trajectory is initiated and completed at a far larger R than would otherwise be necessary, because of a slowly varying centrifugal potential term. Instead, one may use the readily derived equivalent expression, valid at any point outside the interaction region,[18]

TABLE I. Comparison of classically accessible transition probabilities, in the atom–rigid rotor collision obtained from Eq. (2.1) with the corresponding quantum results. Here $N=11$.

J	(l_1, j_1)	(l_2, j_2)	Integral	Quantum
18	10,10	8,12	0.143	0.169
		10,12	0.053	0.066
		12,8	0.163	0.165
		12,10	0.099	0.087
		10,10	0.347	0.39
16	10,6	8,8	0.287	0.296
		12,4	0.295	0.297
		10,6	0.179	0.202
14	10,4	8,6	0.280	0.289
		12,2	0.261	0.275
		10,4	0.180	0.209
6	16,10	14,8	0.240	0.240
		16,10	0.520	0.52
16	6,10	4,12	0.240	0.288
		8,8	0.285	0.285
		6,10	0.250	0.3
6	12,10	10,8	0.203	0.201
		14,12	0.187	0.184
		12,10	0.533	0.54
18	16,4	14,6	0.126	0.124

$$\bar{q}_i^0 = q_i^0 + \frac{\nu_i \mu R_1 p_{R_1}}{p_{R_1}^2 + (\hat{l}_1^2/R_1^2)}\,, \qquad \bar{q}_i = q_i + \frac{\nu_i \mu R_2 p_{R_2}}{p_{R_2}^2 + (\hat{l}_2^2/R_2^2)}\,, \tag{3.11}$$

where p_{R_1} and p_{R_2} are now the instantaneous values of p_R at R_1 and R_2 and where ν_i is, in the case of the orbital coordinate, equal to $(\partial/\partial \hat{l})\,(\hat{l}^2/2\mu R^2)$ and so, unlike any other ν_i, varies with R at a finite R.

The trajectory data employed the system parameters I, a, and $\hbar_0^2$ indicated earlier. The quantum state variables for fixed values of these system parameters include the initial values of j, l, and J (the rotational, orbital, and total angular momentum numbers, respectively) and the initial value of the reduced energy K.

TABLE II. Comparison of classically inacessible transition probabilities, in the atom–rigid rotor collision, obtained from Eq. (2.1) with the corresponding quantum results. Here $N=11$.

J	(l_1, j_1)	(l_2, j_2)	Integral	Quantum
18	(10,10)	(8,10)	0.025	0.022
		(10,8)	0.025	0.019
16	(10,6)	(10,8)	0.022	0.024
		(12,6)	0.040	0.027
14	(10,4)	(12,4)	0.063	0.042
		(10,6)	0.030	0.033
6	(16,10)	(14,10)	0.0002	0.0013
		(18,12)	0.198	0.20
16	(6,10)	(6,12)	0.024	0.027
		(8,10)	0.044	0.029
6	(12,10)	(12,12)	0.009	0.008
		(10,10)	0.015	0.014
		(14,10)	0.007	0.007
		(12,8)	0.008	0.007

TABLE III. Convergence of value integral with increasing number of integration points N^2, for the case of no sign changes in $|\partial \bar{q}_i/\partial \bar{q}_j^0|$.

J	(l_1, j_1)	(l_2, j_2)	$N^2=7^2$	$N^2=11^2$	$N^2=15^2$	$N^2=19^2$	Quantum
18	(16,4)	(14,4)	0.050	0.047	0.048	0.047	0.037
		(14,6)	0.120	0.123	0.123	0.124	0.124
		(16,2)	0.057	0.055	0.054	0.053	0.050
		(16,4)	0.317	0.306	0.301	0.298	0.376
		(16,6)	0.140	0.109	0.105	0.101	0.100
		(18,2)	0.053	0.050	0.052	0.053	0.046
		(18,4)	0.143	0.136	0.126	0.126	0.116
		(18,6)	0.026	0.022	0.025	0.024	0.024

A comparison of the values of S_{mn} given by Eq. (3.5) for the above set of values of the system parameters and for $K=1$ is given in Table I. For all of the systems in this table no sign changes in the pre-exponential factor $|\partial \bar{q}_i/\partial \bar{q}_k^0|$ were observed. All results there were obtained using $N=11$, i.e., 121 integration points and are for transitions which are classically accessible, that is, transitions for which at least some of the stationary phase points of the integrand are real. (Those with high transition probability have four real stationary phase points in a π^2 region and those with low probability in Table I only two.)

In Table II are given similar results for transitions which are classically inaccessible, i.e., for which none of the stationary phase points are real. The conditions are otherwise the same as those in Table I.

An example of the convergence of the value of the integral with increasing the number of trajectories N^2, when no sign changes occurred, is given in Table III which also serves to supplement the comparisons in Tables I and II. A comparison of the integral values with the exact results for the case when sign changes in the Jacobian occurred is given in Table IV. The nature of the convergence of the value of the integral for this case, when the number of integration points N^2 was increased, is also indicated in Table IV.

IV. DISCUSSION

The results in Tables I–III have no sign changes in the Jacobian $|\partial \bar{q}_i/\partial \bar{q}_j^0|$ and are seen to agree well with the

TABLE IV. Convergence problems for case of sign changes in $|\partial \bar{q}_i/\partial \bar{q}_j^0|$. Value of integral vs number of integration points N^2.

J	(l_1, j_1)	(l_2, j_2)	$N^2=7^2$	$N^2=11^2$	$N^2=15^2$	$N^2=19^2$	Quantum
		(4,4)	0.073	0.040	0.057	0.073	0.078
		(6,2)	0.143	0.151	0.121	0.092	0.109
		(2,4)	0.302	0.286	0.291	0.266	0.220
		(6,0)	0.152	0.136	0.171	0.195	0.176
		(6,4)	0.165	0.090	0.072	0.072	0.020
		(4,2)	0.163	0.185	0.215	0.120	0.270
Fraction of negative Jacobians			4/49	11/121	23/225	33/361	

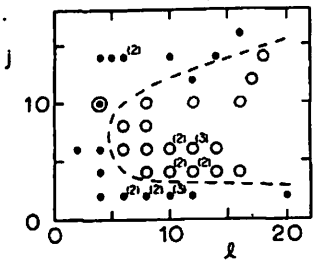

FIG. 1. Effect of initial rotational and orbital quantum numbers on sign changes of $|\partial\bar{q}_i/\partial\bar{q}_j^0|$, for $I=0.4$, $a=0.25$, and $K=1.0$. Filled circles indicate sign changes; unfilled circles, no sign changes.

quantum results. Interestingly enough, this agreement extends to what might be termed "clinging vine transitions," where $j_2=j_1$ and $l_2=l_1$, which are not well described by the *usual* uniform approximations. (This transition is discussed in a later paper.) In Table III it is seen that with increase in number of integration points N^2 the integral converges.

A contrasting behavior is provided by systems with Jacobian sign changes. In Table IV a series of transitions is considered. The difficulty in convergence with increasing N^2 is clearly demonstrated, and the accuracy of the integral is seen to be inferior to that in Tables I–III, where no Jacobian sign changes occurred. Even so, apart from the one case involving a low transition probability, the answer is typically better than a factor of 2 in this case of Jacobian sign changes.

To investigate the conditions, causing sign changes, about 60 sets of conditions were studied, with various values of j, l, and J and with some variation in the parameters a, I, and K: If the internal motion in the collision is unperturbed, the Jacobian $|\partial(\bar{q}_1, \bar{q}_j)/\partial(\bar{q}_1^0, \bar{q}_j^0)|$ is unity. A strong perturbation can cause appreciable departures from unity and a sufficiently strong one can make the sign negative. In Fig. 1 points are given with $a=0.25$, $I=0.4$, $K=1$, and with J varied from 6 to 18. With j and l as axes the points with sign changes are indicated by filled circles, those with no sign changes by unfilled circles, and a dashed line is drawn separating the two sets of points. Only two exceptions are seen to occur on either side of this line. The sign changes are seen to occur at small j and at small l (i.e., small impact parameter). They also occur at very large j. Some variations in the parameters K, a, and I were made: As expected, variation in the asymmetry parameter a had a substantial effect on the number of sign changes. For example, when a was reduced from 0.25 to 0.15 the sign changes at a (j, l, J) of (2, 4, 6), disappeared. When a was increased to 0.35 at (10, 10, 18) sign changes were produced where none existed at $a=0.25$. In other trajectories, I was increased from 0.4 to 3.0 at $j=2$, with $J=6$ and 8, and at various l's. It had no major effect on the sign changes which had occurred at $I=0.4$. A decrease in translational energy at a (j, l, J) of (10, 10, 18) from a total energy of 1.0 to one of 0.6 (at fixed J) caused sign changes to occur where none had occurred before.

In summary the integral method is an effective way of evaluating S_{mn} when there are no Jacobian sign changes (Tables I–III). It is simpler to apply than the uniform method (e.g., it applies to "clinging vine transitions"). In the case of small transition probabilities it is less accurate than the uniform method, it was seen in an earlier paper of this series,[1d] because of large cancellations.

When Jacobian sign changes occur, the integral is less accurate than before, as expected, but even then is not inaccurate by more than a facor of 2 in the cases treated (Table IV) except for the one case of low transition probability. In the cases of Jacobian sign changes one can seek new canonical transformations.

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[14]Semiclassically, $\hat{l}$ equals $(l+\frac{1}{2})\hbar$, i.e., equals $(l+\frac{1}{2})$ when $\hbar=1$. Thus, $2\pi w_l$ is canonically conjugate to $(l+\frac{1}{2})$ and so w_l is canonically conjugate to $2\pi(l+\frac{1}{2})$. Use of Poisson brackets then also shows that w_l is also canonically conjugate to $2\pi l$. Similar remarks apply to w_j and $2\pi j$.[1h]

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[16]Equation (3.5), taken from Ref. 1(g), is the same as the equation in Ref. 2(c), apart from the last term in (3.6).
[17](a) K. W. Hamming, J. Assoc. Comp. Mach. 6, 37 (1959). (b) A. Ralston, Maths. Comput. 16, 431 (1962). (c) A. Ralston, *Mathematical Methods for Digital Computers* (Wiley New York, 1965), Chap. 8.
[18]We are indebted to Dr. Richard Ellis of this laboratory for these equations.