IVR Formulation of Miller's Correspondence Relations†

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The correspondence rules of Miller, determining semiclassical approximations for general quantum amplitudes $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$, are formulated in a way that is analogous to the initial value representation (IVR) treatments of the propagator. The semiclassical formulas obtained in this way do not require numerical searches, are free from caustic singularities, and are often uniform approximations. However, to develop treatments that retain the power and generality of Miller's rules, it is necessary to overcome boundary condition difficulties that arise when the **x**'s are not Cartesian coordinates. Such problems can be solved by replacing Gaussian factors, analogous to those appearing in existing IVR treatments of the propagator, with more general non-Gaussian functions. It is suggested that factors of this kind can be obtained from certain IVR representations for wave functions that are exact for particular model systems. Examples of such factors are presented, and the resulting theory is illustrated. In one application, an IVR expression for the elastic scattering differential cross section that is uniform for all angles is developed and tested.

I. Introduction

W. H. Miller is widely and justifiably recognized as one of the key leaders in the development of modern semiclassical theory. It is safe to say that almost everyone who has engaged in the application of semiclassics to molecular dynamical processes over the past thirty-plus years has been strongly influence by his pioneering work. Of his many highly important contributions to this field, however, perhaps his most fundamental and elegant work is his formulation of the general classical/quantum correspondence relations. First developed as tools for the derivation of classical *S*-matrix expressions,[1,2] these relations were subsequently elaborated and presented in a more general context in his classic *Advances in Chemical Physics* articles.[3,4] In these latter works, Miller demonstrated that most objects of quantum mechanical importance can be expressed as inner products (or quantum amplitudes) of the form $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$, where the $|\mathbf{x}\rangle$'s are states corresponding to classical position or momentum variables. Miller showed that semiclassical approximations to these quantum amplitudes can be expressed compactly and generally in terms of the classical generating functions for canonical transformations between the variables $\mathbf{x}_1$ and $\mathbf{x}_2$. The resulting expressions, which we refer to as the Miller correspondence relations (MCRs), provide short cuts to the derivation of semiclassical formulas for wave functions, propagators, *S* -matrix elements, Franck−Condon factors, Clebsch-Gordan coefficients, and many additional quantities.

The purpose of the present work is to re-express the MCR in a form that makes them more useful for numerical applications. We thus begin, in section II, with a short review of the MCR and a discussion of certain known problems that arise in their application. In section III, we present an alternative formulation of the correspondence relations that alleviates some of these difficulties but that still has disadvantages that obstruct its general use. In section IV, we suggest some modifications to our treatment that overcome these problems, and in section V, we present some examples of the new treatment including numerical results. Finally, in section VI, we summarize and discuss our work.

II. The Miller Correspondence Relations

Miller's semiclassical formulas for the quantum amplitudes $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ are expressed in terms of the classical generating function $F(\mathbf{x}_2,\mathbf{x}_1)$ for the canonical transformation from variables $(\mathbf{x}_1,\mathbf{y}_1)$ to variables $(\mathbf{x}_2,\mathbf{y}_2)$. In the notation used here, $\mathbf{x}_1$ and $\mathbf{x}_2$ are *N*-dimensional vectors containing elements x_{1i} and x_{2i}, where *N* is the number of degrees of freedom for the system treated and x_{ki} is a classical canonical variable for the *i*-th degree of freedom. Each such variable may, independently, be either a coordinate- or momentum-type variable. Similarly, $\mathbf{y}_1$ and $\mathbf{y}_2$ are *N*-dimensional vectors containing elements y_{1i} and y_{2i} that are conjugate to x_{1i} and x_{2i}; i.e., if x_{kj} is a coordinate, then y_{kj} will be a momentum, and vice versa. If all elements in $\mathbf{x}_1$ are of the same gender (coordinate or momentum) and all elements of $\mathbf{x}_2$ are also of a particular gender, the generating functions can be classified as being of types F_1, F_2, F_3, or F_4 in Goldstein's[5] notation. The transformation[5] from $(\mathbf{x}_1,\mathbf{y}_1)$ to $(\mathbf{x}_2,\mathbf{y}_2)$ can be obtained from the generating function *F* by applying the relations

$$\frac{\partial F(\mathbf{x}_2,\mathbf{x}_1)}{\partial \mathbf{x}_2} = \mathbf{S}_2\mathbf{y}_2 \tag{2.1}$$

$$\frac{\partial F(\mathbf{x}_2,\mathbf{x}_1)}{\partial \mathbf{x}_1} = -\mathbf{S}_1\mathbf{y}_1 \tag{2.2}$$

and solving for $(\mathbf{x}_2,\mathbf{y}_2)$ in terms of $(\mathbf{x}_1,\mathbf{y}_1)$. Here we have defined $\mathbf{S}_1$ and $\mathbf{S}_2$ to be $N \times N$ diagonal matrixes with elements $(\mathbf{S}_1)_{ij} = (s_{1i})\delta_{ij}$ and $(\mathbf{S}_2)_{ij} = (s_{2i})\delta_{ij}$, where $s_{ki} = +1$ if x_{ki} is a coordinate and -1 if x_{ki} is a momentum.

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In terms of this notation, Miller's correspondence relations[1−4] for the quantum amplitudes $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ can be expressed compactly as

$$\langle \mathbf{x}_2|\mathbf{x}_1\rangle = \sum \sqrt{\left(\frac{-1}{2\pi i\hbar}\right)^N \det\left[\mathbf{S}_2 \frac{\partial^2 F}{\partial \mathbf{x}_2 \partial \mathbf{x}_1} \mathbf{S}_1\right]}\, e^{iF(\mathbf{x}_2,\mathbf{x}_1)/\hbar} \quad (2.3)$$

The sum appearing in eq 2.3 arises because F is generally a multivalued function of $(\mathbf{x}_2,\mathbf{x}_1)$ and all values of F consistent with $(\mathbf{x}_2,\mathbf{x}_1)$ contribute to $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$.

Despite the great theoretical and practical importance of the MCR, a few important difficulties surface when applications are attempted. One problem is related to the nature of the second derivatives appearing in eq 2.3. It is known that these quantities can become infinite for certain values of $\mathbf{x}_1$ or $\mathbf{x}_2$, referred to as caustics, so that the semiclassical approximation of eq 2.3 breaks down at such points. Thus, the MCR formulas are only primitive semiclassical (PSC) expressions: they do not tend to the exact quantum results uniformly as $\hbar \rightarrow 0$ for all $\mathbf{x}_1,\mathbf{x}_2$. This limits the usefulness of the MCR for direct applications. As a consequence, the MCRs are often used as starting points for the derivation of uniform semiclassical (USC) approximations[6−12] that remain valid at the caustics. Generally, the development of such uniform treatments can be complicated for multidimensional systems.[7−13]

A second problem that arises in applications of the MCR is associated with the multivalued property of F and the appearance of the summation in eq 2.3. We note that each term in the summation corresponds to a particular point $(\mathbf{x}_1,\mathbf{y}_1)$ [or, equivalently, $(\mathbf{x}_2,\mathbf{y}_2)$] in phase space that is consistent with the given values of the variables $(\mathbf{x}_1,\mathbf{x}_2)$. Finding such points generally requires a numerical search. In some cases, the number of points and, thus, the number of terms contributing to eq 2.3 can be very large, and their determination can be difficult.[14]

In cases where the $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ represent propagators[15] and wave functions,[16,17] it is known that the problems described above can be alleviated by expressing these quantities as certain integrals over classical trajectories. For the propagator case, these integral expressions are usually known as initial value representation (IVR) formulas,[6,15,18−58] and we will use this term to describe analogous integral expressions that arise for other cases, even when this name is not literally appropriate. Our objective in this paper is to convert the MCR directly to the IVR form so that the problems described above can be reduced for more general kinds of $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$.

III. Gaussian IVR Treatment of the MCR

A. Expressions. IVR expressions of the MCR can essentially be written down by inspection, in direct analogy with existing IVR formulas for the propagator.[15] As in the propagator case, there are three principal forms for these expressions. We refer to these as being of types LR, L, or R, depending on whether they contain Gaussian factors that depend on both $\mathbf{x}_2$ and $\mathbf{x}_1$, only $\mathbf{x}_2$, or only $\mathbf{x}_1$, respectively. Explicitly, the three forms are:

1. LR-Form. In this case, the quantum amplitude is given by

$$\langle \mathbf{x}_2|\mathbf{x}_1\rangle = \left(\frac{1}{2\pi\hbar}\right)^N \int d\mathbf{x} \int d\mathbf{y}\, G_{\mathbf{\Gamma}_2}(\mathbf{x}_2;\bar{\mathbf{x}},\bar{\mathbf{y}}) \times C(\bar{\mathbf{x}},\bar{\mathbf{y}};\mathbf{x},\mathbf{y})\, e^{iF(\bar{\mathbf{x}},\mathbf{x})/\hbar} G^*_{\mathbf{\Gamma}_1}(\mathbf{x}_1;\mathbf{x},\mathbf{y}) \quad (3.1)$$

where the G is the N-dimensional Gaussian coherent state function of the form

$$G_{\mathbf{\Gamma}}(\mathbf{x}_1;\mathbf{x},\mathbf{y}) = e^{-(\mathbf{x}_1-\mathbf{x})^T\mathbf{\Gamma}(\mathbf{x}_1-\mathbf{x})/\hbar}\, e^{i\mathbf{y}^T\mathbf{S}(\mathbf{x}_1-\mathbf{x})/\hbar} \quad (3.2)$$

with $\mathbf{S}_{ij} = s_i\delta_{ij}$ and $s_i = \pm 1$, according to whether x_i is a coordinate or momentum, respectively. In this expression, $\mathbf{\Gamma}$ is a complex symmetric matrix; it may be chosen arbitrarily, provided that the real part of each eigenvalue is positive and finite. The pre-exponential factor C is given by

$$C(\bar{\mathbf{x}},\bar{\mathbf{y}};\mathbf{x},\mathbf{y}) = \left(\frac{1}{2\pi i\hbar}\right)^{N/2} \times \left[\det\left(-\frac{\partial\bar{\mathbf{y}}}{\partial\mathbf{x}}\mathbf{S} + 2i\bar{\mathbf{S}}\mathbf{\Gamma}_2\frac{\partial\bar{\mathbf{x}}}{\partial\mathbf{x}}\mathbf{S} + 2i\frac{\partial\bar{\mathbf{y}}}{\partial\mathbf{y}}\mathbf{\Gamma}_1^* + 4\bar{\mathbf{S}}\mathbf{\Gamma}_2\frac{\partial\bar{\mathbf{x}}}{\partial\mathbf{y}}\mathbf{\Gamma}_1^*\right)\right]^{1/2} \quad (3.3)$$

where $\bar{\mathbf{S}}_{ij} = \bar{s}_i\delta_{ij}$ and $\bar{s}_i = \pm 1$, according to whether $\bar{x}_i$ is a coordinate or momentum, respectively. As before, $\mathbf{x}_1$ and $\mathbf{x}_2$ are N-dimensional vectors whose elements are variables that may be of either gender (coordinate or momentum), while $\mathbf{y}_1$ and $\mathbf{y}_2$ are vectors containing the variables conjugate to $\mathbf{x}_1$ and $\mathbf{x}_2$, respectively. The N-dimensional vectors $\mathbf{x}$ and $\mathbf{y}$ contain variables of same gender as $\mathbf{x}_1$ and $\mathbf{y}_1$, respectively, so if x_{1j} is a momentum, then x_j is also a momentum, while y_{1j} and y_j are coordinates. Similarly, $\bar{\mathbf{x}}$ and $\bar{\mathbf{y}}$ contain variables of same gender as $\mathbf{x}_2$ and $\mathbf{y}_2$, respectively.

In eq 3.1, the barred variables $(\bar{\mathbf{x}},\bar{\mathbf{y}})$ are considered to be functions of the integration variables $(\mathbf{x},\mathbf{y})$ and are obtained by applying the canonical transformation generated by $F(\bar{\mathbf{x}},\mathbf{x})$ to $(\mathbf{x},\mathbf{y})$. It is important to note this procedure yields a unique value for the variables $(\bar{\mathbf{x}},\bar{\mathbf{y}})$ and for the function $F(\bar{\mathbf{x}},\mathbf{x})$ for each value of $(\mathbf{x},\mathbf{y})$.

The validity of this IVR expression can be established by noting that that it reduces to the MCR expression for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ [eq 2.3] when the integrals are evaluated by the lowest-order stationary phase (SP) approximation. The details of the proof are almost identical to those given in ref 15 and will not be repeated here. Since such a SP treatment becomes exact in the classical limit (except at caustics), our expression approaches the MCR in the classical limit (except at caustics where the MCR break down). This establishes that eq 3.1 is a semiclassical approximation.

It may seem surprising that eq 3.1 apparently lacks the symmetry implied by the relation $\langle \mathbf{x}_2|\mathbf{x}_1\rangle = \langle \mathbf{x}_1|\mathbf{x}_2\rangle^*$. Nevertheless, this symmetry property is obeyed by this expression. This can be shown by (a) using the result that the Jacobian for a canonical transformation is unity to replace the integration variables in eq 3.1 with $(\bar{\mathbf{x}},\bar{\mathbf{y}})$, i.e.

$$\langle \mathbf{x}_2|\mathbf{x}_1\rangle = \left(\frac{1}{2\pi\hbar}\right)^N \int d\bar{\mathbf{x}} \int d\bar{\mathbf{y}}\, G_{\mathbf{\Gamma}_2}(\mathbf{x}_2;\bar{\mathbf{x}},\bar{\mathbf{y}}) \times C(\bar{\mathbf{x}},\bar{\mathbf{y}};\mathbf{x},\mathbf{y})\, e^{iF(\bar{\mathbf{x}},\mathbf{x})/\hbar} G^*_{\mathbf{\Gamma}_1}(\mathbf{x}_1;\mathbf{x},\mathbf{y}) \quad (3.4)$$

and (b) applying the "direct conditions" for a canonical transformation[59] to express C as

$$C(\bar{\mathbf{x}},\bar{\mathbf{y}};\mathbf{x},\mathbf{y}) = \left(\frac{1}{2\pi i\hbar}\right)^{N/2} \times \left[\det\left(\frac{\partial\mathbf{y}}{\partial\bar{\mathbf{x}}}\bar{\mathbf{S}} + 2i\frac{\partial\mathbf{y}}{\partial\bar{\mathbf{y}}}\mathbf{\Gamma}_2 + 2i\mathbf{S}\mathbf{\Gamma}_1^*\frac{\partial\mathbf{x}}{\partial\bar{\mathbf{x}}}\bar{\mathbf{S}} - 4\mathbf{S}\mathbf{\Gamma}_1^*\frac{\partial\mathbf{x}}{\partial\bar{\mathbf{y}}}\mathbf{\Gamma}_2\right)\right]^{1/2} \quad (3.5)$$

In the new expression for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$, the unbarred variables $(\mathbf{x},\mathbf{y})$ are regarded as functions of the barred variables $(\bar{\mathbf{x}},\bar{\mathbf{y}})$. Comparing eq 3.5 with eq 3.3, we see that $C(\bar{\mathbf{x}},\bar{\mathbf{y}};\mathbf{x},\mathbf{y}) = C(\mathbf{x},\mathbf{y};\bar{\mathbf{x}},\bar{\mathbf{y}})^*$, if

$\mathbf{\Gamma}_1$ and $\mathbf{\Gamma}_2$ are switched. Thus, recognizing that $F(\bar{\mathbf{x}},\mathbf{x}) = -F(\mathbf{x},\bar{\mathbf{x}})$ [as implied by eq 2.2], it is clear that eqs 3.1 and 3.4 are consistent with the expected symmetry property.

2. L-Form. For this case, the amplitude $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ is given by

$$\langle \mathbf{x}_2|\mathbf{x}_1\rangle = \left(\frac{1}{2\pi\hbar}\right)^N \int d\mathbf{y}_1\, G_{\mathbf{\Gamma}}(\mathbf{x}_2;\bar{\mathbf{x}},\bar{\mathbf{y}}) B(\bar{\mathbf{x}},\bar{\mathbf{y}};\mathbf{y}_1)\, e^{iF(\bar{\mathbf{x}},\mathbf{x}_1)/\hbar} \quad (3.6)$$

where

$$B(\bar{\mathbf{x}},\bar{\mathbf{y}};\mathbf{y}_1) = \left[\det\left(\frac{\partial\bar{\mathbf{y}}}{\partial\mathbf{y}_1} - 2i\bar{\mathbf{S}}\mathbf{\Gamma}\frac{\partial\bar{\mathbf{x}}}{\partial\mathbf{y}_1}\right)\right]^{1/2} \quad (3.7)$$

and $(\bar{\mathbf{x}},\bar{\mathbf{y}})$ are regarded as functions of $(\mathbf{x}_1,\mathbf{y}_1)$. Equations 3.6 and 3.7 may be derived from eqs 3.1 and 3.3 by considering the special case where $\mathbf{\Gamma}_1 = \gamma_1\mathbf{1}$ and then by letting $\gamma_1 \rightarrow \infty$, which produces an N-dimensional δ function $\delta(\mathbf{x} - \mathbf{x}_1)$ in the integral. As in the case of the LR expression, eq 3.6 also reduces to the PSC MCR formula when the integral over $\mathbf{y}_1$ is evaluated by a SP treatment.

3. R-Form. Here, the quantum amplitude is given by the expression

$$\langle \mathbf{x}_2|\mathbf{x}_1\rangle = \left(\frac{1}{2\pi\hbar}\right)^N \int d\mathbf{y}_2\, A(\mathbf{y}_2;\mathbf{x},\mathbf{y})\, e^{iF(\mathbf{x}_2,\mathbf{x})/\hbar} G^*_{\mathbf{\Gamma}}(\mathbf{x}_1;\mathbf{x},\mathbf{y}) \quad (3.8)$$

where

$$A(\mathbf{y}_2;\mathbf{x},\mathbf{y}) = \left[\det\left(\frac{\partial\mathbf{y}}{\partial\mathbf{y}_2} + 2i\mathbf{S}\mathbf{\Gamma}^*\frac{\partial\mathbf{x}}{\partial\mathbf{y}_2}\right)\right]^{1/2} \quad (3.9)$$

and $(\mathbf{x},\mathbf{y})$ are treated as functions of $(\mathbf{x}_2,\mathbf{y}_2)$. This result may be derived from eqs 3.4 and 3.5 by examining the case where $\mathbf{\Gamma}_2 = \gamma_2\mathbf{1}$ in the limit as $\gamma_2 \rightarrow \infty$. When the integral over $\mathbf{y}_2$ is performed by the SP technique, eq 3.8 again reduces to Miller's PSC expression for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$, verifying its status as a semiclassical approximation.

It is possible to relate the IVR expressions presented above to earlier work by Heller[60] and Weissman,[61] who generalized the MCR to situations where $|\mathbf{x}_1\rangle$, $|\mathbf{x}_2\rangle$, or both may be Gaussian coherent states. At least in some cases, our IVR expressions can be derived from their formulas for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ by a technique analogous to that recently applied by Grossmann and Xavier[62] to obtain the Herman−Kluk[18] formula from the coherent state representation of the propagator. However, the approach to the verification of our results used above is simpler and more easily applicable for the treatment to be presented in section IV.

B. Examples. It is useful to verify that our general IVR expressions reduce to familiar results in special cases.

1. Propagator. The time-dependent propagator (in the coordinate representation) may be defined as

$$K_t(\mathbf{q}_2,\mathbf{q}_1) = \langle \mathbf{q}_2|\mathbf{q}_{1t}\rangle \quad (3.10)$$

where

$$|\mathbf{q}_{1t}\rangle = \exp(-i\hat{H}t/\hbar)|\mathbf{q}_1\rangle \quad (3.11)$$

$\hat{H}$ is the Hamiltonian operator, and $\mathbf{q}_i$ are coordinates. The generator F for the dynamical transformation from variables $(\mathbf{q}_1,\mathbf{p}_1)$ at time 0 to $(\mathbf{q}_2,\mathbf{p}_2)$ at time t is given by the action integral (Hamilton's principal function)

$$S(\mathbf{q}_2,\mathbf{q}_1) = \int_0^t [\mathbf{p}_\tau^{\mathrm{T}}\dot{\mathbf{q}}_\tau - H(\mathbf{q}_\tau,\mathbf{p}_\tau)]\, d\tau \quad (3.12)$$

where H is the classical Hamiltonian function and $\mathbf{q}_\tau$ and $\mathbf{p}_\tau$ are the coordinate and momentum at time τ along a classical trajectory from $\mathbf{q}_1$ to $\mathbf{q}_2$.

If this choice for generating function is substituted into the MCR expression, eq 2.3, and the phase of the pre-exponential factor is correctly interpreted, one obtains the well-known Van Vleck[63]−Gutzwiller[64] semiclassical expression for the propagator.[3] On the other hand, if this generating function is substituted into our LR-form IVR expression, eqs 3.1 and 3.3, we obtain

$$K_t(\mathbf{q}_2,\mathbf{q}_1) = \left(\frac{1}{2\pi\hbar}\right)^N \int_0^t d\mathbf{q}_0 \int_0^t d\mathbf{p}_0\, G_{\mathbf{\Gamma}_2}(\mathbf{q}_2;\mathbf{q}_t,\mathbf{p}_t) \times C(\mathbf{q}_t,\mathbf{p}_t;\mathbf{q}_0,\mathbf{p}_0)\, e^{iS(\mathbf{q}_t,\mathbf{q}_0)/\hbar} G^*_{\mathbf{\Gamma}_1}(\mathbf{q}_1;\mathbf{q}_0,\mathbf{p}_0) \quad (3.13)$$

and

$$C(\mathbf{q}_t,\mathbf{p}_t;\mathbf{q}_0,\mathbf{p}_0) = \left(\frac{1}{2\pi i\hbar}\right)^{N/2} \times \left[\det\left(-\frac{\partial\mathbf{p}_t}{\partial\mathbf{q}_0} + 2i\mathbf{\Gamma}_2\frac{\partial\mathbf{q}_t}{\partial\mathbf{q}_0} + 2i\frac{\partial\mathbf{p}_t}{\partial\mathbf{p}_0}\Gamma_1^* + 4\mathbf{\Gamma}_2\frac{\partial\mathbf{q}_t}{\partial\mathbf{p}_0}\Gamma_1^*\right)\right]^{1/2} \quad (3.14)$$

where $(\mathbf{x},\mathbf{y})$ has been replaced by $(\mathbf{q}_0,\mathbf{p}_0)$, the initial coordinates and momenta of the system at time 0, and $(\bar{\mathbf{x}},\bar{\mathbf{y}})$ has been replaced by $(\mathbf{q}_t,\mathbf{p}_t)$, the values of these variables after their classical propagation to time t. Neither $\mathbf{q}_0$ nor $\mathbf{q}_t$ need to be identical with $\mathbf{q}_1$ or $\mathbf{q}_2$. We can recognize eq 3.13 as a slight generalization of the well-known Herman−Kluk[18] semiclassical propagator expression to the case where the matrixes $\mathbf{\Gamma}_k$ may be nondiagonal.

If we apply the generating function of eq 3.12 to our L-form IVR expression, we obtain the following result for the propagator:

$$K_t(\mathbf{q}_2,\mathbf{q}_1) = \left(\frac{1}{2\pi\hbar}\right)^N \int d\mathbf{p}_1\, G^*_{\mathbf{\Gamma}}(\mathbf{q}_2;\mathbf{q}_t,\mathbf{p}_t)\, B(\mathbf{q}_t,\mathbf{p}_t;\mathbf{p}_1)\, e^{iS(\mathbf{q}_t,\mathbf{q}_1)/\hbar} \quad (3.15)$$

with

$$B(\mathbf{q}_t,\mathbf{p}_t;\mathbf{p}_1) = \left[\det\left(\frac{\partial\mathbf{p}_t}{\partial\mathbf{p}_1} - 2i\mathbf{\Gamma}\frac{\partial\mathbf{q}_t}{\partial\mathbf{p}_1}\right)\right]^{1/2} \quad (3.16)$$

where $(\bar{\mathbf{x}},\bar{\mathbf{y}})$ has been replaced by and $(\mathbf{q}_t,\mathbf{p}_t)$, the variables obtained by running a trajectory from point $(\mathbf{q}_1,\mathbf{p}_1)$ at time 0 to time t. Equation 3.15 has been used, in various forms, as an IVR expression for the propagator in several calculations.[26,32,37] Generally, it appears to be less accurate than the Herman−Kluk approximation.[26]

Finally, if the generating function of eq 3.12 is applied to our R-form IVR expression, the semiclassical propagator becomes

$$K_t(\mathbf{q}_2,\mathbf{q}_1) = \left(\frac{1}{2\pi\hbar}\right)^N \int d\mathbf{p}_2\, A(\mathbf{p}_2;\mathbf{q}_0,\mathbf{p}_0)\, e^{iS(\mathbf{q}_2,\mathbf{q}_0)/\hbar}\, G^*_{\mathbf{\Gamma}}(\mathbf{q}_1;\mathbf{q}_0,\mathbf{p}_0) \quad (3.17)$$

with

$$A(\mathbf{p}_2;\mathbf{q}_0,\mathbf{p}_0) = \left[\det\left(\frac{\partial\mathbf{p}_0}{\partial\mathbf{p}_2} + 2i\mathbf{\Gamma}^*\frac{\partial\mathbf{q}_0}{\partial\mathbf{p}_2}\right)\right]^{1/2} \quad (3.18)$$

where $(\mathbf{x},\mathbf{y})$ in eqs 3.8 and 3.9 has been replaced by $(\mathbf{q}_0,\mathbf{p}_0)$, the variables obtained by propagating $(\mathbf{q}_2,\mathbf{p}_2)$ backward from time t to time 0. Equation 3.17 is a final value representation (FVR)

formula and is related to "time-reversed" expressions for the propagator used in some semiclassical treatments.[23−25,57]

2. Time-Independent Wave Function. In the notation of the MCR, time-independent wave functions for integrable systems are denoted by $\psi_{\mathbf{J}}(\mathbf{q}) = \langle \mathbf{q}|\mathbf{J}\rangle$, where $\mathbf{q}$ denotes the coordinate variables and $\mathbf{J}$ represents the quantized action variables associated with the state. The F_2-type generating function $F(\mathbf{q},\mathbf{J})$ for the transformation from action-angle variables $(\mathbf{J},\boldsymbol{\theta})$ to ordinary coordinates and momenta $(\mathbf{q},\mathbf{p})$ is Hamilton's characteristic function

$$W(\mathbf{q},\mathbf{J}) = \int^{\mathbf{q}} \mathbf{p}^{\mathrm{T}}\, \mathrm{d}\mathbf{q} \tag{3.19}$$

If this choice for F is substituted into the MCR expression, eq 2.3, and the phases of the various terms in the sum are correctly interpreted, one obtains the standard multidimensional WKB semiclassical formula for the wave function. If, on the other hand, this expression for the generating function is substituted into our L-type IVR expression, eqs 3.6, we obtain

$$\psi_{\mathbf{J}}(\mathbf{q}) = \left(\frac{1}{2\pi\hbar}\right)^N \int \mathrm{d}\boldsymbol{\theta}\; G_{\boldsymbol{\Gamma}}(\mathbf{q};\bar{\mathbf{q}},\bar{\mathbf{p}})\, B(\bar{\mathbf{q}},\bar{\mathbf{p}};\boldsymbol{\theta})\, \mathrm{e}^{iW(\bar{\mathbf{q}},\mathbf{J})/\hbar} \tag{3.20}$$

where

$$B(\bar{\mathbf{q}},\bar{\mathbf{p}};\boldsymbol{\theta}) = \left[\det\left(\frac{\partial \bar{\mathbf{p}}}{\partial \boldsymbol{\theta}} - 2i\boldsymbol{\Gamma}\frac{\partial \bar{\mathbf{q}}}{\partial \boldsymbol{\theta}}\right)\right]^{1/2} \tag{3.21}$$

To obtain these results, we have identified the following: $(\mathbf{x}_1,\mathbf{y}_1)$ with the action and angle variables $(\mathbf{J},\boldsymbol{\theta})$; $\mathbf{x}_2$ with $\mathbf{q}$, the Cartesian coordinate at which the wave function is to be evaluated; and $(\bar{\mathbf{x}},\bar{\mathbf{y}})$ with $(\bar{\mathbf{q}},\bar{\mathbf{p}})$, the Cartesian coordinate and momentum corresponding to $(\mathbf{J},\boldsymbol{\theta})$.

The IVR expression for the wave function, eq 3.20, has been previously presented and studied.[16,17] It resembles the frozen Gaussian approximation (FGA) formula for the wave function proposed earlier by Heller.[65] However, unlike the FGA, eq 3.20 becomes exact in the classical limit and is thus a true semiclassical approximation. In addition, it has been shown that, with appropriate choices for $\boldsymbol{\Gamma}$, eq 3.20 is actually a USC approximation that tends to the exact wave function uniformly for all $\mathbf{q}$ as $\hbar \to 0$.[16,17] Calculations verify that this semiclassical treatment is capable of high accuracy.[16,17]

In additional to the L-type formula, eq 3.20, it is clearly possible to propose LR- and R-type expressions for the wave function on the basis of eqs 3.1 and 3.8. However, such expressions suffer from problems to be described toward the end of this Section and are not useful in their present form.

C. Properties of the IVR Expressions. It is worthwhile to review some of the properties of eqs 3.1, 3.6, and 3.8 and discuss how they overcome some of the difficulties of the MCR expressions.

We first note that, unlike the MCR expressions, the IVR expressions for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ are free from infinite caustic singularities. The reason is that the canonical transformations generated by, e.g., $F(\bar{\mathbf{x}},\mathbf{x})$ produce $(\bar{\mathbf{x}},\bar{\mathbf{y}})$ that are finite, continuous functions of $(\mathbf{x},\mathbf{y})$, so that the derivatives appearing in the pre-exponential factors do not cause the integrals to diverge. Additionally, unlike the MCR formulas, calculations based on the IVR expressions do not require searches: the variables $\mathbf{x}_1$ and $\mathbf{x}_2$ are fixed, while the remaining coordinates and momenta are either integration variables or are determined uniquely from the above variables by applying a single-valued transformation. In many cases of interest (including those of the propagator and wave function), this transformation can be immediately obtained by a procedure that involves running specified classical trajectories.

If $\boldsymbol{\Gamma} = \gamma\mathbf{1}$ and $\gamma \to \infty$, the L- and R-type IVR expressions reduce to the PSC MCR formulas, eq 2.3. On the other hand, if $\gamma \to 0$, these expressions tend to known integral forms for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ that appear as intermediate quantities in the derivation of the MCR.[3] Such integrals are evaluated by the SP approximation to obtain the final PSC results summarized in eq 2.3. Integral expressions of this kind were used computationally many years ago by Miller,[6] Marcus,[66,67] and others[68] in the original semiclassical IVR and FVR treatments of the S-matrix. More recently, such $\gamma = 0$ expressions have sometimes been used in semiclassical treatments of the propagator.[20,22−25,31,57] It should be pointed out that although such $\gamma = 0$ integral forms do not diverge, they are, generally, only PSC approximations. Like the $\gamma \to \infty$ forms, they do not always approach the exact quantum mechanical results for all values of $(\mathbf{x}_1,\mathbf{x}_2)$.[15,16,26]

The above choices for $\boldsymbol{\Gamma}$ violate the condition that the real part of all of its eigenvalues be positive and finite. In contrast, choosing $\boldsymbol{\Gamma}$ to obey to this condition results in a number of advantages:

1. The formulas for the propagator [eqs 3.13, 3.15, and 3.17] and the wave function [eq 3.20] are then USC approximations.[15−17]
2. It is then unnecessary to include Maslov phase factors[15,22,23] in expressions for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$, thus simplifying semiclassical calculations. Such factors are needed in cases where $\gamma = 0$ or ∞, since the pre-exponential factor can then become zero or infinite for certain values of its arguments, causing the phase of this factor to change discontinuously. However, when $\boldsymbol{\Gamma}$ is chosen to obey the condition described above, an extension of the analysis presented in refs 15 and 69 shows that the pre-exponential factors C of eq 3.3 are always finite and do not vanish for real values of their arguments, making Maslov indices unnecessary.
3. Finally, for the case of the propagator, such choices for $\boldsymbol{\Gamma}$ improve the numerical convergence of the integrals by causing the integrands to decay in regions where their phase varies rapidly.[26,32] This benefit should apply to the more general IVR expressions presented here.

Unfortunately, despite these advantages, the IVR expressions presented above are not as generally useful as are the original MCR. We recall that much of the power of the MCR lies in their applicability to arbitrary classical canonical variables $(\mathbf{x}_1,\mathbf{x}_2)$, including choices such as spherical coordinates and action-angle variables. This feature allows the MCR to simplify the treatment of many systems by taking full advantage of conservation laws and leads to natural and efficient semiclassical expressions for the amplitudes of transitions between energy eigenstates. However, the above IVR approximations cannot be applied with arbitrary choices of variables. The reason for this limitation is that such choices require the $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ to obey certain characteristic boundary conditions at finite values of $\mathbf{x}_2$ and $\mathbf{x}_1$. Typical examples are periodic boundary conditions at 0 and 2π when $\mathbf{x}_i$ is an angle and regular boundary conditions at the origin when $\mathbf{x}_i$ is a radial distance. The IVR expressions are, however, generally unable satisfy these conditions due to the properties of the Gaussian factors $G_{\boldsymbol{\Gamma}}(\mathbf{x}_i,\mathbf{x},\mathbf{y})$ which are not adapted to obeying specific forms of behavior at finite $\mathbf{x}_i$. Thus, the L-type expression for $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ cannot be made to satisfy specific boundary conditions at finite values of $\mathbf{x}_2$, the R-type expression cannot obey such conditions at finite $\mathbf{x}_1$, and the LR-type expression cannot be made to obey such conditions at finite values of either $\mathbf{x}_2$ or $\mathbf{x}_1$. Although these expressions are able to satisfy boundary conditions at $\mathbf{x} \to \pm\infty$, this only qualifies them for use when the variables $\mathbf{x}$ appearing in the Gaussians

are Cartesian; they cannot be used for other kinds of variables. As a result, our present expressions lack the power and generality of the MCR.

A closely related problem with use of the IVR expressions in their present forms concerns the behavior of the factor $G_{\mathbf{\Gamma}}(\mathbf{x}_1;\mathbf{x},\mathbf{y})$ as a function of $\mathbf{x}$ when this variable and $\mathbf{x}_1$ are defined for only a restricted range of values. Examples of such variables are the radial distance and the vibrational action, which are defined only for positive values. In such cases, we cannot rely on the SP method to make the IVR expressions accurate for values of $\mathbf{x}_1$ is near a boundary. We recall that the usual SP method is based on the assumptions that the integrand can be approximated by a Gaussian expression near the stationary point $\mathbf{x} = \mathbf{x}_1$ and that the integration limits can be extended to $\pm\infty$ in both directions about such a point. However, these conditions will not be obeyed when the integral contains only values for $\mathbf{x}$ on one side of the stationary point. Thus, the accuracy of an IVR expression near such a boundary must rely on very specific properties of the integrand in this region. It can be anticipated that the Gaussian form of G will not possess these necessary properties in all cases.

Although the boundary condition difficulties can sometimes be sidestepped when the quantities to be calculated are not sensitive to values of $\mathbf{x}$ near the boundary points,[43] these problems cannot always be ignored. Some of the consequences of doing so are illustrated in ref 58 where use of the Herman−Kluk propagator for non-Cartesian variables is shown to produce errors in the computed autocorrelation spectrum.

IV. Non-Gaussian IVR Treatment of the MCR

A. General Requirements for *G*. Fortunately, it is possible to generalize our expressions to make them valid for arbitrary choices of canonical variables, thus recovering the advantages of the original MCR. We have mentioned that the feature limiting the boundary behavior of the present IVR expressions is the nature of the Gaussian factors G in the integrals. Therefore, to allow more general boundary behavior, it is necessary to somehow replace the G with more appropriate functions.

One possiblity is to replace Gaussians G with particular sums of Gaussians that enforce the desired boundary conditions. This leads to IVR expressions that can be written as sums over integrals, each being of the form given in eqs 3.1, 3.6, or 3.8, containing Gaussian integrands. This approach was applied by Reimers and Heller[70] to adapt the FGA to periodic boundary conditions. More recently, similar approaches were used by Sun and Miller,[43] Maitra,[51] and McCormack[52] to adapt IVR propagator expressions to such boundary conditions. Here, we describe a more general strategy that includes the Gaussian sum method as a special case.

In our approach, we recognize that the Gaussian factors in our IVR expressions can be replaced by a wide variety of other forms, including those that allow the resulting $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ to obey desired boundary conditions. This is possible because in order for an IVR expression to be a semiclassical approximation, it needs only to reduce to the PSC result when the integral is approximated by the SP method to the lowest order in $\hbar$. But this is a rather weak condition. For it to be satisfied, it is sufficient that the factors G satisfy[15,17,71]

$$\lim_{\hbar\to 0} G_{\mathbf{\Gamma}}(\mathbf{x}';\mathbf{x},\mathbf{y}) = \mathrm{e}^{i\Phi(\mathbf{x}';\mathbf{x},\mathbf{y})/\hbar} \tag{4.1}$$

where

$$\Phi(\mathbf{x}';\mathbf{x},\mathbf{y}) \approx \mathbf{y}^{\mathrm{T}}\mathbf{S}(\mathbf{x}' - \mathbf{x}) + O(|\mathbf{x}' - \mathbf{x}|^2) \tag{4.2}$$

In terms of this expression, the matrix $\mathbf{\Gamma}$ appearing in the pre-exponential factors should be defined by

$$\Gamma_{i,j} = \frac{1}{2i}\left(\frac{\partial^2\Phi}{\partial x_i'\partial x_j'}\right)_{\mathbf{x}'=\mathbf{x}} \tag{4.3}$$

Note that the G defined in this way no longer needs to be Gaussian.

In addition to the factors G, the expressions for the pre-exponential factors A, B, and C appearing in the IVR formulas may be generalized by adding terms to them that only contribute higher powers of $\hbar$ to the integrals. Even further generalizations of the IVR forms are possible[15] but need not be considered here.

For the cases of the wave function and the propagator, it is possible to show that the IVR expressions remain USC approximations, even under the relaxed conditions described above.[15,17] Thus, the factors G may be replaced by more general non-Gaussian forms—including those appropriate for desired boundary conditions—without losing the basic advantages of the IVR treatments.

B. *G* from Classical Exact IVR Expressions. The appropriate functional expressions for the factors G are, however, not always obvious. One approach to determining these expressions is based on the observation that, with the Gaussian restriction removed, the new IVR form for the wave function [eq 3.20 as modified by eq 4.1] is so general that it allows one to express exact quantum mechanical wave functions for a variety of systems in this ostensibly "semiclassical" form.[71,72] Such reference systems include some that are described in terms of non-Cartesian variables so that the wave functions obey the appropriate corresponding boundary conditions. The functions G appearing in these classical exact (CE) expressions can be used to form IVR expressions for other target systems obeying similar boundary conditions. Note that such choices for $G(\mathbf{x}_1,\mathbf{x},\mathbf{y})$ contain not only the correct dependence on $\mathbf{x}_1$ to satisfy the desired boundary conditions but, less trivially, the correct dependence on $\mathbf{x}$ to yield accurate IVR results, at least for the treatment of wave functions for target systems resembling the reference systems.

Examples of reference systems for which CE expressions have been obtained include:[71−73]

1. Harmonic Oscillator, Linear Potential, and Free Particle in Cartesian Coordinates. For such systems, the IVR wave function, eq 3.20, with the Gaussian form for G, eq 3.2, becomes identical to the FGA wave function of Heller.[65] It is furthermore known that the FGA wave function can be made identical to the exact quantum wave function, for the special systems listed above, by choosing $\mathbf{\Gamma}$ to have certain values.[65] Of course, such wave functions obey specific boundary conditions at $\pm\infty$, as is appropriate for the Cartesian coordinate representation. Thus, this example simply confirms that Gaussian functions are appropriate choices for the factors G in IVR treatments of target systems that are described in terms of Cartesian variables.

2. Free Two-Dimensional Rotational Motion. For rotational motion in two dimensions, the IVR wave function, eq 3.20, can be expressed as

$$\psi_L(\phi') = N\int_0^{2\pi} \mathrm{d}\theta\, G_\gamma(\phi';\phi,p_\phi) \times (\partial p_\phi/\partial\theta - 2i\gamma\partial\phi/\partial\theta)^{1/2}\,\mathrm{e}^{iW/\hbar} \tag{4.4}$$

where N is a normalization constant, ϕ is the rotational angle coordinate, p_ϕ is the momentum conjugate to ϕ, L is the quantized action variable for the state of interest, and θ is the

angle variable conjugate to L. For the special case of free rotational motion, $\phi = \theta$, $p_\phi = L = l\hbar$, with $l = 0, 1, ...$, and $W = L\theta$, so that the IVR wave function becomes

$$\psi_L(\phi') = N' \int_0^{2\pi} d\phi \, G_\gamma(\phi';\phi,p_\phi) \, e^{il\phi} \tag{4.5}$$

where N' is another constant. By changing the integration variable, it is clear that ψ of eq 4.5 will be equal to the exact quantum wave function $\propto \exp(il\phi')$ for any choice of $G(\phi';\phi,p_\phi)$ that is a 2π-periodic function of $\phi' - \phi$. One example of such a function G, that is compatible with conditions of eqs 4.1 and 4.2, is

$$G_\gamma(\phi';\phi,p_\phi) = \sum_{k=-\infty}^{\infty} e^{-\gamma(\phi'-\phi-2\pi k)^2/\hbar} \, e^{ip_\phi(\phi'-\phi-2\pi k)/\hbar} \tag{4.6}$$

which is similar to the choice applied in refs 43, 51, 52, and 70. Another possibiity, that we will examine numerically in section V, is

$$G_\gamma(\phi';\phi,p_\phi) = e^{\gamma[\cos(\phi'-\phi)-1]/\hbar + ip_\phi \sin(\phi'-\phi)/\hbar} \tag{4.7}$$

Clearly, there is an infinite variety of other choices for G that also yield the exact quantum wave function in this case. This situation illustrates that, quite generally, CE expressions for wave functions are not unique.

It is important to note that since these G functions obey the conditions of eqs 4.1 and 4.2, despite their non-Gaussian forms, a SP treatment of the integral in eq 4.4 still yields the correct PSC result. Furthermore, since these choices for G satisfy periodic boundary conditions at $\phi' = 0$ and 2π, they can be used to form IVR expressions for wave functions (or other quantities $\langle\phi'|x\rangle$) for more general systems that obey similar boundary conditions.

3. Radial Wave Functions for the Isotropic Three-Dimensional Harmonic Oscilator, the Coulombic System, and the Free Particle. For the above systems, it can be shown[71,72] that the radial wave functions $R_l(r')$, associated with angular momentum quantum number l, can be expressed exactly in IVR form [eq 3.20] if the factor G is taken as

$$G_\gamma(r';r,p_r) = (r'/r)^l \, e^{-(\gamma/\hbar)(r'-r)^2 - (l+1/2)(r'/r-1)} \, e^{ip_r(r'-r)/\hbar} \tag{4.8}$$

and the parameter γ is chosen appropriately. We observe that this form guarantees that $R_l(r')$ obeys regular boundary conditions at $r' = 0$. We also note that this form satisfies the conditions of eqs 4.1 and 4.2. Thus, our IVR expressions with this form of G can be used to obtain semiclassical approximations for radial wave functions of other systems and for other quantities $\langle r'|\mathbf{x}\rangle$, when state $|\mathbf{x}\rangle$ is characterized by a definite value for the angular momentum.

4. Free Orbital Motion. The wave functions for free orbital motion corresponding to azimuthal quantum number $m = 0$ are the Legendre polynomials, $P_l(\cos\theta)$. These functions can be expressed exactly in IVR form, using eq 3.20, if the factor G in eq 3.20 is chosen as[71]

$$G_\gamma(\theta;\chi,L) = \sqrt{-2\pi i \sin\theta} \times (\lambda\cos\chi - ic\sin\chi)^{1/2} \, e^{-c+\cos\theta(c\cos\chi - i\lambda\sin\chi)} \times J_0[\sin\theta(\lambda\cos\chi - ic\sin\chi)] \tag{4.9}$$

where χ is the orbital angle, $L = \lambda\hbar$ is the angular momentum conjugate to χ, $c = 2\gamma/\hbar$, and J_0 is the Bessel function of the first kind.

In order for this form of G to give the exact wave function for free orbital motion, the parameter γ must be chosen as $L/2$. However, even with more general values of γ, this form still obeys the conditions of eqs 4.1 and 4.2, as can be proven by examining the asymptotic approximation for the Bessel function with large argument,[74] consistent with $\hbar \to 0$. Thus, since this choice for G enforces the boundary conditions associated with orbital motion at $\theta = 0$ and π, it can be used to form IVR expressions for more general quantities $\langle\theta|\mathbf{x}\rangle$ that obey similar boundary conditions

It should be mentioned that the boundary conditions for orbital motion generally depend on the value of the azimuthal quantum number m. The expression for G presented here is valid only for $m = 0$. A somewhat more complicated expression for G is available for the more general case.[71]

C. *G* for Action Variables. In the above examples, the variable $\mathbf{x}_2$ in $\langle\mathbf{x}_2|\mathbf{x}_1\rangle$ was a particular kind of coordinate. To find forms for G that are appropriate for L- and LR-type IVR expressions when $\mathbf{x}_2$ is an action variable $\mathbf{J}$, we use a somewhat different approach which we outline below for the one-dimensional case $\langle J|x\rangle$.

We first, express the quantity of interest, $\langle J|x\rangle$, in the form

$$\langle J|x\rangle = \int \langle J|q\rangle\langle q|x\rangle \, dq \tag{4.10}$$

$$= \int \psi_J(q)^* \langle q|x\rangle \, dq \tag{4.11}$$

where q is a coordinate variable and $\psi_J(q) = \langle q|J\rangle$ is the time-independent wave function for state $|J\rangle$. Substituting the L- or LR-IVR forms for $\langle q|x\rangle$ into eq 4.11, we find that we can express $\langle J|x\rangle$ in terms of an integral containing the quantity

$$D_\gamma(J;\bar{q},\bar{p}) = \int dq \psi_J(q)^* G_\gamma(q;\bar{q},\bar{p}) \tag{4.12}$$

On the basis of the IVR form of $\langle J|x\rangle$, we expect the evaluation of D to yield a factor $G'(J;\bar{J},\bar{\theta})$ obeying the conditions of eqs 4.1 and 4.2, where $\bar{J}$ and $\bar{\theta}$ are action and angle variables corresponding to $(\bar{q},\bar{p})$. It is this factor that we wish to determine. For the general case, we could proceed by evaluating the integral in eq 4.12 by the SP method using a WKB expression for ψ, but this technique is not powerful enough to describe the precise form of G' for general values of J and $\bar{J}$. Instead, to learn how G' should look in order that it incorporate the boundary conditions for variables J and $\bar{J}$, we consider model cases where the IVR expression for $\psi_J(q)$ is exact, the corresponding $G_\gamma(q;\bar{q},\bar{p})$ is known, and the integral over q in eq 4.12 can be performed analytically.

As an example of such a model treatment, we consider the case of the one-dimensional harmonic oscillator in state n so that $\psi_J(q)$ [with $J = (n + 1/2)\hbar$] is known analytically. Furthermore, as mentioned above, the IVR expression for $\psi_J(q)$ [eq 3.20] is exact in this case if $G_\gamma(q;\bar{q},\bar{p})$ is chosen to be a Gaussian [eq 3.2] with a certain value for γ. This value turns out to be $\mu\omega/2$,[65] where μ and ω are, respectively, the oscillator mass and frequency. Since eq 3.20 for $\psi_J(q)$ is an L-type IVR formula for $\langle q|J\rangle$, (i.e., it is equivalent to an R-type expression for $\langle J|q\rangle$) it does not, by itself, contain the desired factor $G'(J;\bar{J},\bar{\theta})$. Nevertheless, such a factor can

be deduced by evaluating the integral for D_γ analytically to obtain[75]

$$D_\gamma(J;\bar{q},\bar{p}) = d(\bar{J},\bar{\theta})\, e^{-iF_2(\bar{q},\bar{J})/\hbar} G'_1(J;\bar{J},\bar{\theta}) \qquad (4.13)$$

where

$$F_2(\bar{q},\bar{J}) = \int^{\bar{q}} \bar{p}(\bar{J})\, d\bar{q} \qquad (4.14)$$

$$d(\bar{J},\bar{\theta}) = \left(\frac{\hbar\, e^{i\bar{\theta}}}{\sqrt{2\bar{J}\mu\omega}}\right)^{1/2} \qquad (4.15)$$

and the function G'_1 is given by

$$G'_\alpha(J;\bar{J},\bar{\theta}) = \left(\frac{\sqrt{2\pi/\hbar}}{\hbar^n n!}\right)^{\alpha/2} e^{\alpha(J\ln\bar{J}-\bar{J})/(2\hbar)+i\bar{\theta}(\bar{J}-J)/\hbar} \qquad (4.16)$$

for the special case $\alpha = 1$. When J is large, eq 4.16 can be somewhat simplified using Stirling's approximation to obtain

$$G'_\alpha(J;\bar{J},\bar{\theta}) = e^{\alpha(J\ln\bar{J}/J-\bar{J}+J)/(2\hbar)}\, e^{i\bar{\theta}(\bar{J}-J)/\hbar} \qquad (4.17)$$

Equation 4.13 is just the form for D needed to convert eq 4.11 to the expected IVR form. The factor $\exp(-iF_2/\hbar)$ combines with the factor containing the generating function in $\langle q|x\rangle$ to form the exponential factor $\exp(iF/\hbar)$ for $\langle J|x\rangle$, while d combines with the pre-exponential factor in $\langle q|x\rangle$ to yield the appropriate pre-exponential factor for $\langle J|x\rangle$. The function G'_1 is the Gaussian-replacement factor we have sought. Indeed, when $\hbar \to 0$ (so that $J/\hbar$ is large) and $|J - \bar{J}|$ small, a Taylor expansion of the exponent in eq 4.17 shows that G'_α becomes a Gaussian $G_{\alpha/4J}(J;\bar{J},\bar{\theta})$ as defined by eq 3.2, consistent with the requirements of eqs 4.1 and 4.2.

Thus, G'_α (with α not necessarily equal to 1) can serve as the appropriate factor G for a semiclassical L- or LR-type IVR treatment of $\langle J|x\rangle$, where J is a vibrational action. Although derived for the harmonic oscillator, numerical results confirm that this form can be used semiclassically to describe vibrational states of more general anharmonic oscillators as well.[76] In contrast, the use of Gaussian expressions for $G'(J;\bar{J},\bar{\theta})$ in L- and LR-type IVR treatments of $\langle J|x\rangle$ is found to yield results of much lower accuracy for small values of J, even for harmonic systems.[75,76]

Since the vibrational actions J and $\bar{J}$ are defined only for nonnegative values, it is of interest to examine the limiting boundary behavior of G' when these variables become zero. From eq 4.16, we see that G' has a finite value at $J = 0$ (G' would be 0 at $J = -\hbar/2$ corresponding to $n = -1$). Perhaps more significantly, eqs 4.16 and 4.17 show that G' approaches zero as a positive power of $\bar{J}$ in the limit $\bar{J} \to 0$ (except when $J = 0$). Gaussian expressions for G' cannot produce this behavior that is apparently required for the accurate description of vibrational states with low values of J.

Methods similar to the one illustrated here can be used to find factors G' that are appropriate for actions associated with other kinds of motion. For example, such a factor for rotational actions can be derived by treating the case where $\langle \mathbf{q}|\mathbf{x}\rangle$ is the spherical harmonic, in which case a CE expression is again known[71] and D can again be evaluated analytically.

V. Examples

In this Section we present some examples that illustrate how IVR methods can be applied, with non-Gaussian factors G, to obtain semiclassical approximations for quantities $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ in cases where the $\mathbf{x}_i$ are not Cartesian variables.

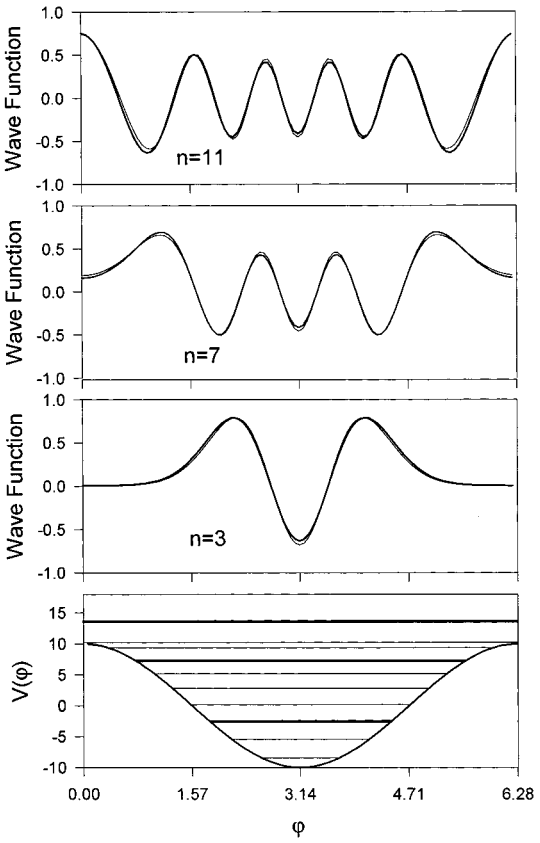

Figure 1. Semiclassical IVR wave functions (heavy curves) and quantum wave functions (light curves) for three states of the hindered rotor. The bottom panel shows the potential energy curve $V(\phi) = V_0 \cos \phi$ for the system with the energy levels for the states treated indicated by heavy horizontal lines.

A. Hindered Rotor. We begin with a simple numerical example in which we use an IVR treatment to calculate wave functions obeying periodic boundary conditions associated with nonfree two-dimensional rotational motion.

We wish to obtain semiclassical eigenfunctions of the hindered rotor Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{d\phi'^2} + V_0 \cos\phi' \qquad (5.1)$$

for parameter values $\mu = \hbar = 1$, and $V_0 = 10.0$. Our treatment is based on eq 4.4 for the wave function $\psi_L(\phi')$ with eq 4.7 for the factor $G_\gamma(\phi';\phi,p_\phi)$.

The quantities $\phi(\theta,L)$, $p_\phi(\theta,L)$, $W(\theta,L)$, etc., appearing in eq 4.4 for the state with quantum number l, must be calculated at the semiclassical energy E_l for that state, as determined by the WKB quantization condition. For levels above the potential barrier, this condition yields two degenerate levels, and the IVR treatment produces two corresponding wave functions. For comparison with the quantum results, we form linear combinations of such semiclassical wave functions to create functions having definite inversion symmetry about π.

The IVR wave functions obtained were found to be not very sensitive to the value of parameter γ. The value $\gamma = 6.6$, consistent with the condition $\gamma = \mu\omega/2$ for harmonic-like low energy states, was used for all levels in our calculation. Some resulting semiclassical wave functions are shown in Figure 1, where they are compared with accurate quantum results. It is

apparent that the semiclassical wave functions obey the correct periodic boundary conditions at angles 0 and 2π and are in very good agreement with the quantum wave functions for all values of the angle. Although the figure shows results for only three states, the degree of semiclassical/quantum agreement was found to be no worse for other states examined.

B. *S*-Matrix for Collinear Scattering. We now apply the IVR form of the correspondence relations to derive a useful semiclassical expression for the *S*-matrix describing transitions between vibrational states $\mathbf{n}_1$ and $\mathbf{n}_2$ in a collinear collision at energy E.

Our treatment begins with the well-known PSC expression for the *S*-matrix derived by Miller[1−4,6,77,78] and Marcus[66,67]

$$S_{\mathbf{n}_2,\mathbf{n}_1}(E) = i \sum \left[\frac{\partial^2 \Phi(\mathbf{n}_2,\mathbf{n}_1)/\partial \mathbf{n}_2 \partial \mathbf{n}_1}{(-2\pi i\hbar)^{N-1}} \right]^{1/2} \exp\left[\frac{i\Phi(\mathbf{n}_2,\mathbf{n}_1)}{\hbar} \right] \quad (5.2)$$

where the $\mathbf{n}_i$'s are defined as $\bar{\mathbf{J}}_i/\hbar - {}^1/_2$, in terms of the initial ($i = 1$) and final ($i = 2$) vibrational actions $\bar{\mathbf{J}}_i$. The $\mathbf{n}_i$ are thus momentum-type classical variables corresponding to vibrational quantum numbers. The coordinate variables conjugate to the $\mathbf{n}_i$ are denoted here by $\mathbf{q}_i = \hbar(\boldsymbol{\theta}_i - \boldsymbol{\omega}_i \mu R_i/P_i)$, where $\boldsymbol{\theta}_i$'s are the initial or final vibrational angle variables, μ is the reduced mass for the collision, $\boldsymbol{\omega}$'s are the vibrational frequencies of the fragments, and (R_i,P_i)'s are the initial or final translational distance and momentum. In the work of Miller and Marcus, the coordinates $\mathbf{q}_i$ are denoted by symbols with overbars, but we do not adopt this notation here to avoid confusion with our variables $(\bar{\mathbf{x}},\bar{\mathbf{y}})$. Finally, the quantity

$$\Phi(\mathbf{n}_2,\mathbf{n}_1) = \int_{-\infty}^{\infty} \mathrm{d}t\, [-R(t)\dot{P}(t) - \hbar \boldsymbol{\theta}(t)^{\mathrm{T}} \dot{\mathbf{n}}(t)] \quad (5.3)$$

appearing in eq 5.2 is the generating function for the transformation between $(\mathbf{n}_1,\mathbf{q}_1)$ and $(\mathbf{n}_2,\mathbf{q}_2)$ for the $N - 1$ vibrational degrees of freedom.

Referring to eq 2.3, we see that we can express eq 5.2 as

$$S_{\mathbf{n}_2,\mathbf{n}_1}(E) = i\langle \mathbf{n}_2 | \mathbf{n}_1 \rangle \quad (5.4)$$

in MCR notation. This immediately allows us to use eq 3.6 to express the *S*-matrix as an L-type IVR formula. We need only substitute: $\mathbf{x}_1 = \mathbf{n}_1$, $\mathbf{y}_1 = \mathbf{q}_1$, $\mathbf{x}_2 = \mathbf{n}_2$, $\mathbf{y}_2 = \mathbf{q}_2$, and $\bar{\mathbf{x}} = \mathbf{n}(\mathbf{n}_1,\mathbf{q}_1)$, $\bar{\mathbf{y}} = \mathbf{q}(\mathbf{n}_1,\mathbf{q}_1)$, where $\mathbf{n}$ and $\mathbf{q}$ are the final values of the classical quantum number and coordinate variables obtained from initial values $(\mathbf{n}_1,\mathbf{q}_1)$. Of course, these final values need not be equal to $(\mathbf{n}_2,\mathbf{q}_2)$. In addition, we use a multidimensional generalization of $G'_\alpha(J;\bar{J},\bar{\theta})$ [eq 4.17] in place of the function G since our variables $\mathbf{n}$ are related to vibrational actions. The final result is

$$S_{\mathbf{n}_2,\mathbf{n}_1}(E) = i\left(\frac{1}{2\pi\hbar}\right)^{N-1} \int \mathrm{d}\mathbf{q}_1\, G'_\alpha(\mathbf{n}_2;\mathbf{n},\mathbf{q})\, B(\mathbf{n},\mathbf{q};\mathbf{q}_1)\, \mathrm{e}^{i\Phi(\mathbf{n},\mathbf{n}_1)/\hbar} \quad (5.5)$$

where

$$G'_\alpha(\mathbf{n}_2;\mathbf{n},\mathbf{q}) = \exp\left\{ \sum_{k=1}^{N-1} \frac{\alpha_k}{2} \left[(n_{2k} + 1/2) \ln\left(\frac{n_k + {}^1/_2}{n_{2k} + {}^1/_2} \right) - n_k + n_{2k} \right] \right\} \times \exp[i\mathbf{q}^T(\mathbf{n} - \mathbf{n}_2)/\hbar] \quad (5.6)$$

$$B(\mathbf{n},\mathbf{q};\mathbf{q}_1) = [\det(b_{ij})]^{1/2} \quad (5.7)$$

with

$$b_{ij} = \frac{\partial q_i}{\partial q_{1j}} + i\left(\frac{\hbar\alpha_i}{2n_i + 1} \right) \frac{\partial n_i}{\partial q_{1j}} \quad (5.8)$$

and the α_k are parameters.

The above derivation is simple and direct. An alternate approach derives eq 5.5 from an asymptotic analysis of the IVR expression for the wave function, eq 3.20.[75] This requires much more effort but provides several important insights. For example, since eq 3.20 is a USC expression and the derivation of eq 5.5 with $0 < R\alpha_k < \infty$ does not involve steps that degrade its uniform quality, it is possible to conclude that eq 5.5 is itself a USC approximation, provided that the α_k are chosen to obey these conditions.

Further aspects of our IVR expression for S are discussed elsewhere,[75] where numerical results are also reported for the Secrest-Johnson[79] collisional model. Here we only summarize some of the major characteristics of eq 5.5.

1. This expression reduces to the PSC formula for the *S*-matrix, eq 5.2, as $\alpha_k \rightarrow \infty$ and becomes identical to the original Miller−Marcus IVR expression[6,66,67] for the *S*-matrix as $\alpha_k \rightarrow 0$, for all k.
2. The numerical studies confirm expectations [based on the uniform properties of eq 5.5] that choices for α_k obeying $0 < R\alpha_k < \infty$ give results that are generally much more accurate than either eq 5.2 or the Miller−Marcus IVR treatment.
3. The non-Gaussian form of G' given in eq 5.6 is found to be essential for achieving such accuracy for low values of $\mathbf{n}_2$.

Since our IVR expression involves only an $N-1$-fold integration, it yields the *S*-matrix at a particular energy using far fewer trajectories than would be needed for a treatment directly based on the semiclassical IVR propagator.[36,40] In the latter case, the dimensionality of the integrations is $2N$[36] or $2N - 1$,[40,53,54] depending on the formulation. The difference between $N - 1$ and, say, $2N - 1$ is extremely important in practice since the computational labor in typical IVR calculations increases exponentially with the dimensionality of the integrations.[30]

It is clear that, in additional to the L-type expression obtained above, it is possible to derive R-type LR-type expressions for the *S*-matrix, in analogy with the FVR[67,68] and double-integral IVR treatments[66,77] of classical *S*-matrix theory. The usefulness of such treatments remains to be fully investigated.

C. Differential Cross Section for Elastic Scattering. As a final example, we use our form of the correspondence relations to derive an IVR expression for the differential cross section of elastic atom−atom scattering. We begin by recalling some basic quantum mechanical results that we will need. The differential cross section for scattering from a spherically symmetric potential is given by

$$\mathrm{d}\sigma/\mathrm{d}\Omega = |f(\theta)|^2 \quad (5.9)$$

The scattering amplitude f can be expressed in terms of the partial wave sum

$$f(\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1)[\mathrm{e}^{2i\eta_l} - 1] P_l(\cos\theta) \quad (5.10)$$

where η_l are phase shifts for the scattering of the l-th partial wave and $k = \sqrt{(2mE/\hbar^2)}$, where E is the energy of the system and m is the reduced mass for the collision partners.

The scattering amplitude can be approximated semiclassically by the well-known PSC formula[12,80,81]

$$f(\theta) = -i\sum\left(\frac{L}{\hbar^2 k^2 \sin\theta}\left|\frac{\partial L}{\partial \chi}\right|\right)^{1/2} e^{i[2\hbar\eta(L)-L\chi]/\hbar \pm i\pi/4} \qquad (5.11)$$

where the sum is taken over impact parameters b for particles that are initially moving parallel to the z-axis at $z = -\infty$ and that are scattered into angle θ (measured from the positive z-axis) from the target located at the origin. χ is the deflection function describing the signed asymptotic angle between the outgoing particle and the positive z-axis as $z \rightarrow \infty$. Thus, the observed scattering angle, θ, is an unsigned version of χ restricted to the range $[0,\pi]$. $L = b\hbar k$ is the angular momentum of the particle, and $\eta(L)$ is the semiclassical phase shift, given by

$$\eta(L) = \lim_{R\rightarrow\infty}\left\{\int_{R_-}^{R}\frac{1}{\hbar}\left[2mE - 2mV(R) - \frac{\hbar^2 L^2}{R^2}\right]^{1/2} dR - kR + \frac{L\pi}{2\hbar}\right\} \qquad (5.12)$$

where $V(R)$ is the potential energy function and R_- is the distance of closest approach of the particle to the target. The choice of sign in the $\pm$ phase term of eq 5.11 depends on the branch of the deflection function.[12,80,81]

To derive an IVR expression for f, we temporarily consider a more general scattering scenario in which the particles in the incoming beam do not necessarily move parallel to z-axis but are incident at an asymtotic angle ϕ, as measured from the *negative* z-axis. We will eventually set ϕ to zero. Then the quantity

$$F(\phi,\chi) = 2\hbar\eta(L) - L\chi \qquad (5.13)$$

appearing in the exponent of eq 5.11 can be identified as a F_1-type generating function for the canonical tranformation between the asymptotic variables (ϕ,L) and (χ,L), where the angular momentum L is conserved. Indeed, using the known relation $2\hbar\partial\eta/\partial L = \chi$,[12,80,81] and recalling that ϕ and χ are measured from different directions along the z-axis, it is easy to show that

$$\partial F(\phi,\chi)/\partial\phi = L \qquad \partial F(\phi,\chi)/\partial\chi = -L \qquad (5.14)$$

consistent with eq 2.2. This observation allows us to express the derivative the $|\partial L/\partial\chi|$ appearing in eq 5.11 as $|\partial^2 F/\partial\phi\partial\chi|$. Comparison with eq 2.3 thus shows that the PSC formula for f, eq 5.11, can be written as

$$f(\theta') = \frac{1}{ik}\left(\frac{-2\pi i L'}{\hbar \sin\theta'}\right)^{1/2}\langle\phi|\chi'\rangle \qquad (5.15)$$

in terms of MCR notation, where we have added primes to the final scattering variables for future convenience.

We are now in a position to derive an R-type IVR expression for the scattering amplitude. We simply apply eq 3.8 for the inner product $\langle x_2|x_1\rangle$ with the substitutions of (χ',L') for (x_1,y_1), (ϕ,L) for (x_2,y_2), and $(\chi(L),L)$ for (x,y). In this treatment, the quantity $\chi(L)$ is the deflection function for particles with angular momentum L and needs not coincide with χ', the deflection function for particles with angular momentum L'. The IVR expression obtained in this way is

$$f(\theta') = \frac{1}{2\pi\hbar ik}\left(\frac{-2\pi i L'}{\hbar \sin\theta'}\right)^{1/2} \times \int_0^\infty dL\, A(L;\chi,L)\, e^{i[2\hbar\eta(L)-L\chi(L)]/\hbar}\, G_\gamma^*(\theta';\chi,L) \qquad (5.16)$$

which we henceforth apply for the case $\phi = 0$. Using eq 3.9, we immediately find the pre-exponential factor A to be

$$A(L;\chi,L) = (1 + 2i\gamma\partial\chi/\partial L)^{1/2} \qquad (5.17)$$

Since $f(\theta')$ must obey boundary conditions for orbital motion, the appropriate choice for the function G in eq 5.16 is the form given in eq 4.9. Substituting that expression gives

$$f(\theta') = \frac{1}{ik}\int_0^\infty d\lambda\, \lambda^{1/2}(1 + ic\partial\chi/\partial\lambda)^{1/2}\, e^{i(2\eta-\lambda\chi)} \times (\lambda\cos\chi + ic\sin\chi)^{1/2}\, e^{-c}\, e^{\cos\theta'(c\cos\chi + i\lambda\sin\chi)} \times J_0[\sin\theta'(\lambda\cos\chi + ic\sin\chi)] \qquad (5.18)$$

where $\lambda = L/\hbar$ and $c = 2\gamma^*/\hbar$. In presenting this result, we have brought the factor $L'^{1/2}$ in eq 5.16 within the integral as $L^{1/2}$. This is valid since a SP treatment of the integral will produce the entire pre-exponential factor at the stationary phase point, where $L = L'$.

To allow a comparison with the quantum expression for f, we examine eq 5.18 in the special case $c = \lambda$, where we can simplify our expression using[74]

$$e^{z\cos\theta'} J_0(z\sin\theta') = \sum_{l=0}^{\infty}\frac{z^l}{l!}P_l(\cos\theta') \qquad (5.19)$$

When this identity is substituted into eq 5.18 and the resulting integral is evaluated term by term in the SP approximation, we obtain

$$f(\theta') = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+2)\, e^{2i\eta_l}P_l(\cos\theta') \qquad (5.20)$$

where, in this expression, $\eta_l = \eta[L = (l + 1/2)\hbar]$. The form of this result differs from that of the exact partial wave expression, eq 5.10, in two ways: the first factor in each term here is $(2l + 2)$ instead $(2l + 1)$, and the second factor in each term here is $e^{2i\eta_l}$ instead of $e^{2i\eta_l} - 1$.

The first difference becomes negligible in the classical limit where many partial waves contribute to f. Still, this discrepancy can be removed by replacing the factor $\lambda^{1/2}$ in the integrand of eq 5.18 with $\lambda^{1/2} - 1/(2\lambda^{1/2})$. This step is justified since it only adds a term to the pre-exponential factor that is of higher order in $\hbar$ than is the factor itself. As explained in the paragraph following eq 4.3, such modifications of IVR expressions are permissible.

Concerning the second difference, it is known that the additional term in the quantum expression for the scattering amplitude is singular and affects only the value of $f(\theta')$ at $\theta' = 0$.[12,80,81] Its role is to remove from f an infinite contribution arising from the flux in the forward direction due to the free motion of particles with large impact parameters. This correction can be incorporated in our IVR treatment simply by subtracting from eq 5.18 the expression that would be obtained by applying eq 5.18 for free particle motion (in which case $\chi = 0$, $\eta = 0$).

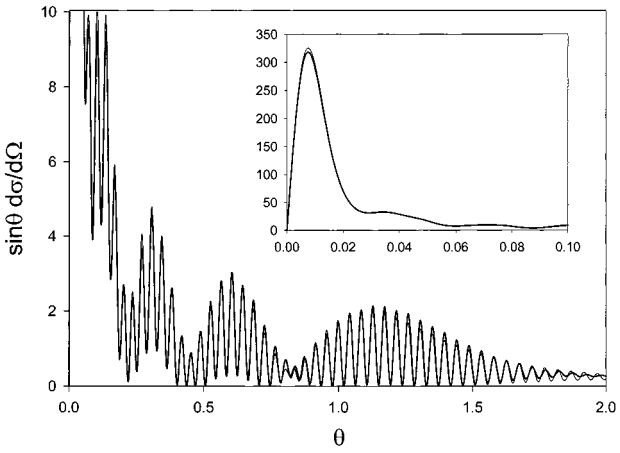

Figure 2. Differential cross section for elastic scattering. The heavy curve is obtained from the IVR approximation, while the light curve is obtained from the partial wave expansion. The inset shows the cross section for small values of the angle.

With these modifications our final result for the scattering amplitude becomes

$$f(\theta') = \frac{1}{ik}\int_0^\infty d\lambda(\lambda - {}^1/_2)\, e^{-c}\{(1 + ic\partial\chi/\partial\lambda)^{1/2}(\lambda\cos\chi + ic\sin\chi)^{1/2}\,\lambda^{-1/2}\; e^{i(2\eta-\lambda\chi)}\, e^{\cos\theta'(c\cos\chi+i\lambda\sin\chi)}\, J_0[(\lambda\cos\chi + ic\sin\chi)\sin\theta'] - e^{c\cos\theta'}\, J_0(\lambda\sin\theta')\} \quad (5.21)$$

This expression can also be derived, albeit with more effort, from an asymptotic analysis of the IVR expression for the scattering wave function, eq 3.20. Since this wave function expression is a USC approximation and no steps are introduced in the derivation of eq 5.21 that degrade this property, eq 5.21 is itself a uniform approximation. It thus yields accurate semiclassical results for all values of θ', including those for which the PSC expression, eq 5.11, diverges. These values include the rainbow angle, θ'_r, where $d\chi'/dL = 0$, the forward direction, $\theta' = 0$, and the backward direction, $\theta' = \pi$.

Our IVR result is somewhat reminiscent of certain semiclassical expressions for $f(\theta')$ that are obtained by replacing the partial wave sum with an integral and substituting various asymptotic approximations for the Legendre polynomials (some of which involve the Bessel function J_0).[12,80,81] However, unlike the present result, these non-IVR approximations break down either at $\theta' = 0$ or π or at both angles. Other semiclassical expressions for f that are uniform in various restricted regions are known.[80−82] A uniform expression that is valid both for glory ($\theta' = 0, \pi$) and rainbow scattering was derived by Miller.[83]

To test the accuracy our result, we apply it to scattering from the Lennard−Jones potential

$$V(R) = 4\epsilon[(R_0/R)^{12} - (R_0/R)^6] \quad (5.22)$$

We set the parameters in our calculation to $E/\epsilon = 1.6$ and $(2mE)^{1/2}R_0/\hbar = 60$ so that the numerical results can be readily compared with those of other semiclassical treatments.[12] The scattering amplitudes are not strongly dependent on the value of γ or c used in the IVR calculation. The results shown here are obtained using $c = 0.2\lambda$.

Figure 2 compares the semiclassical differential cross section, calculated from eq 5.21, with that obtained from the partial wave expansion, eq 5.10, using semiclassical phase shifts. These results, in turn, may be compared with those reported in ref 12 for additional treatments of this system. We see that the IVR method yields good agreement with the partial wave results for all values of θ, including those in the rainbow scattering region ($\theta_r = 1.5$ rad in the present case) and the small-angle region, where the PSC results become highly innacurate. However, the quality of the IVR cross section for $\theta > \theta_r$, which contains an oscillatory contribution from classically forbidden scattering, deteriorates when $\theta - \theta_r$ becomes too large. This is an example of a known difficulty[37] that limits the accuracy of the IVR treatment for strongly forbidden classical processes.

It is important to note that, for the case treated, our expression for $f(\theta')$ requires only about 75 trajectories [each corresponding to a value of L, $\chi(L)$, and $\eta(L)$] to achieve convergence for all angles θ'. This is about $^1/_4$ the number of trajectories needed by the partial wave sum or its integral approximants to achieve convergence. Indeed, these other approximations, when applied with only 75 trajectories, are unable to reproduce the converged results even qualitatively. Furthermore, our treatment requires fewer trajectories than would be needed by the PSC or the more conventional USC treatments[12,80,83] to produce the approximately 50 oscillations appearing in Figure 2. Thus, the present IVR treatment makes efficient use of trajectories to describe the semiclassical differential cross section.

The significance of these results is that they show that calculations of cross sections can be performed accurately by IVR methods that directly parallel the classical approach and avoid partial wave summations. It should be possible to generalize the work described here to develop similar IVR treatments of molecular inelastic and reactive scattering cross sections.

VI. Summary and Discussion

We have investigated the possibility of re-expressing the Miller correspondence rules in IVR form as a means of alleviating a number of difficulties that arise in their application. Although it is rather obvious how to do so in terms of integrals containing Gaussian factors, such expressions do not capture the power and generality of the original MCR since they are only appropriate for Cartesian variables. The key to a more useful generalization of the MCR is to replace the Gaussian factors with functions obeying the specific boundary conditions needed to treat non-Cartesian variables. We have suggested that such non-Gaussian functions can be chosen as factors appearing in IVR expressions for the exact wave functions of certain reference systems. We have presented examples of such factors and have illustrated the theory with a few applications.

These applications demonstrate that the IVR formulation of the MCR is capable of producing semiclassical results that obey the correct boundary conditions, are free of caustic singularities, and are uniformly accurate for the full range of variables. From the computational standpoint, IVR treatments are convenient since they do not require numerical searches and, when properly formulated, do not require calculation of Maslov indices.

The IVR expressions presented here for the S-matrix and the elastic cross section illustrate the value of formulating IVR treatments so that they directly produce the final quantities of interest and make use of the specific sets of variables that simplify the physical problems. This can lead to great savings in computational labor over the extraction of such quantities from IVR treatments of the propagator or the wave function in the Cartesian coordinate representation. For example, a brute-force calculation of the elastic scattering cross section based on the Herman−Kluk IVR propagator would involve a full three-dimensional treatment of the collision and would require the numerical evaluation of a six-dimensional integral. This

would necessitate several orders of magnitude more computational effort than the evaluation of the single integral of eq 5.21. Although such a propagator-based calculation would have the advantage of producing the cross section for a range of energies rather than at a single energy, this would come at a price far too high to make such a treatment worthwhile in any realistic case. The focus of our work here has been to address difficulties concerning boundary conditions, to allow the development of such efficient IVR treatments that are taylored specifically to the quantities and systems of interest.

It should be clear that, beyond the few examples presented here, many other applications of the present formalism are possible. Indeed, some further simple examples of this approach have been presented elsewhere.[71] However, in addition to these, several more potential applications readily come to mind. The most intriguing of such ideas involve the further exploitation of expressions such as eq 4.17 that ultimately allow matrix elements between energy eigenstates to be expressed directly in IVR form. This should make it possible to develop novel semiclassical treatments of spectroscopic, photochemical, and collisional transition amplitudes that may be more efficient than those currently in use. Several of these applications are being actively investigated.[76]

However, to develop many further applications, it will be necessary to derive expressions for additional factors G that are appropriate for the treatment of a wider variety of boundary conditions. It is clear that the quantities $\langle \mathbf{x}_2|\mathbf{x}_1\rangle$ that are of interest for polyatomic systems satisfy many different forms of boundary conditions, depending on the cases treated and identity of the variables $\mathbf{x}_i$. The set of G presented in this paper does not suffice to cover all situations of practical importance. As a particular example, expressions analogous to eq 5.5, describing the matrix elements $S^J_{j'l',jl}(E)$ for rotational scattering from an anisotropic potential, would require an as-yet unknown form of G that is consistent with the boundary conditions for l' and j' arising from conservation of the total angular momentum J. More work is needed to derive such expressions and the development of CE treatments for additional reference systems would be a useful step in this direction.

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