Quantum and semiclassical Green's functions in chemical reaction dynamics

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A variety of quantities related to chemical reaction dynamics (state-selected and cumulative probabilities for chemical reactions, photo-dissociation or detachment cross-sections, and others) can be expressed compactly (and exactly) in terms of the quantum mechanical Green's function (actually an operator) \( \mathcal{G}(E) \equiv (E + i\varepsilon - \hat{H})^{-1} \), where \( \hat{H} \) is the Hamiltonian for the molecular system and \( i\varepsilon \) an absorbing potential. It is emphasized that these 'formal' quantum expressions can serve as the basis for practical calculations by utilizing a straightforward \( L^2 \) matrix representation of the operator \( (E + i\varepsilon - \hat{H}) \). It is also shown how the semiclassical initial value representation (IVR) can be used to construct approximations for general matrix elements of the Green's function, so that these same formally exact quantum expressions can also be used to provide semiclassical approximations for all of these dynamical quantities. Recent applications of the quantum and semiclassical methodologies are discussed.

1 Introduction

For a molecular system characterized by a time-independent Hamiltonian operator \( \hat{H} \) it is clear that all dynamical phenomena of the system, including its reaction dynamics, are described by the time evolution operator \( \exp(-i\hat{H}t/\hbar) \), or equivalently by the Green's function, which is its (half) Fourier transform,

\[
\mathcal{G}(E) \equiv (E + i\varepsilon - \hat{H})^{-1} \quad \quad (1a)
\]

\[
\mathcal{G}(E) = (i\hbar)^{-1} \int_0^\infty dt \exp(iEt/\hbar) \exp[-i(\hat{H} - i\varepsilon)/\hbar] \quad \quad (1b)
\]

[In eqn. (1) \( i\varepsilon \) is a positive operator inserted to provide convergence for the integrand in the \( t \to \infty \) limit, and some kind of limit \( \varepsilon \to 0 \) is implied.] This paper surveys a variety of the dynamical quantities related to chemical reactions that can be compactly expressed in terms of the Green's function and describes general approaches whereby these formally exact quantum expressions can be evaluated either fully quantum mechanically or within a semiclassical approximation.

Quantum mechanical calculations involving the Green's function can be made especially straightforward by using an absorbing potential: the convergence parameter \( \varepsilon \) in eqn. (1) is taken to be a potential-energy operator (a 'negative imaginary potential' in \( \hat{H} - i\varepsilon \)). In this way \( \mathcal{G}(E) \) can be chosen to be zero in the interaction region where the interesting dynamics takes place, and only 'turned on' in the entrance and exit regions (cf. Fig. 1) to absorb flux and prevent reflection of probability amplitude, thus enforcing outgoing wave boundary conditions for the Green's function. The \( \varepsilon \to 0 \) limit in this case is that \( \mathcal{G}(E) \) must be turned on sufficiently far from the region where the dynamics of interest takes place so as not to perturb it, and also turned on sufficiently slowly so as not to cause reflection. In practical calculations one must check these aspects of the absorbing potential, along with other convergence tests (e.g. number of basis functions or grid points).

A generic matrix element of the Green's function is then given by a naive matrix representation of eqn. (1a),

\[
\langle \Psi_2 | \mathcal{G}(E) | \Psi_1 \rangle = \sum_{n,n'} \langle \Psi_2 | u_n \rangle \times \langle u_n | E + i\varepsilon - \hat{H} | u_{n'} \rangle^{-1} \langle u_{n'} | \Psi_1 \rangle \quad (2)
\]

where \( \langle u_n | E + i\varepsilon - \hat{H} | u_{n'} \rangle^{-1} \) is short-hand for the \( (n,n') \) element of the inverse of the matrix \( \langle u_n | ... | u_{n'} \rangle \). In eqn. (2) \( | u_n \rangle \) is any convenient \( L^2 \) basis, including a 'basis of grid points', i.e. a discrete variable representation, that spans the region between the absorbing potentials.

It is interesting to compare this representation of the Green's function with that given by the Kohn variational principle (KVP).

Section 2 first surveys a variety of dynamical quantities relevant to chemical reaction dynamics that can all be conveniently expressed in a unified framework in terms of the Green's function. With eqn. (2) it is possible to carry out practical quantum mechanical calculations directly from all these 'formal' quantum expressions. Section 3 then shows how a semiclassical approximation for the Green's function can be constructed, thus providing a straightforward procedure for implementing semiclassical approximations for all these quantities. Examples of various types of these calculations are discussed.

2 Summary of Green's function expressions

2.1 State-to-state reactive scattering

The most detailed description of a chemical reaction is the reactive scattering \( S \) matrix, from which all state-to-state differential scattering cross-sections can be calculated. The \( S \)
matrix for a chemical reaction from reactant state \( n_r \) to product state \( n_p \) can be expressed in terms of the Green’s function as follows:

\[
S_{n_p,n_r}(E) = \frac{1}{i\hbar} \langle \Phi_{n_p} | \hat{\xi} \hat{G}(E) \hat{\xi} | \Phi_{n_r} \rangle
\]  
(3)

where \( \hat{\xi} \) is the part of the absorbing potential in the reactant (product) region (see Fig. 1), and \( \hat{\xi} = \xi_{t} + \xi_{p} \). The reactant and product wavefunctions have the standard incoming wave form

\[
\Phi_{n} = \phi_{n}(q) \exp(-i\hbar v_{n} R_{n})
\]
(4)

for \( n = n_{r} \) or \( n_{p} \), where \( \phi_{n} \) is the eigenfunction for the internal degrees of freedom in the reactant or product asymptotic region, and \( v_{n} \) is the asymptotic translational velocity. [In the present notation the translational part of \( \phi_{n} \) is not complex-conjugated in the bra symbol in eqn. (3).] In eqn. (4) \( R_{n} \) is the radial Jacobi coordinate for arrangement \( \gamma \), and \( q_{e} \) denotes all the other Jacobi coordinates of that arrangement.

### 2.2 Half-state selected reaction probability

A less detailed quantity of interest in reactive scattering is the ‘half-state selected reaction probability’, i.e. the total reaction probability from a given initial reactant state \( n_{r} \),

\[
P_{n_{r}}(E) = \sum_{n_{p}} |S_{n_{p},n_{r}}(E)|^{2}
\]
(5)

This is expressed in terms of the Green’s function as follows:

\[
P_{n_{r}}(E) = \frac{2}{\hbar} \langle \Phi_{n_{r}}^{*} | \hat{\xi} \hat{G}(E) \hat{\xi}_{p} \hat{G}(E) \hat{\xi} | \Phi_{n_{r}} \rangle
\]
(6)

where the only information about the product region that appears is the product absorbing potential \( \hat{\xi}_{p} \). (An analogous expression gives the reaction probability for a specific product state \( n_{p} \), summed over all initial reactant states.)

### 2.3 Cumulative reaction probability

The least detailed (but most common) characterization of a chemical reaction is its thermal, or microcanonical, rate constant \( k(T) \), or \( k(E) \), both of which are given in terms of the cumulative reaction probability \^\(^5\) (CRP), \( N(E) \),

\[
N(E) = \sum_{n_{r},n_{p}} |S_{n_{p},n_{r}}(E)|^{2}
\]
(7a)

as follows

\[
k(E) = [2\pi\hbar \rho_{e}(E)]^{-1} N(E)
\]
(7b)

\[
k(T) = [2\pi\hbar Q_{e}(T)]^{-1} \int_{-\infty}^{\infty} dE \exp(-E/kT)N(E)
\]
(7c)

where \( \rho_{e} \) and \( Q_{e} \) are the density of reactant states per unit energy and reactant partition function per unit volume, respectively. The CRP is given in terms of the Green’s function by

\[
N(E) = 4\pi\rho_{e}(E)^{2} \langle \hat{\xi}_{p} \hat{G}(E) \hat{\xi} \rangle
\]
(8)

The thermal rate constant can also be expressed more directly in terms of the time evolution operator as follows:

\[
k(T) = Q_{e}(T)^{-1} \int_{0}^{\infty} dt \exp[-i(H - i\hbar e)/(2kT)]
\]
\[
\times \exp[-i(H - i\hbar e)/(2kT)] \langle \hat{\xi}_{p} \hat{G}(E) \hat{\xi} \rangle
\]
(9a)

where \( \hat{F} \) is a flux operator and \( t_{e} = t - i\hbar/(2kT) \), or as

\[
k(T) = Q_{e}(T)^{-1} \frac{1}{\hbar} \int_{0}^{\infty} dt \exp[i(H + i\hbar e)/(2kT)] \langle \hat{\xi}_{p} \hat{G}(E) \hat{\xi} \rangle
\]
(9b)

### 2.4 Franck–Condon intensities

Total photodissociation cross-sections and photodetachment cross-sections (cf. Fig. 2) are proportional (within the Franck–Condon approximation) to the Franck–Condon intensity \( I(E) \),

\[
I(E) = \langle \Psi | \delta(E - \hat{H}) | \Psi \rangle = -\frac{1}{\pi} \Im \langle \Psi | \hat{G}^{+}(E) | \Psi \rangle
\]
(10)

For photodissociation the state \( | \Psi \rangle \) is

\[
| \Psi \rangle = (\mu_{21} \cdot \hat{e}) | \Psi_{a} \rangle
\]
(11)

where \( \mu_{21} \) is the transition dipole connecting the two electronic states (for which the curves in Fig. 2 depict the Born–Oppenheimer potential-energy surfaces), \( \hat{e} \) is the polarization vector of the photon, and \( E = E_{a} + \hbar \omega \) being the energy of the initial state and \( \hbar \omega \) that of the photon. For photodetachment \(^{1} | \Psi \rangle = | \Psi_{a} \rangle \) is the nuclear wavefunction for the negative ion bound state (the lower potential-energy surface), and \( E = E_{a} + \hbar \omega - \epsilon \), where \( \epsilon \) is the kinetic energy of the electron.

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Fig. 1 Sketch of the contour diagram of a potential-energy surface for a chemical reaction, where the points indicate the grid points for a discrete variable representation (the ‘basis functions’ in this case). The parallel lines indicate the absorbing potential in the reactant and product valleys.

Fig. 2 Sketch of the potential-energy surfaces relevant to the photodissociation or photodetachment, as discussed in the text.
the detached electron. In both cases the Hamiltonian in the Green's function is that for the upper ('reactive') potential-energy surface.

2.5 Continuum resonance Raman cross-sections

The resonance Raman cross-section, where the excited electronic state is reactive (cf. Fig. 3), is given in terms of the reactive Green's function (i.e. where the Hamiltonian is that of the excited state) by

\[ \sigma_{2\rightarrow 1} = \frac{\alpha_1 \alpha_2}{c} |\langle \chi_2 | \hat{G}(E) | \chi_1 \rangle |^2 \]  (12)

where states \(| \chi_i \rangle, i = 1 \text{ and } 2, \) are given by

\[ | \chi_i \rangle = (\mu_{21} \cdot \hat{E}) | \Psi_i \rangle \]  (13)

\( \mu_{21} \) again being the transition dipole between the two Born-Oppenheimer electronic states, and

\[ E = E_1 + h\omega_1 = E_2 + h\omega_2 \]  (14)

2.6 Golden rule for electronically non-adiabatic transitions

If \(| \Psi_1 \rangle \) is an initial bound state on the upper Born-Oppenheimer potential surface in Fig. 4, then the 'golden rule' expression for the rate of non-adiabatic transitions to the dissociative state is given by

\[ k_{2\rightarrow 1} = \frac{2\pi}{\hbar} \langle \Psi_1 | \delta(E - \hat{H}) | \Psi \rangle \]

\[ = -\frac{2}{\hbar} \text{Im} \langle \Psi_1 | \hat{G}(E) | \Psi \rangle \]  (15)

where \( E = E_1 \) and

\[ | \Psi \rangle = V_{21} | \Psi_1 \rangle \]  (16)

where \( V_{21} \) is the non-adiabatic coupling between the two electronic states and the Hamiltonian in \( \hat{G}(E) \) is that for the lower (reactive) potential surface in Fig. 4.

2.7 Time-dependent expressions

It is also clear from eqn. (1b) that all of the above expressions can be written in terms of the time evolution operator if this proves more convenient in specific applications. For example eqn. (10) becomes

\[ I(E) = \frac{1}{\pi \hbar} \text{Re} \int_0^\infty dt \exp(iEt/\hbar) \]

\[ \times \langle \Psi_1 | \exp[-i(\hat{H} - i\hat{p})t/\hbar] | \Psi \rangle \]  (10’)

2.8 Applications

As noted in the Introduction, all of the quantum expressions surveyed above involving the Green's function can be evaluated by the straightforward use of eqn. (2) to calculate matrix elements of the Green's function. The practical considerations are that one wishes to locate the absorbing potential as close to the interaction region as possible (cf. Fig. 1) so that the \( I(E) \) basis can be as small as possible, but if it is brought in too close it will perturb the true dynamics one is trying to simulate. The final result of the calculation must of course be independent of the precise location of the absorbing potential, and this is a convergence test that must be checked.

A number of quantum calculations of this type have been carried out. Some state-to-state calculations have been made to illustrate the principle, but most applications have been to cumulative reaction probabilities since other approaches do not exist for obtaining this quantity directly, i.e. without first calculating the state-specific quantities.

The first CRP calculations were for the standard test case \( \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}, \) collinear and three-dimensional, and then more interesting and challenging applications were carried out for the reactions

\[ \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \]  (I)

and

\[ \text{O} + \text{H}_2 \rightarrow \text{OH} + \text{O} \]  (II)

where the primary quantity of interest is the thermal rate constant \( k(T) [\text{cf. eqn. (7)}]. \) Reaction (I) is a simple barrier reaction, complicated only by the fact that it is a four-atom system, while reaction (II) is complicated by the presence of a deep potential well in the interaction region (stable \( \text{HO}_2 \)) that causes a long-lived collision complex.

A particularly interesting application was to the isomerization of ketene

\[ \text{H}_2\text{C}==\text{C}==\text{O} \rightarrow \text{C}==\text{C}==\text{O} \rightarrow \text{O}==\text{C}==\text{C}==\text{H}_2 \]  (III)

which involves the metastable intermediate oxirene. Because of this there is a resonance structure in the microcanonical
rate \(k(E)\) [cf. eqn. (7)] which has been seen in elegant experiments by Lovejoy and Moore.\(^{1,2}\) The calculations showed structure very similar to that seen experimentally.

A more recent application\(^{3,4}\) has been a calculation of the thermal rate constant for the reaction

\[
O + HCl \rightarrow OH + Cl
\]

which is challenging because of the heavy–light–heavy mass combination. The calculation here utilized the time-dependent version of the rate expressions, eqn. (9a).

There have also been applications to photodetachment cross-sections\(^3,5\) [i.e. eqn. (10)],

\[
H_2F^- + h\nu \rightarrow \{HF + F\} + e^-
\]

and

\[
OH^- + h\nu \rightarrow \{OH + H\}_2O\} + e^-
\]

that are relevant to experiments carried out by Neumark's group.\(^6\)

Finally, there has been a variety of interesting work by other research groups on the 'direct' calculation of CRPs and thermal rate constants that should be noted.\(^{1,5}\) The various approaches used have many similarities to that described above though also significant differences.

3 Semiclassical Green's function

As noted above, quantum expressions involving the Green's function can be evaluated by the straightforward matrix representation in eqn. (2), and for small systems (i.e. those with a few degrees of freedom) quantum calculations are in fact often more efficient than the corresponding classical mechanics calculations. For the collinear \(H + H_2 \rightarrow H_3 + H\) reaction (a system of two degrees of freedom), for example, it typically takes less computer time for a quantum reactive scattering calculation than to run a few hundred classical trajectories to determine the reaction probability.

The difficulty of carrying out quantum mechanical calculations, however, scales badly with the size (i.e. number of degrees of freedom) of a molecular system, primarily because of the geometric growth in the number of functions (or grid points) needed in the basis. For example, if \(n\) is the number of basis functions (or grid points) needed to characterize one degree of freedom (\(n \approx 10\)–20, say), then \(n^2\) functions are needed to space the span of \(F\) degrees of freedom.

The number of classical equations of motion (and therefore the effort of computing a classical trajectory) however, only grows linearly with the number of degrees of freedom, so classically based theories have the chance of being more efficient than a quantum description for large systems. (Classical phase space also grows exponentially, i.e. as \(n^2\), with dimensionality, though, so that more trajectories are required to describe the dynamics of larger systems. Monte Carlo sampling methods, however, ameliorate this aspect of the problem.)

Our interest is in using classical mechanics semiclassically, i.e. as input to an approximate quantum theory, so as to be able to describe quantum features such as interference and tunnelling at least approximately. Thus consider a generic matrix element of the time evolution operator

\[
\langle \Psi_2 | \exp[-i(\hat{H} - i\nu)/\hbar] | \Psi_1 \rangle
\]

\[
= \sum_{\text{roots}} \int dq_2 \int dq_1 \Psi_2(q_2)^* \Psi_1(q_1) \left(2\pi i\hbar\right)^{-1/2} \times i^{-n_0} \exp[iS(q_2, q_1)/\hbar] \exp(-\epsilon_i/\hbar)
\]

(17)

Replacing the coordinate matrix representation of the propagator with the standard semiclassical (Van Vleck) approximation yields\(^{16,17}\)

\[
\langle \Psi_2 | \exp[-i(\hat{H} - i\nu)/\hbar] | \Psi_1 \rangle = \sum_{\text{roots}} \int dq_2 \int dq_1 \Psi_2(q_2)^* \Psi_1(q_1) \left(2\pi i\hbar\right)^{-1/2} \times i^{-n_0} \exp[iS(q_2, q_1)/\hbar] \exp(-\epsilon_i/\hbar)
\]

(18)

where

\[
S(q_2, q_1) = \int_0^t dt'[\rho(t')\cdot q(t') - H[\rho(t'), q(t')]]
\]

(19a)

is the classical action for the trajectory that goes from \(q_1\) to \(q_2\) in time \(t\), and \(\epsilon_i\) is the time integral of the absorbing potential along this trajectory,

\[
\epsilon_i = \int_0^t dt'\epsilon(q(t'))
\]

(19b)

The absorbing potential is much easier to deal with semiclassically than it is quantum mechanically because it appears only in the absorptive factor \(\exp(-\epsilon_i/\hbar)\), and not in the equations of motion, and therefore cannot cause reflection.

To apply eqn. (18) as written, one needs to solve the following non-linear boundary value problem: if \(q(p_1, q_1)\) is the coordinate at time \(t\) that evolves from the initial \((t = 0)\) conditions \((p_1, q_1)\), then for a given \(q_1\) one must find values of \(p_1\) that satisfy

\[
q(p_1, q_1) = q_2
\]

(20)

There will, in general, be multiple roots to this equation (since \(q_2\) need not be a monotonic function of \(p_1\)), and the summation in eqn. (18) is over all such roots. The Jacobian factor in eqn. (18)

\[
\frac{\partial q_2}{\partial p_1} = \frac{\partial q(p_1, q_1)}{\partial p_1}
\]

(21)

is evaluated at the roots of eqn. (20), and \(\nu(t)\) is the number of zeros experienced by the determinant \(|\partial q/\partial p_1|\) in the time interval \((0, t)\).

The idea of the initial value representation (IVR)\(^{18–23}\) is to change the integral over the final coordinates in eqn. (18) to one over the initial momenta, giving

\[
\langle \Psi_2 | \exp[-i(\hat{H} - i\nu)/\hbar] | \Psi_1 \rangle = \int dq_1 \int dp_1 \left(\frac{\partial q_2}{\partial p_1}\right)^{-1/2} \times i^{-n_0} \exp[iS(p_1, q_1)/\hbar] \exp(-\epsilon_i/\hbar)\Psi_2(q_2)^*\Psi_1(q_1)
\]

(22)

where \(S(p_1, q_1) = S[q(p_1, q_1), q_1]\). Eqn. (22), though formally identical to eqn. (18), has several advantages over it, most importantly that the classical trajectories needed to evaluate the integral are specified by the initial conditions \((p_1, q_1)\) and not by the double-ended boundary conditions \((q_2, q_1)\). This also means that the summation in eqn. (18) is no longer present because initial conditions determine a unique classical trajectory. Stated more precisely, for a given \(q_1\),

\[
\sum_{\text{roots}} \int dq_2 \rightarrow \int dp_1 \frac{\partial q_2}{\partial p_1}
\]

(23)

Another benefit of the IVR is that the Jacobian from the change of integration variables in eqn. (23) combines with the denominator in eqn. (18), so that the square root of the Jacobian now appears in the numerator of eqn. (22). Since this
factor can go through zero, it is clearly preferable for purposes of numerical integration to have it in the numerator rather than the denominator. Furthermore, this Jacobian factor causes the integrand to be zero when v(t) changes discontinuously, so that the integrand itself is continuous at these points.

The IVR version of the semiclassical approximation, eqn. (22), has all of the interference structure that is in the hallmark of semiclassical theory; e.g. if the integrals in eqn. (22) were all evaluated by the stationary phase approximation, and WKB wavefunctions were used for $\Psi_1$ and $\Psi_2$, then classical $S$-matrix-like results would be obtained, with interference between different stationary phase trajectories. The IVR also provides an approximate description of classically forbidden processes (sometimes called ‘dynamical tunnelling’), where there are no real stationary phase contributions to the integral. In fact, this was the first application of an IVR and the principal reason it was originally introduced, i.e. as a way to treat classically forbidden processes with real-valued trajectories.

Another important aspect of a semiclassical IVR calculation is the manner of evaluating the integral over the phase space of initial conditions in eqn. (22). Since the integrand is oscillatory and the integral will be of large dimension for interesting applications, various ways of smoothing, or filtering out the high-frequency oscillations of the integrand have been considered. Heller’s ‘cellular dynamics’ is one approach to doing this and closely related to it is the Filinov transformation (or stationary phase Monte Carlo) that has been used for similar purposes in evaluating real-time path integrals.

The above discussion has dealt with the semiclassical approximation to matrix elements of the time evolution operator, but it is clear that the corresponding semiclassical approximation to matrix elements of the Green’s function is obtained via the time integral in eqn. (1b), i.e.

$$
\langle \Psi_2 | \hat{G}(E) | \Psi_1 \rangle = (i\hbar)^{-1} \int dq_1 \int dp_1 \Psi_2(q_1) \times \int_0^\infty \frac{dt}{\sqrt{2\pi i\hbar}} \left[ \frac{\partial q}{\partial p_1} \right]^{1/2} \times i^{-\nu_0} \exp[iEt/\hbar] \exp[iS(p_1, q_1)/\hbar] \exp(-\epsilon/\hbar)
$$

Note that in eqn. (24) the time integral [cf. eqn. (1b)] has been moved inside the integral over the phase space of initial conditions, a useful way to organize the calculation because the integral over $r$ can be evaluated at essentially no additional cost while the trajectory with initial conditions $(q_1, p_1)$ is being integrated.

Eqn. (24) is thus the semiclassical result for a generic matrix element of the Green’s function, the semiclassical counterpart to the quantum result in eqn. (2). Semiclassical approximations to all of the dynamical quantities surveyed in Section 2 can thus be obtained by using eqn. (24) for the various matrix elements of the Green’s functions.

Applications of these semiclassical approaches are at an earlier stage of development than the corresponding quantum calculations. Transmission through a one-dimensional potential barrier (i.e. a one-dimensional model of a chemical reaction) has been treated, showing that a modest degree of tunnelling (reaction probabilities as low as $10^{-6}$) can be treated by these methods. A somewhat more realistic model of a chemical reaction, the collinear H H, $\rightarrow$ H + H reaction, has been treated by three different research groups using these types of semiclassical methods (though different in some specifics), all with very good results. Specifically, it is seen that these approaches are able to describe quantization of the collision complex (i.e. scattering resonances) which arises semiclassically from interference between different trajectories connecting the same initial and final states. Resonance structure is thus an inherently quantum effect, and it is a significant triumph for semiclassical theory to be able to describe it accurately.

Very recently semiclassical IVR approaches similar to these have been used to calculate the photodetachment spectra [cf. eqn. (10)] of I– clustered with up to six argon atoms, obtaining good agreement with the experimental determination of these spectra by Neumark and co-workers. Although the dynamics involved here is not reactive (i.e. bond-breaking or -making), it is nevertheless very encouraging that semiclassical IVR approaches are able to handle systems with this many degrees of freedom. Theoretically, recent developments have also shown that these semiclassical IVR methods can be generalized to treat electronically non-adiabatic processes, and preliminary applications indicate that a variety of non-adiabatic phenomena can be accurately described. This has the possibility of being a significant extension of the semiclassical IVR methodology.

In summary, the evidence to date is that these semiclassical IVR approaches are capable of describing quantum effects to a useful degree of accuracy for a wide range of applications. Perhaps more of a question is the extent to which they can be applied. It is fair to say that for simple systems (e.g. collinear H H) they are at present more difficult to apply than the corresponding quantum methods. The difficulties have to do with the integral of an oscillatory integrand over the phase space of the initial conditions in eqn. (24). The potential for being a major contribution to dynamical methodology definitely exists provided one can continue to improve the efficiency of carrying out these phase space integrals.

4 Concluding remarks

The point of this paper has been to emphasize that the ‘formal’ quantum mechanical expressions involving Green’s functions (or time evolution operators) for various dynamical quantities can all be evaluated essentially directly as written either fully quantum mechanically [via eqn. (2)] or semiclassically [via eqn. (24)]. The quantum calculations are more straightforward, and typically easier to carry out for simple systems, than are the semiclassical calculations, but the computational expense of fully quantum calculations grows exponentially with system size. Semiclassical IVR methods have the potential of being more efficient for large molecular systems, and the preliminary evidence is that they provide a sufficiently accurate description of quantum interference and tunnelling effects to be of wide utility.

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