Quantum mechanics in phase space: New approaches to the correspondence principle

Go. Torres-Vega
Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557, and Departamento de Fisica, Centro de Investigación y de Estudios Avanzados del IPN, Apartado Postal 14-740, 07000, México D.F.

John H. Frederick
Department of Chemistry, University of Nevada, Reno, Reno, Nevada 89557

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We present a time evolution equation that provides a novel basis for the treatment of quantum systems in phase space and for the investigation of the quantum-classical correspondence. Through the use of a generalized Husimi transform, we obtain a phase space representation of the time-dependent Schrödinger equation directly from the coordinate representation. Such an equation governs the time evolution of densities such as the Husimi density entirely in phase space, without recourse to a coordinate or momentum representation. As an application of the phase-space Schrödinger equation, we compute the eigenfunctions of the harmonic oscillator in phase space, relate these to the Husimi transform of coordinate representation eigenstates, and investigate the coherent state, its time evolution, and classical limit ($\hbar \to 0$) for the probability density generated by this state. Finally, we discuss our results as they relate to the quantum-classical correspondence, and quasiclassical trajectory simulations of quantum dynamics.

I. INTRODUCTION

Recent advances in the theoretical understanding of the classical mechanics of nonlinearly coupled systems have motivated a new wave of interest in the nature of the quantum-classical correspondence, especially as it applies to molecular systems. In order to explore the relationship between classical and quantum mechanics more fully, several authors have introduced various schemes for generating quantum analogs of classical trajectories. Two such schemes that have become well-established are the Wigner and Husimi transforms. In a parallel development, there has also been a great effort invested in the pursuit of semiclassically and quasiclassically related quantum mechanical quantities, we hope to identify the kinds of classical dynamics that are most representative of the quantum dynamics. In contrast, the standard semiclassical approach typically begins with the classical dynamics of a system and attempts to generalize it to the appropriate quantum dynamics.

This approach to the correspondence principle is not without precedent. Both the Wigner and Husimi transforms have been used to project quantum dynamics onto classical phase space. For example, the time evolution of the Wigner or Husimi density can be determined by allowing a nonstationary state to evolve according to the Schrödinger equation in a coordinate representation and then transforming it into a density in phase space. More direct propagation of these densities in time has also been achieved by using the Wigner or Husimi equivalent of the quantum Liouville operator, and by using the quantum mechanical Fokker–Planck equation for Wigner densities or Husimi densities. Recently, Skodje and co-workers have introduced a means for propagating a Husimi density in phase space by making use of a hydrodynamic-like conservation equation. Unlike these methods, however, we utilize a Schrödinger equation in phase space which allows us to construct wave functions, eigenfunctions and eigenvalues, and densities directly in phase space.

The very nature of expressing quantum mechanics in a phase space representation is nonunique and all such meth-
ods for constructing a quantum density in phase space suffer a degree of arbitrariness. For example, the presence of the arbitrary parameter \( \lambda \) in the definition of the coherent state, 

\[
\phi(q'; q, p, \lambda) = (\lambda / \pi \hbar)^{1/4} \times \exp\left[ -\frac{\lambda}{2\hbar}(q' - q)^2 - \frac{i\hbar}{\lambda}(q' - q) \right],
\]

introduces some indeterminacy into the Husimi transform. Changing this parameter effectively changes the relative weighting given to the coordinate and momentum dimensions of the coherent state in phase space and can introduce large qualitative changes in the appearance of the Husimi density. Moreover, the physical interpretation of such projections is not often easy to determine. For instance, the feature the use of a family of generalized pseudotransition matrix elements for constructing a quantum density in phase space suffer from the problem of indeterminacy introduced some indeterminacy into the Husimi transform. Changing this parameter effectively changes the relative weighting given to the coordinate and momentum representations and that the properties of this representation support the idea that this equation provides an adequate description of the dynamics in quantum phase space. As an example, we treat the harmonic oscillator in the phase space representation in Sec. III. We first solve for the eigenfunctions, then discuss the time evolution of the coherent state, both in phase space. Following our treatment of the harmonic oscillator is a general discussion of our results in Sec. IV. In particular, we discuss implications for the quantum-classical correspondence, quasiclassical trajectory simulations, and the semiclassical computation of quantum expectation values. Finally, Sec. V summarizes our findings.

II. SCHRÖDINGER EQUATION IN "PHASE SPACE"

Any attempt to cast the Schrödinger equation into a phase space representation must be consistent with a transformation of the quantum state itself into a phase space representation. Although we shall eventually show that a more general choice could be made with the same result, we begin by using the Husimi transform, in which the coherent state can be written as a pseudotransition matrix element, 

\[
\langle \Gamma | q' \rangle = (\lambda / \pi \hbar)^{1/4} \times \exp\left[ -\lambda(q' - q)^2 / 2\hbar - \frac{i\hbar}{\lambda}(q' - q) \right],
\]

is used as a pseudotransition matrix element, \( \langle \Gamma | q' \rangle \), between the \( q' \)-basis and the \( \Gamma \)-basis. In Eq. (2.1), \( \lambda \) is an arbitrary constant with units of mass times angular frequency. \( \langle \Gamma | q' \rangle \) is used to obtain a wave function \( \langle \Gamma | \psi \rangle \), in the phase space representation, from the wave function \( \langle q' | \psi \rangle \), in the coordinate representation according to

\[
\langle \Gamma | \psi \rangle = \int_{-\infty}^{+\infty} dq' \langle \Gamma | q' \rangle \langle q' | \psi \rangle.
\]

We can extend this idea and make use of \( \langle \Gamma | q' \rangle \) to find an equation that governs the time evolution of the wave function \( \langle \Gamma | \psi \rangle \) in phase space from the Schrödinger equation in configuration space.

To obtain the time evolution equation in the phase space representation, we start with the one-dimensional Schrödinger equation in configuration space (the generalization to three dimensions is straightforward):

\[
i\hbar \frac{\partial}{\partial t} \langle q' | \psi \rangle = \left\{ \frac{1}{2\mu} \left( -i\hbar \frac{\partial}{\partial q'} \right)^2 + V(q') \right\} \langle q' | \psi \rangle.
\]

Multiplying both sides by \( \langle \Gamma | q' \rangle \), Eq. (2.1), and integrating the result over \( q' \), we find

\[
i\hbar \frac{\partial}{\partial t} \int_{-\infty}^{+\infty} dq' \langle \Gamma | q' \rangle \langle q' | \psi \rangle
\]

\[
= \int_{-\infty}^{+\infty} dq' \langle \Gamma | q' \rangle \left\{ \frac{1}{2\mu} \left( -i\hbar \frac{\partial}{\partial q'} \right)^2 + V(q') \right\} \langle q' | \psi \rangle
\]

\[
= \int_{-\infty}^{+\infty} dq' \left\{ \left[ \frac{1}{2\mu} \left( i\hbar \frac{\partial}{\partial q'} \right)^2 + V(q') \right] \langle \Gamma | q' \rangle \right\} \langle q' | \psi \rangle,
\]

where, as usual, we have assumed that the boundary terms vanish to obtain the last equality.

The coherent state satisfies the equalities

\[
\left( \frac{\partial}{\partial q'} \right)^n \langle \Gamma | q' \rangle = \left( -\frac{\partial}{\partial q'} \right)^n \langle \Gamma | q' \rangle
\]

and

\[
q^n \langle \Gamma | q' \rangle = \left( q + i\hbar \frac{\partial}{\partial p} \right)^n \langle \Gamma | q' \rangle.
\]

If we assume that the potential function \( V(q') \) can be written as a power series in \( q' \), we can recast Eq. (2.4) into the form...
\[ \frac{i\hbar}{\partial t} \langle \Gamma | \psi \rangle = \left[ \frac{1}{2\mu} \left( -i\hbar \frac{\partial}{\partial q} \right)^2 + V(q + i\hbar \frac{\partial}{\partial p}) \right] \langle \Gamma | \psi \rangle. \]  

(2.7)

In Eq. (2.7) \( V(q + i\hbar \frac{\partial}{\partial p}) \) is the potential function, \( V(q) \), evaluated at \( q + i\hbar \frac{\partial}{\partial p} \), and \( \langle \Gamma | \psi \rangle \) is given by Eq. (2.2). This is the time evolution equation in "phase space" inferred from the coherent state, Eq. (2.1), and the Schrödinger equation in the configuration representation, Eq. (2.3). Each time that the coherent state is used to obtain a wave function in phase space, it is implicitly assumed that Eq. (2.7) governs the time evolution in phase space of such a wave function.

It is possible to use the coherent state to generate other identities for \( \frac{\partial}{\partial q'} \) and \( q' \) in terms of \( \frac{\partial}{\partial q}, \frac{\partial}{\partial p}, q, \) and \( p \); however, these other choices would inevitably lead to transformations dependent on the arbitrary parameter \( \lambda \). However, Eq. (2.7) may be obtained from Eq. (2.3) by making use of any pseudotransition matrix with elements of the form

\[ \langle \Gamma | q' \rangle = f(q' - q) e^{-ip(q' - q)/\hbar}, \]  

(2.8)

where \( f(q' - q) \) is an arbitrary nonzero function of \( (q' - q) \) that can be differentiated at least once. On the other hand, Eq. (2.7) may also be obtained from the Schrödinger equation written in the momentum representation if we make use of the pseudotransition matrix element

\[ \langle \Gamma | p' \rangle = g(p' - p) e^{i\phi/q'/\hbar}. \]  

(2.9)

where \( g(p' - p) \) is an arbitrary nonzero function of \( (p' - p) \) that can be differentiated at least once (see Appendix A). Clearly, the coherent state given by Eq. (2.1), is a pseudotransition matrix that conforms to Eq. (2.8) with \( f(q' - q) = (\lambda/\pi\hbar)^{1/4} \exp\left[-\lambda(q' - q)^2/2\hbar \right] \), and, when the coherent state (2.1) is assumed, the appropriate form for \( \langle \Gamma | p' \rangle \) is given by

\[ \langle \Gamma | p' \rangle = \int_{-\infty}^{+\infty} dq' \langle \Gamma | q' \rangle \langle q' | p' \rangle = \frac{1}{2\mu} \left( p' - i\hbar \frac{\partial}{\partial q} \right)^2 \frac{1}{2\lambda^2 \hbar + iq'/\hbar}. \]  

(2.10)

Of course, none of the quantities given by Eqs. (2.1), (2.8), (2.9), or (2.10) can be used as the actual transition matrix elements between the \( q' \)-basis or the \( p' \)-basis and the \( \Gamma \)-basis, respectively.

From the definitions that led to Eq. (2.7), we can determine expressions for the operators \( \hat{Q} \) and \( \hat{P} \) in the phase space representation:

\[ \langle \Gamma | \hat{Q} | \psi \rangle = \left( q + i\hbar \frac{\partial}{\partial p} \right) \langle \Gamma | \psi \rangle \]  

\[ \langle \Gamma | \hat{P} | \psi \rangle = -i\hbar \frac{\partial}{\partial q} \langle \Gamma | \psi \rangle. \]  

(2.11)

For any operator functions \( \hat{f}(\hat{Q}) \) and \( \hat{g}(\hat{P}) \) that can be written as a power series of \( \hat{Q} \) and \( \hat{P} \), respectively, the following also holds

\[ \langle \Gamma | \hat{f}(\hat{Q}) | \psi \rangle = f(q + i\hbar \frac{\partial}{\partial p}) \langle \Gamma | \psi \rangle \]  

\[ \langle \Gamma | \hat{g}(\hat{P}) | \psi \rangle = g(q - i\hbar \frac{\partial}{\partial q}) \langle \Gamma | \psi \rangle. \]  

(2.12)

These relations suggest that the phase space representation is a combination of the coordinate and momentum representations. The commutator \([\hat{Q},\hat{P}]\) in the phase space representation takes the form

\[ \langle \Gamma | [\hat{Q},\hat{P}] | \psi \rangle = \left( q + i\hbar \frac{\partial}{\partial p} \right) \left( q - i\hbar \frac{\partial}{\partial q} \right) \langle \Gamma | \psi \rangle \]  

(2.13)

which is in agreement with the Heisenberg uncertainty principle, that is \([\hat{Q},\hat{P}] = i\hbar\). Another interesting property of Eq. (2.7) and its solutions is based on our physical interpretation of the wave function in phase space. If we assume that, as in configuration and momentum space, the quantity of physical interest is the square magnitude of the wave function (representing a quantum density in phase space), then the wave functions \( \langle \Gamma | \psi \rangle \) and \( e^{-ip/q}/\hbar \langle \Gamma | \psi \rangle \) will contain the same information. Now, by taking advantage of the transformations

\[ e^{-ip/q}/\hbar \left( -i\hbar \frac{\partial}{\partial q} \right) e^{ip/q}/\hbar = \left( p - i\hbar \frac{\partial}{\partial q} \right), \]  

(2.14)

and

\[ e^{-ip/q}/\hbar \left( q + i\hbar \frac{\partial}{\partial p} \right) e^{ip/q}/\hbar = \left( i\hbar \frac{\partial}{\partial p} \right), \]  

(2.15)

we find, from Eq. (2.7), that the time evolution equation of motion for \( e^{-ip/q}/\hbar \langle \Gamma | \psi \rangle \) is given by

\[ i\hbar \frac{\partial}{\partial t} \left[ e^{-ip/q}/\hbar \langle \Gamma | \psi \rangle \right] = \left[ \frac{1}{2\mu} \left( p - i\hbar \frac{\partial}{\partial q} \right)^2 + V(q + i\hbar \frac{\partial}{\partial p}) \right] \left[ e^{-ip/q}/\hbar \langle \Gamma | \psi \rangle \right]. \]  

(2.16)

More symmetric expressions for the operators \( \hat{Q} \) and \( \hat{P} \) can be obtained in this representation if we consider the transformation

\[ e^{-ip/q}/\hbar \left( -i\hbar \frac{\partial}{\partial q} \right) e^{ip/q}/\hbar = \frac{1}{2} p - i\hbar \frac{\partial}{\partial q} \]  

(2.17)

and

\[ e^{-ip/q}/\hbar \left( q + i\hbar \frac{\partial}{\partial p} \right) e^{ip/q}/\hbar = \frac{1}{2} q + i\hbar \frac{\partial}{\partial p}. \]  

(2.18)

We find, from Eq. (2.7), that the time evolution equation of motion for \( e^{-ip/q}/\hbar \langle \Gamma | \psi \rangle \) is given by

\[ i\hbar \frac{\partial}{\partial t} \left[ e^{-ip/q}/\hbar \langle \Gamma | \psi \rangle \right] = \left[ \frac{1}{2\mu} \left( \frac{1}{2} p - i\hbar \frac{\partial}{\partial q} \right)^2 + V(q + i\hbar \frac{\partial}{\partial p}) \right] \times \left[ e^{-ip/q}/\hbar \langle \Gamma | \psi \rangle \right]. \]  

(2.19)
Hence, since the solutions to Eqs. (2.7), (2.16), and (2.19) are postulated to contain the same physical information, these equations are dynamically equivalent. All of the above expressions for \( \tilde{P} \) and \( \tilde{Q} \) deduced from these equations are equally valid and the only effect on the wave packet is an overall phase factor. So, we are free to choose the equation that is most convenient for the problem at hand.

We can also show that the transformation to a phase space representation can be inverted back to a coordinate representation by using a pseudotransition matrix element of the form

\[
\langle q'|\Gamma \rangle = u(q'-q)\mathcal{e}^{i(p'-q)/\hbar},
\]

where \( u(q'-q) \) is an arbitrary nonzero function that can be differentiated at least once. Applying this inverse transformation on \( \langle \Gamma|\psi \rangle \), we should obtain a wave function which evolves according to the coordinate space representation of the Schrödinger equation. If we assume that the potential \( \tilde{P}(\tilde{Q}) \) can be written as a power series in \( \tilde{Q} \) and that all the derivatives \( \partial^n \langle \Gamma|\psi \rangle / \partial p^n \), for \( n = 0,1,\ldots \), vanish at \( p = \pm \infty \) and \( q = \pm \infty \), we find, after multiplying Eq. (2.7) by \( \langle q'|\Gamma \rangle \) and integrating over \( \Gamma \), that

\[
i\hbar \frac{\partial}{\partial t} \int d\Gamma \langle q'|\Gamma \rangle \langle \Gamma|\psi \rangle \\
= \int d\Gamma \langle q'|\Gamma \rangle \left[ \frac{1}{2\mu} \left( -i\hbar \frac{\partial}{\partial q} \right)^2 + V(q) \right] \langle \Gamma|\psi \rangle \\
= \int d\Gamma \langle q'|\Gamma \rangle \langle \Gamma|\psi \rangle.
\]

(2.21)

In other words, the quantity \( \int d\Gamma \langle q'|\Gamma \rangle \langle \Gamma|\psi \rangle \) obeys the Schrödinger equation in coordinate representation and thus corresponds to a coordinate representation of the wave function, \( |\psi \rangle \). In the same way, if we multiply Eq. (2.17) by \( \langle p'|\Gamma \rangle = \mathcal{v}(p' - p) e^{i p'/\hbar} \) and take the integral over \( \Gamma \), we find that

\[
i\hbar \frac{\partial}{\partial t} \int d\Gamma \langle p'|\Gamma \rangle \langle \Gamma|\psi \rangle \\
= \int d\Gamma \langle p'|\Gamma \rangle \left[ \frac{1}{2\mu} \left( -i\hbar \frac{\partial}{\partial q} \right)^2 + V(q) \right] \langle \Gamma|\psi \rangle \\
= \int d\Gamma \langle p'|\Gamma \rangle \langle \Gamma|\psi \rangle.
\]

(2.22)

In this transformation, we once again allow \( \mathcal{v}(p' - p) \) to be an arbitrary nonzero function of \( (p' - p) \) so long as it is differentiable at least once, and we assume that \( \langle \Gamma|\psi \rangle \) and \( \partial \langle \Gamma|\psi \rangle / \partial q \) vanish at \( p = \pm \infty \) and \( q = \pm \infty \). As before, the quantity \( \int d\Gamma \langle p'|\Gamma \rangle \langle \Gamma|\psi \rangle \) obeys the Schrödinger equation in the momentum representation and can be thought of as corresponding to \( \langle p'|\psi \rangle \).

It is well known that when one integrates the Wigner density over momentum space, one obtains the probability density in configuration space.\(^4\) If we formally allow the function \( u(q'-q) \) to be the delta function \( \delta(q'-q) \), then the transformation described by Eq. (2.21) represents a similar "projection" of \( \langle \Gamma|\psi \rangle \) onto configuration space. From Eq. (2.20)

\[
\langle q'|\psi \rangle = \int dp' \int dq' \langle q'|\Gamma \rangle \langle \Gamma|\psi \rangle \\
= \int dp' \int dq' \delta(q'-q) \mathcal{e}^{i(p'-q)/\hbar} \langle \Gamma|\psi \rangle \\
= \int dp \langle \Gamma|\psi \rangle \delta(q'-q).
\]

(2.23)

Thus, in this instance, the projection results in a coordinate space representation of the wave function, instead of the probability density. A similar result can be obtained for an effective projection of \( \langle \Gamma|\psi \rangle \) onto momentum space. Interestingly, these relationships demonstrate a fundamental difference between statistical and quantum mechanics: in statistical mechanics, \( \rho(q;t) \sim \delta_{\pm q} \rho(q',t) \) and \( \rho(q;t) \sim \delta_{\pm q} \rho(q',t) \) but in quantum mechanics, \( \langle q|\psi \rangle \sim \delta_{\pm q} \rho(G|\psi) \) and \( \langle q|\psi \rangle \sim \delta_{\pm q} \rho\rho_{-q}/\hbar \langle \Gamma|\psi \rangle \).

In deriving the time evolution equation, Eq. (2.7), we have introduced a certain degree of arbitrariness by not specifying the function \( f(q'-q) \) other than demanding that its first derivative exist, and that it be nonzero. While this affords us some flexibility in the way we construct the transformation to a phase space representation, it is useful to have some guidelines for making the transformation that do not depend on arbitrary choices. One way of eliminating the arbitrariness is to solve for the dynamics of a model system completely in phase space without reference to configuration or momentum space. Interestingly, for the simplest model system, the free particle, Eqs. (2.7), (2.16), and (2.19) reduces to the corresponding Schrödinger equation in configuration space. In the next section, we will make use of Eq. (2.7) to analyze another simple model system, the harmonic oscillator.

### III. THE HARMONIC OSCILLATOR IN PHASE SPACE

From Eq. (2.7), the time evolution equation for a wave function \( \langle \Gamma|\psi \rangle \) in the harmonic oscillator potential is given by

\[
i\hbar \frac{\partial}{\partial t} \langle \Gamma|\psi \rangle \\
= \left[ -\hbar^2 (\partial^2 / \partial q^2) + V(q) + i\hbar (\partial / \partial p) \right] \langle \Gamma|\psi \rangle.
\]

(3.1)

in the phase space representation. In this section, we find the eigenfunctions of the right hand side of Eq. (3.1) and, later examine the time evolution of coherent states in phase space.

#### A. Eigenfunctions

We begin by finding the ground state solution, \( \langle \Gamma|\psi_0 \rangle \) of Eq. (3.1), i.e., the phase space function which satisfies...
One solution of this equation is given by
\[
\psi_0(\Gamma) = \frac{1}{\sqrt{2\pi\hbar}} \times \exp\left[ -\frac{1}{2\hbar\omega} \left( \frac{1}{2} \mu \omega^2 q^2 + \frac{1}{2\mu} p^2 \right) + \frac{i p q}{2\hbar} \right];
\]

\[
(3.3)
\]

however, in the phase space representation, we find that several, indeed an infinite number of solutions, satisfy Eq. (3.2). From Eq. (3.3), additional solutions can be generated by inserting \(\psi_0(\Gamma)(\Gamma)\), where \(\mathcal{I}(\Gamma)\) is a function to be determined, into Eq. (3.2). We then find that the function \(f(\mathcal{I})\) has to satisfy the partial differential equation,
\[
\left( \mu \omega - ip - \hbar \left( \frac{\partial}{\partial q} - i \mu \omega \frac{\partial}{\partial p} \right) \right) \times \left[ \frac{\partial f(\mathcal{I})}{\partial q} + \mu \omega \frac{\partial f(\mathcal{I})}{\partial p} \right] = 0.
\]

\[
(3.4)
\]

One possible choice for \(f(\mathcal{I})\) is
\[
f(\mathcal{I}) = f - \frac{\alpha}{2} \mu \omega q^2 \hbar + \alpha p^2 \hbar \omega - ip q \hbar,
\]

i.e., any differentiable function of \(- \frac{\alpha}{2} \mu \omega q^2 \hbar + \alpha p^2 \hbar \omega - ip q \hbar\), where \(\alpha\) is a real number, will satisfy Eq. (3.4) since it has the property that \(\frac{\partial f(\mathcal{I})}{\partial q} + \mu \omega \frac{\partial f(\mathcal{I})}{\partial p} = 0\). A particularly interesting choice for \(f(\mathcal{I})\) is the exponential function which gives rise to the following set of ground state eigenfunctions
\[
\psi_0(\Gamma;\alpha) = \left( \frac{1}{4\pi^2 \hbar^2} \right)^{1/4} \exp \left[ -\frac{1}{\hbar} \left( \frac{1}{2} \mu \omega^2 q^2 + \frac{1}{2\mu} p^2 \right) + \frac{i p q}{\hbar} \right] \left( \frac{1}{2} - \alpha \right)^{1/2} + \frac{i}{\hbar} \left( \frac{1}{2} - \alpha \right)^{1/2} \right) + \frac{i}{\hbar} \left( \frac{1}{2} - \alpha \right)^{1/2} \right) \]

\[
(3.5)
\]

with \(-1/2 < \alpha < 1/2\). We note that the set of solutions (3.5) can also be obtained by Husimi transforming the coordinate representation of the harmonic oscillator ground state and taking \(\lambda = \mu \omega (1/2 + \alpha)/(1/2 - \alpha)\) in Eq. (1.1).

To find the remaining eigenstates, we can make use of the ladder operators\(^{14}\)
\[
\hat{A} = (\sqrt{\mu \omega/2\hbar} \hat{Q} + \hat{P}/\sqrt{2\mu \hbar \omega})
\]

and
\[
\hat{A}^\dagger = (\sqrt{\mu \omega/2\hbar} \hat{Q} - \hat{P}/\sqrt{2\mu \hbar \omega})
\]
in the usual manner. In this representation, the recursion relationships for the eigenfunctions \(\psi_n(\Gamma)\) become
\[
\sqrt{\frac{\mu \omega}{2\hbar}} \left( q + i \hbar \frac{\partial}{\partial p} \right) + \sqrt{\frac{\hbar}{2\mu \omega}} \frac{\partial}{\partial q} \psi_n(\Gamma) = \sqrt{n + 1} \psi_{n+1}(\Gamma),
\]

\[
(3.6)
\]

and
\[
\int d\Gamma \psi_n^*(\Gamma) \psi_m(\Gamma) = \delta_{n,m},
\]

\[
(3.10)
\]

where \(d\Gamma = dp \, dq\) and the integration is carried over \(-\infty < q < \infty\) and \(-\infty < p < \infty\).

Now, according to Eq. (2.23), we expect to get the eigenfunctions \(\phi(q')\) of the harmonic oscillator in the configuration representation from the eigenfunctions (3.9). As before, we let \(\langle q' | \Gamma \rangle = \delta(q' - q)e^{ip(q' - q)/\hbar}\), then integrate the ground state eigenfunction, Eq. (3.3), over \(\Gamma\), we get

\[
\int \sqrt{\frac{\mu \omega}{2\hbar}} \left( q + i \hbar \frac{\partial}{\partial p} \right) + \sqrt{\frac{\hbar}{2\mu \omega}} \frac{\partial}{\partial q} \psi_n(\Gamma) = \sqrt{n + 1} \psi_{n+1}(\Gamma),
\]

\[
(3.7)
\]

If Eq. (3.7) is used to generate the remaining eigenfunctions for \(n > 0\), we find that
\[
\psi_n(\Gamma;\alpha) = \frac{2}{\sqrt{n}} \left[ \frac{1}{\sqrt{\hbar \omega}} \left( \sqrt{\frac{\mu \omega^2}{2\hbar}} \frac{1}{2} + \alpha \right) q - \frac{1}{\sqrt{\mu \omega}} \left( \frac{1}{2} - \alpha \right) p \right] \psi_{n-1}(\Gamma;\alpha)
\]

\[
(3.8)
\]

Although the set of ground state functions (3.5) lead to different densities (square magnitudes \(\langle |\psi_n(\Gamma)|^2 \rangle\) in phase space, all are eigenfunctions of Eq. (3.1) and all have the same values for the uncertainties in position and momentum,
\[
\sqrt{\langle \psi_n(\hat{Q})^2 |\psi_n \rangle - \langle \psi_n |\hat{Q} |\psi_n \rangle^2}
\]

and
\[
\sqrt{\langle \psi_n(\hat{P})^2 |\psi_n \rangle - \langle \psi_n |\hat{P} |\psi_n \rangle^2}.
\]

The uncertainty principle is built into the set (3.8). For example, when \(\alpha\) is close to \(-1/2\), \(\psi_n(\Gamma;\alpha)\) has appreciable density on a wider region of \(p\) \([q]\) as compared with that for \(q\) \([p]\). However, a density with an exact value for \(q\) or \(p\) \((\alpha = \pm 1/2)\) is not possible since \(\psi_0(\Gamma;\alpha)\) vanishes.

Among the possible choices for \(f(\mathcal{I})\) is a real number, will satisfy Eq. (3.2), only the solution obtained by taking the value \(f(\mathcal{I}) = 1\) allows us to make direct contact with the classical model since the resulting density is not only a function of the classical Hamiltonian, but also a stationary solution to the classical Liouville equation (see below). Therefore, we will only consider the solutions based on Eq. (3.3) hereafter and the eigenfunctions will take the simple form
\[
\psi_n(\Gamma) = (2\hbar \omega + i \pi n \hbar \omega)^{-1/2} \left( \sqrt{\mu \omega^2 / 2q} - ip/\sqrt{2\mu} \right)^n \times \exp \left[ - (1/2\hbar \omega) (\mu \omega^2 q^2 / 2 + p^2 / 2\mu) + ip q / \hbar \right].
\]

Further investigations of the connection between the quantum and classical Liouville equations are in progress.

As expected, the eigenfunctions \(\{\psi_n(\Gamma)\}\) are orthonormal in the phase space, that is,
\[
\psi_n(\Gamma) = \int d\Gamma \psi_n^*(\Gamma) \psi_m(\Gamma)
\]

\[
(\delta_{n,m})
\]

where \(d\Gamma = dp \, dq\) and the integration is carried over \(-\infty < q < \infty\) and \(-\infty < p < \infty\).

Now, according to Eq. (2.23), we expect to get the eigenfunctions \(\phi(q')\) of the harmonic oscillator in the configuration representation from the eigenfunctions (3.9). As before, we let \(\langle q' | \Gamma \rangle = \delta(q' - q)e^{ip(q' - q)/\hbar}\), then integrate the ground state eigenfunction, Eq. (3.3), over \(\Gamma\), we get...
we can obtain the recursion relationships for the harmonic oscillator in the coordinate representation. Similarly, we can obtain the recursion relationships for the ladder operator recursion relations that are applicable in the coordinate representation.\(^{15}\) In Eqs. (3.12) and (3.13), we have used the simplified notation \(\phi_n(q,p')\) to represent \(|\psi_n(q,p')\rangle\) by integrating Eqs. (3.6) and (3.7) over \(q\) after multiplying by \(\langle q|\Gamma\rangle\)

\[
\sqrt{\frac{2\hbar}{\mu\omega}} \int_{-\infty}^{+\infty} dp \phi_n(q,p')
\]

Thus obtaining the ladder operator recursion relations that are applicable in the coordinate representation. It is interesting to note that, were we to use the more general form of the harmonic oscillator eigenstates in phase space \([Eq. (3.38)]\), we would obtain the same result given in Eq. (3.14) with an extra factor of \((1/2+\alpha)^{1/4}\). These wave functions will vanish for \(\alpha = -1/2\), but not for \(\alpha = +1/2\). [See Eq. (3.8) and the discussion that follows.]

By analogy with the coordinate and momentum representations, we associate the square magnitude of the wave function, \(|\psi_n(\Gamma)|^2\), with the quantum density in the phase space representation. For the case of the harmonic oscillator, \(|\psi_n(\Gamma)|^2\) has the simple form

\[
|\psi_n(\Gamma)|^2 = \left(\frac{1}{2\pi\hbar}\right)^2 \frac{1}{n!} \frac{\mu^{3/2}q^2 + \alpha^2}{\mu^{3/2}}
\]

where \(\phi_n(q',p')\) is the ground state eigenfunction for the harmonic oscillator in the coordinate representation. Similarly, we can obtain the recursion relationships for the harmonic oscillator in the coordinate representation. Thus, we can write

\[
\sqrt{\frac{2\hbar}{\mu\omega}} \int_{-\infty}^{+\infty} dp \phi_n(q,p')
\]

and

\[
|\psi_0(\Gamma)|^2 = \left(\frac{1}{2\pi\hbar}\right)^2 \left(\frac{\mu^{3/2}q^2 + \alpha^2}{\mu^{3/2}}\right)
\]

This equality allows us to rewrite Eq. (3.18) so that

\[
\langle \Gamma|a\rangle = \langle \Gamma|a\rangle = \langle \Gamma|a\rangle
\]

where the complex constant \(\alpha\) and the expectation values \(\langle a|\hat{Q}|\hat{P}\rangle\) of \(\hat{Q}\) and \(\hat{P}\), respectively, are related by

\[
\alpha = \sqrt{\mu\omega/2h(a|\hat{Q}|a) + (i/\sqrt{2\mu\hbar}) (a|\hat{P}|a)}.
\]

This equality allows us to rewrite Eq. (3.18) so that

\[
\langle \Gamma|a\rangle = \langle \Gamma|a\rangle = \langle \Gamma|a\rangle
\]

and then the quantum density is given by

\[
|\psi_n(\Gamma)|^2 = \left(\frac{1}{2\pi\hbar}\right)^2 \left(\frac{\mu^{3/2}q^2 + \alpha^2}{\mu^{3/2}}\right)
\]

\[
\times \exp \left(\frac{1}{2\hbar}\right)^2 \left(\frac{\mu^{3/2}q^2 + \alpha^2}{\mu^{3/2}}\right)
\]

The choice we have made for representing the ground state density in phase space,
This is a Gaussian density in p and q with center at the point $(p,q) = (\langle a|\hat{P}|a\rangle, \langle a|\hat{Q}|a\rangle)$ in phase space. It is interesting to note that the above density resembles the stationary solution $p_{EQ} = (1/Z)\exp[-E_{CI}/\hbar E]$ to the classical Liouville equation of motion with variables $(q - (a|\hat{Q}|a\rangle)$ and $(p - (a|\hat{P}|a\rangle)$, where $Z = \int d\Gamma \exp[-E_{CI}/\hbar E]$, $E_{CI} = (\mu \omega^2/2)q^2 + p^2/2\mu$, and $\hbar \omega$ plays the role of $k_B T$. Hence, the classical picture that can be associated with this state is that of an ensemble of particles with the appropriate value for the average energy.

The time evolution of the coherent state, Eq. (3.20), in a harmonic oscillator potential, is found to be

$$\langle \Gamma|a|\rangle = \langle \Gamma|\exp(-i\hat{H}t/\hbar)|a\rangle$$

$$= \exp(-|a|^2/2) \sum_{n=0}^{\infty} \left(\frac{a^n}{\sqrt{n!}}\right) \exp\left[-i(n+1/2)\omega t\right] \psi_n(\Gamma)$$

$$= (1/\sqrt{2\pi\hbar}) \exp\left[-(\mu\omega/4\hbar)(q^2 + p^2/\mu - 2ip\hbar/\mu) - |a|^2/2 - i\hbar/\mu \right]$$

$$= (1/\sqrt{2\pi\hbar}) \exp\left[-(\mu\omega/4\hbar)[q - q_{av}(t)]^2 - (1/4\hbar\mu)(p - p_{av}(t))^2\right]$$

$$\quad + (i/2\hbar) [pq - pq_{av}(t) + qp_{av}(t)] - i\hbar/2\right]\right],$$

where

$$q_{av}(t) = \langle a|\hat{Q}|a\rangle \cos(\omega t) + (1/\omega) \langle a|\hat{P}|a\rangle \sin(\omega t)$$

(3.23)

and

$$p_{av}(t) = \langle a|\hat{P}|a\rangle \cos(\omega t) - \omega \langle a|\hat{Q}|a\rangle \sin(\omega t).$$

(3.24)

The square magnitude of the coherent state

$$|\langle \Gamma|a|\rangle|^2 = (1/2\pi\hbar) \exp\left[-(1/\hbar\omega) (\mu\omega^2/2)\right]$$

$$\times (q - q_{av}(t))^2 + (1/4\mu)(p - p_{av}(t))^2\right]\right]$$

(3.25)

represents the quantum density of the system in phase space at time $t$. This is just the initial distribution, Eq. (3.21), but now centered at the point $(p,q) = [p_{av}(t),q_{av}(t)]$, which is moving in a classical manner [see Eqs. (3.23) and (3.24)] with initial conditions $(p,q) = (\langle a|\hat{P}|a\rangle, \langle a|\hat{Q}|a\rangle)$, and classical energy $E_{CI} = \langle a|\hat{P}|a\rangle^2/2\mu + \mu \omega^2 \langle a|\hat{Q}|a\rangle^2/2$. This is reminiscent of the results one obtains for the motion of a coherent state in a harmonic potential in the coordinate representation.\(^{17}\)

Once more, Eq. (3.25) resembles the stationary classical distribution of the Liouville equation, but with variables $q - q_{av}(t)$ and $p - p_{av}(t)$. By combining the derivatives $\partial |\langle \Gamma|a|\rangle|^2/\partial q_{sv}, \partial |\langle \Gamma|a|\rangle|^2/\partial p_{sv}$, and $\partial |\langle \Gamma|a|\rangle|^2/\partial t$, we find that the time evolution equation for $|\langle \Gamma|a|\rangle|^2$ is given by

$$\frac{\partial}{\partial t} |\langle \Gamma|a|\rangle|^2 = \left[\hat{q}_{sv} \frac{\partial}{\partial q_{sv}} + \hat{p}_{sv} \frac{\partial}{\partial p_{sv}}\right] |\langle \Gamma|a|\rangle|^2.$$  

(3.26)

This equation is reminiscent of the classical Liouville equation of motion with variables $(p_{sv}, q_{sv})$ (Ehrenfest theorem\(^{14}\)). We note that the expectation value of the energy of the system in this state is

$$\langle a(t)|\hat{H}|a(t)\rangle = \frac{1}{2\mu} \langle a|\hat{P}^2|a\rangle + \frac{1}{2} \mu \omega^2 \langle a|\hat{Q}^2|a\rangle$$

$$= \frac{1}{2\mu} \langle a|\hat{P}^2\rangle^2$$

$$+ \frac{1}{2} \mu \omega^2 \langle a|\hat{Q}|a\rangle^2 + \frac{1}{2} \hbar \omega$$

(3.27)

as compared to the classical value for the energy,

$$E_{CI} = \frac{1}{2\mu} \langle a|\hat{P}^2|a\rangle^2 + \frac{1}{2} \mu \omega^2 \langle a|\hat{Q}|a\rangle^2.$$  

(3.28)

So the quantum and classical values for the energy once again differ by the amount of the zero-point energy. We also note that, in the limit $\hbar \to 0$, the density (3.25) becomes the classical density for a particle moving in a harmonic potential,

$$\lim_{\hbar \to 0} |\langle \Gamma|a|\rangle|^2 = \delta|\langle q_{av}(t) - q_{av}(t) - \delta|\langle p - p_{av}(t)\rangle|\right].$$  

(3.29)

These observations suggest that the classical dynamics which most closely corresponds to the dynamics of a quantum wave packet is that which occupies the same region of phase space and not that which has the same energy.

Finally, if we combine the derivatives $\partial |\langle a(t)|\rangle|^2/\partial q, \partial |\langle a(t)|\rangle|^2/\partial p$ and $\partial |\langle a(t)|\rangle|^2/\partial t$, we find that

$$\frac{\partial}{\partial t} |\langle a(t)|\rangle|^2 + \frac{\partial}{\partial q} J_q(t) + \frac{\partial}{\partial p} J_p(t) = 0,$$

(3.30)

where $J_q(t) = q_{av}(t)|\langle a(t)|\rangle|^2$ and $J_p(t) = p_{av}(t)|\langle a(t)|\rangle|^2$. This represents a conservation equation for the "probability fluid" in phase space.\(^{18}\) When we take the limit $\hbar \to 0$, $J_q(t) = (q_{av}(t)|\langle a(t)|\rangle|^2$ and $J_p(t) = (p_{av}(t)|\langle a(t)|\rangle|^2$. This represents the classical expression for the flux of a particle moving in a harmonic potential, $J_q(t) = (q_{av}(t)|\langle a(t)|\rangle|^2)$ $\delta |q - q_{av}(t)| + (p - p_{av}(t)|\right].$  

(3.30)

IV. DISCUSSION

The expression of the $\hat{Q}$ and $\hat{P}$ operators in a phase space representation offers us a new, direct way to generate information about quantum mechanics that can easily be compared with classical mechanics. As long as the potential function is expressible as a power series in $q$, we are able to write down an effective Schrödinger equation for the system which is applicable in phase space and which maintains the conjugate relationship between the coordinates and momenta (i.e., $[\hat{Q},\hat{P}] = i\hbar$). Most importantly, this representation of the Schrödinger equation provides a means for computing the exact time evolution of a nonstationary state completely in phase space. The drawbacks in the present development are that (i) in the phase space representation,
the operator $\hat{Q}$ now depends in part on $\partial / \partial p$ which means that the Schrödinger equation will generally be a high order partial differential equation and (ii) there may be more solutions than one would obtain from the coordinate or momentum representations. In addition, since phase space contains $2N$ variables for an $N$ degree of freedom system, all functions have twice the dimensionality they would have if expressed in configuration or momentum space which accelerates the complexity of the problem as $N$ increases; however, this same difficulty is found in the description of classical systems.

Despite the difficulties associated with finding and characterizing quantum states directly in phase space, we note that one does not necessarily have to solve a partial differential equation in phase space to find such states. Indeed, one could in principal generate the desired states in a configuration representation, then convert them to a phase space representation by means of the generalized Husimi transform discussed in Sec. II—their subsequent time evolution would then be governed by Eq. (2.7). Another possible approach, since we have found expressions for one set of harmonic oscillator eigenstates in phase space, is to expand the solutions of other bound well systems in a basis formed by these states, compute the matrix elements of the Hamiltonian operator, and solve for the expansion coefficients variationally. In principle, we should be able to express the eigenfunctions of a system. The time evolution of the Wigner distribution in phase space is not given by the classical equations of motion, although these equations are exact for potentials or order $q^2$ or less. As a result, the propagation of an ensemble of classical trajectories which initially conform to a Wigner transform of some initial quantum state, will only be representative of the quantum dynamics so long as the potential is well approximated by a quadratic function. We should note that the Wigner density does in general contain negative values—the subsequent evaluation of average values over an ensemble of trajectories must then be handled carefully.

In our view, it is misleading to consider the energy at all when attempting to model intramolecular quantum dynamics using semiclassical trajectories, but it is more important to study the regions of phase space, which are most important to the dynamics. The quantum expectation value for energy represents a property of the system that has been averaged over an entire wave function. In effect it is the spatial spread of the wave function that gives rise to the zero-point energy. This is best illustrated by considering the ground state of the harmonic oscillator in coordinate space (see Fig. 1). While the expectation value of the energy for this state is $\hbar \omega$, the most probable location for the oscillator is clearly at zero displacement from equilibrium. A similar result follows for all the excited states as well: the most probable locus of points in phase space for the nth eigenstate corresponds to a classical energy of $E_n = n \hbar \omega$ not $(n + \frac{1}{2}) \hbar \omega$ (see Fig. 2).

Since we contend that the regions of phase space explored by a time-evolving quantum state play an important role in making the correspondence to classical dynamics, we arrive at the interesting conclusion that the classical analog of a quantum ground state resides in a region of phase space centered around a "trajectory" which sits precisely at the bottom of the potential well. This does not contradict the semiclassical theory for calculating eigenvalues. In the WKB theory, for $N = 1$, or EBK theory, for $N > 2$, the energy eigenvalue of a bound vibrational system is related to the energy of a classical trajectory whose actions, $J$, are given by

$$J = \left( n + \frac{1}{2} \right) \hbar,$$

(4.1)
where the $n$ are the quantum numbers of the quantum state. This theory, which is good to $O(h^2)$,\textsuperscript{32} takes into account the properties of the wave function at the classical turning points which leads to the added factor of $\frac{1}{2}$. In deriving Eq. (4.1), the emphasis is on the energy expectation value and the theory has essentially picked out the classical dynamics which will approximate this energy. It says nothing, however, about the classical dynamics which best represents the quantum eigenstate—this occurs for trajectories in the vicinity of the classical manifold with actions given by

\[ J = nh. \] (4.2)

This has implications for the construction of semiclassical eigenstates as well. In the methods developed by Heller and co-workers,\textsuperscript{33} a semiclassical eigenstate is constructed by placing Gaussian wave packets uniformly on a classical manifold (invariant torus) whose actions obey the relations Eq. (4.1) and weighting them with a phase factor that incorporates the proper nodal structure. This implicitly assumes that the semiclassical analog of a quantum eigenstate is a uniform probability distribution on the manifold defined by...
Eq. (4.1). Given our arguments, this assumption should be amended so that the semiclassical analog is a uniform probability distribution on the classical manifold defined by Eq. (4.2). For the ground eigenstate, it is easy to see that such an amendment leads to the correct result. While the difference in semiclassical eigenstates created using Eq. (4.2) in place of Eq. (4.1) will not be great for systems with only a couple of degrees of freedom, large systems could show great differences as the additional $\hbar \omega$ of energy in each degree of freedom might place the classical manifold in a region of phase space with a very different dynamical topology (due to nonlinear resonances or chaos).

Large systems also present difficulties in the quasiclassical treatment of molecular dynamics if one uses energy as a criterion for establishing initial conditions, rather than location in phase space. For example, it has been found that a classical model for benzene (with 30 vibrational degrees of freedom) displays chaotic dynamics when given zero-point energy, that is, $\hbar \omega$ of energy in each vibrational mode. The energy criterion for establishing initial conditions for large molecules can also lead to the unfortunate result that the zero-point energy is sufficient to dissociate some or all of the bonds in the molecule. These problems are exacerbated as one goes to larger and larger systems—one would quickly reach a limit in which the zero-point energy is sufficient to break the strongest known chemical bonds.

In light of our results, initial conditions in which $\hbar \omega$ of energy is placed in each vibration would correspond to having half a quantum of excitation in each and every mode in the molecule. It is not so surprising that such an initial state might be chaotic. The classical dynamics in this case would correspond to regions of phase space in which the density of quantum states is extremely high and energy flow in the molecule is essentially statistical. The idea that a molecule would then have enough residual energy in its ground state to dissociate is counterintuitive. Once again, by concentrating on the region of phase space which is most important to the quantum dynamics, we would model the ground state of a large molecule classically using a set of trajectories whose energy distribution is peaked about zero energy. Simulations in which residual zero-point energy is placed in each vibrational mode run the risk of exploring regions of phase space that are completely different from that of most of the quantum dynamics, especially for large molecular systems.

Several workers have devised ways to keep large molecules from dissociating during quasiclassical simulations by artificially maintaining at least zero-point energy in each vibrational mode. Miller, Hase and Darling, and Bowman and co-workers have recently introduced such an algorithm and have applied it to the classical dynamics of linear HC4 and a Hcn-Heiles model Hamiltonian, respectively. Our findings indicate that not only is such a procedure unnecessary, but also that it excludes regions of phase space which are likely to be important in the intramolecular dynamics. For example, consider a two degree of freedom system which is initially displaced in only one direction. Quantum mechanically, one might envision a wave packet which flows back and forth in the displaced degree of freedom (see Fig. 3). The classical analog of such motion, obtained by following the maximum in the probability density, is a periodic orbit. This trajectory has no displacement in the second degree of freedom—effectively, its energy in the second degree of freedom is zero throughout the dynamics. This analogy applies also to large molecular systems: maintaining zero-point energy in nonactivated vibrations precludes motion through the phase space origin in those degrees of freedom which can clearly be a major part of the quantum dynamics.

One should be careful in exercising the idea that the appropriate classical mechanics is only that which corresponds to the motion of the maximum in the probability density. The actual quantum dynamics generally involves a wave function which has spatial extent in all directions in phase space and can be thought of as incorporating many different types and energies of classical motion (although this analogy is not strictly correct—see below). As a result, there may be important parts of the quantum dynamics which would not be represented by a single classical trajectory, no matter how well-placed it is in phase space. This is particularly true in cases where the quantum wave packet bifurcates into two or more pieces, or becomes very delocalized within the time scale of interest.

A particularly insidious example of this involves motion along a periodic orbit as in the motion described in Fig. 3.
For many degree of freedom systems in which only a few vibrations are activated, this kind of motion predominates as the inactive vibrations are all at zero displacement and the classical dynamics lies along a periodic orbit (fixed point) in most of the degrees of freedom. In classical dynamics, periodic orbits and their stability properties are very important in determining the topology of a region of phase space.\cite{34,35} If a periodic orbit is stable, then small displacements from the orbit will result in dynamics that is qualitatively similar to the dynamics on the orbit. A small displacement from an unstable periodic orbit, however, results in classical dynamics that is very different qualitatively from the motion on the periodic orbit.

Now, consider the quantum dynamics in such regions of phase space. Wave packet motion along a stable periodic orbit is generally well-behaved, as in Fig. 3, with the wave packet remaining more or less localized as it moves along the orbit. When motion is along an unstable periodic orbit, however, the wave packet no longer stays nicely localized (see Fig. 4).\cite{34} In such cases, it is clear that quasiclassical simulations of the quantum dynamics must account for more than the motion of the center of the wave packet. These cases correspond to the situation where the coupling between the "stationary" mode and an "active" mode is significant, but will be fixed at zero when there is zero displacement in the stationary vibration. Without computing the quantum dynamics first, the only way one might account for dynamics such as that shown in Fig. 4 is by thoroughly investigating the phase space topology in the neighborhood of a given initial configuration in phase space.

Evidently, the use of quasiclassical trajectories to simulate quantum dynamics is fraught with potential pitfalls. In all but the simplest systems, it is probably inadequate to simulate the dynamics using a single trajectory or even a set of trajectories, all with the same energy. A reasonable way to use classical mechanics to represent the motion of a quantum state might be to run an ensemble of trajectories whose initial conditions are weighted by the phase space density of the initial quantum state. In this case, it is preferable to use a density that allows a correspondence between the quantum and classical Liouville equations which govern the time evolution of densities in phase space.\cite{35} However, even this approach will not be able to account for interference effects or the "global" effects of the wave function on its dynamics. These global effects come into play because the action of the time propagation operator, $e^{-i\hat{H}t/\hbar}$, on the wave function cannot be expressed as the sum of its actions on several small, localized pieces of the wave function. This point is also discussed in slightly different language in the hydrodynamic treatment of quantum dynamics introduced by Skodje and co-workers.\cite{13}

Finally, another application of the quantum-classical correspondence principle is the computation of expectation values using semiclassical theory. There are two major approaches for doing this: (i) computing a classical average over the Wigner density, and (ii) constructing a semiclassical eigenstate and evaluating the expectation value using a quantum operator. The second method is philosophically the same as the quantum expectation value, the only difference being the approximate nature of the state over which the property is being evaluated. In the present discussion, we shall focus on the first method since our approach to the correspondence principle is based on selecting the classical dynamics appropriate to various quantum mechanical quantities.

The expectation value of a dynamical quantity for a given quantum state is a global property of that state. The most appropriate semiclassical analogy, that of computing a classical average over a Wigner distribution, reflects this need for global information. Conversely, a classical average over a single trajectory manifold, or over a single energy shell samples an infinitesimal part of the phase space spanned by a given quantum state and cannot, in general, be equivalent to a quantum expectation value. Consequently, as in the case of studying intramolecular dynamics, one should generally be careful to include a distribution of classical manifolds (or energy shells as the case may be) that span the entire applicable region of phase space.

Another way to compute expectation values in phase space according to our scheme involves constructing the operators for dynamical quantities from the operators $\hat{Q} = q + i\hbar \frac{\partial}{\partial p}$ and $\hat{P} = -i\hbar \frac{\partial}{\partial q}$, for example, then evaluating

\begin{equation}
\langle \hat{Q}\rangle = \langle q \rangle + i\hbar \langle \frac{\partial}{\partial p} \rangle,
\end{equation}

\begin{equation}
\langle \hat{P}\rangle = -i\hbar \langle \frac{\partial}{\partial q} \rangle.
\end{equation}

FIG. 4. Six snapshots of the motion of a nonstationary state (wave packet) in a two dimensional coupled oscillator potential. Here, the wave packet spreads as it oscillates up and down in the potential due to the fact that the underlying classical phase space corresponds to an unstable periodic orbit. Such motion cannot be adequately represented by a single classical trajectory.
\[ \langle \hat{A}(\hat{\mathbf{q}}, \hat{\mathbf{p}}) \rangle = \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} dq \, \psi^* (\Gamma) \times A \left( q + i\hbar \frac{\partial}{\partial p}, -i\hbar \frac{\partial}{\partial q} \right) \psi (\Gamma). \] (4.3)

Unfortunately, there is no simple classical analog for this computation. As a result, the choice of the classical dynamics which is most representative of quantum dynamics has no bearing on the accuracy of semiclassical expectation values when they are computed as classical averages on trajectory manifolds. The one instance in which choosing the classical dynamics according to phase space criteria might improve a semiclassical expectation value would be when semiclassical eigenstates are constructed from classical trajectory manifolds and used to compute desired expectation values, as in the methods of Heller and co-workers.\(^{13}\) We note, however, that the general scheme given in Eq. (4.3) is applicable to any distribution in phase space, \(\psi (\Gamma)\), that represents a quantum state.

V. SUMMARY

The quantum time evolution equation presented here provides a formal means for describing the dynamics of a quantum system completely in phase space. By casting the Schrödinger equation directly in phase space, we now have a basis for deriving eigenfunctions, quantum densities, probability conservation equations, coherent states, and the time evolution of wave packets directly in phase space. The use of the “phase space Schrödinger equation” also makes it easier to compare quantum states with the corresponding classical dynamics and determine to what extent the classical picture of the dynamics carries over to the quantum world. As simple examples of this idea, the harmonic oscillator and the nonstationary coherent state have been treated using this formalism.

The implications of our results are significant for the simulation of quantum dynamics using quasiclassical trajectory calculations and the computation of semiclassical expectation values. In the case of quasiclassical simulations, we find that the usual inclusion of zero-point energy in the definition of initial conditions is not only unnecessary, but could cause the classical dynamics to avoid regions of phase space which are important to the corresponding quantum dynamics. The region of phase space most representative of the ground state of a bound system appears to be the area centered about the potential minimum. Our approach has emphasized identifying appropriate regions of phase space for making a connection between classical and quantum mechanics and, as a result, we have pointed out the inadequacy of using single trajectories (or even single energy shells) in the simulation of quantum dynamics or in the calculation of expectation values. The most reliable means for semiclassically approximating expectation values remains the use of classical averages over the Wigner density or the use of semiclassical eigenstates in the quantum prescription for computing such averages.

The understanding of the correspondence between quantum and classical mechanics is of fundamental importance to our study of molecular systems. Since our perceptions of the world are inevitably based on classical intuition, it is useful to know when that intuition will break down in the case of molecular dynamics. In the present work, our aim has been to provide a time-evolution equation for quantum states that have been cast in phase space via a generalized Husimi transform, to obtain a consistent description of quantum mechanics in phase space, and to clarify the relationship between quantum and classical mechanics as a guide for our innate classical intuition. In future work, we will examine the phase space representation of the time evolution equation for a quantum density (Liouville equation) and explore the manifestations of purely quantum mechanical phenomena, such as tunneling, in phase space to better understand the differences between quantum and classical dynamics.

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APPENDIX

In this appendix, we show that the pseudotransition matrix element

\[ \langle \Gamma | \psi' \rangle = g(p' - p) \exp (ip'q/\hbar) \] (A1)

leads to a time evolution equation for the phase space wave function

\[ \langle \Gamma | \psi_t \rangle = \int_{-\infty}^{\infty} dp' \langle \Gamma | \langle p' | \psi_t \rangle, \] (A2)

from the wave function in momentum representation \( \langle p' | \psi_t \rangle = \langle p' | \psi_t \rangle \).

Multiplying both sides of the Schrödinger equation in the momentum representation,

\[ i\hbar \frac{\partial}{\partial t} \langle p' | \psi_t \rangle = \left[ \frac{1}{2\mu} p'^2 + V \left( \frac{\hbar}{\mu} \frac{\partial}{\partial p'} \right) \right] \langle p' | \psi_t \rangle, \] (A3)

by \( \langle \Gamma | p' \rangle \) and integrating the result over \( p' \), we obtain

\[ i\hbar \frac{\partial}{\partial t} \int_{-\infty}^{\infty} dp' \langle \Gamma | p' \rangle \langle p' | \psi_t \rangle = \int_{-\infty}^{\infty} dp' \langle \Gamma | p' \rangle \left[ \frac{1}{2\mu} p'^2 + V \left( -i\hbar \frac{\partial}{\partial p'} \right) \right] \langle p' | \psi_t \rangle \]

\[ = \int_{-\infty}^{\infty} dp' \left[ \frac{1}{2\mu} p'^2 + V \left( -i\hbar \frac{\partial}{\partial p'} \right) \right] \langle \Gamma | p' \rangle \langle p' | \psi_t \rangle \] (A4)
where we have assumed that \( \langle p'|\psi_t \rangle \) and its derivatives vanish at \( p = \pm \infty \), and that \( V(q) \) can be written as a power series in \( q \).

Since the pseudotransition matrix element (A1) satisfies the equalities

\[
\rho^n(\Gamma|p') = \left( -i\hbar \frac{\partial}{\partial q} \right)^n \langle \Gamma|p' \rangle,
\]

\[
\left( -i\hbar \frac{\partial}{\partial p} \right)^n \langle \Gamma|p' \rangle = \left( q + i\hbar \frac{\partial}{\partial p} \right)^n \langle \Gamma|p' \rangle,
\]

we can recast Eq. (A4) into the form

\[
i\hbar \frac{\partial}{\partial t} \langle \Gamma|\psi_t \rangle = \left[ \frac{1}{2\mu} \right] \left( -i\hbar \frac{\partial}{\partial q} \right)^2
+ V \left( q + i\hbar \frac{\partial}{\partial p} \right) \langle \Gamma|\psi_t \rangle,
\]

which is Eq. (2.7) in the text.