

Phase space deformation and basis set optimization

Matthew C. Cargo and Robert G. Littlejohn

Department of Physics, University of California, Berkeley, California 94720

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By deforming a given region of phase space—occupied by some unknown eigenfunctions one wishes to find—into a standard, integrable region, effective reductions in basis set size can be achieved. In one-dimensional problems we are able to achieve $B/C = 1 + O(\hbar)$, where B is the basis set size and C is the number of “converged” eigenfunctions. This result is confirmed by numerical examples, which also indicate exponential convergence as the basis set size is increased. In higher dimensions we prove that such an optimistic result is impossible; we expect that the best one can do in this case is $B/C = a + o(1)$, where $a > 1$ has a geometric interpretation in terms of ratios of volumes in phase space.

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I. INTRODUCTION

In this paper we develop a strategy which is based on mapping regions of the classical phase space into one another, for optimizing basis sets for diagonalizing quantum Hamiltonians. The goal is to minimize the basis set size when a quantum Hamiltonian must be solved by numerical means, that is, by finding the eigenvectors of its matrix representation in some truncated basis. The selection of the optimized basis set is based on semiclassical notions, but the method we develop is not a semiclassical approximation, since the quantum Hamiltonian is ultimately diagonalized in a complete and orthonormal basis. Semiclassical notions arise, however, because both the basis set and the collection of unknown eigenfunctions that one wishes to find are represented by regions in the classical phase space. When the region occupied by the basis set covers the region occupied by the unknown eigenfunctions with a sufficient margin, the unknown eigenfunctions will be well converged in that basis. This paper explores the element of flexibility inherent in using canonical transformations to map one region of phase space into another, thereby transforming standard basis sets into new ones that are more efficient for covering a given region of phase space.

In view of the practical importance of diagonalizing Hamiltonian matrices and the rapidly increasing computational effort as a function of the basis set size, the problem of optimizing the basis set for a given quantum Hamiltonian is one that has attracted some attention. The importance of this issue is not restricted to bound state calculations, since popular methods for doing scattering calculations involve repetitive diagonalizations of the Hamiltonian restricted to a submanifold of configuration space (the hypersphere or a quotient space thereof) [1–3]. All the methods for basis set optimization that we are aware of involve or are elucidated by phase space concepts, although this has often not been explicitly acknowledged. Moreover, the specific approach, studied in this paper, of transforming phase space regions into a standard region, lies behind several methods—both semiclassical and exact—which have been used in the past.

For example, in the semiclassical method of comparison equations [4] a point transformation is used to transform a one-dimensional problem into a solvable problem with a

standard turning point structure, plus correction terms. (A point transformation is a special case of a canonical transformation in which the new Q is a function only of the old q .) The same point transformation will emerge in our one-dimensional analysis below. It seems, however, that the method of comparison equations is not usually viewed from a phase space standpoint.

Another example arises in the method of distributed Gaussians [5], which uses an array of Gaussian wave packets in configuration space as a nonorthonormal basis. The Gaussians are unmodulated (that is, their momentum expectation values are zero). In this method one can use a uniform array of Gaussians of equal width, but in one-dimensional problems there is an alternative, or “semiclassical,” spacing rule that reduces the basis set size. Under the semiclassical spacing rule, the Gaussians are spaced nonuniformly, and their widths must also be nonuniform in a prescribed manner. As it turns out, the semiclassical spacing rule emerges by performing a canonical transformation on the phase space of the original system, which transforms the original oval of the one-dimensional oscillator one is trying to solve into a rectangle (the phase space region for a particle in a box). This transformation is singular at the turning points, so in later versions of the method of distributed Gaussians [6] the transformation is softened out at the turning points. There does not seem to exist a good multidimensional generalization of the semiclassical spacing rule, a fact which is probably related to the impossibility of transforming a nonintegrable level set into an integrable one (a fact discussed below). As far as we know, this point of view regarding the semiclassical spacing rule for distributed Gaussians (one which relates it to a canonical transformation that transforms the energy contour into a standard shape) is new, but it is not far beneath the surface in Ref. [5]. More recent work on distributed Gaussians [7] (involving random distributions) raises new considerations, which, however, are outside the main thrust of this paper.

A related idea has been pursued by Gygi [8,9] in applications to solid state physics. Gygi considers point transformations in three-dimensional configuration space that preserve the periodicity of a lattice, but reduce the size of the basis set required in quantum calculations. Special attention is given to density functional methods. Gygi uses a variational

principle to optimize the point transformation, which in his applications can be expanded in a Fourier series. But, he does not take any semiclassical ideas into account or develop the phase space point of view, as far as we know. For example, it is not clear how his variational principle is related to the volume of the energy shell in the six-dimensional phase space. Nevertheless, effective reductions in basis set size are achieved, and in any case, regardless of interpretation, it may be that point transformations are the only practical means for transforming phase space regions.

In another study, Fattal, Baer, and Kosloff [10] have examined point transformations that improve the efficiency of a Fourier series basis for solving quantum problems. These authors emphasize the phase space point of view, and are explicit about transforming a complicated phase space region into a rectangle (a standard form covered by a Fourier series basis). In their paper, they do not attempt to find the exact transformation that will produce a desired shape of the region in the target phase space, even for one-dimensional problems. Instead, they work with a specific transformation, which is apparently obtained heuristically, and apply it to several model problems.

This approach is improved upon in a later paper [11], in which the authors study molecular bound states near dissociation in potentials with the asymptotic behavior $V \sim 1/r^n$. This paper deals with coordinate transformations based both on bounding potentials with the same asymptotic behavior as the exact potential as well as on the exact potential itself. In both cases, either the bounding or exact phase space region is transformed into a rectangle. The authors advocate a “Fourier grid method” (essentially a sinc-type discrete variable representation) for solving the transformed wave equation, although it appears that they only actually solve the transformed wave equation for transformations based on bounding potentials at zero total energy, for which the action integral can be evaluated in simple analytic form. This is a reasonable approach in practice, because the exact action integrals are often difficult, but it means that one does not have a test of the maximum possible efficiency of the method of phase space mapping.

Several novel approaches to the problem of optimizing basis sets have been adopted by Poirier [12–14] and by Poirier and Light [15,16]. In Ref. [12], Poirier develops a variational criterion for the “weakly” separable basis that is as close as possible to the eigenbasis of a given Hamiltonian (that is, the basis is optimized for this Hamiltonian). This theory is applied to reactive scattering in Ref. [13]. Although this part of the work does not involve phase space concepts very much, such concepts enter in a much more important way in Ref. [15], which uses “quasiclassical” (phase space) approximations to find the optimal “strongly” separable bases for a variety of multidimensional Hamiltonians. (Strongly separable bases are Cartesian products of one-dimensional bases, which can be cast into discrete variable representation form for efficient computations.) This paper also develops deformed grids for dealing with multidimensional problems, and in this respect is similar to the work of Gygi. Poirier has further developed the phase space point of view in Ref. [14], in which he develops the “quasiclassical”

approximation (one which uses the Wigner-Weyl correspondence and carries expansions only to lowest order in \hbar). Finally, we mention the study of optimized, nonorthonormal, Gaussian bases in Ref. [16], which achieves a very high efficiency in sample problems, comparable to the efficiency we achieve in this paper, but at the expense of near linear dependencies of the basis states.

Another approach that attempts to directly target a desired region of phase space is the one that uses lattices of states in phase space. The lattices are created by taking discrete subgroups of some continuous group that supports coherent states, in the generalized sense of Perelemov [17]. If the Heisenberg-Weyl group is chosen, then we obtain rectangular lattices of states (coherent states in the usual sense [18], if the “fiducial state” is Gaussian) in phase space. If the dilation-translation group is used, then we obtain wavelets, in the usual sense of the word.

The idea of using rectangular lattices of coherent states in phase space as a basis set has a long history, which goes back to von Neumann [19] and continues to the present time [20]. One study that has used such lattices for quantum calculations is that of Davis and Heller [21]. Although much can be said about this approach, it does not usually involve transforming phase space regions, and so lies outside the main line of development of this paper. We merely remark that it seems to us that lattices of coherent states in phase space are not competitive with other methods for minimizing basis set size, especially in multidimensional problems (in spite of the attractiveness of the basic idea). We will say more about coherent state lattices in future publications.

The subject of wavelets [22–25] is an important development in applied mathematics in recent years, which has had a big impact on signal processing and other areas. Wavelets have also been used for few-body quantum calculations [26,27], as well as in many-body density functional calculations [28]. The idea of resolving wave functions on different scales is closely related to phase space representations of wave functions, as is made clear in the founding literature on wavelets. The formalism of multiresolution analysis is an elegant way of implementing this idea. However, the wavelets that are used in multiresolution analysis are nonanalytic functions possessing long-range (algebraic) tails in momentum space. Although the order may be high, these tails will ultimately result in power law (not exponential) convergence for analytic eigenfunctions, and therefore will ultimately result in slower convergence than the analytic basis functions discussed below. Moreover, as far as we know, wavelets have not been used in combination with transformations of phase space.

Our main results are presented in Sec. II. We begin with an outline of the method. Although the basic ideas have been presented previously, most explicitly by Fattal, Baer, and Kosloff [10] and by Kokoouline *et al.* [11], these authors discussed only the case in which the target region is a rectangle, while we generalize to transformations between arbitrary regions of a fixed topology, including the multidimensional case. Moreover the presentation of these authors of the idea of phase space mapping is tangled up with the mapped Fourier method for solving the transformed wave equation, and

these two parts of the theory are logically distinct. In addition, we discuss quite a few issues not dealt with by these authors, including the importance of the analyticity of the transformation, the relation between classical canonical transformations and unitary transformations, the suggestion of using the metaplectic operators, the analyticity of the transformation function $X(x)$ even at the turning points, formulas for the Jacobian at the turning points, and the relation of the present method to the (old) method of comparison equations. For all these reasons we felt it was important to present an independent and self-contained presentation of the basic ideas, which we do in Secs. II A and II B. After this we present numerical results on using harmonic oscillator bases to solve the Morse oscillator, and we present a theorem that shows that optimal phase space coverage, in the sense achieved for the one-dimensional case, is impossible in general in the multidimensional case. Conclusions are presented in Sec. III.

II. THE METHOD OF PHASE SPACE DEFORMATION

In this section we begin by outlining the basic idea of the method of phase space deformation for optimizing basis sets in quantum mechanics, and by discussing a simple example. Next we develop the theory of phase space deformation for one-dimensional problems, which is based on finding a coordinate transformation $X=X(x)$ that transforms a given region of phase space into a standard region (for example, a circle). This part of the presentation should be compared to that of Fattal, Baer, and Kosloff [10] and Kokoouline *et al.* [11], who treat similar subjects. Next we apply this theory to the Morse oscillator. We work out the transformation analytically, as far as possible, and then use it to reduce the basis set size required in numerical work. We find that we are able to achieve ratios B/C quite close to unity. We also examine various approximate schemes for deforming phase space, which are easier to implement than the exact one. Some of these give substantial improvements in basis set size, which, however, are not as great as in the exact case. Finally, we present a theorem on the multidimensional case, which shows that in general an exact mapping of a given phase space region into a standard region (for example, a sphere) is impossible.

A. Outline of the basic idea

Consider a quantum Hamiltonian \hat{H} of a few degrees of freedom. Suppose for simplicity that it is desired to find the first C converged eigenvalues, where “converged” means to some prescribed accuracy. A basis set is chosen in terms of which the Hamiltonian matrix can be computed. The basis set is truncated at some finite number B of basis functions, whereupon the eigenvalues of the Hamiltonian are estimated by the eigenvalues of the truncated, $B \times B$ matrix. The size B of the truncation must be chosen large enough so that the first C eigenvalues of the matrix are converged to the prescribed accuracy. The computational effort is a strongly increasing function of B .

What is the minimum value of B that can be achieved? The answer depends on the basis. Obviously if we were clever enough to choose the exact eigenbasis of the Hamiltonian \hat{H} , or a basis such that the first C basis functions were linear combinations of the first C exact eigenfunctions of \hat{H} , then the answer would be $B=C$. In other cases we have $B > C$, exact the ratio $B/C \geq 1$ is a measure of the goodness of our choice.

We will suppose that C is large enough that semiclassical reasoning can be used to guide us in the choice of a basis set. In particular, we use the semiclassical rule that all quantum states occupy a region of phase space with volume h^f , where $h=2\pi\hbar$. and f is the number of degrees of freedom. This rule applies both to the unknown eigenstates of \hat{H} we wish to find as well as to the basis states.

For example, in a one-dimensional oscillator, we can view the first C energy eigenstates as occupying the region of the classical phase space inside the orbit $H(x,p)=E_0$, where E_0 is chosen in such a way that the area enclosed by the orbit is Ch . Here $H(x,p)$ is the classical Hamiltonian corresponding to the quantum Hamiltonian \hat{H} , where the hat distinguishes quantum operator from its classical counterpart. On the other hand, many common choices of basis sets are eigenbases of some analytically solvable operator, which itself may be a Hamiltonian (the harmonic oscillator Hamiltonian, for example). Call this operator \hat{D} , the “basis generating operator,” which corresponds to the classical function $D(x,p)$. Then the B basis functions can be thought of as occupying the interior of the region $D(x,p)=D_0$, where D_0 is chosen in such a way that the region has area Bh .

In terms of these regions, the minimum value of B needed to find C converged eigenvalues of \hat{H} has a geometrical meaning. Holding C fixed, we increase B and consider the errors in the first C eigenvalues of \hat{H} . The smallest value of B for which all C eigenvalues of \hat{H} are even qualitatively correct is the one for which the region $D(x,p)=D_0$ just covers the region $H(x,p)=E_0$. Then, as we increase B beyond this value, we find that the eigenvalues converge exponentially in the basis set size.

Figure 1 illustrates these ideas. The curve MO in the figure is the contour in the classical phase space of the Morse oscillator Hamiltonian

$$H(x,p) = \frac{p^2}{2} + (e^{-x} - 1)^2 - 1, \quad (1)$$

where $H(x,p)=E_0=-0.1$ in the figure ($E=-1$ at the bottom of the well, and $E=0$ is the dissociation energy). The curve is the energy shell or level set of the Morse Hamiltonian. (In this paper, “level set of the Hamiltonian” and “energy shell” are synonymous. In one dimension, these are the same as a classical orbit of a given energy.) The chosen value of E_0 is sufficiently close to dissociation that the classical motion of the Morse oscillator is strongly anharmonic, as evidenced by the stretched and pointed shape of the contour. The number of quantum states contained inside this energy shell is the area divided by h , the value of which [in

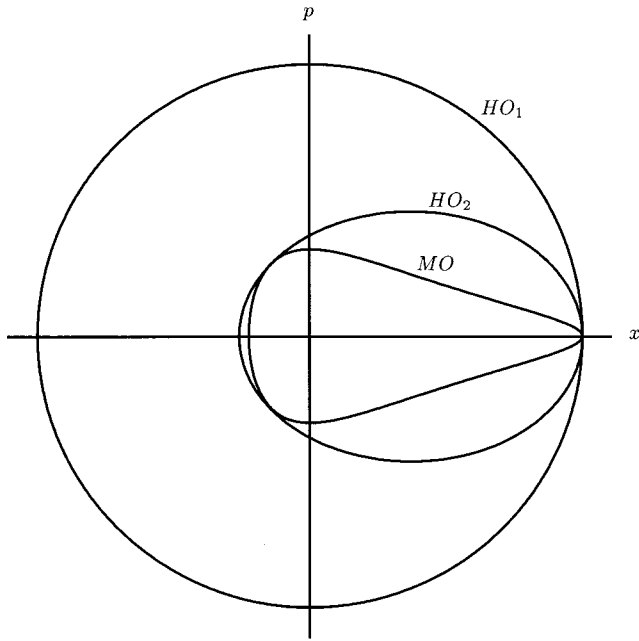


FIG. 1. Phase space contours of classical Hamiltonians. Contour MO is a Morse oscillator with an energy of $E = -0.1$. The large circle HO_1 is the contour of a harmonic oscillator with parameters based on small vibrations at the bottom of the Morse oscillator well. The ellipse HO_2 is the contour of a different harmonic oscillator, with shifted origin and frequency. Both harmonic oscillator contours are chosen to be just large enough to cover the area inside the Morse oscillator contour.

the dimensionless units used in Eq. (1)] depends on the problem, that is, the type of molecular bond being modeled by the Morse oscillator, the masses of the atoms, etc. In any case, the number of quantum states is proportional to the area.

A simple strategy for finding the energy levels of the quantum Morse oscillator is to use a harmonic oscillator basis, which is centered at the bottom of the well of the Morse potential (at $x=0$ in the figure) with the same frequency as that of small vibrations in the Morse potential. The Hamiltonian of this harmonic oscillator is

$$D(x,p) = \frac{p^2}{2} + x^2 - 1. \quad (2)$$

We estimate the number of basis states needed with this basis by finding the smallest contour value D_0 such that the region inside $D(x,p) = D_0$ just covers the region inside $H(x,p) = E_0$. The level set $D(x,p) = D_0$ is the large circle HO_1 in Fig. 1. In the limit $\hbar \rightarrow 0$, the ratio B/C approaches the ratio of the area of the circle $D = D_0$ to that enclosed by the Morse contour $H = E_0$.

It is obvious from the figure that this ratio is relatively unfavorable, because of the large amount of “wasted area.” A different harmonic oscillator basis would do better, such as the one with the elliptical contour HO_2 in Fig. 1. This second harmonic oscillator has a shifted origin and a different

frequency from the first oscillator and achieves a ratio of areas of approximately 2:1, which is not too bad for a one-dimensional problem.

The idea of using shifted and scaled harmonic oscillators to improve basis set efficiency is an old one, which evidently has been used in multidimensional scattering problems, reaction path Hamiltonians, and model problems. As far as we know, however, these approaches have not made use of the notion of the covering of a desired region of phase space by a basis set, which we believe is a fundamental issue in basis set efficiency.

For any nonzero value of \hbar , the actual number of basis states required is larger than that estimated by the enclosed area, because the actual wave functions tunnel into the classical forbidden regions (both in configuration space and momentum space). However, the wave functions die off exponentially in the tunneling regions, giving us exponential convergence as B is increased beyond the area estimate.

The following is a semiclassical way of understanding the exponential convergence that sets in as B increases after the area of the classical oscillator is covered. Let the exact (presumed unknown) eigenstates of the problem we are trying to solve (the Morse oscillator in the example) be $|n\rangle$, and the basis states be $|\alpha\rangle$. Then the expansion coefficients of the exact eigenstates in terms of the basis states are $\langle\alpha|n\rangle$. If we evaluate this scalar product by using the semiclassical approximations to the exact eigenfunctions and the basis functions, then the integral is dominated by the stationary phase points of the integrand. But these stationary phase points are geometrically just the intersections of the curves $H = E_n$ for the Hamiltonian with unknown eigenfunctions and $D = D_\alpha$ for the basis generating operator (more generally, they are the intersections of Lagrangian manifolds in phase space [29]). However, if the classical contour $D = D_\alpha$ lies outside the contour $H = E_n$, then there are no (real) intersections. There will, however, be complex ones, corresponding to complex actions S whose imaginary parts increase as the basis contours expand. Thus, expansion coefficients $\langle\alpha|n\rangle$, which go as $e^{iS/\hbar}$, decrease exponentially. Notice that this argument relies on the analyticity of the functions $H(x,p)$ and $D(x,p)$; indeed, exponential convergence does not usually hold when either function has singularities (divergences or discontinuities in some derivative of the potential, for example).

To return to our example, Fig. 1 shows that even the best choice of harmonic oscillator basis will have some wasted area, because the Morse level sets are not ellipses. If, however, we could perform a canonical transformation on the phase space of the Morse oscillator, which would transform the energy shell $H = E_0$ into (say) a circle, then a circular harmonic oscillator basis would precisely cover the interior of the transformed Morse oscillator energy shell. Notice that we are not trying to transform the Morse oscillator into a harmonic oscillator; this cannot be done in any case, since the harmonic oscillator has a constant frequency and the Morse oscillator has a frequency that depends on the amplitude. All we are trying to do is to transform one specific contour of the Morse oscillator $H = E_0$ into a circle. The

other level sets of the Morse oscillator, for $H < E_0$ and $H > E_0$, will have images under the canonical transformation that are not circles.

More generally, we may seek a canonical transformation that will transform the level set of some classical Hamiltonian whose quantum counterpart we wish to solve out to some energy E_0 into the level set of some conveniently solvable problem. There is then the practical matter of using the eigenbasis of the solvable problem in the transformed variables to solve the original quantum problem in the original variables. We may wish to carry out this program in one or more degrees of freedom.

B. Phase space deformation in one dimension

We now develop the theory of phase space deformation in one dimension. The multidimensional case raises new issues and will be discussed below. We begin with a Hamiltonian \hat{H} whose classical counterpart is $H(x,p)$ and a conveniently solvable Hamiltonian \hat{D} whose classical counterpart is $D(X,P)$. The use of capitalized variables (X,P) for the arguments of D will be explained momentarily. As explained above, the basis functions will be the eigenfunctions of \hat{D} . For simplicity we will assume that both H and D have kinetic-plus-potential form

$$H(x,p) = \frac{p^2}{2m} + V(x), \quad D(X,P) = \frac{P^2}{2} + U(X), \quad (3)$$

with analytic potentials $V(x)$ and $U(X)$, although our results are easily generalized to analytic Hamiltonians of a more general form. Many of the steps below are independent of the specific form of these Hamiltonians. The variables (X,P) are assumed to be suitably dimensionless, hence the absence of a mass parameter in $D(X,P)$.

Now suppose that some energy E_0 is given, such that it is desired to find all energy eigenvalues and eigenfunctions of \hat{H} below E_0 . The level set $H(x,p) = E_0$ of the classical Hamiltonian is some curve in phase space with some topology. Because of the time-reversal invariance of H , this curve is symmetric about the x axis. In general, this curve consists of one or more disconnected pieces. We assume that one of these pieces is a topological circle, that is, an oval of some kind centered on the x axis, with two turning points that we denote by x_0 and x_1 ($x_0 < x_1$). These are the roots in x of $H(x,0) = E_0$. If there are other disconnected pieces of the level set $H(x,p) = E_0$, then we have tunneling from one oscillatory region (between x_0 and x_1) to perhaps other oscillatory regions or perhaps unbounded (scattering) regions. For simplicity, we will assume for now that the level set $H = E_0$ consists only of a single topological circle, so that there is no tunneling. We will comment below about more complicated cases.

We now seek a canonical transformation $(x,p) \rightarrow (X,P)$ such that the level set $H(x,p) = E_0$ in the old variables is mapped into a level set of $D(X,P) = D_0$ in the new variables for some value of D_0 . Since canonical transformations preserve area, the area of the old level set must be equal to the area of the new one

$$\oint p(x,E_0)dx = \oint P(X,D_0)dX, \quad (4)$$

where $p(x,E_0)$ and $P(X,D_0)$ are the respective local momenta

$$p(x,E_0) = \sqrt{2m[E_0 - V(x)]}, \quad P(X,D_0) = \sqrt{2[D_0 - U(X)]}. \quad (5)$$

Thus, Eq. (4) defines D_0 as a function of E_0 . It is assumed that $D(X,P)$ has a level set of the required area, and that it is a topological circle. Once D_0 is known, we can find the turning points of the curve $D(X,P) = D_0$, call them X_0 and X_1 ($X_0 < X_1$).

The functional form of H changes upon carrying out the canonical transformation. We call the new functional form $K(X,P)$, so that

$$K(X,P) = H(x(X,P),p(X,P)). \quad (6)$$

By construction, the level set $K(X,P) = E_0$ is the same curve in the new phase space as the level set $D(X,P) = D_0$. The two functions $K(X,P)$ and $D(X,P)$ are not expected to have other level sets in common, however (only for the contour values E_0 and D_0).

Since our entire approach is based on semiclassical notions, in which the wave function varies on a scale much smaller than that of the classical Hamiltonian, we require that our canonical transformation does not introduce any short scale lengths of its own. This means that our canonical transformation should be analytic (at least in the region of interest) and independent of \hbar . In particular, we must exclude canonical transformations that have discontinuities, either in the transformation itself or in one of its derivatives. One case in practice where this condition has not been met is in approaches in which the standard region in the transformed phase space is a rectangle.

Our strategy will be to use the eigenfunctions of \hat{D} , the quantum analog of $D(X,P)$, as a basis to find the eigenfunctions of \hat{K} , the quantum analog of $K(X,P)$, and hence the eigenfunctions of \hat{H} . However, to pursue this idea we must have the quantum analog of the classical canonical transformation $(x,p) \rightarrow (X,P)$, which would be some unitary transformation. In general, the relationship between canonical transformations in classical mechanics and unitary transformations in quantum mechanics is not simple, due to ordering issues, topological matters, phase factors, higher order terms in \hbar , etc. In cases where the classical transformation is smooth and certain topological conditions are met, Miller [30] has presented a theory that associates a canonical transformation with a semiclassical approximation to the matrix elements of a corresponding unitary transformation. However, Miller's matrix elements have caustics and do not exactly satisfy the unitarity conditions (they do so only in a semiclassical sense). Therefore, they are not suitable for our purposes where it is necessary to carry out an exact unitary transformation on wave functions.

Therefore, we must restrict the consideration to canonical transformations that correspond semiclassically to some

known unitary transformation. The correspondence need not be exact (for example, there might be higher order terms in \hbar), because our purpose is merely to optimize the basis. But the corresponding transformation on the quantum wave functions should be exactly unitary, and, as a practical matter, it should be easy to implement.

There are two classes of canonical transformations that come to mind satisfying these requirements. The first consists of the point transformations, which in the present notation are canonical transformations of the form

$$X=X(x), \quad P=(\partial x/\partial X)p, \quad (7)$$

where $X(x)$ is a given function, which are generated by the type-2 generating function [31] $F_2(x,P)=PX(x)$. Point transformations can be regarded as merely changes of coordinates in configuration space, which are promoted into canonical transformations by appending the momentum transformation law [the second of Eqs. (7)]. The latter is written more transparently as $p dx = P dX$.

If we denote the old and new wave functions under a point transformation by $\psi(x)$ and $\Psi(X)$, and demand that the normalization integrals transform according to

$$\int dx |\psi(x)|^2 = \int dX |\Psi(X)|^2, \quad (8)$$

then the relation between the old and new wave functions is

$$\psi(x) = J^{1/2} \Psi(X), \quad (9)$$

where $J = \partial X/\partial x$ is the Jacobian of the transformation. We will assume that the transformation $X(x)$ is monotonically increasing, so $J > 0$ everywhere.

The second class consists of the linear canonical transformations, which correspond in quantum mechanics to the unitary metaplectic transformations [32]. The point transformations form a rather restricted set of canonical transformations, but by composing them with linear canonical transformations in various orders it is possible to generate a much larger set [33]. However, the action of the metaplectic operators on wave functions is given by an integral transform, which at first sight seems more difficult to use than Eq. (9), although probably fast metaplectic transforms could be implemented. Also, it would seem that linear canonical transformations would complicate the computation of matrix elements of the potential energy.

Therefore in this paper we have restricted the consideration to just the point transformations. This is the same class of transformations considered previously by Gygi [8,9] and Fattal, Baer, and Kosloff [10], so we have nothing new in this respect, except for a larger conceptual framework and the possibility of a larger class of transformations in future work. However, thinking in terms of canonical transformations has definite advantages, as will be apparent in our discussion of the multidimensional case.

If we were to seek an unrestricted canonical transformation that would map the given level set $H(x,p)=E_0$ into the level set $D(X,P)=D_0$, with D_0 defined by Eq. (4), then

there would be many possible solutions. However, if we restrict to point transformations, then the solution is essentially unique, as we will show now.

Let us seek a point transformation $X(x)$ such that the level set $H(x,p)=E_0$ is mapped into the level set $D(X,P)=D_0$. The transformation should also map turning points into one another, $X(x_0)=X_0$ and $X(x_1)=X_1$. In view of Eq. (7), the transformation function $X(x)$ must satisfy the differential equation

$$\frac{dX}{dx} = \frac{p(x,E_0)}{P(X,D_0)}. \quad (10)$$

The single constant of integration is fixed by the condition $X(x_0)=X_0$, which gives

$$\int_{x_0}^x p(x,E_0) dx = \int_{X_0}^X P(X,D_0) dX. \quad (11)$$

This is an implicit solution for $X(x)$. The right turning point condition $X(x_1)=X_1$ is not an extra condition, but rather is satisfied automatically in view of Eq. (4).

Equation (11) defines $X(x)$ between the turning points, but for transforming the wave function as in Eq. (9) we need $X(x)$ for all x (or at least for x far enough outside the turning points that ψ becomes negligible). It turns out that the solution (11) has a well behaved analytic continuation outside the turning points, although the differential equation (10) itself is quite singular at the turning points, as are all of its solutions except the one given by Eq. (11), with the value of D_0 determined by Eq. (4).

Regarding singularities, consider first the left turning point x_0 . If the transformation function $X(x)$ does not satisfy the condition $X(x_0)=X_0$, then dX/dx vanishes at $x=x_0$ and diverges at $X=X_0$. Thus the condition $X(x_0)=X_0$ is necessary for the point transformation to be smooth and single valued. Similarly, if the value of D_0 does not satisfy the area condition (4) (perhaps due to numerical error), then when the integrals in Eq. (11) are carried to the right turning point there will be zeros or infinities in dX/dx .

However, if the turning point conditions are satisfied, then although both p and P go to zero at a turning point, their ratio remains finite and well behaved as the turning point is approached. In fact, by expanding both $V(x)$ and $U(X)$ about the turning point and taking the limit, it is easy to show that the Jacobian approaches the value

$$J = \frac{dX}{dx} = \left(\frac{mV'(x)}{U'(X)} \right)^{1/3}, \quad (12)$$

where V' and U' are evaluated at the turning point. We will assume that V' and U' are nonzero at the turning points, so J has a positive value there. Similarly higher order derivatives of $X(x)$ can be evaluated at the turning points in terms of derivatives of the two potentials, although the expressions rapidly become complicated.

The differential equation (10) can be analytically continued outside the turning points by choosing branches of the square roots for p and P (now both purely imaginary) such

that their real ratio approaches the value (12) as the turning points are approached from the classically forbidden regions. In this way a single transformation function $X(x)$ is defined, which is analytic in all regions, classically allowed and classically forbidden. If, however, there are more than two turning points, and if x is taken as far as one of these extra turning points, then the solution $X(x)$ will develop a singularity.

The transformation $X(x)$ developed above is the same that is used in the method of comparison equations [4] for analyzing two-turning point problems (where D is taken to be a harmonic oscillator). The method of comparison equations is not able to handle systems with three or more turning points, for lack of a solvable comparison equation with the same turning point structure. In our method, however, larger numbers of turning points are not necessarily a problem. Consider, for example, a double well oscillator. If the tunneling is deep for a given energy E_0 , then the communication between wells may be negligible, and we can just use the solution $X(x)$ developed above for a single well. In this case we need take x only halfway to the other well, where the wave function is negligible, and we never encounter any singularity in $X(x)$. On the other hand, if the tunneling is shallow, then we can always raise the cutoff energy E_0 above the top of the barrier, and we have once again a system with two turning points, and both wells can be handled at once.

However, this approach will not work if there is tunneling to an unbounded region (meaning we have a resonance in a scattering problem). For simplicity we will exclude unbounded or scattering problems from our consideration in this paper.

We now transform the Schrödinger equation under the point transformation (7). The old Schrödinger equation is $\hat{H}\psi = E\psi$, where

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}), \quad (13)$$

with $\hat{p} = -i\hbar(\partial/\partial x)$. Then writing $\hat{P} = -i\hbar(\partial/\partial X)$ we have $\hat{p} = J\hat{P}$ and the operator identity

$$J\hat{P}J^{1/2} = J^{1/2}\left(\frac{\hat{P}J + J\hat{P}}{2}\right). \quad (14)$$

Thus we can write the new Schrödinger equation in the form $\hat{K}\Psi = E\Psi$, where

$$\hat{K} = \frac{1}{2m}\left(\frac{\hat{P}J + J\hat{P}}{2}\right)^2 + V(x(\hat{X})). \quad (15)$$

We wish to solve this in the eigenbasis of $\hat{D} = \hat{P}^2/2 + U(\hat{X})$.

We remark that if we use the Weyl symbol correspondence to map quantum operators into classical functions, then the classical Hamiltonian corresponding to Eq. (15) is

$$K(X, P) = \frac{J^2 P^2}{2} + V(x(X)), \quad (16)$$

which coincides with the result of carrying out the classical canonical transformation (7) on the Hamiltonian $H(x, p)$. The Weyl transform provides an elegant way of making semiclassical approximations on Hamiltonians of a rather general functional form [34].

C. Results for the Morse oscillator

We will now test the effectiveness of the phase space deformation method by using it to solve the Morse oscillator. The Morse oscillator is especially useful for our purposes, because the curve $H(x, p) = E_0$ becomes increasingly distorted as E_0 approaches the oscillator's dissociation energy. This allows us to test the deformation method under arbitrarily severe deformations.

The Morse oscillator Hamiltonian of Eq. (1) has been presented in dimensionless units in which the physical properties are parametrized by \hbar . In these units, the energy E of a bound orbit satisfies $-1 \leq E < 0$. The exact energy eigenvalues are given by [35]

$$E_n = -\frac{1}{2}(I - \sqrt{2})^2, \quad (17)$$

where $I = (n + 1/2)\hbar$ and $n = 0, 1, \dots$ [the maximum value of n is the last one before the peak of the quadratic function $E_n(I)$]. Typical values of \hbar for molecular systems range from about $10^{-1} - 10^{-2}$, corresponding to approximately 10–100 bound states. We choose $D(X, P)$ of Eq. (3) to be the harmonic oscillator Hamiltonian

$$D(X, P) = P^2/2 + X^2/2. \quad (18)$$

We will now use Eq. (11) to determine the function $x(X)$ that, for correctly chosen D_0 , maps the level set $H(x, p) = E_0$ into $D(X, P) = D_0$. At energy E_0 , the Morse oscillator has turning points $x_0 = -\ln(1 + \kappa)$ and $x_1 = -\ln(1 - \kappa)$, where $\kappa = \sqrt{1 + E_0}$. At energy D_0 , the harmonic oscillator has turning points $X_1 = -X_0 = \sqrt{2D_0}$. We define $f(x) = \int_{x_0}^x p(x, E_0) dx$ and $F(X) = \int_{X_0}^X P(X, D_0) dX$, so that the implicit solution is $f(x) = F(X)$. For $X_0 < X < X_1$ and $x_0 < x < x_1$, we find

$$F(X) = \frac{XP}{2} + D_0 \tan^{-1}(X/P) + \frac{\pi}{2} D_0, \quad (19)$$

and

$$f(x) = -p + \sqrt{2} \left[\sin^{-1}\left(\frac{1 - e^{-x}}{\kappa}\right) + \sqrt{1 - \kappa^2} \sin^{-1}\left(\frac{e^{-x} - 1 + \kappa^2}{\kappa e^{-x}}\right) + \frac{\pi}{2}(1 - \sqrt{1 - \kappa^2}) \right], \quad (20)$$

where $P = P(X, D_0)$ and $p = p(x, E_0)$. Equation (4) now fixes $D_0 = f(x_1)/\pi = \sqrt{2}(1 - \sqrt{1 - \kappa^2})$.

Similarly, for $X < X_0$ and $x < x_0$ or $X > X_1$ and $x > x_1$, the solution is $g(x) = G(X)$, where

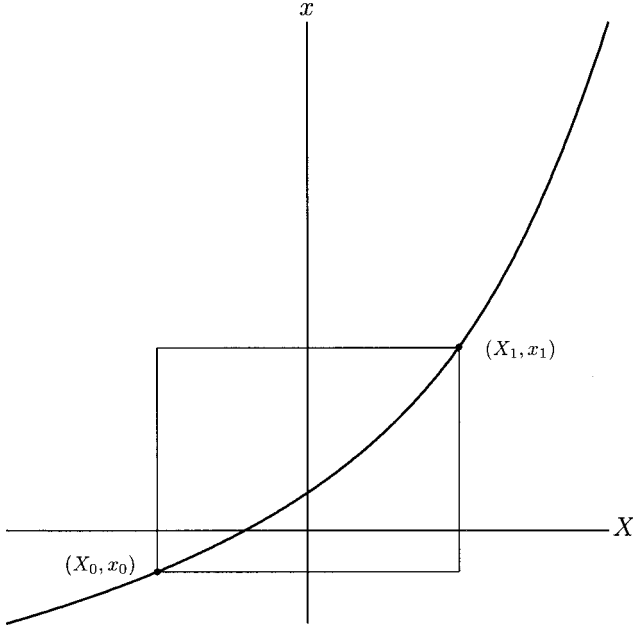


FIG. 2. Function $x(X)$ that deforms the $E_0 = -0.1$ shell of the Morse oscillator into a circle. Vertical and horizontal lines mark the turning points of the harmonic oscillator and the Morse oscillator, respectively.

$$G(X) = \frac{X\bar{P}}{2} - D_0 \ln \left| \frac{X + \bar{P}}{X_0} \right|, \quad (21)$$

and

$$g(x) = -\bar{p} + \sqrt{2} \ln \left| \frac{(\bar{p}/\sqrt{2}) + e^{-x} - 1}{\kappa} \right| + \sqrt{2(1 - \kappa^2)} \ln \left| \frac{e^{-x} - 1 + \kappa^2 - (\bar{p}/\sqrt{2})\sqrt{1 - \kappa^2}}{\kappa e^{-x}} \right|, \quad (22)$$

where $\bar{P} = \sqrt{X^2 - 2D_0}$ and $\bar{p} = \sqrt{2[V(x) - E_0]}$.

It turns out later that we will need to evaluate the function $x(X)$ numerically. We do this by finding the roots of equations $f(x) = F(X)$ or $g(x) = G(X)$. In this process, one must take considerable care in evaluating Eqs. (19)–(22) to avoid loss of precision. A related numerical difficulty appears when we need to evaluate J near the turning points, due to the loss of precision in computing p or P according to Eq. (5). In fact, it does not seem to be easy to evaluate J to maximum precision near the turning points. We have found, however, that the error introduced by simply using Eq. (5) did not seem to adversely affect our results.

In spite of the numerical difficulties of evaluating $x(X)$ near the turning points, the function itself is perfectly well behaved there. This is shown quite clearly in Fig. 2, which is a plot of $x(X)$ for $E_0 = -0.1$. The turning points are indicated in the figure; were this not done, it would be impossible to locate them from the plot itself.

Now we turn to the diagonalization of \hat{K} in the harmonic oscillator basis. We will be interested in testing the convergence of the eigenvalues of \hat{K} (which of course are the same as the eigenvalues of \hat{H}) as the size B of the basis is increased.

First we need the matrix elements of the potential energy $V(x(X))$. In principle, these could be evaluated by any quadrature formula (such as Simpson's rule) with a sufficient number of integration points, but nowadays in problems, such as this, it is popular to transform to the so-called discrete variable representation (DVR) basis [36,37]. In this basis, the potential energy (or any other function of only X) is diagonal to a good approximation, and the matrix elements are trivial. It is also easy to transform back to the original basis (the harmonic oscillator basis in this case), because the unitary transformation between the bases can be expressed exactly in terms of the original basis functions evaluated at a set of DVR grid points. The latter are the zeros of a certain one of the original basis functions. The DVR method is so convenient for finding matrix elements of operators, which depend only on X , that we wanted to use it for our calculation.

However, the DVR method for evaluating matrix elements introduces a certain error, because functions of X are not exactly diagonal in the DVR basis. Since the purpose of this paper is to test the error in the method of phase space deformation, we did not want to contaminate the results with additional errors. Therefore, when we switched to the DVR basis we used a larger number of DVR grid points than the number B of harmonic oscillator basis functions we were using. The number of DVR grid points we chose was sufficiently large that we got convergence in the matrix elements, typically, this was about $B + 10$.

In this manner, we determined the matrix elements of $V(x(X))$. Similarly, we determined the matrix elements of the Jacobian J , which is also a function only of X . The matrix elements of the momentum P are easy in the harmonic oscillator basis. From these, by matrix multiplication, we determined the matrix elements of the operator PJ , whose Hermitian part is $(PJ + JP)/2$. Finally, squaring the matrix of the latter operator, we obtained the matrix elements of the kinetic energy term in \hat{K} , seen in Eq. (15). In these matrix multiplications, we used a basis whose size was somewhat larger than B , again in order to avoid introducing extra error. If one were interested in a practical algorithm, rather than testing the method, it would probably be more convenient to carry out the entire calculation in bases of a fixed size (which would have to be somewhat larger than the B values we quote to get the same accuracy).

Finally, we diagonalized the matrix to obtain approximate energy eigenvalues. We defined an accuracy parameter ϵ for an eigenvalue to be the fractional error relative to the bottom of the well, that is,

$$\epsilon = |E - \tilde{E}|/(E + 1), \quad (23)$$

where E is the exact eigenvalue and \tilde{E} is the approximate one.

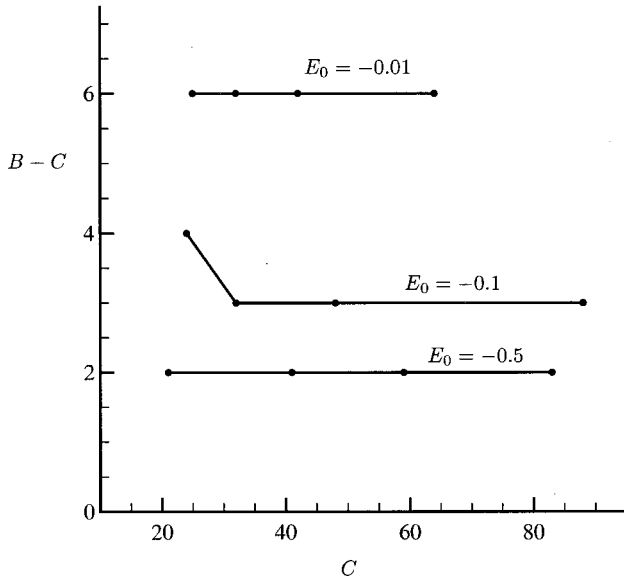


FIG. 3. Excess of basis states over converged eigenstates (difference $B - C$) versus number of converged eigenstates C , for three different energies. Eigenstates are considered converged when the relative error $\epsilon < 10^{-7}$. For given E, C is varied by varying \hbar . The difference $B - C$ is approximately constant for given E .

In one study, we examined how the number of basis states B required to achieve convergence depends on the energy cutoff E_0 and on the number of converged eigenstates C . We varied C for the fixed E_0 by changing \hbar . In this study, we considered the C eigenstates to be converged if the state with the maximum relative error (which was always the last eigenstate with $E \leq E_0$) had $\epsilon < 10^{-7}$. The results are shown in Fig. 3. It turns out that the difference $B - C$ is nearly constant for a given E_0 , so we plotted $B - C$ versus C at different energies. As expected, it requires a larger number of basis states to converge when the cutoff energy E_0 is closer to dissociation, but even at $E_0 = -0.01$ (a strongly distorted oval) we find $B/C \approx 1.1$ for $C = 60$. The results can be summarized by

$$\frac{B}{C} = 1 + \frac{k}{C}, \quad (24)$$

where k is a constant depending on E_0 but not on C . Equivalently, since for fixed E_0 C is proportional to $1/\hbar$, we can say $B/C = 1 + O(\hbar)$.

In another study we examined the convergence for fixed energy cutoff E_0 and fixed C (hence fixed \hbar) as the number of basis states B is increased. We defined ϵ_{\max} as the maximum value of ϵ , given by Eq. (23), for the first C eigenstates. In all cases, the maximum occurred either for the last state (usually), or occasionally for the next to the last state. This maximum error is plotted as a function of B for two different cases in Fig. 4. The convergence is rapid, but apparently not as fast for energies nearer the separatrix, as would be expected.

Finally, we present in Fig. 5 a plot of the relative error ϵ as a function of the quantum number n for the cutoff energy

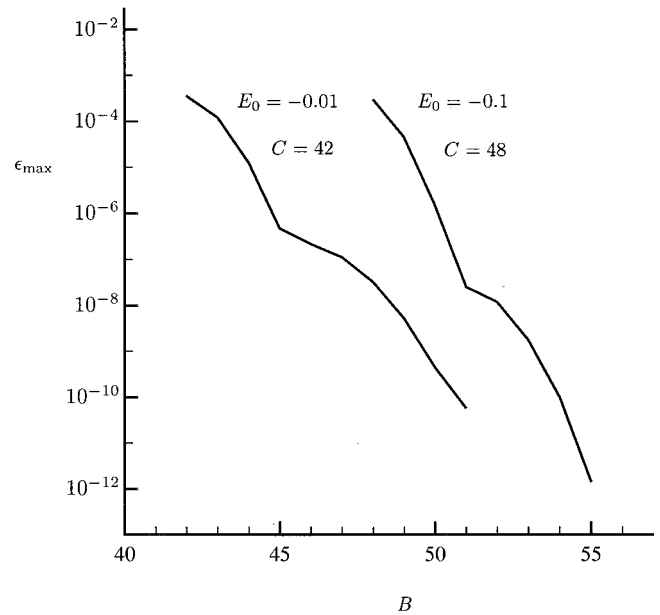


FIG. 4. Maximum relative error ϵ among first C computed eigenvalues as a function of basis set size B .

$E_0 = -0.1$ and a value of h chosen to give $C = 24$ states ($n = 0$ to $n = 23$). The number of basis states used was $B = 28$. Note the sharp decrease in accuracy for states that are not within the target region; effectively, our basis has used all its energies for the states inside the target region, and has none left for states outside.

An obvious drawback to the method we have presented so far is that the function $x(X)$ is difficult to compute. In the

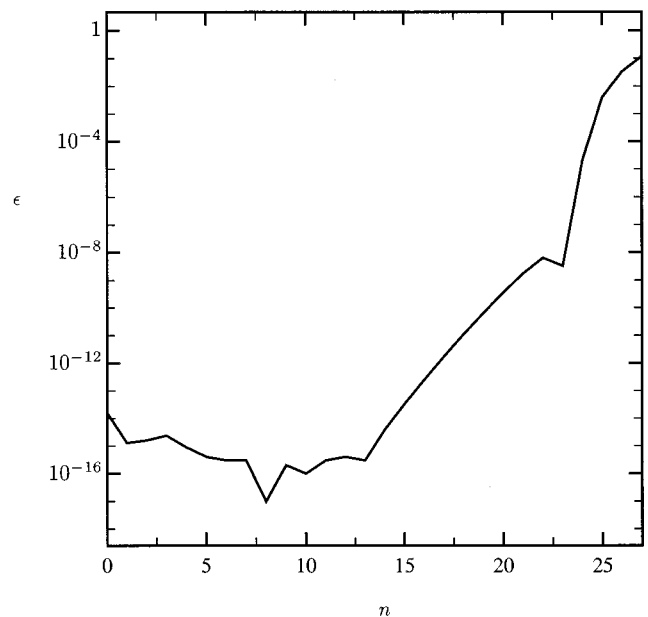


FIG. 5. Relative error ϵ versus quantum number n for $E_0 = -0.1$, which corresponds to 24 bound states ($n = 0 - 23$). $B = 28$ basis states were used.

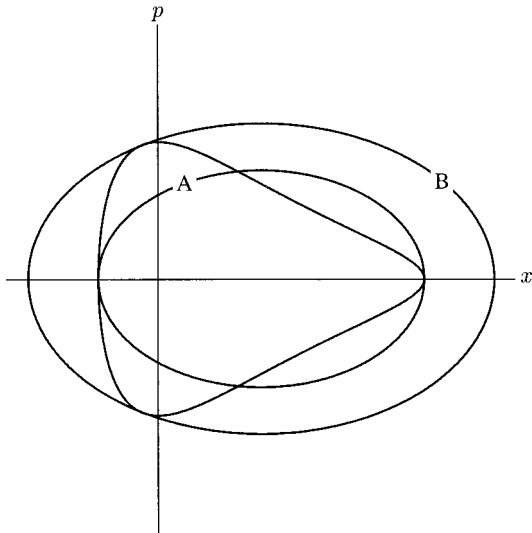


FIG. 6. Harmonic oscillator coverage of the Morse oscillator for $E_0 = -0.1$. The harmonic oscillator contour A has the same turning points and same area as the Morse oscillator cutoff contour. Harmonic oscillator contour B has twice the energy of harmonic oscillator A . This is not the most efficient harmonic oscillator for covering the Morse oscillator.

case of the Morse potential we were able to do the action integrals yielding $f(x)$ and $g(x)$ analytically, but the final forms were not simple. For other potentials it will be impossible to do these integrals analytically. Moreover, even given an analytic form, the functions $f(x)$ and $g(x)$ may be subject to loss of precision near turning points, as we have found in the case of the Morse potential.

On the other hand, Fig. 2 shows that the function $x(X)$ is a rather featureless, monotonic function, which it should be possible to approximate with functions of simple analytic form. Such approximations would not be as effective as the exact $x(X)$ in reducing basis set size, of course, but they might still be useful. In fact, it occurred to us that even a crude numerical evaluation of the function $x(X)$, say, with 10% accuracy, might still be very effective in reducing the basis set size. To test these ideas we studied various simple approximations to $x(X)$. In all of the following studies, we took $E_0 = -0.1$.

The simplest approximation is a linear one. Any linear function $x(X)$ will map harmonic oscillators into other harmonic oscillators. Thus, the standard harmonic oscillator (18) in the (X, P) phase space will correspond to another harmonic oscillator in the original (x, p) phase space, but with elliptical contours. The first example we looked at was a straight line fit between the turning points (X_0, x_0) and (X_1, x_1) in Fig. 2. This corresponds to choosing a harmonic oscillator back in the original (x, p) phase space that has the same turning points as the Morse oscillator, and the same area between those turning points. In this case, we found that achieving $\epsilon = 10^{-3}$ required B to be about $2C$. For comparison, 10^{-3} accuracy could be achieved as early as $B = C$ using the exact $x(X)$, as shown in Fig. 4. Figure 6 shows the

Morse oscillator and the mapped harmonic oscillator (marked A in the figure) in the original (x, p) phase space. It is clear that the wasted area is due to the strong deformation of the Morse oscillator contour, which does not fit an ellipse very well. To cover the area of the Morse oscillator with a harmonic oscillator of these parameters, the harmonic oscillator energy must be increased to approximately $2D_0$, as indicated by the contour B in the figure.

Other linear approximations $x(X)$ work better. For example, by changing the two linear fit parameters, we found an $x(X)$ that covers the Morse oscillator with an energy of $1.7D_0$ (this is the ellipse HO_2 in Fig. 1). Indeed, with $\hbar = 0.03$, 54 basis states are needed to converge the 32 interior states to $\epsilon < 10^{-3}$.

Finally, we investigated some nonlinear fits to $x(X)$. One, a combination of a quadratic and an exponential, fit particularly well in the classically allowed region. Here, for $\hbar = 0.03$, $B = 38$ states were needed to obtain $C = 32$ states to $\epsilon < 10^{-7}$. This is three basis states more than required by the exact $x(X)$, but still considerably better than any linear fit.

In the problem of determining approximate fits to the function $x(X)$, high accuracy may not be required, but it is important that the approximate function be smooth. For example, piecewise analytic functions would not do (owing to the nonanalyticities where the functions are pieced together). Thus it is not trivial to design approximate fits. We could be more motivated to pursue this question if determining a large number of eigenvalues for one-dimensional problems on \mathbb{R} were a common problem in practice. However, the same issues are certainly present in more realistic problems (multi-dimensional problems on spaces of less trivial topology).

D. The multidimensional case

We turn now to the multidimensional case. Our main result here is to show that it is impossible, by means of any canonical transformation, to transform the level set $H = E_0$ of a generic, multidimensional Hamiltonian system into the level set $D = D_0$ of a solvable (that is, integrable) system. Not surprisingly, this result depends on the impossibility of transforming nonintegrable motion into integrable motion. But it is not quite as trivial as it seems, because we are not trying to transform a nonintegrable Hamiltonian entirely into an integrable one, merely a single level set.

As before, let $H(x, p)$ be the classical analog of a quantum Hamiltonian \hat{H} whose eigenvalues and eigenfunctions we wish to find out to energy E_0 . Now, however, x and p are n -dimensional vectors (their components are x_i and p_i). Similarly, $D(X, P)$ is an integrable Hamiltonian of n degrees of freedom whose quantum counterpart we will use as a basis generating operator. We assume that $H(x, p)$ is chaotic (it has at least one chaotic orbit of energy E_0 , which would be the usual case in practice). On the other hand, $D(X, P)$ has only regular orbits (the level set $D = D_0$ is foliated into invariant tori, on which the classical orbits are quasiperiodic). Then there does not exist any smooth canonical transformation $(x, p) \rightarrow (X, P)$ that maps the given level set $H(x, p) = E_0$ into a level set $D(X, P) = D_0$ for any value of D_0 .

Suppose on the contrary that such a canonical transformation exists, and let $K(X,P)$ be the new Hamiltonian, as in Eq. (6). Then the level set $K(X,P)=E_0$ in the new phase space coincides with some level set $D(X,P)=D_0$, for some value of D_0 . These level sets have dimensionality $2n-1$. Let $Z=(X,P)$ be the $2n$ phase space coordinates in the new phase space, with components Z^μ , $\mu=1,\dots,2n$. Consider Hamilton's equations for the two Hamiltonians $K(X,P)$ and $D(X,P)$. The respective flow vectors are given by

$$\dot{Z}_K^\mu = \Gamma^{\mu\nu} \frac{\partial K}{\partial Z^\nu}, \quad \dot{Z}_D^\mu = \Gamma^{\mu\nu} \frac{\partial D}{\partial Z^\nu}, \quad (25)$$

where $\Gamma^{\mu\nu}$ is the unit cosymplectic form [38]. But on the coincident level sets, the differential forms dK and dD (essentially the phase space gradients of the two Hamiltonians) are proportional, because the contour surfaces are the same. That is, we can write $dK=f dD$, where f is a function whose value depends on where we are on the common level set, $K=K_0$ or $D=D_0$. This means that the flow vectors are proportional, $\dot{Z}_K=f\dot{Z}_D$, which implies that the classical orbits generated by these two Hamiltonians, $Z_K(t)$ and $Z_D(t)$ are the same, to within a time parametrization. But the orbits $Z_K(t)$ are the images under the canonical transformation of the orbits $z_H(t)$ in the original phase space, that is, the orbits in $z=(x,p)$ generated by the Hamiltonian $H(x,p)$. Therefore at least one of the orbits $Z_K(t)$ is chaotic. However, the orbits $Z_D(t)$ are all regular. Therefore these orbits cannot be the same, and our assumption, that a smooth canonical transformation exists with the required properties, must be wrong.

III. CONCLUSION

We have shown that phase space concepts offer a good way to understand the effectiveness of a basis set. In particular, we have used phase space concepts to construct a basis distinct from the actual eigenbasis of the Hamiltonian that covers the target phase space with high efficiency and has fast exponential convergence as the basis set is expanded. We have also proven a theorem, which shows that optimal coverage is not possible, in general, in the multidimensional case.

Any study involving one-dimensional problems on \mathbb{R} is at best useful mainly for its suggestive value, since practical problems take place on multidimensional configuration spaces, often with a nontrivial topology and in the presence of gauge fields (rotational or Coriolis effects). Thus, there are several interacting issues at work in the problem of basis set optimization in practical problems. However, the problem of phase space coverage is definitely a piece of the puzzle.

In regard to our results on the multidimensional case, we have shown that achieving $B/C=1+O(\hbar)$ is impossible in general in the multidimensional case. The best one can hope for is $B/C=a+o(1)$, where $a>1$ is some constant (it is the ratio of the volume of the smallest integrable level set enclosing the cutoff energy shell to the volume of that energy shell), and where $o(1)$ indicates terms that go to 0 as $\hbar \rightarrow 0$. It is an open question as to how to find this value of a , or how to come close to it in practice in a multidimensional problem. We mention that we believe our theorem for the multidimensional case is related to the apparent impossibility of finding a semiclassical spacing rule for distributed Gaussians in this case. We will report on this and other aspects of this problem in the future.

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- [1] V. Aquilanti, S. Cavalli, and D. De Fazio, *J. Chem. Phys.* **109**, 3792 (1998).
 - [2] V. Aquilanti, S. Cavalli, D. De Fazio, and A. Volpi, *J. Chem. Phys.* **109**, 3805 (1998).
 - [3] Aron Kuppermann, *J. Phys. Chem.* **100**, 11 202 (1996).
 - [4] M. V. Berry and K. E. Mount, *Rep. Prog. Phys.* **35**, 315 (1972).
 - [5] I. P. Hamilton and J. C. Light, *J. Chem. Phys.* **84**, 306 (1986).
 - [6] Z. Bačić and J. C. Light, *J. Chem. Phys.* **85**, 4594 (1986).
 - [7] Sophya Garashchuk and John C. Light, *J. Chem. Phys.* **114**, 3929 (2001).
 - [8] François Gygi, *Phys. Rev. B* **48**, 11 692 (1993).
 - [9] François Gypi, *Phys. Rev. B* **51**, 11 190 (1995).
 - [10] Eyah Fattal, Roi Baer, and Ronnie Kosloff, *Phys. Rev. E* **53**, 1217 (1996).
 - [11] V. Kokoouline, O. Dulieu, R. Kosloff, and F. Masnou-Seeuws, *J. Chem. Phys.* **110**, 9865 (1999).
 - [12] Bill Poirier, *Phys. Rev. A* **56**, 120 (1997).
 - [13] Bill Poirier, *J. Chem. Phys.* **108**, 5216 (1998).
 - [14] Bill Poirier *Found. Phys.* **30**, 1191 (2000).
 - [15] Bill Poirier and J. C. Light, *J. Chem. Phys.* **111**, 4869 (1999).
 - [16] Bill Poirier and J. C. Light, *J. Chem. Phys.* **113**, 211 (2000).
 - [17] A. Perelemov, *Generalized Coherent States and Their Applications* (Springer-Verlag, New York, 1986).
 - [18] John R. Klauder and Bo-Sture Skagerstam, *Coherent States* (World Scientific, Singapore, 1986).
 - [19] J. von Neumann, *Z. Phys.* **57**, 30 (1929).
 - [20] Ingrid Daubechies, Stéphane Jaffard, and Jean-Lin Journé, *SIAM (Soc. Ind. Appl. Math.) J. Math. Anal.* **22**, 554 (1991).
 - [21] Michael J. Davis and Eric J. Heller, *J. Chem. Phys.* **71**, 3383 (1979).
 - [22] I. Daubechies, *IEEE Trans. Inf. Theory* **36**, 961 (1990).
 - [23] I. Daubechies, *Ten Lectures on Wavelets* (SIAM, Philadelphia, 1992).
 - [24] Charles K. Chui, *Wavelets: A Tutorial in Theory and Applications* (Academic, New York, 1992).
 - [25] *Different Perspectives on Wavelets*, Proceedings of Symposia in Applied Mathematics, edited by Ingrid Daubechies (American Mathematical Society, Providence, RI 1993), Vol. 47.
 - [26] C. J. Tymczak and Xiao-Qian Wang, *Phys. Rev. Lett.* **78**, 3654 (1997).
 - [27] Koichiro Yamaguchi and Takeshi Mukoyama, *J. Phys. B* **29**, 4059 (1996).
 - [28] T. A. Arias, *Rev. Mod. Phys.* **71**, 267 (1999).
 - [29] Robert G. Littlejohn, *J. Math. Phys.* **31**, 2952 (1990).
 - [30] William H. Miller, *Adv. Chem. Phys.* **25**, 69 (1974).
 - [31] Herbert Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, MA, 1980).

- [32] Robert G. Littlejohn, Phys. Rep. **138**, 193 (1986).
- [33] F. Leyvraz and T. H. Seligman, J. Math. Phys. **30**, 2512 (1989).
- [34] Robert G. Littlejohn and William G. Flynn, Phys. Rev. A **44**, 5239 (1991).
- [35] Philip M. Morse, Phys. Rev. **34**, 57 (1929).
- [36] J. V. Lill, G. A. Parker, and J. C. Light, Chem. Phys. Lett. **89**, 483 (1982).
- [37] D. Baye and P.-H. Heenen, J. Phys. A **19**, 2041 (1986).
- [38] V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer-Verlag, New York, 1989).