Model Systems and Approximate Constants of Motion

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We present a framework to quantify the extent to which an approximate Hamiltonian is a suitable model for a real Hamiltonian, based on the degree of stability of the approximate constants of motion that are exact constants in the model. By observing the evolution under the real Hamiltonian of packets prepared initially as eigenstates of the model Hamiltonian, we are able to define quantitative criteria for the quality of the approximation represented by the model. Quantitative measures emerge for the concepts of "approximate constant of the motion" and "pretty good quantum number". This approach is intended for evaluating alternative starting points for perturbational and variational calculations, and for extracting physical insights from elaborate calculations of real systems. The use of the analysis is illustrated with examples of a one-dimensional Morse oscillator approximated by a harmonic oscillator and by another Morse oscillator, and then by a less trivial system, an anharmonic, nonseparable two-dimensional oscillator, specifically a Henon–Heiles potential modified with a fourth-order term to keep all states bound. The higher the angular momentum within any given band, the better the angular momentum is conserved. The square of the angular momentum is less well conserved than the angular momentum itself.

I. Introduction

The concept of the "approximate constant of the motion" has never been given a precise, useful, quantitative meaning. Undoubtedly, this is in no small part because the approximate nature of the concept does not beg for rigor; we all have an intuitive idea of what the term connotes, and for most of us this is sufficient.

By asking "How approximate?", however, we can gain insight into the applicability of various trial systems as models for a real system. This is especially important to the researcher who makes extensive use of perturbational or variational techniques. The choice of basis set in perturbational or variational calculations is intimately tied to this concept. The choice of basis set implies a choice of model system, each of which has its own set of constants of the motion. The extent to which these constants are maintained under conditions of the true Hamiltonian determine the suitability of the model system for emulating the true one. Manifestations of this success are the rate of convergence and quality of convergence of the representation.

The earliest allusion that we could find to an approximate constant of the motion was due to van Vleck, when he wrote in 1932 on the quantization of electronic angular momentum in diatomic molecules. More recently, the idea has been used in the context of chaotic dynamics in molecules. Additionally, a method has been developed for the determination of exact and approximate constants of the motion for systems whose Hamiltonians can be expressed as polynomials in positions and momenta.

We define an approximate constant of the motion to be an observable \( \lambda \) associated with an operator \( \hat{\lambda} \) such that \( \hat{\lambda} \) does not commute with the exact Hamiltonian, \( \hat{H} \), but does commute with \( \hat{H}_0 \), an approximation of the exact Hamiltonian. To be an approximate constant of the motion, it must also satisfy one more condition: fluctuations of \( \lambda \) about its mean value should be smaller than the spacing of the levels of the quantum number of the approximate Hamiltonian. Quantifying this and other useful criteria is the goal of this study.

In section 2 we define the problem more precisely and derive expressions to evaluate the aforementioned set of criteria. In section 3 we present the model analysis that we use to demonstrate the utility of the framework, and in section 4 we present and discuss the results from this model. Concluding remarks and future directions are to be found in section 5. In section 6 we introduce the anharmonic, nonseparable two-dimensional rotor that serves as our first nontrivial model system. Section 7 presents the results of the analysis of this system. Section 8 contains a summary of our conclusions.

II. Framework

We wish to know how an observable that is a constant of the motion for \( \hat{H}_0 \), an approximate Hamiltonian, changes in time if the observable is not a constant of the motion of \( \hat{H} = \hat{H}_0 + \hat{H}_1 \), the exact Hamiltonian. More specifically, we wish to know under what circumstances such an approximation will yield approximate quantum numbers that are indicative of the behavior of the exact system. Most often, the term \( \hat{H}_1 \) will be only a perturbation on the potential.

When we describe a quantum number, say \( \lambda \), corresponding to the operator \( \hat{\lambda} \), as "approximate", what we are really saying is that \( \lambda \) remains near its expectation value for almost all times. That is, if we allow a system prepared in an eigenstate of the approximate Hamiltonian to evolve under conditions of the exact Hamiltonian, there will be little variability evident in successive measured values of the observable \( \hat{\lambda} \).

Let \( \hat{H}_0 \), the approximate Hamiltonian, have bound stationary orthonormal eigenstates \( |0\rangle, |1\rangle, ..., |n\rangle \). Similarly, let \( \hat{H} \) have bound stationary orthonormal eigenstates \( |\lambda\rangle, |\mu\rangle, ..., |\Omega\rangle \) and let \( \omega_0 = E(\langle \lambda \rangle) / \hbar \). Furthermore, let the operator \( \hat{\lambda} \) commute with \( \hat{H}_0 \) with eigenvalues given by \( \langle \lambda \rangle = \lambda \). The superscript 0 on the operator is a reminder that it commutes with \( \hat{H}_0 \) and not with \( \hat{H} \). It is also convenient to define the density operators:

\[
\rho_k = |k\rangle \langle k| \quad I = 0, 1
\]

In the following derivation, the continuum regions that may be present for both Hamiltonians have been disregarded. The reason for this will be discussed below.

Now, let us assume that \( \lambda \) is a candidate approximate constant of the motion for some system. The system is prepared in state \( \rho_0 \) at time \( t = 0 \). We ask how the wavepacket evolves under the...
influence of $H$. First expand $|0\rangle$ in terms of the basis set of $H$ as follows:

$$\Psi(t=0) = |0\rangle = \sum_{k=0}^{N} a_{kl} |k\rangle = \sum_{k=0}^{N} \rho_{kl} |0\rangle$$

(1)

where $a_{kl} = \langle 0 | k \rangle$. The situation will sometimes arise that we cannot adequately express the initial eigenstate of $H_0$ in terms of the discrete eigenstates of $H$. In such cases, the continuum, therefore dissociative, solutions of $H$ must then be included in the expansion in order to be able to express the exact initial eigenstate of $H_0$. This is one way in which $H_0$ may not be a good approximation to $H_0 + H_1$, at least for the specific $|0\rangle$ being tested. Because at this point we are only interested in the bound portion of the wave packet, we require that the "expansion efficacy", defined as $\sum |a_{kl}|^2$ for orthonormal $|k\rangle$, approaches unity as closely as possible so that the approximate state, which is bound, can be satisfactorily expressed as a bound wavepacket.

The effective number of states, or $n^*$, given by

$$n^* = 1 / \sum_{k=0}^{N} |a_{kl}|^2$$

(2)

is an indicator of the number of states that contribute significantly to the dynamics of the wavepacket. When $\Psi(t)$ is an eigenfunction of $H$, then $n^* = 1$, and when $K$ states all participate equally in $\Psi(t)$, $n^* = K$. For all other distributions of $K$ states, $n^*$ ranges between these two values. A usual way in which a model system may yield good approximate quantum numbers is that each model eigenstate has a large overlap with an exact eigenstate and the remaining model eigenstates contribute only fine-tuning. This is one situation in which, when eigenstates of $H_0$ are expanded in the exact basis set of $H_0 + H_1$, small values of $n^*$ are indicative of a good model system.

The initial state, represented by eq 1, evolves according to

$$\Psi(t) = \sum_{k=0}^{N} \rho_{kl} e^{-i H_0 t}$$

(3)

If we now expand $\Psi(t)$ in the $H_0$ basis, we get

$$\Psi(t) = \sum_{m=0}^{M} b_m(t) |m\rangle$$

(4)

Premultiply eq 4 by $\langle 0 |$ and integrate to get an expression for coefficients $b_m$, then recombine this with eqs 3 and 4 to obtain

$$\Psi(t) = \sum_{m=0}^{M} \sum_{k=0}^{N} e^{i \omega_{mk} t} \rho_{mk} |0\rangle e^{-i H_0 t}$$

(5)

which is a time-dependent wave function expressed in terms of the stationary states of the approximate Hamiltonian. We now can determine $\langle \hat{A}^0 \rangle(t)$, the time-dependent expectation value of $\hat{A}$ in the exact system:

$$\langle \hat{A}^0 \rangle(t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle = \sum_{m=0}^{M} \sum_{k=0}^{N} e^{i \omega_{mk} t} \rho_{mk} |0\rangle e^{-i H_0 t}$$

(6)

which defines the coefficients $A_{mk}$. $\langle \hat{A}^0 \rangle(t)$, is in the most general case, nonconstant since $[\hat{A}, H] \neq 0$; it is, however, necessarily real-valued despite the fact that its terms are in general complex. The newly defined coefficients $A_{mk}$ prove to be very important quantities for determining the behavior of a proposed approximate quantum number. As shown in eq 6, the $A_{mk}$ for $j \neq n$ give rise to oscillations in $\langle \hat{A}^0 \rangle(t)$, thus are indicators of the "badness" of $\hat{A}^0$. The coefficients $A_{mj}$, on the other hand, lend time-independent contributions to $\langle \hat{A}^0 \rangle(t)$, thus are indicators of the "goodness" of $\hat{A}^0$.

More specifically, the sum in eq 6 is composed of terms of two types: those of nonzero frequency and those of zero frequency. The terms of nonzero frequency oscillate in time and in the long run each averages to zero. The terms of zero frequency are constant in time, so that the average value of $\langle \hat{A}^0 \rangle(t)$, denoted by $\langle \hat{A}^0 \rangle$ is given by

$$\langle \hat{A}^0 \rangle = \sum_{j=0}^{N} a_{j0} = \sum_{m=0}^{M} \sum_{k=0}^{N} \langle 0 | \rho_{m} | k \rangle a_{j0} |0\rangle$$

(7)

The variance of any linear combination of sine and cosine terms is easily shown to be one-half of the sum of the squares of the amplitudes, so that we can find the standard deviation, $\sigma_n$, of the above quantity from

$$\sigma^2 = \frac{1}{2} \sum_{j=0}^{N} |a_{j0}|^2$$

(8)

We define the badness of a certain quantum level of the zeroth-order Hamiltonian as

$$\text{badness} = 2^{1/2} \sigma_n / \text{(spacing)}$$

(9)

where "spacing" is the mean spacing of quantum levels in the vicinity of the corresponding $\langle \hat{A}^0 \rangle$. If $\langle \hat{A}^0 \rangle(t)$ were simply a cosine curve, then the badness would be the curve's amplitude divided by the spacing. An approximate constant of the motion must have small values of the badness, whether this is due to small $\sigma_n$, large spacing, or a combination of the two.

When a wave packet which is an eigenfunction of the zeroth-order Hamiltonian is allowed to evolve under conditions of the exact Hamiltonian, the magnitude of the overlap of the wave packet at later times with the initial wave packet is almost certainly less than 1. Since this self-overlap, or autocorrelation, is in general complex-valued, we look at its magnitude squared:

$$S^2(t) = |(\Psi(t)|\Psi(0))|^2 = \sum_{j=0}^{N} \cos((\omega_j - \omega_k)t) \langle 0 | \rho_{m} | k \rangle \langle 0 | \rho_{m} | k \rangle$$

(10)

whose long-time average can be found from

$$\text{long-time average} = \sum_{j=0}^{N} |\langle 0 | \rho_{m} | k \rangle|^2$$

(11)

Up to this point, a critical objection to the entire formulation is that we need to know too much about $H$, the exact Hamiltonian. We need to known not only the energy levels and degeneracies of $H$, but also the overlaps of its eigenfunctions with those of $H_0$, the zeroth-order Hamiltonian. If we already have all of this information, then there seems to be no need for an approximation to the exact Hamiltonian, but we can now recast the above formulation in a way to make it applicable to those cases in which we known little, if anything, about the solutions of the true Hamiltonian. Such an approach only requires looking at the above equations from a slightly different point of view. There are several techniques for the numerical propagation of a wavepacket on a potential energy surface. If we prepare the initial state $|0\rangle$ and numerically propagate it according to $H$, the exact Hamiltonian, we can determine $S^2(t)$ and $S^2$ from the
time-dependent overlaps. Furthermore, and rather surprisingly, $S^2$ is just the inverse of $n^2$, the effective number of states. Thus the effective number of states, whose calculation one might have thought one needed detailed information of the solutions of the first-order Hamiltonian, turns out to be calculated even from just a numerical propagation of the wavepacket on the accurate potential.

According to eqs 4 and 6, when the wave packet is expanded in the basis set of the zeroth-order Hamiltonian, the coefficients exhibit individual time dependencies rather than the simple factorable phase factor $e^{-iE/t}$. Given that the initial state was $|\Psi(t)\rangle$, an eigenstate of $H_0$, we wish to know how much another state, say $|\Psi(t)\rangle$, contributes at a later time and how much, in the long run, that state contributes to $\Psi(t)$. The time dependent density of $|\Psi(t)\rangle$, given the initial state $|\Psi(t)\rangle$, in $\Psi(t)$ is given by

$$P(m|l) = b_m(t)^* b_n(t) = \sum_{j=0}^{N} \langle \Psi(t) | \rho_j(0) | \Psi(t) \rangle e^{-i(\omega_j-\omega) t}$$

(12)

Because only the diagonal terms survive averaging, the long time average of $P(m|l)$ is given by

$$P_\omega(m|l) = \sum_{j=0}^{N} \langle \Psi(t) | \rho_j(0) | \Psi(t) \rangle$$

(13)

and it is evident that $P(m|l) = |\langle \Psi(t) | \rho_j(0) | \Psi(t) \rangle|^2$ and that $P_{\omega}(ii) = S^2$. In a numerical treatment of the propagation of the wave packet, the $P(m|l)$ and therefore the $P_{\omega}(m|l)$ can be calculated, thus even in the absence of any knowledge of the full solutions of the exact system, we can still use eq 6 to analyze candidate approximate constants of the motion.

The approximated constant of the motion can be calculated by recalling that $P(m|l)$ is just $|b_n(t)|^2$ so that eq 6 can still be used to find $\langle \Psi(t) | \rho_j(0) | \Psi(t) \rangle$ and, if desired, the $\alpha_{jk}$ can be determined by Fourier transform.

The above framework can be considered from a time-independent view or a time-dependent view. The former is natural when the solutions of the true Hamiltonian are known. In the time-independent approach, we regard the approximation of the zeroth-order Hamiltonian as introducing a dispersion of eigenvalues. All of the functions and quantities that we may need can be expressed in terms of the time-independent parameters of energy levels and overlaps. Unfortunately, however, we rarely have detailed knowledge of the solutions of the true Hamiltonian, and it is in these cases that the time-dependent view comes into play. In this approach, we rely on measurements of the evolution of a prepared state, "naturally chosen" as an eigenstate of $H_0$. By recording a time series of the overlap of the initial state with eigenfunctions of $H_0$, we can calculate the same dynamical information that we could get from detailed knowledge of the true Hamiltonian. Additionally, the time-dependent approach yields information on the spacing of energy levels of the true Hamiltonian.

III. System and Method

In the early days of quantum mechanics, Morse proposed a model potential for diatomics and derived analytic wave functions for it.3 For the most part,4 the Morse potential displays the behavior of diatomic molecule. To illustrate the use of the above framework, we take the true Hamiltonian to be that of a nonrotating $F_2$ molecule modeled by the Morse potential. This particular molecule was chosen because its Morse parameters5,6 yield a large enough number of bound states ($N = 28$) to alleviate problems of convergence and yet few enough bound states to make the problem tractable.

The analysis of the previous section was applied to $F_2$ using three approximate Hamiltonians. Two of these Hamiltonians were Morse oscillators, and the third was a simple harmonic oscillator. The two approximate Morse oscillators differ from that of the "true Hamiltonian" in that the potential is either wider or narrower by an amount sufficient either to increase or decrease the number of bound state by 4. We judged this difference large enough to have a significant impact on the higher-energy states, yet small enough to have a nominal effect on the very lowest states. Because of Morse and harmonic oscillations have analytic solutions, we applied the time-independent approach in this study.

The parameters for the harmonic oscillator were chosen to maximize the overlap between the ground states of $H_0$ and $H$. If the Morse ground state is expanded as an exponential of a power series in the displacement, it can be shown that the overlap is maximized when the curvatures at the minima are identical, which is to be expected on intuitive grounds. Three of the above four potentials are plotted in Figure 1.

These two sorts of approximation to the true Hamiltonian serve as examples of two sorts of perturbations to $H$. The first of these, represented by the wider and the narrower Morse potentials, illustrates the case in which the perturbation $H_1$ actually is only a small perturbation on $H$. This is, of course, the ideal situation from which to approach a problem utilizing variational or perturbational methods. Even in the cases presented here, however, $H_1$ is still large enough that the higher energy states differ significantly from the corresponding eigenstates of $H$.

The second sort of approximation arises when the perturbation is large compared to the true Hamiltonian. This situation is represented by the case of the harmonic approximation. The harmonic potential is a poor approximation to a molecular stretching vibration (except possibly for the very lowest energy levels) for many reasons, among which are (1) different boundary conditions, (2) an infinite number of discrete states and no continuum states, and (3) parity of wave functions. Nevertheless, the harmonic oscillator is so easy to use that it is commonly used as the first approximation for actual molecular vibrations.9

Throughout this work we used analytic Morse and harmonic wave functions. The overlaps between the wave functions of $H$ and those of $H_1$ were determined numerically using a variable step size Runge–Kutta differential equations solver.10 The equations of the previous section were then applied exactly. All calculations were done on a Silicon Graphics 4D290 computer.

IV. Results

The results for the narrow and wide Morse approximations were qualitatively similar, so we shall only present those of the narrow Morse approximation and of the harmonic approximation.
The expansion efficacies, defined in section 2, of the narrow Morse and the harmonic approximations in are shown in Figure 2. Despite the failure of convergence for the narrow Morse case at high energy levels, the expansions are quite good for a very wide range of energy. Contrast this with the harmonic approximation in Figure 2b, for which the expansion can be said to succeed only for the very lowest energy levels.

These results alone do not imply that the Morse approximation is good for a wide range of levels or that the harmonic approximation is good only for a small range of energy levels. The success of an expansion is not in itself an indicator of a good model system. It is, rather, the failure of the expansion in particular regimes that tells us of the limitations of the model system. Where the expansion succeeds, the analysis may continue, but where the expansion fails, continuation of the analysis is of questionable value.

The effective numbers of states for the energy levels of both model systems are presented in Figure 3. Note how for the narrow Morse potential \( n^* \) rises slowly and how even at the sixteenth excited state \( n^* \) is still less than 2. This is markedly different from the harmonic potential, for which \( n^* \) rises very rapidly with the approximate state, skyrocketing past 6.0 even at the fifth excited state. When examining Figure 3, one should also recall that \( S^2 \) for each initial state is just the inverse of \( n^* \) for that state.

We can gain further insight into the nature of \( n^* \) by examining more closely two states selected from each approximation.

In each of the two cases wherein the initial wave packet is chosen as the ground state of the zeroth-order system, the magnitude of the overlap with the first-order ground state is near unity. The effective numbers of states for these two wave packets are correspondingly small. Such is not necessarily the case for the excited states, however. The coefficients of the tenth excited state of the narrow Morse potential, Figure 4b, show a much broader distribution than does the ground state, but as this distribution is also highly peaked, \( n^* \) is not substantially greater than one.

According to Figure 2b, the third excited state of the harmonic Hamiltonian can be expanded very successfully in the exact basis, but the coefficients of this expansion, shown in Figure 4d, reveal a very broad distribution of states and a high effective number of states. We can expect, therefore, that even for energies as low as the third excited state, the harmonic approximation to the \( F_2 \) potential is poor.

In Figure 5 we trace the evolution of \( \langle H_o \rangle(t) \) for several states of each approximate Hamiltonian. The first dozen or so levels within the Morse approximation have quite small values of the badness, but then they rise steeply, initially mostly due to the larger fluctuations in \( H_o \). The fluctuations of \( \langle H_o \rangle(t) \) under the harmonic approximation, Figure 5b, are much larger and are attained at much lower energies. This behavior is reiterated in Figure 6 in which we follow the evolution of \( S^2(t) \) for the same states as in Figure 5. The good correlation at low energies is seen to decay with increasing quantum number of the initial state.

Values of the badness are plotted in Figure 7 for the two zeroth-order Hamiltonians. The first dozen or so levels within the Morse approximation have quite small values of the badness, but then they rise steeply, initially mostly due to the larger fluctuations in \( H_o \). Within the harmonic approximation the spacing of the levels is constant, and the rise in the badness is solely attributable to the increasing fluctuations of \( H_o \) with increasing energy.

Figure 6 vividly illustrates how the wave packet rapidly—in the ones or tens of femtoseconds—moves away from its initial
configuration. For the lower energy states, the wave packet never ventures far from, and often returns near to, the initial state. As the initial approximate quantum number is increased, however, $S^2$ decreases and the returns to the initial state are much weaker.

V. System and Method for the Two-Dimensional Rotor

We constructed an anisotropic two-dimensional model potential to be used in this study; it is a modified Hénon–Heiles potential.\(^{11}\) The difference between the Hénon–Heiles potential and the present one

$$V = \frac{1}{2}r^2 + \frac{1}{3}kr^3 \cos \theta + \frac{1}{10}k^2r^4$$

is in the fourth-order term. This term is just large enough to ensure the existence of exactly one minimum, located at the origin. Its purpose is to eliminate the exit channels, located at $\theta = \pi/3$, $\pi$, and $5\pi/3$ in the unmodified potential, which can cause complications in quantum mechanical studies. The terms containing the perturbation parameter $k$ in this potential comprise the perturbation, $V_1$. When $k = 0$, then $V_1 = 0$ and $H_1 = H$. When $k \neq 0$, the angular momentum is no longer a constant of the motion. This potential is plotted in Figure 8 for the two values of $k$ used in the present work.

There are two independent constants of the motion for the zeroth-order potential, $V = \frac{1}{2}r^2$. We shall designate the states which are eigenfunctions of $H_1$ and $L = xp_y - yp_x$ as $|n, n_0\rangle$ where $n_0$ is the principal quantum number and $n_0$ is the angular quantum number. These eigenfunctions have been discussed by Cohen-Tannoudji et al.\(^{12}\) In atomic units the energy levels of this system are given by $n_0 + 1$ and the angular momentum by $n_0$ where $n_0 = m, n_0 - 1, \ldots , -n_0$. Note that because the system is only two-dimensional, measurements of $L^2$ give eigenvalues of $n_0^2$.

For nonzero $k$ the eigenfunctions are at most 2-fold degenerate. This is readily seen because the perturbed potential belongs to the point group $C_{3v}$, which has only one- and two-dimensional representations.

Because the expectation values of products of operators that commute with the zeroth-order Hamiltonian bear no obvious relationship to their components in the first-order system and to lay the groundwork for future work with three-dimensional systems, we studied the conservation of both the angular momentum and its square in the present work.

Suppose that we have some arbitrary initial wave packet $\Psi(t_0)$ and Hamiltonian $H$. If we propagate the system to time $t$, we find the evolved wave packet in state $\Psi(t)$. Now reflect both $\Psi(t_0)$ and $H$ through some axis (as this is a two-dimensional system) and propagate the transformed system also to time $t$. The two final states must be identical (apart from the reflection) because space is inherently achiral. That is, in the absence of spin, if there are two systems which are at any moment related by a reflection, then those systems retain that relation throughout their respective evolutions. (Spin, if present, should be reversed in order to preserve this property.) Applying this result to the case at hand, we can plainly see that such a reflection on the initial state $|n, n_0\rangle$ and $H_1$, through a reflection element of $H_1$, results in an initial state of opposite angular momentum, $|n, -n_0\rangle$, while leaving $H_1$ unaffected. If we express the angular momenta of these states as $\langle \hat{L}_z \rangle (t)$ and $\langle \hat{L}_z \rangle (-t)$, respectively, we conclude that

$$\langle \hat{L}_z \rangle (t) = -\langle \hat{L}_z \rangle (-t)$$

and we note that as a corollary, $\langle \hat{L}_z \rangle (t) = 0$ for any zeroth-order initial state of zero angular momentum. Similar reasoning can be applied to $\langle \hat{L}_z^2 \rangle (t)$ to show that

$$\langle \hat{L}_z^2 \rangle (t) = \langle \hat{L}_z^2 \rangle (-t)$$
TABLE I: Results for All Initial States with $n, \leq 6$. Initial States Given as $[n, \ell]$

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<th>$B_{Lz}$</th>
<th>$\bar{L}_z$</th>
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again, regardless of the form of the perturbation. Here, however, we cannot draw any new conclusions concerning the nature of the zero angular momentum initial state. We can show similarly that

$$P_n(t) = P_n(0)$$

(17)

that is, that the autocorrelation is unaffected by the sign of the initial angular momentum. With these results, the number of states that we need to consider has been cut roughly in half.

We know only very little about the eigenfunctions of $\mathcal{H}$, so we employed the time-dependent approach outlined previously. We modified a wave-packet propagation program written for a Thinking Machines CM-2, a massively parallel computer. Details of the Chebyshev algorithm used by the code and details of the code itself may be found elsewhere. We then calculated $P(t)$, $\bar{L}_z(t)$, and $B_{\bar{L}z}(t)$ directly from the evolving wave packet. These data were then analyzed on an IBM RS6000 computer. We studied initial states with $n, \leq 6$ for all $|n, \ell|$ with a perturbation of $k = 0.1$, for a total of 16 states. As a test of both theory and the computer code, eqs 15–17 were verified computationally for several states.

VI. Results for the Rotor

The actual energies of the evolving wavepackets, listed in Table 1, deviated only slightly from the energies of the unperturbed eigenfunctions. All energies and momenta are expressed in atomic units. The energy of the initial state $(6,0)$ was 7.046, only 0.66% off from 7, the zeroth-order energy. The energies, therefore, are quite insensitive to the perturbation and are poor indicators of the quality of the model system. In this section we will discuss results for $L_z$ and $\bar{L}_z$, both of which are much more sensitive indicators.

Figure 9 is a plot of $\bar{L}_z$ for 13 of the 16 studied states with $n, \leq 6$. The error bars extend $2\sqrt{\sigma_{\bar{L}_z}}$ in each direction in order to show the magnitude of the fluctuations.

Three states did not converge sufficiently to be used reliably; these are the states $[3,3]$, $[5,3]$, and $[6,6]$. We hypothesize that in each of these cases the 3-fold symmetry of the initial state resulted in enhanced overlaps with nearly degenerate states of the 3-fold symmetric potential. Interference between these states in turn caused the long-term oscillations and lack of convergence. This hypothesis is supported by the fact that $n^*$ for each of these states is appreciably larger than for the other states of similar energy.

In Figure 10 we have plotted $\langle L_z(t) \rangle$ for the initial states $[3,1]$ and $[3,3]$ to illustrate the qualitative differences between the two situations. The evolution displayed by state $[3,1]$ is typical of states with nonzero $n_\ell$ where $n_\ell$ is not a multiple of three. In these cases, quantities such as $n^*$ and $\bar{L}_z$ converge rapidly as a function of time. This is obviously not the situation with state $[3,3]$, whose evolution is typical of those states where $n_\ell$ is a multiple of three. Even though the short-time oscillations for state $[3,3]$ are smaller than for $[3,1]$, there is also a very-long-time oscillation of period 102 fs. This long-time behavior is caused by interference between states separated by about 0.0015 au in energy. The effect is not quite so large for state $[5,3]$ owing to a greater lifting of degeneracy at the higher energy but gets appreciably worse for state $[6,6]$, most likely because this latter state is both 3-fold and 6-fold symmetric, leading to a greater overlap with other states than in the simply 3-fold ($n_\ell = 3$) case.

As expected, when $n_\ell = 0$, $\langle L_z(t) \rangle = \bar{L}_z$. With the preceding exception, the most obvious effect of the perturbation is the dramatic increase in the deviations of $\langle L_z(t) \rangle$ with increasing energy. This effect is less pronounced for states of maximal angular momentum, $|n, n_\ell|$, but is nevertheless noticeable present. It is interesting to note that in the short term, this even holds true when $n_\ell$ is a multiple of three. See Figure 10.

We can also see from Figure 9 that for a given $n_\ell$, the angular momentum is conserved well with decreasing $n_\ell$ (with the exception of $n_\ell = 0$). The average angular momenta for states of maximal angular momentum fit quite well to a straight line. This is also true for the states $[n, n_\ell=2]$ and possibly $[n, n_\ell=4]$, but lack of data prevents further extrapolation.

Now let's consider a set of states with a given $n_\ell$ and varying, $n$. If in Figure 9 we connect $\bar{L}_z$ for those states with a straight line, we can see that the slope of this line is negative and increases in magnitude with increasing $n$. The main effect of the perturbation on $\bar{L}_z$ is one of decreasing $\langle \bar{L}_z \rangle$ from its initial value.

In Figure 11 we plot the results for the square of the angular momentum. Every state converged to give a stable expectation.
value for \( L_z^2 \). However, those states that did not converge for \( L_z \) required appreciably longer runs than were required for the other states.

A qualitative interpretation of the previously discussed observations regarding 3-fold symmetric states is that the symmetry shared by the initial wavepacket and the noncentral potential causes periodic reversal of the angular momentum. If this is true then we can expect determinations of \( \langle L_z^2 \rangle (t) \) for these states to converge at a rate comparable to other states. This, in fact turns out to be the case.

As in the case of \( \langle L_z \rangle(t) \), for a given \( n_z \), \( L_z^2 \) is conserved better with increasing \( n_z \). Here, however, the initial states with \( n_z = 0 \) are not immune to the spoiling of \( L_z^2 \), and as the energy is increased, the magnitudes of fluctuations increase far more rapidly than they do for \( L_z \).

The fluctuations also behave quantitatively differently from those of \( L_z \). For states with large \( |n_l| \) relative to \( n_z \), we still have \( L_z^2 < n_z^2 \), but for smaller \( n_z \) the direction of the inequality changes. This contributes to the overlapping of \( \langle L_z^2 \rangle(t) \) (see Figure 11) that spoils the usefulness of \( n_z^2 \).

VII. Conclusions

In this study, we have derived a framework within which we can test and quantify the utility of a model quantum system. When several model systems are available, one can apply the methods shown here to determine which model system is best suited for the investigator’s purpose.

The first sections dealt with a one-dimensional, nondegenerate system. For such a system, the effective number of states \( n^* \) is a useful concept. For systems with degeneracies, such as the isotropic rotor or oscillator in two or more dimensions, the concept can be extended by making it an “effective number of eigenvalues” or of energy levels.

In the two-dimensional rotor, the perturbation that spoils the zero-order Hamiltonian manifests itself in two ways. First, as the energy of the wave packet is increased, the angular momentum is increasingly spoiled. Second, within the manifold of states corresponding to the same principal quantum number in zeroth order, those states with smaller \( |k| \) are more affected with respect to spoilage of their angular momentum; the exceptions are states of zero angular momentum, whose angular momentum is conserved by symmetry.

Although these same trends are exhibited by \( L_z^2 \), this latter quantity tends to be more spoiled than \( L_z \) itself, as shown by the corresponding larger \( B \) values. We speculate that this is because the third- and four-order perturbations cause the energy levels of the perturbed system to diverge more quickly than those of the unperturbed system, which has constant spacings.

At this point a comment is in order about the energies of the initial wave packets. Even when the effective number of states is large, or when the angular momentum is ill conserved, the energies of the wave packets are very nearly those of the unperturbed system. Comparison of this result with our observations about the angular momentum and its square shows that similarity of the energies of the two systems is not a reliable indicator of the quality of a model system. The quantities—\( B \) and \( n^* \)—derived in this study are more powerful indices of the validity of the model.

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References and Notes

(5) Morse, P. M. Phys. Rev. 1929, 34, 57.
(8) Braier, P. A.; Berry, R. S.; Wales, D. J. J. Chem. Phys. 1990, 93, 8745.
(13) Wave-packet propagation code written by D. Chasman and M. D’Mello.