Optimal separable bases and series expansions

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(Received 18 October 1996; revised manuscript received 28 February 1997)

A method is proposed for the efficient calculation of the Green's functions and eigenstates for quantum systems of two or more dimensions. For a given Hamiltonian, the best possible separable approximation is obtained from the set of all Hilbert-space operators. It is shown that this determination itself, as well as the solution of the resultant approximation, is a problem of reduced dimensionality. Moreover, the approximate eigenstates constitute the optimal separable basis, in the sense of self-consistent field theory. The full solution is obtained from the approximation via iterative expansion. In the time-independent perturbation expansion for instance, all of the first-order energy corrections are zero. In the Green's function case, we have a distorted-wave Born series with optimized convergence properties. This series may converge even when the usual Born series diverges. Analytical results are presented for an application of the method to the two-dimensional shifted harmonic-oscillator system, in the course of which the quantum $\tanh^2$ potential problem is solved exactly. The universal presence of bound states in the latter is shown to imply long-lived resonances in the former. In a comparison with other theoretical methods, we find that the reaction path Hamiltonian fails to predict such resonances. [S1050-2947(97)01307-3]

PACS number(s): 03.65.Ca, 03.80.+r, 03.65.Ge, 02.30.Mv

I. INTRODUCTION

Since the time of Newton, if not earlier, physicists have tried to solve complicated problems by breaking them down into simpler components. The trick lies in ''carving up'' the initial problem in just the right way so that the components are independent of one another and can be solved separately. In classical mechanics, for instance, one seeks the first integrals or action-angle variables because these partition the Hamiltonian in the most natural way. Of course, finding the best way to slice a particular problem may be very difficult, if not impossible. Even in such cases, however, one may still be able to find a *separable substitute* that accurately approximates the true system.

In this paper, we consider separable approximations of quantum-mechanical systems. For a given multidimensional Hamiltonian $\hat{H}$, a separable approximation $\hat{H}_0$ is an operator whose eigenstates are products of coordinate functions. The simplest class of such functions are the direct-product basis sets, which have been utilized, for example, in vibrational problems [1]. These basis sets correspond to what we shall in Sec. II call ''strongly separable'' $\hat{H}_0$'s. However, the general case also includes *weakly* separable $\hat{H}_0$'s, which may provide more accurate approximations of $\hat{H}$. One such $\hat{H}_0$ gives rise to the ''dressed'' eigenfunctions of the truncation-recoupling method [2].

It would clearly be desirable if we could somehow examine all possible separable $\hat{H}_0$'s and select from that pool the best approximation to the true Hamiltonian. Such a procedure would first require a rigorous definition of the ''distance'' between two operators. The closest $\hat{H}_0$ could then be obtained by applying the variational calculus to the set of all Hilbert-space *operators*. At first glance, this appears far more formidable than the original problem. Nevertheless, we shall demonstrate that with a suitable operator metric, specifically, the Frobenius norm of the residual $(\hat{H}-\hat{H}_0)$, the variational problem *itself* corresponds to a conventional quantum problem of reduced dimensionality.

The optimal $\hat{H}_0$ obtained in this manner can be usefully exploited in a variety of ways. The eigenstates of $\hat{H}_0$ turn out to be the best mutually orthogonal separable approximations to the true eigenstates, in the sense of self-consistent field theory. This ''optimal separable basis'' is therefore a natural starting point for a time-independent perturbation expansion of $\hat{H}$. In scattering applications, the stationary scattering states of $\hat{H}_0$ are the so-called distorted waves [3]. These give rise to an optimized distorted-wave Born expansion of the energy Green's function. This expansion may converge quickly even if the standard Born series is slowly convergent or *divergent*, as is the case for many scattering systems of interest.

The remainder of the paper is organized as follows. Section II provides the mathematical preliminaries, including precise definitions of the operator metric and separability. Section III comprises the bulk of the theory underlying the optimal separable basis approach. Section IV applies the method to series expansions, examines convergence, and establishes a link with numerical preconditioning. Section V discusses a simplification that arises when the method is applied to Hamiltonians of a standard form. Section VI presents analytical results for a benchmark two-dimensional system. This ''shifted harmonic-oscillator'' problem has not, to the author's knowledge, been previously considered.

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II. MATHEMATICAL PRELIMINARIES

A. Separability

Let $\hat{H}\equiv H(\hat{q}_1,\hat{p}_1,\ldots,\hat{q}_n,\hat{p}_n)$ be an arbitrary n-dimensional Hamiltonian for which the generalized position operators $\hat{q}_1,\ldots,\hat{q}_n$ and associated $\hat{p}_1,\ldots,\hat{p}_n$ satisfy

$$[\widehat{q_i},\widehat{q_j}]=[\widehat{p_i},\widehat{p_j}]=0, \tag{2.1}$$

$$[\widehat{q_i},\widehat{p_j}]=\delta_{ij}F_i(\widehat{q_i},\widehat{p_i}).$$

Let the first k degrees of freedom be designated as the *inner coordinates* and the remaining $n-k$ as the *outer coordinates*. This partitioning is completely arbitrary and in practice is decided by analytic or computational convenience (Sec. V B).

We define a ''separable basis'' as a basis whose position representation is separable by inner and outer coordinates. In other words, each basis function is a product of an inner function and an outer function. We must distinguish between two distinct types of separability: ''strong'' and ''weak.'' The former corresponds to inner and outer factors that are completely independent, i.e.,

$$\Phi_{lm}=\phi_l(q_1,\ldots,q_k)\varphi_m(q_{k+1},\ldots,q_n). \tag{2.2}$$

This symmetric form corresponds to the eigenfunctions of a strongly separable

$$\hat{H}_0=H_{\text{in}}(\hat{q}_1,\hat{p}_1,\ldots,\hat{q}_k,\hat{p}_k) + H_{\text{out}}(\hat{q}_{k+1},\hat{p}_{k+1},\ldots,\hat{q}_n,\hat{p}_n), \tag{2.3}$$

which follows directly from the commutation relations as specified in Eqs. (2.1).

As an approximation to $\hat{H}$, the class of such $\hat{H}_0$'s is somewhat limited. The range of possible eigenvalue spectra, for example, is restricted to additive spectra only. Fortunately, there is a much broader class of separable bases, i.e., those satisfying the weak separability condition and characterized by eigenfunctions

$$\Phi_{lm}=\phi_l^{(m)}(q_1,\ldots,q_k)\ \varphi_m(q_{k+1},\ldots,q_n). \tag{2.4}$$

Here a lack of symmetry arises because the inner functions depend on the quantum numbers of the outer functions: a familiar situation encountered often in quantum mechanics. Equations (2.1) now imply a corresponding $\hat{H}_0$ conforming to

$$\hat{H}_0=H_{\text{in}}(\hat{q}_1,\hat{p}_1,\ldots,\hat{q}_k,\hat{p}_k, H^1_{\text{out}}(\hat{q}_{k+1},\hat{p}_{k+1},\ldots,\hat{q}_n,\hat{p}_n),H^2_{\text{out}}\cdots), \tag{2.5}$$

where the H^i_{out} comprise an independent set of commuting operators whose simultaneous eigenstates are the $\varphi_m(q_{k+1},\ldots,q_n)$. Note that, in addition to being manifestly asymmetric, Eq. (2.5) is seen to incorporate a much broader range of operators than Eq. (2.3). Moreover, the corresponding energy eigenspectra are completely unrestricted.

B. Defining the operator metric

In order to apply the variational calculus, we must define a metric functional on pairs of operators. In analogy with the complex vector space notion of a dot product, we define the inner product of two *operators* $\hat{A}$ and $\hat{B}$ as

$$\hat{A}*\hat{B}\equiv\text{tr}(\hat{A}^\dagger\hat{B}). \tag{2.6}$$

The norm of $\hat{A}$ is then given by $|\hat{A}|^2=\text{tr}(\hat{A}^\dagger\hat{A})$ and the distance between $\hat{A}$ and $\hat{B}$ by $|\hat{B}-\hat{A}|$.

In any explicit matrix representation, the above definition of the norm becomes

$$|\hat{A}|^2\equiv\sum_{i,j}|A_{ij}|^2, \tag{2.7}$$

where the A_{ij} are the individual matrix elements. In this form, Eq. (2.7) is known as the ''Frobenius norm'' [4]. The Frobenius norm is but one of several competing matrix norm definitions, of which the so-called Euclidean norm [5,6] is usually preferred. Nevertheless, for our purposes, the Frobenius norm turns out to be the appropriate one (Sec. III).

III. OBTAINING THE OPTIMAL SEPARABLE BASIS

The problem of obtaining the optimal $\hat{H}_0$ is now well formulated; namely, we seek to minimize $|\hat{H}-\hat{H}_0|$ with respect to variations of $\hat{H}_0$ subject to the weak separability constraint. This is best approached in two stages. First, for a particular choice of outer basis φ_m, we determine the best $\hat{H}_0$ and corresponding inner bases $\phi_l^{(m)}$. This gives rise to a new interpretation of $\hat{H}_0$. The second stage is to optimize with respect to a variation of the outer basis set.

A. Optimization with respect to a fixed outer basis

Consider the explicit representations of $\hat{H}$ and $\hat{H}_0$ in the partially diagonal basis

$$|q_1,\ldots,q_k,m\rangle=|q_1,\ldots,q_k\rangle|\varphi_m\rangle \tag{3.1}$$

for some choice of outer basis φ_m. Now consider all weakly separable variations of $\hat{H}_0$ for which φ_m is fixed. The explicit form of $\hat{H}_0$ is constrained to be block diagonal in m (i.e., a $\delta_{mm'}$ factor is present), but is otherwise completely arbitrary. From Eq. (2.7), however, it is clear that *the minimal* $|\hat{H}-\hat{H}_0|$ *ensues when* $\hat{H}_0$ *is defined as the block-diagonal portion of* $\hat{H}$.

This finding is true because the block-diagonal and the off-block-diagonal portions of $\hat{H}$ contribute to the total Frobenius norm independently. Adopting the former as our choice for $\hat{H}_0$, the latter becomes the residual matrix $\hat{\Delta}\equiv\hat{H}-\hat{H}_0$. We shall find it very convenient to interpret $\hat{H}_0$ as a collection of k-dimensional inner subsystems that are parametrized by the outer indices m and coupled together by $\hat{\Delta}$.

It remains only to minimize $|\hat{\Delta}|$ with respect to a variation of the outer basis. In terms of coupled subsystems, this is

equivalent to *minimizing the total subsystem coupling* in the usual least-squares sense. This intuitively satisfying interpretation holds only by virtue of the Frobenius norm metric; indeed, the coupled subsystem picture *itself* would be inappropriate if one were to use a different definition of the matrix norm.

B. Optimizing the outer basis

Variations of the outer basis correspond to unitary [7] transformations $\hat{U}$ involving *only* the outer coordinates $\hat{q}_{k+1},\hat{p}_{k+1},\ldots,\hat{q}_n,\hat{p}_n$. In other words,

$$\hat{H}'=\hat{U}^\dagger\hat{H}\hat{U},\quad \hat{U}=U(\hat{q}_{k+1},\hat{p}_{k+1},\ldots,\hat{q}_n,\hat{p}_n). \quad (3.2)$$

This restriction has two advantages. First, Eqs. (2.1) ensure that $\hat{U}$ has no effect on the $\hat{q}_1,\hat{p}_1,\ldots,\hat{q}_k,\hat{p}_k$, so that the $\hat{H}$ dependence on these coordinates is unaffected by the transformation. Second, determining the optimal outer basis is a problem of reduced dimensionality.

Mathematically, we have a constrained eigenvector problem where the *inner* coordinates are the parameters. The k-dimensional constraint on $\hat{U}$ generally disallows complete block diagonalization of $\hat{H}$; nevertheless, minimizing $|\hat{\Delta}|$ has the effect of removing all *unessential* nonseparability from the system. Indeed, if $\hat{H}$ happens to be weakly separable to begin with, then it can be block diagonalized by some $\hat{U}$ of the form Eq. (3.2), in which case *all* of the coupling is removed, as is intuitively appropriate. In the general case $|\hat{\Delta}|$ cannot be made to vanish altogether, but can be greatly reduced, via the optimal choice of outer basis, so as to reflect only the minimal coupling actually inherent in the system.

As with all variational methods, optimization is signaled by candidates that satisfy an appropriate stationarity condition. In our case, $|\hat{\Delta}|$ must be stationary with respect to all infinitesimal outer unitarity transformations, of which we need only consider the elementary (pairwise) transformations explicitly. By evaluating all pairs independently, we obtain

$$\widetilde{H}_{mm'}{}^*(\widetilde{H}_{mm}-\widetilde{H}_{m'm'})=0 \quad \text{for all } m,m', \quad (3.3)$$

where $\widetilde{H}_{mm'}\equiv\langle\varphi_{m'}|\hat{H}|\varphi_m\rangle$. The operators $\widetilde{H}_{mm'}$, etc., being blocks of the full Hamiltonian in the partially diagonal representation, act on the inner coordinates only. The * operation is simply the inner coordinate version of the Eq. (2.6) matrix dot product affiliated with the Frobenius norm metric.

Equation (3.3) above is thus the desired optimization condition and a central result of this paper. Note that this equation can be naturally interpreted as a *mutual orthogonality condition* on the blocks of $\hat{H}$. Although Eq. (3.3) is simple and intuitive, it applies only in the φ_m representation. It does not, for instance, provide us with some differential equation in the *original* coordinates, as do many other applications of the variational method. Nevertheless, Eq. (3.3) still serves as a very useful guide in particular applications. The optimal outer basis can always be determined numerically, for example, using a simple block algorithm that is the focus of another paper [8]. Analytically, any intuitively selected candidate for the optimal φ_m can always be checked directly against Eq. (3.3). Even if the equality fails, the lack of orthogonality can be used as a measure of ''efficiency'' or proximity to optimality. If the optimal basis is analytically intractible, then a nearly optimal subsitute should do almost as well (Sec. V B).

This situation is somewhat analogous to that of Weinberg's quasiparticle approach to converging the Born series [9]. Weinberg's approach allows us to define a quasiparticle however we like; a physically intuitive choice is almost always beneficial even if the mathematically optimal solution is unattainable. In the Weinberg formalism, however, there is no analog of Eq. (3.3), and thus no way to determine whether or not a given choice is close to optimal.

C. Existence, uniqueness, and infinities

It is important to note that Eq. (3.3) is in principle applicable even to non-square-integrable Hamiltonians, i.e., to systems for which the Frobenius norm of $\hat{H}$ is infinite. This does *not* imply that $|\hat{\Delta}|$ is also infinite, indeed, $|\hat{\Delta}|$ is finite for all systems that conform to the standard scattering criteria [10,3]. Nevertheless, there are undoubtedly certain physically interesting cases for which $|\hat{\Delta}|$ *is* infinite in all representations (Sec. VI), as a result of which it may not be intuitively obvious which one is the best. Even in such cases, however, the stationarity condition is still meaningful because Eq. (3.3) relies only on the *orthogonality* of the $\widetilde{H}_{mm'}$ and not on their normalizability.

Normalizability in and of itself is therefore not the principal concern. Of greater importance is whether or not an optimal solution actually exists for a given system. Equation (3.3) is silent on this subject; it merely reflects the conditions that would have to be satisfied should a solution exist. There might be no stationary solutions or several. In the latter event, one would like to be able to distinguish the true minimal solutions from the maxima and saddle points. Although we do not at present know how to resolve these questions for a completely arbitrary system, we can nevertheless prove that at least one stationary minimum exists if certain reasonable conditions are maintained.

Consider a parametrized, outer coordinate unitary transformation operator

$$\hat{U}(\phi_1,\phi_2,\ldots) \quad (3.4)$$

such that $\hat{U}$ is periodic in each of the parameters ϕ_i and such that any arbitrary unitary operator can be obtained by plugging in an appropriate set of parameter values. This could be constructed from a (possibly infinite) product of successive elementary unitary transformations between different (m,m') pairs. Each elementary operator, being a 2×2 (unimodular) unitary matrix, is parametrized by three angles and is periodic in those angles. The collection of all such angles can thus be taken to be the ϕ_i above; by incorporating an arbitrarily large number and variety of elementary operators, we can generate any desired $\hat{U}$. (It does not matter if the set of all $\hat{U}$'s is overspecified).

By incorporating the parametrized $\hat{U}$ above, the residual norm in any representation is conveniently expressed as a real-valued function of the parameters, i.e.,

$|\hat{\Delta}|^2 \equiv F(\phi_1, \phi_2, \ldots)$. A stationary outer basis is therefore presented to us whenever the first partial derivatives of F with respect to the ϕ_i are all zero. If F is continuous and differentiable everywhere, then at least one stationary minimum exists. This is true because the parameter space, being a product of compact spaces, is itself compact by virtue of Tychonoff's theorem [11,12].

The above result can be extended to noncontinuous F's by requiring only that continuous first partial derivatives

$$\frac{\partial F(\phi_1, \phi_2, \ldots)}{\partial \phi_i} = f_i(\phi_1, \phi_2, \ldots) \tag{3.5}$$

exist everywhere and by invoking the finite intersection property for the family of contour sheets defined by $(f_i = 0)$ [12]. This enables us to prove the existence of a stationary point even when F is infinite [13]. However, the partial derivative condition is still more restrictive than is necessary. Section VI, for example, presents a system for which the partial derivatives can be infinite even though a stationary point exists. Consequently, we suspect that a more comprehensive existence proof can be obtained, and this possibility is currently being investigated.

D. Self-consistent field interpretation

We conclude this section with a brief comparison between the optimal separable basis approach and the Hartree-Fock or self-consistent field theories. In the latter, one considers separable approximations of the form

$$\Phi_{lm} = \phi_l^{(m)}(q_1, \ldots, q_k)\varphi_m^{(l)}(q_{k+1}, \ldots, q_n). \tag{3.6}$$

The optimal Φ_{lm}'s are usually defined as those for which the expectation value of the energy is stationary. Since both inner and outer functions depend on *all* the quantum numbers, the Φ_{lm} are not generally orthogonal and do not form a basis.

In contrast, the optimal separable basis consists of Φ_{lm} wave functions that *are* mutually orthogonal. Moreover, the stationarity criterion is *identical* to that of the self-consistent field. The comparison is most easily made by representing $\hat{H}$ in the optimal separable basis itself. $\hat{H}_0$ now comprises the diagonal matrix elements of $\hat{H}$, which are nothing more than the energy expectation values of the Φ_{lm}. Because $|\hat{H}|^2 = |\hat{H}_0|^2 + |\hat{\Delta}|^2$ is representation independent, we have a stationarity condition on the *sum* of the energy expectation value square moduli rather than on the individual expectation values themselves. Our approach can therefore be considered a self-consistent field approximation of the complete energy *basis* rather than of the individual energy eigenfunctions.

IV. SERIES EXPANSIONS

A separable basis approximation of the eigenstates of a multidimensional Hamiltonian is certainly desirable in its own right, particularly one that is ''best'' in the self-consistent field sense. It is also of interest, however, to obtain more accurate results via series expansions that use the optimal $\hat{H}_0$ as a starting point. When actually performing such expansions, whether analytically or numerically, the issue of series convergence always arises. Intuitively, we expect convergence to improve as the residual $\hat{\Delta}$ is diminished. Thus the optimal $\hat{H}_0$ suggested above should result, heuristically speaking, in the fastest convergence. Rigorously speaking however, it is not always clear what constitutes ''optimal convergence'' for an operator series.

A. Time-independent perturbation theory

Let the optimal separable $\hat{H}_0$ of Sec. III be the zeroth-order approximation in a time-independent perturbation expansion of $\hat{H}$. To obtain the zeroth-order eigenfunctions, we must obtain the $\phi_l^{(m)}$ by diagonalizing $\hat{H}_0$: a comparatively simple task, in light of $\hat{H}_0$'s block-diagonal structure. Since each of the blocks can be diagonalized separately, we have a k-dimensional eigenproblem parametrized by the outer indices m.

It can be shown that our choice for $\hat{H}_0$ is always sufficiently close to $\hat{H}$ that the first-order corrections to the energies are all *zero*. In the partially diagonal basis, the block-diagonal nature of $\hat{H}_0$ implies outer coordinate wave functions that are δ functions. On the other hand, the matrix elements of $\tilde{\Delta}_{mm'} = (1 - \delta_{mm'})\tilde{H}_{mm'}$ are by definition zero for m equal to m', thus proving the claim.

The first-order corrections to the eigenfunctions are

$$C_{lm,l'm'} = \frac{\langle \Phi_{l'm'} | \hat{\Delta} | \Phi_{lm} \rangle}{E_{lm}^{(0)} - E_{l'm'}^{(0)}}. \tag{4.1}$$

Equation (4.1) informs us that the optimal basis is the one that minimizes, in the usual least-squares sense, the collection of first order eigenfunction corrections weighted by the energy differences. This interpretation cannot be extended beyond the first order. Nevertheless, corrections of any given order involve as many factors of the $\hat{\Delta}$ matrix elements, and it is clear that convergence will improve, generally speaking, as $|\hat{\Delta}|$ is diminished.

B. Born series expansion

In scattering applications, the main object of interest is the energy Green's function $\hat{G}(E) = \lim_{\epsilon \to 0}(E + i\epsilon - \hat{H})^{-1}$. We consider a separation of $\hat{H}$ into two pieces so that

$$\hat{H} = \hat{H}_0 + \hat{\Delta}, \tag{4.2}$$

where, for the moment, $\hat{H}_0$ is arbitrary. It is assumed only that $\hat{H}_0$ is invertible, so that the corresponding $\hat{G}_0(E) = \lim_{\epsilon \to 0}(E + i\epsilon - \hat{H}_0)^{-1}$ is well defined.

In the usual distorted-wave methodology, the perturbation $\hat{\Delta}$ has the form of a potential (i.e., it depends on the $\hat{q}_i$ only), and $\hat{G}_0$ is called the distorted-wave Green's function [3]. It makes sense to use the same terminology, however, even when $\hat{\Delta}$ takes on a more general form.

The full Green's function $\hat{G}$ can be expressed in terms of the distorted-wave Green's function $\hat{G}_0$ via the distorted-wave Born expansion

$$\hat{G}=\hat{G}_0+\hat{G}_0\hat{\Delta}\hat{G}_0+\hat{G}_0\hat{\Delta}\hat{G}_0\hat{\Delta}\hat{G}_0+\cdots. \tag{4.3}$$

In principle, one attempts to partition as much of $\hat{H}$ into $\hat{H}_0$ as possible, so that the resultant expansion converges quickly. On the other hand, $\hat{G}_0$ must be known explicitly, so that nothing is gained unless inverting $E+i\epsilon-\hat{H}_0$ is significantly more tractable than the original problem.

In the optimal separable $\hat{H}_0$ case, block diagonality can again be exploited so as to render the inversion a parametrized k-dimensional problem rather than an n-dimensional one. At the same time, the minimization of $|\hat{\Delta}|$ is expected to improve the convergence of Eq. (4.3). Thus both of our criteria for a good distorted-wave Green's function are satisfied.

Insofar as a rigorous analysis of convergence is concerned, we can make some progress by acknowledging that Eq. (4.3) is essentially a geometric series of the dimensionless kernel matrix $\hat{A}\equiv\hat{G}_0\hat{\Delta}$. In fact, if $\hat{\Delta}$ satisfies certain conventional scattering criteria, then the convergence of the Born series is determined solely by the eigenvalues of $\hat{A}$ [9,14]. In particular, Eq. (4.3) converges if and only if

$$|\lambda_i|<1 \quad \text{for all } i, \tag{4.4}$$

where the λ_i are the eigenvalues of $\hat{A}$.

One can derive, in terms of the λ_i, an expression for the rate of convergence out to any finite-indexed term in the Eq. (4.3) expansion. Unfortunately, the result depends on the level of expansion, so that a general definition of ''optimal'' convergence for all orders of expansion is not in general possible. Nevertheless, it is clear from Eq. (4.3) that convergence will, as a rule, improve as $|\hat{\Delta}|$ is decreased since both $\hat{\Delta}$ and $\hat{G}_0$ diminish with $|\hat{\Delta}|$.

C. Preconditioners

One is often interested in calculating the action of the Green's function on a scattering wave, rather than the Green's function itself. In numerical applications, where $\hat{G}$ is a matrix and $\vec{x}$ a vector representing the scattering wave, we have the standard linear algebra problem

$$(E+i\epsilon-\hat{H})\vec{y}=\vec{x}. \tag{4.5}$$

Numerical ''preconditioning'' consists of multiplying both sides of this equation with the same matrix—the preconditioner—prior to obtaining a solution. Preconditioning is most effective when the preconditioner matrix is closest to $\hat{G}$. This situation is very analogous to that of $\hat{G}_0$ in the distorted-wave Born expansion. In fact if we simply *define* the preconditioner to be the matrix representation of $\hat{G}_0$, and multiply Eq. (4.5) by Eq. (4.3), we find that numerical preconditioning and subsequent iterative expansion of the linear algebra problem correspond exactly to the distorted-wave Born expansion of $\hat{G}$.

This correlation provides us with an analytic means of evaluating different numerical preconditioning schemes. For example, for Hamiltonians of the standard $\hat{T}+\hat{V}$ form, the Born series proper [15] is generated by choosing $\hat{\Delta}\equiv\hat{V}$. The corresponding preconditioner, known as the ''kinetic-energy preconditioner'' [16], is effective when $\hat{V}$ is much smaller than $\hat{T}$. In contrast the ''diagonal preconditioner'' [16], for which $\hat{H}_0$ consists of the diagonal matrix elements of $\hat{H}$ in the position representation, is effective when $\hat{V}$ is much *larger* than $\hat{T}$. The ''optimized preconditioner,'' obtained from the optimal separable $\hat{H}_0$, is more efficient than either of these, although it can be shown to subsume the other two in the appropriate limits.

V. APPLICATION TO $T+V$ HAMILTONIANS

A. Orthogonality condition

Although the method presented in Sec. III is certainly applicable to arbitrary quantum systems, the analysis is greatly simplified if the Hamiltonian can be written in kinetic-plus-potential form. Specifically, we ask that the potential $\hat{V}$ depend on the position coordinates only and that the kinetic energy $\hat{T}$ satisfy the generic form

$$\hat{T}=T_{\text{in}}(\hat{q}_1,\hat{p}_1,\ldots,\hat{q}_k,\hat{p}_k) + T_{\text{out}}(\hat{q}_1,\ldots,\hat{q}_k;\hat{q}_{k+1},\hat{p}_{k+1},\ldots,\hat{q}_n,\hat{p}_n). \tag{5.1}$$

The kinetic energy thus separates into an inner term and an outer term, each of which may depend on position. There is an asymmetry, however, in that T_{out} may depend on the inner coordinates, but not vice versa.

Hamiltonians of the form of Eq. (5.1), i.e., $\hat{H}=\hat{V}+\hat{T}_{\text{in}}+\hat{T}_{\text{out}}$, exhibit a large amount of *sparsity*, in that each term is a tensor of reduced dimensionality. Moreover, the sparse form of Eq. (5.1) is *retained under a unitary transformation of the outer coordinates*. The $\hat{T}_{\text{in}}$ term is unaffected by such a transformation, whereas $\hat{T}_{\text{out}}+\hat{V}$ remains block diagonal in $(q_1,\ldots,q_k)$.

These facts are very beneficial from the standpoint of trying to find the optimal outer basis. $\hat{T}_{\text{in}}$, for instance, can be completely ignored, as a result of which the orthogonality condition [Eq. (3.3)] reduces to a simple integral

$$\int H_{\text{out}}^{mm'*}(q)[H_{\text{out}}^{mm}(q)-H_{\text{out}}^{m'm'}(q)]dq=0 \quad \text{for all } m,m', \tag{5.2}$$

where $\hat{H}_{\text{out}}\equiv\hat{T}_{\text{out}}+\hat{V}$ and $q\equiv(q_1,\ldots,q_k)$.

Note that where the outer basis is concerned, $\hat{H}_{\text{out}}$ has replaced $\hat{H}$ as the relevant operator. It is natural to interpret the former as a collection of $(n-k)$-dimensional *outer* subsystems parametrized by the *inner* coordinates. By optimizing the outer basis, we are in effect trying to *simultaneously diagonalize the entire collection*. In the general case, one cannot *actually* diagonalize all of the subsystems using a single basis, but the optimal choice is the best compromise in the least-squares sense.

B. Partitioning of coordinates

For an n-dimensional problem, there are 2^n distinct partitionings of coordinates into inner and outer categories, each

of which can potentially lead to a different optimal $\hat{H}_0$. In deciding which particular partitioning should be adopted, the results of the preceding subsection can serve as a useful guide.

One should, if possible, choose a (nontrivial) partitioning that satisfies Eq. (5.1), for, in addition to simplifying the analysis, the majority of the coupling constants will be *zero* by virtue of the sparse form of $\hat{H}_{\text{out}}$. The availability of such choices is related to the separability of the kinetic energy. If $\hat{T}$ is completely separable, as in the standard rectilinear case, then any partitioning will do. Only when the kinetic energy is completely *nonseparable* can no such partitioning be found, in which case a change of coordinates might be employed to induce a separation.

As is evident from Eq. (5.1), the kinetic energy need not be *strongly* separable, as $\hat{T}_{\text{out}}$ may depend on all of the position coordinates. In practice, however, $\hat{T}$ often *is* strongly separable, in which case exchanging the inner for the outer coordinates also satisfies Eq. (5.1). To determine which is the better choice, the simultaneous diagonalization interpretation of Sec. V A can be fruitfully called upon. If $\hat{T}_{\text{out}}+\hat{V}$ were to vary only *slightly* with the inner coordinate parameters, then the various subsystems would be almost identical and would therefore be almost entirely diagonalized by the best-fit outer basis. One is thus led to select, as inner coordinates, those $\hat{q}_i$ upon which the original Hamiltonian has the *least* dependence.

As a special case, consider a completely separable position-independent kinetic energy

$$\hat{T}=T(\hat{p}_1,\ldots,\hat{p}_n)=\sum_{i=1}^{n} T_i(\hat{p}_i), \tag{5.3}$$

where the coordinates have been mass weighted so that the T_i's are all of identical form. The subsystems of $\hat{T}_{\text{out}}+\hat{V}$ are now identical except for the potential energy $\hat{V}$, which depends on the positions only; thus, selecting inner coordinates involves nothing more than a straightforward analysis of the function $V(q_1,\ldots,q_n)$. A simple intuitive candidate for the optimal basis is suggested, namely, that basis which diagonalizes $\hat{T}_{\text{out}}+\langle\hat{V}\rangle_q$, where $\langle\hat{V}\rangle_q$ is the collection-averaged potential-energy function. While this choice may not be the optimal one—indeed, the true optimum may not even be of the form $T_{\text{out}}(\hat{p}_{k+1},\ldots,\hat{p}_n)+V(\hat{q}_{k+1},\ldots,\hat{q}_n)$—it should nevertheless reduce the coupling significantly and is in any case readily obtainable.

C. Inelastic scattering

In inelastic scattering applications, the above $\hat{T}_{\text{out}}+\langle\hat{V}\rangle_q$ candidate is closely related to the coupled-channel approximation, for which one uses the asymptotic rather than the average potential. In fact, if we were to generate our outer basis from $\hat{T}_{\text{out}}+V_{\text{as}}(\hat{q}_{k+1},\ldots\hat{q}_n)$ and restrict ourselves to the energetically accessible bound states only (the open channels), then exactly the coupled-channel approximation would result. In such inelastic applications, a natural separation between internal (intrafragment) and translational (interfragment) coordinates arises. The potential usually varies less with the latter, which is why the internal coordinates are chosen to be the *outer* coordinates.

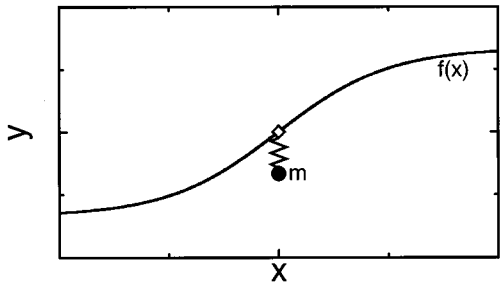

FIG. 1. Physical schematic of the shifted harmonic oscillator.

A primary advantage of the coupled-channel approach is that $\hat{G}(E)$ can be accurately determined using a small and finite outer basis, provided the energy E is sufficiently lower than some cutoff value used to truncate the basis set. Although finite, the various channels are still coupled together. An uncoupled approximation can be obtained by ignoring the off-block-diagonal matrix elements of $\hat{H}$. This is, in fact, a standard way to *define* distorted waves in the multichannel case.

It is clear that the uncoupled-channel approximation above constitutes, in our language, a choice of $\hat{H}_0$. We can therefore think of the *optimal* $\hat{H}_0$ as the choice that redefines the channels in the best possible way, vis-à-vis minimizing the interchannel coupling. This should generally improve the convergence of the resultant multichannel distorted-wave Born expansion, although very little is rigorously known about this subject [3].

VI. RESULTS: SHIFTED HARMONIC OSCILLATOR

As an analytical benchmark problem, we consider the two-dimensional shifted harmonic-oscillator Hamiltonian, i.e.,

$$\hat{H}=\frac{\widehat{p_x}^2}{2m}+\frac{\widehat{p_y}^2}{2m}+\frac{\kappa}{2}[\hat{y}-f(\hat{x})]^2, \tag{6.1}$$

where $f(x)$ is the shifting function (Fig. 1). Since the kinetic energy is completely separable and position independent, Eq. (5.1) is satisfied by any partitioning. The only nontrivial value for k is unity; so we are left with deciding whether x or y is the inner coordinate. We expect $V(x,y)$ to vary less with x than with y, which is particularly valid as $f(x)$ becomes small. The natural choice for the inner coordinate is thus x. If $f'(x)$ approaches zero in the infinite limits, then separable asymptotic states exist in those limits, and we can think of this as a scattering system with channels defined along y.

The first task is to optimize the outer basis via a unitary transformation in $\hat{y}$ and $\hat{p}_y$. This is equivalent to finding the basis that best diagonalizes the following x-parametrized collection of one-dimensional Hamiltonians:

$$\hat{H}_{\text{out}}(x)=\frac{\widehat{p_y}^2}{2m}+\frac{\kappa}{2}[\hat{y}-f(x)]^2. \tag{6.2}$$

In light of Sec. V C, we choose the eigenfunctions of $\widehat{p_y}^2/2m+\frac{1}{2}\kappa(\hat{y}-\langle f\rangle)^2$ as our initial guess, where $\langle f\rangle$ is the mean value of $f(x)$. For convenience, we force $\langle f\rangle=0$ by constraining $f(x)$ to be an odd function.

Our candidate outer basis functions then are the harmonic-oscillator eigenstates. We have not yet proven that this is an optimal choice; but we will soon do so, even for $f(x)$ not small, by demonstrating that Eq. (5.2) is satisfied. When expressed in the partially diagonal basis, $\hat{H}_{\rm out}$ takes on a *block-tridiagonal* form, where the off-block-diagonal terms arise from the $yf(x)$ cross terms in the potential. Specifically, we have

$$H_{\rm out}^{ll'}(x)=\frac{(2l+1)\hbar\omega+m\omega^2 f^2(x)}{2} \quad \text{for } l-l'=0, \tag{6.3}$$

$$H_{\rm out}^{ll'}(x)=-\sqrt{\frac{\max(l,l')\hbar\omega^3 m}{2}}f(x) \quad \text{for } |l-l'|=1, \tag{6.4}$$

$$H_{\rm out}^{ll'}(x)=0 \quad \text{otherwise}, \tag{6.5}$$

where $\omega=\sqrt{\kappa/m}$ and $\{l,l'\}$ index the y-oscillator states. Clearly, Eq. (5.2) is zero for $|l-l'|\neq 1$. When $|l-l'|=1$, the result is proportional to $\int f(x)\,dx$, which is also zero by virtue of $f(x)$ being odd. The candidate outer basis is therefore optimal. The coupling, which in the general two-dimensional case would be a tensor of rank 4, is seen above to be a rank-2 function of l and x only. Note also that $H_{\rm out}^{ll'}$ is proportional to $f(x)$, i.e., the inherent coupling vanishes as the shifting approaches zero, as expected.

We now examine the inner coordinate problem, i.e., the diagonalization of the diagonal blocks $\hat{T}_{\rm in}+\hat{H}_{\rm out}^{ll}$ that comprise $\hat{H}_0$. Note that even though the original potential involved cross terms, the new potential $\hat{H}_{\rm out}^{ll}(x)$ is completely additive in x and l. Consequently, all blocks of $\hat{H}_0$ are diagonalized by the *same* inner basis, so that for this particular problem the optimal *weakly* separable basis happens to be strongly separable.

Apart from an l-dependent constant, all $\hat{H}_0$ blocks are equivalent to the one-dimensional Hamiltonian in x,

$$\hat{H}_{\rm in}=\frac{\widehat{p_x}^2}{2m}+\frac{m\omega^2}{2}f^2(\hat{x}). \tag{6.6}$$

Since $f(x)$ is odd, we have an even potential well that is concave and centered at the origin. Such a well may admit bound-state solutions.

To proceed any further, however, we must specify a particular form of the shifting function $f(x)$. The choice $f(x)=T_0\tanh(\alpha x)$ is a useful one in that it represents a smooth, sigmoid progression from a $(-T_0)$-centered oscillator to a T_0-centered one. The amount of coupling can be adjusted by varying the parameter T_0, whereas the rate of change is determined by α. Moreover, the resultant inner Hamiltonian

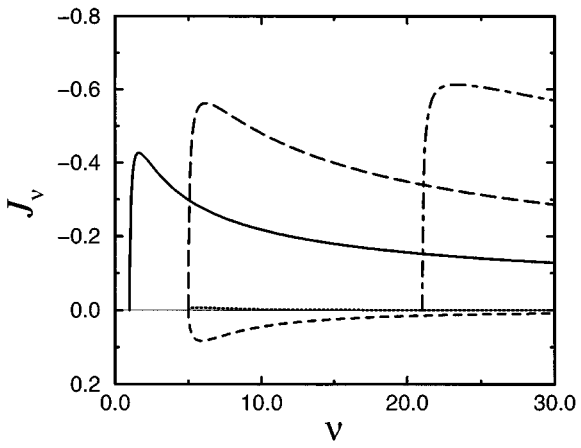

FIG. 2. $J_\nu^{(n',n)}$ as a function of ν for several values of (n',n): ——, (0,1); · · · · ·, (0,5); – – – –, (2,5); — — —, (4,5); – — – — –, (20,21). The curves all reach an extremum at some $\nu_{\rm max}$ on the order of n and then approach zero monotonically as ν is increased.

$$\hat{H}_{\rm in}=\frac{\widehat{p_x}^2}{2m}+\frac{m\omega^2 T_0^2}{2}\tanh^2(\alpha\hat{x}) \tag{6.7}$$

can be diagonalized analytically.

In the Appendix, the (normalized) bound-state eigenfunctions of Eq. (6.7) are shown to be

$$\phi_n^{(\nu)}(\eta)=\frac{\sqrt{(\nu-n)\Gamma(2\nu-n+1)}}{n!^{1/2}2^\nu\Gamma(\nu+1)} \times(1-\eta^2)^{-(\nu-n)/2}\left(\frac{d}{d\eta}\right)^n(1-\eta^2)^\nu, \tag{6.8}$$

where $\eta=\tanh(\alpha x)$, $\sqrt{\nu(\nu+1)}=m\omega T_0/\alpha\hbar$, and $n=\{0,1,\ldots,\text{int}(\nu)\}$. Curiously, a bound state always exists even in the limit $T_0\alpha\to 0$ (see the Appendix).

This fact reveals an interesting feature of $\hat{H}$. If there is no shifting, there are no bound states; however, *any* amount of shifting, no matter how small, *necessarily induces at least one bound state* in $\hat{H}_0$. In the small coupling limit, $\hat{H}_0$ becomes a valid replacement for $\hat{H}$. However, since the latter has no actual bound states, the bound states of $\hat{H}_0$ must correspond to *long-lived resonances* of $\hat{H}$. This result can be used as a benchmark for comparisons with other separable or adiabatic approximation methods, such as those based on the ''reaction path'' [17]. We have found that even the most rigorous adiabatic reaction path Hamiltonian [18] fails to predict any resonances for this system in the small coupling limit.

The optimal $\hat{H}_0$ leads to the zeroth-order eigenfunctions and eigenvalues

$$\Phi_{nl}(\eta,y)=\phi_n(\eta)\varphi_l(y), \tag{6.9}$$

$$E_{nl}=\frac{m\omega^2 T_0^2}{2}\left[1-\frac{(\nu-n)^2}{\nu(\nu+1)}\right]+(l+1/2)\hbar\omega, \tag{6.10}$$

where the $\varphi_l(y)$ are the harmonic-oscillator eigenstates. Since the first-order energy corrections are all zero, the additive Eq. (6.10) result is correct to first order. The first-order eigenfunction corrections $C_{nl,n'l'}$ are all zero except when $|l-l'|=1$, and $|n-n'|$ is odd. We choose $l=l'+1$, $n>n'$, and define $C_{l,n'n}\equiv C_{nl,n'l'}$, which are given by

$$C_{l,n'n}=\frac{\sqrt{l\hbar\omega m/2}\; T_0\; J_\nu^{(n',n)}}{\hbar+m\omega T_0^2[(n^2-n'^2)/\nu-2(n-n')]/(\nu+1)}. \tag{6.11}$$

The corrections specified in Eq. (6.11) are obtained from the one-dimensional integrals

$$J_\nu^{(n',n)}\equiv\int_{-1}^{1}\phi_{n'}^{(\nu)}(\eta)\;\phi_n^{(\nu)}(\eta)\;\frac{\eta}{(1-\eta^2)}\,d\eta, \tag{6.12}$$

whose closed-form expressions for the bound states are derived in the Appendix. Generally speaking, the magnitudes of these integrals are much less than unity (Fig. 2). The largest magnitudes are of order unity only when $n\approx n'\approx\nu$ and in general diminish as $|n-n'|$ or ν is increased.

The limit $T_0\alpha\to 0$, in which the shifting function and coupling approach zero, is of interest. We find that

$$C_{l,n'n}\approx\nu\sqrt{lT_0\alpha/2}\;J_\nu^{(n',n)}\quad\text{for}\quad\nu^2(T_0\alpha)\ll 1. \tag{6.13}$$

Thus the number of bound states ν may be fairly high, even as the $C_{l,n'n}$ approach zero. In the large-ν limit, the highly excited and continuum corrections to the low-lying eigenstates become negligible even in a relative sense. The corresponding resonances of $\hat{H}$ are therefore expected to be very long-lived indeed.

Our final task is to evaluate the kernel matrix $\hat{A}$ pertaining to the generalized Born expansion of Eq. (4.3). Using the Φ_{nl} basis, the representations of $\hat{H}_0$ and $\hat{H}$ are diagonal and block tridiagonal, respectively, even with the addition of the $E+i\epsilon$ terms appropriate for a Green's-function analysis. In the corresponding representation of $\hat{A}$, only the $|l-l'|=1$ blocks are nonzero. Again with $l=l'+1$, we have

$$A_{l,n'n}=\frac{\sqrt{l\hbar\omega^3 m/2}\; T_0\; J_\nu^{(n',n)}}{m\omega^2 T_0^2[1-(\nu-n)^2/\nu(\nu+1)]/2+(l+1/2)\hbar\omega-E-i\epsilon}. \tag{6.14}$$

In the limit $T_0\alpha\to 0$ this reduces to

$$A_{l,n'n}\approx\frac{\nu\sqrt{lT_0\alpha/2}\;J_\nu^{(n',n)}}{\left(l+\frac{1}{2}\right)-(E+i\epsilon)/\hbar\omega}\quad\text{for}\quad\nu^2(T_0\alpha)\ll 1, \tag{6.15}$$

which is small, as expected, provided E is sufficiently far from a resonance. We shall not consider higher-order terms in the present analysis, except insofar as to comment that a treatment of the continuum states should first be applied.

VII. CONCLUSION

The primary purpose of this paper has been to demonstrate that an optimal separable basis can be defined for an arbitrary quantum Hamiltonian in a mathematically rigorous fashion. Separable approximations are invaluable in physics and chemistry not only for their simplicity, but also for the intuitive insights they provide. One is especially interested in approximations that are not only *separable*, but also *accurate*; what has been lacking thus far is a systematic way to obtain such operators. The mutual orthogonality criterion of Eqs. (3.3) and (5.2) goes a long way towards this goal by providing *the* separable $\hat{H}_0$ that most closely approximates the true Hamiltonian, for a given factorization of configuration space.

The optimal separable basis also provides an advantageous starting point for series expansions. The fact that this method is useful for both Green's-function and eigenfunction expansions is not surprising, as both involve the same perturbation $\hat{\Delta}$. Similarly, the applicability of the method to both analytical and computational pursuits is also to be expected, as in either case it is of great benefit to be able to lower the dimensionality. It is significant that in the latter case a computer algorithm has been developed to perform the optimization automatically [8]. The corresponding analytical problem may in individual cases prove to be intractible, albeit dimensionally reduced, but even then the physical picture developed in Secs. III and V can be used to obtain a worthy substitute. It is also significant that the method, though applicable to arbitrary multidimensional operators, is particularly suited to sparse Hamiltonians.

The results for the shifted harmonic-oscillator system of Sec. VI are quite encouraging. Not only were we able to obtain the analytically optimal outer basis for any shifting function $f(x)$, our physical intuition led us immediately to the correct answer. All that was required was a simple integral verification of Eq. (5.2). Although this situation is to some extent fortuitous, it nevertheless indicates that the average potential probably does lead to an excellent, if not optimal, outer basis in the general case.

Having obtained the optimal outer basis for the generic shifted oscillator system, the inner problem was also reduced to a particularly simple form. The separability of the new potential allowed us to solve the full $\hat{H}_0$ problem by simply diagonalizing a *single* one-dimensional system rather than a *collection* of systems. In addition, the inherent residual coupling was found to be of rank 2 only. Thus, with comparatively little effort we were able to obtain the most accurate zeroth- and first-order approximations for this nontrivial two-dimensional system and to prove the existence of resonances

even in the limit of infinitesimal shifting.

In higher dimensions, the optimal separable basis method is expected to be even more effective, at least for numerical applications. One reason is that there is generally more freedom of choice with respect to coordinate partitionings as the dimensionality is increased. Another reason is that the sparsity usually increases with dimensionality, so that a greater percentage of the matrix elements of $\hat{\Delta}$ will be zero. If the kinetic energy is more separable than indicated in Eq. (5.1), one might wonder whether the present approach could be modified to exploit this additional sparsity. For calculations of the Sec. IV C variety, this could easily be accomplished via a *recursive* application of the method. Instead of just two tiers of coordinates, one winds up with three or more layers. Under the most favorable scenario of Eq. (5.3), each coordinate would constitute a separate layer, to be ''peeled off'' one at a time. Moreover, the tremendous initial sparsity of such a system would be preserved throughout.

Although a recursive approach may be advantageous in some cases, a straightforward application as presented in this paper should be suitable for just about any reasonably small system of interest. Moreover, there are plenty of applications for which a two-tiered approach is most natural. In molecular systems, for example, there is an obvious distinction between electronic and nuclear degrees of freedom. In nonrigid rotors, three global rotational degrees of freedom are naturally distinguished from the others. This partitioning results in the so-called Coriolis coupling, whose minimization via the optimal separable basis we plan to consider in a future paper. Scattering Hamiltonians also exhibit a separation between internal and translational coordinates by virtue of the asymptotic form of the potential. Numerical results for a simple molecular reactive scattering system are obtained in a concurrent paper [8], wherein we also present an efficient algorithm for obtaining the optimal outer basis.

ACKNOWLEDGMENTS

The author is indebted to Professor W.H. Miller for many reasons, including useful discussions of the multichannel distorted-wave methodology. Professor A. Weinstein and Professor B.N. Parlett of the UC Berkeley Mathematics Department are also acknowledged, as is M. Aotani. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

APPENDIX: THE $\tanh^2$ POTENTIAL HAMILTONIAN

The $\tanh^2$ potential is equivalent to a $-\mathrm{sech}^2$ potential, apart from a constant of unity. The latter, also known as the Eckart well or the symmetric Poschl-Teller hole [19], was introduced by Rosen and Morse [20] who first solved the quantum problem in an analysis of polyatomic molecular vibration energies. It has since been reconsidered in various other fields, including soliton research [21]. Despite a long-standing interest, however, exact wave-function normalization constants were not obtained until comparatively recently [22].

1. Solving the eigenproblem

We wish to find the eigenfunctions and discrete eigenvalues of the one-dimensional differential equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x)+\frac{m\omega^2 T_0^2}{2}\tanh^2(\alpha x)\ \phi(x)=E\phi(x). \tag{A1}$$

By transforming to the coordinate $\eta=\tanh(\alpha x)$, we obtain (with $\eta'\equiv 1-\eta^2$)

$$-\frac{\hbar^2}{2m}\alpha^2\eta'\left(\eta'\frac{d^2}{d\eta^2}\phi(\eta)-2\eta\frac{d}{d\eta}\phi(\eta)\right)+\left(\frac{m\omega^2 T_0^2}{2}\eta^2-E\right)\phi(\eta)=0. \tag{A2}$$

Dividing by $-\alpha^2\eta'\hbar^2/2m$ yields Legendre's differential equation [23]

$$(1-\eta^2)\ \ddot{\phi}(\eta)-2\eta\ \dot{\phi}(\eta)+[\nu(\nu+1)-\mu^2/(1-\eta^2)]\phi(\eta)=0, \tag{A3}$$

provided $\nu(\nu+1)\equiv(m\omega T_0/\alpha\hbar)^2$ and $\mu^2\equiv\nu(\nu+1)[1-2E/m\omega^2 T_0^2]$.

If μ and ν are taken to be positive (imaginary) square roots, then the solutions to Eq. (A3) are the associated Legendre functions of the first and second kinds $P_\nu^{\pm\mu}$ and $Q_\nu^{\pm\mu}$. For energies $E>\frac{1}{2}m\omega^2 T_0^2$, the parameter μ is pure imaginary as is appropriate for the continuum states. Bound states arise when E is less than $\frac{1}{2}m\omega^2 T_0^2$, in which case μ is real.

For integral ν, we know that the P_ν^μ are square integrable if μ is an integer less than or equal to ν. The generalization for nonintegral values of ν turns out to be that the *difference* between ν and μ must be integral, in which case $P_\nu^{-\mu}$ is the appropriate bound state solution. These functions are closely related to the Gegenbauer or ''ultraspherical'' polynomials [22]. Defining $n\equiv\nu-\mu$, the bound-state solutions $\phi_n(\eta)$ are thus proportional to $P_\nu^{n-\nu}(\eta)$, where n ranges from zero to the largest integer less than ν. The corresponding energy values are

$$E_n=\frac{1}{2}m\omega^2 T_0^2\left[1-\frac{(\nu-n)^2}{\nu(\nu+1)}\right], \tag{A4}$$

from which the ground-state energy is seen to be $E_0=\hbar^2\alpha^2\nu/2m$.

The bound-state solutions satisfy a somewhat unusual orthonormality condition. Because the coordinate η is used instead of x, we have

$$\int_{-1}^{1}\phi_{n'}^{(\nu)}(\eta)\ \phi_n^{(\nu)}(\eta)\ \frac{1}{(1-\eta^2)}\,d\eta=\delta_{nn'}. \tag{A5}$$

In terms of the $P_\nu^{n-\nu}$, the above integral can be analytically evaluated to determine the proper normalization constants [24]. This yields

$$\phi_{n'}^{(\nu)}(\eta)=\sqrt{\frac{(\nu-n)\Gamma(2\nu-n+1)}{n!}}P_{\nu}^{n-\nu}(\eta). \quad \text{(A6)}$$

Alternatively, we can use the Leibnitz and Rodrigues formulas [25] to derive the excited states by differentiating the following expression for the ground state [23]:

$$\phi_0(x)\propto P_{\nu}^{-\nu}[\tanh(\alpha x)]\propto \sin^{\nu}(\theta), \quad \text{(A7)}$$

where $\sin^2(\theta)\equiv 1-\tanh^2(\alpha x)$. This results in the normalized formula of Eq. (6.8).

The limiting case behavior of the bound-state solutions is also quite interesting. Since ν must be positive, there is always a bound state, even in the limit as the well depth (T_0) or width $(1/\alpha)$ approaches zero, and the corresponding action becomes arbitrarily small in relation to Planck's constant. This egregious departure from WKB theory is in marked contrast to other solved potentials. Only one bound state remains in these limits, however, since $\nu\to 0$. According to Eq. (A7), it must be proportional to $(1-\eta^2)^{(\nu/2)}$. Thus the ground state is in essence simply a power of the original potential. As ν approaches zero, ϕ_0 approaches a uniform distribution; moreover, the corresponding energy is seen from Eq. (A4) to approach the continuum threshold. These results are consistent with the limiting functional form of the potential itself, which approaches a constant in the small-ν limit.

2. Obtaining the $J_{\nu}^{(n',n)}$

We wish to evaluate the J_ν integrals of Eq. (6.12). Using a well-known recursion relation of the P_{ν}^{μ} to expand $\phi_{n'}$ [25], we can write

$$J_{\nu}^{(n',n)}=-\frac{1}{2}\sqrt{\frac{(2\nu-n')(n'+1)}{(\nu-n'-1)(\nu-n')}}I_{\nu}^{(n'+1,n)} -\frac{1}{2}\sqrt{\frac{(2\nu-n'+1)n'}{(\nu-n'+1)(\nu-n')}}I_{\nu}^{(n'-1,n)}, \quad \text{(A8)}$$

$$I_{\nu}^{(n',n)}\equiv\int_{-1}^{1}\phi_{n'}^{(\nu)}(\eta)\ \phi_{n}^{(\nu)}(\eta)(1-\eta^2)^{-1/2}d\eta. \quad \text{(A9)}$$

The quantity I_ν is nonzero only when $n,n'\geqslant 0$ and $n-n'$ is even. Using the Leibnitz formula, the (unnormalized) eigenfunctions can be expressed as a sum of algebraic functions of η:

$$\tilde{\phi}_{n}^{(\nu)}\equiv(1-\eta^2)^{-(\nu-n)/2}\left(\frac{d}{d\eta}\right)^{n}(1-\eta^2)^{\nu} =\sum_{i=0}^{n}(-1)^{i}\binom{n}{i}\frac{\nu!}{(\nu-i)!}\frac{\nu!}{(\nu-n+i)!} \times(1-\eta)^{\nu/2+[n/2-i]}(1+\eta)^{\nu/2-[n/2-i]}. \quad \text{(A10)}$$

The integral in Eq. (A9) can be analytically evaluated by expanding both ϕ_n and $\phi_{n'}$ using Eq. (A10) above. The result is

$$I_{\nu}^{(n',n)}=\frac{1}{2}\sqrt{\left(1-\frac{n}{\nu}\right)\left(1-\frac{n'}{\nu}\right)}\ \frac{\binom{2\nu}{\nu}}{\left[\binom{2\nu}{n}\binom{2\nu}{n'}\right]^{1/2}} \times\sum_{\substack{0\leqslant i\leqslant n\\ 0\leqslant j\leqslant n'}}(-1)^{i+j}\frac{\binom{\nu}{i}\binom{\nu}{n-i}\binom{\nu}{j}\binom{\nu}{n'-j}}{\binom{2\nu-1}{\nu+(n+n')/2-(i+j)-\frac{1}{2}}}. \quad \text{(A11)}$$

The right-hand side of Eq. (A11) is a somewhat unwieldy double summation involving $(n+1)(n'+1)$ terms. A simpler expression involving a sum of only $(\frac{1}{2}n'+1)$ terms can be obtained by deriving a recursion relation for the I_ν. It turns out to be more convenient to derive the relation for the $\tilde{I}_\nu$, defined via Eq. (A9) with respect to the $\tilde{\phi}_n$ rather than the ϕ_n. Using integration by parts and Eq. (A8), the following recursion relation is easily derived:

$$(n-n')\tilde{I}_{\nu}^{(n'+1,n)}=n'(2\nu-n'+1)(2\nu-n'-n)\tilde{I}_{\nu}^{(n'-1,n)} -2(\nu-n')\tilde{I}_{\nu}^{(n',n+1)}. \quad \text{(A12)}$$

Thus an arbitrary $\tilde{I}_\nu$ can always be expressed in terms of the $\tilde{I}_\nu$ for which $n'=0$. These are analytically obtained via direct integration of Eq. (A9), resulting in [26]

$$\tilde{I}_{\nu}^{(0,n)}=(-1)^{n/2}\pi^{1/2}[(n-1)!!]^2\frac{\left(\nu-\frac{n}{2}-\frac{1}{2}\right)!}{\left(\nu-\frac{n}{2}\right)!} \quad \text{(A13)}$$

for n even.

By combining the results of the preceding paragraph, any particular $\tilde{I}_\nu$ value can be determined. The first few are

$$\tilde{I}_{\nu}^{(0,0)}=\pi^{1/2}(\nu-\tfrac{1}{2})!/\nu!, \quad (n+n')=0, \quad \text{(A14)}$$

$$\left.\begin{aligned}\tilde{I}_{\nu}^{(0,2)}&=[-\pi^{1/2}(\nu-\tfrac{3}{2})!/(\nu-1)!]\\ \tilde{I}_{\nu}^{(1,1)}&=[2\nu\pi^{1/2}(\nu-\tfrac{3}{2})!/(\nu-1)!]\end{aligned}\right\}, \quad (n+n')=2, \quad \text{(A15)}$$

$$\left.\begin{aligned}
\widetilde{I}_\nu^{(0,4)} &= [9\pi^{1/2}(\nu-\tfrac{5}{2})!/(\nu-2)!] \\
\widetilde{I}_\nu^{(1,3)} &= [-6\nu\pi^{1/2}(\nu-\tfrac{5}{2})!/(\nu-2)!] \\
\widetilde{I}_\nu^{(2,2)} &= \left[12\nu(\nu-1)\left[1-\frac{1}{3}\left(\frac{\nu-3/2}{\nu-1}\right)^2\right]\right. \\
&\quad \left.\times\pi^{1/2}(\nu-\tfrac{5}{2})!/(\nu-2)!\right]
\end{aligned}\right\}, \quad (n+n')=4 \tag{A16}$$

In general, the factor in square brackets is a sum over $\mathrm{int}(1/2n')+1$ terms. The properly normalized formula for an arbitrary I_ν is

$$\begin{aligned}
I_\nu^{(n',n)} &= (-1)^{(n-n')/2}\pi^{1/2}(n-n'-1)!! \\
&\quad\times\sqrt{(2\nu-n)!(2\nu-n')!} \\
&\quad\times\frac{\sqrt{(\nu-n)(\nu-n')(n'!/n!)}}{\nu!\,2^{2\nu}} \\
&\quad\times\sum_{i=0}^{\mathrm{int}(n'/2)}(-1)^i 2^{(n'-i)}\binom{\nu-(n+n')/2+i-\frac{1}{2}}{k} \\
&\quad\times\frac{(n+n'-2i-1)!!}{(\nu-n'+i)!(n'-2i)!}\,\frac{(\nu-(n+n')/2+i-\frac{1}{2})!}{(\nu-(n+n')/2+i)!}.
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