Using Genetic Programming To Solve the Schrödinger Equation

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In a recent paper [Makarov, D. E.; Metiu, H. *J. Chem. Phys.* **1998**, *108*, 590], we developed a directed genetic programming approach for finding the best functional form that fits the energies provided by ab initio calculations. In this paper, we use this approach to find the analytic solutions of the time-independent Schrödinger equation. This is achieved by inverting the Schrödinger equation such that the potential is a functional depending on the wave function and the energy. A genetic search is then performed for the values of the energy and the analytic form of the wave function that provide the best fit of the given potential on a chosen grid. A procedure for finding excited states is discussed. We test our method for a one-dimensional anharmonic well, a double well, and a two-dimensional anharmonic oscillator.

1. Introduction

The solution of most mathematical problems in physical chemistry can be obtained by minimizing a certain functional. This is so even in the absence of a "true" variational principle: we can always search for a solution that gives the smallest error when inserted in the equation of interest. Let us say that we want to solve a problem that can be written as

$$\mathrm{LHS}(y(x;a),x) = \mathrm{RHS}(y(x;a),x) \tag{1}$$

where $y(x;a)$ is the function we want to extract from eq 1, x is a set of variables, and a is a set of numerical parameters. LHS and RHS can contain derivatives, nonlinear terms in y, or integrals. The problem is solved if we can find a function $f(x;a)$ that minimizes the error

$$F[f;a] = \sum_i w_i\{\mathrm{RHS}(f(x_i;a),x_i) - \mathrm{LHS}(f(x_i;a),x_i)\}^2 \tag{2}$$

Here, $\{x_i\}_{i=1}^n$ is a set of grid points, and w_i is a positive numerical weight associated with the grid point x_i. The variable f is a function that approximates $y[x;a]$; the better the approximation, the smaller $F[f;a]$ will be. The values of w_i are chosen to emphasize the importance of some grid points x_i (by taking $w_i > 1$) or to diminish the importance of some points x_j (by taking $w_j < 1$).

The traditional use of eq 2 requires the user to guess a functional form $f(x;a)$, which is supposed to describe $y[x;a]$ fairly well, and to find the values of the parameters a that minimize $F[f;a]$. The user can do this without great difficulties for those problems in which the qualitative properties of the solution are known. Of course, these are the least interesting problems. Those cases where little is known about the solution are more interesting. For these, a good guess is hard to make, and a lengthy and tedious succession of guesses must be undertaken.

An alternative is provided by genetic programming (GP),[1,2] which uses the computer to find not only the values of the parameters but also the functional form of f. In other words, in minimizing $F[f;a]$, one considers as variables not only the parameters a but also the function f.

In this article, we explore the use of a version of genetic programming[3] called directed genetic programming (DGP) to solve the time-independent Schrödinger equation. If successful, the procedure will provide analytic formulas for the wave functions of the ground and excited states and numerical values for the corresponding energies.

In principle, this method can solve any physics problem that can be written in the form of eq 1. This probably includes every conceivable problem. The real limitation is practical: the procedure might not be as efficient as its competitors. At this time, the method is so new and so little tested that such a comparison has not been made. In general, it is unfair and unwise to compare a new method with procedures that have benefited from decades of development and improvements. We hope that future work, by many investigators, will find classes of problems for which this method is useful.

2. Writing the Schrödinger Equation as a Minimum-Error Problem

We want to solve the equation

$$-{}^1\!/_2(d^2/dx^2)\psi(x) + V(x)\psi(x) = E\psi(x) \tag{3}$$

A straightforward application of eq 2 would be to define the error by

$$F[f;a] = \sum_{i=1}^n w_i\left\{-{}^1\!/_2\left.\frac{\partial^2 f(x;a)}{\partial x^2}\right|_{x=x_i} + V(x)f(x_i;a) - Ef(x_i;a)\right\}^2 \tag{4}$$

Unfortunately, this definition has two shortcomings: (1) the smallest error is given by $f(x;a) = 0$, which is a solution but not a useful one; (2) when used in the GP program, this definition leads to an inefficient search and a solution of low accuracy.

We found that a better definition of the error (the search ends faster and the results are more accurate) is

$$F[f;a] = \sum_{i=1}^n\left\{V(x_i) - \left[\frac{1}{2f(x_i;a)}\left.\frac{\partial^2 f(x;a)}{\partial x^2}\right|_{x=x_i}\right] - E\right\}^2 \tag{5}$$

This can be regarded as a fitting problem: we are given the potential energy $V(x)$, and we want to find a function $f(x;a)$ and

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a number E such that

$$W(x_i) = \frac{1}{2f(x_i;a)} \frac{\partial^2 f(x;a)}{\partial x^2}\bigg|_{x=x_i} + E \tag{6}$$

fits $V(x_i)$. The error of $F[f;a]$ defined by eq 5 is very small when the values of $f(x;a)$ on the grid points are close to those of an eigenfunction (ground or excited) of the Hamiltonian defined by eq 3 and when E is close to the corresponding eigenvalue.

In calculating the error, we treat the energy E on a different footing than f and a. We insert $f(x;a)$ in eq 5 and obtain a second-order expression in E. Then we minimize this expression with respect to E and subject it to the constraint that E is a real number. When we search for an excited state, we impose the additional constraint that E is larger than the energies of all lower-lying states.

There are other ways to rewrite eq 3 as a minimization problem. For instance, to find the ground state, we can directly use the variational principle and minimize $\langle E\rangle = \langle f|H|f\rangle/\langle f|f\rangle$ with respect to f. Such a procedure, however, involves the evaluation of integrals for each trial function f and is orders of magnitude slower than the previously described method.

We want to minimize the expression (eq 5) with respect to variations of the functional form of f, the numerical values of the parameters a, and the value of E. To do that, we use the genetic programming approach. An excellent review of genetic programming can be found in Koza's books.[1,2] Our implementation of GP[3] uses the Mathematica programming language and draws heavily on a paper by Nachbar.[4]

In GP, each function $f(x,a)$ is represented as a tree[1,2] with nodes for various functions or operators and "leaves" for parameters (a) or variables (x). The program generates a random list, or "population", of trial functions $\{f_i(x;a_i)\}_{i=1}^{m}$, each having different parameters. The population is then allowed to evolve according to a Monte Carlo procedure, which is designed to promote and improve the fitter population members (i.e., the ones having the smaller error $F[f_i,a_i]$) and to eliminate nonperformers. In the course of evolution, each population member can undergo random changes (genetic operations) similar to Monte Carlo moves in stochastic minimization methods. The search is continued until a population member is created, for which the error (eq 5) is smaller than a given value. Details of our approach are described in ref 3.

3. The Ground State of a One-Dimensional Well

In this section, we use directed genetic programming to find the ground state of a particle of unit mass in the Eckart well

$$V(x) = -2/\cosh^2(x/2) \tag{7}$$

This potential supports four bound states, as shown in Figure 1. The exact eigenfunctions can be written in terms of hypergeometric functions.[6]

We use a uniform grid $\{x_j\}$, with $x_j = x_{\min} + j(x_{\max} - x_{\min})/(N-1)$ ($j = 0, ..., N-1$), where $N = 26$, $x_{\min} = -3$, and $x_{\max} = 3$. A straightforward GP search for $f(x,a)$ that minimizes the error (eq 5) leads to poor results: it takes a long time, and its accuracy is not very good. Why does this happen? The ground-state wave function of a particle confined in a well has rather unique properties. It has no zeros and decays to zero at $|x| \to \infty$. The computer does not know about this: it generates random functions $f(x,a)$, most of which do not have the required properties. The search space is too large, while its relevant domain (containing $f(x,a)$ terms that can be ground-state wave functions of some potentials) is much smaller.

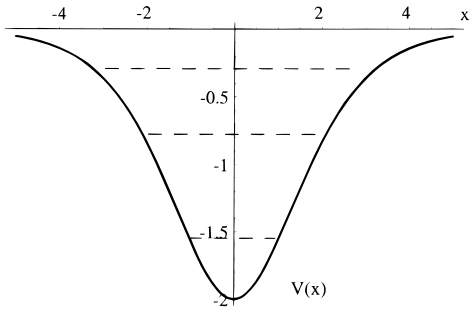

Figure 1. Potential of eq 7. Dashed lines indicate the energies of the bound states.

To circumvent this problem, we use the directed GP (DGP) approach.[3] Instead of directly searching for the $f(x)$ that is an (approximate) solution of eq 3, we guide the search by seeking a function $\chi(x)$ such that

$$f(x) = 1/\cosh[\chi(x)] \tag{8}$$

The use of eq 8 is suggested by the fact that $f(x) = 1/\cosh(x)$ has the bell shape expected for the ground-state wave function. One may therefore hope that replacing x by some simple function $\chi(x)$ will lead to a better approximate solution of eq 3. And indeed, it does.

The set of elementary functions (nodes)[3] from which all the trial functions $\chi(x)$ are built are the four arithmetic operations: addition, subtraction, multiplication, and division. Typically, we worked with a population of $M = 100$ trial functions and terminated the search after a total of 25 000 genetic operations were performed. We ran many independent searches, and most produced a wave function whose energy was within 0.5% of the dissociation energy. It is emphasized that the energy E corresponding to the wave function $f(x)$ is calculated by minimizing $F[f]$ with respect to E. This is not exactly equal to the expectation value of the energy $\langle E\rangle = \langle f|H|f\rangle/\langle f|f\rangle$, where $f(x)$ is the function giving the smallest error in eq 5.

One of the searches produced the following (unnormalized) wave function:

$$f(x) = 1/\cosh[1.086x + 0.023x(-1.78 + 1.086x)(1.658 + 1.086x)] \tag{9}$$

The energy obtained for this function is $E_0 = -1.5576$ eV, which compares well with the exact energy of -1.5586 eV. The expectation value of energy for this function is $\langle E\rangle = -1.5577$ eV, which is very close to the exact value. Thus, we have confidence that the wave function can be used for computing matrix elements.

An important question is whether our success is dependent on the particular choice of the directing function eq 8. To see if this is the case, we have carried out a guided search using a different function

$$f(x) = 1/I_0(\chi(x)) \tag{10}$$

where I_0 is the Bessel function of zeroth order. The genetic algorithm easily finds the ground state

$$f(x) = \frac{1}{I_0\left(1.77\left(x - \frac{1.93x}{7.51 + x^2}\right)\right)} \tag{11}$$

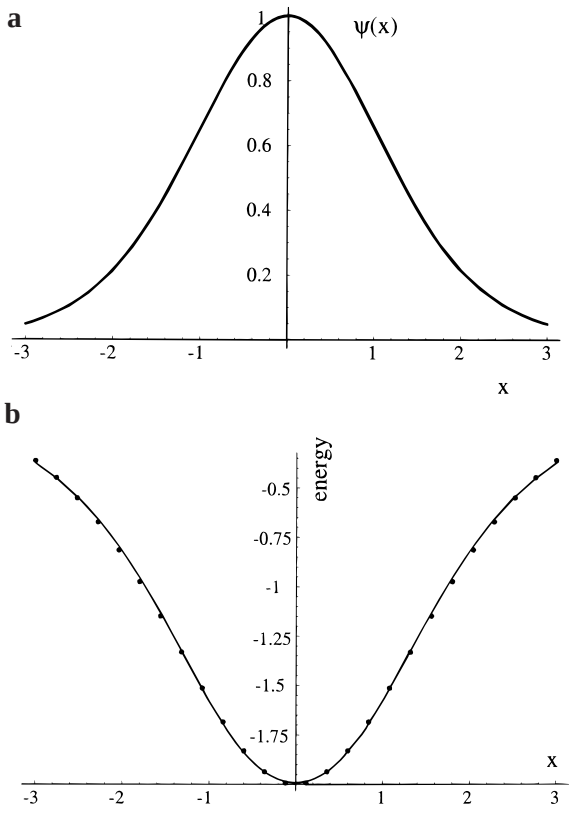

Figure 2. (a) Ground-state wave function for the potential of eq 7. (b) Equation 6 evaluated at grid points (dots) and a plot of eq 7 (solid line).

with $E_0 = -1.559$ eV and $\langle E \rangle = -1.5586$ eV. In Figure 2a, we plot this wave function and the exact wave function; within the resolution of the graph, the two functions are identical. In Figure 2b, we plot $V(x)$ (given by eq 7) as a continuous line and $W(x)$ (eq 6) as points on the graph. If the fit is good, the points representing the values of eq 6 at the grid points fall on the solid line.

The two guiding functions (eqs 8 and 10) have a bell-shaped curve and the correct asymptotic behavior (exponential) at $|x| \rightarrow \infty$. One might argue that the guiding function contains too many details which may not be known in more complicated cases. For this reason, we have performed a search using the function

$$f(x) = \exp[-\chi(x)^2] \tag{12}$$

This function does not have the proper asymptotic behavior. Furthermore, since we did not include square root among the elementary functions, we did not offer the search an easy way of creating a function with the proper asymptotic behavior. Nevertheless, our search finds

$$f(x) = \exp[-0.236x^2(1 + 2/(5.716 + x^2))^2] \tag{13}$$

to have $E_0 = -1.556$ eV and $\langle E \rangle = -1.5584$ eV. Both are within 0.003 eV of the exact value.

We conclude that our algorithm is relatively insensitive to the choice of the guiding function as long as the latter has the "proper ground-state shape". Note that the proper choice of the grid is important here. Had we chosen $|x_{min}|$ and $|x_{max}|$ to be too large, we would have included points that were far away from the origin and would have required an accurate fitting of the wave function in those regions. However, the wave function is practically zero there, so its exact value is unimportant as far as the energy is concerned. That is exactly why the precise asymptotic form of the guiding function is not important, as we only need to fit the wave function at points where it is large. This is true for the ground state, which is well-localized in space. However for higher-lying states that are more extended in space, failure to reproduce the tails of the wave function may lead to quite poor solutions. Moreover, if the wave function were later used in tunneling calculations, we would have to emphasize the asymptotic region, since this dominates tunneling.

4. The Excited States of the One-Dimensional Well (eq 7)

The "fitting error" of eq 5 is equal to zero when f is equal to any of the eigenfunctions ψ_n. Therefore, an undirected search can, in principle, generate higher eigenstates. Without an additional constraint, we should be unable to control which eigenstate the computer will find. While this may be a problem in principle, this is never a problem in practice. In all the undirected searches we made, the computer found the ground state. We do not fully understand why this happened, but we believe that it is reasonable to expect that the computer will more readily find the solution that has the simplest functional form. In our case, this is the ground state.

As a consequence, excited states are difficult to find without designing a proper guiding procedure that excludes the lower-lying states. One such procedure builds the nth excited state from the $(n - 1)$-st state by applying the raising operator $a^\dagger$

$$f_n(x) = a^\dagger f_{n-1}(x) \tag{14}$$

Had we known the exact $a^\dagger$, there would have been no need for a genetic search for the excited states. Since we do not know it, we use the harmonic oscillator creation operator

$$a^\dagger = \sqrt{\omega/2}(x - (1/\omega)(d/dx)) \tag{15}$$

The frequency ω is an adjustable parameter which we most often chose to be equal to the harmonic frequency of the well $\sqrt{V''(x_{eq})/\mu}$; x_{eq} is the equilibrium position of the particle (zero in our case), and μ is its reduced mass (1 in our case).

The application of the harmonic oscillator creation operator (eq 15) to $f_{n-1}(x)$ gives a guess for $f_n(x)$, which is used as a guiding function for the genetic search. We have used two procedures.

Method 1. To search for the first excited-state f_1 we use the guiding function

$$f_1(x;a) = a^\dagger \Phi(\chi(x;a)) \tag{16}$$

where Φ is a bell-shaped function (any one of the functions defined by eq 7, 9, or 12 will do) and χ is the function to be found by the genetic algorithm. The function Φ guides the search to generate the ground state, and $a^\dagger\Phi$ guides it to generate the first excited state. To obtain the second excited state, we use

$$f_2(x;a) = a^\dagger a^\dagger \Phi(\chi(x;a)) \tag{17}$$

To start the genetic search, we use a large population of the form eq 16 (or 17), which corresponds to a large number of different randomly generated functions χ. Then this population is altered by the genetic program (which changes χ) until a satisfactory function is found.

Method 2. Another method uses

$$f_1(x) = a^\dagger f_0(x) \tag{18}$$

to find the first excited state. Here, $f_0(x)$ is the approximate ground state found in a preliminary genetic search. To find the second excited state, we use

$$f_2(x) = a^\dagger f_1(x) \tag{19}$$

In this procedure, we generate a large population in which all individuals are equal to each other and given by eq 18 (or 19). Then the genetic program alters these functions and allows the survival of those that give smaller errors. This method counts on the fact that some of the alterations do not destroy the desired nodal structure, and therefore, the program has a chance of finding the excited state. Another helpful feature is to give a function a large error if the corresponding energy (obtained by minimizing eq 5) is less than some lower bound for the excited state. This feature did not help when used in method 1.

Both methods work. We find that method 2 is in general more efficient, but it is less accurate.

Using method 1, we obtained in one of the searches

$$f_1(x) = a^\dagger \operatorname{sech}\left(0.855\left(x + \frac{0.176(0.045 + 3.689x^3)}{15.411 + x^2}\right)\right)$$

with $E_1 = -0.8003$ eV and $\langle E\rangle = \langle f_1|H|f_1\rangle/\langle f_1|f_1\rangle = -0.8008$ eV. The exact energy is -0.8008 eV. Unfortunately, using $a^\dagger a^\dagger \operatorname{sech}[\chi(x)]$ as a guiding function for the second excited state was unsuccessful; we found no acceptable solution in the allotted time (about a week on a Power Macintosh with a 75 MHz processor).

Using method 2 and starting from the f_0 given by eq 9, we found the first two excited states of the potential (eq 7). For $n = 1$ one of the searches produced

$$\begin{aligned} f_1(x) = {} & (1.844 \times 10^{19} + (2.44(1.80 - x) + 1.084x)(1.686 + \\ & 8.767x + 0.573x^5))(x(1.012 + 0.06x^2)\operatorname{sech}(x + \\ & 0.022x(-3.31 + x^2)) + x\operatorname{sech}(x + 0.044x(-0.636 + x^2))) \end{aligned} \tag{20}$$

with $E_1 = -0.803$ eV and $\langle E\rangle = \langle f_1|H|f_1\rangle/\langle f_1|f_1\rangle = -0.7998$ eV. For $n = 2$, we obtained in one of the searches

$$\begin{aligned} f_2(x) = {} & \\ & 0.707(-0.729(5.03 \times 10^9 - 1.887/x)(70928.4 - x) \times \\ & (x - 67207.4)x^2((1.012 + 0.053x^2)\operatorname{sech}(0.965x) + \\ & \operatorname{sech}(0.044x(x^2 + 22.06))) - 1.115(0.839x(x + x^2) + \\ & 57189.9(x + 70927.9)(x^2 + x + 5.03 \times 10^9) \times \\ & (\operatorname{sech}(0.027x(x^2 + 7.494)\tanh(0.039x(x^2 + 22.0634))) + \\ & \operatorname{sech}(0.022x(x^2 + 31.68))(1.012 + 0.179x^2 - \\ & 0.00396x(13.9865 + x^2) \times \\ & (16.94 + x^2)\tanh(0.021x(x^2 + 34.085)))))) \end{aligned} \tag{21}$$

with $E_2 = -0.293$ eV and $\langle E\rangle = \langle f_2|H|f_2\rangle/\langle f_2|f_2\rangle = -0.290$ eV. The exact value is $E_2^{ex} = -0.293$ eV.

The potential (eq 7) is rather anharmonic. The energies for the harmonic approximation to eq 9 are $E_0 = -1.5$ eV, $E_1 = -0.5$ eV, and $E_2 = 0.5$ eV. Note that the second excited state of the harmonic approximation lies in the continuum of the true potential. Despite this strong anharmonicity, the harmonic oscillator creation operator $a^\dagger$ helps us find the anharmonic wave functions.

These methods become more and more inefficient as we try to calculate higher excited states. It is likely that we need new ideas if we intend to calculate highly excited eigenstates.

5. The Eigenstates of a Symmetric Double Well

In this section, we investigate whether our method is capable of describing tunneling and consider finding the lowest two states of the symmetric double-well potential

$$V(x) = (1 - (x/2)^2)^2 \tag{22}$$

Obviously, the method used in section 4 for guiding the wave function for a single well is inadequate for a double-well problem. To find a guiding function for the double well, we need to invoke the physics of the problem. If we neglect tunneling between the wells, the ground state is doubly degenerate, and we can construct an eigenfunction ψ_L that is localized in the left well and an eigenfunction ψ_R that is localized in the right well. By symmetry, these wave functions are related through

$$\psi_L(x) = \psi_R(-x) \tag{23}$$

Tunneling lifts this degeneracy. From near-degenerate perturbation theory, the ground-state and the first excited-state wave functions are, respectively, the symmetric (ψ_+) and antisymmetric (ψ_-) combinations of the localized wave functions

$$\psi_\pm(x) = \{\psi_R(x) \pm \psi_R(-x)\}/\sqrt{2} \tag{24}$$

This suggests looking for the solution in the form of symmetric and antisymmetric combinations of functions localized in the left and the right wells, i.e., using eq 24 as a template. We further guide the search for $\psi_R(x)$ by using a bell-shaped template function such as the one in eq 8

$$\psi_R(x) = 1/\cosh(\chi(x)) \tag{25}$$

where $\chi(x)$ will be determined by the genetic search. Thus, the function used in the genetic algorithm is

$$f_\pm(x) = 1/\cosh[\chi(x)] \pm 1/\cosh[\chi(-x)] \tag{26}$$

We emphasize that in choosing this functional form, we do not assume the validity of near-degenerate perturbation theory. Rather, we use eq 26 as a physically motivated template function to guide the search.

One of the searches produced the following (unnormalized) ground-state wave function:

$$f_+(x) = (\psi_R(x) + \psi_R(-x))/\sqrt{2} \tag{27}$$

with $\chi(x)$ in eq 25 taking the form

$$\begin{aligned} \chi(x) = {} & 1.63 + 0.85(-4.07 + x) + 0.19x + \\ & 0.005(-0.98 + 0.945x)x^2(-2.94 + x^2) \end{aligned} \tag{28}$$

The wave function $f_+(x)$ has an energy of 0.570 eV and $\langle f_+|H|f_+\rangle/\langle f_+|f_+\rangle = 0.573$ eV, while the exact energy is 0.572 eV. Figure 3 shows how $f_+''(x)/2f_+(x) + E$ fits the potential (eq 22) at the grid points used in the search.

If the near-degenerate perturbation theory were valid, then forming an antisymmetric combination

$$f_-(x) = (\psi_R(x) - \psi_R(-x))/\sqrt{2} \tag{29}$$

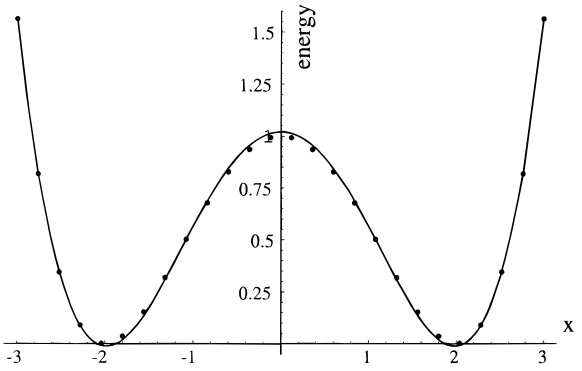

Figure 3. Equation 6 evaluated at grid points (dots) and a plot (solid line) of the exact potential, eq 22, for the ground-state function (eqs 25, 27, and 28) found in a genetic search.

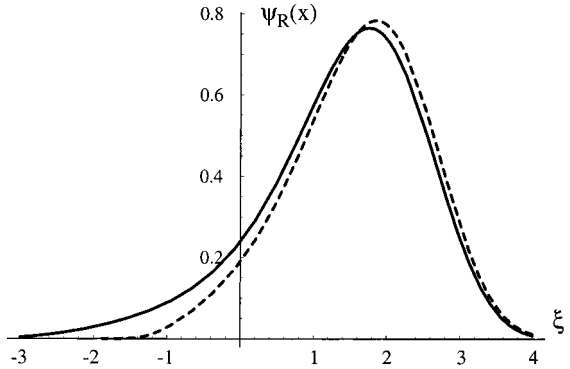

Figure 4. Localized wave function $\psi_R(x)$ found in the genetic search for the ground state (solid line) and the first excited state (dashed line).

with ψ_R determined from eqs 25 and 28 would give the wave function for the first excited state. It turns out that eq 29 gives an error of about 20% in the value of the tunneling splitting between the energies of the two lowest states.

We have performed a new search for the best function $\chi(x)$ in eqs 25 and 29. This search yields the energy (of the first excited state) of 0.688 eV, which is equal to the exact value. The excited-state wave function is given in eq 29 with

$$\psi_R(x) = 1/\cosh[3.52 - 0.55(-3.20 + 1.14(-0.38 + 1.06(x - 1.05))) + 0.13x(x + 0.018)(1.10x - 1.63) - (1.03(3x + 0.024))/((x + 2.32)(2.20 + x - 0.24(0.023 + x)))] \quad (30)$$

In Figure 4, we compare the localized wave function ψ_R (eqs 25 and 28), found by the genetic search for the ground state, to the function ψ_R (eq 30), used to construct the first excited state (eq 29). Note that eq 25 is not normalized while the functions in Figure 4 are. The two localized wave functions are seen to have similar shapes except in the barrier region, where they decay at different rates. This is the region having the most effect on the magnitude of the tunneling splitting.

6. The Eigenstates of a Two-Dimensional Anharmonic Oscillator

We now use DGP to find the eigenstates of an anharmonic oscillator in two dimensions. Our model is a particle of unit mass described by the Hamiltonian

$$H = p_x^2/2 + p_y^2/2 + V(x,y) \quad (31)$$

with

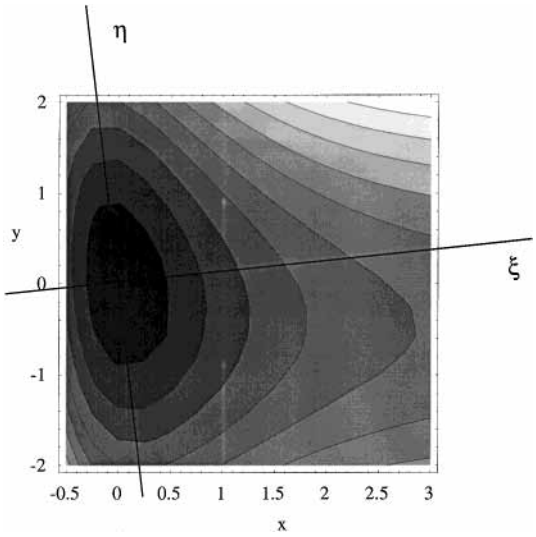

Figure 5. Contour plot of the potential (eq 32) and its normal coordinates.

$$V(x,y) = 3(1 - e^{-x})^2 + 0.5(1 - e^{-x})y + y^2/2 \quad (32)$$

A contour plot of $V(x,y)$ is shown in Figure 5.

The error for this search is defined by

$$F[f;a] = \sum_i \left\{ V(x_i,y_i) - \frac{1}{2f(x_i,y_i;a)} \times \left[\frac{\partial^2 f(x,y;a)}{\partial x^2} + \frac{\partial^2 f(x,y;a)}{\partial y^2} \right]\Bigg|_{x=x_i,y=y_i} - E \right\}^2 \quad (33)$$

A brute-force, undirected search did not succeed in yielding any eigenstates of this potential within the allotted time. In the same amount of time, a directed search, consisting of the following three steps, was successful:

Step 1. Expand $V(x,y)$ to second order in x and y, and find the normal coordinates, ξ and η. For the potential (eq 32), the normal coordinates are

$$x = 0.995\xi - 0.0985\eta,\ y = 0.0985\xi - 0.995\eta \quad (34)$$

They are schematically shown in Figure 5.

Step 2. Use the directed genetic program to search for the best wave function within the Hartree approximation

$$f(\xi,\eta) = \phi(\xi)\varphi(\eta) \quad (35)$$

It is well known that the normal coordinates give a much better Hartree approximation than the Cartesian coordinates.

As in the one-dimensional case, we further set

$$\phi(\xi) = \Phi(\chi(\xi)) \quad \text{and} \quad \varphi(\eta) = \Phi(\lambda(\eta)) \quad (36)$$

where $\Phi(x)$ is a suitable bell-shaped curve and χ and λ are the functions to be optimized by the genetic program. For Φ, we use the harmonic oscillator ground state

$$\Phi(x) = (1/\pi)^{1/4} \exp(-x^2/2) \quad (37)$$

As we have shown in the case of the one-dimensional well, the choice of the bell-shaped curve does not seem to affect the ability of the program to find a good wave function. The search for the best functions $\chi(\xi)$ and $\lambda(\eta)$ starts with a population of randomly created functions.

Step 3. While the Hartree approximation is often rather good, we were interested in finding a wave function that includes correlation effects. For this, we relax the constraint imposed by the Hartree approximation eq 35 and allow the functions χ and λ in eq 36 to depend on both ξ and η. To do so, we initiate a new search with an initial population in which each individual is the best Hartree solution, obtained at step 2. However, when we modify these individuals, we allow the modifications to be functions of both variables ξ and η.

A search in which these three steps have been performed came up with

$$f(\xi,\eta) = \exp[-{}^1/_2(-0.269 + 0.927(0.074 + 0.936\xi))^2 \times (1.67 - 0.264\xi + 0.07\eta)^2 - {}^1/_2(0.116 + \eta + \xi/(25 + \exp(-0.55 + \xi) + \exp(\xi) + \exp(2\xi) + \exp(\eta) - 7.056\xi + \eta + \exp(-\eta)\eta + (0.631 + \eta)(\xi + 3.51\eta)))^2] \quad (38)$$

Unlike in the other searches, we included the exponential function among the elementary functions used to construct new functions. The grid used for the data points was the 10×10 grid that fills uniformly the frame of Figure 6. The wave function of eq 38 is characterized by $E_0 = 1.544$ eV, while the exact energy is 1.587 eV. We also notice that anharmonic effects are significant for the ground state of this potential and are properly accounted for by the wave function (eq 38), as the harmonic approximation gives for the ground-state energy $E_0 = 1.72$. This is also seen from the contour plot of the potential "generated by eq 38", $W(x,y) = E + [f''_{xx}(x,y) + f''_{yy}(x,y)]/[2f(x,y)]$, shown in Figure 6a, as compared with the potential $V(x,y)$ of eq 32, shown in Figure 6b. Both potentials are plotted in Figure 6 as functions of the normal coordinates ξ and η.

When the potential is not too anharmonic, excited states can be built from the known lower states using the approach described in section 4. As functions $f(x,y)$ become more complex in two dimensions, the CPU time required to evaluate eq 33 becomes larger, so finding excited states is rather time-consuming. We have built an approximation to the wave function of the first excited state by applying the harmonic creation operator for the η coordinate

$$a_\eta^+ = \sqrt{\omega/2}\left(\eta - \frac{1}{\omega}\frac{d}{d\eta}\right) \quad (39)$$

to the wave function (eq 38). The adjustable frequency ω was chosen to be equal to the harmonic frequency in the η direction. The resulting expression was used as an initial guess in performing an undirected genetic search.

The wave function

$$f_1(\xi,\eta) = 0.48\exp(-0.46(0.14 - 0.87\xi)^2(1.67 - 0.24\xi + 0.073\eta)^{1.64} - 0.58\eta^2)\eta - 0.62\exp(-0.49(0.2 - 0.87\xi)^2 \times (1.67 - 0.26\xi + 0.069\eta)^{2.242} - 0.47(0.14\eta + \xi/(20.61 + \exp(2\xi) + \exp(\eta) + (x - 6.43)\xi + 5.51\eta + 3.02\eta^2)^{0.9})^2 \times (-0.094(0.31 + \xi^2)^2 - 2.15(0.011 + \eta + \xi/(29.4 + \exp(2.17\xi) + \exp(\eta) + 2.3(\eta - 6.43) + \eta + \xi\eta^2)^{1.39})) \quad (40)$$

found in this way gives $E = 2.534$. The exact value is 2.554.

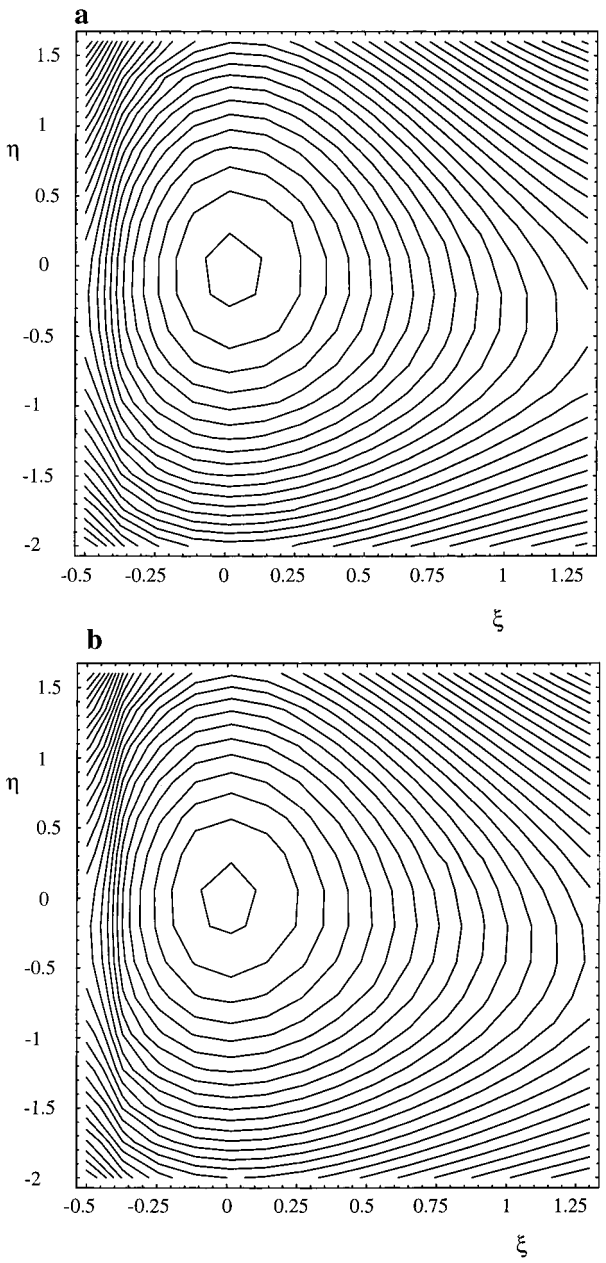

Figure 6. Contour plots, as a function of the normal coordinates, of (a) the potential $W(x,y)$ "generated by eq 38" and (b) $V(x,y)$ from eq 32.

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References and Notes

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