BASIS FUNCTIONS FOR LOCALIZED QUANTUM POTENTIALS

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ABSTRACT: A set of orthogonal functions was constructed for use as a basis set in quantum mechanical energy calculations. Specifically, the functions have the correct asymptotic behavior appropriate for all one-dimensional localized potentials. The results of these calculations are reported for several potential wells and compared with calculations using Hermite Functions.

KEYWORDS: Computational physics, orthogonal polynomials, quantum mechanics.

INTRODUCTION

In classical physics, a particle confined to an attractive potential will oscillate, and the details of the motion, such as frequency and amplitude, are determined by the particle's energy. This energy can take any value from zero (no motion) up to the binding energy of the potential. According to quantum mechanics, however, the energy of oscillation is constrained to take on a value from a discrete set of allowed energies or eigenvalues. The calculation of the energy eigenvalues for a particular potential is a central problem of quantum mechanics, and many methods have been developed to solve it.

Fundamentally, all methods must find the eigenvalues of the time-independent Schrödinger Equation. In one dimension, this takes the form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad .$$

Here, m is the particle's mass, V(x) is the potential, ψ is the particle's wavefunction, and $\hbar$ is Planck's Constant divided by 2π. When appropriate boundary conditions are applied to ψ, the particle's energy, E, is found to have a discrete spectrum.

A powerful method for solving the Schrödinger Equation is the Variational Method (Schiff, 1968). This method takes advantage of the fact that the wavefunction is an element of a Hilbert Space. Specifically, one can choose a complete set of functions as a basis and express the wavefunction as a linear combination of these basis functions. The choice of basis is essentially arbitrary, but each basis function must satisfy the boundary conditions of the problem. As a practical matter, the basis is chosen to be orthonormal, for then the calculations are

greatly simplified. By orthonormal, we mean: let the nth basis function be $\phi_n(x)$, and its complex conjugate be $\phi_n^*(x)$. Then, for every pair of m and n

$$\int_{-\infty}^{\infty} \phi_m^*(x)\phi_n(x)dx = \delta_{m,n} \quad .$$

Here, $\delta_{m,n}$ is the Kronecker Delta, which equals one if m = n and is zero otherwise.

Once the basis is chosen, the calculations are almost rote. A Hamiltonian matrix, H, is constructed, the elements of which are

$$H_{m,n} = \int_{-\infty}^{\infty} \phi_m^* \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} +V \right)\phi_n dx \quad .$$

(Normally, for time-independent problems, ϕ is chosen to be a real function and ϕ^* becomes ϕ.) The eigenvalues of the matrix are the allowed energies of the potential, and the eigenvectors give the wavefunctions as a linear combination of the basis functions.

The size of the basis set, and hence of the H matrix, is chosen by the investigator with the understanding that only an infinite basis can be expected to produce exact eigenvalues. A finite basis set produces approximate energies, and normally, enlarging the set improves the accuracy. The rate of convergence, however, is sensitive to the choice of basis.

CHOICE OF BASIS

Since little is required of the basis functions other than the necessity of satisfying the boundary conditions, it seems reasonable to look at these conditions when selecting the basis. In this work, we are interested in all one dimensional, localized potential wells. By localized, we mean that $V(x) \rightarrow 0$ as $x \rightarrow \pm \infty$. For such potentials, the wavefunction tends to zero as $x \rightarrow \pm \infty$. However, we can be more specific. For $|x|$ large, $V \rightarrow 0$ and the energy of the system is all kinetic. Therefore, $p^2/2m \approx E$ and $p \approx \sqrt{2mE}$. Expressing this in the language of quantum operators, we have

$$-i\hbar \frac{d\psi}{dx} \approx \sqrt{2mE}\psi = i\sqrt{2m|E|}\psi$$

(E < 0 for bound states). This equation has the solution

$$\psi = ce^{\pm kx}, \quad k = \sqrt{2m|E|} / \hbar,$$

with c an arbitrary constant. The boundary conditions require choosing the sign so that $\psi \to 0$ as $|x| \to \infty$. Therefore, $\psi \sim ce^{+kx}$ for $x < 0$ and $\psi \sim ce^{-kx}$ for $x > 0$.

A common choice of basis is $H_n(x) e^{-x^2/2}$, where H_n is a (normalized) Hermite Polynomial. The Hermite Polynomials satisfy the Schrödinger Equation for the case $V(x) = x^2/2$, and, therefore, are automatically orthogonal (with respect to the weight function $e^{-x^2/2}$) and form a complete set (Abramowitz and Stegun, 1964; Erdélyi, 1953; Szegö, 1975). However, since $V(x) = x^2/2$ is not localized, the Hermite Functions vanish more rapidly than e^{-x}, going to zero as e^{-x^2} as x goes to infinity. In light of the previous discussion, then, it seems reasonable to search for a set of functions that share the above properties but vanish as $e^{\pm x}$. One such function is sech(x), since

$$\text{Sech}(x) = \frac{2}{e^x + e^{-x}} \quad .$$

Therefore, it is necessary to construct polynomials $V_n(x)$, orthogonal with respect to $\text{sech}^2(x)$ for then our basis functions could be chosen as $V_n(x)$ sech(x). The orthonormality condition becomes

$$\int_{-\infty}^{\infty} V_m(x)V_n(x)\text{sech}^2(x)dx = \delta_{m,n}$$

Pickett (in press) has constructed these polynomials. The first few are

$V_0(x) = 1$
$V_1(x) = x$
$V_2(x) = x^2 - 1/12$
$V_3(x) = x^3 - (7/20)x$
$V_4(x) = x^4 - (13/14)x^2 + 27/560$

(Actually, these polynomials have been constructed to be orthogonal with respect to $\text{sech}^2(\pi x)$ rather than $\text{sech}^2(x)$. This constitutes a minor detail and was done to avoid cumbersome powers of π in the coefficients.) As written, these functions are not normalized. Each must be multiplied by

$$h_n = \sqrt{\frac{(2/\pi)(n!)^4}{4^n(2n+1)\left[(2n-1)!!\right]^2}}$$

All orthogonal polynomials satisfy a three term recurrence relation (Abramowitz and Stegun, 1964; Erdélyi, 1953; Szegö, 1975). The polynomials $V_n(x)$ satisfy

$$V_{n+1}(x) = xV_n(x) - C_nV_{n-1}(x), \quad C_n = \frac{n^4}{4(2n-1)(2n+1)}$$

The recurrence provides a relatively simple method for calculating the basis functions.

CALCULATIONS

We tested the polynomials by using them to calculate energies for three potentials: the finite square well, e^{-x^2}, and $\text{sech}^2(x)$. We began with sixteen functions in the basis, then enlarged it to twenty, and then to twenty-six. Each calculation was timed and compared to calculations using Hermite Functions as well as to the actual energy values. All of the basis set calculations were performed with Mathematica® on an Intel® 486 33 MHZ processor.

For purposes of numerical solution, the Schrödinger Equation must be cast into dimensionless form. Since our potentials are chosen rather than determined by data, this is easily done by adopting machine units for the various physical dimensions of the problem. In our calculations, we have set m = 1 mass unit, $\hbar = 1$ action unit, and x can be taken as a dimensionless variable measuring length units.

$V(x) = V_0\text{sech}^2(x)$. This potential was chosen because it is localized and the energies are known exactly (Landau and Lifshitz, 1977). The well depth, V_0, was chosen as follows. For this potential, the number of bound states is given as the largest integer not exceeding s, where

$$s = \frac{1}{2}\left(1 + \sqrt{1 - 8V_0}\right)$$

We wanted all of our trial potentials to have a depth that was about midway between those that would bind six and seven states. Therefore, we chose $V_0 = -143/8$ (s = $6^1/_2$).

In the calculations, it is possible to generalize the basis functions by writing them as $V_n(bx/\pi)\text{sech}(bx)$ with b an adjustable parameter. A similar conversion is possible for the Hermite Functions. We chose b by finding the value that minimized the maximum error in the 16 x 16 cases. That is, in each calculation, six energies are computed, and b is chosen to minimize the largest of the six errors. In general, the optimum value of b for the 16 x 16 case will not optimize the 20 x 20 case, or any other basis set size. However, once the parameter had been chosen in this way, its value was considered permanent, even when the basis was enlarged. This reflects the fact that, in practice, one doesn't know the energies in advance and has no way to compute a new parameter as the basis is

Table 1. A comparison of the calculated energies of the potential well $V(x) = (-143/8)\text{sech}^2(x)$ using Hermite Functions and Sech Functions.

| | True Energies | Basis Set Size | | |
		16 x 16	20 x 20	26 x 26
Hermite Functions				
E_0	-15.125000	-15.122276	-15.124390	-15.124926
E_1	-10.125000	-10.114147	-10.122343	-10.124646
E_2	-6.125000	-6.085141	-6.114609	-6.123532
E_3	-3.125000	-3.081641	-3.112872	-3.123165
E_4	-1.125000	-1.067728	-1.108258	-1.122517
E_5	-0.125000	-0.057308	-0.096037	-0.116561
Calculational Time		220 sec	550 sec	1754 sec
Sech Functions				
E_0	-15.125000	-15.124807	-15.124951	-15.124991
E_1	-10.125000	-10.123977	-10.124714	-10.124942
E_2	-6.125000	-6.120332	-6.123705	-6.124741
E_3	-3.125000	-3.119102	-3.123217	-3.124610
E_4	-1.125000	-1.116973	-1.122574	-1.124475
E_5	-0.125000	-0.120390	-0.123903	-0.124684
Calculational Time		356 sec	1091 sec	4948 sec

Table 2. A comparison of the relative errors (%) of the calculated energies of the potential $V(x) = (-143/8)\text{sech}^2(x)$ using Hermite Functions and Sech Functions.

| | Basis Set Size | | |
	16 x 16	20 x 20	26 x 26
Hermite Functions			
E_0	0.018010	0.004033	0.000492
E_1	0.107188	0.026241	0.003498
E_2	0.650764	0.169649	0.023960
E_3	1.387501	0.388096	0.058724
E_4	5.090839	1.488143	0.220687
E_5	54.153337	23.170524	6.750982
Sech Functions			
E_0	0.001273	0.000322	0.000058
E_1	0.010108	0.002825	0.000568
E_2	0.076219	0.021137	0.004227
E_3	0.188726	0.057062	0.012493
E_4	0.713498	0.215644	0.046691
E_5	3.688075	0.877895	0.252670

enlarged. The optimizing parameter for the Hermite Functions in this case has the value b = 1.197566, while that for the sech polynomials is b = 3.9291591.

The results of the calculations for this potential are shown in Tables 1 and 2 along with the correct energies and the results using the Hermite Functions. A proper comparison must also include the amount of time spent computing, and those data are also listed in the tables.

The Finite Square Well (V(x) = 0 for x > 1 and x < -1; for -1 < x < 1, V_0 = $-121\pi^2/32$). The well depth was chosen as the mean of the values that would just accommodate six and seven states. The actual energies are transcendental but can easily be calculated numerically (French and Taylor, 1978; Schiff, 1968). For this potential, the optimizing parameters take on the values b = 3.442024 for the Hermite Functions and b = 12.024734 for the sech polynomials. The results are shown in Tables 3 and 4.

$V(x) = V_0 e^{-x^2}$. Using the same criterion for depth as for the square well, we arrive at V_0 = -27.44171. To obtain the actual energy eigenvalues, we used a numerical method known as the Numerov Technique (French and Taylor, 1978; Griffin and McGhie, 1973). The idea is to numerically integrate the Schrödinger Equation from x = 0 out to x → ∞, starting with $\psi(0)$ = 0 and $\psi'(0)$ = 1 for odd states and $\psi(0)$ = 1 and $\psi'(0)$ = 0 for even states. Energy values in the equation are chosen by trial and error; the quality of the choice is judged by how close ψ fits the boundary condition. For these potentials that condition is ψ → 0 as x → ∞. A poor choice of E results in ψ diverging quickly, while better choices of E keep ψ near zero over a larger range of values. Again, parameter values were chosen to minimize the maximum error in the 16 x 16 case; the values are b = 1.645977 for the Hermite Functions and b = 5.247306 for the sech polynomials. The results for this potential are shown in Tables 5 and 6. The true energy values given in the tables are accurate to the number of digits shown.

CONCLUSIONS

The results given in Tables 1-6 show some consistent patterns. First, except for the square well potential, the calculations using the sech polynomials give better energies than those using Hermite Functions. This is true for the small basis sets and remains so as the sets are enlarged, although the low energy states of the e^{-x^2} potential calculated with Hermite Functions have "caught up" in the 26 x 26 case.

The square well is the exception. We do not know what, if anything, makes this case different. With only three potentials investigated, a sweeping generalization should not be made, but should it prove true that the sech polynomials give better accuracy for the general case, the square well results are anomalous. It may be that the discontinuity in the potential's derivative is responsible; however, it is not clear why that should affect the Sech Functions so much more than the Hermite Functions. Clearly, more work is warranted here.

A second observation is that the calculations are much faster using Hermite Functions. All of the computation times, for both basis sets, show a con-

Table 3. A comparison of the calculated energies of the square well potential using Hermite Functions and Sech Functions.

| | True Energies | Basis Set Size | | |
		16 x 16	20 x 20	26 x 26
Hermite Functions				
E_0	-36.329354	-36.326241	-36.327061	-36.328040
E_1	-33.370612	-33.356871	-33.361853	-33.365399
E_2	-28.481947	-28.453676	-28.460959	-28.470079
E_3	-21.746346	-21.692373	-21.709459	-21.725061
E_4	-13.346977	-13.268379	-13.286394	-13.314615
E_5	-3.853913	-3.733395	-3.737808	-3.801060
Calculational Time		199 sec	517 sec	1708 sec
Sech Functions				
E_0	-36.329354	-36.318742	-36.320752	-36.324656
E_1	-33.370612	-33.320784	-33.342425	-33.354259
E_2	-28.481947	-28.373490	-28.398686	-28.435904
E_3	-21.746346	-21.535710	-21.611499	-21.677984
E_4	-13.346977	-12.927119	-13.108181	-13.199459
E_5	-3.853913	-3.485023	-3.514844	-3.709793
Calculational Time		347 sec	1042 sec	4960 sec

Table 4. A comparison of the relative errors (%) of the calculated energies of the square well potential using Hermite Functions and Sech Functions.

| | Basis Set Size | | |
	16 x 16	20 x 20	26 x 26
Hermite Functions			
E_0	0.008570	0.006313	0.003617
E_1	0.041176	0.026247	0.015622
E_2	0.099258	0.073688	0.041669
E_3	0.248192	0.169622	0.097878
E_4	0.588883	0.453909	0.242463
E_5	3.127162	3.012638	1.371418
Sech Functions			
E_0	0.029212	0.023679	0.012931
E_1	0.149318	0.084466	0.049002
E_2	0.380791	0.292327	0.161655
E_3	0.968603	0.620089	0.314360
E_4	3.145717	1.789137	1.105252
E_5	9.571833	8.798044	3.739581

Table 5. A comparison of the calculated energies of the potential well $V(x) = V_0 exp(-x^2)$ using Hermite Functions and Sech Functions.

| | True Energies | Basic Set Size | | |
		16 x 16	20 x 20	26 x 26
Hermite Functions				
E_0	-23.92594	-23.925830	-23.925927	-23.925938
E_1	-17.29571	-17.295096	-17.295643	-17.295705
E_2	-11.50453	-11.499700	-11.503953	-11.504522
E_3	-6.642870	-6.635298	-6.641860	-6.642747
E_4	-2.856653	-2.834841	-2.853567	-2.856632
E_5	-0.442474	-0.393145	-0.425211	-0.437564
Calculational Time		227 sec	558 sec	1763 sec
Sech Functions				
E_0	-23.92594	-23.925920	-23.925930	-23.925936
E_1	-17.29571	-17.295640	-17.295666	-17.295696
E_2	-11.50453	-11.504378	-11.504399	-11.504461
E_3	-6.642870	-6.642563	-6.642688	-6.642748
E_4	-2.856653	-2.854934	-2.856453	-2.856485
E_5	-0.442474	-0.441446	-0.442270	-0.442378
Calculational Time		367 sec	1078 sec	5004 sec

Table 6. A comparison of the relative errors (%) of calculated energies of the potential $V(x) = V_0 exp(-x^2)$ using Hermite Functions and Sech Functions.

| | Basis Set Size | | |
	16 x 16	20 x 20	26 x 26
Hermite Functions			
E_0	0.000461	0.000051	0.000007
E_1	0.003549	0.000388	0.000027
E_2	0.041981	0.005019	0.000071
E_3	0.113993	0.015200	0.001838
E_4	0.763535	0.108046	0.000751
E_5	11.148594	3.901441	1.109789
Sech Functions			
E_0	0.000085	0.000043	0.000016
E_1	0.000404	0.000253	0.000080
E_2	0.001319	0.001142	0.000602
E_3	0.004618	0.002735	0.001843
E_4	0.060183	0.007016	0.005864
E_5	0.232454	0.046211	0.021732

sistent trend, independent of potential. Therefore, we conclude that the time-limiting step involves the evaluation and integration of the basis functions. It is not known to the authors what method Mathematica uses to evaluate Hermite Polynomials, but the numerical analysis references such as Abramowitz and Stegun (1964) give very efficient methods for well known functions such as these. The Sech Polynomials have not been so thoroughly studied; in our investigations, we could find no faster method than the recurrence relation. Should a faster method become available in the future, Sech Polynomials may provide the best basis functions for calculating bound state energies of localized potentials.

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