Tunneling in a Quartic, Symmetric, Double Well Potential

A Simple Solution Using a Hermite Basis

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Quantum leakage or tunneling is normally presented to undergraduate students in the study of a particle moving in a region of more than one constant potential. Such potentials have many pedagogical advantages but are not realistic. Real systems do not seem to have potentials with steps. However, when realistic potentials are used, the solution of the Schrödinger equation usually requires mathematical expertise beyond that of most undergraduate and first-year graduate students.

We give a relatively simple method for solving the Schrödinger equation for a particle moving in a realistic double well. We shall use Galerkin's variational method (*1*). Galerkin's technique is more straightforward in application than the more popular Rayleigh–Ritz method because it does not require taking derivatives of the energy with respect to the variational parameters when a linear variation function is used. Surprisingly, Galerkin's method is not generally used in the classroom.

The Problem

Consider a particle of mass m moving under the influence of a potential.

$$V(x) = \alpha x^4 - \beta x^2 + \gamma$$

For convenience we want $V(x) \geq 0$ for all x. Therefore

$$V(x) = \alpha x^4 - \beta x^2 + \frac{\beta^2}{4\alpha} \qquad (1)$$

$$\alpha, \beta > 0$$

This potential has minima at

$$x = \pm\left(\frac{\beta}{2\alpha}\right)^{1/2}$$

and a central potential barrier of height

$$\gamma = \left(\frac{\beta^2}{4\alpha}\right)$$

(See Fig. 1.)

Potential functions similar to the one in Figure 1 have been used extensively to study

- hydrogen bonding (*2*)
- proton transfer in DNA (*3*)
- Jahn–Teller effects in cyclooctatetraenes (*4*)
- inversion doubling in ammonia (*5*)
- internal rotation (*6*)
- tunneling in sandwich compounds (*7*)
- many other chemical, physical, and engineering processes (*8*)

The Schrödinger equation for this one-dimensional problem can be written as

$$(H - \lambda)\psi(x) = 0 \qquad (2)$$

where

$$H \equiv \frac{d^2}{dx^2} - \left(\frac{2m}{\hbar^2}\right)V(x)$$

$$\lambda \equiv -\left(\frac{2mE}{\hbar^2}\right)$$

Galerkin's Method

Galerkin's method for solving a differential equation like eq 2 consists of expressing $\psi(x)$ as a linear combination of some basis functions, and then making each and every one of the basis functions orthogonal to $(H - \lambda)\psi(x)$. As trivial as this may look, it leads to the Rayleigh–Ritz secular determinant. Galerkin's method minimizes the energy by appealing directly to the variational aspects of the eigenvalue problem (*9*).

Use of Hermite Functions

To illustrate Galerkin's method consider an approximation to $\psi(x)$ to be a linear combination of r Hermite functions.

$$\psi(x) = \sum_{n=0}^{r-1} c_n \varphi_n(x) \qquad (3)$$

Equation 3 describes a curtailed Gram–Charlier series. In the limit of $r \to \infty$ exact results are obtained. We have chosen the Hermite functions because they

- span the space $(-\infty, +\infty)$
- satisfy the boundary conditions
- form a complete orthonormal set

We define the Hermite functions by

$$\varphi_n(x) = N_n\left(e^{-x^2/2}\right)H_n(x) \qquad (4)$$

where N_n is the normalization constant, and $H_n(x)$ is the nth Hermite polynomial.

We now substitute eq 3 in eq 2, multiply on the left by one of the r basis functions, for example, the ith, and integrate over all space.

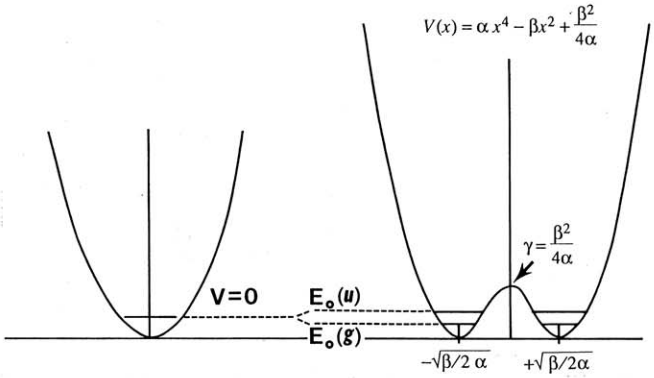

Figure 1. The symmetric double well can be considered as the overlap of two single-well oscillator potentials. The energy levels of the single well are split in the double well. Only the splitting of the $v = 0$ level is shown.

$$\sum_{n=0}^{r-1} c_n \langle \varphi_i | H - \lambda | \varphi_n \rangle = 0 \tag{5}$$

$$i = 0, 1, 2, \ldots, (r-1)$$

We suppress the x dependence for clarity. It is clear from eq 5 that we have obtained the identical determinant as that obtained using the Rayleigh–Ritz method. Notice that it was not necessary to take derivatives of E with respect to the variational parameters c_n. An advantage of using the Hermite functions is that we can change the differential operator in H to a multiplicative operator using the following relation.

$$\varphi_n''(x) = (x^2 - (2n+1))\varphi_n(x) \tag{6}$$

Combining eqs 6, 2, and 5, and multiplying by –1, we get

$$\sum_{n=0}^{r-1} c_n \langle \varphi_i \left| \left(2m/\hbar^2\right) V(x) - x^2 + (2n+1) - \left(2mE/\hbar^2\right) \right| \varphi_n \rangle = 0 \tag{7}$$

All the integrals in eq 7 are of the type

$$\langle \varphi_i | x^{2s} | \varphi_n \rangle \tag{8}$$

$$s = 0, 1, 2$$

The integrals in eq 8, for $s = 1$ and 2, can be evaluated using the recursion relation for the Hermite polynomials. In particular,

$$x^2 H_n(x) = \frac{1}{4} H_{n+2}(x) + \left(n + \frac{1}{2}\right) H_n(x) + n(n-1) H_{n-2}(x) \tag{9}$$

To simplify the nonzero elements of the secular determinant obtainable from eq 7 we arbitrarily set

$$\frac{m}{\hbar^2} = 1$$

The energy values will then be in arbitrary units.

From eqs 7–9 and the orthogonality properties of the Hermite functions, we see that we need calculate only three matrix elements: $i = n$, $n + 2$, and $n + 4$. The expressions for the nonzero matrix elements are

$$H_{n,n} = \left(\frac{3\alpha}{2}\right)(2n^2 + 2n + 1) - (2\beta + 1)\left(n + \frac{1}{2}\right) + (2n+1) + \frac{\beta^2}{2\alpha} \tag{10}$$

$$H_{n,n+2} = \left((n+1)(n+2)\right)^{1/2} \left((2n+3)\alpha - \frac{2\beta+1}{2}\right) \tag{11}$$

$$H_{n,n+4} = \frac{\alpha}{2}\left((n+1)(n+2)(n+3)(n+4)\right)^{1/2} \tag{12}$$

To study the tunneling process as a function of the barrier height we set the distance between the minima at a fixed value, for example, 2. Therefore, $\beta = 2\alpha$. From eqs 10–12, we get the following case with fixed separation.

Fixed Separation between the Minima: $\beta = 2\alpha$

$$\therefore \text{ barrier height} = \frac{\beta}{2}$$

$$\therefore V(x) = \frac{\beta}{2}(x^4 - 2x^2 + 1)$$

$$H_{n,n} = \frac{3\beta}{4}(2n^2 + 2n + 1) + n(1 - 2\beta) + \frac{1}{2} \tag{13}$$

$$H_{n,n+2} = \left((n+1)(n+2)\right)^{1/2} \left(\frac{\beta(2n+1) - 1}{2}\right) \tag{14}$$

$$H_{n,n+4} = \frac{\beta}{4}\left((n+1)(n+2)(n+3)(n+4)\right)^{1/2} \tag{15}$$

Using the above equations we can choose values of β, solve the secular determinants, and obtain the eigenvalues.[1] We can then investigate how each of the eigenvalues varies with respect to changes in the barrier height. To see the effect of changing the separation between the minima while maintaining a fixed barrier height, we set $\beta^2 = 4\alpha$. From eqs 10–12 we get the following case.

Fixed Barrier Height: $\beta^2 = 4\alpha$

$$\text{distance between minima} = \sqrt{8/\beta}$$

$$V(x) = \frac{\beta^2}{4}x^4 - \beta x^2 + 1$$

$$H_{n,n} = \frac{3\beta^2}{8}(2n^2 + 2n + 1) - \beta(2n+1) + n + \frac{5}{2} \tag{16}$$

$$H_{n,n+2} = \left((n+1)(n+2)\right)^{1/2} \left((2n+3)\frac{\beta^2}{4} - \frac{2\beta+1}{2}\right) \tag{17}$$

$$H_{n,n+4} = \frac{\beta^2}{8}\left((n+1)(n+2)(n+3)(n+4)\right)^{1/2} \tag{18}$$

Computer Software and Procedures

We have done calculations for values of β from 0.10 to 10.0 and for determinants of orders up to 100. For determinants of orders greater than 4 the calculations were done using readily available programs both in BASIC and FORTRAN. The BASIC program uses a Jacobi diagonalization procedure (*10*), whereas the FORTRAN program uses the more efficient Givens–Householder–Wilkinson algorithm.

The BASIC Jacobi program was chosen to show that the calculations can be carried out with many inexpensive microcomputers as purchased. With the BASIC Jacobi program we have gone up to 50 basis functions with our IBM-compatible microcomputer. The diagonalization of the 40 × 40 matrix took only a few minutes.

To verify the BASIC Jacobi results, we ran the calculations again using the FORTRAN program in our mainframe (IBM-4381) using double and quadruple precision and going up to 100 basis functions. The more extensive calculations confirm the single-precision results obtained using the BASIC Jacobi program on the microcomputer.

Discussion

Tunneling Probability and Time

For most values of β that we tried, convergence to 4 significant figures in the lower eigenvalues was obtained using 40 or fewer basis functions in the BASIC Jacobi program. Previous theoretical studies for step potentials indicate that the tunneling probability

- decreases with increasing mass of the particle
- decreases with increasing separation between the minima
- decreases with increased barrier height

Our results are in agreement with those studies. As required by theory, the approximate eigenvalues found by us appear in ordered pairs. We shall use

$$(E_v(u), E_v(g))$$

[1] For symmetric potentials it is advantageous to write eq 3 as two distinct sums: one over the even Hermite functions and the other over the odd Hermite functions. Then a $2n$ term expansion can be done with two determinants of order n.

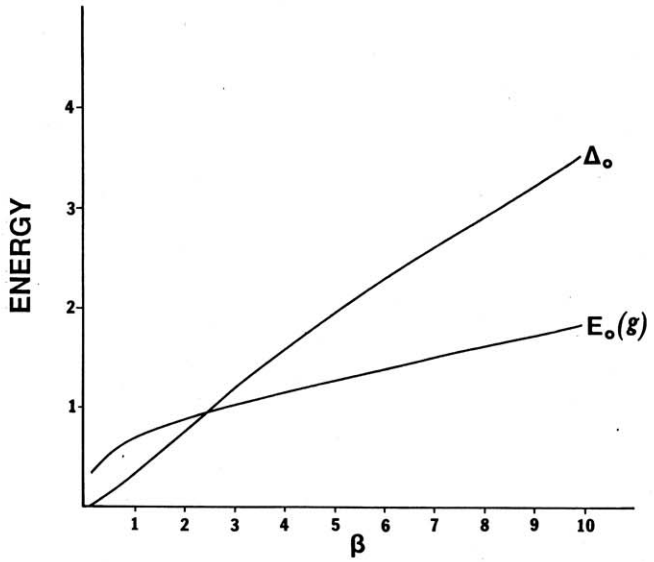

Figure 2. Fixed barrier height is 1.

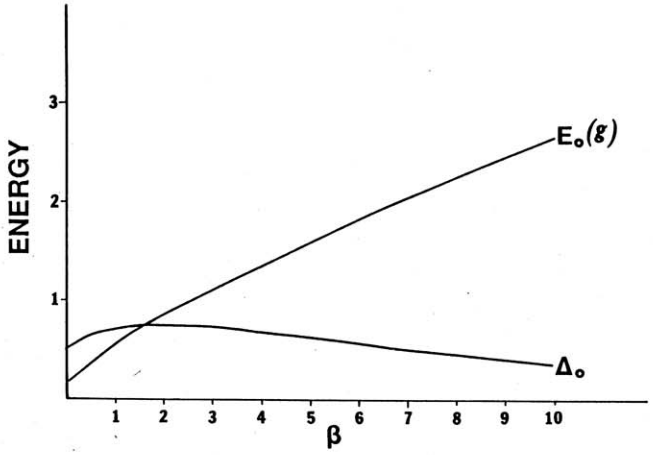

Figure 3. Fixed minima separation is 2.

to designate the ordered pairs that correspond to the same vibrational quantum number v.

We find, as expected, that the ungerade level is higher than the corresponding gerade level. Thus, each of the nondegenerate levels of the harmonic oscillator gives rise to two levels in the double well (Fig. 1). This means that vibrationless transitions between gerade and ungerade levels can occur. Because the g–u transitions need not occur within the same well, we have the possibility of tunneling from one well to the other if $E_0(g)$ lies below the maximum. The average time that a particle takes to effect the passage from one well to the other varies inversely with Δ_v (*11*).

$$t = \frac{1}{2c(E_v(u) - E_v(g))} \equiv \frac{1}{2c\Delta_v} \tag{19}$$

where c is the speed of light, and Δ_v is in cm^{-1}.

Behavior of the Potential Function

To examine the behavior of our potential function with respect to tunneling let us first discuss the case of fixed barrier height (see Fig. 2). Our results show that for $\beta < 3$ the $E_0(g)$ level lies below the barrier height. As β increases, the separation between the minima decreases, and one expects that more tunneling will occur. That, indeed, is what our calculations show. We also find that Δ_v increases with v, a result observed for other potentials (*12*).

When we maintain the separation between the minima constant and vary the barrier height (see Fig. 3), we find that $E_0(g)$ lies below the barrier height for $\beta > 1.5$. However, Δ_0 increases with β, goes through a maximum at $\beta = 1.5$, and then decreases with β. This result should not be interpreted as implying that the tunneling rate increases as the barrier height increases. After all, the term tunneling applies only when a particle passes through a potential energy barrier whose height is greater than the particle's energy. For $\beta > 1.5$, $E_0(g)$ is already above the barrier height, and the term tunneling does not apply.

Barrier Thickness and Area

We also find that as β increases the barrier "thickness" increases (for fixed minima separation). The "thickness" of the barrier can be defined as the horizontal distance between two points $(\pm x, k)$ with

$$V(x) = k$$

$$0 \le k \le \beta/2$$

$$|x| \le 1$$

With this definition the "thickness" of the barrier is

$$2\sqrt{1 - \sqrt{\frac{2k}{\beta}}} \tag{20}$$

For a given value of $\beta > 1.5$, the doublet splitting Δ_v will determine the rate of tunneling. The area of the barrier above the kth energy level has been correlated with the tunneling probability (*13*). That area is readily found to be

$$\frac{2\beta\sqrt{1 - \sqrt{2k/\beta}}}{15}\left(4 + 2\sqrt{\frac{2k}{\beta}} - 6\left(\frac{2k}{\beta}\right)\right) \tag{21}$$

Our result for the area cut off is similar to the one reported in the literature (*13*). Both α and β can be calculated from spectroscopic data (*13*) or from other data taken from the literature. Finally, it can be shown that increasing the mass of the particle is equivalent to increasing the barrier height for our potential.

Conclusion

Our treatment has several advantages.

- The student is introduced to the Galerkin version of the variational method.
- Mathematical techniques learned in other courses are used.
- Most of the known features of quantum leakage are obtained from a relatively simple, realistic potential.
- Reliable calculations can be carried out using a short, published program in BASIC—a language widely available in microcomputers.
- The method outlined here can be applied to other potentials and other bases.
- Nontrivial undergraduate research in quantum chemistry can be carried out.
- No artificial step functions are needed because many real systems can be approximated using simple polynomial potentials.

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