Application of Hermite Polynomials
In the Quantum Simple Harmonic Oscillator

Physical Chemistry I Legacy Project
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I. Introduction

The Quantum Simple Harmonic Oscillator (QSHO) is a very useful model in Quantum Mechanics. According to Dr. Ulness, it is “arguably the single most important model in all of physics.” Although the QSHO is simply the quantum equivalent of the classical mass-spring problem, solving the Schrödinger’s equation for QSHO to obtain a set of wave functions is not that simple. It involves solving a non-linear second-order ordinary differential equation and the solutions contain special functions called the Hermite polynomials. However, most aspects of this process are still accessible to undergraduate students with enough coursework in mathematics. In this presentation, we will explore the step-by-step process of solving the Schrödinger's equation for QSHO.

II. Schrödinger’s Equation for QSHO

After substituting proper expressions for the energy E, the Schrödinger’s equation for QSHO can be described as follows:

$$-\frac{\hbar^2}{2m}\Psi''(x)+\frac{kx^2}{2}\Psi(x)-E\Psi(x)=0\,, \qquad \textbf{[1]}$$

where $\hbar$ is the Planck constant, m is the mass of the particle, k is the spring constant and E is the energy of the particle.

However, it is usually convenient to write the differential equations in a form where the coefficient of the highest order derivative of the function is one. Therefore, [1] becomes

$$\Psi''(x)+\left(\frac{2mE}{\hbar^2}-\frac{mkx^2}{\hbar^2}\right)\Psi(x)=0 \qquad \textbf{[2]}$$

Solving this differential equation directly can be quite difficult and probably unwise. But this differential equation is quite similar to another nonlinear differential equation called the Hermite differential equation whose solution is a set of polynomials under proper circumstances. Therefore, let us consider the Hermite differential equation first.

III. Hermite Polynomials

Following differential equation is called the Hermite differential equation.

$$y''(x) - 2xy'(x) + 2ny(x) = 0 \qquad \textbf{[3]}$$

It is shown in the Appendix that the solutions to this equation are polynomials called the Hermite polynomials for non-negative integer values of *n*. Please see Table 1 for first few Hermite polynomials. Therefore, if we can somehow transform [2] to [3], then we can solve [2] using [3]. Then, it is only reasonable to expect the Hermite polynomials in the solution of [2]. However, Table 1 shows that Hermite polynomials are not bounded as *x* approaches ±∞. Since the solutions of [2] must be wave functions, their normalizability requires them to be bounded. Hence, it is clear that there will be something else "enveloping" the Hermite polynomials so that the solutions of [2] will be wave functions.

It can also be shown with the assist of an operator defined as $\hat{L}y = -e^{x^2}[e^{-x^2}y']'$ that the Hermite polynomials form an "orthogonal" set with the weight function e^{-x^2}. (We will not go into detail since it is just a matter of mathematical manipulation and needs undergraduate coursework in differential equation and linear algebra to fully understand this.) In another word,

$$\int_{-\infty}^{\infty} H_m(x) H_n(x) e^{-x^2}\, dx = 0 \qquad \textbf{[4]}$$

where H_m and H_n are Hermite polynomials with $m \neq n$. Here, the use of the weight function e^{-x^2} needs to be emphasized. Without it, the integral will not equal to zero. And we also need to note that with the weight function the Hermite polynomials can become bounded. Therefore, it seems convenient to absorb part of the weighting function into the Hermite polynomial. Let us then define

$$Y_n(x) = e^{-x^2/2} H_n(x) \qquad \textbf{[5]}$$

Then, repetitively using product rule of taking derivatives, we have

$$\begin{aligned} H_n(x) &= Y_n(x) e^{x^2/2} \\ H_n'(x) &= Y_n'(x) e^{x^2/2} + Y_n(x)(x e^{x^2/2}) = e^{x^2/2}\left(Y_n'(x) + xY_n(x)\right) \\ H_n''(x) &= e^{x^2/2}\left[Y_n''(x) + Y_n(x) + xY_n'(x)\right] + xe^{x^2/2}\left[Y_n'(x) + xY_n(x)\right] \end{aligned} \qquad \textbf{[6]}$$

But, $H_n(x)$ is a solution to [3], i.e., $y(x) = H_n(x)$. Substituting [6] in [3],

$$\begin{aligned}&e^{x^2/2}Y_n''(x)+(2xe^{x^2/2})Y_n'(x)+(e^{x^2/2}+x^2e^{x^2/2})Y_n(x)\\&-(2xe^{x^2/2})Y_n'(x)-(2x^2e^{x^2/2})Y_n(x)+2ne^{x^2/2}Y_n(x)=0\\&\Rightarrow e^{x^2/2}Y_n''(x)+e^{x^2/2}\left[1+x^2-2x^2+2n\right]Y_n(x)=0\\&\Rightarrow Y_n''(x)+\left[(2n+1)-x^2\right]Y_n(x)=0\end{aligned} \qquad \textbf{[7]}$$

This means that $Y_n(x)$ satisfies the differential equation [7].

IV. Solving Schrödinger's Equation for QSHO

Please note that [7] is now more like [2], which is the Schrödinger's equation we are trying to solve. Only the coefficient of x^2 in [2] seems troubling. However, please note that merely factoring out $\frac{mk}{\hbar^2}$ will not work because we also need to maintain the coefficient of $\Psi''(x)$ to be 1 so that [2] will look like [7]. The chain rule comes into play here. We now need to substitute $\Psi(x)$ with a more convenient function $\psi(z)$ such that

(i) $\psi(z(x)) = \Psi(x)$, and
(ii) $\psi(z(x))$ satisfies [7].

We now need to determine a simple relation between z and x, i.e. the function $z(x)$, so that the above requirements (i) and (ii) are met. Then let

$$\begin{aligned}&z=\alpha x\\&\Rightarrow x=z/\alpha\end{aligned} \qquad \textbf{[8]}$$

But (i) says $\Psi(x) = \psi(z)$. Then

$$\Psi(x)=\Psi(z/\alpha)=\psi(z) \qquad \textbf{[9]}$$

Therefore,

$$\frac{d}{dz}\Psi(x)=\frac{d}{dz}\psi(z) \qquad \textbf{[10]}$$

Using chain rule, [10] becomes

$$\frac{d}{dx}\Psi(x)\frac{dx}{dz}=\frac{d}{dz}\psi(z)$$
$$\Rightarrow \Psi'(x)\frac{d}{dz}\left(z/\alpha\right)=\psi'(z)$$
$$\Rightarrow \Psi'(x)(1/\alpha)=\psi'(z) \qquad \textbf{[11]}$$
$$\Rightarrow \Psi''(x)(1/\alpha)^2=\psi''(z)$$
$$\Rightarrow \Psi''(x)=\alpha^2\psi''(z)$$

Here, we need to note that $\Psi'(x)$ and $\Psi''(x)$ are derivatives with respect to *x*, but $\psi'(x)$ and $\psi''(x)$ are derivatives with respect to *z*.

By substituting [11] in [2], the equation [2] (the Schrödinger's Equation for QSHO) becomes

$$\alpha^2\psi''(z)+\left(\frac{2mE}{\hbar^2}-\frac{mkz^2}{\hbar^2\alpha^2}\right)\psi(z)=0$$
$$\Rightarrow \psi''(z)+\left(\frac{2mE}{\alpha^2\hbar^2}-\frac{mkz^2}{\hbar^2\alpha^4}\right)\psi(z)=0 \qquad \textbf{[12]}$$

It is now important not to lose track of what we are trying to achieve. We are trying to transform the equation [2] to look like [7] which we know how to solve. Now that we have equation [12], we want it to look like [7]. Then,

$$\frac{mk}{\hbar^2\alpha^4}=1\Rightarrow \alpha^4=\frac{mk}{\hbar^2}\Rightarrow \alpha=\frac{(mk)^{1/4}}{\hbar^{1/2}} \qquad \textbf{[13]}$$

Now, substituting [13] in [12], it becomes

$$\psi''(z)+\left(\frac{2E}{\hbar}\sqrt{\frac{m}{k}}-z^2\right)\psi(z)=0 \qquad \textbf{[14]}$$

Now, [14] has exactly the same form as [7] whose solutions are in the form of [5]. Therefore, solutions to [14] also are in the form of

$$\psi_n(z)=e^{-z^2/2}H_n(z) \qquad \textbf{[15]}$$

where $z = \alpha\, x$ with the value of α given by [13].

Recall that only for integer values of n, the solutions of [3] converge to H_n. For non-integer values of n, the solutions of [3] are infinite series with the power of x going to ∞. Therefore, the boundary conditions that must be satisfied by wave functions

$$\lim_{x \to \pm\infty} \Psi(x) = 0$$

cannot be met since the function will increase without bound as x approaches to ±∞. Therefore, n being an integer also makes sense physically.

By comparing [14] with [7], we can see that multiple values of E exist since

$$\frac{2E}{\hbar}\sqrt{\frac{m}{k}} = 2n + 1 \qquad \textbf{[16]}$$

where $n = 0, 1, 2, 3, \ldots$.

But, as seen in our familiar classical mass-spring problems, $\sqrt{\frac{k}{m}} = \omega$. Therefore, [16] becomes:

$$\frac{2E}{\hbar\omega} = 2n + 1 \Rightarrow E = \left(n + \tfrac{1}{2}\right)\hbar\omega \qquad \textbf{[17]}$$

Note that [17] is our energy level formula we learnt in our class!

The problem of normalizing [15] to make a useful wave function remains. It can be done using a series formula for H_n. However, the Hermite polynomials are described using recursive relations as shown in the Appendix, therefore obtaining a non-recursive formula for H_n by recognizing the patterns of coefficients can be difficult, and proving it by mathematical induction can be tedious. Another way of obtaining the non-recursive series formula from the so-called generating functions is ‘nicer’ but it is beyond our scope for the moment. Once we have obtained that non-recursive formula for H_n, ψ_n can be normalized. Again, this involves the use of the orthogonality of Hermite polynomials and putting them in self-adjoint form. Skipping all these details, the normalized version of ψ_n is as follows:

$$\psi_{norm,n}(z) = \left[2^{-n/2}\pi^{-1/4}(n!)^{-1/2}\right]e^{-z^2/2}H_n(z) \qquad \textbf{[18]}$$

which is the formula given in our class notes.

Conclusion

As shown in this presentation, *analytically* solving even a *single simple* harmonic oscillator in quantum mechanics can be this long and complicated. Then solving *billions* of *complex* quantum models is beyond question. This underlines the importance of numerical methods for solving differential equations and the physical approximations such as the Born-Oppenheimer Approximation. Moreover, by going through a relatively detailed process of finding solutions to a Schrödinger's equation can help us appreciate all the mathematical hard work and ingenuity behind something that we easily 'solve' by just typing in the Mathematica.

Appendix: Solving the Hermite Differential Equation

The Hermite differential equation is

$$y''(x) - 2xy'(x) + 2ny(x) = 0 \qquad \textbf{[20]}$$

Since we want to use n as an index in series formula, we can rewrite [20] replacing n with m.

$$y''(x) - 2xy'(x) + 2my(x) = 0 \qquad \textbf{[21]}$$

Here *n* is the index and *m* is not a mass or anything; it is just a parameter in the differential equation. Please remember that the mathematical entities in this Appendix have no direct link to physical quantities.

Let $y = \sum_{n=0}^{\infty} c_n x^n$.

Then,

$$y' = \sum_{n=1}^{\infty} nc_n x^{n-1}, y'' = \sum_{n=2}^{\infty} n(n-1)c_n x^{n-2} .$$

Then,

$$\sum_{n=2}^{\infty} n(n-1)c_n x^{n-2} + \sum_{n=1}^{\infty} (-2nc_n)x^n + \sum_{n=0}^{\infty} 2mc_n x^n = 0$$

$$\Rightarrow 2c_2 x^0 + \sum_{n=3}^{\infty} n(n-1)c_n x^{n-2} + \sum_{n=1}^{\infty} (-2nc_n)x^n + 2mc_0 + \sum_{n=1}^{\infty} 2mc_n x^n = 0$$

$$\Rightarrow 2c_2 + 2mc_0 = 0, and \sum_{n=3}^{\infty} n(n-1)c_n x^{n-2} + \sum_{n=1}^{\infty} (-2nc_n)x^n + \sum_{n=1}^{\infty} 2mc_n x^n = 0$$

$$\Rightarrow c_2 = -mc_0, and \sum_{k=1}^{\infty} (k+2)(k+1)c_{k+2}x^k + \sum_{k=1}^{\infty} (-2kc_k)x^k + \sum_{k=1}^{\infty} 2mc_k x^k = 0$$

Collecting the like-terms on the series part, we have

$$(k+2)(k+1)c_{k+2} - 2kc_k + 2mc_k = 0$$

Solving for the highest-indexed c,

$$c_{k+1} = \frac{2(k-m)}{(k+2)(k+1)} c_k , k = 1,2,3,...$$

Finding first few values of c_k,

$$c_0 = c_0 , c_1 = c_1$$

$$c_2 = (-m)c_0 , c_3 = \frac{2(1-m)}{3!} c_1$$

$$c_4 = \frac{2^2(2-m)(-m)}{4!} c_0 , c_5 = \frac{2^2(3-m)(1-m)}{5!} c_1$$

$$c_6 = \frac{2^3(4-m)(2-m)(-m)}{6!} c_0 , c_7 = \frac{2^3(5-m)(3-m)(1-m)}{7!} c_1$$

$$\therefore y(x) = c_0 + c_1 x^1 + c_2 x^2 + c_3 x^3 + c_4 x^4 + c_5 x^5 + c_6 x^6 + c_7 x^7 + ...$$

$$= c_0 \left[1 + (-m) + \frac{2^2(2-m)(-m)}{4!} + \frac{2^3(4-m)(2-m)(-m)}{6!} + ... \right]$$

$$+ c_1 \left[\frac{2(1-m)}{3!} + \frac{2^2(3-m)(1-m)}{5!} + \frac{2^3(5-m)(3-m)(1-m)}{7!} + ... \right]$$

Therefore,

$$\begin{aligned} y_1(x) &= c_0\left[1+(-m)+\frac{2^2(2-m)(-m)}{4!}+\frac{2^3(4-m)(2-m)(-m)}{6!}+\ldots\right], and \\ y_2(x) &= \left[\frac{2(1-m)}{3!}+\frac{2^2(3-m)(1-m)}{5!}+\frac{2^3(5-m)(3-m)(1-m)}{7!}+\ldots\right] \end{aligned} \qquad \textbf{[22]}$$

are the two fundamental solutions of [21].

In [22], we can see that for non-negative integer values for m, the power series collapse into finite sum, i.e., polynomials. Following is a table of first few values for m. The last column is the scaled version of the solutions so that the coefficient of the higher power of *x* is in the form of 2^m, which are called the Hermite polynomials.

Talbe 1. Hermite Polynomials for 0 to 4.

$$m=0, y_1=1 \Rightarrow H_0=1$$

$$m=1, y_1=x \Rightarrow H_1=2x$$

$$m=2, y_1=1-2x^2 \Rightarrow H_2=2^2x^2-2$$

$$m=3, y_1=x-\frac{2^2x^3}{3!} \Rightarrow H_3=2^3x^3-12x$$

$$m=4, y_1=1-4x^2+\frac{2^2(-2)(-4)x^4}{4!} \Rightarrow H_4=2^4x^4-48x^2+12$$

■

Reference:

Afkan's *Mathematical Methods for Physicists*.