Workshop: Curvature based solution of the Schrödinger equation

Quantum aspects of physical chemistry

http://quantum.bu.edu/courses/PLTL/1/1.pdf
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The best way to understand the curvature form of the Schrödinger equation,

$$\begin{aligned}
&\text{curvature of } \psi \text{ at } x\\
&\qquad = -\frac{2\,m}{\hbar^2}\,\text{kinetic energy at } x \times \psi \text{ at } x\\
&\qquad = -\frac{2\,m}{\hbar^2}\,[E - V(x)]\,\psi(x)
\end{aligned}$$

is to see how it works for an example.

It is very convenient to use units of energy and length chosen so that the proportionality constant, $2\,m/\hbar^2$, is equal to one, so that the Schrödinger equation becomes

$$\text{curvature of } \psi \text{ at } x = -[E - V(x)]\,\psi(x).$$

The energy and length units that correspond to setting $2\,m/\hbar^2$ equal to one depend on the problem at hand.

> 1. Show that if energy is measured in multiples of the zero point energy of an infinite square well of width L, namely $h^2/(8\,m\,L^2)$, then setting $2\,m/\hbar^2$ equal to one means the zero point energy will have the numerical value $(\pi/L)^2$. That is, if the well is width $L = \pi$, then the zero point energy will be 1.

We have seen how to use the Schrödinger equation to find a next value of the function ψ from two adjacent, preceding values.

$$\begin{aligned}
\psi_3 &= \text{newSlope} \times (x_3 - x_2) + \psi_2\\
&= (\text{initialSlope} + \text{changeInSlope}) * (x_3 - x_2) + \psi_2\\
&= \left\{\frac{\psi_2 - \psi_1}{x_2 - x_1} + \text{slopeOfSlope}[x_2] \times (x_3 - x_2)\right\} \times (x_3 - x_2) + \psi_2\\
&= \left\{\frac{\psi_2 - \psi_1}{x_2 - x_1} - T(x_2) \times \psi_2 \times (x_3 - x_2)\right\} \times (x_3 - x_2) + \psi_2\\
&= \left\{\frac{\psi_2 - \psi_1}{x_2 - x_1} - [E - V(x_2)] \times \psi_2 \times (x_3 - x_2)\right\} \times (x_3 - x_2) + \psi_2
\end{aligned}$$

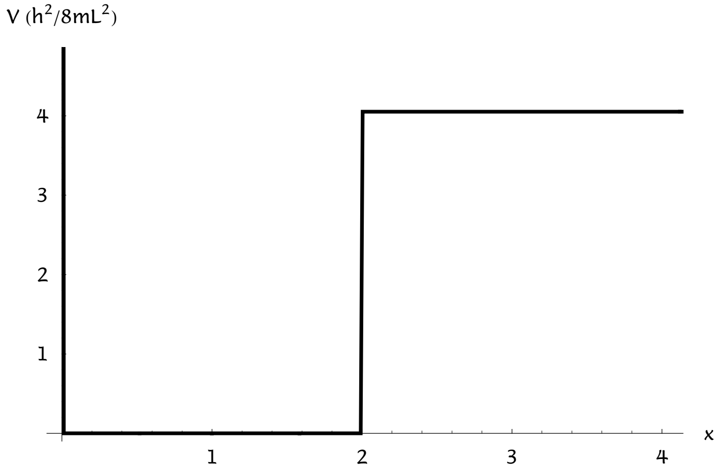
The set of points x_1, x_2, x_3, … is known as the integration mesh. It is easiest to use a mesh of evenly spaced points.

> 2. Show that it we denote the even mesh spacing as $s = x_{j+1} - x_j$, then $\psi_3 = \left\{ 2 - s^2 [E - V(x_2)] \right\} \psi_2 - \psi_1$.

This last expression shows that each new value, $\psi_{3,}$ depends on: the previous two values, $\psi_1$and ψ_2; the previous two positions, $x_1$and x_2; the new position, x_3; the potential energy at the immediately preceding position, $V(x_2)$; and the total energy, E.

Once we have the new value of ψ we can use it, and the immediately preceding value, to get a next new value of ψ. We can continue in this way to determine the how the function ψ changes along a set of successive positions.

To carry out the stepwise solution of the Schrödinger equation, we need a potential energy function, the values of the wavefunction at the first two mesh points, and value of the energy. Here is the potential energy function that we will use.



The potential energy is infinite for $x < 0$, zero for $0 \leq x \leq 2$, and 10 units high for $x > 2$.

> 3. If the potential energy for $x > 2$ were infinite, what would the lowest energy be?

> 4. How do you expect the actual lowest energy to compare with its value when the potential energy is infinite for $x > 2$.

> 5. If the potential energy for $x > 2$ were infinite, what would the lowest energy wavefunction look like?

> 6. How do you expect the actual lowest energy wavefunction to compare with the lowest energy wavefunction when the potential energy is infinite for $x > 2$?

> 7. Assume a mesh of spacing 0.2, and initial wavefunction values $\psi(x_1) = 0$ and $\psi(x_2) = 0.01$. Use the Schrödinger equation to find the values of $\psi(x_j)$ out to $x_n = 4.0$ for energy $E = 1$ unit, that is, using the numerical value $(\pi/2)^2 = 2.47$. Plot your wavefunction values versus x.

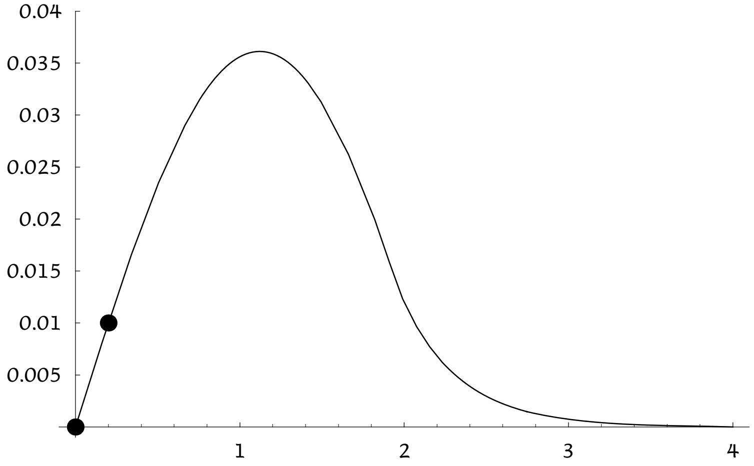
> 8. Assume a mesh of spacing 0.2, and initial wavefunction values $\psi(x_1) = 0$ and $\psi(x_2) = 0.01$. Use the Schrödinger equation to find the values of $\psi(x_j)$ out to $x_n = 4.0$ for energy $E = 1$ unit, that is, using the numerical value $(\pi/2)^2 = 2.47 - 1 = 1.47$. Plot your wavefunction values versus x.

> 9. Assume a mesh of spacing 0.2, and initial wavefunction values $\psi(x_1) = 0$ and $\psi(x_2) = 0.01$. Use the Schrödinger equation to find the values of $\psi(x_j)$ out to $x_n = 4.0$ for

energy $E = 1$ unit, that is, using the numerical value $(\pi / 2)^2 = 2.47 - 0.50 = 1.97$. Plot your wavefunction values versus x.

10. From the plots of your wavefunctions for the previous questions, estimate the energy of the lowest energy level.

11. The figure below is a plot of the wavefiunction of the lowest energy level, with the first two values of the wavefunction marked with dots. Explain why the same value of the energy would be gotten if instead another value was chosen for the $\psi(x = 0.2)$. *Hint*: Consider if a solution to the Schrödinger equation may be multiplied by a constant and still be a solution at the same energy.



12. The integral of the square of the wavefiunction of the lowest energy level, shown above, is $\int_0^4 \psi(x)^2 \, dx = 0.0015$. Plot the normalized wavefunction of the lowest energy level, with the first two values of the wavefunction marked with dots. Are the first two values or the normalized waveunction different from those of the unnormalized wavefunction? If they are different, does this mean that prior to normalization we may use anything for the second wavefunction value?