Mathematica Exercise: Particles in 2D Boxes

Physical Chemistry I
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M. Francl

Phenyl rings and related structures are one of the most common structura organic chemistry. Let's consider some simple quantum mechanical models simple model imagines the π electrons moving in freely over a hexagonal plane, a particle in a 2 dimensional hexagonal box. Solving this problem, perhaps not surprisingly, is not trivial, but we can begin by simplifying the model even further and consider benzene to be a square box.

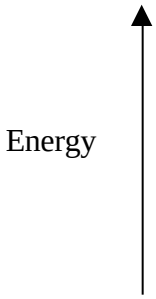
Begin by writing down the Schrodinger equation for a single particle inside a square box, where the sides of the box have length *a*. Be sure to specify the boundary conditions.

Now, by analogy to our solution for the 3 dimensional problem, write down the solutions for the energy and the wavefunction, $\psi(x,y)$.

E = $\psi(x,y)$ =

Using these results, make a sketch, to scale, of the energy levels for the π electrons in benzene. You will need to make an estimate of the parameter *a*. It may be helpful to recall that the length of the CC bond in benzene is 1.40Å. There are several reasonable ways to choose *a*; be sure to write down your reasoning.

a =



Use *Mathematica* to plot the corresponding wavefunctions. Recall that the command to plot a function in 3 dimensions is **Plot3D[func[x,y],{x,xstart,xend},{y, ystart,yend}]**. For example, to plot f(*x*,*y*)=(sin*x*)(sin*y*) for $-\pi \le x \le \pi$ and $-\pi \le y \le \pi$, use
Plot3D[Sin[x]*Sin[y],{x,-Pi,Pi},{y, -Pi,Pi}]

Print out your plots. To print out only the plots and not all the rest of the notebook, select your graph and under the **File** menu choose **Print Selection**. Sketch the MOs for benzene, can you see any similarities between your wavefunctions and the MOs?

Based on the energy level sketch and the wavefunctions, do you think this model is an adequate or useful description of benzene.

Going further

A next step might be to consider other simple geometric models related to the shape of benzene. For example, it might be reasonable to consider modeling benzene's electrons as particles trapped on a circle, or inside a disk. One might also be able to build up a model using the wavefunctions from the solution of the 2D square box problem along with solutions for a particle trapped in a triangular shaped box.

Start with a box in the form of an equilateral triangle. What are the boundary conditions for this sort of box?

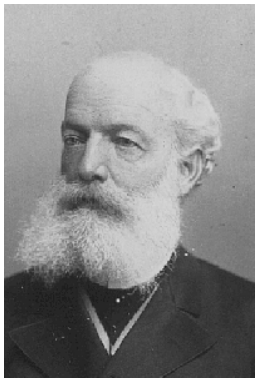
A solution for the ground state wavefunction is [ref. G.B. Shaw, "Degeneracy in the particle-in-a-box problem", *J.Phys. A.* **1974**, *7*, 1537-1546]

Two solutions for this problem are

$$\psi_{n_1}(x,y) = 2(\sin y - 2\sin\tfrac{1}{2}y\cos\tfrac{\sqrt{3}}{2}x) \qquad \psi_{n_2}(x,y) = \sin 2y - 2\sin y\cos\sqrt{3}x$$

Plot these. Can you determine which of these is the ground state, based on what you learned above?

The Culture of Chemistry



August Kekule von Stradonitz
Benzene structure

Kekule was a German of Czech decent. His family had wanted him to study architecture, but he grew interested in chemistry after attending lectures by the famous chemist Liebig at the University of Giessen. While working as a research assistant in London, he was riding home on a bus after visiting a chemist friend. While daydreaming, he "saw" carbon atoms join together in a "giddy dance". This was the beginning of his idea for carbons linking together in chains.

Kekule is credited with writing the first organic chemistry textbook called "Lehrbuch der organischen chemie". Some people feel this book was the birth of organic chemistry as a separate and distinct subject. The following is a quote from Kekule about a dream he had while working on this book....

> "I was sitting writing at my text book, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows, sometimes more closely fitted together; all twisting and turning in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth."

from Prof. Maryellen Nerz-Stormes, "History of Chemistry" web site.
http://www.brynmawr.edu/Acads/Chem/mnerzsto/couper-stradonitz.htm