

# An Alternative Derivation of the Energy Levels of the “Particle on a Ring” System

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The wave functions that result from solving the Schrödinger equation for micro systems must be made subject to four restrictions, namely:

1. They must be normalized.
2. They must be finite.
3. They must be single-valued.
4. They must be continuous.

Application of the third of these conditions usually results in the emergence of quantum numbers that are a crucial feature of wave mechanics. The fourth condition, however, is seldom applied specifically. This paper illustrates how this fourth condition can be used to derive the wave functions and energies of a ring system from those of a simpler linear system.

Elementary courses in wave mechanics commonly include the simple derivation of the energy levels of a particle in a one-dimensional box. The Schrödinger equation for this system includes only one variable, the distance along the box, and it is readily solved to give values of the energy of the particle equal to  $n^2h^2/8ml^2$ , where  $n$  is a quantum number taking integer values from one upwards (1, 2). The system can be used as a simple model of an electron in a long-chain molecule such as a conjugated hydrocarbon and can be used to show, for instance, that the UV absorption wavelength becomes longer as the chain length increases.

If the particle is constrained, not to a straight chain but to a ring (for example as a model of an electron in a benzene ring), the algebra becomes more complex. The Schrödinger equation now has two variables, since the flat ring is two-dimensional, and it is best solved by converting it to polar coordinates—which is not a trivial exercise. The problem, however, can readily be solved by analogy with the particle in a one-dimensional box, since a ring is simply a straight chain bent round into a circle. Provided the wave function remains continuous at the “join”, the resulting functions and energies are allowed solutions of the Schrödinger equation for this system.

## Energy Levels

Table 1 shows the first four energy levels and the associated wave functions for the particle in a one-dimensional box. Consider the first ( $n = 1$ ) function. If the chain is bent round into a ring the first function is no longer an acceptable wave function, since the slope is positive immediately before the “join” and negative immediately after. Conversion from chain to ring therefore causes the function to become discontinuous and therefore forbidden for the ring system. Now consider the second ( $n = 2$ ) function. This has a positive slope at each end of the chain. When converted to a ring, therefore, the function remains continuous and is “allowed” by this criterion of wave mechanics. It is obvious by inspection that the wave functions of the particle in a box model become alternately forbidden and allowed when converted to the particle on

a ring model, only those functions corresponding to an even quantum number being allowed. Thus we can readily formulate the allowed energy levels for the particle on a ring as:

$$\begin{aligned} E &= \frac{(2n)^2h^2}{8ml^2} \\ &= \frac{(2n)^2h^2}{8m(2\pi r)^2} \text{ for a ring of radius } r \\ &= \frac{n^2h^2}{8\pi^2mr^2} \end{aligned}$$

in agreement with the result obtained conventionally.

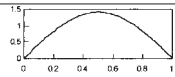
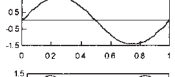

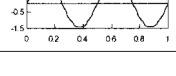
## Wave Functions

So far we have used sine functions as the wave functions of the particle in a box model. Cosine functions are equally acceptable as solutions to the Schrödinger equation but, as shown in Table 2, are all nonzero and hence discontinuous at the end of the linear box. They are therefore forbidden as wave mechanical functions for the straight-chain system. On forming the ring, however, alternate functions, namely those of even  $n$  (including  $n = 0$ ) become continuous and hence are allowed. The resulting energy levels are the same as those for the sine functions with the addition of a value of zero:

$$E = \frac{n^2h^2}{8\pi^2mr^2} \quad [n = 0, 1, 2, \dots]$$

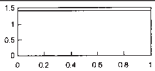
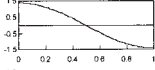
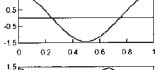
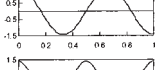
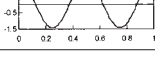
The effect of including the cosine functions is thus to add an energy of zero to the allowed values and to make all other energy levels doubly degenerate. Again this result agrees with that obtained conventionally.

**Table 1. Energies and Wave Functions for the Particle in a One-Dimensional Box and the Effect of Forming a Ring**

$n$	$E(\text{chain})$	Chain wave function	Ring wave function	$E(\text{ring})$
1	$h^2/8ml^2$		discontinuous	—
2	$4h^2/8ml^2$		continuous	$4h^2/8m(2\pi r)^2$
3	$9h^2/8ml^2$		discontinuous	—
4	$16h^2/8ml^2$		continuous	$16h^2/8m(2\pi r)^2$

**Table 2. Energies and Cosine Wave Functions for the Particle in a One-Dimensional Box and the Effect of Forming a Ring**

$$\Psi = \sqrt{\frac{2}{l}} \cos \frac{n\pi x}{l}$$

<i>n</i>	<i>E</i> (chain)	Chain wave function	Ring wave function	<i>E</i> (ring)
0	—		continuous	0
1	—		discontinuous	—
2	—		continuous	$4h^2/8m(2\pi r)^2$
3	—		discontinuous	—
4	—		continuous	$16h^2/8m(2\pi r)^2$

The wave functions for the particle on a ring are best expressed in terms of the polar coordinate,  $\phi$ , an angle around the ring from 0 to  $2\pi$ . We can then make the substitution:

$$\phi = \frac{2\pi x}{l}$$

in the functions for the linear box and obtain:

$$\psi = N \sin \frac{n\phi}{2} \quad [n = 2, 4, 6, \dots] \text{ and } \psi = N \cos \frac{n\phi}{2} \quad [n = 0, 2, 4, 6, \dots]$$

or:

$$\psi = N \sin n\phi \quad [n = 1, 2, 3, \dots] \text{ and } \psi = N \cos n\phi \quad [n = 0, 1, 2, 3, \dots]$$

as the acceptable wave functions for the ring system where  $N$  is a normalization constant to be determined.

### Normalization

Acceptable wave functions must be normalized to make the probability of finding the particle somewhere in space equal to unity. This is achieved by finding a value for the normalization constant,  $N$ , such that:

$$\int N^2 \psi^2 d\tau = 1$$

where the integration is over all space.

Thus for the linear sine function we can write:

$$N^2 \int_0^l \sin^2 \left( \frac{n\pi x}{l} \right) dx = 1$$

Recalling the trigonometrical relationships:

$$\cos^2 \theta + \sin^2 \theta = 1$$

and

$$\cos^2 \theta - \sin^2 \theta = \cos 2\theta$$

it follows that:

$$2\sin^2 \theta = 1 - \cos 2\theta$$

or

$$\sin^2 \theta = \frac{1}{2} - \frac{1}{2} \cos 2\theta$$

The normalization equation therefore becomes:

$$N^2 \int_0^l \left( \frac{1}{2} - \frac{1}{2} \cos \left( \frac{2n\pi x}{l} \right) \right) dx = 1$$

hence

$$N^2 \left( \left[ \frac{x}{2} \right]_0^l - \left[ \frac{l}{4n\pi} \sin \left( \frac{2n\pi x}{l} \right) \right]_0^l \right)$$

and

$$\frac{N^2 l}{2} - 0 = 1$$

and

$$N = \sqrt{\frac{2}{l}}$$

For the ring system, the corresponding equation is:

$$N^2 \int_0^{2\pi} \sin^2 n\phi d\phi = 1$$

giving:

$$N^2 \int_0^{2\pi} \left( \frac{1}{2} - \frac{1}{2} \cos 2n\phi \right) d\phi = 1$$

$$N^2 \left( \left[ \frac{\phi}{2} \right]_0^{2\pi} - \left[ \frac{1}{4n} \sin 2n\phi \right]_0^{2\pi} \right) = 1$$

$$N^2 (\pi - 0) = 1$$

and

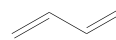
$$N = \frac{1}{\sqrt{\pi}}$$

The cosine function for the ring system also has a normalization constant of the same value.

Again we can notice a similarity between the two models. In both cases the normalization constant equals  $(2/\text{total length})^{1/2}$ . For the linear system this gives  $(2/l)^{1/2}$ ; for the ring, it gives (in polar coordinates)  $(2/2\pi)^{1/2}$ .

### Some Chemical Applications

The particle-in-a-box model can be used to calculate the allowed energy levels of the  $\pi$ -electrons in conjugated hydrocarbons such as ethene, butadiene, hexatriene, etc. In this approach the hydrocarbon is treated as a one-dimensional box and its length is regarded as extending half a bond length beyond the last carbon atom at each end of the molecule. Thus for butadiene:



the length of the molecule is  $135 \times 2 + 146 = 416$  pm, to which can be added another 140 pm giving a total of 556 pm. The four  $\pi$ -electrons then fill the two lowest-lying orbitals as follows:

$n$	$E = n^2 h^2 / 8ml^2$	Electrons in the level
4	$3.12 \times 10^{-18}$	0
3	$1.75 \times 10^{-18}$	0
2	$7.80 \times 10^{-19}$	2
1	$1.95 \times 10^{-19}$	2

The energy required to promote an electron from the  $n = 2$  to the  $n = 3$  level is  $9.74 \times 10^{-19}$  J, which corresponds to a quantum of radiation of wavelength 203 nm.

A similar calculation for a molecule of hexatriene ( $l = 837$  pm) gives the result:

$n$	$E = n^2 h^2 / 8ml^2$	Electrons in the level
5	$2.15 \times 10^{-18}$	0
4	$1.38 \times 10^{-18}$	0
3	$7.74 \times 10^{-19}$	2
2	$3.44 \times 10^{-19}$	2
1	$8.60 \times 10^{-20}$	2

The promotion energy is now reduced to  $6.02 \times 10^{-19}$  J, which corresponds to a wavelength of 330 nm (a value closer to the visible region of the spectrum).

Calculations of this sort show in a simple way how the ultraviolet absorption spectra of conjugated hydrocarbons move steadily towards the visible region as the chain length increases. The model is a very simple one and the results cannot be relied upon to predict accurate UV absorption maxima. They do, however, correctly demonstrate

the trend as the chain length of the molecule increases. The best-known ultimate example of the trend is, of course, the molecule  $\beta$ -carotene, one of the compounds responsible for the color of carrots, which has a conjugated chain containing 22 carbon atoms.

Two-dimensional compounds can be approximated by the particle on a ring model. Benzene is the simplest example, and since the C–C bond length in benzene is 138 pm we can use a model in which the radius of the ring is also 138 pm. The six  $\pi$ -electrons of benzene will then occupy the two lowest energy levels as follows:

$n$	$n^2 h^2 / 8\pi^2 m r^2$	Degeneracy	Electrons in the level
2	$1.28 \times 10^{-18}$	2	0
1	$3.21 \times 10^{-19}$	2	4
0	0	1	2

The promotion energy is now  $9.59 \times 10^{-19}$  J, corresponding to a wavelength of 207 nm, compared to an actual UV absorption maximum for benzene of 204 nm.

Extension of this model to polycyclic aromatics is not easy because few compounds even approximate circles. The remarkably close agreement between the calculated and observed UV absorption wavelength, however, is encouraging for such a simple model.

#### Literature Cited

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2. Linnett, J. W. *Wave Mechanics and Valency*; Methuen: London, 1960.