

Particle in a One-Dimensional Box as a Model for the Description of Conjugated Systems**

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Abstract: The usual «particle in a one-dimensional box» model for the description of the first absorption band of conjugated polyenes is criticized because it leads to the wrong prediction that the energy of the highest occupied molecular orbital (HOMO) is independent of the chain length, which means that the redox potential change for the oxidation of these dyes with increasing chain length cannot be described. It is shown how this serious deficiency of the otherwise still very useful model can be eliminated without loss of simplicity.

The simplest way to generate spatial dependence for a wave function to produce a varying probability of finding a particle at different points in space, is to leave the particle as free as possible but within the confines of a box from which it cannot escape. Physically, this means that within the box, the particle's potential energy is independent of its position, but that no matter how much kinetic energy it has, it cannot get beyond the walls^[1]. This simple model is very useful to explain important consequences of quantization. Asymptotic behaviour of the energy levels can be introduced by lowering the potential energy at the walls from infinity to some finite value. 1948 *Kuhn*^[2] has shown that the behaviour of a particle in a one-dimensional box can be used to describe the color of many conjugated systems by introducing only one parameter, the length of the box. One year later *Platt*^[3] has worked out an elegant description of the electronic absorption spectra of aromatic systems by using a particle on a closed bond path as model. This description was extended by *Ruedenberg* and *Scherr*^[4] to a free-electron network theory. A little later^[5] it was shown how electron-electron interaction can be treated within this simple approach. Other extensions of the now called free-electron molecular-orbital theory (FEMO) have been discussed by several authors. The most important features of this model are very well explained in a textbook written by *Mc Glynn* et al.^[6]. In 1966 *Baumann* and *Heilbronner* have reported that the analogy be-

tween the «electron-in-a-box» and the «LCAO-MO» model does not go as far as had been assumed before^[7]. The wavelength for a linear system (e.g. a one-dimensional «electron-in-a-box» model) is directly connected with the momentum of the electron and therefore with its kinetic energy according to the de Broglie relation. There exists no such simple relationship in the LCAO-MO description, however.

Since the treatment of *Kuhn*^[2], the FEMO model has been used in many elementary and specialized publications. Unfortunately, only the agreement of calculated and observed electronic transition energies has been considered. It has therefore escaped attention that the asymptotic behaviour of the highest occupied molecular orbital (HOMO) is wrong. This makes it difficult to teach the model to critical students. Regarding the success of the frontier-orbital approach to describe chemical reactions, developed by *Hoffmann*, *Fukui*^[8] and others, one has to analyze not only the HOMO-LUMO energy difference as for the description of electronic spectra, but also the behaviour of the HOMO and LUMO themselves. I will show how this serious deficiency of the otherwise still very useful model can easily be eliminated.

The energy of a particle in a one-dimensional box is described by

$$E_n = \frac{h^2}{8mL^2} \cdot n^2 \quad n = 1, 2, 3, \dots \quad (1)$$

h is Planck's constant, m is the mass of the particle, and L is the length of the box. The number of π electrons, Z_π , in a linear conjugated molecule



is equal to $2 \cdot (k + 1)$ and in cyanine molecules



it is equal to $2 \cdot (k + 2)$. Each orbital is occupied by two electrons. Therefore we get for the quantum numbers n_{HOMO} of the highest occupied molecular orbital and n_{LUMO} of the lowest unoccupied molecular orbital the following relations:

$$\begin{aligned} n_{\text{HOMO}} &= Z_\pi/2 \\ n_{\text{LUMO}} &= Z_\pi/2 + 1 = (Z_\pi + 2)/2 \end{aligned} \quad (2)$$

The resulting orbital energies $\varepsilon_{\text{HOMO}}$, $\varepsilon_{\text{LUMO}}$ are:

$$\begin{aligned} \varepsilon_{\text{LUMO}} &= \frac{h^2}{8m} \cdot \frac{(Z_\pi + 2)^2}{4L^2} \\ \varepsilon_{\text{HOMO}} &= \frac{h^2}{8m} \cdot \frac{Z_\pi^2}{4L^2} \end{aligned} \quad (3a)$$

The transition energy $S_1 \leftarrow S_0$ is equal to the difference:

$$\begin{aligned} h\nu = \Delta E &= \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \\ &= \frac{h^2}{8m \cdot 4L^2} [(Z_\pi + 2)^2 - Z_\pi^2] \\ \Delta E &= \frac{h^2}{8m \cdot L^2} \cdot (Z_\pi + 1) \end{aligned} \quad (3b)$$

In order to calculate $\varepsilon_{\text{LUMO}}$, $\varepsilon_{\text{HOMO}}$ and ΔE , an assumption about the length of the box, L , has to be made. *Kuhn* has introduced the following:

$$L = Z_\pi \cdot d_0 = 2(j + 1)d_0 \quad (4)$$

where d_0 is equal to the C-C bond length and j is equal to k for the linear conjugated molecules and equal to $k + 1$ for the cyanine dyes^[2,10]. Introducing this assumption we get:

$$\begin{aligned} \varepsilon_{\text{LUMO}} &= \frac{h^2}{8m} \cdot \frac{1}{4d_0^2} \left(\frac{Z_\pi + 2}{Z_\pi} \right)^2 \\ &= \frac{h^2}{8m} \cdot \frac{1}{4d_0^2} \left(1 + \frac{2}{Z_\pi} \right)^2 \end{aligned} \quad (5a)$$

$$\varepsilon_{\text{HOMO}} = \frac{h^2}{8m} \cdot \frac{1}{4d_0^2} = \text{constant} \quad (5b)$$

$$\begin{aligned} \Delta E &= \frac{h^2}{8m} \cdot \frac{1}{d_0^2} \cdot \frac{Z_\pi + 1}{Z_\pi} \\ &= \frac{h^2}{8m} \cdot \frac{1}{d_0^2} \left(\frac{Z_\pi + 1}{Z_\pi} \right)^2 \cdot \frac{1}{Z_\pi + 1} \end{aligned} \quad (5c)$$

The behaviour of equations (5a) and (5c) as a function of Z_π is reasonable but the prediction of (5b) is wrong. We know very well that the redox potential for the oxidation of polyenes as a function of their chain length is not a constant, but becomes smaller as $Z_\pi/2$ increases.

It is astonishingly simple to correct this deficiency. We only have to replace equation (4) by the following expression:

$$L = (Z_\pi + 1)d_0 \quad (6)$$

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This leads to the new equations:

$$\begin{aligned} \varepsilon'_{\text{LUMO}} &= \frac{h^2}{8m} \cdot \frac{1}{4d_0^2} \left(\frac{Z_\pi + 2}{Z_\pi + 1} \right)^2 \\ &= \frac{h^2}{8m} \cdot \frac{1}{4d_0^2} \left(1 + \frac{1}{Z_\pi + 1} \right)^2 \end{aligned} \quad (7a)$$

$$\begin{aligned} \varepsilon'_{\text{HOMO}} &= \frac{h^2}{8m} \cdot \frac{1}{4d_0^2} \left(\frac{Z_\pi}{Z_\pi + 1} \right)^2 \\ &= \frac{h^2}{8m} \cdot \frac{1}{4d_0^2} \left(1 - \frac{1}{Z_\pi + 1} \right)^2 \end{aligned} \quad (7b)$$

$$\begin{aligned} \Delta E' &= \frac{h^2}{8m} \cdot \frac{1}{d_0^2} \cdot \frac{Z_\pi + 1}{(Z_\pi + 1)^2} \\ &= \frac{h^2}{8m} \cdot \frac{1}{d_0^2} \cdot \frac{1}{Z_\pi + 1} \end{aligned} \quad (7c)$$

Since we know, that ΔE calculated by equation (5c) can be well used for the interpretation of absorption spectra of e.g. cyanine and azacyanine dyes, it is important to check whether in this respect (7c) is inferior or not. The two equations differ from one another by the factor:

$$\left(\frac{Z_\pi + 1}{Z_\pi} \right)^2 \quad (8)$$

This means that the asymptotic behaviour of both equations is the same with respect to large conjugated chains. It is shown in Fig. 1, where equations (5a), (5b) – dotted lines – are compared with the new equations (7a), (7b) – solid lines. Fortunately, the behaviour of $\varepsilon'_{\text{HOMO}}$ and $\varepsilon'_{\text{LUMO}}$ as a function of number of double bonds, Z_π , is now correct and can be used to describe the redox potential change of cyanine dyes with increasing chain-length^[9].

We have not yet discussed d_0 , a parameter which should be in the order of 1 to 1.5 Å to be physically reasonable. This parameter can be determined by setting ΔE or $\Delta E'$ equal to the observed transition energy, ΔE_{obs} . From equations (5c) and (7c) we get:

$$d_0 = \left[\frac{1}{\Delta E_{\text{obs}}} \cdot \frac{h^2}{8m} \left(\frac{Z_\pi + 1}{Z_\pi} \right)^2 \cdot \frac{1}{Z_\pi + 1} \right]^{1/2} \quad (9a)$$

$$d'_0 = \left(\frac{1}{\Delta E_{\text{obs}}} \cdot \frac{h^2}{8m} \cdot \frac{1}{Z_\pi + 1} \right)^{1/2} \quad (9b)$$

The obvious way to compare d_0 and d'_0 is the ratio:

$$\frac{d_0}{d'_0} = \frac{Z_\pi + 1}{Z_\pi} \quad (9c)$$

This means that the difference between d_0 and d'_0 is only significant for small conjugated systems. Correct asymptotic behaviour is far more important for a simple model than very good numerical agreement. Nevertheless, it is interesting that equation (7c) does not seem to be inferior

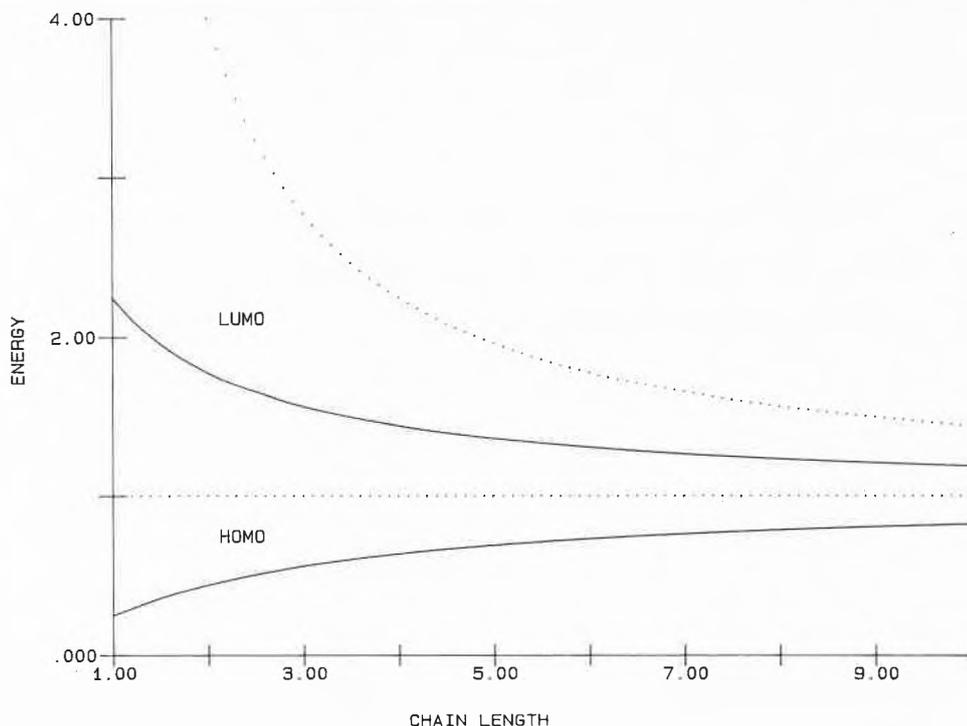
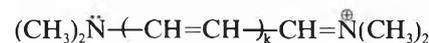


Fig. 1. Comparison of the correct HOMO, LUMO behaviour (solid lines) with the one used up to now (dotted line) in units of $h^2/(8md_0^2)$.

Table 1. Comparison of experimental electronic transition energies with energies calculated by formula (10a) and (10b) in units of $[\text{cm}^{-1}]$.

k	Z_π	ΔE_{exp}	ΔE (equation (10a))	$\Delta E/\Delta E_{\text{exp}}$	$\Delta E'$ (equation (10b))	$\Delta E'/\Delta E_{\text{exp}}$
0	4	44643	44643	1.0	44643	1.0
1	6	31949	27778	0.869	31888	0.998
2	8	24038	20089	0.836	24802	1.032
3	10	19268	15714	0.815	20292	1.053
4	12	16000	12897	0.806	17170	1.073
5	14	13605	10933	0.804	14881	1.094
6	16	11792	9487	0.804	13130	1.11

to (5c) for the prediction of electronic transition energies, even from a numerical point of view. This is demonstrated by the comparison given in Table 1. The experimental data for the cyanine dyes



have been taken from Table 7.7 of Ref.^[10] (note, however, that the comparison is made in units of energy and not in wavelength).

The equations (5c) and (7c) can be written as follows:

$$\Delta E = \text{const} \cdot \frac{Z_\pi + 1}{Z_\pi^2} \quad (10a)$$

$$\Delta E' = \text{const}' \cdot \frac{1}{Z_\pi + 1} \quad (10b)$$

The simplest way to determine a set of (const, const') in order to compare equations (10a) and (10b) is the following:

$$\text{const} = 44643 \cdot \frac{4^2}{4 + 1} = 142857$$

From (9c) we get:

$$\text{const}' = \text{const} \cdot \left(\frac{5}{4} \right)^2 = 223215$$

Finally I would like to draw the attention to a problem which cannot be solved by simple parametrization. Setting $\varepsilon'_{\text{HOMO}}$ approximately equal to the first ionization energy we get a qualitatively correct asymptotic behaviour. However, it is easy to show that the magnitude of the predicted ionization energy IP_1 is wrong. Comparing $\varepsilon'_{\text{HOMO}}$ with $\Delta E'$ we get:

$$\frac{IP_1}{\Delta E_{\text{S}_1 \leftarrow \text{S}_0}} \rightarrow \frac{\varepsilon'_{\text{HOMO}}}{\Delta E'} = \frac{1}{4} \cdot \frac{Z_\pi^2}{Z_\pi + 1} \quad (11)$$

A comparison of this prediction with experimental values for ethylene and butadiene (Table 2) shows that it is basically wrong.

Table 2. Comparison of equation (11) with experimental values [cm^{-1}].

	$\Delta E(S_1 \leftarrow S_0)$	IP_1	$IP_1/\Delta E(S_1 \leftarrow S_0)$	$0.25 \cdot \frac{Z_\pi^2}{Z_\pi + 1}$
Ethylene	61250	84763	1.384	1/3
Butadiene	46080	73149	1.587	4/5

It is not astonishing that equation (11) fails and it is obvious that parametrization does not really help. The way to improve the model is to lower the potential energy at the walls to, let us say, E_μ and to approximate the ionization energy by the difference $E_\mu - \epsilon_{\text{HOMO}}^{(1)}$, but at this point a simple MO picture as provided by the HMO (Hückel Molecular Orbitals) or the

EHMO (Extended Hückel Molecular Orbitals) theory becomes more useful.

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