

### 1.3: Quantum Mechanics of Some Simple Systems

The simple quantum-mechanical problem we have just solved can provide an instructive application to chemistry: the *free-electron model* (FEM) for delocalized  $\pi$ -electrons. The simplest case is the 1,3-butadiene molecule

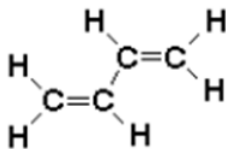


Figure 4) by

$$\rho = 2\psi_1^2 + 2\psi_2^2 \quad (1.3.1)$$

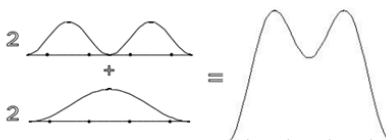
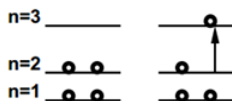


Figure 4. Pi-electron density in butadiene.

A chemical interpretation of this picture might be that, since the  $\pi$ -electron density is concentrated between carbon atoms 1 and 2, and between 3 and 4, the predominant structure of butadiene has double bonds between these two pairs of atoms. Each double bond consists of a  $\pi$ -bond, in addition to the underlying  $\sigma$ -bond. However, this is not the complete story, because we must also take account of the residual  $\pi$ -electron density between carbons 2 and 3. In the terminology of valence-bond theory, butadiene would be described as a *resonance hybrid* with the contributing structures  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  (the predominant structure) and  ${}^{\circ}\text{CH}_2.\text{CH}=\text{CH}-\text{CH}_2^{\circ}$  (a secondary contribution). The reality of the latter structure is suggested by the ability of butadiene to undergo 1,4-addition reactions.

The free-electron model can also be applied to the electronic spectrum of butadiene and other linear polyenes. The lowest unoccupied molecular orbital (LUMO) in butadiene corresponds to the  $n=3$  particle-in-a-box state. Neglecting electron-electron interaction, the longest-wavelength (lowest-energy) electronic transition should occur from  $n=2$ , the highest occupied molecular orbital (HOMO).



The energy difference is given by

$$\Delta E = E_3 - E_2 = (3^2 - 2^2) \frac{h^2}{8mL^2} \quad (1.3.2)$$

Here  $m$  represents the mass of an electron (not a butadiene molecule!),  $9.1 \times 10^{-31}$  Kg, and  $L$  is the effective length of the box,  $4 \times 1.40 \times 10^{-10}$  m. By the Bohr frequency condition

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad (1.3.3)$$

The wavelength is predicted to be 207 nm. This compares well with the experimental maximum of the first electronic absorption band,  $\lambda_{max} \approx 210$  nm, in the ultraviolet region.

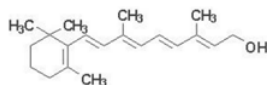
We might therefore be emboldened to apply the model to predict absorption spectra in higher polyenes  $\text{CH}_2=(\text{CH}-\text{CH})_{n-1}\text{CH}_2$ . For the molecule with  $2n$  carbon atoms ( $n$  double bonds), the HOMO  $\rightarrow$  LUMO transition corresponds to  $n \rightarrow n + 1$ , thus

$$\frac{hc}{\lambda} \approx [(n+1)^2 - n^2] \frac{h^2}{8m(2nL_{CC})^2} \quad (1.3.4)$$

A useful constant in this computation is the [Compton wavelength](#)

$$\frac{h}{mc} = 2.426 \times 10^{-12} m. \quad (1.3.5)$$

For  $n=3$ , hexatriene, the predicted wavelength is 332 nm, while experiment gives  $\lambda_{max} \approx 250$  nm. For  $n=4$ , octatetraene, FEM predicts 460 nm, while  $\lambda_{max} \approx 300$  nm. Clearly the model has been pushed beyond range of quantitative validity, although the trend of increasing absorption band wavelength with increasing  $n$  is correctly predicted. Incidentally, a compound should be colored if its absorption includes any part of the visible range 400-700 nm. Retinol (vitamin A), which contains a polyene chain with  $n=5$ , has a pale yellow color. This is its structure:



## Contributors and Attributions

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