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.

$$\rho = 2\psi_1^2 + 2\psi_2^2$$  \(\text{(28)}\)

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

\[ \Delta E = E_{3} - E_{2} = (3^2 - 2^2) \frac{h^2}{8mL^2} \tag{29} \]

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

\[ \Delta E = h\upsilon = \frac{hc}{\lambda} \tag{30} \]

The wavelength is predicted to be 207 nm. This compares well with the experimental maximum of the first electronic absorption band, \( \lambda_{\text{max}} \approx 210 \) 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 \( \text{HOMO} \rightarrow \text{LUMO} \) transition corresponds to \( n \rightarrow n + 1 \), thus

\[ \frac{hc}{\lambda} \approx \begin{bmatrix} (n+1)^2 - n^2 \end{bmatrix} \frac{h^2}{8m(2nL_{\text{CC}})^2} \tag{31} \]

A useful constant in this computation is the Compton wavelength

\[ \frac{h}{mc} = 2.426 \times 10^{-12} \text{ m}. \]

For \( n=3 \), hexatriene, the predicted wavelength is 332 nm, while experiment gives \( \lambda_{\text{max}} \approx 250 \) nm. For \( n=4 \), octatetraene, FEM predicts 460 nm, while \( \lambda_{\text{max}} \approx 300 \) 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:

![Retinol structure](image)

**Contributors and Attributions**

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