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

\[
\rho = 2\psi_1^2 + 2\psi_2^2 \label{28}
\]

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 CH\(_2\)=CH-CH=CH\(_2\) (the predominant structure) and CH\(_2\)-CH=CH-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

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

\[
\Delta E = h \nu = \frac{hc}{\lambda}\label{30}
\]

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 \( \text{CH}_2=(\text{CH-CH=})_{n-1}\text{CH}_2 \). For the molecule with \( 2n \) carbon atoms (\( n \) double bonds), the HOMO → LUMO transition corresponds to \( n \rightarrow n + 1 \), thus

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

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 \( \lambda \approx 250 \) nm. For \( n=4 \), octatetraene, FEM predicts 460 nm, while \( \lambda \approx 300 \) nm. Clearly the model has been pushed beyond range of quantitate 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:

![Chemical Structure](image)

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**Contributors and Attributions**

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