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\(_2\)=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

\[
\Delta E = E_3 - E_2 = (3^2 - 2^2)\frac{h^2}{8mL^2} \label{29}
\]
Here \( m \) represents the mass of an electron (not a butadiene molecule!), \( 9.1 \times 10^{-31} \text{ Kg} \), and \( L \) is the effective length of the box, \( 4 \times 1.40 \times 10^{-10} \text{ m} \). By the Bohr frequency condition

\[
\Delta E = h\nu = \frac{hc}{\lambda} \quad \text{(label 30)}
\]

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

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

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

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 \( \lambda_{\text{max}} \approx 250 \text{ nm} \). For \( n=4 \), octatetraene, FEM predicts 460 nm, while \( \lambda_{\text{max}} \approx 300 \text{ nm} \). 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: