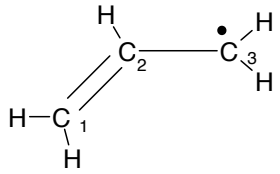
Approximations: variational method

1. π electrons in the allyl system

We will approximate the one-electron wave functions of the π electrons in the allyl system by linear combinations of normalized atomic orbitals $p_{z_i}(\mathbf{r})$ (simply denoted $p_i(\mathbf{r})$ in the following), which are centered on carbon atoms C_i (see figure below).



A trial wave function can thus be written as

$$\Phi(\mathbf{r}) = \lambda\, p_1(\mathbf{r}) + \mu\, p_2(\mathbf{r}) + \nu\, p_3(\mathbf{r}),$$

where λ, μ and ν are real coefficients. The following approximations and notations will be used for deriving the secular equation:

- the overlap integrals $\langle p_i|p_j\rangle = \int d\mathbf{r}\; p_i^*(\mathbf{r})\;.\; p_j(\mathbf{r})$ are equal to δ_{ij},
- the energies $H_{ii} = \langle p_i|\hat{H}|p_i\rangle$ (associated to the atomic orbitals p_i) where $\hat{H}$ is a one-electron Hamiltonian describing the molecule, are all equal to a real number α,
- the so-called "coupling integrals" $H_{ij} = \langle p_i|\hat{H}|p_j\rangle$ are all equal to a real number β when C_i and C_j are adjacent carbon atoms. They are assumed to be zero if C_i and C_j are not adjacent (Hückel approximation),
- α and β are negative.

1. Derive the secular determinant in terms of α, β and the one-electron energy E. Rewrite it in terms of the variable x defined as $x = \dfrac{\alpha - E}{\beta}$.

2. Solve the secular equation in x.

3. Deduce from question 2. what are the energy levels of the π electrons in the allyl system. Draw the corresponding energy diagram.

4. Using arrows for spin states ($\uparrow$ or $\downarrow$), give on three separate energy diagrams the electron distribution corresponding to the ground state configuration of the π electrons in (a) the allyl radical (3 electrons), (b) the allyl cation and (c) the allyl anion.

5. Give the three wave functions Φ_1, Φ_2 and Φ_3 (referred to as molecular orbitals) which correspond to the three energy levels found in question 3.

6. Normalize these three molecular orbitals.

2. The 1D harmonic oscillator

Consider a 1D harmonic oscillator whose Hamiltonian equals

$$\hat{H} = \frac{\hat{p_x}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2.$$

This Hamiltonian is even (i.e. invariant under reflection $x \to -x$), so its ground state has even parity. Consequently it is described by an even function. As an attempt to find an approximation to the exact ground state wave function, we consider an even trial wave function depending on a single α parameter: $\Phi_\alpha(x) = e^{-\alpha x^2}$ $(\alpha > 0)$.

Using the variational method, find the ground state energy of the 1D harmonic oscillator as well as the expression of the associated wave function. For that purpose proceed as follows:

a) Derive the expectation value E_α of the energy over the trial wave function Φ_α (use integration by parts).

b) Minimize E_α with respect to α.

c) Comment the result.

Useful formula: $\displaystyle\int_0^{+\infty} e^{-u^2} du = \frac{\sqrt{\pi}}{2}$

I- The π-electrons in the allyl system

1- On calcule d'abord $E_\phi = \dfrac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$

puis on minimise E_ϕ par rapport aux trois paramètres réels λ, μ et ν

$$\langle\phi|\hat{H}|\phi\rangle = \langle\lambda p_1+\mu p_2+\nu p_3|\hat{H}|\lambda p_1+\mu p_2+\nu p_3\rangle$$

$$= \lambda^2\underbrace{\langle p_1|\hat{H}|p_1\rangle}_{\alpha} + \mu^2\underbrace{\langle p_2|\hat{H}|p_2\rangle}_{\alpha} + \nu^2\underbrace{\langle p_3|\hat{H}|p_3\rangle}_{\alpha} + \lambda\mu\underbrace{\langle p_1|\hat{H}|p_2\rangle}_{\beta} + \lambda\nu\underbrace{\langle p_1|\hat{H}|p_3\rangle}_{0}$$
$$+ \mu\nu\underbrace{\langle p_2|\hat{H}|p_3\rangle}_{\beta} + \mu\lambda\underbrace{\langle p_2|\hat{H}|p_1\rangle}_{\beta} + \nu\lambda\underbrace{\langle p_3|\hat{H}|p_1\rangle}_{0} + \nu\mu\underbrace{\langle p_3|\hat{H}|p_2\rangle}_{\beta}$$

$$= (\lambda^2+\mu^2+\nu^2)\alpha + 2\lambda\mu\beta + 2\mu\nu\beta$$

$$\langle\phi|\phi\rangle = \lambda^2+\mu^2+\nu^2$$

$$\Rightarrow E_\phi = \frac{(\lambda^2+\mu^2+\nu^2)\alpha + (2\lambda\mu+2\mu\nu)\beta}{\lambda^2+\mu^2+\nu^2}$$

$$\Leftrightarrow (\lambda^2+\mu^2+\nu^2)E_\phi = (\lambda^2+\mu^2+\nu^2)\alpha + (2\lambda\mu+2\mu\nu)\beta \quad (1)$$

Pour minimiser E_ϕ, je cherche où ses dérivées s'annulent :

$$\frac{\partial(1)}{\partial\lambda} \to 2\lambda E_\phi = 2\lambda\alpha + 2\mu\beta \quad \text{avec} \quad \frac{\partial E_\phi}{\partial\lambda} = 0$$

$$\frac{\partial(1)}{\partial\mu} \to 2\mu E_\phi = 2\mu\alpha + (2\lambda+2\nu)\beta \quad \frac{\partial E_\phi}{\partial\mu} = 0$$

$$\frac{\partial(1)}{\partial\gamma} \to 2\nu E_\phi = 2\nu\alpha + 2\mu\beta \quad \frac{\partial E_\phi}{\partial\nu} = 0$$

$$\Rightarrow \begin{cases} (2\alpha-2E_\phi)\lambda + 2\mu\beta = 0 \\ 2\lambda\beta + (2\alpha-2E_\phi)\beta + 2\alpha\nu = 0 \\ 2\mu\beta + (2\alpha-2E_\phi)\nu = 0 \end{cases}$$

$$\Leftrightarrow \begin{pmatrix} \alpha-E_\phi & \beta & 0 \\ \beta & \alpha-E_\phi & \beta \\ 0 & \beta & \alpha-E_\phi \end{pmatrix}\begin{pmatrix}\lambda\\ \mu\\ \nu\end{pmatrix} = \begin{pmatrix}0\\0\\0\end{pmatrix} \quad (2)$$

L'équation (2) a une solution non triviale si

$$\begin{vmatrix} \alpha-E_\phi & \beta & 0 \\ \beta & \alpha-E_\phi & \beta \\ 0 & \beta & \alpha-E_\phi \end{vmatrix} = 0$$

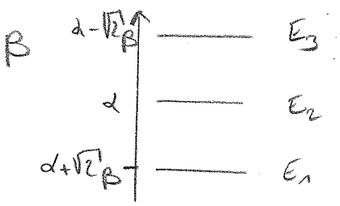
ce déterminant est appelé déterminant séculaire

$x = \dfrac{\alpha-E_\phi}{\beta}$ d'où $\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$

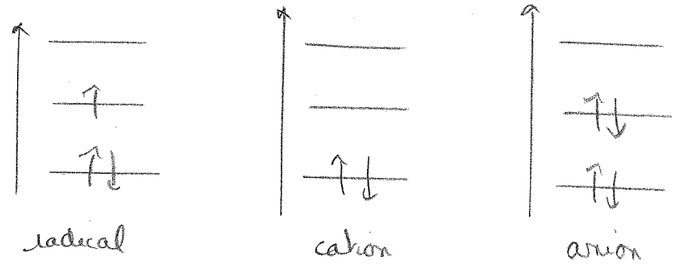
2) $x(x^2-1) - x = 0 \iff x(x^2-2) = 0$

$$\Leftrightarrow \begin{cases} x = 0 \\ x = \pm\sqrt{2} \end{cases}$$

3) $E_\phi = \alpha$ ou $E_\phi = \alpha \pm \sqrt{2}\beta$ ($\beta<0$)



4)



5) Pour chacun les fonctions d'ondes associées à chaque énergie, on part de l'équation (2) et on remplace E_ϕ par la valeur trouvée

- Pour $E_2 = \alpha$

$$\begin{pmatrix} 0 & \beta & 0 \\ \beta & 0 & \beta \\ 0 & \beta & 0 \end{pmatrix}\begin{pmatrix}\lambda\\ \mu\\ \nu\end{pmatrix} = \begin{pmatrix}0\\0\\0\end{pmatrix} \iff \begin{cases}\mu = 0 \\ \lambda = -\nu\end{cases}$$

$\Rightarrow \phi_2 = p_1 - p_3$ normalisation $\Rightarrow$ $\boxed{\phi_2 = \dfrac{1}{\sqrt{2}}(p_1-p_3)}$

* Pour $E_1 = \alpha + \sqrt{2}\beta$

$$(2) \Leftrightarrow \begin{pmatrix} -\sqrt{2}\beta & \beta & 0 \\ \beta & -\sqrt{2}\beta & \beta \\ 0 & \beta & -\sqrt{2}\beta \end{pmatrix} \begin{pmatrix} \lambda \\ \mu \\ \nu \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \Leftrightarrow \begin{cases} \mu = \sqrt{2}\lambda \\ \lambda - \sqrt{2}\mu + \nu = 0 \\ \mu = \sqrt{2}\nu \end{cases}$$

$$\Rightarrow \quad \phi_1 = p_1 + \sqrt{2}p_2 + p_3$$

* Pour $E_3 = \alpha - \sqrt{2}\beta$, on trouve de même $\phi_3 = p_1 - \sqrt{2}p_2 + p_3$

6) Normalisation :

$$\langle \phi_1 | \phi_1 \rangle = \int \phi_1^* \phi_1 \, d\tau = 1 \Leftrightarrow N^2(1+2+1) = 1 \Leftrightarrow N = \frac{1}{2}$$

$$\Rightarrow \boxed{\begin{aligned} \phi_1 &= \frac{1}{2}\left(p_1 + \sqrt{2}p_2 + p_3\right) \\ \phi_3 &= \frac{1}{2}\left(p_1 - \sqrt{2}p_2 + p_3\right) \end{aligned}}$$

II. The linear harmonic oscillator

a) $E_\alpha = \dfrac{\langle \phi_\alpha | \hat{H} | \phi_\alpha \rangle}{\langle \phi_\alpha | \phi_\alpha \rangle}$ avec $\phi_\alpha(x) = e^{-\alpha x^2}$

- $\hat{H}\phi_\alpha(x) = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} e^{-\alpha x^2} + \dfrac{1}{2} m\omega^2 x^2 e^{-\alpha x^2}$

$$= +\frac{\hbar^2}{2m} 2\alpha e^{-\alpha x^2} + \left(\frac{1}{2}m\omega^2 - \frac{\hbar^2}{2m}4\alpha^2\right) x^2 e^{-\alpha x^2}$$

- $\langle \phi_\alpha | \hat{H} | \phi_\alpha \rangle = \displaystyle\int_{-\infty}^{+\infty} + \frac{\hbar^2}{2m} 2\alpha e^{-2\alpha x^2} dx + \left(\frac{1}{2}m\omega^2 - \frac{\hbar^2}{2m}4\alpha^2\right) \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx$

$$\int_{-\infty}^{+\infty} e^{-2\alpha x^2} dx = 2\int_0^{+\infty} e^{-2\alpha x^2} dx \qquad \left(\text{changement de variable } u = \sqrt{2\alpha}\,x,\ du = \sqrt{2\alpha}\,dx\right)$$

$$= 2\int_0^{+\infty} e^{-u^2} \frac{du}{\sqrt{2\alpha}} = \frac{\sqrt{\pi}}{\sqrt{2\alpha}}$$

$$\int_{-\infty}^{+\infty} x^2 e^{-2\alpha x^2} dx = ? \qquad \text{intégration par partie } \int uv' = uv - \int u'v$$

$u = x \quad u' = 1$

$v' = x e^{-2\alpha x^2} \quad v = -\dfrac{1}{4\alpha} e^{-2\alpha x^2}$

$$\Rightarrow \int_{-\infty}^{+\infty} x^2 e^{-2\alpha x^2} dx = \left[-\frac{x}{2\alpha} e^{-2\alpha x^2}\right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} -\frac{1}{4\alpha} e^{-2\alpha x^2} dx$$

$$= 0 + \frac{1}{4\alpha}\frac{\sqrt{\pi}}{\sqrt{2\alpha}}$$

$$\Rightarrow \langle \phi_\alpha | \hat{H} | \phi_\alpha \rangle = \frac{\hbar^2}{2m} 2\alpha \frac{\sqrt{\pi}}{\sqrt{2\alpha}} + \left(\frac{1}{2}m\omega^2 - \frac{\hbar^2}{2m}4\alpha^2\right)\frac{1}{4\alpha}\frac{\sqrt{\pi}}{\sqrt{2\alpha}}$$

$$= \frac{1}{2}m\omega^2 \times \frac{1}{4\alpha}\frac{\sqrt{\pi}}{\sqrt{2\alpha}} + \frac{\hbar^2}{2m}\alpha\frac{\sqrt{\pi}}{\sqrt{2\alpha}}$$

- $\langle \phi_\alpha | \phi_\alpha \rangle = \displaystyle\int e^{-2\alpha x^2} dx = \frac{\sqrt{\pi}}{\sqrt{2\alpha}}$

$$\Rightarrow \boxed{E_\alpha = \frac{\langle \phi_\alpha | \hat{H} | \phi_\alpha \rangle}{\langle \phi_\alpha | \phi_\alpha \rangle} = \frac{1}{2}m\omega^2 \times \frac{1}{4\alpha} + \frac{\hbar^2}{2m}\alpha}$$

b) $\dfrac{dE_\alpha}{d\alpha} = \dfrac{1}{8} m\omega^2 \times (-)\dfrac{1}{\alpha^2} + \dfrac{\hbar^2}{2m} = 0$

$$\Leftrightarrow \alpha = \frac{1}{2}\frac{m\omega}{\hbar}$$

$$\Rightarrow E_\alpha = \frac{1}{2}m\omega^2 \times \frac{1}{4} \times \frac{2\hbar}{m\omega} + \frac{\hbar^2}{2m} \times \frac{1}{2}\frac{m\omega}{\hbar} = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4}$$

$$\Leftrightarrow \boxed{E_\alpha = \frac{\hbar\omega}{2}}$$

c) On obtient le résultat exact (cf TD oscillateur harmonique)

$$\Rightarrow \psi_0 = e^{-\frac{1}{2}\frac{m\omega}{\hbar}x^2} = \phi_{\frac{m\omega}{2\hbar}}$$