13. Apply the particle in a ring model to the π-electrons of benzene.

$$E_k = \frac{k^2 \hbar^2}{2mr^2} \qquad k = 0, \pm 1, \pm 2 \ldots$$

Taking $r = 1.35$ Å

$$E = qk^2 \qquad q = \frac{\hbar^2}{8\pi^2 mr^2} \sim 1.69 \times 10^4 \text{ cm}^{-1}$$

Check!

$k=2$ ═══ $E = 4q$ LUMO

$k=1$ ═══ $E = q$ HOMO $\quad \Delta E = 3q \sim 50700 \text{ cm}^{-1}$

$k=0$ ═══ $E = 0$

14. Calculate the bond orders and π-e density for the first excited state of butadiene (HMO method)

ϕ_4 —— $0.372\,\pi_1 - 0.602\,\pi_2 + 0.602\,\pi_3 - 0.372\,\pi_4$

ϕ_3 —+— $0.602\,\pi_1 - 0.372\,\pi_2 - 0.372\,\pi_3 + 0.602\,\pi_4$

ϕ_2^* —+— $0.602\,\pi_1 + 0.372\,\pi_2 - 0.372\,\pi_3 - 0.602\,\pi_4$

ϕ_1 —#— $0.372\,\pi_1 + 0.602\,\pi_2 + 0.602\,\pi_3 + 0.372\,\pi_4$

B.O. $1-2 = (.372 \times .602) \times 2 + (.602 \times -.372) + (.602 \times -.372)$

$= 0.448$

$2-3 = 0.725$

$Q_1 = .372^2 \times 2 + .602^2 + .602^2 = 1.00$

$Q_2 = 1.00$