

ph237 Quantum Physics workshop 4 (RW) – solutions

1. Benzene - a delocalised electron system

Benzene, C_6H_6 , is a molecule shaped like a regular hexagon of carbon atoms, with a hydrogen atom bonded to each one of them. All six carbon atoms are equivalent, and each of them contributes one electron to a shared, delocalised, electron system spanning the whole ring. This situation can be described in two alternative ways: as a linear combination of atomic states, or by *ab initio* solution of the Schrödinger equation for the delocalised electrons, neglecting the localised electrons and atom cores.

Linear combination approach:

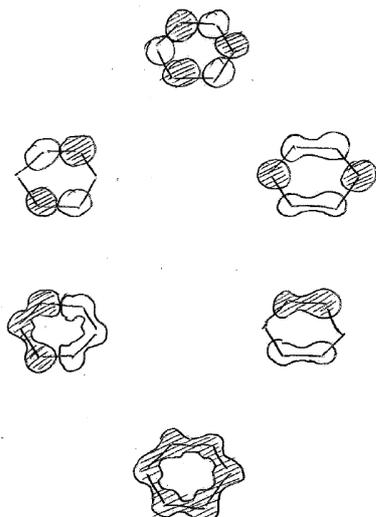
- (a) Which atomic state (identified by n, l, m) contributes to the delocalised system?

If the ring is in the xy plane, the overlapping atomic states are $2p_z$ states. The other two $2p$ states and the $2s$ state of each atom are mixed into three $2sp^2$ hybrid states forming σ bonds between each pair of carbon atoms and with the $1s$ state of the attached hydrogen atom.

- (b) How many molecular states exist for the delocalised electron system? How many of them are bonding, *i.e.* energetically advantages compared to the atomic states?

As six atomic states are linear-combined, there are also six molecular states. Three of them are bonding, three anti-bonding.

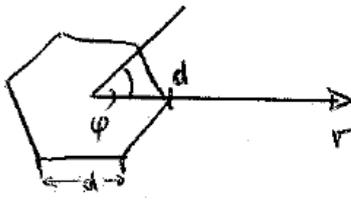
- (c) Sketch the locations of the nodes of the wave functions of all molecular states.



Because of the symmetry of the ring, the number of nodes must be even. The state with the lowest energy has no nodes, the other two bonding states have two nodes each (either through two atoms, or through the centre of two bonds). The two lower anti-bonding states have four nodes, two of which are located in the centre of bonds, and the other two either at atom positions or also in the centre of bonds. The highest-energy state has nodes between each pair of atoms. Given that there are only six delocalised electrons present, only the bonding states are occupied in the ground state configuration.

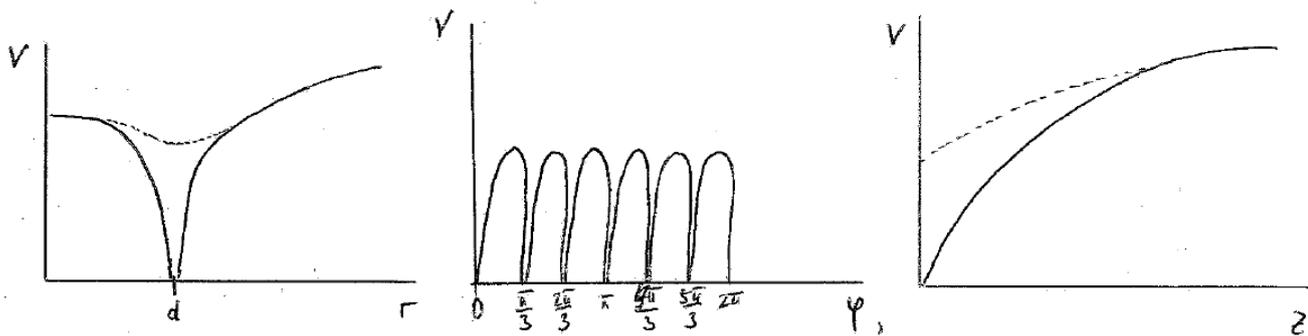
Ab initio approach:

- (d) Choose a suitable reference frame for quantum-mechanical calculations of the benzene molecule and sketch the geometry of the system and its position in the reference frame. Let d be the C-C bond length and ignore the hydrogen atoms.



Cylindrical co-ordinates with the z axis normal to the ring. Origin at the centre of the molecule. $\phi = 0$ either in the direction of an atom (shown) or centre of a bond.

- (e) Plot the potential that the delocalised electrons experience against each of the three coordinates of your chosen reference frame (keeping the other coordinates constant).



- (f) Write down the Schrödinger equation for the delocalised electron system.

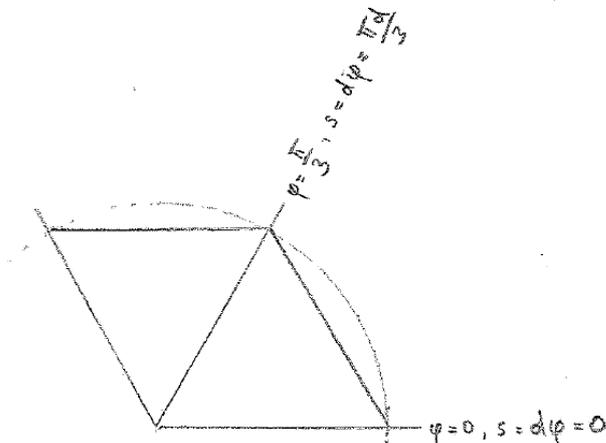
Here we need the ∇^2 operator for cylindrical co-ordinates, which we can get by simplifying the one for spherical co-ordinates (by removing all the θ terms) and adding a 2nd derivative with respect to z:

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}$$

Next, we need the potential. Each carbon atom is a Coulomb well, so

$$V(s) = -\frac{Z_{eff}e^2}{4\pi\epsilon_0 s}$$

where Z_{eff} is the effective nuclear charge of the carbon nuclei shielded by the localised electrons, and s is the position along the C-C bond, with $s = 0$ at the nucleus (i.e. s is the radius of a single atom - not to be confused with r , the radius of the molecule!).



If $\phi = 0$ points in the direction of an atom, then the next atom will be at $\phi = 60^\circ$, so there are origins of the Coulomb potentials spaced 60° apart. Neglecting the bulge of the corners of the hexagon (i.e. modelling the hexagon as a circle), we can substitute $s = d\phi$. This means that the next atom occurs at $s = \frac{\pi}{3}d \sim 1.047d$ rather than at $s = d$. A more accurate substitution can be found geometrically. Using this approximation in the potential results in

$$V(\phi) = -\frac{Z_{eff}e^2}{4\pi\epsilon_0d\phi}$$

for the ring potential originating from a single atom. Each of the other five atoms causes the same potential, but offset by multiples of 60° . Thus we have

$$V(\phi) = -\frac{Z_{eff}e^2}{4\pi\epsilon_0d} \sum_{n=0}^5 \frac{1}{\phi + \frac{n\pi}{3}}$$

Then the Schrödinger equation for the delocalised electron system in benzene is

$$\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m_e}{\hbar^2} \left(E + \frac{Z_{eff}e^2}{4\pi\epsilon_0d} \sum_{n=0}^5 \frac{1}{\phi + \frac{n\pi}{3}} \right) = 0$$

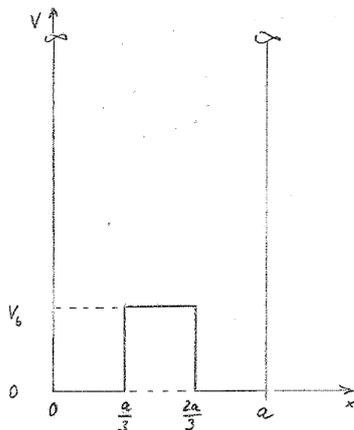
(g) What boundary conditions do we need to impose on the solutions? Give formulae.

Any wave function must be periodic over the whole ring, i.e. $\psi(\phi = 0) = \psi(\phi = 2\pi)$.

2. Perturbation - double well potential

In many crystal structures, there are two crystallographically equivalent sites very close to each other, which can only be occupied by a single atom because of their proximity. At low temperatures, the thermal energy of the atoms is not sufficient to jump out of one minimum and into the other one, and an ordered structure with relatively low symmetry results. A phase transition occurs at a certain critical temperature where the thermal energy is just enough to overcome the internal barrier between the two wells. In the high temperature phase, each atom occupies the whole well rather than either minimum, and the symmetry of the structure increases suddenly (as measurable by diffraction).

(a) Sketch a crude symmetric double well potential based on rectangular wells (to keep the maths simple). Express your chosen potential as an equation.



$V(x) = \infty$ for $x < 0$ and $x > a$, $V(x) = 0$ for $0 < x < \frac{a}{3}$ and $\frac{2a}{3} < x < a$, $V(x) = V_b$ for $\frac{a}{3} < x < \frac{2a}{3}$. By comparison with the unperturbed particle in a well, the perturbation potential is $V'(x) = V_b$ for $\frac{a}{3} < x < \frac{2a}{3}$ and $V'(x) = 0$ elsewhere.

(b) Calculate the 1st order energy correction

$$E_n^{(1)} = \int_{-\infty}^{\infty} \psi_n^{(0)*} \hat{H}_1 \psi_n^{(0)} dx$$

of the double well, using the wave function of the standard particle in a well as the unperturbed base system.

The wave function of the unperturbed particle in a 1D well is $\psi_n^{(0)} = ce^{ikx}$.

$$\begin{aligned} E &= \int_{-\infty}^{\infty} ce^{-ikx} V'(x) ce^{ikx} dx \\ &= c^2 V_b \int_{\frac{a}{3}}^{\frac{2a}{3}} dx \\ &= c^2 V_b \left(\frac{2a}{3} - \frac{a}{3} \right) \\ &= \frac{c^2 a V_b}{3} \end{aligned}$$

- (c) How does the transition temperature depend on the height of the internal potential hump separating the two minima?

The energy correction is proportional to the area of the hump in the $V(x)$ graph. Thermal energy, $E_{th} = k_b T$, is proportional to temperature. Thus the transition temperature increases linearly with both the height and the width of the hump.