

ph237 Quantum Physics workshop 4 (RW)

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:

- Which atomic state (identified by n, l, m) contributes to the delocalised system?
- 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?
- Sketch the locations of the nodes of the wave functions of all molecular states.

Ab initio approach:

- 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.
- Plot the potential that the delocalised electrons experience against each of the three coordinates of your chosen reference frame (keeping the other coordinates constant).
- Write down the Schrödinger equation for the delocalised electron system.
- What boundary conditions do we need to impose on the solutions? Give formulae.

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).

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

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