

Session 5 - This session is intended as a reminder to cover the basics of nuclear motion in aperiodic systems.

1. a) Write the non-relativistic, four-body hamiltonian for hydrogen molecule. Is the energy spectrum discrete or continuous? Is it bound from below or above or both/neither? what are the symmetries of the system ?
 b) **Born-Oppenheimer approximation** for nuclear motion: Rewrite the four-body hamiltonian assuming that electrons adiabatically follow the nuclear motion, i.e. the total wavefunction is separable and electronic wavefunctions depend on nuclear coordinates only parametrically. Identify conditions where this is no longer a valid approximation.
 c) Within the B.O. approximation, write the hamiltonian for H_2^+ . Assume a linear combination of atomic orbital description for the molecular wavefunction. Obtain eigenvalues and eigenfunctions.
 d) Qualitatively, extend the previous example to the case of H_2 with two electrons.
 e) discuss the consequences of Pauli principle.

2. **Vibrating molecule:** The Hydrogen molecule has a binding energy of 4.52 eV and an equilibrium interatomic distance of 0.74 Å. Assume the molecule is in its electronic ground state and consider the nuclear motion of a non-rotating but vibrating H_2 molecule.
 a) Determine the vibrational spectrum of H_2 in the harmonic approximation assuming using the Morse-potential for the internuclear interaction: $V(R) = D(e^{-2a(R-R_0)} - 2e^{-a(R-R_0)})$ where parameter a is related to the decay length of overlap matrix element between orbitals centered on the two atoms. Assume $a = 1\text{bohr}^{-1}$.
 b) Determine the vibrational spectrum of H_2 in the harmonic approximation assuming the Lennard-Jones potential for the internuclear interaction: $V(R) = \epsilon \left(-2\left(\frac{R_0}{R}\right)^6 + \left(\frac{R_0}{R}\right)^{12} \right)$
 Are the two estimates comparable? how they compare with the experimental molecular frequencies ? which model potential is more appropriate in your opinion ?

3. a) **Rigid rotor:** Let us solve the nuclear hamiltonian for H_2 molecule assuming B.O. approximation and using rigid-rotor model. What is the rotational energy of this dimer at equilibrium bond length?
 b) **Non-rigid rotor:** Derive a low order correction to the rotational energy using non-rigid rotor model with an internuclear distance close to the equilibrium bond length.

4. a) **Roto-vibration:** For a simultaneously rotating and vibrating Morse molecule, what is the mean rotational energy over a vibrational cycle?