

## LECTURE 21

### Content

In this lecture we will commence a study of molecules by devoting ourselves to the **Born-Oppenheimer approximation**. In general the solution of a Hamiltonian for a molecule is complicated due to the electron-nuclei interaction which makes it inseparable.

The Born-Oppenheimer approximation provides a method for performing an approximate separation.

### Outcomes

At the end of this lecture you will:

- know how to write the Hamiltonian for a complete molecule
- know and be able to apply the Born-Oppenheimer approximation
- be able to show how it leads to a Schrödinger equation for nuclear motion in an effective potential due to the electrons

## LECTURE 21 SUMMARY

- the Hamiltonian for a **molecule** is complicated by the fact that it does not separate into nuclear and electronic parts
- by applying the **Born-Oppenheimer approximation** we can achieve an approximate separation
- we assume that the nuclei move much more slowly than the electrons, which can adjust instantaneously to changes in the nuclear positions
- we may derive an equation for nuclear motion in which the electrons provide an **effective potential** within which the nuclei move

## LECTURE 22

### Content

In this lecture we will examine the simplest molecule we can make: the hydrogen molecular ion  $\text{H}_2^+$ . We will apply the Born-Oppenheimer approximation we learned about in the previous lecture to obtain a molecular wavefunction that is a **linear combination of atomic orbitals** (LCAO).

### Outcomes

At the end of this lecture you will:

- be able to apply the Born-Oppenheimer approximation to simple molecules
- be able to calculate the form of the electronic wavefunction of  $\text{H}_2^+$
- become familiar with the linear combination of atomic orbitals for constructing a molecular wavefunction
- know that the form of the wavefunction suggests a covalent bond in  $\text{H}_2^+$

## LECTURE 22 SUMMARY

- the simplest molecule we can make is  $\text{H}_2^+$
- we can apply the Born-Oppenheimer approximation to find the electronic wavefunction of the molecule
- the molecular wavefunction is a linear combination of the atomic wavefunctions centred on each of the nuclei
- both symmetric (gerade) and antisymmetric (ungerade) combinations arise corresponding to a covalent bonding orbital and an antibonding orbital respectively

## LECTURE 23

### Content

In this lecture we will continue our study of the hydrogen molecular ion  $\text{H}_2^+$  by calculating the electronic **energies** of the lowest states, the wavefunctions of which we calculated in the last lecture. We will demonstrate that the symmetric (gerade) combination leads to a **bonding** orbital, and the antisymmetric (ungerade) combination is unstable and leads to an **antibonding** orbital.

### Outcomes

At the end of this lecture you will:

- be able to calculate the electronic energies of the lowest states of  $\text{H}_2^+$
- be able to express the energy in terms of *Coulomb*, *Exchange* and *Overlap* integrals
- be able to interpret the results in terms of bonding and antibonding orbitals

## LECTURE 23 SUMMARY

- the electronic energies are found by evaluating the normalised expectation value of the electronic Hamiltonian
- we can write the energy in terms of Coulomb, Exchange and Overlap integrals
- for the antisymmetric wavefunction the energy is always higher than the energy of the separated atoms, so it is an antibonding orbital
- for the symmetric wavefunction the energy is less than that of the separated atoms for some parameters
- the energy has a minimum, and this corresponds to a bonding orbital and a stable molecule

## LECTURE 24

### Content

In this lecture we will build on our acquired knowledge of the hydrogen molecular ion, and examine the simplest *neutral* molecule,  $\text{H}_2$ . We will approach the problem in a similar manner, using the Born-Oppenheimer approximation and looking at the electronic wavefunction, but unlike the case for  $\text{H}_2^+$  we now have two electrons and so must also consider the effects of the Pauli Exclusion Principle.

### Outcomes

At the end of this lecture you will:

- know how to calculate the electronic energies of the  $\text{H}_2$  molecule using the Born-Oppenheimer approximation
- know how to apply the Pauli Exclusion Principle to the  $\text{H}_2$  molecule
- be able to describe the energies in terms of overlap, Coulomb and exchange integrals
- be able to show that the exchange interaction raises the energy of the spin triplet state, in contrast with the case in Helium

## LECTURE 24 SUMMARY

- the neutral hydrogen molecule wavefunction can be approximated as a combination of hydrogen atom wavefunctions
- as the molecule contains two electron the Pauli Exclusion Principle must be taken into account
- the molecule can have spin triplet and spin singlet state, with spatial wavefunctions of the appropriate symmetry
- the energy can be evaluated in term of overlap, Coulomb and exchange integrals
- the exchange interaction raises the energy of the spin triplet state, unlike in the helium atom

## LECTURE 25

### Content

In this lecture we will turn our attention to the nuclear motion of a molecule. We will return to the nuclear Schrödinger equation of earlier lectures and consider the motion in the effective potential due to the electrons. We will find solutions that describe **rotational** and **vibrational** motion, both of which are **quantized**.

### Outcomes

At the end of this lecture you will:

- know how to solve the nuclear Schrödinger equation in the Born-Oppenheimer approximation
- know that the nuclei move in an *effective potential* due to the electrons
- be able to show that the nuclear motion has rotational and vibrational components, both of which are quantised

## LECTURE 25 SUMMARY

- in a molecule the nuclei move in an effective potential - the electronic energies we evaluated previously
- the nuclear motion has rotational and vibrational parts
- both of these are quantised
- the total energy is therefore the sum of the electronic energy (at equilibrium), the rotational energy and the vibrational energy

## LECTURE 26

### Content

In this lecture we will the expression for the energy of an *ideal* molecule that we obtained in the previous lecture with that for a *real* molecule. We will see that differences arise when we consider centrifugal distortion, vibration of the bond and anharmonicity of the potential. To account for these the rotational energy will be modified, and the more realistic **Morse potential** will be introduced.

We will then examine the spectra of diatomic molecules that arise from pure rotational, rotation-vibrational, and electronic-vibration-rotational transitions, and see that each of these has selection rules.

### Outcomes

At the end of this lecture you will:

- be able to compare the energy of an ideal molecule with that of a real molecule and explain the differences
- be able to use the Morse potential to describe the electronic energy
- be able to describe the spectra of a diatomic molecule in terms of pure rotational, rotation-vibrational, and electronic-vibration-rotational transitions
- be able to evaluate parameters of the molecule from molecular spectra

## LECTURE 26 SUMMARY

- a real molecule deviates from the energy of the ideal case due to centrifugal distortion of the bond, the variation of rotational constant with the vibrational quantum number, and the anharmonicity of the potential
- these factors are important at large  $J$  and  $v$
- they can be described by a modifying the expression for the molecular energy and introducing the Morse potential
- spectra of diatomic molecules arise from rotational, vibration-rotational and electronic-vibration-rotational transitions
- these lie in the microwave, infra-red and ultra-violet regions of the spectrum respectively
- each obeys selection rules and has a characteristic form that allows parameters of the molecule to be calculated from data

## LECTURE 27

### Content

In this lecture we will look at **ionic** bonds. We will introduce the concept of *electron affinity*, and (re-) introduce the *ionisation energy*. We will use these parameters, and the Coulomb interaction between ions to estimate the binding energy of an ionic bond.

### Outcomes

At the end of this lecture you will:

- know the definitions of electron affinity and ionisation energy
- apply this knowledge to calculate the energy required to produce oppositely charged ions from neutral atoms
- be able to relate this to the Coulomb interaction energy to evaluate the stability of an ionic bond
- explain the difference between this simple model and measured bond energies
- evaluate and compare electric dipole moments of ionic molecules to determine the fractional ionic character

## LECTURE 27 SUMMARY

- the electron affinity is the energy required to add an electron to an atom
- the ionisation energy is the energy required to remove an electron from an atom
- the difference between these may be compensated by the Coulomb attraction to form a stable ionic molecule
- to calculate the binding energy we must take account of the repulsion of the electron clouds
- the electric dipole moment gives an indication of the fractional ionic character of the bond

**END OF LECTURE COURSE**