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

5 MOLECULES

Atoms rarely remain isolated. Instead, more commonly, they combine to form molecules. As in the atomic case, Coulomb interactions and atomic properties dominate. But molecules are not just sums of atomic properties. They are qualitatively different since we must consider motion of nuclei *and* electrons.

We shall consider the simplest molecules, H_2^+ and H_2, examples of **covalent bonding** where the nuclei share the electrons. We shall also consider another type of molecules, held together by **ionic bonding** (e.g. LiH).

As it is for atoms, the structure of molecules can be probed by *scattering* and *spectroscopy*. Molecular spectra are more complicated than atomic ones because, in addition to electronic transitions, there are other energy changes arising from the **rotational** and **vibrational** motion of nuclei.

5.1 SCHRÖDINGER EQUATION FOR MOLECULES

For our molecule we will define:
$\underline{R}_N$ and Z_N = Position vector and charge of Nth nucleus
$\underline{r}_i$ = Position vector of ith electron

The time independent Schrödinger equation, including nuclear ($\underline{R}_N$) and electronic ($\underline{r}_i$) coordinates is written:

$$\hat{H}\Psi(\underline{R}_1, \underline{R}_2..., \underline{r}_1, \underline{r}_2...) = E\Psi(\underline{R}_1, \underline{R}_2..., \underline{r}_1, \underline{r}_2...)\ . \tag{1}$$

The Hamiltonian is:

$$\begin{aligned}\hat{H}(\underline{R}_1, \underline{R}_2..., \underline{r}_1, \underline{r}_2...) &= \underbrace{\sum_N \frac{-\hbar^2}{2M_N}\nabla_R^2}_{\substack{\text{K.E. of}\\ \text{nuclei}}} + \underbrace{\sum_i \frac{-\hbar^2}{2m}\nabla_i^2}_{\substack{\text{K.E. of}\\ \text{electrons}}} \\ &+ \underbrace{V(\underline{R}_N, \underline{r}_i)}_{\substack{\text{Coulomb}\\ \text{Interactions}}} \end{aligned} \tag{2}$$

where the potential is :

$$\begin{aligned} V(\underline{R}_N, \underline{r}_i) &= \underbrace{\sum_{\substack{i,j\\ i>j}} \frac{1}{|\underline{r}_i - \underline{r}_j|}}_{e^-\text{–}e^-\text{ repulsion}} \\ &+ \underbrace{\sum_{\substack{N,M\\ N>M}} \frac{Z_N Z_M}{|\underline{R}_N - \underline{R}_M|}}_{\substack{\text{Repulsion}\\ \text{between nuclei}}} \\ &- \underbrace{\sum_{N,i} \frac{Z_N}{|\underline{R}_N - \underline{r}_i|}}_{\substack{\text{Attraction}\\ \text{between nuclei}\\ \text{and electrons}}} \quad . \end{aligned} \tag{3}$$

Because of the interaction between electrons and nuclei (last term in equation (**??**)), the solution cannot be simply separated into nuclear and electronic components, i.e.

$$\Psi(\underline{R}_N, \underline{r}_i) \neq \nu(\underline{R}_N)\psi(\underline{r}_i)$$

N. B. To simplify the notation, sometimes we will write $\Psi(\underline{R}_N, \underline{r}_i)$ but it should be understood that here $\underline{R}_N$ stands for **all** nuclear position vectors and $\underline{r}_i$ for **all** electronic positions

So, solution is difficult. But an *approximate separation* (of electronic and nuclear parts) can be achieved through the **Born-Oppenheimer** approximation—arguably one of the most effective tools in molecular physics.

5.2 BORN-OPPENHEIMER APPROXIMATION

The Born-Oppenheimer approximation is underpinned by fact that *nuclei move much more slowly than electrons*, since they are much heavier, i.e., $\frac{m_e}{M_N} \ll 1$

Using this fact we will be able to write the total wavefunction for any molecule as a product of an electronic and nuclear part. For simplicity we will use a general *diatomic* molecule to explain the approximation.

After separation of the centre of mass motion, the Hamiltonian can be written:

$$\hat{H}(\underline{R}, \underline{r}_i) = -\frac{\hbar^2}{2\mu}\nabla^2_R + \sum_i \frac{-\hbar^2}{2m}\nabla^2_i + V(\underline{R}, \underline{r}_i) \qquad (4)$$

with μ the reduced mass of the nuclei.

BORN-OPPENHEIMER IN SIX EASY STEPS

1. First fix the **nuclei** in place, i.e. set the internuclear coordinate to a constant value:

   $$\underline{R} = \text{ constants}$$

   We can therefore neglect the nuclear kinetic energy term, $-\frac{\hbar^2}{2\mu}\nabla_R^2$, in the Hamiltonian (**??**).

2. Having 'pinned' the nuclei, now solve the Schrödinger Equation for electronic motion (in the field of nuclei fixed in position):

   $$\hat{H}_{\text{el}}(\underline{r}_i; \underline{R})\psi(\underline{r}_i; \underline{R}) = E_{\text{el}}(R)\psi(\underline{r}_i; \underline{R}) \qquad (5)$$

   where

   $$\hat{H}_{\text{el}}(\underline{r}_i; \underline{R}) = \underbrace{\sum_i \frac{-\hbar^2}{2m}\nabla_i^2}_{\substack{\text{K.E. of} \\ \text{electrons}}} + \underbrace{V(\underline{r}_i; \underline{R})}_{\substack{\text{P.E. with} \\ \text{fixed nuclei}}} \qquad (6)$$

   Note that $\underline{R}$ is now a parameter on which the wavefunction and Hamiltonian depend. To indicate this we write $(\underline{r}_i; \underline{R})$.

   The above is known as the **electronic Schrödinger equation**. Setting $\underline{R}$ equal to a different value, we can solve this equation until we have a complete description of the electron wavefunctions in terms of nuclear positions.

3. Assume the solution of the Schrödinger equation has the form:

$$\Psi(\underline{R}, \underline{r}_i) = \nu(\underline{R})\psi(\underline{r}_i; \underline{R}) \tag{7}$$

   that is, a product of a nuclear part that depends on $\underline{R}$, and an electronic part that depends on $(\underline{r}_i; \underline{R})$.

4. Plug this form into the **full** Schrödinger Equation *including the nuclear kinetic energy term*:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + \sum_i -\frac{\hbar^2}{2m}\nabla_i^2 + V(\underline{R}, \underline{r}_i)\right]\nu(\underline{R})\psi(\underline{r}_i; \underline{R}) \\ = E\nu(\underline{R})\psi(\underline{r}_i; \underline{R}) \tag{8}$$

5. We look at the result of applying the operator associated with the kinetic energy of the nuclei to the wavefunction:

$$\frac{-\hbar^2}{2\mu}\nabla_R^2\Psi(\underline{R}, \underline{r}_i) = -\frac{\hbar^2}{2\mu}\nabla_R^2\nu(\underline{R})\psi(\underline{r}_i; \underline{R}) \\ = -\frac{\hbar^2}{2\mu}\left[\psi\nabla_R^2\nu + 2\nabla_R\psi \cdot \nabla_R\nu + \nu\nabla_R^2\psi\right].$$

   The major physical insight of Born and Oppenheimer is that *electronic wavefunctions are quite insensitive to changes in nuclear positions*, so gradients of ψ (with respect to nuclear coordinates)

$$\nabla_R\psi \qquad \text{and} \qquad \nabla_R^2\psi$$

   are negligible.

Hence, we can write:

$$\frac{-\hbar^2}{2\mu}\nabla_R^2\Psi(\underline{R},\underline{r}_i) = -\frac{\hbar^2}{2\mu}\psi(\underline{r}_i;\underline{R})\nabla_R^2\nu(\underline{R}) \qquad (9)$$

The key point of the Born-Oppenheimer approximation is this simplification.

6. Using this result we can simplify the Schrödinger Equation (**??**) in step 4:

$$\begin{aligned}\left[\psi\left(-\frac{\hbar^2}{2\mu}\nabla_R^2\nu(\underline{R})\right)\right] &+ \underbrace{\left[\sum_i -\frac{\hbar^2}{2m}\nabla_i^2 + V\right]\psi}_{=\hat{H}_{\mathrm{el}}(\underline{r}_i;\underline{R})=E_{\mathrm{el}}\psi(\underline{r}_i;\underline{R})}\nu(\underline{R}) \\ &= E\nu(\underline{R})\psi\end{aligned}$$

Re-arranging:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + E_{\mathrm{el}}(R)\right]\nu(\underline{R}) = E\nu(\underline{R})\ . \qquad (10)$$

This gives a **Schrödinger Equation for nuclear motion**. The electronic energies, $E_{\mathrm{el}}(R)$, act as an **effective potential** in which the nuclei move.

SUMMARY of Born-Oppenheimer approximation

1. Nuclei move much more slowly than electrons (much more massive $M_P \gg m_e$). We calculate electronic energies and wavefunctions neglecting $\nabla_R^2/2\mu$ term. Solution for electrons depends on position of nuclei, **not** their motions: the electrons adjust **instanteously** to changes in position of nuclei.
2. The total solution is separable (but not exactly) into (nuclear) × (electron) part.
3. In the equation for the nuclear motion, the electronic energies at different internuclear distances provide a potential in which the nuclei move.

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 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 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 H_2^+

5.3 THE H_2^+ MOLECULE

The hydrogen molecular ion H_2^+ is the simplest molecule possible: it has one electron and two protons.

In the Born-Oppenheimer approximation we need to solve two separate Schrödinger equations: the **electronic** equation and the **nuclear** one. First, we will fix the positions of the nuclei and concentrate on the **electronic part**.

So we use the electronic Hamiltonian of the previous lecture (Lecture 21, equation **??**) and we solve:

$$\left[-\frac{\nabla_r^2}{2} - \frac{1}{|\underline{R}_A - \underline{r}|} - \frac{1}{|\underline{R}_B - \underline{r}|} + \frac{1}{|\underline{R}_A - \underline{R}_B|}\right] \psi(\underline{r_i}; \underline{R}) \\ = E_{\mathrm{el}}(R)\psi(\underline{r}; \underline{R})$$

(note atomic units have been used, $e = m_e = \hbar = 1$) or

$$\begin{aligned} \left(-\frac{\nabla_r^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}\right) & \psi \quad (\underline{r}_A, \underline{r}_B; \underline{R}) \\ & = \quad E_{\mathrm{el}}(R)\psi(\underline{r}_A, \underline{r}_B; \underline{R}) \end{aligned} \quad (11)$$

where we define the realtive positions:

$$\underline{R}_A - \underline{R}_B = \underline{R}$$
$$\underline{R}_A = -\underline{R}_B = \underline{R}/2$$
$$\underline{r}_A = \underline{R}_A - \underline{r}\ ; \qquad r_A = |\underline{R}_A - \underline{r}|$$
$$\underline{r}_B = \underline{R}_B - \underline{r}\ ; \qquad r_B = |\underline{R}_B - \underline{r}|$$

When r_A is small (i.e. the electron is very close to nucleus A), we will have:

(A)—a neutral hydrogen atom in the ground state and
(B)—a proton, i.e., we have :

$$\text{H–H}^+: \qquad \psi(\underline{r}_A, \underline{r}_B, \underline{R}) \underset{r_A \to 0}{\longrightarrow} \Phi_{1\text{s}}(\underline{r}_A)$$

(remember that ψ is the *electronic* wavefunction, and we know the electronic wavefunction for the ground state of a hydrogen atom) and vice versa when r_B is small:

$$\text{H}^+\text{–H}: \qquad \psi(\underline{r}_A, \underline{r}_B, \underline{R}) \underset{r_B \to 0}{\longrightarrow} \Phi_{1\text{s}}(\underline{r}_B)$$

$\Phi_{1\text{s}}(\underline{r})$ is the ground 1s wavefunction of the hydrogen atom. When $r{=}r_A$, Φ is centred on the nucleus A and when $r{=}r_B$ it is centred on B.

In between these limits, we suppose we have some **superposition**

$$\psi \sim C_1 \Phi_{1\text{s}}(\underline{r}_A) + C_2 \Phi_{1\text{s}}(\underline{r}_B)$$

where C_1 and C_2 are unknown constants.

Now, because H_2^+ is a **homonuclear** molecule (i.e. both nuclei are the same, A=B), the probability of the electron being around A is the same as that of being around B, i.e.

$$|C_1|^2 = |C_2|^2$$

or, $C_1 = \pm C_2 = C$.

In other words, the electronic wavefunction is either **symmetric** or **antisymmetric** with respect to exchange of A and B. The wavefunction must reflect this symmetry so:

$$\begin{aligned} \psi_+ &= C[\Phi_{1\mathrm{s}}(\underline{r}_A) + \Phi_{1\mathrm{s}}(\underline{r}_B)] \qquad &\text{(symmetric)} \\ \psi_- &= C[\Phi_{1\mathrm{s}}(\underline{r}_A) - \Phi_{1\mathrm{s}}(\underline{r}_B)] \qquad &\text{(antisymmetric)} \end{aligned}$$

with $C = 1/\sqrt{2}$ for a 50:50 split.

The symmetric combination is known as '**gerade**', and the antiymmetric as '**ungerade**' often denoted with subscripts g and u rather than + and -.

Building a *molecular* wavefunction from a superposition of *atomic* orbitals is a standard technique of molecular physics known as LCAO = **Linear Combination of Atomic Orbitals**.

Let's have a look at the wavefunctions and electron distributions:

(See diagram of wavefunctions and electron distributions of H_2^+ from lecture or website.)

ψ_+ provides plenty of electron density between protons A and B to neutralize mutual Coulomb repulsion.(ψ_+ represents an example of a **covalent bond**, where an electron is shared between two nuclei.)

For a ψ_- state, electrons avoid middle region. As we will see later, this leads to a state that is not stable.

For now we will say that the gerade state corresponds to a **bonding orbital** that is stable as the presence of the electon helps reduce the Coulomb repulsion of the two nucleo. The ungerade state corresponds to an **antibonding orbital** as there is very little probability of finding the electron between the nuclei their Coulomb repulsion pushes them apart, the molecule is unstable and breaks up.

LECTURE 22 SUMMARY

- the simplest molecule we can make is 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 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 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

5.4 CALCULATION OF ELECTRONIC ENERGIES FOR LOWEST STATES OF $\mathbf{H_2^+}$

To find the electronic energies we must evaluate:

$$\begin{aligned}\int \psi_\pm^* \hat{H}_{\mathrm{el}} \psi_\pm \mathrm{d}\tau &= \langle \psi_\pm | \hat{H}_{\mathrm{el}} | \psi_\pm \rangle \\ &= \langle \psi_\pm | E_\pm(R) | \psi_\pm \rangle \\ &= E_\pm \langle \psi_\pm | \psi_\pm \rangle\end{aligned}$$

and so the energy of the $\psi_\pm$ states is:

$$\begin{aligned}E_\pm(R) &= \frac{\int \psi_\pm^* \hat{H}_{\mathrm{el}} \psi_\pm d\tau}{\int \psi_\pm^* \psi_\pm d\tau} \\ &= \frac{A_\pm}{N_\pm} \\ &= \frac{\text{expectation value of } \hat{H}_{\mathrm{el}}}{\text{normalization constant}} \ .\end{aligned}$$

Then the normalization term is:

$$\begin{aligned}N_\pm &= \frac{1}{2} \int \left[\Phi_{1\mathrm{s}}^*(\underline{r}_A) \pm \Phi_{1s}^*(\underline{r}_B)\right] \left[\Phi_{1\mathrm{s}}(\underline{r}_A) \pm \Phi_{1\mathrm{s}}(\underline{r}_B)\right] d\tau \\ &= \frac{1}{2} \left[1 + 1 \pm 2 \int \Phi_{1\mathrm{s}}^*(\underline{r}_A) \Phi_{1\mathrm{s}}(\underline{r}_B) d\tau\right] \\ &= 1 \pm I(R) \ ,\end{aligned}$$

since:

$$\int \Phi_{1\mathrm{s}}^*(\underline{r}_{A,B}) \Phi_{1\mathrm{s}}(\underline{r}_{A,B}) d\tau = 1$$

and

$$I(R) = \int \Phi_{1\mathrm{s}}^*(\underline{r}_B) \Phi_{1\mathrm{s}}(\underline{r}_A) d\tau = \int \Phi_{1\mathrm{s}}(\underline{r}_B) \Phi_{1\mathrm{s}}^*(\underline{r}_A) d\tau$$

I(R) is the **overlap** between $\Phi_{1\mathrm{s}}(\underline{r}_A)$ and $\Phi_{1\mathrm{s}}(\underline{r}_B)$. It is non-zero since they are **not orthogonal** as they are centered on different origins.

For the expectation values, $A_{\pm}$, we again use the electronic Hamiltonian of **Lecture 22**, equation (**??**):

$$\hat{H}_{\text{el}} = -\frac{1}{2}\nabla_r^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

First we recall from the treatment of atomic hydrogen that:

$$\left[-\frac{1}{2}\nabla_r^2 - \frac{1}{r_A}\right] \Phi_{1\text{s}}(\underline{r}_A) = E_{1\text{s}}\Phi_{1\text{s}}(\underline{r}_A) \qquad (12)$$

and

$$\left[-\frac{1}{2}\nabla_r^2 - \frac{1}{r_B}\right] \Phi_{1\text{s}}(\underline{r}_B) = E_{1\text{s}}\Phi_{1\text{s}}(\underline{r}_B)\ ,$$

where $E_{1\text{s}}$ is ground state energy of H atom.

We want:

$$\begin{aligned} A_{\pm} &= \int \frac{1}{\sqrt{2}}\left[\Phi_{1\text{s}}^*(\underline{r}_A) \pm \Phi_{1\text{s}}^*(\underline{r}_B)\right] \\ &\times \hat{H}_{\text{el}}\frac{1}{\sqrt{2}}\left[\Phi_{1\text{s}}(\underline{r}_A) \pm \Phi_{1\text{s}}(\underline{r}_B)\right] d\tau\ . \end{aligned}$$

that we will re-write as:

$$A_{\pm} = \langle \hat{H}_{\text{el}} \rangle = \frac{1}{2}\left[H_{AA} + H_{BB}\right] \pm H_{AB} \qquad (13)$$

where

$$\begin{aligned} H_{AA} &= \int \Phi_{1\text{s}}^*(\underline{r}_A)\hat{H}_{\text{el}}\Phi_{1s}(\underline{r}_A)d\tau \\ &= E_{1\text{s}} && \text{(Energy of H atom)} \\ &+ \frac{1}{R}\int \Phi_{1\text{s}}(\underline{r}_A)\Phi_{1\text{s}}(\underline{r}_A)d\tau && \text{(internuclear repulsion)} \\ &- \int \Phi_{1\text{s}}^*(\underline{r}_A)\frac{1}{r_B}\Phi_{1\text{s}}(\underline{r}_A)d\tau && \text{(Coulomb Integral)} \\ &= E_{1s} + \frac{1}{R} - J(R) \end{aligned}$$

where $J(R)$ is due to the interaction with the other atom, B.

There is a similar term H_{BB} from the other atom, B:

$$H_{BB} = E_{1s} + \frac{1}{R} - J(R) \tag{14}$$

Also:

$$H_{AB} = H_{BA} = \int \Phi^*_{1\mathrm{s}}(\underline{r}_A)\hat{H}_{\mathrm{el}}\Phi_{1\mathrm{s}}(\underline{r}_B)d\tau \tag{15}$$

and

$$H_{AB} = \pm \left[\left(E_{1\mathrm{s}} + \frac{1}{R}\right) I(R) - \underbrace{\int \Phi^*_{1\mathrm{s}}(\underline{r}_A)\frac{1}{r_A}\Phi_{1\mathrm{s}}(\underline{r}_B)d\tau}_{\text{`}K\text{' exchange integral}} \right] .$$

So

$$H_{AB} = \pm \left(E_{1\mathrm{s}} + \frac{1}{R}\right) I(R) \mp K(R) \; . \tag{16}$$

Putting these results together, the electronic energy is:

$$\begin{aligned} E_\pm &= A_\pm/N_\pm \\ &= \frac{\left(E_{1\mathrm{s}} + \frac{1}{R}\right) - J \pm \left(E_{1\mathrm{s}} + \frac{1}{R}\right) I \mp K}{1 \pm I} \\ &= \underbrace{E_{1\mathrm{s}} + \frac{1}{R}}_{\substack{\text{H atom +} \\ \text{Coulomb repulsion}}} + \frac{-J \mp K}{1 \pm I} \; . \end{aligned}$$

The integrals J, K, I depend parametrically on $\underline{r}$ and can be evaluated *analytically*. It turns out that:

$$\begin{gathered} -J = e^{-2R} > 0. \\ K = (1+R)e^{-R} > 0. \\ I = (1 + R + \tfrac{R^2}{3})e^{-R} \end{gathered}$$

and since $\quad 0 < I < 1 \quad$ so $\quad 1 \pm I > 0.$

FORM OF $E_{\pm}(R)$

1. As $R \rightarrow \infty$, $J, K, I \rightarrow 0$, so:
$$E_{-} \simeq E_{+} \rightarrow E_{1s} + \frac{1}{R}$$
2. The splitting
$$\frac{2K(R)}{(1 \pm I)}$$
lowers E_+ and increases E_-.
3. As $R \rightarrow 0$

   $E_{\pm} \rightarrow \infty$

   because of repulsion between nuclei.
4. $E_+(R)$ has a minimum. This leads to a stable molecule.

   Wavefunction associated with this eigenvalue (ψ_+) is a **bonding orbital**.

   $E_-(R)$ is higher than the energy of the separated atoms.

   Wavefunction associated with this eigenvalue (ψ_-) is an **antibonding orbital**. If the electron is excited to this state, the molecule falls apart.
5. FOR STABLE MOLECULE:
$$D_e = \text{DISSOCIATION ENERGY},$$
$$R_e = \text{EQUILIBRIUM DISTANCE OF NUCLEI.}$$

When does the approximation fail? At small internuclear separation R the wavefunction should tend to that of the ground state of He^+ with $Z = 2$, which our LCAO wavefunction ψ_+ does not. Hence the actual binding energy is slightly greater than that given by Born-Oppenheiner.

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, 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 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 H_2 molecule using the Born-Oppenheimer approximation
- know how to apply the Pauli Exclusion Principle to the 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

5.5 THE H_2 MOLECULE

H_2 is the simplest neutral molecule.

We will proceed in a similar manner to that which we used for H_2^+, although we must bear in mind that:

As for H_2^+:

- We look at electronic wavefunction first, following B-O approximation.
- Also have covalent bond (nuclei identical so share electron).
- Also have definite symmetry with respect to exchange of **nuclei** (symmetric or antisymmetric under $\hat{P}_{\mathrm{AB}}$).

But unlike H_2^+:

- There are now two electrons so must consider **Pauli Exclusion Principle**: ψ must be *anti-symmetric* with respect to exchange of **electrons**.

The electronic Hamiltonian for H_2 is:

$$\hat{H}_{\mathrm{el}} = \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2}_{\text{K.E. of electrons 1 and 2}} - \underbrace{\frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}}}_{\text{Nucleus-electron attraction}} + \underbrace{\frac{1}{R} + \frac{1}{r_{12}}}_{\text{Repulsion between nuclei and between electrons}} \tag{17}$$

Of course, the wavefunction must include **spin**:

$$\psi^{S,T} = \psi(\underline{r}_i; \underline{R})\chi^{S,T} \tag{18}$$

where $S = 0$ or 1 since we have two electrons each with spin $\frac{1}{2}$. The χ (spin wavefunctions) are the same as we obtained for **Helium** (i.e. two-electron wavefunctions).

Remember that for $\psi^{S,T}$ to be antisymmetric overall:

- if $\psi(\underline{r}_i; \underline{R})$ is anti-symmetric with respect to exchange of electrons then χ^S (spin part) must be symmetric ⇒ **spin triplet**.
- if $\psi(\underline{r}_i; \underline{R})$ is symmetric with respect to exchange of electrons then χ^S must be anti-symmetric ⇒ **spin singlet**.

As for H_2^+ we can build the low-lying states of H_2 from atomic orbitals of 1s hydrogen. The antisymmetric $\psi = \psi_-$, will give us a spin **triplet** state:

$$\psi^{\mathrm{T}} \simeq \frac{1}{\sqrt{2}}\left[\Phi_{1\mathrm{s}}(\underline{r}_{A1})\Phi_{1\mathrm{s}}(\underline{r}_{B2}) - \Phi_{1\mathrm{s}}(\underline{r}_{A2})\Phi_{1\mathrm{s}}(\underline{r}_{B1})\right]\chi^{T} \tag{19}$$

and the symmetric $\psi = \psi_+$, will give us a spin **singlet** state:

$$\psi^{\mathrm{S}} \simeq \frac{1}{\sqrt{2}}\left[\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) + \Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1})\right]\chi^{S} \tag{20}$$

As before, to obtain the energy associated to these two states we work out expectation value of Hamiltonian, normalized for either singlet or triplet states:

$$\begin{aligned} E_\pm(R) &= \frac{\int \psi^{*S,T}\hat{H}_{\mathrm{el}}\psi^{S,T}d\tau}{\int \psi^{*S,T}\psi^{S,T}d\tau} \\ E_+ &\rightarrow \psi^{\mathrm{S}} \\ E_- &\rightarrow \psi^{\mathrm{T}} \end{aligned}$$

Optional: Working through these integrals, like we did for H_2^+, gives the denominator, $\int \psi^{*S,T}\psi^{S,T}d\tau =$

$$\begin{aligned}
& \frac{1}{2}\int\left(\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) \pm \Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1})\right)^* \\
\times \; & \left(\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) \pm \Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1})\right) dr_1 dr_2 \\
= \; & \frac{1}{2}\int \Phi^*_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{A1})dr_1 \int \Phi^*_{1s}(\underline{r}_{B2})\Phi_{1s}(\underline{r}_{B2})dr_2 \\
+ \; & \frac{1}{2}\int \Phi^*_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{A2})dr_2 \int \Phi^*_{1s}(\underline{r}_{B1})\Phi_{1s}(\underline{r}_{B2})dr_1 \\
\pm \; & \frac{1}{2}\int \Phi^*_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B1})dr_1 \int \Phi^*_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B2})dr_2 \\
\pm \; & \frac{1}{2}\int \Phi_{1s}(\underline{r}_{A1})\Phi^*_{1s}(\underline{r}_{B1})dr_1 \int \Phi_{1s}(\underline{r}_{A2})\Phi^*_{1s}(\underline{r}_{B2})dr_2
\end{aligned} \tag{21}$$

which, remembering that the $\Phi_{1s}(\underline{r}_{N,i})$ (for $N = A, B$ and $i = 1, 2$) are normalised, and defining the **overlap integral**:

$$I = \int \Phi^*_{1s}(\underline{r}_{N,i})\Phi_{1s}(\underline{r}_{M,i})dr_i \tag{22}$$

we see that:

$$\int \psi^{*S,T}\psi^{S,T}d\tau = 1 \pm I^2 \tag{23}$$

remembering that the '+' corresponds to the spin singlet, and the '-' to the spin triplet.

For the numerator we need to evaluate four parts. First:

$$\int \Phi^*_{1s}(\underline{r}_{A1})\Phi^*_{1s}(\underline{r}_{B2})\hat{H}_{\mathrm{el}}\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) \tag{24}$$

Breaking up $\hat{H}_{\mathrm{el}}$ we can identify the $-\frac{1}{2}\nabla^2_1 - \frac{1}{r_{A1}}$ and $-\frac{1}{2}\nabla^2_2 - \frac{1}{r_{B2}}$ as being the hydrogen atom Hamiltonians, and so both will integrate to E_{1s}.

We can also recognise

$$\frac{1}{R}\int |\Phi_{1s}(\underline{r}_{A1})|^2|\Phi_{1s}(\underline{r}_{B2})|^2 d\tau = \frac{1}{R} \tag{25}$$

the nuclear repulsion term that was present in the H_2^+ solution.

The rest of the Hamiltonian gives rise to:

$$\int |\Phi_{1s}(\underline{r}_{A1})|^2|\Phi_{1s}(\underline{r}_{B2})|^2 \left(-\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}}\right) d\tau = J(R) \tag{26}$$

which we can identify as a **Coulomb integral** (not exactly the same as in the previous H_2^+ solution)

And so we find the first part of the numerator is

$$2E_{1s} + \frac{1}{R} + J \tag{27}$$

The second term to evaluate is:

$$\int \Phi^*_{1s}(\underline{r}_{A2})\Phi^*_{1s}(\underline{r}_{B1})\hat{H}_{el}\Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1}) \tag{28}$$

which, as only the electon number labels have changed clearly integrates to the same as the above.

The third term is a 'cross term':

$$\int \Phi^*_{1s}(\underline{r}_{A2})\Phi^*_{1s}(\underline{r}_{B1})\hat{H}_{el}\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) \tag{29}$$

Adopting the same procedure as above, the first part we tackle is the hydrogen atom Hamiltonians $-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}}$ and $-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{B2}}$ which will produce two terms equal to

$$\pm E_{1s} I^2 \tag{30}$$

where I is the overlap as defined before which occurs because we now have to evaluate terms like $\int \Phi^*(\underline{r}_{B1})\Phi(\underline{r}_{A1})dr_1$.

We can also identify the nuclear repulsion term:

$$\pm \frac{1}{R} I^2 \tag{31}$$

remembering the '+' and '-' are spin singlet and triplet respectively.

This leaves only the part:

$$\int \Phi^*(\underline{r}_{A2})\Phi^*(\underline{r}_{B1})\Phi(\underline{r}_{A1})\Phi(\underline{r}_{B2})\left(-\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}}\right) d\tau \tag{32}$$

which we will denote $K(R)$, the **Exchange Integral**.

So the contribution from this third term is

$$\pm(2E_{1s} + \frac{1}{R})I^2 + K \tag{33}$$

The fourth term is the other cross-term, which again differs only by the electron labels being swapped, and so integrates to the same result.

Adding together all four terms (and remembering the factor of $\frac{1}{2}$ from the initial wavefunction normalisation), we get:

$$\langle \psi^{S,T} | \hat{H}_{\mathrm{el}} | \psi^{S,T} \rangle = (2E_{1s} + \frac{1}{R})(1 + I^2) + J \pm K \tag{34}$$

where the sign of K depends on the symmetry of the wavefunction.

Normalising we find an expression for the energy:

$$E_{\pm} = 2E_{1s} + \frac{1}{R} + \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} \tag{35}$$

Back to core material: The energies for the spin singlet (+) and spin triplet (-) states are:

$$E_\pm = \underset{\substack{\downarrow \\ \text{2 hydrogen} \\ \text{atoms}}}{2E_{1s}} + \underset{\substack{\downarrow \\ \text{Nuclear} \\ \text{repulsion}}}{\frac{1}{R}} + \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} \tag{36}$$

As for H_2^+: I is the **overlap** integral, J is the **Coulomb** integral and K is the **exchange** integral.

Let's look at the integrals in this case more closely:

OVERLAP:

$$I(R) = \int \Phi_{1\mathrm{s}}^*(\underline{r}_{A1})\Phi_{1\mathrm{s}}(\underline{r}_{B1})d\tau \ . \tag{37}$$

$$I < 1$$

So $1 \pm I^2 > 0$ is **always positive**.

COULOMB:

$$J(R) = \int |\Phi_{1\mathrm{s}}(\underline{r}_{A1})|^2 \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}}\right) |\Phi_{1\mathrm{s}}(\underline{r}_{B2})|^2 d\tau \tag{38}$$

In general, J represents a **positive** contribution to the energy.

EXCHANGE:

$$\begin{aligned} K(R) &= \int \Phi^*_{1\mathrm{s}}(\underline{r}_{A1})\Phi^*_{1\mathrm{s}}(\underline{r}_{B2}) \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}}\right) \\ &\times \Phi_{1\mathrm{s}}(\underline{r}_{A2})\Phi_{1\mathrm{s}}(\underline{r}_{B1}) d\tau \end{aligned} \tag{39}$$

which, in general, represents a **negative** contribution.

What are E_+ and E_- like? Does the term $(J \pm K)/(1 \pm I^2)$ **lower** energy below that of separated H atoms ⇒ stable H_2 molecule or does it **raise** it ⇒ unstable H_2 molecule ?

From the previous analysis, the behaviour depends on the sign of $\pm K$, the exchange term.

So the spin singlet (add the negative contibution of K) lies **below** the spin triplet (subtract the negative contribution of K).

Compare and contrast H_2 (simplest two electron molecule) with Helium (simplest two electron atom).

For Helium, triplet lies below singlet.

Why ? The triplet in Helium is lower energetically because electrons avoid each other. Remember that:

$$\psi \rightarrow 0 \quad \text{as} \quad r_{12} \rightarrow 0$$

because the antisymmetric helium spatial wavefunction was zero when $r_1 = r_2$. This means there is a *low probability of overlap*. Previously we described this as the electron 'keeping away' from each other.

For the molecule, the triplet ψ has a zero at the midpoint of H_2.

There is a *low probability of finding an electron between protons* in the antisymmetric ψ (triplet spin) case.

For a molecule, the most important factor for stability is that **electrons should neutralize mutual repulsion of nuclei**, i.e., the $1/R$ term. So the molecules are more stable if there is a significant probability that the electrons are between the nuclei. This does not happen for the spin triplet - the electrons 'keep away' from each other, but in doing so expose the nuclei to each other.

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

5.6 NUCLEAR MOTION OF MOLECULES

Now we have solved the electronic Schrödinger equation for two examples we will move on to the nuclear equation.

A molecule with N nuclei has $3N$ nuclear degrees of freedom and three types of motion:

- **Translation**—Free motion of the molecule as a whole in x, y, z direction: 3 degrees of freedom.
- **Rotation**—Rotation about centre of mass. In general 3 rotational axes for a solid body but only 2 for a linear molecule (3 or 2 degrees of freedom).
- **Vibtation**—Nuclei vibrate about equilibrium positions: $3N-6$ (or $3N-5$ for linear molecules) vibrational modes.

5.7 NUCLEAR MOTION OF A DIATOMIC MOLECULE

Consider a diatom AB and its nuclear Schrödinger equation (**??**):

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + E_{\mathrm{el}}(R)\right]\nu(\underline{R}) = E\nu(\underline{R})\ .$$

where $\underline{R}$ is the internuclear vector and μ is the nuclear reduced mass:

$$\mu = \frac{M_A M_B}{M_A + M_B} \tag{40}$$

Expressing ∇_R^2 in spherical polar coordinates:

$$-\frac{\hbar^2}{2\mu}\nabla_R^2 = \underbrace{-\frac{\hbar^2}{2\mu}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)}_{\text{Radial}} + \underbrace{\frac{\hat{J}^2}{2\mu R^2}}_{\text{Angular}} \tag{41}$$

with:

$$\hat{J}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \tag{42}$$

The solution of the Schrödinger equation proceeds analogously to that of the hydrogen atom, by separation of radial and angular coordinates:

$$\nu_{vJ}(\underline{R}) = \underbrace{\frac{F_v(R)}{R}}_{radial}\underbrace{Y_{JM_J}(\theta,\phi)}_{angular}\ . \tag{43}$$

5.7.1 ROTATION

The spherical harmonics, Y_{JM_J}, describe the rotational motion of the molecule with **angular momentum quantum numbers J and M_J**. They are eigenfunctions of:

$$\hat{J}^2 Y_{JM_J}(\theta,\phi) = \hbar^2 J(J+1)\, Y_{JM_J}(\theta,\phi) \tag{44}$$

The molecule behaves like a **rigid rotor** that rotates about an axis perpendicular to the internuclear axis through the centre of mass. Its **moment of inertia** is:

$$I_e = M_A\,(R-x)^2 + M_B x^2$$

But if the centre of mass is at the origin of coordinates, then:

$$I_e = \mu R_e^2 \tag{45}$$

The eigenvalues associated to the rotational motion are:

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2} = BJ(J+1) \tag{46}$$

where B is the **rotational constant**:

$$B = \frac{\hbar^2}{2\mu R_e^2} = \frac{\hbar^2}{2I_e} \qquad \text{so} \qquad \omega_{\text{rot}} \propto \frac{1}{\mu}\,,$$

If J=0, then E_{rot} is zero.

5.7.2 VIBRATIONS

If we substitute solution (**??**) in the nuclear Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 + E_{\mathrm{el}}(R)\right]\frac{F_v(R)}{R}Y_{JM_J} = E\frac{F_v(R)}{R}Y_{JM_J}\ ,$$

and take into account that:

$$-\frac{\hbar^2}{2\mu}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)\frac{F_v(R)}{R} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{d^2F_v(R)}{dR^2}\ .$$

we can eliminate the Y_{JM_J} and the $1/R$ term to get:

$$\underbrace{\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{\hbar^2 J(J+1)}{2\mu R^2} + E_{\mathrm{el}}(R)\right]}_{\text{K.E.+Rotational+electronic}} F_v(R) = \underbrace{E}_{\text{Total}}\ F_v(R)\ . \tag{47}$$

The functions $F_v(R)$, solutions of (**??**), describe the vibrational motion of the molecule. We could solve (**??**) numerically, but for a stable molecule, $E_{\mathrm{el}}(R)$ has a minimum at $R{=}R_e$:

This potential well supports quantum states. The nuclear motion is generally confined to a small region around R_e. We can show that for motion close to equilibrium i.e. $R \simeq R_e$,

$$E_{\mathrm{el}}(R) \sim \text{parabolic} \qquad \Rightarrow \qquad \text{motion} \sim \text{harmonic.}$$

We can expand $E_{\rm el}(R)$ as a Taylor series about $R = R_e$:

$$\begin{aligned} E_{\rm el}(R) = E_{\rm el}(R_e) \ &+ \ (R - R_e) \left.\frac{dE_{\rm el}}{dR}\right|_{R=R_e} \\ &+ \ \frac{(R-R_e)^2}{2} \left.\frac{d^2E_{\rm el}}{dR^2}\right|_{R=R_e} \cdots . \end{aligned} \quad (48)$$

Since $R - R_e$ is small, we neglect terms higher than quadratic.

At the minimum,

$$\left.\frac{dE}{dR}\right|_{R=R_e} = 0$$

So, to 2nd order,

$$E_{\rm el}(R) = E_{\rm el}(R_e) + \frac{1}{2}k(R - R_e)^2 \ , \quad (49)$$

i.e. the potential in which the nuclei move is a constant plus a harmonic term $\equiv \frac{1}{2}kx^2$ where k is the harmonic oscillator constant (spring constant):

$$k = \left.\frac{d^2E}{dR^2}\right|_{R=R_e} .$$

We can now re-write equation (**??**):

$$\begin{aligned} \Rightarrow \ & \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + E_{\rm el}(R_e) + \frac{1}{2}k(R - R_e)^2\right] F_v(R) \\ = \ & (E - E_{\rm rot})F_v(R) \end{aligned} \quad (50)$$

Rearranging:

$$\begin{aligned} \Rightarrow \ & \underbrace{\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{1}{2}k(R - R_e)^2\right]}_{\text{Quantum harmonic oscillator}} \ F_v(R) \\ = \ & \underbrace{(E - E_{\rm rot} - E_{\rm el}(R_e))}_{E_v} F_v(R) \\ = \ & E_v F_v(R) \ . \end{aligned}$$

Hence, we have:

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right) \ , \qquad v = 0, 1, 2, \dots \ ,$$

with v the **vibrational quantum number**. E_v is the energy of a harmonic oscillator of frequency

$$\omega = \sqrt{\frac{k}{\mu}}$$

so that the energy can be written:

$$E_v = \hbar \sqrt{\frac{k}{\mu}} \left(v + \frac{1}{2} \right) \ . \tag{51}$$

For $v = 0$

$$E_v = \frac{1}{2}\hbar\omega$$

is referred to as the **zero-point energy**.

The energy of a quantum harmonic oscillator, unlike the classical harmonic oscillator, is **never** zero.

ENERGY OF A DIATOMIC MOLECULE

$$\begin{aligned} E &\simeq \underbrace{E_{\text{el}}}_{\substack{\text{electronic}\\ \text{energy at}\\ \text{equilibrium}}} + \underbrace{BJ(J+1)}_{\substack{\text{Rotational}\\ \text{energy}}} + \underbrace{\left(v+\frac{1}{2}\right)\hbar\omega}_{\substack{\text{Vibrational}\\ \text{energy}}} \\ &\simeq E_{\text{el}} + E_{vJ} \end{aligned}$$

This is the total energy for an **ideal** diatomic molecule. For a real molecule, this is valid as long as:

1. v is small: the harmonic approximation is best near the bottom of the well
2. J is also small: centrifugal distortion tends to stretch the molecule and lower the rotational energy.

EXAMPLE

A molecule AB has nuclei of mass, $M_A = 4m$ and $M_B = 6m$. It emits photons at a frequency of

$$\begin{aligned} &\nu_v \quad \text{for} \quad v = 1 \rightarrow 0 \text{ transitions} \\ &\nu_R \quad \text{for} \quad J = 1 \rightarrow 0 \text{ transitions} \end{aligned}$$

The atom, A, is replaced by an isotope of half the mass. Estimate the new values for:
(a) $v = 1 \rightarrow 0$ line; (b) $J = 1 \rightarrow 0$ line.

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

5.8 REAL MOLECULES

The energy expression we obtained in the previous lecture:

$$E = \underbrace{E_{el}(R_e)}_{electronic} + \underbrace{BJ(J+1)}_{E_J} + \underbrace{\hbar\omega\left(v+\frac{1}{2}\right)}_{E_v} \tag{52}$$

applies only to an *ideal* molecule. *Real* molecules deviate from the ideal case:

1. *Centrifugal distortion*: As J increases, internuclear distance **stretches**. In effect this lowers the rotational energy. This is important for high $J \geq 10$
2. The rotational constant B depends on v. Since molecules *vibrate*, effective bondlength $\neq R_e$. Combining the effects of (1) and (2) means E_J becomes:

   $$E_J = B_v J(J+1) - \underbrace{D_v J^2(J+1)^2}_{\substack{\text{centrifugal}\\ \text{distortion}}} \ .$$

3. Potential E_{el} is not really parabolic, except approximately, for low v. For high v, corrections due to the *anharmonicity* of the potential are needed.

   A more realistic description of vibration in diatomic molecules can be achieved by the use of the **Morse potential**. This addresses the deviation stated in point 3.

5.8.1 MORSE POTENTIAL

For many covalent molecules (e.g. H_2, H_2^+) a better description of the potential well provided by E_{el} is given by the empirically determined **Morse potential**.This potential has the form:

$$V_{\text{Morse}}(R) = D_e \left(e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)} \right) \tag{53}$$

where R_e = equilibrium bond length, and D_e = potential minimum D_e, R_e and α are constants for a given molecule. Note that $V_{\text{Morse}}(R)$ is attractive at large R, has a minimum and then becomes repulsive at short distances.

Some values are shown in the table below:

Molecule	R_e / Å	D_e / eV	αR_e
H_2	0.742	4.75	1.44
I_2	2.66	1.56	4.95
HCl	1.27	4.62	2.38

The parameter α determines how fast the potential energy falls off with distance. It can be related to the force constant, k, by expanding $V_{\text{Morse}}(R)$ in powers of $(R - R_e)$:

$$V_{\text{Morse}}(R) \simeq D_e \left(-1 + \alpha^2 (R - R_e)^2 + ... \right) \tag{54}$$

for small displacements from equilibrium, and comparing this equation with equation (**??**) of **Lecture 25** we see that:

$$\alpha = \sqrt{\frac{1}{2}\frac{k}{D_e}} \tag{55}$$

5.9 SPECTRA OF DIATOMIC MOLECULES

5.9.1 PURE ROTATIONAL TRANSITIONS

Pure rotational transitions can take place between rotational states corresponding to the same electronic state. Only relevant to molecules with a permanent electric dipole moment (e.g. LiF, HCl, but **not** homonuclear diatomics) that the oscillating electric field can rotate.

Pure **rotational** transitions occur at **microwave** frequencies. The selection rules are:

$$\Delta J = \pm 1 \ .$$

(Remember this is the nuclear angular momentum)

Molecules such as O_2, H_2 and H_2^+ have no dipole: They have a much weaker spectrum of 'forbidden' $\Delta J = 2$ transitions. (*Non-linear molecules* can have $\Delta J = 0$).

Frequencies of transition lines are given by:

$$\frac{E_{rot}(J) - E_{rot}(J-1)}{h} = \frac{2BJ}{h}$$

so the spectral lines are **equally** spaced with separation $2B/h$.

Answer: $H^{35}Cl$ has a rotational spectrum with line spacing of $\Delta\tilde{\nu} \approx 21.2$ cm^{-1}. Find B, I_e and R_e.

Solution: $\Delta\tilde{\nu} = 2B$, so $B \approx 10.6$ cm^{-1}. And from B we can calculate the moment of inertia, as $B = \frac{\hbar^2}{2I_e}$, so $I_e = \frac{\hbar^2}{2\times 2.11\times 10^{-22}} = 2.63 \times 10^{-47}$ kgm^2. Also $I_e = \mu R_e$, so $R_e = \sqrt{\frac{2.63\times 10^{-47}}{\frac{35}{36}1.67\times 10^{-27}}} = 1.27$ Å as in table on previous page.

5.9.2 VIBRATION-ROTATION SPECTRA

Vibration-rotation transitions occur at **infra-red** frequencies. For harmonic approximation, the selection rules are:

$$\Delta v = \pm 1 \qquad |J - J'| = 1$$

(Transitions with $\Delta v = \pm 2, \pm 3, ...$ occur but are much less likely). $\Delta v = \pm 1$ comes from the selection rules of the harmonic oscillator. The change in J is as for the rotational spectra above.

Ro-vibrational transitions give rise to spectra with 2 branches, the '**R-branch**' ($\Delta J = +1$):

$$\begin{aligned} \hbar\omega^{(R)}_{\mathrm{ro-vib}} &= E(v+1, J+1) - E(v, J) \\ &= 2B(J+1) + \hbar\omega_0, \qquad J = 0, 1, 2... \end{aligned}$$

and the '**P-branch**' ($\Delta J = -1$):

$$\begin{aligned} \hbar\omega^{(P)}_{\mathrm{ro-vib}} &= E(v+1, J-1) - E(v, J) \\ &= -2BJ + \hbar\omega_0, \qquad J = 1, 2, 3... \end{aligned}$$

with a line missing at $\hbar\omega_0$ due to ΔJ=0 being forbidden.

Note that the line spacing gives us B (and hence I_e and even R_e) as before, and ω_0 (the missing line) can give us the spring constant.

Example: the missing line in the rotation-vibration spectrum of $H^{35}Cl$ is at $\tilde{\nu} = 2990.6\mathrm{cm}^{-1}$. What is the spring constant of the bond?

Answer: Recall that $\omega_0 = \sqrt{\frac{k}{\mu}}$ we have $k = \mu\omega_0^2$. So: $k = \frac{35}{1+35} \times 1.67 \times 10^{-27} \times (2\pi)^2 \times (8.96 \times 10^{13})^2 = 515\mathrm{Nm}^{-1}$.

5.9.3 ELECTRONIC TRANSITIONS

Diatomic molecules have *axial symmetry*, not spherical symmetry as in atoms. Hence, the *electronic* eigenfunctions are simultaneous eigenfunctions of $\hat{H}_{\mathrm{el}}$ and $\hat{L}_z$, i.e., $\hat{L}_z$ gives us the good quantum number:

$$\hat{L}_z\psi = M_L\hbar\psi = \pm\Lambda\hbar\psi \tag{56}$$

Λ is the absolute value in atomic units of the projection of the total *electronic* angular momentum on the internuclear ($z-$) axis. As with atomic spectroscopic notation (S, P, D, F,....) we use letters to denote the angular momentum, but for molecules we use Greek letters:

$$\begin{aligned}\Lambda &= 0 \longrightarrow \Sigma\\ \Lambda &= 1 \longrightarrow \Pi\\ \Lambda &= 2 \longrightarrow \Delta\\ \Lambda &= 3 \longrightarrow \Phi\\ &\ldots\ldots.\end{aligned}$$

If we want to label a one-electron function (a molecular orbital) we use λ=0,1,2,... $\longrightarrow \sigma$, π, δ, etc..

As for atoms, the spin multiplicity is indicated as a superscript, so we have:

$$^{2S+1}\Lambda_{g,u}$$

where g and u denote gerade or ungerade and only applies for *homonuclear* molecules.

Molecular electronic transitions are always accompanied by rotational and vibrational transitions. The selection rules for changes in the electronic state are:

$$\begin{gathered}\Delta\Lambda = 0, \pm 1 \\ g \rightarrow u \text{ but } \textbf{not } g \rightarrow g \text{ or } u \rightarrow u \\ \Delta S = 0\end{gathered}$$

5.9.4 ELECTRONIC-VIBRATIONAL-ROTATIONAL

The energy difference between electronic levels is much larger than those corresponding to transitions without a change in the electronic state, hence these transitions are usually observed in the **ultra-violet**. We have discussed the selection rules for the electronic part in section **??**. For the nuclear part we have:

$$\begin{aligned} &\Delta v && \text{can take any value.} \\ &\Delta J = && 0 \ \pm 1 \end{aligned}$$

But the bond length, and hence the rotational constant, B, can differ substantially for the initial and final states. Hence:

$$\Delta E_J = [BJ(J+1) - B'J'(J'+1)]$$

does not lead to evenly spaced lines. Since,

$$E_n, E_v \gg E_{\rm rot}$$

this just spreads the electronic-vibration frequency into a **band** of closely spaced lines.

EXAMPLE

The carbon monoxide (CO) molecule is observed to have a set of spectral lines with frequencies:

$$\begin{aligned} f_1 &= 1.15 \times 10^{11}\,\mathrm{Hz} \\ f_2 &= 2.30 \times 10^{11}\,\mathrm{Hz} \\ f_3 &= 3.46 \times 10^{11}\,\mathrm{Hz} \\ f_4 &= 4.61 \times 10^{11}\,\mathrm{Hz} \end{aligned}$$

What sort of transitions do these correspond to ?

5.9.5 FRANCK-CONDON PRINCIPLE

In most cases, the electron ‘jumps’ so quickly in electronic transitions that nuclei cannot relax. If this is the case, the distribution of final vibrational states after the transition takes place is determined by the **overlap** of vibrational wavefunctions between the ground and excited state.

The overlap between $v'' = 0$ and $v' = 0$ is very small so transitions are very weak.

Transition $v'' = 0 \rightarrow v' = n$ is big as the $v' = n$ state is large at inner turning point.

More formally, the transition probability is proportional to:

$$I_{v''v'} = \left[\int_0^\infty \nu^*_{v''}(\underline{R})\nu_{v'}(\underline{R})d\tau\right]^2$$

where $\nu_{v''}$ is the vibrational wavefunction of the lower state and $\nu_{v'}$ that of the upper state.

I is known as the **Franck-Condon Factor**.

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

5.10 IONIC BONDS

Previously, for example when we studied the H_2 molecule, we have looked at **covalent** bonds, where the electrons are ‘shared’ between the two nuclei.

Now we will look at **ionic** bonds, where the electron is much more likely to be found near one of the atoms in the molecule.

Ionic bonds frequently occur for alkali-halogen molecules. **Alkalis** (e.g., Li, Na, Rb, Cs) have *one electron outside* a closed shell. **Halogens** are *one electron short* of being closed shell. Hence NaCl, KCl, LiF, etc form ionic bonds.

Example: Sodium Chloride (NaCl). We consider two properties of atoms:

1. Electron affinity, A

This is the binding energy of an *additional* electron, e.g. F → F^-. Some examples (for the halogens) are shown below. Note that the energies are *negative*, i.e. energy is *released*.

element	electron affinity, A /eV
F	-3.40
Cl	-3.62
Br	-3.36
I	-3.06

Cl → Cl^-: A(Cl) = -3.62 eV
Na → Na^-: A(Na) = -0.54 eV

2. Ionisation energy, I.

Energy 'cost' of *removing* outer electron, e.g. Na → Na^+. Some examples (for the alkalis) are shown below. Note that the energies are *positive*, i.e. energy must be *put in*.

element	ionisation energy, I /eV
Li	5.39
Na	5.14
K	4.34
Rb	4.18
Cs	3.89

$$\begin{aligned}&I(\mathrm{Na}) = 5.14\,\mathrm{eV}\\&I(\mathrm{Cl}) = 12.97\,\mathrm{eV} \;\;\rightarrow\;\; \text{much more energy needed}\end{aligned}$$

Energy cost of removing an electron from Na and adding it to Cl is $I(\mathrm{Na}) + A(\mathrm{Cl})$:

$$E = 5.14\,\mathrm{eV} - 3.62\,\mathrm{eV} = 1.52\,\mathrm{eV} = 0.056\,\mathrm{a.u.}\;.$$

That is, we need to provide energy to 'transfer' an electron from Na to Cl (notice that if $I < A$ then the process would be *exothermic*). **But**, we now have $\mathrm{Na}^+\mathrm{Cl}^-$ and the ions attract each other. For what R does the Coulomb attraction overcome the energy loss due to ionisation? When:

$$E = 0.056\,\mathrm{a.u.} = \frac{1}{R} \rightarrow R \sim 17.9 \text{ a.u}$$

Net energy exchange will be zero if $R \sim 17.9\,\mathrm{a.u.}$ Any closer and it will be negative, i.e., $\mathrm{Na}^+\mathrm{Cl}^-$ is more stable than Na-Cl.

If we want the *dissociation energy*, i.e., the energy required to separate Na and Cl as **neutral atoms** then we could calculate the Coulomb attration using the bond length determined from spectroscopy to be $R_0 = 0.24\,\mathrm{nm} = 4.54$ a.u., which makes $E_{\mathrm{Coulomb}} = 0.22$ a.u. $\equiv 6$ eV

$$\begin{aligned} D_e = \underbrace{0.22}_{\text{separate ions}} - \underbrace{(I(\mathrm{Na}) + A(\mathrm{Cl}))}_{\text{transfer electron}} &= 0.22 - 0.056\,\text{a.u.} \\ &= 0.164\,\text{a.u.} \\ &= 4.46\ \text{eV} \end{aligned} \qquad (57)$$

The measured dissociation energy $D_e = 4.22$ eV (0.155 a.u. or in chemistry terms 411 kJ mol^{-1}). So our simple calculation is within about 10%. Corrections come from the fact that the ions are **not** point charges, and at these small distances the electron clouds overlap, raising the energy slightly. A more realistic form for the potential would be:

$$E(R) = \underbrace{E(\infty)}_{I(\mathrm{Na})+A(\mathrm{Cl})} - \underbrace{\frac{1}{R}}_{\text{Coulomb}} + \underbrace{b\mathrm{e}^{cR}}_{\text{overlap}}$$

where the parameters b and c may be derived from spectroscopic measurements. The depth of this potential for NaCl is at -5.7 eV $= -0.21$ a.u. rather than -6.0 eV.

We should also take into account that small correction ($\approx$ 0.02 eV) from the zero point energy - the first vibrational level lies $\frac{1}{2}\hbar\omega_0$ above the minimum of the potential.

5.11 IONIC CHARACTER OF THE BOND

In reality, most bonds are not purely ionic. For NaCl we have $R = 4.54\,\mathrm{a}_0$. If we had $\mathrm{Na}^+\ \mathrm{Cl}^-$ then the electric dipole moment would be $\mu = eR_0 = 4.54$a.u.. The experimentally measured value for the dipole moment is, however, $p_{\text{expt}} \simeq 3.54$a.u., indicating that the electron still maintains some probability of remaining on Na.

Some properties of selected alkali halide molecules:

molecule	bond length, R_0 / a.u.	dipole moment, $\lvert p\rvert$ / a.u.
Li F	2.96	2.49
Li Cl	3.82	2.81
Na Cl	4.46	3.54
Na Br	4.73	3.59
K Cl	5.04	4.04
K Br	5.33	4.18
Rb Cl	5.27	4.14
Cs Cl	5.49	4.09

The fractional ionic character of the bond may be expressed as:

$$\frac{p}{eR_0} = \frac{3.54}{4.54} = 0.78$$

for the sodium chloride bond.

$\frac{p}{eR_0} = 1 \longrightarrow$ completely ionic

$\frac{p}{eR_0} = 0 \longrightarrow$ completely covalent

LECTURE 27 SUMMARY

- the electron affinity is the energy required to add an electon 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 from a stable ionic molecule
- to calculate the binding energy we nust 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