5 MOLECULES

5.1 SCHRÖDINGER EQUATION FOR MOLECULES

(See text books or lecture notes for figure of molecular coordinates)

$$\underline{R}_N \text{ and } \mathrm{Z}_N = \text{Position vector and charge of } N\text{th nucleus}$$
$$\underline{r}_i = \text{Position vector of } i\text{th electron}$$

Time independent Schrödinger equation:

$$\hat{H}\Psi(\underline{R}_1, \underline{R}_2, \underline{R}_3, ..., \underline{r}_1, \underline{r}_2, ...) = E\Psi(\underline{R}_1, \underline{R}_2, \underline{R}_3, ..., \underline{r}_1, \underline{r}_2, ...)\ . \tag{1}$$

The Hamiltonian is:

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

where the potential is :

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

Because of the interaction between electrons and nuclei, the solution cannot be simply separated into nuclear and electronic components, i.e.

$$\Psi(\underline{R}_N, \underline{r}_i) \neq \nu(\underline{R}_N)\psi(\underline{r}_i)^1$$

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., $\frac{m_e}{M_N} \ll 1$. For simplicity we will use a general diatomic molecule to explain the approximation.

(See text books or lecture notes for figure of diatomic coordinates)

Hamiltonian can be written:

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

with μ the reduced mass of the nuclei.

BORN-OPPENHEIMER APPROXIMATION

1. Clamp nuclei in place. In other words, set the internuclear coordinate to a constant value:

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

   Hence, neglect nuclear kinetic energy term, $-\frac{\hbar^2}{2\mu}\nabla_R^2$, in the Hamiltonian (4).

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[1] 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

2. Having 'pinned' the nuclei, now solve the Schrödinger Equation for electronic motion:

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

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

Note that $\underline{R}$ is now a parameter on which the wavefunction and Hamiltonian depend. To indicate this we write $(\underline{r}_i;\underline{R})$. This is the **electronic Schrödinger equation**, solve for different values of R,

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

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

where $\psi(\underline{r}_i;\underline{R})$ is the solution to eq. 5

Put this form into the **<u>full</u>** Schrödinger Equation including the nuclear kinetic energy term:

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

4. Kinetic energy operator for the nuclei:

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

The key point of the B–O approximation is that electronic wavefunctions are quite insensitive to changes in nuclear positions $\nabla_R\psi$ and $\nabla_R^2\psi$ are negligible and

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

5. Finally, using this result we can simplify the Schrödinger Equation (8) in step 4:

$$\left[\psi\left(-\frac{\hbar^2}{2\mu}\nabla_R^2\nu(\underline{R})\right)\right] + \underbrace{\left[\sum_i \frac{-\hbar^2}{2m}\nabla_i^2 + V\right]\psi}_{\substack{\text{our clamped solu-}\\\text{tions from 1}\\= E_{\rm el}\psi(\underline{r}_i;\underline{R})}}\nu(\underline{R}) = E\nu(\underline{R})\psi$$

Re-arranging and cancelling ψ as we are not operating on it anymore:

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

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

SUMMARY of Born-Oppenheimer approximation

1. Nuclei move much more slowly than electrons ($M_P \gg m_e$), take R a constant value.
2. Calculate electronic energies and wavefunctions using electronic Hamiltonian, i.e. neglecting $\nabla_R^2/2\mu$ term in $\hat{H}$.

   E and Ψ for electrons depend parametrically on R.

3. The total wavefunction is separable (but not exactly) into nuclear × electron part and put it into total Hamiltonian.
4. In total $\hat{H}$, as e^- adjust instantaneously to changes in position of nuclei, KE term of nuclei does not act on the electronic wavefunction.
5. End up with a Shrodinger eq. for the nuclear motion (1D for diatomic), where the electronic energies at different internuclear distances provide a potential in which the nuclei move.

5.3 THE H_2^+ MOLECULE

H_2^+ is simplest molecule possible: it only has one electron and two protons. (See diagram in text books or in lecture notes) B–O approximation: fix the positions of the nuclei and concentrate on the **electronic part**.

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

$$\underline{R}_A - \underline{R}_B = \underline{R} \text{ and } \underline{R}_A = -\underline{R}_B = \underline{R}/2$$

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

When R is large , we will have either :

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

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

or

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

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

In between, we suppose we have some superposition

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

where C_1 and C_2 are unknown constants.

Now, because H_2^+ is a **homonuclear** molecule (A=B), the probability of the electron being around A is the same as that of being around B and the wavefunction must reflect this symmetry so:

$$\psi_+ = 1/\sqrt{2}[\Phi_{1s}(\underline{r}_A) + \Phi_{1s}(\underline{r}_B)] \qquad \text{(symmetric or gerade)}$$
$$\psi_- = 1/\sqrt{2}[\Phi_{1s}(\underline{r}_A) - \Phi_{1s}(\underline{r}_B)] \qquad \text{(antisymmetric or ungerade)}$$

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

Electron distributions (see figure 5.1) 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.

5.4 CALCULATION OF ELECTRONIC ENERGIES FOR LOWEST STATES OF H_2^+

The energy of the $\psi_\pm$ states is:

$$E^\pm(R) = \frac{\int \psi^*_\pm \hat{H}_{el}\psi_\pm d\tau}{\int \psi^*_\pm\psi_\pm d\tau} = \frac{A_\pm}{N_\pm} = \frac{\text{expectation value of } \hat{H}_{el}}{\text{normalization constant}}.$$

Then, the normalization term is:

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

I(R) is the <u>OVERLAP</u> between $\Phi_{1\mathrm{s}}(\underline{r}_A)$ and $\Phi_{1\mathrm{s}}(\underline{r}_B)$. It is non-zero since they are NOT <u>ORTHOGONAL</u>; they are centered on different origins.

Now for the $A_{\pm}$. We use again the electronic Hamiltonian that we used in (11):

$$\hat{H}_{\mathrm{el}} = -\frac{1}{2}\nabla^2_r - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

First we recall from the treatment of atomic hydrogen that:

$$\left[-\frac{1}{2}\nabla^2_r - \frac{1}{r_i}\right]\Phi_{1\mathrm{s}}(\underline{r}_i) = E_{1\mathrm{s}}\Phi_{1\mathrm{s}}(\underline{r}_i) \qquad i = A, B \tag{12}$$

We want:

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

that we will re-write as:

$$A_{\pm} =< \hat{H}_{\mathrm{el}} >= \frac{1}{2}\left[H_{AA} + H_{BB}\right] \pm H_{AB} \tag{13}$$

where

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

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: Also:

$$H_{AB} = H_{BA} = \int \Phi_{1\mathrm{s}}^*(\underline{r}_A)\hat{H}_{\mathrm{el}}\Phi_{1\mathrm{s}}(\underline{r}_B)d\tau \tag{14}$$

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

$$H_{AB} = \pm\left(E_{1\mathrm{s}} + \frac{1}{R}\right) I(R) \mp K(R) \ . \tag{15}$$

Putting these results together, the electronic energy is:

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

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

$$-J = Re^{-2R} > 0.$$

$$K = (1+R)e^{-R} > 0.$$

$$I = (1 + R + \tfrac{R^2}{3})e^{-R} \qquad \text{and} \qquad 0 < I < 1 \qquad \text{so} \qquad 1 \pm I > 0.$$

FORM OF $E_\pm(R)$

See figure in text book or lecture notes.

1. As $R \to \infty$, $J, K, I \to 0$, so: $E_- \simeq E_+ \to E_{1s} + \frac{1}{R}$

2. The splitting $2K(R)/(1 \pm I)$ lowers E_+ and increases E_-.
3. As $R \to 0$ $\quad E_\pm \to \infty$ because of repulsion between nuclei.
4. $E_+(R)$ has a minimum. This leads to a stable molecule. Wavefunction associated to this eigenvalue is a **BONDING ORBITAL**.

   $E_-(R)$ is higher than the energy of the separated atoms. Wavefunction associated to this eigenvalue is an **ANTIBONDING ORBITAL**. If electron is excited to this state, molecule falls apart.
5. FOR STABLE MOLECULE:

$$D_e = \text{DISSOCIATION ENERGY},$$
$$R_e = \text{EQUILIBRIUM DISTANCE OF NUCLEI.}$$

5.5 THE H_2 MOLECULE

See textbook or lecture notes for diagram of coordinates for H_2.

As for H_2^+:

- Electronic wavefunction first, B-O approximation.
- Covalent bond (nuclei identical so share electron).
- Also have symmetry with respect to exchange of nuclei.

But unlike H_2^+:

- 2 electrons, must consider Pauli Principle: ψ must be antisymmetric w.r.t. exchange of electrons.

The electronic Hamiltonian for H_2 is:

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

Of course, the wavefunction must include SPIN:

$$\psi^{S,T} = \psi(\underline{r}_i;\underline{R})\chi^{S,T} \tag{16}$$

where $S = 0$ or 1 since we have two electrons each with spin $\frac{1}{2}$. The $\chi^{S,T}$ are the same as we obtained for He. So,

if $\psi(\underline{r}_i;\underline{R})$ is anti-symmetric w.r.t. exchange of e^- then χ must be symm. $\Rightarrow$ SPIN TRIPLET.

if $\psi(\underline{r}_i;\underline{R})$ is symmetric w.r.t. exchange of e^- then χ must be anti-symm. $\Rightarrow$ 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 triplet state:

$$\psi^{\mathrm{T}} \simeq \frac{1}{\sqrt{2}}\left[\Phi_{1\mathrm{s}}(\underline{r}_{A1})\Phi_{1\mathrm{s}}(\underline{r}_{B2}) - \Phi_{1\mathrm{s}}(\underline{r}_{A2})\Phi_{1\mathrm{s}}(\underline{r}_{B1})\right]\chi^T \tag{17}$$

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

$$\psi^{\mathrm{S}} \simeq \frac{1}{\sqrt{2}}\left[\Phi_{1\mathrm{s}}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) + \Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1})\right]\chi^S \tag{18}$$

As before

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

Working through these integrals, like for H_2^+, gives:

$$E_\pm = \underbrace{2E_{1s}}_{\downarrow \text{ 2 hydrogen atoms}} + \underbrace{\frac{1}{R}}_{\downarrow \text{ Nuclear repulsion}} + \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} \tag{19}$$

OVERLAP:

$$I(R) = \int \Phi_{1s}^*(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B1})d\tau \ . \tag{20}$$

$$I < 1$$

So $1 \pm I^2 > 0$ is always <u>POSITIVE</u>.

COULOMB:

$$J(R) = \int |\Phi_{1s}(\underline{r}_{A1})|^2 \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}}\right) |\Phi_{1s}(\underline{r}_{B2})|^2 d\tau \tag{21}$$

In general, J represents a <u>POSITIVE</u> contribution.

EXCHANGE:

$$K(R) = \int \Phi_{1s}^*(\underline{r}_{A1})\Phi_{1s}^*(\underline{r}_{B2}) \left(\frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}}\right) \Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1})d\tau \tag{22}$$

which, in general, represents a <u>NEGATIVE</u> contribution.

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

See text books or lecture notes for diagram of E_{el} for H_2

So <u>SINGLET</u> lies below <u>TRIPLET</u>.

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, $\psi \to 0 \quad \text{as} \quad r_{12} \to 0$, so there is a low probability of overlap.

For the molecule, the triplet ψ has a zero at the midpoint of H_2. (similar to H_2^+ in figure 5.1). 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.

5.6 NUCLEAR MOTION OF MOLECULES

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

- TRANSLATION—Free motion 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).
- VIBRATION—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 (10):

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

$$-\frac{\hbar^2}{2\mu}\nabla_R^2 = \underbrace{-\frac{\hbar^2}{2\mu}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)}_{\text{Radial}} + \underbrace{\frac{\hat{J}^2}{2\mu R^2}}_{\text{Angular}} \tag{23}$$

with $\hat{J}^2$ same as $\hat{L}^2$ in section 2. Solution with separate radial and angular coordinates:

$$\nu_{vJ}(\underline{R}) = \frac{F_v(R)}{R}Y_{JM_J}(\theta,\phi) \ . \tag{24}$$

5.7.1 ROTATION

The spherical harmonics, Y_{JM_J}.**angular momentum quantum numbers J and M_J**. Eigenfunctions of:

$$\hat{J}^2 Y_{JM_J}(\theta,\phi) = \hbar^2 J(J+1)\, Y_{JM_J}(\theta,\phi) \tag{25}$$

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

The eigenvalues associated to the rotational motion are:

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2} = BJ(J+1) \tag{26}$$

where B is the ROTATIONAL CONSTANT:

$$B = \frac{\hbar^2}{2\mu R_e^2} = \frac{\hbar^2}{2I_e} \qquad \text{and} \qquad I_e \text{moment of inertia}$$

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

5.7.2 VIBRATIONS

If we substitute solution (24) in the nuclear Schrödinger equation:

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

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:

$$\underbrace{\left[\frac{-\hbar^2}{2\mu}\frac{d^2}{dR^2}+\frac{\hbar^2 J(J+1)}{2\mu R^2}+E_{\rm el}(R)\right]}_{\simeq \text{ K.E. + Rotational energy + electronic energy}} F_v(R) = \underbrace{E}_{\text{Total energy}} F_v(R)\ . \tag{27}$$

The functions $F_v(R)$, solutions of (27), describe the vibrational motion of the molecule. For a stable molecule, $E_{\rm el}(R)$ has a minimum at R=R_e (see figure 5.2) and supports quantum states. We can show that for motion close to equilibrium i.e. $R \simeq R_e$, $E_{\rm el}(R) \sim$ parabolic ⇒ motion $\sim$ harmonic.

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

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

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,

$$E_{\rm el}(R) = E_{\rm el}(R_e) + \frac{1}{2}k(R-R_e)^2\ , \tag{28}$$

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/force constant:

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

We can now re-write equation (27):

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

Rearranging:

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

Hence, we have:

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

with v the **vibrational quantum number**. $E_v=\hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right)$ is the energy of a harmonic oscillator of frequency $\omega=\sqrt{\frac{k}{\mu}}$. 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

$$\begin{aligned}E &\simeq \underbrace{E_{\text{el}}}_{\substack{\text{electronic}\\ \text{energy at}\\ \text{equilibrium}\\ \approx 10\text{eV}}} + \underbrace{BJ(J+1)}_{\substack{\text{Rotational energy}\\ \approx 0.001\text{eV}}} + \underbrace{\left(v+\frac{1}{2}\right)\hbar\omega}_{\substack{\text{Vibrational energy}\\ \approx 0.1\text{eV}}} \\ &\simeq E_{\text{el}} + E_{vJ}\end{aligned}$$

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.

5.8 REAL MOLECULES

The energy expression. eq. 29, applies only to an ideal molecule. Real molecules deviate from ideal case:

1. 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.
2. The rotational constant B depends on v. Since molecules vibrate, effective bond-length $\neq R_e$.
3. Centrifugal distortion. As J increases, internuclear distance STRETCHES. In effect this lowers the rotational energy and E_J becomes:

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

   This is important for high $J \geq 10$

5.8.1 MORSE POTENTIAL

For many covalent molecules (e.g. H2, H_2^+) a better description of the potential well provided by E_e is given by the empirically determined **Morse potential**. (see figure in text books or lecture notes)

R$_e$= equilibrium bondlengh
D$_e$= potential minimum
D$_0$= dissociation energy for v=0

This potential has the form:

$$V(R) = D_e \left(e^{-2\alpha(R-R_e)} - 2e^{-\alpha(R-R_e)}\right) \tag{29}$$

D_e, R_e and α are constants for a given molecule. Note that $V(R)$ is attractive at large R, has a minimum and then becomes repulsive at short distances. The parameter α determines how fast the potential energy falls off with distance. It can be related to the force constant, k, by expanding $V(R)$ in powers of $(R - R_e)$:$\alpha = \sqrt{\frac{1}{2}\frac{k}{D_e}}$

5.9 IONIC BONDS

Ionic bonds occur for alkali-halogen molecules. Alkalies (e.g., Li, Na, Rb, Cs) have one electron outside closed shell. Halogens are one electron short of being closed shell. Example: LiF. We consider two properties of atoms:

1. Electron affinity, A

   This is the binding energy of an additional electron F → F$^-$: A(F) = -3.4 eV = energy released, Li → Li$^-$: A(Li) = -0.62 eV

2. Ionisation energy, I.

   Energy 'cost' of removing outer electron

   $$I(\text{Li}) = 5.4\,\text{eV}$$
   $$I(\text{F}) = 17.4\,\text{eV} \;\rightarrow\; \text{much more energy needed}$$

Energy cost of removing an electron from Li and adding it to F is

$$E = 5.4\,\text{eV} - 3.4\,\text{eV} = 2.0\,\text{eV} = 0.074\,\text{a.u.}\,.$$

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

$$E = 0.074\,\text{a.u.} = \frac{1}{R} \to R \sim 13.6\ a.u$$

Net energy exchange will be zero if $R \sim 13.6\,\text{a.u.}$ Any closer and it will be negative, i.e., Li^+F^- is more stable than LiF.

If we want the dissociation energy, i.e., the energy required to separate Li and F as <u>NEUTRAL</u> atoms, then:

$$D = 0.29 + (I(\text{Li}) - A(\text{F})) = 0.29 - 0.074 = 0.206\,\text{a.u.}$$

In reality, most bonds are not purely ionic. For LiF, the lithium's electron still maintains some probability of remaining on Li.

5.10 SPECTRA OF DIATOMIC MOLECULES

5.10.1 ELECTRONIC TRANSITIONS

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

$$\hat{L}_z\psi = M_L\hbar\psi = \pm\Lambda\hbar\psi \tag{30}$$

Λ is the absolute value in atomic units of the projection of the total electronic angular momentum on the internuclear axis.

$$\begin{gathered}\Lambda = 0 \rightarrow \Sigma \\ \Lambda = 1 \rightarrow \Pi \\ \Lambda = 2 \rightarrow \Delta \\ \Lambda = 3 \rightarrow \Phi \\ \ldots\ldots\ldots\end{gathered}$$

If we want to label a one-electron function (a molecular orbital) we use λ=0,1,2,... → σ, π, δ, etc.. The spin multiplicity is indicated as a superscript,

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

where g and u denote gerade (symm.) or ungerade (anti. symm.) 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:

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

5.10.2 PURE ROTATIONAL TRANSITIONS

Rotational transitions can take place between rotational states corresponding to the same electronic state (see figure 5.3). Only relevant to molecules with permanent electric dipole moment (e.g. LiF, HCl, but **not** homonuclear diatomics).

Pure ROTATIONAL transitions occur at MICROWAVE frequencies. The **selection rules** are:

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

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 $2B/h$ (see figure 5.4).

5.10.3 VIBRATION-ROTATION SPECTRA

VIBRATION-ROTATION transitions occur at INFRA RED frequencies (see figure 5.3).

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)

Ro-vibrational transitions give rise to spectra with 2 branches with a line missing at $\hbar\omega$:

$$\begin{array}{lll} \Delta J = +1 & J \longrightarrow J+1 & \text{('R' BRANCH)} \\ \Delta J = -1 & J \longrightarrow J-1 & \text{('P' BRANCH)} \end{array}$$

Lines are equally spaced by $2B/h$ except for the gap due to ΔJ=0 being forbidden (see figure 5.4).

5.10.4 ELECTRONIC-VIBRATIONAL-ROTATIONAL

These transitions are usually observed in the ULTRA VIOLET (see figure 5.3). We have discussed the selection rules for the electronic part in section (5.10.1). 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,

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

this just spreads the electronic-vibration frequency into a BAND of closely spaced lines (see figure 5.4).

5.10.5 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 (see figure 5.5).

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.