

Lecture 17b: Diatomic Molecules - Long Range Forces

Ionic Binding

We have seen that for homonuclear molecules, the dominant mechanism for chemical bonds is covalent binding - electrons delocalized between nuclei. For heteronuclear molecules, ionicity can dominate even at equilibrium if it is energetically favorable to transfer one or more electrons from one atom to another. The main attraction is the Coulomb attraction between the positive ion and negative ion with potential $\frac{1}{R}$.

For example, consider salt NaCl. The atomic configurations



The 3s electron of Na is weakly bound (small ionization pot) and Cl is strongly electronegative - closing the shell lowers the energy. Thus $Na^+ + Cl^-$ at infinite separations has an energy not much different from $Na + Cl$. However, as R decreases the Coulomb attraction lowers the energy of $Na^+ + Cl^-$ below $Na + Cl$ which barely interact. At very short distances, the interaction between the closed shell of Na^+ and Cl^- is like the repulsion between $He + He$. The strong repulsive exchange force can be empirically modeled by $Ae^{-\alpha R}$

van der Waals forces

For an ionic bond, the charged ions experience a long range force due to the $\frac{1}{R}$ Coulomb attraction between these "monopoles". Neutral atoms also experience a long-range force, but this must be due to higher order multipole interaction.

For neutrals, the lowest order multipole is electric dipole. Assuming the distance between the atoms is in the "quasi-static" zone, the dipole-dipole interaction is

$$\hat{A}_{dd} = \frac{\hat{d}_A \cdot \hat{d}_B - 3(\hat{e}_r \cdot \hat{d}_A)(\hat{e}_r \cdot \hat{d}_B)}{r^3}$$

To understand the nature of the long-range forces, we look at molecular potentials which asymptote to separate atoms $\phi^A + \phi^B$. At these long range separations there is no overlap between the electron wave functions, and exchange forces can be neglected. Thus we speak only of atom-A and atom-B, distinguishable by their positions, and not the indistinguishable electron-1 or electron-2.



$^2S+^2S$ potential

Consider the simple case of H_2 or diatomic alkali

In the absence of interaction the two-atom ground state

$$|\Psi^{(0)}\rangle_{AB} = |\phi_{nS}\rangle_A |\phi_{nS}\rangle_B$$

With energy $E^{(0)} = 2E_{nS} = -2 \times E_{\text{ionisation}}$

The first order shift in the energy

$$E^{(1)} = \langle \Psi^{(0)} | \hat{A}_{dd} | \Psi^{(0)} \rangle$$
$$= \frac{\langle d_A \rangle \cdot \langle d_B \rangle - 3(\vec{e}_R \cdot \langle d_A \rangle)(\vec{e}_R \cdot \langle d_B \rangle)}{R^3}$$

$$= 0$$

Since $\langle \phi_{nS} | d | \phi_{nS} \rangle = 0$ (No permanent dipole moment in state of definite parity)

We must thus go to second order

$$E^{(2)} = \sum_{\substack{n', n'' \\ \neq nS}} \frac{|\langle \phi_{nR} | \langle \phi_{n''} | \hat{A}_{dd} | \Psi^{(0)} \rangle|^2}{2E_{nS} - (E_{n'} + E_{n''})} \propto \frac{1}{R^6}$$

Now consider $\langle \phi_{nR} | d | \phi_{nS} \rangle$

By Wigner-Ekart, since d is rank-1 as for an s -state, no any momentums, we must have $l=1$ (virtual p -states)

Explicitly for hydrogen, $E_{nc} = -\frac{1}{2n^2}$ (a.u.)

$$\Rightarrow E^{(2)} = -2 \sum_{n, n'=2}^{\infty} \frac{|\langle \phi_{n'l} | \langle \phi_{n'l} | \hat{V}_{dd} | \phi_{n's} \rangle | \phi_{n's} \rangle|^2}{1 - (\frac{1}{n^2} + \frac{1}{n'^2})}$$

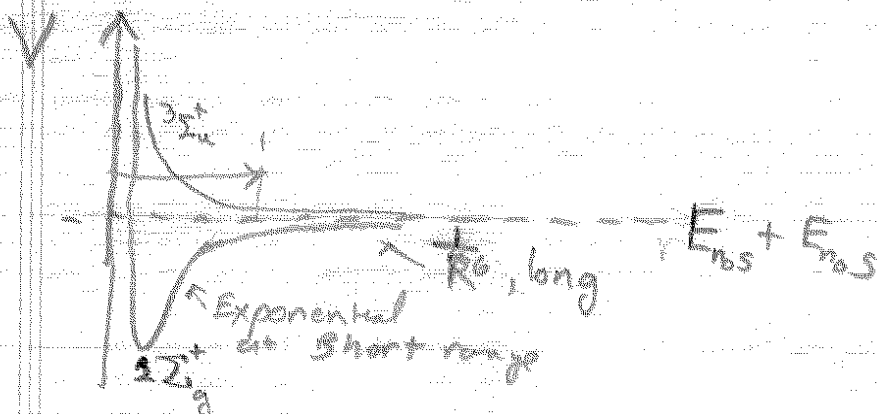
$E^{(2)} < 0 \Rightarrow$ Attractive interaction.

Responsible for long-range binding of noble gases which have no ^{attractive} exchange forces for separated atoms, only repulsion of electron clouds.

Order of magnitude estimate (using a.u.)

$$E_{\text{van der Waals}} \sim - \left[\frac{1}{(R/a_0)^3} \right]^2 \times \frac{e^2}{a_0} = -\frac{e^2}{R} \left(\frac{a_0}{R} \right)^5$$

reduce from coulomb attraction by $\left(\frac{a_0}{R} \right)^5$



van der Waals "range" of potential

$$\sim \frac{1}{2} \left(\frac{2m_{red} C_6}{\hbar} \right)^{\frac{1}{2}}$$

$$\frac{C_6}{R^6}$$

Excited States

Consider now an excited electronic molecular state which asymptotes to atomic levels (ns) & $(n'p)$. There are two degenerate manifolds

$$|\Psi_1\rangle = |\phi_{ns}\rangle_A |\phi_{n'p}\rangle_B \quad \text{and} \quad |\phi_{n'p}\rangle_A |\phi_{ns}\rangle_B \equiv |\Psi_2\rangle$$

We must do degenerate perturbation theory with \hat{V}_{dd}

$$\hat{V}_{dd} = \begin{bmatrix} 0 & -\frac{C_3}{R^3} \\ \frac{C_3}{R^3} & 0 \end{bmatrix} \begin{matrix} |\Psi_1\rangle \\ |\Psi_2\rangle \end{matrix}$$

$$\text{where } C_3 = |\langle \phi_{n'p} | \hat{d} | \phi_{ns} \rangle|^2 - 3 | \vec{e}_R \cdot \langle \phi_{n'p} | \hat{d} | \phi_{ns} \rangle |^2$$

Thus, there is a first order dipole-dipole interaction

$$\begin{cases} E_{dd}^{(0)} = \mp \frac{C_3}{R^3} & \text{with corresponding eigenstates} \end{cases}$$

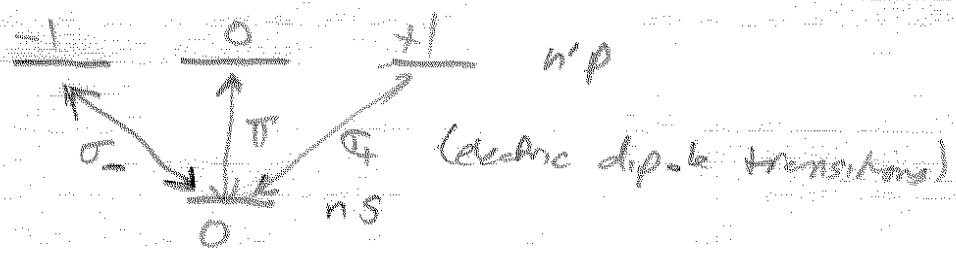
$$|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}} (|\phi_{ns}\rangle_A |\phi_{n'p}\rangle_B \pm |\phi_{n'p}\rangle_A |\phi_{ns}\rangle_B)$$

Since in the states $|\Psi_{\pm}\rangle$ $\langle \vec{d}_A | \vec{d}_B \rangle \neq 0$

To more precisely understand the nature of these long range forces, we must determine the matrix elements $\langle \phi_{n'p} | \hat{d} | \phi_{ns} \rangle$ which

requires us to consider "direction information" which is contained in the m_l q -number.

m_l



Remember, when dealing with molecules, the quantization axis (symmetry axis) is chosen to be along the internuclear axis.

There are four energy states corresponding to

- Dipole \parallel or \perp to internuclear axis
- Dipoles along same or opposite directions

Dipole along $\vec{e}_r \Rightarrow \pi$ -polarization $\Rightarrow M_l = 0 \Rightarrow \Sigma$ state
 Dipoles \perp to $\vec{e}_r \Rightarrow \sigma_{\pm}$ -polarization $\Rightarrow M_l = \pm 1 \Rightarrow \Pi$ state

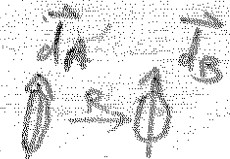
Four possibilities



$$\sum_{\text{same}}, V_{dd} = -\frac{2\langle d_{eg} \rangle^2}{R^3}$$



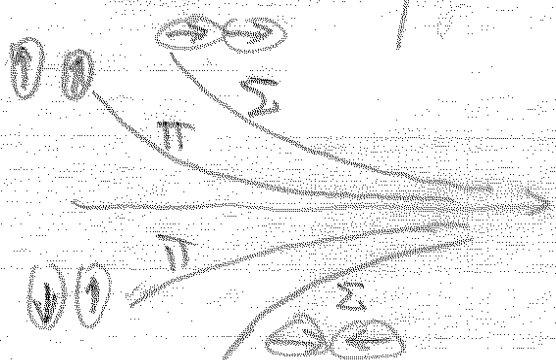
$$\sum_{\text{opp}}, V_{dd} = \frac{2\langle d_{eg} \rangle^2}{R^3}$$



$$\Pi \text{ state}, V_{dd} = +\frac{\langle d_{eg} \rangle^2}{R^3}$$



$$\Pi \text{ state}, V_{dd} = -\frac{\langle d_{eg} \rangle^2}{R^3}$$



Ignoring electron exchange symmetry these states are formed atomic states

$$\Psi_{\Lambda=1, m_{el}}^{(\pm)} = \frac{1}{\sqrt{2}} \left(|\phi_{ns}^A\rangle |\phi_{n'p, m_{el}}^B\rangle \pm |\phi_{n'p, m_{el}}^A\rangle |\phi_{ns}^B\rangle \right)$$

Ignoring spin, the $\Lambda=1, \Pi$ states are doubly degenerate.

To obtain the full molecular potentials, which asymptote to these long-range potentials we must include electron exchange symmetry. For this one-valence electron case, a properly symmetrized wave function is

$$\overset{\text{spin}}{\Lambda}_{\rho} = \Psi_{S, \rho}(\vec{x}_1, \vec{x}_2) \chi_S(1, 2)$$

↑ $\Psi_{S, \rho}$ ↑ $\chi_S(1, 2)$
↑ ρ ↑ spin-state (singlet/triplet)
↑ parity

$$\Psi_{S, \rho}(\vec{x}_1, \vec{x}_2) = \frac{1}{2} \left[\phi_{ns}^{(A)}(\vec{x}_1) \phi_{np}^{(B)}(\vec{x}_2) - \rho (-1)^S \phi_{np}^{(A)}(\vec{x}_1) \phi_{ns}^{(B)}(\vec{x}_2) \right. \\ \left. + (-1)^S \left(\phi_{ns}^A(\vec{x}_1) \phi_{np}^{(B)}(\vec{x}_2) - \rho (-1)^S \phi_{np}^{(A)}(\vec{x}_1) \phi_{ns}^{(B)}(\vec{x}_2) \right) \right]$$

$$\text{w.r.t } \vec{r} = \frac{\vec{r} - 3.5 \vec{R}}{R^3}$$

$$\langle V_{dd} \rangle = -\frac{\rho (-1)^S}{2} \left[\langle \phi_s^A | \vec{d}_1 | \phi_p^A \rangle \cdot \vec{r} \cdot \langle \phi_s^B | \vec{d}_2 | \phi_p^B \rangle + h.c. \right]$$

$$+ \frac{(-1)^S}{2} \left[\langle \phi_s^A | \vec{d}_1 | \phi_p^B \rangle \cdot \vec{r} \cdot \langle \phi_p^B | \vec{d}_2 | \phi_s^A \rangle + h.c. \right]$$

$$- \frac{\rho}{4} \left[\langle \phi_p^B | \vec{d}_1 | \phi_p^A \rangle \cdot \vec{r} \cdot \langle \phi_s^A | \vec{d}_2 | \phi_s^B \rangle + h.c. \right]$$

The last two terms correspond to the electron being delocalized between the two nuclei and these exchange effects are negligible for $R \gg a_0$.

$$\text{Thus the states } \Psi^{\pm} = \frac{1}{\sqrt{2}} \left(|\phi_A^A\rangle |\phi_B^B\rangle \pm |\phi_A^B\rangle |\phi_B^A\rangle \right)$$

are each associated with two different cases

$$+1 = p(-)^S \Rightarrow \text{gerade, singlet or ungerade, triplet}$$

$$-1 = p(-)^S \Rightarrow \text{gerade, triplet or ungerade, singlet}$$