VALENCE

Prof M. Brouard   *8 Lectures*

SUMMARY

The aim of this lecture course is to provide an introduction to *valence theory*. This is the theory used to describe the chemical bond. The goal of the theory is the prediction of molecular structure, and of the forces which drive chemical change. Valence therefore lies at the very heart of chemistry. The main topics to be covered in the lecture course are:

1. The Born-Oppenheimer Approximation

2. Bonding in H_2^+

   - the LCAO approximation

3. Many electron molecules

   - the orbital approximation, its strengths and weaknesses
   - binding in H_2
   - splitting of degenerate configurations
   - dissociation of H_2

4. Application of the variation principle to find LCAO's

   - the secular equations

5. Binding of the first row diatomics

   - splitting into terms, and
   - levels

6. Walsh diagrams

   - Bond angles in AH_2 systems

7. Hückel theory

   - use of symmetry
   - aromaticity
   - bond order, electron densities, and organic reactivity

8. Correlation Diagrams

   - predicting chemical reactivity

RECOMMENDED TEXTS

1. P.W. Atkins and J. de Paula, *Physical Chemistry*, (O.U.P., 7th Edition, 2002)

2. P.W. Atkins and R.S. Friedman, *Molecular Quantum Mechanics*, (O.U.P., 4th edition, 2004).

3. N.J.B.Green, *Quantum Mechanics I and II* (O.U.P., Chemistry Primers 48 and 65).

4. J.N. Murrell, S.F.A. Kettle and J.M. Tedder, *Valence Theory* (Wiley and Sons, 1974). Unfortunately out of print but widely available in libraries.

5. J.M. Brown, *Molecular Spectroscopy*, (O.U.P., Chemistry Primer 55).

VALENCE PROBLEM SHEET 1

1. Derive the secular equations for the trial wavefunction of the form

$$\psi = c_A \phi_A + c_B \phi_B$$

where ϕ_i is the normalized atomic orbital on atom i, and the c_i are coefficients.

2. Show that, when the atomic orbitals, ϕ_i, are orthogonal (such that $S_{ij} = 0$ for $i \neq j$), the roots of the secular equations derived in question 1 are given by:

$$E_\pm = \frac{H_{AA} + H_{BB}}{2} \pm \frac{1}{2} \left[(H_{AA} - H_{BB})^2 + 4H_{AB}^2 \right]^{1/2}$$

3. Find the coefficients c_i for the molecular orbitals associated with E_+ and E_- for the special cases $H_{AA} = H_{BB}$ (i.e. a homonuclear diatomic), and $H_{AA} = 2H_{BB} = \alpha$, $H_{AB} = \alpha/4$.

4. Two states, characterized by the wavefunctions ψ_1 and ψ_2, arise as eigenfunctions of some simple approximate Hamiltonian for a diatomic molecule, and have energies ϵ_1 and ϵ_2, respectively. When the full Hamiltonian is considered, a small interaction $\langle \psi_1 | \hat{H} | \psi_2 \rangle = \Delta$ between these states occurs. By considering trial wavefunctions of the form $\Psi = c_1 \psi_1 + c_2 \psi_2$, and using the variational principle, find general expressions for the two lowest energy levels.

[Hint: the procedure leads to secular equations - use your knowledge of the properties of eigenfunctions to find the matrix elements, then make use of the result in question 2 above.]

5. In question 4, the energies ϵ_1 and ϵ_2 vary with internuclear separation R as $\epsilon_1 = K(R-3)$, $\epsilon_2 = -K(R-3)$, whereas $\Delta = K/10$ is a constant. Evaluate and plot the two lowest energy levels at $R = 3.0$, 3.0 ± 0.1, 3.0 ± 0.2, 3 ± 0.5, and 3 ± 1.0. Plot also the ratio $|c_1/c_2|$ as a function of R for each associated eigenfunction.

[This question illustrates the origin of the 'non-crossing rule'.]

VALENCE PROBLEM SHEET 2

1. Discuss the data on the following diatomic molecules, showing how they reflect the character of the occupied molecular orbitals.

	r/pm	ω_e/cm^{-1}	D_e/eV	$E^\star$/eV	I/eV
N_2	110	2359	9.76	6.22	15.58
N_2^+	112	2207	8.71	1.14	
NO	115	1904	6.50	0.015	9.26
NO^+	106	2376	10.84	6.47	
O_2	121	1580	5.12	0.98	12.07
O_2^+	112	1905	6.66	0.024	

[ω_e is the harmonic vibrational wavenumber, D_e the bond dissociation energy, $E^\star$ the energy of the first excited electronic state, and I is the first ionization energy.]

2. Some of the spectroscopically determined properties of the low lying states of the C_2 molecule are shown below:

Term symbol	Energy/cm^{-1}	Vibrational frequency/cm^{-1}	Bondlength/Å
$^1\Sigma_g^+$	0	1856	1.242
$^3\Pi_u$	610	1641	1.311
$^1\Pi_u$	8392	1608	1.318
$^1\Sigma_u^+$	43240	1830	1.238

Describe how these properties are related to the character of the molecular orbitals occupied in these states (note that the π_g orbitals are not involved).

3. The eigenfunctions for an electron (j) confined to a circular ring are

$$\psi_m(j) = \sqrt{\frac{1}{2\pi}} e^{im\phi_j}$$

where m is the quantum number and ϕ_j is the angular position of electron j on the ring, and the spin functions for electron j are $\alpha(j)$ and $\beta(j)$. A selection of model, two-electron wavefunctions can be written

(a) $\Psi_a = \dfrac{1}{\sqrt{2}} \left[\psi_1(1)\psi_{-1}(2) - \psi_1(2)\psi_{-1}(1)\right]\alpha(1)\alpha(2)$

(b) $\Psi_b = \dfrac{1}{2}\left[\psi_1(1)\psi_{-1}(2) + \psi_1(2)\psi_{-1}(1)\right]\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$

(c) $\Psi_c = \dfrac{1}{2}\left[\psi_1(1)\psi_{-1}(2) - \psi_1(2)\psi_{-1}(1)\right]\left(\alpha(1)\beta(2) + \alpha(2)\beta(1)\right)$

(d) $\Psi_d = \dfrac{1}{\sqrt{2}}\left[\psi_1(1)\psi_1(2)\right]\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right).$

For each of these wavefunctions in turn

i. Show that it satisfies the Pauli Principle (i.e. is antisymmetric with respect to exchange of the labels of electrons 1 and 2).

ii. Show that it is an eigenfunction of the operator $\hat{L}_Z = -i\hbar\left(\frac{\partial}{\partial\phi_1} + \frac{\partial}{\partial\phi_2}\right)$, and hence assign a spectroscopic term symbol Σ, Π, Δ, etc. depending on the eigenvalue obtained (i.e. $\Lambda \equiv M = m_1 + m_2 = 0 \Rightarrow \Sigma$, etc.).

iii. If the answer to (i) is Σ, determine the effect of changing ϕ_1 and ϕ_2 to $2\pi - \phi_1$ and $2\pi - \phi_2$ (equivalent to reflecting the coordinates of each electron in a plane perpendicular to the ring) and assign the symbol Σ^+ and Σ^- accordingly.

iv. Determine the effect of interchange of ϕ_1 and ϕ_2. Note that the spatial parts of triplet wavefunctions are antisymmetric and singlet functions are symmetric under this operation.

The motion of an electron around the internuclear axis of a diatomic molecule is analogous to motion on a ring. Use the above results to explain why the spectroscopic term symbol for the ground electronic state of O_2 is $^3\Sigma_g^-$.

4. Account *for all* of the following observations:

(a) the term symbols for the electronic ground states of Si_2 and C_2 are $^3\Sigma_g^-$ and $^1\Sigma_g^+$ respectively;

(b) the lowest two electronic states of S_2 have term symbols $^3\Sigma_g^-$ and $^1\Delta_g$; they are separated by about $4000\,\text{cm}^{-1}$ ($0.5\,\text{eV}$) and have very similar bond lengths;

(c) The dissociation energy of Mg_2 is only $0.1\,\text{eV}$;

(d) The first excited electronic state of NO lies only $0.015\,\text{eV}$ about the ground state.

VALENCE PROBLEM SHEET 3

1. Use Hückel theory to construct the secular equations for the π orbitals of the allyl radical shown below.
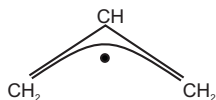
Determine the molecular orbital energies and the linear combinations of atomic orbitals associated with them. Estimate the electron spin densities at each carbon atom of the allyl radical, and use your result to predict the ESR spectrum of the allyl radical radical in solution, stating clearly any approximations that you make. [If you are unfamiliar with ESR spectroscopy, you might find it helpful to read Atkins and de Paula pp 615 -621.]

Show that the charge density arising from the π electrons is uniform at each carbon atom in the allyl radical. Suggest the most likely point of attack on the allyl cation by a nucleophilic reagent.

2. The kth molecular orbital for a linear chain of N carbon atoms has the form

$$\Psi_k = \sum_{m=1,N} \phi_m \sin\left[\frac{m\,k\,\pi}{N+1}\right]$$

where ϕ_m is a p_π orbital on atom m. Find its energy within Hückel theory by direct substitution into the secular equations.

Sketch the lowest three orbitals for a six-membered chain. By considering the relative phases of each molecular orbital on the first and last atoms, show that orbitals with even values of k are destabilized, and those with odd values of k are stabilized if the chain is converted to a ring.

3. To model the steric interactions in *cis*-butadiene an interaction between terminal atoms 1 and 4 is introduced ($H_{14} = H_{41} = -\beta/10$). Using perturbation theory, examine how the normal Hückel molecular orbital energies for butadiene are affected by this additional term. (Use the m.o.'s obtained in the lectures.)

4. An end-on view of the biphenyl molecule is sketched in the figure, defining the torsional angle ϕ between the planes of the benzene rings.

If the inter-ring interaction is ignored the Hamiltonian is simply:

$$H_0 = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}$$

where I is the appropriate moment of inertia. Show that

$$\psi_m = \sqrt{\frac{1}{2\pi}}\,\mathrm{e}^{im\phi}$$

is an eigenfunction of this Hamiltonian, determine the possible values of m, and the associated energy levels for the torsional motion.

To allow for inter-ring interactions, a term

$$V = V_2 \cos 2\phi$$

is added to the Hamiltonian. Discuss the form of this term, and the likely sign of V_2.

The effect of V on the low-lying excited states of the torsional motion may be found (approximately) by taking a trial wavefunction

$$\chi = c_{+1}\psi_{+1} + c_{-1}\psi_{-1}$$

and solving the secular equations in the basis (ψ_{+1}, ψ_{-1}). Determine the new excited state energy levels, and sketch the probability distribution for ϕ in the first excited state.

Discuss the limitations of this approach as V_2 increases.