

## 3.012 Bonding-Structure: Review Session

### 1 Keywords

- Hydrogen-like atoms: *Lecture 5*
- *Aufbau*: *Lecture 8; Engel, Reid 21.5*
- Screening, Hartree equations: *Lecture 7; Lecture 11; Recitation 4 II*
- Trends in the periodic table: *Lecture 8; Engel, Reid 21.6; Recitation 4 II*
- Variational principle: *Engel, Reid 21.4; Recitation 4 I and 5*
- Spin, Stern-Gerlach experiment: *Lecture 8; Engel, Reid 17.2*
- Hartree-Fock equations: *Lecture 11; Engel, Reid 21.5*
- $H_2^+$  molecule: *Lecture 9; Engel, Reid 23.1-3; Recitation 5 I-II*
- LCAO: *Lecture 9; Engel, Reid 24.2*
- Electronic Hybridization  $sp$ ,  $sp^2$ ,  $sp^3$ , Chemical bonding: *Lecture 10; Engel, Reid 25.1-2, 25.4*
- Stability of liquids: *Lecture 10; PS 4.4*
- Bond energy, bond length, bond order: *Lecture 10; Engel, Reid 24.6*
- Pauli exclusion principle, Antisymmetry requirement: *Lecture 11*
- Many-electron wavefunction, Slater determinant: *Lecture 11; Engel, Reid 24.2; PS 4.2*
- Homonuclear diatomic molecules  $\sigma_g 1s$ ,  $\sigma_u^* 1s$ ,  $\sigma_g 2s$ ,  $\sigma_u^* 2s$ ,  $\sigma_g 2p_z$ ,  $\sigma_u^* 2p_z$ ,  $\pi_u 2p_x$ ,  $\pi_u 2p_y$ ,  $\pi_g^* 2p_x$ ,  $\pi_g^* 2p_y$ : *Lecture 11; Engel, Reid 24.4-5; PS 4.5*
- Hückel model, HOMO-LUMO gap: *Lecture 12; Engel, Reid 25.7; PS 4.6*
- Quantum oscillator, Energies of a quantum oscillator: *Lecture 12, 13; Engel, Reid 18.1*

## 2 Hydrogen-like atoms

The quantized states of an electron in the presence of a hydrogen nucleus are obtained by solving the S.S.E:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right\} \psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \quad (1)$$

It is convenient to rewrite the preceding equation as:

$$\left\{ -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hat{L}^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right\} \psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \quad (2)$$

We moreover introduce spherical harmonics:

$$\hat{L}^2 Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi) \quad (3)$$

$$\hat{L}_z Y_{lm}(\theta, \phi) = \hbar m Y_{lm}(\theta, \phi) \quad (4)$$

$$\langle Y_{lm} | Y_{lm} \rangle = 1 \text{ (if same indices)} \quad (5)$$

$$\langle Y_{lm} | Y_{l'm'} \rangle = 0 \text{ (if different indices)} \quad (6)$$

We then make the *ansatz*:  $\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$ . As a result, the  $R(r)$  must satisfy:

$$\left\{ -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right\} R(r) = ER(r) \quad (7)$$

The eigenfunctions  $R_{nl}(r)$  are called radial wavefunctions. The eigenvalues are  $E_n = -\frac{1}{n^2}$  Ryd (for hydrogen-like atom,  $E_n = -\frac{Z^2}{n^2}$ ).

The function  $Y_{lm}(\theta, \phi)$  and  $R_{nl}(r)$  are essential to understand molecular and crystalline structures.

References and Examples: *Recitation 3*

## 3 Variational Principle

Solving the S.S.E analytically can be extremely complex. As a consequence, one often adopts another approach, the variational method. Broadly speaking, this method consists in finding the eigenstates of a quantum system by minimization of the total energy. The variational method can be described as follows:

1. Select a set of trial wavefunctions  $\{\psi_I, \psi_{II}, \psi_{III}, \dots\}$ .
2. calculate the expectation value for the total energy of each trial wavefunction:  $E_I = \frac{\langle \psi_I | \hat{H} | \psi_I \rangle}{\langle \psi_I | \psi_I \rangle}$ ,  $E_{II} = \frac{\langle \psi_{II} | \hat{H} | \psi_{II} \rangle}{\langle \psi_{II} | \psi_{II} \rangle}, \dots$

3. The wavefunction  $\psi_{min}$  corresponding to the lowest total energy among the trial wavefunctions is the best approximation for the ground-state wavefunction  $\psi_0$ .

References and Examples: *Recitation 4 I; PS 4.3*

## 4 Hückel Method, LCAO Method

The Hückel method consists in reformulating the S.S.E  $\hat{H}|\psi\rangle = E|\psi\rangle$  into a matrix eigenvalue problem. Given a complete set of orthogonal and normalized wavefunctions  $\{\phi_i\}$ , the S.S.E can indeed be rewritten as:

$$\begin{bmatrix} H_{11} & H_{12} & H_{13} & \cdot & \cdot & \cdot \\ H_{21} & H_{22} & H_{23} & & & \\ H_{31} & H_{32} & H_{33} & & & \\ \cdot & & & \cdot & & \\ \cdot & & & & \cdot & \\ \cdot & & & & & \cdot \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} \quad (8)$$

where  $E$  is the eigenenergy,  $\{c_i\}$  are the coefficients of the linear combination defining the eigenfunction  $\psi$  (that is,  $|\psi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle + c_3|\phi_3\rangle + \dots$ ),  $H_{ij}$  is defined as  $\langle\phi_i|\hat{H}|\phi_j\rangle$ .

Consequently, the eigenvalues  $E$  are obtained by solving a determinant equation:

$$\det \begin{bmatrix} H_{11} - E & H_{12} & H_{13} & \cdot & \cdot & \cdot \\ H_{21} & H_{22} - E & H_{23} & & & \\ H_{31} & H_{32} & H_{33} - E & & & \\ \cdot & & & \cdot & & \\ \cdot & & & & \cdot & \\ \cdot & & & & & \cdot \end{bmatrix} = 0 \quad (9)$$

In Lecture 12, the Hückel method was applied to solve for the energy levels of a benzene molecule. The following six-by-six determinant equation was obtained:

$$\det \begin{bmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{bmatrix} = 0 \quad (10)$$

where  $\alpha = \langle p_z^1 | \hat{H} | p_z^1 \rangle = \langle p_z^2 | \hat{H} | p_z^2 \rangle = \dots = \langle p_z^6 | \hat{H} | p_z^6 \rangle$  ( $p_z^i$  denotes the  $p_z$  orbital centered on the  $i^{\text{th}}$  carbon atom of the benzene ring) and  $\beta = \langle p_z^1 | \hat{H} | p_z^2 \rangle = \langle p_z^2 | \hat{H} | p_z^3 \rangle = \langle p_z^3 | \hat{H} | p_z^4 \rangle =$

... =  $\langle p_z^6 | \hat{H} | p_z^1 \rangle$ . The other  $\langle p_z^i | \hat{H} | p_z^j \rangle$  coefficients are zero.

The LCAO variational method consists in selecting linear combinations of atomic orbitals as trial wavefunctions in the variational method.

References and Examples: *Lecture 12; Engel, Reid 25.7; Recitation 4 I; Recitation 5; PS 4.2, PS 4.6*