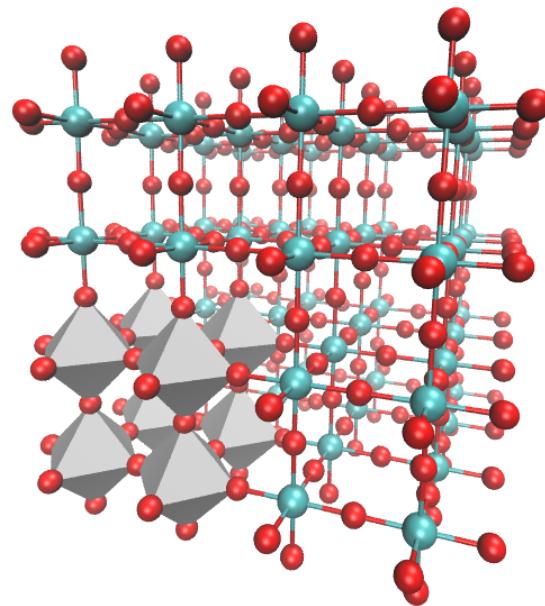


Atomic and Molecular Orbitals



Prof. Lee M. Thompson

Hydrogenic Orbitals

Hydrogen atom

- We solved the Schrödinger equation for the hydrogen atom exactly and briefly discussed the solutions
- Wavefunction can be written as functions of radial and angular parts

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta, \phi)\Phi(\phi)$$

- Angular part is obtained from spherical harmonics

$$Y_{l,m_l} = \Theta(\theta, \phi)\Phi(\phi)$$

- Radial part is exponential decay function

$$R(r) \propto e^{-Ar}$$

- Each function has associated quantum numbers from boundary conditions
 - Principle quantum number (n)
 - Angular quantum numbers (l)
 - Magnetic quantum number (m_l)
- Set (n, l, m_l) uniquely describes each solution

Hydrogenic Orbitals

Hydrogen atom

- Orbitals can be grouped into **shells** by their principle quantum number (n)

n	1	2	3	4
	K	L	M	N

- Each shell can be further divided into **sub-shells** by the angular quantum number (l)

l	0	1	2	3	4	5	6
	s	p	d	f	g	h	i

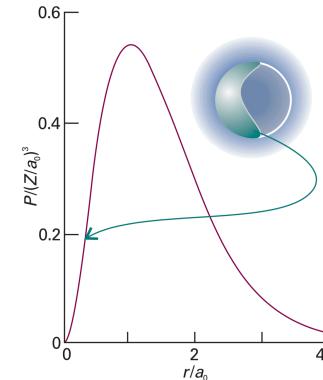
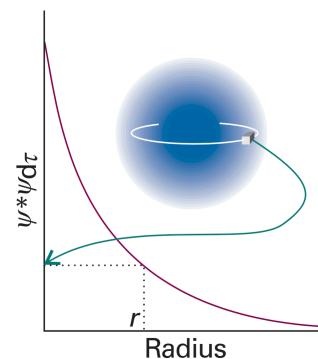
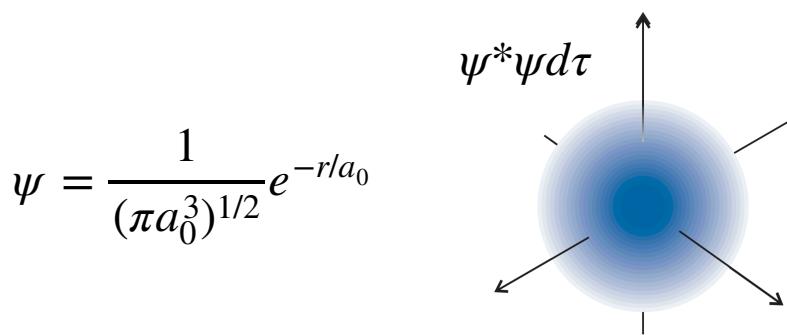
- As $l=0\dots n-1$, there are n sub-shells in each shell
- The degeneracy of each sub shell is $2l+1$ as determined by the magnetic quantum number (m_l) which has values $m_l=-l\dots l$
- Each shell therefore is n^2 degenerate

n	1	2	3	4
g_n	1	4	9	16

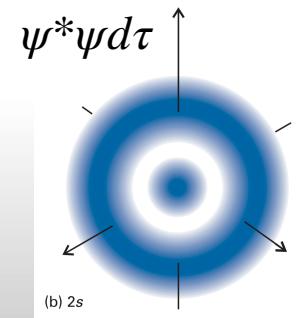
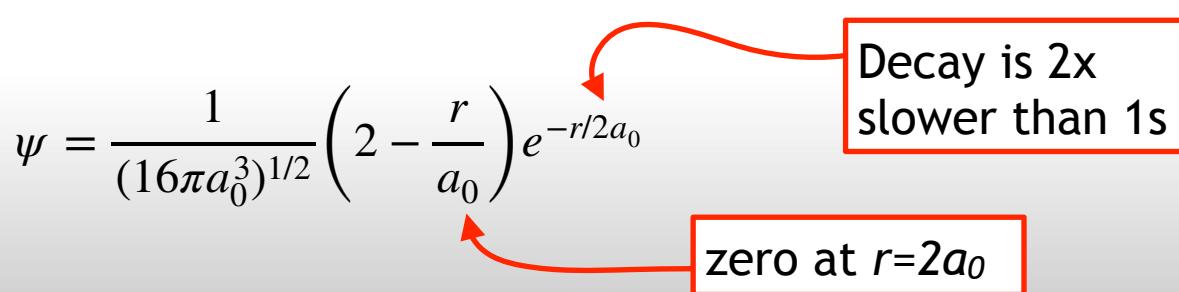
Hydrogenic Orbitals

Hydrogen atoms

- What do the hydrogen atom wavefunctions look like?
- For $Z=1$, $n=1$, $l=0$ and $m_l=0$ (hydrogen 1s) we have a function that is independent of angle



- For $Z=1$, $n=2$, $l=0$ and $m_l=0$ (hydrogen 2s)



Hydrogenic Orbitals

Hydrogen atoms

- What do the p orbitals look like?
- For Z=1, n=2, l=1 and ml=0 (hydrogen 2p):

$$\psi = \frac{1}{(32\pi a_0^5)^{1/2}} r \cos(\theta) e^{-r/2a_0} \Rightarrow \psi = \frac{1}{(32\pi a_0^5)^{1/2}} z e^{-r/2a_0}$$

- For Z=1, n=2, l=1 and ml=±1:

$$\psi_{\pm} = \mp \frac{1}{(16\pi a_0^5)^{1/2}} r \sin(\theta) e^{\pm i\phi} e^{-r/2a_0}$$

Recall solutions to
particle on a ring

- Linear combinations of degenerate orbitals yield equally valid solution of the Schrödinger equation

$$\psi_{\pm} = \mp \frac{1}{(16\pi a_0^5)^{1/2}} r \sin(\theta) \{ \cos(\phi) \pm i \sin(\phi) \} e^{-r/2a_0}$$

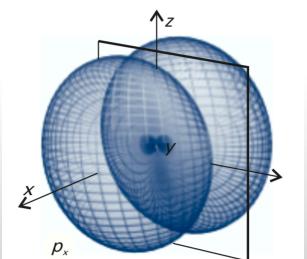
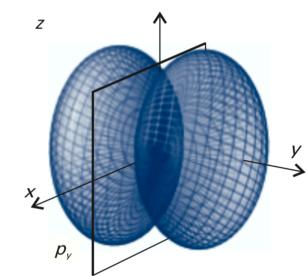
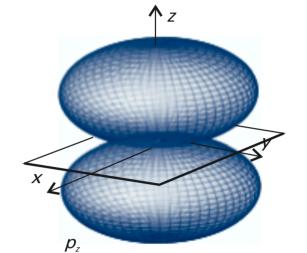
$$i(\psi_+ + \psi_-) = - \frac{i^2}{(4\pi a_0^5)^{1/2}} r \sin(\theta) \sin(\phi) e^{-r/2a_0} \Rightarrow \frac{1}{(4\pi a_0^5)^{1/2}} y e^{-r/2a_0}$$

$$-(\psi_+ - \psi_-) = \frac{1}{(4\pi a_0^5)^{1/2}} r \sin(\theta) \cos(\phi) e^{-r/2a_0} \Rightarrow \frac{1}{(4\pi a_0^5)^{1/2}} x e^{-r/2a_0}$$

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

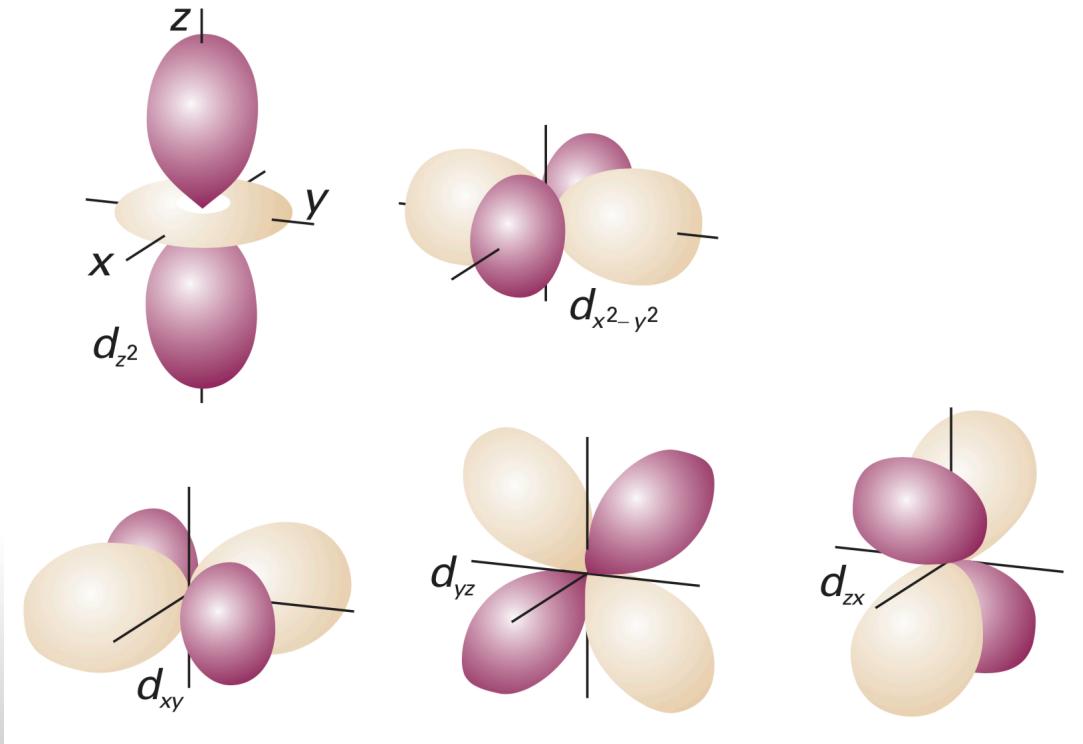
$$z = r \cos \theta$$



Hydrogenic Orbitals

Hydrogen atoms

- What do the d orbitals look like?
- For $Z=1$, $n=3$, $l=2$ and $m_l=-2, 1, 0, 1, 2$ (hydrogen 3d orbitals):



$$d_{xy} = xyf(r)$$

$$d_{xz} = xz f(r)$$

$$d_{yz} = yz f(r)$$

$$d_{x^2-y^2} = \frac{1}{2}(x^2 - y^2)f(r)$$

$$d_{z^2} = \frac{1}{2}\sqrt{3}(3z^2 - r^2)f(r)$$

$$f(r) = \frac{1}{(32\pi)^{1/2}} \left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0}$$

Many-Electron Atoms

Orbital approximation

- Beyond one-electron system, wavefunction is complicated function of all coordinates

$$\psi(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k \dots)$$

- Approximate that each electron has defined one-electron wavefunction - it's own orbital

$$\psi(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k \dots) = \psi(\mathbf{r}_i)\psi(\mathbf{r}_j)\psi(\mathbf{r}_k) \dots$$

- Each orbital is similar to hydrogenic orbital, but adapted to modified nuclear charge and repulsion with other electrons

Electron configuration

- Orbital approximation allows us to write down electron configuration
- Electron configuration determined by listing quantum number labels for n and l , along with occupancy e.g. vanadium atom:

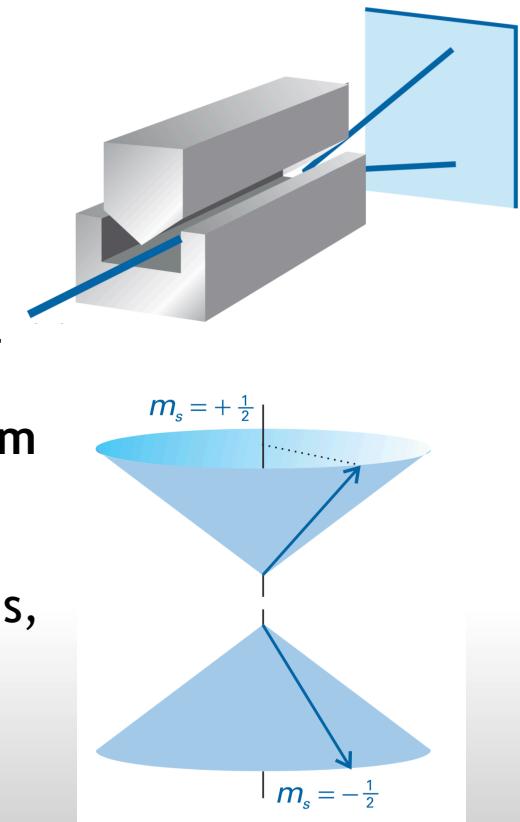
$$1s^2 2s^2 2p^6 3s^2 3d^5$$

- Each eigenstate is uniquely defined by quantum numbers, so how can we have two electrons per orbital?

Many-Electron Atoms

Electron spin

- Stern-Gerlach experiment showed two bands of particles
- $2l+1$ orientations for given angular momentum l
- For two bands, $l=1/2$ but we derived that l is integer
- Stern-Gerlach result not due to orbital angular momentum but due to spin angular momentum
- Spin is an intrinsic angular momentum analogous to orbital angular momentum (although with no classical analogue)
- **Spin quantum number (s)** and **spin magnetic quantum number (m_s)** used to describe spin state
- Spin depends on particle
 - Fermions have half integer spin (electrons, protons, neutrons etc.)
 - Bosons have integer spin (photons, some nuclei)
- Dirac equation provides theoretical basis to spin



Many-Electron Atoms

Pauli principle

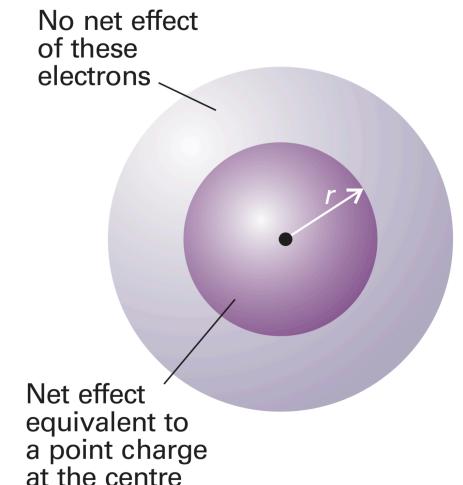
- No more than two electrons may occupy any given orbital, and if two do occupy one orbital, then their spins must be paired
- More on the Pauli principle later

Penetration and shielding

- Electron in many-electron system experiences modified Coulomb forces
- Attracted to **effective nuclear charge (Z_{eff})**

$$Z_{eff} = Z - \sigma$$

- Difference between actual nuclear charge and effective nuclear charge is the **shielding constant (σ)** arising from electron-electron repulsion
- Lower angular momentum orbitals of the same shell are more likely to be found closer to the nucleus - their **penetration** is greater
- Result is that energies of subshell follows s<p<d<f



Many-Electron Atoms

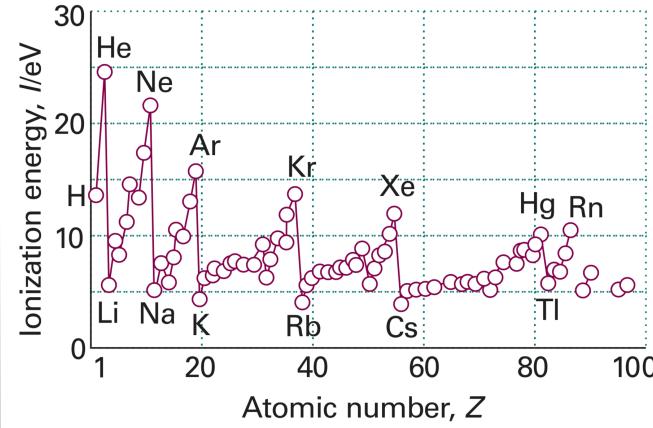
Aufbau principle

- The ground state of atoms is obtained by filling the lowest energy orbitals first
 $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p \rightarrow 5s \rightarrow 4d \rightarrow 5p \rightarrow 6s$
- Electrons occupy different orbitals of a given sub shell before doubly occupying any one of them

Hund's rule

- An atom in its ground state adopts a configuration with the greatest number of unpaired electrons

Ionization energies

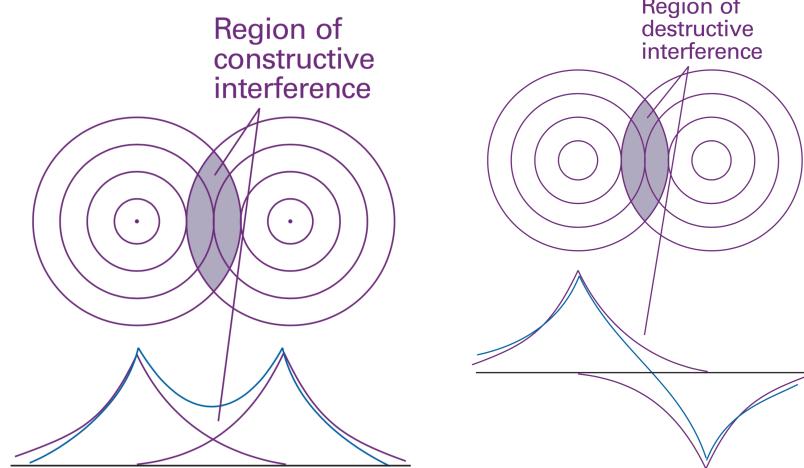
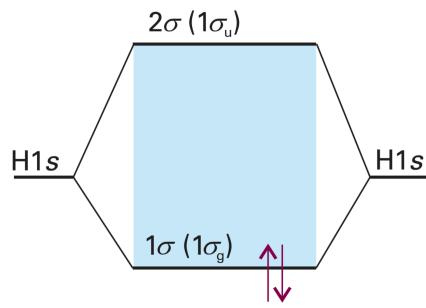


Molecular Orbitals

Homonuclear diatomic molecules

- Wavefunction of hydrogen molecule
 - Start at noninteracting limit - each electron in 1s atomic orbital
 - Atomic orbitals interact both in-phase and out-of-phase to form molecular orbitals

$$\psi_{\pm} = N(\chi_A(\mathbf{r}_1) \pm \chi_B(\mathbf{r}_2))$$

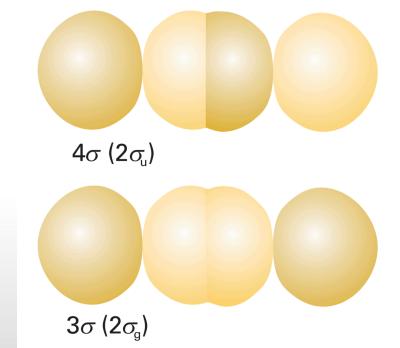
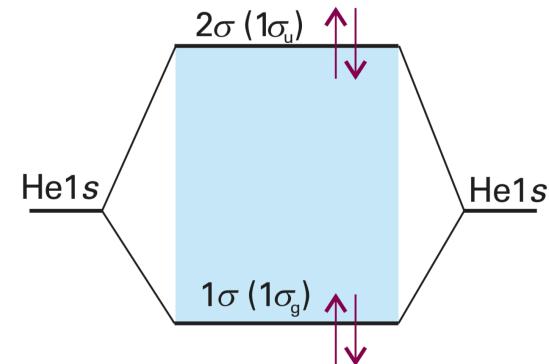


- Bonding orbitals not as stabilized as antibonding orbital destabilized
 - Greater electron-electron repulsion in bonding orbitals as electrons on average are closer together

Molecular Orbitals

σ orbitals

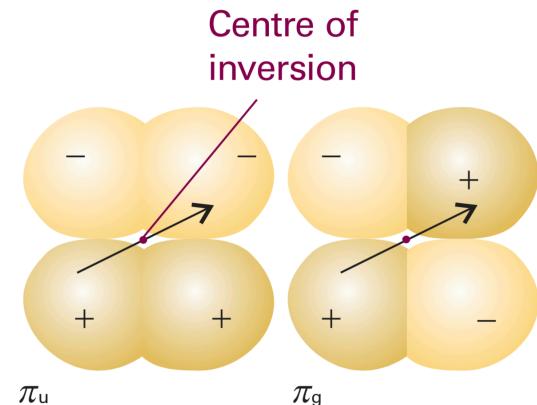
- Molecular orbital theory explains why helium is monoatomic
- σ bond as spherical symmetry around bonding axis
 - Atomic orbital components can be of any angular momentum type
- Formally all atomic orbitals with correct symmetry should be included when building a molecular orbital
 - In reality as subshells are separated in energy the contributions to molecular orbitals can also be separated



Molecular Orbitals

π orbitals

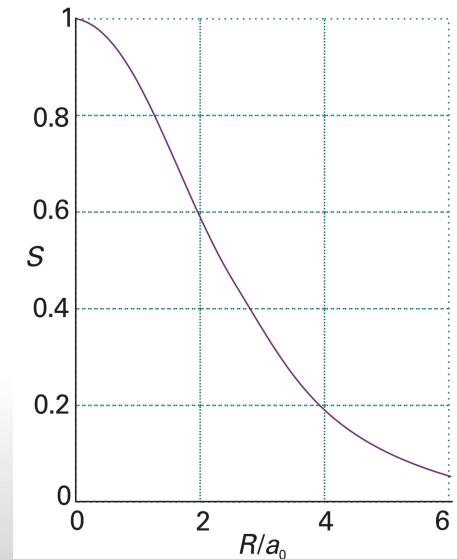
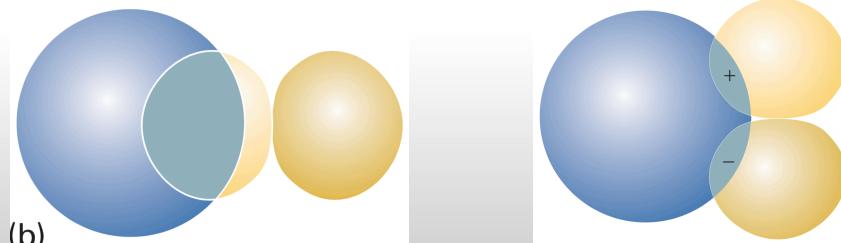
- What about p orbitals with non-spherical symmetry around bonding axis
- Inversion symmetry around bond axis results in π -orbital



Overlap integral

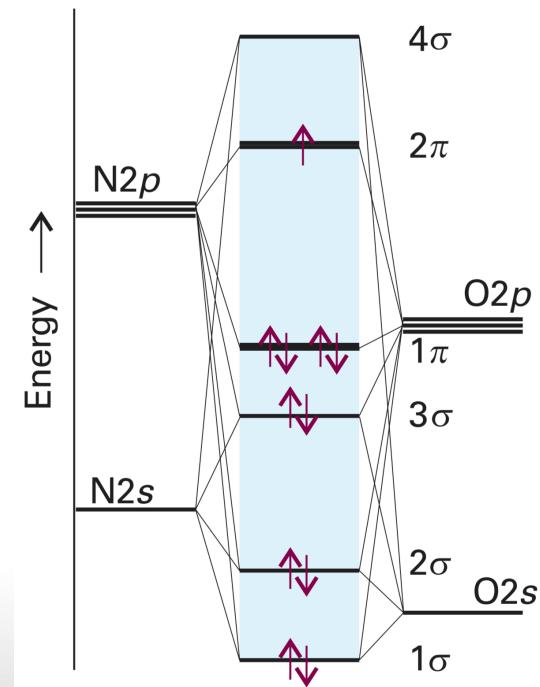
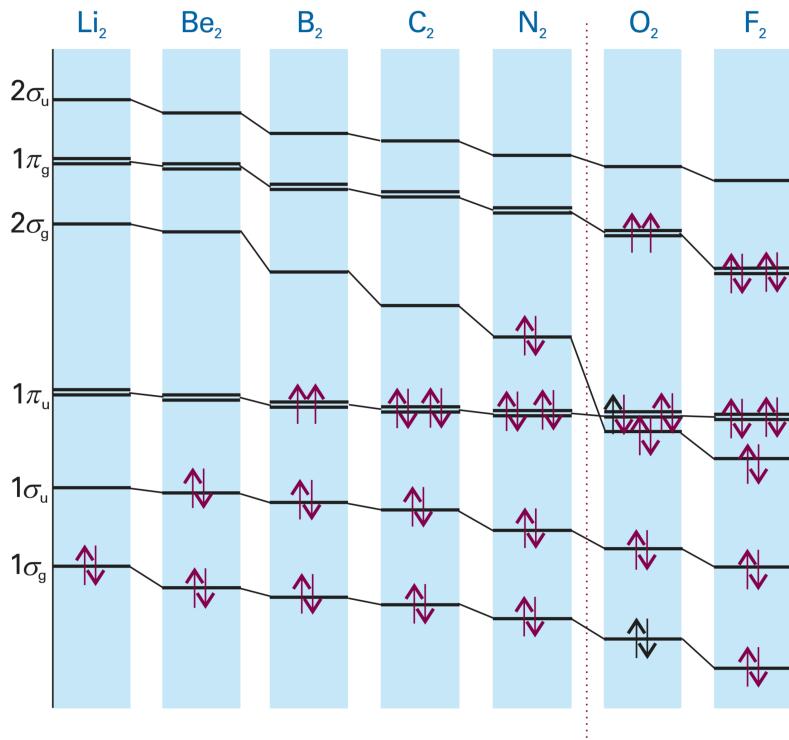
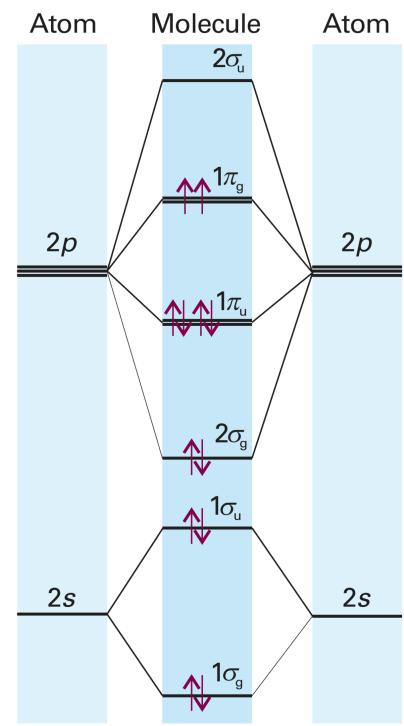
- Interaction between atomic orbitals depends on extent to which orbitals overlap
- Atomic overlap measured by overlap integral

$$S = \int \chi_A^* \chi_B d\tau$$



Molecular Orbitals

Molecular orbital diagrams



Hückel Theory

Polyatomic molecular orbitals

- More generally molecular orbitals can be written as linear combination of any number of atomic orbitals

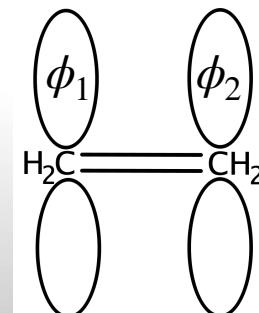
$$\psi_i = \sum_{\mu} c_{i\mu} \phi_{\mu}$$

- What are the coefficients and energies of these molecular orbitals?
 - From the variational theorem we have a set of coupled differential equations to solve

$$\sum_{\mu} c_{i\mu} (H_{\mu\nu} - E_i S_{\mu\nu}) = 0 \quad H_{\mu\nu} = \langle \phi_{\mu} | \hat{H} | \phi_{\nu} \rangle \quad S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle$$

- Integrals can be solved numerically as form of the functions is known
- Hückel suggested qualitative approach to solve MO diagram for π systems using Hückel approximations
 - Electron-electron interaction is neglected
 - σ - π manifolds are separated

- $S_{\mu\nu} = \delta_{\mu\nu}$
- $H_{\mu\mu} = \alpha, \quad H_{\mu\mu\pm 1} = \beta, \quad H_{\mu\mu\pm > 1} = 0$



Hückel Theory

Polyatomic molecular orbitals

- Solve the secular determinant for the energies

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0 \Rightarrow \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$(\alpha - E)^2 - \beta^2 = 0 \Rightarrow E = \alpha \pm \beta$$

- Solve for the coefficients by normalization

$$\begin{bmatrix} \alpha & \beta \\ \beta & \alpha \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

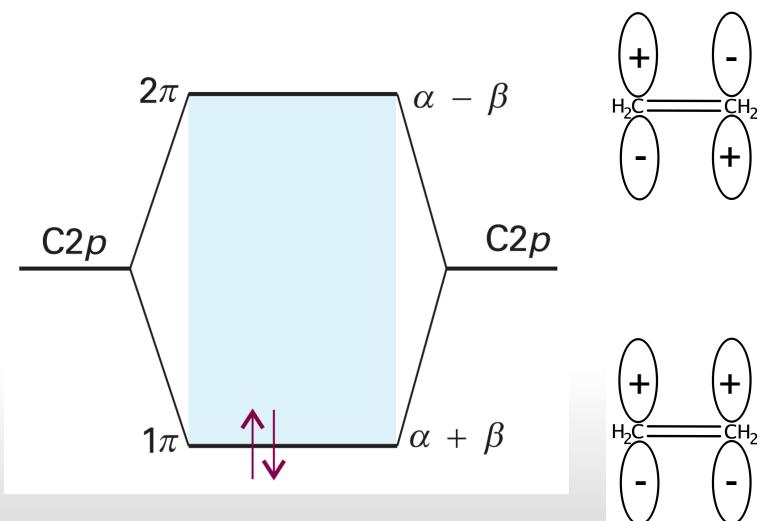
$$E = \alpha + \beta$$

$$\begin{bmatrix} \alpha c_1 + \beta c_2 \\ \beta c_1 + \alpha c_2 \end{bmatrix} = \begin{bmatrix} \alpha c_1 + \beta c_1 \\ \alpha c_2 + \beta c_2 \end{bmatrix} \Rightarrow c_1 = c_2$$

$$E = \alpha - \beta$$

$$\begin{bmatrix} \alpha c_1 + \beta c_2 \\ \beta c_1 + \alpha c_2 \end{bmatrix} = \begin{bmatrix} \alpha c_1 - \beta c_1 \\ \alpha c_2 - \beta c_2 \end{bmatrix} \Rightarrow c_1 = -c_2$$

$$2c_1^2 = 1 \Rightarrow c_1 = \frac{1}{\sqrt{2}}$$

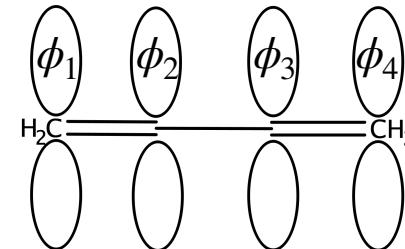


Hückel Theory

Polyatomic molecular orbitals

- Butadiene has four atomic orbitals

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$



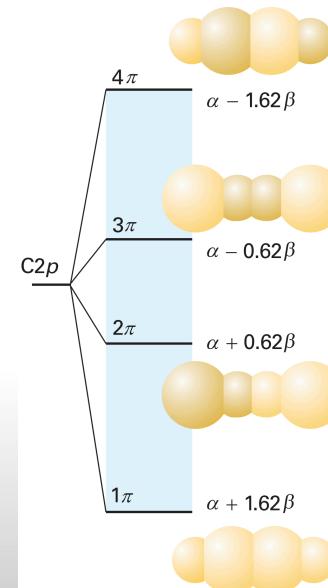
- To solve this can use substitution $-x = (\alpha - E)/\beta$ and then divide by β

$$\begin{vmatrix} -x & 1 & 0 & 0 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 0 & 0 & 1 & -x \end{vmatrix} = 0 \Rightarrow x^4 - 3x^2 + 1 = 0$$

Let $y = x^2$, then $y^2 - 3y + 1 = 0$

$$y = \frac{3 \pm \sqrt{9 - 4}}{2} = 2.618, 0.382$$

$$x = \pm 1.618, \pm 0.618$$



Hückel Theory

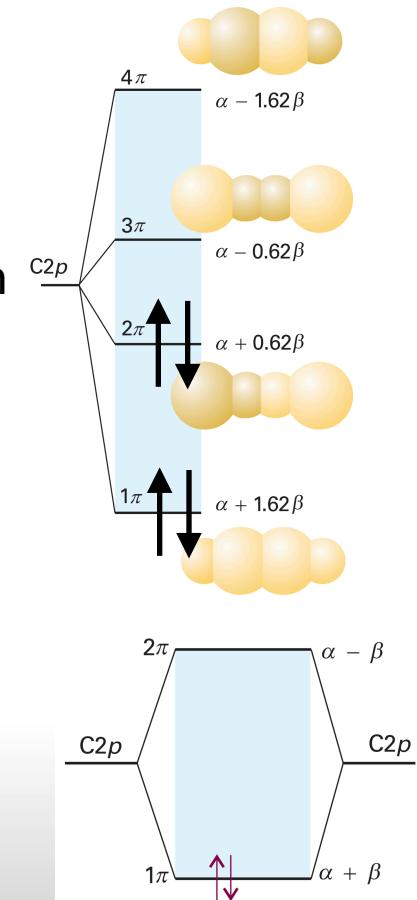
Delocalization Energy

- Butadiene has four atomic orbitals and four electrons
 - In the ground state, two electrons are in orbital with $\varepsilon_1 = (\alpha + 1.62\beta)$ and two electrons are in orbital with $\varepsilon_2 = (\alpha + 0.62\beta)$
 - Total energy is (because we neglect electron-electron interactions so $E = \sum \varepsilon_i$):
$$E = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$$

- Energy of two ethylene molecules is

$$E = 2 \times 2(\alpha + \beta) = 4\alpha + 4\beta$$

- Due to delocalization, resonance in butadiene lowers energy by -0.48β compared with two localized π bonds



Summary

- Hydrogenic orbitals
- Multi-electron atomic orbitals
- Molecular orbitals
- Hückel molecular orbital theory