

Atomic and molecular orbitals

$$h^2/4\pi^2me^2 = 0.53 \times 10^{-8} \text{ cm)}$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a} \right)^{3/2} e^{-Zr/a}$$

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a} \right)^{3/2} \left(2 - \frac{Zr}{a} \right) e^{-Zr/2a}$$

$$\psi_{2pz} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \cos \theta$$

$$\psi_{2px} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \cos \varphi$$

$$\psi_{2py} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a} \right)^{5/2} r e^{-Zr/2a} \sin \theta \sin \varphi$$

$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a} \right)^2 \left(27 - 18 \frac{Zr}{a} + 2 \frac{Z^2 r^2}{a^2} \right) r e^{-Zr/3a}$$

$$\psi_{3pz} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a} \right)^{5/2} \left(6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \cos \theta$$

$$\psi_{3px} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a} \right)^{5/2} \left(6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \cos \varphi$$

$$\psi_{3py} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a} \right)^{5/2} \left(6 - \frac{Zr}{a} \right) r e^{-Zr/3a} \sin \theta \sin \varphi$$

$$\psi_{3d_z^2} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a} \right)^{7/2} \left(\frac{Z}{a} \right) r^2 e^{-Zr/3a} (3 \cos^2 \theta - 1)$$

$$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin\theta \cos\theta \cos\varphi$$

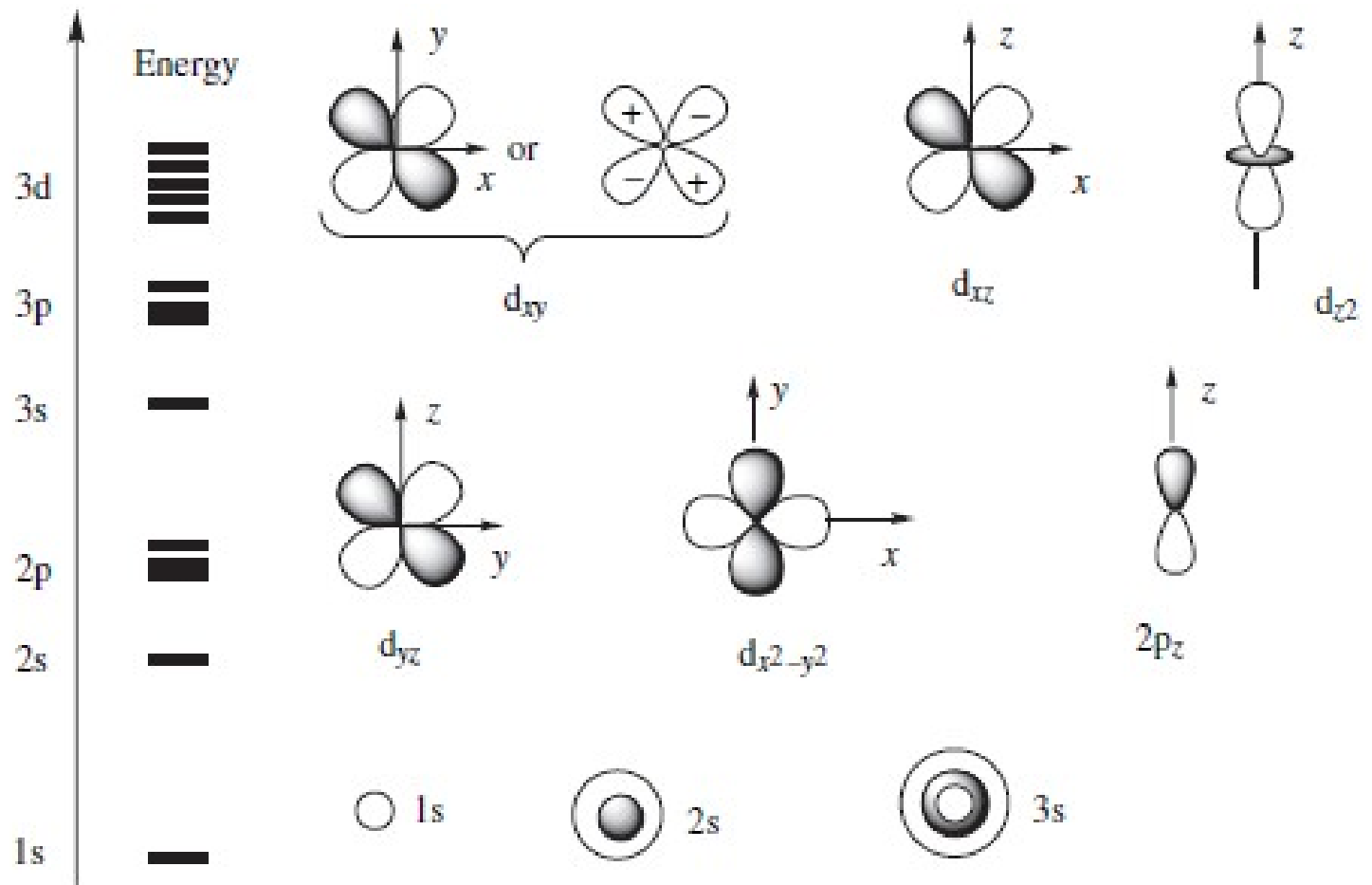
$$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin\theta \cos\theta \sin\varphi$$

$$\psi_{3d_{x^2-y^2}} = \frac{\sqrt{2}}{81\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin^2\theta \cos 2\varphi$$

$$\psi_{3d_{xy}} = \frac{\sqrt{2}}{81\sqrt{2\pi}} \left(\frac{Z}{a}\right)^{\frac{7}{2}} r^2 e^{-Zr/3a} \sin^2\theta \sin 2\varphi$$

$$h^2/4\pi^2me^2 = 0.53 \times 10^{-8} \text{ cm)}$$

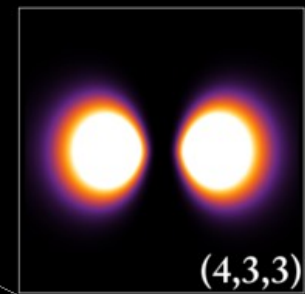
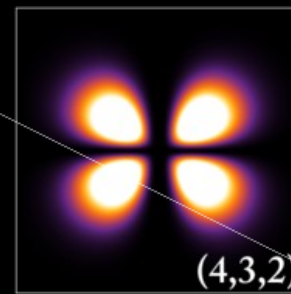
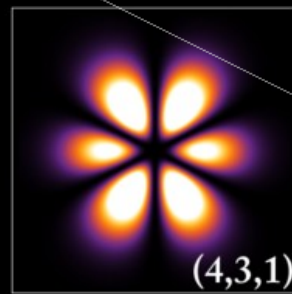
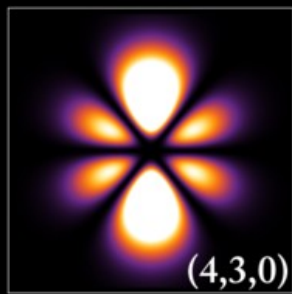
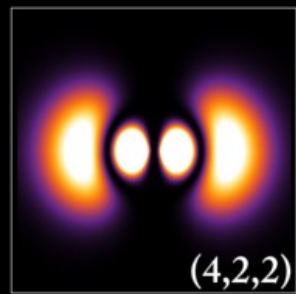
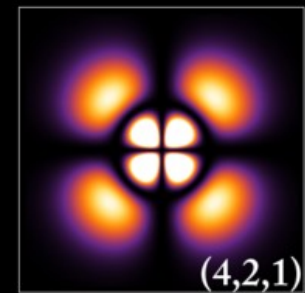
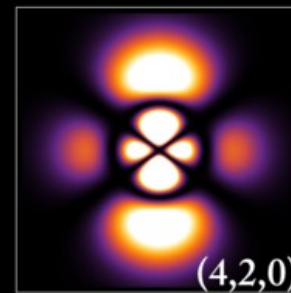
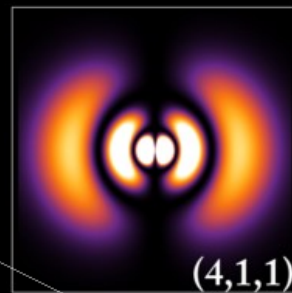
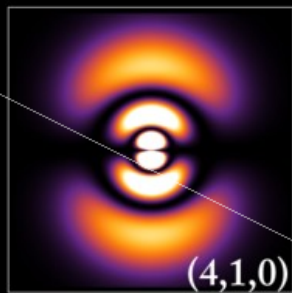
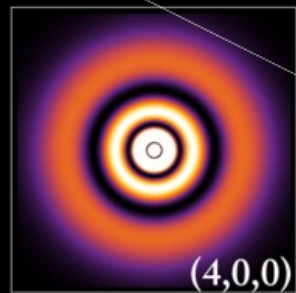
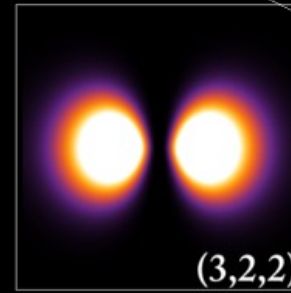
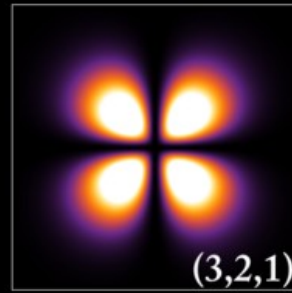
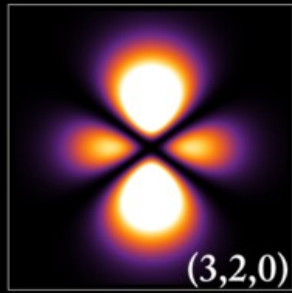
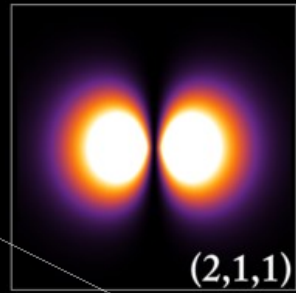
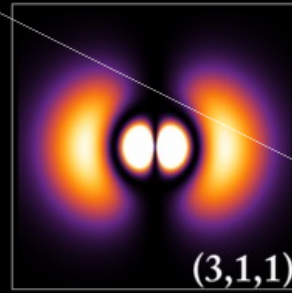
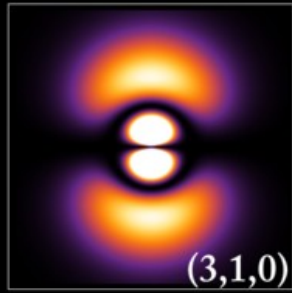
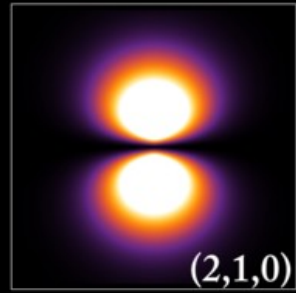
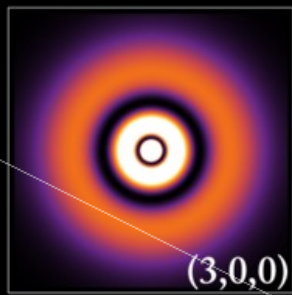
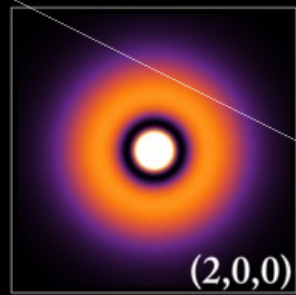
Atomic and molecular orbitals



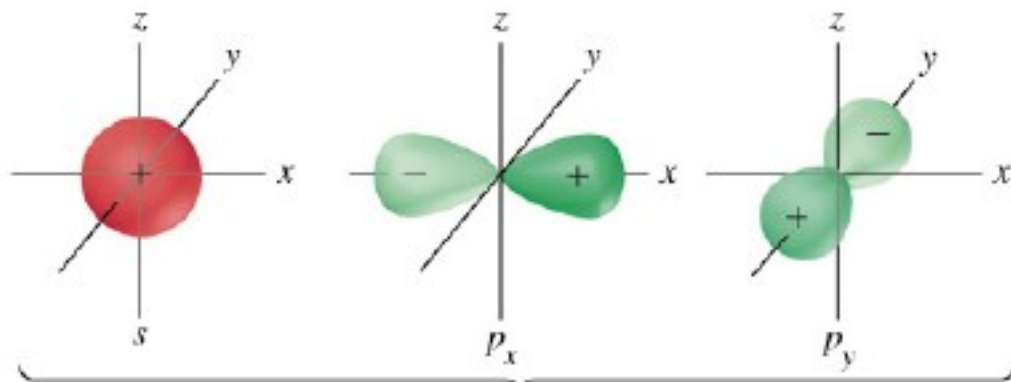
Hydrogen Wave Function

Probability density plots.

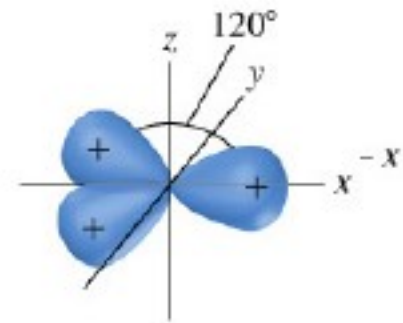
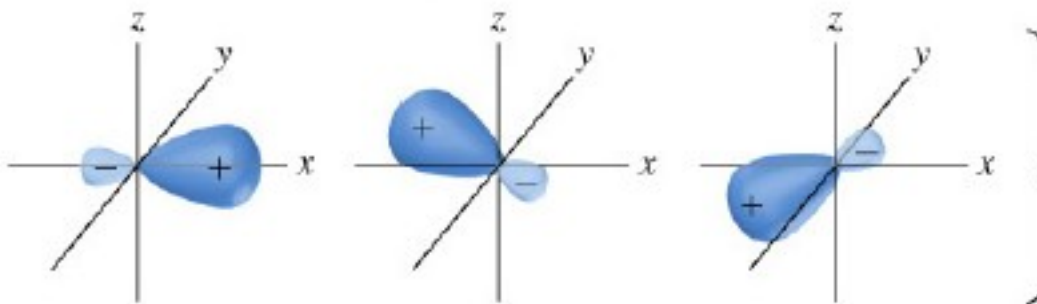
$$\psi_{nlm}(r, \vartheta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta, \varphi)$$



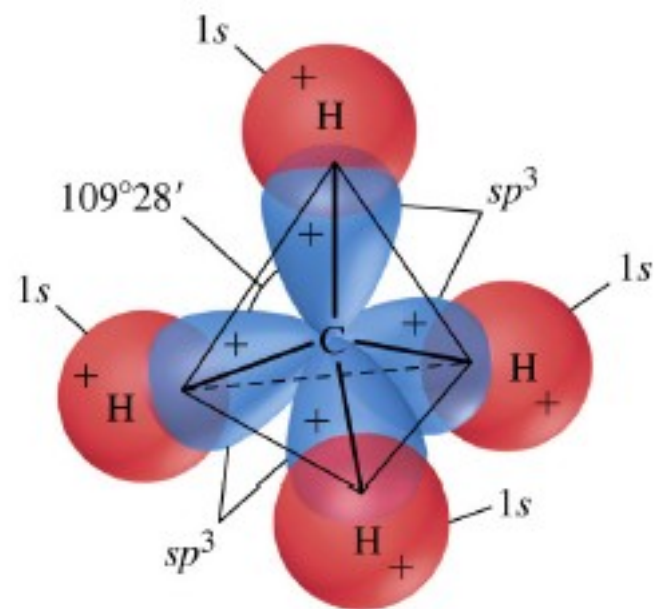
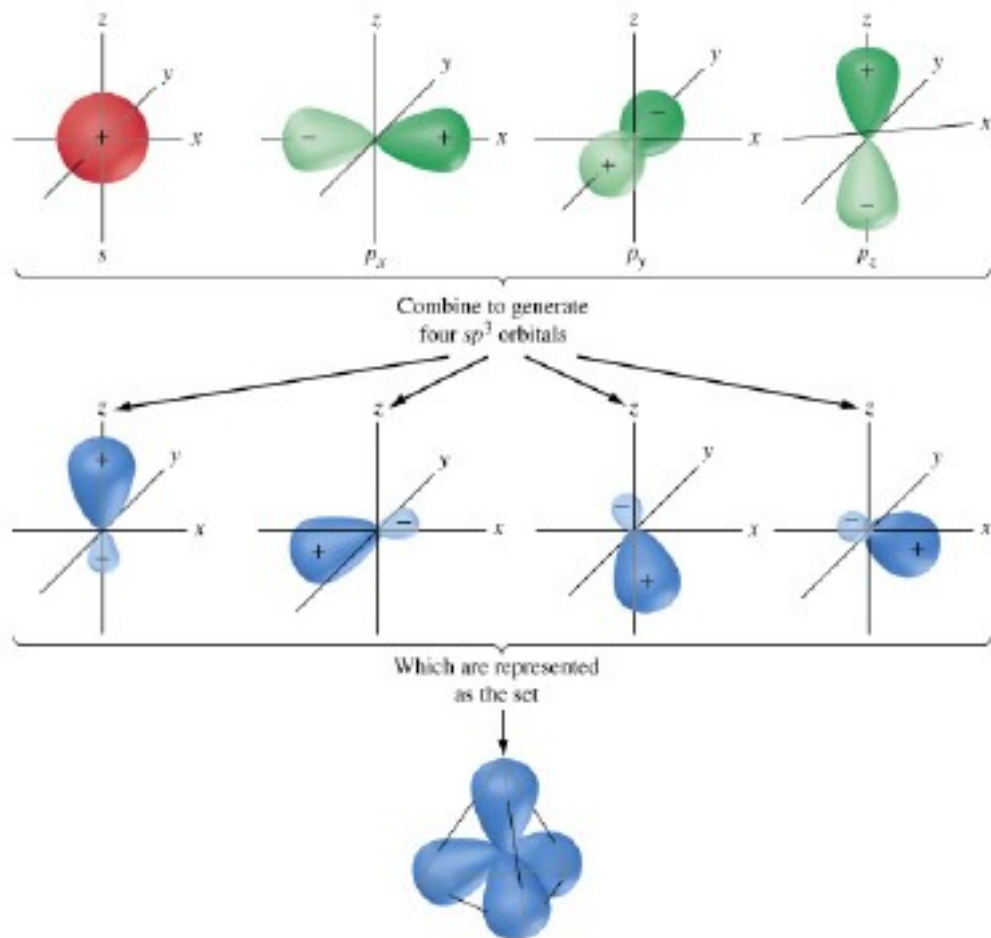
sp^2 Hybrid atomic orbitals



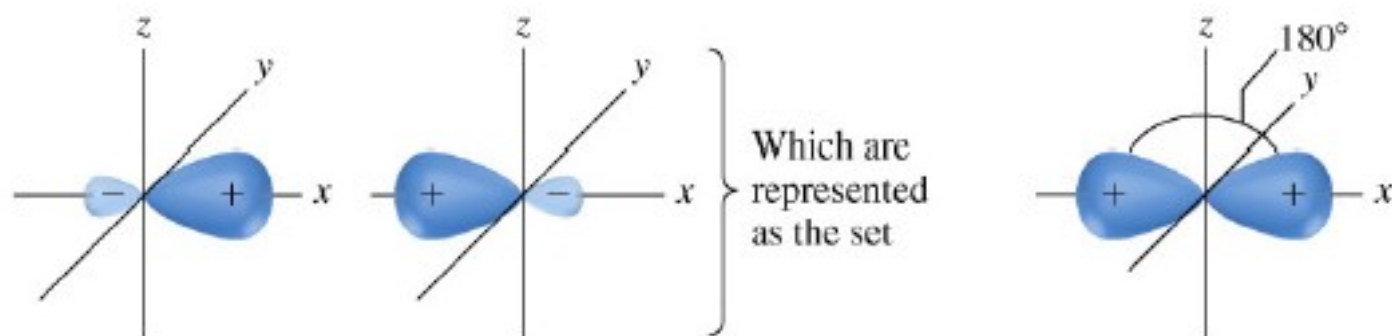
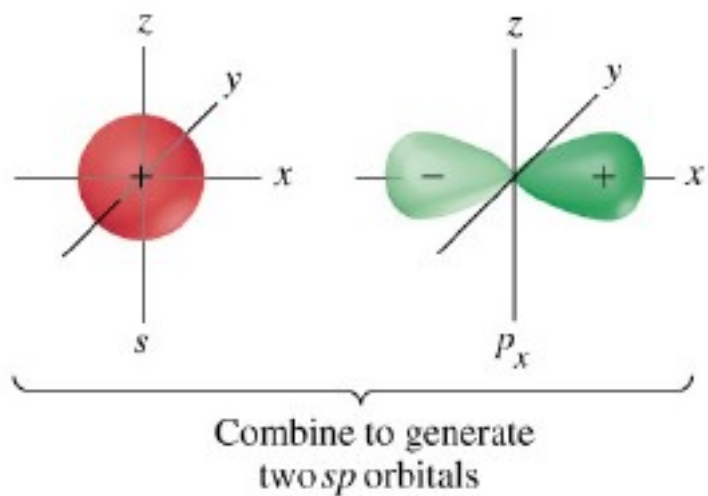
Combine to generate three sp^2 orbitals



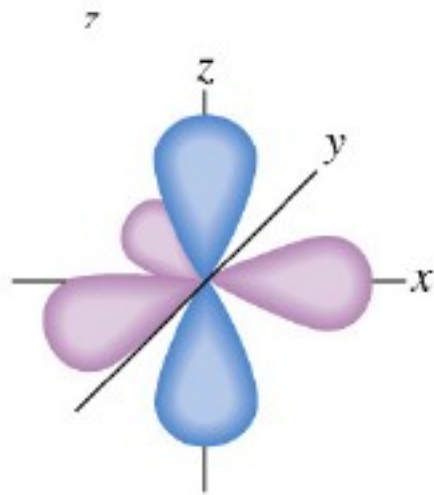
sp^3 Hybrid atomic orbitals



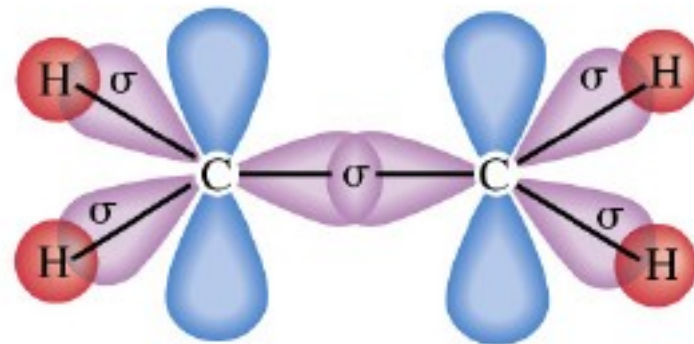
sp Hybrid atomic orbitals



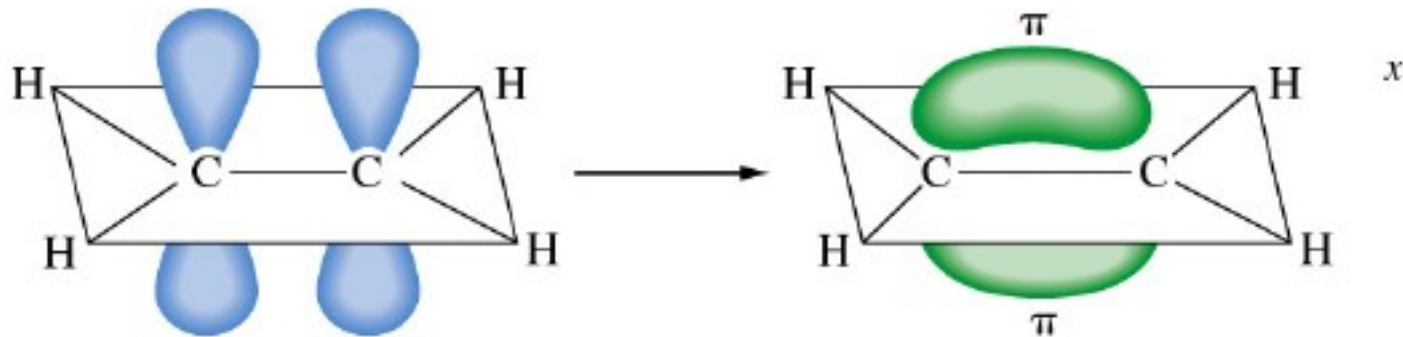
Multiple bonds with VB



The set of orbitals $sp^2 + p$

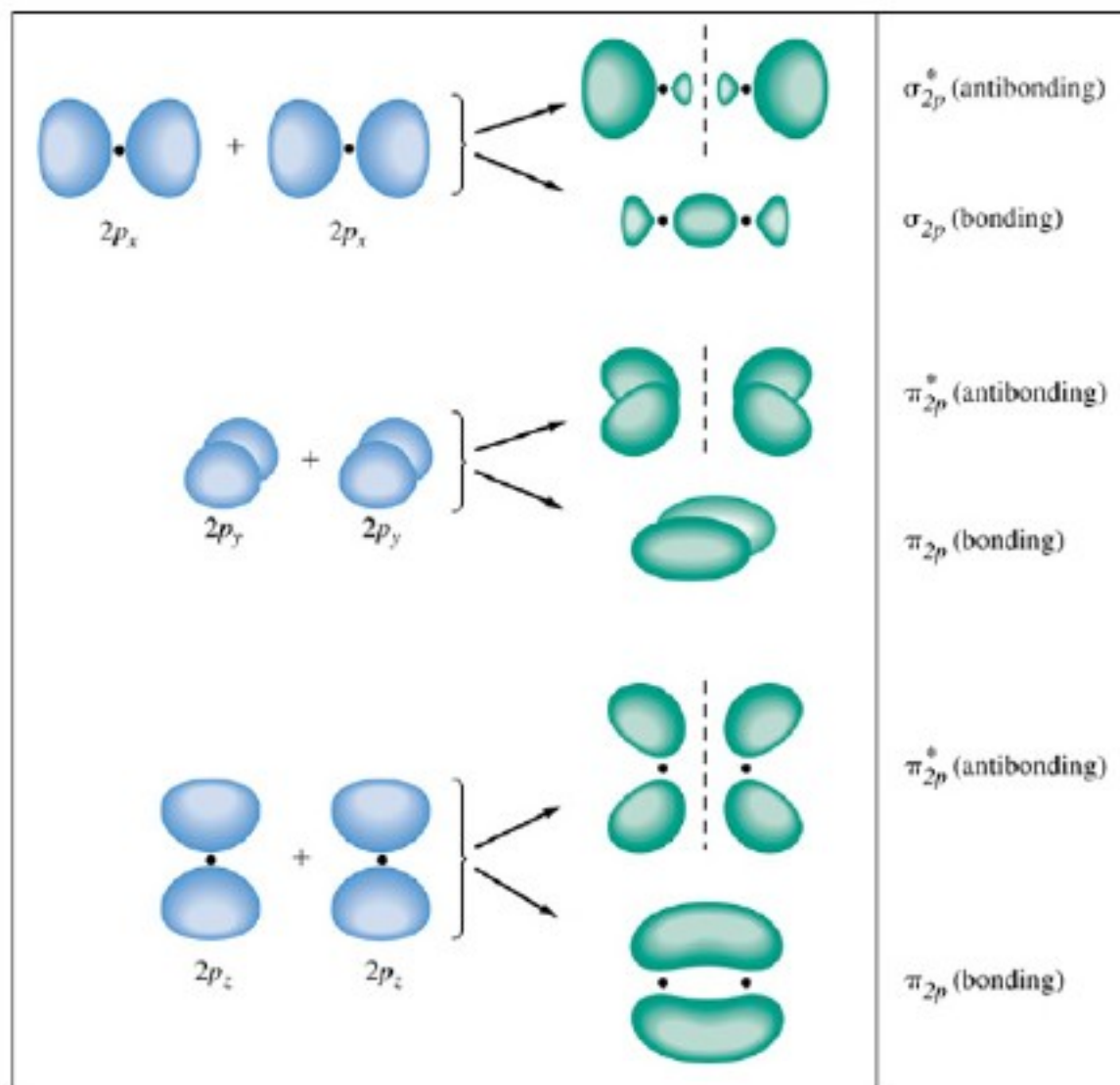


Sigma (σ) bonds

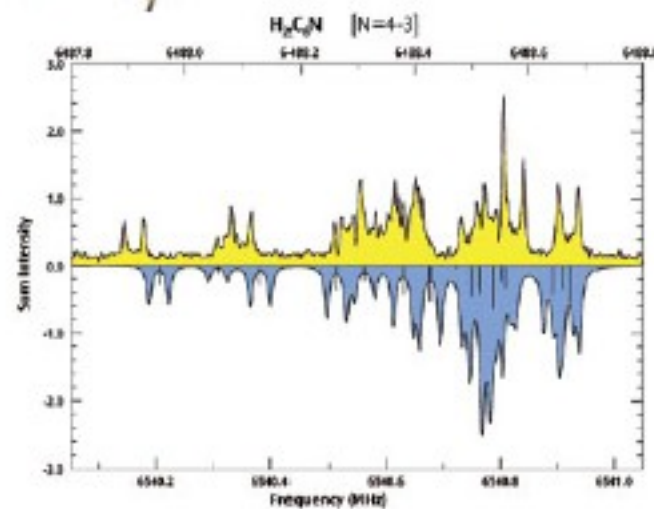
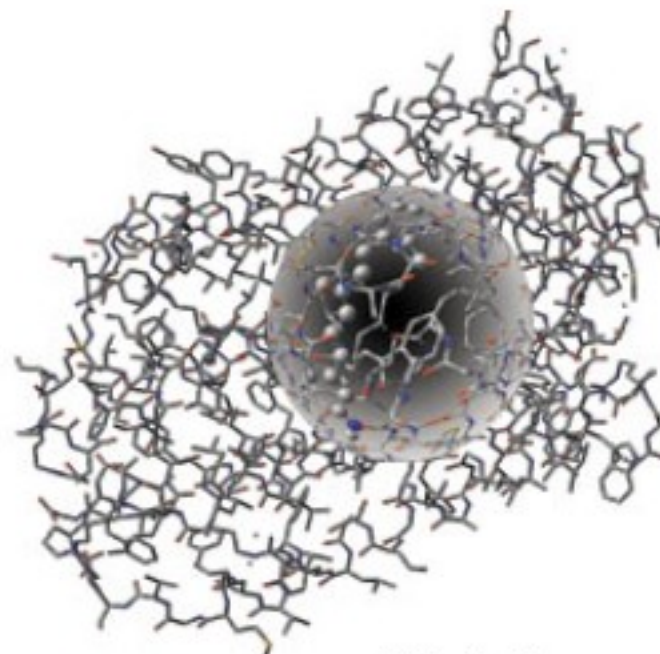
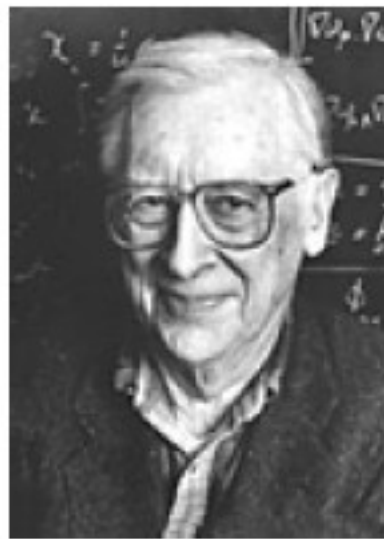


Overlap of p orbitals leading to pi (π) bond

Molecular Orbitals from p A.O.



Modern MO calculations



W. Kohn
(1923-)

J. A. Pople
(1925-2004)

Nobel prize in Chemistry
1998

TB (tight-binding) formalism

tzw. przybliżenie „sztywnego wiązania”

LCAO – Linear Combination of Atomic Orbitals

$$\tilde{H} - E\tilde{S} = 0$$

$$H_{nm} = \sum_{R_j} \exp i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i) \int \varphi_n^*(\mathbf{r} - \mathbf{R}_i) H \varphi_m(\mathbf{r} - \mathbf{R}_j) d\mathbf{v}$$

$$S_{nm} = \sum_{R_j} \exp i\mathbf{k} \cdot (\mathbf{R}_j - \mathbf{R}_i) \int \varphi_n^*(\mathbf{r} - \mathbf{R}_i) \varphi_m(\mathbf{r} - \mathbf{R}_j) d\mathbf{v}$$

$$R_c = [\sum_m \sum_n c_m^* c_n H_{mn}] / [\sum_m \sum_n c_m^* c_n S_{mn}]$$

where

$$H_{nm} = \int \phi_m^* H \phi_n d\mathbf{r}$$

and

$$S_{nm} = \int \phi_m^* \phi_n d\mathbf{r}$$

Coulomb integral

Overlap intergral

$$\sum_n (H_{nn} - E S_{nn}) C_n = 0$$



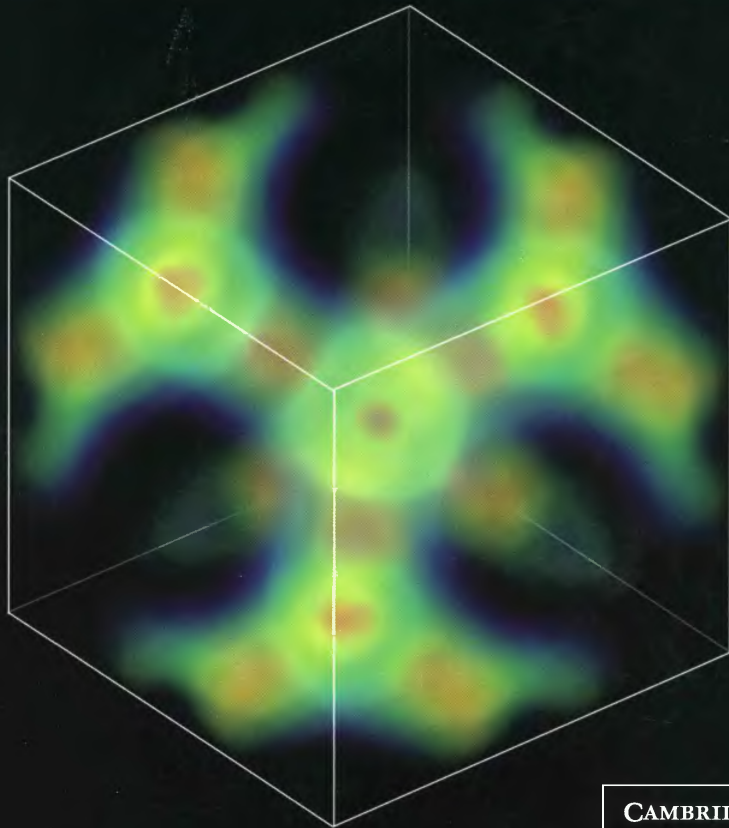
$$HC = ESC$$

Metody obliczeń struktury elektronowej: pseudopotencjały, ..

Richard M. Martin

Electronic Structure

Basic Theory and Practical Methods



CAMBRIDGE

Single-particle Methods of Solution

1. Local orbitals; LCAO-Hückel
2. Plane waves
3. Augmented plane waves (APW)
4. Orthogonalized plane waves (OPW)
5. Green's function methods (KKR)
6. **Pseudopotentials**
7. PAW



Walter Kohn

Pseudopotentials (~1959) were born before DFT (1964)

Bloch's theorem: **can choose** eigenstates of a periodic Hamiltonian in the form

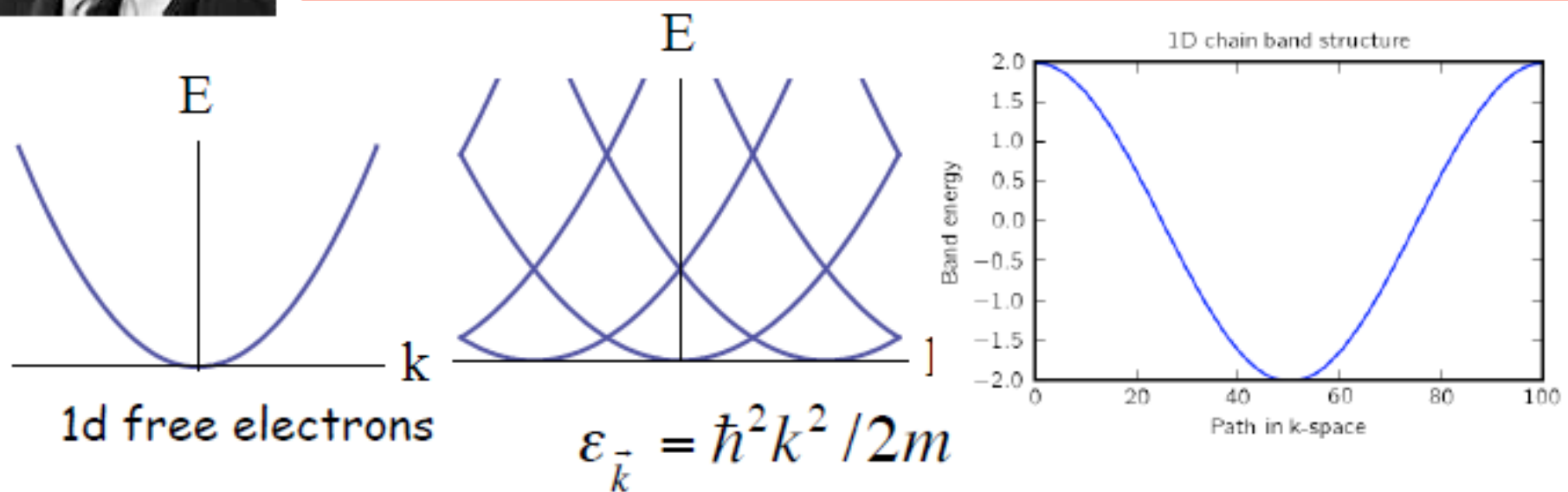


$$\hat{T}(\vec{R})\psi(\vec{r}) \equiv \psi(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R})\psi(\vec{r}) \quad (\text{label as } \psi_{\vec{k}})$$

(eigenvalue of \hat{H} labeled as $\varepsilon_{\vec{k}}$)

(eigenvalue of translation $\hat{T}(\vec{R})$ is $\exp(i\vec{k} \cdot \vec{R})$)

\vec{k} and $\vec{k} + \vec{G}$ give the same translation eigenvalue.



1d free electrons

$$\varepsilon_{\vec{k}} = \hbar^2 k^2 / 2m$$

1d free electrons with periodicity of k -space (the reciprocal lattice)

1d single-orbital tight-binding band

$$\text{LCAO: } \psi_{\vec{k}} = \sum \exp(i\vec{k} \cdot \vec{R}) \phi(\vec{r} - \vec{R}) \quad \varepsilon_{\vec{k}} = -2t \cos(ka)$$

PHYSICAL REVIEW
volume 51 (1937)
Wave Functions in a Periodic Potential

J. C. SLATER*

Augmented Plane Waves (APW)

The wave function is expanded in spherical harmonics and radial solutions of the wave equation within the spheres, and in plane waves outside the spheres, joining continuously at the surface. A single unperturbed function consists of a single plane wave outside the spheres, together with the necessary spherical functions within the spheres. ... It is hoped that the method will be useful for comparatively low energy excited electrons, for which the usual method of expansion in plane waves converges too slowly.

Birth of computational electronic structure theory?



students:

Leland Allen
Don Ellis
Art Freeman
Frank Herman
George Koster
Len Mattheiss
Dick Watson
John Wood

Birth of the pseudopotential

New Method for Calculating Wave Functions in Crystals and Molecules¹



JAMES C. PHILLIPS[†] AND LEONARD KLEINMAN[‡]
Department of Physics, University of California, Berkeley, California

Phys. Rev. 116, 287 (1959)

[†] National Science Foundation Postdoctoral Fellow.

[‡] National Science Foundation Predoctoral Fellow.

¹ C. Herring, Phys. Rev. 57, 1169 (1940).

² V. Heine, Proc. Roy. Soc. (London) A240, 340 (1957).

³ F. Herman, Phys. Rev. 88, 1210 (1952); 93, 1214 (1954).

⁴ J. C. Slater, Phys. Rev. 92, 603 (1953).



We begin by imagining that we *know* the exact crystal wave function ψ_α which transforms according to an irreducible representation of the cubic point group Γ_α which has *s* or *p* atomic symmetry.⁷ Since ψ_α must be orthogonal to the core states of similar symmetry, we have

$$\psi_\alpha = \varphi_\alpha + \sum_n a_n^\alpha \varphi_\alpha^n, \quad (2.1)$$

$$a_n^\alpha = -(\varphi_\alpha, \varphi_\alpha^n). \quad (2.2)$$

If we had chosen φ to be a single plane wave Herring's¹ results would follow.



Conyers Herring

Schemat obliczeń samouzgodnionych struktury elektronicznej

- Supercell geometry: lattice vectors + atoms in the unit cell
- Plane-wave basis set, determined by the lattice and by a single parameter (*cutoff*)
- Atom-based pseudopotentials representing the electron-nuclei potential (V_{nuc} in the figure)
- Charge density with valence electrons only

