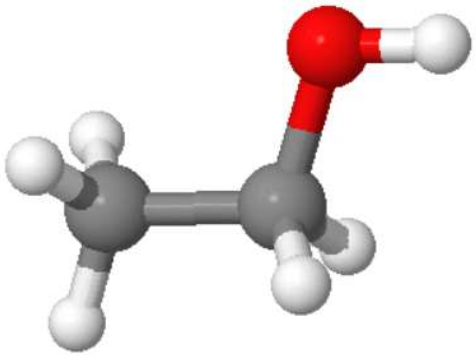
Technische Universität Graz

Molecular and Solid State Physics

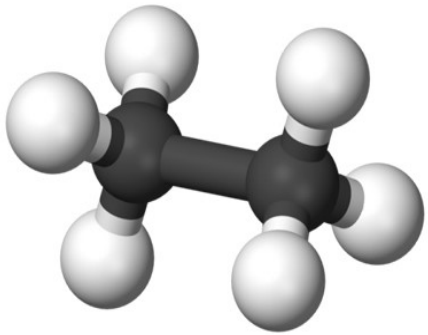
Goal

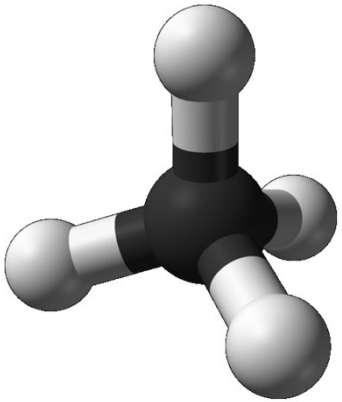
From the microscopic structure



calculate any property of any molecule or any solid.

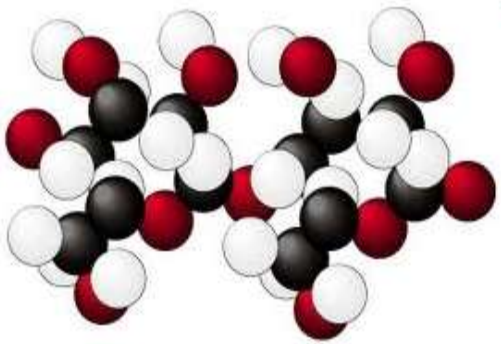
Molecules

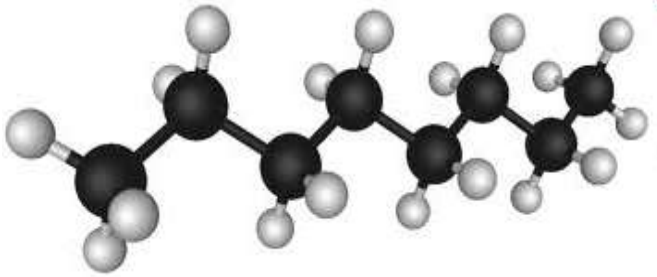


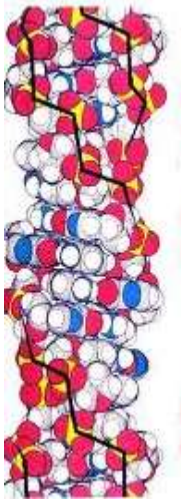


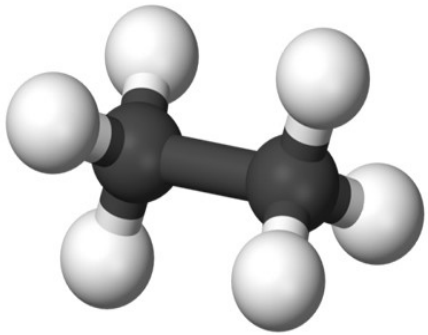
There are billions of useful molecules.

Acids, esthers, alkanes, ...
Biological molecules: DNA, RNA, proteins









Molecules

Every property of a molecule can be calculated using multi-particle quantum mechanics.

$$H_{\mathrm{mp}} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a}\nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0|\vec{r}_a - \vec{r}_b|}$$

We will calculate:

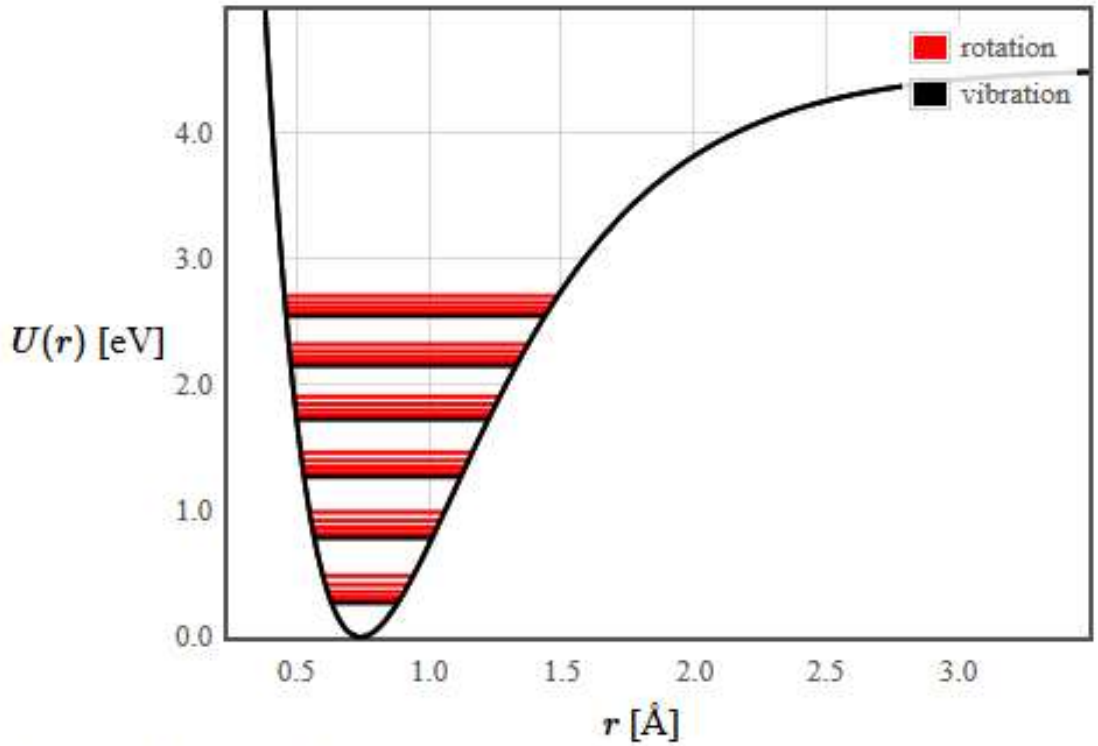
- bond length
- bond strength
- molecular energy levels

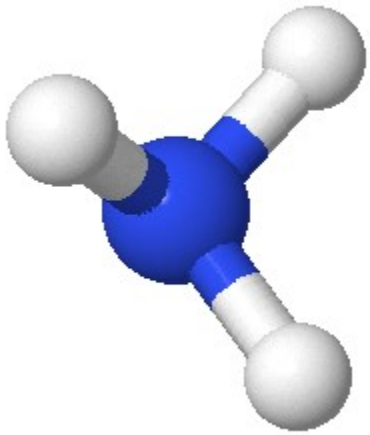
http://en.wikipedia.org/wiki/File:Erwin_Schr%C3%B6dinger.jpg

Molecules

$$H_{\mathrm{mp}} = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a}\nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}$$

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

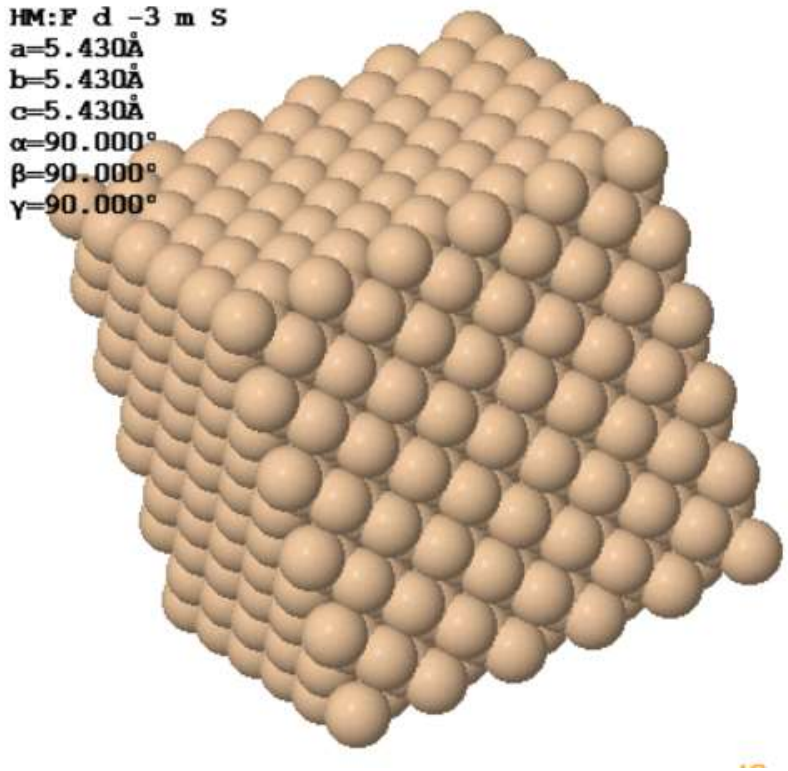




Bond length: 0.74144 Å.
Dissociation energy: 4.52 eV.

Solids

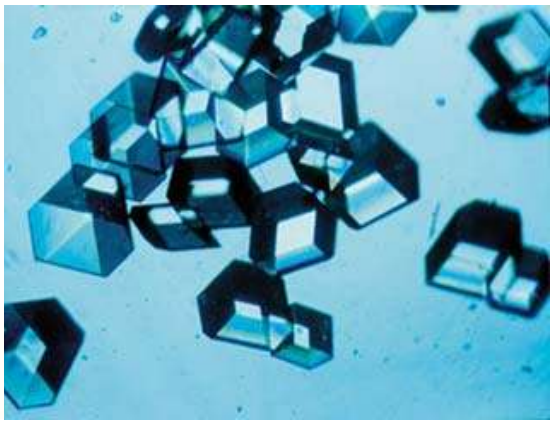
Solids are large molecules



Crystal = periodic arrangement of atoms

Gallium crystals

quartz



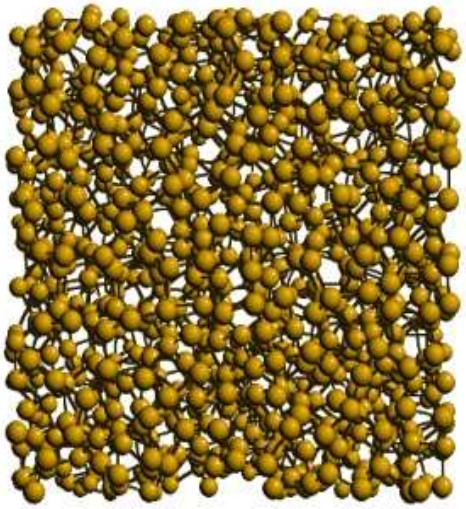
Insulin crystals

http://www.pmc.umontreal.ca/~mousseau/site_an/uploads/Main/si1000.jpg

http://www.wikipedia.org

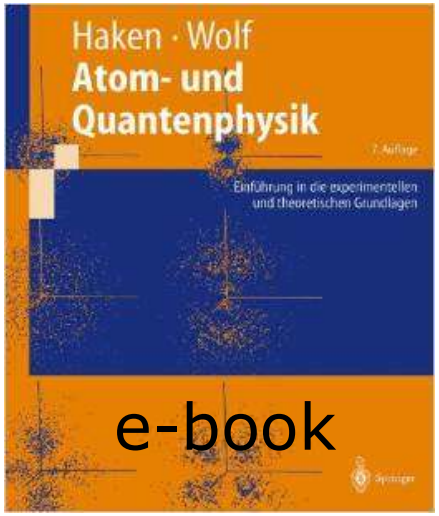
amorphous metal

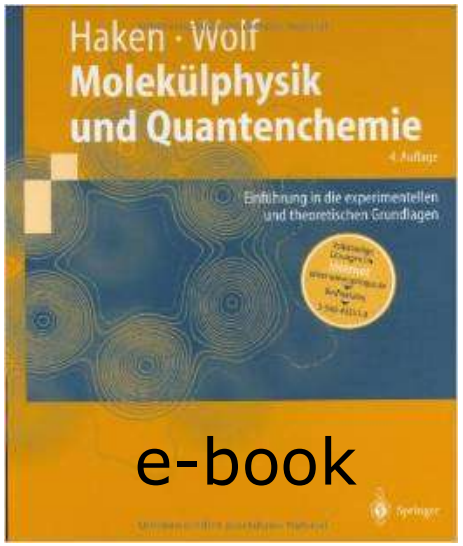
glass

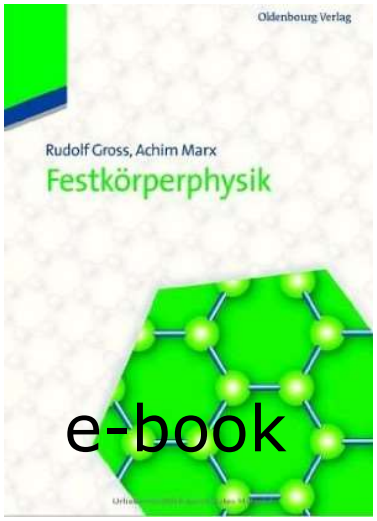


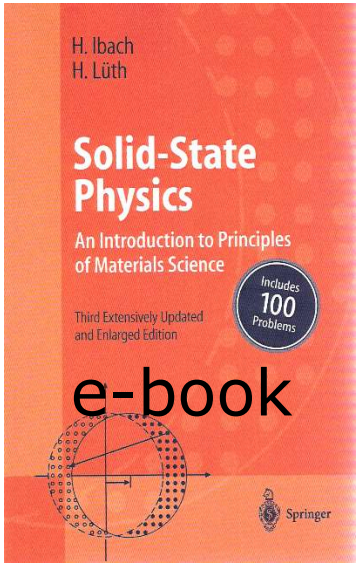
amorphous silicon

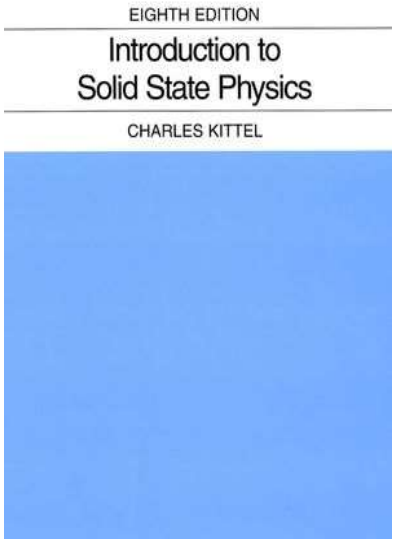
Books


Haken · Wolf
Atom- und Quantenphysik
Einführung in die experimentellen und theoretischen Grundlagen
e-book


Haken · Wolf
Molekülphysik und Quantenchemie
Einführung in die experimentellen und theoretischen Grundlagen
e-book


Oldenbourg Verlag
Rudolf Gross, Achim Marx
Festkörperphysik
e-book


H. Ibach
H. Lüth
Solid-State Physics
An Introduction to Principles of Materials Science
Third Extensively Updated and Enlarged Edition
Includes 100 Problems
e-book
Springer


EIGHTH EDITION
Introduction to Solid State Physics
CHARLES KITTEL

http://www.if.tugraz.at/ss1.html

TU Graz NAWI Graz UNI GRAZ

Menu | Sections | PHY.F20 Molecular and Solid State Physics

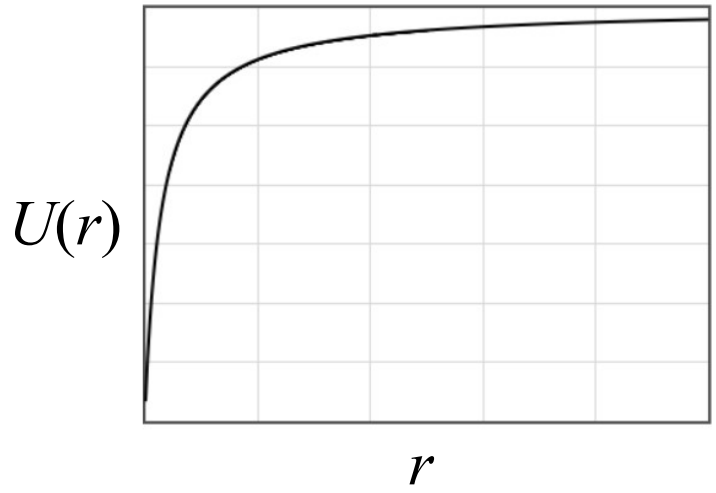
Course outline

- **Introduction** ▶ EN 6:45
- **Review of atomic physics**
  - The solutions to the Schrödinger equation for the hydrogen atom ▶ DE 5:13
    - Plots of the atomic orbitals
  - Helium
  - Many-electron wavefunctions
  - Slater determinants W
  - Singlet and triplet states
  - Exchange W
  - The intractability of the Schrödinger equation
  - Many-electron atoms
- **Molecules**
  - Molecular orbital theory W
    - Solving the total molecular Hamiltonian W
      - The Born-Oppenheimer approximation W
      - Many-electron wavefunctions
      - Bond potentials
      - Vibrational states
      - Rotational states
    - Solving the molecular orbital Hamiltonian

Hydrogen atom, Atomic Orbitals

Estimate the size of a hydrogen atom

Potential energy $$U(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$



Uncertainty relation $$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

For an atom: $\Delta x \sim r_0$

$$\Delta p_x \geq \frac{\hbar}{2r_0}$$

Estimate the size of a hydrogen atom

$$\Delta p_x \geq \frac{\hbar}{2r_0}$$

$$\Delta p_x = \sqrt{\left\langle p_x^2 \right\rangle - \left\langle p_x \right\rangle^2} \qquad \left\langle p_x \right\rangle = 0$$

$$\left(\Delta p_x\right)^2 = \left\langle p_x^2 \right\rangle \geq \left(\frac{\hbar}{2r_0}\right)^2$$

$$E_{kin} = \frac{mv^2}{2} = \frac{p^2}{2m}$$

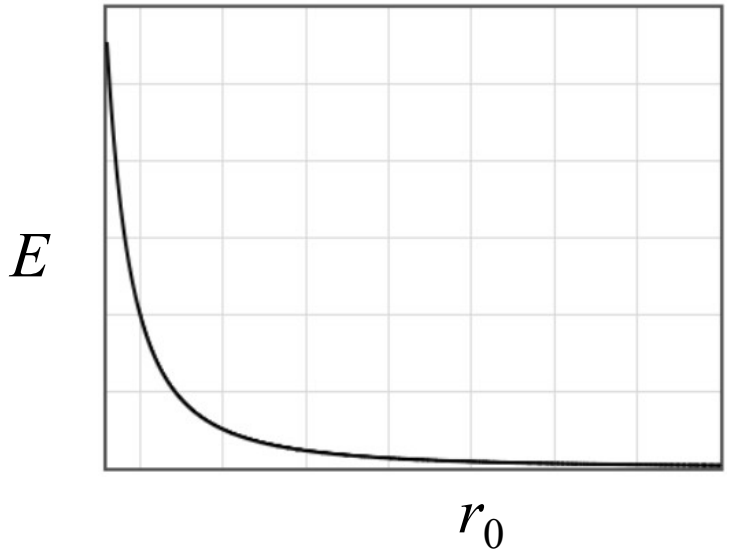
Kinetic energy in x-direction = $\left\langle E_{kin} \right\rangle = \frac{\left\langle p_x^2 \right\rangle}{2m} \geq \frac{\hbar^2}{8mr_0^2}$

Confinement energy

Kinetic energy in x-direction = $\left\langle E_{kin} \right\rangle = \frac{\left\langle p_x^2 \right\rangle}{2m} \geq \frac{\hbar^2}{8mr_0^2}$

Confinement energy:

$$\frac{\left\langle p_x^2 \right\rangle}{2m} + \frac{\left\langle p_y^2 \right\rangle}{2m} + \frac{\left\langle p_z^2 \right\rangle}{2m} \geq \frac{3\hbar^2}{8mr_0^2}$$



Estimate the size of a hydrogen atom

Total energy = Kinetic + Potential

$$E_{tot} = \frac{3\hbar^2}{8mr^2} - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\frac{dE_{tot}}{dr} = \frac{-3\hbar^2}{4mr^3} + \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$r_0 = \frac{3\hbar^2\pi\varepsilon_0}{me^2} = 4.0\times10^{-11}\ \text{m}$$

$$a_0 = 5.3\times10^{-11}\ \text{m}$$

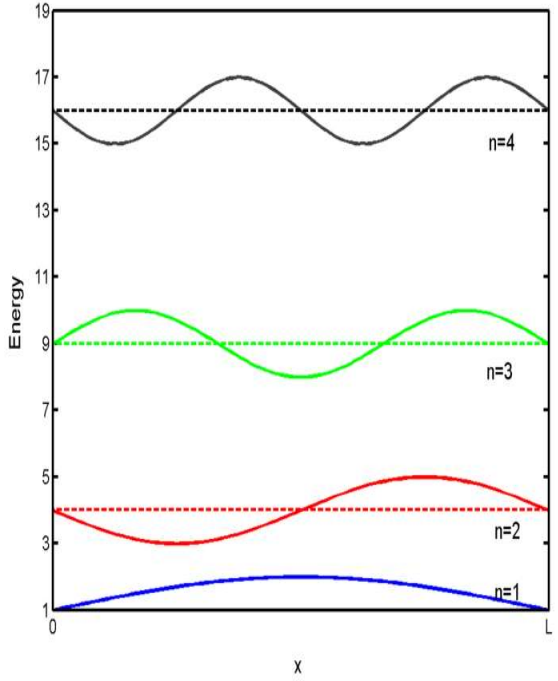
Confinement energy

$$\frac{-\hbar^2}{2m}\nabla^2\Psi - \frac{e^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$$

The kinetic energy term increases as the wavelength gets smaller

$$E_{kin} = \tfrac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$p = mv \quad p = \hbar k \quad k = \frac{2\pi}{\lambda}$$



Atomic orbitals

$$\frac{-\hbar^2}{2m}\nabla^2\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$$

Z = effective nuclear charge

Solve with the boundary condition $\Psi \to 0 \quad \text{as} \quad \left|\vec{r}\right| \to \infty$

Assume $\Psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$

Atomic orbitals

Z is the effective nuclear charge

$$\phi_{1s}^{Z} = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{Zr}{a_0}},$$

$$\phi_{2s}^{Z} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}}\left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}},$$

$$\phi_{2px}^{Z} = \frac{1}{8}\sqrt{\frac{Z^3}{\pi a_0^3}}\,\frac{Zr}{a_0}\, e^{-\frac{Zr}{2a_0}} \sin\theta\cos\varphi,$$

$$\phi_{2py}^{Z} = \frac{1}{8}\sqrt{\frac{Z^3}{\pi a_0^3}}\,\frac{Zr}{a_0}\, e^{-\frac{Zr}{2a_0}} \sin\theta\sin\varphi,$$

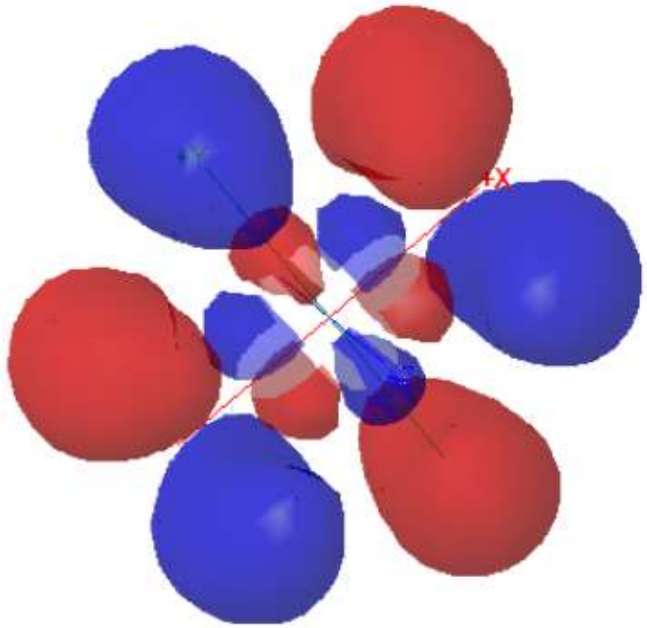
$$\phi_{2pz}^{Z} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}}\,\frac{Zr}{a_0}\, e^{-\frac{Zr}{2a_0}} \cos\theta,$$

$$E = -\frac{Z^2 m e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{13.6 Z^2}{n^2}\ \text{eV}.$$

Atomic orbitals

http://lampx.tugraz.at/~hadley/ss1/molecules/atoms/AOs.php

5f



Atomic orbitals:

1s								
2s						2px	2py	2pz
3s						3px	3py	3pz
4s	3d xy	3d yz	3d xz	3d z²	3d x²-y²	4px	4py	4pz
5s	4d xy	4d yz	4d xz	4d z²	4d x²-y²	5px	5py	5pz
6s	5d xy	5d yz	5d xz	5d z²	5d x²-y²	6px	6py	6pz

4f	4f	4f	4f	4f	4f	4f
5f	5f	5f	5f	5f	5f	5f

$$\langle \phi_m | H | \phi_n \rangle = \frac{-\hbar^2}{2m} \langle \phi_m | \nabla^2 | \phi_n \rangle - \frac{2e^2}{4\pi\varepsilon_0} \langle \phi_m | \frac{1}{|\vec{r}|} | \phi_n \rangle$$