Molecular and Solid State Physics

Calculate the macroscopic properties from the microscopic structure.

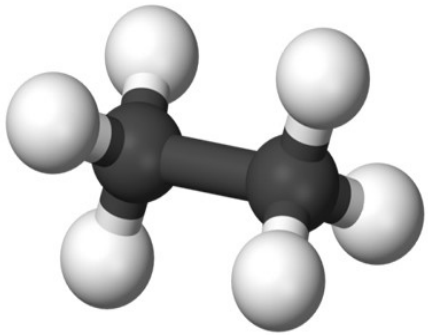
Goals

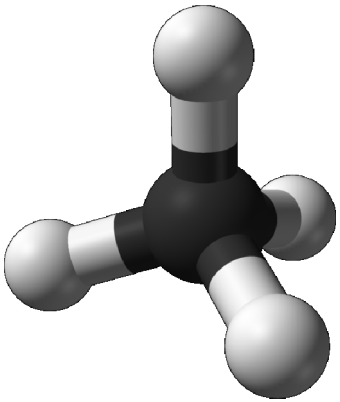
The microscopic structure determines the macroscopic properties.

At the end of this course you should be able to explain how any property of any molecule or solid can be calculated using quantum mechanics and statistical physics.

For example: knowing how the atoms are arranged in a crystal, you must be able to say if it is an electrical conductor or not.

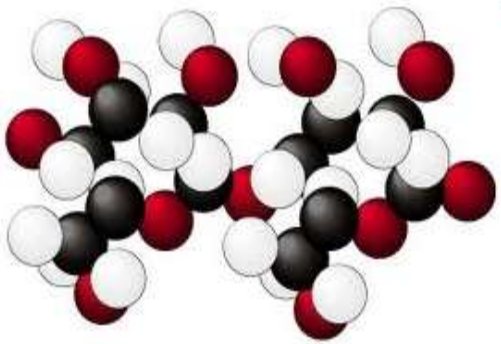
Molecules

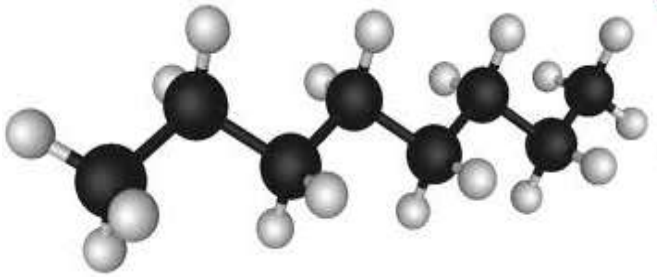


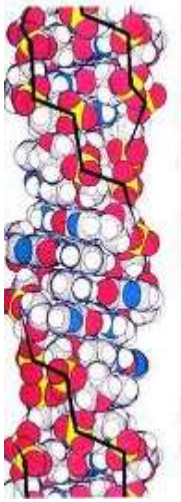


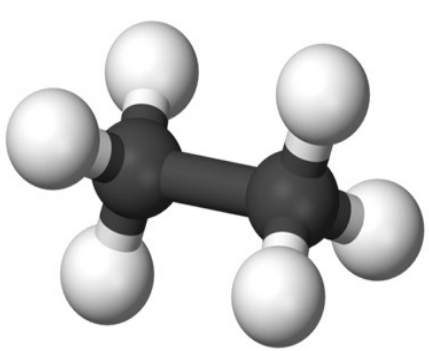
There are billions of useful molecules.

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









Molecules

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

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

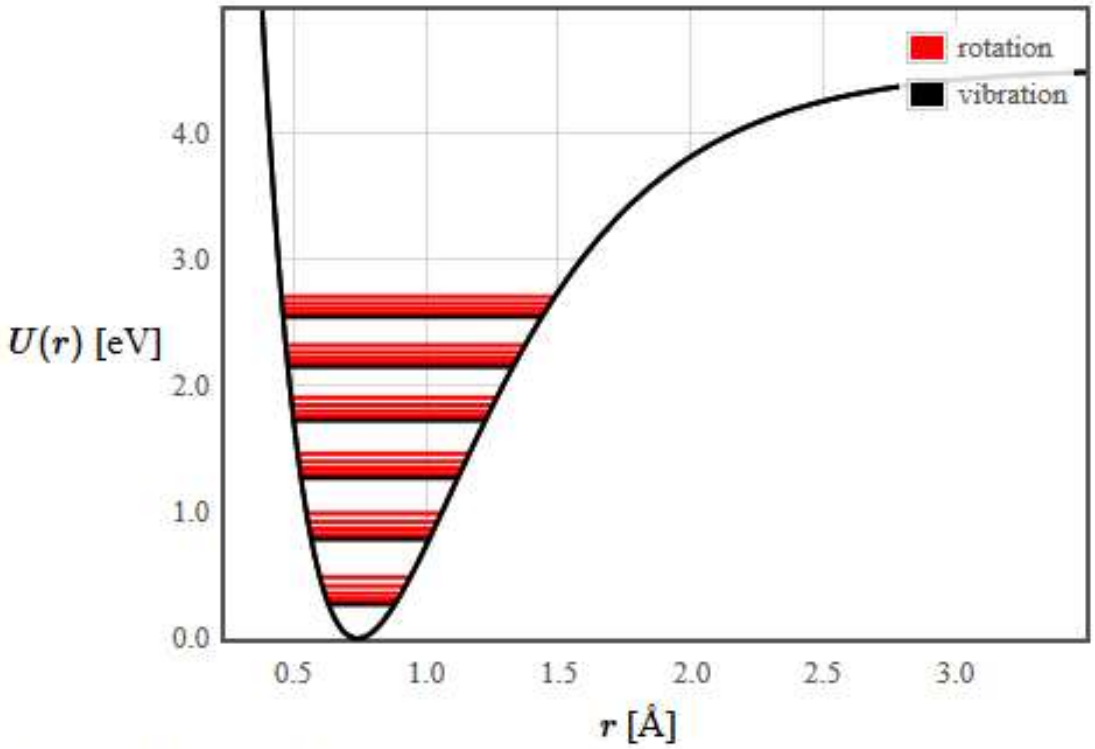
We will calculate:

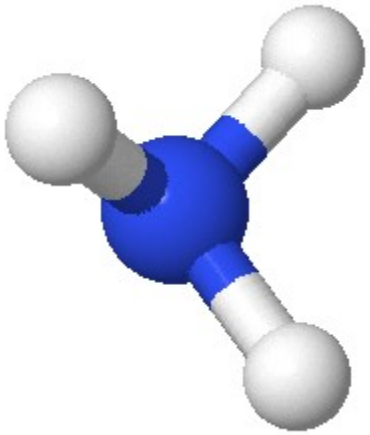
- bond length
- bond strength
- molecular energy levels

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

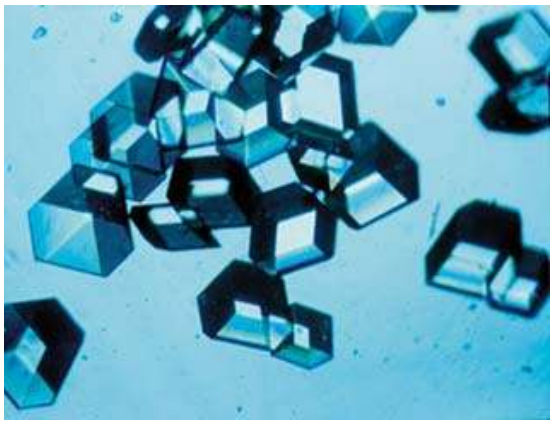
Solids are large molecules

Crystal structures
Determining crystal structures with x-ray diffraction
Photons in solids
Phonons in solids (lattice vibrations)
Thermal properties
Free electron model
Band structure (metals, semiconductors, insulators)
Semiconductors

Crystal = periodic arrangement of atoms

Gallium crystals

quartz



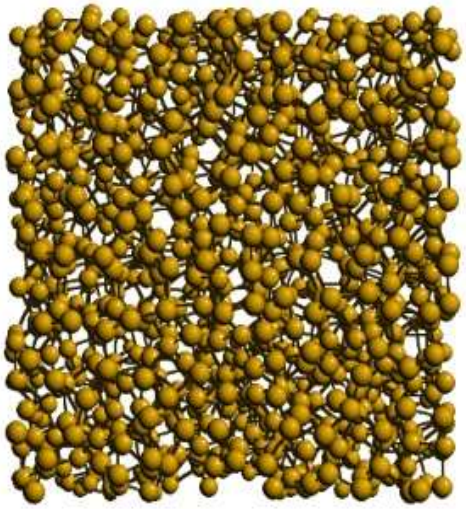
Insulin crystals

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

http://www.wikipedia.org

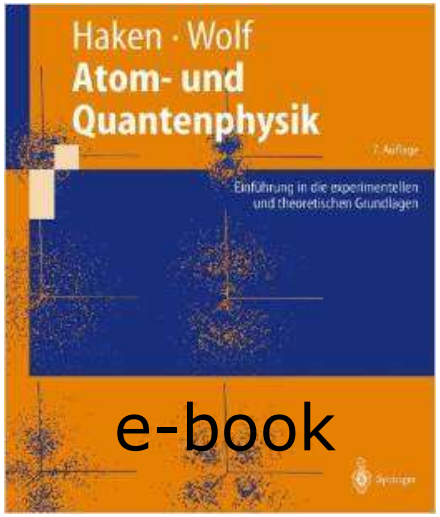
amorphous metal

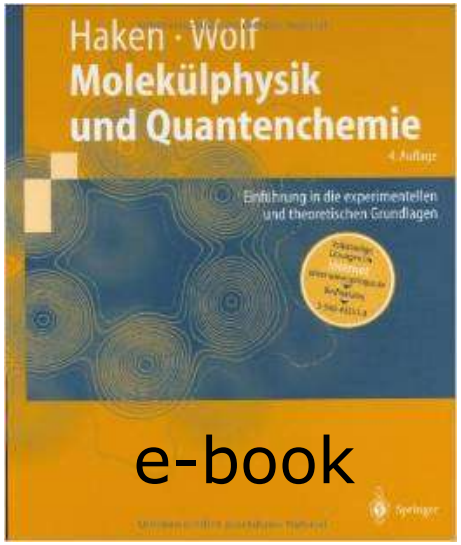
glass

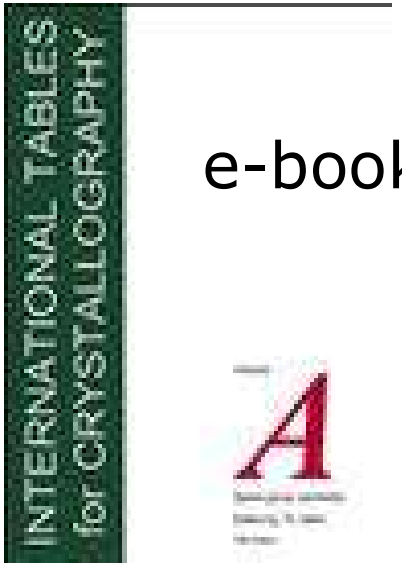


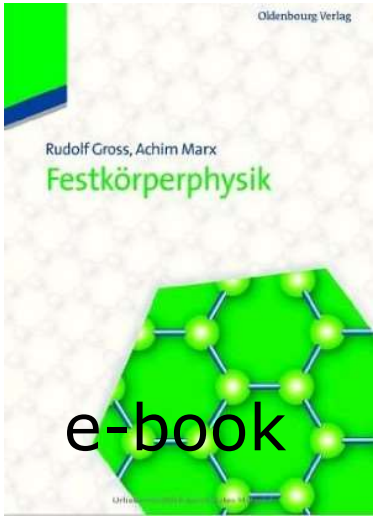
amorphous silicon

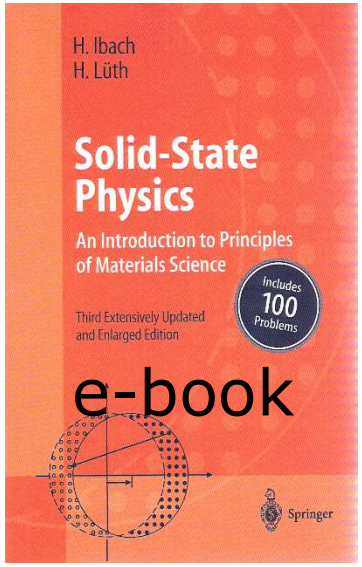
Books

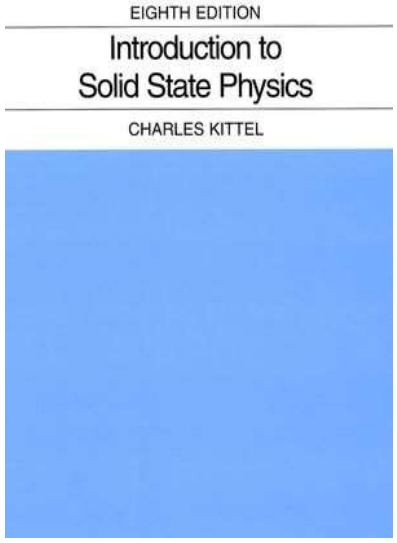

Haken · Wolf
Atom- und Quantenphysik
Einführung in die experimentellen und theoretischen Grundlagen
e-book

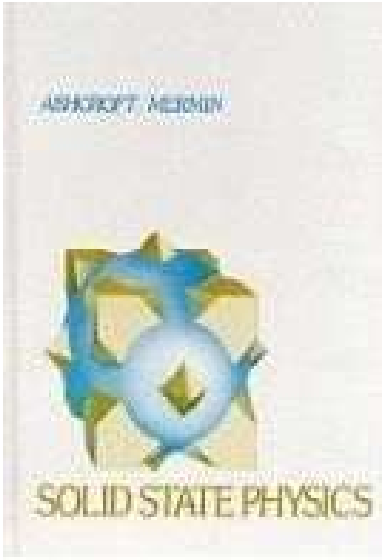

Haken · Wolf
Molekülphysik und Quantenchemie
Einführung in die experimentellen und theoretischen Grundlagen
e-book


INTERNATIONAL TABLES for CRYSTALLOGRAPHY
A
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
Includes 100 Problems
Third Extensively Updated and Enlarged Edition
e-book
Springer


EIGHTH EDITION
Introduction to Solid State Physics
CHARLES KITTEL


ASHCROFT MERMIN
SOLID STATE PHYSICS

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

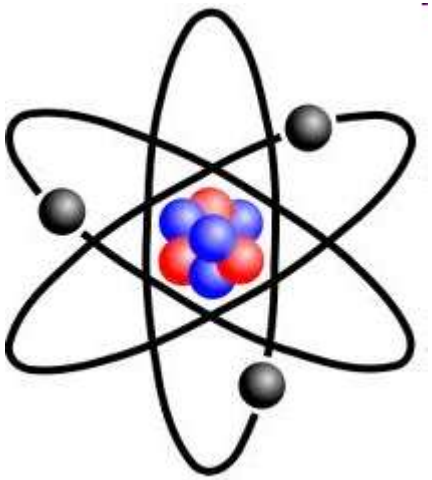
Student Projects

Do something that will help other students

- Write a program to calculate the time evolution of the wave function of a multi-electron atom. The program would be about a page long but if mor involved it will take more than the age of the universe to run it.
- Calculate the molecular orbitals of ethylene, butadiene, and benzene.
- Use valence bond theory to calculate the bond potential (like a Morse potential) for H_2.
- Write a solution to the Singlet-triplet problem
- Make a multimedia presentation (~5 minutes) that explains some topic better than it was explained during the lectures. See making presentations f
- Make patterns that can be printed on paper, cut out and folded to make three dimensional models of the Brillouin zones.
- Implement the triclinic crystal system in the Brillouin zone applet.
- Make a web page that specifies the symmetry points and lines of a Brillouin zone like the one for fcc.
  - Triclinic
  - Simple Monoclinic
  - Base centered Monoclinic
  - Simple Orthorhombic
  - Base centered Orthorhombic
  - Face centered Orthorhombic
  - Body centered Orthorhombic
  - Simple Tetragonal

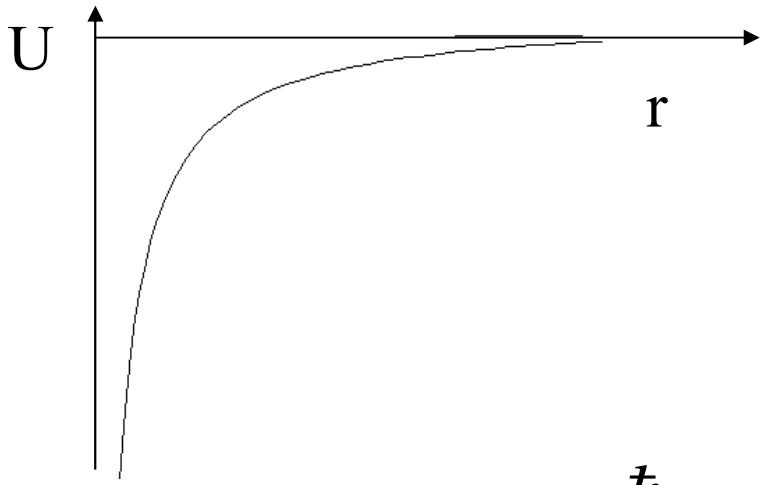
Review of atomic physics

Estimating the size of an atom
The hydrogen atom
The helium atom
Many electron atoms



Estimate the size of a hydrogen atom

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



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

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

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

Estimate the size of a hydrogen atom

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

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

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

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

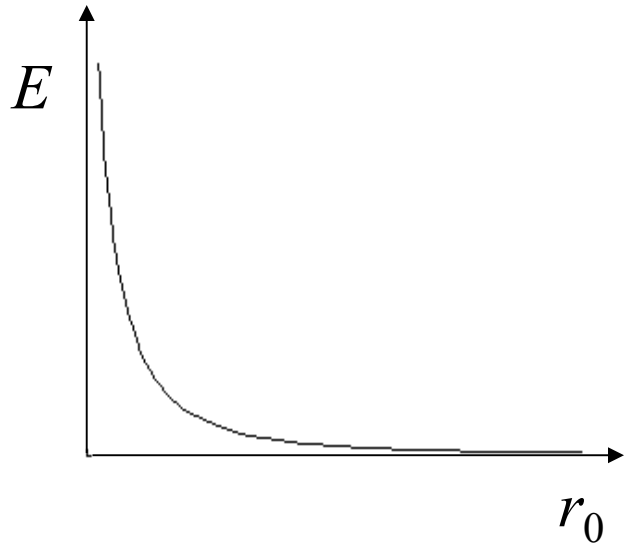
Kinetic energy in x-direction = $\left\langle E_{kin} \right\rangle = \frac{\left\langle p_x^2 \right\rangle}{2m} \geq \frac{\hbar^2}{8mr_0^2}$

Confinement energy

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

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

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

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

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

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

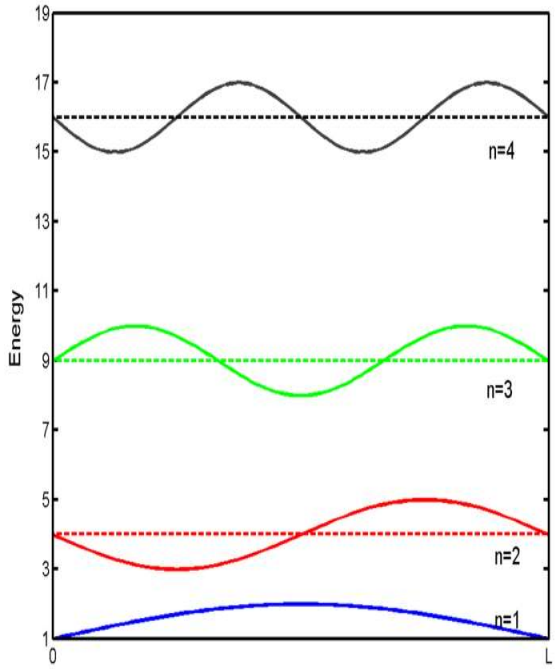
Confinement energy

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

The kinetic energy term increases as the wavelength gets smaller

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

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



Wave functions of hydrogen

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

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

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

Hydrogen atom

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

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

$\rho = \dfrac{2r}{na_0}$ $\quad a_0$ = Bohr radius

$L_{n-l-1}^{2l+1}(\rho)$ = generalized Laguerre polynomials

$Y_{lm}(\theta,\varphi)$ = spherical harmonics (appear in centrosymmetric problems)

Hydrogen wavefunctions

quantum numbers n,l,m

$l = 0 \ldots n\text{-}1$

$m = -l \ldots 0 \ldots l$

$l = 0 \rightarrow$ s
$l = 1 \rightarrow$ p
$l = 2 \rightarrow$ d
$l = 3 \rightarrow$ f

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}},$$

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

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

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

$$\psi_{2pz} = \frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos\theta.$$