Pázmány Péter Catholic University
Faculty of Information Technology and Bionics

“Fides et Ratio”

Physics of Information Technology II
Physics of Molecular Bionics II
2014 Autumn

Lecture 3
Schrödinger’s Quantum Wave Mechanics
Postulates
Expectation Value, Heisenberg’s Relation
The Single Electron Problem
Electrons in ‚Boxes’
Hydrogen and Hydrogen-like Atoms

The Postulates of Schrödinger's Quantum Wave Mechanics

Postulate 1. (P.1) *Information we can know about a state*

The state of a system is fully described by its state-function (wave-function) $\psi(q_1, q_2, ..., q_\mathrm{f}, t)$, which is bounded, single-valued, continuous, and continuously differentiable function of the configuration-space-coordinates $(q_1, q_2, ..., q_f)$ and of time t .

Postulate 2. (P.2) *Interpretation of the wave-function*

The probability that the system in state ψ can be found in the volume-element dV of the configuration space is $\psi\psi^*\mathrm{d}V$.
From this it follows that

$$\int_V \psi\psi^* \,\mathrm{d}V = 1$$ i.e. ψ is square-integrable.

Postulate 3. (P.3) *Observables*

There is a linear operator L assigned to every observable (measurable dynamical variable) *L.*

If we perform a "strong" measurements on the system then the observable's values of *L* are the λ eigen-values of operator L

$$\hat{\mathbf{L}}\psi = \lambda\psi$$

The rules of the operator assignment are as follows:

a) The operators of the space coordinates are multiplication by the coordinate : $\hat{\mathbf{q}}_i \quad \rightarrow \quad q_i; \quad \hat{\mathbf{r}} \Rightarrow \mathbf{r}\,\cdot$

b) The operator assigned to the momentum: $\hat{\mathbf{p}} \quad \rightarrow \quad -\mathrm{j}\hbar\nabla$

c) We assign operators to dynamical variables which are functions of the space coordinates moments by substituting the operators of the space coordinates and moments into the functions:

$$E_{\text{kin}} = \frac{1}{2} m\mathbf{v}^2 = \frac{1}{2m}\hat{\mathbf{p}}^2 \rightarrow \quad \hat{\mathbf{E}}_{\text{kin}} = -\frac{\hbar^2}{2m}\nabla^2$$

The operator of the total energy of a particle $\quad E = E_{\text{kin}} + E_{\text{pot}}$

$$\mathbf{H} = -\frac{\hbar^2}{2m}\Delta + E_{\text{pot}}(\mathbf{r})$$

where $\nabla^2 = \Delta$, which in Descartes-coordinates: $\quad \Delta \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$

The operator of a particle’s angular momentum:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \qquad \rightarrow \qquad \hat{\mathbf{L}} = -\mathrm{j}\hbar\mathbf{r} \times \nabla$$

Hamilton operator of a many-body system

$$E = E_{\text{kin}} + E_{\text{pot}} = \sum_{i=1}^{n} \frac{1}{2m_i}\mathbf{p}_i^2 + E_{\text{pot}} \;\; \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$$

$$\hat{E} = \hat{E}_{\text{kin}} + \hat{E}_{\text{pot}} = \sum_{i=1}^{n} \frac{1}{2m_i}\hat{\mathbf{p}}_i^2 + E_{\text{pot}} \;\; \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n \; = \hat{\mathbf{H}}$$

Postulate 4. (P.4) *The outcome of strong measurements*

If the state of a physical system is ψ, and we observe the dynamic *observable L with operator L, then the expectation value and deviation of L are:*

$$\langle L \rangle = \int_V \psi^* \hat{\mathbf{L}} \psi \, \mathrm{d}V \qquad \Delta L = \sqrt{\langle L^2 \rangle - \langle L \rangle^2}$$

Postulate 5. (P.5) *Time-evolution of the wave-function*

In a closed system the wave-function evolves in time according to the time-dependent Schrödinger equation:

$$\mathrm{j}\hbar \frac{\partial \psi}{\partial t} = \hat{\mathbf{H}} \psi$$

(From the initial sate-function ψ_{t_0} we can determine the future of the wave-function ψ_t for $t > t_0$).

$$h = 6.625 \cdot 10^{-34} \ \mathrm{Ws}^2; \quad \hbar = h / 2\pi = 1.05 \cdot 10^{-34} \ \mathrm{Ws}^2$$

Consequences of the Postulates

Frequency, period in time

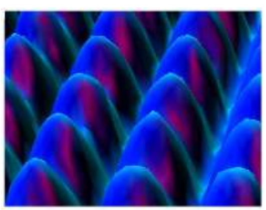
1. Total energy $E = h \cdot \nu = \hbar \cdot \omega$ $\Rightarrow \quad e^{-j \cdot \omega t} = e^{-j \frac{E}{\hbar} t}$

2. Momentum $\mathbf{p} = \hbar \cdot \overline{\mathbf{k}}$ $\quad p = \hbar \cdot k = \dfrac{h}{\lambda}$

Wavelength, period in space

3. Electrons are either ‘bounded’ or ‘free’

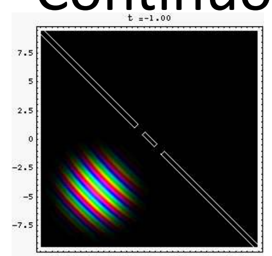
“Bounded” electron
Discrete energy spectrum



$E_1, E_2, \ldots, E_n, \ldots$

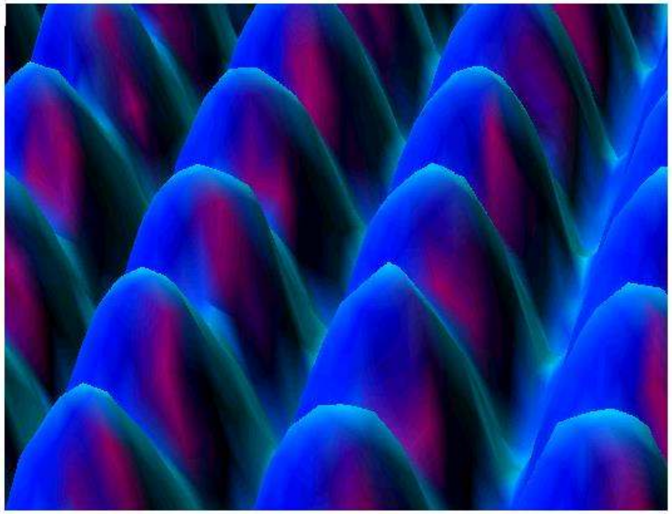
Orbitals
Standing waves

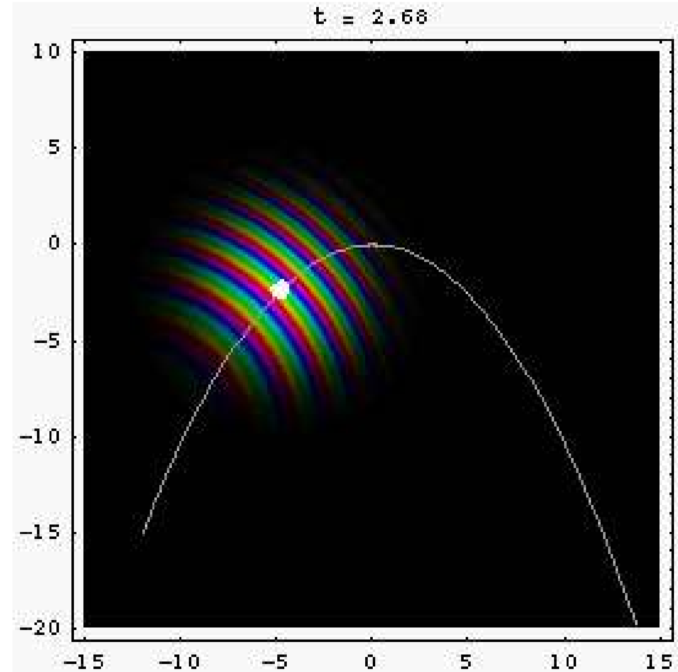
„Free” electron
Continuous energy spectrum



$E(k)$ Wave pocket

$$\psi(x,t) = \int_{-\infty}^{+\infty} A(k) e^{\mathrm{j}(kx - \frac{E}{\hbar} t)} \mathrm{d}k$$

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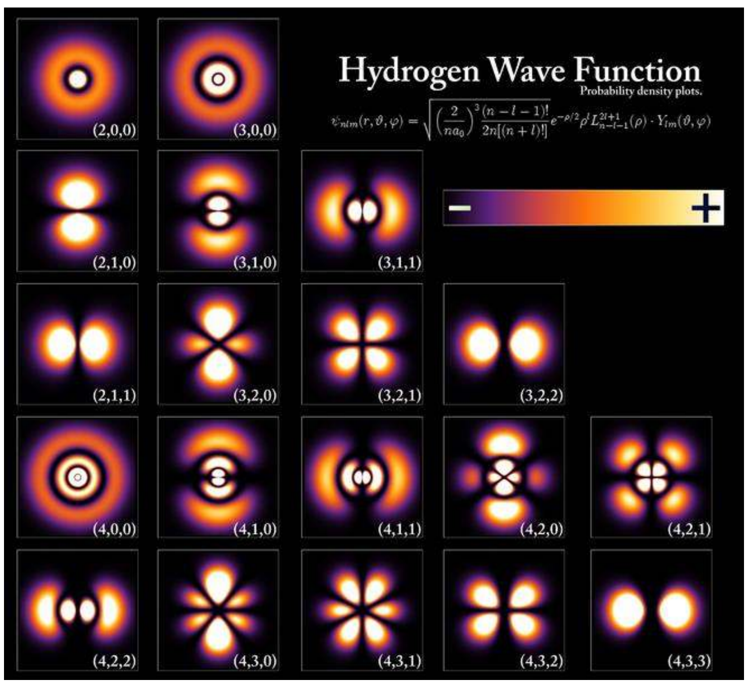
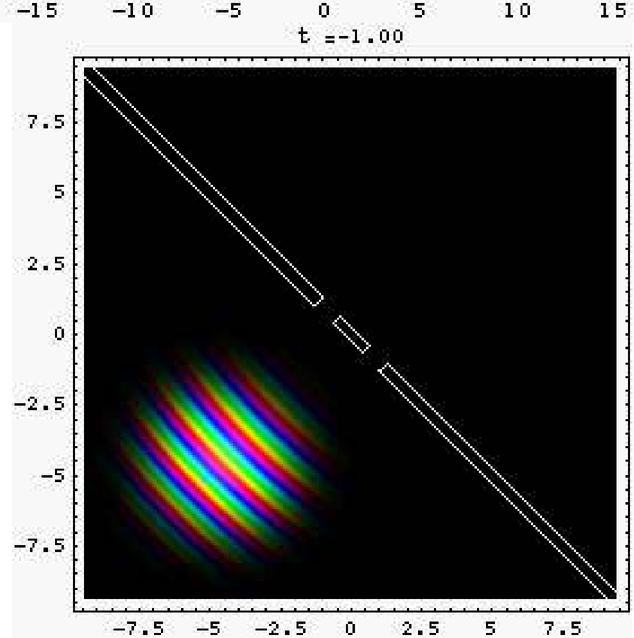
10
5
0
-5
-10
-15
-20
-15
-10
-5
0
5
10
15


Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2}\rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$
−
+
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
(2,1,1)
(3,2,0)
(3,2,1)
(3,2,2)
(4,0,0)
(4,1,0)
(4,1,1)
(4,2,0)
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)


t =-1.00
7.5
5
2.5
0
-2.5
-5
-7.5
-7.5
-5
-2.5
0
2.5
5
7.5

3. The Expectation Value of Measurements Change in Time

$$\frac{\mathrm{d}\langle L\rangle}{\mathrm{d}t} = \frac{\mathrm{j}}{\hbar}\langle\psi|\hat{\mathbf{H}}\hat{\mathbf{L}} - \hat{\mathbf{L}}\hat{\mathbf{H}}|\psi\rangle$$

$$\hat{\mathbf{H}}\hat{\mathbf{L}} - \hat{\mathbf{L}}\hat{\mathbf{H}} \equiv \left[\hat{\mathbf{H}}, \hat{\mathbf{L}}\right]$$

„Commutator” of $\hat{\mathbf{H}}$ and $\hat{\mathbf{L}}$

Ehrenfest theorem

$$\frac{\mathrm{d}\langle p\rangle}{\mathrm{d}t} = \frac{\mathrm{d}\langle\psi|\hat{\mathbf{p}}|\psi\rangle}{\mathrm{d}t} = \langle\psi|-\nabla V_{\mathrm{pot}}|\psi\rangle$$

$$\hat{\mathbf{F}} = -\nabla V_{\mathrm{pot}}$$

4. Heisenberg’s Relation

$$q_1, q_2, \ldots, q_i, \ldots q_f \,.$$

Schrödinger Equation

$$\mathrm{j}\hbar \frac{\partial \psi\left(q_1,\ldots,q_f,t\right)}{\partial t} = \mathbf{H}\psi\left(q_1,\ldots,q_f,t\right)$$

$$\psi\left(q_1,\ldots,q_f,t\right) = \Psi\left(q_1,\ldots,q_f\right)\cdot\varphi\left(t\right)$$

$$\mathbf{H}\Psi = E\Psi \qquad \mathrm{d}\varphi\left(t\right)/\,\mathrm{d}t = -\mathrm{j}\frac{E}{\hbar}\varphi\left(t\right)$$

$$E_1, E_2, \ldots, E_n, \ldots$$

$$\Psi_1, \Psi_2, \ldots, \Psi_n, \ldots \qquad e^{-\mathrm{j}\frac{E_n}{\hbar}t}$$

$$\psi\left(q_1,\ldots,q_f,t\right) = \sum_n C_n \Psi_n\left(q_1,\ldots,q_f\right)\cdot e^{-j\frac{E_n}{\hbar}t}$$

The Single Electron Problem Time t

Configuration space $\mathbf{r}$ $\left(q_1, q_2, q_3\right)$; $\left(x, y, z\right)$; $\left(r, \vartheta, \varphi\right)$

Hamilton Operator $$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\Delta + E_{\text{pot}}(\mathbf{r})$$

Descartes x, y, z

$$\Delta\psi = \left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right]$$

Spherical r, ϑ, φ

$$\Delta\psi = \frac{1}{r^2\sin\vartheta}\left[\frac{\partial}{\partial r} r^2 \sin\vartheta \frac{\partial\psi}{\partial r} + \frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial\psi}{\partial\vartheta} + \frac{\partial}{\partial\varphi}\frac{1}{\sin\vartheta}\frac{\partial\psi}{\partial\varphi}\right]$$

Schrödinger Equation $$\mathrm{j}\hbar\frac{\partial\psi\left(\mathbf{r},t\right)}{\partial t} = \hat{\mathbf{H}}\psi\left(\mathbf{r},t\right)$$

$$\hat{\mathbf{H}}\Psi\left(\mathbf{r}\right) = E\cdot\Psi\left(\mathbf{r}\right)$$

$$\psi_1(\mathbf{r},t), \quad \psi_2(\mathbf{r},t), \quad \ldots \quad ,\psi_n(\mathbf{r},t),\ldots$$

$$E_1, \quad E_2, \quad \ldots \quad ,E_n,\ldots$$

$$\Psi_1\left(\mathbf{r}\right)e^{-j\frac{E_1}{\hbar}t}, \Psi_2\left(\mathbf{r}\right)e^{-j\frac{E_2}{\hbar}t}, \ldots, \Psi_n\left(\mathbf{r}\right)e^{-j\frac{E_n}{\hbar}t}, \ldots$$

$$\Psi_1\left(\mathbf{r}\right), \Psi_2\left(\mathbf{r}\right), \ldots, \Psi_n\left(\mathbf{r}\right), \ldots$$

Time-dependent Schrödinger Equation

$$\mathrm{j}\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t}=\hat{\mathbf{H}}\psi(\mathbf{r},t)$$

Time-independent Schrödinger Equation

$$\hat{\mathbf{H}}\psi(\mathbf{r})=E\cdot\psi(\mathbf{r})$$

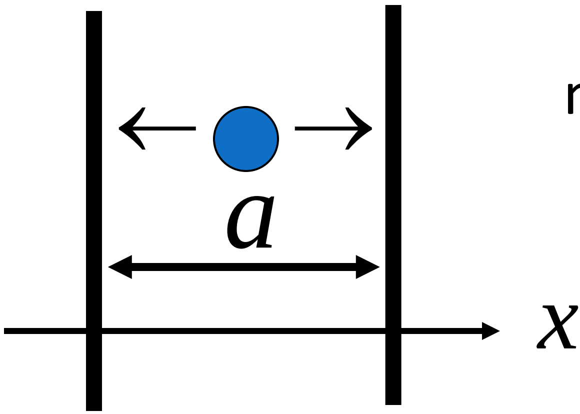
Ervin Schrödinger, Quantisierung als Eigenwert Problem, 1926

Energy eigenvalues $E_1, \quad E_2, \quad \ldots \quad , E_n, \ldots$

Eigen-functions $\psi_1(\mathbf{r}),\psi_2(\mathbf{r}),\ldots,\psi_n(\mathbf{r}),\ldots$

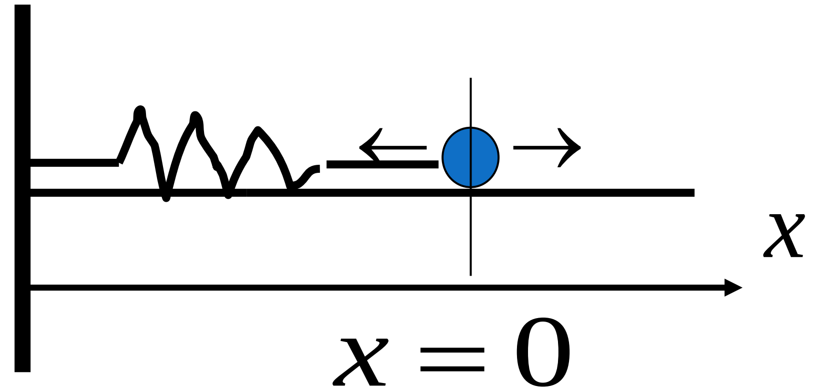
Stationary eigen-states
(No radiation) $\psi_1(\mathbf{r})e^{-j\frac{E_1}{\hbar}t},\psi_2(\mathbf{r})e^{-j\frac{E_2}{\hbar}t},\ldots,\psi_n(\mathbf{r})e^{-j\frac{E_n}{\hbar}t},\ldots$

One-dimensional Single Electron Examples



Quantum mechanically

$$\psi(x,t) \quad ?$$

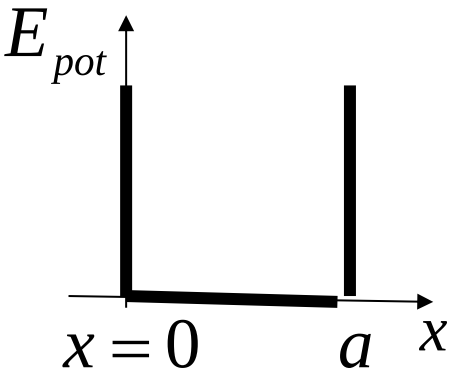


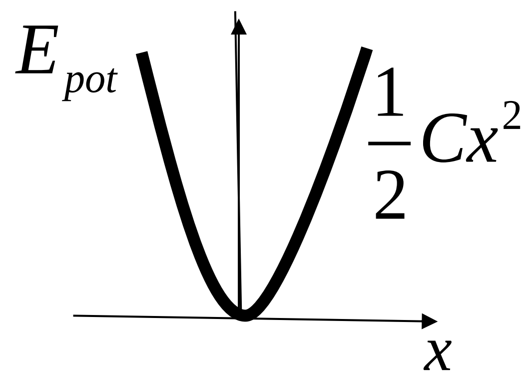
Classically:
‚ping-pong' ball

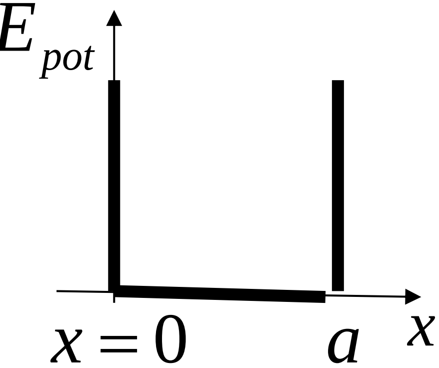
Classically:
Harmonic oscillator

$$\hat{\mathbf{H}}\psi(\mathbf{r}) = E\cdot\psi(\mathbf{r}) \rightarrow$$

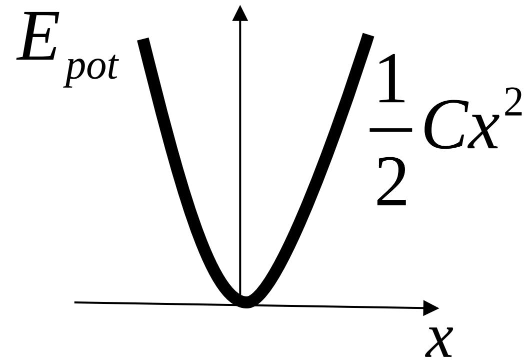
$$\hat{\mathbf{H}}\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + E_{\mathrm{pot}}(x)\right]\psi(x) = E\psi(x)$$







$$\hat{\mathbf{H}}\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + E_{\mathrm{pot}}(x)\right]\psi(x) = E\psi(x)$$



$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x)$$

$$0 < x < a$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + \frac{1}{2}Cx^2\psi(x) = E\psi(x)$$

$$-\infty < x < +\infty$$

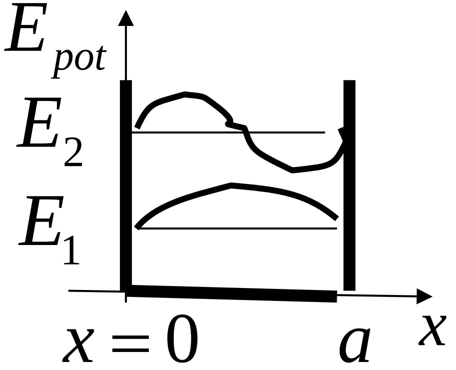
$$\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = -\frac{2m}{\hbar^2}E\cdot\psi(x) = -k^2\cdot\psi(x) \qquad \psi(0) = B = 0 \qquad \psi(a) = A\sin ka = 0$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$k\cdot a = n\cdot\pi \quad n = 1, 2, \ldots \qquad k_n = n\cdot\frac{\pi}{a} \quad n = 1, 2, \ldots$$

$$\psi(x) = A\sin kx + B\cos kx$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} \rightarrow E_n = \hbar^2\frac{k_n^2}{2m} = \frac{h^2}{4\pi^2}\frac{n^2\pi^2}{2m\cdot a^2} = n^2\frac{h^2}{8ma^2}$$



$$\psi_n(x) = A\sin k_n x$$

$$\int_0^{+a} A^2 \sin^2 \frac{n\pi x}{a}\,\mathrm{d}x = 1 \rightarrow A_n = \sqrt{\frac{2}{a}}$$

Energy eigenvalues $\quad E_1 = \frac{h^2}{8ma^2} \qquad E_2 = 4 \cdot E_1 \qquad E_3 = 9 \cdot E_1$

Eigen-functions $\quad \psi_1(x) = \sqrt{\frac{2}{a}}\sin\frac{\pi}{a}x \qquad \psi_2(x) = \sqrt{\frac{2}{a}}\sin\frac{2\pi}{a}x \qquad \psi_3(x) = \sqrt{\frac{2}{a}}\sin\frac{3\pi}{a}x$

Stationary eigen-states (No radiation)

$$\psi_1(x,t) \qquad \psi_2(x,t) \qquad \psi_3(x,t)$$

$$\left(\sqrt{\frac{2}{a}}\sin\frac{\pi}{a}x\right)e^{-\mathrm{j}\frac{E_1}{\hbar}t} \qquad \left(\sqrt{\frac{2}{a}}\sin\frac{2\pi}{a}x\right)e^{-\mathrm{j}\frac{E_2}{\hbar}t} \qquad \left(\sqrt{\frac{2}{a}}\sin\frac{3\pi}{a}x\right)e^{-\mathrm{j}\frac{E_3}{\hbar}t}$$

Null-point energy
‚Ground state energy'

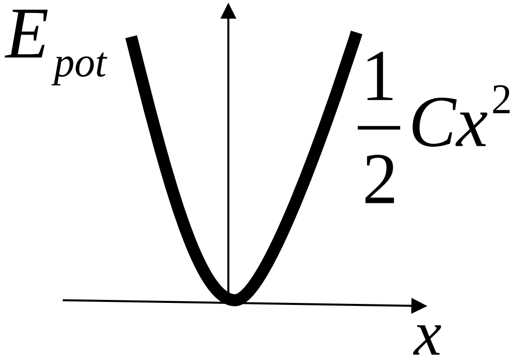
$$E_1 = \frac{h^2}{8ma^2}$$

$$a = 1\,\mu\text{m} \qquad E_1 = 0.376 \cdot 10^{-6}\ \text{eV}$$

$$a = 1\,\text{nm} \qquad E_1 = 0.376\,\text{eV}$$

$$a = 0.1\,\text{nm} \qquad E_1 = 37.6\,\text{eV}$$

$$a = 10^{-15}\ \text{m} \qquad E_1 = 376\,\text{GeV}$$



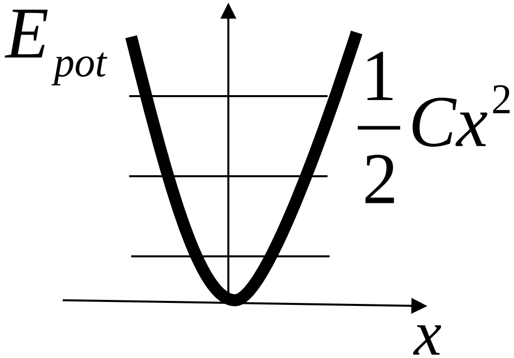
Harmonic oscillator

$$\omega = \sqrt{\frac{C}{m}}; \quad u = \alpha . x = \sqrt{\frac{\sqrt{Cm}}{\hbar}}x; \quad A_n = \sqrt{\frac{\alpha}{\sqrt{\pi}\,2^n\, n!}}$$

$$E_n = \hbar\,\omega\,(n + \frac{1}{2}), \quad n = 0, 1, 2, \ldots$$

$$\psi_n(x) = A_n H_n(u) \cdot e^{-\frac{u^2}{2}};$$

$$H_0(u) = 1; \quad H_1(u) = 2u; \quad H_2(u) = 4u^2 - 2; \ldots$$



$$\omega = \sqrt{\frac{C}{m}}; \quad u = \alpha . x = \sqrt{\frac{\sqrt{Cm}}{\hbar}}x; \quad A_n = \sqrt{\frac{\alpha}{\sqrt{\pi}\, 2^n n!}}$$

Energy eigenvalues $E_0 = \frac{1}{2}\hbar\omega; \quad E_1 = \frac{3}{2}\hbar\omega; \quad E_2 = \frac{5}{2}\hbar\omega; ....$

Eigen-functions

$$\psi_0 \ u \ = A_0 \cdot e^{-\frac{u^2}{2}}; \qquad \psi_1 \ u \ = 2A_1 u \cdot e^{-\frac{u^2}{2}}; \qquad \psi_2 \ u \ = 2A_1 \ u^2 - 1 \ \cdot e^{-\frac{u^2}{2}};$$

Stationary eigen-states (No radiation)

$$\psi_0 \ u \ e^{-j\frac{E_0}{\hbar}t} \qquad \psi_1 \ u \ e^{-j\frac{E_1}{\hbar}t} \qquad \psi_2 \ u \ e^{-j\frac{E_2}{\hbar}t}$$

CUPS – Consortium of Upper-level Physics Software

CUPSQM

– BOUND1D

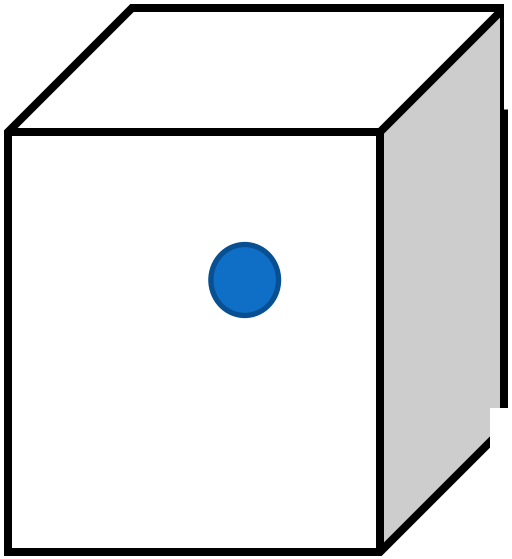
– LATICE1D

Energy eigenvalues

Eigen-functions

Probabilities

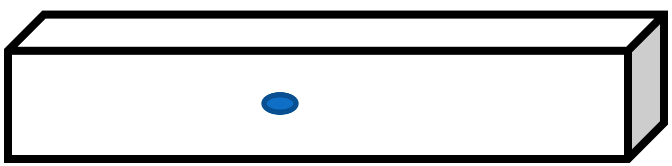
Single Electron in a three-dimensional cubic box
(“big box”, “long box”, “small box”)



$$\hat{\mathbf{H}}\psi(x,y,z,t) = \mathrm{j}\hbar\frac{\partial \psi(x,y,z,t)}{\partial t} \qquad \hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\Delta + E_{\mathrm{pot}}$$

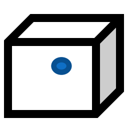
$$\Delta\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \qquad E_{\mathrm{pot}} = \begin{cases} 0, & if \quad 0 < x < a, \\ & \quad 0 < y < b, \\ & \quad 0 < z < c, \\ \infty & \text{otherwise.} \end{cases}$$

$$\hat{\mathbf{H}}\psi(x,y,z) = E\cdot\psi(x,y,z)$$



$$\psi\left(\mathrm{x,y,z,t}\right) = \psi\left(\mathrm{x,y,z}\right)e^{-\mathrm{j}\frac{E}{\hbar}t}$$

We are looking for the solution as



$$\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z)$$

$$\mathbf{H}\psi(x,y,z) = -\frac{\hbar^2}{2m}\Delta\psi(x,y,z) = E\psi(x,y,z) \qquad \Delta\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \qquad \psi(x,y,z) = \psi_1(x)\,\psi_2(y)\,\psi_3(z)$$

$$\Delta\psi_1(x)\psi_2(y)\psi_3(z) = \psi_2(y)\psi_3(z)\frac{\mathrm{d}^2\psi_1}{\mathrm{d}x^2} + \psi_1(x)\psi_3(z)\frac{\mathrm{d}^2\psi_2}{\mathrm{d}y^2} + \psi_1(x)\psi_2(y)\frac{\mathrm{d}^2\psi_3}{\mathrm{d}z^2}$$

$$-\frac{\hbar^2}{2m}\left[\psi_2(y)\psi_3(z)\frac{\mathrm{d}^2\psi_1}{\mathrm{d}x^2} + \psi_1(x)\psi_3(z)\frac{\mathrm{d}^2\psi_2}{\mathrm{d}y^2} + \psi_1(x)\psi_2(y)\frac{\mathrm{d}^2\psi_3}{\mathrm{d}z^2}\right] = E\cdot\psi_1(x)\psi_2(y)\psi_3(z)$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{\psi_1(x)}\frac{\mathrm{d}^2\psi_1}{\mathrm{d}x^2} + \frac{1}{\psi_2(y)}\frac{\mathrm{d}^2\psi_2}{\mathrm{d}y^2} + \frac{1}{\psi_3(z)}\frac{\mathrm{d}^2\psi_3}{\mathrm{d}z^2}\right] = E$$

The sum of three functions is constant.

This is possible if and only if

$$\frac{\mathrm{d}^2\psi_1(x)}{\mathrm{d}x^2} = -\frac{2m}{\hbar^2}E_1\psi_1(x) \qquad \frac{\mathrm{d}^2\psi_2(y)}{\mathrm{d}y^2} = -\frac{2m}{\hbar^2}E_2\psi_2(y) \qquad \frac{\mathrm{d}^2\psi_3(z)}{\mathrm{d}z^2} = -\frac{2m}{\hbar^2}E_3\psi_3(z)$$

$$E = E_1 + E_2 + E_3$$

$$\frac{\mathrm{d}^2\psi_1(x)}{\mathrm{d}x^2} = -\frac{2m}{\hbar^2}E_1\psi_1(x) \qquad \psi_{n_1}(x) = A\sin n_1\pi\frac{x}{a}, \qquad n_1 = 1,2,\ldots,$$

$$\frac{\mathrm{d}^2\psi_2(y)}{\mathrm{d}y^2} = -\frac{2m}{\hbar^2}E_2\psi_2(y) \qquad \psi_{n_2}(y) = B\sin n_2\pi\frac{y}{b}, \qquad n_2 = 1,2,\ldots,$$

$$\frac{\mathrm{d}^2\psi_3(z)}{\mathrm{d}z^2} = -\frac{2m}{\hbar^2}E_3\psi_3(z) \qquad \psi_{n_3}(z) = C\sin n_3\pi\frac{z}{a}, \qquad n_3 = 1,2,\ldots,$$

$$\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z) \quad = A\sin n_1\pi\frac{x}{a}\cdot\sin n_2\pi\frac{y}{b}\cdot\sin n_3\pi\frac{z}{c}$$

$$A^2\int_0^a\int_0^b\int_0^c \sin^2 n_1\pi\frac{x}{a}\cdot\sin^2 n_2\pi\frac{y}{b}\cdot\sin^2 n_3\pi\frac{z}{c}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 1 \qquad A = \sqrt{\frac{8}{abc}}$$

$$\psi_{n_1n_2n_3}(x,\ y,\ z;\ t) = \sqrt{\frac{8}{abc}}\sin n_1\pi\frac{x}{a}\cdot\sin n_2\pi\frac{y}{b}\cdot\sin n_3\pi\frac{z}{c}\cdot\mathrm{e}^{-\mathrm{j}\frac{E_{n_1n_2n_3}}{\hbar}t}$$

$$\psi_{n_1 n_2 n_3}(x, y, z; t) = \sqrt{\frac{8}{abc}} \sin n_1\pi \frac{x}{a} \cdot \sin n_2\pi \frac{y}{b} \cdot \sin n_3\pi \frac{z}{c} \cdot \mathrm{e}^{-\mathrm{j}\frac{E_{n_1 n_2 n_3}}{\hbar} t}$$

The admitted energies of the electron in the box:

$$E_{n_1 n_2 n_3} = E_1 + E_2 + E_3 = \frac{\mathrm{h}^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

If the box is symmetric, e.g. $b = a$ then

$$E_{n_1 n_2 n_3} = \frac{h^2}{8m}\left(\frac{n_1^2 + n_2^2}{a^2} + \frac{n_3^2}{c^2}\right)$$

Degenerate stationary states

To an energy it belongs more than a single eigen-state

Two eigenstates *n1 n2 and n2 n1* belong to the same energy

$$\psi_{n_1 n_2 n_3} \qquad \psi_{n_2 n_1 n_3}$$

If $c = b = a$, then there are even more degeneracies

$$E_{n_1 n_2 n_3} = \frac{h^2}{8ma^2}\, n_1^2 + n_2^2 + n_3^2 \ , \qquad n_1 = 1, 2, ...; \quad n_2 = 1, 2, ...; \quad n_3 = 1, 2...$$

$$\psi_{n_1 n_2 n_3} = \sqrt{\frac{8}{a^3}} \sin n_1 \pi \frac{x}{a} \cdot \sin n_2 \pi \frac{y}{a} \cdot \sin n_3 \pi \frac{z}{a}$$

The state is determined by the eigen-function

In case of a cubic box (n_1, n_2, n_3) quantum numbers specify the eigen-values (energies)

The null-point energy, E_1 , belongs to quantum numbers (1, 1, 1).

The ground state $$\psi_{111} = \sqrt{\frac{8}{a^3}} \sin \pi \frac{x}{a} \cdot \sin \frac{y}{a} \cdot \sin \frac{z}{a}$$

Next energy level is $E_2 = 2E_1$. There are three dufferent states which belong to E_2: (2, 1, 1), (1, 2, 1) and (1, 1, 2)

$$\psi_{211} = \sqrt{\frac{8}{a^3}} \sin 2\pi \frac{x}{a} \cdot \sin \frac{y}{a} \cdot \sin \frac{z}{a} \qquad \psi_{121} = \sqrt{\frac{8}{a^3}} \sin \pi \frac{x}{a} \cdot \sin 2\frac{y}{a} \cdot \sin \frac{z}{a} \quad \psi_{112} = \sqrt{\frac{8}{a^3}} \sin \pi \frac{x}{a} \cdot \sin \frac{y}{a} \cdot \sin 2\frac{z}{a}$$

Third energy level is E_3=3E_1, the fourth is E_4=(11/3)E_1.

Three states belong to E_3 and E_4 -hez.

The energy level E_5= 4E_1 is not degenerate (2, 2, 2).

To the energy level E_6=(14/3)E_1 belong six stationary eigenstates:

(1, 2, 3), (1, 3, 2), (2, 1, 3), (2, 3, 1),(3, 1, 2), (3, 2, 1)

Quantum numbers: (n_1, n_2, n_3)

There is a fourth quantum number which belongs to spin of the electron: s=$\pm$(1/2) „spin quantum number".

$$\psi_{+1/2} = \psi_{n_1 n_2 n_3}(x, y, z)\,\psi_s\left(+\frac{1}{2}\right) \qquad \psi_{-1/2} = \psi_{n_1 n_2 n_3}(x, y, z)\,\psi_s\left(-\frac{1}{2}\right)$$

There are two ψ states which belong to the null-point energy E_1

To $E_2 = 2E_1$, $E_3 = 3E_1$, $E_4 = (11/3)E_1$ six, and to energy level

$E_6 = (14/3)E_1$ 12 different stationary states

E

$$\psi_{123+1/2} \quad \psi_{123-1/2} \quad \psi_{132+1/2} \quad \psi_{132-1/2} \quad \psi_{213+1/2} \quad \psi_{213-1/2}$$

$$\psi_{231+1/2} \quad \psi_{231-1/2} \quad \psi_{312+1/2} \quad \psi_{3121-1/2} \quad \psi_{321+1/2} \quad \psi_{321-1/2}$$

$$E_6 = \frac{14}{3} E_1$$

$$E_5 = \\ = 4E_1$$

$$\psi_{222+1/2} \quad \psi_{222-1/2}$$

$$E_4 = \frac{11}{3} E_1$$

$$\psi_{133+1/2} \quad \psi_{133-1/2} \quad \psi_{313+1/2} \quad \psi_{313-1/2} \quad \psi_{331+1/2} \quad \psi_{331-1/2}$$

$$E_3 = 3E_1$$

$$\psi_{122+1/2} \quad \psi_{122-1/2} \quad \psi_{212+1/2} \quad \psi_{212-1/2} \quad \psi_{221+1/2} \quad \psi_{221-1/2}$$

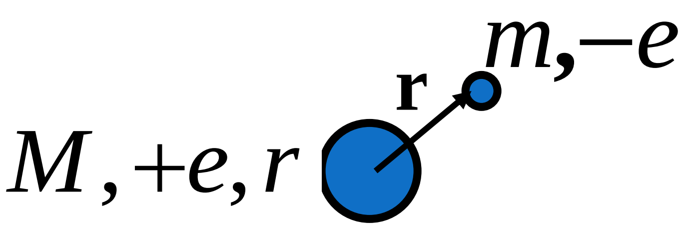
$$E_2 = 2E_1$$

$$\psi_{112+1/2} \quad \psi_{112-1/2} \quad \psi_{121+1/2} \quad \psi_{121-1/2} \quad \psi_{211+1/2} \quad \psi_{211-1/2}$$

$$E_1$$

$$\psi_{111+1/2} \quad \psi_{111-1/2}$$

Hydrogen and hydrogen molecule



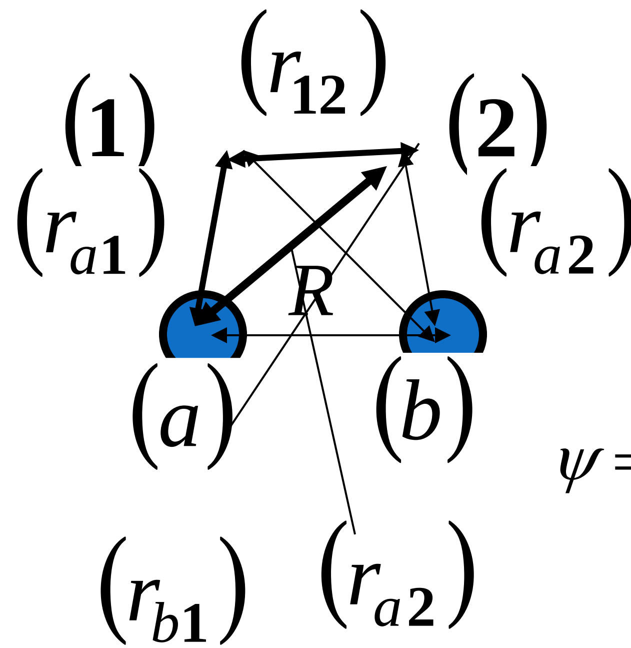
Hydrogen atom

$$E_{pot} = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}|}$$

$$\mathbf{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\mathbf{H} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

The hydrogen molecule



$$\psi = \psi(\mathbf{r}_1; \mathbf{r}_2; R)$$

$$\mathbf{H} = -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{\hbar^2}{2M}\Delta_\mathrm{M} +$$
$$+\frac{1}{4\pi\varepsilon_0}\left(-\frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}} + \frac{e^2}{R} + \frac{e^2}{r_{12}}\right)$$

$$E_n = -\frac{mZ^2e^4}{8\varepsilon_0{}^2h^2n^2}; \quad r_1 = \frac{\varepsilon_0 h^2}{\pi mZe^2}$$

$$n = 1, 2, 3, \ldots; \quad \ell = 0, 1, 2, \ldots, n-1; \quad m = -\ell, \ldots, -1, 0, 1, \ldots, \ell$$

$$\psi_{n\ell m}(r, \vartheta, \phi) = A\mathrm{e}^{-\frac{r}{nr_1}} \cdot \left(\frac{2r}{nr_1}\right)^{\ell} \cdot L_{n+\ell}^{2\ell+1}\left(\frac{2r}{nr_1}\right) \cdot P_\ell^m(\cos\vartheta) \cdot \mathrm{e}^{\mathrm{j}m\phi}$$

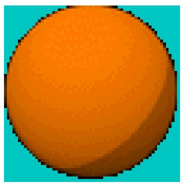
$$P_\ell^m(x) = \left(1-x^2\right)^{\frac{|m|}{2}} \frac{d^{|m|}P_\ell(x)}{dx^{|m|}}; \quad L_\ell^p(x) = \frac{\mathrm{d}^p L_\ell(x)}{\mathrm{d}x^p}; \quad L_\ell(x) = \sum_{k=0}^{\ell} \frac{(-1)^k}{k!}\binom{\ell}{k} x^k$$

$$P_0(x) = 1; \quad P_1(x) = x; \quad P_2(x) = \frac{1}{2}\left(3x^2 - 1\right); \quad P_3(x) = \frac{1}{2}\left(5x^3 - 3x\right), \ldots$$

$$E_1 = -\frac{mZ^2e^4}{8\varepsilon_0{}^2\mathrm{h}^2} = $$

$$= -Z^2 \cdot 13.6\,\mathrm{eV},$$

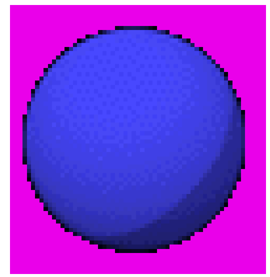
1s



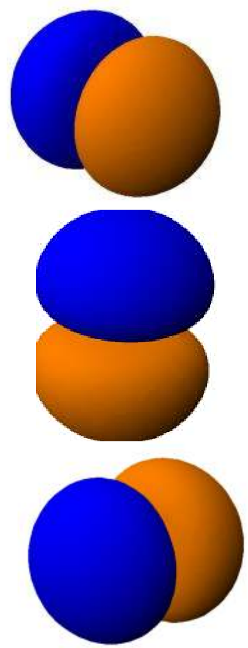
$$E_2 = -\frac{E_1}{4} = $$

$$= -\mathrm{Z}^2\, 3.4\,\mathrm{eV},$$

2s



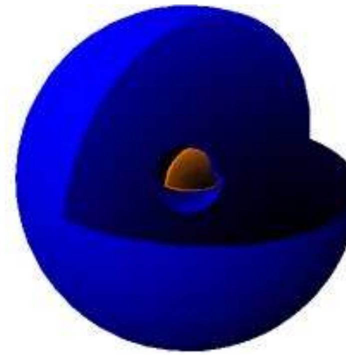
2p



$$E_3 = -\frac{E_1}{9} = $$

$$= -Z^2 1.5\,\mathrm{eV}$$

3s



In case of the Hydrogen Atom (Z = 1)

$$1s \qquad \psi_{1,0,0} = \frac{1}{\sqrt{\pi r_1^3}} e^{-\frac{r}{r_1}} \quad ;$$

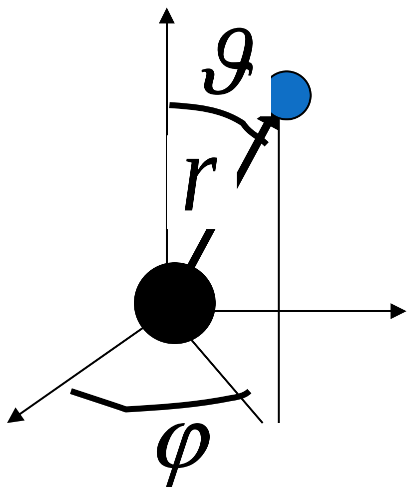
$$2s \qquad \psi_{2,0,0} = -\frac{1}{4\sqrt{2\pi}} \frac{1}{r_1^{3/2}} \left(\frac{r}{r_1} - 2 \right) e^{-\frac{r}{2r_1}}$$

$$2p \qquad \psi_{2,1,-1} = \frac{1}{8\sqrt{\pi}} \frac{1}{r_1^{3/2}} \frac{r}{r_1} e^{-\frac{r}{2r_1}} \sin\vartheta \sin\varphi$$

$$2p \qquad \psi_{2,1,0} = \frac{1}{4\sqrt{2\pi}} \frac{1}{r_1^{3/2}} \frac{r}{r_1} e^{-\frac{r}{2r_1}} \cos\vartheta$$

$$2p \qquad \psi_{2,1,1} = \frac{1}{8\sqrt{\pi}} \frac{1}{r_1^{3/2}} \frac{r}{r_1} e^{-\frac{r}{2r_1}} \sin\vartheta \cos\varphi$$

Up to Z=20 atoms are ‚hydrogen-like'



$$E_{pot} = q_e U = -\frac{Ze^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}$$

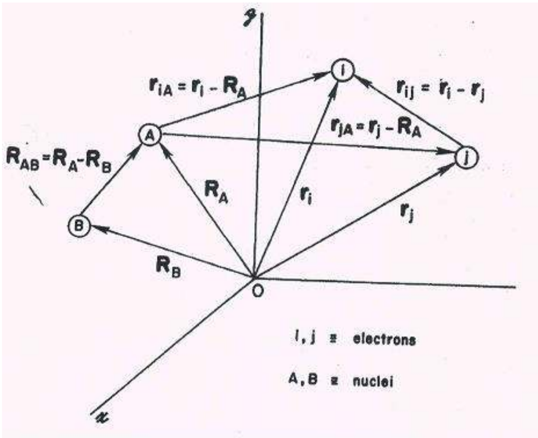
$$E_n = -\frac{mZ^2e^4}{8\varepsilon_0{}^2\mathbf{h}^2n^2}, \qquad r_1 = \frac{\varepsilon_0\mathbf{h}^2}{\pi m Z e^2}$$

$$\psi_{n\ell m}(r,\vartheta,\varphi) = A\mathbf{e}^{-\frac{r}{nr_1}}\cdot\left(\frac{2r}{nr_1}\right)^{\ell}\cdot L_{n+\ell}^{2\ell+1}\left(\frac{2r}{nr_1}\right)\cdot P_{\ell}^{m}(\cos\vartheta)\cdot\mathbf{e}^{\mathbf{j}m\varphi}$$

$n = 1,2,3,\ldots$ $\quad \ell = 0,1,2,\ldots,n-1$ $\quad m = -\ell,\ldots,-1,0,1,\ldots,\ell$

Z			
1	H	21	Sc
2	He	22	Ti
3	Li	23	V
4	Be	24	Cr
5	B	25	Mn
6	C	26	Fe
7	N	27	Co
8	O	28	Ni
9	F	29	Cu
10	Ne	30	Zn
11	Na	31	Ga
12	Mg	32	Ge
13	Al	33	As
14	Si	34	Se
15	P	35	Br
16	S	36	Kr
17	Cl	37	Rb
18	Ar	38	Sr
19	K	39	Y
20	Ca	40	Zr

The Schrödinger equation for molecules



$$\sum_{A=1}^{M} \frac{p_A^2}{2M_A} + \sum_{i=1}^{N} \frac{p_i^2}{2m_i} - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{1}{4\pi\varepsilon_0} \frac{e \cdot Z_A e}{r_{iA}} +$$

$$+ \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{1}{4\pi\varepsilon_0} \frac{Z_A e \cdot Z_B e}{R_{AB}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_{ij}}$$

$$\Downarrow$$

i, j Electrons $-e$

A, B Nuclei $+Z_A e$ e

$$\mathbf{H} = -\hbar^2 \sum_{A=1}^{M} \frac{1}{2M_A} \Delta_A - \hbar^2 \sum_{i=1}^{N} \frac{1}{2m_i} \Delta_i - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{1}{4\pi\varepsilon_0} \frac{e \cdot Z_A e}{r_{iA}} +$$

$$+ \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{1}{4\pi\varepsilon_0} \frac{Z_A e \cdot Z_B e}{R_{AB}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_{ij}}$$