Theoretical Chemistry

Marek Kręglewski
Wydział Chemii UAM

Course content

I. **Experimental background of quantum mechanics**

II. **Observables and operators**

III. **Models in quantum chemistry**

IV. **Hydrogen atom and orbitals**

V. **Multi-electron atom, spin and Pauli Exclusion Principle**

VI. **Molecule H_2^+**

VII. **Two-atomic molecules**

VIII. **Ab initio calculation**

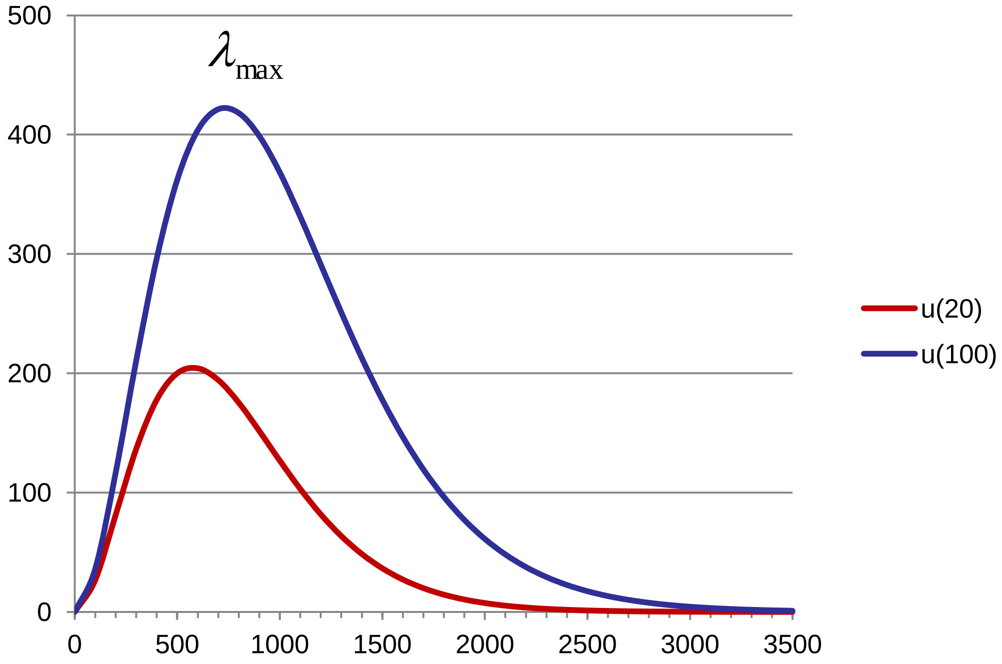
IX. **Vibrations of molecules**

X. **Rotations of molecules**

Literature

1) Peter Atkins & Julio de Paula, Atkin’s Physical Chemistry (Part2), Oxford University Press 2014
2) Andrew R.Leach, Molecular Modelling – Principles and Applications, Pearson Education Limited 2001
3) Lucjan Piela, Idee chemii kwantowej, PWN, Warszawa 2001
4) Włodzimierz Kołos, Chemia kwantowa, PWN, Warszawa 1991.

Black body emission spectrum



Spectral density:

$$u(\nu,T)=\frac{8\pi\nu^2}{c^3}*\frac{h\nu}{e^{\frac{h\nu}{kT}}-1}$$

$$\lambda_{\max}=\frac{b}{T}$$

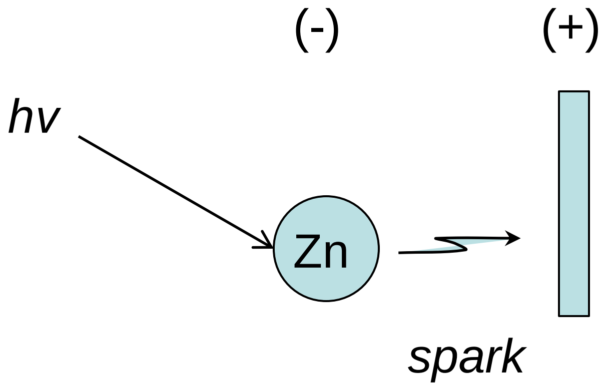
Planck hypothesis (1900): $\Delta E=h\nu$ (quantum of energy)

$h = 6{,}62\cdot10^{-34}$ J s

$c = 2{,}99792458\cdot10^{8}$ m s^{-1}

$k = 1{,}380662\cdot10^{-23}$ J K^{-1}

Photoelectric effect



The Lenard laws (1899)

1) The number of emitted electrons is proportional to the intensity of light
2) The maximum velocity of electrons depends on wavelength not on intensity of light

Einstein formula (1905, Nobel prize in 1921):

$$h\nu = \frac{1}{2} m_e v^2 + W$$

„In fact, it seems to me that the observations on "black-body radiation", photoluminescence, the production of cathode rays by ultraviolet light and other phenomena involving the emission or conversion of light can be better understood on the assumption that the energy of light is distributed discontinuously in space. According to the assumption considered here, when a light ray starting from a point is propagated, the energy is not continuously distributed over an ever increasing volume, but it consists of a finite number of energy quanta, localised in space, which move without being divided and which can be absorbed or emitted only as a whole.”

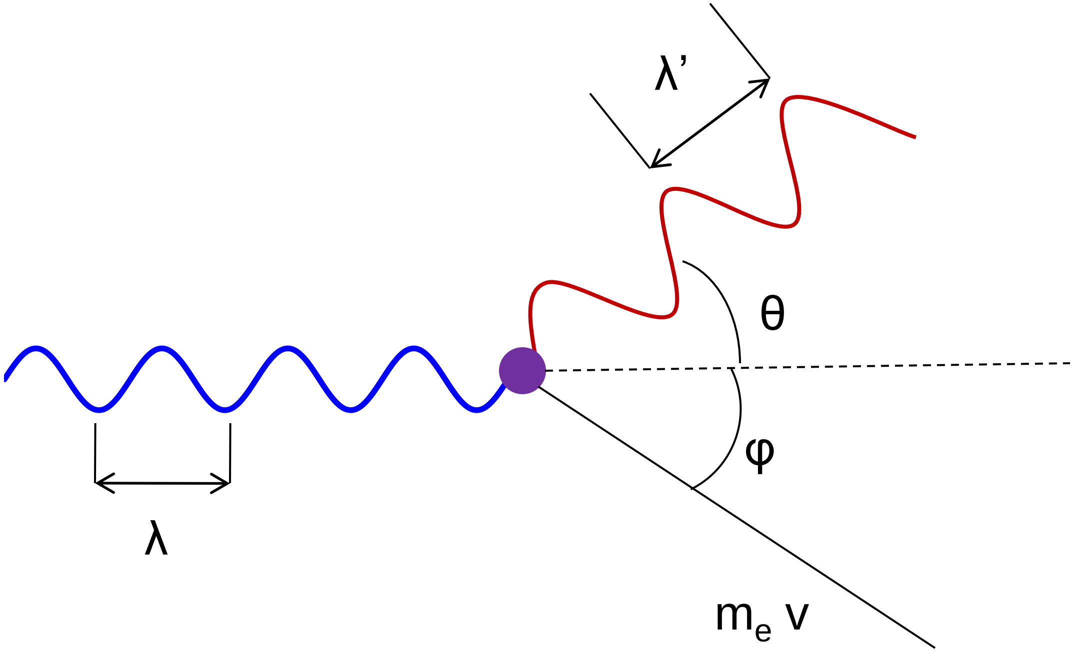
Albert Einstein, 1905

Photoelectric effect

Es scheint mir nun in der Tat, daß die Beobachtungen über die „schwarze Strahlung‟, Photolumineszenz, die Erzeugung von Kathodenstrahlen durch ultraviolettes Licht und andere die Erzeugung bez. Verwandlung des Lichtes betreffende Erscheinungsgruppen besser verständlich erscheinen unter der Annahme, daß die Energie des Lichtes diskontinuierlich im Raume verteilt sei. Nach der hier ins Auge zu fassenden Annahme ist bei Ausbreitung eines von einem Punkte ausgehenden Lichtstrahles die Energie nicht kontinuierlich auf größer und größer werden der Räume verteilt, sondern es besteht dieselbe aus einer endlichen Zahl von in Raumpunkten lokalisierten Energiequanten, welche sich bewegen, ohne sich zu teilen und nur als Ganze absorbiert und erzeugt werden können.

"Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt”. Albert Einstein, Annalen der Physik. Vol. 322 No. 6 (1905): 132–148.

Compton effect / scattering (1923)



$\lambda' > \lambda$

$p_e = m_e v$

$p_f = h/\lambda$

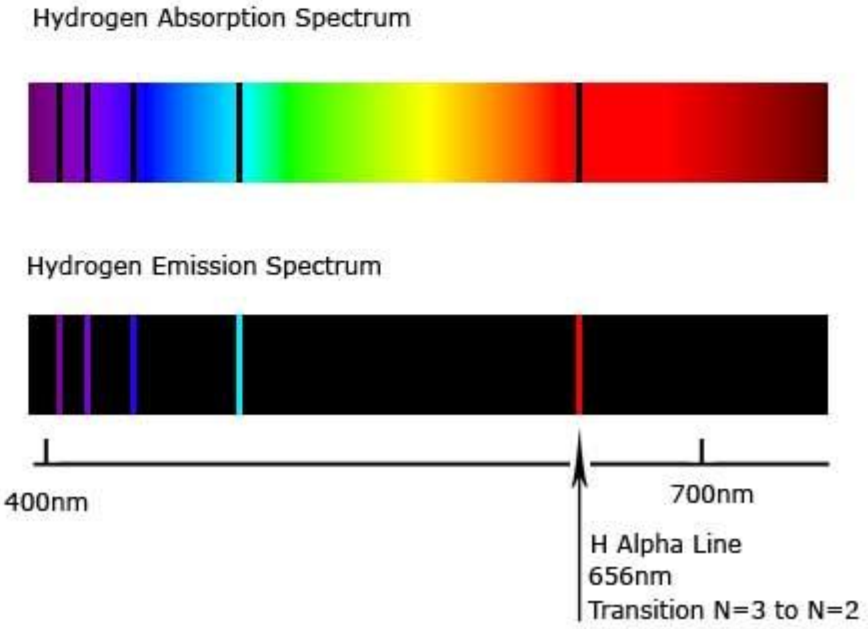
$p_e = p_f$

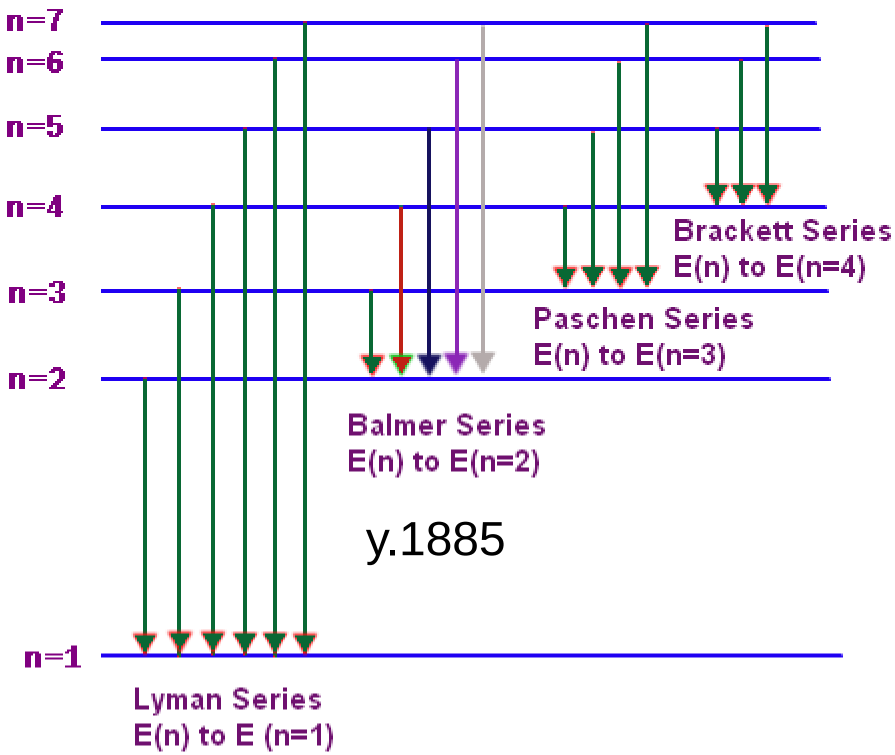
$m_e v = h/\lambda$

$$\Delta\lambda = \lambda' - \lambda = 2\Lambda \sin^2\frac{\theta}{2}$$

$$\Lambda = \frac{h}{m_e c} = 2{,}426 \bullet 10^{-12} m = 0{,}02426\,\overset{\circ}{A}$$

Spectrum of the hydrogen atom





y.1885

$$\Delta E(i \leftarrow j) = T_i - T_j$$

$$\lambda = hc / \Delta E$$

de Broglie hypothesis (1923)

$$p = \frac{h}{\lambda} \qquad \lambda = \frac{h}{p}$$

Why is the duality not observed in classical mechanics?

m = 2g v = 1000 m/s p = 2 kg m /s

h = $6{,}62 \cdot 10^{-34}$ J s c = $2{,}99792458 \cdot 10^{8}$ m /s

$\lambda = (6{,}62 \cdot 10^{-34} / 2)$ m = $3{,}31 \cdot 10^{-25}$ nm

Wave-particle duality: a key concept of quantum mechanics

Uncertainty principle

$$\Delta p_x \bullet \Delta x \geq \frac{\hbar}{2}$$

$$\Delta E \bullet \Delta t \geq \hbar$$

1923 - Werner Heisenberg

Exact formula:

$$\left\langle \Delta p_x^2 \right\rangle \bullet \left\langle \Delta x^2 \right\rangle \geq \frac{\hbar^2}{4}$$

Wavefunction
Postulate I

All information about a system are included in its wavefunction.

The square of the wavefunction $|\Psi|^2$ describes the probability density

$$\int_{-\infty}^{+\infty} \left|\Psi(x,y,z)\right|^2 dx\,dy\,dz = 1$$

The wavefunction must be square-integrable.

Operators in Quantum Mechanics
Postulate II

Operators of position $\hat{x} = x \bullet$

and momentum $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

The operator is defined through its action on a function.

In order to build an operator of a complex physical quantity the positions and momenta in classical Newtonian expression are replaced by corresponding operators.

Hamiltonian – the operator of total mechanical energy

$$E_{total} = E_{kin} + E_{pot} = \frac{m\vec{v}^{\,2}}{2} + V(x,y,z) = \frac{\vec{p}^{\,2}}{2m} + V(x,y,z) = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V(x,y,z)$$

$$\hat{H} = \hat{T} + \hat{V} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) + \hat{V}(x,y,z)$$

Time evolution of a wavefunction Postulate III

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Time evolution

If potential energy does not change with time the Schrödinger equation converts to:

$$\hat{H}\Psi = E\Psi$$

Values of observables
Postulate IV

If a wavefunction Ψ is the eigenfunction of the operator Â

$$\hat{A}\psi = a\psi$$

The experimental measurement can give the value a, only.

Expectation (mean) value of the operator

$$\left\langle \hat{A} \right\rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{A} \psi dV}{\int_{-\infty}^{\infty} \psi^* \psi dV}$$

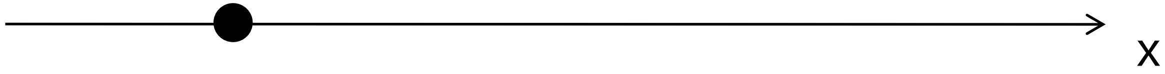
$$\left\langle \hat{A} \right\rangle = a$$

when Ψ is an eigenfunction of the operator Â

$$\left\langle \hat{A} \right\rangle \neq a$$

when Ψ is not an eigenfunction of the operator Â

Model 1: Free particle in space



$$E_{total} = E_{kin} + E_{pot} = \frac{mv_x^2}{2} + 0 = \frac{p_x^2}{2m} + 0$$

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}_x^2}{2m} + 0 = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\hat{H}\psi(x) = E\psi(x)$$

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

$$\psi_1(x) = Ne^{iax}$$

$$\psi_2(x) = Ne^{-iax}$$

Test of solutions:

$$\psi_1(x) = Ne^{iax}$$

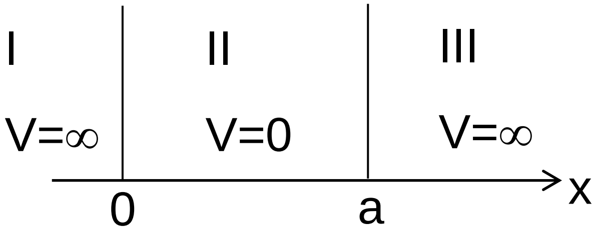
$$\frac{d}{dx}\psi_1(x) = Niae^{iax}$$

$$\frac{d^2}{dx^2}\psi_1(x) = N(ia)^2 e^{iax} = -Na^2e^{i\hbar x}$$

$$-\frac{\hbar^2}{2m}\left(-Na^2\right)e^{iax} = ENe^{iax}$$

$$E = \frac{\hbar^2 a^2}{2m}$$

Model 2: Particle in a box



The motion of a particle limited to the well <0,a>.

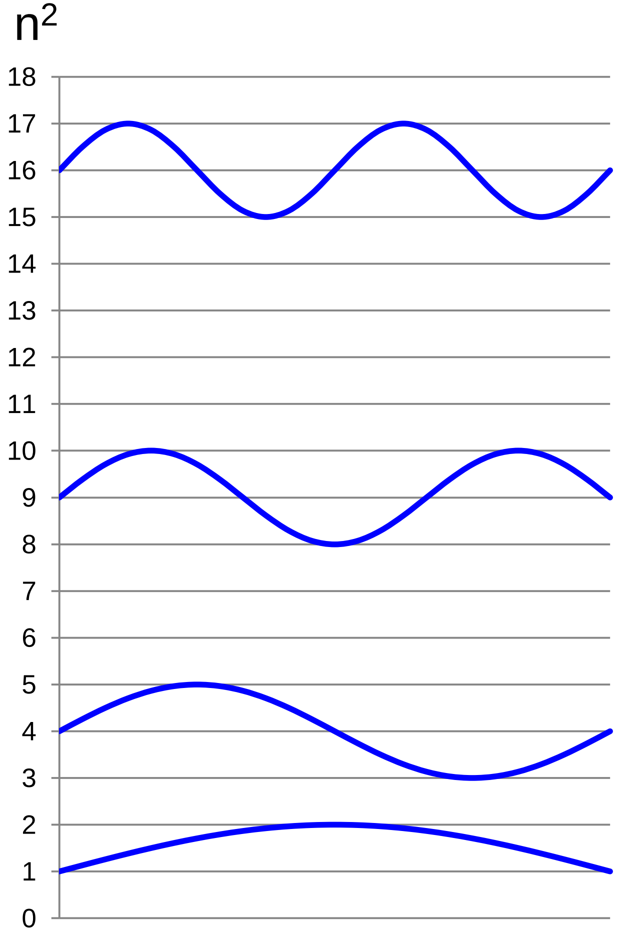
$$\hat{H}\psi = E\psi$$

$$\psi_I(x) = 0$$

$$\psi_{II}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

$$\psi_{III}(x) = 0$$

$$E = \frac{\hbar^2\pi^2}{2ma^2}n^2$$



Particle in a box

Expectation values of energy, momentum, momentum squared and position

$$\left\langle E\right\rangle = \frac{\int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)dx}{\int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)dx} = \frac{\frac{2}{a}\left(-\frac{\hbar^2}{2m}\right)\int_0^a \sin\left(\frac{n\pi}{a}x\right)\left(\frac{d^2}{dx^2}\right)\sin\left(\frac{n\pi}{a}x\right)dx}{\frac{2}{a}\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx} = \frac{-\frac{2}{a}\left(-\frac{\hbar^2}{2m}\right)\left(\frac{n\pi}{a}\right)^2\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx}{\frac{2}{a}\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx} = \frac{\hbar^2\pi^2}{2ma^2}n^2$$

$$\left\langle p_x\right\rangle = \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\left(-i\hbar\frac{d}{dx}\right)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)dx = \frac{2}{a}(-i\hbar)\frac{n\pi}{a}\int_0^a \sin\left(\frac{n\pi}{a}x\right)\cos\left(\frac{n\pi}{a}x\right)dx = \frac{1}{a}(-i\hbar)\frac{n\pi}{a}\int_0^a \sin\left(\frac{2n\pi}{a}x\right)dx = 0$$

$$\left\langle p_x^2\right\rangle = \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\left(-\hbar^2\frac{d^2}{dx^2}\right)\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)dx = \frac{2}{a}\left(\hbar^2\right)\left(\frac{n\pi}{a}\right)^2\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)dx = \frac{2}{a}\left(\hbar^2\right)\left(\frac{n\pi}{a}\right)^2\frac{1}{2}\int_0^a \left[1-\cos\left(\frac{2n\pi}{a}x\right)\right]dx = \frac{\hbar^2\pi^2}{a^2}n^2$$

$$\left\langle x\right\rangle = \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)x\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)dx = \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi}{a}x\right)dx = \frac{2}{a}x\frac{1}{2}\left[x-\frac{a}{2n\pi}\sin\left(\frac{2n\pi}{a}x\right)\right]\Bigg|_0^a - \frac{2}{a}\frac{1}{2}\int_0^a \left[x-\frac{a}{2n\pi}\sin\left(\frac{2n\pi}{a}x\right)\right]dx =$$

$$= a-\frac{1}{a}\left[\frac{x^2}{2}+\left(\frac{a}{2n\pi}\right)^2\cos\left(\frac{2n\pi}{a}x\right)\right]\Bigg|_0^a = a-\frac{a}{2}=\frac{a}{2}$$

Particle in a box

Expectation values of position squared

$$\langle x^2\rangle = \int_0^a \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)x^2\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)dx = \frac{2}{a}\int_0^a x^2\sin^2\left(\frac{n\pi}{a}x\right)dx = \frac{2}{a}\frac{1}{2}\int_0^a x^2dx - \frac{2}{a}\frac{1}{2}\int_0^a x^2\cos\left(\frac{2n\pi}{a}x\right)dx =$$

$$= \frac{1}{a}\frac{x^3}{3}\Bigg|_0^a - \frac{1}{a}x^2\frac{a}{2n\pi}\sin\left(\frac{2n\pi}{a}x\right)\Bigg|_0^a + \frac{1}{a}2\frac{a}{2n\pi}\int_0^a x\sin\left(\frac{2n\pi}{a}x\right)dx = \frac{a^3}{3} - \frac{1}{n\pi}x\frac{a}{2n\pi}\cos\left(\frac{2n\pi}{a}x\right)\Bigg|_0^a + \frac{1}{n\pi}\frac{a}{2n\pi}\int_0^a\cos\left(\frac{2n\pi}{a}x\right)dx =$$

$$= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} + \frac{a}{2n^2\pi^2}\frac{a}{2n\pi}\sin\left(\frac{2n\pi}{a}x\right)\Bigg|_0^a = a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right)$$

Test of the uncertainty principle for the particle in a box:

$$\Delta x = x - \langle x\rangle \qquad\qquad \Delta p_x = p_x - \langle p_x\rangle$$

$$\langle\Delta x^2\rangle\langle\Delta p_x^2\rangle = \left\langle(x-\langle x\rangle)^2\right\rangle\left\langle(p_x-\langle p_x\rangle)^2\right\rangle = \left\langle\left(x^2 - 2x\langle x\rangle + \langle x\rangle^2\right)\right\rangle\left\langle\left(p_x^2 - 2p_x\langle p_x\rangle + \langle p_x\rangle^2\right)\right\rangle = \left\langle\left(x^2 - \langle x\rangle^2\right)\right\rangle\left\langle\left(p_x^2 - \langle p_x\rangle^2\right)\right\rangle =$$

$$= \left(\langle x^2\rangle - \langle x\rangle^2\right)\left(\langle p_x^2\rangle - \langle p_x\rangle^2\right) = \left[a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \left(\frac{a}{2}\right)^2\right]\left[\frac{\hbar^2\pi^2n^2}{a^2} - 0\right] = \left(\frac{1}{3} - \frac{1}{4} - \frac{1}{2n^2\pi^2}\right)\hbar^2\pi^2n^2 = \left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)\hbar^2\pi^2n^2 =$$

$$= \frac{\hbar^2}{4}\left(\frac{1}{3}\pi^2n^2 - 2\right) > \frac{\hbar^2}{4}$$

Particle in a box

Eigenfunction (exact) $\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$

Trial functions (approximate): $\phi_1(x) = Nx(a-x)$

$\phi_2(x) = Nx^2(a-x)$ $\phi_3(x) = Nx(a-x)^2$

$\phi_4(x) = Nx^2(a-x)^2$

$$N^2 \int_0^a [x(a-x)]^2 dx = N^2 \int_0^a \left(a^2x^2 - 2ax^3 + x^4\right) dx = N^2 \left(a^2 \frac{x^3}{3} - 2a\frac{x^4}{4} + \frac{x^5}{5} \right)\Bigg|_0^a = N^2 \left(\frac{a^5}{3} - 2\frac{a^5}{4} + \frac{a^5}{5} \right) = N^2 \frac{a^5}{30} = 1$$

$N^2 = \frac{30}{a^5}$ $N = \sqrt{\frac{30}{a^5}}$ $\phi_1(x) = \sqrt{\frac{30}{a^5}} x(a-x)$

$$N^2 \int_0^a \left[x^2(a-x)\right]^2 dx = N^2 \int_0^a \left(a^2x^4 - 2ax^5 + x^6\right) dx = N^2 \left(a^2 \frac{x^5}{5} - 2a\frac{x^6}{6} + \frac{x^7}{7} \right)\Bigg|_0^a = N^2 \left(\frac{a^7}{5} - \frac{a^7}{3} + \frac{a^7}{7} \right) = N^2 \frac{a^7}{105} = 1$$

$N^2 = \frac{105}{a^7}$ $N = \sqrt{\frac{105}{a^7}}$ $\phi_2(x) = \sqrt{\frac{105}{a^7}} x^2(a-x)$

$$N^2 \int_0^a \left[x(a-x)^2\right]^2 dx = N^2 \int_0^a \left(a^4x^2 - 4a^3x^3 + 6a^2x^4 - 4ax^5 + x^6\right) dx = N^2 \left(a^4 \frac{x^3}{3} - 4a^3\frac{x^4}{4} + 6a^2\frac{x^5}{5} - 4a\frac{x^6}{6} + \frac{x^7}{7} \right)\Bigg|_0^a = N^2 \left(\frac{a^7}{3} - a^7 + \frac{6a^7}{5} - 2\frac{a^7}{3} + \frac{a^7}{7} \right) = N^2 \frac{a^7}{105} = 1$$

$N^2 = \frac{105}{a^7}$ $N = \sqrt{\frac{105}{a^7}}$ $\phi_3(x) = \sqrt{\frac{105}{a^7}} x(a-x)^2$

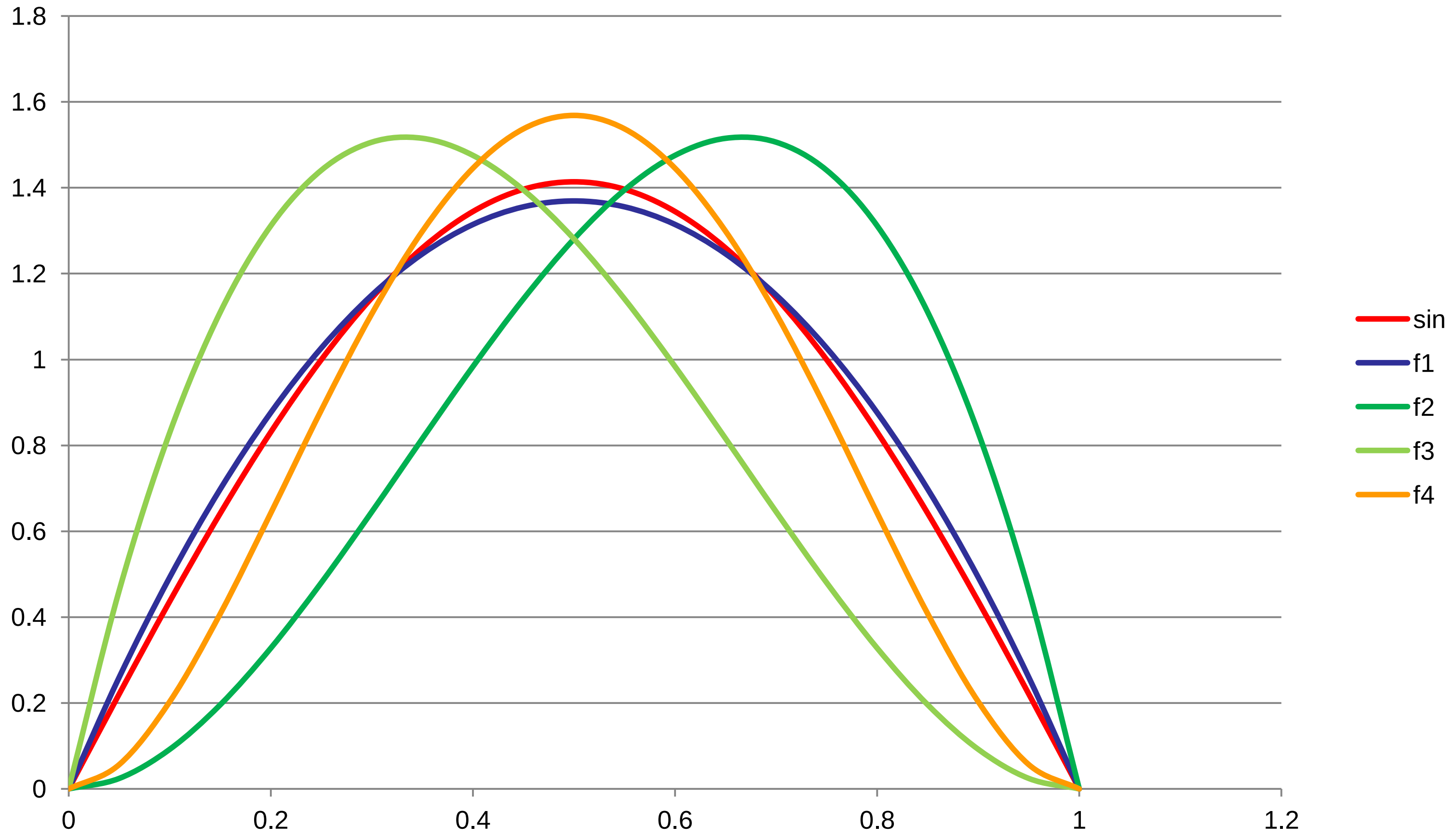
$$N^2 \int_0^a \left[x^2(a-x)^2\right]^2 dx = N^2 \int_0^a \left(a^4x^4 + 4a^2x^6 + x^8 - 4a^3x^5 + 2a^2x^6 - 4ax^7\right) dx = N^2 \int_0^a \left(x^8 - 4ax^7 + 6a^2x^6 - 4a^3x^5 + a^4x^4\right) dx =$$

$$= N^2 \left(\frac{x^9}{9} - 4a\frac{x^8}{8} + 6a^2\frac{x^7}{7} - 4a^3\frac{x^6}{6} + a^4\frac{x^5}{5} \right)\Bigg|_0^a = N^2 a^9 \left(\frac{1}{9} - \frac{1}{2} + \frac{6}{7} - \frac{2}{3} + \frac{1}{5} \right) = N^2 \frac{a^9}{630} = 1$$

$N^2 = \frac{630}{a^9}$ $N = \sqrt{\frac{630}{a^9}}$ $\phi_4(x) = \sqrt{\frac{630}{a^9}} x^2(a-x)^2$

Particle in a box

The graph of the eigenfunction and trial functions



Particle in a box

$$\psi(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right) \qquad E_1=\frac{\hbar^2\pi^2}{2ma^2}$$

$$\phi_1(x)=\sqrt{\frac{30}{a^5}}x(a-x) \qquad \phi_2(x)=\sqrt{\frac{105}{a^7}}x^2(a-x) \qquad \phi_3(x)=\sqrt{\frac{105}{a^7}}x(a-x)^2 \qquad \phi_4(x)=\sqrt{\frac{630}{a^9}}x^2(a-x)^2$$

$$\varepsilon=\int_0^a\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right)dx=\frac{2}{a}\left(\frac{\hbar^2}{2m}\right)\left(\frac{\pi}{a}\right)^2\int_0^a\sin^2\left(\frac{\pi}{a}x\right)dx=\frac{2}{a}\left(\frac{\hbar^2}{2m}\right)\left(\frac{\pi}{a}\right)^2\frac{1}{2}\int_0^a\left[1-\cos\left(\frac{2\pi}{a}x\right)\right]dx=\frac{\hbar^2\pi^2}{2ma^2}=\frac{\hbar^2 9{,}87}{2ma^2}$$

$$\varepsilon=\int_0^a\sqrt{\frac{30}{a^5}}x(a-x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{30}{a^5}}x(a-x)dx=\frac{30}{a^5}\left(\frac{\hbar^2}{2m}\right)\int_0^a x(a-x)dx=\frac{30}{a^5}\left(\frac{\hbar^2}{2m}\right)\left(a\frac{x^2}{2}-\frac{x^3}{3}\right)\Bigg|_0^a=\frac{\hbar^2 10}{2ma^2}$$

$$\varepsilon=\int_0^a\sqrt{\frac{105}{a^7}}x^2(a-x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{105}{a^7}}x^2(a-x)dx=\frac{105}{a^7}\left(-\frac{\hbar^2}{2m}\right)\int_0^a x^2(a-x)(2a-6x)dx=$$

$$=\frac{105}{a^7}\left(-\frac{\hbar^2}{2m}\right)\int_0^a\left(2a^2x^2-8ax^3+6x^4\right)dx=\frac{105}{a^7}\left(-\frac{\hbar^2}{2m}\right)\left(2a^2\frac{x^3}{3}-8a\frac{x^4}{4}+6\frac{x^5}{5}\right)\Bigg|_0^a=\frac{\hbar^2 14}{2ma^2}$$

$$\varepsilon=\int_0^a\sqrt{\frac{105}{a^7}}x(a-x)^2\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{105}{a^7}}x(a-x)^2dx=\frac{105}{a^7}\left(-\frac{\hbar^2}{2m}\right)\int_0^a x(a-x)^2(-4a+6x)dx=$$

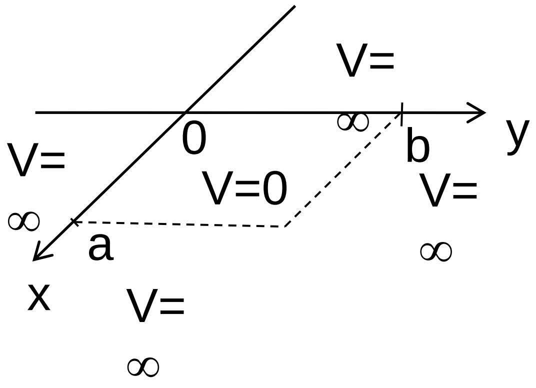
$$=\frac{105}{a^7}\left(-\frac{\hbar^2}{2m}\right)\int_0^a\left(-4a^3x+14a^2x^2-16ax^3+6x^4\right)dx=\frac{105}{a^7}\left(-\frac{\hbar^2}{2m}\right)\left(-4a^3\frac{x^2}{2}+14a^2\frac{x^3}{3}-16a\frac{x^4}{4}+6\frac{x^5}{5}\right)\Bigg|_0^a=\frac{\hbar^2 14}{2ma^2}$$

$$\varepsilon=\int_0^a\sqrt{\frac{630}{a^9}}x^2(a-x)^2\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{630}{a^9}}x^2(a-x)^2dx=\frac{630}{a^9}\left(-\frac{\hbar^2}{2m}\right)\int_0^a x^2(a-x)^2\left(2a^2-12ax+12x^2\right)dx=$$

$$=\frac{630}{a^9}\left(\frac{\hbar^2}{2m}\right)\int_0^a\left(-2a^4x^2+16a^3x^3-38a^2x^4+36ax^5-12x^6\right)dx=$$

$$=\frac{630}{a^9}\left(\frac{\hbar^2}{2m}\right)\left(-2a^4\frac{x^3}{3}+16a^3\frac{x^4}{4}-38a^2\frac{x^5}{5}+36a\frac{x^6}{6}-12\frac{x^7}{7}\right)\Bigg|_0^a=\frac{630}{a^2}\left(\frac{\hbar^2}{2m}\right)\left(-\frac{2}{3}+\frac{16}{4}-\frac{38}{5}+\frac{36}{6}-\frac{12}{7}\right)=\frac{\hbar^2 12}{2ma^2}$$

Two-dimensional box



$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\right]\Psi(x,y)=E\Psi(x,y)$$

$$\Psi(x,y)=\psi_x(x)\psi_y(y)$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\right]\psi_x(x)\psi_y(y)=E\psi_x(x)\psi_y(y)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_x(x)\psi_y(y)-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi_x(x)\psi_y(y)=E\psi_x(x)\psi_y(y)$$

$$-\frac{\hbar^2}{2m}\psi_y(y)\frac{\partial^2}{\partial x^2}\psi_x(x)-\frac{\hbar^2}{2m}\psi_x(x)\frac{\partial^2}{\partial y^2}\psi_y(y)=E\psi_x(x)\psi_y(y) \qquad /\psi_x(x)\psi_y(y)$$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi_x(x)}\frac{\partial^2}{\partial x^2}\psi_x(x)-\frac{\hbar^2}{2m}\frac{1}{\psi_y(y)}\frac{\partial^2}{\partial y^2}\psi_y(y)=E$$

$$-\frac{\hbar^2}{2m}\frac{1}{\psi_x(x)}\frac{\partial^2}{\partial x^2}\psi_x(x)=E_x \qquad -\frac{\hbar^2}{2m}\frac{1}{\psi_y(y)}\frac{\partial^2}{\partial y^2}\psi_y(y)=E_y \qquad E_x+E_y=E$$

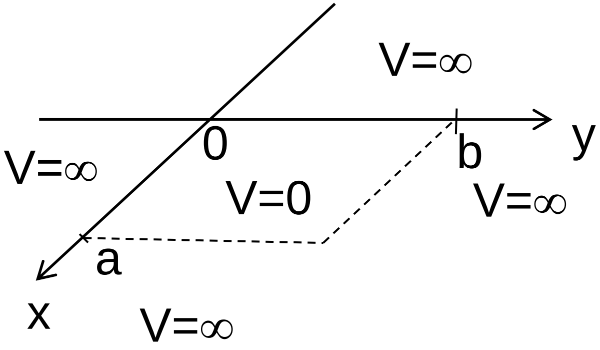
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_x(x)=E_x\psi_x(x) \qquad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi_y(y)=E_y\psi_y(y)$$

$$E_x(n)=\frac{\hbar^2\pi^2}{2m}\frac{n^2}{a^2} \qquad \Psi_n(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

Two-dimensional box

$$E_{n,k}=\frac{\hbar^2\pi^2}{2m}\left(\frac{n^2}{a^2}+\frac{k^2}{b^2}\right)$$

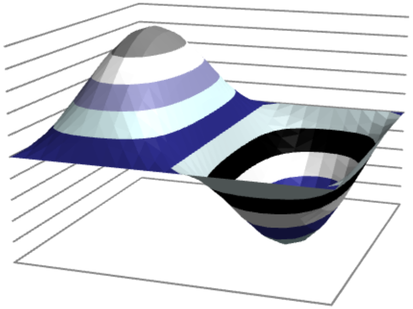
$$\Psi_{n,k}(x,y)=\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)\sqrt{\frac{2}{b}}\sin\left(\frac{k\pi}{b}y\right)$$



Degenarate states:

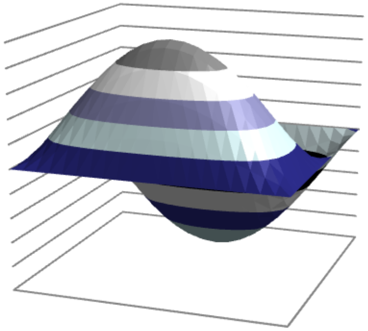
If a=b

then $E_{1,2=}E_{2,1}$



$$E_{1,2}=\frac{\hbar^2\pi^2}{2m}\left(\frac{1^2}{a^2}+\frac{2^2}{a^2}\right)$$

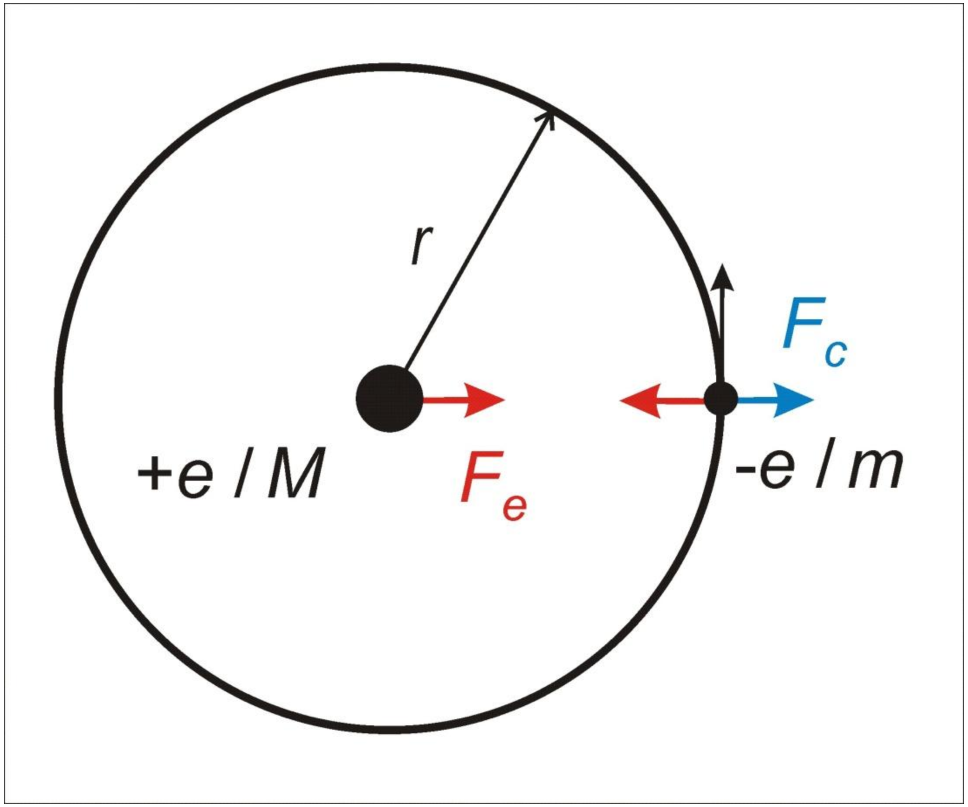
$$\Psi_{1,2}(x,y)=\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right)\sqrt{\frac{2}{a}}\sin\left(\frac{2\pi}{a}y\right)$$



$$E_{2,1}=\frac{\hbar^2\pi^2}{2m}\left(\frac{2^2}{a^2}+\frac{1^2}{a^2}\right)$$

$$\Psi_{2,1}(x,y)=\sqrt{\frac{2}{a}}\sin\left(\frac{2\pi}{a}x\right)\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}y\right)$$

Hydrogen atom – classical picture



$$F_c = \frac{m\mathrm{v}^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = F_e$$

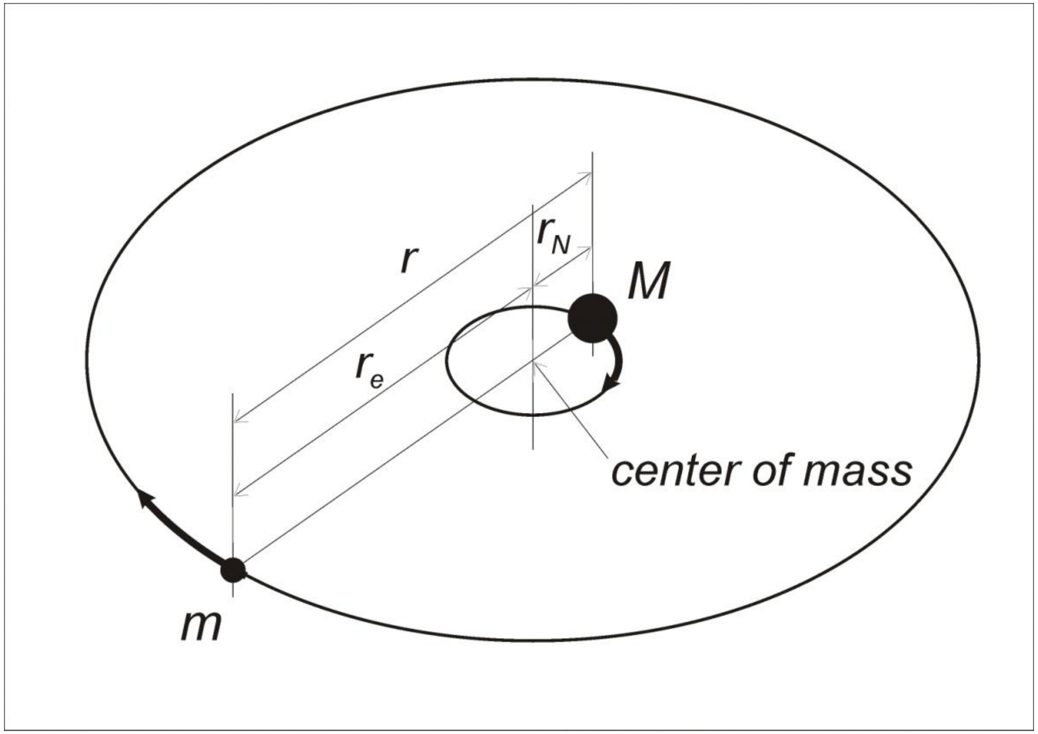
$$\mathrm{v} = \frac{e}{(4\pi\varepsilon_0\, mr)^{1/2}} \approx 2.10^6\ ms^{-1}$$

$$E = T + V \approx 13.6\, eV$$

$$\nu = \frac{1}{T} \approx 6.10^{15}\ s^{-1}$$

Reduced mass

⇒ motion of the reduced mass around a center of mass



$$mr_e = Mr_N \qquad r = r_e + r_N$$

$$m\omega r_e^2 + M\omega r_N^2 = n\hbar$$

$$\frac{mM}{m+M}\omega r^2 = n\hbar$$

$$\boxed{\frac{mM}{m+M} = \mu}$$

$$\mu / m_e = \begin{matrix} 0.99945\ \text{(H)} \\ 0.99972\ \text{(D)} \end{matrix}$$

Hydrogen atom

$$\hat{H}_e = \frac{\hbar^2}{2\mu}\left[-\frac{\partial^2}{\partial x^2}-\frac{\partial^2}{\partial y^2}-\frac{\partial^2}{\partial z^2}\right]-\frac{e^2}{r}$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

Schrödinger equation:

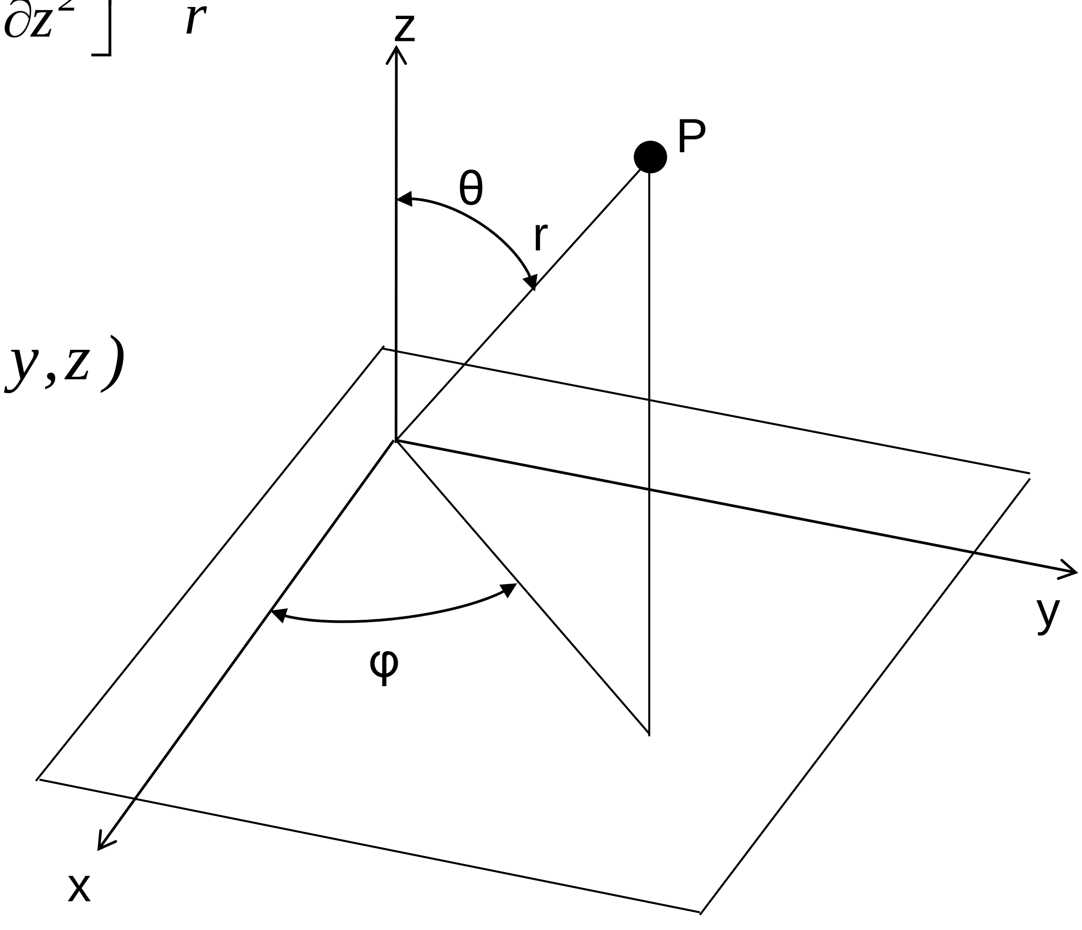
$$\hat{H}_e\psi(x,y,z) = E\psi(x,y,z)$$

Spherical coordinates:

x = r sinθ cosφ

y = r sinθ sinφ

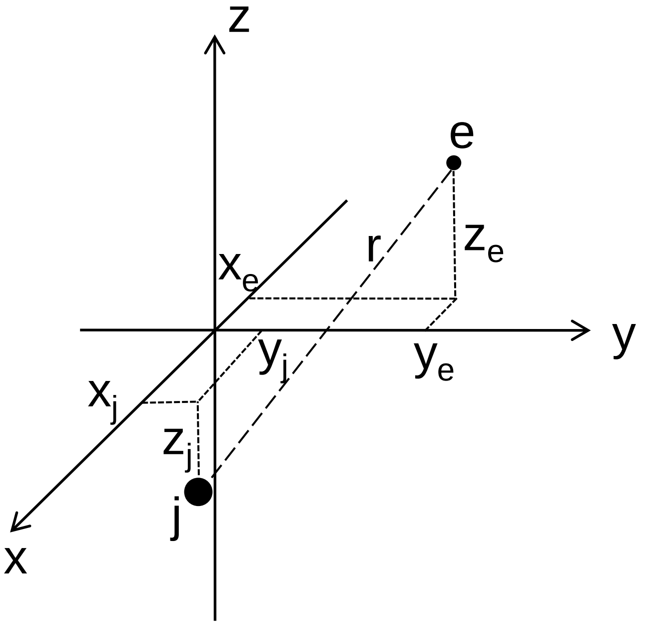
z = r cosθ



Hydrogen atom 1

$$\hat{H} = -\frac{\hbar^2}{2M_j}\left[\frac{\partial^2}{\partial x_j^2}+\frac{\partial^2}{\partial y_j^2}+\frac{\partial^2}{\partial z_j^2}\right]-\frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right]-\frac{e^2}{r}$$

$$r = \sqrt{\left(x_j - x_e\right)^2 + \left(y_j - y_e\right)^2 + \left(z_j - z_e\right)^2}$$



Center of mass coordinates:

$$X = \frac{M_j x_j + m_e x_e}{M_j + m_e}$$

$$Y = \frac{M_j y_j + m_e y_e}{M_j + m_e}$$

$$Z = \frac{M_j z_j + m_e z_e}{M_j + m_e}$$

Relative coordinates:

$$x = x_e - x_j$$

$$y = y_e - y_j$$

$$z = z_e - z_j$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\hat{H}\Psi\left(x_j, y_j, z_j, x_e, y_e, z_e\right) = E_c \Psi\left(x_j, y_j, z_j, x_e, y_e, z_e\right)$$

Hydrogen atom 2

Transformation of the Hamiltonian to the center of mass and relative coordinates

$$\frac{\partial}{\partial x_e}=\frac{\partial X}{\partial x_e}\frac{\partial}{\partial X}+\frac{\partial x}{\partial x_e}\frac{\partial}{\partial x}=\frac{m}{m+M}\frac{\partial}{\partial X}+\frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial x_j}=\frac{\partial X}{\partial x_j}\frac{\partial}{\partial X}+\frac{\partial x}{\partial x_j}\frac{\partial}{\partial x}=\frac{M}{m+M}\frac{\partial}{\partial X}-\frac{\partial}{\partial x}$$

$$\frac{\partial^2}{\partial x_e^2}=\left(\frac{m}{m+M}\frac{\partial}{\partial X}+\frac{\partial}{\partial x}\right)^2=\frac{m^2}{(m+M)^2}\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial x^2}+\frac{2m}{m+M}\frac{\partial^2}{\partial X\partial x}$$

$$\frac{\partial^2}{\partial x_j^2}=\left(\frac{M}{m+M}\frac{\partial}{\partial X}-\frac{\partial}{\partial x}\right)^2=\frac{M^2}{(m+M)^2}\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial x^2}-\frac{2M}{m+M}\frac{\partial^2}{\partial X\partial x}$$

$$-\frac{\hbar^2}{2}\left[\frac{1}{m}\frac{\partial^2}{\partial x_e^2}+\frac{1}{M}\frac{\partial^2}{\partial x_j^2}\right]=-\frac{\hbar^2}{2}\left[\frac{m}{(m+M)^2}\frac{\partial^2}{\partial X^2}+\frac{1}{m}\frac{\partial^2}{\partial x^2}+\cancel{\frac{2}{m+M}\frac{\partial^2}{\partial X\partial x}}+\frac{M}{(m+M)^2}\frac{\partial^2}{\partial X^2}+\frac{1}{M}\frac{\partial^2}{\partial x^2}-\cancel{\frac{2}{m+M}\frac{\partial^2}{\partial X\partial x}}\right]=$$

$$=-\frac{\hbar^2}{2(m+M)}\frac{\partial^2}{\partial X^2}-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}$$

$$\frac{1}{\mu}=\frac{1}{m}+\frac{1}{M}$$

Similarly for Y, Z, y, z:

$$\hat{H}=-\frac{\hbar^2}{2(M_j+m_e)}\left[\frac{\partial^2}{\partial X^2}+\frac{\partial^2}{\partial Y^2}+\frac{\partial^2}{\partial Z^2}\right]-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]-\frac{e^2}{r}$$

Hydrogen atom 3

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\left(M_j + m_e\right)}\left[\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right]}_{H_{trans}} \underbrace{-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] - \frac{e^2}{r}}_{H_e}$$

Translation of atom

relative motion of nucleus and electron

$$\Psi\left(x_j, y_j, z_j, x_e, y_e, z_e\right) = \Psi\left(X, Y, Z, x, y, z\right) = \Phi\left(X, Y, Z\right)\psi\left(x, y, z\right)$$

Schrödinger equation after the separation of coordinates:

$$\hat{H}_{trans}\Phi\left(X, Y, Z\right) = E_{trans}\Phi\left(X, Y, Z\right)$$

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

$$E_{total} = E_{tr} + E$$

Hydrogen atom 4

$$\hat{H}_e = -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]-\frac{e^2}{r}$$

$$r = \sqrt{x^2+y^2+z^2}$$

Schrödinger equation:

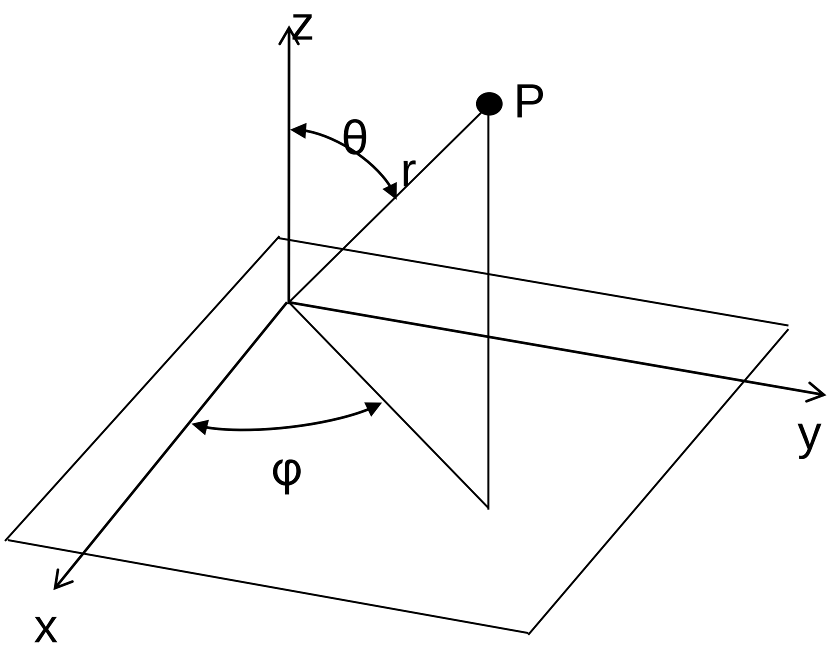
$$\hat{H}_e\psi(x,y,z) = E\psi(x,y,z)$$

Współrzędne sferyczne:

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

$y = r\sin\theta\sin\varphi$

$z = r\cos\theta$



$0 \le r < \infty, \quad 0 \le \theta \le \pi, \quad 0 \le \varphi < 2\pi$

Hydrogen atom 5

$$\hat{H}_e = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]-\frac{e^2}{r}$$

$$\hat{H}_e\psi(r,\theta,\varphi)=E\psi(r,\theta,\varphi)$$

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

The equation
in spherical
coordinates

After the separation a set of 3 equations:

equations:
azimuthal

$$-i\hbar\frac{\partial}{\partial\varphi}\Phi_m(\varphi)=\boxed{m}\Phi_m(\varphi)$$

horizontal

$$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{\boxed{m}^2}{\sin^2\theta}\right]\Theta_{lm}(\theta)=\boxed{l(l+1)}\Theta_{lm}(\theta)$$

radial

$$\left\{-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\boxed{l(l+1)}\right]-\frac{e^2}{r}\right\}R_{nlm}(r)=E_nR_{nlm}(r)$$

Hydrogen atom 6

The boundary conditions generate quantum numbers

Asymuthal equation:

$\Phi(\varphi) = \Phi(\varphi + 2\pi)$ m=0,±1, ±2, ±3, …

Horizontal equation:

$\Theta(\theta)$ Square-integrable *l=0, 1, 2, 3, …* *m=-l,-l+1,…,0,…,+l*

Radial equation:

R(r) Square-integrable *n=1, 2, 3, …* *l=0,1,…,n-1*

Energy of the hydrogen atom $\boxed{E = -\frac{\mu e^4}{2\hbar^2 n^2} = -R_H \frac{1}{n^2}}$ $R_H = \frac{\mu e^4}{2\hbar^2} = 109677 cm^{-1}$

$R_\infty = \frac{m_e e^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = 109737.3 cm^{-1}$ Rydberg constant

Hydrogen atom 7

The wavefunctions of the H atom

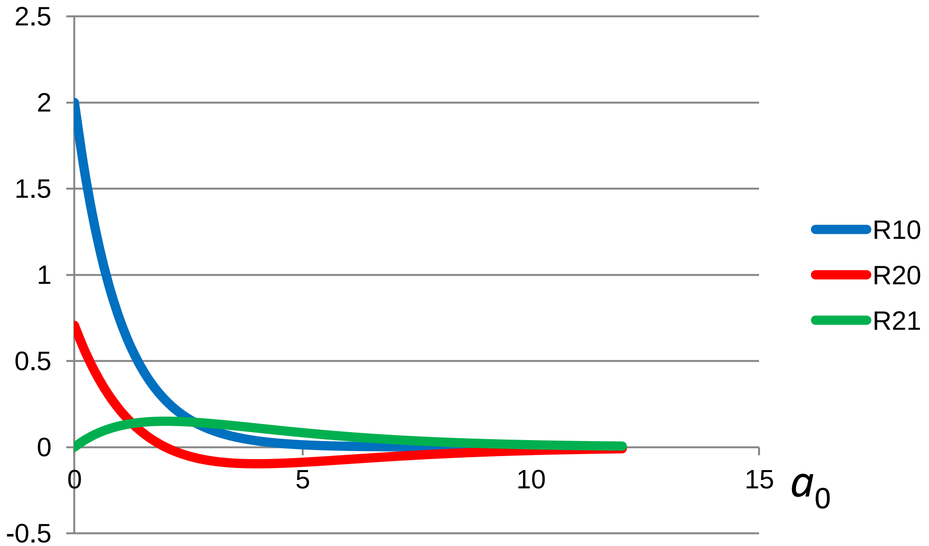
$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\,Y_l^m(\theta,\varphi)$$

Radial functions:

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{5/2} r\,e^{-Zr/2a_0}$$



a_0 = 0,529 Å = 0,529 · 10^{-10} m Bohr radius

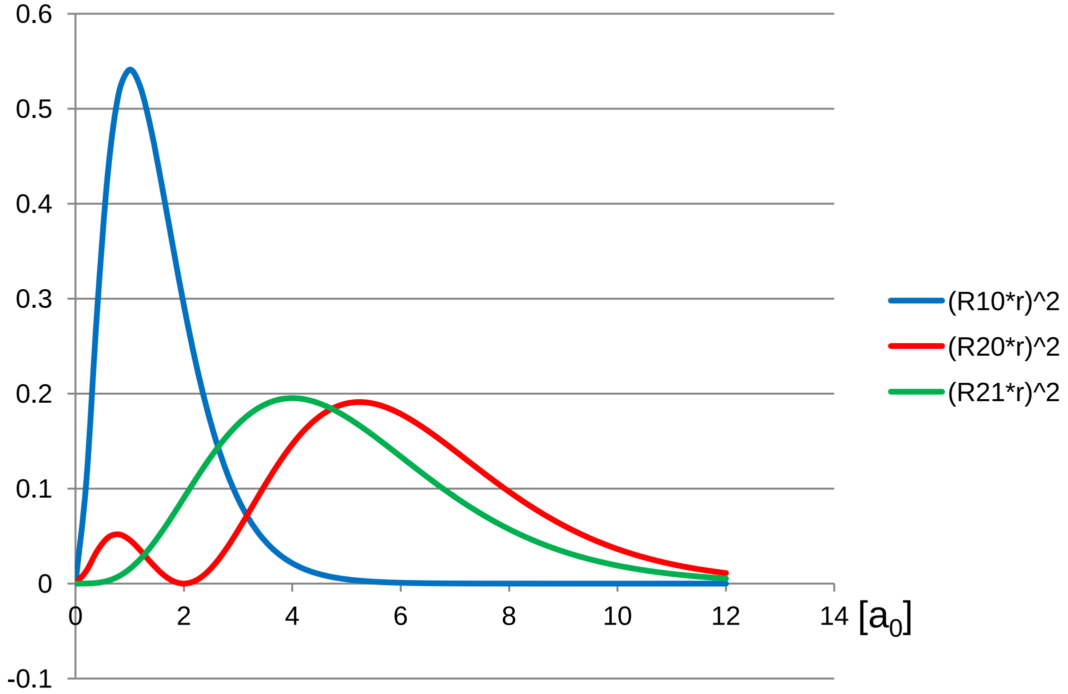
Hydrogen atom 8

Volume element: $dV = dx\,dy\,dz = r^2 \sin\theta\, dr\, d\theta\, d\varphi$

Normalization integral:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \left|\psi_{nlm}(r,\theta,\varphi)\right|^2 r^2 \sin\theta\, dr\, d\theta\, d\varphi = \int_0^\infty \left|R(r)\right|^2 r^2 dr \int_0^\pi \int_0^{2\pi} \left|Y_l^m(\theta,\varphi)\right|^2 \sin\theta\, d\theta\, d\varphi = 1$$

Radial probability density: $R^2(r)\, r^2$

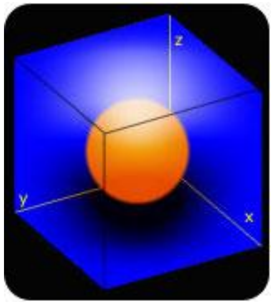


Notice:

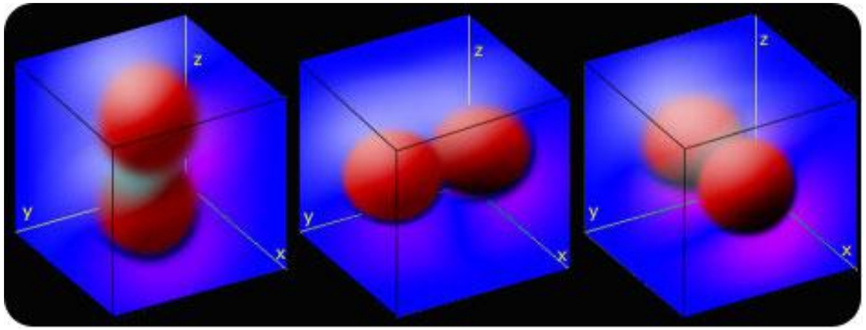
For l=n-1 there is a single maximum at $r=n^2 * a_0$

Hydrogen atom 9

Qualitative graphs of orbitals of type: s, p, d

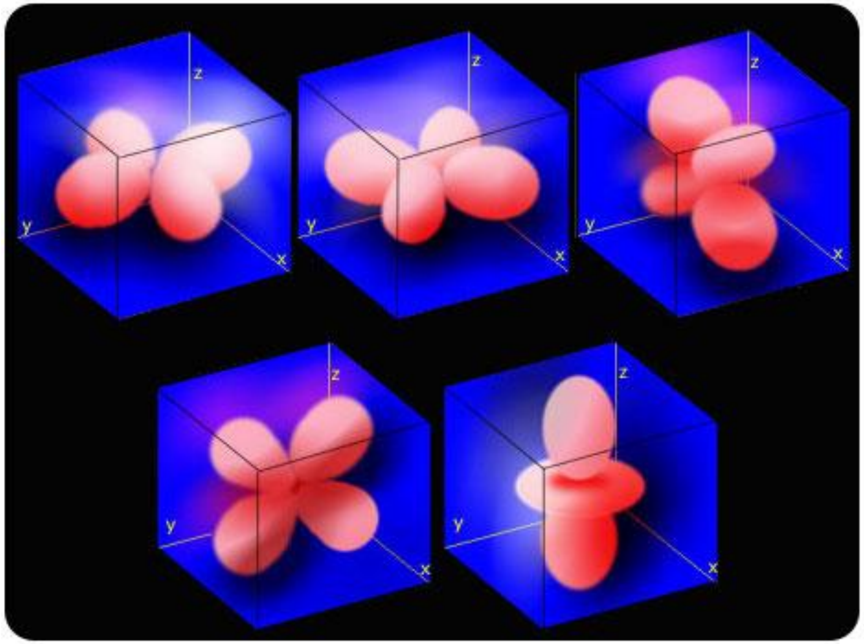


s



p_z p_y p_x

d_{x2-y2} d_{xy} d_{xz}



d_{yz} d_{z2}

Hydrogen atom 10

Atomic orbitals

$$\psi_{100} = N_{1s}\, e^{-Zr/a_0} \qquad N_{1s} = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^{3/2}$$

$$\psi_{200} = N_{2s}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0} \qquad N_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}$$

$$\psi_{210} = N_{2p} r e^{-Zr/2a_0} \cos\theta \qquad N_{2s} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2}$$

$$\psi_{211} = \frac{1}{\sqrt{2}} N_{2p} r e^{-Zr/2a_0} \sin\theta\, e^{i\varphi}$$

$$\psi_{21-1} = \frac{1}{\sqrt{2}} N_{2p} r e^{-Zr/2a_0} \sin\theta\, e^{-i\varphi}$$

Linear combinations of atomic orbitals

$$\frac{1}{\sqrt{2}}\left(\psi_{211} + \psi_{21-1}\right) \qquad \frac{-i}{\sqrt{2}}\left(\psi_{211} - \psi_{21-1}\right)$$

$$2p_x = N_{2p} r e^{-Zr/2a_0} \sin\theta\, \frac{\left(e^{i\varphi} + e^{-i\varphi}\right)}{2} = N_{2p} r e^{-Zr/2a_0} \sin\theta \cos\varphi = N_{2p} x e^{-Zr/2a_0}$$

$$2p_y = N_{2p} r e^{-Zr/2a_0} \sin\theta\, \frac{\left(e^{i\varphi} - e^{-i\varphi}\right)}{2i} = N_{2p} r e^{-Zr/2a_0} \sin\theta \sin\varphi = N_{2p} y e^{-Zr/2a_0}$$

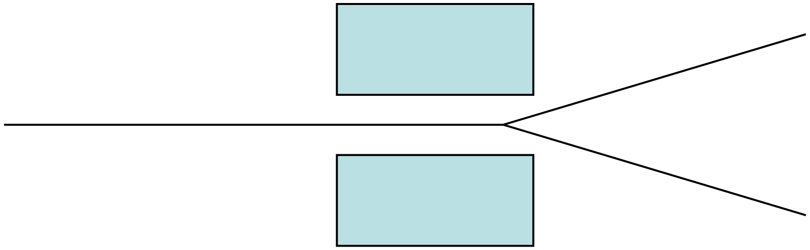
Spin

The Stern-Gerlach experiment

The beam of silver atoms passing through the magnetic field

Electron configuration of silver:

Ag: $1s^2/2s^22p^6/3s^23p^63d^{10}/4s^24p^64d^{10}/5s^1$



magnet

$m_s = +½$

$m_s = -½$

State of an electron

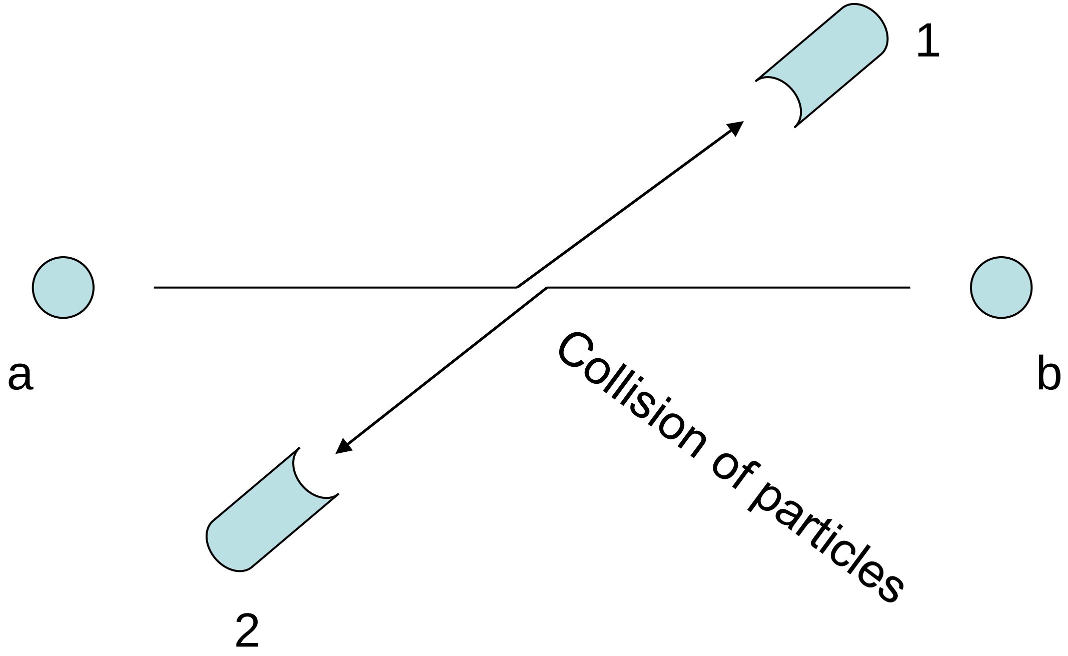
α

β

Spinorbital

$$\varphi_{nlmm_s} = \psi_{nlm}\sigma_{m_s}$$

Indistinguishable particles



a,b – particles

1,2 - detectors

Probability of detecting different particles $P_1 = |\varphi_a(1)\ \varphi_b(2)|^2$

$P_2 = |\varphi_a(2)\ \varphi_b(1)|^2$

If particles identical $P_1 = P_2$, then: $\varphi_a(1)\ \varphi_b(2) = \pm\ \varphi_a(2)\ \varphi_b(1)$

The particles can interfere with each other.

Indistinguishable particles

The amplitude of interference of identical particles:

Bosons	$\varphi_a(1)\,\varphi_b(2) + \varphi_a(2)\,\varphi_b(1)$	integer spin
Fermions	$\varphi_a(1)\,\varphi_b(2) - \varphi_a(2)\,\varphi_b(1)$	half-integer spin

The wavefunction for fermions is antisymmetrical with respect to permutation:

$\Phi(1,2,3,\ldots) = -\Phi(2,1,3,\ldots)$

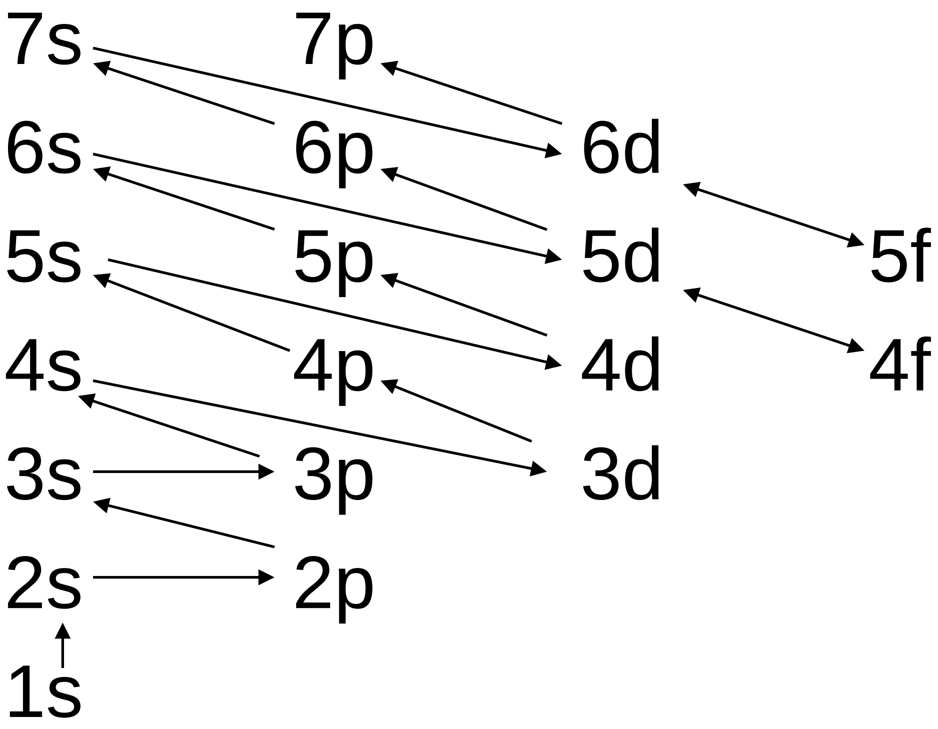
If two fermions occur in the same state1=2, thus $\varphi_a(1)\,\varphi_b(1) - \varphi_a(1)\,\varphi_b(1) \equiv 0$

It is the content of the Pauli exclusion principle.

The wavefunction for bosons is symmetrical.

Bosons tend to occupy the same state – thus the superfluidicity of helium ^{4}He.

Multielectron atoms



7s 7p

6s 6p 6d

5s 5p 5d 5f

4s 4p 4d 4f

3s 3p 3d

2s 2p

1s

Electron shells:

n = 1,2,3,… → K,L,M,…

l = 0,1,2,…→ s,p,d,…

Hund’s rule:

For a given electron configuration, the lowest energy term is the one with the greatest value of spin multiplicity

Multielectron atoms

The electronic term $^{2S+1}L_J$

2S+1 means multiplicity, where S is the total spin.

How to determine the values of L, J, S ? J = L+S, L+S-1, … , |L-S|

The carbon atom electronic configuration $1s^2\ 2s^2\ 2p^2$

Closed shells give the total spin S = 0

l_1 l_2	s_1 s_2	m_1 m_2	M_L	L	M_S	S
1 1	+½ -½	1 1	2	2	0	0
	±½ ±½	1 0	1	1	+1,0,-1, 0	1
	±½ ±½	1 -1	0	0	+1,0,-1, 0	0
	+½ -½	0 0	0		0	
	±½ ±½	0 -1	-1		+1,0,-1, 0	
	+½ -½	-1 -1	-2		0	

Terms: $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^1S_0$

Helium atom1

$$\hat{H} = -\frac{\hbar^2}{2M_j}\left[\frac{\partial^2}{\partial x_j^2} + \frac{\partial^2}{\partial y_j^2} + \frac{\partial^2}{\partial z_j^2}\right] - \frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right] - \frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\right] - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

$$\hat{H} = -\frac{\hbar^2}{2M_j}\Delta_j - \frac{\hbar^2}{2m_e}\Delta_1 - \frac{\hbar^2}{2m_e}\Delta_2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

$$\hat{H}_e = \sum_{i=1}^{2}\left(-\frac{\hbar^2}{2m_e}\Delta_i - \frac{2e^2}{r_i}\right) + \frac{e^2}{r_{12}}$$

The electronic Hamiltonian in the approximation of the infinitely heavy nucleus

$$\hat{H}_e(i) = -\frac{\hbar^2}{2m_e}\Delta_i - \frac{2e^2}{r_i}$$

$$\hat{H}(i)\psi_n(i) = E_n\psi_n(i)$$

The one-electron Hamiltonian

$$\Psi(1,2) = \psi_1(1)\psi_2(2)$$

The one-electron approximation

$$\varphi_1(1) = \psi_1(1)\sigma_1(1)$$

Spinorbital = orbital * spin_function

$$\Phi(1,2) = \varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)$$
$$\Phi(2,1) = \varphi_1(2)\varphi_2(1) - \varphi_2(2)\varphi_1(1)$$
$$\Phi(1,2) = -\Phi(2,1)$$

Antisymmetrized multi-electron function

Helium atom 2

$$\Phi(1,2) = \Psi(1,2)\sigma(1,2)$$

Spinorbital function = orbital function * spin function

$$\Psi_s(1,2) = \frac{1}{\sqrt{2}}\left[\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)\right] = \Psi_s(2,1)$$

Symmetry of the orbital function

$$\Psi_a(1,2) = \frac{1}{\sqrt{2}}\left[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)\right] = -\Psi_a(2,1)$$

$$\sigma_a(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] = -\sigma_a(2,1)$$

$$\sigma_s(1,2) = \alpha(1)\alpha(2) = +\sigma_s(2,1)$$

$$\sigma_s(1,2) = \beta(1)\beta(2) = +\sigma_s(2,1)$$

Symmetry of the spin function

$$\sigma_s(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] = +\sigma_s(2,1)$$

$$\Phi_{\text{singlet}}(1,2) = \frac{1}{\sqrt{2}}\left[\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

The singlet (S=0)

and

and triplet (S=1)

$$\Phi_{\text{triplet}}(1,2) = \frac{1}{\sqrt{2}}\left[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)\right]\begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \end{cases}$$

functions

Multielectron atoms

$$\hat{H}_e = \sum_{i=1}^{n}\left(-\frac{\hbar^2}{2m_e}\Delta_i - \frac{ne^2}{r_i}\right) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{e^2}{r_{ij}}$$

$$\Phi(1,2) = \tfrac{1}{\sqrt{2}}\left[\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)\right] = \tfrac{1}{\sqrt{2}}\begin{vmatrix} \varphi_1(1) & \varphi_1(2) \\ \varphi_2(1) & \varphi_2(2) \end{vmatrix}$$

Determinant form of the electron function for the helium atom

$$\Phi(1,2,\ldots,n) = \tfrac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \ldots & \varphi_1(n) \\ \varphi_2(1) & \varphi_2(2) & \ldots & \varphi_2(n) \\ \ldots & \ldots & \ldots & \ldots \\ \varphi_n(1) & \varphi_n(2) & \ldots & \varphi_n(n) \end{vmatrix}$$

The antisymmetrized function for the n electron system fulfills the Pauli exclusion principle

E_{HF} : the Hartree-Fock energy – the lowest energy in the frame of one-electron approximation

$E_{correlation} = E_{acurate} – E_{HF}$ The correlation energy

Variational method

How to solve a Schrödinger equation when the exact solution is not possible?
We search for a trail function Φ which gives the lowest ground state energy.

$$\hat{H}\psi = E\psi$$

$$\varepsilon = \frac{\int \Phi^* \hat{H} \Phi dV}{\int \Phi^* \Phi dV}$$

$$\Phi = \sum_{i=1}^{N} c_i \varphi_i$$

$$H_{ij} = \int \varphi_i^* \hat{H} \varphi_j dV$$

$$S_{ij} = \int \varphi_i^* \varphi_j dV$$

If Φ is the same as ψ, then ε is equal to E_0.

If Φ is an approximation of ψ, then ε is higher than E_0.

<u>Linear combinations method:</u>

The best trial function Φ is searched as a linear combination of functions φ_i, which form a set of basis functions. ε is minimized with respect to coefficients c_i:

$$\frac{\partial \varepsilon}{\partial c_i} = 0 \qquad dla\ i = 1, \ldots, N$$

A set of linear equations on coefficients c_i:

$$c_i\left(H_{ii} - \varepsilon\right) + \sum_{j \neq i} c_j\left(H_{ij} - S_{ij}\varepsilon\right) = 0 \qquad dla\ i = 1, \ldots, N$$

The variational method for a particle in a box (1)

$$\varphi_1(x)=\sqrt{\frac{30}{a^7}}x(a-x)$$

$$\varphi_2(x)=\sqrt{\frac{630}{a^9}}x^2(a-x)^2$$

$$\Phi(x)=c_1\varphi_1(x)+c_2\varphi_2(x)$$

The basis functions φ$_1$ i φ$_2$ are normalized, thus $S_{11}=1$ i $S_{22}=1$.

The set of secular equations:

$$\begin{cases} c_1(H_{11}-\varepsilon)+c_2(H_{12}-S_{12}\varepsilon)=0 \\ c_1(H_{21}-S_{21}\varepsilon)+c_2(H_{22}-\varepsilon)=0 \end{cases}$$

The necessary conditions for the existence of non-trivial solutions:

$$\begin{vmatrix} H_{11}-\varepsilon & H_{12}-S_{12}\varepsilon \\ H_{21}-S_{21}\varepsilon & H_{22}-\varepsilon \end{vmatrix}=0 \qquad H_{12}=H_{21} \qquad S_{12}=S_{21}=S$$

$$\begin{vmatrix} H_{11}-\varepsilon & H_{12}-S\varepsilon \\ H_{12}-S\varepsilon & H_{22}-\varepsilon \end{vmatrix}=0$$

The normalization of the function Φ(x):

$$\int\Phi^*(x)\Phi(x)dx=\int\Phi^2(x)dx=\int[c_1\varphi_1(x)+c_2\varphi_2(x)]^2dx=c_1^2\int\varphi_1^2dx+c_2^2\int\varphi_2^2dx+2c_1c_2\int\varphi_1\varphi_2dx=1$$

$$c_1^2+c_2^2+2c_1c_2S=1$$

The variational method for a particle in a box (2)

$$\begin{cases} c_1\left(H_{11}-\varepsilon\right)+c_2\left(H_{12}-S\varepsilon\right)=0 \\ c_1\left(H_{12}-S\varepsilon\right)+c_2\left(H_{22}-\varepsilon\right)=0 \end{cases}$$

$$c_1^2+c_2^2+2c_1c_2S=1$$

$$c_2=-c_1\,\frac{H_{11}-\varepsilon}{H_{12}-S\varepsilon}$$

$$\begin{vmatrix} H_{11}-\varepsilon & H_{12}-S\varepsilon \\ H_{12}-S\varepsilon & H_{22}-\varepsilon \end{vmatrix}=0$$

$$\left(H_{11}-\varepsilon\right)\left(H_{22}-\varepsilon\right)-\left(H_{12}-S\varepsilon\right)^2=0$$

$$\left(1-S^2\right)\varepsilon^2-\left(H_{11}+H_{22}-2H_{12}S\right)\varepsilon+H_{11}H_{22}-H_{12}^2=0$$

$$\Delta=\left(H_{11}+H_{22}-2H_{12}S\right)^2-4\left(1-S^2\right)\left(H_{11}H_{22}-H_{12}^2\right)=$$

$$=\left(H_{11}-H_{22}\right)^2+4H_{12}^2+4S\left(H_{11}H_{22}S-H_{11}H_{12}-H_{22}H_{12}\right)$$

$$\varepsilon_1=\frac{1}{2\left(1-S^2\right)}\left[H_{11}+H_{22}-2H_{12}S-\sqrt{\Delta}\right]$$

$$\varepsilon_2=\frac{1}{2\left(1-S^2\right)}\left[H_{11}+H_{22}-2H_{12}S+\sqrt{\Delta}\right]$$

For every calculated energy ε_1 or ε_2 the set of equations on coefficients c_1 i c_2 is solved.

The variational method for a particle in a box (3)

The calculation of integrals :

$$S_{12}=S_{21}=S=\int_0^a \sqrt{\frac{30}{a^5}}x(a-x)\sqrt{\frac{630}{a^9}}x^2(a-x)^2\,dx=\frac{\sqrt{30*630}}{a^7}\int_0^a x^3\left(a^3-3a^2x+3ax^2-x^3\right)dx=$$

$$=\frac{30\sqrt{21}}{a^7}\left[a^3\frac{x^4}{4}-3a^2\frac{x^5}{5}+3a\frac{x^6}{6}-\frac{x^7}{7}\right]_0^a=30\sqrt{21}\left[\frac{1}{4}-\frac{3}{5}+\frac{1}{2}-\frac{1}{7}\right]=30\sqrt{21}\,\frac{35-84+70-20}{140}=\boxed{\frac{3\sqrt{21}}{14}}$$

$$H_{12}=\int_0^a\sqrt{\frac{30}{a^5}}x(a-x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{630}{a^9}}x^2(a-x)^2\,dx=\frac{\hbar^2}{2m}\frac{\sqrt{30*630}}{a^7}\int_0^a\left(ax-x^2\right)\left(-2a^2+12ax-12x^2\right)dx=$$

$$=\frac{\hbar^2}{2m}\frac{30\sqrt{21}}{a^7}\int_0^a\left(-2a^3x+12a^2x^2-12ax^3+2a^2x^2-12ax^3+12x^4\right)dx=$$

$$=\frac{\hbar^2}{2m}\frac{30\sqrt{21}}{a^7}\left[-2a^3\frac{x^2}{2}+14a^2\frac{x^3}{3}-24a\frac{x^4}{4}+12\frac{x^5}{5}\right]_0^a=\frac{\hbar^2}{2m}\frac{30\sqrt{21}}{a^2}\left[-1+\frac{14}{3}-6+\frac{12}{5}\right]=\boxed{\frac{\hbar^2}{2m}\frac{2\sqrt{21}}{a^2}}$$

$$H_{21}=\int_0^a\sqrt{\frac{630}{a^9}}x^2(a-x)^2\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{30}{a^5}}x(a-x)\,dx=\frac{\hbar^2}{2m}\frac{30\sqrt{21}}{a^7}\int_0^a\left(a^2x^2-2ax^3+x^4\right)2\,dx=$$

$$=\frac{\hbar^2}{2m}\frac{30\sqrt{21}}{a^7}\left[2a^2\frac{x^3}{3}-4a\frac{x^4}{4}+2\frac{x^5}{5}\right]_0^a=\frac{\hbar^2}{2m}\frac{30\sqrt{21}}{a^2}\left[\frac{2}{3}-1+\frac{2}{5}\right]=\boxed{\frac{\hbar^2}{2m}\frac{2\sqrt{21}}{a^2}}$$

The variational method for a particle in a box (4)

The calculation of integrals :

The integrals for energy in units of $\frac{\hbar^2}{2ma^2}$

$$H_{12} = H_{21} = \frac{\hbar^2}{2m}\frac{2\sqrt{21}}{a^2} \qquad S = \frac{3\sqrt{21}}{14}$$

$$H_{11} = \int_0^a \sqrt{\frac{30}{a^5}}x(a-x)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{30}{a^5}}x(a-x)dx = \frac{\hbar^2}{2m}\frac{10}{a^2}$$

$$H_{22} = \int_0^a \sqrt{\frac{630}{a^9}}x^2(a-x)^2\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\sqrt{\frac{630}{a^9}}x^2(a-x)^2 dx = \frac{\hbar^2}{2m}\frac{12}{a^2}$$

The set of secular equations:

$$c_1(10-\varepsilon)+c_2\left(2\sqrt{21}-\varepsilon\frac{3\sqrt{21}}{14}\right)=0$$

$$c_1\left(2\sqrt{21}-\varepsilon\frac{3\sqrt{21}}{14}\right)+c_2(12-\varepsilon)=0$$

$$\begin{vmatrix} 10-\varepsilon & 2\sqrt{21}-\frac{3\sqrt{21}}{14}\varepsilon \\ 2\sqrt{21}-\frac{3\sqrt{21}}{14}\varepsilon & 12-\varepsilon \end{vmatrix} = 0$$

A solution:

$$\left(1-\frac{9*21}{196}\right)\varepsilon^2-\left(10+12-2*2*\sqrt{21}*3*\sqrt{21}/14\right)\varepsilon+10*12-4*21=0$$

$$\frac{1}{28}\varepsilon^2-4\varepsilon+36=0$$

$$\Delta = 16-4*(1/28)*36 = 76/7 \qquad \sqrt{\Delta} = 3{,}295017884$$

$$\varepsilon_1 = (4-3{,}295017884)*(28/2) = \boxed{9{,}869719621}$$

$$\varepsilon_2 = (4+3{,}295017884)*(28/2) = \boxed{102{,}13025038}$$

The variational method for a particle in a box (5)

Calculation of the linear combination coefficients:

$$c_1^2 + c_2^2 + 2c_1c_2S = 1$$

$$c_2 = -c_1 \frac{H_{11} - \varepsilon}{H_{12} - S\varepsilon}$$

$$\varepsilon_1 = 9{,}869719621$$

$$c_2 = -c_1 \frac{10 - 9{,}869719621}{2 * \sqrt{21} - 9{,}869719621 * 3 * \sqrt{21}/14}$$

$$c_2 = 0{,}247271562 c_1$$

$$c_1 = \sqrt{\frac{1}{1 + 0{,}247271562^2 + 2 * 0{,}247271562 * 2 * \sqrt{21}/14}}$$

$$c_1 = 0{,}80405626$$

$$c_2 = 0{,}19882025$$

$$\Phi_1 = 0{,}80405626\varphi_1 + 0{,}19882025\varphi_2$$

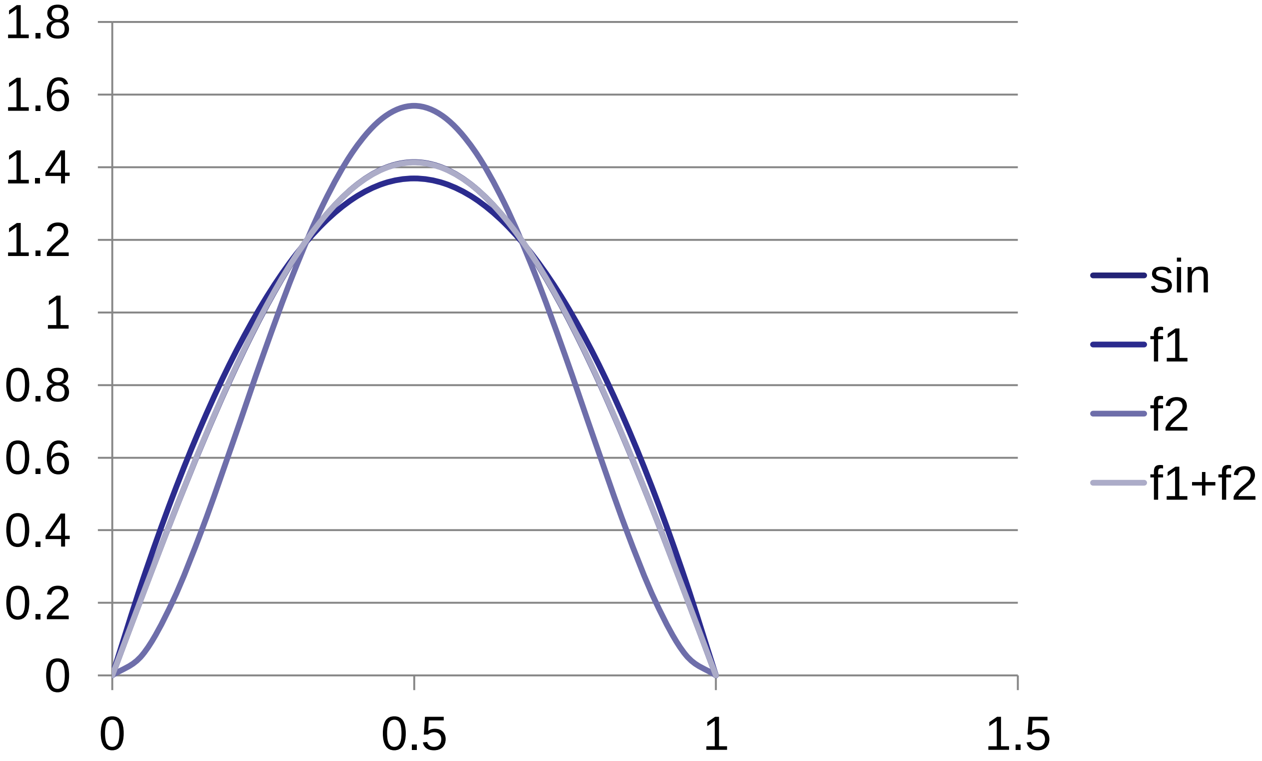
The exact value of energy E_1 for a particle in a box [in units of $\frac{\hbar^2}{2ma^2}$]

$$E_1 = \pi^2 = 9{,}869604401$$

$$\varepsilon_1 > E_1$$

The variational method for a particle in a box (6)

A graph of the functions:



The function sin(x) and the linear combination of functions φ_1 and φ_2 overlap in a scale of the graph

The Hartree-Fock method for an atom

$$\hat{H}_e = \sum_{i=1}^{n}\left(-\frac{\hbar^2}{2m_e}\Delta_i - \frac{Ze^2}{r_i}\right) + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{e^2}{r_{ij}}$$

The Hamiltonian for N-electron atom

$$\Psi(1,2,\ldots,n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \phi_1(1) & \phi_1(2) & \ldots & \phi_1(n) \\ \phi_2(1) & \phi_2(2) & \ldots & \phi_2(n) \\ \ldots & \ldots & \ldots & \ldots \\ \phi_n(1) & \phi_n(2) & \ldots & \phi_n(n) \end{vmatrix}$$

$$\phi_p(i) = \varphi_p(i)\sigma_p(i)$$

$$\sigma_p = \alpha \text{ lub } \beta$$

$$\hat{F}(i)\phi_p(i) = \varepsilon_p\phi_p(i)$$

$$p = 1,2,3,\ldots,n$$

The orbital energy

$$\hat{F}(1) = \hat{h}(1) + \hat{J}(1) - \hat{K}(1)$$

$$\hat{h}(1) = -\frac{\hbar^2}{2m_e}\Delta_1 - \sum_{A}\frac{Z_A e^2}{r_{1A}}$$

One-electron operator

$$\hat{J}(1)\phi_i(1) = \left[\int \phi_j^*(2)\frac{e^2}{r_{12}}\phi_j(2)dV_2\right]\phi_i(1)$$

$$\hat{K}(1)\phi_i(1) = \left[\int \phi_j^*(2)\frac{e^2}{r_{12}}\phi_i(2)dV_2\right]\phi_j(1)$$

Two-electron operators:

Coulomb

Exchange

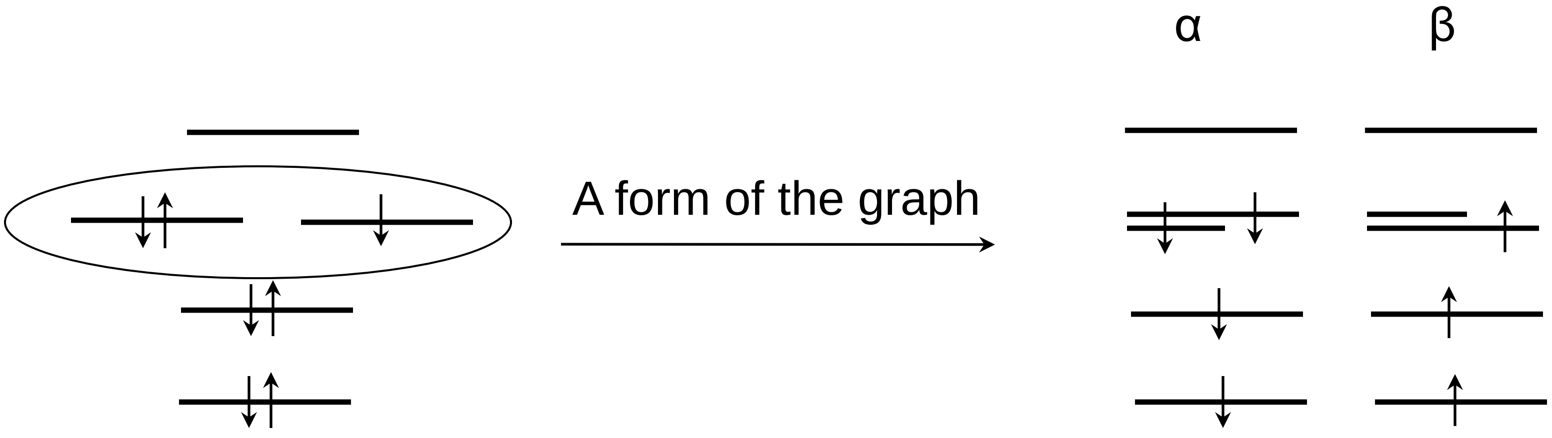
Unrestricted Hartree-Fock method (UHF)

$$\phi_p(i) = \varphi_p(i)\sigma_p(i) \qquad\qquad \sigma_p = \alpha \ or \ \beta$$

where: φ_p is real, and numbers of electrons with spin α and β are not equal

Used for the open-shell systems (atoms or molecules)

(different orbital energies for spins α and β)



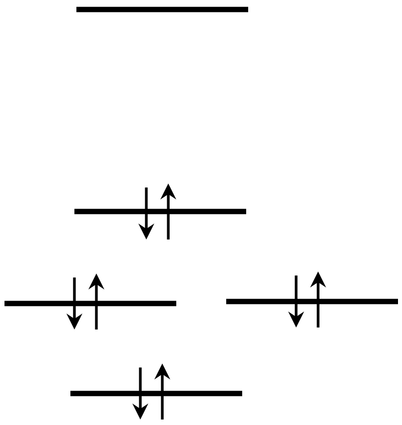
Restricted Hartree-Fock (RHF)

Even number of electrons, equal number of electrons of spin α and β.

The number of spinorbitals is twice as many as that of occupied orbitals.

$$\phi_{2p-1}(i) = \varphi_p(i)\alpha(i)$$
$$\phi_{2p}(i) = \varphi_p(i)\beta(i)$$

The number of spinorbitals is equal to the number of electrons, wheras each orbital is occupied by two electrons.



LUMO (Lowest unoccupied molecular orbital)

HOMO (Highest occupied molecular orbital)

Basis functions 1

The method of Hartree-Fock-Roothan SCF-LCAO-MO

(Self consistent field-linear combination of atomic orbitals- molecular orbitals)

One-electron approximation:

$$\Psi(1,2,\ldots,n)=\frac{1}{\sqrt{n!}}\begin{vmatrix} \phi_1(1) & \phi_1(2) & \ldots & \phi_1(n) \\ \phi_2(1) & \phi_2(2) & \ldots & \phi_2(n) \\ \ldots & \ldots & \ldots & \ldots \\ \phi_n(1) & \phi_n(2) & \ldots & \phi_n(n) \end{vmatrix}$$

$$\phi_i(k)=\varphi_i(k)\sigma_i(k) \qquad \sigma_i=\alpha \text{ or } \beta$$

LCAO (Linear Combination of Atomic Orbitals)

One-electron finctions as linear combinations of basis functions:

$$\varphi_i(1)=\sum_{j=1}^{m} c_{ij}\chi_j(1)$$

Basis functions 2

In a molecule: expansion of molecular orbitals $\varphi_i(r)$
using the basis functions – atomic orbitals $\chi_j(r)$

$$\varphi_i(\vec{r}) = \sum_{j=1}^{m} c_{ij} \chi_j(\vec{r})$$

Atomic orbitals $\chi_j(r)$ are usually centered on atomic nuclei

Atomic orbital AO = radial function × angular function

$$\chi(\vec{r}) = \chi(r, \theta, \varphi) = R(r) Y_{lm}(\theta, \varphi)$$

Basis functions 3

Angular function l=	**0**	**1**	**2**	**3**
	s	p	d	f

AO are grouped in shells of a given l having the same radial function

Radial function– 2 types of basis sets:

Slater R(r)= polynomial(r) * exp($-\alpha r$)

Gauss R(r)= polynomial(r) * exp($-\alpha r^2$)

The Slater functions have a proper asymptotic behavior for small and large values of r, but the calculation of integrals with r_{12} are time-consuming and the Gaussian functions are used much more often.

Contracted Gaussian basis sets

$$\chi_j(r) = \sum_{k=1}^{K} a_{jk} G_k(r)$$

where:

χ_j is a Contracted Gaussian Type Orbital CGTO

G_k is a primitive Gaussian Type Orbital PGTO

The linear expansion coefficients are determined by the software authors, are not further optimized in the process of the SCF calculations.

Example in Excel

Basis functions

Minimum basis set (single zeta SZ)

one radial function R(r) for each shell

Example:

atom C $1s^2$ $2s^2$ $2p^2$

Basis function: one radial function to represent the orbital 1s

one radial function to represent the orbital 2s

one radial function to represent the orbital 2p

Thus, there are 5 basis functions

χ_{1s} , χ_{2s} , χ_{2px} , χ_{2py} , χ_{2pz}

Basis functions

Double zeta basis set (DZ)

two radial functions R(r) for each shell

Example:

atom C $1s^2$ $2s^2$ $2p^2$

Basis function: two radial functions to represent the orbital 1s

two radial functions to represent the orbital 2s

two radial functions to represent the orbital 2p

Thus, there are 10 basis functions

$\chi_{1s;1}$, $\chi_{1s;2}$, $\chi_{2s;1}$, $\chi_{2s;2}$, $\chi_{2px;1}$, $\chi_{2px;2}$, $\chi_{2py;1}$, $\chi_{2py;2}$, $\chi_{2pz;1}$, $\chi_{2pz;2}$

Basis functions

Double zeta valence basis set (DZV)

one radial function R(r) for each shell of core electrons

two radial functions R(r) for each shell of valence electrons

Example:

atom C $1s^2\ 2s^2\ 2p^2$

Basis function: one radial function to represent the orbital 1s

two radial functions to represent the orbital 2s

two radial functions to represent the orbital 2p

Thus, there are 9 basis functions

χ_{1s} , $\chi_{2s;1}$, $\chi_{2s;2}$, $\chi_{2px;1}$, $\chi_{2px;2}$, $\chi_{2py;1}$, $\chi_{2py;2}$, $\chi_{2pz;1}$, $\chi_{2pz;2}$

Basis functions

By analogy, the triple zeta valence basis set (TZV)

one radial function R(r) for each shell of core electrons

three radial functions R(r) for each shell of valence electrons

Example:

atom C $1s^2\ 2s^2\ 2p^2$

Basis function: one radial function to represent the orbital 1s

three radial functions to represent the orbital 2s

three radial functions to represent the orbital 2p

Thus, there are 13 basis functions

χ_{1s} , $\chi_{2s;1}$, $\chi_{2s;2}$, $\chi_{2s;3}$, $\chi_{2px;1}$, $\chi_{2px;2}$, $\chi_{2px;3}$, $\chi_{2py;1}$, $\chi_{2py;2}$, $\chi_{2py;3}$, $\chi_{2pz;1}$, $\chi_{2pz;2}$, $\chi_{2pz;2}$

Basis functions

Polarization functions– additional functions for unoccupied orbitals

Example:

atom C $1s^2$ $2s^2$ $2p^2$

Double zeta valence polarization functions (DZVP)

Basis functions: one radial function to represent the orbital 1s

three radial functions to represent the orbital 2s

three radial functions to represent the orbital 2p

one radial function to represent the orbital 3s

Thus, there are 15 basis functions

1 function 1s, 2 functions 2s, 2 functions 2px, 2 functions 2py, 2 functions 2pz,

In addition 6 functions 3d (d_{xy}, d_{yz}, d_{xz}, d_{x2}, d_{y2}, d_{z2})

Basis functions

Diffusion functions – additional radial function with small value of the exponent i.e. expanding far from the nucleus

Used for calculations for anions

Pople basis sets

6-31G VDZ

core function: 1 contraction of 6 PGTO

valence functions: 2 contractions (of 3 and 1 PGTO)

3-21G VDZ the same number of contractions by smaller number of PGTO

6-311G VTZ

core function: 1 contraction of 6 PGTO

valence functions: 3 contractions (of 3, 1 and 1 PGTO)

Typical description of the basis set

STO-2G

```
BASIS="STO-2G"
H   0
S   2   1.00
        1.30975638   0.43012850
        0.23313597   0.67891353
 ****
C 0
S   2   1.00
      27.38503303   0.43012850
        4.87452205   0.67891353
SP  2  1.00
        1.13674819   0.04947177   0.51154071
        0.28830936   0.96378241   0.61281990
```

Primitive GTO

$$GTO = \frac{2\alpha}{\pi^{0,75}} e^{-\alpha r^2} = N_\alpha e^{-\alpha r^2}$$

For H (1s): $\psi_{1s}^{H} = 0{,}43012850 \; * N_\alpha e^{-1{,}30975638 r^2} + 0{,}67891353 \; * N_\alpha e^{-0{,}233313597 r^2}$

For C (1s): $\psi_{1s}^{C} = 0{,}43012850 \; * N_\alpha e^{-27{,}38503303 r^2} + 0{,}67891353 \; * N_\alpha e^{-4{,}87452205 r^2}$

(2s): $\psi_{2s}^{C} = 0{,}04947177 \; * N_\alpha e^{-1{,}13674819 r^2} + 0{,}96378241 \; * N_\alpha e^{-0{,}28830936 r^2}$

($2p_z$): $\psi_{2p}^{C} = 0{,}51154071 * N_\alpha e^{-1{,}13674819 r^2} + 0{,}61281990 * N_\alpha e^{-0{,}28830936 r^2}$

Pople basis sets

For larger basis sets supplement of polarization functions(of higher value of l)

6-31G* = 6-31(d) = VDZP

core function: 1 contraction of 6 PGTO

valence functions: 2 contractions (of 3 and 1 PGTO)

polarization functions: 1 contraction of 1 PGTO

Diffusion functions:

6-31+G* ditto + low exponent function (far-expanding)

Summary of basis sets

Effective basis set – look for hints in bibliography or in your own experience (generally: different basis set required for different molecular properties)

Routine calculations – basis sets ≥ VDZP

Gaussian basis sets:

- Pople 6-311G(d)
  - (for H usually the polarization functions p are not added)
- for correlation type calculations (MP2, CI)
  - correlation consistent cc-pVnZ (n=D,T,Q,5,…)
  - augmented aug-cc-pVnZ

Ion H_2^+ - the simplest molecule

$$\varepsilon = \frac{\int \psi^* \hat{H} \psi \, dV}{\int \psi^* \psi \, dV}$$

$$\varepsilon \int \psi^* \psi \, dV = \int \psi^* \hat{H} \psi \, dV$$

$$\varepsilon \int \left(c_1 \chi_a + c_2 \chi_b\right)^2 dV = \int \left(c_1 \chi_a + c_2 \chi_b\right) \hat{H} \left(c_1 \chi_a + c_2 \chi_b\right) dV$$

$$\varepsilon \left[c_1^2 \int \chi_a^2 dV + c_2^2 \int \chi_b^2 dV + 2c_1 c_2 \int \chi_a \chi_b dV\right] = c_1^2 \int \chi_a \hat{H} \chi_a dV + c_2^2 \int \chi_b \hat{H} \chi_b dV + 2c_1 c_2 \int \chi_a \hat{H} \chi_b dV$$

$$\varepsilon \left[c_1^2 + c_2^2 + 2c_1 c_2 S\right] = c_1^2 H_{aa} + c_2^2 H_{bb} + 2c_1 c_2 H_{ab}$$

$$\frac{\partial \varepsilon}{\partial c_1} \left[c_1^2 + c_2^2 + 2c_1 c_2 S\right] + \varepsilon \left[2c_1 + 2c_2 S\right] = 2c_1 H_{aa} + 2c_2 H_{ab}$$

$$\frac{\partial \varepsilon}{\partial c_2} \left[c_1^2 + c_2^2 + 2c_1 c_2 S\right] + \varepsilon \left[2c_2 + 2c_1 S\right] = 2c_2 H_{bb} + 2c_1 H_{ab}$$

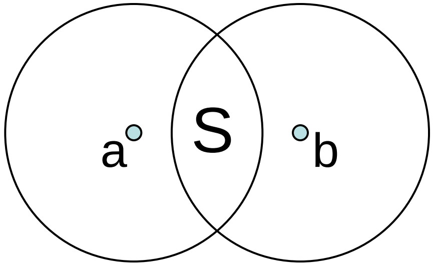
$$H_{aa} = H_{bb}$$

$$E\left[2c_1 + 2c_2 S\right] = 2c_1 H_{aa} + 2c_2 H_{ab}$$

$$E\left[2c_2 + 2c_1 S\right] = 2c_2 H_{aa} + 2c_1 H_{ab}$$

$$c_1\left(H_{aa} - E\right) + c_2\left(H_{ab} - SE\right) = 0$$

$$c_1\left(H_{ab} - SE\right) + c_2\left(H_{aa} - E\right) = 0$$



Ion H_2^+

$$\begin{vmatrix} H_{aa}-E & H_{ab}-SE \\ H_{ab}-SE & H_{aa}-E \end{vmatrix} = 0$$

$$(H_{aa}-E)^2 - (H_{ab}-SE)^2 = 0$$

$$H_{aa}-E = \pm(H_{ab}-SE)$$

$$H_{aa}-E = -H_{ab}+SE \qquad H_{aa}-E = H_{ab}-SE$$

$$E+SE = H_{aa}+H_{ab} \qquad E-SE = H_{aa}-H_{ab}$$

$$E_+ = \frac{H_{aa}+H_{ab}}{1+S} \qquad E_- = \frac{H_{aa}-H_{ab}}{1-S}$$

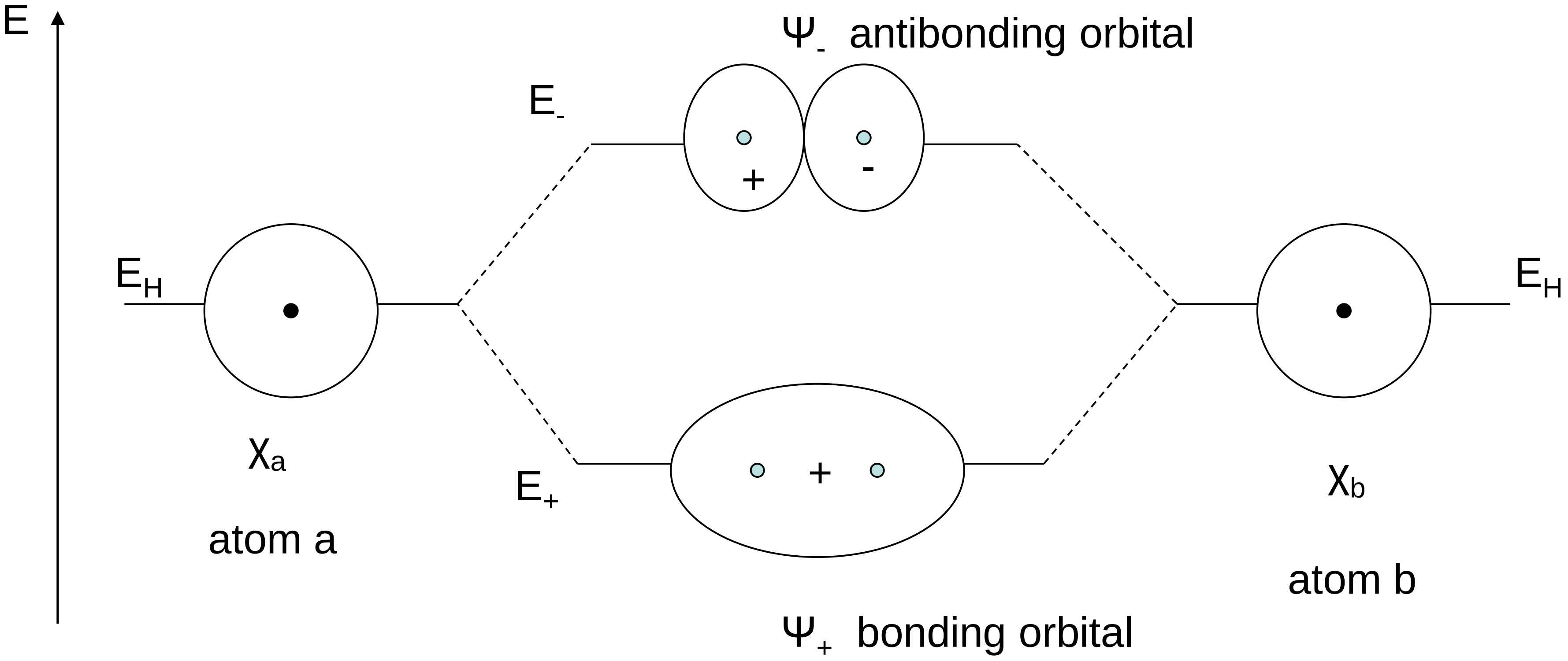
$$H_{aa} \approx E_H = -R\,\tfrac{1}{n^2} < 0 \qquad H_{ab} \leq 0 \qquad S << 1 \qquad E_+ < E_-$$

Since both centers a and b are equivalent $c_1^2 = c_2^2 \quad thus \quad c_1 = \pm c_2$

$$for\ E_+ \rightarrow \psi_+ = c_1\chi_a + c_1\chi_b = N_+(\chi_a+\chi_b) \qquad N_+ = \frac{1}{\sqrt{2+2S}}$$

$$for\ E_- \rightarrow \psi_- = c_1\chi_a - c_1\chi_b = N_-(\chi_a-\chi_b) \qquad N_- = \frac{1}{\sqrt{2-2S}}$$

Ion H_2^+

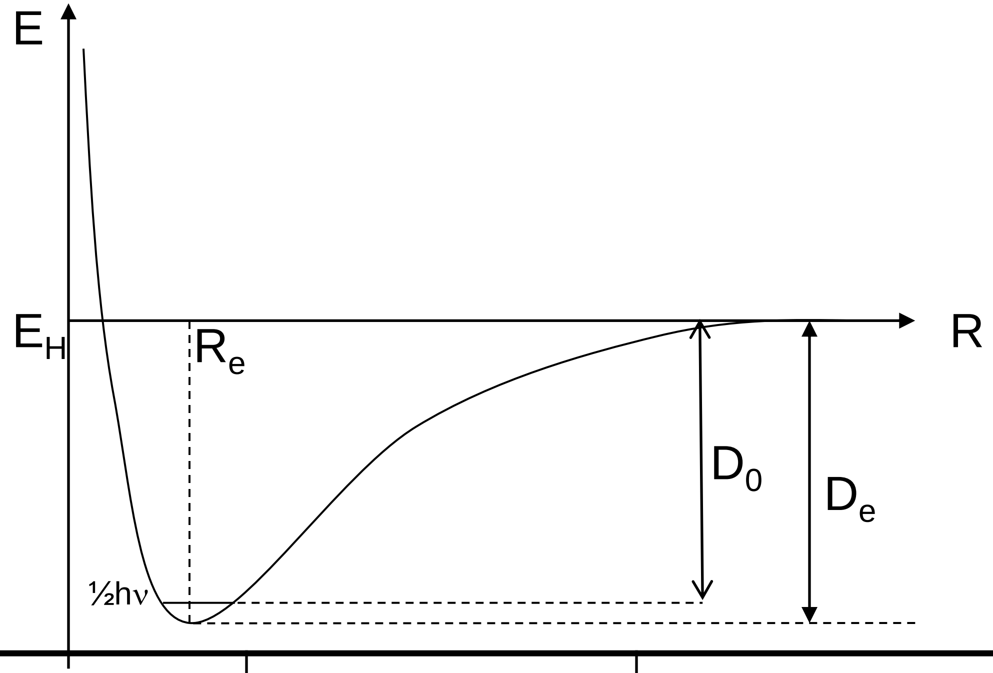


If R decreases, then $|H_{ab}|$ increases

Ion H_2^+

Total energy of a molecule:

$$E_c = E_+ + \frac{e^2}{R}$$

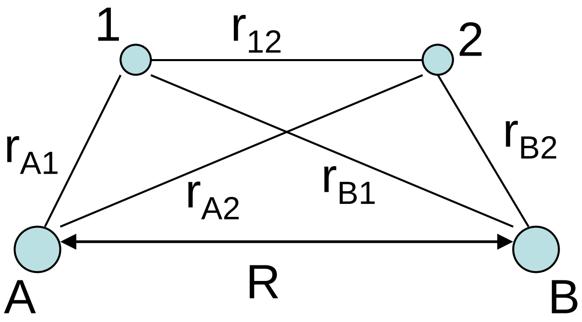


	D_e	R_e
Experiment	2,793 eV	1,057 Å
Calculated	1,78 eV	1,32 Å
Variational calc.	2,35 eV	1,06 Å

$$\chi_a = N\,e^{-r/a_0}$$

$$\chi_a = N\,e^{-\zeta r/a_0} \qquad \zeta = 1{,}24$$

Molecular Hamiltonian H_2



$$\hat{H} = -\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 + \frac{e^2}{|\vec{R}|} - \frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{e^2}{r_{12}} - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} - \frac{e^2}{r_{B2}}$$

$$\hat{H}\,\Psi\left(\{r\},\vec{R}\right) = E\,\Psi\left(\{r\},\vec{R}\right)$$

Adiabatic approximation:
(Born-Oppenheimer appr.)

$$\Psi\left(\{r\},\vec{R}\right) = \psi_e\left(\{r\};R\right)\Psi_{vr}\left(\vec{R}\right)$$

The molecular wave function presented as a product of the electronic wave function and the function for a motion of nuclei.

$\psi_e\left(\{r\};R\right)$ The function describes a distribution of electrons for the instantaneous position of nuclei R

$\Psi_{vr}\left(\vec{R}\right)$ The function describes a distribution of nuclei – their distance R and the direction of the vector $\vec{R}$

Separation of molecular Schrödinger equation

$$\hat{H} = \hat{H}_e + \hat{H}_{vr}$$

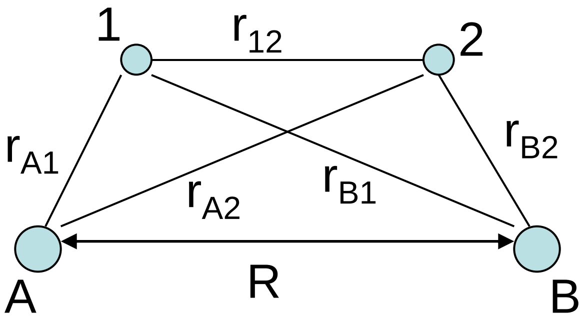
$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{e^2}{r_{12}} - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}} - \frac{e^2}{r_{B2}} + \frac{e^2}{\left|\vec{R}\right|}$$

$$\hat{H}_e \psi_e\left(\{r\}; R\right) = E_e(R)\psi_e\left(\{r\}; R\right) \qquad R = \left|\vec{R}\right|$$

$$\hat{H}_{vr} = -\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 + E_e(R)$$

$$\hat{H}_{vr}\left(\vec{R}\right)\Psi_{vr}\left(\vec{R}\right) = E_{vr}\,\Psi_{vr}\left(\vec{R}\right)$$

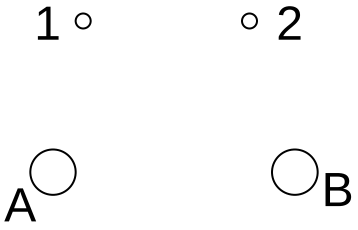
H_2 molecule



$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2+\nabla_2^2\right)+\frac{e^2}{R_{AB}}+\frac{e^2}{r_{12}}-\frac{e^2}{r_{A1}}-\frac{e^2}{r_{A2}}-\frac{e^2}{r_{B1}}-\frac{e^2}{r_{B2}}$$

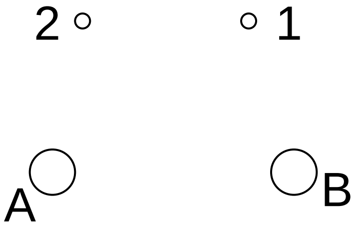
Borna-Oppenheimer approximation: R_{AB} = const

One-electron approximation:



$$\psi_1 = \psi_A(1)\psi_B(2)$$

$$\psi = c_1\psi_1 + c_2\psi_2$$



$$\psi_2 = \psi_A(2)\psi_B(1)$$

H_2 molecule

Slater determinant

$$\psi = N\begin{vmatrix} \varphi_A(1)\alpha(1) & \varphi_A(2)\alpha(2) \\ \varphi_B(1)\beta(1) & \varphi_B(2)\beta(2) \end{vmatrix} = N\left[\varphi_A(1)\varphi_B(2)+\varphi_A(2)\varphi_B(1)\right]\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]$$

Total energy:

$$E_e = 2\sum_{i=1}^{n/2} h_{ii} + \sum_{i=1}^{n/2}\sum_{j=i}^{n/2}\left(2J_{ij} - K_{ij}\right) + V_{nn}$$

$$h_{ii} = \int \varphi_i^*(1)\left[-\frac{\hbar^2}{2m_e}\nabla_1^2 - \sum_A \frac{Z_A e^2}{r_{1A}}\right]\varphi_i(1)\,dV_1$$

$$J_{ij} = \int \varphi_i^*(1)\varphi_i(1)\frac{e^2}{r_{12}}\varphi_j^*(2)\varphi_j(2)\,dV_1 dV_2$$

$$K_{ij} = \int \varphi_i^*(1)\varphi_j(1)\frac{e^2}{r_{12}}\varphi_i^*(2)\varphi_j(2)\,dV_1 dV_2$$

Orbital energy:

$$\varepsilon_i = h_{ii} + \sum_{j}^{n/2}\left(2J_{ij} - K_{ij}\right)$$

Average energy of electron repulsion:

$$V_{ee} = \sum_{i}^{n/2}\sum_{j}^{n/2}\left(2J_{ij} - K_{ij}\right)$$

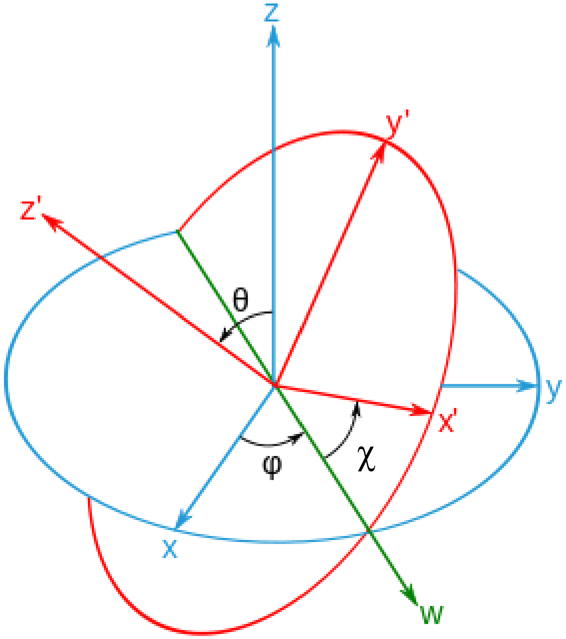
The total energy is not equal to the sum of orbital energies

$$E_e = \sum_{i}^{n/2} 2\varepsilon_i - V_{ee}$$

Rovibrational equation

$$\hat{H}_{vr} = -\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 + E_e(R)$$

$$\hat{H}_{vr}(\vec{R})\Psi_{vr}(\vec{R}) = E_{vr}\Psi_{vr}(\vec{R})$$



Euler angles

Separation of rotational and vibrational equations:

$$\Psi_{vr}(\vec{R}) = \Psi_v(R)\Psi_r(\chi,\theta,\varphi)$$

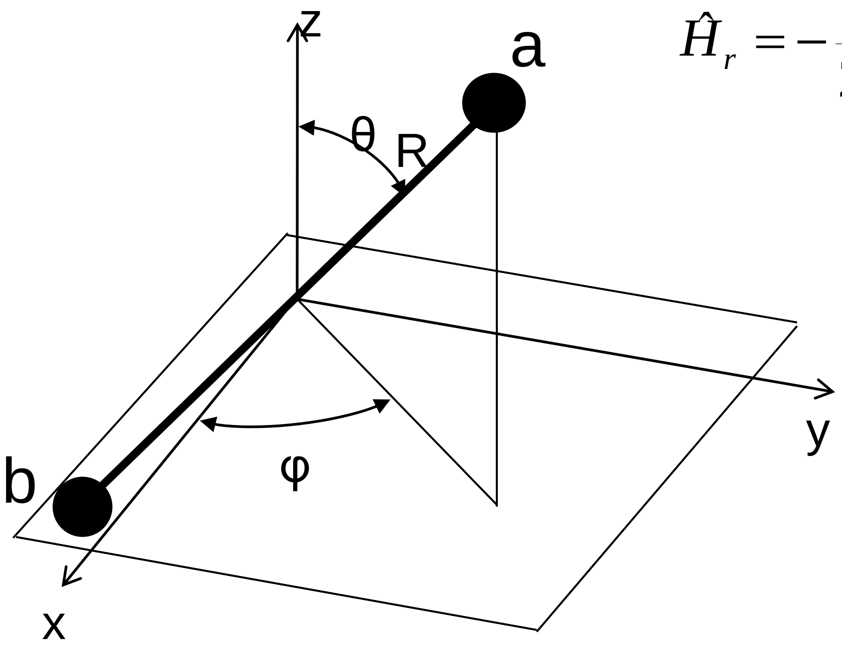
$$\hat{H}_v(R)\Psi_v(R) = E_v\Psi_v(R)$$

$$H_r(\chi,\theta,\varphi)\Psi_r(\chi,\theta,\varphi) = E_r\Psi_r(\chi,\theta,\varphi)$$

Total energy of a molecule in the adiabatic approximation

$$E = E_e + E_v + E_r$$

Rigid rotor (E_r)



$$\hat{H}_r = -\frac{\hbar^2}{2\mu R^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

$$\hat{H}_r(\theta,\varphi)Y_J^M(\theta,\varphi) = E_r Y_J^M(\theta,\varphi)$$

$$E_r(J) = \frac{\hbar^2}{2\mu R^2}J(J+1)$$

$J= 0, 1, 2, ...$

$M=-J, -J+1,...,0,..., J$

(2J+1) – fold degeneracy of a rotational state

Reduced mass:

$$\frac{1}{\mu} = \frac{1}{m_a} + \frac{1}{m_b}$$

Rigid rotor (E_r)

$$E_r(J) = \frac{\hbar^2}{2\mu R^2} J(J+1)$$

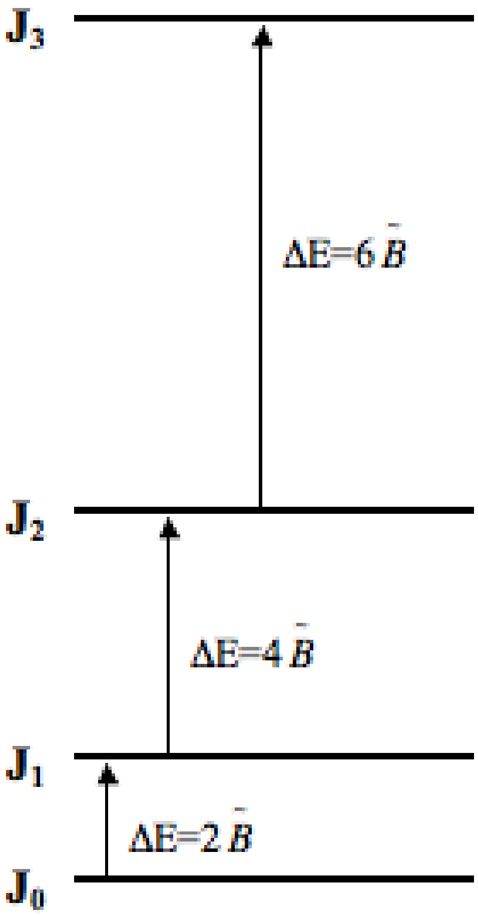
$J = 0, 1, 2, \ldots$

Moment of inertia $I = \mu R^2$

Rotational constant B $B = \frac{\hbar^2}{2\mu R^2} = \frac{\hbar^2}{2I}$

$$E_J = BJ(J+1)$$

Energy levels of a rigid rotor

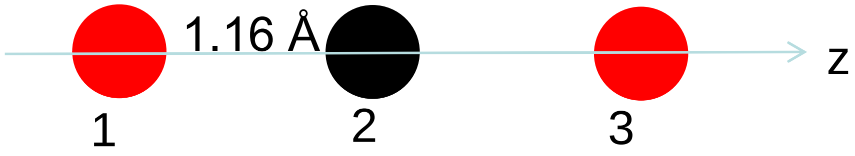


$$E_J = BJ\left(J+1\right)$$

Moment of inertia - CO_2

$$I_x = \sum_{i=1}^{n} m_i \left(y_i^2 + z_i^2 \right)$$

The coordinates of nuclei measured in the center of mass molecular axis system



Constants:

μ = 1.660538921*10^{-27} kg

ħ = 1.0545919*10^{-34} J*s

c = 299792400 m/s

hc = 1.9865*10^{-25} J*m = 1.9865*10^{-27} J*cm

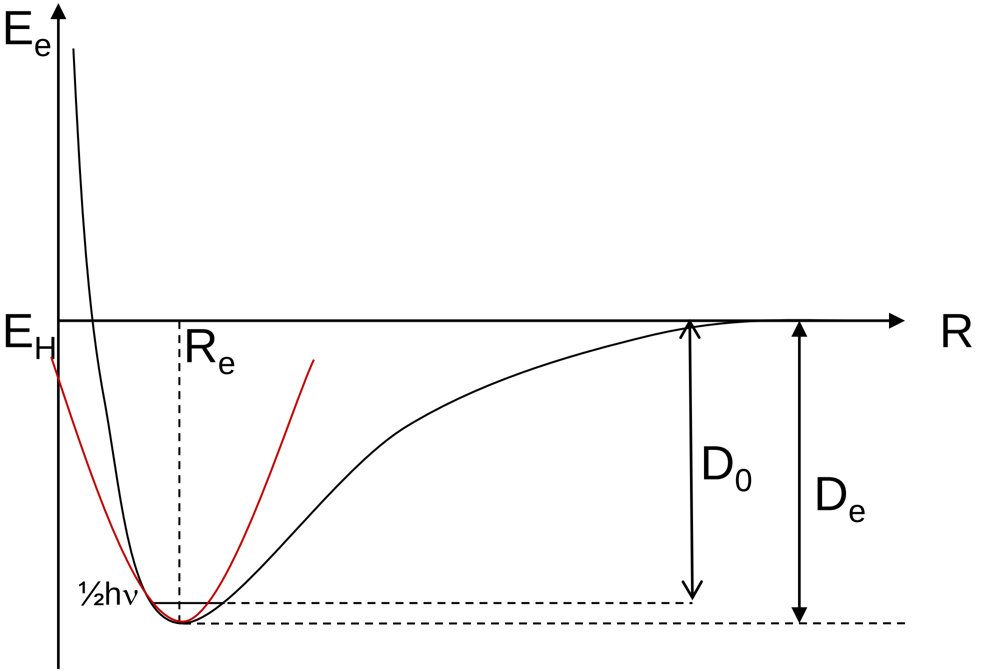
I= 7.1501*10^{-42} kg*m^{2}

B= 7.7772*10^{-28} J

B/(hc) = 0.3915 cm^{-1}

B*c = 1.1737*10^{+06} s^{-1} = 1.1737 MHz

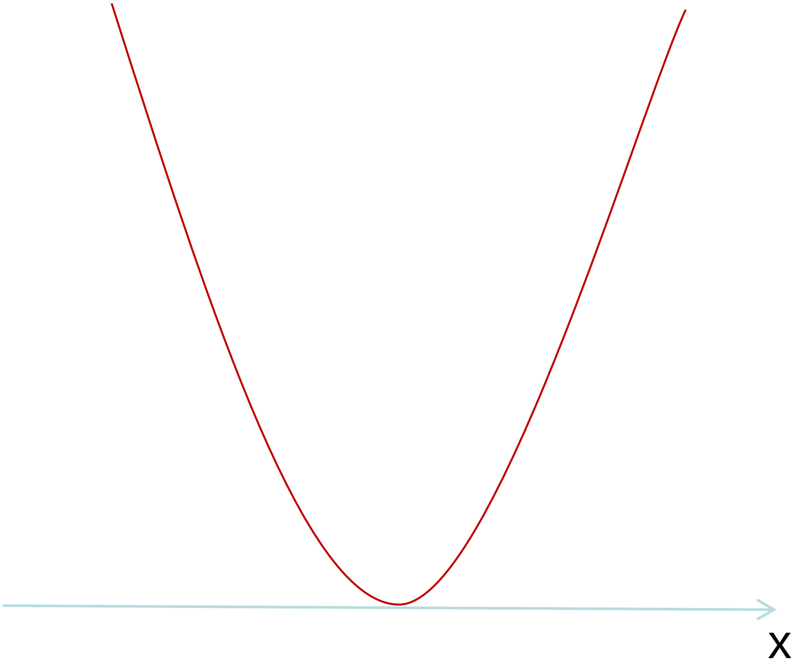
Vibrational energy (E_v)



At the minimum the potential energy curve is approximated with a parabola, what leads to the Schrödinger equation for a harmonic oscillator

Harmonic oscillator

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}+\boxed{\tfrac{1}{2}kx^2}\Psi = E\Psi$$



The energy of a harmonic oscillator

$$E=\hbar\omega\left(n+\tfrac{1}{2}\right)$$

$$\Psi_n(x)=e^{-\frac{1}{2}x^2}H_n(x)$$

$$\hbar=\frac{h}{2\pi}\qquad \omega=2\pi\nu\qquad \hbar\omega=h\nu$$

2-dimensional harmonic oscillator

$$-\frac{\hbar^2}{2m}\left[\frac{d^2\Psi}{dx^2}+\frac{d^2\Psi}{dy^2}\right]+\tfrac{1}{2}k\left(x^2+y^2\right)\Psi=E\Psi$$

$$x=r\cos\varphi \qquad\qquad 0<r<\infty$$

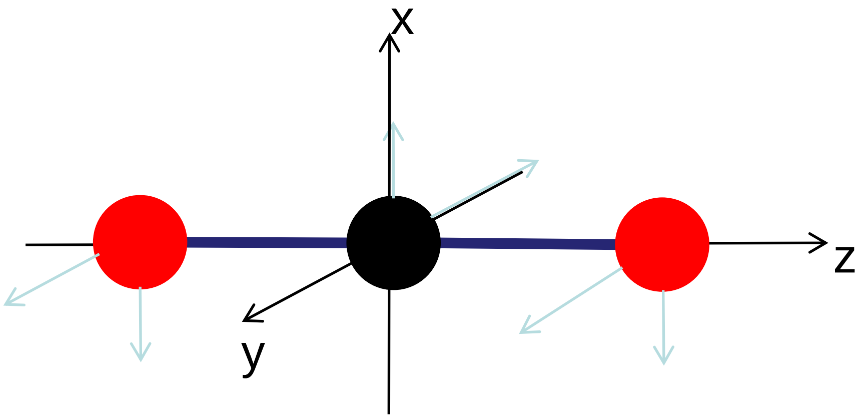
$$y=r\sin\varphi \qquad\qquad 0<\varphi<2\pi$$

$$\Psi_{n,l}(r,\varphi)=N_{n.l}e^{-r^2/2}r^{|l|}\left[L^{|l|}_{(n+|l|)/2}(r)\right]\left[e^{il\varphi}\right]$$

$$E=\hbar\omega(n+1)$$

$$n=0,1,2,\ldots$$

$$l=n,n-2,\ldots,-n+2,-n$$



Vibrations in the Morse potential

Morse potential– closer to a real one than the harmonic potential

takes into account the anharmonicity and dissociation limit

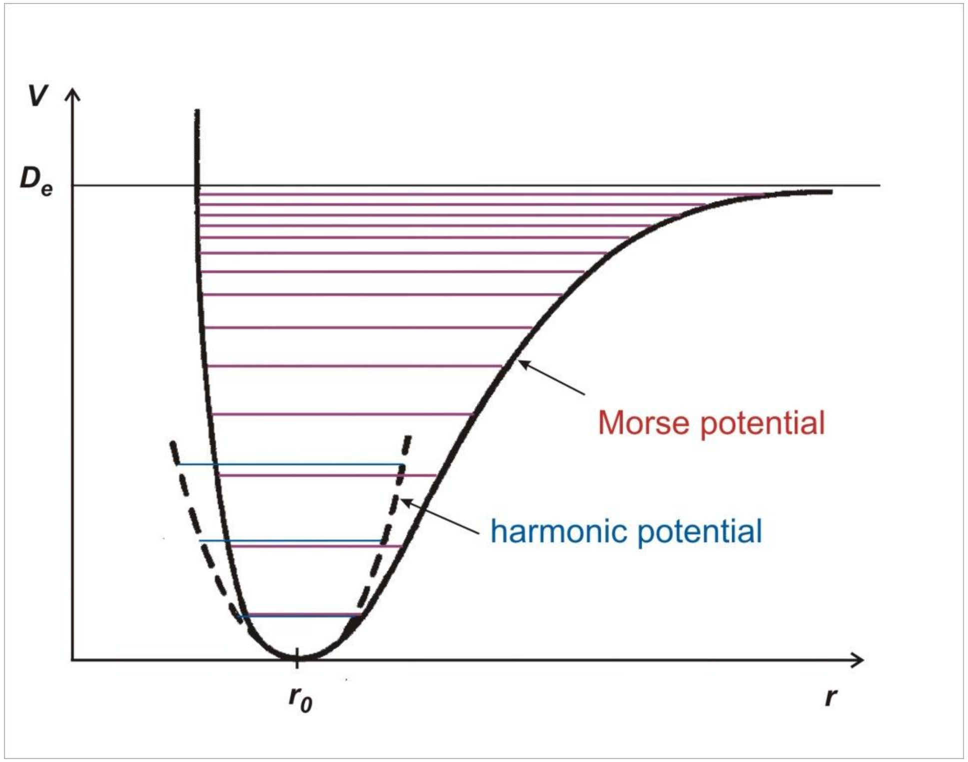
The exact solution of the Schrödingera equation with the Morse potential

$$V(r) = D_e\left[1 - e^{-\alpha(r-r_0)}\right]^2$$

$$\alpha = \left(\frac{k}{2D_e}\right)^{1/2} \qquad k = \left(\frac{\partial^2 V}{\partial r^2}\right)_{r_0}$$

$$E_v = \left(v + \tfrac{1}{2}\right)\hbar\omega - \left(v + \tfrac{1}{2}\right)^2 \hbar\omega x_e$$

$$\boxed{\omega x_e = \frac{\alpha\hbar}{2\mu}}$$



Effective rovibrational Hamiltonian for a diatomic molecule

$$E_{vib-rot}(v,J)=\left(v+\tfrac{1}{2}\right)\hbar\omega-\left(v+\tfrac{1}{2}\right)^{2}\hbar\omega x_{e}+BJ(J+1)-DJ^{2}(J+1)^{2}$$

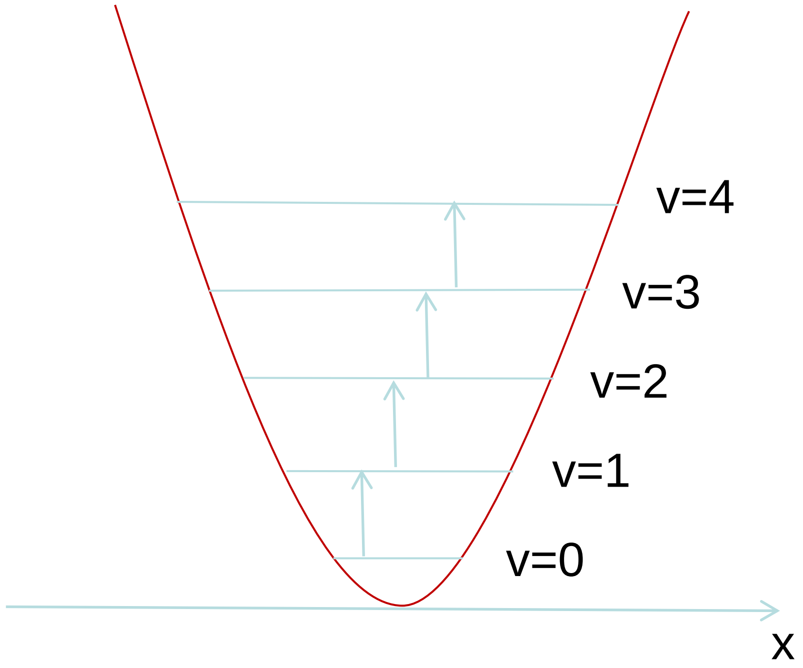
Harmonic term

Anharmonic term

Rigid rotor term

Nonrigid rotor term

Vibrational selection rules



$\Delta v=+1$

Notation for a vibrational transition

$v' \leftarrow v''$

Upper state ← lower state

Fundamental bands

$v' \leftarrow v'' = 1 \leftarrow 0$

Hot bands

$v' \leftarrow v'' = 2 \leftarrow 1$

$v' \leftarrow v'' = 3 \leftarrow 2$

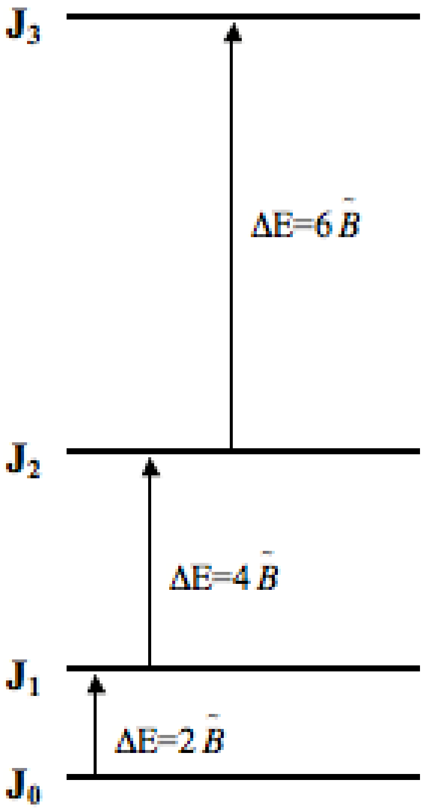
When the potential is anharmonic, allowed transitions $\Delta v=+2, +3$,

Like overtones $v' \leftarrow v'' = 2 \leftarrow 0$

Rotational selection rules

Transitions within a single vibrational state

$\Delta J=+1$

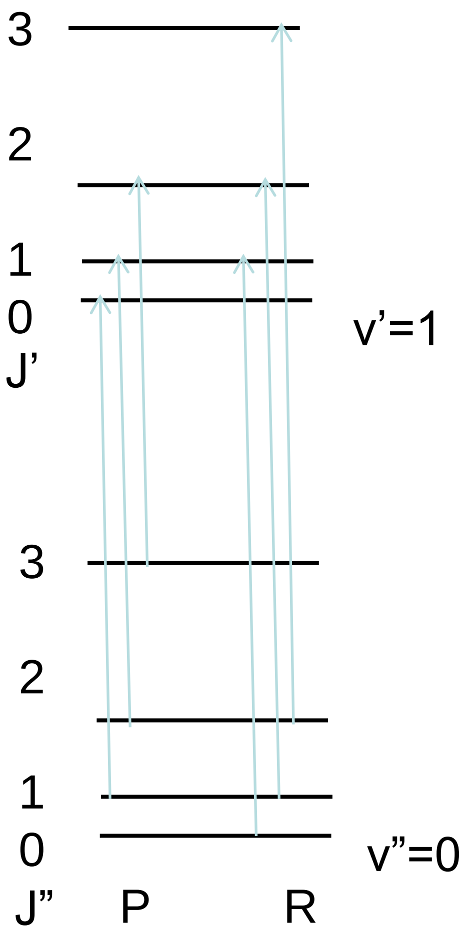


Rovibrational transitions

Δv=+1 ΔJ=±1

$$E_{vib-rot}\left(0,J\right)=\tfrac{1}{2}v_0+B''J(J+1)-D''J^2\left(J+1\right)^2$$

$$E_{vib-rot}\left(1,J\right)=\tfrac{3}{2}v_0+B'J(J+1)-D'J^2\left(J+1\right)^2$$



P branch: Δv=+1 , J-1←J

$$\Delta E=E_{vib-rot}\left(1,J-1\right)-E_{vib-rot}\left(0,J\right)=$$

$$=v_0+B'(J-1)J-D'\left(J-1\right)^2J^2-B''J(J+1)+D''J^2\left(J+1\right)^2=$$

$$=v_0+-\left(B'+B''\right)J+\left(B'-B''-D'+D''\right)J^2+2\left(D'+D''\right)J^3+\ldots$$

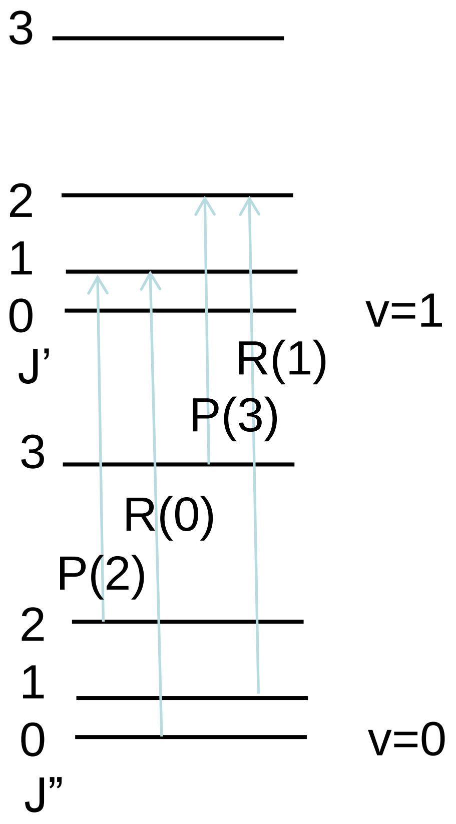
R branch: Δv=+1 , J+1←J

$$\Delta E=E_{vib-rot}\left(1,J+1\right)-E_{vib-rot}\left(0,J\right)=$$

$$=v_0+B'(J+1)\left(J+2\right)-D'\left(J+1\right)^2\left(J+2\right)^2-B''J(J+1)+D''J^2\left(J+1\right)^2=$$

$$=v_0+\left(2B'-4D'\right)\left(J+1\right)+\left(B'-B''-4D'\right)J\left(J+1\right)+\ldots$$

Ground state combination differences (GSCD)



Energy differences E(v,J) in the ground state

$E(0,2)-E(0,0)=R(0)-P(2)$

$E(0,3)-E(0,1)=R(1)-P(3)$

$E(0,4)-E(0,2)=R(2)-P(4)$

...

$E(0,J+2)-E(0,J)=B_0[(J+2)(J+3)-J(J+1)]-$

$-D_0[(J+2)^2(J+3)^2-J^2(J+1)^2]=$

$=R(J)-P(J+2)$

From sufficient number of P i R transitions having common upper levels, the accurate values of B_0 i D_0 constants for the ground state can be determined using a linear regression.

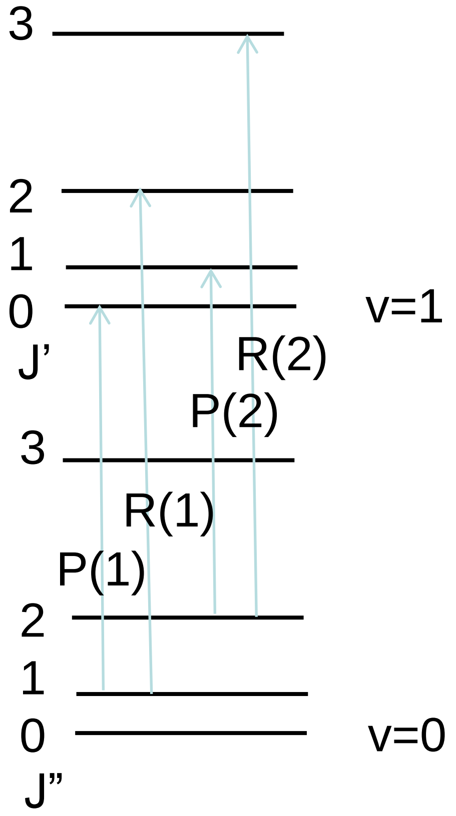
GSCD – example for $^{12}C^{16}O$

P	v'	J'	v"	J"	R	v'	J'	v"	J"	R-P(exp)	obl	(e-o)^2
2135.5473	2	1	1	2	2147.0823	2	1	1	0	11.5350	11.5349	3.53E-09
2131.6326	2	2	1	3	2150.8571	2	2	1	1	19.2245	19.2244	7.74E-09
2127.6832	2	3	1	4	2154.5967	2	3	1	2	26.9135	26.9131	1.23E-07
2123.6999	2	4	1	5	2158.3008	2	4	1	3	34.6009	34.6009	1.52E-09
2119.6819	2	5	1	6	2161.9694	2	5	1	4	42.2875	42.2873	6.16E-08
2115.6301	2	6	1	7	2165.6022	2	6	1	5	49.9721	49.9720	5.07E-09
2111.5442	2	7	1	8	2169.1991	2	7	1	6	57.6549	57.6549	1.44E-12
2107.4244	2	8	1	9	2172.7599	2	8	1	7	65.3355	65.3356	4.67E-09
2103.2709	2	9	1	10	2176.2846	2	9	1	8	73.0137	73.0137	1.93E-09
2099.0838	2	10	1	11	2179.7730	2	10	1	9	80.6892	80.6891	4.58E-09
2094.8635	2	11	1	12	2183.2249	2	11	1	10	88.3614	88.3614	1.6E-09
2090.6098	2	12	1	13	2186.6402	2	12	1	11	96.0304	96.0304	6.92E-10
2086.3231	2	13	1	14	2190.0188	2	13	1	12	103.6957	103.6956	3.61E-09
2082.0034	2	14	1	15	2193.3603	2	14	1	13	111.3569	111.3569	2.04E-09
2077.6508	2	15	1	16	2196.6648	2	15	1	14	119.0140	119.0140	1.37E-11
2073.2656	2	16	1	17	2199.9322	2	16	1	15	126.6666	126.6665	1.01E-08
2068.8479	2	17	1	18	2203.1620	2	17	1	16	134.3141	134.3142	3.86E-09
2064.3980	2	18	1	19	2206.3547	2	18	1	17	141.9567	141.9567	9.85E-11
2059.9158	2	19	1	20	2209.5094	2	19	1	18	149.5936	149.5938	3.62E-08
2055.4015	2	20	1	21	2212.6266	2	20	1	19	157.2251	157.2252	4.77E-09
2050.8552	2	21	1	22	2215.7057	2	21	1	20	164.8505	164.8505	1.11E-09
2046.2770	2	22	1	23	2218.7466	2	22	1	21	172.4696	172.4696	1.1E-10
2041.6677	2	23	1	24	2221.7494	2	23	1	22	180.0817	180.0820	1.19E-07
2037.0262	2	24	1	25	2224.7141	2	24	1	23	187.6879	187.6876	8.75E-08
2032.3539	2	25	1	26	2227.6397	2	25	1	24	195.2858	195.2860	3.1E-08
2027.6500	2	26	1	27	2230.5270	2	26	1	25	202.8770	202.8769	1.79E-08
2022.9153	2	27	1	28	2233.3754	2	27	1	26	210.4601	210.4600	1.41E-08
											∑=	5.46E-07

Call file CO_assign

B0= 1.922527
D0= 6.112E-06

Upper State Combination Differences (USCD)



Energy differences E(v,J) in the upper state:

$E(1,2)-E(1,0)=R(1)-P(1)$

$E(1,3)-E(1,1)=R(2)-P(2)$

$E(1,4)-E(1,2)=R(3)-P(3)$

...

$E(1,J+1)-E(1,J-1)=B_1[(J+1)(J+2)-(J-1)J]-$

$-D_1[(J+1)^2(J+2)^2- (J-1)^2J^2]=$

$=R(J)-P(J)$

From sufficient number of P i R transitions having common lower levels, the accurate values of B_1 i D_1 constants for the upper state can be determined using a linear regression.

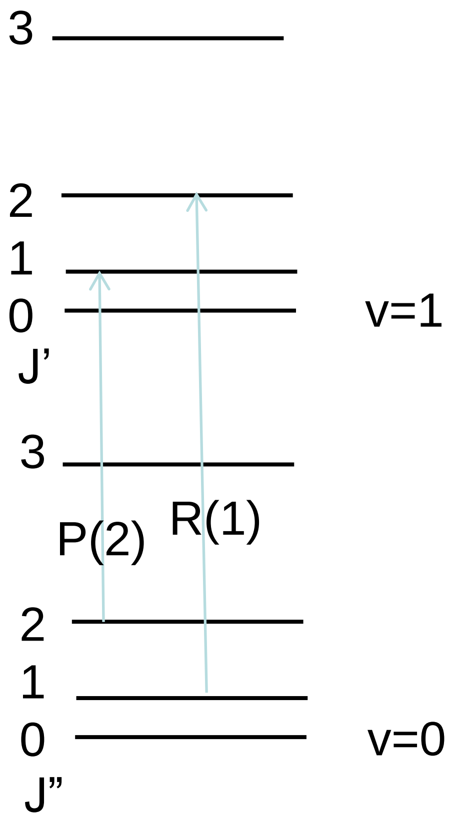
USCD – example for $^{12}C^{16}O$

P	v'	J'	v"	J"	R	v'	J'	v"	J"	R-P(exp)	obl	(e-o)^2
2135.5473	2	1	1	2	2154.5967	2	3	1	2	19.0494	19.0494	1.27E-10
2131.6326	2	2	1	3	2158.3008	2	4	1	3	26.6682	26.6681	6.85E-09
2127.6832	2	3	1	4	2161.9694	2	5	1	4	34.2862	34.2858	1.45E-07
2123.6999	2	4	1	5	2165.6022	2	6	1	5	41.9023	41.9022	1E-08
2119.6819	2	5	1	6	2169.1991	2	7	1	6	49.5172	49.5170	5.41E-08
2115.6301	2	6	1	7	2172.7599	2	8	1	7	57.1298	57.1298	7.55E-10
2111.5442	2	7	1	8	2176.2846	2	9	1	8	64.7404	64.7405	7.57E-09
2107.4244	2	8	1	9	2179.7730	2	10	1	9	72.3486	72.3487	2.75E-09
2103.2709	2	9	1	10	2183.2249	2	11	1	10	79.9540	79.9540	9.24E-10
2099.0838	2	10	1	11	2186.6402	2	12	1	11	87.5564	87.5563	5.26E-09
2094.8635	2	11	1	12	2190.0188	2	13	1	12	95.1553	95.1553	2.48E-09
2090.6098	2	12	1	13	2193.3603	2	14	1	13	102.7505	102.7505	2.75E-11
2086.3231	2	13	1	14	2196.6648	2	15	1	14	110.3417	110.3418	9.82E-09
2082.0034	2	14	1	15	2199.9322	2	16	1	15	117.9288	117.9288	1.47E-09
2077.6508	2	15	1	16	2203.1620	2	17	1	16	125.5112	125.5113	1.68E-08
2073.2656	2	16	1	17	2206.3547	2	18	1	17	133.0891	133.0890	1.45E-08
2068.8479	2	17	1	18	2209.5094	2	19	1	18	140.6615	140.6615	2.85E-11
2064.3980	2	18	1	19	2212.6266	2	20	1	19	148.2286	148.2286	3.43E-10
2059.9158	2	19	1	20	2215.7057	2	21	1	20	155.7899	155.7899	2.17E-09
2055.4015	2	20	1	21	2218.7466	2	22	1	21	163.3451	163.3453	3.87E-08
2050.8552	2	21	1	22	2221.7494	2	23	1	22	170.8942	170.8943	1.91E-08
2046.2770	2	22	1	23	2224.7141	2	24	1	23	178.4371	178.4368	1.04E-07
2041.6677	2	23	1	24	2227.6397	2	25	1	24	185.9720	185.9723	1.04E-07
2037.0262	2	24	1	25	2230.5270	2	26	1	25	193.5008	193.5007	1.49E-08
2032.3539	2	25	1	26	2233.3754	2	27	1	26	201.0215	201.0216	2.61E-09
2027.6500	2	26	1	27	2236.1849	2	28	1	27	208.5349	208.5346	6.31E-08
2022.9153	2	27	1	28	2238.9549	2	29	1	28	216.0396	216.0397	6.02E-09
											∑=	6.33E-07

B1= 1.905024
D1= 6.113E-06

Call file CO_assign

The band centre v_0



The band centre:

$v_0 = P(J) – E(1,J-1) + E(0,J)$

$v_0 = R(J) – E(1,J+1) + E(0,J)$

$v_0 = P(J) – B_1(J-1)J+D_1 (J-1)^2J^2 +B_0J(J+1) -D_0 J^2 (J+1)^2$

$v_0 = R(J) – B_1(J+1)(J+2)+D_1 (J+1)^{2(}J+2)^2 +B_0J(J+1) -D_0 J^2 (J+1)^2$

The average of the calculated band centre for each line in the P and R branches.

v_0 - example for $^{12}C^{16}O$

P	v'	J'	v"	J"	nu
2135.5473	2	1	1	2	2143.2722
2131.6326	2	2	1	3	2143.2721
2127.6832	2	3	1	4	2143.2719
2123.6999	2	4	1	5	2143.2722
2119.6819	2	5	1	6	2143.2720
2115.6301	2	6	1	7	2143.2722
2111.5442	2	7	1	8	2143.2722
2107.4244	2	8	1	9	2143.2722
2103.2709	2	9	1	10	2143.2722
2099.0838	2	10	1	11	2143.2721
2094.8635	2	11	1	12	2143.2722
2090.6098	2	12	1	13	2143.2722
2086.3231	2	13	1	14	2143.2722
2082.0034	2	14	1	15	2143.2722
2077.6508	2	15	1	16	2143.2721
2073.2656	2	16	1	17	2143.2721
2068.8479	2	17	1	18	2143.2720
2064.3980	2	18	1	19	2143.2722
2059.9158	2	19	1	20	2143.2722
2055.4015	2	20	1	21	2143.2723
2050.8552	2	21	1	22	2143.2722
2046.2770	2	22	1	23	2143.2720
2041.6677	2	23	1	24	2143.2724
2037.0262	2	24	1	25	2143.2721
2032.3539	2	25	1	26	2143.2723
2027.6500	2	26	1	27	2143.2721
2022.9153	2	27	1	28	2143.2721

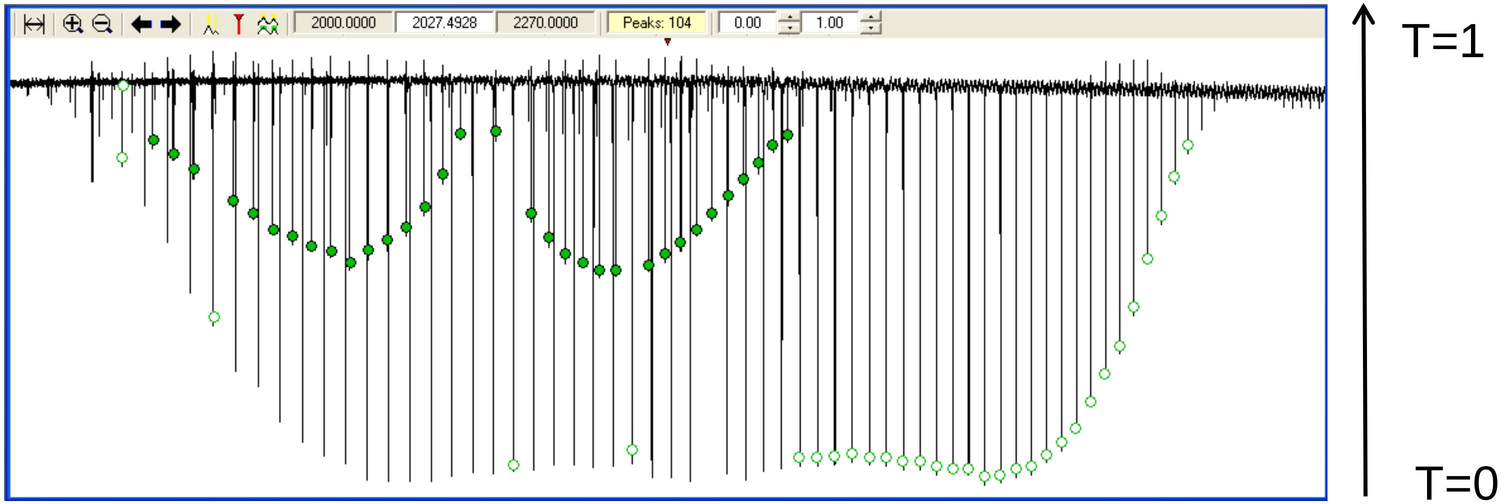
R	v'	J'	v"	J"	nu
2147.0823	2	1	1	0	2143.2723
2150.8571	2	2	1	1	2143.2722
2154.5967	2	3	1	2	2143.2722
2158.3008	2	4	1	3	2143.2722
2161.9694	2	5	1	4	2143.2723
2165.6022	2	6	1	5	2143.2723
2169.1991	2	7	1	6	2143.2722
2172.7599	2	8	1	7	2143.2722
2176.2846	2	9	1	8	2143.2722
2179.7730	2	10	1	9	2143.2722
2183.2249	2	11	1	10	2143.2722
2186.6402	2	12	1	11	2143.2722
2190.0188	2	13	1	12	2143.2723
2193.3603	2	14	1	13	2143.2721
2196.6648	2	15	1	14	2143.2721
2199.9322	2	16	1	15	2143.2722
2203.1620	2	17	1	16	2143.2720
2206.3547	2	18	1	17	2143.2722
2209.5094	2	19	1	18	2143.2720
2212.6266	2	20	1	19	2143.2722
2215.7057	2	21	1	20	2143.2722
2218.7466	2	22	1	21	2143.2721
2221.7494	2	23	1	22	2143.2721
2224.7141	2	24	1	23	2143.2724
2227.6397	2	25	1	24	2143.2721
2230.5270	2	26	1	25	2143.2722
2233.3754	2	27	1	26	2143.2722
2236.1849	2	28	1	27	2143.2723
2238.9549	2	29	1	28	2143.2720
2241.6858	2	30	1	29	2143.2719

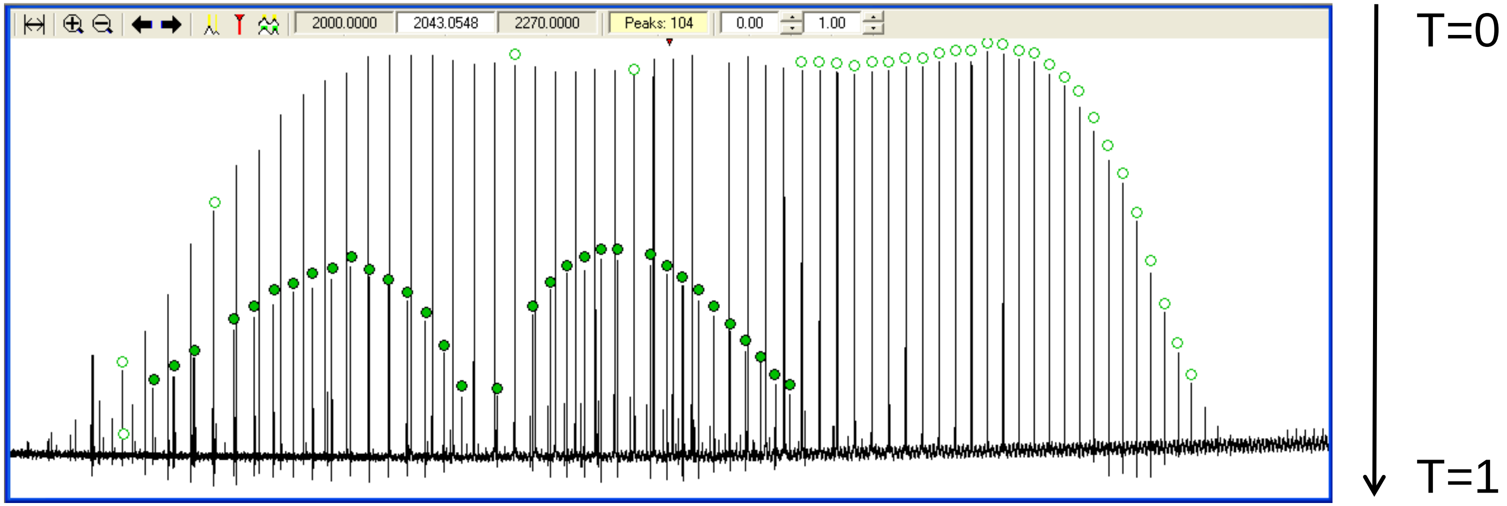
B0= 1.922527
D0= 6.11E-06
B1= 1.905024
D1= 6.11E-06

nu= 2143.2722

wywołaj plik
CO_assign

The spectrum of $^{13}C^{16}O$





The spectrum of $^{13}C^{16}O$

Transmission $T = \frac{I}{I_0}$

I – the intensity of light passing through the sample

I_0 – the initial intensity of light

Absorbance $A = \log\left(\frac{1}{T}\right) = \log\left(\frac{I_0}{I}\right)$

Absorbance determines, how much of the radiation was absorbed:

A=0 no absorbance of the sample T=1

A=∞ total absorbance of the sample T=0

Usually spectrometers use the transmission scale.

The IR spectrum of $^{13}C^{16}O$

The analysis of the P and R branches of $^{13}C^{16}O$ leads to the following results:

B_0 = 1,837964 cm^{-1}
D_0 = 5,575*10^{-6} cm^{-1}

B_1 = 1,821605 cm^{-1}
D_1 = 5,571*10^{-6} cm^{-1}

v_0 = 2096,0680 cm^{-1}

Reminder:

$$B = \frac{\hbar^2}{2\mu R^2} = \frac{\hbar^2}{2I}$$

Thus:

$$\frac{B_0\left[{}^{12}C^{16}O\right]}{B_0\left[{}^{13}C^{16}O\right]} = \frac{I_0\left[{}^{13}C^{16}O\right]}{I_0\left[{}^{12}C^{16}O\right]} = \frac{\mu R_0^2\left[{}^{13}C^{16}O\right]}{\mu R_0^2\left[{}^{12}C^{16}O\right]} = \frac{\mu\left[{}^{13}C^{16}O\right]}{\mu\left[{}^{12}C^{16}O\right]} = \frac{\frac{13*16}{13+16}}{\frac{12*16}{12+16}} = 1,046119$$

The test:

$$\frac{B_0\left[{}^{12}C^{16}O\right]}{B_0\left[{}^{13}C^{16}O\right]} = \frac{1,922527}{1,837964} = 1,046009$$

It is a proof that the weak band can be attributed to $^{13}C^{16}O$.

The intensity of rotational transitions

In the ground vibrational state

$$I_{rot} \approx \left|\vec{\mu}\right|^2 \left(2J+1\right) e^{-\frac{E_{rot}}{kT}}$$

The rovibrational transition from the ground vibrational state

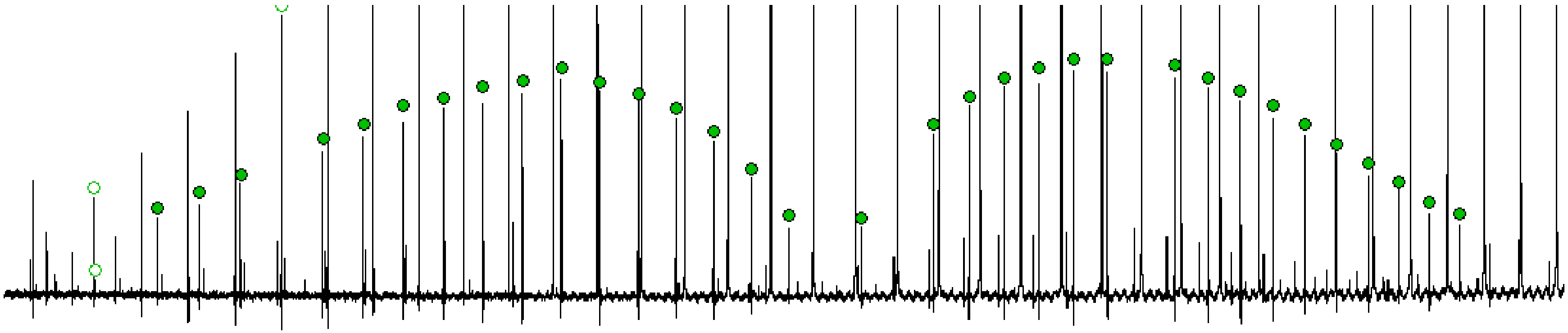
$$I_{wib,rot} \approx \left(P_{v' \leftarrow v''}\right)^2 \left(2J+1\right) e^{-\frac{E_{rot}}{kT}}$$

(2J+1) – degeneracy of the lower state

k = 1.380658E-23 J/deg   (Boltzmana constant)

T – temperature in K

Determination of the rotational temperautre for $^{13}C^{16}O$



P branch

J	E(J)	Int_obl	Int_exp_P	(e-o)^2
0	0	0.052421		
1	3.675905	0.154936	0.211749	0.003228
2	11.02758	0.250642	0.305692	0.00303
3	22.05476	0.335554	0.378366	0.001833
4	36.75704	0.406458	0.43172	0.000638
5	55.13389	0.461109	0.459239	3.5E-06
6	77.18464	0.498335	0.485285	0.00017
7	102.9085	0.518045	0.514058	1.59E-05
8	132.3045	0.521143	0.489271	0.001016
9	165.3716	0.509364	0.479119	0.000915
10	202.1085	0.485063	0.446468	0.00149
11	242.5141	0.450972	0.439332	0.000135
12	286.5867	0.409966	0.399873	0.000102
13	334.3247	0.364839	0.370603	3.32E-05
14	385.7265	0.318137		
15	440.7902	0.272024	0.294809	0.000519
16	499.5136	0.228215	0.259272	0.000965
17	561.8949	0.187949	0.224834	0.00136

Solver:

k=	6.95E-01cm-1/K
T=	**354.81365K**
kT=	246.60924cm-1
N=	0.0524209