Approximation Methods: Time-independent perturbation theory for a non-degenerate level

Rayleigh-Schrodinger perturbation theory:

I- First order (without proof)

$$H = H_0 + \lambda H'$$

$$H_0 \psi_n^0 = E_n^0 \psi_n^0$$

$$\int (\psi_n^0)^* \psi_m^0 d\tau = \delta_{nm}$$

$\lambda H'$ is small enough so that the perturbed energy level E_n is much close to E_n^0

E_n^0 is the unperturbed energy level (we assume to be non - degenerate)

ψ_n^0 is the unperturbed wave function

The problem that we want to solve is

$$H\psi_n = E_n \psi_n$$

The basic idea of the perturbation theory is to assume that both
The eigenvalues and eigenfunctions of H can be expanded in
Powers of the perturbation parameter λ

$$E_n = \sum_{j=0}^{\infty} \lambda^j E_n^j = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

J is the order of the perturbation

put $\lambda = 1$,

$$\boxed{E_n = E_n^0 + \underbrace{E_n^1}_{\text{First order correction}} + \underbrace{E_n^2}_{\text{Second order correction}} + \cdots}$$

$$\psi_n = \sum_{j=0}^{\infty} \lambda^j \psi_n^j = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \cdots$$

put $\lambda = 1$

Second order correction to the wave function

$$\boxed{\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 + \cdots}$$

First order correction to the wave function

First order energies (without proof ☺)

$$\boxed{E_n^1 = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^0 \right\rangle}$$

It says that the first-order correction to the energy is the expectation value Of the perturbation in the unperturbed state.

The above equation is the first-order correction to the energy.

First order wave functions:

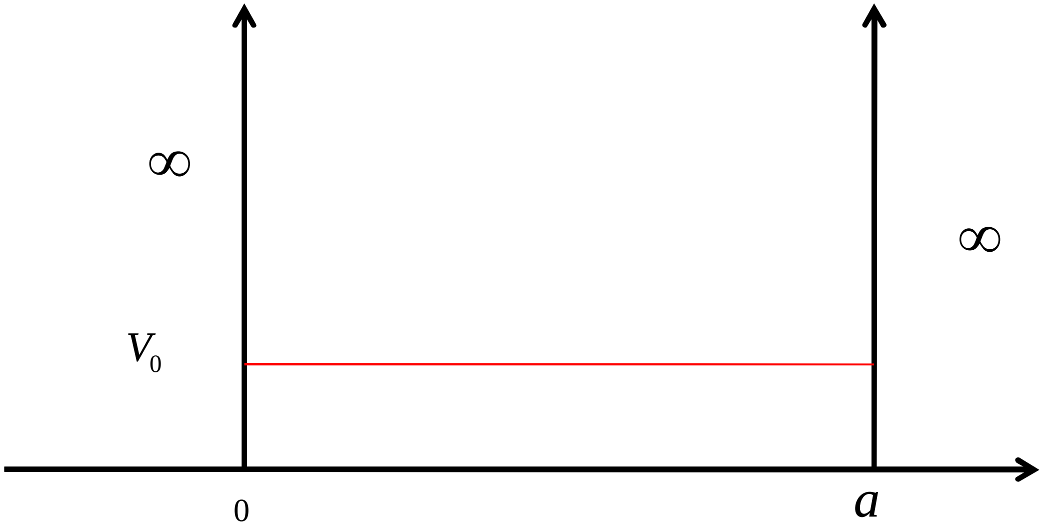
$$\boxed{\psi_n^1 = \sum_{m\neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{\left(E_n^0 - E_m^0\right)} \psi_m^0}$$

The above equation is the first-order correction to the wave function.

Example:

suppose that we perturb the system by simply raising the floor of the well by a constant amount V_0. What is the first-order correction to the energy and wave functions?

$$V_0 << \infty$$



unperturbed wave function for the infinite square well are

$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$

First order correction to the energy levels

$$H' = V_0$$

$$E_n^1 = \left\langle \psi_n^0 \middle| V_0 \middle| \psi_n^0 \right\rangle = \frac{2}{a} V_0 \int_0^a \sin^2\left(\frac{n\pi}{a} x\right) dx = V_0$$

$$E_n = E_n^0 + E_n^1 = \frac{\pi^2 \hbar^2}{2ma^2} n^2 + V_0$$

This means all the energy levels has been shifted up by V0. this means the difference between the energy levels does not changed

First order correction to the wave functions

$$\psi_n^1 = \sum_{m\neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0$$

$$\psi_n^1 = \sum_{m\neq n} \frac{\langle \psi_m^0 | V_0 | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0 = V_0 \sum_{m\neq n} \frac{\langle \psi_m^0 | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0$$

$$= V_0 \sum_{m\neq n} \frac{Zero}{(E_n^0 - E_m^0)} \psi_m^0 = 0$$

This means there is no change in the wave functions

Example

Suppose we put a delta-function bump in the center of the infinite square well:

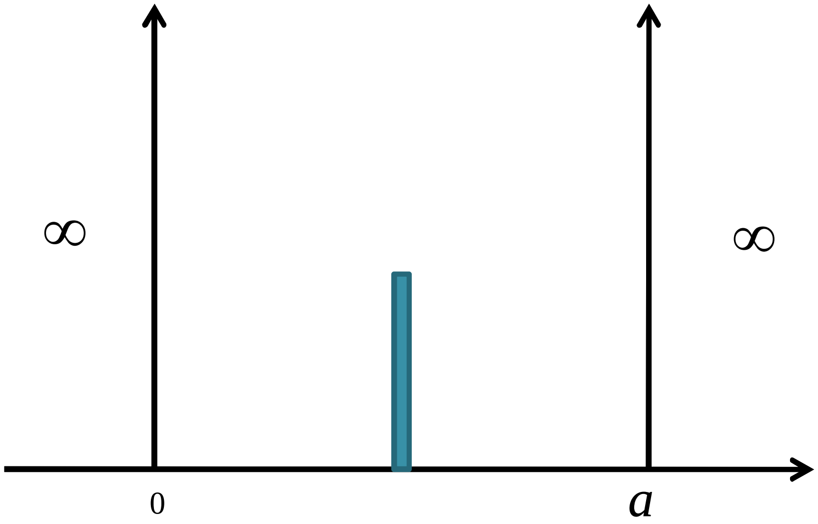
$$H' = \alpha\delta(x - \frac{a}{2})$$

where α is a constant

a)- Find the first-order correction to the allowed energies. Explain why the energies are not perturbed for even n.

The unperturbed wave function for the infinite square well are

$$\psi_n^0(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

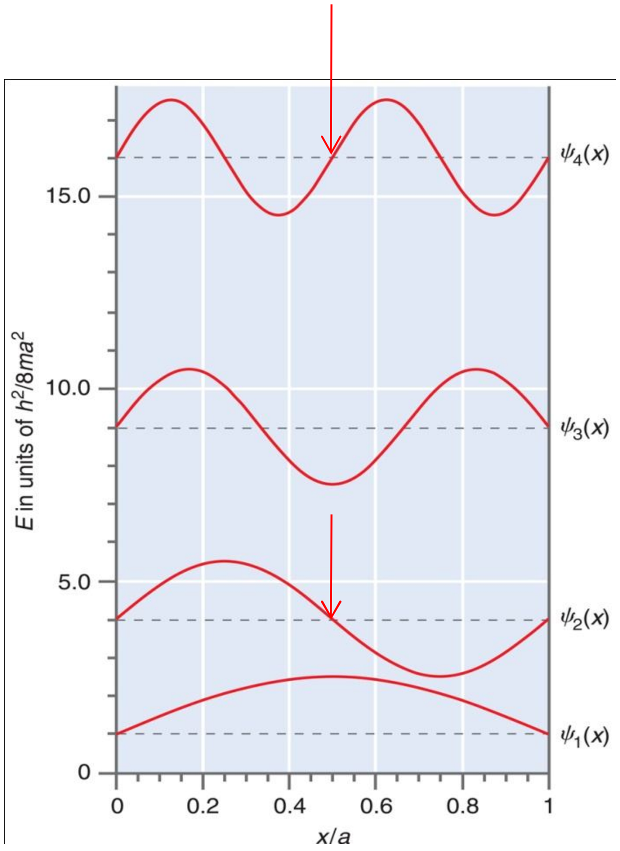


$$H' = \alpha\delta\left(x-\frac{a}{2}\right)$$

$$E_n^1 = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^0 \right\rangle = \frac{2}{a}\alpha\int_0^a \sin^2\left(\frac{n\pi}{a}x\right)\delta\left(x-\frac{a}{2}\right)dx$$

$$= \frac{2\alpha}{a}\sin^2\left(\frac{n\pi}{a}\frac{a}{2}\right) = \frac{2\alpha}{a}\sin^2\left(\frac{n\pi}{2}\right) = \begin{cases} 0 & \text{if n is even} \\ \dfrac{2\alpha}{a} & \text{if n is odd} \end{cases}$$

For even n the wave function is zero at the location of the perturbation ($x = a/2$), so it never feel H'.



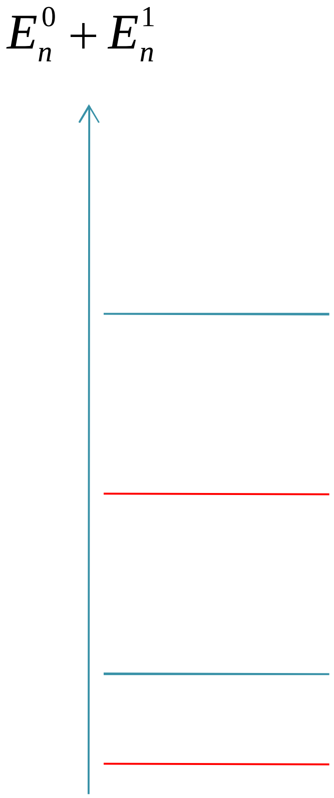
$\alpha = 1$

$a = 1$

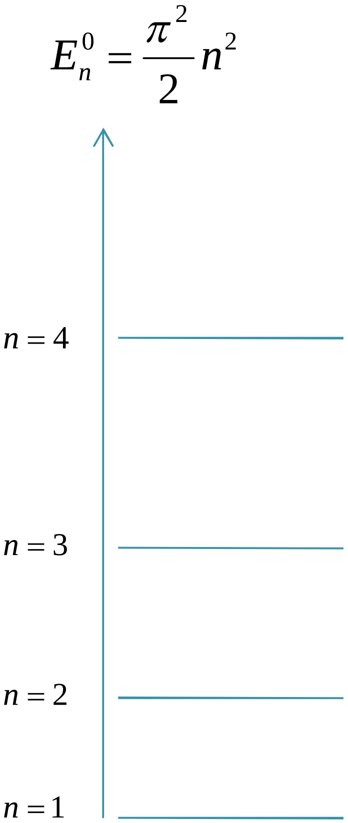
$m = 1$

$\hbar = 1$

$$E_n = E_n^0 + E_n^1 = \boxed{\frac{\pi^2}{2}n^2 + \begin{cases} 0 & \text{if n = even} \\ 2 & \text{if n = odd} \end{cases}}$$



After perturbation



Before perturbation

b)- What is the first order correction to the ground state wave function

$$\psi_1^1 = \sum_{m\neq 1} \frac{\langle \psi_m^0 | H' | \psi_1^0 \rangle}{\left(E_1^0 - E_m^0\right)} \psi_m^0$$

$$\text{Here n} = 1,$$

$$\langle \psi_m^0 | H' | \psi_1^0 \rangle = \frac{2\alpha}{a} \int \sin\left(\frac{m\pi}{a} x\right) \delta\left(x - \frac{a}{2}\right) \sin\left(\frac{\pi}{a} x\right) dx$$

$$= \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{\pi}{2}\right) = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right)$$

This is zero for even m, so the first three nonzero terms will be m=3, m=5, and m=7

$$E_1^0 - E_m^0 = \frac{\pi^2 \hbar^2}{2ma^2}\left(1 - m^2\right)$$

$$
\begin{aligned}
\psi_1^1 &= \sum_{m=3,5,7,\ldots} \frac{(2\alpha / a)\sin(m\pi/2)}{E_1^0 - E_m^0}\psi_m^0 \\
&= \frac{2\alpha}{a}\frac{2ma^2}{\pi^2\hbar^2}\left[\frac{-1}{1-9}\psi_3^0 + \frac{1}{1-25}\psi_5^0 + \frac{-1}{1-49}\psi_7^0 + \cdots\right] \\
&= \frac{4\alpha ma}{\pi^2\hbar^2}\sqrt{\frac{2}{a}}\left[\frac{1}{8}\sin\left(\frac{3\pi}{a}x\right) - \frac{1}{24}\sin\left(\frac{5\pi}{a}x\right) + \frac{1}{48}\sin\left(\frac{7\pi}{a}x\right) + \cdots\right] \\
&= \frac{\alpha m}{\pi^2\hbar^2}\sqrt{\frac{a}{2}}\left[\sin\left(\frac{3\pi}{a}x\right) - \frac{1}{3}\sin\left(\frac{5\pi}{a}x\right) + \frac{1}{6}\sin\left(\frac{7\pi}{a}x\right) + \cdots\right]
\end{aligned}
$$

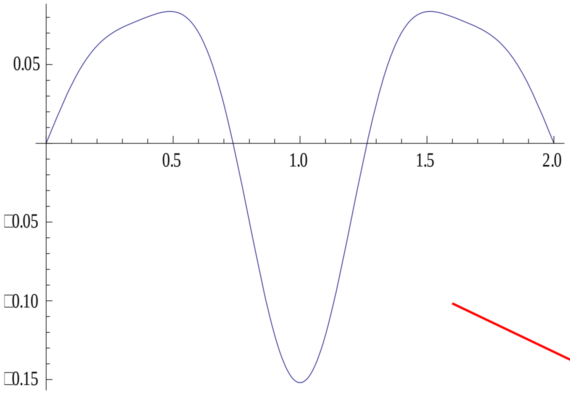
$$\psi_1 = \psi_1^0 + \psi_1^1$$

$m=1$

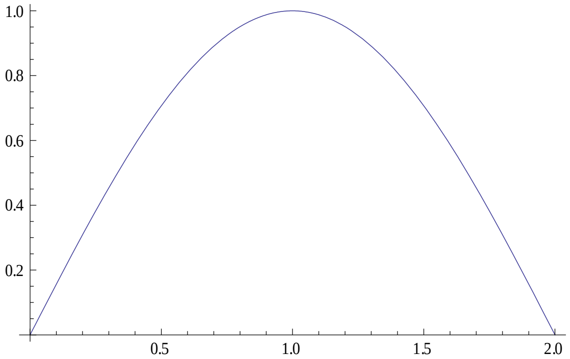
$a=2$

$\hbar=1$

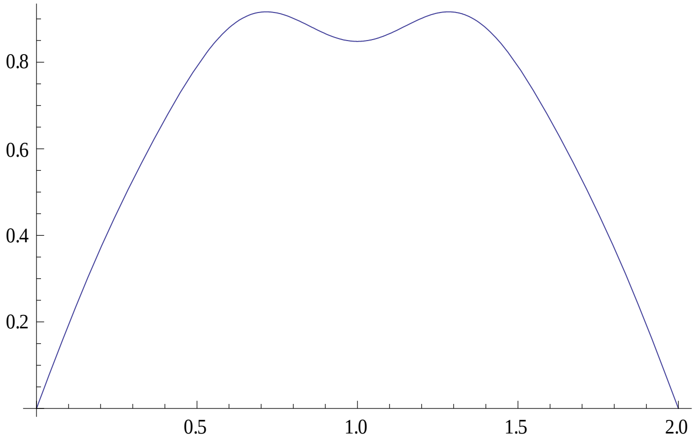
ψ_1^1



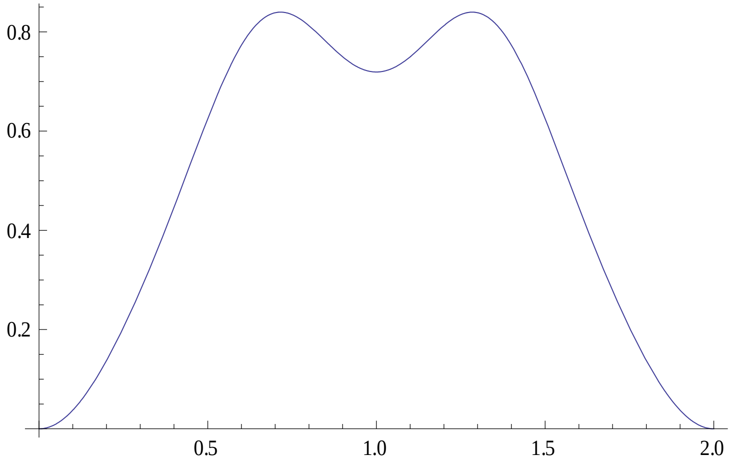
ψ_1^0



$\psi_1=\psi_1^0+\psi_1^1$



$|\psi_1|^2$



Application: Spin-orbit coupling

Little electrodynamics

Imagine the electron in orbit around the nucleus; from the electron's point Of view, the proton is circling around it. This orbiting positive charge sets up A magnetic field B in the electron frame, which exerts a torque on the Spinning electron, tending to align its magnetic moment along the direction Of the field. The (potential energy) Hamiltonian is

Magnetic field due to the moving Proton (in the electron rest frame)

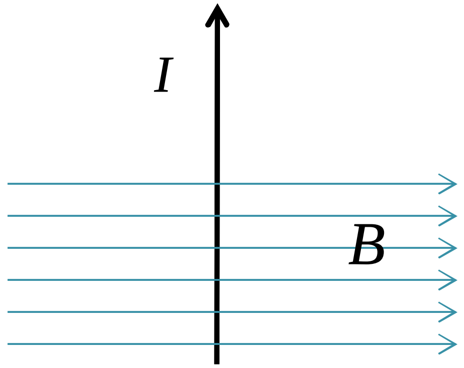
$$\boxed{U = -\vec{\mu}\cdot\vec{B}}$$

Electron magnetic moment

Derivation of the potential energy

Force

$$F = ILB\sin\theta$$

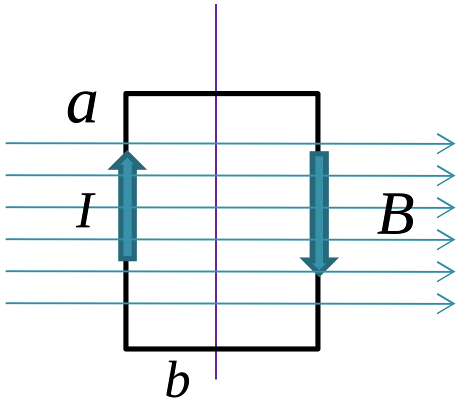


Torque

$$T = F\cdot\frac{b}{2} + F\cdot\frac{b}{2} = Fb$$

$$T = IabB\sin\theta$$

$$T = IAB\sin\theta = \mu B\sin\theta$$



$\mu = IA =$ magnetic dipole moment

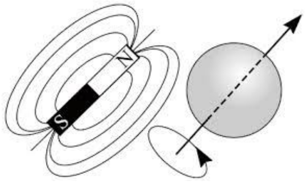
Potential energy

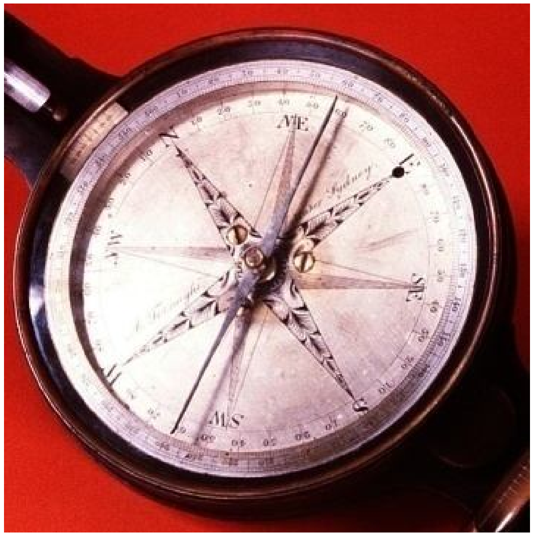
$$U = W = \int T d\theta$$

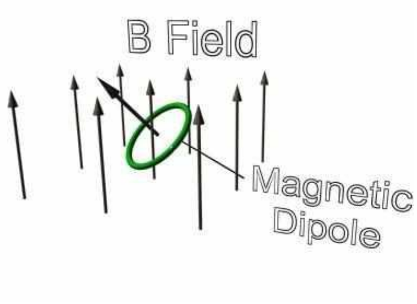
$$U = \mu B \int \sin\theta d\theta$$

$$U = -\mu B \cos\theta = -\mu \cdot B$$

The work require to rotate
The dipole through an angle theta.
Review rotational motion in L4







The magnetic field of the proton:

$$B = \frac{\mu_0 I}{2r}$$

$$B = \frac{e}{4\pi\varepsilon_0}\frac{1}{mc^2}\frac{rmv}{r^3}$$

$$I = \frac{e}{T}\,, \qquad T = \frac{2\pi r}{v}$$

$$I = \frac{ev}{2\pi r}, \qquad \mu_0 = \frac{1}{\varepsilon_0 c^2}$$

The orbital angular momentum of the electron (in the nucleus rest frame)
Is L=rmv.

$$B = \frac{e}{4\pi\varepsilon_0}\frac{1}{mc^2}\frac{\vec{L}}{r^3}$$

Electron orbital
Angular momentum
(in the proton rest frame)

The magnetic dipole moment of a charge q (classical calculation):

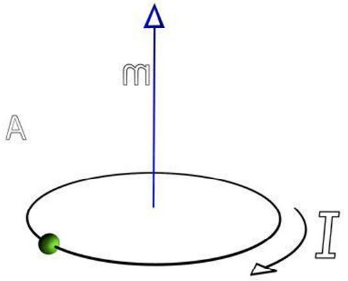
$$\mu = AI = \pi r^2 \frac{q}{T}$$

$$T = 2\pi r / v$$

$$\mu = \frac{q}{2} rv = \frac{q}{2m} mrv$$

$$\mu = \frac{q}{2m} \vec{S}$$

Electron spin



In the above calculation we picture the electron as a spinning sphere.
But this is not the case, so we can not use the above magnetic moment
For the electron. Quantum electrodynamics gives the correct answer that is

$$\boxed{\mu_e = -\frac{e}{m}\vec{S}}$$

The minus sign is due to the electron charge

The extra factor of 2 was explained by Dirac in this relativistic theory of electron

The Spin-Orbit Interaction:

$$U = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{L}\cdot\vec{S}$$

We have done the calculation in the rest frame of the electron, but that is not an inertial frame (it accelerates as the electron orbits around the nucleus). So we have correct this kinematic problem. We introduce kinematic correction, Known as the Thomas precession. In this context it throws in a factor of ½.

$$\boxed{U = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{L}\cdot\vec{S}}$$

The Physical reason for Spin-Orbit interaction

In the Electron’s instantaneous rest frame.
The spin-orbit interaction is due to the torque exerted on the magnetic dipole Moment of the spinning electron, by the magnetic field of the proton.

In the nucleus (proton) rest frme.
Moving magnetic dipole (of the electron) acquires an electric dipole moment.
So, the spin-orbit interaction is due to the interaction of the electric field of the Nucleus with the electric dipole moment of the electron

Of course both of them gives the same results, but the second one need sophisticated Electrodynamics, so we used the first one.
For more information see : Am. J. Phys., 57 (1989) 171.

Return to quantum mechanics

$$H'_{s.o}=\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2r^3}L\cdot S$$

$$E_n^1=\left\langle\psi_n^0\middle|H'_{s.o}\middle|\psi_n^0\right\rangle$$

In the presence of spin-orbit interaction the orbital angular momentum and the spin angular momentum are not separately conserved, i.e they are not constant of motion (they does not commute with H.).The conserved quantities are J^2, J_z, L^2, S^2

$$J^2 = (L+S)\cdot(L+S) = L^2 + S^2 + 2L\cdot S$$

$$L\cdot S = \frac{1}{2}\left[J^2 - L^2 - S^2\right]$$

$$\left[J^2 - L^2 - S^2\right]\psi_{jm_j ls} = \hbar^2\left[j(j+1) - l(l+1) - s(s+1)\right]\psi_{jm_j ls}$$

$$E_n^1 = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{m^2c^2}\frac{\hbar^2\left[j(j+1) - l(l+1) - 3/4\right]}{2}\left\langle\frac{1}{r^3}\right\rangle$$

$$\left\langle\frac{1}{r^3}\right\rangle = \frac{1}{l(l+1/2)(l+1)n^3a^3}$$

a is the Bohr radius

$$E_n^1 = \left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{1}{m^2c^2}\right)\left(\frac{\hbar^2}{2}\right)\frac{1}{n^3a^3}\left\{\frac{\left[j(j+1)-l(l+1)-3/4\right]}{l(l+1/2)(l+1)}\right\}$$

$$E_n^1 = \frac{(E_n^0)^2}{mc^2}\left\{\frac{n\left[j(j+1)-l(l+1)-3/4\right]}{l(l+1/2)(l+1)}\right\}$$

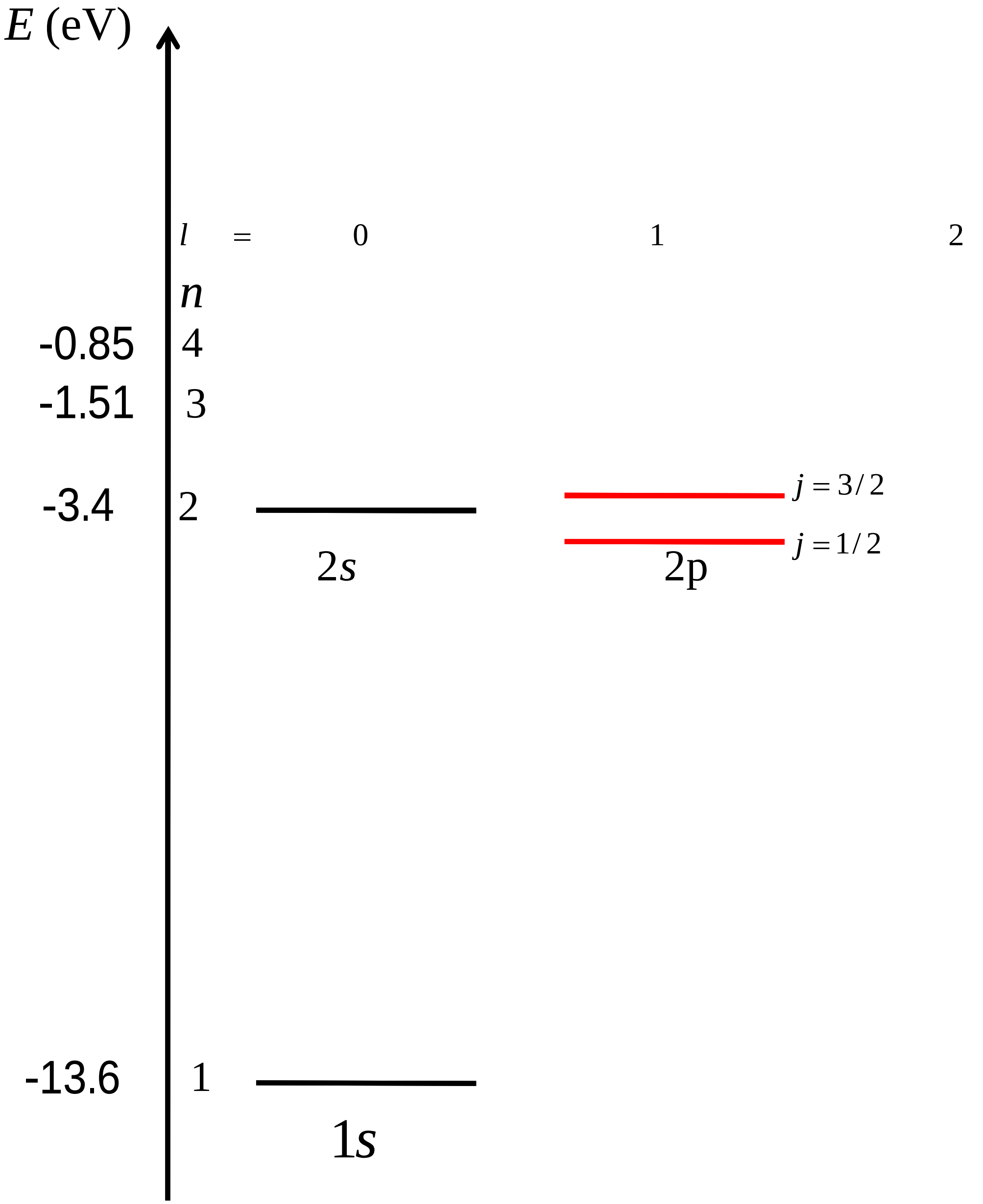
$$E_n = E_n^0 + \frac{(E_n^0)^2}{mc^2}\left\{\frac{n\left[j(j+1)-l(l+1)-3/4\right]}{l(l+1/2)(l+1)}\right\}$$

$$E_n = \frac{-13.6}{n^2} + \left(\frac{-13.6}{n^2}\right)^2 \frac{1}{0.5\times10^6}\left\{\frac{n\left[j(j+1)-l(l+1)-3/4\right]}{l(l+1/2)(l+1)}\right\}$$

$n = 2$

$l = 1$

$$E = -3.4 + 2.3\times10^{-5}\begin{cases} 2/3 & j = 3/2 \\ -4/3 & j = 1/2 \end{cases}$$


E (eV)
l = 0 1 2
n
-0.85 4
-1.51 3
-3.4 2
-13.6 1
$j = 3/2$
$j = 1/2$
$2s$
2p
$1s$