$~~c_1 x + c_2 = 0~~$

$~~c_1 + c~~$

$C_n + C$

Pertubation theory

Variation theory → for ground state

pert. → for sto sta.

$\hat{H}\psi_n = E_n \psi_n$

$\hat{H}^{\circ}\psi_n^{\circ} = E_n^{(0)}\psi_n^{(0)}$

different → pertubation b/w two hamiltonian.

$\hat{H}' = \hat{H} - \hat{H}^{\circ}$

---

when $\lambda = 0$
pertabation is not added.

when $\lambda = 1$
petab. present.

(limit 0 to 1 → gradually)

$\hat{H} = \hat{H}^{\circ} + \lambda \hat{H}'$

we look at <u>nondegenerate level.</u>

$$\hat{H}\psi_n = (\hat{H}^{\circ} + \lambda \hat{H}')\psi_n = E_n\psi_n$$

$$= \left(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots + \lambda^k\psi_n^{(k)} \dots\right)$$

$$\left(E_n^{\circ}\right) + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \lambda^k E_n^{(k)} +$$

$$= (\hat{H}^{\circ} + \lambda \hat{H}')(\psi_n^{\circ})$$

↓ derivation.

First order correction to Energy,

$$E_n^{(1)} = \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} \, d\tau$$

$$\boxed{\text{ex: } E_n = \underbrace{E_n^{(0)}}_{\text{without pert. we know this}} + \lambda \underbrace{E_n^{(1)}}_{\text{this should calculate.}}}$$

$$\underbrace{E_n}_{\text{Energy of pert. system.}} = E_n^{(0)} + \int \psi_n^{(0)*} \hat{H}' \psi_n^{(0)} \, d\tau.$$

<u>wave function of pert. system with first-order correction</u>

when $\lambda = 1$

$$\psi_n = \psi_n^{(0)} + \underbrace{\left[\sum_{m \neq n} \left(\frac{\int \psi_m^{(0)*} \hat{H}' \psi_n^{(0)} \, d\tau}{E_n^{(0)} - E_m^{(0)}} \right) \psi_m^{(0)} \right]}_{\text{first order correction to the wave function. } \psi_n^{(1)}}$$

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \dots$$

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ercise

lculate the first order correction to the ground state
ergy of the following Hamiltonian for the 1-D anh. Oscillator.

$$\hat{H} = -\hbar^2/2m \; d^2/dx^2 + 1/2\, kx^2 + cx^4$$

$$\psi_0 = (\beta/\pi)^{1/4} e^{-\beta x^2/2}$$

Hint $\int_0^\infty x^{2n} e^{-bx^2} dx$.

$$\frac{n^2 h^2}{8ml^2} = E_n^{(0)}$$

$$= \frac{1 \ldots 3 \ldots \overset{5}{\cancel{8}} \ldots (2n-1)}{\cancel{2} \; 2^{n+1}} \left(\frac{\pi}{b^{2n+1}}\right)^{1/2}.$$

$$e^{-\beta x^2/2}$$

$$e^x = e^x.$$

$$e^{-1/2 \cdot \beta x^2}$$

$$\boxed{-1/2 \cdot e^{-\beta x^2/2} \cdot \beta 2x}$$

$$\hat{H}' = \hat{H} - \hat{H}^0$$

$$= -\frac{\hbar^2}{2m} d^2/dx^2 + 1/2\, kx^2 + cx^4 -$$

$$\hat{H}^0 \psi_n^0 = E_n^{(0)} \psi_n^{(0)}$$

$$\hat{H}^0 = \cancel{\frac{n^2 h^2}{8ml^2}}$$

$$1/2\, \beta^2$$

$$\boxed{1/2\, \beta . 2x}$$

$$(n+1/2)h\nu.$$

$$e^{-\beta x^2/2}$$

$$(n+1/2)h\nu.$$

$$\hat{H}' = cx^4$$

$$(\beta/\pi)^{1/2} c \int_{-\infty}^{+\infty} x^4 e^{-\beta x^2} dx.$$

$n = 2$
$b = \beta$

$$\int^{+\infty} (\beta/\pi)^{1/4} e^{-\beta x^2/2} \, cx^4 \, (\beta/\pi)^{1/4} e^{-\beta x^2/2} dx.$$

K-E β l-n

Other case:

$$\frac{1\times 3}{2^3}\left(\frac{\pi}{\beta 5}\right)^{1/2}$$

$$(\beta/\pi)^{1/2}\, c\times 2\times 3/8\,(\pi/\beta 5)^{1/2} = (\beta/\pi)^{1/2} c\left(\frac{3}{4\beta^2}\right)\left(\frac{\pi}{\beta}\right)$$

$$= \frac{3c}{4\beta^2}$$

24/23

past pp

$$l = \sqrt{\frac{mb}{\hbar}}$$

Atomic units

$$E_n = \frac{1}{2}\hbar\omega + \frac{3c}{4\beta^2}$$

$$\hat{H} = \frac{-\hbar^2}{2m_e}\nabla^2 + \left(\frac{-e^2}{4\pi\varepsilon_0 r}\right)$$

SI units

Quantity	SI units	Atomic units.
Mass	kg	electron mass = 1 (m_e). $(9.11\times 10^{-31}$ kg)
Charge	C	proton charge = 1 - (e) $(1.602\times 10^{-19}$ C)
energy	J	1 Hartree = 27.21 eV $= 4.36\times 10^{-18}$ J
Angular momentum	$kg^2 m^2 s^{-1}$	$\hbar = 1$
permittivity	$C^2 N^{-1} m^{-2}$	$4\pi\varepsilon_0 = 1$
		Bohr radius $a_0 = 1$

$$\frac{-(1)^2}{2\cdot(1)}\nabla^2 - \frac{(1)^2}{1\times r} = \frac{1}{2}\nabla^2 - \frac{1}{r}$$

Eigen values of $\hat{L}_z = m_l \hbar$ Splitting.

$\hat{S}_z \Rightarrow m_s \hbar$ $\boxed{\begin{matrix} \frac{1}{2}\hbar \\ -\frac{1}{2}\hbar \end{matrix}}$

$m_s = -s, -s+1, \ldots +s.$

spin quantum number.

$-\frac{1}{2}$ $+\frac{1}{2}.$

For electron $\hat{S}^2$

$s(s+1)\hbar^2$

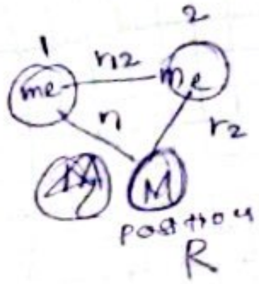
$\frac{1}{2}(\frac{1}{2}+1)\hbar^2$

$= \frac{3}{4}\hbar^2$

E ($c_1 + c_2 \, 2 * n$ ... $= 0$

-S cm' g.s H atom:

$$= \frac{-e^2}{8\pi\varepsilon_0 a_0} = \frac{-(1)^2}{2(1)(1)} = \underline{\underline{-1/2}}$$



Multi electrons : He

M: mass of the nucleus

∇^2: lap operator. for nucleus.

∇_1^2 / ∇_2^2 : for 2 electron.

3 elec + 3 p.t.

$$\cancel{= \frac{-\hbar^2}{2m_e}\nabla_1^2 + \frac{-\hbar^2}{}}$$

$$= \left[\frac{-\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) + \frac{-\hbar^2}{2M}\nabla^2\right]\psi_{(R,r_1,r_2)} + \left(\left[\frac{-e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right] + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi_{(R,r_1,r_2)}$$

$$= E\psi_{(R,r_1,r_2)}$$

$M \gg m_e$.

∴ ignore the motion of nucleus.

with Born-Opp. approximation

$$\cancel{\frac{-(1)^2}{2(1)}}$$

$$\left(\underbrace{\frac{-\hbar^2}{2m_e}\nabla_1^2}_{H(1)} - \underbrace{\frac{\hbar^2}{2m_e}\nabla_2^2}_{H(2)}\right)\psi + \left(\underbrace{\frac{-2e^2}{4\pi\varepsilon_0 r_1}}_{H(1)} - \underbrace{\frac{2e^2}{4\pi\varepsilon_0 r_2}}_{H(2)} + \frac{e^2}{4\pi\varepsilon_0 (r_{12})}\right)\psi$$

$$= \left(\frac{-(1)^2}{2(1)}\nabla_1^2 - \frac{(1)^2}{2(1)}\right) + \left(\frac{-2(1)^2}{(1)r_1} - \frac{2(1)^2}{(1)(r_2)} + \frac{(1)2}{(1)r_{12}}\right)$$

$$= \frac{-1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \left(\frac{-2}{r_1} - \frac{-2}{r_2} + \frac{2}{r_{12}}\right) \text{ at. units}$$

-C_2 ≈ -c x

$| m \ \ - E | = 0.$

$\hat{H}_H(1) + \hat{H}_H(2) + \dfrac{e^2}{4\pi\varepsilon_0 r_{12}}$ ∴ have to use approximation method

H

H_1

~~Spin angular momentum~~

Electron spin → Spin angular momentum.

e.g. E^n spin around axis which doesn't have physical observables

$$\hat{L}^2 = \hat{L}_x^2 + L_y^2 + \hat{L}_z^2$$

$$\hat{S}^2 = \hat{S}_x^2 + S_y^2 + \hat{S}_z^2$$

total spin angular mom. operator

$[\hat{L_x}, \hat{L_y}] = i\hbar \hat{L_z}$ $\qquad$ $[\hat{S_x}, \hat{S_y}] = i\hbar \hat{S}_z$

$[\hat{L_y}, \hat{L_z}] = i\hbar \hat{L_x}$ $\qquad$ $[\hat{S_y}, \hat{S_z}] = i\hbar \hat{S}_x$

$[\hat{L_z}, \hat{L_x}] = i\hbar \hat{L_y}$ $\qquad$ $[\hat{S_z}, \hat{S_x}] = i\hbar \hat{S}_y$

$$[\hat{L}^2, \hat{L_x}] = [\hat{L}^2, \hat{L_y}] = [\hat{L}^2, \hat{L_z}] = 0$$

$$[\hat{S}^2, \hat{S}_x] = [\hat{S}^2, \hat{S}_y] = [\hat{S}^2, \hat{S_z}] = 0.$$

$\hat{L}^2$ eigen value → have to remember.

$l(l+1)\hbar^2$

eigen val. of $\hat{S}^2$: $s(s+1)\hbar^2$

$s = 0, 1/2, 1, 3/2, \ldots$