Tuesday, January 22, 2013

Improvements to the basic hydrogen atom Hamiltonian

Basic hydrogen Hamiltonian : $H_0 = \frac{P^2}{2\mu} - \frac{e^2}{r}$; $\mu \sim m_e$

↳ it works fairly well at first glance : { predicts the basic hydrogen spectrum; $E_I = 13.6\,eV$

A. Relativistic Energy

$$E_{rel}^2 = m_e^2 c^4 + \vec{P}_{rel}^2 c^2 \Rightarrow E_{rel} = \pm c\underbrace{\sqrt{\vec{P}_{rel}^2 + m_e^2 c^2}} \stackrel{?}{=} H_{rel}$$

Taylor expand

$$\Rightarrow H_{rel\,\text{hydrogen}} = m_e c^2 + \frac{P_{rel}^2}{2m_e} - \frac{P_{rel}^4}{8m_e^3 c^2} + \cdots - \frac{e^2}{R}$$

$$= m_e c^2 + H_0 - \frac{P_{rel}^4}{8m_e^3 c^2} + \cdots$$

4^{th} order ~~deriv~~ differential equation

B. Hydrogen with ~~Including~~ Spin

~~Exact~~ Spin-orbit coupling:

(interaction of e^- spin with $\vec{B}$ in the frame of e^-)

fine structure term : $H_{LS} = \frac{1}{2}\frac{e^2}{m_e^2 c^2}\frac{1}{R^3}\underbrace{\vec{L}\cdot\vec{S}}$

mixes spatial and spin parts of ~~Ham~~ wavefunction (Hamiltonian

↳ $H = H_0 + H_{LS}$

Hyperfine interaction : including the spin $\vec{I}$ of the nucleus

$$H_{HF} = \alpha\,\vec{L}\cdot\vec{I} + \beta\frac{1}{R^3}\underbrace{\left[3(\vec{S}\cdot\hat{r})(\vec{I}\cdot\hat{r}) - \vec{S}\cdot\vec{I}\right]}$$

nuclear spin-orbit

magnetic dipole-dipole interaction between $\vec{I}$ & $\vec{S}$

$$+ \gamma\,\vec{I}\cdot\vec{S}\,\delta(\vec{R})$$

e^- spin interacts with $\vec{B}$-field magnetic moment inside nucleus → contact term ~~for $\vec{I}\cdots\vec{S}$ interaction~~

Interaction of an atom with an $\vec{E}$ or $\vec{B}$ field:

$\cancel{H = \frac{P^2}{2\mu} - \frac{e^2}{R}}$ Canonical momentum changes:

$$\vec{P} \longrightarrow \vec{P} - q\vec{A}$$

$\vec{A}$ = vector potential

So we have

$$H_0 \rightarrow H = \frac{(\vec{P} - q\vec{A})^2}{2\mu} - \frac{e^2}{R}$$

DC $\vec{E}$-field : $H = H_0 - q\,\vec{E}\cdot\vec{R}$

DC $\vec{B}$-field : $H = H_0 + \beta\,\vec{B}\cdot(\vec{L} + 2\vec{S}) + \gamma\,\vec{B}\cdot\vec{I}$

Conclusion: Improving on our hydrogen atom generally requires adding "small" terms to the basic Hamiltonian

perturbations

(I) Time-Independent Perturbation Theory

Non-degenerate case

We consider a generic Hamiltonian H_0 with eigenbasis $\{|\varphi_1\rangle, |\varphi_2\rangle, \ldots, |\varphi_n\rangle\}$ and distinct eigenvalues $E_1, E_2, \ldots, E_n$.

Thus in the eigen basis:

$$H_0 = \begin{array}{c c} & \begin{array}{cccc} |\varphi_1\rangle & |\varphi_2\rangle & \cdots & |\varphi_n\rangle \end{array} \\ \begin{array}{c} \langle\varphi_1| \\ \langle\varphi_2| \\ \vdots \\ \langle\varphi_n| \end{array} & \begin{bmatrix} E_1 & & & 0 \\ & E_2 & & \\ & & \ddots & \\ 0 & & & E_n \end{bmatrix} \end{array}$$

$\Rightarrow$ no level crossing ...

Next we add a perturbing term to H_0 ; $W = \lambda \hat{W}$
with $\lambda \ll 1$ and $\langle \varphi_i | W | \varphi_j \rangle \ll E_m - E_n$

matrix elements of W are much smaller than energies (energy differences) of H_0.

then the Hamiltonian is

$$H = H_0 + W = H_0 + \lambda \hat{W}$$

Matrix elements of $\hat{W}$ are of the order $E_i - E_j$.

objective: obtain approximate corrections to E_i and $|\varphi_i\rangle$ due to W to a given order in λ.

We want to solve:

$$H(\lambda)\,|\psi(\lambda)\rangle = E(\lambda)\,|\psi(\lambda)\rangle$$

(time-independent Schrodinger eq.)

we start by assuming that we can write a series solution

$$E(\lambda) = \varepsilon_0 + \lambda \varepsilon_1 + \dots + \lambda^n \varepsilon_n + \dots$$

$\{E_i\}$

$$|\psi(\lambda)\rangle = |0\rangle + \lambda|1\rangle + \dots + \lambda^n|n\rangle + \dots$$

$\{|\varphi_i\rangle\}$

our objective is to get expressions for $\begin{cases} \lambda\varepsilon_1, \lambda^2\varepsilon_2, \dots \\ \lambda|1\rangle, \lambda^2|2\rangle, \dots \end{cases}$

Plug assumptions into Schrodinger Eq.

$$\left(H_0 + \lambda\hat{W}\right)\left(\sum_{n=0}^{\infty} \lambda^n |n\rangle\right) = \left(\sum_{m=0}^{\infty} \lambda^m \varepsilon_m\right)\left(\sum_{n=0}^{\infty} \lambda^n |n\rangle\right)$$

$$\Leftrightarrow \quad H_0|0\rangle + \lambda\left(H_0|1\rangle + \hat{W}|0\rangle\right) + \lambda^2\left(H_0|2\rangle + \hat{W}|1\rangle\right) + \dots = \varepsilon_0|0\rangle + \lambda\left(\varepsilon_1|0\rangle + \varepsilon_0|1\rangle\right) + \lambda^2\left(\varepsilon_2|0\rangle + \varepsilon_1|1\rangle + \varepsilon_0|2\rangle\right) + \dots$$

We require that the expanded schrodinger eq. hold for arbitrary but small λ, so ~~the~~ the terms of a given order must ~~match~~ be matched

λ^0: $H_0|0\rangle = \varepsilon_0|0\rangle$

original equation for which we know the solution $\begin{cases}\varepsilon_0 = \{E_i\} \\ |0\rangle = \{|\varphi_i\rangle\}\end{cases}$

thus $\begin{cases}|0\rangle = |\varphi_j\rangle \\ \varepsilon_0 = E_j\end{cases}$

λ^1: $H_0|1\rangle + \hat{W}|0\rangle = \varepsilon_1|0\rangle + \varepsilon_0|1\rangle$

λ^2: $H_0|2\rangle + \hat{W}|1\rangle = \varepsilon_2|0\rangle + \varepsilon_1|1\rangle + \varepsilon_0|2\rangle$

1st order perturbation theory:

apply $\langle\varphi_j|$

$$\lambda^1: \underbrace{\langle\varphi_j|H_0|1\rangle}_{\cancel{E_j\langle\varphi_j|1\rangle}} + \langle\varphi_j|\hat{W}|\varphi_j\rangle = \varepsilon_1\overset{1}{\cancel{\langle\varphi_j|\varphi_j\rangle}} + \cancel{\langle\varphi_j|1\rangle E_j}$$

~~we require~~

$$\Longrightarrow \varepsilon_1 = \langle\varphi_j|\hat{W}|\varphi_j\rangle \iff \lambda^1\varepsilon_1 = \langle\varphi_j|W|\varphi_j\rangle$$

thus to 1st order (energy correction) $\boxed{E_j(\lambda) = E_j' = E_j + \langle\varphi_j|W|\varphi_j\rangle}$

However, we can also apply $\langle\varphi_i|$ (with $i \neq j$) to the λ^1 equation

$$\underbrace{\langle\varphi_i|H_0|1\rangle}_{E_i\langle\varphi_i|} + \langle\varphi_i|\hat{W}|\varphi_j\rangle = \varepsilon_1\underbrace{\cancel{\langle\varphi_i|\varphi_j\rangle}}_{0} + E_j\langle\varphi_i|1\rangle$$

$$\Rightarrow E_i \langle \varphi_i | 1 \rangle + \langle \varphi_i | \hat{W} | \varphi_j \rangle = E_j \langle \varphi_i | 1 \rangle$$

$$\Leftrightarrow \langle \varphi_i | 1 \rangle = \frac{\langle \varphi_i | \hat{W} | \varphi_j \rangle}{E_j - E_i}$$

if we require that at 1st order $|\psi(\lambda)\rangle$ ~~$= |0\rangle + \lambda |1\rangle$~~ be normalized and pick its overall phase such that $\langle 0 | \psi(\lambda)\rangle$ is real then

$$1 = \langle \psi(\lambda) | \psi(\lambda) \rangle = (\langle 0| + \lambda \langle 1|)(|0\rangle + \lambda |1\rangle)$$
$$= \langle \varphi_j | \varphi_j \rangle + \lambda (\langle 1 | \varphi_j \rangle + \langle \varphi_j | 1 \rangle) + \mathcal{O}(\lambda^2)$$
$$= 1 + 2\lambda \langle 1 | \varphi_j \rangle + \mathcal{O}(\lambda^2)$$

$$\Rightarrow \langle 1 | \varphi_j \rangle = \langle \varphi_j | 1 \rangle = 0$$

$\langle \varphi_j | 1 \rangle = 0$

thus

$$\lambda |1\rangle = \sum_n \lambda |\varphi_n\rangle \langle \varphi_n | 1 \rangle = \sum_{i \neq j} \lambda \langle \varphi_i | 1 \rangle |\varphi_i\rangle$$

$$= \sum_{i \neq j} \frac{\langle \varphi_i | \lambda \hat{W} | \varphi_j \rangle}{E_j - E_i} |\varphi_i\rangle$$

1st order correction to eigenstate:

$$\boxed{\Rightarrow |\psi\rangle = |\psi_j'\rangle = |\varphi_j\rangle + \sum_{i \neq j} \frac{\langle \varphi_i | W | \varphi_j \rangle}{E_j - E_i} |\varphi_i\rangle}$$

↳ must be re-normalized (only normalized to λ^1) not λ^2 or higher

2^{nd} order perturbation theory

we apply $\langle\varphi_j|$ to λ^2 equation

$$\underbrace{\langle\varphi_j|\cancel{\lambda^2}H_0|2\rangle}_{\cancel{E_j\langle\varphi_j|2\rangle}} + \langle\varphi_j|\cancel{\lambda}\hat{W}|1\rangle = \cancel{\lambda^2}\varepsilon_2\overset{1}{\cancel{\langle\varphi_j|\varphi_j\rangle}} + \cancel{\lambda}\varepsilon_1\overset{0}{\cancel{\langle\varphi_j|1\rangle}} + \cancel{\lambda^2}\cancel{E_j\langle\varphi_j|2\rangle}$$

$$\Rightarrow \cancel{\lambda}\varepsilon_2 = \langle\varphi_j|\cancel{\lambda}\hat{w}|1\rangle$$

$$\Leftrightarrow \cancel{\lambda}\varepsilon_2 = \langle\varphi_j|\hat{w}\cancel{\lambda}\left(\sum_{i\neq j}\frac{\langle\varphi_i|\hat{w}|\varphi_j\rangle|\varphi_i\rangle}{E_j-E_i}\right)$$

$$\Leftrightarrow \varepsilon_2 = \sum_{i\neq j}\frac{|\langle\varphi_i|\hat{w}|\varphi_j\rangle|^2}{E_j-E_i}$$

the 2^{nd} order correction to the energy is thus

$$\boxed{E_j(\lambda) = E_j'' = \underbrace{E_j + \langle\varphi_j|W|\varphi_j\rangle}_{E_j'} + \sum_{i\neq j}\frac{|\langle\varphi_i|W|\varphi_j\rangle|^2}{E_j-E_i}}$$

Example: perturbation of a 2-level system

Consider $H_0 = \begin{array}{c} \\ \langle\varphi_1| \\ \langle\varphi_2| \end{array}\!\!\begin{array}{c} \begin{array}{cc} |\varphi_1\rangle & |\varphi_2\rangle \end{array} \\ \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \end{array}$ and $W = \begin{pmatrix} \cancel{0}\ \varepsilon_1 & V \\ V^* & \cancel{0}\ \varepsilon_2 \end{pmatrix}$

1st order: $E_1' = E_1 + \cancel{\langle\varphi_1|W|\varphi_1\rangle}\ \varepsilon_1 = E_1 + \varepsilon_1$

$E_2' = E_2 + \cancel{\langle\varphi_2|W|\varphi_2\rangle}\ \varepsilon_2 = E_2 + \varepsilon_2$

Stopped here

~~2nd order~~ $|\varphi_1\rangle' = |\varphi_1\rangle + \dfrac{\langle\varphi_2|W|\varphi_1\rangle}{E_1 - E_2}|\varphi_2\rangle$

$= |\varphi_1\rangle + \dfrac{V^*}{E_1 - E_2}|\varphi_2\rangle$

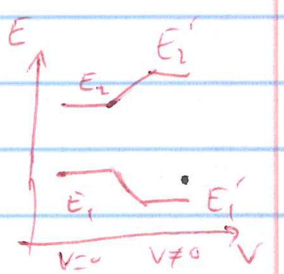
note: $\langle\varphi_1'|\varphi_2'\rangle = 0$

$|\varphi_2\rangle' = |\varphi_2\rangle + \dfrac{\langle\varphi_1|W|\varphi_2\rangle}{E_2 - E_1}|\varphi_1\rangle$

$= |\varphi_2\rangle + \dfrac{V}{E_2 - E_1}|\varphi_1\rangle$

2nd order: $E_1'' = \cancel{E_1'}\ E_1 + \cancel{\sum_{i\neq j}} \dfrac{|\langle\varphi_2|W|\varphi_1\rangle|^2}{E_1 - E_2} = E_1 + \dfrac{|V|^2}{E_1 - E_2}$

$E_2'' = \cancel{E_2'}\ E_2 + \dfrac{|\langle\varphi_1|W|\varphi_2\rangle|^2}{E_2 - E_1} = E_2 + \dfrac{|V|^2}{E_2 - E_1}$



note: - if $E_1 < E_2$, then ~~both~~ perturbed level ~~are~~ repelled by off-diagonal coupling ~~V~~ $V = \langle\varphi_1|W|\varphi_2\rangle$

- if $E_2 > E_1$, same thing.

$\Longrightarrow$ no level crossing theorem.