

Perturbation theory

or how to use a ~~sg~~ simple model to describe complex interactions

So far we have considered several rather over-simplified quantum systems

- isolated spin in a magnetic field
- (in)finite ~~square~~ potential well / steps / barrier (rectangular or spherical)
- Simple harmonic oscillator
- Hydrogen atom

In all these cases we were able to obtain exact solutions for eigenstates and energy eigen values.

However, for most even slightly more complicated system and interaction this approach is impractical.

Instead, it is more convenient to first model the system using one of the "ideal" ones, and then use the corresponding eigen vectors to calculate the deviations ~~to~~ due to their differences

[Time-independent] perturbation theory

Ideal system: $\hat{H}_0 |n_0\rangle = E_n^{(0)} |n_0\rangle$
 we know how to solve it

Unknown system: $\hat{H} = \hat{H}_0 + \lambda \cdot \hat{\delta H}$
 perturbation
 λ - "smallness" indicator

A crucial assumption: the new eigenstates/values are almost like the old ones (perturbation is small)

$$\hat{H} |n\rangle = E_n |n\rangle \rightarrow \text{need to find } E_n, |n\rangle$$

$$|n\rangle = |n_0\rangle + \lambda \sum_{k \neq n} c_k^{(1)} |k_0\rangle + \dots$$

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

Let's substitute this into the SE, keeping up to only the first order of smallness λ

$$\begin{aligned} \hat{H} |n\rangle &= (\hat{H}_0 + \lambda \hat{\delta H}) (|n_0\rangle + \lambda \sum_{k \neq n} c_k^{(1)} |k_0\rangle) = \\ &= E_n |n\rangle = (E_n^{(0)} + \lambda E_n^{(1)}) (|n_0\rangle + \lambda \sum_{k \neq n} c_k^{(1)} |k_0\rangle) \\ &\hat{H}_0 |n_0\rangle + \lambda \left[\hat{\delta H} |n_0\rangle + \sum_{k \neq n} c_k^{(1)} \hat{H}_0 |k_0\rangle \right] = \\ &= E_n^{(0)} |n_0\rangle + \lambda \left[E_n^{(1)} |n_0\rangle + E_n^{(0)} \sum_{k \neq n} c_k^{(1)} |k_0\rangle \right] \end{aligned}$$

$$\hat{\delta H} |n_0\rangle + \sum_{k \neq n} c_k^{(1)} E_k^{(0)} |k_0\rangle = E_n^{(1)} |n_0\rangle + E_n^{(0)} \sum_{k \neq n} c_k^{(1)} |k_0\rangle$$

To find the first-order energy correction, we take the inner product with $\langle n_0 |$

$$\langle n_0 | \hat{S}H | n_0 \rangle = E_n^{(1)} \langle n_0 | n_0 \rangle \quad \text{since } \langle n_0 | k_0 \rangle = 0 \text{ for any } n \neq k$$

$$\underline{E_n^{(1)}} = \langle n_0 | \hat{S}H | n_0 \rangle$$

The first-order correction coefficient for the wave function, we take the inner product with $\langle m_0 |$ (where $m \neq n$)

$$\langle m_0 | \hat{S}H | n_0 \rangle + \sum_{k \neq n} c_k^{(1)} E_k^{(0)} \underbrace{\langle m_0 | k_0 \rangle}_{\delta_{mk}} = E_n^{(1)} \langle m_0 | n_0 \rangle + E_n^{(0)} \sum_k c_k^{(1)} \underbrace{\langle m_0 | k_0 \rangle}_{\delta_{mk}} = 0$$

$$\langle m_0 | \hat{S}H | n_0 \rangle + c_m^{(1)} E_m^{(0)} = E_n^{(0)} c_m^{(1)}$$

$$c_m^{(1)} = \frac{\langle m_0 | \hat{S}H | n_0 \rangle}{E_n^{(0)} - E_m^{(0)}} \quad m \neq n$$

If necessary, one can go to higher-order corrections. Calculating the second-order energy correction is quite common if $\langle n_0 | \hat{S}H | n_0 \rangle = 0$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle n_0 | \hat{S}H | m_0 \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

Simple example: a spin-zero molecule in a magnetic field. For

Assuming ground vibrational state

$$\hat{H}_0 = \hat{H}_{\text{rot}} = \frac{\hat{L}^2}{2I} \quad \hat{S}H = -\vec{\mu} \cdot \vec{B}_z = \omega_0 \hat{L}_z$$

$$E_{lm}^{(1)} = \langle l m | \hat{S}H | l m \rangle = \langle l m | \omega_0 \hat{L}_z | l m \rangle = \hbar \omega_0 \cdot m \quad \text{Zeeman effect}$$

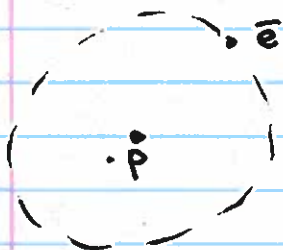
Note that for the case of $\vec{B} = (0, 0, B)$
 $[\hat{S}_H, \hat{L}_z] = [\hat{S}_H, \hat{L}^2] = [\hat{S}_H, \hat{H}_0] = 0$, so the same
 eigenstates $|l, m\rangle$ can be used.

$B=0$
 l, m

— $m=l$
 — $m=l-1$
 ...
 ... $m=-l+1$
 — $m=-l$

Magnetic field lifts
 the degeneracy

More complex example: let's take a ~~look~~
 closer look at the hydrogen atom



$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu_e} \leftarrow \frac{ke^2}{r}$$

Here we use non-relativistic expression
 for the electron kinetic energy

$$\Delta x \cdot \Delta p \sim a_0 \cdot \mu_e \cdot v \sim \hbar$$

$$v \sim \frac{\hbar}{a_0 \mu_e} = \frac{10^{-34} \text{ J}\cdot\text{s}}{10^{-10} \text{ m} \cdot 10^{-30} \text{ kg}} \sim 10^6 \text{ m/s}$$

$$\frac{v}{c} \sim 10^{-2} \quad \text{small effect, but not negligible}$$

Relativistic corrections

$$- K = \sqrt{(\mu_e c^2)^2 + (pc)^2} - \mu_e c^2 \approx p^2/2\mu_e + \frac{3}{4} \frac{p^4}{\mu_e^3 c^2}$$

$$- \text{Spin-orbit interaction} \quad \cancel{A \hat{S} \cdot \hat{L}} \quad A \hat{S} \cdot \hat{L}$$

Intuitive explanation: moving electron creates
 magnetic field that affects its spin state
 and vice versa

- Darwin term (affects only s-electrons)

Because of spin-orbit interaction, neither spin \hat{S} nor orbital \hat{L} angular momenta ~~are~~ operators commute with \hat{H}_0 .

However the total angular momentum does

$$\hat{J} = \hat{S} + \hat{L} \quad \text{total angular momentum}$$

$$\hat{J}^2 = (\hat{S} + \hat{L})^2 = \hat{S}^2 + \hat{L}^2 + 2\hat{S} \cdot \hat{L} \Rightarrow \hat{S} \cdot \hat{L} = \frac{\hat{J}^2 - \hat{S}^2 - \hat{L}^2}{2}$$

Original (unperturbed) quantum states

$$|n, l, m_l, m_s\rangle \Rightarrow |n, l, s=1/2, j, m_j\rangle$$

$$\hat{J}^2 |n, l, s, j, m_j\rangle = \hbar^2 j(j+1) |n, l, s, j, m_j\rangle$$

$$\hat{J}_z |n, l, s, j, m_j\rangle = \hbar m_j |n, l, s, j, m_j\rangle$$

We can now use the perturbation theory to calculate the first-order corrections to hydrogen energy levels \rightarrow fine structure

corrections $\frac{\Delta E_{FS}}{E_R} \sim \frac{\alpha}{2} = \frac{1}{137}$ fine-structure constant

Energy ~~change~~ correction for all relativistic ~~and~~ corrections

$$\Delta E_{n,j} = \frac{dE_n^{(0)}}{n} \left[\frac{1}{j+1/2} - \frac{3}{4n} \right]$$

depends only on n, j (not l)

Zeeaman effect $\delta H_{\text{magn}} = \omega_0 \hat{J}_z$

$$\Delta E_{\text{magn}} = \hbar \omega_0 \cdot m_j$$

Even finer corrections

Lamb shift - small shift in $l=0$ (s) electronic energy due to quantum fluctuations of the e-m field (vacuum)

One of proofs of e-m field quantization

Hyperfine structure - arises because of interaction of electron and nuclear angular momenta (hence magnetic moments)

$$\hat{H}_{HFS} = A_{HF} \cdot \hat{\mathbf{I}} \cdot \hat{\mathbf{S}} \quad (\text{for } l=0 \text{ case})$$

↙ nuclear spin operator

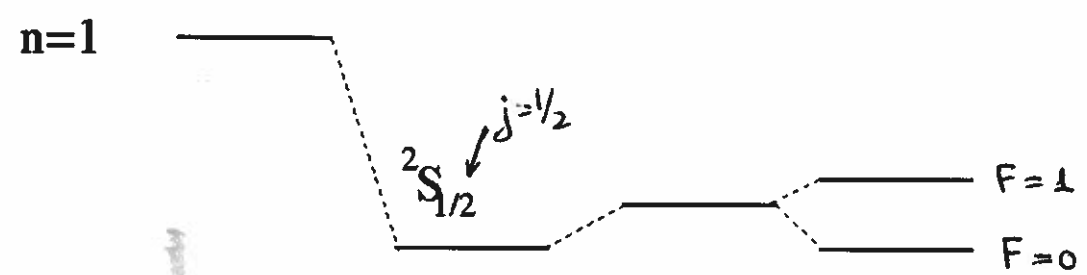
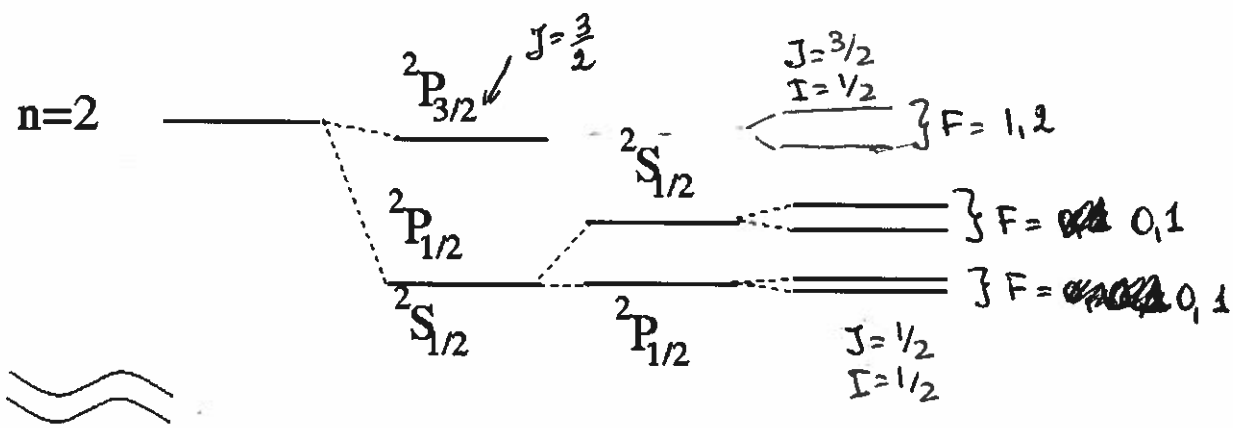
In this case $\hat{\mathbf{J}}$ is no longer commutes with \hat{H}_0 and \hat{H}_{HFS} , so people use total angular momentum

$$\hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}}$$

$$\Delta E_{HFS} \sim \frac{\mu_e}{\mu_{nuclei}} \Delta E_{FS} \sim 10^{-3} \Delta E_{FS}$$

So how many quantum numbers do we need

$$|n \ell s j I F m_F \rangle$$



Coulomb Fine Structure Lamb Shift Hyperfine Splitting

Spectroscopic notation

$$2S+1 L_j$$

$$2S_{1/2} \Rightarrow s=1/2, l=0, j=1/2$$

$$2P_{3/2} \Rightarrow s=1/2, l=1, j=3/2$$

$$2P_{1/2} \Rightarrow s=1/2, l=1, j=1/2$$