Quantum Mechanics II

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Contents

Introduction

This book is a collection of the lectures on Quantum Mechanics II course given by Professor Mowbray Duncan and digitalised by the student Gabriel Balarezo. The purpose of this book is to serve as a guide for the students about to take the mentioned course. We consider the student to be familiarised with the basics of quantum mechanics (Quantum Mechanics I course is required), since this course covers the second part of the book *Introduction to Quantum Mechanics* by David Griffits which is focused on the applications of quantum mechanics.
Here we will cover the following main topics:

0.1 Time Independent Perturbation Theory

Zeeman Effect

Fine structure of the hydrogen.

- Relativistic effects
- Spin-Orbit Coupling

Known $\hat{H}_o$, ψ_n and E_n, apply a perturbation $V = \hat{E}_n$, and find $\hat{\psi}_n$, $\hat{E}_n$ to $V + \hat{E}_n$.

0.2 Variational Principle

Known hamiltonian $\hat{H}$ we want the ground state energies.

Choose a $\hat{\psi}$ (trial wave function) and $\langle\hat{\psi}|\hat{H}|\hat{\psi}\rangle \geq Egs$

Since $\hat{H} = \frac{-\hbar^2}{2m}\nabla + V$, known $\langle\psi|\frac{-\hbar^2}{2m}\nabla|\psi\rangle$

Calculate $\langle\psi|V|\psi\rangle$, requires $\langle\psi|\psi\rangle = 1$.

0.3 WKB Approximation

$$\psi = \frac{c}{\sqrt{|p|}} e^{\frac{-i}{\hbar}\int |p| dx}, \quad p = \sqrt{2m(E - V(x))}$$

0.4 Time Dependent Perturbation Theory

Time dependent problem,

$$V(t) \text{ time-dependent potential}$$

Selection Rules: $\Delta l = \pm 1, \;\; \Delta m = 0, \pm 1$

Hydrogenic atom: $\langle nlm|\vec{r}|n'lm'\rangle$

0.5 Absorption and Emission of Light

Interaction of a time-dependent electromagnetic field with an atomic system.

$$E(t) = E_o Cos(\omega t)\hat{k} \longrightarrow V(t) = E_o Cos(\omega t)\hat{z}$$

0.6 Quantum Information

Qubits, Computational Trackability, Quantum Teleportation, etc,.

Chapter 1

Time Independent Non-Degenerate Perturbation Theory

1.1 Lecture 1

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Suppose we have a "known" system with hamiltonian, eigenfunctions and eigenenergies H_o, Ψ_n and E_n respectively.

$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$$

Where

$$\langle\hat{\Psi}|\hat{H}|\hat{\Psi}\rangle = E_n, \quad \langle\Psi_n|\Psi_{n'}\rangle = \delta_{nn'}$$

So that $\{\Psi_n\}$ forms an orthonormal basis over the Hilbert spaces of H_o.

We apply a perturbative potential $\tilde{V}$ to H_o, yielding a new Hamiltonian for the perturbated system,

$$\tilde{H} = \hat{H}_o + \lambda\tilde{V}, \text{ let } \lambda \in [0,1]$$

Assumption:

$\tilde{V}$ is small compared to $\hat{H}_o$

let a "bookkeeping parameter" to keep track of the relative signs of from in order of the perturbated potential.

1.1.1 Method

Express the wave functions and eigenenergies of the perturbated Hamiltonian H, $\tilde{\psi}$, $\tilde{E}_n$ as a power series equation in orders of λ.

$$\tilde{E}_n = \tilde{E}_o^{(0)} + \lambda \tilde{E}_n^{(1)} + \lambda^2 \tilde{E}_n^{(2)} + \cdots = \sum_k \lambda^k \tilde{E}_n^{(k)}$$
$$\tilde{\psi}_n = \tilde{\psi}_n^{(0)} + \lambda \tilde{\psi}_n^{(1)} + \lambda^2 \tilde{\psi}_n^{(2)} + \cdots = \sum_k \lambda^k \tilde{\psi}_n^{(k)}$$

Time Independent Schrodinger Equation

$$\tilde{H}\big|\tilde{\psi}_n\big\rangle = \tilde{E}_n\big|\tilde{\psi}_n\big\rangle$$
$$(\hat{H} + \hat{V}) \sum_k \lambda^k \big|\psi_n^{(k)}\big\rangle = \sum_k \lambda^k \tilde{E}_n^{(k)} \sum_k \lambda^k \big|\psi_n^{(k)}\big\rangle$$
$$\sum_k (\lambda^k \hat{H}_o + \lambda^{k+1}\hat{V})\big|\hat{\psi}_n^{(k)}\big\rangle = \sum_{k'} \sum_k \lambda^{k'+k} \hat{E}_n^{(k)} \big|\hat{\psi}_n^{(k)}\big\rangle$$

$$\sum_k \left(\lambda^k \hat{H}_o + \lambda^{k+1}\hat{V} - \sum_{k'} \lambda^{k'+k} \hat{E}_n^{(k')} \right) \big|\psi_n^{(k)}\big\rangle = 0$$
$$\sum_k \lambda^k \left(\hat{H}_o\big|\hat{\psi}_n^{(k)}\big\rangle + \underbrace{(1-\delta_{k0})}_{k\neq 0} \hat{V}\big|\hat{\psi}^{(k-1)}\big\rangle - \sum_{k=0}^{k} \hat{E}_n^{(k')} \big|\hat{\psi}_n^{(k-k')}\big\rangle \right) = 0$$

Since (9) holds for arbitrary λ, it must hold independently for each powers of λ:

$$\mathcal{O}(1)_{k=0} = \hat{H}\big|\hat{\psi}_n^{(0)}\big\rangle + (1-\delta_{k0})\hat{V}\big|\hat{\psi}_n^{(-1)}\big\rangle$$
$$= \sum_{k'=0}^{0} \hat{E}_n^{(k')} \big|\hat{\psi}_n^{(0-k')}\big\rangle$$
$$\Longrightarrow \hat{H}_o\big|\hat{\psi}_n^{(0)}\big\rangle = \hat{E}_n^{(0)}\big|\hat{\psi}_n^{(0)}\big\rangle$$
$$\big\langle \psi_n \big| \underbrace{H_o}_{\text{hermitian}} \big|\hat{\psi}_n^{(0)}\big\rangle = \hat{E}_n^{(0)} \big\langle \psi_n \big| \hat{\psi}_n^{(0)}\big\rangle$$

$$\big\langle \psi_{n'} \big| \hat{H}_o^\dagger = E_{n'} \big\langle \psi_{n'} \big|$$
$$(E_{n'} - \hat{E}_n^{(0)}) \big\langle \psi_{n'} \big| \hat{\psi}_n^{(0)} \big\rangle = 0$$

So,

$$\hat{E}_n^{(0)} = E_n \;\text{ or }\; \big\langle \psi_n \big| \hat{\psi}_n^{(0)} \big\rangle = 0$$

If the system $\hat{H}_o$ is nondegenerate:

$$\Longrightarrow \big|\hat{\psi}_n^{(0)}\big\rangle = \big|\psi_n\big\rangle$$

If the system is degenerate, then:

$$\hat{H}_o\big|\psi_{n'}\big\rangle = E_n\big|\psi_{n'}\big\rangle \;\text{ for } n' \in \{n,\cdots,n+k\}$$

Then:

$$\big|\hat{\psi}_n^{(0)}\big\rangle = \sum_{k'=0}^{k} C_{n+k'}\big|\psi_{n+k'}\big\rangle$$

$$\hat{E}_n = E_n\mathcal{O}(\lambda)$$

$$\big|\hat{\psi}_n\big\rangle = \big|\psi_n\big\rangle + \mathcal{O}(\lambda)$$

$$\mathcal{O}(\lambda) : \hat{H}_o\big|\hat{\psi}_n^{(1)}\big\rangle + \hat{V}\big|\hat{\psi}_n^{(0)}\big\rangle = E_n^{(0)}\big|\hat{\psi}_n^{(1)}\big\rangle + \hat{E}_n^{(1)}\big|\hat{\psi}_n^{(0)}\big\rangle$$

multiply by $\big\langle\psi_{n'}\big|$:

$$\big\langle\psi_{n'}\big|\hat{H}_o\big|\hat{\psi}_n^{(1)}\big\rangle + \big\langle\psi_{n'}\big|\hat{V}\big|\hat{\psi}_n^{(0)}\big\rangle = E_n^{(0)}\big\langle\psi_{n'}\big|\hat{\psi}_n^{(1)}\big\rangle + \hat{E}_n^{(1)}\big\langle\psi_{n'}\big|\hat{\psi}_n^{(0)}\big\rangle$$

$$\big\langle\psi_{n'}\big|\hat{H}_o = E_{n'}\big\langle\psi_{n'}\big|$$

$$\big|\hat{\psi}_n^{(0)}\big\rangle = \big|\psi_n\big\rangle \;\text{ (non-degenerate)},\;\; \hat{E}_n^{(0)} = E_n$$

$$(E_{n'} - E_n)\big\langle\psi_{n'}\big|\hat{\psi}_n^{(1)}\big\rangle + \big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle = \hat{E}_n^{(1)}\delta_{n'n}$$

if $\mathbf{n' = n}$:

$$\cancelto{0}{(E_{n'} - E_n)}\big\langle\psi_{n'}\big|\hat{\psi}_n^{(1)}\big\rangle + \big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle = \hat{E}_n^{(1)}\delta_{n'n}$$

$$\implies \hat{E}_n^{(1)} = \big\langle\psi_n\big|\hat{V}\big|\hat{\psi}_n^{(1)}\big\rangle$$

$$\hat{E}_n = E_n + \big\langle\psi_{n'}\big|\hat{V}\big|\hat{\psi}_n^{(1)}\big\rangle + \mathcal{O}(\lambda^2)$$

$$\big|\hat{\psi}_n\big\rangle = \big|\psi_n\big\rangle + \mathcal{O}(\lambda)$$

if $\mathbf{n' \neq n}$:

$$(E_{n'} - E_n)\big\langle\psi_{n'}\big|\hat{\psi}_n^{(1)}\big\rangle = -\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle + \hat{E}_n^{(1)}\cancelto{0}{\delta_{n'n}}$$

$$\big\langle\psi_{n'}\big|\hat{\psi}_n^{(1)}\big\rangle = \frac{\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle}{E_n - E_{n'}}$$

Since $\{\psi_n\}$ forms an orthonormal basis,

$$\implies \sum_{n'}\big|\psi_{n'}\big\rangle\big\langle\psi_{n'}\big| = \mathbb{1} \;\text{ Identity matrix}$$

$$\begin{aligned}\big|\hat{\psi}_n^{(1)}\big\rangle = \mathbb{1}\big|\hat{\psi}_n^{(1)}\big\rangle &= \sum_{n'}\big|\psi_{n'}\big\rangle\big\langle\psi_{n'}\big|\hat{\psi}_n^{(1)}\big\rangle \\ &= \sum_{n'=n}\frac{\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle}{E_n - E_{n'}}\big|\psi_{n'}\big\rangle\end{aligned}$$

Since $\big|\hat{\psi}_n^{(0)}\big\rangle = \big|\psi_n\big\rangle$, then $\big|\hat{\psi}_n^{(1)}\big\rangle$ cannot depend on $\big|\psi_n\big\rangle$.

1.2 Lecture 2

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$$\underbrace{\tilde{H}}_{\text{perturbed hamiltonian}} = \underbrace{\hat{H}_o}_{\text{unperturbed hamiltonian}} + \underbrace{\lambda}_{\text{lookkeeping parameter [0,1]}} * \underbrace{\hat{V}}_{\text{perturbing potential}}$$

$\hat{V}$ needs to be smaller than $\hat{H}_o$, λ keeps track of this, i.e., dependence on $\hat{V}$

Schrodinger Equation

$$(\hat{H}_o + \lambda\hat{V})\hat{\psi}_n = \tilde{E}_n\tilde{\psi}_n$$

$\tilde{E}_n$ and $\tilde{\psi}_n$ are eigenenergies and wavefunctions for the perturbated hamiltonian.

Expand $\tilde{E}_n$ and $\tilde{\psi}_n$ in power of lambda:

$$\tilde{E}_n = \hat{E}_n^{(0)} + \lambda\tilde{E}_n^{(1)} + \lambda^2\tilde{E}_n^{(2)} + \mathcal{O}(\lambda^3)$$
$$\tilde{\psi}_n = \hat{\psi}_n^{(0)} + \lambda\tilde{\psi}_n^{(1)} + \lambda^2\tilde{\psi}_n^{(2)} + \mathcal{O}(\lambda^3)$$

Substitute for $\tilde{E}_o$ and $\tilde{\psi}_n$ into the (SE) and collect terms of like powers of λ.

$$\mathcal{O}(1) : \hat{H}_o\big|\tilde{\psi}_n^{(0)}\big\rangle = \tilde{E}_o^{(0)}\big|\psi_n^{(0)}\big\rangle$$

multiply by $\big\langle\psi_{n'}\big|$:

$$\big\langle\psi_{n'}\big|\hat{H}_o\big|\tilde{\psi}_n^{(0)}\big\rangle = \tilde{E}_o^{(0)}\big\langle\psi_{n'}\big|\psi_n^{(0)}\big\rangle$$

$\hat{H}_o = H_o^\dagger$ since $\hat{H}_o$ is hermitian.

$$\big\langle\psi_{n'}\big|\hat{H}_o^\dagger = E_{n'}\big\langle\psi_{n'}\big| \text{ (SE) for } \hat{H}_o$$

$$\implies E_{n'}\big\langle\psi_{n'}\big|\psi_n^{(0)}\big\rangle = \hat{E}_o^{(0)}\big\langle\psi_{n'}\big|\psi_n^{(0)}\big\rangle$$

$$E_{n'}^{(0)} = E_{n'} \quad \text{or} \quad \big\langle\psi_{n'}\big|\psi_n^{(0)}\big\rangle = 0$$

$\mathbb{1} = \sum_{n'}\big|\psi_{n'}\big\rangle\big\langle\psi_{n'}\big|$

$\tilde{\psi}_n^{(0)} = \sum_{n'}\big\langle\psi_{n'}\big|\psi_n^{(1)}\big\rangle$

If E_n is k-level degenerate, then:

$$\big|\tilde{\psi}_n^{(0)}\big\rangle = \sum_{n'=n}^{n+k-1}\big\langle\psi_{n'}\big|\psi_n^{(0)}\big\rangle\big|\psi_{n'}\big\rangle$$

Consider $\hat{H}_o$ to be nondegenerate:

$$\implies E_n^{(0)} = E_n, \quad \big|\big\langle\psi_n\big|\tilde{\psi}_n^{(0)}\big\rangle\big|^2 = 0$$

$$\sum_{n'=n}^{n+k-1} \left|\left\langle \psi_{n'} \middle| \psi_n^{(0)} \right\rangle\right|^2 = 1$$

Since $\left\langle \psi_{n'} \middle| \psi_n^{(0)} \right\rangle = 0$ for $n' \neq n$:

$$\implies \left|\tilde{\psi}_n^{(0)}\right\rangle = \left|\psi_{n'}\right\rangle$$

The n^{th} eigenenergy of the perturbated system (hamiltonian) $\tilde{E}_n$ is the n^{th} eigenenergy of the unperturbed system to Zeroth order in the perturbation, i.e $\mathcal{O}(\lambda^0) = \mathcal{O}(1),\ \lambda = 0$.

$\iff$ If we turn the perturbation off we get the eigenenergy of the unperturbed system.

$\because$ The n^{th} wavefunction for the perturbed hamiltonian $\tilde{\Psi}_n$ is a linear combination of the unperturbed hamiltonian's degenerate wavefunctions with energy E_n to Zeroth order in the perturbation, i.e $\mathcal{O}(\lambda^0) = \mathcal{O}(1)$ or $\lambda = 0$

$$\implies \left|\hat{\psi}_n^{(0)}\right\rangle = \sum_{n'=n}^{n+k-1} \left\langle \psi_{n'} \middle| \tilde{\psi}_n^{(0)} \right\rangle \left|\psi_{n'}\right\rangle$$

,where

$$\sum_{n'=n}^{n+k-1} \left|\left\langle \psi_{n'} \middle| \tilde{\psi}_n^{(0)} \right\rangle\right|^2 = 1$$

Even if we "turn off" the perturbation, it can still left the degeneracy of $\{\left|\psi_n\right\rangle, \cdots, \left|\psi_{n+k-1}\right\rangle\}$ for k-fold degenerate systems, unless the unperturbed wavefunctions are eigenstates of the perturbation.

Assuming $\hat{H}_o$ is non-degenerate

$$\implies \left|\left\langle \psi_{n'} \middle| \tilde{\psi}_n^{(0)} \right\rangle\right|^2 = 1$$

wlog $\psi_n = \tilde{\psi}_n^{(0)}$ (Choice of 1 for phase factor).

$$\tilde{E}_n = E_n + \mathcal{O}(\lambda)$$
$$\tilde{\psi}_n = \psi_n + \mathcal{O}(\lambda)$$

Gather together terms of order 1 in λ in the (SE):

$$\mathcal{O}(\lambda) : \lambda \left(\hat{H}_o \left|\tilde{\psi}_n^{(1)}\right\rangle + \hat{V}\left|\tilde{\psi}_n^{(0)}\right\rangle\right) = \lambda \left(E_n \left|\tilde{\psi}_n^{(1)}\right\rangle + E_n^{(1)}\left|\psi_n\right\rangle\right)$$

Set $\lambda = 1$,

$$\hat{H}_o \left|\tilde{\psi}_n^{(1)}\right\rangle + \hat{V}\left|\tilde{\psi}_n^{(0)}\right\rangle = E_n \left|\tilde{\psi}_n^{(1)}\right\rangle + E_n^{(1)}\left|\psi_n\right\rangle$$

This is a recursive equation relating the 1st order corrections in $\tilde{E}_n$ and $\tilde{\psi}_n$ to the Zeroth ordec̊orrections, in the unperturbed eigenenergy and wavefunction, E_n and ψ_n respectively $\because$ the $\mathcal{O}^{th}$ relates the kth order corrections to all previous orders.

1.2.1 Two Unknowns

Use the fact that:

$$\langle\psi_{n'}|\psi_n\rangle = \delta_{n'n} \quad \text{and} \quad \hat{H}_o|\psi_{n'}\rangle = E_{n'}|\psi_{n'}\rangle$$

To obtain equations for $\tilde{E}_n^{(1)}$ and $\tilde{\psi}_n^{(1)}$.

multiply by $\langle\psi_{n'}|$:

$$\langle\psi_{n'}|\hat{H}_o^{\dagger}|\tilde{\psi}_n^{(1)}\rangle + \langle\psi_{n'}|\hat{V}|\tilde{\psi}_n^{(0)}\rangle = E_n\langle\psi_{n'}|\tilde{\psi}_n^{(1)}\rangle + E_n^{(1)}\underbrace{\langle\psi_{n'}|\psi_n\rangle}_{\delta_{n'n}}$$

$$(E_{n'} - E_n)\langle\psi_{n'}|\tilde{\psi}_n^{(1)}\rangle + \langle\psi_{n'}|\hat{V}|\psi_n\rangle = \tilde{E}_n^{(1)}\delta_{n'n} \tag{1.2.1}$$

$\langle\psi_{n'}|\tilde{\psi}_n^{(1)}\rangle$: Coefficient of $|\psi_{n'}\rangle$.

$\tilde{E}_n^{(1)}$: First order correction to the eigenenergy.

If $n' = n$, (2.2.1) yields to: $\tilde{E}_n^{(1)}$

$$\boxed{\tilde{E}_n^{(1)} = \langle\psi_n|\hat{V}|\psi_n\rangle}$$

is the expectation value of the perturbation in the n^{th} eigenstate of the unperturbed hamiltonian.

If $n' \neq n$, (2.2.1) yields to: coefficients of $|\tilde{\psi}_n^{(1)}\rangle$ and $\lambda = 1$.

$$\langle\psi_{n'}|\hat{\psi}_n^{(1)}\rangle = \frac{\langle\psi_{n'}|\hat{V}|\psi_n\rangle}{E_n - E_{n'}}$$

$$|\tilde{\psi}_n^{(1)}\rangle = \sum_{n'\neq n}\frac{\langle\psi_{n'}|\hat{V}|\psi_n\rangle}{E_n - E_{n'}}|\psi_{n'}\rangle$$

$$\tilde{E}_n = E_n + \langle\psi_n|\hat{V}|\psi_n\rangle + \mathcal{O}(\lambda^2)$$

$$|\tilde{\psi}_n\rangle = |\psi_n\rangle + \sum_{n'\neq n}\frac{\langle\psi_{n'}|\hat{V}|\psi_n\rangle}{E_n - E_{n'}}|\psi_{n'}\rangle + \mathcal{O}(\lambda^2)$$

The first order correction to the eigenenergy is the energy of the perturbation of you stay in the n^{th} eigenstate of the unperturbed system. So V has to be "weak" so that you can remain in $|\psi_n\rangle$ under its action.

Note: if $\hat{V}$ (the perturbation) is an odd function,

$$\Longrightarrow \hat{E}_n^{(1)} = \int d^3\vec{r}\,|\underbrace{\psi(\vec{r})}_{\text{even}}|^2\,\overbrace{\hat{V}(\vec{r},t)}^{\text{odd}} = 0$$

The first order corrections to wavefunctions are proportional to the matrix elements:

$$\langle \psi_{n'} | \hat{V} | \psi_n \rangle,$$

i.e., that under the action of the perturbation you can transition from n^{th} to n'^{th} eigenstate of the unperturbed hamiltonian and inversely proportional to the difference (energy) between the eigenenergies of the n^{th} and n'^{th} eigenstates of the perturbed hamiltonian.

Note:

$$\left| \langle \psi_{n'} | \hat{V} | \psi_n \rangle \right| \ll \left| E_n - E_{n'} \right|$$

Otherwise our expression for the wavefunctions of the perturbed system won't converge.

$$\left| \langle \psi_{n'} | \hat{V} | \psi_n \rangle \right| \ll \left| E_n - E_{n'} \right|$$

for our application of perturbation theory to apply.

$$\implies \lambda \gg 1$$

$$\mathcal{O}(\lambda^2) : \hat{H}_o | \tilde{\psi}_n^{(2)} \rangle + \hat{V} | \tilde{\psi}_n^{(1)} \rangle = E_n | \tilde{\psi}_n^{(2)} \rangle + \tilde{E}_n^{(1)} | \tilde{\psi}_n^{(1)} \rangle + \tilde{E}_n^{(2)} | \psi_n \rangle$$

Multiply by $\langle \psi_{n'} |$:

$$\langle \psi_{n'} | \hat{H}_o | \tilde{\psi}_n^{(2)} \rangle + \langle \psi_{n'} | \hat{V} | \tilde{\psi}_n^{(1)} \rangle = E_n \langle \psi_{n'} | \tilde{\psi}_n^{(2)} \rangle + \tilde{E}_n^{(1)} \langle \psi_{n'} | \tilde{\psi}_n^{(1)} \rangle + \tilde{E}_n^{(2)} \langle \psi_{n'} | \psi_n \rangle$$

$$(E_{n'} - E_n) \langle \psi_{n'} | \hat{\psi}_n^{(2)} \rangle + \langle \psi_{n'} | \hat{V} \sum_{k \neq n} \frac{\langle \psi_k | \hat{V} | \psi_n \rangle}{E_n - E_k} | \psi_k \rangle$$

$$= \langle \psi_n | \hat{V} | \psi_n \rangle \langle \psi_{n'} | \sum_{n=k} \frac{\langle \psi_k | \hat{V} | \psi_n \rangle}{E_n - E_k} | \psi_k \rangle + \tilde{E}_n^{(2)} \delta_{n'n}$$

$$(E_{n'} - E_n) \langle \psi_{n'} | \hat{\psi}_n^{(2)} \rangle + \sum_{k=n} \frac{\langle \psi_k | \hat{V} | \psi_n \rangle \langle \psi_{n'} | \hat{V} | \psi_k \rangle}{E_n - E_k}$$

$$= \frac{\langle \psi_n | \hat{V} | \psi_n \rangle \langle \psi_{n'} | \hat{V} | \psi_n \rangle}{E_n - E_{n'}} \left(1 - \delta_{n'n} \right) + \tilde{E}_n^{(2)} \delta_{n'n}$$

If $n' = n$:

$$\boxed{\tilde{E}_n^{(2)} = \sum_{k \neq n} \frac{\left| \langle \psi_k | \hat{V} | \psi_n \rangle \right|^2}{E_n - E_k}}$$

If $n' \neq n$:

$$\langle \psi_{n'} | \tilde{\psi}_n^{(2)} \rangle = \sum_{k \neq n} \frac{\langle \psi_k | \hat{V} | \psi_n \rangle \langle \psi_{n'} | \hat{V} | \psi_k \rangle}{(E_n - E_k)(E_n - E_{n'})} + \frac{\langle \psi_n | \hat{V} | \psi_n \rangle \langle \psi_{n'} | \hat{V} | \psi_n \rangle}{E_n - E_{n'}}$$

$$| \tilde{\psi}_n^{(2)} \rangle = \sum_{n' \neq n} \left| \psi_{n'} \right\rangle \left[\frac{\langle \psi_{n'} | \hat{V} | \psi_k \rangle \langle \psi_k | \hat{V} | \psi_n \rangle}{(E_n - E_K)(E_n - E_{n'})} + \frac{\langle \psi_{n'} | \hat{V} | \psi_n \rangle \langle \psi_n | \hat{V} | \psi_n \rangle}{E_n - E_{n'}} \right]$$

1.3 Lecture 3

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$$\tilde{H} = \hat{H}_o + \lambda \hat{V}$$

, where $\hat{H}_o \big|\psi_n\big\rangle = E_n \big|\psi_n\big\rangle$ and $\big\langle \psi_{n'} \big| \psi_n \big\rangle = \delta_{n'n}$.

if

$$\left| \big\langle \psi_{n'} \big| \hat{V} \big| \psi_n \big\rangle \right|^2 \ll (E_n - E_{n'})^2$$

then,

$$\hat{H} \big| \tilde{\psi}_n \big\rangle = \hat{E}_n \big| \tilde{\psi}_n \big\rangle$$

where

$$\hat{E}_n = E_n + \lambda \big\langle \psi_{n'} \big| \hat{V} \big| \psi_n \big\rangle + \lambda^2 \sum_{n' \neq n} \frac{\left| \big\langle \psi_{n'} \big| \hat{V} \big| \psi_n \big\rangle \right|^2}{E_n - E_{n'}} + \mathcal{O}(\lambda^3)$$

$$\psi_n = \psi_n + \lambda \sum_{n' \neq n} \frac{\big\langle \psi_{n'} \big| \hat{V} \big| \psi_n \big\rangle}{E_n - E_{n'}} \big| \psi_{n'} \big\rangle + \mathcal{O}(\lambda^2)$$

here,

E_n: Unperturbed eigenenergy.

$\big\langle \psi_{n'} \big| \hat{V} \big| \psi_n \big\rangle$: Expectation value of the perturbation in the unperturbed state.

$\big\langle \psi_{n'} \big| \hat{V} \big| \psi_n \big\rangle$: Matrix element fot $n \to n' \to n$

$E_n - E_{n'}$: Energy difference between ψ_n and $\psi_{n'}$.

1.3.1 Example 1: 1D Infinite Square Well + Perturbative Potential $V = V_o$

$$\begin{aligned} \tilde{H} &= \hat{H}_o + \lambda \hat{V} \\ &= \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V_o, \quad x \in [0, L] \end{aligned}$$

Schrodinger Equation

$$\frac{-\hbar^2}{2m} \frac{d^2 \tilde{\psi}_n(x)}{dx^2} + \lambda \tilde{V}_o \tilde{\psi}_n(x) = \tilde{E}_n \tilde{\psi}_n(x)$$

for the perturbated system.

For the unperturbated system:

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

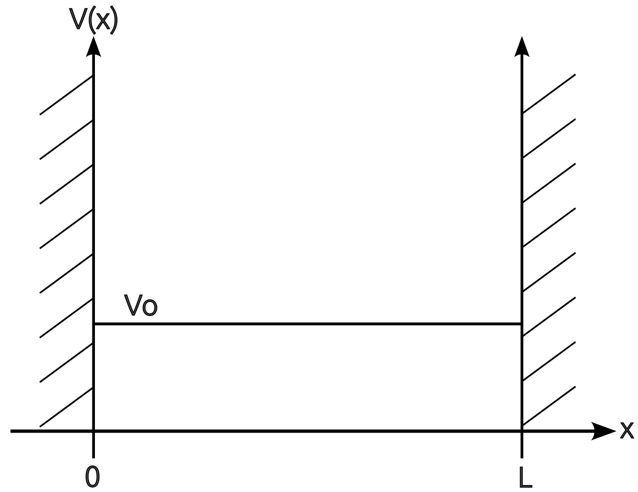


Figure 1.1: Infinite Square Well

(ODE):

$$\psi_n''(x) = \frac{-2mE_n\psi_n(x)}{\hbar^2} \longrightarrow \psi_n(x) = A\cos\left(\sqrt{\frac{2mE_n}{\hbar^2}}x\right) + B\sin\left(\sqrt{\frac{2mE_n}{\hbar^2}}x\right)$$

(B.C):

$$\psi(0) = \psi(L) = 0$$
$$\psi(0) = A\cancelto{1}{\cos(0)} + B\cancelto{0}{\sin(0)} + \implies A = 0$$
$$\psi(L) = B\sin\left(\sqrt{\frac{2mE_n}{\hbar^2}}L\right) = 0 \implies \sqrt{\frac{2mE_n}{\hbar^2}}L = n\pi, \quad n \in \mathbb{N}\ wlog$$

$$\implies E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \longleftarrow \text{Eigenenergies of the unperturbed infinite square well.}$$
$$\psi(x) = B\sin\left(\frac{\sqrt{2m}}{\hbar}\left(\frac{n^2\pi^2\hbar^2}{2mL^2}\right)^{1/2} x\right) = B\sin\left(\frac{n\pi x}{L}\right)$$

1.3.2 Normalisation

$$\begin{aligned}\langle\psi_n|\psi_n\rangle &= 1\\ &= B^2\int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx\\ &= B^2\frac{L}{2} = 1\\ \implies B &= \sqrt{\frac{2}{L}}\end{aligned}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

$$\hat{E}_n = E_n + \left\langle\psi_n\middle|\hat{V}\middle|\psi_n\right\rangle + \sum_{n'\neq n}\frac{\left|\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle\right|^2}{E_n - E_{n'}}$$

$$\tilde{E}_n = \frac{n^2\pi^2\hbar^2}{2mL^2} + \int_0^L \cancelto{1}{\frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)}.V_o dx + \sum_{n\neq n'}\frac{\left|\cancelto{0}{\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n,\pi x}{L}\right)dx}\right|^2}{n^2 - n'^2}V_o^2\frac{2mL^2}{\pi^2\hbar^2}$$

$$\boxed{\tilde{E}_n = \frac{n^2\pi^2\hbar^2}{2mL} + V_o}$$

Basically, if we add a constant potential V_o everywhere, this just shifts the eigenenergies by V_o.

The 2^{nd} order term is zero because V_o does not alter the wavefunction ψ_n and $\left\langle\psi_{n'}\middle|\psi_n\right\rangle = \delta_{n'n}$.

If we half the potential, the eigenenergies will be shifted by $V_o/2$.

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \int_0^{\frac{L}{2}} V_o\sin^2\left(\frac{n\pi x}{L}\right)\frac{2}{L}dx$$
$$+ \sum_{n\neq n'}\frac{V_o^2}{n^2 - n'^2}\frac{2mL^2}{\pi^2\hbar^2}\left|\int_0^{\frac{L}{2}}\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n'\pi x}{L}\right)dx\right|^2\left(\frac{2}{L}\right)^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + V_o\frac{2}{L}\left(\frac{L}{2\cdot 2}\right) + \frac{2mL^2}{\pi^2\hbar^2}V_o^2\sum_{n'\neq n}\frac{1}{n^2 - n'^2}\cdot\left|\frac{1}{2}\int_0^{\frac{L}{2}}\cos\left(\frac{(n-n')\pi x}{L}\right)\right.$$
$$\left. + \cos\left(\frac{(n+n')\pi x}{L}\right)dx\right|^2\cdot\left(\frac{2}{L}\right)^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \frac{V_o}{2} + \frac{2mL^2V_o^2}{\pi^2\hbar^2}\sum_{n'\neq n}\frac{1}{n^2 - n'^2}\frac{1}{4}\cdot\left|\frac{L}{\pi}\left(\frac{\sin\left(\frac{(n-n')x\pi}{L}\right)}{n-n'}\right)\right.$$
$$\left. - \left(\frac{\sin\left(\frac{(n+n')x\pi}{L}\right)}{n+n'}\right)\right|_0^{\frac{L}{2}}\Bigg|^2\left(\frac{2}{L}\right)^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \frac{V_o}{2} + \frac{2mL^2V_o^2}{\pi^2\hbar^2}\sum_{n'\neq n}\frac{1}{n^2 - n'^2}\left|\frac{\sin((n-n')\pi/2)}{n-n'} + \frac{\sin((n+n')\pi/2)}{n+n'}\right|^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \frac{V_o}{2} + \frac{2mL^2V_o^2}{\pi^2\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left|\frac{(1-(-1)^{n-n'})}{2}\frac{(-1)^{\frac{n-n'-1}{2}}}{n-n'} + \frac{(1-(-1))^{n+n'}(-1)^{\frac{n+n'}{2}}}{n+n'}\right|^2$$

If $n+n,$ is even, then $n-n,$ is even.
Proof:

$$\begin{aligned} n+n' &= 2k \\ n-n' &= n+n'-2n' = 2k-2n' \implies \text{Which is even.} \end{aligned}$$

If $n+n,$ is odd, then $n-n,$ is odd.
Proof:

$$\begin{aligned} n+n' &= 2k+1 \\ n-n' &= n+n'-2n' = 2k+1-2n' \\ &= 2(k-n')+1 \implies \text{is odd.} \end{aligned}$$

Then:

$$\frac{1-(-1)^{n-n'}}{2} = \frac{1-(-1)^{n+n'}}{2}$$

$$\tilde{E}_n^{(2)} = \frac{2mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left|\frac{1-(-1)^{n+n'}}{2}\right|\left|\frac{(-1)^{\frac{n-n'-1}{2}}}{n-n'} + \frac{(-1)^{\frac{n+n'}{2}}}{n+n'}\right|^2$$

Only when $n+n'$ is odd we have a correction.

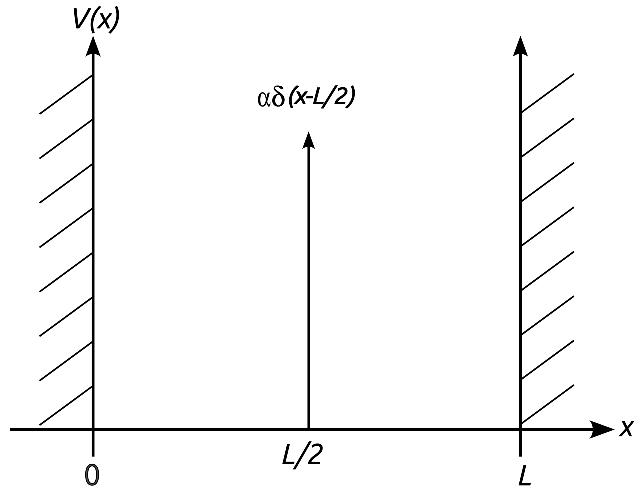
$$\begin{aligned} \tilde{E}_n^{(2)} &= \frac{2mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left|\frac{1-(-1)^{n+n'}}{2}\right|\left|(-1)^{\frac{n+n'}{2}}\right|^2\left|\frac{1}{n+n'} - \frac{1}{n-n'}\right|^2 \\ &= \frac{2mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left(\frac{1-(-1)^{n+n'}}{2}\right)\left|\frac{n-n'-(n+n')}{(n+n')(n-n')}\right|^2 \\ &= \frac{8mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{n'^2}{(n^2-n'^2)^3}\frac{1-(-1)^{n+n'}}{2} \end{aligned}$$

We only have a 2nd order correction when we go odd $\rightarrow$ even or even $\rightarrow$ odd.

Suppose n is even:

$$\begin{aligned} n = 2k \implies \Psi_{2k}\left(\frac{L}{2}\right) &= 0 \\ \Psi_{2k+1}\left(\frac{L}{2}\right) &= \pm\sqrt{\frac{2}{L}} \end{aligned}$$

1.3.3 Example: 1D Infinite Square Well Potential + Perturbative Potential $V(x) = \alpha\delta(x - \frac{L}{2})$.



Criteria for using the perturbation theory:

$$\left|\langle\psi_{n'}|\hat{V}|\psi_n\rangle\right|^2 \ll (E_n - E_{n'})^2$$

$$\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \qquad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

$$\begin{aligned}
\left|\langle\psi_{n'}|\hat{V}|\psi_n\rangle\right|^2 &= \left|\alpha\int_0^L \frac{2}{L}\sin\left(\frac{n'\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\delta\left(x - \frac{L}{2}\right)dx\right|^2 \\
&= \frac{4}{L^2}\alpha^2\sin^2\left(\frac{n'\pi}{L}\right)\sin^2\left(\frac{n\pi}{L}\right) \\
&= \left(\frac{2\alpha}{L}\right)^2 \underbrace{\left(\frac{1-(-1)^{n'}}{2}\right)}_{\text{n' is odd}}\underbrace{\left(\frac{1-(-1)^{n}}{2}\right)}_{\text{n is odd}}
\end{aligned}$$

$$(E_n - E_{n'})^2 = \left(\frac{\pi^2\hbar^2}{2mL^2}\right)(n^2 - n'^2)^2$$

$$\frac{4\alpha^2}{L^2} \ll \frac{\pi^4\hbar^4}{4m^2L^4}(n-n')^2(n+n')^2$$

$$\alpha \ll \frac{\pi^2\hbar^2}{2mL}\left|n^2 - n'^2\right| = \frac{\pi^2 - n'^2}{2mL}\underbrace{(n-n')}_{\geq 2}\underbrace{(n+n')}_{\geq 4}$$

$$\alpha << \frac{4\pi^2\hbar^2}{mL}$$

$$\begin{aligned}
\tilde{E}_n^{(1)} &= \left\langle \psi_n \middle| \hat{V} \middle| \psi_n \right\rangle \\
&= \int_2^L \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right) \alpha\delta\left(x - \frac{L}{2}\right) dx \\
&= \frac{2}{L} \sin^2\left(\frac{n\pi L}{2L}\right) \cdot \alpha \cancelto{0}{\int_0^L \delta\left(x - \frac{L}{2}\right)} \\
&= \frac{2}{L}\left(\frac{1-(-1)^n}{2}\right)
\end{aligned}$$

$$\tilde{E}_{2k} = \frac{\pi^2\hbar^2(2k)^2}{2mL^2} + 0$$

when ψ_{2k} has no 1^{st} order correction to their eigenenergies.

$$\tilde{E}_{2k-1} = \frac{\pi^2\hbar^2(2k-1)^2}{2mL^2} + \frac{2\alpha}{L}$$

odd ψ_{2k-1} have a constant shift by $\frac{2}{L}\alpha$.

$$\psi_{2k}\left(\frac{L}{2}\right) = \sqrt{\frac{2}{L}} \sin\left(\frac{2k\pi L}{2L}\right) = \sqrt{\frac{2}{L}} \sin(\pi k) = 0$$

even n index wavefunctions all have a node @ $\frac{L}{2} \to \left(\psi_{2k}\left(\frac{L}{2}\right) = 0\right)$.

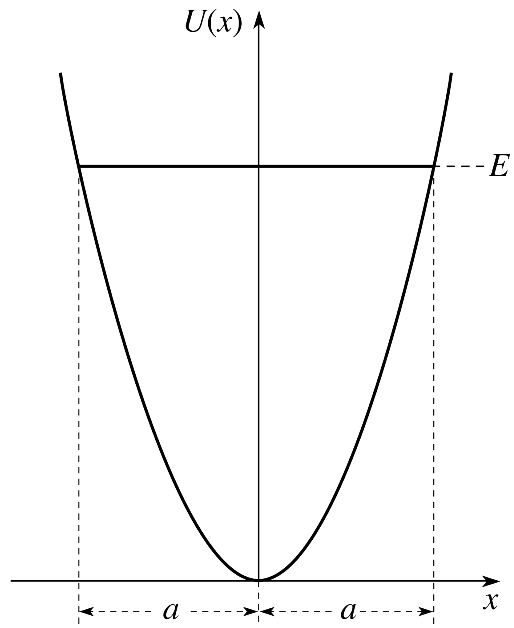
Since $V(x) = \alpha\delta\left(x - \frac{2}{L}\right)$ is non-zero only @ $\frac{L}{2}$ it does nothing to the even n wavefunctions.

$\because$ a particle in the $2k-1$, odd n, state ψ_{2k-1} has a probability $\left|\psi_{2k-1}\left(\frac{L}{2}\right)\right|^2 = \frac{2}{L}$ of being @ $\frac{L}{2}$.

1.4 Lecture 4

May 02, 2023

1.4.1 Example: Harmonic Oscillator



$$V(x) = kx^2 = \omega^2 m x^2, \quad \omega = \sqrt{\frac{k}{m}} : \text{ The frequency of oscillation}$$

Hamiltonian for the Harmonic Oscillator:

$$\hat{H}_o = \underbrace{\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}}_{K.E} + \underbrace{\omega^2 m x^2}_{P.E=\hat{V}}$$

Eigenenergies

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

x^2 can be written in terms of rising and lowering operators $\hat{a}_+ + \hat{a}_-$, respectively as:

$$\hat{x} = C\left(\hat{a}_+ + \hat{a}_-\right)$$

where if $\big|n\big\rangle$ are the eigenstates of the SHO:

Rising operator

$$\hat{a}_+\big|n\big\rangle = \sqrt{n+1}\big|n+1\big\rangle$$

Lowering operator

$$\hat{a}_-\big|n\big\rangle = \sqrt{n}\big|n-1\big\rangle$$

$$\langle n|\hat{H}_o|n\rangle = \langle n|\hat{T}|n\rangle + \underbrace{\langle n|\hat{V}|n\rangle}_{\text{the eigenenergy } E_n}$$

The particle has zero average K.E, 1/2 time to the left, and 1/2 time to the right.

Then,

$$\langle n|\omega^2 m x^2|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right) = E_n$$

but what is C?

$$\begin{aligned}
\hbar\omega\left(n+\frac{1}{2}\right) &= \omega^2 m \langle n|C^2\left(\hat{a}_+ + \hat{a}_-\right)\left(\hat{a}_+ + \hat{a}_-\right)|n\rangle \\
&= C^2\omega^2 m \cdot \langle n|\hat{a}_+\hat{a}_+ + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-\hat{a}_-|n\rangle \\
&= C^2\omega^2 m \left(\langle n|\sqrt{n+2}\sqrt{n+1}|n+2\rangle + \langle n|n\rangle n + (n+1)\langle n|n\rangle + \langle n|n-2\rangle\sqrt{n-1}\sqrt{n}\right) \\
&= C^2\omega^2 m \left(\sqrt{n+2}\sqrt{n+1}\cdot\cancelto{0}{\delta_{n,n+2}} + (2n+1)\cdot\cancelto{1}{\delta_{n,n}} + \sqrt{n-1}\sqrt{n}\cdot\cancelto{0}{\delta_{n,n-2}}\right) \\
&= C^2\omega^2 m \cdot (2n+1)
\end{aligned}$$

$$C^2 = \frac{\hbar\omega\left(n+\frac{1}{2}\right)}{\omega^2 m(2n+1)} \Rightarrow C = \sqrt{\frac{\hbar}{2\omega m}}$$

Thus,

$$\hat{x} = \sqrt{\frac{\hbar}{2\omega m}}\left(\hat{a}_+\hat{a}_-\right)$$

$$\langle n|\hat{a}_-\hat{a}_+|n\rangle = n+1 \quad \text{and} \quad \langle n|\hat{a}_+\hat{a}_-|n\rangle = n$$

$$\hat{a}_+|n\rangle = \sqrt{n+1}|n+1\rangle \quad \text{and} \quad \hat{a}_-|n\rangle = \sqrt{n}|n-1\rangle$$

Let $|n\rangle$ be the n^{th} eigenstate of the SHO with eigenenergy $E_n = \hbar\omega\left(n+\frac{1}{2}\right)$.

Perturbation

Suppose we increase the spring constant k to $k+\epsilon$ where $\epsilon << 1$, e.g. reduce the temperature.

What are the "new" perturbed eigenenergies?

$$\begin{aligned}
E_n &= \hbar\sqrt{\frac{k}{m}}\left(n+\frac{1}{2}\right) \\
\tilde{E}_n &= \hbar\sqrt{\frac{k}{m}}\left(n+\frac{1}{2}\right)\cdot\sqrt{1+\epsilon} \\
&= E_n\cdot\sqrt{1+\epsilon} \approx E_n\cdot\left(1+\frac{\epsilon}{2}-\frac{\epsilon^2}{8}+\frac{\epsilon^3}{16}\right)
\end{aligned}$$

expanding using the Tylor series.

Applying T.I.N.D.P.T

The perturbed hamiltonian is:

$$\tilde{H} = \frac{-\hbar}{2m}\frac{d^2}{dx^2} + k\hat{x}^2 + k\epsilon\hat{x}^2$$

, so, our perturbation is $\hat{V} = k\epsilon\hat{x}^2$.

$$\tilde{E}_n = E_n + \left\langle n\middle|\hat{V}'\middle|n\right\rangle + \sum_{n'\neq n}\frac{\left|\left\langle n'\middle|\hat{V}'\middle|n\right\rangle\right|^2}{E_n - E_{n'}}$$

where:

E_n: Unperturbed eigenenergy.

$E_n - E_{n'}$: Energy difference between $\left|n\right\rangle$ and $\left|n'\right\rangle$.

$\left|\left\langle n'\middle|\hat{V}'\middle|n\right\rangle\right|^2$: Probability of $\left|n\right\rangle \rightarrow \left|n'\right\rangle \rightarrow \left|n\right\rangle$ under the action of $\hat{V}$. Note that $\{\left|n\right\rangle\}$ are not usually eigenstates of $\hat{V}'$.

Note:

$$\left|\left\langle n'\middle|\hat{V}'\middle|n\right\rangle\right|^2 \lll \left|E_n - E_{n'}\right|^2, \forall n' \neq n$$

for TINDPT to apply to $\tilde{E}_n$.

Remember: If we need to go to 3^{RD} order, TINDPT does not apply unless both 1^{ST} and 2^{ND} order terms are zero, in which case the 3^{RD} order term probably is zero as well.

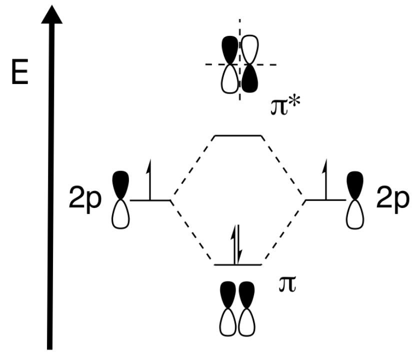
If $E_{n'} > E_n \Longrightarrow E_n - E_{n'} < 0$

If $E_{n'} < E_n \Longrightarrow E_n - E_{n'} > 0$

The second order correction to the energy,

$$\sum_{n'\neq n}\frac{\left|\left\langle n'\middle|\hat{V}'\middle|n\right\rangle\right|^2}{E_n - E_{n'}}$$

has positive terms for states below E_n, and negative terms for states above E_n. This is known as **level repulsion.**



- Same phase: bonding orbital.
- Opposite phase: antibonding orbital.

Hint: Levels repell each other.

$$\tilde{E}_n = \hbar\omega\left(n + \frac{1}{2}\right) + \frac{\epsilon}{2}E_n$$

$$\begin{aligned}\left\langle n\middle|\hat{V}'\middle|n\right\rangle = \left\langle n\middle|\frac{k\epsilon}{2}\hat{x}^2\middle|n\right\rangle &= \frac{m\omega^2}{2}\frac{\epsilon\hbar}{2m}\left\langle n\middle|(\hat{a}_+\hat{a}_-)^2\middle|n\right\rangle \\ &= \frac{\epsilon\hbar\omega}{2}\frac{(2n+1)}{2} = \frac{\epsilon}{2}\hbar\omega\left(n+\frac{1}{2}\right) \\ &= \frac{\epsilon}{2}E_n\end{aligned}$$

Virial Theorem

$$\left\langle\hat{T}\right\rangle = \left\langle\hat{V}\right\rangle$$

Schrodinger Equation:

$$\left\langle\hat{T}\right\rangle + \left\langle\hat{V}\right\rangle = E_n \Longrightarrow \left\langle\hat{V}\right\rangle = \frac{1}{2}E_n$$

$$\hat{V} = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$$

1.4.2 2^{nd} Order Correction

$$
\begin{aligned}
\tilde{E}_n^2 &= \sum_{n'\neq n} \frac{\left|\left\langle n'\middle|\hat{V}'\middle|n\right\rangle\right|^2}{E_n - E_{n'}} = \sum_{n'\neq n} \frac{\left|\left\langle n'\middle|\frac{\epsilon}{2}kx^2\middle|n\right\rangle\right|^2}{\hbar\omega\left(n+\frac{1}{2}\right) - \hbar\omega\left(n'+\frac{1}{2}\right)} \\
&= \frac{\epsilon^2}{4}\frac{m^2\omega^4}{\hbar\omega}\left(\frac{\hbar}{2m\omega}\right)^2 \sum_{n'\neq n} \frac{1}{n-n'}\left|\left\langle n\middle|\hat{a}_+\hat{a}_+ + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-\hat{a}_-\middle|n\right\rangle\right|^2 \\
&= \frac{\epsilon^2}{4}\hbar\omega \sum_{n'\neq n} \frac{1}{n-n'}\Big|\sqrt{n+2}\sqrt{n+1}\left\langle n'\middle|n+2\right\rangle + \left\langle n'\middle|n\right\rangle n + (n+1)\left\langle n\middle|n'\right\rangle \\
&+ \left\langle n'\middle|n-2\right\rangle\sqrt{n-1}\sqrt{n}\Big|^2 \\
&= \frac{\epsilon^2}{16}\hbar\omega \sum_{n'\neq n} \frac{1}{n-n'}\left|\sqrt{n+1}\sqrt{n+2}\cdot\delta_{n',n+2} + (2n+1)\cdot\cancelto{0}{\delta_{n'n}} + \sqrt{n}\sqrt{n-1}\cdot\delta_{n',n-2}\right|^2 \\
&= \frac{\epsilon^2}{16}\hbar\omega \sum_{n'\neq n} \frac{1}{n-n'}\Big|(n+1)(n+2)\cdot\delta^2_{n',n+2} + 2\sqrt{n}\sqrt{n+2}\sqrt{n+1}\sqrt{n-1}\cdot\cancelto{0}{\delta_{n',n+2}\delta_{n',n-2}} \\
&+ n(n+2)\delta^2_{n',n-2}\Big|^2
\end{aligned}
$$

Note that n' can't equal $n+2$ and $n-2$ at the same time, that is why the delta functions cancel.

1.5 Lecture 5

May 03, 2023

1.5.1 Example: SHO

$k \longrightarrow (1+\epsilon)k$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$\omega = \sqrt{\frac{k}{m}}, \quad \hat{V} = \frac{1}{2}kx^2$$

Exact Solution

$$\begin{aligned}\tilde{E}_n &= \hbar\sqrt{\frac{k(1+\epsilon)}{m}}\left(n + \frac{1}{2}\right)\\ &= \hbar\omega\left(n + \frac{1}{2}\right)\sqrt{1+\epsilon}\\ &= E_n\sqrt{1+\epsilon}\end{aligned}$$

$$\boxed{\tilde{E}_n \approx E_n\left(1 + \frac{\epsilon}{2} - \frac{\epsilon^2}{8} + \mathcal{O}(\epsilon^3)\right)}$$

Perturbation Theory

$$\tilde{E}_n = E_n + \langle n|\hat{V}|n\rangle + \sum_{n'\neq n}\frac{\left|\langle n'|\hat{V}|n\rangle\right|^2}{E_n - E_{n'}}$$

Level repulsion scales the energy.

$$|\tilde{n}\rangle = |n\rangle \sum_{n'\neq n}\frac{\langle n'|\hat{V}|n\rangle}{E_n - E_{n'}}|n'\rangle$$

In general, the appropiate wavefunctions from TINDPT are not very accurate.

$$\tilde{E}_n = \hbar\omega\left(n + \frac{1}{2}\right) + \langle n|\frac{\epsilon}{2}kx^2|n\rangle + \sum_{n'\neq n}\frac{\left|\langle n'|\frac{\epsilon}{2}kx^2|n\rangle\right|^2}{E_n - E_{n'}}$$

$$\langle n|\frac{\epsilon}{2}kx^2|n\rangle = \frac{m\omega^2}{2}\frac{\hbar\epsilon}{2m\omega}\left|\langle n|\hat{a}_+\hat{a}_+ + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-\hat{a}_-|n\rangle\right|^2$$

But,

$$\hat{x} \equiv \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}_+ + \hat{a}_-\right), \quad \hat{a}_+|n\rangle = \sqrt{n+1}|n+1\rangle, \quad \hat{a}_-|n\rangle = \sqrt{n}|n-1\rangle$$

Then

$$\langle n|\hat{V}|n\rangle = \frac{\epsilon}{4}\hbar\omega\,(n+n+1) = \frac{\epsilon}{2}\hbar\omega\left(n+\frac{1}{2}\right) = \boxed{\frac{\epsilon}{2}E_n}$$

Now, let's compute the second order correction:

$$\begin{aligned}
\tilde{E}_n^{(2)} &= \left(\frac{\epsilon}{2}m\omega^2\right)^2\left(\frac{\hbar}{2m\omega}\right)^2\frac{1}{\hbar\omega}\sum_{n'\neq n}\frac{\left|\langle n'|\hat{a}_+\hat{a}_+ + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-\hat{a}_-|n\rangle\right|^2}{n+\frac{1}{2}-\left(n+\frac{1}{2}\right)} \\
&= \frac{\epsilon^2}{16}\hbar\omega\sum_{n'\neq n}\left|\sqrt{n+2}\sqrt{n+1}\,\underbrace{\langle n'|n+2\rangle}_{\delta_{n',n+2}} + \sqrt{n-1}\sqrt{n}\,\underbrace{\langle n'|n-2\rangle}_{\delta_{n',n-2}}\right|^2 \\
&= \frac{\epsilon^2}{16}\hbar\omega\left(\sum_{n'\neq n}\frac{(n+2)(n+1)\delta_{n',n+2}}{n-(n-2)} + \frac{(n-1)n\cdot\delta_{n',n-2}}{n-(n-2)}\right) \\
&= \frac{\epsilon^2}{16}\hbar\omega\left(\frac{n^2-n-n^2-2n-n-2}{|2|}\right) \\
&= \frac{\epsilon^2\hbar\omega}{16}\left(\frac{-4n-2}{2}\right)^{1/2}
\end{aligned}$$

$$\boxed{\tilde{E}_n^{(2)} = \frac{-\epsilon^2\hbar\omega}{8}\left(n+\frac{1}{2}\right)}$$

Then,

$$\tilde{E} = E_n\left(1+\frac{\epsilon}{2}-\frac{\epsilon^2}{8}\right) = E_n\sqrt{1+\epsilon} \quad \text{to} \quad \mathcal{O}(\epsilon^3)$$

1.5.2 Example: Interacting Bosons

Consider two bosons which interact weakly in an infinite square well potential of width L which weakly interact via $V(x_1,x_2) = -LV_o\delta(x_1-x_2)$ where V_o is a constant with dimensions of energy, δ is the Dirac delta function and x_1 and x_2 are the positions of the 1^{st} and 2^{nd} boson.
Recall: the dimension of the Dirac δ-function is the inverse of its arguments so that:

$$\int_{-\infty}^{\infty}\delta(x)dx = 1 \quad \text{(dimensionless)}$$

So, $\delta(x_1-x_2)$ has units of 1/Lenght, this is why we have a factor of L in the def'n of $V(x_1,x_2)$.

Note: $V(x_1,x_2)\longrightarrow\infty$ as $x_1\longrightarrow x_2$, but so does the Coulomb interaction. Moreover, it is the expectation of the potential which is important and this will go as V_o, i.e. $\langle n|V|n\rangle \sim V_o$, when $x_1\neq x_2$, $V(x_1,x_2)=0$, so the two particles only interact when they reach or occupy the same point in space.

- Bosons: many bosons can occupy the same state (spin 0).
- Fermions: Only one fermion can occupy the same state (spin $\frac{1}{2}$)

Bosons:

$$\Psi(x_1, x_2) = \Psi_a(x_1)\Psi_b(x_2) + \Psi_a(x_2)\Psi_b(x_1)$$

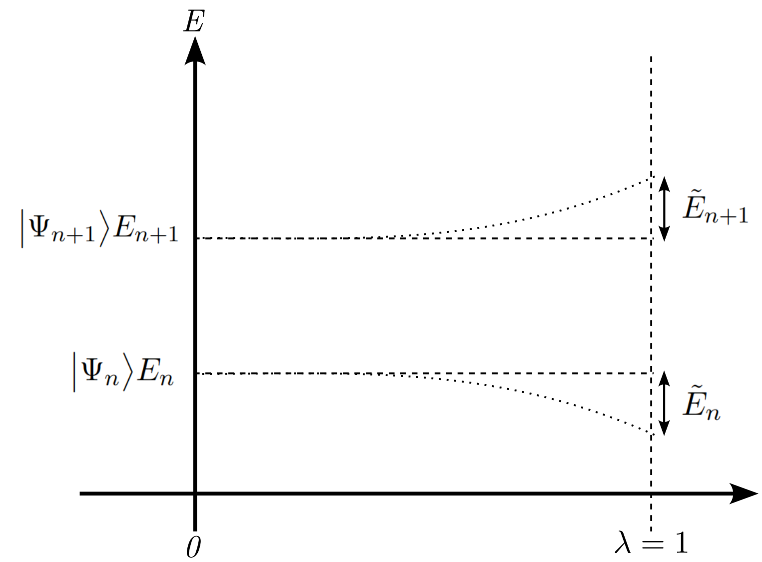
$$\Psi(x_1, x_2) = \Psi(x_1)\Psi(x_2) \quad \text{Bosons are symmetric under exchange.}$$

Fermions:

$$\Psi(x_1, x_2) = \Psi_a(x_1)\Psi_b(x_2) + \Psi_a(x_2)\Psi_b(x_1)$$

$$\Psi(x_1, x_2) = -\Psi(x_2, x_1) \quad \text{Fermions are antisymmetric under exchange.}$$

The n-particle wavefunction in terms of single particle wavefunctions can be written as a **Slater Determinant**, i.e. the determinant of an $n \times n$ matrix of single particle wavefunctions at positions χ to χ_n.



$$\tilde{H} = \underbrace{\hat{H}_o}_{E_n\left|\psi_n\right\rangle} + \lambda\hat{V}$$

$$\tilde{\mathcal{E}}_n \approx \mathcal{E}_n + \big\langle n\big|\hat{V}\big|n\big\rangle + \sum_{n' \neq n} \frac{\big|\big\langle n'\big|\hat{V}\big|n\big\rangle\big|^2}{\mathcal{E}_n - \mathcal{E}_{n'}}$$

1.6 Lecture 6

May 08, 2023

1.6.1 Example: two bosons in an infinite square well

$$-LV_o\delta(x_1, x_2)$$

where,

$$V_o(x_1, x_2) = \begin{cases} 0 & 0 \le x_1,\ x_2 \le 1 \\ \infty & \text{Otherwise} \end{cases}$$

For non-interacting bosons

Let $\Psi_{n_1,n_2}(x_1, x_2)$ be the two body wavefunction for the two bosons.

Schrodinger Equation:

$$\hat{H}_o(x_1, x_2)\Psi(x_1, x_2) = E\Psi(x_1, x_2)$$

$$\begin{aligned} \hat{H}_o(x_1, x_2) &= \hat{T}(x_1, x_2) + \hat{V}(x_1, x_2) \\ &= \frac{-\hbar}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right)\Psi(x_1, x_2) = E\Psi(x_1, x_2) \end{aligned}$$

$$\boxed{\frac{\partial^2\Psi}{\partial x_1^2} + \frac{\partial^2\Psi}{\partial x_2^2} = \frac{-2mE}{\hbar^2}\Psi}$$

Since the two particles are bosons, then the wavefunction is symmetric, i.e.,

$$\Psi(x_1, x_2) = \Psi(x_2, x_1)$$

$$\Psi_{n_1,n_2}(x_1, x_2) = \underbrace{\Psi_{n_1}(x_1)\Psi_{n_2}(x_2)}_{\text{separable}} + \underbrace{\Psi_{n_1}(x_2)\Psi_{n_2}(x_1)}_{\text{ensures symmetry}}$$

$$\begin{aligned} &\Psi''_{n_1}(x_1)\Psi''_{n_2}(x_2) + \Psi_{n_1}(x_2)\Psi''_{n_2}(x_1) + \Psi_{n_1}(x_1)\Psi''_{n_2}(x_2) + \Psi'' + \Psi''_{n_1}(x_2)\Psi_{n_1}(x_1) \\ &\qquad = \frac{-2mE}{\hbar^2}\left[\Psi_{n_1}(x_1)\Psi_{n_2}(x_2) + \Psi_{n_1}(x_2)\Psi_{n_2}(x_1)\right] \end{aligned}$$

Separation of variables

$$\Psi''_{n_1}(x_1)\Psi_{n_2}(x_2) + \Psi_{n_1}(x_1)\Psi''_{n_2}(x_2) = \frac{-2mE}{\hbar^2}\Psi_{n_1}(x_1)\Psi_{n_2}(x_2)$$

$$\Psi_{n_1}(x_2)\Psi''_{n_2}(x_1) + \Psi''_{n_1}(x_2)\Psi_{n_1}(x_2) = \frac{-2mE}{\hbar^2}\Psi_{n_1}(x_2)\Psi_{n_2}(x_1)$$

Divide (7.4) by $\Psi_{n_1}(x_1)\Psi_{n_2}(x_2)$ on both sides:

$$\frac{\Psi''_{n_1}(x_1)}{\Psi_{n_1}(x_1)} + \frac{\Psi''_{n_2}(x_2)}{\Psi_{n_2}(x_2)} = \frac{-2mE}{\hbar^2} \longleftarrow \text{Eigenvalue}$$

$$\frac{\Psi''_{n_1}(x_1)}{\Psi_{n_1}(x_1)} = \frac{-2mE}{\hbar^2} - \frac{\Psi''_{n_2}(x_2)}{\Psi_{n_2}(x_2)} = -\lambda_{n_1} \longleftarrow \text{Eigenvalue}$$

then,

$$\Psi''_{n_1}(x_1) = -\Psi_{n_1}(x_1)\lambda_{n_1}$$

$$\Longrightarrow \boxed{\Psi_{n_1}(x_1) = A\cos\left(\sqrt{\lambda_{n_1}}x_1\right) + B\sin\left(\sqrt{\lambda_{n_1}}x_1\right)}$$

$$\Psi_{n_1}(0) = 0 = A \quad \Psi_{n_1}(L) = 0 = B_1\sin\left(\sqrt{\lambda_{n_1}}L\right)$$

$$\Longrightarrow \sqrt{\lambda_{n_1}}L = n_1\pi \Rightarrow \begin{cases} n_1 = 0, & \text{no particle} \\ \Psi_{n_1}(x_1) = -\Psi_{n_1}(x_1) \longrightarrow n_1 \in \mathbb{R} \end{cases}$$

Then,

$$\Psi_{n_1}(x_1) = B_1\sin\left(\frac{n_1\pi x}{L}\right) \Longrightarrow \lambda_1 = \frac{n_1^2\pi^2}{L^2}$$

$$\because \Psi_{n_2}(x_2) = B_2\sin\left(\frac{n_2\pi x}{L}\right) \Longrightarrow \lambda_2 = \frac{n_2^2\pi^2}{L^2}$$

$$\Longrightarrow \frac{-2mE}{\hbar^2} = -\lambda_1 - \lambda_2 = \frac{-\pi^2}{L^2}\left(n_1^2 - n_2^2\right)$$

$$\boxed{E_{n_1n_2} = \frac{\pi^2\hbar^2}{2mL^2}\left(n_1^2 + n_2^2\right)}$$

$$\Psi_{n_1n_2}(x_1, x_2) = \underbrace{B_1B_2}_{A}\left(\sin\left(\frac{n_1\pi x_1}{L}\right)\sin\left(\frac{n_2\pi x_2}{L}\right) + \sin\left(\frac{n_1\pi x_2}{L}\right)\sin\left(\frac{n_2\pi x_1}{L}\right)\right)$$

We need to normalise the wave function, i.e. find A,

$$\left\langle\Psi_{n_1n_2}(x_1, x_2)\middle|\Psi_{n_1n_2}(x_1, x_2)\right\rangle = 1$$

$$\Longrightarrow A^2\int_0^L\int_0^L dx_1dx_2\left(\sin^2\left(\frac{n_1\pi x_1}{L}\right)\sin^2\left(\frac{n_2\pi x_2}{L}\right) + 2\sin\left(\frac{n_1\pi x_1}{L}\right)\sin\left(\frac{n_2\pi x_1}{L}\right)\right.$$
$$\left.\cdot\sin\left(\frac{n_2\pi x_2}{L}\right)\sin\left(\frac{n_1\pi x_2}{L}\right) + \sin^2\left(\frac{n_1\pi x_2}{L}\right)\sin^2\left(\frac{n_2\pi x_1}{L}\right)\right)$$

$$= A^2\left(\frac{L}{2}\times\frac{L}{2} + 2\frac{L}{2}\delta_{n_1n_2}\times\delta_{n_1n_2} + \frac{L}{2}\times\frac{L}{2}\right) = A^2\frac{L^2}{4}2\left(1 + \delta_{n_1n_2}\right)$$

$$= A^2\frac{L^2}{2}\left(1+\delta_{n_1n_2}\right) \implies \boxed{A = \frac{\sqrt{2}}{L}\frac{1}{\sqrt{1+\delta n_1 n_2}}}$$

Then, our normalised wavefunction is

$$\Psi_{n_1n_2}(x_1,x_2) = \frac{\sqrt{2}}{L}\frac{1}{\sqrt{1+\delta_{n_1n_2}}}\left(\sin\left(\frac{n_1\pi x_1}{L}\right)\sin\left(\frac{n_2\pi x_2}{L}\right)+\sin\left(\frac{n_1\pi x_2}{L}\right)\sin\left(\frac{n_2\pi x_1}{L}\right)\right)$$

and the eigenenergy

$$E_{n_1n_2} = \frac{\pi^2\hbar^2}{2mL^2}\left(n_1^2+n_2^2\right) = E_{n_1}+E_{n_2}$$

Ground State

$$E_{gs} = E_{11} = \frac{\pi^2\hbar^2}{mL^2}$$

$$\Psi_{gs} = \frac{2}{L}\sin\left(\frac{\pi x_1}{L}\sin\left(\frac{\pi x_2}{L}\right)\right)$$

1st Excited State

$$E_{ex} = E_{12} = E_{21} = \frac{5\pi^2\hbar^2}{2mL^2} = 5E_1 = E_1+E_2$$

$$\Psi_{ex} = \frac{2}{L}\frac{\sin\left(\frac{2\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)+\sin\left(\frac{2\pi x_2}{L}\right)\sin\left(\frac{\pi x_1}{L}\right)}{\sqrt{2}}$$

Perturbed Hamiltonian

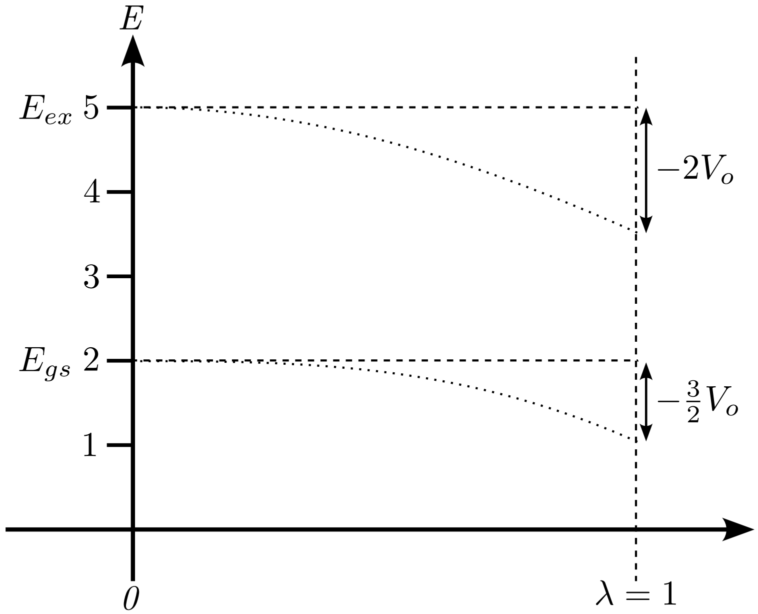
$$\hat{H} = \hat{H}_o - LV_o\delta(x_1-x_2)$$

$$\tilde{E}_n = E_{gs} + \left\langle\Psi_{gs}\middle| -LV_o\delta(x_1-x_2)\middle|\Psi_{gs}\right\rangle$$

$$\begin{aligned}
\tilde{E}^{(1)}_{gs} &= \int_0^L\int_0^L\left(\frac{2}{L}\right)^2\sin^2\left(\frac{\pi x_1}{L}\right)\sin^2\left(\frac{\pi x_2}{L}\right)\delta(x_1-x_2)dx_1dx_2(-LV_o)\\
&= \frac{4}{L^2}(-LV_o)\int_0^L\sin^4\left(\frac{\pi x_1}{L}\right)dx_1\\
&= \frac{-4V_o}{L}\left(\frac{3L}{8}\right)
\end{aligned}$$

$$\boxed{\tilde{E}^{(1)}_{gs} = -\frac{3}{2}V_o}$$

Trig. Identity $\displaystyle\int\sin^4(\alpha x)dx = \frac{3x}{8}-\frac{\sin(2\alpha x)}{4\alpha}+\frac{\sin(4\pi x)}{32\alpha}$



$$\begin{aligned}
\tilde{E}_{ex}^{(1)} &= \int_0^L \int_0^L \frac{2}{L^2}\left(\sin\left(\frac{2\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)+\sin\left(\frac{2\pi x_2}{L}\right)\sin\left(\frac{\pi x_1}{L}\right)\right)^2\left(-LV_o\delta(x_1,x_2)\right)dx_1dx_2 \\
&= \frac{L}{L^2}V_o 2\int_0^L\left(2\sin\left(\frac{2\pi x_1}{L}\right)\sin\left(\frac{\pi x_1}{L}\right)\right)^2 dx_1 \\
&= \frac{-8V_o}{L}\int_0^L \sin^2\left(\frac{2\pi x_1}{L}\right)\sin^2\left(\frac{\pi x_1}{L}\right)dx_1
\end{aligned}$$

We solved this integral using a trigonometrical identity:

$$\begin{aligned}
Sin^2(A)Sin^2(B) &= Sin^2(A) - Sin^2(A)Cos^2(B) \\
&= Sin^2(A) - \left(\frac{Sin(A+B)-Sin(A-B)}{2}\right)^2 \\
&= Sin^2(A) - \frac{1}{4}\left(Sin^2(A+B) - 2Sin(A+B)Sin(A-B) + Sin^2(A-B)\right)
\end{aligned}$$

then,

$$\begin{aligned}
&= \frac{-8V_o}{L}\int_0^L \cancelto{\frac{L}{2}}{Sin^2\left(\frac{2\pi x_1}{L}\right)} - \frac{1}{4}\left(\cancelto{\frac{L}{2}}{Sin^2\left(\frac{3\pi x_1}{L}\right)} + \cancelto{\frac{L}{2}}{Sin^2\left(\frac{\pi x_1}{L}\right)} - \cancelto{\delta_{mn}=0}{2Sin^2\left(\frac{3\pi x_1}{L}\right)Sin\left(\frac{\pi x_1}{L}\right)}\right)dx_1 \\
&= \frac{-8V_o}{L}\left(\frac{L}{2}-\frac{L}{4}\right)
\end{aligned}$$

$$\boxed{\tilde{E}_{ex}^{(1)} = -2V_o}$$

Chapter 2

Time Independent Degenerate Perturbation Theory

2.1 Lecture 7

May 09, 2023

1D infinite square well with two bosons

$$\Psi_{n_1n_2}(x_1,x_2) = \frac{2}{L}\frac{1}{\sqrt{2}\sqrt{1+\delta_{n_1n_2}}}\left(\sin\left(\frac{n_1\pi x_1}{L}\right)\sin\left(\frac{n_2\pi x_2}{L}\right)+\sin\left(\frac{n_1\pi x_2}{L}\right)\sin\left(\frac{n_2\pi x_1}{L}\right)\right)$$

Now, let's compute $\tilde{E}_{11}^{(2)}$

$$\begin{aligned}
\tilde{E}_{11}^{(2)} &= \left(1-\delta_{n_1n_2}\delta_{n_11}\right)\sum_{n_1,n_2=1}^{\infty}\frac{\left|\left\langle\Psi_{n_1n_2}\right|-LV_o\delta(x_1-x_2)\left|\Psi_{11}\right\rangle\right|^2}{E_{11}-E_{n_1n_2}} \\
&= \frac{2mL^2}{\pi^2\hbar}\sum_{n_1,n_2}\frac{L^2V_o^2\left(1-\delta_{n_1n_2}\delta_{n_11}\right)}{2-n_1^2-n_2^2}\left(\frac{4}{L^2}\right)\frac{1}{2\left(1+\delta_{n_1n_2}\right)} \\
&\cdot\left|\int_0^L\int_0^L\left[Sin\left(\frac{n_1\pi x_1}{L}\right)Sin\left(\frac{n_2\pi x_2}{L}\right)+Sin\left(\frac{n_1\pi x_2}{L}\right)\right.\right. \\
&\cdot\left.\left. Sin\left(\frac{n_2\pi x_1}{L}\right)\right]\delta(x_1-x_2)\right|^2\underbrace{\frac{2}{L}Sin\left(\frac{\pi x_1}{L}\right)Sin\left(\frac{\pi x_2}{L}\right)}_{\Psi_{11}(x_1,x_2)}dx_1dx_2 \\
&= \frac{16mV_o^2}{\pi^2\hbar^2}\sum_{n_1,n_2=1}^{\infty}\frac{1-\delta_{n_1n_2}\delta_{n_11}}{2-n_1^2-n_2^2}\frac{1}{1+\delta_{n_1n_2}}\left|\int_0^L 2Sin\left(\frac{n_1\pi x}{L}\right)Sin\left(\frac{n_2\pi x}{L}\right)\underbrace{Sin^2\left(\frac{\pi x}{L}\right)}_{1-Cos^2\left(\frac{\pi x}{L}\right)}dx\right|^2 \\
&= \frac{2^6mV_o^2}{\pi^2\hbar^2}\sum_{n_1,n_2=1}\frac{1-\delta_{n_1n_2}\delta_{n_11}}{1+\delta_{n_1n_2}}\frac{1}{2-n_1^2-n_2^2}\left|\underbrace{\int_0^L Sin\left(\frac{n_1\pi x}{L}\right)Sin\left(\frac{n_2\pi x}{L}\right)Sin^2\left(\frac{\pi x}{L}\right)dx}_{(*)}\right|^2
\end{aligned}$$

Let's solve the integral $(*)$:

$$\int_0^L Sin\left(\frac{n_1\pi x}{L}\right) Sin\left(\frac{n_2\pi x}{L}\right) \underbrace{Sin^2\left(\frac{\pi x}{L}\right)}_{1-Cos^2\left(\frac{\pi x}{L}\right)} dx = \overbrace{\int_0^L Sin\left(\frac{n_1\pi x}{L}\right) Sin\left(\frac{n_2\pi x}{L}\right) dx}^{\frac{L}{2}\delta_{n_1n_2}}$$

$$- \int_0^L Sin\left(\frac{n_1\pi x}{L}\right) Cos\left(\frac{\pi x}{L}\right) Sin\left(\frac{n_2\pi x}{L}\right) Cos\left(\frac{\pi x}{L}\right) dx$$

$$= \frac{L}{2}\delta_{n_1n_2} - \frac{1}{4}\int_0^L Sin\left(\frac{(n_1+1)\pi x}{L}\right) Sin\left(\frac{(n_2+1)\pi x}{L}\right)$$

$$+ Sin\left(\frac{(n_1+1)\pi x}{L}\right) Sin\left(\frac{(n_2-1)\pi x}{L}\right)$$

$$+ Sin\left(\frac{(n_1-1)\pi x}{L}\right) Sin\left(\frac{(n_2+1)\pi x}{L}\right)$$

$$+ Sin\left(\frac{(n_1-1)\pi x}{L}\right) Sin\left(\frac{(n_2-1)\pi x}{L}\right) dx$$

$$= \frac{L}{2}\delta_{n_1n_2} - \frac{1}{4}\frac{L}{2}\left(\underbrace{\delta_{n_1+1,n_2+1}}_{\delta_{n_1n_2}} + \delta_{n_1+1,n_2-1}\right.$$

$$\left. + \delta_{n_1-1,n_2+1} + \underbrace{\delta_{n_1-1,n_2-1}}_{\delta_{n_1n_2}}\right)$$

Finally,

$$\tilde{E}_{11}^{(2)} = \frac{2^4 m L^2 V_o^2}{\pi^2\hbar^2}\sum_{n_1,n_2=1}\frac{1-\delta_{n_1n_2}\delta_{n_11}}{1+\delta_{n_1n_2}}\frac{1}{2-n_1^2-n_2^2}\left|\frac{\delta_{n_1n_2}}{2} - \frac{\delta_{n_1+1,n_2-1}+\delta_{n_1-1,n_2+1}}{4}\right|^2$$

we can notice that $n_1 - n_2 = \pm 2 \Rightarrow \Delta n = \pm 2$

Selection Rule

$\Delta n = \mathcal{O}n \pm 2$

$$\tilde{E}_{11}^{(2)} = \frac{2V_o^2}{E_1}\sum_{n_1,n_2=1}\frac{1-\delta_{n_1n_2}\delta_{n_11}}{1+\delta_{n_1n_2}}\frac{1}{2-n_1^2-n_2^2}\left|\underbrace{\delta_{n_1n_2}}_{\Delta n=0} - \underbrace{\frac{\delta_{n_1+1,n_2-1}}{4}}_{\Delta n=-2} + \underbrace{\frac{\delta_{n_1-1,n_2+1}}{4}}_{\Delta n=+2}\right|^2$$

So, the ground state of two bosons only couples two exited states with the same or a difference 0f ± 2 between the n's.

Time-Ind. Degenerate Perturbation Theory

Suppose states $\mathbf{n}, \mathbf{n+1}, \cdots, \mathbf{n+k-1}$ are k-fold degenerate i.e. $\mathcal{E}_{\mathbf{n}} = \mathcal{E}_{\mathbf{n+1}} = \cdots = \mathcal{E}_{\mathbf{n+k-1}}$, where $\mathbf{k}$ is the number of states with the same eigenenergy as $\mathcal{E}_{\mathbf{n}}$ for the unperturbed hamiltonian $\hat{\mathbf{H}}_{\mathbf{o}}$.

$$\hat{H}_o \big|\psi_n\big\rangle = \mathcal{E}_n \big|\psi_n\big\rangle$$
$$\big\langle {\psi_n}' \big|\psi_n\big\rangle = \delta_{n'n} \quad \text{(Orthonormality)}$$

Apply the perturbation $\hat{V}'$.

The perturbed hamiltonian is $\tilde{H} = \hat{H}_o + \lambda V$, where $\lambda \in [0,1]$ is a bookkeeping parameter, and we expand the eigenenergies and eigenfunctions of the perturbed hamiltonian in powers of λ.

$$\tilde{\mathcal{E}}_n = \tilde{\mathcal{E}}_n^{(0)} + \lambda \tilde{\mathcal{E}}_n^{(1)} + \lambda^2 \tilde{\mathcal{E}}_n^{(2)} + \cdots = \sum_{k=0} \lambda^k \tilde{\mathcal{E}}_n^{(k)}$$

so, λ keeps track of the dependence on the perturbation $\hat{V}'$.

$$\therefore \tilde{\psi}_n = \tilde{\psi}_n^{(0)} + \lambda \tilde{\psi}_n^{(1)} + \lambda^2 + \lambda^2 \tilde{\psi}_n^{(2)} + \cdots = \sum_{k=0}^{\infty} \lambda^k \tilde{\psi}_n^{(k)}$$

TISE

$$\tilde{H} \big|\tilde{\psi}_n\big\rangle = \tilde{\mathcal{E}} \big|\hat{\psi}_n\big\rangle$$

Substituting for $\hat{H}, \big|\hat{\psi}_n\big\rangle$ and $\tilde{\mathcal{E}}_n$:

$$\left(\hat{H}_o + \lambda \hat{V}'\right) \sum_{k=0}^{\infty} \lambda^k \big|\tilde{\psi}_n^{(k)}\big\rangle = \sum_{k=0}^{\infty} \lambda^{k'} \tilde{\mathcal{E}}_n^{(k')} \sum_{k=0}^{\infty} \lambda^k \big|\tilde{\psi}_n^{(k)}\big\rangle$$

$$\sum_{k=0}^{\infty} \left[\lambda^{k'} \hat{H}_o \big|\tilde{\psi}_n^{(k)}\big\rangle + \lambda^{k+1} \hat{V}' \big|\tilde{\psi}_n^{(k)}\big\rangle - \sum_{k'=0}^{k} \lambda^{k+k'} \tilde{\mathcal{E}}_n^{(k')} \big|\tilde{\psi}_n^{(k)}\big\rangle \right] = 0$$

Gather together like powers of λ;

$$\sum_{k=0}^{\infty} \lambda^k \left[\hat{H}_o \big|\tilde{\psi}_n^{(k)}\big\rangle + \hat{V}_o (1 - \delta_{k0}) \big|\tilde{\psi}_n^{(k-1)}\big\rangle - \sum_{k'=0}^{k} \tilde{\mathcal{E}}_n^{(k')} \big|\tilde{\psi}_n^{(k-k')}\big\rangle \right] = 0$$

for this sum to be zero $\forall$ values of λ we need the term in $[\cdots]$ to be zero $\forall$ values of k $\forall$ powers of λ.

$\mathcal{O}(\lambda^0) = \mathcal{O}(1) = k = 0$:

$$\hat{H}_o \big|\tilde{\psi}_n^{(0)}\big\rangle = \tilde{\mathcal{E}}_n^{(0)} \big|\tilde{\psi}_n^{(0)}\big\rangle \quad \text{(alternatively set } \lambda = 0 \text{ in TISE)}$$

multiply by $\langle \psi_{n'} |$:

$$\langle \psi_{n'} | \hat{H}_o | \psi_n^{(0)} \rangle = \tilde{\mathcal{E}}_n^{(0)} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle$$

$$\begin{aligned}
\langle \psi_{n'} | \hat{H}_o^{\dagger} | \psi_n^{(0)} \rangle - \tilde{\mathcal{E}}_n^{(0)} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle &= 0 \\
\mathcal{E}_{n'} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle - \tilde{\mathcal{E}}_n^{(0)} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle &= 0 \\
\left(\mathcal{E}_{n'} - \tilde{\mathcal{E}}_n^{(0)} \right) \tilde{\mathcal{E}}_n^{(0)} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle &= 0
\end{aligned}$$

then,

$$\Rightarrow \mathcal{E}_{n'} = \tilde{\mathcal{E}}_n^{(0)} \quad \text{or} \quad \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle = 0$$

if $n' \in \{n, \cdots, n+k-1\}$, then $\mathcal{E}_{n'} = \mathcal{E}_n = \tilde{\mathcal{E}}_n^{(0)}$

$$\Rightarrow \boxed{ | \tilde{\psi}_n^{(0)} \rangle = \sum_{n'=n}^{n+k-1} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle | \psi_{n'} \rangle }$$

So, the Zeroth order wave function for the n^{th} perturbed eigenstate isn't just $| \psi_{n'} \rangle$, but a linear combination of all the **degenerate** unperturbed eigenfunctions with the same eigenvalue $\mathcal{E}_n$, i.e.

$$\begin{aligned}
| \tilde{\psi}_n^{(0)} \rangle &= \sum_{n'=n}^{n+k-1} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle | \psi_{n'} \rangle \\
&= \sum_{n'=n}^{n+k-1} C_{nn'} | \psi_{n'} \rangle
\end{aligned}$$

- Sum over all degenerate unperturbed eigenstates.

and,

$$\sum_{n'=n}^{n+k-1} \left| C_{n'n} \right|^2 = 1$$

Idea: the perturbation $\hat{V}'$ "lifts" the degeneracy between the k-fold degenerate eigenstates of the unperturbed hamiltonian.

The zeroth order eigenstate for the perturbed hamiltonian need to be eigenstates of the perturbation. If the eigenstates of the unperturbed hamiltonian are also eigenstates of the perturbation, then we can just directly apply non-degenerate perturbation theory.

$$\text{Recall:} \quad \tilde{\mathcal{E}}_n^{(1)} = \langle \psi_n | \hat{V} | \tilde{\psi}_n^{(0)} \rangle$$

So, we need to find $| \tilde{\psi}_n^{(0)} \rangle$.

2.2 Lecture 8

May 10, 2023

Zeroth order term in the perturbed n^{th} wavefunction,

$$\tilde{\psi}_n^{(0)} = \sum_{n'=n}^{n+k-1} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle | \psi_{n'} \rangle$$

where $\hat{H}_0 | \psi_{n'} \rangle = \mathcal{E}_n | \psi_{n'} \rangle \; \forall n' \in \{n_1 \ldots, n+k, -1\}$ (k-fold degenerate)

$$\sum_{n'=n}^{n+k-1} \left| \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle \right|^2 = 1$$

$$\mathcal{O}(\lambda) : \hat{H}_o | \tilde{\psi}_n^{(1)} \rangle + \hat{V}' | \tilde{\psi}_n^{(0)} \rangle = \tilde{\mathcal{E}}_n^{(o)} | \tilde{\psi}_n^{(1)} \rangle + \tilde{\mathcal{E}}_n^{(1)} | \tilde{\psi}_n^{(0)} \rangle \tag{2.2.1}$$

We need to find $| \tilde{\psi}_n^{(1)} \rangle$ and $\tilde{\mathcal{E}}_n^{(1)}$,

Multiply (3.2.1) by $\langle \psi_{n'} |$:

$$\langle \psi_{n'} | \hat{H}_o | \tilde{\psi}_n^{(1)} \rangle + \langle \psi_{n'} | \hat{V}' | \tilde{\psi}_n^{(0)} \rangle = \tilde{\mathcal{E}}_n^{(o)} \langle \psi_{n'} | \tilde{\psi}_n^{(1)} \rangle + \tilde{\mathcal{E}}_n^{(1)} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle$$

$$(\mathcal{E}_{n'} - \mathcal{E}_n) \langle \psi_{n'} | \tilde{\psi}_n^{(1)} \rangle + \langle \psi_{n'} | \hat{V}' | \tilde{\psi}_n^{(0)} \rangle = \tilde{\mathcal{E}}_n^{(1)} \langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle$$

if $n' \in \{n, \cdots, n+k-1 \quad \text{and} \quad \mathcal{E}_{n'} = \mathcal{E}_n\}$, then:

$$\begin{aligned}
\mathcal{E}_n^{\tilde{(1)}} &= \frac{\langle \psi_{n'} | \hat{V}' | \psi_n^{(0)} \rangle}{\langle \psi_{n'} | \tilde{\psi}_n^{(0)} \rangle} = \frac{\langle \psi_{n'} | \hat{V}' \sum_{n''=n}^{n+k-1} \langle \psi_{n''} | \tilde{\psi}_n^{(0)} \rangle | \psi_{n''} \rangle}{\langle \psi_{n'} | \sum_{n''=n}^{n+k-1} \langle \psi_{n''} | \tilde{\psi}_n^{(0)} \rangle | \psi_{n''} \rangle} \\
&= \frac{\sum_{n''=n}^{n+k-1} C_{n''n} \langle \psi_{n'} | \hat{V} | \psi_{n''} \rangle}{\sum_{n''=n}^{n+k-1} C_{n''n} \langle \psi_{n'} | \psi_{n''} \rangle} \\
&= \frac{\sum_{n''=n}^{n+k-1} C_{n''n} \langle \psi_{n'} | \hat{V} | \psi_{n''} \rangle}{C_{n'n}}
\end{aligned}$$

$$\boxed{\tilde{\mathcal{E}}_n^{(1)} = \sum_{n''=n}^{n+k-1} \frac{C_{n''n}}{C_{n'n}} \langle \psi_{n'} | \hat{V} | \psi_{n''} \rangle}, \quad n' \in \{n, \cdots, n+k-1\}$$

This is a set of k independet equations for $\tilde{\mathcal{E}}_n^{(1)}$, with different $C_{n'n}$:

- $1 + k$ equations
- $1 + k$ unknowns

$\Rightarrow$ Closed system

Matrix elements: $W_{n'n''} = \langle \psi_{n'} | \hat{V}' | \psi_{n''} \rangle$
Expectation value of the perturbation $|\psi_{n''}\rangle \longrightarrow \langle \psi_{n'}|$

$$\tilde{\mathcal{E}}_n^{(1)} = \sum_{n''=n}^{n+k-1} \frac{C_{n''n}}{C_{n'n}} W_{n'n''}$$

Consider k=*2*, doubly degenerate system,

$$\{n, n+1\} \equiv \{\alpha, \beta\}$$

$$\tilde{\mathcal{E}}_n^{(1)} = \frac{C_{\alpha\alpha}}{C_{\alpha\alpha}} W_{\alpha\alpha} + \frac{C_{\beta\alpha} W_{\alpha\beta}}{C_{\alpha\alpha}}, \quad n' = \alpha$$

$$\tilde{\mathcal{E}}_n^{(1)} = \frac{C_{\alpha\alpha}}{C_{\beta\alpha}} W_{\beta\alpha} + \frac{C_{\beta\alpha} W_{\beta\beta}}{C_{\beta\alpha}}, \quad n' = \beta$$

Suppose $W_{\alpha\alpha} = W_{\beta\beta} = 0 \Rightarrow$ Perturbation between swaps eigenstates of $\hat{H}_o$

$$\Rightarrow \tilde{\mathcal{E}}_\alpha^{(1)} = \frac{C_{\beta\alpha}}{C_{\alpha\alpha}} W_{\alpha\beta} = \frac{C_{\alpha\alpha}}{C_{\beta\alpha}} W_{\beta\alpha}$$

$$|C_{\alpha\alpha}|^2 + |C_{\beta\alpha}|^2 = 1$$

$$\tilde{\mathcal{E}}_\alpha^{(1)} = \frac{|C_{\beta\alpha}|^2}{C_{\alpha\alpha} C_{\beta\alpha}} W_{\alpha\beta} = \frac{|C_{\alpha\alpha}|^2}{C_{\alpha\alpha} C_{\beta\alpha}} W_{\beta\alpha}$$

$$C_{\alpha\alpha} = \frac{C_{\beta\alpha} W_{\alpha\beta}}{\tilde{\mathcal{E}}_\alpha^{(1)}}$$

$$\tilde{\mathcal{E}}_\alpha^{(1)} = \cancelto{1}{\frac{C_{\beta\alpha}}{C_{\beta\alpha}}} \frac{W_{\beta\alpha} W_{\alpha\beta}}{\tilde{\mathcal{E}}_\alpha^{(1)}}$$

$$|\tilde{\mathcal{E}}_\alpha^{(1)}|^2 = |W_{\alpha\beta}|^2$$

$$\boxed{\tilde{\mathcal{E}}_\alpha^{(1)} = \pm |\langle \psi_\alpha | \hat{V} | \psi_\beta \rangle|}$$

1. $C_{\alpha\alpha} \tilde{\mathcal{E}}_\alpha^{(1)} = C_{\alpha\alpha} W_{\alpha\alpha} + C_{\beta\alpha} W_{\alpha\beta}$

   Solve for $C_{\beta\alpha}$:

$$C_{\beta\alpha} = C_{\alpha\alpha} \frac{\left(\tilde{\mathcal{E}}_\alpha^{(1)} - W_{\alpha\alpha}\right)}{W_{\alpha\beta}}$$

2. $C_{\beta\alpha}\tilde{\mathcal{E}_\alpha^{(1)}} = C_{\alpha\alpha}W_{\beta\alpha} + C_{\beta\alpha}W_{\beta\beta}$

   Substituting in for $C_{\beta\alpha}$:

$$C_{\alpha\alpha}\frac{\left(\tilde{\mathcal{E}_\alpha^{(1)}} - W_{\alpha\alpha}\right)}{W_{\alpha\beta}}\tilde{\mathcal{E}_\alpha^{(1)}} = C_{\alpha\alpha}W_{\beta\alpha} + C_{\alpha\alpha}\frac{\left(\tilde{\mathcal{E}_\alpha^{(1)}} - W_{\alpha\alpha}\right)}{W_{\alpha\beta}}W_{\beta\beta}$$

Factor out $C_{\alpha\alpha}$ and multiply by $W_{\alpha\beta}$, and rearrange in powers of $\tilde{\mathcal{E}}_\alpha^{(1)}$:

$$C_{\alpha\alpha}\left[\left(\tilde{\mathcal{E}}_\alpha^{(1)}\right)^2 - \left(W_{\alpha\alpha} + W_{\beta\beta}\right)\tilde{\mathcal{E}}_\alpha^{(1)} - \left|W_{\alpha\beta}\right|^2 + W_{\alpha\alpha}W_{\beta\beta}\right] = 0$$

$$\therefore C_{\beta\alpha}\left[\left(\tilde{\mathcal{E}}_\alpha^{(1)}\right)^2 - \left(W_{\alpha\alpha} + W_{\beta\beta}\right)\tilde{\mathcal{E}}_\alpha^{(1)} - \left|W_{\alpha\beta}\right|^2 + W_{\alpha\alpha}W_{\beta\beta}\right] = 0$$

So, either $C_{\alpha\alpha} = 0, C_{\beta\alpha} = 0$, or $\left(\tilde{\mathcal{E}}_\alpha^{(1)}\right) - \left(W_{\alpha\alpha} + W_{\beta\beta}\right)\tilde{\mathcal{E}}_\alpha^{(1)} - \left|W_{\alpha\beta}\right|^2 + W_{\alpha\alpha}W_{\beta\beta} = 0$

If $C_{\alpha\alpha} = 0 \Rightarrow \left|\tilde{\psi}_\alpha^{(0)}\right\rangle = \left|\psi_\beta\right\rangle$, if $C_{\beta\alpha} = 0 \Rightarrow \left|\tilde{\psi}_\alpha^{(0)}\right\rangle = \left|\tilde{\psi}_\alpha\right\rangle$

Since $\left|C_{\alpha\alpha}\right|^2 + \left|C_{\beta\alpha}\right|^2 = 1$, and we can just use T.I.N.D.P.T

Otherwise

$$\tilde{\mathcal{E}}_\alpha^{(1)} = \frac{W_{\alpha\alpha} + W_{\beta\beta}}{2} \pm \sqrt{\frac{\left(W_{\alpha\alpha} + W_{\beta\beta}\right)^2}{4} + \left|W_{\alpha\beta}\right|^2 - W_{\alpha\alpha}W_{\beta\beta}}$$

Then we've got two solutions $\pm W$

Figure

$$\tilde{\mathcal{E}}_\alpha^{(1)} = \underbrace{\frac{W_{\alpha\alpha} + W_{\beta\beta}}{2}}_{(*)} \pm \sqrt{\frac{W_{\alpha\alpha}^2 + 2W_{\alpha\alpha}W_{\beta\beta} + W_{\beta\beta}^2}{4} - W_{\alpha\alpha}W_{\beta\beta} + \left|W_{\alpha\beta}\right|^2}$$

here $(*)$ is the average of *T.I.N.D.P.T* results for $\tilde{\mathcal{E}}_\alpha$ and $\tilde{\mathcal{E}}_\beta$.

$$= \frac{W_{\alpha\alpha}W_{\beta\beta}}{2} \pm \sqrt{\left(\frac{W_{\alpha\alpha} - W_{\beta\beta}}{2}\right)^2 + \left|W_{\alpha\beta}\right|^2}$$

- $\frac{W_{\alpha\alpha} - W_{\beta\beta}}{2}$ is half the absolute difference between $W_{\alpha\alpha}$ and $W_{\beta\beta}$

two eigenvalues of the matrix:

$$\det\begin{vmatrix}\lambda - W_{\alpha\alpha} & W_{\alpha\beta} \\ W_{\beta\alpha} & \lambda - W_{\beta\beta}\end{vmatrix} = 0$$

If $W_{\alpha\beta} = 0$ (i.e. $\left|\psi_\alpha\right\rangle$ and $\left|\psi_\beta\right\rangle$ are eigenstates of the perturbation $\hat{V}'$) then:

$$\begin{aligned}
\tilde{\mathcal{E}}_\alpha^{(1)} &= \frac{W_{\alpha\alpha} + W_{\beta\beta}}{2} \pm \frac{\left|W_{\alpha\alpha} - W_{\beta\beta}\right|}{2} = \max/\min\left(W_{\alpha\alpha}, W_{\beta\beta}\right) \\
\tilde{\mathcal{E}}_\alpha^{(1)} &= \min\left(W_{\alpha\alpha}, W_{\beta\beta}\right) \\
\tilde{\mathcal{E}}_\beta^{(1)} &= \max\left(W_{\alpha\alpha}, W_{\beta\beta}\right)
\end{aligned}$$

$$\mathcal{W}_{n'n} = \left\langle\psi_n\middle|\hat{V}\middle|\psi_{n'}\right\rangle \Rightarrow \mathcal{W} = \begin{pmatrix} \left\langle\psi_n\middle|\hat{V}\middle|\psi_n\right\rangle & \dots & \left\langle\psi_n\middle|\hat{V}\middle|\psi_{n+k-1}\right\rangle \\ \vdots & \ddots & \vdots \\ \left\langle\psi_{n+k-1}\middle|\hat{V}\middle|\psi_n\right\rangle & \dots & \left\langle\psi_{n+k-1}\middle|\hat{V}\middle|\psi_{n+k-1}\right\rangle \end{pmatrix}$$

Solve the eigen problem:

$$\det[\lambda I - \mathcal{W}] = 0$$

What are $\left|\tilde{\psi}_\alpha^{(0)}\right\rangle$ and $\left|\tilde{\psi}_\beta^{(0)}\right\rangle$? i.e. $\left|\psi_\pm\right\rangle = C_{\alpha\pm}\left|\psi_\alpha\right\rangle + C_{\beta\pm}\left|\psi_\beta\right\rangle$

$$C_{\alpha\pm}W_{\alpha\alpha} + C_{\beta\pm}W_{\alpha\beta} = \tilde{\mathcal{E}}_\pm^{(1)}C_{\alpha\pm}$$

$$\begin{gathered}
C_{\alpha\pm}W_{\beta\alpha} + C_{\beta\pm}W_{\beta\beta} = \tilde{\mathcal{E}}_\pm^{(1)}C_{\beta\pm} \\
\left|C_{\alpha\pm}\right|^2 + \left|C_{\beta\pm}\right|^2 = 1
\end{gathered}$$

$$\boxed{\begin{aligned}
C_{\alpha\pm} &= \frac{C_{\beta\pm}W_{\alpha\beta}}{\tilde{\mathcal{E}}_\pm^{(1)} - W_{\alpha\alpha}} \\
C_{\beta\pm} &= C_{\alpha\pm}\frac{\left(\tilde{\mathcal{E}}_\pm^{(1)} - W_{\alpha\alpha}\right)}{W_{\alpha\beta}}
\end{aligned}}$$

$$\begin{aligned}
\left\langle\psi_\mp\middle|\psi_\pm\right\rangle &= \left(C_{\alpha\mp}\left\langle\psi_\alpha\right| + C_{\beta\mp}\left\langle\psi_\beta\right|\right)\left(C_{\alpha\pm}\left|\psi_\alpha\right\rangle + C_{\beta\pm}\left|\psi_\beta\right\rangle\right) \\
&= C_{\alpha\mp}C_{\alpha\pm}\left\langle\psi_\alpha\middle|\psi_\alpha\right\rangle + C_{\alpha\mp}C_{\beta\pm}\left\langle\psi_\alpha\middle|\psi_\beta\right\rangle + C_{\beta\mp}C_{\alpha\pm}\left\langle\psi_\beta\middle|\psi_\alpha\right\rangle + C_{\beta\mp}C_{\beta\pm}\left\langle\psi_\beta\middle|\psi_\beta\right\rangle \\
&= C_{\alpha\mp}C_{\alpha\pm}\cancelto{1}{\delta_{\alpha\alpha}} + C_{\alpha\mp}C_{\beta\pm}\cancelto{0}{\delta_{\alpha\beta}} + C_{\beta\mp}C_{\alpha\pm}\cancelto{0}{\delta_{\beta\alpha}} + C_{\beta\mp}C_{\beta\pm}\cancelto{1}{\delta_{\beta\beta}} \\
&= C_{\alpha\mp}C_{\alpha\pm} + C_{\beta\mp}C_{\beta\pm}
\end{aligned}$$

$$\boxed{\tilde{\mathcal{E}}_\pm^{(1)} = \frac{W_{\alpha\alpha} + W_{\beta\beta}}{2} \pm \sqrt{\left(\frac{W_{\alpha\alpha} - W_{\beta\beta}}{2}\right)^2 + \left|W_{\alpha\beta}\right|^2}}$$

2.3 Lecture 9

May 15, 2023

Suppose we have two degenerate wavefunctions with energy $\mathcal{E}$ for the unperturbed hamiltonian, α, β

$$\hat{H}_o\big|\psi_\alpha\big\rangle = \mathcal{E}\big|\psi_\alpha\big\rangle$$

$$\hat{H}_o\big|\psi_\beta\big\rangle = \mathcal{E}\big|\psi_\beta\big\rangle$$

We know that:

$$\begin{aligned}
&\big\langle\psi_i\big|\psi_j\big\rangle = \delta_{ij} \\
&\hat{H} = \hat{H}_o + \lambda\hat{V}' \\
&\big|\tilde{\psi}_\pm\big\rangle = C_{\alpha\pm}\big|\psi_\alpha\big\rangle + C_{\beta\pm}\big|\psi_\beta\big\rangle \\
&\big|C_{\alpha\pm}\big|^2 + \big|C_{\beta\pm}\big|^2 = 1
\end{aligned}$$

$$\tilde{\mathcal{E}}_\pm^{(1)} = \frac{\big\langle\psi_\alpha\big|\hat{V}'\big|\psi_\alpha\big\rangle + \big\langle\psi_\beta\big|\hat{V}'\big|\psi_\beta\big\rangle}{2} + \sqrt{\left(\frac{\big\langle\psi_\alpha\big|\hat{V}'\big|\psi_\alpha\big\rangle - \big\langle\psi_\beta\big|\hat{V}'\big|\psi_\beta\big\rangle}{2}\right)^2 + \big|\big\langle\psi_\alpha\big|\hat{V}'\big|\psi_\beta\big\rangle\big|^2}$$

- The first term is the average of $T.I.N.D.P.T$ $\mathcal{O}(\lambda)$ correction for $\tilde{\mathcal{E}}_\alpha^{(1)}$ and $\tilde{\mathcal{E}}_\beta^{(1)}$.
- The first term in the root is the difference between $\tilde{\mathcal{E}}_\alpha^{(1)}$ and $\tilde{\mathcal{E}}_\beta^{(1)}$ and their average.
- The last term in the root is the cross term non-zero when $\big|\psi_\alpha\big\rangle$ and $\big|\psi_\beta\big\rangle$ are not eigenstates of $\hat{V}'$.

Let $\omega_\pm = \tilde{\mathcal{E}}_\pm^{(1)}$:

$$\omega_\pm = \frac{W_{\alpha\alpha} + W_{\beta\beta}}{2} \pm \sqrt{\left(\frac{W_{\alpha\alpha} - W_{\beta\beta}}{2}\right)^2 + \big|W_{\alpha\beta}\big|^2} \tag{2.3.1}$$

($TISE$) to $\mathcal{O}(\lambda)$ and multiply by $\big\langle\psi_\alpha\big|$:

$$\big\langle\psi_\alpha\big|\hat{V}'\left(C_{\alpha\pm}\big|\psi_\alpha\big\rangle + C_{\beta\pm}\big|\psi_\beta\big\rangle\right) = \mathcal{E}_\pm C_{\alpha\pm}$$

$$C_{\alpha\pm}\left(\mathcal{E}_\pm - W_{\alpha\alpha}\right) = C_{\beta\pm}W_{\alpha\beta} \Rightarrow C_{\beta\pm} = C_{\alpha\pm}\frac{\left(\tilde{\mathcal{E}}_\pm - W_{\alpha\alpha}\right)}{W_{\alpha\beta}} \tag{2.3.2}$$

$\therefore$ multiply by $\big\langle\psi_\beta\big|$:

$$\big\langle\psi_\beta\big|\hat{V}'\left(C_{\alpha\pm}\big|\psi_\alpha\big\rangle + C_{\beta\pm}\big|\psi_\beta\big\rangle\right) = \mathcal{E}_\pm C_{\beta\pm}$$

$$C_{\beta\pm}\left(\mathcal{E}_\pm - W_{\beta\beta}\right) = C_{\alpha\pm}W_{\beta\alpha}$$

$$C_{\alpha\pm}\left[\left(\mathcal{E}_\pm - W_{\alpha\alpha}\right)\left(\mathcal{E}_\pm - W_{\beta\beta}\right) - W_{\alpha\beta}W_{\beta\alpha}\right] = 0$$

Are the eigenstates we got orthogonal?

$$\langle\psi_+|\psi_-\rangle = \left(C^*_{\alpha+}\langle\psi_\alpha| + C^*_{\beta+}\langle\psi_\beta|\right)\left(C_{\alpha\mp}|\psi_\alpha\rangle + C_{\beta-}|\psi_\beta\rangle\right)$$

$$\begin{aligned}
\langle\psi_i|\psi_j\rangle = \delta_{ij}, &\quad \text{Using orthonormality of the eigenstates} \\
= C_{\alpha+}C_{\alpha-} + C_{\beta+}C_{\beta-}, &\quad \text{Substitute in (3.3.2) for } C_{\beta\pm} \\
= C^*_+C_-\left[1 + \frac{(\mathcal{E}_+ - W_{\alpha\alpha})}{W_{\alpha\beta}}\frac{(\mathcal{E}_- - W_{\alpha\alpha})}{W_{\alpha\beta}}\right]&
\end{aligned}$$

Substitute in (3.3.1) for $\mathcal{E}_\pm$:

$$= C^*_{\alpha+}C_{\alpha-}\left[1 + \frac{\left(\frac{W_{\alpha\alpha}+W_{\beta\beta}}{2} + \sqrt{\left(\frac{W_{\alpha\alpha}+W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2} - W_{\alpha\alpha}\right)}{(W_{\alpha\beta})^2}\right.$$

$$\left.\cdot\left(\frac{W_{\alpha\alpha}+W_{\beta\beta}}{2} - W_{\alpha\alpha} - \sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2}\right)\right]$$

$$= C^*_{\alpha+}C_{\beta-}\left[1 + \frac{1}{|W_{\alpha\beta}|^2}\left(\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2} + \sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2}\right)\right.$$

$$\left.\cdot\left(\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2} - \sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2}\right)\right]$$

Since $(x+y)(x-y) = x^2 - y^2$, cross terms cancel:

$$= C_{\alpha+}C_{\beta-}\left[1 + \frac{1}{|W_{\alpha\beta}|^2}\left[\left|\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2}\right|^2 - \left|\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right|^2 + |W_{\alpha\beta}|^2\right]\right]$$

$$\boxed{= C_{\alpha+}C_{\alpha-}[1-1] = 0}$$

$$\boxed{\langle\psi_\pm|\psi_\mp\rangle = 0}$$

$$\langle\psi_\pm|\psi_\mp\rangle = \left(C^*_{\alpha\pm}\langle\psi_\alpha| + C^*_{\beta\pm}\langle\psi_\beta|\right)\left(C_{\alpha\mp}|\psi_\alpha\rangle + C_{\beta\mp}|\psi_\beta\rangle\right)$$
$$\langle\psi_\pm|\psi_\mp\rangle = C^*_{\alpha\pm}C_{\alpha\mp}\langle\psi_\alpha|\psi_\alpha\rangle + C^*_{\alpha\pm}C_{\beta\mp}\langle\psi_\alpha|\psi_\beta\rangle + C^*_{\beta\pm}C_{\alpha\mp}\langle\psi_\beta|\psi_\alpha\rangle + C^*_{\beta\pm}C_{\beta\mp}\langle\psi_\beta|\psi_\beta\rangle$$
$$\langle\psi_\pm|\psi_\mp\rangle = C^*_{\alpha\pm}C_{\alpha\mp} + C^*_{\beta\pm}C_{\beta\mp} = C^*_{\alpha\pm}C_{\alpha\mp} + C^*_{\alpha\pm}\left(\frac{\mathcal{E}_\pm - W_{\alpha\alpha}}{W_{\alpha\beta}}\right)^* C_{\alpha\mp}\left(\frac{\mathcal{E}_\mp - W_{\alpha\alpha}}{W_{\alpha\beta}}\right)$$
$$\langle\psi_\pm|\psi_\mp\rangle = C^*_{\alpha\pm}C_{\alpha\mp}\left[1 + \frac{1}{|W_{\alpha\beta}|^2}\left(\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2} \pm \sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|}\right)^*\right.$$
$$\left.\cdot\left(\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2} \mp \sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2}\right)\right]$$
$$\langle\psi_\pm|\psi_\mp\rangle = C^*_{\alpha\pm}C_{\alpha\mp}\left[1 + \frac{1}{|W_{\alpha\beta}|^2}\left(\left|\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2}\right|^2 - \left|\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right|^2 + |W_{\alpha\beta}|^2\right)\right.$$
$$= C^*_{\alpha\pm}C_{\alpha\mp}(1-1) = 0$$

$$\begin{aligned}\langle\psi_\pm|\psi_\pm\rangle &= \left(C^*_{\alpha\pm}\langle\psi_\alpha| + C^*_{\beta\pm}\langle\psi_\beta|\right)\left(C_{\alpha\pm}|\psi_\alpha\rangle + C_{\beta\pm}|\psi_\beta\rangle\right)\\ &= C^*_{\alpha\pm}C_{\alpha\pm}\langle\psi_\alpha|\psi_\alpha\rangle + C^*_{\alpha\pm}C_{\beta\pm}\langle\psi_\alpha|\psi_\beta\rangle + C^*_{\beta\pm}C_{\alpha\pm}\langle\psi_\beta|\psi_\alpha\rangle + C^*_{\beta\pm}C_{\beta\pm}\langle\psi_\beta|\psi_\beta\rangle\\ &= |C_{\alpha\pm}|^2 + |C_{\beta\pm}|^2 = 1 \quad \text{by construction!}\end{aligned}$$

$$C_{\beta\pm} = C_{\alpha\pm}\frac{(\mathcal{E}_\pm - W_{\alpha\alpha})}{W_{\alpha\beta}} = \frac{C_{\alpha\pm}}{W_{\alpha\beta}}\left(\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2} \pm \sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2}\right)$$

$$\begin{aligned}\langle\psi_\pm|\hat{V}|\psi_\mp\rangle &= \left(C^*_{\alpha\pm}\langle\psi_\alpha|C^*_{\beta\pm}\langle\psi_\beta|\right)\hat{V}'\left(C_{\alpha\mp}|\psi_\alpha\rangle + C_{\beta\mp}|\psi_{\beta\mp}\rangle\right)\\ &= C^*_{\alpha\pm}C_{\alpha\mp}\langle\psi_\alpha|\hat{V}'|\psi_\alpha\rangle + C^*_{\alpha\pm}C_{\beta\mp}\langle\psi_\alpha|\hat{V}'|\psi_\beta\rangle + C^*_{\beta\pm}C_{\alpha\mp}\langle\psi_\beta|\hat{V}'|\psi_\alpha\rangle + C^*_{\beta\pm}C_{\beta\mp}\langle\psi_\beta|\hat{V}'|\psi_\beta\rangle\\ &= C^*_{\alpha\pm}C_{\alpha\mp}W_{\alpha\alpha} + \frac{C^*_{\alpha\pm}C_{\alpha\mp}}{\cancel{W_{\alpha\beta}}}(\mathcal{E}_- - W_{\alpha\alpha})\cancel{W_{\alpha\beta}} + C^*_{\alpha\pm}C_{\alpha\mp}\left(\frac{\mathcal{E}_+ - W_{\alpha\alpha}}{\cancel{W_{\alpha\beta}}}\right)^*\cancel{W_{\beta\alpha}}\\ &+ C^*_{\alpha\pm}C_{\alpha\mp}\left(\frac{\mathcal{E}_+ - W_{\alpha\alpha}}{W_{\alpha\beta}}\right)^*\left(\frac{\mathcal{E}_- - W_{\alpha\alpha}}{W_{\alpha\beta}}\right)W_{\beta\beta}\\ &= C^*_{\alpha\pm}C_{\alpha\mp}\left[W_{\alpha\alpha} + \mathcal{E}_- - W_{\alpha\alpha} + \mathcal{E}_+ - W_{\alpha\alpha} + \frac{W_{\beta\beta}}{|W_{\alpha\beta}|^2}\left(\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2}\right.\right.\\ &\left.\left.+\sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2}\right)^*\cdot\left(\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2} - \sqrt{\left(\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right)^2 + |W_{\alpha\beta}|^2}\right)\right]\end{aligned}$$

$$
\begin{aligned}
&= C^*_{\alpha\pm}C_{\alpha\mp}\left[W_{\alpha\alpha}+W_{\beta\beta}-W_{\alpha\alpha}+\frac{W_{\beta\beta}}{\cancel{\left|W_{\alpha\beta}\right|^2}}\left(\cancel{\left|\frac{W_{\beta\beta}-W_{\alpha\alpha}}{2}\right|^2}\right.\right.\\
&\left.\left.-\cancel{\left|\frac{W_{\alpha\alpha}-W_{\beta\beta}}{2}\right|^2}-\cancel{\left|W_{\alpha\beta}\right|^2}\right)\right]\\
&= \boxed{C^*_{\alpha\pm}C_{\alpha\mp}\left(W_{\alpha\alpha}+W_{\beta\beta}-W_{\alpha\alpha}-W_{\beta\beta}\right)=0}
\end{aligned}
$$

$\Rightarrow \left|\psi_\pm\right\rangle$ are eigenstates of $\hat{V}'$

What are their eigenvalues? i.e $\hat{V}'\left|\psi_\pm\right\rangle = \mathcal{E}_\pm\left|\psi_\pm\right\rangle$

$$
\begin{aligned}
\left\langle\psi_\pm\middle|\hat{V}\middle|\psi_\pm\right\rangle &= \left(C^*_{\alpha\pm}\left\langle\psi_\alpha\right|C^*_{\beta\pm}\left\langle\psi_\beta\right|\right)\hat{V}'\left(C_{\alpha\pm}\left|\psi_\alpha\right\rangle+C_{\beta\pm}\left|\psi_{\beta\mp}\right\rangle\right)\\
&= C^*_{\alpha\pm}C_{\alpha\pm}\left\langle\psi_\alpha\middle|\hat{V}'\middle|\psi_\alpha\right\rangle + C^*_{\alpha\pm}C_{\beta\pm}\left\langle\psi_\alpha\middle|\hat{V}'\middle|\psi_\beta\right\rangle + C^*_{\beta\pm}C_{\alpha\pm}\left\langle\psi_\beta\middle|\hat{V}'\middle|\psi_\alpha\right\rangle\\
&+ C^*_{\beta\pm}C_{\beta\pm}\left\langle\psi_\beta\middle|\hat{V}'\middle|\psi_\beta\right\rangle\\
&= \left|C_{\alpha\pm}\right|^2 W_{\alpha\alpha} + C^*_{\alpha\pm}C_{\beta\pm}W_{\alpha\beta} + C^*_{\beta\pm}C_{\alpha\pm}W_{\beta\alpha} + \left|C_\beta\right|^2 W_{\beta\beta}
\end{aligned}
$$

whe know that:

$$
C_{\alpha\pm} = C_{\beta\pm}\left(\frac{\mathcal{E}_\pm - W_{\beta\beta}}{W_{\beta\alpha}}\right), \quad C_{\beta\pm} = C_{\alpha\pm}\left(\frac{\mathcal{E}_\pm - W_{\alpha\alpha}}{W_{\alpha\beta}}\right)
$$

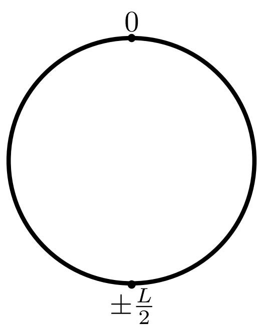
then,

$$
\begin{aligned}
\left\langle\psi_\pm\middle|\hat{V}\middle|\psi_\pm\right\rangle &= \left|C_{\alpha_\pm}\right|^2\left(\cancel{W_{\alpha\alpha}}+\frac{\mathcal{E}_\pm-\cancel{W_{\alpha\alpha}}}{\cancel{W_{\alpha\beta}}}\cdot\cancel{W_{\alpha\beta}}\right)+\left|C_{\beta_\pm}\right|^2\left(\cancel{W_{\beta\beta}}+\frac{\mathcal{E}_\pm-\cancel{W_{\beta\beta}}}{\cancel{W_{\beta\alpha}}}\cdot\cancel{W_{\beta\alpha}}\right)\\
&\boxed{= \mathcal{E}_\pm\left(\left|C_{\alpha\pm}\right|^2+\left|C_{\beta\pm}\right|^2\right) = \mathcal{E}_\pm}
\end{aligned}
$$

So, $\left|\psi_\pm\right\rangle$ are eigenstates of the perturbation $\hat{V}'$ and their eigenvalues are $\mathcal{E}_\pm$, i.e, the first order correction in $\hat{V}'$ to the eigenenergies of the perturbed hamiltonian $\hat{H} = \hat{H}_o + \hat{V}'$.

If $W_{\alpha\beta} = 0 = \left\langle\psi_\alpha\middle|\hat{V}'\middle|\psi_\beta\right\rangle$, then $\left|\psi_\alpha\right\rangle$ and $\left|\psi_\beta\right\rangle$ are eigenstates of $\hat{V}'$ and we can use non-degenerate perturbation theory.

2.3.1 Example: A 1D periodic space of length L, i.e, a Ring.



Find the eigenstates of a particle to a 1D ring.

$$TISE: \quad \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x) = \mathcal{E}\Psi(x)$$

(B.C):

$$\Psi(\pm L) = 0$$
$$\Psi''(x) = \frac{-2m}{\hbar^2}\mathcal{E}\Psi(x)$$

$$\Rightarrow \Psi\left(\frac{L}{2}\right) = Ae^{\left(i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)} + Be^{\left(-i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)} = \Psi\left(\frac{-L}{2}\right)$$
$$= Ae^{\left(-i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)} + Be^{\left(i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)}$$

$$(A-B)\, e^{\left(i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)} = (A-B)\, e^{\left(-i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)}$$

$$(A-B)\left(e^{\left(i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)} - 1\right) = 0$$

$$\Rightarrow e^{\left(i\sqrt{\frac{2m\mathcal{E}}{\hbar^2}}\frac{L}{2}\right)} = 1 \longrightarrow e^{i2\pi n} = 0, \quad \forall n \in \mathbb{Z}$$
$$\Rightarrow \sqrt{\frac{2m\mathcal{E}}{\hbar^2}}L = 2\pi n, \quad n \in \mathbb{Z}$$

Then, the eigenenergies are given by:

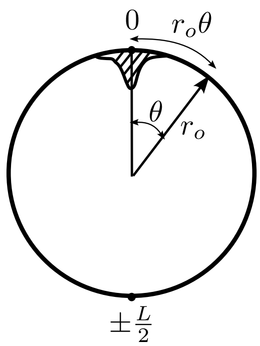
$$\mathcal{E}_n = \frac{4\hbar^2\pi^2n^2}{2mL^2} = \frac{2\hbar^2\pi^2n^2}{mL^2}$$

$$\boxed{\begin{array}{ll} \text{Eigenstates:} & e^{i2\pi n\frac{x}{L}}, \quad n \in \mathbb{Z} \\ & \\ \text{Eigenvalues:} & \mathcal{E}_n = \dfrac{2\hbar^2\pi^2n^2}{mL^2} \end{array}}$$

$\mathcal{E}_{n\pm} = \mathcal{E}_n$, for $n \neq 0$ doubly degenerate.

2.4 Lecture 10

May 16, 2023



Let's continue with the example from the last class:

$$r_o\theta = x, \quad x \in \left[\frac{-L}{2}, \frac{L}{2}\right]$$

$$\hat{H}_o = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$$\text{(B.C)}: \quad \Psi_n\left(\frac{-L}{2}\right) = \Psi\left(\frac{L}{2}\right)$$

Unperturbed eigenenergies and wavefunctions:

$$\mathcal{E}_n = \frac{2\hbar^2\pi^2 n^2}{mL^2}, \quad \Psi_n = e^{i2\pi n\frac{x}{L}}, \quad n \in \mathbb{Z}$$

n can be positive or negative, to describe clockwise/counterclockwise motion around the ring, but $\mathcal{E}_{-n} = \mathcal{E}$, $n \neq 0$, so Ψ_n is doubly degenerate for $n \neq 0$ ($\mathcal{E} \sim n^2$)

Check:

$$\begin{aligned}
\langle \Psi_n | \Psi_n \rangle &= A^2 \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{-i2\pi n\frac{x}{L}} e^{i2\pi n\frac{x}{L}} dx = A^2 L = 1 \\
&= A^2 \int_{-\frac{L}{2}}^{\frac{L}{2}} dx \\
&\Rightarrow \boxed{A = \frac{1}{\sqrt{L}}}
\end{aligned}$$

$$\begin{aligned}
\langle \Psi_{n'} | \Psi_n \rangle &= \frac{1}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} e^{i2\pi(n-n')\frac{x}{L}} dx \\
&= \frac{1}{L}\frac{L}{2i\pi(n-n')} e^{i2\pi(n-n')\frac{x}{L}}\Big|_{-\frac{L}{2}}^{\frac{L}{2}} \\
&= \frac{L}{2i\pi(n-n')}\left(e^{i\pi(n-n')} - e^{-i\pi(n-n')}\right) = 0 \\
&= \frac{(-1)^{n-n'} - (-1)^{n-n'}}{2\pi(n-n')} = \begin{cases} 0, & n \neq n' \\ 1, & n = n' \end{cases}
\end{aligned}$$

$$\langle \Psi_n | \Psi_n \rangle = \delta_{n'n}$$

Perturbation

$$\hat{V}' = -V_o\, e^{x^2/\Delta^2}, \quad \Delta \ll L$$

A gaussian well centered @ $x = 0$ is a "trap" for the particle, e.g. bent the wire @ $x = 0$ that forms the ring.

For $n = 0$,

$$\Psi_0(x) = \frac{1}{\sqrt{L}}, \quad \text{in non-degenerate}$$

$$\hat{\tilde{H}} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} - V_0\, e^{-x^2/\Delta^2}, \qquad \text{we can use } \textit{TINDPT} \text{ for } n = 0$$

$$\begin{aligned}
\tilde{\mathcal{E}}_0^{(1)} = \langle \Psi_0 | \hat{V}' | \Psi_0 \rangle &= \int_{-\frac{L}{2}}^{\frac{L}{2}} \left(\frac{1}{\sqrt{L}}\right)^2 \left(-V_0 e^{-x^2/\Delta^2}\right) dx \\
&= \frac{-V_0}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} \underbrace{e^{-x^2/\Delta^2}}_{\text{even in x}} \\
&= \frac{-2V_0}{L} \int_0^{\frac{L}{2}} e^{-x^2/\Delta^2}
\end{aligned}$$

Since $\Delta \ll L$, we can approximate the integral by extending the boundary to $\frac{L}{2} \longrightarrow \infty$. Then,

$$\mathcal{E}_0^{(1)} = -\frac{2V_0}{L}\left[\int_0^\infty e^{-x^2/\Delta^2} dx - \underbrace{\int_{\frac{L}{2}}^\infty e^{-x^2/\Delta^2}}_{\text{negligeble for } L \gg \Delta}\right]$$

$$\boxed{\mathcal{E}_0^{(1)} = -\frac{V_0}{L}\sqrt{\pi}\Delta}$$

Recall: We're using a perturbation theory, so all results are approximate in any case.

For $n \neq 0$, $\Psi_{\pm n}(x)$ are degenerate! use *TIDPT*

$$\mathcal{E}_{\pm n} = \frac{W_{n,n} + W_{-n,-n}}{2} \pm \sqrt{\left(\frac{W_{n,n} - W_{-n,-n}}{2}\right)^2 + \left|W_{n,-n}\right|^2}, \quad \text{where } W_{n'n} = \langle \psi_{n'} | \hat{V}' | \psi_n \rangle$$

$$\begin{aligned}
W_{n,n} &= \int_{-L/2}^{L/2} \left|\psi_n(x)\right|^2 \hat{V}'(x) dx = -\frac{V_0}{L}\int_{-L/2}^{L/2} e^{-x^2/\Delta^2} e^{i2\pi nx/L} e^{-i2\pi nx/L} dx \\
&= -2\frac{V_0}{L}\int_0^{L/2} e^{-x^2/\Delta} dx \\
&\cong -2\frac{V_0}{L}\left(\frac{1}{2}\sqrt{\pi}\Delta\right) = \frac{-V_0}{L}\sqrt{\pi}\Delta, \quad \text{i.e. the } \textit{TIDPT} \text{ is the same } \forall n \\
&\Rightarrow \boxed{W_{n,n} = W_{-n,-n} = \frac{-V_0}{L}\sqrt{\pi}\Delta}
\end{aligned}$$

$(\mathbf{\Delta \ll L})$

Since $W_{n,n} - W_{n,-n} = 0$

$$\mathcal{E}_{\pm n} = \frac{-V_0}{L}\sqrt{\pi}\Delta \pm \left|W_{n,-n}\right|$$

$$W_{n,-n} = \frac{-V_0}{L}\int_{-L/2}^{L/2} e^{-x^2/\Delta^2} e^{i4\pi nx/L} dx$$

We will use:

$$\boxed{\int_{-\infty}^{+\infty} e^{-(ax^2+bx+c)}dx = \sqrt{\frac{\pi}{a}}\, e^{\frac{b^2-4ac}{4a}}} \tag{2.4.1}$$

$$\begin{aligned}\mathcal{E}_{\pm n} &= \frac{V_0}{L}\sqrt{\pi}\Delta \pm \frac{-V_0}{L}\sqrt{\pi}\Delta\, e^{-(2\pi n\Delta/L)^2} \\ &= \boxed{\frac{-V_0}{L}\sqrt{\pi}\Delta\left(1 \pm e^{-\left(\frac{2\pi n\Delta}{L}\right)^2}\right)}\end{aligned}$$

Alternatively: $V'(x) = -V_0 e^{-x^2/\Delta^2}$ is an even function of x, so, if our wavefunction, i.e. linear combinations of Ψ_n and Ψ_{-n} were even/odd, they would be eigenfunction of the perturbation!

Even part of $\Psi_n(x)$:

$$\frac{\psi_n(x) + \psi_n(-x)}{2} = \frac{e^{i2\pi nx/L + e^{-i2\pi nx/L}}}{2\sqrt{L}} = \frac{1}{\sqrt{L}} Cos\left(\frac{2\pi nx}{L}\right)$$

Odd part of $\Psi_n(x)$:

$$\frac{\psi_n(x) - \psi_n(-x)}{2} = \frac{e^{i2\pi nx/L - e^{-i2\pi nx/L}}}{2\sqrt{L}} = \frac{\psi_n(x)}{2} - \frac{\psi_{-n}(x)}{2} = \frac{i}{\sqrt{L}} Sin\left(\frac{2\pi nx}{L}\right)$$

$$\begin{aligned}W_{\alpha\beta} &= \left\langle \frac{i}{\sqrt{\pi}} Sin\left(\frac{2\pi nx}{L}\right) \middle| V_0 e^{-x^2/\Delta^2} \middle| \frac{1}{\sqrt{L}} Cos\left(\frac{2\pi nx}{L}\right) \right\rangle \\ &= \frac{-iV_0}{L}\int_{-L/2}^{L/2} \underbrace{\underbrace{Sin\left(\frac{2\pi nx}{L}\right)}_{\text{odd}} \underbrace{Cos\left(\frac{2\pi nx}{L}\right)}_{\text{even}} \underbrace{e^{-x^2/\Delta^2}}_{\text{even}}}_{\text{odd}} dx = 0\end{aligned}$$

Sine and Cosine are eigenfunctions of the perturbation.

$$\begin{aligned}W_{\alpha\alpha} &= \int_{-L/2}^{L/2} Cos^2\left(\frac{2\pi nx}{L}\right)\left(\frac{-V_0}{L}\right) e^{-x^2/\Delta^2} dx \\ &= \frac{-2V_0}{L}\int_0^{L/2} Cos^2\left(\frac{2\pi nx}{L}\right) e^{-x^2/\Delta^2} dx\end{aligned}$$

Professor made a bunch of mistakes here, so tried to correct them using other approach, but as you may have noticed, we corrected them, and it is not necessary to introduce Sines and Cosines. Anyway, in the next lecture he sure will correct this problem and shows us a plot of the eigenenergies.

2.5 Lecture 11

May 17, 2023

$$\boxed{\begin{gathered} \psi_n(x) = \frac{1}{\sqrt{L}} e^{2i\pi x/L} \\ \mathcal{E}_n = \frac{2\hbar^2\pi^2 n^2}{mL^2} \\ \hat{V}(x) = -V_0 e^{-x^2/\Delta^2} \end{gathered}}$$

We will use:

$$\boxed{\int_{-\infty}^{+\infty} e^{ax^2+bx+c} dx = \sqrt{\frac{\pi}{a}}\, e^{\frac{b^2-4ac}{4a}}} \tag{2.5.1}$$

$$\begin{aligned} W_{nn} &= \left\langle \psi_n \middle| \hat{V} \middle| \psi_n \right\rangle \\ &= \frac{-V_0}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} \cancelto{1}{\left| e^{2\pi inx/L} \right|^2} e^{-x^2/\Delta^2} dx \end{aligned}$$

then, following (3.5.1):

$$a = \frac{1}{\Delta^2}, \quad b = 0, \quad c = 0$$

$$\boxed{= \frac{-V_0}{L}\sqrt{\pi}\Delta = -\sqrt{\pi}V_0 \frac{\Delta}{L}, \quad \Delta \ll L}$$

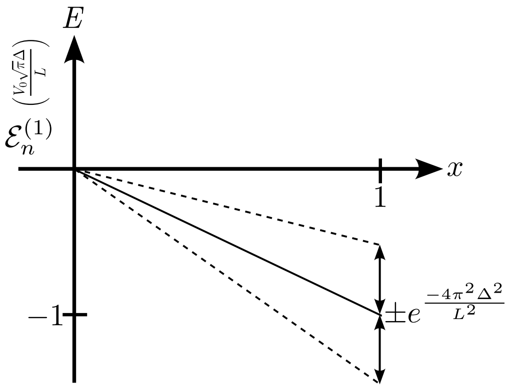
$$W_{n,-n} = \frac{-V_0}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{4\pi inx/L} e^{-x^2/\Delta^2} dx$$

$$a = \frac{1}{\Delta^2}, \quad b = 4\pi in/L, \quad c = 0, \quad \text{Let } L \longrightarrow \infty$$

Then,

$$W_{n,-n} = \frac{-V_0}{L} e^{\frac{-16\pi^2 n^2 \Delta^2}{4L^2}} = \frac{-V_0}{L}\sqrt{\pi}\Delta e^{-\left(\frac{2\pi n\Delta}{L}\right)^2}$$

$$\Rightarrow \boxed{\tilde{\mathcal{E}}_{\pm n}^{(1)} = \frac{-V_0\sqrt{\pi}\Delta}{L}\left(1 \pm e^{-\left(\frac{2\pi n\Delta}{L}\right)^2}\right)}$$



Splitting around $\frac{-V_0\sqrt{\pi}\Delta}{L}$ of $e^{-\left(\frac{2\pi n\Delta}{L}\right)^2}$, so the strongest effect is for:

$$n = 1 : \pm e^{\frac{-4\pi^2\Delta^2}{L^2}}$$
$$n = 2 : \pm e^{\frac{-16\pi^2\Delta^2}{L^2}}$$
$$n = 3 : \pm e^{\frac{-32\pi^2\Delta^2}{L^2}} \quad \text{(very small!)}$$

i.e. splitting is significant only for $n = 1$, (and 2), remember $\Delta \ll L$, so $\Delta^2/L^2 \ll 1$, so $\frac{4\pi^2 n^2\Delta^2}{L^2} \gg 1 \Leftrightarrow n \gg \frac{L}{2\pi\Delta}$ for the splitting to be negligible. **Consider the k-fold degenerate state**

$$\begin{pmatrix} W_{n,n} & \dots & W_{n,n+k-1} \\ \vdots & \ddots & \vdots \\ W_{n+k-1} & \dots & W_{n+k-1,n+k-1} \end{pmatrix} \begin{pmatrix} C_n \\ \vdots \\ C_{n+k-1} \end{pmatrix} = \mathcal{E} \begin{pmatrix} C_n \\ \vdots \\ C_{n+k-1} \end{pmatrix} \tag{2.5.2}$$

where $C_{n'} = \langle \psi_{n'} | \tilde{\psi}^{(0)} \rangle$ are the coefficients of the Zeroth order eigenstate of the perturbation in the basis of the unperturbed hamiltonian's k-fold degenerate eigenstates, where $\hat{H}_0 |\psi_{n'}\rangle = \mathcal{E} |\psi_{n'}\rangle \quad \forall n' \in \{n, \cdots, n+k-1\}$

Recall: $W_{n'n} = \langle \tilde{\Psi}_{n'} | \hat{V}' | \tilde{\Psi}_n \rangle$, are the matrix elements for the perturbation in this basis.

Idea

$\{\Psi_n, \cdots, \Psi_{n+k-1}\}$ forms an orthogonal basis which spans the space of the states with unperturbed eigenenergies $\mathcal{E}$.
You can express any eigenstate of the perturbation with unperturbed eigenenergy $\mathcal{E}$ as a linear combination of the k-fold degenerate eigenstates of the unperturbed hamiltonian $\hat{H}_0$.

Want:

$$\langle \tilde{\Psi}^{(0)} | \hat{V} | \tilde{\Psi}^{(0)} \rangle = \tilde{\mathcal{E}}^{(1)}$$

So, $\hat{V} |\tilde{\Psi}^{(0)}\rangle = \tilde{\mathcal{E}}^{(1)} |\tilde{\Psi}^{(0)}\rangle$, since it spans the the space:

$$\sum_{n'n''=n}^{n+k-1} |\psi_{n'}\rangle\langle\psi_{n'}| = \sum_{n'=n}^{n+k-1} |\psi_{n'}\rangle\langle\psi_{n'}| = \mathbb{1}$$

$$\hat{V} \sum_{n'n''=n}^{n+k-1} |\psi_{n'}\rangle\langle\psi_{n'}|\tilde{\psi}^{(0)}\rangle = \tilde{\mathcal{E}}^{(1)} \sum_{n'=n}^{n+k-1} |\psi_{n'}\rangle \underbrace{\langle\psi_{n'}|\tilde{\psi}^{(0)}\rangle}_{C_{n'}} = \mathbb{1}$$

Multiply by $\langle\psi_{n'}|$:

$$\sum_{n'=n}^{n+k-1}\langle\psi_{n''}|\hat{V}|\psi_{n'}\rangle C_{n'}=\tilde{\mathcal{E}}^{(1)}\sum_{n'}\delta_{n''n}C_{n'}=\tilde{\mathcal{E}}^{(1)}C_{n'}$$

For k = 2:

$$\begin{pmatrix} W_{nn} & W_{n,n+1} \\ W_{n+1,n} & W_{n+1,n+1}\end{pmatrix}\begin{pmatrix} C_n \\ C_{n+1}\end{pmatrix}=\tilde{\mathcal{E}}^{(1)}\begin{pmatrix} C_n \\ C_{n+1}\end{pmatrix} \tag{2.5.3}$$

$$W_{n+1,n}C_n+W_{n,n+1}C_{n+1}=\tilde{\mathcal{E}}^{(1)}C_n\Longrightarrow C_{n+1}=\left(\frac{\tilde{\mathcal{E}}^{(1)}-W_{nn}}{W_{n,n+1}}\right)C_n \tag{2.5.4}$$

$$W_{n+1,n}C_n+W_{n+1,n+1}C_{n+1}=\tilde{\mathcal{E}}^{(1)}C_{n+1},\quad \text{substitute here (3.5.4)}$$

$$C_n\left(W_{n+1,n}+W_{n+1,n+1}\left(\frac{\tilde{\mathcal{E}}^{(1)}-W_{n,n}}{W_{n,n+1}}\right)-\tilde{\mathcal{E}}^{(1)}\left(\frac{\tilde{\mathcal{E}}^{(1)}-W_{nn}}{W_{n,n+1}}\right)\right)=0$$

if $C_n\neq 0$: multiply $W_{n,n+1}$ and get:

$$W_{n+1,n}W_{n,n+1}+\left(W_{n+1,n+1}+W_{nn}\right)\tilde{\mathcal{E}}^{(1)}-W_{n+1,n+1}W_{nn}-\tilde{\mathcal{E}}^{(1)2}=0$$

$$\tilde{\mathcal{E}}^{(1)2}-\left(W_{nn}+W_{n+1,n+1}\right)\tilde{\mathcal{E}}^{(1)}+W_{nn}W_{n+1,n+1}-\left|W_{n,n+1}\right|^2=0$$

$$\boxed{\tilde{\mathcal{E}}^{(1)}=\frac{W_{nn}+W_{n+1,n+1}}{2}\pm\sqrt{\left(\frac{W_{nn}-W_{n+1,n+1}}{2}\right)^2+\left|W_{n,n+1}\right|^2}} \tag{2.5.5}$$

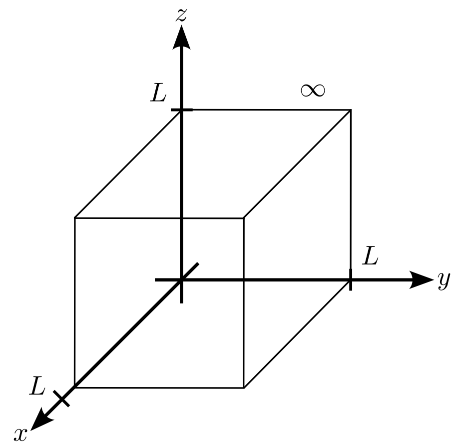
$$det\left(W-\tilde{\mathcal{E}}^{(1)}\mathbb{1}\right)=0 \tag{2.5.6}$$

$$\left(W_{nn}-\mathcal{E}\right)\left(W_{n+1,n+1}-\mathcal{E}\right)-W_{n,n+1}W_{n+1,n}=0$$

$$\mathcal{E}^2-\left(W_{nn}+W_{n+1,n+1}\right)\mathcal{E}+W_{nn}W_{n+1,n+1}-\left|W_{n,n+1}\right|^2=0$$

$$\boxed{\mathcal{E}_{\pm}=\frac{W_{nn}+W_{n+1,n+1}}{2}\pm\sqrt{\left(\frac{W_{nn}-W_{n+1,n+1}}{2}\right)^2+\left|W_{n,n+1}\right|^2}} \tag{2.5.7}$$

2.5.1 Example



Consider a 3D infinite cubic square well of dimension L

$$V_\infty(x,y,z) = \begin{cases} 0, & \text{for } 0 \le x,y,z \le L \\ \infty, & \text{otherwise} \end{cases} \tag{2.5.8}$$

$$\hat{H}_0 = \frac{-\hbar^2}{2m}\nabla^2 \Rightarrow$$

$$(TISE): \quad \frac{-\hbar^2}{2m}\nabla^2\Psi(x,y,z) = \mathcal{E}\Psi(x,y,z)$$

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} = \frac{-2m\mathcal{E}}{\hbar^2}$$

Assume $\Psi(x,y,z) = X(x)Y(y)Z(z)$:

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} = \frac{-2m\mathcal{E}}{\hbar^2}$$

$$\frac{X''(x)}{X(x)} = \frac{-2m\mathcal{E}}{\hbar^2} - \left(\frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)}\right) = -\lambda_x = \frac{-n_x^2\pi^2}{L^2}$$

$$X''(x) = -\lambda_x X(x) \Rightarrow X(x) = A\,Cos\left(\sqrt{\lambda_x}x\right) + B\,Sin\left(\sqrt{\lambda_x}x\right)$$

(B.C):

$$X(0) = X(L) = 0 \Rightarrow X(0) = \boxed{A=0}, \quad X(L) = B\,Sin\left(\sqrt{\lambda_x}x\right) = 0$$

$$(B \neq 0) \Rightarrow \sqrt{\lambda_x}L = n_x\pi, \quad n_x \in \mathbb{N}$$

$-n$ gives the same $X_{-n}(x) = -X(x)$ up to a factor of -1 so no linearly independent. $n_x = 0 \Rightarrow$ no particle, empty state.

$$\Rightarrow \boxed{\lambda_x = \frac{n_x^2\pi^2}{L^2}}$$

$$X(x) = B_x\,Sin\left(\frac{n_x\pi x}{L}\right) \tag{2.5.9}$$

$$Y(y) = B_y\,Sin\left(\frac{n_y\pi y}{L}\right) \tag{2.5.10}$$

$$Z(z) = B_z\,Sin\left(\frac{n_z\pi z}{L}\right) \tag{2.5.11}$$

$$\frac{-2m\mathcal{E}}{\hbar^2} = \lambda_x - \lambda_y - \lambda_z = \frac{\pi^2}{L^2}\left(n_x^2 + n_y^2 + n_z^2\right) \Rightarrow \boxed{\mathcal{E}_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)} \tag{2.5.12}$$

$$\boxed{\Psi_{n_x,n_y,n_z} = B_xB_yB_z\,Sin\left(\frac{n_x\pi x}{L}\right)Sin\left(\frac{n_y\pi y}{L}\right)Sin\left(\frac{n_z\pi z}{L}\right)} \tag{2.5.13}$$

Now, we need to find $B_x B_y B_z$:

$$\begin{aligned}\left\langle \Psi_{n'_x,n'_y,n'_z} \middle| \Psi_{n_x,n_y,n_z} \right\rangle &= B_x^2 B_y^2 B_z^2 \int_0^L Sin\left(\frac{n'_x \pi x}{L}\right) Sin\left(\frac{n_x \pi x}{L}\right) dx \\ &\cdot \int_0^L Sin\left(\frac{n'_y \pi y}{L}\right) Sin\left(\frac{n_y \pi y}{L}\right) dy \\ &\cdot \int_0^L Sin\left(\frac{n'_z \pi z}{L}\right) Sin\left(\frac{n_z \pi z}{L}\right) dz \\ &= B_x^2 B_y^2 B_z^2 \left(\delta_{n'_x,n_x}\frac{L}{2}\right)\left(\delta_{n'_y,n_y}\frac{L}{2}\right)\left(\delta_{n'_z,n_z}\frac{L}{2}\right) \\ &\Rightarrow B_x = B_y = B_z = \sqrt{\frac{2}{L}}\end{aligned}$$

$$\boxed{\Psi_{n_x,n_y,n_z} = \left(\frac{2}{L}\right)^{3/2} Sin\left(\frac{n_x \pi x}{L}\right) Sin\left(\frac{n_y \pi y}{L}\right) Sin\left(\frac{n_z \pi z}{L}\right)} \tag{2.5.14}$$

Then,

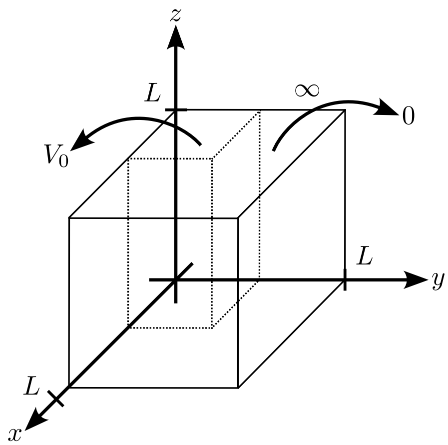
$$\Psi_{111}(x,y,z) = \left(\frac{2}{L}\right)^{3/2} Sin\left(\frac{\pi x}{L}\right) Sin\left(\frac{\pi y}{L}\right) Sin\left(\frac{\pi z}{L}\right)$$

$$\mathcal{E}_{111} = \frac{\pi^2\hbar^2}{2mL^2}(1+1+1) = \frac{3\pi\hbar^2}{2mL^2} \quad \boxed{\begin{array}{l}\text{(ground state)}\\ \text{non-degenerate}\end{array}}$$

1^{st} **excited state:**

$$\mathcal{E}_{211} = \mathcal{E}_{121} = \mathcal{E}_{112} = \frac{\pi^2\hbar^2}{2mL^2}(1+1+4) = \frac{3\pi^2\hbar^2}{mL^2} \quad \boxed{\begin{array}{l}\text{three-fold}\\ \text{degenerate}\end{array}}$$

Now, let's introduce a perturbation:



$$\hat{V}'(x,y) = \begin{cases} V_0 & , \quad \text{for} 0 \le x, y \le L/2 \\ 0 & , \quad \text{otherwise} \end{cases}$$

$$\begin{aligned} V'(x,y) &= V_0\left(1 - \Theta\left(x - \frac{L}{2}\right)\Theta\left(y - \frac{L}{2}\right)\right) \\ &= V_0\left(\Theta\left(x - \frac{L}{2}\right)\Theta\left(y - \frac{L}{2}\right)\right) \end{aligned}$$

where:

$$\Theta(x) = \begin{cases} 1 & , \quad x \ge 0 \\ 0 & , \quad x \le 0 \end{cases}$$

is the Heaviside step function.

Ground State:

$$\begin{aligned} \tilde{\mathcal{E}}_{111}^{(1)} &= \left\langle \Psi_{111} \middle| \hat{V}' \middle| \Psi_{111} \right\rangle \quad (TINDPT) \\ &= \int_0^L \int_0^L \int_0^L \left(\frac{2}{L}\right) Sin^2\left(\frac{\pi x}{L}\right) Sin^2\left(\frac{\pi y}{L}\right) Sin^2\left(\frac{\pi z}{L}\right) V_0 \Theta\left(x - \frac{L}{2}\right)\Theta\left(y - \frac{L}{2}\right) dxdydz \\ &= \frac{8V_0}{L^3}\int_0^{L/2} Sin^2\left(\frac{\pi x}{L}\right) dx \int_0^{L/2} Sin^2\left(\frac{\pi y}{L}\right) dy \int_0^L Sin^2\left(\frac{\pi z}{L}\right) dz \\ &= \frac{8V_0}{L^3}\left(\frac{L}{4}\right)\left(\frac{L}{4}\right)\left(\frac{L}{2}\right) = \frac{V_0}{4} \quad \boxed{V_0 \text{ acts on a quarter of the well.}} \end{aligned}$$

$$\begin{aligned} \Psi_{211}(x,y,z) &= \left(\frac{2}{L}\right)^{3/2} Sin\left(\frac{2\pi x}{L}\right) Sin\left(\frac{\pi y}{L}\right) Sin\left(\frac{\pi z}{L}\right) \\ \Psi_{121}(x,y,z) &= \left(\frac{2}{L}\right)^{3/2} Sin\left(\frac{\pi x}{L}\right) Sin\left(\frac{2\pi y}{L}\right) Sin\left(\frac{\pi z}{L}\right) \\ \Psi_{112}(x,y,z) &= \left(\frac{2}{L}\right)^{3/2} Sin\left(\frac{\pi x}{L}\right) Sin\left(\frac{\pi y}{L}\right) Sin\left(\frac{2\pi z}{L}\right) \end{aligned}$$

$$\begin{aligned} \left\langle \Psi_{211} \middle| \hat{V}' \middle| \Psi_{211} \right\rangle &= \left(\frac{2}{L}\right)^3 \int_0^{L/2} Sin^2\left(\frac{2\pi x}{L}\right) dx \int_0^{L/2} Sin^2\left(\frac{\pi y}{L}\right) dy \int_0^L Sin^2\left(\frac{\pi z}{L}\right) dz \\ &= \frac{8V_0}{L}\left(\frac{L}{4}\right)\left(\frac{L}{4}\right)\left(\frac{L}{2}\right) = \frac{V_0}{4} = \left\langle \Psi_{121} \middle| \hat{V}' \middle| \Psi_{121} \right\rangle \end{aligned}$$

$$\left\langle \Psi_{211} \middle| \hat{V}' \middle| \Psi_{121} \right\rangle = \left(\frac{2}{L}\right)^3 \int_0^{\frac{L}{2}} Sin\left(\frac{\pi x}{L}\right) Sin\left(\frac{2\pi x}{L}\right) dx \int_0^{\frac{L}{2}} Sin\left(\frac{2\pi y}{L}\right) Sin\left(\frac{\pi x}{L}\right) dy \int_0^L \cancelto{L/2}{Sin^2\left(\frac{\pi z}{L}\right)} dz$$

Using

$$\boxed{Sin(A)Sin(B) = \frac{1}{2}\left(Cos(A-B) - Cos(A+B)\right)}$$

$$\left\langle\Psi_{211}\middle|\hat{V}'\middle|\Psi_{121}\right\rangle = \left\langle\Psi_{121}\middle|\hat{V}'\middle|\Psi_{211}\right\rangle = \frac{4V_0}{L^2}\left[\int_0^{\frac{L}{2}}\left(Cos\left(\frac{\pi x}{L}\right)\right) - Cos\left(\frac{3\pi x}{L}\right)dx\right]^2$$

$$= \frac{V_0}{L^2}\left[\left(\frac{L}{\pi}Sin\left(\frac{\pi x}{L}\right) - \frac{L}{3\pi}Sin\left(\frac{3\pi x}{L}\right)\right)\Big|_0^{L/2}\right]^2$$

$$= \frac{V_0}{L^2}\frac{L^2}{\pi^2}\left[1 - \frac{(-1)}{3}\right]^2$$

$$= \frac{16V_0}{9\pi^2} = \left(\frac{8}{3\pi}\right)^2\frac{V_0}{4}, \quad \text{let} \quad k = \frac{8}{3\pi}$$

Note:

$$\frac{2}{L}\int_0^L Sin\left(\frac{2\pi z}{L}\right)Sin\left(\frac{\pi z}{L}\right)dz = \delta_{21} = 0$$

Finally, we have that:

$$\mathcal{W} = \begin{pmatrix} \frac{V_0}{4} & \frac{V_0}{4}k^2 & 0 \\ \frac{V_0}{4}k^2 & \frac{V_0}{4} & 0 \\ 0 & 0 & \frac{V_0}{4} \end{pmatrix} = \frac{V_0}{4}\begin{pmatrix} 1 & k^2 & 0 \\ k^2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{2.5.15}$$

$$(1-\mathcal{E})\left((1-\mathcal{E})^2 - k^2\right) = 0$$
$$\Rightarrow \mathcal{E} = 1$$
$$\Rightarrow \mathcal{E} = 1 \pm \sqrt{1 - 4(1-k)^2}$$

2.6 Lecture 12

May 22, 2023

Example

3D infinite square well

$$E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)$$
$$\Psi_{n_x,n_y,n_z} = \left(\frac{2}{L}\right)^{3/2} Sin\left(\frac{n_x\pi x}{L}\right) Sin\left(\frac{n_y\pi y}{L}\right) Sin\left(\frac{n_z\pi z}{L}\right)$$
$$\hat{V}' = V_0\left(\Theta\left(x-\frac{L}{2}\right)\Theta\left(y-\frac{L}{2}\right)\right)$$

$$\underbrace{W_{n_xn_yn_z,n_x'n_y'n_z'}}_{W-\text{matrix}} = \underbrace{\left\langle \Psi_{n_x,n_y,n_z}\middle|\hat{V}'\middle|\Psi_{n_x',n_y',n_z'}\right\rangle}_{\text{matrix elements}}$$

$$W_{211,211} = W_{121,121} = W_{112,112} = \frac{V_0}{4}$$

$$W_{211,121} = W^*_{121,211} = \frac{V_0}{4}\left(\frac{8}{3\pi}\right)^2 = \frac{V_0}{4}k^2$$

$$\frac{2}{L}\int_0^L Sin\left(\frac{2\pi z}{L}\right) Sin\left(\frac{\pi z}{L}\right) dz = \delta_{21} = 0$$

if $n_z' = 2, n_z = 1, W_{n_xn_y1,n_x'n_y'2} = 0, \quad \forall\, n_x, n_y, n_x', n_y' \in \mathbb{N}$

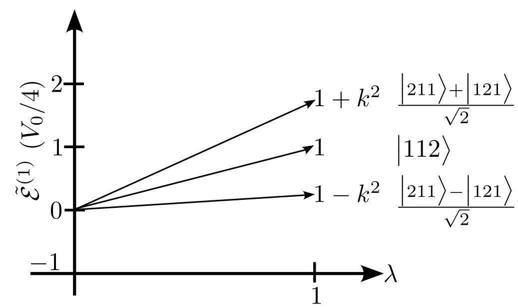
$$\mathcal{W} = \frac{V_0}{4}\begin{pmatrix}1 & k^2 & 0\\ k^2 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} = \tilde{\mathcal{E}}^{(1)}\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} \tag{2.6.1}$$

To solve for $\tilde{\mathcal{E}}^{(1)}$, the first order corrections to $E_{211} = E_{121} = E_{112} = \frac{3\pi^2\hbar^2}{mL^2}$ let $\tilde{\mathcal{E}}^{(1)} = \frac{V_0}{4}\omega$

$$\det\begin{pmatrix}1-\omega & k^2 & 0\\ k^2 & 1-\omega & 0\\ 0 & 0 & 1-\omega\end{pmatrix} = 0$$

$$(1-\omega)\det\begin{pmatrix}1-\omega & k^2\\ k^2 & 1-\omega\end{pmatrix} = 0$$
$$(1-\omega)\left((1-\omega)^2 - k^4\right) = 0$$

Solutions:



$$\hat{\omega} = 1$$
$$\hat{\omega} = 1 \pm k^2$$

$$\tilde{\mathcal{E}}^{(1)} = \begin{cases} \frac{V_0}{4} \\ \frac{V_0}{4}\left(1+\left(\frac{8}{3\pi}\right)^2\right) \\ \frac{V_0}{4}\left(1-\left(\frac{8}{3\pi}\right)^2\right) \end{cases} \tag{2.6.2}$$

$$= \frac{V_0}{4}\begin{cases} 0.28 \\ 1.00 \\ 1.72 \end{cases}$$

Solve for the eigenstates of $\hat{V}'$ in $|211\rangle, |121\rangle, |112\rangle$ basis:

Method: Substitute the eigenenergies into (3.6.1) and solve for the coefficients α, β, γ

$$\tilde{\mathcal{E}}^{(1)} = \frac{V_0}{4}: \quad \alpha + k^2\beta = \alpha \Rightarrow \beta = 0$$

$$k^2\alpha + \beta = \beta \Rightarrow \alpha = 0 \quad \Rightarrow \boxed{|112\rangle \text{ is the eigenstate with energy } V_0/4}$$

$$\gamma = \gamma \Rightarrow |\gamma|^2 = 1$$

$$\tilde{\mathcal{E}}^{(1)} = \frac{V_0}{4}\left(1+k^2\right): \quad \alpha + k^2\beta = \left(1+k^2\right)\alpha$$
$$k^2\beta = k^2\alpha \Rightarrow \alpha = \beta$$
$$k^2\alpha + \beta = \left(1+k^2\right)\beta \Rightarrow \alpha = \beta$$
$$\gamma = k^2\gamma \Rightarrow \gamma = 0$$

Normalisation: $|\alpha|^2 + |\alpha|^2 = 1 \Rightarrow \alpha = \frac{1}{\sqrt{2}} = \beta$

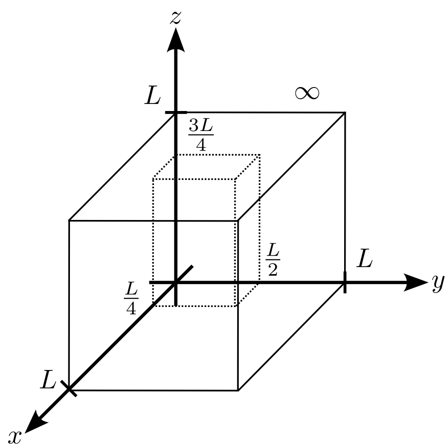
$$\Rightarrow \frac{|211\rangle + |121\rangle}{\sqrt{2}} \quad \boxed{\text{is the eigenstate with energy } V_0/4(1+k^2)}$$

$$\tilde{\mathcal{E}}^{(1)} = \frac{V_0}{4}\left(1+k^2\right): \quad \alpha + \beta k^2 = \left(1-k^2\right)\alpha \Rightarrow \alpha = -\beta$$
$$k^2\alpha + \beta = \left(1-k^2\right)\beta \Rightarrow \alpha = \beta$$
$$\gamma = \left(1-k^2\right)\gamma \Rightarrow \gamma = 0$$

Normalisation: $|\alpha|^2 + |\beta|^2 + |\gamma|^2 = 2|\alpha|^2 = 1 \Rightarrow \alpha = \frac{1}{\sqrt{2}}$ and $\beta = \frac{-1}{\sqrt{2}}$.

$$\Rightarrow \frac{|211\rangle - |121\rangle}{\sqrt{2}} \quad \boxed{\text{is the eigen-state with energy } V_0/4(1-k^2)}$$

Example



Now: $\hat{V} = L^3 V_0 \delta\left(x - \frac{L}{4}\right)\delta\left(y - \frac{L}{2}\right)\delta\left(z - \frac{3L}{4}\right)$

δ "bump" @ $\left(\frac{L}{4}, \frac{L}{2}, \frac{3L}{4}\right)$

$$\begin{aligned}
\tilde{\mathcal{E}}^{(1)}_{111} &= \langle 111|\hat{V}'|111\rangle, \quad \text{Since } |111\rangle \text{ is non-degenerate} \\
&= \left(\frac{2}{L}\right)^3 \int_0^L \int_0^L \int_0^L Sin^2\left(\frac{\pi x}{L}\right) Sin^2\left(\frac{\pi y}{L}\right) Sin^2\left(\frac{\pi z}{L}\right) \\
&\quad \delta\left(x - \frac{L}{4}\right)\delta\left(y - \frac{L}{2}\right)\delta\left(z - \frac{3L}{4}\right) dxdydz \\
&= V_0\, 8\, Sin^2\left(\frac{\pi}{4}\right) Sin^2\left(\frac{\pi}{2}\right) Sin^2\left(\frac{3\pi}{4}\right) \\
&= 8\, V_0 \left(\frac{1}{\sqrt{2}}\right)^2 (1) \left(\frac{-1}{\sqrt{2}}\right) \\
&= \frac{8}{4} V_0 = \boxed{2\, V_0}
\end{aligned}$$

Calculate the matrix elements for $\{|211\rangle, |121\rangle, |112\rangle\}$

$$\begin{aligned}
W_{211,211} = \langle 211|\hat{V}'|211\rangle &= \frac{8V_0L^3}{L^3} \int_0^L Sin^2\left(\frac{2\pi x}{L}\right)\delta\left(x - \frac{L}{4}\right) dx \\
&\quad \int_0^L Sin^2\left(\frac{\pi y}{L}\right)\delta\left(y - \frac{L}{2}\right) dy \int_0^L Sin^2\left(\frac{\pi z}{L}\right)\delta\left(z - \frac{3L}{4}\right) dz \\
&= 8\, V_0 \cancelto{1}{\left(Sin^2\left(\frac{2\pi}{4}\right)\right)} \cancelto{1}{\left(Sin^2\left(\frac{\pi}{2}\right)\right)} \cancelto{1/2}{\left(Sin^2\left(\frac{3\pi}{4}\right)\right)} = 4V_0
\end{aligned}$$

$$\begin{aligned}
W_{121,121} = \langle 121|\hat{V}'|121\rangle &= \frac{8V_0L^3}{L^3} \int_0^L Sin^2\left(\frac{\pi x}{L}\right)\delta\left(x - \frac{L}{4}\right) dx \\
&\quad \int_0^L Sin^2\left(\frac{2\pi y}{L}\right)\delta\left(y - \frac{L}{2}\right) dy \int_0^L Sin^2\left(\frac{\pi z}{L}\right)\delta\left(z - \frac{3L}{4}\right) dz \\
&= 8\, V_0 \cancelto{1/2}{\left(Sin^2\left(\frac{\pi}{4}\right)\right)} \cancelto{0}{\left(Sin^2(\pi)\right)} \cancelto{1/2}{\left(Sin^2\left(\frac{3\pi}{4}\right)\right)} = 0
\end{aligned}$$

Note: $\left|n_x, 2kn_y\right\rangle$ are even in y, node @ $y = L/2$, so particles have zero probability of being @ $y = L/2$, ergo they do not feel $\hat{V}'$.

$$\begin{aligned} W_{112,112} &= \left\langle 112\middle|\hat{V}'\middle|112\right\rangle \\ &= 8V_0 Sin^2\left(\frac{\pi}{4}\right) Sin^2\left(\frac{pi}{2}\right) Sin^2\left(\frac{3\pi}{4}\right) = 4V_0 \end{aligned}$$

$$\begin{aligned} W_{211,121} = \left\langle 211\middle|\hat{V}'\middle|121\right\rangle = \frac{8V_0L^3}{L^3} &\int_0^L Sin\left(\frac{2\pi x}{L}\right) Sin\left(\frac{\pi x}{L}\right) \delta\left(x - \frac{L}{4}\right) dx \\ &\int_0^L Sin\left(\frac{\pi y}{L}\right) Sin\left(\frac{2\pi y}{L}\right) \delta\left(y - \frac{L}{2}\right) dy \int_0^L Sin^2\left(\frac{\pi z}{L}\right) \delta\left(z - \frac{3L}{4}\right) dz \\ &= 0 = W_{112,121} = W^*_{211,121} = W_{112,121} \end{aligned}$$

$$\begin{aligned} W_{211,112} = \left\langle 211\middle|\hat{V}'\middle|112\right\rangle = \frac{8V_0L^3}{L^3} &\int_0^L Sin\left(\frac{2\pi x}{L}\right) Sin\left(\frac{\pi x}{L}\right) \delta\left(x - \frac{L}{4}\right) dx \\ &\int_0^L Sin^2\left(\frac{\pi y}{L}\right) \delta\left(y - \frac{L}{2}\right) dy \int_0^L Sin\left(\frac{\pi z}{L}\right) Sin\left(\frac{2\pi z}{L}\right) \delta\left(z - \frac{3L}{4}\right) dz \\ &= 8\,V_0 \left(Sin\left(\frac{\pi}{2}\right) Sin\left(\frac{\pi}{4}\right)\right) \left(Sin^2\left(\frac{\pi}{2}\right)\right) \left(Sin\left(\frac{3\pi}{4}\right) Sin\left(\frac{3\pi}{2}\right)\right) = -4V_0 \end{aligned}$$

Then,

$$\mathcal{W} = 4V_0 \begin{pmatrix} 1 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1 \end{pmatrix} \tag{2.6.3}$$

Solve $\det(\mathcal{W} - \tilde{\mathcal{E}}^{(1)}\mathbb{1}) = 0$, let $\tilde{\mathcal{E}}^{(1)} = 4V_0\omega$

$$\det\begin{pmatrix} 1-\omega & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 1-\omega \end{pmatrix} = 0 \Longleftrightarrow \omega = 0 \text{ for } \left|121\right\rangle$$

$$\det\begin{pmatrix} 1-\omega & -1 \\ -1 & 1-\omega \end{pmatrix} = 0$$

$$\begin{aligned} \left(1-\omega^2\right) - 1 &= 0 \\ 1 - \omega &= \pm 1 \\ \omega &= 1 \pm 1 \end{aligned}$$

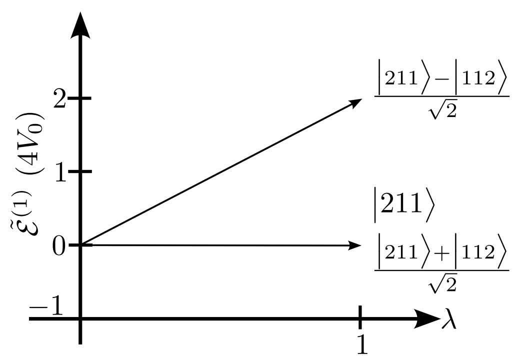
$$\omega = \begin{cases} 0, & \left|121\right\rangle \\ 0, & \frac{\left|211\right\rangle + \left|112\right\rangle}{\sqrt{2}} \\ 2, & \frac{\left|211\right\rangle - \left|112\right\rangle}{\sqrt{2}} \end{cases}$$

$$\omega = 0: \quad \alpha - \gamma = 0$$
$$-\alpha + \gamma = 0$$

$$\Rightarrow \alpha = \gamma \Rightarrow \alpha = \frac{1}{\sqrt{2}} = \gamma$$

$$\omega = 2: \quad \alpha - \gamma = 2\alpha$$
$$\gamma = -\alpha$$
$$\alpha = -\gamma$$

$$\Rightarrow \alpha = -\gamma = \frac{1}{\sqrt{2}}$$



Example

$$\tilde{H} = \begin{pmatrix} 1-\epsilon & 0 & 0 \\ 0 & 1 & \epsilon \\ 0 & \epsilon & 2 \end{pmatrix} \quad \text{Hamiltonian in matrix form}$$

For $\epsilon \ll 1$:

$$\tilde{H} = \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}}_{\hat{H}_0} + \epsilon \underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}}_{\mathcal{W}}$$

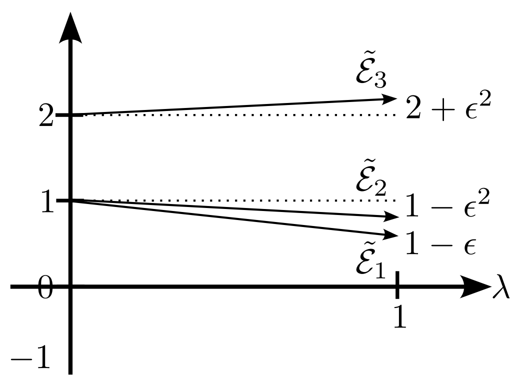
$$\mathcal{E}_1 = \mathcal{E}_2 = 1, \quad \mathcal{E}_3 = 2$$
$$\Rightarrow |\Psi_1\rangle + |\Psi_2\rangle \quad \text{are degenerate}$$

But $\left|\Psi_1\right\rangle + \left|\Psi_2\right\rangle$ are linearly independent in the perturbation.
We can use *TINDPT* (non-degenerate for $\left|\Psi_1\right\rangle \& \left|\Psi_2\right\rangle$)

$$\tilde{\mathcal{E}}_1 = 1 + \cancelto{\epsilon}{\left\langle \Psi_1 \middle| \hat{V}' \middle| \Psi_1 \right\rangle} + \sum_{n \neq 1} \frac{\left\langle \Psi_{n'} \middle| \hat{V}' \middle| \Psi_1 \right\rangle}{\mathcal{E}_1 - \mathcal{E}_{n'}} = 1 - \epsilon$$

$$\tilde{\mathcal{E}}_2 = 1 + \cancelto{0}{\left\langle \Psi_2 \middle| \hat{V}' \middle| \Psi_2 \right\rangle} + \sum_{n \neq 2} \frac{\left\langle \Psi_{n'} \middle| \hat{V}' \middle| \Psi_2 \right\rangle}{\mathcal{E}_2 - \mathcal{E}_{n'}} = 1 - \epsilon^2$$

$$\tilde{\mathcal{E}}_3 = 2 + \cancelto{0}{\left\langle \Psi_3 \middle| \hat{V}' \middle| \Psi_3 \right\rangle} + \frac{\epsilon^2}{2-1} = 2 + \epsilon^2$$



$$\det \begin{pmatrix} 1-\omega & 0 & 0 \\ 0 & 1-\omega & \epsilon \\ 0 & \epsilon & 2-\omega \end{pmatrix} = 0$$

$$\omega = 1 - \epsilon \quad (1-\omega)(2-\omega) - \epsilon^2 = 0$$

$$\omega^2 - 3\omega + 2 - \epsilon^2 = 0$$

$$\boxed{\omega_\pm = \frac{3}{2} \pm \sqrt{\frac{9}{4} - 2 + \epsilon^2} = \frac{3}{2} \pm \sqrt{\frac{1}{4} + \epsilon^3}}$$

Chapter 3

Fine Structure of the Hydrogen

3.1 Lecture 13

May 23, 2023

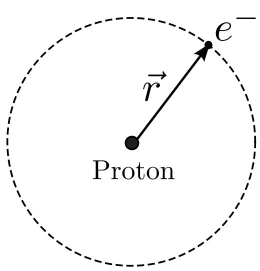


Figure 3.1: Boohr model of the Hydrogen atom.

Hamiltonian

$$\hat{H}_{0,\text{Bohr}} = \frac{-\hbar^2}{2m}\nabla^2_{\vec{r}} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} = \boxed{\frac{\vec{\nabla}_{\vec{r}}}{2} - \frac{1}{r^2}}$$

In atomic units

Atomic units

$$\hbar = m_e = e = 4\pi\epsilon_0 = 1 = a_0$$

but why?

3.1.1 Fine Structure Constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \cong \frac{1}{137,036}$$

A universal dimensionless constant relating $4\pi\epsilon_0, e^2, \hbar\,\&\,c$.

$$\Rightarrow c = \frac{1}{\alpha} \approx 137 \quad \text{in atomic units.}$$

$\hat{H}_{\text{Bohr}}$ is the Bohr model for the hamiltonian of the hydrogen atom.

Idea: Find corrections to the Bohr model hamiltonian $\hat{H}_{\text{Bohr}}$, and include them via *TIPT*.

$$\hat{H}_{\text{Bohr}} + \underbrace{\hat{H}'}_{\text{corrections}} \longrightarrow \tilde{E}_n \approx E_n + \langle \varphi_n | \hat{H}' | \varphi_n \rangle$$

In fact, $\langle \varphi_n | \hat{H}' | \varphi_n \rangle$ are of order $\alpha^4 mc^2$, whereas:

$$\begin{aligned} E_n = \frac{E_1}{n^2} &= \frac{-m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2}\left(\frac{1}{n^2}\right) \\ &= \frac{-m_e}{2}\underbrace{\left(\frac{e^2}{4\pi\epsilon_0\hbar c}\right)^2}_{\alpha} \cdot c^2 \frac{1}{n^2} \\ &= \frac{-m_e c^2}{2}\alpha^2\frac{1}{n^2} = \mathcal{O}(mc^2\alpha^2) \end{aligned}$$

$$\hat{H}_{\text{Bohr}}(r) \longleftarrow \begin{array}{l}\text{Angular}\\ \text{symmetry}\end{array} \implies \varphi_{nlm}(r,\theta,\varphi)\zeta_n(r)Y_l^m(\theta,\varphi)$$

are l and m degenerate. So $\hat{H}'$ could split/ break this angular degeneracy.

Fine Structure $\mathcal{O}(\alpha^2 m_e c^2)$

1. Relativistic corrections to the Kinetic Energy.
2. Spin-Orbit Coupling: this interaction between the electron's spin and its orbit around the proton.
   $\hat{H}_{SO} = -\vec{\mu}\cdot\vec{B}$
   - $\vec{\mu}$ electron's spin dipole proton orbit induced.
   - $\vec{B}$ magnetic field.

$$\hat{T}_{\text{Bohr}} = \frac{1}{2}(m\hat{p})^2, \quad \hat{p} = i\hbar\nabla_r$$

3.1.2 Relativistic corrections to the Kinetic Energy

Relativistic effects

$$\text{Total Energy} = \text{Kinetic E} + \text{Rest E}$$

$$E_0 = mc^2, \quad \gamma = \frac{1}{\sqrt{1-v^2/c^2}}, \quad \hat{p} = \gamma m v$$

$$\begin{array}{l}\text{Total}\\ \text{Energy}\end{array} = \gamma E_0 = \frac{mc^2}{\sqrt{1-v^2/c^2}}$$

$$\begin{array}{l}\text{Kinetic}\\ \text{Energy}\end{array} = \begin{array}{l}\text{Total}\\ \text{Energy}\end{array} - \begin{array}{l}\text{Rest}\\ \text{Energy}\end{array} = \frac{mc^2}{\sqrt{1-v^2/c^2}} - mc^2$$

$$
\begin{pmatrix}\text{Total}\\ \text{Energy}\end{pmatrix}^2 = \left(\frac{m^2c^4}{1-v^2/c^2}\right), \quad p^2 = \frac{m^2v^2}{1-v^2/c^2}
$$

$$
\begin{aligned}
&= \left(\frac{m^2v^2c^2 + m^2c^4 - m^2v^4}{1-v^2/c^2}\right)\\
&= p^2c^2 + \frac{m^2c^4(1-v^2/c^2)}{1-v^2/c^2}\\
&= p^2c^2 + m^2c^4
\end{aligned}
$$

Steps

1. Square $E_{\text{tot}} = \gamma E_0$ so as to avoid the root.
2. Separate out $p = \gamma mv$ by substracting $\gamma^2m^2v^2c^2$.
3. Express in terms of p alone to avoid v because it is not a good quantum operator.

$$
\begin{pmatrix}\text{Total}\\ \text{Energy}\end{pmatrix}^2 = (T+E_0)^2 = \left(T+mc^2\right)^2 = p^2c^2 + m^2c^4
$$

An expression relating T to p including relativistic effects but without γ & v.

$$
\begin{aligned}
\Rightarrow \hat{T} &= \sqrt{p^2c^2 + m^2c^4} - mc^2, \quad \sqrt{1+x^2} \approx 1 + \frac{x^2}{2} - \frac{x^4}{8} + \mathcal{O}(x^6)\\
&= mc^2\left(\sqrt{1+\frac{p^2}{mc^2}} - 1\right)\\
&= mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \mathcal{O}\left(\frac{p^6}{m^6c^6}\right) - 1\right)\\
&= \underbrace{\frac{p^2}{2m}}_{\text{classic K.E}} - \underbrace{\frac{p^4}{8m(mc)^2}}_{\text{1st order relativistic correction}} + \mathcal{O}\left(\frac{p^6}{m^5c^4}\right)
\end{aligned}
$$

$$
\hat{H}_{\text{rel}} = \frac{-p^4}{8m^3c^2}
$$

The reletivistic correction to the Bohr model hamiltonian. This hamiltonian is dependent only on $(p^2)^2$ and so has the same eigenvalues as the unperturbed Bohr hamiltonian.

$$
E^{(1)}_{\text{rel}} = \left\langle \varphi_n \middle| \frac{-p^4}{8m^3c^2} \middle| \varphi_n \right\rangle
$$

There is no angular dependence, so it does not lift the degeneracy between φ_{nlm}, and we can use non-degenerate perturbation theory.

$$
\Rightarrow \varphi_{nlm} \quad \text{are eigenstates of } \hat{H}_{\text{rel}}
$$

We can use non-degenerate perturbation theory.

Treat $\hat{p}^2$ as an hermitian operator:

$$p^2 = \hbar^2\nabla^2$$

$$E_n^{(1)} = \frac{-1}{8m^3c^2}\langle\varphi_n|(\hat{p}^2)^\dagger(\hat{p}^2)|\varphi_n\rangle$$

From the Bohr Model

$$E_{\text{tot}} = T + V$$

$$\Rightarrow p^2 = 2m(E_{\text{tot}} - \hat{V})$$

this is a further approximation, but is justified as we are calculating $\langle\hat{H}_{\text{rel}}\rangle$ perturbately.

$$E_n^{(1)} = \frac{-1}{8m^3c^2}\langle\varphi_n|2m(E_{\text{tot}} - \hat{V}^\dagger)2m(E_{\text{tot}} - \hat{V})|\varphi_n\rangle$$

But $E_{\text{tot}} = E_n$ when operating on φ_n

$$\begin{aligned} &= \frac{-1}{2mc^2}\langle\varphi_n|(E_{\text{tot}} - \hat{V}^\dagger)(E_{\text{tot}} - \hat{V})\varphi_n\rangle \\ &= \frac{-1}{2mc^2}\left(E_n^2 - 2E_n\langle\varphi_n|\hat{V}|\varphi_n\rangle + \left|\langle\varphi_n|\hat{V}|\varphi_n\rangle\right|^2\right) \end{aligned}$$

let $\langle\hat{V}\rangle = \langle\varphi_n|\hat{V}|\varphi_n\rangle$:

$$\frac{-1}{2mc^2}\left(E_n^2 - 2E_n\langle\hat{V}\rangle + \left|\langle\hat{V}\rangle\right|^2\right)$$

$\hat{V} = \frac{-e^2}{4\pi\epsilon_0}\frac{1}{r}$:

$$\tilde{E}_{\text{rel},n}^{(1)} = \frac{-1}{2mc^2}\left(E_n^2 - 2E_n\left(\frac{-e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \left(\frac{-e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{1}{r^2}\right\rangle\right)$$

$$E_n = \underbrace{\frac{-me^4}{2(4\pi\epsilon_0)^2}\frac{1}{\hbar^2}}_{E_1}\left(\frac{1}{n^2}\right) = \frac{-m}{2}\left(\frac{-e^2}{4\pi\epsilon_0}\right)^2\frac{1}{\hbar^2}\frac{1}{n^2}$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}, \quad E_1 = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{m}{2\hbar^2} \rightarrow$$ Negative, since the Bohr model hydrogen atom is stable.

Then:

$$\begin{aligned} \tilde{E}_{\text{rel},n}^{(1)} &= \frac{-1}{2mc^2}\left[\frac{E_1^2}{n^4} - 2\frac{E_1}{n^2}\left(\frac{-e^2}{4\pi\epsilon_0}\right)\left\langle\frac{a_0}{r}\right\rangle\left(\frac{e^2m}{4\pi\epsilon_0\hbar^2}\right) + \left(\frac{-e^2}{4\pi\epsilon_0}\right)^2\left\langle\frac{a_0^2}{r^2}\right\rangle\left(\frac{e^2m}{4\pi\epsilon_0\hbar^2}\right)^2\right] \\ &= \boxed{\frac{-E_1^2}{2mc^2}\left[\frac{1}{n^4} - \frac{4}{n^2}\left\langle\frac{a_0}{r}\right\rangle + 4\left\langle\frac{a_0^2}{r^2}\right\rangle\right]} \end{aligned}$$

We know that: (*This results were taken from Griffits*)

$$\left\langle \varphi_n \middle| \frac{1}{r} \middle| \varphi_n \right\rangle = \frac{1}{n^2 a_0}$$
$$\left\langle \varphi_n \middle| \frac{1}{r^2} \middle| \varphi_n \right\rangle = \frac{1}{(l+1/2)n^3 a_0^2}$$

so,

$$\begin{aligned}
\tilde{E}^{(1)}_{\mathrm{rel},n} &= \frac{-E_1^2}{2mc^2}\left[\frac{1}{n^4} - \frac{4}{n^4} + \frac{4}{(l+1/2)n^3}\right] \quad \text{factor out } \tfrac{1}{n^4} \text{ to get } E_n^2 \\
&= \frac{-E_n^2}{2mc^2}\left[1 - 4 + \frac{4n}{(l+1/2)}\right] \\
\end{aligned}$$
$$\boxed{\tilde{E}^{(1)}_{\mathrm{rel},n} = \frac{-E_n^2}{2mc^2}\left[\frac{4n}{(l+1/2)} - 3\right]}$$

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$$\boxed{\tilde{E}^{(1)}_{\text{rel}} = \frac{-E_n^2}{2mc^2}\left[\frac{4n}{(l+1/2)} - 3\right]} \tag{3.2.1}$$

So, $\left|\varphi_{nlm}\right\rangle$ are eigenfunctions of $\hat{H}_{\text{rel}}$ and non-degenerate perturbation theory is valid.

3.2.1 Spin-Orbit

$$\hat{\hat{H}}_{SO} = -\vec{\mu}\cdot\vec{B}_{\text{ind}}, \quad \text{where:}$$

- $\vec{\mu}$ is the electric spin dipole of the electron.
- $\vec{B}_{\text{ind}}$ is the magnetic field induced by the proton orbit.

From the electron's perspective

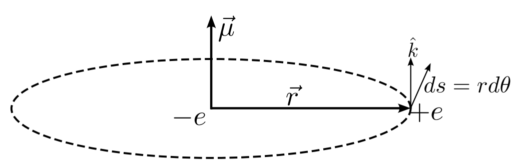

Figure 3.2: Hydrogen atom from the electron's perspective.

$$\vec{B}_{\text{ind}} = \frac{\mu_0 I}{2r}, \quad \text{Biot-Savart law}$$

$$\begin{aligned}
\vec{B}_{\text{ind}} &= \mu_0 \int \frac{\vec{r}\times d\vec{l}}{r^3} I, \quad d\vec{l} = r\vec{e}_\theta d\theta \\
&= \frac{\mu_0}{r^3} r^2 \int_0^{2\pi} \frac{\hat{e}_r \times \hat{e}_\theta}{4\pi} d\theta I \\
&= \frac{\mu_0 I}{2r}\hat{k}
\end{aligned}$$

Idea: We'd prefer to have the hamiltonian in terms of "good" quantum operators of $\hat{H}_{\text{Bohr}}$, i.e. operators which have $\left|nlm\right\rangle$ as eigenstates.

Why? So we can use non-degenerate perturbation theory.
Can we express the current I in terms of a quantum operator with $\left|nlm\right\rangle$ as eigenstates?

Current is the speed of the proton as it orbits around the electron.

Try to express I in terms of the electron-proton system's angular momentum L.

$$current = \frac{charge}{orobit\ period} \quad \text{assuming quasi-circular orbit}$$

$$I = \frac{e}{T}$$

angular momentum of the electron around proton $= rm_e v$

$$r m_e v = r m_e \frac{2\pi r}{T}$$

$$\begin{aligned}\vec{B}_{\text{ind}} &= \frac{\mu_0}{2r}\left(\frac{e}{T}\right)\cdot\hat{k}\\ &= \frac{\mu_0 e}{2r}\frac{1}{2\pi m_e r^2}\underbrace{\left(\frac{2\pi m_e r^2}{T}\right)}_{L}\hat{k}\end{aligned}$$

$$\begin{aligned}\vec{B}_{\text{ind}} &= \frac{\mu_0 e}{4\pi m_e r^3}\vec{L}, \quad c^2 = \frac{1}{\mu_0\epsilon_0}, \quad \mu_0 = \frac{1}{\epsilon_0 c^2}\\ &= \frac{e}{4\pi\epsilon_0 r^3}\frac{\vec{L}}{m_e c^2}\end{aligned}$$

Can we express $\vec{\mu}$ in terms of a "good" quantum operator for $\hat{H}_{\text{Bohr}}$?

The magnetic dipole momentum of the electron considers the electron to be a "ring" of charge of radius r with units of charge q distributed over the string.

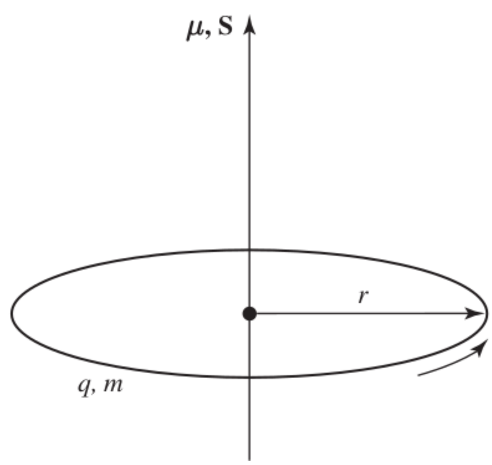

Figure 3.3: A ring of charge, rotating aorund the axis.

$$v = \frac{2\pi r}{T}$$

$$\begin{aligned}|\vec{\mu}| &= I\cdot A \longrightarrow \text{current}\times\text{area}\\ &= \frac{q}{T}\times\pi r^2\end{aligned}$$

Can we relate $\vec{\mu}$ to the electron spin operator $\vec{S}$.

$$\begin{aligned}\text{angular momentum of a spinning ring} &= \text{moment of inertia} \times \text{angular velocity}\\ &= m\, r^2 \times \frac{2\pi}{T}\end{aligned}$$

$$S = \frac{2\pi r^2 m_e}{T}$$

$$\vec{S} = \frac{2\pi r^2 m_e \vec{k}}{T}$$

$$\vec{\mu} = \frac{q\pi r^2}{T}\vec{k} = \frac{q\vec{S}}{2m_e}$$

$$\left.\vec{\mu}_e = \frac{-e\vec{S}}{2m_e}\right\} \qquad \text{classical result}$$

Using Dirac's relativistic quantum mechanics we obtain an extra factor of 2, so that:

$$\left.\vec{\mu}_e = \frac{e\vec{S}}{m_e}\right\} \quad \text{quantum mechanical result for an electron} \quad \left(\text{Dirac Eqn}\right)$$

However, we treated the proton's motion around the electron as if the electron was in an inertial frame of reference. This in not the case as the electron has an acceleration.

$$\vec{B}_{\text{ind}} = \frac{e\vec{L}}{4\pi\epsilon_0 r^3 m_e c^2}$$

To account for this, we need to include the Thomas Precession correction, a factor of 1/2 in $\vec{B}_{\text{ind}}$.

$$\left.\vec{B}_{\text{ind}} = \frac{e\vec{L}}{8\pi\epsilon_0 r^3 m_e c^2}\right\} \quad \text{including relativistic effects} \quad \left(\text{Thomas Precession}\right)$$

In any case:

$$\hat{\tilde{H}}_{SO} = -\vec{\mu}\cdot\vec{B}_{\text{ind}}$$

Negative ensures $\left\langle \hat{H}_{SO} \right\rangle$ is positive when $\vec{\mu}$ and $\vec{B}$ are parallel.

Substituting in:

$$\begin{aligned}\hat{\tilde{H}}_{SO} &= -\left(\frac{e\vec{S}}{m_e}\right)\left(\frac{e\vec{L}}{8\pi\epsilon_0 r^3 m_e c^2}\right)\\ &= \frac{e^2}{8\pi\epsilon_0 r^3}\frac{\vec{S}\vec{L}}{m_e m_p c^2}\end{aligned}$$

Since $\left|\varphi_{nlm}\right\rangle$ have S and L as quantum numbers, $\vec{S}$ and $\vec{L}$ have $\left|nlm\right\rangle$ as eigenstates, and we can use non-degenerate perturbation theory.

$$\begin{aligned}\tilde{E}^{(1)}_{SO} &= \left\langle \varphi_{nlm} \middle| \frac{e^2\vec{S}\cdot\vec{L}}{8\pi\epsilon_0 m_e m_p c^2 r^3} \middle| \varphi_{nlm} \right\rangle\\ &= \frac{e^2}{8\pi\epsilon_0 m_e m_p c^2}\left\langle \frac{\vec{S}\cdot\vec{L}}{r^3}\right\rangle\end{aligned}$$

but $\vec{S}$ and $\vec{L}$ commute with r:

$$\tilde{E}_{SO}^{(1)} = \frac{e^2}{8\pi\epsilon_0 m_e m_p c^2}\left\langle \vec{S}\cdot\vec{L}\right\rangle\left\langle\frac{1}{r^3}\right\rangle$$

$$\begin{aligned}\left\langle L^2\right\rangle &= \hbar^2\, l(l+1)\\ \left\langle S^2\right\rangle &= \hbar^2\, s(s+1)\\ \left\langle J^2\right\rangle &= \hbar^2\, j(j+1)\end{aligned}$$

$$\vec{J} = \vec{S}+\vec{L}$$

$$J^2 = \left(\vec{S}+\vec{L}\right)^2 = S^2 + 2\,\vec{S}\cdot\vec{L} + L^2$$

$$\Rightarrow \vec{S}\cdot\vec{L} = \frac{1}{2}\left(J^2 - S^2 - L^2\right)$$

$$\begin{aligned}\left\langle\vec{S}\cdot\vec{L}\right\rangle &= \frac{\left\langle J^2\right\rangle - \left\langle S^2\right\rangle - \left\langle L^2\right\rangle}{2}\\ &= \frac{\hbar^2}{2}\left(j(j+1) - s(s+1) - l(l+1)\right)\end{aligned}$$

$$\left\langle\frac{a_0^3}{r^3}\right\rangle = \frac{1}{l(l+1/2)(l+1)n^3}$$

$$\tilde{E}_{SO}^{(1)} = \frac{e^2}{2(4\pi\epsilon_0)m_e m_p c^2 a_0^3}\frac{\hbar^2}{2}\frac{j(j+1)-s(s+1)-l(l+1)}{l(l+1/2)(l+1)n^3}$$

$$E_n = \frac{-m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2}$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$

$$\begin{aligned}\tilde{E}_{SO}^{(1)} &= \frac{e^2}{4(4\pi\epsilon_0)m_e m_p c^2}\left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)^3\hbar^2\frac{j(j+1)-s(s+1)-l(l+1)}{l(l+1/2)(l+1)n^3}\\ &= \underbrace{\left(\frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2}\right)^2\frac{1}{n^4}}_{E_n^2}\frac{1}{mc^2}\frac{n[j(j+1)-s(s+1)-l(l+1)]}{l(l+1/2)(l+1)}\end{aligned}$$

$$\boxed{\tilde{E}_{SO}^{(1)} = \frac{E_n^2}{mc^2}\frac{n[j(j+1)-s(s+1)-l(l+1)]}{l(l+1/2)(l+1)}} \tag{3.2.2}$$

The relativistic and spin-orbit corrections have the same "order":

$$\frac{E_n^2}{mc^2} = \frac{\alpha^4 mc^2}{n^4} = \frac{\alpha^2 E_n}{n^2}$$

Idea: We must include both corrections or neither.

3.2.2 Fine Structure Correction

$$
\begin{aligned}
E_{fs} = \tilde{E}^{(1)}_{\text{rel}} + \tilde{E}^{(1)}_{SO} &= \frac{E_n^2}{mc^2}\left[\frac{-2n}{l+1/2} + \frac{3}{2} + \frac{n[j(j+1) - s(s+1) - l(l+1)]}{l(l+1/2)(l+1)}\right] \\
&= \frac{E_n^2}{mc^2}\left[\frac{3}{2} + \frac{n}{l+1/2}\frac{j(j+1) - s(s+1) - l(l+1) - 2l(l+1)}{l(l+1)}\right] \\
&= \frac{E_n^2}{mc^2}\left[\frac{3}{2} + \frac{n}{l+1/2}\frac{j(j+1) - s(s+1) - 3l(l+1)}{l(l+1)}\right]
\end{aligned}
$$

Note: $s = 1/2$, $j = l \pm s = l \pm 1/2$, $\Rightarrow -s(s+1) = -1/2(3/2) = -3/4$

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

if $j = l + s = l + 1/2$ (angular and spin angular momentum are parallel) $\Rightarrow l = j - 1/2, l+1 = j + 1/2, l + 1/2 = j$

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

if $j = l - s = l - 1/2$, $l = j + 1/2$, $l + 1 = j + 3/2$, $l + 1/2 = j + 1$ (l and s are anti-parallel)

$$
\begin{aligned}
E_{fs} &= \frac{E_n^2}{mc^2}\left[\frac{3}{2} + \frac{n[j(j+1) - 3/4 - 3(j+1/2)(j+3/2)]}{(j+1/2)(j+1)(j+3/2)}\right] \\
&= \frac{E_n^2}{mc^2}\left[\frac{3}{2} + \frac{n[j^2 + j - 3/4 - 3(j^2 + 2j + 3/4)]}{(j+1/2)[j^2 + 5/2j + 3/2]}\right] \\
&= \frac{E_n^2}{mc^2}\left[\frac{3}{2} + \frac{n\cancelto{2}{[-2j^2 - 5j - 3]}}{(j+1/2)\cancel{[j^2 + 5/2j + 3/2]}}\right] \\
&= \frac{E_n^2}{mc^2}\left[\frac{3}{2} - \frac{2n}{j+1/2}\right] \\
&= \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+1/2}\right]
\end{aligned}
$$

Finally

$$
\tilde{E} = E_n + \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+1/2}\right] \tag{3.2.3}
$$

3.3 Lecture 15

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$$\hat{H}_{Bohr} = \frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$$\begin{aligned}
\hat{T} &= \underbrace{mc^2}_{E_0}\left(\sqrt{1-\frac{p^2}{m^2c^2}}-1\right) \\
&\approx \cancel{mc^2}\left(\frac{p^2}{2\cancel{m^2c^2}} - \frac{p^4}{8\cancel{m^4c^4}} + \mathcal{O}\left(\frac{p^6}{m^6c^6}\right)\right) \\
&= \underbrace{\frac{p^2}{2m}}_{\hat{T}} + \underbrace{\frac{p^4}{8m^3c^2}}_{\hat{H}_{rel}} + \cdots
\end{aligned}$$

Where $\hat{H}_{rel}$ is the first order relativistic correction to the kinetic energy.

$$E_{rel} = \tilde{\mathcal{E}}^{(1)}_{rel} = \frac{-1}{8m^3c^2}\left(\langle\psi_n|p^4|\psi_n\rangle\right)$$

Treating the momentum as a quantum operator we had: $\hat{p} = i\hbar\vec{\nabla}$ (a semiclassical approximation).

$$\frac{\hat{p}^2}{2m}|\psi_n\rangle = \left(E_n - \hat{V}\right)|\psi_n\rangle \qquad \begin{pmatrix}\text{to first order in} \\ \text{the relativistic} \\ \text{correction}\end{pmatrix}$$

$$\begin{aligned}
E_{rel} &= \langle\psi_n|\hat{p}^{2\dagger}\hat{p}^2|\psi_n\rangle\left(\frac{-1}{8m^3c^2}\right) \\
&= \frac{-1}{8m^3c^2}\langle\psi_n|(E_n-\hat{V}^\dagger)2m\cdot 2m(E_n-\hat{V})|\psi_n\rangle \\
&= \frac{-1}{2mc^2}\left(\langle\psi_n|E_n^2 - 2E_n\hat{V} + |\hat{V}|^2|\psi_n\rangle\right)
\end{aligned}$$

$$E^{(1)}_{rel,n} = -\frac{E_n^2 - 2E_n\langle\hat{V}\rangle + \langle\hat{V}^2\rangle}{2mc^2}$$

Example: Harmonic Oscillator

$$\mathcal{E}_n = \hbar\omega\left(n-\frac{1}{2}\right), \qquad n\in\mathbb{N}, \qquad \omega^2 = \frac{k}{m}$$

$$\hat{V}_{harm} = \frac{1}{2}kx^2 = \frac{\omega^2 m x^2}{2}$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a}_+ - \hat{a}_-\right)$$

Recall:

$$\left\langle \hat{T} \right\rangle + \left\langle \hat{V} \right\rangle = E_{tot} \Rightarrow \left\langle \hat{V} \right\rangle = \frac{\hbar\omega}{2}\left(n - \frac{1}{2}\right)$$

Virial Theorem:

$$\left\langle \hat{T} \right\rangle = \left\langle \hat{V} \right\rangle \Rightarrow \left\langle \hat{V} \right\rangle = \frac{E_{tot}}{2}$$

$$\begin{aligned}\left\langle \hat{V} \right\rangle &= \frac{\hbar^2}{4m^2\omega^2}\left(\hat{a}_+ - \hat{a}_-\right)^4 \frac{\omega^4 m^2}{4} \\ &= \left(\frac{\hbar\omega}{4}\right)^2 \left(\hat{a}_+ - \hat{a}_-\right)^4\end{aligned}$$

$$\begin{aligned}a_+|n\rangle &= \sqrt{n+1}|n+1\rangle \\ a_-|n\rangle &= \sqrt{n}|n-1\rangle\end{aligned}$$

$$\begin{aligned}\left(\hat{a}_+ + \hat{a}_-\right)^4 &= \left(\hat{a}_+^2 + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-^2\right)\left(\hat{a}_+^2 + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+ + \hat{a}_-^2\right) \\ &= \left(\hat{a}_+^4 + \hat{a}_+^2\hat{a}_+\hat{a}_- + \hat{a}_+^2\hat{a}_-\hat{a}_+ + \hat{a}_+^2\hat{a}_-^2 + \hat{a}_+\hat{a}_-\hat{a}_+^2 + \hat{a}_+\hat{a}_-\hat{a}_+\hat{a}_- + \hat{a}_+\hat{a}_-\hat{a}_-\hat{a}_+\right. \\ &\quad + \hat{a}_+\hat{a}_-\hat{a}_-^2 + \hat{a}_-\hat{a}_+\hat{a}_+^2 + \hat{a}_-\hat{a}_+\hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+\hat{a}_-\hat{a}_+ + \hat{a}_-\hat{a}_+\hat{a}_-^2 \\ &\quad \left. + \hat{a}_-^2\hat{a}_+^2 + \hat{a}_-^2\hat{a}_+\hat{a}_- + \hat{a}_-^2\hat{a}_-\hat{a}_+ + \hat{a}_-^2\hat{a}_-^2\right)\end{aligned}$$

$$\begin{aligned}\left\langle n\middle| \left(\hat{a}_+ + \hat{a}_-\right)^2 \middle|n\right\rangle &= \left\langle n\middle|\hat{a}_+^4\middle|n\right\rangle + \left\langle n\middle|\hat{a}_+^2\hat{a}_+\hat{a}_-\middle|n\right\rangle + \left\langle n\middle|\hat{a}+^2\hat{a}_-\hat{a}_+\middle|n\right\rangle \\ &\quad + \left\langle n\middle|\hat{a}_+^2\hat{a}_-^2\middle|n\right\rangle + \left\langle n\middle|\hat{a}_+\hat{a}_-\hat{a}_+^2\right\rangle \\ &\quad + \left\langle n\middle|\hat{a}_+\hat{a}_-\hat{a}_+\hat{a}_-\middle|n\right\rangle + \left\langle n\middle|\hat{a}_+\hat{a}_-\hat{a}_-\hat{a}_+\middle|n\right\rangle + \left\langle n\middle|\hat{a}_+\hat{a}_-\hat{a}_-^2\middle|n\right\rangle \\ &\quad + \left\langle n\middle|\hat{a}_-\hat{a}_+\hat{a}_+^2\middle|n\right\rangle + \left\langle n\middle|\hat{a}_-\hat{a}_+\hat{a}_+\hat{a}_-\middle|n\right\rangle + \left\langle n\middle|\hat{a}_-\hat{a}_+\hat{a}_-\hat{a}_+\middle|n\right\rangle \\ &\quad + \left\langle n\middle|\hat{a}_-\hat{a}_+\hat{a}_-^2\middle|n\right\rangle + \left\langle n\middle|\hat{a}_-^2\hat{a}_+^2\middle|n\right\rangle + \left\langle n\middle|\hat{a}_-^2\hat{a}_+\hat{a}_-\middle|n\right\rangle \\ &\quad + \left\langle n\middle|\hat{a}_-^2\hat{a}_-\hat{a}_+\middle|n\right\rangle + \left\langle n\middle|\hat{a}_-^4\middle|n\right\rangle\end{aligned}$$

$$\begin{aligned}&= n(n-1) + n^2 + n(n+1) + n(n+1) + (n+1)^2 + (n+2)(n+1) \\ &= n^2 - n + n^2 + 2n^2 + 2n + n^2 + 2n + 1 + n^2 + 3n + 2 \\ &= 6n^2 + 6n + 3 = 6\left(n^2 + n + 1/2\right)\end{aligned}$$

$$\left\langle \hat{V}^2 \right\rangle = \frac{3}{8}\hbar^2\omega^2\left(n^2 + n + \frac{1}{2}\right), \qquad E_n^2 = \hbar^2\omega^2\left(n - \frac{1}{2}\right)^2 = \hbar^2\omega^2\left(n^2 - n + \frac{1}{4}\right)$$

$$-2E_n\left\langle \hat{V} \right\rangle = -2E_n\frac{E_n}{2} = -E_n^2, \qquad \text{recall:} \quad \left\langle n\middle|\hat{V}\middle|n\right\rangle = \frac{E_n}{2}$$

$$\begin{aligned}E_{rel} &= \frac{1}{2mc^2}\left(E_n^2 - 2E_n\frac{E_n}{2} + \frac{3}{8}\hbar^2\omega^2\left(n^2 + n + \frac{1}{2}\right)\right) \\ &= \frac{3\hbar^2\omega^2}{16mc^2}\left(n^2 + n + \frac{1}{2}\right), \qquad \omega^2 = \frac{k}{m}, \qquad E_1 = \frac{\hbar\omega}{2} \\ &= \frac{3E_1^2}{4mc^2}\left(n^2 + n + \frac{1}{2}\right), \qquad E_{tot} = E_1\left[(2n-1) + \frac{3E_1}{4mc^2}\left(n^2 + n + \frac{1}{2}\right)\right], \qquad \frac{E_1}{mc^2} \ll 1\end{aligned}$$

$$E_1 = \frac{\hbar\omega}{2} = \frac{\hbar}{2}\sqrt{\frac{k}{m}} \Rightarrow \frac{\hbar\omega}{2} = \sqrt{\frac{k}{m}} \ll mc^2$$

Then:

$$\tilde{\mathcal{E}}^{(1)}_{rel} = \frac{1}{2mc^2}\left(E_n^2 - 2E_n\left\langle nlm\middle|\frac{-e^2}{4\pi\epsilon_0 r}\middle|nlm\right\rangle + \left\langle nlm\middle|\frac{e^4}{(4\pi\epsilon_0)^2 r^2}\middle|nlm\right\rangle\right)$$

$$E_1 = \frac{-me^4}{2(4\pi\epsilon_0)^2\hbar^2}, \qquad a_0 = \frac{4\pi\epsilon_0\hbar}{m_e e^2}, \qquad \text{(for the Bohr atom)}$$

$$\tilde{\mathcal{E}}^{(1)}_{rel} = \frac{-E_1^2}{2mc^2}\left(\frac{1}{n^4} - \frac{4}{n^2}\left\langle\frac{a_0}{r}\right\rangle + 4\left\langle\frac{a_0^2}{r^2}\right\rangle\right)$$

$$\left\langle nlm\middle|\frac{1}{r}\middle|nlm\right\rangle = \frac{1}{n^2 a_0}$$

$$\left\langle nlm\middle|\frac{1}{r^2}\middle|nlm\right\rangle = \frac{1}{(l+1/2)n^3 a_0^2}$$

$$\boxed{\tilde{\mathcal{E}}^{(1)}_{rel,n} = \frac{-E_n^2}{2mc^2}\left(\frac{4n}{l+1/2} - 3\right)}$$

$$E_1 = \frac{\alpha^2 mc^2}{2} = 13.8\,eV = -Rdy = \frac{-Ha}{2}$$

3.3.1 Spin-Orbit Coupling

$$\boxed{\hat{H}_{SO} = -\vec{\mu}\cdot\vec{B}_{ind}}$$

$$\vec{\mu} = \frac{-e\vec{S}}{m}$$

$$\vec{B}_{ind} = \frac{e\vec{L}}{8\pi\epsilon_0 mc^2 r^3}$$

then:

$$\hat{H}_{SO} = \frac{e^2\,\vec{S}\cdot\vec{L}}{8\pi\epsilon_0 m^2c^2r^3}$$

$$\langle nlm|S^2|nlm\rangle = \hbar^2\,s(s+1) = \frac{3}{4}\hbar^2$$

$$\langle nlm|L^2|nlm\rangle = \hbar^2\,l(l+1)$$

Let $\vec{J} = \vec{L} + \vec{S}$, be the total angular momentum.

$$\langle nlm|J^2|nlm\rangle = \hbar^2\,j(j+1)$$

Note:

$$J^2 = \left(\vec{L}+\vec{S}\right)^2 = L^2 + S^2 + 2\,\vec{L}\cdot\vec{S}$$

$$\Rightarrow \vec{S}\cdot\vec{L} = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$$

$$\begin{aligned}
\left\langle nlm\middle|\hat{H}_{SO}\middle|nlm\right\rangle &= \frac{e^2}{8\pi\epsilon_0 m^2c^2}\left\langle\frac{\vec{S}\cdot\vec{L}}{r^3}\right\rangle \\
&= \frac{e^2}{16\pi\epsilon_0 m^2c^2}\left\langle\frac{J^2 - L^2 - S^2}{r^3}\right\rangle \\
&= \frac{e^2}{16\pi\epsilon_0 m^2c^2}\left(\left\langle J^2\right\rangle - \left\langle L^2\right\rangle - \left\langle S^2\right\rangle\right)\left\langle\frac{1}{r^3}\right\rangle \\
&= \frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\cdot\frac{j(j+1) - s(s+1) - l(l+1)}{l(l+1/2)(l+1)n^3a_0^3}, \qquad \frac{1}{a_0^3} = \left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)^3 \\
&= \underbrace{\frac{1}{4}\left(\frac{e^4}{(4\pi\epsilon_0)^2}\right)^2\cdot\frac{m^2}{\hbar^4}}_{E_1^2}\frac{1}{mc^2}\left(\frac{1}{n^4}\right)\cdot\frac{n[j(j+1) - s(s+1) - l(l+1)]}{l(l+1/2)(l+1)}
\end{aligned}$$

$$\begin{aligned}
E_{SO} &= \frac{E_n^2}{mc^2}\cdot\frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)} \\
&= \frac{\alpha^4 mc^2}{4n^4}\frac{n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)}
\end{aligned}$$

$$\begin{aligned}
E_{fs} &= E_{rel} + E_{SO} \\
&= \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{j+1/2}\right] \\
&= \frac{\alpha^4 mc^2}{8n^4}\left[3 - \frac{4n}{j+1/2}\right]
\end{aligned}$$

$$\begin{aligned}
E_{tot} &= E_n + E_{rel} + E_{SO} \\
&= -\frac{\alpha^2 mc^2}{2n^2}\left[1 + \frac{\alpha^2}{n^2}\left[\frac{n}{j+1/2} - \frac{3}{4}\right]\right]
\end{aligned}$$

$$E_{fs} \sim \frac{\alpha^2}{n^2} \sim \frac{1}{10^6\cdot n^2}$$

$$E_{fs} \sim \frac{1}{n}$$

The fine structure correction to H is quite small, and most important for the ground state.

3.4 Lecture 16

May 30, 2023

$$\tilde{E}_n = \frac{E_n}{2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right], \quad \text{where } \alpha^2 = \left(\frac{1}{137.0}\right)^2 \approx 5.328 \times 10^{-6}$$

$\tilde{E}_1 = -13.605\, eV$
$E_{fs} \sim 0.725\, meV \sim 8.4\, K$
$k_B T \sim 25\, meV$ @ room temperature.

Fine structure corrections are quite small, almost negligible, but definitely measurable @ liquid nitrogen temperatures $\sim 7 - 8\, K$. E_{fs} is of the same order as these thermal fluctuations.

Note: $E_{fs} \approx \frac{E_1 \alpha^2}{n^4}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)$

$$E_{fs,n=1} \approx E_1 \alpha^2 \left(\frac{1}{1/2 + 1/2} - \frac{3}{4}\right) = \frac{E_1 \alpha^2}{4}$$

But for $n > 1$, E_{fs} lifts the degeneracy over angular momentum l, since $j = l + s = l \pm \frac{1}{2}$

$$l \ll n - 1, \qquad j = l \pm 1/2$$

$l = 1, \quad j = 3/2$ or $1/2$

$$\begin{aligned} E_{fs} &= \frac{E_1 \alpha^2}{16}\left(\frac{2}{3/2 + 1/2} - \frac{3}{4}\right) \\ &= \frac{E_1 \alpha^2}{16}\left(\frac{1}{4}\right) \end{aligned}$$

$n = 3, \quad l = 0$

$$\begin{aligned} E_{fs} &= \frac{E_1 \alpha^2}{81}\left(\frac{3}{1/2 + 1/2} - \frac{3}{4}\right) \\ &= \frac{E_1 \alpha^2}{81}\left(\frac{9}{4}\right) = \frac{E_1 \alpha^2}{36} \end{aligned}$$

$l = 1, \quad s = -1/2, \quad j = 1/2$

$$E_{fs} = E_{fs}(n = 3, l = 0)$$

$l = 1, \quad s = 1/2, j = 3/2$

$$E_{fs} = \frac{E_1 \alpha^2}{81}\left(\frac{3}{3/2 + 1/2} - \frac{3}{4}\right) = \frac{E_1 \alpha^2}{108}$$

$l = 2, \quad j = 2 \pm 1/2 = 5/2 \text{ or } 3/2$
For $j = 5/2$

$$E_{fs}(3, j = 5/2) = \frac{E_1\alpha^2}{81}\left(\frac{3}{5/2 + 1/2} - \frac{3}{4}\right)$$
$$= \frac{E_1\alpha^2}{324}$$

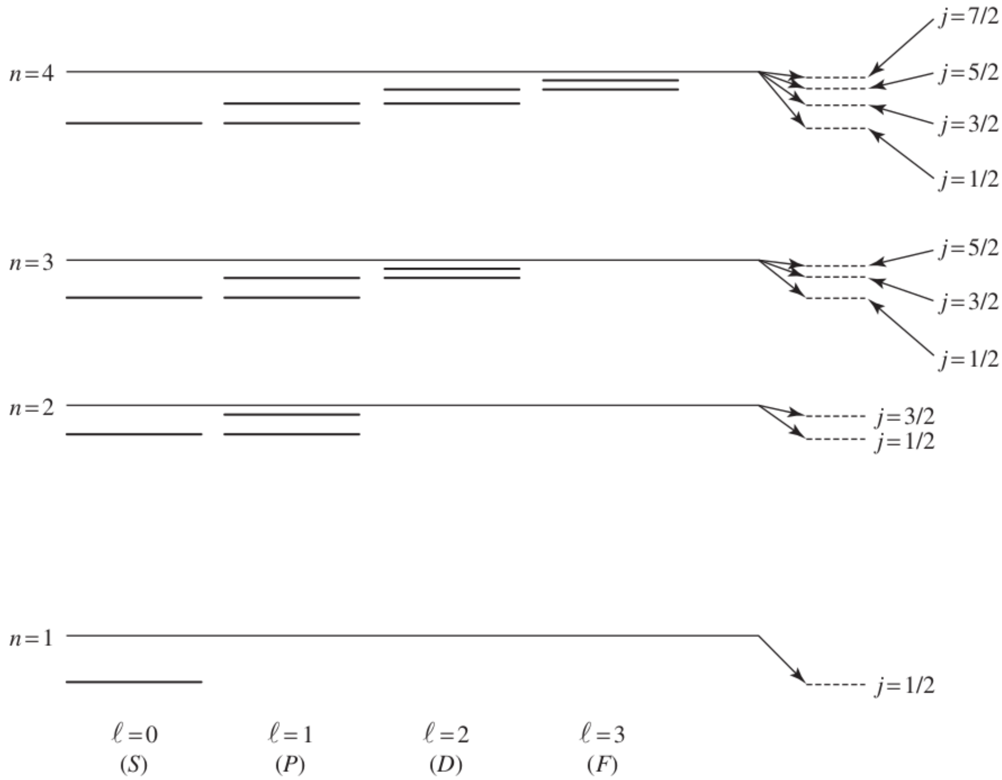

Figure 3.4: Energy levels of hydrogen, including fine structure (*Griffits*)

Note: splitting is over j in the energies. States with the same total angular momentum j are degenerate.

The "good" quantum numbers, i.e. the operators which commute with the states are $n, j, m_j, l, s \Longleftrightarrow \vec{J}, J_z, \vec{L}, \vec{S}$.

$$\Rightarrow |n, j\rangle, \quad m_l, \quad m_s, \quad (L_z, S_z)$$

are no longer "good" quantum numbers/ operators.

$$|n, j\rangle \longrightarrow \sum_{l, m_s, s, m_s} C_{n,j} |lm_l\rangle |sm_s\rangle \qquad \text{(Clebsk-London Coefficients)}$$

3.5 Exact solution via solving the Dirac's Eqn.

$$\tilde{E}_{nj} = mc^2 \left[\left(1 + \left(\frac{\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2}} \right)^2 \right)^{-1/2} + 1 \right]$$

Expand to order $\alpha^4 mc^2$:

$$\text{Let} \qquad f_{nj}(x) = \frac{\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2}}$$

$$\tilde{E}_{nj} = mc^2 \left[\frac{1}{\sqrt{1 - f_{nj}^2(\alpha)}} - 1 \right]$$

$$\frac{1}{\sqrt{1-x}} = 1 - \frac{x}{2} + \frac{3}{8}x^2$$

$$\begin{aligned}
\tilde{E}_{nj} &= mc^2 \left[1 - \frac{f_{nj}^2(\alpha)}{2} + \frac{3}{8} f_{nj}^4(\alpha) - 1 \right] \\
&= \frac{-mc^2}{2} \frac{\alpha^2}{(n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2})^2} + \frac{3}{8} \frac{mc^2 \alpha^4}{(n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2})^4} \\
&= \frac{-mc^2 \alpha^2}{2} \left[\frac{1}{n^2} + \frac{\alpha^4}{2n^2 (j+1/2)^4} \right]
\end{aligned}$$

$$\frac{\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2}} = \frac{\alpha}{(j+1/2) \left(\frac{n}{j+1/2} - 1 + \sqrt{1 - \frac{\alpha^2}{(j+1/2)^2}} \right)}$$

$$\sqrt{1-x} \approx 1 + \frac{x}{2} - \frac{x^2}{8} + \mathcal{O}(x^3)$$

$$\sqrt{1 - \frac{\alpha^2}{(j+1/2)^2}} \approx 1 - \frac{\alpha^2}{2(j+1/2)^2} - \frac{\alpha^4}{8(j+1/2)^4}$$

$$\frac{\alpha}{n - (j+1/2) + \sqrt{(j+1/2)^2 - \alpha^2}} = \frac{\alpha}{(j+1/2) \left(\frac{n}{j+1/2} - 1 + \sqrt{1 - \frac{\alpha^2}{(j+1/2)^2}} \right)}$$

Well, there were some messy steps, I will return later. But here is the answer:

$$\boxed{\tilde{E}_{nj} = \frac{-mc^2 \alpha^2}{2n^2} \left[1 + \frac{\alpha^2}{n^2} \left[\frac{n}{j+1/2} - \frac{3}{4} \right] + \mathcal{O}(\alpha^6) \right]}$$

Chapter 4

Zeeman Effect

4.1 Lecture 17

May 31, 2023

Consider the effect of an external magnetic field $\vec{B}_{ext}$ an the H atom. This is the so called Zeeman Effect.

$$\hat{H}_{Zeeman} = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}_{ext}$$

where:

- (-): more stable when dipoles are aligned.
- $\vec{\mu}_l$: magnetic dipole of the orbital angular momentum l.
- $\vec{\mu}_s$: magnetic dipole due to the electrons spin.

$$\vec{\mu}_s = \frac{-e\vec{S}}{m} \qquad \left(\text{Same as for the spin orbit coupling.}\right)$$

$$\vec{\mu}_l = \frac{q}{2m}\vec{L} = \frac{-e}{2m}\vec{L}$$

$$\hat{H}_{Zeeman} = \frac{-e}{2m}\left(\vec{L} + 2\vec{S}\right) \cdot \vec{B}_{ext}$$

Recall:

$$\hat{H}_{SO} = \frac{e^2}{8\pi\epsilon_0} \cdot \frac{1}{m^2c^2} \cdot \frac{\vec{S} \cdot \vec{S}}{r^3}$$

in atomic units:

$$\left\langle \hat{H}_{SO} \right\rangle = \frac{1}{2c^2}\langle \vec{S} \cdot \vec{L} \rangle \left\langle \frac{a_0^3}{r^3} \right\rangle \sim \frac{1}{2c^2}\left(\frac{1}{2n^3}\right) \frac{j(j+1) - l(l+1) - 3/4}{l(l+1/2)(l+1)}$$

$$\hat{H}_{Zeeman} = \frac{\left|\vec{B}_{ext}\right|}{2}\left(\vec{L}+2\vec{S}\right)\cdot\hat{k}$$
$$= \frac{-e}{2m}\left(L_z+2S_z\right)B_{ext}$$
$$\left\langle\hat{H}_{Zeeman}\right\rangle = \frac{-Bext}{2}\left(m_l+2m_s\right)$$

$$\frac{-\cancel{e}B_{ext}}{2\cancel{m}}\left(m_l+2m_s\right)\hbar \sim \frac{e^{\cancel{2}}}{8\pi\epsilon_0}\frac{1}{m^{\cancel{2}}c^2}\left(\frac{\hbar^{\cancel{2}}}{\cancel{2}n^3}\right)\frac{j(j+1)-l(l+1)-3/4}{l(l+1/2)(l+1)}$$

$$B_{ext} \sim \frac{-e}{8\pi\epsilon_0}\frac{\hbar}{mc^2}\frac{1}{n^3}\frac{1}{(m_l+2m_s)}\frac{j(j+1)-l(l+1)-3/4}{l(l+1/2)(l+1)}$$

$$\boxed{\vec{B}_{ext} \sim 12.5\ T}$$

for $\left\langle\hat{H}_{Zeeman}\right\rangle \sim \left\langle\hat{H}_{SO}\right\rangle$

$$B[a.u] = 235051.806\ T$$
$$\frac{1}{c^2}[a.u] = 5.328\times10^{-5}\,[a.u] = 12.5\ T$$

Since the strongest electromagnetics operating at liquid nitrogen temperature provide field strengths on the order of 13 T, we will mostly work/ see the weak Zeeman effect limit experimentally.

4.1.1 Weak Zeeman effect $(B_{ext} \ll B_{ind})$ or $(B_{ext} \ll 12.5\ T)$

$$\left\langle\hat{H}_{Zeeman}\right\rangle = \frac{-eB_{ext}}{2m}\left\langle L_z 2S_z\right\rangle, \quad \text{where} \quad \vec{B}_{ext} = B_{ext}\hat{K}$$

if m_l & m_s are "good" quantum numbers, i.e. the basis functions for the unperturbed Hamiltonian commute with L_z and S_z, then

$$\left\langle m_l m_s\middle|\hat{H}_{Zeeman}\middle|m_l m_s\right\rangle = \frac{-eB_{ext}}{2m}\hbar\left(m_l+2m_s\right)$$

However, m_l and m_s do not commute with the eigenstates of $\hat{H}_{SO}$ which are $\left|n,l,j,m_j\right\rangle$

$$\vec{L}+2\vec{S} = \vec{J}+\vec{S}$$

and total angular momentum $\vec{J}$ has $\left|n,l,j,m_j\right\rangle$ as eigenstates.

$$\left\langle n,l,j,m_j\middle|H_{Zeeman}\middle|n,l,j,m_j\right\rangle = \frac{-eB_{ext}\hbar}{2m}\left\langle(\vec{J}+\vec{S})\cdot\hat{k}\right\rangle$$

$$\left\langle\vec{S}\right\rangle_{avg} \approx \left\langle\frac{\vec{J}\cdot\vec{S}}{\vec{J}}\right\rangle \approx \left\langle\frac{J^2-L^2+S^2}{2\vec{J}}\right\rangle$$

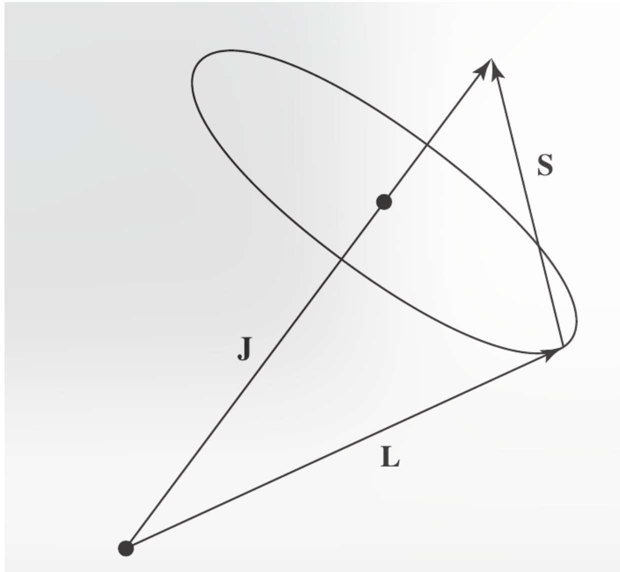

Figure 4.1: In the presence of spin-orbit coupling, $\vec{L}$ and $\vec{S}$ are separately conserved; they precess about the fixed total angular momentum $\vec{J}$

.

since j and m_j are "good" quantum numbers for a given eigenstate of the system under $\hat{H}_{\text{Bohr}} + \hat{H}_{\text{rel}} + \hat{H}_{\text{SO}}$, then the total momentum $\left|\vec{J}\right|$ and its direction, so $\vec{J}$ is fixed, and since l is also a "good" quantum number, $\left|\vec{L}\right|$ is fixed, but as m_l is not a "good" quantum number, its direction can precess. Similarly, s is a "good" quantum number as $\left|\vec{S}\right| = 1/2$, but its direction is indeterminate as m_s is NOT a good quantum number.

For a given state $\left|n\,l\,j\,m_j\,s\right\rangle$, the magnitude and direction of $\left|\vec{J}\right|$ is fixed, whereas $\left|\vec{L}\right|$ and $\left|\vec{S}\right|$ are fixed, but their directions can vary. However on average

$$\left\langle\vec{S}\right\rangle_{\text{avg}}^2 = \frac{\left\langle\vec{S}\cdot\vec{J}\right\rangle}{\left\langle\vec{J}\right\rangle}$$

In other words, after averaging $\vec{S}$ over a given cycle around $\vec{J}$, the components of $\vec{S}$ perpendicular to $\vec{J}$ cancel, and only the components of $\vec{S}$ parallel to $\vec{J}$, i.e. $\frac{\vec{S}\cdot\vec{J}}{\left|\vec{J}\right|}$, remain.

Similarly

$$\begin{aligned}
\vec{L} &= \vec{J} - \vec{S} \\
L^2 &= \left(\vec{J} - \vec{S}\right)^2 = J^2 - 2\vec{J}\cdot\vec{S} + \vec{S} \\
\Rightarrow \vec{J}\cdot\vec{S} &= \frac{J^2 - L^2 + S^2}{2}
\end{aligned}$$

Time averaged $\vec{S}$

$$\left\langle \vec{S} \right\rangle_{avg} \approx \left\langle \frac{\vec{S}\cdot\vec{J}}{J^2}\vec{J} \right\rangle$$
$$= \left\langle \frac{J^2 - L^2 + S^2}{2J^2}\vec{J} \right\rangle$$

$$\begin{aligned}
\left\langle n,l,s,j,m_j \middle| \hat{H}_{\text{Zeeman}} \middle| n,l,s,j,m_j \right\rangle &\cong \frac{e\,B_{ext}}{2m}\left\langle n,l,s,j,m_j \middle| \left(\vec{J} + \frac{J^2 - L^2 + S^2}{2J^2}\vec{J}\right)\cdot\hat{k} \middle| n,l,s,j,m_j \right\rangle \\
&\approx \frac{e\,B_{ext}}{2m}\left\langle n,l,s,j,m_j \middle| J_z + \frac{J^2 - L^2 + S^2}{2J^2}J_z \middle| n,l,s,j,m_j \right\rangle \\
&= \frac{e\,B_{ext}}{2m}\left\langle J_z \right\rangle \left(1 + \frac{\left\langle J^2\right\rangle - \left\langle L^2\right\rangle + \left\langle S^2\right\rangle}{2\left\langle J^2\right\rangle}\right) \\
&= \frac{e\,B_{ext}}{2m}\hbar m_j \left(1 + \hbar^2\frac{j(j+1) - l(l+1) + 3/4}{2\hbar^2(j(j+1))}\right) \\
&= \underbrace{\frac{e\,\hbar}{2m}}_{\mu_B} B_{ext} m_j \underbrace{\left(1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}\right)}_{g_J}
\end{aligned}$$

$$\begin{aligned}
\left\langle J_z \right\rangle &= \hbar m_j \\
\left\langle J^2 \right\rangle &= \hbar^2 j(j+1) \\
\left\langle L^2 \right\rangle &= \hbar^2 l(l+1) \\
\left\langle S^2 \right\rangle &= \hbar^2 3/4
\end{aligned}$$

$$\boxed{\mu_B = \frac{e\hbar}{2m} \quad \text{The Bohr Magnetron}}$$

$$\boxed{g_J = 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)} \quad \text{The Landé g-factor (for an e)}}$$

$$\Rightarrow \left\langle \hat{H}_{Zeeman} \right\rangle = \mu_B g_J\, B_{ext} m_j \approx \tilde{E}^{(1)}_{Zeeman}$$

$$\begin{aligned}
\mu_B &\approx 5.788 \times 10^{-5}\, eV/T \\
&= \frac{1}{2} \quad \text{in atomic units}
\end{aligned}$$

for $B_{ext} \sim 10T \to \mu_B\, B_{ext} \sim 0.5788\, MeV$

$$B_{ext} \ll 12.5\, T \quad \text{in the Weak Zeeman Regime}$$

4.2 Lecture 18

June 05, 2023

$$\hat{H}_{Zeeman} = -\vec{\mu}_{tot} \cdot \vec{B}_{ind} = \frac{e\,B_{ind}}{2m\hbar}(\vec{L} + 2\vec{S}) \cdot atk$$

Weak Zeeman Regime

$$B_{ind} \ll B_{SO} \sim 12.7T$$

$$\langle n, l, s, j, m_j | \hat{H}_{Zeeman} | n, l, s, j, m_j \rangle$$

are eigenstates of $\hat{H}_{Bohr}, \hat{H}_{rel}, \hat{H}_{SO}$.

$$E^{(1)}_{Zeeman} \approx \frac{e\hbar}{2m}\left(1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)}\right) B_{ind}\, m_j = \mu_B\, g_L B_{ind}\, m_j$$

4.2.1 Strong Zeeman Regime

$B_{ind} \gg B_{SO} \sim 12.5T$

In this case we will work in the prefered basis of the Zeeman hamiltonian, using the eigenstates of the Zeeman Hamiltonian $\hat{H}$.

$$\langle H_{Zeeman} \rangle = \frac{e\,B_{ind}}{2m}\left\langle L_z + 2S_z \right\rangle = \frac{e\,B_{ind}}{2m}\left(\hbar\, m_l + \hbar\, m_s\right)$$

so $|n, l, s, m_l, m_j\rangle$ are eigenstates of $\hat{H}_{Zeeman}, \hat{H}_{Bohr}, \hat{H}_{rel}$ but not $\hat{H}_{SO}$.

$$\begin{aligned} E_{Zeeman} &= \mu_B\, B_{ind}(m_l + 2m_s) \\ E^{(1)}_{rel} &= \frac{-E_1^2}{2mc^2}\frac{1}{n^4}\left[\frac{4n}{l+1/2} - 3\right] \\ \hat{H}_{SO} &= \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2}\frac{\vec{S}\cdot\vec{L}}{r^3} \end{aligned}$$

This is the same for both basis $|n, l, s, j, m_j\rangle$ and $|n, l, s, m_l, m_s\rangle$

$$\vec{S}\cdot\vec{L} = S_xL_x + S_yL_y + S_zL_z$$

Idea: Evaluate the expectation value of $\langle \hat{H}_{SO} \rangle$ using $|n, l, s, m_l, m_s\rangle$ as eigenstates. This permits the use of nondegenerate perturbation theory.

$$\begin{aligned} E^{(1)}_{SO} &= \langle n, l, s, m_l, m_s | \hat{H}_{SO} | n, l, s, m_l, m_s \rangle = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\left\langle n, l, s, m_l, m_s \left| \frac{\vec{L}\cdot\vec{S}}{r^3} \right| n, l, s, m_l, m_s \right\rangle \\ &= \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\left\langle n, l, s, m_l, m_s \left| \frac{1}{r^3} \right| n, l, s, m_l, m_s \right\rangle \left(\langle L_x\rangle\langle S_x\rangle + \langle L_y\rangle\langle S_y\rangle + \langle L_z\rangle\langle L_z\rangle\right) \end{aligned}$$

$$\langle n, \ell, s, m_j, m_s | L_{x,y} | n, \ell, s, m_\ell, m_s \rangle = 0, \qquad \langle n, \ell, s, m_j, m_s | L_z | n, \ell, s, m_\ell, m_s \rangle = \hbar m_\ell$$

$$\langle n,\ell,s,m_j,m_s\big|S_{x,y}\big|n,\ell,s,m_\ell,m_s\rangle = 0, \qquad \langle n,\ell,s,m_j,m_s\big|S_z\big|n,\ell,s,m_\ell,m_s\rangle = \hbar m_s$$

$$\begin{aligned}
&= \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2}\frac{(\hbar\, m_\ell)(\hbar\, m_s)}{\ell(\ell+1/2)(\ell+1)n^3a_0^3} \\
&= \frac{e^2}{8\pi\epsilon_0}\frac{\hbar^2\, m_\ell\, m_s}{m^2c^2n^3\,\ell(\ell+1/2)}\frac{1}{(\ell+1)a_0^3}
\end{aligned}$$

$$\left(\frac{1}{a_0^3}\right) = \left(\frac{m\,e^2}{4\pi\,\epsilon_0\hbar^2}\right)^3, \quad E_1 = \frac{-m\,e^4}{2(4\pi\epsilon_0)^2\hbar^2}$$

$$\begin{aligned}
&= \frac{e^2\,\hbar^2}{8\pi\epsilon_0\,m^2\,c^2}\left(\frac{m\,e^2}{4\pi\,\epsilon_0\hbar^2}\right)^3\frac{m_\ell\,m_s}{n^3\,\ell(\ell+1/2)(\ell+1)} \\
&= \frac{1}{2}\left(\frac{e^4}{(4\pi\epsilon_0)^2}\right)^2\frac{m^2}{\hbar^4 m\,c^2}\frac{n}{n^4}\frac{m_\ell\,m_s}{\ell(\ell+1/2)(\ell+1)} \\
&= \left[\frac{1}{2}\frac{e^4\,m}{(4\pi\epsilon_0)^2\hbar^2}\right]^2\frac{2}{m\,c^2}\frac{n}{n^4}\frac{m_\ell\,m_s}{\ell(\ell+1/2)(\ell+1)} \\
&= \frac{2E_n^2}{m\,c^2}\frac{n\,m_\ell\,m_s}{\ell(\ell+1/2)(\ell+1)} = E_{SO}^{(1)}
\end{aligned}$$

$$\begin{aligned}
E_{fs}^{(1)} = E_{SO}^{(1)} + E_{rel}^{(1)} &= \frac{E_n^2}{m\,c^2}\left[\frac{2\,n\,m_\ell\,m_s}{\ell(\ell+1/2)(\ell+1)} + \frac{3}{2} - \frac{2\,n}{\ell+1/2}\right] \\
&= \frac{E_n^2}{m\,c^2}\left[\frac{3}{2} - \frac{2\,n[\ell(\ell+1)-m_\ell\,m_s]}{\ell(\ell+1/2)(\ell+1)}\right] \\
&= \frac{2\,E_1^2}{m\,c^2\,n^2}\left[\frac{3}{4\,n} - \frac{\ell(\ell+1)-m_\ell\,m_s}{\ell(\ell+1/2)(\ell+1)}\right] \\
&= \frac{-2\,E_1}{m\,c^2}\left(\frac{-\alpha^2\,m\,c^2}{2}\right)\frac{1}{n^3}\left[\frac{3}{4\,n} - \frac{\ell(\ell+1)-m_\ell\,m_s}{\ell(\ell+1/2)(\ell+1)}\right] \\
&= \frac{E_1\,\alpha^2}{n^3}\left[\frac{3}{4\,n} - \frac{\ell(\ell+1)-m_\ell\,m_s}{\ell(\ell+1/2)(\ell+1)}\right] \\
E_{\mathrm{S\,Z}} &= \frac{E_1}{n^2}\,[1]
\end{aligned}$$

4.3 Lecture 19

June 06, 2023

4.4 Lecture 20

June 07, 2023

Chapter 5

Hyperfine Splitting

5.1 Lecture 21

June 12, 2023

Assigment 1: (Due to June 19th)
Further problems Chapter 6 (Griffiths "Introduction to Quantum Mechanics" vol.1) Problems: 6.27 , 6.28, 6.30, 6.33 (Before the exam)

Midterm exam: 7-10 am June 19th

5.2 Zeeman Effect (Intermediate)

Chapter 6

Variational Principle

6.1 Lecture 22

June 13, 2023

Perturbation theory: Have a known exact solution to an unperturbed hamiltonian and add a minor perturbation:

$$\left|\langle n'|V|n\rangle\right| \ll \mathcal{E}_n - \mathcal{E}_{n'}$$

- Approximating the "effect" of the exact hamiltonian for the perturbed system

$$\begin{array}{c}\text{perturbed}\\\text{hamiltonian}\end{array} \longrightarrow \tilde{H} \sim \tilde{H}_0 \longleftarrow \begin{array}{c}\text{unperturbed}\\\text{hamiltonian}\end{array}$$

Variational Principle: Choose a trial wavefunction $\tilde{\Psi}$ and solve for the exact ground state energy if we were in the trial state $\tilde{\Psi}$. By "varying" the trial wavefunction we obtain a lowest upper bound on the ground state energy.

- Approximating the ground state wavefunction

$$\begin{array}{l}\text{exact wavefunc-}\\\text{tion in the ground}\\\text{state}\end{array} \longrightarrow \Psi_{gs} \sim \tilde{\Psi} \longleftarrow \text{trial wavefunction}$$

6.1.1 Theorem (Variational Principle)

For a hamiltonian $\hat{H}$ with ground state energy E_{gs}, and any normalised trial wavefunction $\tilde{\Psi}$, with $\langle\tilde{\Psi}|\tilde{\Psi}\rangle = 1$

$$\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle \geq E_{gs}$$

Proof:
Let $\{\Psi_n\}$ and $\{\mathcal{E}_n\}$ be the normalised eigenstates and eigenenergies of H, i.e.

$$\hat{H}|\Psi\rangle = \mathcal{E}_n|\Psi\rangle, \quad \text{and} \quad \langle\Psi_n|\Psi_{n'}\rangle = \delta_{nn'}$$

then $\{\Psi_n\}$ form a complete basis which spans the Hilbert space of $\hat{H}$, and

$$\mathbb{1} = \sum_n \big|\Psi_n\big\rangle\big\langle\Psi_n\big|$$

$$\begin{aligned}
\big\langle\tilde{\Psi}\big|\hat{H}\big|\tilde{\Psi}\big\rangle &= \left\langle\tilde{\Psi}\right| \left(\sum_n \big|\Psi_n\big\rangle\big\langle\Psi_n\big|\right) \hat{H} \left(\sum_{n'} \big|\Psi_{n'}\big\rangle\big\langle\Psi_{n'}\big|\right) \left|\tilde{\Psi}\right\rangle \\
&= \sum_n \big\langle\tilde{\Psi}\big|\Psi_n\big\rangle\big\langle\Psi_n\big| \sum_{n'} \underbrace{\hat{H}\big|\Psi_{n'}\big\rangle}_{\mathcal{E}_{n'}\left|\Psi_{n'}\right\rangle} \big\langle\Psi_{n'}\big|\tilde{\Psi}\big\rangle \\
&= \sum_{nn'} \big\langle\tilde{\Psi}\big|\Psi_n\big\rangle \underbrace{\big\langle\Psi_n\big|\mathcal{E}_{n'}\big|\Psi_{n'}\big\rangle}_{\mathcal{E}_{n'}\delta_{nn'}} \big\langle\Psi_{n'}\big|\tilde{\Psi}\big\rangle \\
&= \sum_{nn'} \big\langle\tilde{\Psi}\big|\Psi_n\big\rangle\big\langle\Psi_{n'}\big|\tilde{\Psi}\big\rangle \mathcal{E}_{n'}\delta_{nn'} \\
&= \sum_n \underbrace{\left|\big\langle\tilde{\Psi}\big|\Psi_n\big\rangle\right|^2}_{\hat{C}_n\hat{C}_n^*} \mathcal{E}_n = \sum_n \left|\tilde{C}_n\right|^2 \mathcal{E}_n
\end{aligned}$$

where $\tilde{C}_n$ are the coefficients of $\tilde{\Psi}$ in the $\{\Psi_n\}$ basis.

Since $\mathcal{E}_n \geq E_{gs} \quad \forall n$, i.e. $E_{gs} = \mathcal{E}_1$

$$\begin{aligned}
&\geq \sum_n \left|\tilde{C}_n\right|^2 \mathcal{E}_1 \\
&= \mathcal{E}_1 \sum_n \left|\tilde{C}_n\right|^2 \\
&= E_{gs} \left(\cancelto{1}{\sum_n \left|\tilde{C}_n\right|^2}\right)
\end{aligned}$$

By the Normalisation condition on $\tilde{\Psi}$

$$\sum_n \left|\big\langle\tilde{\Psi}\big|\Psi_n\big\rangle\right|^2 = \sum_n \left|\tilde{C}_n\right|^2 = 1$$

$$\big\langle\tilde{\Psi}\big|\hat{H}\big|\tilde{\Psi}\big\rangle \geq E_{gs} = \mathcal{E}_1$$

6.1.2 Procedure

1. Normalise our trial wavefunction $\tilde{\Psi}(b_1, \cdots, b_n) \rightarrow$ parameters
2. Calculate $\big\langle\tilde{\Psi}\big|\hat{T}\big|\tilde{\Psi}\big\rangle = \big\langle\hat{T}(b_1, \cdots, b_n)\big\rangle$
3. Calculate $\big\langle\tilde{\Psi}\big|\hat{V}\big|\tilde{\Psi}\big\rangle = \big\langle\hat{V}(b_1, \cdots, b_n)\big\rangle$

4. $\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \langle \hat{T}(b_1, \cdots, b_n) \rangle + \langle \hat{V}(b_1, \cdots, b_n) \rangle = \tilde{\mathcal{E}}_{gs}(b_1, \cdots, b_n) \geq E_{gs}$.

5. Minimise $\tilde{\mathcal{E}}_{gs}(b_1, \cdots, b_n)$ w.r.t. the parameters $\{b_1, \cdots, b_n\}$ to obtain the best estimate for E_{gs} and hence:
Set Ψ_{gs} e.g. set:

$$\frac{\partial \tilde{\mathcal{E}}_{gs}}{\partial b} = 0, \quad \text{to find b that minimises} \quad \mathcal{E}_{gs} \quad \left(\frac{\partial^2 \tilde{\mathcal{E}}_{gs}}{\partial b^2} > 0 \right)$$

Note: Steps (1) and (2) only need to be applied once for trial wavefunction, i.e. you may have "pre-prepared" trial wavefunctions that are normalised and have a known $\langle \hat{T}(b_1, \cdots, b_n) \rangle$. E.g. The gaussian wavefunction has an analytic $\langle \hat{T} \rangle$.

6.1.3 Example: 1D Harmonic Oscillator

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2m} \frac{d^2}{dx^2}}_{\hat{T}(x)} + \underbrace{\frac{1}{2} m\omega^2 x^2}_{V(x)}$$

Trial wavefunction:

$$\tilde{\Psi}(x) = A\, e^{-bx^2} \quad \text{(Gaussian)}$$

- A: normalisation constant
- b: parameter

Step 1: normalisation

$$1 = \langle \tilde{\Psi} | \tilde{\Psi} \rangle = A^2 \int_{-\infty}^{+\infty} e^{-2bx^2} dx$$

use:

$$\int_0^{+\infty} e^{-ax^2} = \frac{1}{2} \sqrt{\frac{\pi}{a}} \tag{6.1.1}$$

then,

$$1 = A^2 \sqrt{\frac{\pi}{2b}}$$

$$\boxed{A = \left(\frac{2b}{\pi} \right)^{1/4}}$$

Step 2 and 3: get $\langle \hat{T} \rangle$ and $\langle \hat{V} \rangle$
First we need the 1st and 2nd derivatives:

$$\begin{aligned} \frac{d\tilde{\Psi}}{dx} &= A \left(-2bx\, e^{-bx^2} \right) \\ \frac{d^2\tilde{\Psi}}{dx^2} &= A \left(4b^2x^2 - 2b \right) e^{-bx^2} \\ &= A(2b)(2bx^2 - 1) e^{-bx^2} \\ &= (4b^2x^2 - 2b) \tilde{\Psi}(x) \end{aligned}$$

then,

$$
\begin{aligned}
\langle\tilde{\Psi}|\hat{T}|\tilde{\Psi}\rangle &= \frac{-\hbar^2}{2m}A^2\int_{-\infty}^{+\infty} e^{-2bx^2}(4b^2x^2-2b)dx \\
&= \frac{-\hbar^2}{2m}\sqrt{\frac{2b}{\pi}}\left[4b^2\frac{\sqrt{\pi}}{2}\frac{1}{(2b)^{3/2}} - 2b\sqrt{\frac{\pi}{2b}}\right] \\
&= \frac{\hbar^2 b}{2m}
\end{aligned}
$$

for this integral we've used:

$$
\begin{aligned}
\int_0^\infty e^{-ax^2}x^m dx &= \frac{\Gamma\left(\frac{m+1}{2}\right)}{2a^{\frac{m+1}{2}}} \\
&= \frac{\sqrt{\pi}}{a^{\frac{m+1}{2}}}\frac{(m-1)\cdot(m-3)\cdots(1)}{m/2} \qquad (6.1.2)\\
\int_{-\infty}^{+\infty} e^{-ax^2}x^2 dx &= \frac{\sqrt{\pi}}{2a^{\frac{m+1}{2}}}
\end{aligned}
$$

$$
\begin{aligned}
\langle\tilde{\Psi}|\hat{V}|\tilde{\Psi}\rangle &= A^2\int_{-\infty}^{+\infty} e^{-2bx^2}\left(\frac{1}{2}m\omega^2x^2\right)dx \\
&= \sqrt{\frac{2b}{\pi}}\left(\frac{m\omega^2}{2}\right)\frac{\sqrt{\pi}}{2}\left(\frac{1}{(2b)^{3/2}}\right) \\
&= \frac{m\omega^2}{8b}
\end{aligned}
$$

Step 4: find $\langle\hat{H}\rangle = \langle\hat{T}\rangle + \langle\hat{V}\rangle$

$$
\frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b} = \tilde{\mathcal{E}}_{gs}(b)
$$

b is the parameter estimate of the ground state energy.

Step 6: minimise $\tilde{\mathcal{E}}_{gs}$

$$
\begin{aligned}
\frac{\partial\tilde{\mathcal{E}}_{gs}(b)}{\partial b} &= \frac{\partial}{\partial b}\frac{\hbar^2 b}{2m} + \frac{\partial}{\partial b}\frac{m\omega^2}{8b} \\
&= \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \\
b^2 &= \frac{m\omega^2}{8}\left(\frac{2m}{\hbar^2}\right) = \frac{m^2\omega^2}{4\hbar^2} \\
b_{min} &= \frac{m\omega}{2\hbar}
\end{aligned}
$$

Now, we can compute $\tilde{\mathcal{E}}_{gs}(b_{min})$:

$$
\begin{aligned}
\tilde{\mathcal{E}}_{gs}(b_{min}) &= \frac{\hbar^2}{2m}\left(\frac{m\omega}{2\hbar}\right) + \frac{m\omega^2}{8}\left(\frac{2\hbar}{m\omega}\right) \\
&= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} \\
&= \frac{\hbar\omega}{2} = E_{gs}
\end{aligned}
$$

$$\Rightarrow \boxed{\tilde{\Psi} = \Psi_{gs} = \left(\frac{2b}{\pi}\right)^{1/4} \cdot e^{-\frac{m\omega}{2\hbar}x^2}}$$

6.1.4 Example: δ-function potential

$$\hat{V}(x) = -\alpha\delta(x)$$
$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)$$

Trial wavefunction:

$$\tilde{\Psi}(x) = Ae^{-bx^2}$$

Recall:

$$A = \left(\frac{2b}{\pi}\right)^{1/4}, \qquad \langle\hat{T}\rangle = \frac{\hbar^2 b}{2m}$$

So we already have step (1), and (2)

Step 3:

$$\begin{aligned}\langle\hat{V}\rangle &= A^2\int_{-\infty}^{+\infty} e^{-2bx^2}(-\alpha\delta(x))dx \\ &= -\alpha\sqrt{\frac{2b}{\pi}}\cancelto{1}{e^{-2b(0)^2}} \\ &= -\alpha\sqrt{\frac{2b}{\pi}}\end{aligned}$$

Step 4:

$$\langle\hat{H}\rangle = \langle\hat{T}\rangle + \langle\hat{V}\rangle = \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}} = \tilde{\mathcal{E}}_{gs}(b)$$

Step 5:

$$\begin{aligned}\frac{\partial\tilde{\mathcal{E}}_{gs}(b)}{\partial b} &= \frac{\hbar^2}{2m} - \frac{\alpha}{2}\sqrt{\frac{2}{\pi b}} = 0 \\ \Rightarrow \sqrt{b} &= \frac{\alpha\sqrt{2}}{2\sqrt{\pi}}\frac{2m}{\hbar^2} \\ \Rightarrow b_{min} &= \frac{2\alpha^2 m^2}{\pi\hbar^4}\end{aligned}$$

$$\begin{aligned}\tilde{\mathcal{E}}_{gs}\left(\frac{2\alpha^2m^2}{\pi\hbar^4}\right) &= \frac{\hbar^2}{2m}\left(\frac{2\alpha^2m^2}{\pi\hbar^4}\right) - \alpha\sqrt{\frac{2}{\pi}}\left(\frac{2\alpha^2m^2}{\pi\hbar^4}\right)^{1/2} \\ &= \frac{\alpha^2 m}{\pi\hbar^2} - \alpha\sqrt{\frac{2}{\pi}}\sqrt{\frac{2}{\pi}}\frac{\alpha m}{\hbar^2} \\ &= \frac{\alpha^2 m}{\pi\hbar^2}(1-2) = \frac{-\alpha^2 m}{\pi\hbar^2}\end{aligned}$$

$$E_{gs} = \frac{-\alpha^2 m}{2\hbar^2} < \frac{-\alpha^2 m}{\pi\hbar^2} = \tilde{\mathcal{E}}_{gs}$$
$$\frac{-1}{2} < \frac{-1}{\pi} \sim 30\% \text{ error}$$

For the 1D SHO, the potential *Localises* the wavefunction around $x = 0$, whereas for the δ-function potential, the localisation of the state around $x = 0$ is generally weak (it only acts @ $x = 0$).

A gaussian give a poor description of the quasi-free electron under a δ-function potential.

A free-electron (plane-wave) description might yield better results.

6.2 Lecture 23

June 14, 2023

Choose a trial wavefunction $\tilde{\Psi}$ and minimise $\langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle = \tilde{\mathcal{E}}_{gs} \geq E_{gs}$ where $\langle\tilde{\Psi}|\tilde{\Psi}\rangle = 1$, but $\tilde{\Psi}$ should be a piecewise continuous, but may have discontinuities or be continuous with discontinuities in the derivatives.

6.2.1 Example: 1D Square Well

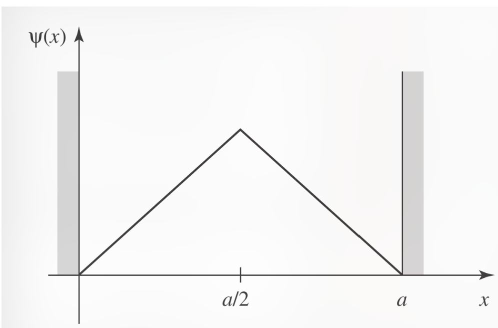

Figure 6.1: Triagular wave function

$$V_\infty = \begin{cases} 0, & 0 \leq x \leq L \\ \infty, & \text{otherwise} \end{cases}$$

$$\tilde{\Psi}(x) = \begin{cases} Ax, & 0 \leq x \leq L/2 \\ A(L-x), & L/2 \leq x \leq L \\ 0, & \text{otherwise} \end{cases}$$

Then, the hamiltonian will be

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V_\infty$$

As before, we need to follow the given steps to accomplish the exercise.

Step 1:

$$\begin{aligned}
1 =& \langle\tilde{\Psi}|\tilde{\Psi}\rangle = \int_0^L \left|\tilde{\Psi}(x)\right|^2 dx \\
&= A^2 \int_0^{L/2} x^2 dx + A^2 \int_{L/2}^{L} (L-x)^2 dx \\
&= A^2 \left[\frac{x^3}{3}\bigg|_0^{L/2} + \frac{(L-x)^3}{3}(-1)\bigg|_{L/2}^{L} \right] \\
&= A^2 \left[\frac{L^3}{24} + \frac{L^3}{24} \right] = A^2 \frac{L^3}{12} = 1
\end{aligned}$$

$$\boxed{A = \sqrt{\frac{12}{L^3}}}$$

Step 2:

$$\frac{d\tilde{\Psi}}{dx} \Longrightarrow$$ We can express $\tilde{\Psi}$ in terms of Heaviside step functions.

$$\Theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \\ 1/2, & x = 0 \end{cases}$$

Then

$$\tilde{\Psi}(x) = \underbrace{Ax\Theta(x)}_{0 \le x \le L/2} + \underbrace{(L-2x)\Theta(x-L/2)}_{L/2 \le x \le L} - \underbrace{(L-x)\Theta(x-L)}_{x \ge L}$$

Note: $\frac{d}{dx}\Theta(x) = \delta(x)$

$$\begin{aligned} \frac{d}{dx}\tilde{\Psi} &= A\left[\frac{d}{dx}(x\,\Theta(x)) + \frac{d}{dx}((L-2x)\,\Theta(x-L/2)) + \frac{d}{dx}((x-L)\Theta(x-L))\right] \\ &= A\left[\Theta(x) + x\,\delta(x) - 2\,\Theta(x-L/2) + (L-2x)\right] \end{aligned}$$

6.3 Lecture 24: Midterm Exam

June 19, 2023

6.4 Lecture 25

June 20, 2023

Chapter 7

Time Dependent Perturbation Theory

7.1 Lecture 25

July 17, 2023

7.1.1 Time Dependent Quantum Mechanics

Time dependent Schrodinger Eq'n

$$\hat{H}\Psi(\vec{r},t) = i\,\hbar\frac{\partial\Psi}{\partial t}$$

Let E be the eigenvalue of $\hat{H}$ i.e., the energy, so that

$$\hat{H}\Psi(\vec{r},t) = E\Psi(\vec{r},t) = i\,\hbar\frac{\partial\Psi}{\partial t}$$

Assume $\Psi(\vec{t},r)$ is separable, i.e., $\Psi(\vec{r},t) = \psi(\vec{r})\varphi(t)$

$$E\cancel{\psi(\vec{r})}\varphi(t) = i\hbar\cancel{\psi(\vec{r})}\frac{\partial\varphi}{\partial t}$$

$$\varphi'(t) = \frac{-i}{\hbar}\varphi(t) \Rightarrow \varphi(t) = e^{-\frac{iE}{\hbar}t}$$

$$\Rightarrow \Psi(\vec{r},t) = \psi(\vec{r})\,e^{-\frac{iE}{\hbar}t}$$

where $\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$.

if we want to consider transitions, excitations, and quantum dynamics, we can express the time dependent state $\Psi(\vec{r},t)$ as a time dependent linear combination of eigenstates of the system.

$$\Psi(\vec{t},r) = \sum_n C_n(t)\,e^{-\frac{i\mathcal{E}_n}{\hbar}t}$$

where

$$\hat{H}\big|\psi_n\big\rangle = \mathcal{E}_n\big|\psi_n\big\rangle$$
$$\big\langle\psi_n\big|\psi_{n'}\big\rangle = \delta_{n'n}$$
$$\big\langle\Psi\big|\psi_n\big\rangle = C_n(t)\, e^{-\frac{i}{\hbar}\mathcal{E}_n\, t}$$

$$\big\langle\psi\big|\psi\big\rangle = 1 \qquad \text{(normalisation)}$$
$$\big\langle\Psi\big|\underbrace{\sum_n \big|\psi_n\big\rangle\big\langle\psi_n\big|}_{\mathbb{1}}\big|\Psi\big\rangle \qquad \text{(Completeness)}$$

$$= \sum_{nn'n''} C_n^\dagger\, e^{\frac{i}{\hbar}\mathcal{E}_n\, t}\big\langle\psi_n\big|\psi_{n'}\big\rangle\big\langle\psi_n'\big|C_{n''}\, e^{-\frac{i}{\hbar}\mathcal{E}_{n''}\, t}\big|\psi_{n''}\big\rangle$$
$$\sum_n C_n^\dagger C_n e^{\frac{i}{\hbar}(\mathcal{E}_n-\mathcal{E}_n)t} = \sum_n \big|C_n\big|^2 = 1$$

A time dependent perturbation will lead to time dependent coefficients $C_n(t)$, but will still be spanned by the eigenbasis $e^{-\frac{i}{\hbar}\mathcal{E}t}\big|\psi_n\big\rangle$.

Suppose

$$\hat{H}(\vec{r},t) = \hat{H}_0(\vec{r}) + V(t)$$

$$\hat{H}(\vec{r},t)\Psi(\vec{r},t) = i\hbar\frac{\partial\Psi}{\partial t}$$
$$\Big(\hat{H}_0(\vec{r}) + V(t)\Big)\sum_n C_n(t)\, e^{-\frac{i}{\hbar}\mathcal{E}_n t}\psi_n(\vec{r}) = i\hbar\frac{\partial}{\partial t}\sum_{n'}\dot{C}_n(t)\, e^{-\frac{i}{\hbar}\mathcal{E}_{n'} t}\psi_{n'}(\vec{r})$$
$$\sum_n C_n(t)e^{-\frac{i}{\hbar}\mathcal{E}_n t}\hat{H}_0(\vec{r})\psi_n(\vec{r}) + V(t)C_n(t)e^{-\frac{i}{\hbar}\mathcal{E}_n t}\psi_n(\vec{r}) = i\hbar\sum_{n'}\left(\dot{C}_{n'}(t) - \frac{i}{\hbar}\mathcal{E}_{n'}C_{n'}(t)\right)e^{-\frac{i}{\hbar}\mathcal{E}_{n'} t}\psi_{n'}(\vec{r})$$

Time Independent Schrodinger Eq'n

$$\hat{H}(\vec{r})\psi_n(\vec{r}) = \mathcal{E}_n\psi_n(\vec{r})$$

Therefore

$$\sum_n \left(\mathcal{E}_n + V(t)\right) C_n(t)e^{-\frac{i}{\hbar}\mathcal{E}_n\, t}\psi_n\vec{r} = \sum_{n'}\Big(i\,\hbar\dot{C}_{n'}(t) + \mathcal{E}_{n'}C_{n'}(t)\Big)\, e^{-\frac{i}{\hbar}\mathcal{E}_{n'} t}\psi_{n'}(\vec{r})$$
$$\sum_n V(t)C_n(t)e^{-\frac{i}{\hbar}\mathcal{E}_n t}\psi_n(\vec{r}) = \sum_{n'} i\hbar\,\dot{C}_n(t)e^{-\frac{i}{\hbar}\mathcal{E}_n t}$$
$$\sum_n \Big(V(t)\, C_n(t) - i\hbar\,\dot{C}_n(t)\Big)\, e^{-\frac{i}{\hbar}\mathcal{E}_n t}\psi_n(\vec{r}) = 0$$

Multiply by $\langle \psi_n' |$:

$$\sum_n \langle \psi_{n'} | V(t) | \psi_n \rangle C_n(t) e^{-\frac{i}{\hbar}\mathcal{E}_n t} = \sum_n i\hbar\, \dot{C}_n(t) e^{-\frac{i}{\hbar}\mathcal{E}_n t} \xcancel{\langle \psi_{n'} | \psi_n \rangle} \to \delta_{nn'}$$

$$= i\hbar\, \dot{C}_{n'}(t) e^{-\frac{i}{\hbar}\mathcal{E}_{n'} t}$$

$$\boxed{\dot{C}_n(t) = -\frac{i}{\hbar} \sum_n C_n(t) \underbrace{e^{-\frac{i}{\hbar}(\mathcal{E}_{n'} - \mathcal{E}_n)t}}_{\omega_{nn'}} \underbrace{\langle \psi_{n'} | V(t) | \psi_n \rangle}_{\text{matrix elements of the perturbation.}}}$$

7.1.2 For a two-level system

$$\dot{C}_a(t) = -\frac{i}{\hbar} \left(C_a(t) \langle \psi_a | \hat{V}(t) | \psi_a \rangle + C_b(t) e^{-i\omega_0 t} \langle \psi_a | \hat{V}(t) | \psi_b \rangle \right)$$
$$\dot{C}_b(t) = -\frac{i}{\hbar} \left(C_a(t) e^{i\omega_0 t} \langle \psi_b | \hat{V}(t) | \psi_a \rangle + C_b(t) \langle \psi_b | \hat{V}(t) | \psi_b \rangle \right)$$

For the special case $\langle \psi_n | \hat{V}(t) | \psi_n \rangle = 0$, where the perturbation transitions between eigenstates which is often the case.

$$\dot{C}_a(t) = -\frac{i}{\hbar} C_b(t)\, e^{-i\omega_0 t} \langle \psi_a | \hat{V}(t) | \psi_b \rangle$$
$$\dot{C}_b(t) = -\frac{i}{\hbar} C_a(t)\, e^{i\omega_0 t} \langle \psi_b | \hat{V}(t) | \psi_a \rangle$$

$$\boxed{\dot{C}_{n'}(t) = -\frac{i}{\hbar} \sum_n C_n(t) e^{i\omega_{nn'} t} \langle \psi_{n'} | \hat{V}(t) | \psi_n \rangle}$$

7.1.3 Example

$$\vec{E}(\vec{r}, t) = E(t)\hat{k}, \qquad \hat{V}(t) = -e\mathcal{E}z\Theta(t) \quad (\text{ Heaviside step function })$$

A constant electric field in the $\hat{k}$ direction which turns on after $t = 0$. For a hydrogen atom, calculate the matrix elements:

$$\varphi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$
$$\varphi_{200}(r) = \frac{(2 - r/a_0)}{4\sqrt{2\pi a_0^3}} e^{-r/2a_0}$$
$$\varphi_{210}(r, \phi) = \frac{r\cos\phi}{4a_0\sqrt{2\pi a_0^3}} e^{-r/2a_0}$$
$$\varphi_{21\pm1}(r, \theta, \phi) = \frac{r\sin\phi}{8a_0\sqrt{\pi a_0^3}} e^{-r/2a_0} e^{\pm i\theta}$$

$$\langle\varphi_{100}|\hat{V}|\varphi_{100}\rangle = \int \underbrace{|\varphi_{100}(r)|^2}_{\text{even}} \underbrace{(e\mathcal{E}z)}_{\text{odd}} drd\Omega = 0$$

$$\langle\varphi_{100}|\hat{V}|\varphi_{200}\rangle = \int \underbrace{\varphi_{100}(r)\varphi_{200}(r)}_{\text{even in z}} \underbrace{(-e\mathcal{E}z)}_{\text{odd in z}} drd\Omega$$

$$\langle\varphi_{100}|\hat{V}|\varphi_{210}\rangle \neq 0$$

$$\begin{aligned}
\langle\varphi_{100}|\hat{V}|\varphi_{210}\rangle &= \int\int\int \frac{e^{-3r/2a_0^4}}{4\pi a_0} r\cos\phi\,(-e\mathcal{E}r\cos\phi)\, r^2\sin\phi dr\, d\theta\, d\phi \\
&= -\frac{e\mathcal{E}}{4\pi a_0^4}\int_0^{2\pi} d\theta \int_0^{\pi} \cos^2\phi\sin\phi\, d\phi \int_0^{\infty} e^{-\frac{3}{2}\frac{r}{a_0}} r^4\, dr \\
&= -\frac{e\mathcal{E}}{2a_0^4}\left(\frac{-\cos^3\phi}{3}\right)\Big|_0^{\pi} \frac{\cancelto{4!}{\Gamma(4+1)}}{(3/2a_0)^5} \\
&= -e\mathcal{E}a_0\frac{2^8}{3^5} = -\frac{2^8}{3^5}e\mathcal{E}a_0
\end{aligned}$$

7.2 Lecture 40

July 18, 2023

7.2.1 Example

H atom in

$$V(z) = -e\mathcal{E}\Theta(t), \qquad \Theta(t) = \begin{cases} 1, & t > 0 \\ 0, & t < 0 \\ 1/2 & t = 0 \end{cases}$$

From the previous class, we know that

$$\langle \varphi_{100} | \hat{V}(z) | \varphi_{210} \rangle = -\frac{e\mathcal{E}a_0 2^8}{3^5}$$

and

$$\dot{C}_n(t) = -\frac{i}{\hbar}\sum_{n'} C_{n'}(t)\, e^{i\omega_{nn'}t}\langle \psi_n | \hat{V} | \psi_{n'} \rangle, \qquad \omega_{nn'} \equiv \frac{\mathcal{E}_n - \mathcal{E}_{n'}}{\hbar}$$

$$\begin{aligned}
\Rightarrow \dot{C}_{210}(t) &= -\frac{i}{\hbar}C_{100}(t)\, e^{i\frac{E_2-E_1}{\hbar}t}\left(-\frac{2^8}{3^5}e\mathcal{E}a_0\right) \\
\dot{C}_{210}(t) &= \frac{i}{\hbar}C_{100}(t)e^{-i\frac{3}{4}\frac{E_1}{\hbar}t}\left(\frac{2^8}{3^5}e\mathcal{E}a_0\right) \\
&= \frac{2^8}{3^5}\frac{i}{\hbar}e\mathcal{E}a_0 C_{100}(t)\, e^{-\frac{i3}{4}\frac{E_1}{\hbar}t}
\end{aligned}$$

Assume @ $t = 0$ $C_{100}(0) = 1$ and $C_{210}(0) = 0$ (initially in the ground state)

$$\begin{aligned}
\frac{dC_{210}}{dt} &= \frac{2^8}{3^5}\frac{i}{\hbar}e\mathcal{E}a_0 e^{-\frac{i3}{4}\frac{E_1}{\hbar}t}C_{100}(t), \quad \left|C_{100}(t)\right|^2 + \left|C_{210}(t)\right|^2 = 1 \\
&\Rightarrow C_{100}(t) = \sqrt{1 - \left|C_{210}(t)\right|^2} \\
C_{210}(t) &= \frac{2^8}{3^5}\frac{i}{\hbar}e\,\mathcal{E}a_0\int_0^t e^{-\frac{i3}{4}\frac{E_1}{\hbar}t}
\end{aligned}$$

7.2.2 Example

Solve

$$\begin{aligned}
\dot{C}_a(t) &= -\frac{i}{\hbar}e^{-i\omega_0 t}C_b(t)\langle \psi_a | \hat{V} | \psi_b \rangle \\
\dot{C}_b(t) &= -\frac{i}{\hbar}e^{i\omega_0 t}C_a(t)\langle \psi_b | \hat{V} | \psi_a \rangle
\end{aligned}$$

where $\hat{V}(\vec{r})$ (time independent) and $C_a(0) = 1, C_b(0) = 0$.

Differentiating:

$$\ddot{C}_a(t) = -\frac{i}{\hbar} e^{-i\omega_0 t} \langle \psi_a | \hat{V} | \psi_b \rangle \left(\dot{C}_b(t) - i\omega_0 C_b(t) \right)$$
$$\therefore \ddot{C}_b(t) = -\frac{i}{\hbar} e^{i\omega_0 t} \langle \psi_b | \hat{V} | \psi_a \rangle \left(\dot{C}_a(t) + i\omega_0 C_a(t) \right) \quad (*)$$

We want to solve for $C_b(t)$, so we need an ODE in $C_b(t)$.

Subtitute

$$\dot{C}_a(t) = -\frac{i}{\hbar} e^{-i\omega_0 t} C_b(t) \langle \psi_a | \hat{V} | \psi_b \rangle$$
$$C_a(t) = \frac{i\hbar \dot{C}_b(t) e^{-i\omega_0 t}}{\langle \psi_b | \hat{V} | \psi_a \rangle}$$

into $(*)$

$$\ddot{C}_b(t) = \frac{i}{\hbar} e^{i\omega_0 t} \langle \psi_b | \hat{V} | \psi_a \rangle \left[\frac{i}{\hbar} e^{-i\omega_0 t} C_b(t) \langle \psi_a | \hat{V} | \psi_b \rangle + i\,\omega_0 (i\hbar) \frac{\dot{C}_b(t) e^{-i\omega_0 t}}{\langle \psi_b | \hat{V} | \psi_a \rangle} \right]$$
$$\ddot{C}_b(t) = -\frac{1}{\hbar^2} C_b(t) \left| \langle \psi_a | \hat{V} | \psi_b \rangle \right|^2 + i\omega_0 \dot{C}_b(t)$$
$$\Rightarrow \ddot{C}_b(t) - i\omega_0 \dot{C}_b(t) + \frac{C_b(t)}{\hbar^2} \left| \langle \psi_a | \hat{V} | \psi_b \rangle \right|^2 = 0$$

A 2^{ND} order ODE with constant coefficients.

$$C_b(t) \sim A\, e^{\lambda_+ t} + B\, e^{\lambda_- t}$$

$$\lambda_\pm = \frac{i\omega_0}{2} \pm \frac{1}{2} \sqrt{-\omega_0^2 - 4 \frac{\left| \langle \psi_a | \hat{V} | \psi_b \rangle \right|^2}{\hbar^2}}$$
$$= \frac{i}{2} \left(\omega_0 \pm \sqrt{\omega_0^2 + 4 \frac{\left| \langle \psi_a | \hat{V} | \psi_b \rangle \right|^2}{\hbar^2}} \right)$$

$$C_b(t) = A \exp\left[\frac{it}{2} \left(\omega_0 + \sqrt{\omega_0^2 + 4 \frac{|V_{ab}|^2}{\hbar^2}} \right) \right] + B \exp\left[\frac{it}{2} \left(\omega_0 - \sqrt{\omega_0^2 + 4 \frac{|V_{ab}|^2}{\hbar^2}} \right) \right]$$
$$= \exp\left(\frac{i\omega_0 t}{2} \right) \left[A \exp\left(\frac{it}{2} \sqrt{\omega_0^2 + \frac{4|V_{ab}|^2}{\hbar^2}} \right) + B \exp\left(-\frac{it}{2} \sqrt{\omega_0^2 + \frac{4|V_{ab}|^2}{\hbar^2}} \right) \right]$$
$$C_b(t) = \exp\left(\frac{i\omega_0 t}{2} \right) \left[C \cos\left(\sqrt{\frac{\omega_0^2}{4} + \frac{|V_{ab}|^2}{\hbar^2}} t \right) + D \sin\left(\sqrt{\frac{\omega_0^2}{4} + \frac{|V_{ab}|^2}{\hbar^2}} t \right) \right]$$

But $C_b(0) = 0$ (initially in $C_a = 1$) therefore $C = 0$ and $D = 1$

$$C_b(t) = \exp\left(\frac{i\omega_0 t}{2}\right)\sin\left(\sqrt{\frac{\omega_0^2}{4} + \frac{|V_{ab}|^2}{\hbar^2}}t\right)$$

$$C_a(t) = \exp\left(-\frac{i\omega_0 t}{2}\right)\cos\left(\sqrt{\frac{\omega_0^2}{4} + \frac{|V_{ab}|^2}{\hbar^2}}t\right)$$

Check $\left|C_a(t)\right|^2 + \left|C_b(t)\right|^2 = 1$

$$\Rightarrow \cos^2\left(\sqrt{\frac{\omega_0^2}{4} + \frac{|V_{ab}|^2}{\hbar^2}}t\right) + \sin^2\underbrace{\left(\sqrt{\frac{\omega_0^2}{4} + \frac{|V_{ab}|^2}{\hbar^2}}t\right)}_{\substack{\text{Rabi frequency}\\ \text{switching between}\\ \psi_a \& \psi_b}} = 1$$

$$V(t) = \mathcal{U}\delta(t - t_0), \quad \mathcal{U}_{aa} = \mathcal{U}_{bb} = 0, \quad \mathcal{U}_{ab} = \mathcal{U}_{ba}^\dagger = \alpha, \quad C_a(-\infty) = 1, \quad C_b(-\infty) = 0$$

$$\left.\begin{aligned} \dot{C}_a(t) &= -\frac{i}{\hbar}C_b(t)e^{-i\omega_0 t}\alpha\delta(t - t_0) \\ \dot{C}_b(t) &= -\frac{i}{\hbar}C_a(t)e^{i\omega_0 t}\alpha^\dagger\delta(t - t_0) \end{aligned}\right\}$$

ODE in C_b alone and its derivatives, differentiating to obtain a 2nd order ODE in $C_b(t)$

$$\begin{aligned} \delta(t - t_0) &= \lim_{\epsilon \to 0} P_\epsilon(t - t_0) = \frac{\Theta(t - t_0 + \epsilon/2) - \Theta(t - t_0 - \epsilon/2)}{\epsilon} \\ &= \begin{cases} 1/\epsilon, & (t - t_0) < \epsilon/2 \\ 0, & \text{otherwise} \end{cases} \end{aligned}$$

$$\ddot{C}_b(t) = -\frac{i}{\hbar}e^{i\omega_0 t}\alpha^\dagger\left[\dot{C}_a(t)\delta(t - t_0) + i\omega_0 C_a(t)\delta(t - t_0) + C_a(t)\frac{d}{dt}\delta(t - t_0)\right]$$

Let $t_0 = 0$ wlog, for $t < -\epsilon/2$, $C_a(t) = 1$, $C_b = 0$
After $t > \epsilon/2$, $C_a(t) = C_a^0$, $C_b(t) = C_b^0$

For $\left|t\right| > \epsilon/2$, then $\delta(t - t_0) = 1/\epsilon$, $\frac{d}{dt}\delta(t - t_0) = 0$

$$\ddot{C}_b(t) = -\frac{i}{\hbar}e^{i\omega_0 t}\alpha^*\left(\frac{\dot{C}_a(t)}{\epsilon} + \frac{i\omega_0 C_a(t)}{\epsilon}\right)$$

$$\begin{aligned} C_a(t) &= \frac{i\hbar\dot{C}_b(t)e^{-i\omega_0 t}\epsilon}{\alpha^*} \\ \dot{C}_a(t) &= -\frac{i}{\hbar}C_b(t)e^{-i\omega_0 t}\frac{\alpha}{\epsilon} \end{aligned}$$

Therefore

$$\ddot{C}_b(t) = -\frac{i}{\hbar}e^{i\omega_0 t}\left[-\frac{i}{\hbar}e^{-i\omega_0 t}C_b(t)\frac{\left|\alpha\right|^2}{\epsilon^2} + i\omega_0(i\hbar)e^{-i\omega_0 t}\dot{C}_b(t)\right]$$

$$\ddot{C}_b(t) + \frac{\left|\alpha\right|^2}{\hbar^2\epsilon^2}C_b(t) - i\omega_0\dot{C}_b(t) = 0$$

A second order ODE with constant coefficients.

$$\lambda_\pm = \frac{i\omega_0}{2} \pm \sqrt{-\omega_0^2 - \frac{4\left|\alpha\right|^2}{\epsilon^2\hbar^2}} = \frac{i}{2}\left(\omega_0 \pm \underbrace{\sqrt{\omega_0^2 + \frac{4\left|\alpha\right|^2}{\epsilon^2\hbar^2}}}_{\omega_R}\right)$$

$$\begin{aligned}
C_b(t) &= \exp\left(\frac{i\omega_0}{2}t\right)\left[A\exp\left(\frac{i\omega_R}{2}t\right) + B\exp\left(-\frac{i\omega_R}{2}t\right)\right] \\
&= \exp\left(\frac{i\omega_0}{2}t\right)\left[C\cos\left(\frac{\omega_R}{2}t\right) + D\sin\left(\frac{\omega_R}{2}t\right)\right] \\
C_b(-\epsilon/2) = 0 &= \exp\left(\frac{-i\omega_0\epsilon}{4}\right)\left[C\cos\left(-\frac{\omega_R\epsilon}{4}\right) + D\sin\left(-\frac{\omega_R\epsilon}{4}\right)\right] \\
C\cos\left(\frac{\omega_R\epsilon}{4}\right) &= D\sin\left(\frac{\omega_R\epsilon}{4}\right)
\end{aligned}$$

$$\Rightarrow C = D\tan\left(\frac{\omega_R\epsilon}{4}\right)$$

$$C_b(t) = \exp\left(\frac{i\omega_0 t}{2}\right)D\left[\tan\left(\frac{\omega_R\epsilon}{4}\right)\cos\left(\frac{\omega_R t}{2}\right) + \sin\left(\frac{\omega_R t}{2}\right)\right]$$

$$\begin{aligned}
C_a(t) &= \frac{i\hbar}{\alpha^*}\dot{C}_b(t)e^{-i\omega_0 t}\epsilon \\
&= \frac{i\hbar}{\alpha^*}\epsilon\exp\left(-\frac{i\omega_0 t}{2}\right)D\left[\left(\frac{i\omega_0}{2}\cos\left(\frac{\omega_R t}{2}\right) - \frac{\omega_R}{2}\sin\left(\frac{\omega_R t}{2}\right)\right)\tan\left(\frac{\omega_R\epsilon}{4}\right)\right. \\
&\quad \left. + \left(\frac{i\omega_0}{2}\sin\left(\frac{\omega_R t}{2}\right) + \frac{\omega_R}{2}\cos\left(\frac{\omega_R t}{2}\right)\right)\right] \\
C_a(-\epsilon/2) = 1 &= \frac{i\hbar\epsilon}{\alpha^*}\exp\left(\frac{i\omega_0\epsilon}{4}\right)D\left[\left(\frac{i\omega_0}{2}\cos\left(\frac{\omega_R\epsilon}{4}\right) + \frac{\omega_R}{2}\sin\left(\frac{\omega_R\epsilon}{4}\right)\right)\tan\left(\frac{\omega_R\epsilon}{4}\right)\right. \\
&\quad \left. + \left(-\frac{i\omega_0}{2}\sin\left(\frac{\omega_R\epsilon}{4}\right) + \frac{\omega_R}{2}\cos\left(\frac{\omega_R\epsilon}{4}\right)\right)\right] \\
1 &= \frac{i\hbar\epsilon}{\alpha^*}\exp\left(\frac{-i\omega_0\epsilon}{4}\right)
\end{aligned}$$

Look for the missing examples in the QM 2 book