PHY 742 Quantum Mechanics II
1-1:50 AM MWF Olin 103

Plan for Lecture 12

Time dependent perturbation theory
Ref: Chapter 15

1. Time harmonic perturbations
2. Fermi Golden Rule
3. Oscillator strength

1

Topics for Quantum Mechanics II

Single particle analysis
- Single particle interacting with electromagnetic fields – EC Chap. 9
- Scattering of a particle from a spherical potential – EC Chap. 14
- More time independent perturbation methods – EC Chap. 12, 13
- Single electron states of a multi-well potential ➔ molecules and solids – EC Chap. 2,6
- Time dependent perturbation methods – EC Chap. 15
- Path integral formalism (Feynman) – EC Chap. 11.C
- Relativistic effects and the Dirac Equation – EC Chap. 16

Multiple particle analysis
- Quantization of the electromagnetic fields – EC Chap. 17
- Photons and atoms – EC Chap. 18
- Multi particle systems; Bose and Fermi particles – EC Chap. 10
- Multi electron atoms and materials
  - Hartree-Fock approximation
  - Density functional approximation

2

Course schedule for Spring 2020

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	Reading	Topic	HW	Due date
1	Mon: 01/13/2020	Chap. 9	Quantum mechanics of electromagnetic forces	#1	01/22/2020
2	Wed: 01/15/2020	Chap. 9	Quantum mechanics of particle in electrostatic field	#2	01/24/2020
3	Fri: 01/17/2020	Chap. 9	Quantum mechanics of particle in magnetostatic field	#3	01/27/2020
	Mon: 01/20/2020	No class	Martin Luther King Holiday		
4	Wed: 01/22/2020	Chap. 14	Scattering theory	#4	01/29/2020
5	Fri: 01/24/2020	Chap. 14	Scattering theory	#5	01/31/2020
6	Mon: 01/27/2020	Chap. 14	Scattering theory	#6	02/03/2020
7	Wed: 01/29/2020	Chap. 12	Variational methods	#7	02/05/2020
8	Fri: 01/31/2020	Chap. 12	Variational and other approximation methods	#8	02/07/2020
9	Mon: 02/03/2020	Chap. 2,6	Single particle states of molecules and solids	#9	02/10/2020
10	Wed: 02/05/2020	Chap. 2,6	H_2^+ molecular ion; Born Oppenheimer approximation	#10	02/12/2020
11	Fri: 02/07/2020	Chap. 15	Time-dependent perturbations	#11	02/14/2020
12	Mon: 02/10/2020	Chap. 15	Time-dependent perturbations	#12	02/14/2020
13	Wed: 02/12/2020				
14	Fri: 02/14/2020				
15	Mon: 02/17/2020				
16	Wed: 02/19/2020				

3

Review: Treatment of time-dependent perturbations

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = H(t)\left|\psi\right\rangle$$

$$H(t) = H^0 + \epsilon H^1(t)$$

We approach the problem using the complete basis set of H^0 :

$$H^0\left|n^0\right\rangle = E_n^0\left|n^0\right\rangle$$

It is reasonable to assume that

$$\left|\psi(t)\right\rangle = \sum_n c_n(t)\left|n^0\right\rangle \equiv \sum_n k_n(t)e^{-iE_n^0 t/\hbar}\left|n^0\right\rangle$$

2/10/2020 PHY 742 -- Lecture 12 4

4

Treatment of time-dependent perturbations -- continued

$$\left|\psi(t)\right\rangle = \sum_n k_n(t)e^{-iE_n^0 t/\hbar}\left|n^0\right\rangle$$

$$i\hbar\frac{\partial}{\partial t}\left|\psi\right\rangle = \left(H^0 + \epsilon H^1(t)\right)\left|\psi\right\rangle$$

$$\sum_n\left(i\hbar\frac{dk_n(t)}{dt} - \epsilon H^1(t)k_n(t)\right)e^{-iE_n^0 t/\hbar}\left|n^0\right\rangle = 0$$

Projecting this equation with a particular zero-order state $\left\langle f^0\right|$:

$$i\hbar\frac{dk_f(t)}{dt} = \epsilon\sum_n\left\langle f^0\right|H^1(t)\left|n^0\right\rangle k_n(t)e^{i\left(E_f^0 - E_n^0\right)t/\hbar}$$

2/10/2020 PHY 742 -- Lecture 12 5

5

Treatment of time-dependent perturbations -- continued

$$i\hbar\frac{dk_f(t)}{dt} = \epsilon\sum_n\left\langle f^0\right|H^1(t)\left|n^0\right\rangle k_n(t)e^{i\left(E_f^0 - E_n^0\right)t/\hbar}$$

Perturbation expansion for time-dependent coefficients:

$$k_n(t) = k_n^0 + \epsilon k_n^1(t) + \epsilon^2 k_n^2(t) + \ldots$$

Zero order equation: $\frac{dk_n^0}{dt} = 0$

s-order equation for $s > 0$:

$$\frac{dk_m^s}{dt} = \frac{1}{i\hbar}\sum_n\left\langle m^0\right|H^1(t)\left|n^0\right\rangle k_n^{s-1}(t)e^{i\left(E_m^0 - E_n^0\right)t/\hbar}$$

2/10/2020 PHY 742 -- Lecture 12 6

6

Treatment of time-dependent perturbations -- continued

1^{st}-order equation, assuming that $k_n^0 = \delta_{nI}$

$$\frac{dk_m^1}{dt} = \frac{1}{i\hbar}\left\langle m^0 \middle| H^1(t) \middle| I^0 \right\rangle e^{i\left(E_m^0 - E_I^0\right)t/\hbar}$$

Example:

Suppose that $H^1(t) = \tilde{H}^1 h(t)$

$$\text{where} \qquad h(t) \equiv \begin{cases} 0 & \text{for } t<0 \text{ and } t>T \\ 2\sin\omega t & \text{for } 0<t<T \end{cases}$$

2/10/2020 PHY 742 -- Lecture 12 7

7

Treatment of time-dependent perturbations -- continued

For this example

$$\frac{dk_m^1}{dt} = 0 \quad \text{for } t<0 \text{ or } t>T$$

$$\frac{dk_m^1}{dt} = \frac{2}{i\hbar}\frac{\left\langle m^0 \middle| \tilde{H}^1 \middle| I^0 \right\rangle}{2i}\left(e^{i(\omega+\omega_{mI})t} - e^{i(-\omega+\omega_{mI})t}\right)$$

$$\text{for } 0<t<T$$

$$\Rightarrow k_m^1(t) = \frac{2}{i\hbar}\frac{\left\langle m^0 \middle| \tilde{H}^1 \middle| I^0 \right\rangle}{2}\left(\frac{e^{i(\omega+\omega_{mI})T}-1}{\omega+\omega_{mI}} - \frac{e^{i(-\omega+\omega_{mI})T}-1}{-\omega+\omega_{mI}}\right)$$

where $\omega_{mI} \equiv \left(E_m^0 - E_I^0\right)/\hbar \qquad \text{for } t>T$

2/10/2020 PHY 742 -- Lecture 12 8

8

For $t > T$

$$k_m^1(t) = \frac{2}{i\hbar}\frac{\left\langle m^0 \middle| \tilde{H}^1 \middle| I^0 \right\rangle}{2}\left(\frac{e^{i(\omega+\omega_{mI})T}-1}{\omega+\omega_{mI}} - \frac{e^{i(-\omega+\omega_{mI})T}-1}{-\omega+\omega_{mI}}\right)$$

where $\omega_{mI} \equiv \left(E_m^0 - E_I^0\right)/\hbar$

$$\left|k_m^1(t)\right|^2 \approx \frac{4}{\hbar^2}\left|\left\langle m^0 \middle| \tilde{H}^1 \middle| I^0 \right\rangle\right|^2 \times$$

$$\left(\frac{\sin^2\left((\omega+\omega_{mI})T/2\right)}{(\omega+\omega_{mI})^2} + \frac{\sin^2\left((-\omega+\omega_{mI})T/2\right)}{(-\omega+\omega_{mI})^2}\right)$$

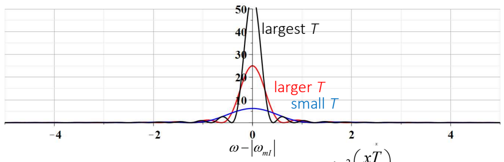
$$\approx \frac{4\pi T}{2\hbar^2}\left|\left\langle m^0 \middle| \tilde{H}^1 \middle| I^0 \right\rangle\right|^2 \left(\delta\left(\omega+\omega_{mI}\right) + \delta\left(-\omega+\omega_{mI}\right)\right)$$

2/10/2020 PHY 742 -- Lecture 12 9

9

Treatment of time-dependent perturbations -- continued

Behavior of $k_m^1(T)$ in the neighborhood of $\omega = |\omega_{mI}|$



$\omega - |\omega_{mI}|$

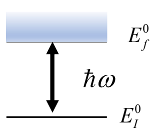
Note that $\int_{-\infty}^{\infty} \frac{\sin^2\left(\frac{xT}{2}\right)}{x^2} dx = \frac{\pi T}{2}$

10

Estimating the rate of transitions $I \rightarrow f$

$$\mathcal{R}_{I\to f} = \frac{\left|k^1_{I\to f}(t)\right|^2}{T} \approx \frac{2\pi}{\hbar}\left|\langle f^0|\tilde{H}^1|I^0\rangle\right|^2 \left(\delta\left(\hbar\omega + E_f^0 - E_I^0\right) + \delta\left(-\hbar\omega + E_f^0 - E_I^0\right)\right)$$

Fermi "Golden" rule



11

Example – Zero order system in the presence of an electromagnetic field

Full Hamiltonian: $H(\mathbf{r},t) = \frac{1}{2m}\left(\mathbf{p} - q\mathbf{A}(\mathbf{r},t)\right)^2 + V(\mathbf{r}) + qU(\mathbf{r},t)$

Zero order Hamiltonian: $H^0(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$

First order Hamiltonian: $H^1(\mathbf{r},t) = \frac{-q}{m}\mathbf{A}(\mathbf{r},t)\cdot\mathbf{p} + \frac{i\hbar q}{2m}\left(\nabla\cdot\mathbf{A}(\mathbf{r},t)\right) + qU(\mathbf{r},t)$

Time dependent electric field: $\mathbf{F}(\mathbf{r},t) = -\nabla U(\mathbf{r},t) - \frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t}$

12

Example – Zero order system in the presence of an electromagnetic field -- continued

Time dependent electric field: $\mathbf{F}(\mathbf{r},t) = -\nabla U(\mathbf{r},t) - \frac{\partial \mathbf{A}(\mathbf{r},t)}{\partial t}$

Suppose $\mathbf{F}(\mathbf{r},t) = \begin{cases} 0 & \text{for } t<0 \text{ or } t>T \\ F_0\hat{\mathbf{z}}(2\sin(\omega t)) & \text{for } 0<t<T \end{cases}$

Possibility #1 -- scalar representation: $U(\mathbf{r},t) = -F_0 z(2\sin(\omega t))$ for $0<t<T$

$\mathbf{A}(\mathbf{r},t) = 0$

Possibility #2 -- vector representation: $U(\mathbf{r},t) = 0$

$\mathbf{A}(\mathbf{r},t) = -\frac{F_0}{\omega}\hat{\mathbf{z}}(2\cos(\omega t))$ for $0<t<T$

2/10/2020 PHY 742 -- Lecture 12 13

13

Example – Zero order system in the presence of an electromagnetic field -- continued

First order Hamiltonian: $H^1(\mathbf{r},t) = \frac{-q}{m}\mathbf{A}(\mathbf{r},t)\cdot\mathbf{p} + \frac{i\hbar q}{2m}(\nabla\cdot\mathbf{A}(\mathbf{r},t)) + qU(\mathbf{r},t)$

Convenient notation: $H^1(\mathbf{r},t) \equiv \tilde{H}^1(\mathbf{r})(2\sin(\omega t))$ for $0<t<T$ **(note slight cheat)**

Possibility #1 -- scalar representation: $\tilde{H}^1(\mathbf{r}) = -qF_0 z$

Possibility #2 -- vector representation: $\tilde{H}^1(\mathbf{r}) = \frac{qF_0}{m\omega}p_z$

Note that for this example, $(\nabla\cdot\mathbf{A}(\mathbf{r},t)) = 0$

2/10/2020 PHY 742 -- Lecture 12 14

14

Example – Zero order system in the presence of an electromagnetic field -- continued

Suppose the charged particle is an electron: $q=-e$

$\tilde{H}^1 = eF_0 z$ representing field as scalar potential

$\tilde{H}'^1 = -\frac{eF_0 p_z}{\omega m}$ representing field as vector potential

Note that these two are equivalent in the exact basis of H^0:

$\frac{p_z}{m} = \frac{1}{i\hbar}\left[z,\frac{\mathbf{p}^2}{2m}\right] = \frac{1}{i\hbar}\left[z,H^0\right]$

$\left\langle f^0\left|\frac{p_z}{m}\right|I^0\right\rangle = \frac{1}{i\hbar}\left\langle f^0\left|\left[z,H^0\right]\right|I^0\right\rangle = -\frac{E_f^0-E_I^0}{i\hbar}\left\langle f^0\left|z\right|I^0\right\rangle$

$= i\omega_{fI}\left\langle f^0\left|z\right|I^0\right\rangle$ for $\hbar\omega_{fI} \equiv E_f^0 - E_I^0$

2/10/2020 PHY 742 -- Lecture 12 15

15

Example – Zero order system in the presence of an electromagnetic field -- continued

$$\left\langle f^0 \left| \tilde{H}^1 \right| I^0 \right\rangle = eF \left\langle f^0 \left| z \right| I^0 \right\rangle \quad \text{representing field as scalar potential}$$

$$\left\langle f^0 \left| \tilde{H}'^1 \right| I^0 \right\rangle = -\frac{eF}{\omega m} \left\langle f^0 \left| p_z \right| I^0 \right\rangle \quad \text{representing field as vector potential}$$

$$= -\frac{eF}{\omega} i\omega_{fi} \left\langle f^0 \left| z \right| I^0 \right\rangle$$

$$\Rightarrow \text{When } \omega = \omega_{fi}, \quad \left| \left\langle f^0 \left| \tilde{H}'^1 \right| I^0 \right\rangle \right|^2 = \left| \left\langle f^0 \left| \tilde{H}^1 \right| I^0 \right\rangle \right|^2$$

Fermi golden rule: $$\mathcal{R}_{I\to f} = \frac{\left| k^1_{I\to f}(t) \right|^2}{T} \approx \frac{2\pi}{\hbar} \left| \left\langle f^0 \left| \tilde{H}^1 \right| I^0 \right\rangle \right|^2 \delta\left(\hbar\left(\omega - \omega_{fi}\right)\right)$$

2/10/2020 PHY 742 -- Lecture 12 16

16

Example -- H-like atom in presence of electric field

$$\tilde{H}^1 = -eFz \quad \text{representing field as scalar potential}$$
$$= -eFr\cos\theta$$

Some H^0 eigenstates for H-like ion:

$$\left| I^0 = 1s \right\rangle = \left(\frac{Z^3}{a_0^3 \pi} \right)^{1/2} e^{-Zr/a_0} \qquad E_I^0 = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0}$$

$$\left| f^0 = 2p_0 \right\rangle = \left(\frac{Z^3}{32 a_0^3 \pi} \right)^{1/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta \qquad E_f^0 = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0} \frac{1}{4}$$

2/10/2020 PHY 742 -- Lecture 12 17

17

$$\left\langle f^0 \left| \tilde{H}^1 \right| I^0 \right\rangle = \left\langle f^0 \left| -eFr\cos\theta \right| I^0 \right\rangle$$

H^0 eigenstates for H-like ion: $\left| I^0 = 1s \right\rangle = \left(\frac{Z^3}{a_0^3 \pi} \right)^{1/2} e^{-Zr/a_0}$

$$\left| f^0 = 2p_0 \right\rangle = \left(\frac{Z^3}{32 a_0^3 \pi} \right)^{1/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$$

$$\left\langle f^0 \left| \tilde{H}^1 \right| I^0 \right\rangle = -eF \frac{Z^3}{a_0^3 \pi} \left(\frac{1}{32} \right)^{1/2} 2\pi \frac{2}{3} \int_0^\infty r^3 dr \frac{Zr}{a_0} e^{-3Zr/2a_0}$$

$$= -eF \frac{Z^3}{a_0^3 \pi} \left(\frac{1}{32} \right)^{1/2} 2\pi \frac{2}{3} \left(\frac{a_0}{Z} \right)^4 \int_0^\infty x^4 dx \; e^{-\frac{3}{2}x}$$

$$= -\frac{eFa_0}{\sqrt{2}Z} \frac{256}{243}$$

2/10/2020 PHY 742 -- Lecture 12 18

18

Summary of results for resonant transitions for H-like ion ***1s→2p₀***

$$\mathscr{R}_{I\to f} \approx \frac{2\pi}{\hbar}\left|\left\langle f^0\right|\tilde{H}^1\left|I^0\right\rangle\right|^2 \delta\left(-\hbar\omega + E_f^0 - E_I^0\right)$$

$$\left\langle f^0\right|\tilde{H}^1\left|I^0\right\rangle = -\frac{eFa_0}{\sqrt{2}Z}\frac{256}{243}$$

$$\hbar\omega = E_f^0 - E_I^0 = \frac{3}{4}\frac{Z^2e^2}{8\pi\epsilon_0 a_0} = 10.204\, Z^2 \text{ eV}$$

19

Digression: Notion of oscillator strength for transition between states ***I→n:***

$$f_{nl} = \frac{2m}{\hbar^2}\left(E_n^0 - E_l^0\right)\left|\left\langle n^0\right|z\left|l^0\right\rangle\right|^2$$

$$\left[z,\left[z,H^0\right]\right] = z^2H^0 + H^0z^2 - 2zH^0z = \frac{i\hbar}{m}\left[z,p_z\right] = -\frac{\hbar^2}{m}$$

$$\left\langle l^0\right|\left[z,\left[z,H^0\right]\right]\left|l^0\right\rangle = 2E_l^0\left\langle l^0\right|z^2\left|l^0\right\rangle - 2\left\langle l^0\right|zH^0z\left|l^0\right\rangle = -\frac{\hbar^2}{m}\left\langle l^0|l^0\right\rangle$$

Inserting resolution of the identity: $1 = \sum_n \left|n^0\right\rangle\left\langle n^0\right|$

$$\sum_n\left(2E_l^0\left\langle l^0\right|z\left|n^0\right\rangle\left\langle n^0\right|z\left|l^0\right\rangle - 2\left\langle l^0\right|z\left|n^0\right\rangle E_n^0\left\langle n^0\right|z\left|l^0\right\rangle\right) = -\frac{\hbar^2}{m}\left\langle l^0|l^0\right\rangle$$

$$\frac{2m}{\hbar^2}\sum_n\left(E_n^0 - E_l^0\right)\left\langle l^0\right|z\left|n^0\right\rangle\left\langle n^0\right|z\left|l^0\right\rangle = \sum_n f_{nl} = \left\langle l^0|l^0\right\rangle = 1$$

sum rule for oscillator strength

20

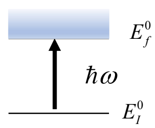
Digression – "selection rules" for transitions between spherically symmetric states in due to interaction with an electromagnetic field in the dipole approximation --

$$\left\langle f^0\right|\tilde{H}^1\left|I^0\right\rangle = \left\langle f^0\right| -eFr\cos\theta\left|I^0\right\rangle$$

Symmetry analysis of the matrix element finds non-trivial matrix elements for $\ell_f - \ell_I = \pm 1$ and $m_f - m_I = 0, \pm 1$.

21

Example when the final state is in the continuum spectrum



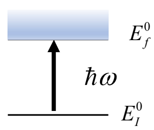
Exact solutions for continuum states of H-like ions are related to confluent hypergeometric functions

22

Absorption of radiation in the case of photo emission

$$\left|f^0\right\rangle = R_{El}(r)Y_{lm}(\hat{\mathbf{r}})$$

$$\left(-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)-\frac{Ze^2}{4\pi\epsilon_0 r}-E\right)R_{El}(r)=0$$



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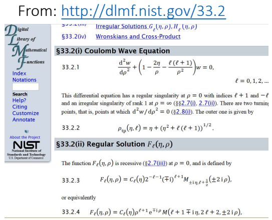

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Irregular Solutions $G_\ell(\eta,\rho), H_\ell^{\pm}(\eta,\rho)$

§33.2(iv) Wronskians and Cross-Product

§33.2(i) Coulomb Wave Equation

33.2.1 $\frac{d^2w}{d\rho^2}+\left(1-\frac{2\eta}{\rho}-\frac{\ell(\ell+1)}{\rho^2}\right)w=0,$ $\ell=0,1,2,\ldots$

This differential equation has a regular singularity at $\rho=0$ with indices $\ell+1$ and $-\ell$ and an irregular singularity of rank 1 at $\rho=\infty$ (§§2.7(i), 2.7(ii)). There are two turning points, that is, points at which $d^2w/d\rho^2=0$ (§2.8(i)). The outer one is given by

33.2.2 $\rho_{tp}(\eta,\ell)=\eta+(\eta^2+\ell(\ell+1))^{1/2}.$

§33.2(ii) Regular Solution $F_\ell(\eta,\rho)$

The function $F_\ell(\eta,\rho)$ is recessive (§2.7(iii)) at $\rho=0$, and is defined by

33.2.3 $F_\ell(\eta,\rho)=C_\ell(\eta)2^{-\ell-1}(\mp i)^{\ell+1}M_{\pm i\eta,\ell+\frac{1}{2}}(\pm 2i\rho),$

or equivalently

33.2.4 $F_\ell(\eta,\rho)=C_\ell(\eta)\rho^{\ell+1}e^{\mp i\rho}M(\ell+1\mp i\eta,2\ell+2,\pm 2i\rho),$

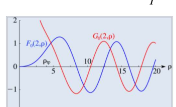

Figure 33.3.3: $F_\ell(\eta,\rho)$, $G_\ell(\eta,\rho)$ with $\ell=0$, $\eta=2$. The turning point is at $\rho_{tp}(2,0)=4$.

23

Absorption of radiation in the case of photo emission approximating final state as a plane wave (Born approximation)

$$\left|f^0\right\rangle \approx \mathcal{N}e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{where } k=\sqrt{(2mE_f^0/\hbar^2)}$$

$$\text{For initial state: } \left|I^0=1s\right\rangle = \left(\frac{Z^3}{a_0^3\pi}\right)^{1/2} e^{-Zr/a_0}$$

$$\mathcal{R}_{I\to f} \approx \frac{2\pi}{\hbar}\left|\left\langle f^0\left|\tilde{H}^1\right|I^0\right\rangle\right|^2 \delta\left(-\hbar\omega+E_f^0-E_I^0\right)$$

$$\left\langle f^0\left|\tilde{H}^1\right|I^0\right\rangle = \left\langle f^0\left|-eFr\cos\theta\right|I^0\right\rangle$$

To be continued …

24