ATOMIC PHYSICS
(PHYS4011) LECTURE NOTES

Lecture notes based on a course given by Tom Kirchner.
The emphasis of the course is on solving atomic systems,
in particular the Hydrogen atom through perturbation theory.
Some relativistic quantum mechanics is introduced at the end

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Presented by: TOM KIRCHNER

LaTeXNotes by: JEFF ASAF DROR

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CONTENTS

I. Introduction: the field-free Schrodinger hydrogen atom 3
A. Reduction to an effective one-body problem 3
B. Central-field problem for relative motion 3
C. Solutions of the Coloumb problem 3
D. Assorted Remarks 5

II. Atoms in electric fields: the Stark effect 7
A. Non-Degenerate perturbation theory (PT) 8
1. Comments 10
B. Degenerate Perturbation Theory 12
C. Effect on excited states: the linear Stark effect 14

III. Interaction of Atoms with Radiation 18
A. The semiclassical Hamiltonian 18
B. Time-Dependent Perturbation Theory 21
1. General Formulation 21
2. Comments 23
3. Discussion of 1^{st} order result 23
4. Example: Slowly varying perturbation 24
5. Solution of TDSE up to 1st order 25
6. Comments 25
7. Example: Sudden Perturbation 26
8. Example:Periodic perturbation 26
C. Photoionization 28
1. Transitions into the continuum: Fermi's golden rule (FGR) 28
2. Dipole Approximation 30
D. Outlook on Field Quantization 31
1. Construction of H_F 32
2. Creation and Annihilation Operators 34
3. Interaction Between Photon Field and Electrons 35
4. The Transition Matrix Elements 36
5. Spontaneous Emission 38

IV. Brief Introduction to Relativistic Quantum Mechanics 43
A. Klien-Gordon Equation 43
1. Setting up a relativistic wave equation 43
B. Discussion of KG equation 43
C. Dirac Equation 44
1. Free Particles 44
2. Solutions of the free Dirac equation 47
3. Add Electromagnetic Potentials 49
4. The relativistic hydrogen problem 49
5. Nonrelativistic limit of the Dirac equations 51

I. INTRODUCTION: THE FIELD-FREE SCHRODINGER HYDROGEN ATOM

A. Reduction to an effective one-body problem

B. Central-field problem for relative motion

$$\hat{H}_{rel} = \frac{\hat{p}^2}{2\mu} + V(r); \qquad \hat{H}_{rel}\phi_{rel}(\mathbf{r}) = E_{rel}\phi_{rel}(\mathbf{r}) \tag{I.1}$$

Note: omit hats from now on. We use the ansatz:

$$\phi_{rel}(\mathbf{r}) = R(r)Y_{\ell,m}(\phi,\theta) \tag{I.2}$$

$$= \frac{y(r)}{r}Y_{\ell,m}(\phi,\theta) \tag{I.3}$$

where $y(r) \equiv rR(r)$. This gives the radial Schrodinger equation which given by

$$y''_\ell(r) + \left[\epsilon - U(r) - \frac{\ell\,(\ell+1)}{r^2}\right] y_\ell(r) = 0 \tag{I.4}$$

where $\epsilon \equiv \frac{2\mu}{\hbar^2}E_{rel},\ U(r) = \frac{2\mu}{\hbar^2}V(r)$.

C. Solutions of the Coloumb problem

Consider the potential

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_o r} \tag{I.5}$$

For now on we will only consider $E_{rel} < 0$ (we don't consider the scattering problems of $E_{rel} > 0$, only the bound

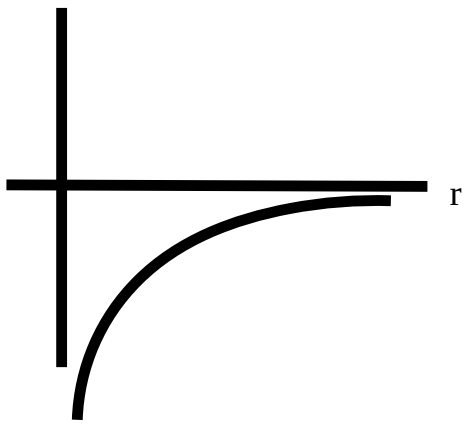

FIG. 1. The Hydrogen potential energy

states). The energy levels as well as the energy states are quantized.

$$\epsilon \to \epsilon_n$$
$$E_{rel} \to E_n = \frac{\hbar^2}{2\mu}\epsilon_n = -\frac{\hbar^2}{2\mu a^2}\frac{Z^2}{n^2} \approx -13.6eV\left(\frac{Z^2}{n^2}\right)$$
$$\psi_{rel} \to \psi_{n,\ell,m} = \frac{y_{n,\ell}(r)}{r}Y_{\ell,m}$$

TABLE I. Some Hydrogen States and Their Properties. $R \equiv \frac{\hbar^2}{2\mu a} \approx 13.6eV$

n	ℓ	m	$n_r = n - \ell - 1$	$state$	$-E_n$
1	0	0	0	$1s$	RZ^2
2	0	0	1	$2s$	$\frac{RZ^2}{4}$
2	1	-1	0	$2p_{-1}$	$\frac{RZ^2}{4}$
2	1	0	0	$2p_0$	$\frac{RZ^2}{4}$
2	1	1	0	$2p_{+1}$	$\frac{RZ^2}{4}$

where $y_{n,\ell} = A_{n,\ell} r^{\ell+1} e^{-\kappa_n r} L^{2\ell+1}_{n-\ell-1}(2\kappa_n r)$ and $\kappa_n = \sqrt{-\epsilon_n} = \frac{Z}{na}$, and L is the associated Laguerre polynomials. n is an integer and it's called the principle quantum number. Lastly, $a \equiv \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \approx 0.53\mathring{A}$ is called the Bohr radius.

There is a degeneracy in the energy since the energies are independent on ℓ, m. For a given ℓ, there are $2\ell + 1$ states. For a given n we have the states $\ell = 0, 1, ..., n-1$. Hence the number of states is

$$\sum_{\ell=0}^{n-1} 2\ell + 1 = n^2 \tag{I.6}$$

Some states are summarized in table I The energy spectrum is shown in figure 2. Probability density is defined as

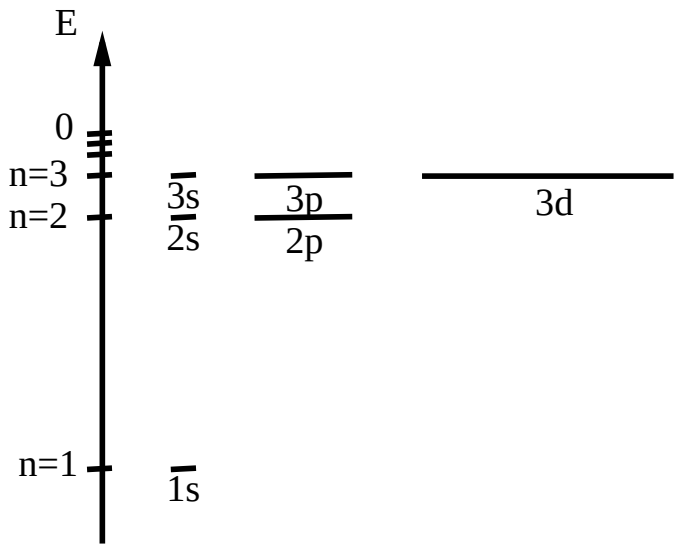

FIG. 2. The energy levels of Hydrogen

$$\rho_{n,\ell,m}(\mathbf{r}) \left|\phi_{n,\ell,m}\right|^2 = R^2_{n,\ell}(r) \left|Y_{n,\ell}(\phi,\theta)\right|^2 \tag{I.7}$$

If

$$\int_{\mathbf{r}} \rho_{n,\ell,m}(\mathbf{r}) dr^3 = \int_0^\infty r^2 R^2_{n,\ell}(r) dr \overbrace{\int \left|Y_{\ell,m}\right|^2 d\Omega}^{1} \tag{I.8}$$

then $\rho_{n,\ell,m}dr^3$ is the probability to find the electron in the interval $[\mathbf{r}, \mathbf{r}+d\mathbf{r}]$. We define the radial probability density by

$$\rho_{n,\ell}(r) = r^2 R_{n,\ell}^2(r) \left|Y_{\ell,m}(\phi,\theta)\right|^2 d\Omega \tag{I.9}$$
$$= r^2 R_{n,\ell}^2(r) \tag{I.10}$$

Lecture 4 - Jan 11, 2012
Next we consider the momentum space representation of the Hydrogen atom. Recall

$$\psi_{n,\ell,m}(\mathbf{r}) = \langle \mathbf{r}|n,\ell m\rangle \tag{I.11}$$

with $H_{rel}\left|n,\ell m\right\rangle = E_n \left|n,\ell,m\right\rangle$. Alternatively we can project our states onto momentum space

$$\psi_{n,\ell,m}(\mathbf{p}) = \langle \mathbf{p}|n,\ell m\rangle \tag{I.12}$$
$$= \langle \mathbf{p}| I \left|n,\ell,m\right\rangle \tag{I.13}$$
$$= \int_{\Re} \langle \mathbf{p}|\mathbf{r}\rangle \langle \mathbf{r}|n,\ell,m\rangle \, d^3r \tag{I.14}$$
$$= \frac{1}{(2\pi\hbar)^{3/2}} \int_{\Re} e^{i\mathbf{p}\cdot\mathbf{r}} \psi_{n,\ell,m}(\mathbf{r}) d^3r \tag{I.15}$$

Use $\mathbf{k} = \frac{\mathbf{p}}{\hbar}$ and

$$e^{-i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-i)^L \overbrace{j_L(kr)}^{Bessel} Y_{LM}(\Omega_k) Y_{LM}^*(\Omega_r) \tag{I.16}$$

where j_L is the spherical Bessel function. Note that here the Ω_r represents normal θ and ϕ while Ω_k represents θ and ϕ in spherical momentum coordinates. Using these relations

$$\psi_{n,\ell,m}(\mathbf{p}) = \frac{4\pi}{(2\pi\hbar)^{3/2}} \sum_{L,M} (-i)^L \int_0^\infty r^2 j_L(kr) R_{n,\ell}(r) dr \overbrace{\int Y_{L,M}^*(\Omega_r) Y_{\ell,m}(\Omega_r) d\Omega_r}^{\delta_{L,\ell}\delta_{M,m}} Y_{L,M}(\Omega_k) \tag{I.17}$$
$$= \frac{4\pi}{(2\pi\hbar)^{3/2}} (-i)^\ell \int_0^\infty r^2 j_\ell(kr) R_{n,\ell}(r) dr Y_{\ell,m}(\Omega_k) \tag{I.18}$$
$$= P_{n,\ell}(p) Y_{\ell,m}(\Omega_p) \tag{I.19}$$

The probability density is

$$\rho_{n,\ell,m}(\mathbf{p}) = \left|\phi_{n,\ell,m}(\mathbf{p})\right|^2 \tag{I.20}$$

While the radial probability density in momentum space is

$$\rho_{n,\ell}(\mathbf{p}) = p^2 \left|\phi_{n,\ell,m}(p)\right|^2 \tag{I.21}$$

Lecture 13th, 2012

D. Assorted Remarks

1. Review Griffith's chapters 4.1-4.3
2. Hydrogen-like ions are also solved (for $Z \geq 2$). Energy scales like $E_n \propto Z^2$.

3. One can also look at a number of exotic systems using the same results as well. e.g. positronium(e^+, e^-), muonium (μ^+, e^-), muonic atom (p, μ^-). When considering these systems the energy change is due to $E_n \propto \mu = \frac{m_1 m_2}{m_1+m_2}$. For more on exotic systems consider C.T. book, volume I

4. There are corrections to be looked at which we will consider in detail later

5. Thus far we have used SI units. In these units we have the Hamiltonian (for Hydrogen)

$$H_{SI} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{I.22}$$

To eliminate some constants we introduce atomic units. To get rid of the constants we

- measure mass in $m_e = 1a.u.$ (atomic unit).
- measure charge in units of $e = 1a.u.$.
- measure angular momentum in units of $\hbar = 1a.u.$
- measure permittivity of $4\pi\epsilon_o = 1a.u.$

In short atomic units, $a.u.$ are defined by $m_e = e = \hbar = 4\pi\epsilon_o = 1$.
As a consequence of this the Hamiltonian in atomic units are given by

$$H_{a.u.} = -\frac{1}{2}\nabla^2 - \frac{1}{r} \tag{I.23}$$

- For length in atomic units we use Bohr's radius, $a_o = \frac{4\pi\epsilon_o\hbar^2}{m_e e^2} = 0.53\mathring{A} = 1a.u.$ (as a consequence of our earlier definitions).
- For energy in atomic units we consider the Hydrogen ground state. $E_{n=1} = -\frac{\hbar^2}{2m_e a_o^2} = -13.6eV = -\frac{1}{2}a.u.$ (as a consequence of earlier definitions). Other units of energy may also be used:

$$1a.u.(\text{of energy}) = 27.2eV = 1\ Hartree = 2\ Rydberg \tag{I.24}$$

- For time in atomic units we use dimensional analysis in SI:

$$\text{time} = \frac{\text{distance}}{\text{speed}} = \frac{\text{distance} \times \text{mass}}{\text{momentum}} = \frac{\text{distance}^2 \times \text{mass}}{\text{angular momentum}} \tag{I.25}$$

Hence we define a unit of time:

$$t_o = \frac{a_o^2 m_e}{\hbar} = 2.4 \times 10^{-17} s = 1a.u. \tag{I.26}$$

The Bohr-like revolution time of the electron around the proton in the Hydrogen ground state is

$$\tau = 2\pi t_o \tag{I.27}$$

- We can now infer a velocity in atomic units:

$$\tau = 2\pi t_o = \frac{2\pi a_o}{v_o} \tag{I.28}$$

$$\Rightarrow v_o = \frac{\hbar}{m_e a_o} = 2.2 \times 10^6 m/s = \frac{1}{137}c = 1a.u. \tag{I.29}$$

- The fine-structure constant is

$$\alpha = \frac{e^2}{4\pi\epsilon_o\hbar c} = \frac{\hbar}{m_e a_o c} = \frac{1}{137} = \left(\frac{1}{c}\right)_{a.u.} \tag{I.30}$$

Lecture 6: January 16th, 2012

II. ATOMS IN ELECTRIC FIELDS: THE STARK EFFECT

From classical electromagnetism we know that a uniform electric field in the z direction with field strength F is

$$\mathbf{E} = F\hat{k} \tag{II.1}$$

The electrostatic potential is

$$\phi(\mathbf{r}) = -\mathbf{E}\cdot\mathbf{r} \tag{II.2}$$
$$= -Fz \tag{II.3}$$
$$\tag{II.4}$$

The potential energy of an electron is

$$W(\mathbf{r}) = -e\phi(\mathbf{r}) \tag{II.5}$$
$$a = Fez \tag{II.6}$$

We need to solve the stationary Schrodinger equation:

$$H\,|\phi_\alpha\rangle = E\,|\phi_\alpha\rangle \tag{II.7}$$

for (in atomic units)

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} + Fz \tag{II.8}$$
$$= \quad H_o \; + \; +W \tag{II.9}$$

To get a better intuition on the problem we sketch the potential energies for $x = y = 0$. This is shown in figure 3. In principle there are no stationary state since "bound" electrons can always tunnel out of the potential well. This is

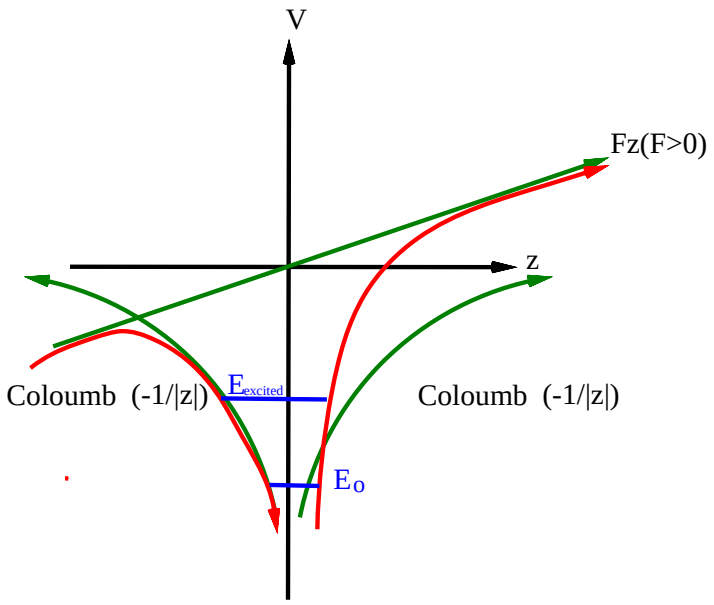

FIG. 3. The potential energies of the Stark effect

called ionization. In practice we only have 'weak' electric fields:

$$F_{lab} \sim 10^4 V/cm$$
$$F_{1s} \sim \frac{e^2}{4\pi\epsilon_o a_o^2} = 5\times 10^9 V/cm$$

Thus in practice the tunnel effect is unimportant for low-lying states. What does happen is the energy levels shift and split.

A. Non-Degenerate perturbation theory (PT)

1. Nondegerenate PT:General formulation
There are different types of perturbation theory.
Consider the Hamiltonian of the form

$$H\left|\phi_\alpha\right\rangle = E_\alpha\left|\phi_\alpha\right\rangle \tag{II.10}$$

where we assume $H = H_o + W$ and $\langle\phi_\alpha|\phi_\beta\rangle = \delta_{\alpha\beta}$. Assume further that

$$H_o\left|\phi_\alpha^o\right\rangle = E_\alpha^{(0)}\left|\phi_\alpha^o\right\rangle \tag{II.11}$$

is known and non degenerate with $\left\langle\phi_\alpha^o|\phi_\beta^o\right\rangle = \delta_{\alpha\beta}$. In other words that ϕ_α forms a basis. If we assume that W is small then

$$W = \lambda w \qquad \lambda \ll 1, \lambda \in \Re \tag{II.12}$$

We can now write

$$H_o + \lambda w\left|\phi_\alpha(\lambda)\right\rangle = E_\alpha(\lambda)\left|\phi_\alpha(\lambda)\right\rangle \tag{II.13}$$

Note that the eigenvalues and eigenvectors should depend on λ since the perturbation changes the system. We can now use Taylor expansions:

$$E_\alpha(\lambda) = E_\alpha^{(0)} + \left.\frac{dE_\alpha}{d\lambda}\right|_{\lambda=0}\lambda + \frac{1}{2}\left.\frac{d^2E_\alpha}{d\lambda}\right|_{\lambda=0}\lambda^2 + ... \tag{II.14}$$

$$\left|\phi_\alpha(\lambda)\right\rangle = \left|\phi_\alpha^0\right\rangle + \left.\frac{d}{d\lambda}\left|\phi_\alpha\right\rangle\right|_{\lambda=0}\lambda + ... \tag{II.15}$$

Consider the derivative of the Schrodinger equation with respect to λ:

$$\frac{d}{d\lambda}\left[\left(H_o + \lambda w - E_\alpha(\lambda)\right)\left|\phi_\alpha(\lambda)\right\rangle\right] = 0 \tag{II.16}$$

$$\left(H_o + \lambda w - E_\alpha(\lambda)\right)\left|\phi'_\alpha(\lambda)\right\rangle + \left(w - E'_\alpha(\lambda)\right)\left|\phi_\alpha(\lambda)\right\rangle = 0 \tag{II.17}$$

$$\tag{II.18}$$

where $\frac{d}{d\lambda}\left|\phi_\alpha(\lambda)\right\rangle \equiv \left|\phi'_\alpha(\lambda)\right\rangle$. Multiplying both sides of the equation by the bra $\langle\phi_\beta(\lambda)|$

$$\left\langle\phi_\beta(\lambda)|H(\lambda) - E_\alpha(\lambda)|\phi'_\beta(\lambda)\right\rangle + \langle\phi_\beta(\lambda)|w - E'_\alpha(\lambda)|\phi(\lambda)\rangle = 0 \tag{II.19}$$

Assume that $\alpha = \beta$

$$\overbrace{\langle\phi_\alpha|\,H(\lambda)}^{\langle\phi_\alpha(\lambda)|E_\alpha(\lambda)} + \langle\phi_\alpha(\lambda)|w|\phi_\alpha(\lambda)\rangle - E'_\alpha(\lambda)\overbrace{\langle\phi_\alpha(\lambda)|\phi_\alpha(\lambda)\rangle}^{1} = 0 \tag{II.20}$$

$$E'_\alpha(\lambda) = \langle\phi_\alpha(\lambda)|\,w\,|\phi_\alpha(\lambda)\rangle \tag{II.21}$$

$$E'_\alpha\left(\lambda = 0\right) = \langle\phi_\alpha^o|\,w\,|\phi_\alpha^o\rangle \tag{II.22}$$

Next we assume that $\alpha \neq \beta$

$$\langle\phi_\beta(\lambda)|\,E_\beta(\lambda) - E_\alpha(\lambda)\,|\phi'_\alpha(\lambda)\rangle + \langle\phi_\beta(\lambda)|\,w\,|\phi_\alpha(\lambda)\rangle = 0 \tag{II.23}$$

$$\left(E_\beta(\lambda) - E_\alpha(\lambda)\right)\langle\psi_\beta(\lambda)|\phi'_\alpha(\lambda)\rangle + \langle\phi_\beta(\lambda)|\,w\,|\phi_\alpha(\lambda)\rangle = 0 \tag{II.24}$$

$$\langle\phi_\beta(\lambda)|\phi'_\alpha(\lambda)\rangle = \frac{\langle\phi_\beta(\lambda)|\,w\,|\phi_\alpha(\lambda)\rangle}{E_\alpha(\lambda) - E_\beta(\lambda)} \tag{II.25}$$

Consider the completeness relation and inserting inside the above equation gives

$$|\phi'_\alpha(\lambda)\rangle = \sum_\beta |\phi_\beta(\lambda)\rangle \langle\phi_\beta(\lambda)|\phi'_\alpha(\lambda)\rangle \tag{II.26}$$

$$\sum_\beta |\phi_\beta(\lambda)\rangle \frac{\langle\phi_\beta(\lambda)| w |\phi_\alpha(\lambda)\rangle}{E_\alpha(\lambda) - E_\beta(\lambda)} \tag{II.27}$$

but this doesn't include $\alpha = \beta$. What about $\langle\phi_\alpha(\lambda)|\phi'_\alpha(\lambda)\rangle$?

$$\frac{d}{d\lambda}\langle\phi_\alpha|\phi_\alpha(\lambda)\rangle = 0 \tag{II.28}$$

$$\langle\phi'_\alpha(\lambda)|\phi_\alpha(\lambda)\rangle + \langle\psi\alpha(\lambda)|\phi'_\alpha(\lambda)\rangle = 0 \tag{II.29}$$

$$\langle\phi_\alpha(\lambda)|\phi'_\alpha(\lambda)\rangle^* + \langle\psi\alpha(\lambda)|\phi'_\alpha(\lambda)\rangle = 0 \tag{II.30}$$

$$2\langle\phi_\alpha(\lambda)|\phi'_\alpha(\lambda)\rangle = 0 \tag{II.31}$$

if $\langle\phi_\alpha|\phi'_\alpha\rangle \in \Re$. However the eigenstate of a Hermitian operator can always be transformed into a basis (by taking linear combinations of them) such that they are real. Hence these overlaps are real. Which means that the overlaps are zero.

$$|\phi'(\lambda)\rangle = \sum_{\beta\neq\alpha} \frac{\langle\phi_\alpha(\lambda)| w |\phi_\alpha(\lambda)\rangle}{E_\alpha(\lambda) - E_\beta(\lambda)} |\phi_\beta(\lambda)\rangle \tag{II.32}$$

and hence

$$|\phi'_\alpha(\lambda = 0)\rangle = \sum_{\beta\neq\alpha} \frac{\left\langle\phi^0_\beta\right| w \left|\phi^0_\alpha\right\rangle}{E^{(0)}_\alpha - E^{(0)}_\beta} \left|\phi^0_\beta\right\rangle \tag{II.33}$$

One can go on to other orders as well

$$\frac{d^2}{d\lambda^2}E_\alpha(\lambda) = \frac{d}{d\lambda}E'_\alpha(\lambda) \tag{II.34}$$

Lecture 7 - January 18th, 2012
We can express the perturbed energies by

$$E_\alpha(\lambda) = E^{(0)}_\alpha + \frac{dE_\alpha}{d\lambda}_{\lambda=0}\lambda + \frac{1}{2}\frac{d^2E}{d\lambda^2}\bigg|_{\lambda=0}\lambda^2 + ... \tag{II.35}$$

$$= E^{(0)}_\alpha + \lambda\left\langle\phi^0_\alpha\right| w \left|\phi^0_\alpha\right\rangle + \lambda^2 \sum_{\beta\neq\alpha} \frac{\left|\left\langle\phi^0_\alpha\right| w \left|\phi^0_\beta\right\rangle\right|^2}{E^{(0)}_\alpha - E^{(0)}_\beta} + ... \tag{II.36}$$

$$= E^{(0)}_\alpha + \left\langle\phi^0_\alpha\right| W \left|\phi^0_\alpha\right\rangle + \sum_{\beta\neq\alpha} \frac{\left|\left\langle\phi^0_\alpha\right| W \left|\phi^0_\beta\right\rangle\right|^2}{E^{(0)}_\alpha - E^{(0)}_\beta} + ... \tag{II.37}$$

$$= E^{(0)}_\alpha + \Delta E^{(1)}_\alpha + \Delta E^{(2)}_\alpha + ... \tag{II.38}$$

$$\tag{II.39}$$

$$|\phi_\alpha(\lambda)\rangle = \left|\phi^0_\alpha\right\rangle + \sum_{\beta\neq\alpha} \frac{\left\langle\phi^0_\alpha\right| W \left|\phi^0_\beta\right\rangle}{E^{(0)}_\alpha - E^{(0)}_\beta} \left|\phi^0_\beta\right\rangle \tag{II.40}$$

1. Comments

(a) These equations are non-defined only when $E_\alpha^{(0)} \neq E_\beta^{(0)} \forall \alpha, \beta$. In other words non-degenerate systems.

(b) Convergence is difficult to check in perturbation theory but consistency checks can be done. One can check that

$$\left| \frac{\left\langle \phi_\alpha^0 \right| W \left| \phi_\beta^0 \right\rangle}{E_\alpha^{(0)} - E_\beta^{(0)}} \right| << 1 \tag{II.41}$$

If this is not fulfilled then it indicates that perturbation theory will likely fail.

(c) Full calculations for the energies, E_α, beyond first order are in general not possible (due to the infinite sum).

(d) Griffith, 6.1; Liboff, B.1

2. Applications to H(1s) in an electric field

$$\phi_{1s}^0(r) = \frac{1}{\sqrt{\pi}} e^{-r} \tag{II.42}$$

$$E_{1s}^0 = -\frac{1}{2} \tag{II.43}$$

$$W = Fz \tag{II.44}$$

We can calculate the first order energy correction:

$$\Delta E_{1s}^{(1)} = \left\langle \phi_{1s}^0 \right| Fz \left| \phi_{1s}^0 \right\rangle \tag{II.45}$$

$$= \frac{F}{\pi} \int e^{-2r} z d^3 r \tag{II.46}$$

$$= \frac{F}{\pi} \int r \cos\theta \sin\theta e^{-2r} r^2 dr d\theta d\phi \tag{II.47}$$

$$= \frac{F}{\pi} \int_0^\infty r^3 e^{-2r} \cancelto{0}{\int_0^\pi \frac{1}{2} \sin 2\theta d\theta} \int d\phi \tag{II.48}$$

$$= 0 \tag{II.49}$$

However this doesn't tell us whether or not the rest of the correction orders are zero or non-zero. To get an idea for the second order correction we check the consistency criterion. Consider the overlap of the contribution of the $2p$ and $1s$ states. Note that this gives the smallest possible denominator (greatest correction).

$$\left| \frac{\left\langle \phi_{1s}^{(0)} \right| Fz \left| \phi_{2p} \right\rangle}{E_{1s}^{(0)} - E_{n=2}^{(0)}} \right| = \left| \frac{\left\langle \phi_{2p0}^{(0)} \right| z \left| \phi_{1s}^0 \right\rangle}{-\frac{1}{2} + \frac{1}{8}} \right| \tag{II.50}$$

$$\approx 2F \tag{II.51}$$

For the Stark effect the $F \approx 10^{-5}$ in atomic units. Hence we expect the second order effect to be small but non zero. Next we estimate the full second order correction

$$\left| \Delta E_{1s}^{(2)} \right| = \left| \sum_{\beta \neq 1s} \frac{\left| \left\langle \phi_\beta^0 \right| Fz \left| \phi_{1s}^0 \right\rangle \right|^2}{E_{1s}^{(0)} - E_\beta^{(0)}} \right| \tag{II.52}$$

To get an upper bound for this estimate we can replace the denominator by it's minimum value which corresponds to $n = 2$.

$$\left| E_{1s}^{(0)} - E_\beta^{(0)} \right| \geq \left| E_{1s}^{(0)} - E_{n=2}^{(0)} \right| = \frac{3}{8} \tag{II.53}$$

Thus we can write

$$\left|\Delta E_{1s}^{(2)}\right| = \frac{8}{3}F^2 \sum_{\beta\neq 1s} \left|\left\langle \phi_\beta^0 \right| z \left|\phi_{1s}^0\right\rangle\right|^2 \tag{II.54}$$

$$= \frac{8}{3}F^2 \sum_{\beta\neq 1s} \left|\left\langle \phi_{1s}^0 \right| z \left|\phi_\beta^0\right\rangle \left\langle \phi_\beta^0 \right| z \left|\phi_{1s}^0\right\rangle\right| \tag{II.55}$$

$$= \frac{8}{3}F^2 \left|\left\langle \phi_{1s}^0 \right| z \sum_{\beta\neq 1s} \left|\phi_\beta^0\right\rangle \left\langle \phi_\beta^0 \right| z \left|\phi_{1s}^0\right\rangle\right| \tag{II.56}$$

but

$$\sum_{\beta\neq 2s} \left|\phi_{\beta^0}\right\rangle \left\langle \phi_\beta^0 \right| = 1 - \left|\phi_{1s}^0\right\rangle \left\langle \phi_{1s}^0 \right| \tag{II.57}$$

Hence

$$\left|\Delta E_{1s}^{(2)}\right| = \frac{8}{3}F^2 \left|\left\langle \phi_{1s}^0 \right| z \left(1 - \left|\phi_{1s}^0\right\rangle \left\langle \phi_{1s}^0 \right|\right) z \left|\phi_{1s}^0\right\rangle\right| \tag{II.58}$$

$$= \frac{8}{3}F^2 \left\{ \left\langle \phi_{1s}^0 \right| z^2 \left|\phi_{1s}^0\right\rangle - \left\langle \phi_{1s}^0 \right| z \left|\phi_{1s}^0\right\rangle \cancelto{0}{\left\langle \phi_{1s}^0 \right| z \left|\phi_{1s}^0\right\rangle} \right\} \tag{II.59}$$

$$= \frac{8F^2}{3} \left\langle \phi_{1s}^0 \right| z^2 \left|\phi_{1s}^0\right\rangle \tag{II.60}$$

It turns out that the integral is easy to do

$$\left|\Delta E_{1s}^{(2)}\right| \leq \frac{8F^2}{3} \tag{II.61}$$

We also know that the energy correction is negative, $\Delta E_{1s}^{(2)} < 0$. One can also calculate the exact result:

$$\Delta E_{1s}^{(2)} = -\frac{9}{4}F^2 \tag{II.62}$$

This is called the "quadratic Stark effect". Since F is small this is a very small correction.

3. Interpretation
Consider a classical charge distribution in an electric field. The classical energy of a charge distribution is given by

$$U = \int \rho(\mathbf{r})\phi(\mathbf{r})d^3r \tag{II.63}$$

$$= -F \int \rho(\mathbf{r}) z d^3r \tag{II.64}$$

$$= -Fp_z \tag{II.65}$$

where $p_z \equiv$ z component of the dipole moment. Connection to QM:

$$\rho(\mathbf{r}) = -\left|\phi_{1s}(\mathbf{r})\right|^2 \tag{II.66}$$

$$p_z = -\int \left|\phi_{1s}(\mathbf{r})\right|^2 z d^3 \tag{II.67}$$

$$= -\left\langle \phi_{1s} \right| z \left|\phi_{1s}\right\rangle \tag{II.68}$$

$$= -\left\langle \phi_{1s}^{(0)} + \lambda\phi_{2s}^{(1)} + ... \right| z \left| \phi_{1s}^{(0)} + \phi_{1s}^{(1)} + ... \right\rangle \tag{II.69}$$

$$= -\left\langle \phi_{1s}^{(0)} \right| z \left|\phi_{1s}^{(0)}\right\rangle - \lambda \left\langle \phi_{1s}^{(1)} \right| z \left|\phi_{1s}^{(0)}\right\rangle - \lambda \left\langle \phi_{1s}^{(0)} \right| z \left|\phi_{1s}^{(1)}\right\rangle + \mathcal{O}(\lambda^2) + ... \tag{II.70}$$

The first term is zero. By choosing real eigenstates we can

$$p_z = -2 \sum_{\beta \neq 1s} \frac{\left\langle \phi_{1s}^{(0)} \right| z \left| \phi_{\beta}^{(0)} \right\rangle \left\langle \phi_{\beta}^{(0)} \right| Fz \left| \phi_{1s}^{(0)} \right\rangle}{E_{1s}^{(0)} - E_{\beta}^{(0)}} \tag{II.71}$$

$$= -2F \sum_{\beta \neq 1s} \frac{\left| \langle \phi_{1s} | z \left| \phi_{\beta}^{(0)} \right\rangle \right|^2}{E_{1s}^{(0)} - E_{\beta}(0)} + \mathcal{O}(\lambda^2) \tag{II.72}$$

$$= -\frac{2}{F} \Delta E_{1s}^{(2)} + \mathcal{O}(\lambda^2) \tag{II.73}$$

$$= \frac{9}{2} F + \mathcal{O}(F^2) \tag{II.74}$$

In summary

(a)

$$\Delta E_{1s}^{(1)} = 0 \iff p_z^{(0)} = -\left\langle \phi_{1s}^{(0)} \right| z \left| \phi_{1s}^{(0)} \right\rangle = 0 \tag{II.75}$$

This is expected since a spherical charge distribution has no static dipole moment (and equivalently for a spherical probability distribution)

(b) $\Delta E_{1s}^{(2)} \neq 0$ reflects that we have a nonzero **induced** dipole moment. This means that we have a nonzero polarizability

$$\alpha_D = \frac{1}{F} p_z^{(1)} = \frac{9}{2} \tag{II.76}$$

B. Degenerate Perturbation Theory

We have a Hamiltonian given by

$$H = H_o + \lambda w \tag{II.77}$$

where

$$H_o \left| \phi_{\alpha,j}^o \right\rangle = E_{\alpha}^{(0)} \left| \phi_{\alpha,j}^o \right\rangle, \qquad j = 1, 2, ..., g_\alpha \tag{II.78}$$

$$H \left| \phi_{\alpha,j} \right\rangle = E_{\alpha,j} \left| \phi_{\alpha,j} \right\rangle \tag{II.79}$$

Here we have assumed that after the perturbation the energy levels are non-degenerate (this is not always the case but it is the case for the Stark effect). The states

$$\left\{ \left| \phi_{\alpha,j}^o \right\rangle, j = 1, 2, ...g_\alpha \right\} \tag{II.80}$$

span the subspace (of Hilbert space) associated with $E_\alpha^{(0)}$. Any linear combination is an eigenstate of H_o for $E_\alpha^{(0)}$. Effect of perturbation theory is shown in figure 4 Note that as the perturbation is increased we encounter a change in state to some linear combination of states.

$$|\phi_{\alpha j}\rangle \to \left| \phi_{\alpha,j}^0 \right\rangle \tag{II.81}$$

We make the ansatz:

$$E_{\alpha,j}(\lambda) = E_\alpha^{(0)} + \lambda E_{\alpha,j}^{(1)} + \lambda^2 E_{\alpha,j}^{(2)} + ... \tag{II.82}$$

$$|\phi_{\alpha,j}(\lambda)\rangle = \left| \phi_{\alpha,j}^0 \right\rangle + \lambda \left| \phi_{\alpha,j}^1 \right\rangle + ... \tag{II.83}$$

Inserting this into the Schrodinger equation:

$$(H_o + \lambda w) \left\{ \left| \phi_{\alpha,j}^0 \right\rangle + \lambda \left| \phi_{\alpha,j}^1 \right\rangle + ... \right\} = \left\{ E_\alpha^{(0)} + \lambda E_{\alpha,j}^{(1)} \right\} \left(\left| \phi_{\alpha,j}^0 \right\rangle + \lambda \left| \phi_{\alpha,j}^{(1)} \right\rangle + ... \right) \tag{II.84}$$

$$H_o \left| \phi_{\alpha,j}^0 \right\rangle + \lambda \left\{ w \left| \phi_{\alpha,j}^0 \right\rangle + H_o \left| \phi_{\alpha,j}^{(1)} \right\rangle \right\} + \mathcal{O}\left(\lambda^2\right) = E_\alpha^{(0)} \left| \phi_{\alpha,j}^0 \right\rangle + \lambda \left\{ E_\alpha^{(1)} \left| \phi_{\alpha,j}^0 \right\rangle + E_\alpha^{(0)} \left| \phi_{\alpha,j}^{(1)} \right\rangle \right\} + \mathcal{O}\left(\lambda^2\right) \tag{II.85}$$

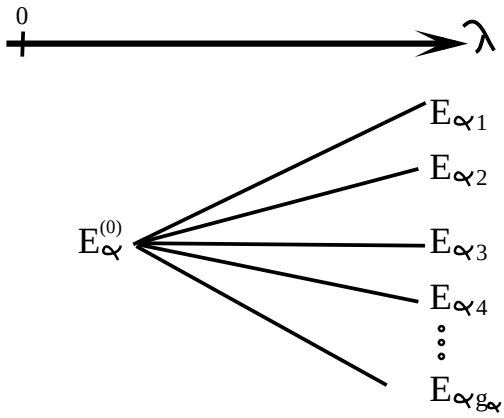

FIG. 4. The effects of perturbation theory: degeneracy is lifted

By equation coefficients we know that

$$\lambda^0: \qquad H_o \left|\phi^o_{\alpha,j}\right\rangle = E^{(0)}_\alpha \left|\phi^0_{\alpha,j}\right\rangle \tag{II.86}$$

$$\lambda^1: \qquad H_o \left|\phi^{(1)}_{\alpha,J}\right\rangle + w\left|\phi_{\alpha,j}(0)\right\rangle - E^{(0)}_\alpha \left|\phi^{(1)}_{\alpha,j}\right\rangle - E^{(1)}_{\alpha,j}\left|\phi_{\alpha,j}\right\rangle = 0 \tag{II.87}$$

The first equation just shows consistency. By adding on a bra to the second equation we get

$$\left\langle\phi^o_{\beta,\ell}\right| H_o - E^{(0)}_\alpha \left|\phi^{(1)}_{\alpha,j}\right\rangle + \left\langle\phi^o_{\beta,\ell}\right| w - E^{(1)}_{\alpha,j}\left|\phi^o_{\alpha,j}\right\rangle = 0 \tag{II.88}$$

$$\left(E^{(0)}_\beta - E^{(0)}_\alpha\right)\left\langle\phi^o_{\beta,\ell}|\phi^{(1)}_{\alpha,j}\right\rangle + \left\langle\phi^o_{\beta,\ell}\right| w\left|\phi^o_{\alpha,j}\right\rangle - E_{\alpha,j}\delta_{\alpha\beta}\delta_{\ell,j} = 0 \tag{II.89}$$

Consider the case of $\alpha = \beta$ and $\ell = j$

$$E^{(1)}_{\alpha,j} = \left\langle\phi^o_{\alpha,j}\right| w\left|\phi^o_{\alpha,j}\right\rangle \tag{II.90}$$

Consider the case of $\alpha = \beta$ and $\ell \neq j$

$$\left\langle\phi^o_{\beta,\ell}\right| w\left|\phi^o_{\alpha,j}\right\rangle = 0 \tag{II.91}$$

This result is a property of the perturbation and it follows due to the ansatz we chose. However this is not true for all perturbations. For example

$$\langle H(2s)|\, z\,|H(2p_o)\rangle \neq 0 \tag{II.92}$$

To ensure that this is always the case we need to diagonalize our perturbations. We modify our ansatz by

$$E_{\alpha,j} = E^{(0)}_\alpha + \lambda E^{(1)}_{\alpha,j} + ... \tag{II.93}$$

$$|\phi_{\alpha,j}\rangle = \left|\tilde{\phi}^o_{\alpha,j}\right\rangle + \lambda\left|\phi^{(1)}_{\alpha,j}\right\rangle + ... \tag{II.94}$$

with $\left|\tilde{\phi}^0_{\alpha,j}\right\rangle = \sum_{k=1}^{g_\alpha} a^\alpha_{k,j}\left|\phi^0_{\alpha,k}\right\rangle$ such that $\left\langle\tilde{\phi}^0_{\alpha,\ell}\right| w\left|\tilde{\phi}^0_{\alpha,j}\right\rangle = 0$.

Insert the two ansatz into the Schrodinger equation, sort, and project on $\left\langle\phi^0_{\alpha,\ell}\right|$

$$\left\langle\phi^0_{\alpha,\ell}\right| w - E^{(1)}_{\alpha,j}\left|\tilde{\phi}^0_{\alpha,j}\right\rangle = 0 \tag{II.95}$$

$$\sum_{k=1}^{g_\alpha}\left\langle\phi^0_{\alpha,\ell}\right| w - E^{(1)}_{\alpha,j}\left|\phi^0_{\alpha,k}\right\rangle a^\alpha_{k,j} = 0; \qquad \ell = 1,2,...g_\alpha \tag{II.96}$$

This can be rewritten in matrix form as

$$\begin{pmatrix} w_{11}^{\alpha}-E_{\alpha,j} & w_{12} & w_{13} & ... \\ w_{21}^{\alpha} & w_{22}^{\alpha}-E_{\alpha,j}^{(1)} & ... & ... \\ \vdots & \vdots & \ddots & \vdots \\ ... & ... & ... & w_{g_\alpha,g_\alpha}-E_{\alpha,j}^{(1)} \end{pmatrix} \begin{pmatrix} a_{1,j}^{\alpha} \\ a_{2,j}^{\alpha} \\ \vdots \\ a_{g_\alpha,j}^{\alpha} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \tag{II.97}$$

The condition for a nontrivial solution is

$$\det(\quad\quad\quad\quad) = 0 \tag{II.98}$$

and has g_α roots $E_{\alpha,j}^{(1)}, j = 1, 2, ...g_\alpha$.

The procedure for using degenerate perturbation theory is as follows

1. Solve "secular" (characteristic) equation and obtain eigenvalues

$$\left\{E_{\alpha,j}^{(1)}, j = 1, ...g_\alpha\right\} \tag{II.99}$$

2. Insert eigenvalues into the matrix equations and obtain the expansion coefficients.

$$\left\{a_{k,j}^{\alpha}; k, j = 1, ...g_\alpha\right\} \tag{II.100}$$

3. One can go further and check that

$$\left\langle \tilde{\phi_{\alpha,\ell}^{0}} \right| w \left|\phi_{\alpha,j}^{0}\right\rangle = E_{\alpha,j}^{(1)}\delta_{\ell,j} \tag{II.101}$$

4. It's possible to go on to calculate wavefunctions and 2nd order energy corrections but it's tedious

C. Effect on excited states: the linear Stark effect

1. Matrix elements

$$w_{\ell,k}^{\alpha} = \left\langle \phi_{\alpha,\ell}^{0} \right| w \left|\phi_{\alpha,k}^{0}\right\rangle \tag{II.102}$$

or for the Hydrogen atom ($w = Fz$):

$$\left\langle \phi_{n\ell m}^{0} \right| z \left|\phi_{n\ell' m'}^{0}\right\rangle \tag{II.103}$$

with $\phi_{n\ell m}(\mathbf{r}) = R_{n\ell}(r)Y_{\ell m}(\Omega), z = r\ \cos\theta\sqrt{\frac{4\pi}{3}}rY_{10}$

$$\left\langle \phi_{n\ell m}^{0} \right| z \left|\phi_{n\ell' m'}^{0}\right\rangle = \sqrt{\frac{4\pi}{3}}\int_0^\infty r^3 R_{n\ell}(r)R_{n\ell'}(r)dr \int Y_{\ell,m}(\Omega)Y_{10}(\Omega)Y_{\ell',m'}(\Omega)d\Omega \tag{II.104}$$

The radial integral is simple enough. We have done similar ones in the past. The angular integral can be done in general using "Wiger-Eckant-Theorem":

$$\sqrt{\frac{4\pi}{2L+1}}\int Y_{\ell m}^{*}(\Omega)Y_{LM}(\Omega)Y_{\ell' m'}(\Omega)d\Omega = (-1)^m\sqrt{(2\ell+1)(2\ell'+1)}\begin{pmatrix} \ell & L & \ell' \\ -m & M & m' \end{pmatrix}\begin{pmatrix} \ell & L & \ell' \\ 0 & 0 & 0 \end{pmatrix} \tag{II.105}$$

with $\overbrace{\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}}^{\text{Wigner's 3j symbols}} = (-1)^{j_1-j_2-m_3}(2j_3+1)^{-1/2} \times \overbrace{\langle j_1, m_1, j_2, m_2 | j_3, -m_3\rangle}^{\text{Clebsch-Gordan Coefficients}}$ For more information on these topics refer to Liboff, chapter 9 or Cohen-T. Chapter 6 and 10.

Lecture 9 - January 25th, 2012 The selection rules can be written in terms of the Wigner 3j symbols.

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \neq \iff \begin{cases} m_1 + m_2 + m_3 = 0 \\ \text{and} \\ |j_1 - j_2| \leq j_3 \leq j_1 + j_2 (\text{triangular condition}) \end{cases} \tag{II.106}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} \neq \iff \begin{cases} \text{triangular condition} \\ \text{and} \\ j_1 + j_2 + j_3 = \text{even} \end{cases} \tag{II.107}$$

Applying these relations to our situation our integral is non zero only if

$$m = m' \tag{II.108}$$

$$\Delta\ell = \ell - \ell' = \pm 1 \tag{II.109}$$

These are sometimes called the electric dipole selection rules (E1) (special case).

2. Linear Stark effect for H($n = 2$)
Consider the degenerate stats

$$\left\{ \phi^o_{2s}, \phi^o_{2p_o}, \phi^o_{2p_{-1}}, \phi^o_{2p_1} \right\} \tag{II.110}$$

We consider the matrix eigenvalue problem:

$$\sum_{\ell', m' (n=2)} \langle \phi^o_{2\ell m} | \, w - E^{(1)}_{n=2} \left| \phi^o_{2n,\ell',m'} \right\rangle a^{n=2}_{\ell,m,\ell',m'} = 0 \tag{II.111}$$

Consider

$$w_{i,j} = \langle \phi^o_{2\ell m} | \, w \left| \phi^o_{2n,\ell' m'} \right\rangle \tag{II.112}$$

If $i = j$ then $w_{i,j} = 0$ because $\Delta\ell = 0$. Further we have a symmetric matrix since the states are real. By using the selection rules we see that

$$w = \begin{pmatrix} 0 & w_{12} & 0 & 0 \\ w_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{II.113}$$

Hence the only potentially nonzero element is the w_{12}. Note that if the radial part is nonzero then the element may still be zero. It's easy to calculate the element explicitly:

$$w_{12} = \langle \phi^o_{2s} | \, z \left| \phi^o_{2p_o} \right\rangle = -3a.u. \tag{II.114}$$

Hence we have the secular equation

$$\begin{vmatrix} -E^{(1)} & w_{12} & 0 & 0 \\ w_{12} & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{vmatrix} = 0 \tag{II.115}$$

This matrix is block diagonal and it's easy to find the equation:

$$\left(E^{(1)} \right)^2 \left\{ \left(E^{(1)} \right)^2 - w^2_{12} \right\} = 0 \tag{II.116}$$

$$E^{(1)} = \{0, 0, w_{12}, -w_{12}\} \tag{II.117}$$

Hence the first order energy corrections are

$$\Delta E^{(1)} = \{0, 0, -3F, 3F\} \tag{II.118}$$

We are left with three lines. Two lines stay degenerate as represented by the zeroes however the originally one line splits into three.
Next we calculate the mixing coefficients of the expansion, $a_{\ell,m,\ell',m'}$. We insert the eigenvalues into our equation.

(a) First consider $E_1^{(1)} = E_2^{(1)} = 0$

$$\begin{pmatrix} 0 & w_{12} & 0 & 0 \\ w_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_{2s} \\ a_{2p_o} \\ a_{2p_{-1}} \\ a_{2p_{+1}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{II.119}$$

This is true only if $a_{2s} = a_{2p_o} = 0$. $a_{2p_{-1}}$ and $a_{2p_{+1}}$ are undetermined. The state that corresponds to this state is any linear combination of the 3rd and 4th states. We choose

$$\left|\tilde{\phi}_{E_1}\right\rangle = \left|\phi^o_{2p_{-1}}\right\rangle \tag{II.120}$$

$$\left|\tilde{\phi}_{E_2}\right\rangle = \left|\phi_{2p_{-1}}\right\rangle \tag{II.121}$$

(b) Next we consider $E_3^{(1)} = +w_{12}$:

$$\begin{pmatrix} -w_{12} & w_{12} & 0 & 0 \\ w_{12} & -w_{12} & 0 & 0 \\ 0 & 0 & -w_{12} & 0 \\ 0 & 0 & 0 & -w_{12} \end{pmatrix} \begin{pmatrix} a_{2s} \\ a_{2p_0} \\ a_{2p_{-1}} \\ a_{2p_{+1}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{II.122}$$

This gives $a_{2p_{-1}} = a_{2p_{+1}} = 0$. The other two equations are

$$-w_{12}a_{2s} + w_{12}a_{2p_o} = 0 \tag{II.123}$$

$$w_{12}a_{2s} - w_{12}a_{2p_o} = 0 \tag{II.124}$$

This requires that $a_{2s} = a_{2p_o}$.

(c) The final eigenvectors for $E_4 = -w_{12}$ are given by $a_{2s} = -a_{2p_0}, a_{2p_{-1}} = a_{2p_{+1}} = 0$.

We have fixed the components of the eigenvectors (the energy corrections). We should fix the normalization of the last two states (we include the previous states for concreteness):

$$\left|\tilde{\phi}_{E_3^{(1)}}\right\rangle = \frac{1}{\sqrt{2}}\left(|\phi^o_{2s}\rangle + \left|\phi^o_{2p_o}\right\rangle\right) \tag{II.125}$$

$$\left|\tilde{\phi}_{E_4^{(1)}}\right\rangle = \frac{1}{\sqrt{2}}\left(|\phi^o_{2s}\rangle - \left|\phi^o_{2p_o}\right\rangle\right) \tag{II.126}$$

$$\left|\tilde{\phi}_{E_1^{(1)}}\right\rangle = \left|\phi^o_{2p_{-1}}\right\rangle \tag{II.127}$$

$$\left|\tilde{\phi}_{E_2^{(1)}}\right\rangle = \left|\phi^o_{2p_{+1}}\right\rangle \tag{II.128}$$

3. Summary and interpretation

(a) Splitting of energy levels is shown in figure

(b) Note that $\left\langle \phi^o_{2\ell,m}\right| z \left|\phi^o_{2\ell m}\right\rangle = 0$ hence the original states $(\phi^o_{2s}, \phi_{2p_0}, \phi^o_{2p_{\pm 1}})$ have no static dipole moment. However the Stark states $\left|\tilde{\phi}_{E_3^{(1)}}\right\rangle, \left|\tilde{\phi}_{E_4^{(1)}}\right\rangle$ do have non zero static dipole moment

$$p^0_{z,3} = -\left\langle \phi_{E_3^{(1)}}\right| z \left|\phi_{E_3^{(1)}}\right\rangle) \tag{II.129}$$

$$= 3a.u. \tag{II.130}$$

$$p_{z,4} = -3a.u. \tag{II.131}$$

(c) The new states are shown in figure 6

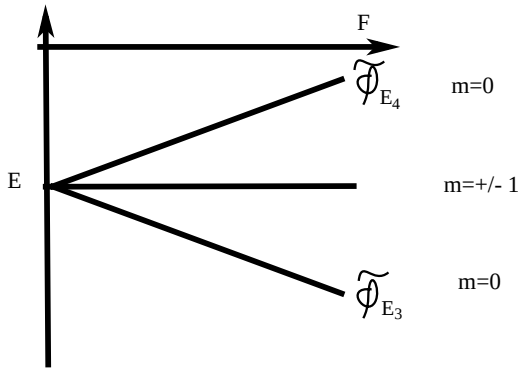

FIG. 5. The linear Stark splitting of energy levels

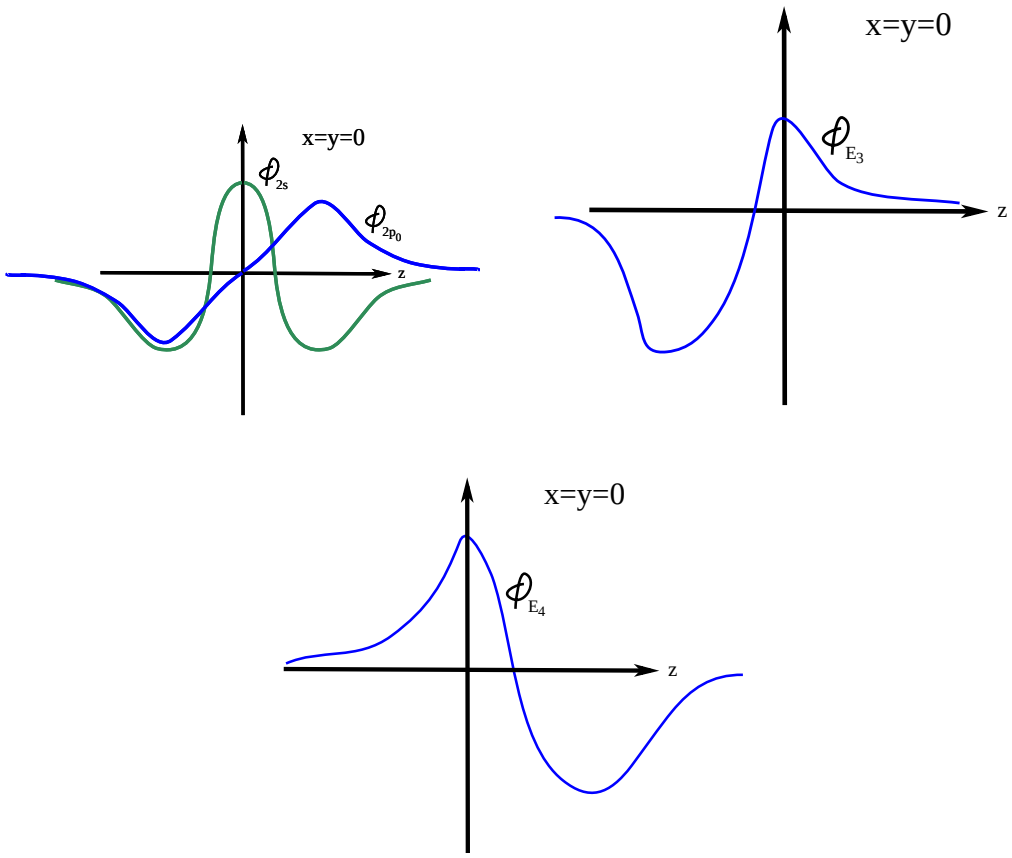

FIG. 6. The Stark states

(d) Note that we still have azimuthal symmetry.

$$[\ell_z, w] = 0 \tag{II.132}$$

Hence m is still a good quantum number

(e) The last question to consider is the effect on the $n = 3$ shell states. We would need to consider the

$$(3s, 3p_o, ..., 3d_{\pm 2}) \tag{II.133}$$

This involves solving the secular equation of a 9×9 matrix.

Lecture 10, January 30th, 2012

(f) To solve the Stark effect on the $n = 3$ states one can decompose the matrix into blocks. To show this method consider the L-shell problem one more time

$$\det \begin{pmatrix} -E^{(1)} & w_{12} & 0 & 0 \\ w_{12} & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{pmatrix} \tag{II.134}$$

The matrix is block diagonal and we have 3 subspaces since the m states don't mix (this can also by seen by $[\ell_z, W] = 0$. For block diagonal matrices of the form:

$$\det \begin{pmatrix} A_1 & 0 & ... \\ 0 & A_2 & \vdots \\ \vdots & ... & \ddots \end{pmatrix} = \det A_1 \det A_2 ... \tag{II.135}$$

$\det A = 0 \iff \det A_i = 0; \qquad \forall i$. For this case:

$$m = \pm 1 \qquad \det\left(-E^{(1)}\right) = 0 \iff E_1^{(1)} = E_1^{(1)} = 0 \tag{II.136}$$

$$m = 0 \qquad \det \begin{pmatrix} -E^{(1)} & w_{12} \\ w_{12} & -E^{(1)} \end{pmatrix} = 0 \iff \left(E^{(1)}\right)^2 - w_{12}^2 = 0 \tag{II.137}$$

In the $n = 3$ shell we can subdivide the states by

$$m = \begin{cases} 0 & 3s, 3p_o, 3d_o \\ -1 & 3p_{-1}, 3d_{-1} \\ 1 & 3p_1, 3d_1 \\ -2 & 3d_{-2} \\ 2 & 3d_2 \end{cases} \tag{II.138}$$

III. INTERACTION OF ATOMS WITH RADIATION

Consider the scheme of Quantum Theory shown in figure 7.

A. The semiclassical Hamiltonian

1. Consider a classical particle with charge q in an electromagnetic field. The force acting on the particle is simply the Lorentzian force.

$$\mathbf{F}_L = q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right) \tag{III.1}$$

Introduce the electromagnetic potentials, A is the vector potential and ϕ is the scalar potential

$$\mathbf{E} = -\nabla\phi - \frac{\partial}{\partial t}\mathbf{A} \tag{III.2}$$

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{III.3}$$

Inserting these equations gives

$$\mathbf{F}_L = q\left(-\nabla\phi - \frac{\partial \mathbf{A}}{\partial t} + \mathbf{v} \times (\nabla \times \mathbf{A})\right) \tag{III.4}$$

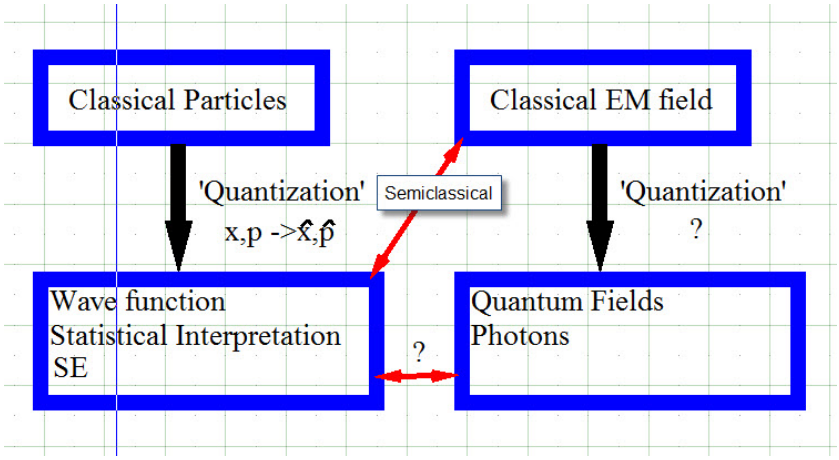

FIG. 7. Scheme of Quantum Theory

Define a generalized potential energy,

$$U = q\left(\phi - \mathbf{A}\cdot\mathbf{v}\right) \tag{III.5}$$

The Lagrangian is given by

$$L = T - U \tag{III.6}$$

$$= \frac{m}{2}v^2 - q\phi + q\mathbf{v}\cdot\mathbf{A} \tag{III.7}$$

The Lagrangian equations of motion

$$\frac{\partial}{\partial t}\frac{\partial L}{\partial v_i} - \frac{\partial L}{\partial x_i} = 0 \iff m\mathbf{a} = \mathbf{F}_L \tag{III.8}$$

Hence the generalize potential energy yields the correct force. The Hamiltonian can now easily be extracted

$$H = \mathbf{p}\cdot\mathbf{v} - L \tag{III.9}$$

Note that

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = m\mathbf{v} + q\mathbf{A} \tag{III.10}$$

is the canonical momentum. We can rearrange this equation for velocity:

$$\mathbf{v} = \frac{1}{m}\left(\mathbf{p} - q\mathbf{A}\right) \tag{III.11}$$

We can now rewrite our Hamiltonian without $\mathbf{v}$ (we need to eliminate this variable to have a proper Hamiltonian):

$$H = \frac{\mathbf{p}}{m}\cdot\left(\mathbf{p} - q\mathbf{A}\right) - \frac{1}{2m}\left(\mathbf{p} - q\mathbf{A}\right)^2 + q\phi - \frac{q}{m}\left(\mathbf{p} - q\mathbf{A}\right)\cdot\mathbf{A} \tag{III.12}$$

$$= \frac{1}{2m}\left(\mathbf{p} - q\mathbf{A}\right)^2 + q\phi \tag{III.13}$$

2. Next consider the quantum mechanical Hamiltonian for an electron.

   - To consider bound states we add another scalar potential, V due to a nucleus.
   - The charge for the electron is $q = -e$

- Next we perform quantization ($\mathbf{p} \to \hat{\mathbf{p}} = \frac{\hbar}{i}\nabla$). Hence

$$H = \frac{1}{2m}\left(\hat{\mathbf{p}} + e\mathbf{A}\right)^2 - e\phi + V \tag{III.14}$$

$$H\psi(\mathbf{r},t) = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla + e\mathbf{A}(\mathbf{r},t)\right)\left(\frac{\hbar}{i}\nabla + e\mathbf{A}(\mathbf{r},t)\right)\phi(\mathbf{r},t) - e\phi(\mathbf{r})\psi(\mathbf{r},t) + V(\mathbf{r})\phi(\mathbf{r},t) \tag{III.15}$$

$$= \frac{1}{2m}\left(-\hbar^2\nabla^2\phi + \frac{\hbar e}{i}\nabla(\mathbf{A}\psi) + \frac{\hbar e}{i}\mathbf{A}\nabla\psi + e^2\mathbf{A}^2\psi\right) - e\phi\psi + V\psi \tag{III.16}$$

$$= \overbrace{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)}^{H_o}\psi + \frac{e\hbar}{mi}\mathbf{A}\cdot\nabla\psi + \left(\frac{e\hbar}{2mi}\nabla\cdot\mathbf{A}\right)\psi + \left(\frac{e^2}{2m}\mathbf{A}^2 - e\phi\right)\psi \tag{III.17}$$

$$= H_o + \overbrace{\frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e}{2m}\mathbf{p}\cdot\mathbf{A} + \frac{e^2}{2m}\mathbf{A}^2 - e\phi}^{W(t)} \tag{III.18}$$

where H_o is the Hydrogen Hamiltonian without electromagnetism and $W(t)$ is the time dependent perturbation.

- Assume for the following the electromagnetic is a free electromagnetic field which is characterized by no charges and no currents, $\rho = 0$; $\mathbf{J} = 0$. Here its convenient to choose the Coloumb gauge, $\nabla\cdot\mathbf{A} = 0$. This is useful because then we arrive at the equations

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = 0 \tag{III.19}$$

and

$$\phi = 0 \tag{III.20}$$

Note this doesn't mean that there is no electric field (since $\mathbf{E} = -\frac{\partial\mathbf{A}}{\partial t}$). Consider the monochromatic solution to the wave equation, a plane wave.

$$\mathbf{A}(\mathbf{r},t) = \hat{\Pi}\,|A_c|\cos(\mathbf{k}\cdot\mathbf{r} - \omega t + \alpha) \tag{III.21}$$

One can perform two checks. Firstly

$$\nabla\cdot\mathbf{A} = -\hat{\Pi}\cdot\mathbf{k}\,|A_c|\sin(\mathbf{k}\cdot\mathbf{r} - \omega t + \alpha) = 0 \tag{III.22}$$

Hence $\hat{\Pi} \perp \mathbf{k}$. Thus the vector potential is a transverse wave. The second check is the wave equation

$$\nabla^2\mathbf{A} = \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} \tag{III.23}$$

$$-k^2\mathbf{A} = -\frac{\omega^2}{c^2}\mathbf{A} \tag{III.24}$$

Thus we see that this is a solution given that $k = \frac{\omega}{c}$. Going back to the perturbation we have (due to the Coloumb gauge $\mathbf{p}\cdot\mathbf{A}$ one term disappears and another disappears because we don't have a scalar potential)

$$\boxed{W(t) = \frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2m}\mathbf{A}^2} \tag{III.25}$$

Assume that $\mathbf{A}$ is weak. If this is the case we can neglect the second term:

$$\boxed{W(t) \approx \frac{e}{m}\mathbf{A}\cdot\mathbf{p}} \tag{III.26}$$

Lecture 11 - February 1st, 2012
Test 1 is up to (and including) last lecture. In other words up to this point.

We can write the Hamiltonian due to an external field by

$$H = H_o + W(t) \tag{III.27}$$

where

$$H_o = \frac{p^2}{2m} + V(\mathbf{r}); \qquad W(t) = \frac{e}{m}\mathbf{A}(\mathbf{r},t)\cdot\mathbf{p} + \frac{e^2}{2m}\mathbf{A}^2(\mathbf{r},t) \tag{III.28}$$

Note that since we have a time dependent Hamiltonian we cannot use the stationary Schrodinger equation. Thus we use time dependent perturbation theory.

B. Time-Dependent Perturbation Theory

1. *General Formulation*

Consider a perturbation $W(t) = \lambda w(t)$ on a Hamiltonian which is stationary.

$$H(t) = H_o + \lambda w(t) \tag{III.29}$$

The goal is to solve the time-dependent Schrodinger equation:

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle \tag{III.30}$$

The SE is a initial value problem. We assume we know the state at some time. Assume for $t \geq t_o$ that

$$W(t) = 0; \qquad |\phi(t_o)\rangle = |\phi_o\rangle \tag{III.31}$$

where $H_o|\psi_j\rangle = \epsilon_j|\psi_j\rangle$ $(j = 0, 1, ...)$. We assume that W is switched on at t_o and we look into how the system develops in time.

Define $|\psi_j(t)\rangle = e^{-i\epsilon_j t/\hbar}|\phi_j\rangle$ then inserting into the SE (before perturbation) by

$$i\hbar\frac{\partial}{\partial t}|\psi_j(t)\rangle = i\hbar\left(\frac{\partial}{\partial t}e^{-i\epsilon_j t/\hbar}|\phi_j\rangle\right) \tag{III.32}$$

$$= \epsilon_j e^{-i\epsilon_j t/\hbar}|\phi_j\rangle \tag{III.33}$$

$$= H_o|\psi_j\rangle \tag{III.34}$$

Hence if $|\phi\rangle$ solves the SE then so does $|\psi\rangle$. We denote the $|\psi(t)\rangle$ by the solution after the perturbation has been turned on. We expand these states as

$$|\psi(t)\rangle = \sum_j c_j|\psi_j(t)\rangle \tag{III.35}$$

and insert into the time dependent SE

$$i\hbar\frac{\partial}{\partial t}\left(\sum_j c_j(t)|\psi_j(t)\rangle\right) = (H_o + W(t))\sum_j c_j(t)|\psi_j(t)\rangle \tag{III.36}$$

$$\sum_j (i\hbar\dot{c}_j(t) + \epsilon_j)e^{-i\epsilon_j t/\hbar}|\phi_j\rangle = (H_o + W(t))\sum_j c_j(t)e^{-i\epsilon_j t/\hbar}|\phi_j(t)\rangle \tag{III.37}$$

$$\tag{III.38}$$

We project these states onto the state $\langle\psi_k(t)| = \langle\phi_k| e^{i\epsilon_k t/\hbar}$:

$$\sum_j e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}\overbrace{\langle\phi_k|\phi_j\rangle}^{\delta_{j,k}}(i\hbar\dot{c}_j(t)+c_j\epsilon_j) = \sum_j e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}c_j(t)\langle\phi_k| H_o + \lambda w(t)|\phi_j\rangle \tag{III.39}$$

$$i\hbar\dot{c}_k(t) + \cancel{c_k(t)\epsilon_k} = \cancel{c_k(t)\epsilon_k} + \sum_j e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}c_j(t)\langle\phi_k|\lambda w(t)|\phi_j\rangle \tag{III.40}$$

$$\boxed{i\hbar\dot{c}_k = \sum_j e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}c_j(t)\lambda w_{kj}} \tag{III.41}$$

where $w_{kj} \equiv \langle\phi_k| w |\phi_j\rangle$. Note that thus far we have not made any approximations. These are sometimes called coupled-channel equations. If we assume that $W(t > t_f) = 0$ then for $t > t_f$ the matrix elements on the right side are 0 and hence

$$\dot{c}_k(t > t_f) = 0 \tag{III.42}$$

and the states are constant. The probabilities for transitions $|\phi_0\rangle \to \langle\phi_k\rangle$ (equivalently $|\psi_0\rangle \to |\psi_k\rangle$). The probability for transition to state k is

$$p_k = |c_k|^2_{t>t_f} = |\langle\psi_k|\psi\rangle|^2_{t>t_f} = |\langle\phi_k|\psi\rangle|^2_{t>t_f} \tag{III.43}$$

To check the answer one can check that $\sum_k p_k = 1$. This turns out to be true. We finally introduce perturbation theory. Notice that the only thing we can expand is the expansion coefficients. We use a power series expansion

$$c_k(t) = c_k^{(0)}(t) + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)} + ... \tag{III.44}$$

We insert this into the coupled channel equations

$$i\hbar\left\{\dot{c}_k^{(1)} + \lambda\dot{c}_k^{(1)} + ...\right\} = \lambda\sum_j e^{\frac{i}{\hbar}w_{kj}(\epsilon_k-\epsilon_j)t}\left\{c_j^{(0)} + \lambda c_j^{(1)} + ...\right\} \tag{III.45}$$

consider zeroth order, λ^0:

$$i\hbar\dot{c}_k^{(0)} = 0 \tag{III.46}$$

Next consider first order

$$i\hbar\dot{c}_k^{(1)} = \sum_j c_j^{(0)}e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}w_{kj} \tag{III.47}$$

Lastly consider second order

$$i\hbar\dot{c}_k^{(2)} = \sum_j c_j^{(1)}e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}w_{kj} \tag{III.48}$$

Notice that you can in principle get a solution for all orders using this method. Once you have first order you can get second order and once you have second order you can get third order etc. In other words we solve these successively. For first order

$$\boxed{c_k^{(0)}(t) = const = \delta_{k,0}} \tag{III.49}$$

Our initial condition was the ground state. Hence the coefficients are zero except the ground state coefficient. In zeroth order we just stay in the ground (initial) state. Input this into higher orders:

$$i\hbar\dot{c}_k^{(1)} = \sum_j \delta_{j,0}e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}w_{k,j} \tag{III.50}$$

$$= e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_0)t}\langle\phi| w(t)|\phi_0\rangle \tag{III.51}$$

$$c_k^{(1)}(t) - \cancel{c_k^{(1)}(t_0)}^{\,0} = -\frac{i}{\hbar}\int_{t_o}^{t} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_0)t'}\langle\phi_k| w(t')|\phi_j\rangle\, dt' \tag{III.52}$$

$$\boxed{c_k^{(1)}(t) = -\frac{i}{\hbar}\int_{t_o}^{t} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_0)t'}\langle\phi_k| w(t')|\phi_j\rangle\, dt'} \tag{III.53}$$

where $c_k^{(1)}(t_0) = 0$ since our initial conditions say that the system is in the ground state. In second order we have

$$i\hbar\dot{c}_k^{(2)} = \sum_j c_j^{(1)} e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t} w_{k,j} \tag{III.54}$$

$$i\hbar c_k^{(2)} = -\frac{i}{\hbar}\sum_j \int_{t_o}^{t'} e^{\frac{i}{\hbar}(\epsilon_j - \epsilon_0)t''} \langle\phi_j| w_j(t'') |\phi_0\rangle dt'' e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t} \langle\phi_k| w(t) |\phi_j\rangle \tag{III.55}$$

$$\boxed{c_k^{(2)}(t) = -\frac{1}{\hbar^2}\sum_j \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t'} e^{\frac{i}{\hbar}(\epsilon_j - \epsilon_0)t''} w_{k,j}(t') w_{j,0}(t'')} \tag{III.56}$$

Lecture 12 - February 6th, 2012

2. *Comments*

1. 'Exact' calculations beyond 1^{st} order are in general impossible (due to infinite sums)

2. Practical calculations of second order often rely on the 'closure approximation '. Notice that the second order calculation is not an infinite sum if the ϵ_j are constant (you can use the completeness relation formed from $w_{k,j}(t')w_{j,0}(t'') = \langle\phi_k| w(t') |\phi_j\rangle \langle\phi_j| w(t'') |\phi_0\rangle$). Thus one can approximate that

   $$\epsilon_j \to \bar{\epsilon} \tag{III.57}$$

   where $\bar{\epsilon}$ is an average energy value. This produces a second order correction of

   $$c_k^{(2)}(t) = -\frac{1}{\hbar^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{\frac{i}{\hbar}(\epsilon_k - \bar{\epsilon})t'} e^{\frac{i}{\hbar}(\bar{\epsilon} - \epsilon_0)t''} \langle\phi_k| w(t')w(t'') |\phi_0\rangle \tag{III.58}$$

3. The interpretation of the results are as follows. The first order result is called a direct transition since

   $$|\phi_0(t_0)\rangle \xrightarrow{w} |\phi_k(t)\rangle \tag{III.59}$$

   One the contrary for second order we have

   $$|\phi_0\rangle \xrightarrow{w} |\phi_j\rangle \xrightarrow{w} |\phi_k\rangle \tag{III.60}$$

   We call this a transition through a 'virtual' state (two steps). The $|\phi_j\rangle$ state serves as an intermediate step. We can see this pictorially as shown in figure 8.

3. *Discussion of 1^{st} order result*

$$c_k(t) \approx c_k^{(0)} + \lambda c_k^{(1)} \tag{III.61}$$

$$= \delta_{k0} - \frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{k0}t'} W_{k0}(t')dt' \tag{III.62}$$

where $\omega_{k0} \equiv \frac{\epsilon_k - \epsilon_0}{\hbar}$ and $W_{k0}(t) = \langle\phi_k| W(t) |\phi_0\rangle = \lambda \langle\phi_k| w(t) |\phi_0\rangle$ is called a transition matrix element. The probability to transition to state $k \neq 0$ (from the initial, ground state) is

$$P_{0\to k}^{1st-order} = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} e^{iw_{k0}t'} W_{k0}(t')dt'\right|^2 \tag{III.63}$$

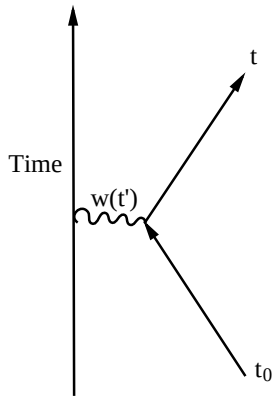

FIG. 8. Diagram of first order perturbation theory

For $k = 0$ we have an elastic collision (the particle stays in the initial state)

$$P_{0\to 0}^{1st-order} = \left| c_0^{(0)} + \lambda c_0^{(1)} + \lambda^2 c_0^{(2)} + ... \right| \tag{III.64}$$

$$\approx 1 + \lambda \left(c_0^{(1)} + c_0^{(1)*} \right) + \lambda^2 \left(\left| c_0^{(1)} \right|^2 + c_0^{(2)} + c_0^{(2)*} \right) \tag{III.65}$$

$$= 1 - \sum_{k\neq 0} P_{0\to k}^{1st-order} \tag{III.66}$$

This shows norm conservation even in first order.

4. Example: Slowly varying perturbation

1. Slowly varying perturbation. An example of such a slowly varying perturbation is shown in figure 9. for $k \neq 0$

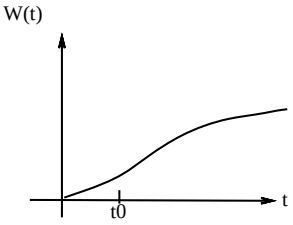

FIG. 9. Slowly varying perturbation

we have

$$c_k(t) = -\frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{k0}t'} W_{k0}(t')dt' \tag{III.67}$$

$$= -\frac{i}{\hbar}\left\{ \frac{1}{i\omega_{k0}} e^{i\omega_{k0}t'} W_{k0}(t')\Big|_{t0}^{t} - \frac{1}{i\omega_{k0}}\int_{t_0}^{t} e^{i\omega_{k0}t'} \overbrace{\dot{W}_{k0}(t')}^{\approx 0} dt' \right\} \tag{III.68}$$

$$\approx -\frac{1}{\hbar\omega_{k0}} W_{k0}(t) e^{i\omega_{k0}t} \tag{III.69}$$

$$= -\frac{\langle\phi_k| W(t) |\phi_0\rangle}{\epsilon_k - \epsilon_0} e^{i\omega_{k0}t} \tag{III.70}$$

$$p_{0\to k} = |c_k|^2 \tag{III.71}$$

$$= \frac{|\langle\phi_k| W(t) |\phi_0\rangle|^2}{(\epsilon_k - \epsilon_0)^2} \tag{III.72}$$

$$= 0(\text{if for } t > t_f,\, W(t_f) = const) \tag{III.73}$$

This only works for a non-degenerate initial state (due to the energies in the denominator).

5. *Solution of TDSE up to 1st order*

Consider the solution to the TDSE and insert in the 1st order coefficient

$$|\psi(t)\rangle = \sum_k c_k(t) e^{-\frac{i}{\hbar}\epsilon_k t} |\phi_k\rangle \tag{III.74}$$

$$= c_0(t) e^{-\frac{i}{\hbar}\epsilon_0 t} |\phi_0\rangle + \sum_{k\neq 0} \frac{\langle\phi_k| W(t) |\phi_0\rangle}{\epsilon_0 - \epsilon_k} e^{-\frac{i}{\hbar}\epsilon_k t} |\phi_k\rangle \tag{III.75}$$

Since we are using perturbation theory we require that $c_0 \approx 1$ in this case we have

$$|\psi(t)\rangle \approx \left(\overbrace{|\phi_0\rangle + \sum_{k\neq 0} \frac{\langle\phi_k| W |\phi_0\rangle}{\epsilon_0 \epsilon_k} |\phi_k\rangle}^{|\tilde{\phi}_0(t)\rangle} \right) e^{-\frac{i}{\hbar}\epsilon_0 t} \tag{III.76}$$

$\left|\tilde{\phi}_0(t)\right\rangle$ describes state of the system at time t up to 1st order corresponding to perturbed energy eigenvalue

$$\epsilon_0^{(1)}(t) = \epsilon_0 + \langle\phi_0| W(t) |\phi_0\rangle \tag{III.77}$$

The system remains in the ground state of the total (instantaneous) Hamiltonian, $H(t)$, at all times. This is often called an adiabatic situation. The approximation of neglecting the time derivative of W is called the adiabatic approximation.

6. *Comments*

1. This argument can be generalized to strong perturbations (all orders). If perturbation varies slowly with time the system is found in an eigenstate of the total Hamiltonian $H(t) = H_0 + W(t)$ at all times ("adiabatic approximation"). Ref: D.Bohm, Quantum Theory, Chapter 20

2. Realizations of this formulism can found in

   - Slow atomic collisions

- Stern-Gerlach experiment

Lecture 13, Feb 13th, 2012

7. *Example: Sudden Perturbation*

Consider the following perturbation:

$$W(t) = \begin{cases} 0 & t \leq t_0 \\ W & t > t_0 \end{cases} \tag{III.78}$$

The first order amplitude is

$$c_k(t) = -\frac{i}{\hbar}\int_0^t e^{i(\omega-\omega_{k0})t} W_{k0}(t')dt' \tag{III.79}$$

where $\omega_{k0} = \frac{\epsilon_k - \epsilon_0}{\hbar}$ and $W_{k0} = \langle k| W(t) |0\rangle$. Thus

$$c_k(t) = -\frac{i}{\hbar} W_{k0} \int e^{i\omega_{k0}} dt' \tag{III.80}$$

$$= -\frac{W_{k0}}{\hbar\omega_{k0}} \left(e^{i\omega_{k0}t} - 1\right) \tag{III.81}$$

$$P_{0\to k}(t) = |c_k(t)|^2 = \frac{|W_{k0}|^2}{\hbar^2}\omega_{k0} \{2 - 2\cos\omega_{k0}t\} \tag{III.82}$$

$$= \frac{4|W_{k0}|^2}{\hbar^2} f(t, \omega_{k0}) \tag{III.83}$$

where $f(t, \omega_{k0}) = \left(\frac{\sin^2\left(\frac{\omega_{k0}t}{2}\right)}{\omega_{k0}^2}\right)$. The function f is independent of the particular perturbation. The perturbation is shown in figure 10. Note that noticeable transitions only occur within $\Delta\Omega = \frac{2\pi}{t}$. This corresponds to an energy range

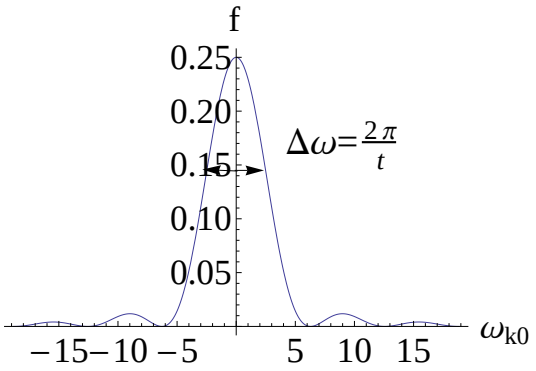

FIG. 10. The function f which determines the probability of transition

$\Delta E = \frac{2\pi\hbar}{t}$.

8. *Example:Periodic perturbation*

Consider the potential below:

$$W(t) = \begin{cases} 0 & t \leq t_0 = 0 \\ Be^{i\omega t} + B^\dagger e^{-i\omega t} & t > t_0 = 0 \end{cases} \tag{III.84}$$

Note that $W = W^\dagger$. We consider the first order amplitude for a transition from state $|i\rangle$ to $|f\rangle$. The amplitude is

$$c_{fi}(t) = -\frac{i}{\hbar}\int_0^t W_{fi}(t')e^{i\omega_{fi}t'}dt' \tag{III.85}$$

where $\omega_{fi} = \frac{\epsilon_f - \epsilon_i}{\hbar}$.

$$c_{fi}(t) = -\frac{i}{\hbar}\left\{\langle f|\, B\,|i\rangle \int_0^t e^{i\left(\omega_{fi}+\omega t' dt'\right)} + \langle f|\, B^\dagger\,|i\rangle \int_0^t e^{i(\omega_{fi}-\omega)t'}dt'\right\} \tag{III.86}$$

we now define $B_{fi} \equiv \langle f|\, B\,|i\rangle$ and note that $\langle f|\, B^\dagger\,|i\rangle = \langle i|\, B\,|f\rangle = B^*_{if}$. We can now write

$$c_{fi}(t) = -\left\{\frac{B_{fi}}{\hbar\left(\omega_{fi}+\omega\right)}\left(e^{i(\omega_{fi}+\omega)t}-1\right) + \frac{B^*_{if}}{\hbar\left(\omega_{fi}-\omega\right)}\left(e^{i(\omega_{fi}-\omega)t}-1\right)\right\} \tag{III.87}$$

$$P_{i\to f}(t) = |c_{fi}(t)|^2 \tag{III.88}$$

$$= \frac{|B_{fi}|^2}{\hbar^2\left(\omega_{fi}+\omega\right)^2}\left|e^{i(\omega_{fi}+\omega)t}-1\right|^2 + \frac{|B_{if}|^2}{\hbar^2\left(\omega_{fi}-\omega\right)}\left|e^{i(\omega_{fi}-\omega)t}-1\right|^2 + \text{cross terms} \tag{III.89}$$

The function is plotted in figure 11.

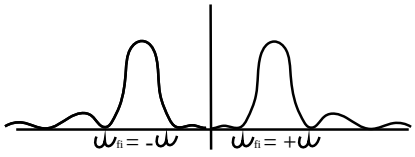

FIG. 11. The probability of a transition with oscillatory perturbation

We summarize the observations below

- Consider the case of $\omega_{fi} = -\omega \iff \epsilon_f = \epsilon_i - \hbar\omega$. Hence we can only have a noticeable transition if the applied frequency corresponds to the difference between energy of the two energy levels is $\hbar\omega$. This is called stimulated emission since this required a perturbation to emit energy. This is also called resonance de-excitation.
- For the second peak we have $\omega_{fi} = \omega \iff \epsilon_f = \epsilon_i - \hbar\omega$. Hence we can only have a noticeable transition if we have absorption of $\hbar\omega$. This is also called resonant excitation.

Now we consider the connection to atom-radiation interaction. We found earlier that

$$W(t) = \frac{e}{m}\mathbf{A}(\mathbf{r},t)\cdot\mathbf{p} \tag{III.90}$$

with

$$\mathbf{A}(\mathbf{r},t) = \hat{\Pi}\,|A_0|\cos\left(\mathbf{k}\cdot\mathbf{r}-\omega t+\alpha\right) \tag{III.91}$$

$$= \frac{\hat{\Pi}}{2}\left\{A_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega)t} + A_0^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right\} \tag{III.92}$$

where $A_0 \equiv |A_0|\, e^{i\alpha}$. Hence we have

$$W(t) = \frac{e}{2m}\left\{A_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\hat{\Pi}\cdot\mathbf{p} + A_0^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right\} \tag{III.93}$$

Recall that we had $W(t) = B^\dagger e^{-\omega t} + Be^{i\omega t}$ thus we an make the identification

$$B = \frac{e}{2m}A_0^* e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\Pi}\cdot\mathbf{p}$$

We need to check the criterion to avoid the overlap of resonances (neglect cross terms) this requires

$$\Delta\omega = \frac{2\pi}{t} \ll \omega \iff t \gg \frac{2\pi}{\omega} \tag{III.94}$$

Now we check the validity of first order time dependent perturbation theory.

$$P_{i\to f} = \frac{4\left|B_{fi}\right|^2}{\hbar^2} \overbrace{f\left(t, \omega_{ji} \pm \omega = 0\right)}^{t^2/4} = \frac{\left|B_{fi}\right|^2}{\hbar^2} t^2 \tag{III.95}$$

To be valid this must be much less then 1. I.e. $\frac{|B_{fi}|^2}{\hbar^2} t^2 \ll 1$. We combine these results to say that

$$\frac{2\pi}{\omega} = \frac{2\pi}{|\omega_{fi}|} \ll \frac{\hbar}{|B_{fi}|} \tag{III.96}$$

This is true only if

$$|\epsilon_f - \epsilon_i| \gg |B_{fi}| \tag{III.97}$$

Hence the matrix element which causes the transition must be small when compared to the energy difference between the states.

Lecture 14th, February 15th, 2012

C. Photoionization

1. *Transitions into the continuum: Fermi's golden rule (FGR)*

Suppose that we don't transition to a single state but into a band of states as shown in figure **??** We need to replace

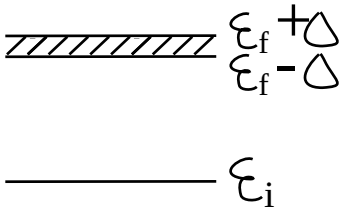

FIG. 12. Jumping into an energy band

$$p_{i\to f} = \left|\langle\phi_f|\psi(t(f))\rangle\right|^2 \tag{III.98}$$

by

$$P_{i\to f} = \int_{\epsilon_f - \Delta\epsilon}^{\epsilon_f + \Delta} p_{i\to f}\left(\epsilon_{f'}\right)\rho\left(\epsilon_{f'}\right) d\epsilon_f \tag{III.99}$$

with $\rho(\epsilon_{f'})$ is the density of states. Free particle continuum states are

$$\phi_f(\mathbf{r}) = \langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \tag{III.100}$$

$$\langle \mathbf{p}|\mathbf{p}'\rangle = \int_r \langle \mathbf{p}|\mathbf{r}\rangle \langle \mathbf{r}|\mathbf{p}'\rangle \, d^3r \tag{III.101}$$

$$= \frac{1}{(2\pi\hbar)^3} \int e^{\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})} d^3r \tag{III.102}$$

$$= \delta(\mathbf{p}-\mathbf{p}') \tag{III.103}$$

Consider

$$1 = \langle \psi|\psi\rangle \tag{III.104}$$

$$= \int \langle \psi|\mathbf{p}\rangle \langle \mathbf{p}|\psi\rangle \, d^3p \tag{III.105}$$

$$= \int |\phi(\mathbf{p})|^2 \, d^3p \tag{III.106}$$

We can transfer this integral to an energy integral using $\epsilon_f = \frac{p^2}{2m}$. We can use

$$d^3p = p^2 dp d\Omega_p = p^2 \frac{dp}{d\epsilon_f} d\epsilon_f d\Omega_p \tag{III.107}$$

We use

$$p = (2m\epsilon_f)^{1/2} \qquad \Rightarrow \qquad \frac{dp}{d\epsilon_f} = \left(\frac{m}{2\epsilon_f}\right)^{1/2} \tag{III.108}$$

This gives

$$d^3p = 2m\epsilon_f \sqrt{\frac{m}{2\epsilon_f}} d\epsilon_f d\Omega_p \tag{III.109}$$

$$= \sqrt{2m^3\epsilon_f} d\epsilon_f d\Omega_p \tag{III.110}$$

We now go back to our normalization equation

$$1 = \int |\psi(\mathbf{p})|^2 \sqrt{2m^3\epsilon_f} d\epsilon_f d\Omega_p \tag{III.111}$$

$$= \int d\epsilon_f \sqrt{2m^3\epsilon_f}^{\rho(\epsilon_f)} \overbrace{\int d\Omega_p \, |\psi(\mathbf{p})|^2}^{p_{i\to f}(\epsilon_f)} \tag{III.112}$$

Note that this was only for free particles. Hence for a free particle he density of states is $\sqrt{2m^3\epsilon_f}$. If we want to discuss photoionization we need to discuss

$$P_{i\to f} = \int_{\epsilon_f-\Delta\epsilon}^{\epsilon_f+\Delta\epsilon} p_{i\to f}(\epsilon'_f)\rho(\epsilon'_f) d\epsilon_f \tag{III.113}$$

Recall our previous result for first order $p_{i\to f}$

$$P_{i\to f} = \frac{4}{\hbar^2} \int_{\epsilon_f-\Delta\epsilon}^{\epsilon_f+\Delta\epsilon} |B_{fi}|^2 \left\{ f\left(t, \omega'_{fi}+\omega\right) + f(t, \omega'_{fi}-\omega) \right\} \rho(\epsilon'_f) d\epsilon'_f \tag{III.114}$$

If we assume that the interval range is small then $\rho(\epsilon'_f)$ and B_{fi} don't vary much accross that interval. In this case. Furthermore the meximan hat (f) functions are only large at particular ω. If we are looking at absorption then only $f\left(t, \omega'_{fi}-\omega\right)$ is large across this band. In this case

$$P^{abs}_{i\to f} \approx \frac{4}{\hbar^2} |B_{fi}|^2 \rho(\epsilon_f) \int_{\epsilon_f-\Delta\epsilon}^{\epsilon_f+\Delta\epsilon} f(t, \omega'_{fi}-\omega) d\epsilon'_f \tag{III.115}$$

To carry out the integral we define $\tilde{\omega} \equiv \omega'_{fi} - \omega$ and hence $d\epsilon_f = \hbar d\tilde{\omega}$

$$P^{abs}_{i\to f} \approx \frac{4}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) \int \frac{\sin^2 \frac{\tilde{\omega}t}{2}}{\tilde{\omega}^2} d\tilde{\omega} \tag{III.116}$$

Technically the integral is from $\epsilon_f - \Delta\epsilon$ to $\epsilon_f + \Delta\epsilon$. However if we are centered on an absorption peak then contributions from other parts of the function are small. Thus we may as well just extend the limits of the integral to $\pm\infty$, which is a well known, analytic integal. With this we have

$$P^{abs}_{i\to f} = \frac{2\pi t}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) t \tag{III.117}$$

with $\epsilon_f = \epsilon_i + \hbar\omega$ One can easily show that we get a similar equation for stimulated emission:

$$P^{SE}_{i\to f} = \frac{2\pi t}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) t \tag{III.118}$$

where $\epsilon_f = \epsilon_i - \hbar\omega$. We define the transition rate by

$$W_{i\to f} = \frac{d}{dt} P_{i\to f} \tag{III.119}$$

This is given by

$$W_{i\to f} = \frac{2\pi}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) \tag{III.120}$$

where $\epsilon_f = \epsilon_i \pm \hbar\omega$. This is called Fermi's Golden Rule (FGR).

2. Dipole Approximation

Typical situation is that the wavelength of the light used is large compared to the characteristic distance of atoms. i.e. $\lambda = \frac{2\pi}{k} \gg a_0$. In this case we use the dipole approximation that says

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + \mathbf{k}\cdot\mathbf{r} + ... \tag{III.121}$$

$$\approx 1 \tag{III.122}$$

Hence the field doesn't change spatially across the atom. On Monday we said that

$$B_{fi} = \frac{e}{2m} A_0^* \hat{\Pi} \langle\phi_f| e^{-i\mathbf{k}\cdot\mathbf{r}} \mathbf{p} |\phi_i\rangle \tag{III.123}$$

Applying the dipole approximation we have

$$B_{fi} \approx \frac{e}{2m} A_0^* \hat{\Pi} \cdot \langle\phi_f| \mathbf{p} |\phi_i\rangle \tag{III.124}$$

We now use a commutator relation:

$$\mathbf{p} = \frac{im}{\hbar} [H_0, \mathbf{r}] \tag{III.125}$$

where $H_o = \frac{p^2}{2m} + V$. With this relation

$$\langle\phi_f| \mathbf{p} |\phi_i\rangle \approx \frac{im}{\hbar} \langle\phi_f| H_o\mathbf{r} - \mathbf{r}H_0 |\phi_i\rangle \tag{III.126}$$

If we have ϕ_f and ϕ_i as eigenstates then we have

$$\langle\phi_f| \mathbf{p} |\phi_i\rangle = \frac{im}{\hbar} (\epsilon_f - \epsilon_i) \overbrace{\langle\phi_f| \mathbf{r} |\phi_i\rangle}^{\text{Dipole Matrix Elements}} \tag{III.127}$$

Thus we have (inserting back into previous equation)

$$B_{fi}^{dip} = \frac{ie}{2\hbar} A_0^* (\epsilon_f - \epsilon_i) \hat{\Pi} \cdot \langle \phi_f | \mathbf{r} | \phi_i \rangle \tag{III.128}$$

For $\hat{\Pi} = \hat{z}$ we have the standard selection rules, $\Delta m = 0, \Delta \ell = \pm 1$. We can now figure out the transition rates using FGR. Using this one will find that

$$W_{i \to f}^{dip, \hat{z}} \propto \cos^2 \theta \tag{III.129}$$

for $\phi_i =$ s-states. This is plotted in figure 13

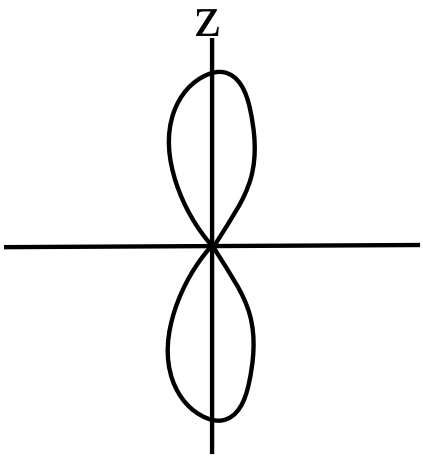

FIG. 13. The transition probability as a function of θ for the 1s state

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Lecture 15th - February 27th, 2012

D. Outlook on Field Quantization

We need to find a Hamiltonian for atom and electromagnetic field

$$H = H_A + H_F + W \tag{III.130}$$

where H_A is the Hamiltonian due to the atom, H_F is the Hamiltonian due to the field, and W represents the interaction of the atom with the field. We can write

$$H = H_o + W \tag{III.131}$$

where $H_o = H_A + H_F$. The steps toward a 1st-order PT treatment are

1. Determine $H_0 = H_A + H_F$. We already know $H_A = \frac{p^2}{2m} + \frac{e^2}{r}$. However we don't know H_F. One requirement we will use is that H_F will be Hermitian, i.e. $H_F = H_F^\dagger$.

2. Solve the eigenvalue problem of H_0. We already know the original eigenstates and energies:

$$H_A |\phi_j\rangle = \epsilon_j |\phi_j\rangle \tag{III.132}$$

but we don't know the states and energies below

$$H_F |\rho_k\rangle = \tilde{\epsilon}_k |\rho_k\rangle \tag{III.133}$$

If we denote $|\psi_\ell\rangle$ as the full unperturbed states then we have

$$H_0 |\psi_\ell\rangle = (H_A + H_F) |\phi_\ell\rangle |\rho_\ell\rangle \tag{III.134}$$
$$= (H_A |\phi_\ell\rangle) |\rho_\ell\rangle + |\phi_\ell\rangle H_F |\rho_\ell\rangle \tag{III.135}$$
$$= \epsilon_\ell |\psi_\ell\rangle + \tilde{\epsilon}_\ell |\psi_\ell\rangle = (\epsilon_\ell + \tilde{\epsilon}_\ell) |\psi\rangle \tag{III.136}$$

3. Determine W. We use the ansatz

$$W = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} \tag{III.137}$$

4. Obtain 1st - order transition rates (apply Fermi's Golden Rule)

   - Need

$$\langle \psi_f | W |\psi_i\rangle \tag{III.138}$$

1. *Construction of H_F*

The energy of a classical electromagnetic field in a vacuum of volume L^3 is (denote this energy W_{EM})

$$W_{EM} = \frac{\epsilon_o}{2} \int \left(E^2 + c^2 B^2\right) d^3 r \tag{III.139}$$

Recall for free electromagnetic waves (electric potential is zero) we have with the Coloumb gauge that

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0 \tag{III.140}$$

Assume periodic boundary conditions for each side of cube

$$\mathbf{A}(x, y, z = 0) = \mathbf{A}(x, y, z = L)$$
$$\mathbf{A}(x, y = 0, z) = \mathbf{A}(x, y = L, z)$$
$$\mathbf{A}(x = 0, y, z) = \mathbf{A}(x = L, y, z)$$

This gives ($k_j = k_x, k_y, k_z$ for $j = 1, 2, 3$)

$$1 = e^{i k_j L} \tag{III.141}$$

and hence

$$k_z = \frac{2\pi}{L} n_z \tag{III.142}$$

The total vector potential is given by

$$\mathbf{A}(\mathbf{r}, t) = \sum_\lambda \mathbf{A}_\lambda(\mathbf{r}, t) \tag{III.143}$$

where

$$\mathbf{A}_\lambda(\mathbf{r}, t) = \frac{\hat{\Pi}}{L^{3/2}} \left\{ q_\lambda e^{i(\mathbf{k}_\lambda \cdot \mathbf{r} - \omega_\lambda t)} + q_\lambda^* e^{-i(\mathbf{k}_\lambda \cdot \mathbf{r} - \omega_\lambda t)} \right\}$$

λ is the mode index. Each mode is characterized by $\left\{ \mathbf{k}_\lambda, \hat{\Pi}_\lambda, \omega_\lambda \right\}$. $\hat{\Pi}_\lambda$ is the unit polarization vector, $\omega_\lambda = c k_\lambda$, and $k_\lambda = \frac{2\pi}{L} \left(n_x^\lambda, n_y^\lambda, n_z^\lambda\right)$ where $n_x^\lambda, n_y^\lambda, n_z^\lambda \in \mathbb{Z}$. We can now calculate $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$ and $\mathbf{B} = \nabla \times \mathbf{A}$. By taking these derivatives and inserting into the equation for W_{EM} above we get (after a lot of manipulations)

$$W_{EM} = 2\epsilon_0 \sum_\lambda w_\lambda^2 q_\lambda^* q_\lambda \tag{III.144}$$

We now perform a substitution amplitudes given by

$$Q_\lambda \equiv \sqrt{\epsilon_0}\,(q_\lambda + q_\lambda^*)$$
$$P_\lambda \equiv i\sqrt{\epsilon_0}\omega_L\,(q_\lambda^* - q_\lambda)$$

This gives

$$q_\lambda = \frac{1}{2\sqrt{\epsilon_0}}\left(Q_\lambda + i\frac{P_\lambda}{\omega_\lambda}\right) \tag{III.145}$$

This gives

$$W_{EM} = 2\epsilon_0 \sum_\lambda x_\lambda^2 \left(\frac{1}{4\epsilon_0}\right)\left(Q_\lambda^2 + \frac{P_\lambda^2}{\omega_\lambda^2}\right) \tag{III.146}$$

$$= \frac{1}{2}\sum_\lambda \left(P_\lambda^2 + \omega_\lambda Q_\lambda^2\right) \tag{III.147}$$

We can now quantize this energy by promoting P_λ and Q_λ to operators. We also demand them to be Hermitian and follow the commutation relations for position and momentum. i.e.$P_\lambda = P_\lambda^\dagger$ and $Q_\lambda = Q_\lambda^\dagger$ and

$$[Q_\lambda, P_{\lambda'}] = i\hbar\delta_{\lambda,\lambda'} \tag{III.148}$$

Since we have a quantized W_{EM} we have H_F:

$$H_F = \frac{1}{2}\sum_\lambda \left(P_\lambda^2 + \omega_\lambda^2 Q_\lambda^2\right) = H_F^\dagger \tag{III.149}$$

We know the eigenvalues of this Hamiltonian if it has the commutation relations of position and momentum. The energies are

$$E_{n_1,n_2,\ldots} = \sum_\lambda \hbar\omega_\lambda \left(n_\lambda + \frac{1}{2}\right) \tag{III.150}$$

where $n_\lambda = 0, 1, 2, \ldots$. Lecture 16th - February 29th, 2012

Consider the following summary and discussion of our results.

1. For our expressions we have assumed that we have periodic boundary conditions. This forced us to have discrete wavelengths inside our system. This enables us to change our integrals to sums

$$\int d^3k \to \sum_\lambda$$

2. Note that

$$W_{EM} = \frac{1}{2}\sum_\lambda \left(P_\lambda^2 + \omega_\lambda^2 Q_\lambda^2\right) \tag{III.151}$$

is independent on time (since the numbers P_λ and Q_λ don't change with time). i.e.

$$\frac{dW_{EM}}{dt} \tag{III.152}$$

This means that the surface integral of the Poynting vector must be zero (from classical electrodynamics).

3. We quantized P_λ and Q_λ by elevating them to Hermitian operators that obey the canonical commutation relations

$$[Q_\lambda, P_{\lambda'}] = i\hbar\delta_{\lambda,\lambda'} \tag{III.153}$$

4. Energy spectrum of our Hamiltonian is given by

$$E = \sum_{\lambda} \hbar\omega_{\lambda} \left(n_{\lambda} + \frac{1}{2} \right) \tag{III.154}$$

with $n_{\lambda} = 0, 1, 2, ...$

5. The "conventional" but wrong interpretation is to associate each mode with a particle in a parabolic potential and then the eigenenergies in this mode $E_{n_\lambda} = \hbar\omega \left(n_{\lambda} + \frac{1}{2} \right)$ are the ground and excited state energy levels

6. The alternate interpretation is to associate each mode with n_λ particles (or quanta) in the same state. All these quanta carry the same energy, $\hbar\omega_\lambda$ (forgetting about the $\frac{1}{2}\hbar\omega_\lambda$ term). Note that this only works because the energy is linear in n_λ otherwise. For example if you had 3 quanta (i.e. $n_\lambda = 3$) we would have and energy of $\hbar\omega + \hbar\omega + \hbar\omega = 3\hbar\omega$. This is the photon interpretation.

7. However we have not yet described the $\frac{1}{2}\hbar\omega_\lambda$ factor. This is the zero-point energy. The full zero-point energy is

$$E_0 = \sum_{\lambda} \frac{\hbar\omega_{\lambda}}{2} \to \infty \tag{III.155}$$

since this is an infinite sum. To make this finite we require a technique called renormalization. The zero-point energy is the energy without any photons there. This relates to the idea that we have energy in a vacuum (which causes effects such as spontaneous emission).

2. Creation and Annihilation Operators

We introduce creation and annihilation operators given by

$$b_{\lambda} = \frac{1}{\sqrt{2\hbar\omega_{\lambda}}} \left(\omega_{\lambda} Q_{\lambda} + i P_{\lambda} \right)$$
$$b_{\lambda}^{\dagger} = \frac{1}{\sqrt{2\hbar\omega_{\lambda}}} \left(\omega_{\lambda} Q_{\lambda} - i P_{\lambda} \right)$$

These operators obey

$$\left[b_{\lambda}, b_{\lambda'}^{\dagger} \right] = \delta_{\lambda,\lambda'} \tag{III.156}$$

and

$$[b_{\lambda}, b_{\lambda'}] = \left[b_{\lambda}^{\dagger}, b_{\lambda'}^{\dagger} \right] = 0 \tag{III.157}$$

This gives

$$H_F = \sum_{\lambda} \hbar\omega_{\lambda} \left(b_{\lambda}^{\dagger} b_{\lambda} + \frac{1}{2} \right) \tag{III.158}$$
$$= \sum_{\lambda} \hbar\omega_{\lambda} \left(n_{\lambda} + \frac{1}{2} \right) \tag{III.159}$$

where $n_\lambda \equiv b_\lambda^\dagger b_\lambda$ is called the occupation number operator. The eigenvalue equation with $H_F = \sum_\lambda H_F^{(\lambda)}$ is

$$H_F^{(\lambda)} = |\psi_{n_\lambda}\rangle = \hbar\omega \left(n_{\lambda} + \frac{1}{2} \right) |\psi_{n_\lambda}\rangle \tag{III.160}$$

where $n_\lambda = 0, 1, 2, ...$ and we have

$$\left\langle \psi_{n_\lambda} | \psi_{n'_\lambda} \right\rangle = \delta_{n_\lambda n'_\lambda} \tag{III.161}$$

The occupation number obeys

$$n_\lambda |\psi_{n_\lambda}\rangle = n_\lambda |\psi_{n_\lambda}\rangle \tag{III.162}$$

We use shorthand notation of $|\psi_{n_\lambda}\rangle = |n_\lambda\rangle$. One must be careful with this notation. Since we may write the following equation

$$\hat{n}_\lambda |n_\lambda + 1\rangle = (n_\lambda + 1) |n_\lambda + 1\rangle \tag{III.163}$$

A ˆ was used to differentiate the operator $\hat{n}_\lambda$ from the number. We now consider the state

$$|n_\lambda = 0\rangle \equiv |0\rangle \tag{III.164}$$

which we call the vacuum state. This gives

$$n_\lambda |0\rangle = |\emptyset\rangle \tag{III.165}$$

This is not the same as $|0\rangle$! This is really the zero state. However since we have a ket on the left side we don't want to write just 0. One can show that

$$\begin{aligned} b_\lambda^\dagger |n_\lambda\rangle &= \sqrt{n_\lambda + 1} |n_\lambda + 1\rangle \\ b_\lambda |n_\lambda\rangle &= \sqrt{n_\lambda} |n_\lambda - 1\rangle \end{aligned}$$

In particular we have

$$b_\lambda |0\rangle = |\emptyset\rangle \tag{III.166}$$

Lecture 17th - March 5th, 2012
Here we generalize these results. We use the rule that if the eigenvalue of your system is the sum of a set of eigenvalues then the resultant eigenvalues are the product of the eigenstates:

$$H_F |n_1, n_2, ...\rangle = E |n_1, n_2, ...\rangle \tag{III.167}$$

where $E = \sum_\lambda \hbar\omega_\lambda \left(n_\lambda + \frac{1}{2}\right) = \sum_\lambda \hbar\omega_\lambda n_\lambda + E_0$ and $|n_1, n_2, ...\rangle = |n_1\rangle \otimes |n_2\rangle \otimes ...$ are the product states. The operator n_λ counts the number of modes in mode λ:

$$\hat{n}_\lambda |n_1, n_2, ..., n_\lambda, ...\rangle = n_\lambda |n_1, n_2, ..., n_\lambda, ...\rangle$$

$$\begin{aligned} b_\lambda^\dagger |n_1, n_2, ..., n_\lambda, ...\rangle &= \sqrt{n_\lambda + 1} |n_1, n_2, ..., n_\lambda + 1, ...\rangle \\ b_\lambda |n_1, n_2, ..., n_\lambda, ...\rangle &= \sqrt{n_\lambda} |n_1, n_2, ..., n_\lambda, ...\rangle \end{aligned}$$

3. Interaction Between Photon Field and Electrons

In the beginning we discussed that we are using the semiclassical interaction with a perturbing Hamiltonian:

$$W = \frac{e}{m} \mathbf{A} \cdot \mathbf{p} \tag{III.168}$$

with

$$\mathbf{A}(\mathbf{r}, t) = \sum_\lambda \frac{\hat{\Pi}_\lambda}{L^3} \left\{ q_\lambda e^{i(\mathbf{k}_\lambda \cdot \mathbf{r} - \omega_\lambda t)} + q_\lambda^* e^{-i(\mathbf{k}_\lambda \cdot \mathbf{r} - \omega_\lambda t)} \right\} \tag{III.169}$$

To quantize this operator we made the transformation given earlier:

$$q_\lambda = \frac{1}{2\sqrt{\epsilon_0}} \left(Q_\lambda + i \frac{P_\lambda}{\omega_\lambda} \right) = \sqrt{\frac{\hbar}{2\epsilon_0 \omega_\lambda}} b_\lambda \tag{III.170}$$

Hence we have the vector potential in its new form given by

$$\mathbf{A}(\mathbf{r},t)=\sum_{\lambda}\hat{\Pi}_{\lambda}\overbrace{\frac{1}{L^{3}}\sqrt{\frac{\hbar}{2\epsilon_{0}\omega_{\lambda}}}}^{\gamma}\left\{b_{\lambda}e^{i(\mathbf{k}_{\lambda}\cdot\mathbf{r}-\omega_{\lambda}t)}+b_{\lambda}^{\dagger}e^{-i(\mathbf{k}_{\lambda}\cdot\mathbf{r}-\omega_{\lambda}t)}\right\} \tag{III.171}$$

This operator is time dependent. However we want an operator thats time independent. To achieve this we define

$$b_{\lambda}^{H}=b_{\lambda}e^{-i\omega_{\lambda}t} \tag{III.172}$$

For this to make sense we need to show that

$$i\hbar\frac{d}{dt}b_{\lambda}^{H}=\left[b_{\lambda}^{H},H_{\lambda}^{H}\right] \tag{III.173}$$

where we denote operators in the Heisenberg picture by superscript H.

Proof of statement above is shown below. The Hamiltonian in the Schrodinger interpretation is the same as in the Heisenberg interpretation. Thus we have

$$RHS=\left[b_{\lambda}^{H},H_{F}^{(\lambda),H}\right]=e^{-i\omega_{\lambda}t}\left[b_{\lambda},\hbar\omega\left(n_{\lambda}+\frac{1}{2}\right)\right] \tag{III.174}$$

$$=\hbar\omega_{\lambda}e^{-i\omega_{\lambda}t}\left[b_{\lambda},n_{\lambda}\right] \tag{III.175}$$

$$=\hbar\omega_{\lambda}e^{-i\omega_{\lambda}t}b_{\lambda} \tag{III.176}$$

$$LHS=i\hbar\omega(-i\omega_{\lambda})b_{\lambda}e^{-i\omega_{\lambda}t}=\hbar\omega_{\lambda}e^{-i\omega_{\lambda}t}b_{\lambda} \tag{III.177}$$

$$=RHS \tag{III.178}$$

Hence our construction gave us an operator in the Heisenberg picture. Thus removing the time dependence is easy and gives (where γ was defined above)

$$A(\mathbf{r})=\gamma\sum_{\lambda}\hat{\Pi}\left\{b_{\lambda}e^{i\mathbf{k}_{\lambda}\mathbf{r}}+b_{\lambda}^{\dagger}e^{-i\mathbf{k}_{\lambda}\cdot\mathbf{r}}\right\} \tag{III.179}$$

This is our quantized vector potential in the Schrodinger picture where the interaction is

$$W=\frac{e}{m}\mathbf{A}\cdot\mathbf{p} \tag{III.180}$$

$$=-i\overbrace{\sqrt{\frac{e^{2}\hbar^{3}}{2\omega_{\lambda}\epsilon_{0}m^{2}L^{3}}}}^{\beta}\hat{\Pi}\left\{e^{ik_{\lambda}\mathbf{r}}\nabla b_{\lambda}+e^{-i\mathbf{k}_{\lambda}\cdot\mathbf{r}}\nabla b_{\lambda}^{\dagger}\right\} \tag{III.181}$$

4. The Transition Matrix Elements

$$\langle\phi_{f}|W|i\rangle=\sum_{\lambda}\langle\phi_{f}|W_{\lambda}|\phi_{i}\rangle \tag{III.182}$$

$$=\sum_{\lambda}\langle\psi_{f}|\otimes\left\langle n_{1}^{f}n_{2}^{f}...\right|(W_{\lambda})\left|n_{1}^{i}n_{2}^{i}...\right\rangle\otimes|\psi_{i}\rangle \tag{III.183}$$

where $|\psi\rangle$ are the electron states while $|n_1 n_2,...\rangle$ are the photon states. We have two parts to the equation the product states are made up of a photon part and an electron part.

$$\langle\phi_{f}|W|\phi_{i}\rangle=-i\beta\sum_{\lambda}\left\{\langle\psi_{f}|e^{i\mathbf{k}_{\lambda}\cdot\mathbf{r}}\hat{\Pi}_{\lambda}\cdot\nabla|\phi_{i}\rangle\otimes\left\langle n_{1}^{f}n_{2}^{f}...\right|b_{\lambda}\left|n_{1}^{i}n_{2}^{i}...\right\rangle+\langle\phi_{f}|e^{-ik_{\lambda}\cdot\mathbf{r}}\hat{\Pi}_{\lambda}\nabla|\phi_{i}\rangle\otimes\left\langle n_{1}^{f}n_{2}^{f}...\right|b_{\lambda}^{\dagger}\left|n_{1}^{i}n_{2}^{i}...\right\rangle\right\} \tag{III.184}$$

Note that we already know the electron matrix elements since we dealt with them earlier (we will get back to them in more detail shortly). We now consider the photon matrix elements.

$$\left\langle n_1^f n_2^f ... n_\lambda^f ... \right| b_\lambda \left| n_1^i n_2^i ... n_\lambda^i ... \right\rangle = (\delta_{n_1^f, n_1^i} \delta_{n_2^f, n_2^i} ... \delta_{n_\lambda^f, n_\lambda^i - 1} ...) \sqrt{n_\lambda^i} \tag{III.185}$$

This matrix element is highly selective. Furthermore we have

$$\left\langle n_1^f n_2^f ... n_\lambda^f ... \right| b_\lambda^\dagger \left| n_1^i n_2^i ... n_\lambda^i ... \right\rangle = (\delta_{n_1^f, n_1^i} \delta_{n_2^f, n_2^i} ... \delta_{n_\lambda^f, n_\lambda^i + 1} ...) \sqrt{n_\lambda^i + 1} \tag{III.186}$$

Hence the condition to have a non zero transition elements are that the photon numbers don't change by more then one. Furthermore there can only be a single photon interaction at a time. The annihilation of a photon corresponds to absorption of a photon, while the creation of a photon corresponds to an emission of a photon.

Summary:

The matrix elements

$$\langle \phi_f | W | \phi_i \rangle \neq 0 \tag{III.187}$$

are non-zero if and only if

1. $$\left| n_1^i n_2^i ... \right\rangle \text{ and } \left| n_1^f n_2^f ... \right\rangle \tag{III.188}$$

   differ in exactly one mode (by one photon).

2. If we apply the dipole approximation then we have the dipole selection rules for the electronic part in the non-zero mode ($e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} \approx 1$). In this case we can use the typical selection rules of $\Delta \ell = \pm 1, \Delta m = 0$

3. Recall that we found in the constant perturbation or sudden approximation that the transition is small unless energy is conserved. i.e.

   $$E_i = E_f \tag{III.189}$$

   $$\begin{aligned} H_0 |\phi_i\rangle &= (H_A + H_F) |\psi_i\rangle \left| n_1^i n_2^i ... \right\rangle && \text{(III.190)} \\ &= (H_A |\phi_i\rangle) + |\phi_i\rangle H_F \left| n_1^i n_2^i ... \right\rangle && \text{(III.191)} \\ &= \left(\varepsilon_i + \sum_{\lambda'} \hbar \omega_{\lambda'} \left(n_{\lambda'}^i + \frac{1}{2} \right) \right) |\phi_i\rangle && \text{(III.192)} \end{aligned}$$

   This gives

   $$E_f = \varepsilon_f + \sum_{\lambda'} \hbar \omega_{\lambda'} \left(n_{\lambda'}^f + \frac{1}{2} \right) \tag{III.193}$$

   Energy conservation $E_i = E_f$ implies that

   $$\begin{aligned} \varepsilon_f &= \varepsilon_i + \sum_{\lambda'} \hbar \omega_{\lambda'} \left(n_{\lambda'}^i - n_{\lambda'}^f \right) && \text{(III.194)} \\ &\varepsilon_i \pm \hbar \omega_\lambda && \text{(III.195)} \end{aligned}$$

   where the plus sign corresponds to absorption while the minus sign corresponds to emission.

Lecture 18 - March 7th, 2012

Note: Look carefully on last question of new assignment, it may be a test question

Recall we can write

$$\langle \phi_f | W | \phi_i \rangle = -i\beta \times \begin{cases} \langle \psi_f | e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}} \hat{\Pi}_\lambda \cdot \nabla |\psi_i\rangle \sqrt{n_\lambda^i + 1} \\ \langle \psi_f | e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} \hat{\Pi}_\lambda \cdot \nabla |\phi_i\rangle \sqrt{n_\lambda^i} \\ 0 \end{cases} \tag{III.196}$$

Note we can only have one of above.

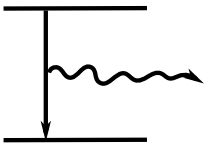
5. *Spontaneous Emission*

Thus is a special case of the term

$$-i\beta \langle\psi_f| e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\hat{\Pi}_\lambda \cdot \nabla |\psi_i\rangle \sqrt{n_\lambda^i + 1} \tag{III.197}$$

with $n_\lambda^i = n_\lambda^f - 1 = 0$. Energy conservation needs to be fulfilled. In other words

$$\varepsilon_f = \varepsilon_i - i\hbar\omega_\lambda \tag{III.198}$$



Fermi's Golden rule says that

$$W_{i\to f}^{spon.emission} = \frac{2\pi}{\hbar} |\langle\phi_f| W |\phi_i\rangle|^2 \rho(E_f) \tag{III.199}$$

where ρ is the density of states. We first need to find the density of states.

$$\text{Initial state} = \begin{cases} |\psi_i\rangle : \text{(discrete) Excited atomic state} \\ |0\rangle : \text{No photon} \end{cases} \tag{III.200}$$

$$\text{Final state} = \begin{cases} |\psi_f\rangle : \text{(discrete) atomic ground state} \\ |1\rangle : \text{One photon with } \omega = \frac{\varepsilon_i - \varepsilon_f}{\hbar} \end{cases} \tag{III.201}$$

We want to find the density of (photon) states. We look at the density of states with respect to $\mathbf{k}$-space. Recall that

$$\mathbf{k}_\lambda = \frac{2\pi}{L}\left(n_x^\lambda, n_y^\lambda, n_z^\lambda\right) \tag{III.202}$$

where $n_i^\lambda \in \mathbb{Z}$.

$$\rho(\mathbf{k}) = \frac{\Delta N}{\Delta V_k} = \frac{\Delta n_x \Delta n_y \Delta n_z}{\Delta k_x \Delta k_y \Delta k_z} \tag{III.203}$$

We use the relation between $\mathbf{k}$ and n shown in equation III.202. It's easy to see that

$$\rho(\mathbf{k}) = \left(\frac{2\pi}{L}\right)^3 \tag{III.204}$$

We can rewrite the differential as

$$d^3k = k^2 dk d\Omega = k^2 \frac{dk}{dE} dE d\Omega \tag{III.205}$$

For photons we have

$$E = \hbar\omega = \hbar ck \tag{III.206}$$

Hence we have

$$\frac{dE}{dk} = \hbar c \iff \frac{dk}{dE} = \frac{1}{\hbar c} \tag{III.207}$$

With this relation we have

$$d^3k = \frac{1}{\hbar c}\left(\frac{E^2}{\hbar^2\omega^2}\right) dE d\Omega \tag{III.208}$$

We can now find the number differential

$$dN = \rho d^3k = \left(\frac{L}{2\pi}\right)^3 \frac{\omega^2}{\hbar c^3} dE d\Omega \tag{III.209}$$

$$\rho(E) dE d\Omega \tag{III.210}$$

Fermi's Golden Rule says that

$$\frac{dW_{i\to f}^{Spon.Emission}}{d\Omega} = \frac{2\pi}{\hbar}\left(\frac{\not{L}}{2\pi}\right)^3 \frac{\omega^2}{\hbar c^3}\left(\frac{e^2\hbar^3}{2\epsilon_0 \omega m^2 \not{L}^3}\right)\left|\langle\psi_f| e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\Pi}\cdot\nabla|\phi_i\rangle\right|^2 \tag{III.211}$$

$$= \frac{\omega}{8\pi^2 c^3}\left(\frac{e^2\hbar}{\epsilon_0 m^2}\right)\left|\langle\psi_f| e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\Pi}\cdot\nabla|\phi_i\rangle\right|^2 \tag{III.212}$$

If we apply the dipole approximation then $e^{-\mathbf{k}\cdot\mathbf{r}} \approx 1$ (this says that the size of the atoms is much smaller then the wavelength of the light). This leaves us to consider

$$\langle\psi_f|\hat{\Pi}\cdot\nabla|\psi_i\rangle = \frac{i}{\hbar}\langle\psi_f|\hat{\Pi}\cdot\mathbf{p}|\psi_i\rangle \tag{III.213}$$

However one can show that

$$\frac{im}{\hbar}[H_A, \mathbf{r}] = \mathbf{p} \tag{III.214}$$

if $H_A = \frac{p^2}{2m} + V(\mathbf{r})$. Using this relation we have

$$\langle\psi_f|\hat{\Pi}\cdot\nabla|\psi_i\rangle = -\frac{m}{\hbar^2}\hat{\Pi}\cdot\langle\psi_f|H_A\mathbf{r} - \mathbf{r}H_A|\psi_i\rangle \tag{III.215}$$

$$= -\frac{m}{\hbar^2}\overbrace{(\varepsilon_f - \varepsilon_i)}^{\hbar\omega}\hat{\Pi}\cdot\langle\psi_f|\mathbf{r}|\psi_i\rangle \tag{III.216}$$

Putting this result together we have

$$\frac{dW_{i\to f}^{Spon.Emission}}{d\Omega} = \frac{e^2\omega^3}{8\pi\epsilon_0\hbar c^3}\times\left|\hat{\Pi}\cdot\langle\psi_f|\mathbf{r}|\psi_i\rangle\right|^2 \tag{III.217}$$

$$= \overbrace{\frac{e^2\omega^3}{8\pi^2\epsilon_0\hbar c^3}}^{\alpha}\left|\hat{\Pi}\cdot\mathbf{r}_{if}\right|^2 \tag{III.218}$$

We now sum over all polarizations thus we integrate. We choose our wave propagation direction, $\mathbf{k}$, such that $\mathbf{r}_{if}$ is along the z axis and define the angle between these two axes as θ. The two linearly independent polarization directions of the light must be perpendicular to the motion of the wave ($\perp \mathbf{k}$). If we choose one polarization to be perpendicular to $\mathbf{r}_{if}$ then this contribution is zero. This sets the other polarization direction to be

$$\hat{\Pi_2}\cdot\mathbf{r}_{if} = |\mathbf{r}|\cos\left(\frac{\pi}{2} - \theta\right) = r_{if}\sin\theta \tag{III.219}$$

Hence we have

$$W_{i\to f}^{S.E} = \int\left(|\Pi_1\cdot\mathbf{r}_{if}|^2 + |\Pi_2\cdot\mathbf{r}_{if}|^2\right)d\Omega \tag{III.220}$$

$$= \alpha\int r_{if}^2\sin^2\theta d\Omega \tag{III.221}$$

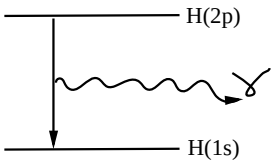
$$= \alpha\frac{8\pi}{3}r_{if}^2 \tag{III.222}$$

Thus the total transition rate in the dipolar approximation is

$$W_{i\to f}^{S.E.} = \frac{e^2\omega^3}{3\pi\epsilon_0\hbar c^3}|\mathbf{r}_{if}|^2 \tag{III.223}$$

where $\mathbf{r}_{if} = \langle\psi_i|\mathbf{r}|\psi_f\rangle$.
Discussion:

1. As an example consider a Hydrogen $2p \to 1s$ transition



The lifetime is given by

$$T^{dip}_{2p\to 1s} = \frac{1}{W^{S.E}_{2p\to 1s}} \approx 1.6 \times 10^{-9} s \tag{III.224}$$

In a classical picture it takes the electron $10^{-16}s$ to circle around the nucleus. Thus this is a very long lifetime with respect to this value.

2. We can consider a different decay of Hydrogen $2s \to 1s$ It turns out that

$$T^{1storder}_{2s\to 1s} = \infty \tag{III.225}$$

However experimentally we have

$$T^{experiment}_{2s\to 1s} = 0.1s \tag{III.226}$$

This state is metastable. We need second order perturbation theory (more then FGR) to do this. This corresponds to a two-photon process.

3. For an N-photon process one needs to consider N^{th} order perturbation theory. The W operator is linear in b and $b^\dagger$ so in order to contribute a N photon process we need to combine more of these operators.

Lecture 19th - March 12th, 2012

Recall that the total transition rate in the dipole approximation is

$$W^{s.e.}_{i\to f} = \frac{e^2\omega^3}{3\pi\epsilon_0\hbar c^3}\left(|x_{if}|^2 + |y_{if}|^2 + |z_{if}|^2\right) \tag{III.227}$$

The lifetime is simplify given by

$$T_{i\to f} = \frac{1}{W^{s.e.}_{i\to f}} \tag{III.228}$$

Consider if we have an electron in the 3p state: $\phi_i = H(3p)$. This is shown in figure 14 The total decay rate is the

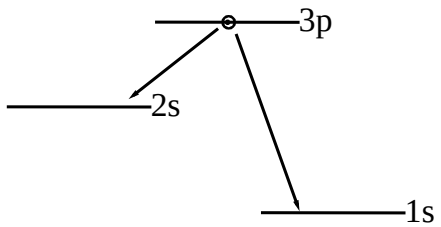


FIG. 14. A decay from a Hydrogen $3p$ state

sum of the two rates:

$$W^{s.e.} = \frac{e^2}{3\pi\epsilon_0\hbar c^3}\sum_{f(\varepsilon_f<\varepsilon_i)} \omega^3_{if}\left|\mathbf{r}_{if}\right|^2 \tag{III.229}$$

Here the rates are uncoupled (the rate of $3p \to 2s$ doesn't effect the rate of $3p \to 1s$). In practice of course this is not the case.

Concluding remarks on photons:

Here we defined photons as the quanta of an electromagnetic field. The properties of the photon are

- Can be created or annihilated (hence they are not stable)
- Carry energy $\hbar\omega_\lambda$
- One can show that they carry momentum $\hbar\mathbf{k}_\lambda$. The reasoning is as follows. One could start from a classical expression for momentum of the electromagnetic field:

$$\mathbf{p}_{EM} = \epsilon_0 \int_{V=L^3} (\mathbf{E} \times \mathbf{B})\, d^3r \tag{III.230}$$

  For our cube we know the vector potential ($A_\lambda(\mathbf{r}, t) = \sum_\lambda ...$) and hence we can find the electromagnetic fields

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$$
$$\mathbf{B} = \nabla \times \mathbf{A}$$

  we can then insert this result into the momentum and find the momentum of the fields:

$$\mathbf{p}^{EM} = 2\epsilon_0 \sum_\lambda \mathbf{k}_\lambda \omega_\lambda q_\lambda^* q_\lambda \tag{III.231}$$

  Quantizing this operator gives

$$\mathbf{p}_F = \sum_\lambda \hbar\mathbf{k}_\lambda b_\lambda^\dagger b_\lambda = \sum \hbar\mathbf{k}_\lambda n_\lambda \tag{III.232}$$

  Hence we have

$$\mathbf{p}_F \left|n_1, n_2, ...\right\rangle = \sum_\lambda \hbar\mathbf{k}_\lambda n_\lambda \left|n_1, n_2, ...\right\rangle \tag{III.233}$$

  From this it is clear that momentum of each mode is $\hbar\mathbf{k}_\lambda$.

- Similarly one can show that photons also carry angular momentum (often called photon spin) given by $\pm\hbar$. This is reasoned as follows. The angular momentum of an electromagnetic field is

$$L_{EM} = \epsilon_0 \int_{L^3} \mathbf{r} \times (\mathbf{E} \times \mathbf{B})\, d^3r \tag{III.234}$$

  This gives a spin of $\pm\hbar$.

- Since one can show that the angular momentum is an integer the photons are bosons. Note that we didn't find any restriction for the number of photons that can be in a given mode. This is another way of showing that photons are bosons.
- The photons move with the velocity of light $v = c$ since that the velocity of electromagnetic waves in a vacuum. By Einstein's theory of special relativity we know that the photons have zero mass
- The photon treatment can be found in the following resources:
  - Friedrich, Theoretical Atomic Physics
  - Sakurai and Napolitano, Modern Quantum Mechanics
  - Schiff, Quantum Mechanics
- The semiclassical atom-radiation interaction can be found in
  - Liboff (Chap 13.5 - 13.9)
  - Cohen-Tannoudiji (Chap 13)

As an aside we now go over the solution to the practice problem put online. Consider the harmonic oscillator Hamiltonian:

$$H_0 = \frac{p^2}{2m} + \frac{m}{2}\omega_0^2 x^2 \tag{III.235}$$

with the perturbation

$$W = \frac{1}{2}m\omega^2 x^2 \cos\omega t \tag{III.236}$$

$$c_k^{1storder}(t) = \delta_{k0} - \frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{k0}t'} \langle k| W(t') |0\rangle \, dt \tag{III.237}$$

We first need to find the matrix elements.

$$\langle k| \tilde{W} |0\rangle \equiv \langle k| x^2 |0\rangle \tag{III.238}$$

Here we use the following

$$x = \sqrt{\frac{\hbar}{2m\omega_0}} \left(a + a^\dagger\right) \tag{III.239}$$

where a and $a^\dagger$ are the annihilation and creation operators respectively.

$$x^2 = \frac{\hbar}{2m\omega_0}\left(a^2 + a^{\dagger\,2} + aa^\dagger a^\dagger a\right) \tag{III.240}$$

$$\langle k| W |0\rangle = \frac{\hbar}{2m\omega_0}\left(\cancelto{0}{\langle k| a^2 |0\rangle} + \langle k| aa^\dagger |0\rangle + \cancelto{0}{\langle k| a^\dagger a |0\rangle} + \langle k| a^{\dagger\,2} |0\rangle\right) \tag{III.241}$$

but $a^\dagger |0\rangle = |1\rangle, a|1\rangle = |0\rangle,$ and $a^\dagger |1\rangle = \sqrt{2}|2\rangle$. Thus

$$\langle k| W |0\rangle = \frac{\hbar}{2m\omega_0}\left(\langle k|0\rangle + \sqrt{2}\langle k|2\rangle\right) \tag{III.242}$$

$$= \frac{\hbar}{2m\omega_0}\left(\delta_{k0} + \sqrt{2}\delta_{k2}\right) \tag{III.243}$$

We now summarize our results as

$$\langle k| W(t) |0\rangle \Big|_{k\neq 0} = \frac{\sqrt{2}\hbar}{2m\omega_0}\frac{m\omega^2}{4}\left(e^{i\omega t} + e^{-i\omega t}\right) \tag{III.244}$$

Thus

$$c_2(t) = -i\frac{\sqrt{2}}{8}\frac{\omega^2}{\omega_0}\int_0^t e^{i2\omega_0 t'}\left(e^{i\omega t'} + e^{-i\omega t}\right)dt' \tag{III.245}$$

where we have $\omega_{20} = 2\omega_0$.

$$c_2(t) = -i\frac{\sqrt{2}}{8}\frac{\omega^2}{\omega_0}\left(\frac{1}{i\left(2\omega_0+\omega\right)}\left(e^{i(2\omega_0+\omega)t} - 1\right) + \frac{1}{i\left(2\omega_0-\omega\right)}\left(e^{i(2\omega_0-\omega)t} - 1\right)\right) \tag{III.246}$$

For the case of $\omega = 2\omega_0$ (the resonance condition) we have (must go back to the integral to show this)

$$c_2(t) = -i\frac{\sqrt{2}}{2}\omega_0 t \tag{III.247}$$

The probability is given by

$$P_2(t) = \frac{\omega_0^2}{2}t^2 \tag{III.248}$$

Lecture 20th, March 19th, 2012

IV. BRIEF INTRODUCTION TO RELATIVISTIC QUANTUM MECHANICS

A. Klien-Gordon Equation

1. Setting up a relativistic wave equation

Recall the non-relativistic case. We start from a classical expression for the energy of a free particle

$$E - \frac{p^2}{2m} = 0 \tag{IV.1}$$

We then quantize this expression by promoting the energy and momentum parts to operators:

$$E \to i\hbar\frac{\partial}{\partial t} \tag{IV.2}$$

$$p^2 \to -i\hbar^2\nabla^2 \tag{IV.3}$$

This gives

$$\left(i\hbar\frac{\partial}{\partial t} + \hbar^2\nabla^2\right)\psi = 0 \tag{IV.4}$$

The relativistic case is as follows. We start with the relativistic energy momentum relation:

$$E^2 = \mathbf{p}^2 + m^2 \tag{IV.5}$$

We then quantize this equation using the prescription above

$$\left(-\hbar^2\frac{\partial^2}{\partial t^2} + \hbar^2c^2\nabla^2 - m^2c^4\right)\psi = 0 \tag{IV.6}$$

or in natural units (KG equation)

$$\left(-\frac{\partial^2}{\partial t^2} + \nabla^2 - m^2\right)\psi = 0 \tag{IV.7}$$

B. Discussion of KG equation

(i) KG equation is a second order PDE in both space and time

(ii) KG equation is Lorentz covariant (this means that this equation behaves under LT the way that it should)

(iii) Time development is determined from two initial conditions (since it's second order in time) for the wavefunction and for the time deriviative. i.e.,

$$\psi(t_0) = \frac{\partial\psi(t_0)}{\partial t} \tag{IV.8}$$

However this is not compatible with one of the postulates of quantum mechanics which says that to get the full wavefunction we just need to act on the wavefunction at a certain time with the time evolution operator.

$$\psi(t_0) \xrightarrow{\hat{U}} \psi(t) \tag{IV.9}$$

(iv) Another problem arises with the continuity equation. One can derive the probability current in the KG equation:

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot\mathbf{J} = 0 \quad , \tag{IV.10}$$

where $\rho = \frac{i\hbar}{2mc^2}\left(\psi^*\frac{\partial\psi}{\partial t} - \psi\frac{\partial\psi^*}{\partial t}\right)$ is the probability density and $\mathbf{J} = \frac{i\hbar}{2m}\left(\psi\nabla\psi^* - \psi^*\nabla\psi\right)$ is the probability current. However ρ is not positive definite and can be negative!

(v) Consider the following trial solution of the KG equation:

$$\psi(\mathbf{r},t) = A\sin\left(\mathbf{k}\cdot\mathbf{r} - \omega t\right) \tag{IV.11}$$

$$\frac{\partial^2\psi}{\partial t^2} = -A\omega^2\sin\left(\mathbf{k}\cdot\mathbf{r} - \omega t\right) = -\omega^2\psi \tag{IV.12}$$

$$\nabla^2\psi = -k^2\psi \tag{IV.13}$$

substitution into the KG equation gives

$$\hbar^2\omega^2\psi = \left(\hbar^2c^2\mathbf{k}^2 + m^2c^4\right)\psi \tag{IV.14}$$

This gives

$$E^2 = c^2p^2 + m^2c^4 \tag{IV.15}$$

with $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$. However this solution doesn't solve the Schrodinger equation! The time dependent Schrodinger equation cannot be solved by a real solution. However this is not true for the KG equation. Subsitution into the current and probability densities given above for this solution gives

$$\mathbf{J} = 0 \tag{IV.16}$$

$$\rho = 0 \tag{IV.17}$$

This solution is clearly problematic. On the other hand we can try another solution for the KG equation:

$$\psi(\mathbf{r},t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \tag{IV.18}$$

with the same energy momentum relation:

$$E^2 = p^2c^2 + m^2c^4 \tag{IV.19}$$

The Klien Gordon equation does not seem to have any restriction on energy thus we can have

$$E = \pm\sqrt{p^2c^2 + m^2c^4} \tag{IV.20}$$

(vi) Adding the Coloumb potential to the free KG equation and solving gives solutions that don't agree with experiments. This is what bothered Schrodinger. This is because the KG equation does not take spin into account.

(vii) In 1934 the KG equation was recognized as correct wave equation for spin 0 particles.

C. Dirac Equation

1. *Free Particles*

Dirac wanted an equation first order in space and time. He hoped this would remove some of the problems with the KG equation. Dirac tried the an satz was

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{IV.21}$$

He had a set of requirements that his equation was to fulfill.

(i) Compatibility with the relativistic energy relation: $E^2 = p^2c^2 + m^2m^4$

(ii) Covariant with respect to Lorentz transformations.

(iii) An equation that is consistent with the continuity equation and probability interpretation

(iv) He didn't want to invent any new quantization rules

We have our energy momentum relation

$$E^2 = \mathbf{p}^2c^2 + m^2c^4 \tag{IV.22}$$

If we had the equation (which is not true!)

$$E = pc + mc^2 \tag{IV.23}$$

then we are first order and space and time. Dirac's idea was to write

$$H = \boldsymbol{\alpha} \cdot \mathbf{p}c + \beta mc^2 \quad . \tag{IV.24}$$

Dirac realized that this an satz can fulfill the energy momentum relation if $\boldsymbol{\alpha}$ and β are matrices. Trying to fulfill the requirements listed above gives the restrictions on α and β. All we know so far is that we have three α matrices and 1 β matrix. We call these $N \times N$ matrices. Since these are matrices we require wavefunctions with a number of components equal to the dimensionality of the matrices. These wavefunctions are called 'spinor wavefunctions'. We can denote this spinor wavefunction as follows

$$\Psi = \begin{pmatrix} \psi_1(\mathbf{r},t) \\ \psi_2(\mathbf{r},t) \\ \vdots \\ \psi_N(\mathbf{r},t) \end{pmatrix} \tag{IV.25}$$

where N is the dimensionality of the matrices. The first requirement says that each component $\psi_i(\mathbf{r},t)$ must fulfill the KG equation.

Lecture 21 - March 21st, 2012

We now go through Dirac's wishlist in order to find conditions for $\boldsymbol{\alpha}$ and β: First each component of $\psi_i(\mathbf{r},t)$ must fulfill the Klien Gordon equation. Consider the Dirac equation:

$$\left(i\hbar\frac{\partial}{\partial t} - H\right)\Psi = 0 \tag{IV.26}$$

iterating the Dirac equation gives

$$\left(i\hbar\frac{d}{dt} - H\right)\left(i\hbar\frac{d}{dt} - H\right)\Psi = 0 \tag{IV.27}$$

$$-\hbar^2\frac{d^2}{dt^2} + H^2 - 2i\hbar\left(\frac{d}{dt}H\right)\Psi = 0 \tag{IV.28}$$

$$-\hbar^2\frac{d^2}{dt^2} + H^2 - 2H^2\Psi = 0 \tag{IV.29}$$

$$-\hbar^2\frac{d^2}{dt^2} = H^2\Psi \qquad 0 \tag{IV.30}$$

$$\begin{aligned} -\hbar^2\frac{\partial^2}{\partial t^2}\Psi &= \left(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2\right)\left(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2\right)\Psi \\ &= \left(c\frac{\hbar}{i}\sum_j \alpha_j\frac{d}{dx_j} + \beta mc^2\right)\left(c\frac{\hbar}{i}\sum_k \alpha_k\frac{d}{dx_k} + \beta mc^2\right)\Psi \\ &= \left\{-\hbar^2c^2\sum_{j,k}\alpha_j\alpha_k\frac{\partial^2}{\partial x_j\partial x_k} + \frac{\hbar mc^3}{i}\sum_j\left(\alpha_j\beta - \beta\alpha_j\right)\frac{d}{dx_j} + \beta^2m^2c^4\right\}\Psi \\ &= \left\{-\hbar^2c^2\sum_{j,k}\frac{\alpha_j\alpha_k + \alpha_k\alpha_j}{2}\frac{\partial^2}{\partial x_j\partial x_k} + \frac{\hbar mc^3}{i}\sum_j\left(\alpha_j\beta - \beta\alpha_j\right)\frac{d}{dx_j} + \beta^2m^2c^4\right\}\Psi \end{aligned} \tag{IV.31}$$

Recall the Klien Gordan equation says that

$$-\hbar^2\frac{\partial^2}{\partial t^2}\psi = \left(-\hbar^2c^2\nabla^2 + m^2c^4\right)\psi \tag{IV.32}$$

The left hand sides are trivially equal to one another. Thus we require certain conditions. Clearly there are no first order derivatives in the KG equation. Thus we require

$$\boxed{\alpha_j\beta + \beta\alpha_j \equiv \{\alpha_j, \beta\} = 0} \quad . \tag{IV.33}$$

The KG equation only has second derivatives in the form of a Laplacian. Thus all the cross terms such as $\frac{\partial^2}{\partial x_1 x_2}$ must be zero. This can be done by introducing a Kronecker delta. However the term must be 1 for each second derivative of a given variable (e.g. $\frac{\partial^2}{\partial x_1^2}$):

$$\boxed{\alpha_j\alpha_k + \alpha_k\alpha_j = 2\delta_{jk}} \tag{IV.34}$$

Lastly we require

$$\boxed{\beta^2 = 1} \tag{IV.35}$$

This conditions must be fulfilled for all $j, k = 1, 2, 3$. Further requirements(one that wasn't mentioned in Dirac's wishlist but important) was that the Dirac Hamiltonian should be Hermitian:

$$H = H^\dagger \tag{IV.36}$$

This requires

$$\boxed{\alpha_j = \alpha^\dagger \quad ; \quad \beta = \beta^\dagger} \quad . \tag{IV.37}$$

Hence they have real eigenvalues. Notice our requirements tell us that

$$\alpha_j^2 = 1 \text{ and } \beta^2 = 1$$

Thus the eigenvalues must be ± 1 for all four of these matrices. Consider the equation

$$\alpha_j\beta + \beta\alpha_j = 0 \quad .$$

If we multiply this equation on the right with β we we have

$$\begin{aligned} \alpha_j\beta^2 &= -\beta\alpha_j\beta \\ \alpha_j &= -\beta\alpha_j\beta \\ \mathrm{Tr}(\alpha_j) &= -\mathrm{Tr}(\beta\alpha_j\beta) \\ \boxed{\mathrm{Tr}(\alpha_j) &= -\mathrm{Tr}(\alpha_j)} \end{aligned} \tag{IV.38}$$

where in the last step we used $\beta^2 = 1$. Hence the trace of α_j must be zero. The same can be shown for β by multiplying by α_j instead of β in the beginning. Thus we have another condition on α_j and β, α_j and β are traceless. Since the matrices are tracelss the sum of the eigenvalues is zero (easy to prove). Since the eigenvalues are ± 1 and the only way to have a sum of 0 we need to have an even dimension! We need 4 anticommuting matrices.

The simplest choice for the dimension would be $N = 2$. However we already know that the Pauli matrices make up three independent anticommuting matrices and there cannot be a fourth. Hence we need to go up to a larger dimension. We choose the next lowest dimension, namely $N = 4$. Matrices are obey all the conditions we have above are

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \; ; \; \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix} \; ; \; \alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} \; ; \; \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{IV.39}$$

Note that we can rewrite these as

$$\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \; ; \; \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \; ; \; \alpha_z = \begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix} ; \;\; \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{IV.40}$$

We now take a look at the Dirac equation more explicitly:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \left\{ c \left(\alpha_x p_x + \alpha_y p_y + \alpha_z p_z \right) + \beta m c^2 \right\} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \tag{IV.41}$$

These are four coupled equations because α have all off-diagonal terms. Working out these equations gives (when you multiply by α and β matrices)

$$i\hbar \frac{\partial}{\partial t} \psi_1 = \frac{\hbar c}{i} \left(\left(\frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) \psi_4 + \frac{\partial}{\partial z} \psi_3 \right) + mc^2 \psi_1 \tag{IV.42}$$

$$i\hbar \frac{\partial}{\partial t} \psi_2 = \frac{\hbar c}{i} \left(\left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) \psi_3 - \frac{\partial}{\partial z} \psi_4 \right) + mc^2 \psi_2 \tag{IV.43}$$

$$i\hbar \frac{\partial}{\partial t} \psi_3 = \frac{\hbar c}{i} \left(\left(\frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) \psi_2 + \frac{\partial}{\partial z} \psi_1 \right) - mc^2 \psi_3 \tag{IV.44}$$

$$i\hbar \frac{\partial}{\partial t} \psi_4 = \frac{\hbar c}{i} \left(\left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) \psi_1 - \frac{\partial}{\partial z} \psi_2 \right) - mc^2 \psi_4 \tag{IV.45}$$

2. *Solutions of the free Dirac equation*

To solve them we use the ansatz

$$\psi_j(\mathbf{r}, t) = u_j e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \tag{IV.46}$$

with $E = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$. This gives four linearly independent solutions. The two solutions

$$u^{(1)} = \begin{pmatrix} 1 \\ 0 \\ \chi_1 \\ \chi_2 \end{pmatrix} \; ; \; u^{(2)} = \begin{pmatrix} 0 \\ 1 \\ \chi_1' \\ \chi_2' \end{pmatrix} \tag{IV.47}$$

correspond to an energy of

$$E = +\sqrt{p^2c^2 + m^2c^4} \tag{IV.48}$$

The factors $\chi_1, \chi_2, \chi_1', \chi_2'$ are kinematic factors. In the limit of $v \ll c$ these factors are zero. The two other solutions,

$$u^{(3)} = \begin{pmatrix} \phi_1 \\ \phi_2 \\ 1 \\ 0 \end{pmatrix} \; ; \; u^{(4)} = \begin{pmatrix} \phi_1' \\ \phi_2' \\ 0 \\ 1 \end{pmatrix} \tag{IV.49}$$

correspond to negative energy, $E = -\sqrt{p^2c^2 + m^2c^4}$ with $\phi_1, \phi_2, \phi_1', \phi_2' \xrightarrow{v \ll c} 0$. These negative solutions are difficult to interpret. Dirac's interpretation is shown in figure 15. Dirac says that the negative energy levels are all occupied by negative energy electrons. Since electrons are fermions they cannot all pile in these negative energy states. These particles make up the vacuum. Thus we use a photon with high enough energy we can excited these particles and create a hole in the Dirac sea. Dirac inferred that these holes are observable as antiparticles called the positrons. These are holes in the negative energy spectrum and hence have positive energy.

This interpretation says that the vacuum is a a fully occupied Dirac sea with no electrons with energy $E > mc^2$.

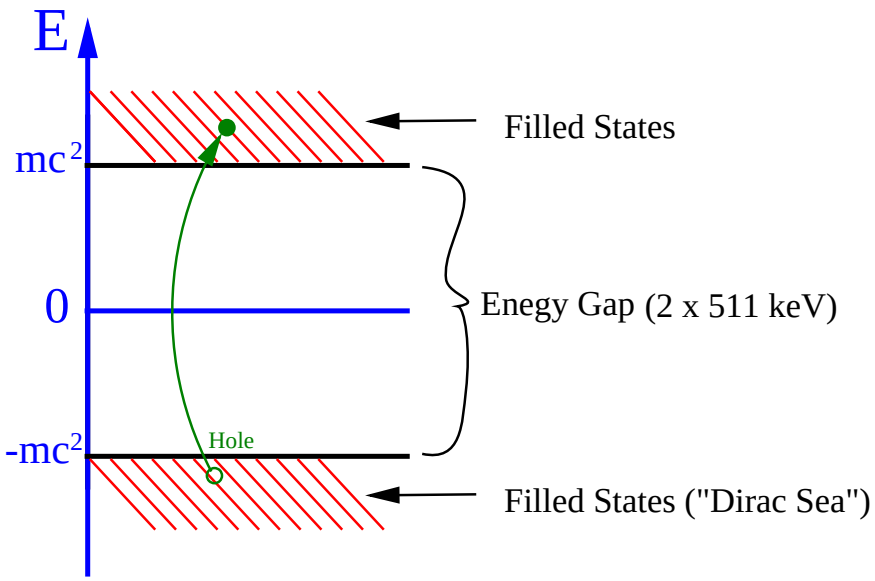


FIG. 15. The Dirac Interpretation of the solutions to the Dirac equation. He says that all the negative energy levels are filled. However we cannot observe these particles

Lecture 22 - March 26th, 2012
As an aside recall that Dirac's problem with the KG equation was that it didn't give physical answers for the continuiuty equation. For the Dirac equation one can show that

$$\rho = \Psi^\dagger \Psi = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + |\psi_4|^2 > 0 \tag{IV.50}$$

$$J_k = c\Psi^\dagger \alpha_k \Psi \tag{IV.51}$$

for $k = 1, 2, 3$. The Dirac equations gives strictly positive probabilities as expected and parallels the probabilities in the Schrodinger equation.

We now come back to the Dirac interpretation. The process of pair creation is given by

$$\gamma \to e^+ + e^- \tag{IV.52}$$

To conserve energy and momentum this process must occur in the presence of a nucleus. Annihilation can produce photons:

$$e^+ + e^- \to 2\gamma \tag{IV.53}$$

The consequence of the Dirac interpretation is that particle number is not conserved in this theory. Not only photons can be created and annihilated but also photons can. This suggests that this is a many-particle theory.

Recall that we have 4 energy solutions. This is called a doublet structure. This represents the spin degree of freedom:

$$u^{(1)}, u^{(3)} \quad \text{“spin up”}$$
$$u^{(2)}, u^{(4)} \quad \text{“spin down”}$$

At this point from our analysis its not clear that this spin has anything to do with angular momentum.

Now consider the components in the u vectors labeled χ. These are non-vanishing 'small' components which implies that e^+ and e^- are intrinsically connected. For small velocity ($v \ll c$) the Schrodinger (Pauli) equation can be recovered from the Dirac equation.

3. Add Electromagnetic Potentials

We now add EM potentials to the Dirac theory. This is often called the "minimal coupling prescription". Recall that the get from the free Schrodinger equation to one with potentials we add a potential:

$$i\hbar\frac{\partial}{\partial t}\psi = \frac{p^2}{2m}\psi \tag{IV.54}$$

In EM field we have

$$i\hbar\frac{\partial}{\partial t}\psi = \frac{1}{2m}\left(\mathbf{p}+e\mathbf{A}\right)^2 - e\phi \tag{IV.55}$$

We can extract a recipe from this.

$$\mathbf{p} \to \mathbf{p} + e\mathbf{A}$$
$$i\hbar\frac{\partial}{\partial t} \to i\hbar\frac{\partial}{\partial t} + e\phi$$

Recall the free Dirac equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \left(\boldsymbol{\alpha}\cdot\mathbf{p}c + \beta mc^2\right)\psi \tag{IV.56}$$

Using our recipe we have

$$i\hbar\frac{\partial\psi}{\partial t} = \left(\boldsymbol{\alpha}\cdot\left(\mathbf{p}+e\mathbf{A}\right) + \beta mc^2 - e\phi\right)\psi \tag{IV.57}$$

One can show that this equation is also Lorentz covariant which says that it has the same form in all inertial reference frames.

4. The relativistic hydrogen problem

This corresponds to a given choice for the potential in the Dirac equation

$$\mathbf{A} = 0; \quad \phi = \frac{Ze}{4\pi\epsilon_0 r} \quad . \tag{IV.58}$$

However this is not Lorentz covariant since we chose a nonconvariant form for the potential (if you have a boost then the vector potential would be nonzero). This introduces a small error. To solve the Dirac equation we use the usual an satz

$$\Psi(\mathbf{r},t) = \Phi(\mathbf{r})e^{-iEt/\hbar} \tag{IV.59}$$

this gives

$$\left\{c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right\}\Phi(\mathbf{r}) = E\Phi(\mathbf{r}) \tag{IV.60}$$

Lecture 23 - March 28th, 2012
The bound-state eigenenergies for the bound states can be obtained and written as

$$E_{n,j} = mc^2\left[-\sqrt{1+\frac{\left(Z\alpha\right)^2}{\left(n-\delta_j\right)^2}}\right] \tag{IV.61}$$

where $\delta_j \equiv j+\frac{1}{2}-\sqrt{\left(j+\frac{1}{2}\right)^2-\left(Z\alpha\right)^2}$ and $\alpha = \frac{\hbar}{ma_0c} \approx \frac{1}{137}$.

$$n = 1, 2, 3, ...$$

is still the principle quantum number and

$$j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ..., n-\frac{1}{2}$$

is the total angular momentum quantum number.
Discussion

(i) $\delta_j \geq 0$ for $Z\alpha \leq 1$

(ii) $E_{n,j} \neq E_{n,j'}$ this accounts for fine-structure.

(iii) One can expand $E_{n,j}$ in powers of the small parameters $(Z\alpha)^2$. This gives

$$E_{n,j} = mc^2 \left(1 - \frac{(Z_\alpha)^2}{2n^2} - \frac{(Z_\alpha)^4}{2n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right) \tag{IV.62}$$

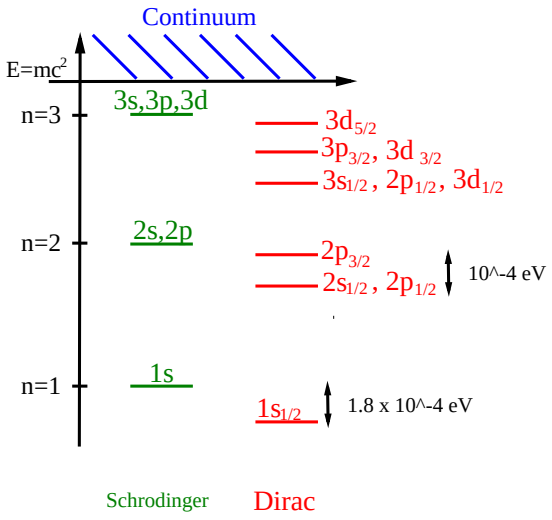
The first term (0^{th} order) is the rest energy mc^2. The second term (1^{st} order) we have the non relativistic binding energy since

$$mc^2\alpha^2 = \frac{\hbar}{ma_0^2} \tag{IV.63}$$

and

$$E_n^{(2)} = -\frac{\hbar}{2ma_0^2}\frac{Z^2}{n^2} \tag{IV.64}$$

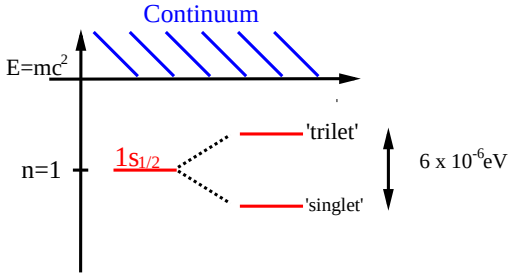
The third term (2^{nd} order) gives a relavistic correction which is j dependent (fine structure). The fine structure is shown in figure **??**:



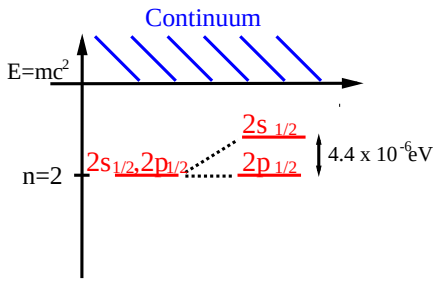
Notice that in Schrodinger's theory our reference frame was zero. On the other hand with Dirac we have relativity and we use $E = mc^2$ as our new reference frame.

Further corrections of bound state hydrogen problem:

(i) Hyperfine structure coupling of magnetic moments of the electron to the nuclear magnetic moment. e.g.



(ii) QED effects (the Lamb shift) e.g.



5. Nonrelativistic limit of the Dirac equations

The starting point is the stationary Dirac equation:

$$\left(c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta mc^2+V(\mathbf{r})\right)\Phi=E\Phi(\mathbf{r}) \tag{IV.65}$$

we write the 4-spinor as

$$\Phi=\begin{pmatrix}\phi\\ \chi\end{pmatrix}=\begin{pmatrix}\phi_1\\ \phi_2\\ \chi_1\\ \chi_2\end{pmatrix} \tag{IV.66}$$

We can write $\alpha_j=\begin{pmatrix}0 & \sigma_j\\ \sigma_j & 0\end{pmatrix}$ with σ_j as the Pauli matrices. Further we have $\beta=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$. Inserting into the Dirac equation gives

$$c\begin{pmatrix}0 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0\end{pmatrix}\cdot\mathbf{p}\begin{pmatrix}\phi\\ \chi\end{pmatrix}=\left(E-V(\mathbf{r})-mc^2\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right)\Phi(\mathbf{r}) \tag{IV.67}$$

This gives two coupled matrices for ϕ and χ:

$$\begin{aligned}c\boldsymbol{\sigma}\cdot\mathbf{p}\chi&=\left(E-V(\mathbf{r})-mc^2\right)\phi\\ c\boldsymbol{\sigma}\cdot\mathbf{p}\phi&=\left(E-V(\mathbf{r})+mc^2\right)\chi\end{aligned}$$

Isolating the second equation for χ gives

$$\chi=\frac{c}{E-V(\mathbf{r})+mc^2}\boldsymbol{\sigma}\cdot\mathbf{p}\phi \tag{IV.68}$$

Inserting this equation into the top equation gives

$$\boldsymbol{\sigma}\cdot\mathbf{p}\left\{\frac{c^2}{E-V(\mathbf{r})+mc^2}\boldsymbol{\sigma}\cdot\mathbf{p}\right\}\phi=\left(E-V(\mathbf{r})-mc^2\right)\phi \tag{IV.69}$$

Lecture 24th, 2012
Isolating for ϕ we have

$$\phi=\frac{1}{(E-V(\mathbf{r})-mc^2)}\boldsymbol{\sigma}\cdot\mathbf{p}\left\{\frac{c^2}{E-V(\mathbf{r})+mc^2}\boldsymbol{\sigma}\cdot\mathbf{p}\right\}\phi \tag{IV.70}$$

We now make a weak relativistic approximation. We define

$$\varepsilon=E-mc^2\ll mc^2$$

Further we assume

$$V(r)\ll mc^2$$

We now expand consider the term in the left hand side of equation IV.69:

$$\left\{\frac{c^2}{\varepsilon+2mc^2-V(\mathbf{r})}\right\}=\frac{1}{2m\left(1+\frac{\varepsilon-V}{2mc^2}\right)}\approx\frac{1}{2m}\left(1-\frac{\varepsilon-V}{2mc^2}\right) \tag{IV.71}$$

This gives

$$\frac{1}{2m}\left[\boldsymbol{\sigma}\cdot\mathbf{p}\left(1-\frac{\varepsilon-V}{2mc^2}\right)\boldsymbol{\sigma}\cdot\mathbf{p}\right]\phi=(\varepsilon-V)\,\phi \tag{IV.72}$$

$$\frac{1}{2m}\left[\left(1-\frac{\varepsilon-V}{2mc^2}\right)(\boldsymbol{\sigma}\cdot\mathbf{p})^2+\frac{\hbar}{i}\boldsymbol{\sigma}\cdot\frac{\nabla V}{2mc^2}\boldsymbol{\sigma}\cdot\mathbf{p}\right]\phi=(\varepsilon-V)\,\phi \tag{IV.73}$$

Now for Pauli matrices we can write

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B})=\nabla(\mathbf{A}\cdot\mathbf{B})+i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B}) \tag{IV.74}$$

In our case we have $\mathbf{A}\times\mathbf{B}=\mathbf{p}\times\mathbf{p}=0$. Further we have that the gradient of a function is (given no radial dependence

$$\nabla V=\frac{1}{r}\frac{dV}{dr}dr \tag{IV.75}$$

Inserting in these relations we have

$$\frac{1}{2m}\left[\left(1-\frac{\varepsilon-V}{2mc^2}\right)p^2+\frac{\hbar}{i}\frac{1}{r}\frac{dV}{dr}\left(\frac{\boldsymbol{\sigma}\cdot\mathbf{r}\boldsymbol{\sigma}\cdot\mathbf{p}}{2mc^2}\right)\right]\phi=(\varepsilon-V)\,\phi \tag{IV.76}$$

$$\frac{p}{2m}\left[\left(1-\frac{\varepsilon-V}{2mc^2}\right)+\frac{\hbar}{i}\frac{1}{4m^2c^2r}\frac{dV}{dr}(\mathbf{r}\cdot\mathbf{p})+\frac{\hbar}{4m^2c^2r}\frac{dV}{dr}\boldsymbol{\sigma}\cdot\mathbf{L}\right]\phi=(\varepsilon-V)\,\phi \tag{IV.77}$$

where we have used equation IV.74 We define these terms T_1, T_2 and T_3 respectively.

Interpretation of Terms

As preparation consider a term acting on a non-relativistic wavefunction

$$\left(\varepsilon-mc^2-V(r)\right)\psi=\frac{p^2}{2m}\psi$$

This is not the term we have. In our case we have

$$T_1\phi=\left(1-\frac{\varepsilon-V}{2mc^2}\right)\frac{p^2}{2m}\approx\frac{p^2}{2m}-\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2 \tag{IV.78}$$

$$=\frac{p^2}{2m}-\frac{p^4}{8m^3c^2} \tag{IV.79}$$

Here we see the relativistic correction of kinetic energy. The second term T_2 is not Hermitian. However it can easily be made Hermitian by considering Hermitian average

$$\bar{T}_2\equiv\frac{1}{2}\left(T_2+T_2^\dagger\right) \tag{IV.80}$$

$$=\frac{1}{2}\left(\frac{\hbar}{i}\frac{1}{r}\frac{dV}{dr}\mathbf{r}\cdot\mathbf{p}-\frac{\hbar}{i}\left(\underbrace{\frac{1}{r}\frac{dV}{dr}}_{\mathbf{F}(\mathbf{r})}\mathbf{r}\cdot\mathbf{p}\right)^\dagger\right) \tag{IV.81}$$

Now

$$(\mathbf{F}\cdot\mathbf{p})^\dagger=\mathbf{p}^\dagger\mathbf{F}^\dagger(\mathbf{r}) \tag{IV.82}$$

$$=\mathbf{p}^\dagger\cdot\mathbf{F}^\dagger \tag{IV.83}$$

$$=\mathbf{p}\cdot\mathbf{F} \tag{IV.84}$$

With this we have

$$\bar{T_2} = \frac{1}{8m^2c^2}\left(\frac{\hbar}{i}\frac{dV}{dr}\mathbf{r}\cdot\mathbf{p} - \frac{\hbar}{i}\mathbf{p}\cdot\mathbf{r}\frac{1}{r}\frac{dV}{dr}\right) \tag{IV.85}$$

By inserting $\mathbf{p} = \frac{\hbar}{i}\nabla$ and doing some algebra (exercise) we get

$$\bar{T_2} = \frac{\hbar^2}{8m^2c^2}\nabla^2 V \equiv H_D \tag{IV.86}$$

This term is called the Darwin hamiltonian. Note that

$$\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta(\mathbf{r}) \tag{IV.87}$$

Thus we finally have

$$H_D = \frac{Ze^2\hbar^2}{8m^2c^2\epsilon_0}\delta(\mathbf{r}) \tag{IV.88}$$

This represents "Zitterbewgung" or trembling motion. Lastly consider the third term

$$T_3 = \frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{dV}{dr}\boldsymbol{\sigma}\cdot\mathbf{L} \tag{IV.89}$$

$$= \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{S}\cdot\mathbf{L} \tag{IV.90}$$

with $\mathbf{S} = \frac{\hbar}{2}\boldsymbol{\sigma}$. This is a spin orbit coupling term. This is the reason we call spin-orbit coupling a relativistic effect. The weak relativistic limit of the Dirac equation takes the form

$$H\left|\phi\right\rangle = \varepsilon\left|\phi\right\rangle \tag{IV.91}$$

with

$$H = fracp^2 2m - \frac{Ze^2}{4\pi\epsilon_0 r} + \left(-\frac{p^4}{8m^3c^2}\right) + H_D + T_3 \tag{IV.92}$$

$$= H_0 + W \tag{IV.93}$$

You can account for W in first order perturbation theory. We obtain

$$\Delta E^{(1)} = \langle W\rangle = \frac{mc^2}{2}\frac{(Z\alpha)^4}{n^3}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) \tag{IV.94}$$