Physics 251b – LECTURE NOTES – Spring 2012

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NOTE: The following lecture notes were originally prepared by graduate student Phil Larochelle, based on the course given by B. I. Halperin at Harvard in spring 2004. Corrections and additions have been made by Prof. Halperin. *Notes for this course are intended for the use of students and other affiliates of Harvard University, and should not be distributed further without the express permission of Prof. Halperin.*

1.1　The Schrödinger and Heisenberg Pictures

1.1.1　Schrödinger Picture

The Schrödinger picture is the method we used throughout P251a. Pure states within the Schrödinger Picture are denoted by $|\psi\rangle$ and obey the Schrödinger equation of the form:

$$i\hbar\frac{\partial |\psi\rangle}{\partial t} = H |\psi\rangle \tag{1.1}$$

Given this equation it is possible to state the time evolution of a state $|\psi\rangle$ in terms of a time evolution operator $T(t,t')$:

$$|\psi(t)\rangle = T(t,t') |\psi(t')\rangle \tag{1.2}$$

The time evolution operator will have the following properties:

- $i\hbar\frac{\partial T}{\partial t} = HT$

- $-i\hbar\frac{\partial T^\dagger}{\partial t} = T^\dagger H$

- $T(t,t) = 1$

- $T(t,t')T(t',t'') = T(t,t'')$,　　$T(t,t')T(t',t) = T(t,t) = 1$,　$T(t,t') = T^{-1}(t',t)$

- By the preservation of normalization we have $\langle\psi(t)|\psi(t)\rangle = \langle\psi(t')|\psi(t')\rangle$ Therefore T must be unitary: $T^\dagger T = 1$.

If H is independent of time then T will take the form of $T(t,t') = e^{-i(t-t')H/\hbar}$.

Observables are associated with operators. In the Schrödinger picture, if an observable has no explicit time dependence, then the operator has no time dependence. However the expectation

value of these operators will have time dependence: $\langle A \rangle_t = \langle \psi(t)|A|\psi(t)\rangle_t$. From Ehrenfest's theorem, derived in p251a, we had a formula for the time dependence of expectation values. If an observable has no explicit time dependence, then

$$\frac{d\langle A \rangle_t}{dt} = \frac{1}{i\hbar}\langle \psi(t)|[A,H]|\psi(t)\rangle_t = \frac{1}{i\hbar}\langle [A,H]\rangle_t \tag{1.3}$$

We can also talk about mixed states, which can be described through the use of a density matrix $W(t)$. We saw that the expectation value of the operator A at time t was given by $\langle A \rangle_t = Tr(AW(t))$. We also found that the time evolution of the density matrix could be obtained by $W(t) = T(t,t_0)W(t_0)T^\dagger(t,t_0)$ and that it obeyed the equation:

$$\frac{dW(t)}{dt} = \frac{-1}{i\hbar}[W(t),H]$$

Therefore we get:

$$\frac{d\langle A \rangle_t}{dt} = Tr\left(A\frac{dW(t)}{dt}\right) = -\frac{1}{i\hbar}Tr(A[W(t),H]) \tag{1.4}$$

$$= \frac{1}{i\hbar}Tr([A,H]W(t)) = \frac{1}{i\hbar}\langle [A,H]\rangle_t , \tag{1.5}$$

giving us the same result as before.

In addition to the Schrödinger picture as a means of analyzing quantum mechanics, there exist other possible pictures. You can make any kind of unitary transformation that you want as long as you are consistent. We will denote our new picture by putting bars on everything. The states and operators without bars are in the old Schrödinger picture. Let $U(t)$ be an arbitrary unitary operator, which may depend on the time t. Then new quantities can be defined:

- States are given by $\left|\bar{\psi}(t)\right\rangle = U(t)\left|\psi(t)\right\rangle$.

- Observables are given by $\bar{A}(t) = U(t)AU^\dagger(t)$.

- Density will be given by: $\bar{W}(t) = U(t)W(t)U^\dagger(t)$

We can see that the expectation values are preserved in this new picture:. For pure states, $\langle \bar{\psi}(t)|\bar{A}(t)|\bar{\psi}(t)\rangle = \langle \psi(t)|A(t)|\psi(t)\rangle = \langle A \rangle_t$, since $U^\dagger U = 1$. Also, using the invariance of the trace under cyclic permutations:

$$\text{Tr}(\bar{W}\bar{A}) = \text{Tr}(UWU^\dagger UAU^\dagger) = \text{Tr}(WA) \tag{1.6}$$

A unitary transformation is a change in basis and preserves eigenvalues, product of operators and commutators.

$$AB = C \quad \Rightarrow \quad \bar{A}\bar{B} = \bar{C}$$

$$[A,B] = C \quad \Rightarrow \quad [\bar{A},\bar{B}] = \bar{C} \tag{1.7}$$

Example: For the kinetic energy K, we have $\bar{K} = \left(\frac{p^2}{2m}\right) = \frac{\bar{p}\cdot\bar{p}}{2m}$, since $K = \frac{p\cdot p}{2m} = \frac{p^2}{2m}$

1.1.2   Heisenberg Picture

Choose the unitary transformation $U(t) = T^\dagger(t,0) = T(0,t)$. This will yield the states:

$$\left|\bar{\psi}(t)\right\rangle = T^\dagger(t,0)\left|\psi(t)\right\rangle = \left|\psi(0)\right\rangle \tag{1.8}$$

This tells us that $\left|\bar{\psi}(t)\right\rangle = \left|\bar{\psi}(0)\right\rangle = \left|\psi(0)\right\rangle$. Therefore our new Heisenberg picture states are independent of time. The density matrix $\bar{W} = T^\dagger(t,0)W(t)T(t,0) = W(0) = \bar{W}(0)$ is also independent of time. For a general Schrödinger operator A, the corresponding Heisenberg operator will be given by

$$\bar{A}(t) = T^\dagger(t,0)A T^{(}t,0)$$

If A has no explicit time dependence, then the time evolution of the Heisenberg operator will be given by:

$$\frac{d\bar{A}(t)}{dt} = \frac{dT^\dagger(t,0)}{dt}A\,T(t,0) + T^\dagger(t,0)A\,\frac{dT(t,0)}{dt} = T^\dagger(t,0)\frac{[A,H]}{i\hbar}T(t,0) = \frac{\left[\bar{A},\bar{H}\right]}{i\hbar} \tag{1.9}$$

Since the state vector or density matrix is independent of time in the Heisenberg picture, we may compute the time derivative of the expectation value of A by taking the expectation value of both sides of this equation. We recover Ehrenfest's equation in the Heisenberg picture:

$$\frac{d\langle\bar{A}(t)\rangle}{dt} = \frac{1}{i\hbar}\langle[\bar{A},\bar{H}]\rangle \tag{1.10}$$

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2.1 Heisenberg Picture (continued)

Consider a situation where, in the Schrödinger picture, the Hamiltonian H is independent of time. From the previous lecture we saw that if an operator A has no explicit time dependence in the Schrödinger picture, then in the Heisenberg picture,

$$\frac{d\bar{A}(t)}{dt} = \frac{\left[\bar{A}(t), \bar{H}(t)\right]}{i\hbar} \tag{2.1}$$

Therefore we can directly obtain

$$\frac{d\bar{H}(t)}{dt} = \frac{\left[\bar{H}(t), \bar{H}(t)\right]}{i\hbar} = 0 \tag{2.2}$$

Since $\bar{H}(t=0) = H$ it follows that $\bar{H} = H$. This is consistent with the transformation law for our Schrödinger $\Rightarrow$ Heisenberg operators;

$$\bar{H} = UHU^\dagger = H \tag{2.3}$$

since, in this case, $[U, H] = [H, U^\dagger] = 0$ where $U(t) = \exp(iHt/\hbar) = T^\dagger(t, 0)$. If H does have time dependence then these relationships cease to hold.

2.1.1 Example: 1 - D particle in a potential $V(x; t)$

The Hamiltonian for a particle in a time-independent one-dimensional potential in the Schrödinger picture will be:

$$H = \frac{p^2}{2m} + V(x; t)$$

Now using the transformation law in equation (2.3) we arrive at:

$$\bar{H} = \frac{\bar{p}^2}{2m} + V(\bar{x}; t) \tag{2.4}$$

Commutators are preserved under unitary transformations, therefore $[\bar{x}, \bar{p}] = i\hbar$ and our equations of motion for the Heisenberg operators will give:

$$\frac{d\bar{x}}{dt} = \frac{1}{i\hbar}\left[\bar{x}, \bar{H}\right] = \frac{\bar{p}}{m} \tag{2.5}$$

$$m\frac{d^2\bar{x}}{dt^2} = \frac{d\bar{p}}{dt} = \frac{1}{i\hbar}\left[\bar{p}, \bar{H}\right] = -V'(\bar{x}; t), \tag{2.6}$$

where $V'(x;t) \equiv \partial V(x;t)/\partial x$.

In this form, the operator equations of motion look very similar to Newton's equations of motion. However, the equations are really much more complicated than in classical mechanics, because $\bar{x}$ and $\bar{p}$ are not just real numbers but are operators, which is to say they are essentially infinite-dimensional matrices. If you think in terms of the matrix elements of the operators in some fixed basis of states, what we have is an infinite set of coupled first-order differential equations, which is not easy to solve in general. There are only a few special cases where one can obtain useful explicit solutions. One is the free particle. Another is the case of the harmonic oscillator.

For the harmonic oscillator we have:

$$V(\bar{x}) = \frac{k}{2}\bar{x}^2 \qquad V'(\bar{x}) = k\bar{x} \tag{2.7}$$

This will yield the formal solutions:

$$\bar{x}(t) = \bar{x}(0)\cos(\omega_0 t) + \frac{\bar{p}(0)}{m\omega_0}\sin(\omega_0 t) \tag{2.8}$$

$$\bar{p}(t) = \bar{p}(0)\cos(\omega_0 t) - \frac{k\bar{x}(0)}{\omega_0}\sin(\omega_0 t) \tag{2.9}$$

with $\omega_0 = (k/m)^{1/2}$. This is like the solution for the classical harmonic oscillator. Now these are operator equations. What you actually do with this is a matter which will discuss later. An important fact is that $[\bar{x}(t), \bar{x}(t')] \neq 0$, unless $\omega_0(t - t')$ is a multiple of π. This means that you can't perfectly know both $\bar{x}(t)$ and $\bar{x}(t')$ Looking back at equation (2.8) we can see why this is true: to know $\bar{x}(t)$ and $\bar{x}(0)$ you would have to perfectly know $\bar{x}(0)$ and $\bar{p}(0)$ which is impossible by the uncertainty principle.

2.1.2   Interaction Representation

Consider a Hamiltonian of the form $H(t) = H_0 + V(t)$ where $V(t)$ is small. This will be used later in time-dependent perturbation theory, We choose our unitary transformation to be $U(t) = \exp(iH_0 t/\hbar)$ and we can see that if $V(t) = 0$ this would just be the Heisenberg picture. This unitary transformation describes the interaction picture description of quantum mechanics. In this picture the time dependence of the operators is due to H_0 and the time dependence of the states will be due to $V(t)$. The transformation of operators[1] will be given by:

$$\bar{A} = e^{iH_0 t/\hbar} A e^{-iH_0 t/\hbar} = UAU^\dagger \tag{2.10}$$

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[1]We are using the bar for objects now in the interaction picture, and unbarred for Schrödinger objects

The time development of the states is not immediately evident, but as we will show, it is given by the modified Schrödinger equations:

$$i\hbar \frac{d\left|\bar{\psi}(t)\right\rangle}{dt} = \bar{V}\left|\bar{\psi}(t)\right\rangle \tag{2.11}$$

where the operator $\bar{V}$ is given by the transformation $\bar{V} = UV(t)U^\dagger$. The proof of the equation follows straight from the transformation $\left|\bar{\psi}(t)\right\rangle = U(t)\left|\psi(t)\right\rangle$ coupled with the Schrödinger picture:

$$i\hbar \frac{d\left|\bar{\psi}(t)\right\rangle}{dt} = i\hbar \frac{\partial U(t)}{\partial t}\left|\psi(t)\right\rangle + i\hbar U(t)\frac{\partial\left|\psi(t)\right\rangle}{\partial t} \tag{2.12}$$

$$= -U(t)H_0\left|\psi(t)\right\rangle + U(t)H_0\left|\psi(t)\right\rangle + U(t)V(t)\left|\psi(t)\right\rangle \tag{2.13}$$

$$= U(t)V(t)U^\dagger(t)\left|\bar{\psi}(t)\right\rangle \tag{2.14}$$

Therefore we recover equation (2.3). Similarly, the time evolution of states results in the time evolution of the density matrix being given by

$$\frac{d\bar{W}}{dt} = -\frac{1}{i\hbar}\left[\bar{W}, \bar{V}\right] \tag{2.15}$$

This new pseudo Schrödinger equation leads us to the formulation of a new time evolution operator $S(t, t')$ which performs time translation between states within the interaction picture;

$$\left|\bar{\psi}(t)\right\rangle = S(t, t')\left|\psi(t')\right\rangle$$

It is clear that $S(t, t')S(t', t'') = S(t, t'')$. Since S preserves lengths of vectors and has an inverse, it must be unitary. Equation (2.11) gives the time evolution of the S operator by:

$$i\hbar \frac{\partial S(t, t_0)}{\partial t} = \bar{V}(t)S(t, t_0) \tag{2.16}$$

Equation (2.4) can be "solved" through the use of the integral equation:

$$S(t, t_0) = 1 + \frac{1}{i\hbar}\int_{t_0}^{t} dt'\, \bar{V}(t')S(t', t_0) \tag{2.17}$$

The 1 in front is a constant of integration which meets the initial condition $S(t_0, t_0) = 1$. In a method similar to what we did for the Born Approximation in p251a, we can iterate this equation [i.e., plug the result for $S(t, t_0)$ back into the RHS of the equation].

$$S(t, t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\bar{V}(t') + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, \bar{V}(t')\bar{V}(t'')S(t'', t_0) \tag{2.18}$$

If we continue iterating, our sum will look like:

$$S(t, t_0) = 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \ldots \int_{t_0}^{t_2} dt_1 \, \bar{V}(t_n)\bar{V}(t_{n-1})\ldots\bar{V}(t_1) \qquad (2.19)$$

The one thing to note which is very important is that the integral expression is time ordered with the potentials $\bar{V}(t_n)$ with the earlier times on the right, later times on the left. This ordering is important because our operators in the interaction picture do not commute with themselves when they are at different times.

If we deal with the situation of small $\bar{V}(t)$ there are two important effects:

- The Sum will hopefully converge

- It is possible, to a reasonable approximation, to only keep the first term in the expansion:

$$S = 1 - \frac{i}{\hbar} \int_{t_0}^t dt' \bar{V}(t') \qquad (2.20)$$

Now a neat formal trick, which will prove very useful, especially in quantum field theory, is that the n-fold integrals can be rewritten through the use of a time ordering operator:

$$\int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \ldots \int_{t_0}^{t_2} dt_1 \quad \bar{V}(t_n)\bar{V}(t_{n-1})\ldots\bar{V}(t_1) \qquad (2.21)$$

$$= \frac{1}{n!}\mathcal{T}\left(\int_{t_0}^t dt_n dt_{n-1} \ldots dt_1 \bar{V}(t_n)\bar{V}(t_{n-1})\ldots\bar{V}(t_1)\right) \quad (2.22)$$

where $\mathcal{T}$ denotes the time ordering operator, which rearranges products of operators putting the earlier times to the right. The $\frac{1}{n!}$ comes from just integrating over one part of a hypercube, and the time ordering operator is necessary because the operators $\bar{V}(t), \bar{V}(t')$ do not commute[2]. Plugging (2.22) into the sum in equation (2.19) we can see that we will arrive at the formal expression:

$$S(t, t_0) = \mathcal{T}\left(\exp\left[-\frac{i}{\hbar}\int_{t_0}^t dt' \, \bar{V}(t')\right]\right) \qquad (2.23)$$

Note that $\mathcal{T}$ is not an operator in the quantum mechanical Hilbert space, as it acts on operators, not on vectors in the Hilbert space.

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[2]This is discussed in more detail in Peskin and Schroder chapter 4

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3.1   Time-Dependent Perturbation Theory

We can consider a small time dependent potential $V(t)$ in the Schrödinger picture. The Hamiltonian and Schrödinger equation will be:

$$H = H_0 + V(t)$$

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

where H_0 is independent of time. Now, suppose that $|\psi\rangle$ is known at a time $t = t_0$. What is $|\psi(t)\rangle$ and the expectation values of operators at a later time t? We assume a discrete spectrum of eigenstates of the unperturbed Hamiltonian $H_0 |n\rangle = E_n^0 |n\rangle$ with the normalization $\langle n|n'\rangle = \delta_{nn'}$.

We can expand out the wavefunction as a sum in the following way:

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

It is perfectly permissable to stick in that phase factor, we are basically just sucking it out of the time dependent $c_n(t)$. We can see with this that if $V(t) = 0$; $c_n(t)$ will be independent of time. If $V(t) \neq 0$, then $\frac{dc_n(t)}{dt} \propto V(t)$. The value of the coefficients will be given by $c_n(t) = \langle n|\psi(t)\rangle \exp(iE_n^0 t/\hbar)$. In the interaction picture the states will be given by $|\bar{\psi}(t)\rangle = \exp(iH_0 t/\hbar) |\psi(t)\rangle$. Therefore the new expansion will just be written:

$$|\bar{\psi}(t)\rangle = \sum_n c_n(t) |n\rangle \tag{3.1}$$

The coefficients can thus be written in the interaction picture as

$$c_n(t) = \langle n|\bar{\psi}(t)\rangle \tag{3.2}$$

Although the vectors $|n\rangle$ and $\langle n|$ were defined as the (time-independent) eigenstates of H_0 in the Schrödinger picture, they may also be interpreted in the Interaction picture as eigenstates of H_0 at time $t = 0$. The Interaction, Schrödinger, and Heisenberg pictures all coincide at $t = 0$.

We recall (from p251b lecture 2) that the time evolution of the interaction picture states is given by:

$$i\hbar \frac{\partial |\bar{\psi}(t)\rangle}{\partial t} = \bar{V}(t) |\bar{\psi}(t)\rangle \tag{3.3}$$

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It should be noted that in the literature there are generally no bars to distinguish operators in the interaction picture from those in the Schrödinger picture, because papers don't normally switch back and forth. However, we keep them here to avoid confusion.

We can write a a set of differential equations to determine $c_n(t)$. Using equations (3.2) and (3.3) we arrive at:

$$i\hbar\frac{\partial}{\partial t}\sum_{n'}c_{n'}\left|n'\right\rangle = \bar{V}(t)\left|\bar{\psi}(t)\right\rangle \tag{3.4}$$

Now, we multiply on both sides by $\langle n|$ which gives:

$$i\hbar\frac{dc_n(t)}{dt} = \langle n|\bar{V}(t)|\bar{\psi}(t)\rangle$$

Now using (3.1) we arrive at:

$$\begin{aligned}i\hbar\frac{dc_n(t)}{dt} &= \sum_{n'}\langle n|\bar{V}(t)|n'\rangle c_{n'}(t)\\ &= \sum_{n'}\bar{V}_{nn'}(t)c_{n'}(t)\end{aligned} \tag{3.5}$$

where we have defined $\langle n|\bar{V}(t)|n'\rangle = \bar{V}_{nn'}(t)$. Now we can derive a form for $\bar{V}_{nn'}$. Starting from $V_{nn'} = \langle n|V(t)|n'\rangle$ we have:

$$\begin{aligned}\bar{V}(t) &= UVU^\dagger = e^{iH_0t/\hbar}V(t)e^{iH_0t/\hbar}\\ \bar{V}_{nn'}(t) &= \langle n|e^{iH_0t/\hbar}Ve^{-iH_0t/\hbar}|n'\rangle\\ \bar{V}_{nn'}(t) &= V_{nn'}(t)e^{i\omega_{nn'}t}\end{aligned} \tag{3.6}$$

where the frequency $\omega_{nn'}$ is given by:

$$\omega_{nn'} = \frac{E_n^0 - E_{n'}^0}{\hbar} \tag{3.7}$$

So far everything we have done is exact, but we now want to start looking at specfic cases for analysis. Consider the case where at some time t_0 the wavefunction is in an eigenstate of H_0: $\left|\bar{\psi}(t_0)\right\rangle = |s\rangle$. We recall then, that the time evolution of the states will be given by:

$$\left|\bar{\psi}(t)\right\rangle = S(t,t_0)\left|\bar{\psi}(t_0)\right\rangle$$

We can translate this into a statement for the coefficients, multiplying by $\langle n|$ and using (3.2) to get:

$$c_n(t) = \langle n|S(t,t_0)|s\rangle \tag{3.8}$$

We consider the case for $t_0 = -\infty$, where $V(t) \to 0$ for $t \to -\infty$. This gives: $\left|\bar{\psi}(t = -\infty)\right\rangle = |s\rangle$ and $c_n(-\infty) = \delta_{ns}$. To first order in V therefore can replace $c_{n'}$ on the RHS of Eq. (3.5) by the value it would have for $V = 0$, namely $c'_n = \delta_{n's}$. Then, using (3.6), we find

$$i\hbar \frac{dc_n(t)}{dt} = V_{ns}(t)\, e^{i\omega_{ns}t'} \tag{3.9}$$

Integrating this and using the initial conditions we get:

$$\text{n} \neq \text{s} \qquad c_n(t) = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' V_{ns}(t') e^{i\omega_{ns}t'} + \mathcal{O}(V^2) \tag{3.10}$$

$$\text{n} = \text{s} \qquad c_s(t) = 1 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' V_{ss}(t') + \mathcal{O}(V^2) \tag{3.11}$$

An alternative derivation results from using the equation 3.8:

$$c_n(t) = \langle n| S(t, -\infty)|s\rangle, \tag{3.12}$$

together with the formula for $S(t, t_0)$ we derived in lecture 2:

$$S(t, t_0 = -\infty) = 1 - \frac{i}{\hbar} \int_{-\infty}^{t} \bar{V}(t)dt' + \mathcal{O}(V^2). \tag{3.13}$$

What is the probability that the system is in some given eigenstate of H_0 at time t? For $n \neq s$ we see that we will get something proportional to V^2

$$P_n(t) = \langle c_n(t)|c_n(t)\rangle = |c_n(t)|^2 \simeq \mathcal{O}(V^2)$$

For $n = s$, at first glance it looks like we might get a term proportional to V. However, the important thing is that the quantity V_{ss} is real; it is the diagonal matrix element of a hermitian operator, and therefore the first order contribution will drop out when we take the magnitude of $c_s(t)$. . So we get:

$$P_{n=s}(t) = |c_s(t)|^2 \simeq 1 + \mathcal{O}(V^2)$$

This shows that it is as least possible to maintain the normalization $\sum_n |c_n|^2 = 1$.

Let us now consider the case where $V(t) \to 0$ for $t \to \infty$ as well as for $t \to -\infty$, and ask what happens to the occupation probabilities for $t \to \infty$. We see that for $n \neq s$,

$$c_n(\infty) = -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt' V_{ns}(t') e^{i\omega_{ns}t'} \tag{3.14}$$

We see that this is proportional to the Fourier transform of $V(t)$. Recall that the way we define Fourier transforms in this class is:

$$\tilde{V}_{ns}(\omega) \equiv \int_{-\infty}^{\infty} \frac{dt}{\sqrt{2\pi}} V_{ns}(t) e^{i\omega t} = \langle n| \int_{-\infty}^{\infty} \frac{dt}{\sqrt{2\pi}} V(t) e^{i\omega t} |s\rangle \tag{3.15}$$

This will give the probability for $n \neq s$:

$$P_n = |c_n(\infty)|^2 = \frac{2\pi}{\hbar^2} |\tilde{V}_{ns}(\omega_{ns})|^2 \tag{3.16}$$

So what is the interpretation of this? The probability statement in equation (3.16) tells us that for there to be a significant probability for the system to make a transition from $|s\rangle \to |n\rangle$, the perturbation must have significant Fourier components around the frequency that corresponds to the energy difference between the two states. (This is true to lowest order in V.)

3.1.1 Linear Response

What is $\langle A \rangle_t$ as predicted by perturbation theory. Suppose that A (in the Schrödinger picture) has no explicit time dependence. Once again the Hamiltonian is assumed to have the form $H = H_0 + V(t)$ and we assume $V(t) \to 0$ for $t \to -\infty$. We take the initial state to be $|s\rangle$. Using all the same expansions we have already used we arrive at:

$$\begin{aligned} \langle A \rangle_t &= \langle \bar{\psi}(t)| \bar{A}(t) |\bar{\psi}(t)\rangle \\ \bar{A}_{nn'}(t) &= A_{nn'} e^{i\omega_{nn'}t} \end{aligned} \tag{3.17}$$

Using the expansion $\left|\bar{\psi}\right\rangle = \sum_n c_n |n\rangle$, we arrive at

$$\begin{aligned} \langle A \rangle_t &= |c_s(t)|^2 A_{ss} + \sum_{n \neq s} [A_{sn} c_n(t) e^{i\omega_{sn}t} c_s^*(t) + A_{ns} c_s(t) e^{i\omega_{ns}t} c_n^*(t)] \\ &\quad + \sum_{n \neq s} \sum_{n' \neq s} A_{nn'} c_n^*(t) c_{n'}(t) e^{i\omega_{nn'}t} \end{aligned}$$

Now it should be noted that we have grouped the terms here in a particular way. Each of the $\left|\bar{\psi}(t)\right\rangle$ expansions contained states which were either $|s\rangle$ or not $|s\rangle$. We have grouped the multiplication of our sum according to terms where both coefficients are equal to $|s\rangle$, where one coefficient is equal to $c_s(t)$ and where neither coefficient is equal to $c_s(t)$. The reason for doing it this way goes back to equations (3.10) and (3.11). Our goal is to work to first order in $V(t)$, and as we can see the forms of those equations tell us that we can disregard the last set of sums

over $n, n' \neq s$. Now we make the substitutions from equations (3.10) and (3.11), and keeping to lowest order in V, we arrive at:

$$\langle A \rangle_t = A_{ss} + \sum_{n \neq s} \left(\frac{-i}{\hbar} \right) \int_{-\infty}^{t} dt' [A_{sn} V_{ns} e^{-i\omega_{ns}(t-t')} - A_{ns} V_{sn}(t') e^{-i\omega_{sn}(t-t')}] + \mathcal{O}(V^2) \quad (3.18)$$

where we have noted that $A_{sn} = A_{ns}^*$, $V_{sn} = V_{ns}^*$ and $\omega_{sn} = -\omega_{sn}$. We have also used $|c_s(t)|^2 = 1 + \mathcal{O}(V^2)$. The minus sign appears because we factored out $-i/\hbar$.

Note that the second term inside the brackets in the integrand of the equation above is the complex conjugate of the first term. Since there is a minus sign between them, the quantity in brackets is pure imaginary, and the result for the expectation value $\langle A \rangle_t$ is real, as it must be, since A is Hermitian.

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4.1   Linear Response to a Time-Dependent Electric Field

We consider here the linear response of a neutral atom or molecule to a time-dependent electric field. We assume that the field is spatially uniform on the scale of the atom.

Thus, we consider a Hamiltonian of the form $H = H_0 + V(t)$ with a small time dependent potential given by $V(t) = -\vec{E}(t) \cdot \vec{d}$, where $\vec{d} = \sum_i q_i \vec{r}_i$ is the electric dipole operator, where q_i, and $\vec{r}_i$ are the charge and the position of the ith particle, and H_0 is the Hamiltonian of the system in the absence of the time-dependent field. We assume that initially, the system is in an eigenstate $|s\rangle$ of H_0, which may or may not be the ground state.

We want to know what will be the induced value of the electric dipole moment $\langle d \rangle_t$, due to the applied electric field. We shall assume that there is no dipole moment in the initial state, $\langle s|\vec{d}|s\rangle = 0$. This is always true for an atom, due to rotational and/or inversion symmetry. It is also true for many molecules, such as H_2 or N_2 or CO_2, all of which have an inversion symmetry, but it is not true for "polar" molecules such as CO. (Here I am assuming the nuclei to be infinitely massive and fixed in space.)

We recall the equation for the expectation value of an operator $\langle A \rangle_t$ we derived in p251b lecture 3:

$$\langle A \rangle_t = A_{ss} + \sum_{n \neq s} \left(\frac{-i}{\hbar} \right) \int_{-\infty}^{t} dt' [A_{sn} V_{ns} e^{-i\omega_{ns}(t-t')} - c.c] \tag{4.1}$$

We used the shorthand $c.c$ for complex conjugate to avoid writing it out again. Let us now chose A to be itself one of the components of the dipole operator, d_μ. Using the above formula, we can arrive at the value for $\langle d_\mu \rangle_t$:

$$\langle d_\mu \rangle_t = \sum_\nu \int_{-\infty}^{\infty} \frac{dt'}{(2\pi)^{1/2}} \tilde{\alpha}_{\mu\nu}(t-t') E_\nu(t') + \mathcal{O}(E^2) \tag{4.2}$$

where

$$\left(\frac{1}{2\pi} \right)^{1/2} \tilde{\alpha}_{\mu\nu}(\tau) = \frac{i\Theta(\tau)}{\hbar} \sum_{n \neq s} (d_{sn}^\mu d_{ns}^\nu e^{-i\omega_{ns}\tau} - c.c) \tag{4.3}$$

The quantity d_{sn}^μ is defined by $d_{sn}^\mu = \langle s|d^\mu|n\rangle$., while the Θ function, $\Theta(\tau)$, is defined to be zero for $\tau < 0$ and one for $\tau > 0$. Although we have introduced a lot of notation here, a quick inspection reveals that equation (4.2) follows directly from equation (4.1) and our definition in (4.3).

There are a couple of important things to note here. Equation (4.2) is more general than any particular situation. It must describe any linear response to an electric field. The details of the atom or molecule are all neatly contained in the tensor $\tilde{\alpha}_{\mu\nu}$, which can differ from situation to situation. However, the form is perfectly general; it does not even depend on quantum mechanics. It merely says that the polarization at time t should depend in a linear way on the electric field at times past, if the applied electric field is sufficiently weak. One might ask why $\tilde{\alpha}_{\mu\nu}$ is a function only of the time difference, $t - t'$, but this is just a direct consequence of the fact that the system is time-independent in the absence of the perturbation, so there is no fixed origin of time other than that provided by the perturbation itself. The physical requirement that the polarization should depend only on the filed at past times, not at future times, ("causality"), is embodied in the requirement that $\tilde{\alpha}_{\mu\nu}$ should vanish for $t' > t$. This is ensured by the Θ function in (4.3) . The specific results of quantum mechanics are contained in the remaining factors of (4.3) .

It will be very useful to express the linear response tensor $\tilde{\alpha}_{\mu\nu}$ in terms of another quantity, the **spectral function** $g_{\mu\nu}(\omega)$ of the dipole operator, defined as

$$g_{\mu\nu}(\omega) = \sum_{n \neq s} d^{\mu}_{sn} d^{\nu}_{ns} \delta(\omega - \omega_{ns}) \tag{4.4}$$

Our equation for the tensor $\tilde{\alpha}_{\mu\nu}(\tau)$ now reads:

$$\left(\frac{1}{2\pi}\right)^{1/2} \tilde{\alpha}_{\mu\nu}(\tau) = \frac{i\Theta(\tau)}{\hbar} \int_{-\infty}^{\infty} d\omega [g_{\mu\nu}(\omega)e^{-i\omega\tau} - g^*_{\mu\nu}(\omega)e^{i\omega\tau}] \tag{4.5}$$

Linear response in the frequency-domain.

In order to go further, we should notice that equation (4.2) has the form of a convolution. The definition of a convolution is[1]:

$$f * g = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t - t')g(t')dt' \tag{4.6}$$

The basic claim of the Fourier convolution theorem is that the Fourier transform of the convolution of two functions is equal to the product of the Fourier transforms of the two functions. Well, that is confusing, so just look at the next equation.

$$\mathcal{F}[f * g] = \mathcal{F}[f]\mathcal{F}[g] \tag{4.7}$$

---

[1]Note: The convolution is defined in parallel with what definition of the Fourier transform you are using in order to satisfy equation (4.7). If someone else is using a different Fourier transform, they will have a different definition of the convolution. This caused the author (Phil Larochelle) much grief in realizing

where the curly $\mathcal{F}$ denotes the Fourier transform. This is easy to prove. First off, note the definitions of the Fourier transforms we are using:

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(\omega) e^{-i\omega t} d\omega \tag{4.8}$$

$$\tilde{f}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt \tag{4.9}$$

Now take the convolution, stick in the value defined in equation (4.4) change the order of integration, and voila:

$$\begin{aligned}
f * g &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(t') \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(w) e^{-i\omega(t-t')} d\omega \right) dt' \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(\omega) \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(t') e^{i\omega t'} dt' \right) e^{-i\omega t} d\omega \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(\omega) \tilde{g}(\omega) e^{-i\omega t} d\omega
\end{aligned}$$

Now take the Fourier transform (equation (4.6)) of both sides:

$$\begin{aligned}
\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} (f * g) e^{i\omega' t} dt &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{f}(\omega) \tilde{g}(\omega) \int_{-\infty}^{\infty} e^{i(\omega'-\omega)t} dt \, d\omega \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{f}(\omega) \tilde{g}(\omega) \, 2\pi \delta(\omega' - \omega) \, d\omega
\end{aligned}$$

Thus[2] we recover equation (4.7).

So now that we have taken that slight detour, using the guidance from equations (4.6) and (4.7) we can make the guess to rewrite[3] the expectation value of the dipole operator in the frequency domain as:

$$\langle d_\mu \rangle_\omega = \sum_\nu \alpha_{\mu\nu}(\omega) E_\nu(\omega) \tag{4.10}$$

where $\alpha_{\mu\nu}(\omega)$ is the *properly defined* Fourier transform (from now on abbreviated PDFT) of $\tilde{\alpha}_{\mu\nu}(\tau)$. If it is correct, this equation is nice, because by working in frequency space, rather than

---

[2] The fact that $\int_{-\infty}^{\infty} e^{i(\omega'-\omega)t} dt = 2\pi \delta(\omega' - \omega)$ is a standard, but non trivial result, which is at the heart of the Fourier inversion theorem. It was quoted, without proof in Lecture 4 of Physics 251a, and references were given there. By arguments you can easily see why it would involve a delta function, since the integral would average out to zero in unless $\omega = \omega'$ in which case it would be infinite. But the 2π pops out of residue theory in complex analysis.

[3] This is a guess right now because $\tilde{\alpha}_{\mu\nu}(\tau)$ may not have a well-defined Fourier transform, as will be described below

in the time domain, we have eliminated one integral. We shall see that the equation is correct, and that the tensor $\alpha_{\mu\nu}$ can be related to the spectral function defined above. However, we need to be careful about how we define the Fourier transform, because as written in equation (4.3), $\tilde{\alpha}_{\mu\nu}(\tau)$ doesn't have a well defined Fourier transform. There are a discrete set of contributions (as for example with the hydrogen atom) that don't go to zero as $\tau \to \infty$. The conventional Fourier transform requires that a function decays at ∞, and the convolution theorem assumes that the Fourier transforms properly exist.

Instead we define the PDFT as follows. We introduce a complex frequency $z = \omega + i\gamma$ where ω is real and $\gamma > 0$ and define:

$$\alpha_{\mu\nu}(z) = \int_{-\infty}^{\infty} \frac{d\tau}{(2\pi)^{1/2}} e^{iz\tau} \tilde{\alpha}_{\mu\nu}(\tau) \tag{4.11}$$

Because the exponential factor is now $e^{i\omega\tau} e^{-\gamma\tau}$ the integrand will go to zero for large times due to the decay factor. For $\tau \to -\infty$ we are also ok, because $\tilde{\alpha}_{\mu\nu}(\tau) = 0$ for $\tau < 0$. The function α is analytic in $z = \omega + i\gamma$, for z in the upper half-plane. For ω real, we define the PDFT as:

$$\alpha_{\mu\nu}(\omega) = \lim_{\gamma \to 0+} \alpha_{\mu\nu}(\omega + i\gamma). \tag{4.12}$$

In other words, we define the PDFT by introducing an infinitesimal imaginary part to the frequency ω when we take Fourier transform of $\tilde{\alpha}_{\mu\nu}(\tau)$. In case of doubt, we should keep the value of γ to be non-zero in intermediate steps of the calculation, and take the limit $\gamma \to 0^+$ at the end.

Evaluating the PDFT in equation (4.11) using the definition of $\tilde{\alpha}_{\mu\nu}(\tau)$ in equation (4.5) we arrive at:

$$\alpha_{\mu\nu}(z) = \frac{1}{\hbar} \int_{-\infty}^{\infty} d\omega' \left[\frac{g_{\mu\nu}(\omega')}{\omega' - z} + \frac{g_{\mu\nu}^*(\omega')}{\omega' + z} \right] \tag{4.13}$$

We can now see that for z in the upper half of the complex plane we are fine, the integer will converge regardless of the form $g_{\mu\nu}$. However when z approaches the real axis, we can see that we will get a pole when $z = \pm\omega'$. We have to be very careful as to how to handle those instances.

Now to justify the choice we made in equation (4.12) we want to show that we can recover equation (4.2) from it. We define a quantity $I(t)$:

$$I(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\sqrt{2\pi}} e^{-i\omega t} \sum_{\nu} \alpha_{\mu\nu}(\omega) E_{\nu}(\omega) \tag{4.14}$$

Note that $E_{\nu}(\omega)$ wlll always be a continuous function of ω, if $E_{\nu}(t) \to 0$ in a reasonable manner for $t \to \infty$.

We want to show that $I(t) = \langle d_\mu \rangle_t$, as given by equation (4.2).

$$I(t) = \lim_{\gamma \to 0^+} \int_{-\infty}^{\infty} \frac{d\omega}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega' \sum_\nu \frac{1}{\hbar} \left[\frac{g_{\mu\nu}(\omega')}{\omega' - \omega - i\gamma} + \frac{g_{\mu\nu}^*(\omega')}{\omega' + \omega + i\gamma} \right] \int_{-\infty}^{\infty} \frac{dt'}{\sqrt{2\pi}} e^{-i\omega(t-t')} E_\nu(t') \,.$$

$$(4.15)$$

We can evaluate this integral by evaluating the ω integral before doing the ω' or t' integrals, so that we get terms like:

$$J_\pm(t - t') = \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega(t-t')}}{\omega + i\gamma \pm \omega'}$$

$$(4.16)$$

This can be evaluated using complex analysis and contour integration. For $(t - t') < 0$ the function will go to zero as $\omega \to i\infty$ so we can complete the contour in the upper half plane, and since there are no poles, we get $J_\pm = 0$.

For $(t - t') > 0$ the function now goes to zero for $\omega \to -i\infty$ so we close the contour in the lower half plane. There is a pole at $\omega = \mp\omega' - i\gamma$ that leaves a residue of $(-i2\pi)$ since the contour is clockwise. Our overall $J_\pm$ for all t is therefore:

$$J_\pm = -2\pi i \Theta(t - t') e^{\mp i\omega'(t-t')} e^{-\gamma(t-t')}$$

$$(4.17)$$

With this we can rewrite $I(t)$:

$$
\begin{aligned}
I(t) &= \lim_{\gamma \to 0^+} \int_{-\infty}^{\infty} \frac{d\omega'}{\sqrt{2\pi}} \sum_\nu \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{dt'}{\sqrt{2\pi}} [g_{\mu\nu}^*(\omega') J_- - g_{\mu\nu}(\omega') J_+] E_\nu(t') \\
&= \lim_{\gamma \to 0^+} \sum_\nu \frac{i}{\hbar} \int_{-\infty}^{\infty} d\omega' dt' \Theta(t - t') [g_{\mu\nu}(\omega') e^{-i\omega'(t-t')} - g_{\mu\nu}^*(\omega') e^{i\omega'(t-t')}] e^{-\gamma(t-t')} E_\nu(t') \\
&= \int_{-\infty}^{\infty} \frac{dt'}{\sqrt{2\pi}} \sum_\nu \tilde{\alpha}_{\mu\nu}(t - t') E_\nu(t')
\end{aligned}
$$

$$(4.18)$$

In the last line we used the definition of $\tilde{\alpha}_{\mu\nu}(\tau)$ given in equation (4.5). We see that (4.18) matches the value for $\langle d_\mu \rangle_t$ given in equation (4.2). We therefore conclude that the assumption we made about the form of $\langle d_\mu \rangle_\omega$ in equation (4.10) was correct.

Note that the fact that (4.17) vanishes for $t < t'$, was a direct consequence of the fact that γ was chosen positive in (4.16). This vanishing, in turn, is necessary for *causality*: the expectation value of d_μ at time t should only depend on the electric field at previous times. Conversely, the fact that $\tilde{\alpha}_{\mu\nu}(\tau)$ vanishes for $\tau < 0$ (causality) ensured that $\alpha_{\mu\nu}(z)$ is analytic in the upper half plane, and that its value goes to zero for $\text{Im}(z) \to +\infty$.

Evaluation of $\alpha_{\mu\nu}(\omega)$

In general, the spectral function $g_{\mu\nu}(\omega')$ on the right hand side of (4.13) will have a continuous contribution arising from final states n, in which one or more electrons have been excited to a high energy continuum state where the electron is unbound from the atom or molecule, as well as a contribution of discrete δ-functions from final states where all the electrons are bound to the atom or molecule. In order to take the limit where z approaches the real axis, in the case where $g_{\mu\nu}$ has a continuum contribution, it is very useful to use the following analysis.

We can always write

$$\frac{1}{\omega - \omega' \pm i\gamma} = \mp i \frac{\gamma}{(\omega - \omega')^2 + \gamma^2} + \frac{\omega - \omega'}{(\omega - \omega')^2 + \gamma^2}$$

In the limit $\gamma \to 0$, the first term becomes essentially a δ-function. Thus, when this is multiplied by a continuous function, and included in an integral, we may write

$$\lim_{\gamma \to 0^+} \left(\frac{1}{\omega - \omega' \pm i\gamma} \right) = \mp i\pi\delta(\omega - \omega') + \mathcal{P}\left(\frac{1}{\omega - \omega'} \right)$$

where the second term denotes the principal value of the function (often referred to as the Cauchy principal value). Specifically, for any continuous function f, we have

$$\mathcal{P}\left(\int_{-\infty}^{\infty} \frac{d\omega' f(\omega')}{\omega - \omega'} \right) = \lim_{\epsilon \to 0^+} \left[\int_{-\infty}^{\omega - \epsilon} \frac{d\omega' f(\omega')}{\omega - \omega'} + \int_{\omega + \epsilon}^{\infty} \frac{d\omega' f(\omega')}{\omega - \omega'} \right] \tag{4.19}$$

The two terms on the right each have log divergences, but ones which exactly cancel each other. Therefore we now have:

$$\lim_{\gamma \to 0^+} \int_{-\infty}^{\infty} \frac{d\omega' f(\omega')}{\omega - \omega' \pm i\gamma} = \mathcal{P}\left(\int_{-\infty}^{\infty} \frac{f(\omega')d\omega'}{\omega - \omega'} \right) \mp i\pi f(\omega) \tag{4.20}$$

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5.1 Dynamic Polarizability $\alpha_{\mu\nu}(\omega)$

First, to recall some important results from the previous lecture. The expectation value of the dipole operator (for some initial state $|s\rangle$) is given by:

$$\langle d_\mu \rangle_\omega = \sum_\nu \alpha_{\mu\nu}(\omega) E_\nu(\omega) + \mathcal{O}(E^2) \tag{5.1}$$

The dynamic polarizability is given by:

$$\alpha_{\mu\nu}(\omega) = \lim_{\gamma \to 0^+} \frac{1}{\hbar} \int_{-\infty}^{\infty} d\omega' \left[\frac{g_{\mu\nu}(\omega')}{\omega' - \omega - i\gamma} + \frac{g_{\mu\nu}^*(\omega')}{\omega' + \omega + i\gamma} \right] \tag{5.2}$$

The spectral functions $g_{\mu\nu}$ are defined as:

$$g_{\mu\nu}(\omega) = \sum_{n \neq s} d_{sn}^\mu d_{ns}^\nu \delta(\omega - \omega_{ns}) \tag{5.3}$$

We note that for an atom or molecule in the absence of an applied magnetic field, if the initial state s is non-degenerate, the spectral function $g_{\mu\nu}(\omega)$ is necessarily real. This is true because the eigenstates of the Hamiltonian can be chosen to be real, so that the matrix-elements of the dipole operator are also real.

Equation (5.2) can be further analyzed with the help of the relation:

$$\lim_{\gamma \to 0^+} \left(\frac{1}{\omega - \omega' \pm i\gamma} \right) = \mp i\pi\delta(\omega - \omega') + \mathcal{P}\left(\frac{1}{\omega - \omega'} \right) \tag{5.4}$$

If ω is real, the diagonal matrix elements of $\alpha_{\mu\nu}(\omega)$ have the property (no implied sums here):

$$\operatorname{Im}\alpha_{\mu\mu}(\omega) = \frac{\pi}{\hbar}[g_{\mu\mu}(\omega) - g_{\mu\mu}(-\omega)] = -\operatorname{Im}\alpha_{\mu\mu}(-\omega) \tag{5.5}$$

This indicates that the imaginary part is an odd function of frequency. It is easy to see that, by contrast, the real part of $\alpha_{\mu\mu}$ is a symmetric function of ω.

We can also see that there is a physical significance to the function $\alpha_{\mu\nu}(z)$ for complex z in the upper half plane. Suppose that there is a time dependent electric field $\vec{E}(t)$ with $\gamma > 0$ such that:

$$\vec{E}(t) = \operatorname{Re}[\vec{E}_0 e^{-i\omega_0 t} e^{\gamma t}] \tag{5.6}$$

That is, we have an oscillating electric field which we turn on at a *finite* rate γ. I claim that the expectation value of the dipole operator can be written (to first order in $\vec{E}$) as[1].

$$\langle d_\mu \rangle_t = \text{Re} \left[\sum_\nu \alpha_{\mu\nu}(\omega_0 + i\gamma) E_\nu^0 e^{-i\omega_0 t} e^{\gamma t} \right] \tag{5.7}$$

In the limit $\gamma \to 0$, we recover the polarization induced by an electric field at the real frequency $\omega = \omega_0$.

There is a bunch of physics we can extract from this. As mentioned before, the spectral functions $g_{\mu\nu}(\omega')$ will have delta functions at the frequencies ω_{ns} of allowed transitions for our system. If we take the hydrogen atom, for example, for energies less than the ionization energy there will be a discrete set of final state energies. Thus if $\hbar\omega$ is less than the ionization energy, and $\omega \neq \omega_{ns}$ for any allowed transition, then using (5.4), we see that $\alpha_{\mu\nu}(\omega)$ will be purely real (since the principal value integral returns a real value) if ω is real but $\omega \neq \omega_{ns}$. In this case the expectation value of the dipole operator will just be proportional to $\pm \cos\omega_0 t$, with its maximum value following the electric field in phase, or 180 degrees out of phase, depending on the sign of α.

For the case of values of $\hbar\omega$ bigger than the ionization energy, the values of ω_{ns} will be a continuum and we will start getting both the real and imaginary parts. The imaginary part gives a part which is a sine wave instead of a cosine wave, and will be 90 degrees out of phase with the electric field.

We now suppose that we have $\omega_0 = 0$ and $\gamma \to 0$. This could be equivalent to an electric field which slowly turns on. The dipole operator will have expectation value:

$$\langle d_\mu \rangle_t = \sum_\nu \alpha_{\mu\nu}(\omega = 0) E_0^\nu \tag{5.8}$$

$$\alpha_{\mu\nu}(\omega = 0) = \frac{1}{\hbar} \int_{-\infty}^\infty d\omega' \frac{g_{\mu\nu}(\omega) + g_{\mu\nu}^*(\omega')}{\omega'} \tag{5.9}$$

If we assume that the ground state $|s\rangle$ is not degenerate, then we don't need to add an imaginary part, since $g_{\mu\nu}(\omega' = 0) = 0$ and there are no poles in the integral.

We now make the claim that if the initial state $|s\rangle$ is not degenerate, $\alpha_{\mu\nu}(\omega = 0)$ is the same as you would obtain from static (time independent) perturbation theory[2]. We also claim that $\alpha_{\mu\nu}(\omega = 0)$ is real and symmetric: $\alpha_{\mu\nu}(\omega = 0) = \alpha_{\nu\mu}(\omega = 0)$.

---

[1]this is proven as a homework problem

[2]this is another homework problem

5.1.1   Kramers Krönig Relations

We now state the following relations, known as the **Kramers Krönig relations**:

$$\text{Re}[\alpha_{\mu\mu}(\omega)] = \frac{1}{\pi}\mathcal{P}\left(\int_{-\infty}^{\infty} \frac{\text{Im}[\alpha_{\mu\mu}(\omega')]d\omega'}{\omega' - \omega}\right) \tag{5.10}$$

$$\text{Im}[\alpha_{\mu\mu}(\omega)] = -\frac{1}{\pi}\mathcal{P}\left(\int_{-\infty}^{\infty} \frac{\text{Re}[\alpha_{\mu\mu}(\omega')]d\omega'}{\omega' - \omega}\right) \tag{5.11}$$

The first relation follows directly from the expression for the real part of $\alpha_{\mu\mu}$ and (5.5). The second relation, as well as the first, is true because you can analytically continue the function to the upper half plane, it has no singularities in the upper half plane and goes to zero as $z \to 0$. Then using complex variables theorem, you can prove the relations are true.

If $|s\rangle$ is the groundstate then $g_{\mu\nu} = 0$ for $\omega < 0$, because there are no states for $\omega < 0$. We also find that $g_{\mu\mu}$ is real and ≥ 0 for $\omega > 0$. This also says $\text{Im}[\alpha_{\mu\mu}] \geq 0$ for $\omega > 0$ and $\text{Im}[\alpha_{\mu\mu}] \leq 0$ for $\omega < 0$

5.1.2 f-Sum Rule

Assume that there is a potential that only depends on positions of the particles. You can have interactions between the different particles, as long as they are functions only of the positions of the particles. So,

$$H_0 = \sum_i \frac{p_i^2}{2m_i} + U\{\vec{r}_i\} \tag{5.12}$$

(Although this assumes no velocity/momentum dependent terms, the theorem we are about to prove is actually also true when there is a magnetic field present.) The theorem is

$$\int_{-\infty}^{\infty} \omega g_{\mu\nu}(\omega)d\omega = \frac{\hbar}{2}\sum_i \frac{q_i^2}{m_i}\delta_{\mu\nu} \approx \frac{\hbar}{2}\frac{Ze^2}{m_e}\delta_{\mu\nu} \tag{5.13}$$

The last step is exact if we reat the nuclei as infinitely massive.

The proof goes as follows. First we note the commutation relations:

$$[z_i, H_0] = \frac{p_z^i i\hbar}{m_i} \qquad [[z_i, H_0], z_j] = \delta_{ij}\frac{\hbar^2}{m_i} \tag{5.14}$$

Now, let us consider the case $\mu = \nu = z$. Using the definition of the dipole moment, $\vec{d_z^i} = \sum_i q^i z_i$ we write:

$$\begin{aligned}
\int_{-\infty}^{\infty} \omega g_{zz}(\omega)d\omega &= \sum_n |\langle n|d_z|s\rangle|^2(E_n - E_s) \\
&= \sum_n \langle s|d_z|n\rangle E_n^0\langle n|d_z|s\rangle - \langle s|d_z|n\rangle\langle n|d_z|s\rangle E_s^0
\end{aligned} \tag{5.15}$$

We can now combine the energies in equation (5.15) with the adjacent bras and the kets, in order to get the Hamiltonian operator H_0 in convenient places:

$$
\begin{aligned}
\int_{-\infty}^{\infty} \omega g_{zz}(\omega) d\omega &= \langle s|d_z H_0 d_z|s \rangle - \frac{\langle s|d_z^2 H_0|s \rangle}{2} - \frac{\langle s|H_0 d_z^2|s \rangle}{2} \\
&= \frac{1}{2}\langle s|[[d_z, H_0], d_z]|s \rangle = \frac{\hbar^2}{2} \sum_i \frac{q_i^2}{m_i}
\end{aligned}
\tag{5.16}
$$

Similar results occur for $\mu = \nu = x$ or y, while the commutator is zero for $\mu \neq \nu$.

6.1   Semiclassical Theory of Optical Absorption

We first recall the results for an atom or molecule in a uniform time dependent electric field $\vec{E}(t)$ derived from a scalar potential $\Phi(\vec{r}, t) = -\vec{E}(t) \cdot \vec{r}$. We can decompose the Hamiltonian into a part H_0, which describes the atom or molecule in zero field, and a perturbation $V(t) = q\Phi(\vec{r}, t) = -\vec{E}(t) \cdot \vec{d}$, such that $H = H_0 + V(t)$. We consider the situation where $\vec{E}(t) \to 0$ for $t = \pm\infty$, and the system is initially in the eigenstate $|s\rangle$, the groundstate of the system. We now want to calculate what the probability that system is in the state $|n\rangle$ at $t = \infty$.

   We have made the approximation that the field is approximately uniform in the neighborhood of the atom. This first approximation is known as the dipole approximation. Sometimes such transitions are not allowed by symmetry and more accurate approximation regimes are required.

   In this approximation though, we would imagine that the answer would be the same whether the electric field was produced from a scalar potential say from capacitor plates or from a vector potential from an electromagnetic wave. Indeed we will see that both of these give the same answer. We will calculate the scalar potential case now and the vector potential case later.

   Referring back to p251b lecture 3 we found that the probability for the system to transition from the ground state $|s\rangle$ to another state $|n\rangle$ is given by:

$$
\begin{aligned}
P_n &= |c_n(t = \infty)|^2 = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} dt \, e^{i\omega_{ns}t} \vec{E}(t) \cdot \vec{d}_{ns} \right|^2 \\
&= \frac{2\pi}{\hbar^2} \left| \tilde{\vec{E}}(\omega = \omega_{ns}) \cdot \vec{d}_{ns} \right|^2
\end{aligned}
\tag{6.1}
$$

We can calculate the total transition probability by summing over the probabilities of transitions to all excited states:

$$
\sum_{n \neq s} P_n = \frac{2\pi}{\hbar^2} \int_{-\infty}^{\infty} d\omega \sum_{\alpha\beta} \tilde{E}_\alpha^*(\omega) \tilde{E}_\beta(\omega) g_{\alpha\beta}(\omega)
\tag{6.2}
$$

The functions $g_{\alpha\beta}$ are the spectral functions defined in p251b lecture 4:

$$
g_{\alpha\beta}(\omega) = \sum_{n \neq s} d_{sn}^\alpha d_{ns}^\beta \delta(\omega - \omega_{ns})
$$

For the case of spherical symmetry the spectral functions will take the form $g_{\alpha\beta} = g(\omega)\delta_{\alpha\beta}$. Then,

$$
\sum_{n \neq s} P_n = \frac{2\pi}{\hbar^2} \int_{-\infty}^{\infty} d\omega \, g(\omega)|\vec{E}(\omega)|^2.
\tag{6.3}
$$

Here, $\vec{E}(\omega)$ denotes the Fourier transform of the vector $\vec{E}(t)$, but we omit the tilde, for simplicity.

Expectation Value of Work Done

The expectation value of the work done by the time dependent electric field will be given by the mean value of change in energy between the initial and final states:

$$
\begin{aligned}
\langle \Delta E \rangle &= \langle E_n^0 - E_s^0 \rangle \\
&= \sum_{n \neq s} P_n (E_n^0 - E_s^0) = \sum_n P_n \hbar \omega_{ns} \\
&= \frac{2\pi}{\hbar^2} \int_{-\infty}^{\infty} d\omega \, \hbar \omega |\vec{E}(\omega)|^2 g(\omega) \; (\text{For Spherical Symmetry})
\end{aligned} \tag{6.4}
$$

Since the value of the electric field must be real this places a constraint on the fourier coefficients of the field: $\vec{E}(\omega) = \vec{E}(-\omega)^*$ From this we can also establish a relation between the magnitudes: $|\vec{E}(\omega)|^2 = |\vec{E}(-\omega)|^2$. We can now use the definition of the response function $\alpha_{\mu\nu}(\omega)$ also defined in p251b lecture 4 and more specifically the imaginary part of the response function discussed in p251b lecture 5 to rewrite the expectation value of the work. Recall:

$$
\text{Im}[\alpha(\omega)] = -\text{Im}[\alpha(-\omega)] = \frac{\pi}{\hbar}[g(\omega) - g(-\omega)]
$$

Using this, the expectation value of the total work can be rewritten:

$$
\begin{aligned}
\langle E_n^0 - E_s^0 \rangle &= \frac{2\pi}{\hbar^2} \int_0^{\infty} \hbar \omega \frac{\hbar}{\pi} |\vec{E}(\omega)|^2 \, \text{Im}[\alpha(\omega)] \, d\omega \\
&= 2 \int_0^{\infty} \omega \, |\vec{E}(\omega)|^2 \, \text{Im}[\alpha(\omega)] \, d\omega \\
&= \int_{-\infty}^{\infty} \omega \, |\vec{E}(\omega)|^2 \, \text{Im}[\alpha(\omega)] \, d\omega
\end{aligned} \tag{6.5}
$$

A quick inspection will verify the validity of this. Since $\omega \, \text{Im}[\alpha(\omega)]$ is independent of the sign of ω, you just get the same thing back twice.

What is the physical significance of this? First, if the Fourier transform of the applied electric field is narrowly centered around one of the allowed transitions of the system, $\omega = \omega_{ns}$, referring to equation (6.4), we can see that the total work done will be $< \Delta E >= \hbar \omega \, P$, where P is the total transition probability. We will later interpret this as the system absorbing a photon of energy $\hbar \omega$, when we talk about optical absorption. Second, if the field has a large spread we can find the energy given to the system by breaking the field down into its fourier components.

There is an alternative way of deriving this without ever having gone back to quantum mechanics, by merely using the definition of $\tilde{\alpha}_{\mu\nu}$. This alternate derivation helps to shed light on the physical significance. If you want to calculate the work done by the electromagnetic field

on a collection of moving charges, in classical mechanics, it should be given by:

$$
\begin{aligned}
< \mathrm{Work\,Done} > \;&=\; \sum_i \int \vec{F} \cdot d\vec{r}_i = \sum_i \int_{-\infty}^{\infty} q\vec{E}(t) \cdot \frac{d\vec{r}_i}{dt}\, dt \\
&=\; \int_{-\infty}^{\infty} \vec{E}(t) \cdot \frac{d}{dt}\langle \vec{d} \rangle_t\, dt
\end{aligned} \tag{6.6}
$$

This is also what you would get quantum mechanically for the mean value of the change in energy, using Ehrenfest's theorem. We found in Physics 251a that

$$
\frac{d\langle H \rangle_t}{dt} = \left\langle \frac{\partial H}{\partial t} \right\rangle_t = -\langle \vec{d} \rangle_t \cdot \frac{\partial \vec{E}}{\partial t}\,.
$$

Then, using integration by parts, we see that

$$
-\int_{-\infty}^{\infty} \langle \vec{d} \rangle_t \cdot \frac{\partial \vec{E}}{\partial t} = \int_{-\infty}^{\infty} \vec{E}(t) \cdot \frac{d}{dt}\langle \vec{d} \rangle_t\, dt
$$

If we now take the Fourier tranform of (6.6), we get:

$$
\int_{-\infty}^{\infty} (-i\omega)\vec{E}^*(\omega) \cdot \langle \vec{d} \rangle_\omega\, d\omega = \int_{-\infty}^{\infty} -i\omega |\vec{E}(\omega)|^2 \alpha(\omega)\, d\omega \tag{6.7}
$$

In the last line we have used result derived in p251b Lecture 4, to first order in E:

$$
\langle d_\mu \rangle_\omega = \sum_\nu \alpha_{\mu\nu}(\omega) E_\nu(\omega) + \mathcal{O}(E^2) = \alpha(\omega) E_\mu(\omega)\,.
$$

Since the expectation value of the work must be real quantity we can see from (6.7) that the only contribution from $\alpha(\omega)$ will come from the imaginary part (to cancel the $-i$) and we recover our previous result from equation (6.5).

6.1.1   Electromagnetic Field from a Transverse Wave

We now consider the response of a system such as the one analyzed above to a transverse electromagnetic field, e.g. from a plane wave. The field for a plane wave is specified by the following vector and scalar potentials:

$$
\Phi(\vec{r},t) = 0 \qquad \vec{A}(\vec{r},t) = \mathrm{Re}[\vec{A}_k e^{i\vec{k}\cdot\vec{r} - i\omega_k t}]
$$

where the quantities listed above (as is standard in E&M) have the following properties.

$$
\omega_k = kc \qquad \vec{A}_k \perp \vec{k} \tag{6.8}
$$

3

The most general transverse wave can be written as a sum of such plane waves. To simplify the problem, we have chosen to work in the Coulomb gauge $\nabla \cdot \vec{A} = 0$, so the vector potential satisfies:

$$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} \qquad \frac{1}{c^2}\frac{\partial^2 \vec{A}}{\partial t^2} = \nabla^2 \vec{A} \tag{6.9}$$

The Hamiltonian for an atom or molecule in this vector potential can be broken up into a free part H_0 which has no vector potential terms and the perturbation terms involving $\vec{A}$, which we demnote $V(t)$. As was covered in Physics 251a, the effect of the vector potential on the Hamiltonian of the system will be to replace the momenta $\vec{p}_i$ in the kinetic energy by the kinetic momenta:

$$\vec{p}_i \Rightarrow \vec{p}_i - \frac{q_i \vec{A}(\vec{r}_i)}{c}$$

If we also take into account the Zeeman interaction with the electron spin, we may then write the total Hamiltonian as $H = H_0 + V(t)$, with

$$V(t) = \frac{|e|}{c}\sum_{i=1}^{Z} \frac{\vec{A}(\vec{r}_i) \cdot \vec{p}_i}{m_e} + \frac{e^2}{2m_e c^2}\sum_{i=1}^{Z}|\vec{A}(\vec{r}_i)|^2 + \frac{g\mu_B}{\hbar}\vec{B}(\vec{r}_i)\cdot\vec{S}_i \tag{6.10}$$

We have used the fact that in the Coulomb gauge, where $\nabla \cdot \vec{A} = 0$, we can write $\vec{p}\cdot\vec{A} = \vec{A}\cdot\vec{p}$.

We begin by ignoring the spin term and only considering term first order in A. Then the perturbation is:

$$V(t) = \frac{|e|}{m_e c}\sum_{i=1}^{Z}\vec{A}(\vec{r}_i)\cdot\vec{p}_i \tag{6.11}$$

6.1.2 Dipole Approximation

Since we are considering the case where the wavevector is much smaller than the reciprocal of the Bohr radius ($ka_H << 1$), in practice we can say that the field is uniform across the span of the atom, therefore $\vec{A}(\vec{r}_i) \simeq \vec{A}(\vec{r} = 0)$. So the perturbation can be written:

$$V(t) = \frac{|e|}{m_e c}\vec{A}(0,t)\sum_{i=1}^{Z}\vec{p}_i \tag{6.12}$$

We now want to use this perturbation to calculate matrix elements and transition probabilities. The transition coefficients first derived in p251b-Lecture 3 are given by:

$$|c_n(\infty)|^2 = \frac{2\pi}{\hbar^2}|\tilde{V}_{ns}(\omega = \omega_{ns})|^2 \tag{6.13}$$

If we want to get the same quantity for the transition coefficients c_n that we had before (in equation (6.1)) which involved the electric field dotted into the dipole matrix element, we should try to find a relationship between the matrix elements of the momentum and those of the dipole operator. We can begin by rewriting the momentum using a commutation relation between the position and the Hamiltonian H_0:

$$\begin{aligned}
\langle n|\vec{p}_i|s\rangle &= \frac{m_e}{i\hbar}\langle n|[\vec{r}_i, H_0]|s\rangle \\
&= \frac{m_e}{i\hbar}(E_s^0 - E_n^0)\langle n|\vec{r}_i|s\rangle
\end{aligned} \tag{6.14}$$

Now substituting in the definition of the dipole operator $\vec{d} = -|e|\sum_{i=1}^{Z}\vec{r}_i$ into (6.13) we can rewrite:

$$\frac{|e|}{m_e}\sum_{i=1}^{Z}\langle n|\vec{p}_i|s\rangle = -i\omega_{ns}\langle n|\vec{d}|s\rangle \tag{6.15}$$

Therefore the transition probability will be:

$$\begin{aligned}
|c_n(\infty)|^2 &= \frac{2\pi}{\hbar^2}|V_{ns}(\omega = \omega_{ns})|^2 = \frac{2\pi}{\hbar^2 c^2}\omega_{ns}^2|\vec{A}_{ns}(\omega_{ns})\cdot\vec{d}_{ns}|^2 \\
&= \frac{2\pi}{\hbar^2}|\vec{E}(\omega_{ns})\cdot\vec{d}_{ns}|^2,
\end{aligned} \tag{6.16}$$

where we again omit the tildes over the Fourier transforms.

Thus we recover the same probability as we did before, and we see that we get the same result regardless of whether the field comes from a vector or scalar potential. In the last line we have used the relationship $\vec{E}(\omega) = \frac{i\omega}{c}\vec{A}(\omega)$ which follows from equations (6.8) and (6.9).

7.1 Semiclassical Theory of Optical Absorption (Continued) and Stimulated Emission

We want to calculate the probability of an electron in an atom making a transition from an initial state $|s\rangle$ to a final state $|n\rangle$ in the presence of some time dependent electromagnetic field which is equal to zero at $t = \pm\infty$. If the atom was initially in its ground state, the only thing it can do is increase in energy, and quantum mechanically we would say it has absorbed a photon and will have gained an energy $\hbar\omega$ where ω is the Fourier component of the electromagnetic wave. This is called **optical absorption**. We haven't quantized the electromagnetic field yet, so we don't see the photons explicitly, but we can see some indications of it from the semiclassical analysis.

If the atom is not initially in its ground state, but in some excited state, there is a possibility for it to make a transition to a lower energy state, if there is an electromagnetic wave with energy tuned to the energy difference between two of the states, This is called **stimulated emission**.

We consider a linearly polarized electromagnetic wave, so that the vector potential is in the z direction.

$$\vec{A}(\vec{r}, t) = \hat{z} \int_{-\infty}^{\infty} \frac{d\omega}{(2\pi)^{1/2}} A_z(\omega) e^{i\frac{\omega}{c}x - i\omega t} \tag{7.1}$$

This is a superposition of plane waves with $\vec{k}||\vec{x}$ and $\vec{A}||\hat{z}$. We have previously established in p251b lecture 3 that a probability for transition from a state $|s\rangle$ to a state $|n\rangle$ will be

$$P_n = \frac{2\pi}{\hbar^2} |\tilde{V}_{ns}|^2$$

If we assume an infinite nuclear mass, the perturbation for our system will be:

$$V(t) = \frac{|e|}{m_e c} \sum_{i=1}^{Z} \vec{A}(\vec{r}_i, t) \cdot \vec{p}_i$$

Likewise, the matrix elements will be[1]:

$$\tilde{V}_{ns}(\omega) = \frac{|e|}{m_e c} A_z(\omega) \sum_{i=1}^{Z} \langle n|e^{i\omega x_i/c} p_z^i|s\rangle$$

---

[1]The notation p_z^i means the z component of the momentum of the *ith* particle

The result above is obtained because in taking the fourier transform of $V(t)$ we should multiply by $\frac{e^{i\omega t}}{(2\pi)^{1/2}}$ and integrate over t. The t integral will give a $2\pi\delta(\omega - \omega')$ (where ω' is the dummy integration variable we have chosen for the form of $\vec{A}(\vec{r}, t)$ given in equation (7.1). This will then cancel the integral over ω' as well as the 2π in the denominator.

If we assume that the wavevector is small compared to the reciprocal of the Bohr radius (the order of the size of an atom) $\frac{\omega}{c} = k << \frac{1}{a_H}$ then we can do a Taylor expansion of $e^{i\omega x/c}$:

$$e^{i\omega x/c}p_z^i = p_z^i + \frac{i\omega}{c}x_i\,p_z^i + ... \tag{7.2}$$

To first order, we only keep the first term p_z^i. Now we see that this is essentially the same quantity we treated in p251b lecture 6. From almost identical analysis we find:

$$P_n = \frac{2\pi}{\hbar^2}\left|\frac{|e|}{m_ec}A_z(\omega)\sum_{i=1}^{Z}\langle n|p_z^i|s\rangle\right|^2 = \frac{2\pi}{\hbar^2}|E_z(\omega_{ns})\langle n|d_z|s\rangle|^2$$

There are many times when this approximation will give a zero transition probability. For example consider a spherically symmetric potential $U(r)$ with initial state $|s\rangle$ which has angular momentum $l = 0$. The wavefunction for this will be:

$$|s\rangle = R(r)Y_0^0(\theta, \phi) \tag{7.3}$$

The z coordinate in spherical coordinates is $z = r\cos(\theta) \simeq rY_1^0(\theta)$. Therefore, by the orthogonality of spherical harmonics we have: $\langle n|z|s\rangle = 0$ unless the final state $|n\rangle$ has $l = 1$ and $m = 0$. If this matrix element vanishes, it doesn't mean that there are no transitions, it just means that there are no electric dipole transitions, there could be other transitions which are higher order in $\frac{\omega}{c}$.

So far we have just considered the situation where there is just one electron. For several electron systems we can still classify the total angular momentum of the system and certain transitions will still be forbidden. More generally there are often symmetry considerations which forbid certain dipole transitions. This will be formalized later in the term, through something called the Wigner Eckart theorem.

So what about terms which go beyond the dipole approximation? As we go to the next higher order in the expansion (7.2) in equation we have a term proportional to $x_ip_z^i$. We can rewrite this quantity using the angular momentum operator[2]:

$$x_ip_z^i = \frac{1}{2}(x_ip_z^i + z_ip_x^i) - \frac{1}{2}L_y^i$$

---

[2]The upper and lower indices have nothing to do with covariant and contravariant quantities.

As in p251b lecture 6 we can reduce the first set of terms in parentheses by rewriting the momentum in terms of the commutator of a position coordinate with the Hamiltonian. When we do this, and take the matrix element between the initial state and the final state, we will obtain something proportional to $\left(\frac{\omega}{m}\right)$ times the matrix element of $x_i z_i$, which is a component of the electric quadrupole operator.

The term containing the angular momentum will look like $\simeq \frac{i\omega}{c} A_z L_y$, but since $\vec{B} = \nabla \times \vec{A}$, we can rewrite this as $\simeq \left(\frac{e}{m_e c}\right) B_y L_y$ which will be a orbital magnetic dipole interaction term. There are also spin interaction terms $\vec{B} \cdot \vec{S}$. If all of these have zero matrix elements between the initial state and any final states with frequency-difference $\omega_{ns} = \omega$, you can keep expanding using more terms in equation (7.2) getting the electric octopole operator etc. each of which will be down by a factor of $\frac{\omega}{c}$.

For an atom, non-relativistically and for no static $\vec{B}$ field, the rotational symmetries tell us that $[\vec{L}, H_0] = [\vec{S}, H_0] = 0$. In that case we can choose the state $|n\rangle$ to be an eigenstate of L_y and S_y. Therefore since L_y, S_y will not change the energies, their associated transitions (magnetic dipole transitions) are not allowed. However, this will change if a static magnetic field is applied in a direction other than the y-direction. Also, when relativistic spin-orbit coupling is included in the Hamiltonian, magnetic dipole transitions may be allowed even in the absence of an applied magnetic field.

7.1.1 Semi-Classical Interpretation

If we just imagine that photons exist, taking it on faith for the moment, we would imagine that the probability of transition is proportional to the number of photons that are coming in. We make the guess that for photons the absorption probability may be written in the form:

$$P_{ABS} = \int_0^\infty N(\omega)\sigma_{ABS}(\omega)d\omega \tag{7.4}$$

where $N(\omega)$ = the number of photons per unit area per unit frequency ω incident on the target, and σ_{ABS} = absorption cross section. From E+M we know that the energy flux is given by the Poynting vector, and for a plane wave this gives the special result:

$$\text{Energy Flux} = \frac{c}{4\pi}(\vec{E}(t) \times \vec{B}(t)) = \frac{c|\vec{E}(t)|^2}{4\pi}$$

We can write the Fourier transform of the electric field as:

$$\vec{E}(\omega) = \int_{-\infty}^\infty \frac{dt}{(2\pi)^{1/2}} e^{-i\omega t}\vec{E}(t) \tag{7.5}$$

3

Since we know that the electric field in the time domain is real we know that the constraint $\vec{E}(\omega) = \vec{E}^*(-\omega)$ must hold. We now use the property that the fourier transform preserves the inner product to write the total energy per unit area as:

$$
\begin{aligned}
\frac{\text{Total Energy}}{\text{cm}^2} &= \int_{-\infty}^{\infty} dt \, \frac{c|\vec{E}(t)|^2}{4\pi} = \int_{-\infty}^{\infty} d\omega \, \frac{c|\vec{E}(\omega)|^2}{4\pi} \\
&= \int_{0}^{\infty} d\omega \, \frac{c|\vec{E}(\omega)|^2}{2\pi} = \int_{0}^{\infty} d\omega N(\omega)\hbar\omega
\end{aligned}
\tag{7.6}
$$

In the last line we have again clairvoyantly assumed the existence of photons, and have assumed that the total energy in the electromagnetic field must be equal to the number of photons per unit frequency, multiplied by the energy carried by each photon $\hbar\omega$, and integrated over all frequencies. If this is to hold for arbitrary forms of $\vec{E}(\omega)$ then the integrands must be the same at every frequency. Thus we find

$$
\boxed{N(\omega) = \frac{c|\vec{E}(\omega)|^2}{2\pi\hbar\omega}}
\tag{7.7}
$$

Now we assume a spherically symmetric atom, and we use the dipole approximation from Lecture 6, with $\vec{E}||\hat{z}$ to get the total transition probability for absorption (i.e., $\omega_{ns} > 0$, hence the integral from 0 to ∞ instead of $-\infty$ to ∞):

$$
P_{ABS} = \sum_{n>s} P_n = \int_{0}^{\infty} \frac{2\pi}{\hbar^2} |E_z(\omega)|^2 g_{zz}(\omega) \, d\omega
$$

where the spectral function, first defined in Lecture 4, is:

$$
g_{zz}(\omega) = \sum_{n\neq s} |d_{ns}^z|^2 \delta(\omega - \omega_{ns})
$$

Now referring back to equation (7.4) we find that:

$$
\sigma_{ABS}(\omega) = g_{zz}(\omega)\left(\frac{4\pi^2\omega}{\hbar c}\right)
\tag{7.8}
$$

Similarly we can guess that for stimulated emission, which requires $\omega_{ns} < 0$, we would have:

$$
P_{SE} = \int_{0}^{\infty} N(\omega)\sigma_{SE}(\omega) \, d\omega = \int_{-\infty}^{0} \frac{2\pi}{\hbar^2} |E_z(\omega)|^2 g_{zz}(\omega) \, d\omega
$$

This will yield (for $\omega > 0$):

$$
\sigma_{SE}(\omega) = g_{zz}(-\omega)\left(\frac{4\pi^2\omega}{\hbar c}\right)
\tag{7.9}
$$

A side remark from the f-sum rule discussed in p251b lecture 5 is:

$$
\begin{aligned}
\int_0^\infty d\omega \left[\sigma_{ABS}(\omega) - \sigma_{SE}(\omega)\right] &= \frac{4\pi^2}{\hbar c} \int_{-\infty}^\infty g_{zz}(\omega)\omega \, d\omega \\
&= \frac{2\pi^2 e^2}{m_e c} Z
\end{aligned}
$$

If you begin in the ground state, there is no stimulated emission cross-section, and the left hand side of the equation involves only absorption. In this case we could also write:

$$
\sigma_{ABS}(\omega) = \sum_{n \neq s} \delta(\omega - \omega_{ns}) \frac{2\pi^2 e^2}{m_e c} f_{ns}
$$

where the quantities $f_{ns} \geq 0$ are called the "oscillator strengths", and

$$
\sum_n f_{ns} = Z
$$

So, are these semiclassical results correct? We will answer this question later by doing a full quantum mechanical calculation, involving the quantization of the electromagnetic field. But before that, we can ask, what does this mean and is it sensible.

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8.1 Photoelectric Cross Section (Continuum States)

We want to continue our discussion of the photon absorption cross section, and now we want to extend our discussion to the situation where the photon comes in with an energy greater than the binding energy of an electron in an atom $\hbar\omega > E_B$ so that when the photon is absorbed it kicks the electron from a bound state to a continuum state.

We assume that we are in a regime where we can make the electric dipole approximation. We assume that the electric field is polarized in the z-direction $\vec{E} = \hat{z}$. From P251b Lecture 6 we had the following formula for the absorption cross section:

$$\sigma_{ABS}(\omega) = \frac{4\pi^2\omega}{\hbar c}g_{zz}(\omega) \tag{8.1}$$

The matrix elements of the spectral functions g_{zz} (first discussed in p251b Lecture 4) are given by:

$$g_{zz} = \sum_{n\neq s}\delta(\omega - \omega_{ns})|\langle n|d_z|s\rangle|^2 \tag{8.2}$$

We want to calculate the total absorption cross section, which includes transitions to both higher energy bound states and also to continuum states. We are now faced with the problem of how do we go from a sum to a continuum?

To address this problem we shall make the simplifying assumption that we can treat the atom as a collection of non-interacting electrons, moving in a self-cosistent electrostatic potential, which we shall take to be spherically symmetric. We shall examine the probability of ejecting an electron that was initially in an s-orbital, i.e., in a state with orbital angular momentum 0. This would be a good approximation, for example, if we want to calculate the cross section for ejecting the outermost electron of an alkali atom, which sits in an s-state outside a spherically symmetric filled shell of tightly bound electrons. The unperturbed Hamiltonian for the valence electron will then be of the form:

$$H_0 = \frac{p^2}{2m} + U(r), \tag{8.3}$$

where $U(r) \to 0$ for $r \to \infty$.

We consider an initial state $|s\rangle$ of zero orbital angular momentum $l = 0$ and a set of continuum final states which will be given by a combination of spherical harmonics and the appropriate radial functions (the solutions for a coulomb potential were discussed in p251a lecture 15 and spherical harmonics were covered in p251a lecture 13). The continuum states may be written

$$|n\rangle \to N^{-1/2}R_l(r, k)Y_l^m(\theta) \tag{8.4}$$

where $N^{-1/2}$ is the normalization factor and $k > 0$ is the wavevector of the outgoing electron, related to the electron's energy by $E = \frac{\hbar^2 k^2}{2m}$, with $E > 0$.

We put the system into a large spherical box of radius R. This imposes the boundary condition that $\psi = 0$ at $r = R$. This allows us to get a discrete set of states rather than a continuum. For large distances from the origin (as was seen in p251a lecture 17) the radial wavefunctions will take the asymptotic form:

$$R_l \simeq \frac{\sin(kr - \frac{l}{2}\pi + \delta_l)}{kr} \tag{8.5}$$

The quantity δ_l is the phase shift due to the presence of the potential, it will be a constant if the potential goes to zero faster than $\frac{1}{r}$. For the Coulomb potential, the phase shift will approximately go like $\delta \simeq \ln r$. To satisfy the boundary condition $\psi(R) = 0$ the argument of the sine function in equation (8.5) must be an integer multiple of π, when $r = R$. So therefore we have:

$$kR - \frac{l\pi}{2} + \delta_l(k) = n\pi \tag{8.6}$$

where n is an integer. We want to convert the integral/sum over n into an integral over k. Taking differentials of both sides of the equation we have:

$$dn = \frac{dk}{\pi}[R + \frac{d\delta_l(k)}{dk}] \tag{8.7}$$

As we are interested in the case for the size of the box going to infinity, we can take the limit as $R \to \infty$, so we can neglect the second term above and write:

$$dn \overset{R \to \infty}{=} \frac{R}{\pi} dk \tag{8.8}$$

Now looking back at equation (8.2) we can rewrite the sum over n as an integral:

$$\sum_{n=0}^{\infty} \Rightarrow \int_0^{\infty} dn = \int_0^{\infty} \frac{R}{\pi} dk \tag{8.9}$$

In principle there could also be a sum over the angular momentum quantum numbers (l, m) in the final state, but in the present problem there will be only one angular momentum component that enters, $(l = 1, m = 0)$, with $Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$.

We now want to look into the normalization. We require that:

$$\int d^3r|\psi(\vec{r})|^2 = 1 \qquad \langle n|n\rangle = 1 \tag{8.10}$$

2

Looking at equation (8.4) we can see that this gives:

$$N = \int_0^R r^2 \, dr \, |R_{l,k}(r)|^2 \overbrace{\int d^2\Omega |Y_{10}(\Omega)|^2}^{\text{normalized}} \tag{8.11}$$

Since we are dealing with $R \to \infty$, we will ignore the contribution from the integral inside of $r < a$ and we can use the asymptotic form of $|R_{l,k}(r)|^2$ given in equation (8.5).

$$N \simeq \int_a^R \frac{r^2 dr}{r^2 k^2} \overbrace{\sin^2(\ldots)}^{1/2} \simeq \frac{1}{2} \frac{R}{k^2} \tag{8.12}$$

Since we will be integrating over many oscillations of the $\sin^2$ function, we can just set it to its average value of $1/2$.

We have assumed that the initial state is an s-state, which we write as:

$$|s\rangle = \psi_s(r) \tag{8.13}$$

As an s state, it is spherically symmetric; its value only depends on the radial distance from the origin. It is a bound state, so we must have $\psi_s(r) \to 0$, for $r \gg a$. We normalize it so that $\langle s|s \rangle = 1$.

The value of the matrix element will be:

$$\langle n|d_z|s \rangle = N^{-1/2} \int_0^R r^2 \, dr \, R_1(r,k) \psi_s(r)(-e)r \overbrace{\int d^2\Omega \cos\theta Y_{10}(\theta)}^{\sqrt{\frac{4\pi}{3}}} \tag{8.14}$$

The dipole is aligned along the z axis and thus contributes the $-er\cos(\theta)$ to the integral. We can rewrite the square of the matrix element as:

$$|\langle n|d_z|s \rangle|^2 = e^2 \frac{4\pi}{3} \frac{2k^2}{R} |I(k)|^2 \tag{8.15}$$

where the function $I(k)$ is defined as:

$$I(k) = \int_0^\infty r^3 \, dr \, R_1(r,k) \psi_s(r) \tag{8.16}$$

Looking back at the value for g_{zz} in equation (8.2), we can see the frequency ω_{ns} will be given by the energy difference of the final state of the electron minus that of the initial state:

$$\omega_{ns} = \frac{\hbar k^2}{2m} + \frac{E_b}{\hbar} \tag{8.17}$$

3

Thus we now have:

$$g_{zz}(\omega) = \int_0^\infty \frac{dk}{\pi} \delta\left(\omega - \frac{\hbar k^2}{2m} - \frac{E_b}{\hbar}\right) \frac{8\pi e^2}{3} k^2 |I(k)|^2 \tag{8.18}$$

This integral is not that complicated due to the delta function. We have to be careful because we have an integral over k while we have a delta function involving k^2, so we need to introduce the jacobian of the transformation. Let us introduce the variable ν such that: $\nu = \frac{\hbar k^2}{2m}$, $dk = \frac{m}{\hbar k} d\nu$ and our delta function becomes $\delta(\omega - \nu - \frac{E_b}{\hbar})$. Now the value for g_{zz} is given by:

$$g_{zz}(\omega) = \frac{8e^2}{3} \frac{mk}{\hbar} |I(k)|^2 \bigg|_{k=\frac{1}{\hbar}\sqrt{\hbar\omega - E_b}} \tag{8.19}$$

We know ω, we know the binding energies, we know the energy of the outgoing electron we know what $\vec{k}$ is, so we just have to evaluate the integral $I(k)$. This is not easy, often involves a numerical integration. For the case of the hydrogen atom, it turns out you can do it analytically. (See, e.g., Gottfried, Section 58.) The result is:

$$\sigma(\omega) \propto \omega^{-7/2} \quad \text{for} \quad \omega \to \infty \tag{8.20}$$

It also turns out that for $\hbar\omega \to E_b$, $\sigma(\omega)$ goes to a finite constant (equal to $6.31 \times 10^{-18} \text{cm}^2$). This is about 15 times smaller than the geometric cross-section of the hydrogen atom, $\pi a_H^2 \approx 10^{-16} \text{cm}^2$.

So far, we have considered just a single initial state $|s\rangle$. If the target atom contains many electrons, we must add up the contributions from each of the possible initial states. (Recall that we are working in an independent electron approximation.) If the incident photon energy is large enough, electrons from more than one initial state can be excited into the continuum. Then for a given photon energy, there will be several different allowed energies for the ejected electron. Measurement of these energies tells us the energies of the various initial states, after subtracting the energy of the photon. We shall se that measurement of the intensities of electrons emitted at different energies, and also their angular distribution, gives us information about the wave functions of the various initial states.

8.1.1   Angular Resolved Photoemission

Suppose we have an experiment where we have a photon coming in parallel to the x axis $(\vec{k}_{in}||\hat{x})$ and the electric field is parallel to the z axis, and we have a target that the photon is incident upon. Let's say we have a small detector whose angular position we can vary. We can see what

the relative probability of finding an electron emitted into a particular direction is. This is called angular resolved photoemission. We can write the differential scattering cross section as:

$$\frac{d\sigma}{d\Omega_e} = \text{differential cross section} = \tilde{P}(\Omega)\sigma_{abs}(\omega) \tag{8.21}$$

where $\tilde{P}(\Omega)$ is the relative probability of the electron being ejected into a particular solid angle Ω. Of course we require $\int \tilde{P}(\Omega)d^2\Omega = 1$. Without doing a complicated calculation we can say a couple of things. First the probability seems like it should be biggest in the $\pm z$-direction. Secondly, we may guess that the probability will be proportional to $|\cos^2(\theta)|$, as we are making a transition to a final state which is proportional to Y_{10}, and we expect that the probability of emission into a given solid angle should be proportional to the square of the magnitude of the wave function in that direction.

Questions for thought: What would you expect the angular distribution of emitted to look like if the photons source is unpolarized? Assume as before that the photons come in along the x-axis.

What would you expect, qualitatively, if the initial state of the ejected electron is a p-state, rather than an s-state?

How would you calculate the angular distribution of the emitted electron in a case of a molecule or a solid, where the Hamiltonian of the system does not have spherical symmetry?

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9.1 Angular-Resolved Photoemission

9.1.1 Photoemission from a target without spherical symmetry.

We will now treat the angular resolved photoemission of a single electron in the case where the target does not have spherical symmetry. As before, we make the independent electron approximation. Then for each electron, the Hamiltonian can be broken into an unperturbed part H_0 and a time dependent perturbation $V(t)$:

$$H = H_0 + V(t)$$

$$H_0 = \frac{p^2}{2m_e} + U(\vec{r})$$

We treat the perturbation using the electric dipole approximation, so that it can be written as:

$$V(t) = \frac{|e|}{m_e c} \vec{A}(\vec{r}) \cdot \vec{p} \simeq \frac{|e|}{m_e c} \vec{A}(0) \cdot \vec{p}$$

Thus the perturbation is due to a time-dependent spatially uniform electric field $\vec{E}(t) = -(1/c)(d\vec{A}/dt)$. As we have seen above, we will obtain the same final results if we assume that the electric field is derived from a scalar potential, so that the perturbation would be

$$V(t) = -\vec{E}(t) \cdot \vec{d}$$

We define the differential scattering cross section $\frac{d\sigma}{d\Omega_e}$ such that the integral over the solid angle will give the total scattering cross section:

$$\int \frac{\partial \sigma}{\partial \Omega_e} \, d^2\Omega_e = \sigma_{ABS}(\omega) \tag{9.1}$$

We can also define a relative probability of scattering per solid angle $\tilde{P}(\Omega_e)$ such that:

$$\frac{\partial \sigma}{\partial \Omega_e} = \tilde{P}(\Omega_e)\sigma_{ABS}(\omega)$$

We now consider a situation with a given initial state $|s\rangle$ and a set of final states $|n\rangle$. To obtain the total optical absorption cross section, we can use any set of final states we want, so long as they are properly normalized and properly counted. (Of course, they need to be eigenstates of the unperturbed Hamiltonian H_0). If we want to calculate the angular-resolved

photoemission cross section, however, it turns out to be most convenient to choose final states of the form:

$$|\vec{k}_{(-)}\rangle = N^{-1/2} \psi_{\vec{k}}^{(-)}(\vec{r})$$

where $\psi_{\vec{k}}^{(-)}(\vec{r})$ is a continuum eigenstate of H_0 with energy $E_k = \frac{\hbar^2 k^2}{2m_e}$, which satisfies the boundary condition that for large r,

$$\psi_{\vec{k}}^{(-)}(\vec{r}) \overset{r\to\infty}{\simeq} \left(\frac{1}{2\pi}\right)^{3/2} \left[e^{i\vec{k}\cdot\vec{r}} + \frac{h_{\vec{k}}(\hat{r})}{r}e^{-i|k|r}\right] \tag{9.2}$$

This is similar to the conditions used to define the scattering wavefunctions $\psi_{\vec{k}}^{(+)}(\vec{r})$ in p251a, starting with p251a lecture 20; however, now we are dealing with an **incoming** spherical wave rather than outgoing spherical wave due to the negative sign on the second exponential (the one with the magnitude of k). The two choices are related by $\psi_{\vec{k}}^{(-)}(\vec{r}) = [\psi_{-\vec{k}}^{(+)}(\vec{r})]^*$. Indeed, we see that for large r,

$$[\psi_k^{(-)}(\vec{r})]^* \overset{r\to\infty}{\simeq} \left(\frac{1}{2\pi}\right)^{3/2} [e^{-i\vec{k}\cdot\vec{r}} + \frac{h_{\vec{k}}^*(\hat{r})}{r}e^{ikr}], \tag{9.3}$$

which has the correct asymptotic form for a scattering wave solution for an incoming plane wave of wave vector $-\vec{k}$. Moreover, if $\psi_{\vec{k}}^{(-)}$ is a solution of the Schrödinger equation at energy E, so is $[\psi_{\vec{k}}^{(-)}]^*$, since H_0 is real. The scattering amplitude $f_{-\vec{k}}(\hat{r})$ is equal to $h_{\vec{k}}^*(\hat{r})$.

We want to normalize this in a box of size L_x, L_y, L_z. This will make the normalization factor:

$$N = \frac{L_x L_y L_z}{(2\pi)^3}$$

The optical absorption cross section is given by

$$\sigma_{ABS}(\omega) = \frac{4\pi^2\omega}{\hbar c} \sum_{\vec{k}}' |\langle \vec{k}_{(-)}|d_z|s\rangle|^2 \delta(\omega - \omega_{ks}) \tag{9.4}$$

where the sum on $\vec{k}$ must be defined consistently with our choice of normalization. The correct definition is

$$\sum_{\vec{k}} \equiv \frac{L_x L_y L_z}{(2\pi)^3} \int d^3k = \frac{L_x L_y L_z}{(2\pi)^3} \int_0^\infty k^2 dk \int d^2\Omega_{\vec{k}} \tag{9.5}$$

To obtain this result, we choose periodic boundary conditions consistent with our box normalization, such that $e^{ik_x L_x} = 1$, $e^{ik_y L_y} = 1$ and $e^{ik_z L_z} = 1$. This leads to $k_x L_x = 2\pi n_x$, $k_y L_y = 2\pi n_y$ and $k_z L_z = 2\pi n_z$, where the n_μ are arbitrary integers. To convert the sum to an integral we used the fact that if $X(\vec{k})$ is any smooth function of $\vec{k}$,

$$\lim_{\Delta\vec{k}\to 0} \sum_{\vec{k}} X = \lim_{\Delta\vec{k}\to 0} \frac{1}{\Delta n_x \Delta n_y \Delta n_z} \sum_{\vec{k}} \Delta n_x \Delta n_y \Delta n_z X = \frac{1}{\Delta n_x \Delta n_y \Delta n_z} \int dn_x\, dn_y\, dn_z X$$

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Taking note that $\Delta n_x = \Delta n_y = \Delta n_z = 1$ and by the relations established above $dn_x = \frac{L_x}{2\pi} dk_x$ etc... we reproduce equation (9.5). We also convert the delta function in ω from equation (9.4) into a delta function in k. Using the various rules for manipulating delta functions the conversion is

$$\delta(\omega - \omega_{ks}) = \frac{m_e}{\hbar k} \delta(k - k_0),$$

where

$$k_0 = [2m_e(\hbar\omega - E_b)]^{1/2} / \hbar \tag{9.6}$$

As before, E_b is the binding energy of the initial state: $E_s^0 = -E_b$. Plugging this into equation (9.4), the volumes of the box in the wavefunction normalizations and the sum-to-integral conversions will cancel and we get:

$$\sigma_{ABS}(\omega) = \frac{4\pi^2 e^2 \omega}{\hbar c} \frac{m_e k_0}{\hbar} \int d^2\Omega_{\vec{k}} \left| \int \psi_{\vec{k}}^{(-)*}(\vec{r}) z \psi_s(\vec{r}) \, d^3r \right|^2 \tag{9.7}$$

where $\vec{k}$ is a wave vector of magnitude k_0 in the direction $\hat{\Omega}_{\vec{k}}$.

Now, I make the further claim, which is not obvious, that we can obtain the differential cross section for angular-resolved photoemission in a specified direction $\hat{\Omega}_e$ by simply omitting the integration over $\hat{\Omega}_{\vec{k}}$ in Eq. (9.7), and choosing $\vec{k}$ in the direction $\hat{\Omega}_e$:

$$\boxed{\frac{\partial\sigma}{\partial\Omega_e} = \frac{4\pi^2 e^2 \omega}{\hbar c} \frac{m_e k_0}{\hbar} \left| \int \psi_{\vec{k}}^{(-)*}(\vec{r}) z \psi_s(\vec{r}) \, d^3r \right|^2} \tag{9.8}$$

with $\vec{k} = k_0 \hat{\Omega}_e$, and k_0 given by Eq. (9.6). In other words:

$$\frac{\partial\sigma}{\partial\Omega_e} = \frac{4\pi^2 \omega}{\hbar c} \frac{1}{\delta\Omega_e} \sum_{\substack{k \\ \hat{k}\epsilon\delta\Omega_e}} |\langle \vec{k}_{(-)}|d_z|s\rangle|^2 \delta(\omega - \omega_{ks})$$

In general, you would **not** get the correct answer for the differential cross section if you were to use $\psi_{\vec{k}}^{(+)}$ instead of $\psi_{\vec{k}}^{(-)}$ in (9.8). However, the total cross section, integrating over all solid angles, would come out the same in either case.

Why is it that the choice $\psi_{\vec{k}}^{(-)}$ leads to the correct angular distribution? The logic behind this is described in detail in the Handout on Photoemission. It is also discussed in Messiah, p. 1007, using a rather different method than in the handout. The topic is not properly discussed in Merzbacher or Sakurai. I will just present the highlights below.

We start off with a state $|s\rangle$ at time $t = -\infty$. Assume that the electric field at the origin, $\vec{E}(t)$, is a pulse with a width in time Δt, and a center frequency ω_0, and which reaches its maximum near time $t = 0$. Therefore when we fourier transform it we get a spread $\Delta\omega \simeq \frac{1}{\Delta t}$

such that we have $\vec{E}(\omega)$ concentrated in the interval $\omega_0 - \Delta\omega < \omega < \omega_0 + \Delta\omega$. For times t much greater than the characteristic time Δt, we would expect from first order time-dependent perturbation theory to have:

$$|\psi(t)\rangle = \exp(-iE_s^0 t/\hbar)|\psi_s\rangle + \sum_{\vec{k}} c_{\vec{k}}(t)e^{-i\omega_k t}|\vec{k}_{(-)}\rangle \tag{9.9}$$

where we can approximate $c(t) \simeq c(\infty)$. This will be given by:

$$c_{\vec{k}}(\infty) = \frac{-i(2\pi)^{1/2}}{\hbar}\langle\vec{k}_{(-)}|\tilde{V}(\omega_{ns})|s\rangle \tag{9.10}$$

The main point is that it is proportional to the matrix element of the fourier transform of the potential at the transition frequency between the initial and final state.

Now, I claim that in the position basis $\langle\vec{r}|\psi(t)\rangle$, the wave function will be concentrated on a spherical shell propagating outward, where $r \approx v_0 t$, with v_0 being the velocity of an electron with energy $\hbar\omega - E_B$. Moreover, due to the rapidly oscillating phase factors, the contribution from the incoming spherical wave turns out to vanish everywhere in space, for $t > 0$. The contribution from the plane waves will cancel everywhere except on the shell; and for a point $\vec{r}$ on the shell, the only wavevectors that contribute are those with $\vec{k}$ oriented very close to the direction $\hat{r}$. Thus, the number of electrons emitted in a direction $\hat{r}$ will be proportional to $|c_{\vec{k}}|^2$, for $\vec{k}$ in the specified direction. (See Handout!)

This does not work if we use basis states $|\vec{k}_{(+)}\rangle$. In this case, the contribution from the outgoing spherical wave is not destroyed by the rapidly varying phase factors, so the a state with a given direction of $\vec{k}$ can contribute to the emission in directions other than $\hat{k}$.

Why don't we simply use plane waves $|\vec{k}\rangle$ as the final states? Well, these are not eigenstates of the Hamiltonian H_0. If the potential U is strong enough to have bound states, then we should not ignore its effect on the final state. Frequently, people approximate the final state by a plane wave; this often referred to as the Born approximation. However, the Born approximation is at best qualitatively correct in most cases. Also, the Born approximation is not a gauge invariant approximation; you get different answers if you evaluate matrix elements of the electric dipole operator d_z or the momentum operator p_z, which means you get different answers if you assume the exciting electric field is derived from a scalar potential or a vector potential.

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10.1 Scattering: Born Approximation Derived from Time-Dependent Perturbation Theory

10.1.1 Elastic Scattering From a Potential $V(\vec{r})$

We will now use a cheat, using time dependent perturbation theory, to re-derive the first Born Approximation for scattering from a time-independent potential. Suppose that for $t < 0$ we have a Hamiltonian with no potential, $H_0 = p^2/2m$. We assume an initial state at $t = 0$ which is a plane wave, normalized in a large box of dimensions $L \times L \times L$, with periodic boundary conditions:

$$|\vec{k}_0\rangle = \frac{1}{L^{3/2}} e^{i\vec{k}_0 \cdot \vec{r}} \tag{10.1}$$

Now, we turn on the potential at $t = 0$, so that for times greater than zero we have the full Hamiltonian $H = H_0 + V(\vec{r})$, where the potential is just a function of the position (independent of time). Since the initial state is no longer an eigenstate of the Hamiltonian, the wave function will be time-dependent. We would guess that after some time, after some initial transients have passed, but before the initial state has had time to be seriously depleted, there will be a constant rate of transition into final states $|\vec{k}\rangle$ traveling in different directions. We shall, in fact calculate this transition rate, and interpret it in terms of a scattering cross-section, which we can thereby calculate.

To get the transition rate we can use time-dependent perturbation theory to get an idea of what fraction of the incoming particles will have made the transition by a given time t. The wave function may be written

$$|\psi(t)\rangle \approx \exp(-iE_0 t/\hbar)|k_0\rangle + \sum_{\vec{k}} \exp(-iE_{\vec{k}} t/\hbar) c_{\vec{k}}(t)|\vec{k}\rangle + \mathcal{O}(V^2) \tag{10.2}$$

where the coefficient $c_{\vec{k}}$ will be given by:

$$c_{\vec{k}}(t) = \frac{1}{i\hbar} \int_0^t dt' e^{i\Delta\omega_k t} \langle \vec{k}|V(\vec{r})|\vec{k}_0\rangle \tag{10.3}$$

with $\Delta\omega_k = (E_k - E_{k_0})/\hbar$ We have assumed that the potential is weak, and the time interval t is not so huge that the initial state is depleted, so we can neglect terms of order V^2 in the wave function $|\psi(t)\rangle$. We can easily perform the time integral, and we note that the matrix element of the potential between the two plane waves will give us a Fourier transform. of V. Thus we find:

$$c_k(t) = \frac{1}{i\hbar} V_{\vec{k}\vec{k}_0} \frac{e^{i\Delta\omega_k t} - 1}{i\Delta\omega_k} \qquad \Delta\omega_k = \frac{E_{\vec{k}} - E_{\vec{k}_0}}{\hbar} \tag{10.4}$$

where:

$$V_{\vec{k}\vec{k}_0} = \frac{(2\pi)^{3/2}}{L^3} \tilde{V}(\vec{k} - \vec{k}_0) \tag{10.5}$$

The probability that a particle has been scattered into a solid angle $\delta\Omega$ about a specified angle $\hat{\Omega}$

$$P_{\hat{\Omega}} \delta\Omega = \sum_{\vec{k}\epsilon\delta\Omega} |c_{\vec{k}}(t)|^2 = \frac{L^3}{(2\pi)^3} \delta\Omega \int_0^\infty k^2 \, dk |c_{\vec{k}}(t)|^2 \tag{10.6}$$

The expression for $c_{\vec{k}}$ given by equation (10.4) implies that

$$|c_{\vec{k}}(t)|^2 = |V_{\vec{k}\vec{k}_0}|^2 \frac{1}{\hbar^2} \left[\frac{4\sin^2(\Delta\omega_k t/2)}{(\Delta\omega_k)^2} \right] \tag{10.7}$$

We want to explore the behavior of this function for the limit where t is large. More specifically we want to look at the regime where $t >> \frac{\hbar}{E_{k_0}}$. As quickly become evident, this function approaches some multiple of a delta function in $\Delta\omega_k$ as $t \to \infty$, with a width in frequency of order $1/t$ and a center peak rising to approximately $\simeq t^2$. More accurately the area under the curve will be given by:

$$A = \int_{-\infty}^\infty d(\Delta\omega_k) \frac{4\sin^2(t\Delta\omega_k/2)}{(\Delta\omega_k)^2} \tag{10.8}$$

The analysis can be simplified with a change of variable $x = \frac{\Delta\omega t}{2}$. This will integrate over all frequency space to give

$$A = \int_{-\infty}^\infty dx \frac{\sin^2 x}{x^2} \left(\frac{4t}{2} \right) \tag{10.9}$$

The integral can be evaluated analytically (see Appendix), and one finds $A = 2\pi t$. The criteria for a standard delta function is that the function is equal to zero everywhere, is infinite where it's argument is equal to zero, and has an overall area of one. The function in equation (10.7) (as $t \to \infty$)meets all the criteria of the delta function, except it has an area equal to $2\pi t$; therefore we can write:

$$\frac{4\sin^2(\Delta\omega_k t/2)}{(\Delta\omega_k)^2} \stackrel{t\to\infty}{=} 2\pi t\delta(\Delta\omega_k) = 2\pi t\hbar\delta(E_k - E_{k_0}) \tag{10.10}$$

Formally, therefore, using this knowledge we can write the coefficient as:

$$|c_{\vec{k}}(t)|^2 \stackrel{t\to\infty}{=} \frac{2\pi}{\hbar} |V_{\vec{k}\vec{k}_0}|^2 t\delta(E_k - E_{k_0}) \tag{10.11}$$

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The transition rate will be given by taking the time derivative of the probability:

$$\frac{d}{dt}|c_k(t)|^2 = \frac{2\pi}{\hbar}|V_{\vec{k}\vec{k}_0}|^2\delta(E_k - E_{k_0}) \tag{10.12}$$

We can generalize this statement for the transition rate from some initial state $|i\rangle$ of H_0 to a final state $|f\rangle$ in the presence of a "switched on" perturbation V. This much used, very important equation is known as **Fermi's Golden Rule**:

$$\boxed{W_{i\to f} = \frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2\,\delta(E_f - E_i)} \tag{10.13}$$

10.1.2   Conditions of Validity for Fermi's Golden Rule

It is important to know when using this equation is valid. The necessary conditions are:

- The initial state needs to be an eigenstate of the unperturbed Hamiltonian H_0, at some time $t = t_0$.

- There is a weak perturbation V, which is independent of time for $t > t_0$. (We do not actually care about V for $t < t_0$, since the initial state is specified at $t = t_0$.)

- There must be a **continuum** of final states.

- The transition rate will only be valid at a time such that the initial transients are gone, but the initial state is not yet significantly depleted. Initial transients will generally be gone if $\Delta\omega \equiv 1/(t-t_0)$ is sufficiently small that we may neglect the variation of the matrix element $V_{\vec{k}\vec{k}_0}$ when the magnitude of $\vec{k}$ varies by an amount corresponding to an energy change $\pm\Delta\omega$.

10.1.3   Application to scattering

The transition rate per solid angle will be given by:

$$\gamma_{\hat{\Omega}} = \frac{1}{\delta\Omega}\sum_{k\epsilon\delta\Omega} W_{\vec{k}_0\vec{k}} = \frac{L^3}{(2\pi)^3}\int_0^\infty k^2\,dk\,|V_{\vec{k}\vec{k}_o}|^2 2\pi\delta(E_k - E_{k_0}) \tag{10.14}$$

In the last integral, it is understood that the wave vector $\vec{k}$ in the matrix element is oriented in the specified direction $\hat{\Omega}$.

Our integral is with respect to $\vec{k}$, but the the delta function is with respect to energy. We choose to convert the integral by using:

$$k = \frac{\sqrt{2mE}}{\hbar} \qquad k\,dk = \frac{m}{\hbar}\,dE$$

Making this substitution, we arrive at:

$$\gamma_{\hat{\Omega}} = \frac{2\pi}{\hbar} |V_{\vec{k}\vec{k}_0}|^2 \frac{L^3}{(2\pi)^3} \frac{mk_0}{\hbar} \tag{10.15}$$

In the matrix element, $|k| = |k_0|$ and therefore that $\vec{k} = |k_0|\hat{\Omega}$. The quantity $\frac{L^3}{(2\pi)^3} \frac{mk}{\hbar}$ is the density of states (per unit energy per unit solid angle). Given this we want to know how to calculate the scattering cross section. We would expect $\gamma_{\hat{\Omega}}$ to be proportional to $\frac{d\sigma}{d\Omega}$ and the incident flux. The density of particles in the initial state (10.1) is equal to $1/L^3$. The incident flux (which needs dimensions of particles per second per unit area) is obtained by multiplying the density by the velocity, and is given by $\frac{1}{L^3} \frac{\hbar \vec{k}_0}{m}$. We would predict that the transition rate is equal to the flux times the differential scattering cross section, therefore:

$$\frac{d\sigma}{d\Omega} = \frac{\gamma_{\hat{\Omega}}}{\frac{\hbar k_0}{m} L^{-3}} \tag{10.16}$$

Now we can use equation (10.16) and the definition of $V_{\vec{k}\vec{k}_0}$ from equation (10.5) and arrive at:

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{2\pi m^2}{\hbar^4} |\tilde{V}(\vec{k} - \vec{k}_0)|^2} \tag{10.17}$$

Thankfully the size of the Universe (L^3) drops out. This is the same result which we obtained from the Born Approximation in p251a lecture 22.

As before, if V is isotropic, the differential scattering cross section depends only on

$$|\vec{k} - \vec{k}_0| = 2k_0 \sin(\theta/2), \tag{10.18}$$

where θ is the scattering angle.

Appendix. Evaluation of integral (10.9).

Integrating by parts, we find

$$I \equiv \int_{-\infty}^{\infty} dx \, \frac{\sin^2 x}{x^2} = \int_{-\infty}^{\infty} dx \, \frac{\sin 2x}{x} \, .$$

We now deform the contour of integration to sit along a line just above the real axis, thus replacing x in the integrand by $(x + i0^+)$. Now we write $\sin 2x = (e^{2ix} - e^{-2ix})/2i$, and consider the two terms separately. The term involving e^{2ix} can be closed in the upper half plane, where the integrand is analytic, so it gives no contribution to I. The other term must be closed in the lower half plane, where there is now a pole at $x = -i0^+$, with residue $-1/2i$. This gives the result $I = \pi$.

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11.1 Inelastic Scattering of a "Probe Particle" from a Target with Internal Degrees of Freedom

We now consider scattering of a probe particle from a target with internal degrees of freedom, and consider the possibility of inelastic scattering, where the target is left in an excited state, and the probe particle scatters with less energy than it started with.

For example, consider a target such as an atom, and assume probe is a charged particle with charge Z_0 and mass m. Let the vector $\vec{R}$ be the position of the probe particle, the vectors $\vec{r}_i$ (i=1...Z) denote the positions of the electrons in the atom and the vector $\vec{r}_0$ denote the position of the nucleus.

If we ignore the spin of the particles, the Hilbert space of this system will be given by a set of functions $\psi(\vec{R}, \vec{r}_i)$ where $i = 0...Z$. We can model the nuclear mass to be infinite (compared to the electrons and probe particles) and so the vector $\vec{r}_0$ can be considered a constant parameter. As before, the Hamiltonian can be written as

$$H = H_0 + V \qquad H_0 = \frac{p^2}{2m} + H^0_{TARGET} \tag{11.1}$$

where p is the momentum of the probe particle, and H^0_{TARGET} is the hamiltonian of the atom without the probe. The perturbation is turned on at time $t = 0$ and is given by the Coulomb interaction between the probe particle and the particles in the target:

$$V = Z_0 e \sum_{i=0}^{Z} q_i \frac{1}{|\vec{R} - \vec{r}_i|} \qquad \begin{array}{c} i = 1...Z \ \ q_i = -e \\ i = 0 \ \ q_0 = Ze \end{array}$$

In our analysis, we shall treat the perturbation V as weak, so that we can use Fermi's Golden Rule and the first Born approximation for scattering. This approximation is generally correct if the probe particle has sufficiently high energy, so that it moves quickly through the target. For low energy charged probes, the Born approximation is likely to be poor. Also, if the probe particle is itself a low-energy electron, one needs to take into account exchange processes, in which the probe particle is absorbed by the target and another electron is ejected in its place. We ignore such possibilities here.

We label the initial state of the probe particle and the atom as $\left| \vec{k}_i; s \right\rangle = |\vec{k}_i\rangle|s\rangle$ and the final state as $\left| \vec{k}_f; n \right\rangle = |\vec{k}_f\rangle|n\rangle$. We assume that the particles of the target are in bound states, so

we may further describe the atom states $|s\rangle$ and $|n\rangle$ by wave functions $\psi_s(\{\vec{r}_i\})$ and $\psi_n(\{\vec{r}_i\})$, which are functions of the of coordinates of the particles in the target, which vanish if any of the particles is far from the origin, and which we assume to be normalized to unity. The probe particle initial state will be given by a plane wave function normalized in a box of volume L^3:

$$|\vec{k}_i\rangle = \frac{1}{L^{3/2}} e^{i\vec{k}_i \cdot \vec{R}} \tag{11.2}$$

and similarly for the final state $|\vec{k}_f\rangle$.

The energy of the system with the probe particle having the wavevector k and the atom being in the unperturbed eigenstate $|n\rangle$ will be:

$$E^0_{k,n} = \frac{\hbar^2 k^2}{2m} + E^0_n = E_k + E^0_n \tag{11.3}$$

Because this system satisfies the requirements for the use of Fermi's Golden Rule (as described in p251b Lecture 10, the transition rate from the initial state to the final state can be computed using it:

$$W_{\vec{k}_f,n} = \frac{2\pi}{\hbar} |\langle \vec{k}_f, n|V|\vec{k}_i, s\rangle|^2 \delta(E_{k_f} + E^0_n - E_{k_i} - E^0_s) \tag{11.4}$$

The total transition rate will be given by the sum of the transition rates over all final probe particle momenta $\vec{k}_f$ and atomic states n. This sum can be rewritten as an integral as follows:

$$\sum_{\vec{k}_f,n} = \frac{L^3}{(2\pi)^3} \sum_n \int d^3 k_f = \frac{L^3}{(2\pi)^3} \sum_n \int_0^\infty k_f^2 \, dk_f \int d\hat{\Omega}_{k_f} \tag{11.5}$$

The total transition rate will therefore be:

$$\boxed{\gamma = \frac{L^3}{(2\pi)^3} \sum_n \int k_f^2 \, dk_f \int d\hat{\Omega}_{k_f} W_{\vec{k}_f,n}} \tag{11.6}$$

We could also break down the transition rate per solid angle. This would give:

$$\gamma_{\hat{\Omega}} = \frac{L^3}{(2\pi)^3} \sum_n \int_0^\infty k_f^2 \, dk_f \, W_{\vec{k}_f,n}. \tag{11.7}$$

Converting the δ-function of energy to a δ-function of wavevector, the integration over k_f becomes trivial, and we find:

$$\gamma_{\hat{\Omega}} = \frac{2\pi}{\hbar} \sum_n |\langle \vec{k}_f, n|V|\vec{k}_i, s\rangle|^2 \frac{L^3}{(2\pi)^3} \frac{m k_f}{\hbar^2} \tag{11.8}$$

where $\vec{k}_f = k_f \hat{\Omega}$ and:

$$k_f = \frac{1}{\hbar} \sqrt{2m \left(\frac{\hbar^2 k^2}{2m} + E_s^0 - E_n^0 \right)} \tag{11.9}$$

The differential scattering cross section will be given by the angular resolved transition rate $\gamma_{\hat{\Omega}}$, divided by the incident flux of particles. As discussed in p251b lecture 10, the flux will be equal to $\frac{\hbar k_i}{m} \frac{1}{L^3}$. Therefore we have:

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{\gamma_{\hat{\Omega}}}{\frac{\hbar k_i}{m} \frac{1}{L^3}} = \frac{2\pi m^2}{\hbar^4} \sum_n |\langle \vec{k}_f, n|V|\vec{k}_i, s\rangle|^2 \frac{L^6}{(2\pi)^3} \frac{k_f}{k_i}} \tag{11.10}$$

We can also restate our equations for an **Energy Resolved Detector**. We want to define an energy resolved differential scattering cross section $\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k_f}}$ such that:

$$\int_{-\infty}^{\infty} dE_{k_f} \frac{\partial^2 \sigma}{\partial \Omega \partial E_{k_f}} = \frac{\partial \sigma}{\partial \Omega} \tag{11.11}$$

By inspection, we can see that the form of this will be:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k_f}} = \frac{2\pi m^2}{\hbar^4} \frac{k_f}{k_i} \frac{L^6}{(2\pi)^3} \sum_n |\langle \vec{k}_f, n|V|\vec{k}_i, s\rangle|^2 \delta(E_{k_f} + E_n^0 - E_{k_i} - E_s^0) \tag{11.12}$$

We can take the quantity k_f outside because the delta function will fix the value such that:

$$k_f = \frac{1}{\hbar} \sqrt{2m E_{k_f}} \qquad \vec{k}_f = k_f \hat{\Omega}$$

We now want to look at the value of the matrix element $\langle \vec{k}_f, n|V|\vec{k}_i, s\rangle$. We can write the general form of the probe-particle interaction as:

$$V = eZ_0 \int \frac{d^3 r}{|\vec{R} - \vec{r}|} \rho(\vec{r}) \qquad \rho(\vec{r}) = \sum_{i=0}^{z} q_i \delta(\vec{r} - \vec{r}_i) \tag{11.13}$$

where $\vec{R}$ is the position of the probe particle, and $\vec{r}$ is a dummy variable. The matrix element can now be written as:

$$\langle \vec{k}_f, n|V|\vec{k}_i, s\rangle = eZ_0 \int d^3 r \langle \vec{k}_f| \frac{1}{|\vec{R} - \vec{r}|} |\vec{k}_i\rangle \langle n|\rho(\vec{r})|s\rangle \tag{11.14}$$

We look at this in pieces;

$$\langle \vec{k}_f| \frac{1}{|\vec{R} - \vec{r}|} |\vec{k}_i\rangle = \frac{1}{L^3} \int d^3 R \frac{e^{i(\vec{k}_i - \vec{k}_f) \cdot \vec{R}}}{|\vec{R} - \vec{r}|} \tag{11.15}$$

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From here we make the variable substitution $\vec{s} = \vec{R} - \vec{r}$ giving:

$$\langle \vec{k}_f | \frac{1}{|\vec{R} - \vec{r}|} | \vec{k}_i \rangle = \frac{1}{L^3} e^{i(\vec{k}_i - \vec{k}_f) \cdot \vec{r}} \int d^3 s \frac{e^{i(\vec{k}_i - \vec{k}_f) \cdot \vec{s}}}{|\vec{s}|} = \frac{e^{i(\vec{k}_i - \vec{k}_f) \cdot \vec{r}}}{L^3} \left(\frac{4\pi}{|\vec{k}_i - \vec{k}_f|^2} \right) \tag{11.16}$$

The integral in equation (11.16) is essentially the Fourier transform of the Coulomb potential; it was evaluated in Physics 251a, as an application of the Born approximation.

We see that it is possible to recast equation (11.14) as a Fourier transform:

$$\langle \vec{k}_f, n | V | \vec{k}_i, s \rangle = \frac{(2\pi)^{3/2}}{L^3} \frac{4\pi}{|\vec{k}_i - \vec{k}_f|^2} Z_0 e \tilde{\rho}_{ns}(\vec{k}_f - \vec{k}_i) \tag{11.17}$$

where $\tilde{\rho}_{ns}(\vec{Q}) = \langle n | \tilde{\rho}(\vec{Q}) | s \rangle$, and the Fourier transform of the density operator can be written as:

$$\boxed{\tilde{\rho}(\vec{Q}) = \int d^3 r \frac{e^{-i\vec{Q} \cdot \vec{r}}}{(2\pi)^{3/2}} \rho(\vec{r}) = \sum_{i=0}^{Z} q_i \frac{e^{-i\vec{Q} \cdot \vec{r}_i}}{(2\pi)^{3/2}}} \tag{11.18}$$

The energy resolved cross section (from equation (11.12)) can now be written as:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k_f}} = \frac{2\pi m^2}{\hbar^4} \frac{k_f}{k_i} \left| \frac{4\pi Z_0 e}{Q^2} \right|^2 f(\vec{Q}, \omega) \tag{11.19}$$

$$f(\vec{Q}, \omega) \equiv \sum_n |\langle n | \tilde{\rho}(\vec{Q}) | s \rangle|^2 \delta(\omega - \omega_{ns}), \tag{11.20}$$

where $\vec{Q} = \vec{k}_f - \vec{k}_i$, $\omega = \frac{1}{\hbar}(E_{k_i} - E_f)$ and $E_{k_f} = \frac{\hbar^2 k_f^2}{2m}$. The function $f(\vec{Q}, \omega)$ has only to do with the properties of a target, and it is generally the quantity one is trying to measure when one does an inelastic scattering experiment.

Elastic scattering

If the target is an atom with an infinitely massive nucleus we can get scattering where the final state is the same as the initial state, since there is no recoil energy and the scattered probe particle has the same energy as the incident particles. Thus we have $|n\rangle = |s\rangle$ and $E_{k_i} = E_{k_f}$. This is called elastic scattering, and we can pick out the contribution from the elastic scattering to $\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k_f}}$ by setting the detector to only detect energies such that $E_{k_f} = E_{k_i}$. Then the cross section we will see can be considered as:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k_f}} \simeq \delta(E_{k_f} - E_{k_i}) \frac{\partial \sigma_{ELASTIC}}{\partial \Omega} \tag{11.21}$$

This cross section will be:

$$\frac{\partial \sigma_{ELASTIC}}{\partial \Omega} = \frac{2\pi}{\hbar^4} m^2 \left| \left(\frac{4\pi Z_0 e}{Q^2} \right) \langle s|\tilde{\rho}(\vec{Q})|s\rangle \right|^2 \tag{11.22}$$

We now define an effective electrostatic potential arising from the charge density in the initial state of the atom as

$$\Phi_S(\vec{r}) = \int \frac{d^3 r'}{|\vec{r} - \vec{r}'|} \langle s|\rho(\vec{r})|s\rangle \tag{11.23}$$

With this we can rewrite the the elastic scattering cross section:

$$\frac{\partial \sigma_{ELASTIC}}{\partial \Omega} = \frac{2\pi m^2}{\hbar^4} Z_0^2 e^2 |\tilde{\Phi}_S(\vec{Q})|^2 \tag{11.24}$$

where $\tilde{\Phi}_S$ is the Fourier transform of Φ_S. This is exactly what we would get from the Born Approximation, as derived in the previous lecture, replacing the potential $V(\vec{r})$ by $Z_0 e \Phi_S(\vec{r})$.

Information obtained from inelastic scattering experiments

The results derived above show that the energy resolved scattering cross section is proportional to a spectral resolution function for the density operator:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E} \propto f(\vec{Q}, \omega),$$

$$f(\vec{Q}, \omega) \equiv \sum_n |\langle n|\tilde{\rho}(\vec{Q})|s\rangle|^2 \delta(\omega - \omega_{ns}),$$

where $\hbar\vec{Q}$ = the momentum transfer and $\hbar\omega$ = the energy transfer to the target. The spectral resolution of the Charge Density operator $f(\vec{Q}, \omega)$ is often written as $S(\vec{Q}, \omega)$ and is called the charge dynamic structure function.

Scattering measurements using a charged particle probe are often done in order to measure the charge dynamic structure function of a selected target. Other types of probes may couple to different operators and measure different quantities. For example, neutrons do not see the electron charge, but do couple to the electron spin. In appropriate circumstances, one can use inelastic neutron scattering to measure the dynamic structure factor for the electron spin density. Neutrons also couple (more strongly) to the positions of various nuclei in a target. Thus, one can also use inelastic scattering to obtain the dynamic structure factor for fluctuations in the positions of the nuclei, say because of lattice vibrations in a solid, or motion of atoms in a liquid. Inelastic light scattering can also be used to obtain information about atomic motions.

For small values of $\vec{Q} \ll \frac{1}{a_H}$, where a_H is the Bohr radius, $\rho(\vec{Q})$ can be expanded:

$$
\begin{aligned}
\rho(\vec{Q}) &= \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{i=0}^{Z} e^{-i\vec{Q}\cdot\vec{r}} q_i \\
&= \frac{1}{(2\pi)^{\frac{3}{2}}} \left(\sum_{i=0}^{Z} q_i - i \sum_{i=0}^{Z} \vec{Q}\cdot\vec{r_i} q_i + \mathcal{O}(\vec{Q}^2) \right) \\
&= \frac{1}{(2\pi)^{\frac{3}{2}}} \left(0 - i\vec{Q}\cdot\vec{d} + \mathcal{O}(\vec{Q}^2) \right)
\end{aligned}
$$

In the last line we have assumed that we are dealing with a neutral atom, so the sum of the charges will go to zero. However, even if we are dealing with an ion or something else where the charge does not go to zero, the sum is just a constant, so its matrix element between any two non-identical states will be zero. Using this expansion, and assuming that $\vec{Q}$ is in the z-direction, then we get for $f(\vec{Q}, \omega)$:

$$
f(\vec{Q}, \omega) \xrightarrow{Q \ll \frac{1}{a_H}} \frac{1}{(2\pi)^3} Q^2 g_{zz}(\omega) \tag{11.25}
$$

where $g_{zz}(\omega)$ is the spectral function of the dipole operator first defined in P251b Lecture 4. These spectral functions not only tell you about optical absorption but can also tell you about the scattering of charged particles if we are in the regime where the momentum transfer is less than one over the Bohr radius.

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12.1 (1) Scattering from a Target with Finite Mass, and (2) The Adiabatic Theorem, Landau-Zener Problem, and Time-Dependence of a 2-Level System beyond Linear Response

12.1.1 Scattering from a Target with Finite Mass

We now want to consider the case where the target is not infinitely massive. We can use Fermi's golden rule and derive a cross section once more. However, now we have to take into account the possible motion of the nucleus of the target, and momentum conservation will play a crucial role in the scattering problem. The energy eigenstates of the target will now be taken to be a product of a plane wave, describing the motion of the center of mass of the target, and a function of the relative coordinates, describing some internal state of the atom.

We are considering Hamiltonians of the form:

$$H = \sum_i \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_i \sum_{j \neq i} V_{ij}(\vec{r}_i - \vec{r}_j) \tag{12.1}$$

For the overall Hamiltonian H, the sum includes the probe particle as well as the particles in the target. For the unperturbed Hamiltonian H_0, we omit the interaction between the probe particle and the target.

Because the interactions V_{ij} depend only on the relative distances of the particles, the overall Hamiltonian is translationally invariant, and it commutes with the total momentum operator, $\vec{P} = \sum_i \vec{p}_i$, so $\vec{P}$ is a constant of the motion. The unperturbed Hamiltonian H_0 conserves separately the momentum of the probe particle and the total momentum of the target. Thus, we may choose the energy eigenstates of the target to be of the form

$$|n\rangle = \frac{1}{L^{\frac{3}{2}}} e^{i\vec{K}_n \cdot \vec{R}} \psi_n(\vec{r}_i - \vec{r}_N), \tag{12.2}$$

where N is the total number of particles in the target, $\vec{r}_i$ is the position of the ith particle, $\hbar\vec{K}_n$ is the total momentum of the state, and $\vec{R} = \sum_i m_i \vec{r}_i / M$ is the center of mass position, with $M = \sum_i m_i$ being the total mass. It is readily seen that the total momentum operator gives zero when acting on the function ψ_n, so the state $|n\rangle$ is indeed an eigenfunction of $\vec{P}$ with momentum $\hbar\vec{K}_n$.

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We now assume an initial state $|\vec{k}_i, s\rangle$ which is a product of a plane wave state of the probe particle, with initial momentum $\vec{k}_s$ and an eigenstate $|s\rangle$ of the target, having the form of (12.2), with momentum $\hbar\vec{K}_s$. The final state $|\vec{k}_f, n\rangle$ is a similar product state with probe particle momentum $\vec{k}_f$ and target state $|n\rangle$. Because the Hamiltonian of the entire system, probe plus target, conserves total momentum, we can only get transitions where $\vec{k}_i + \vec{K}_s = \vec{k}_f + \vec{K}_n$. Indeed, you can check that the matrix element $\langle \vec{k}_f, n|V|\vec{k}_i, s\rangle$, will be zero unless $\vec{k}_i + \vec{K}_s = \vec{k}_f + \vec{K}_n$, where V is here the interaction between probe and target.

These formulas will now allow us to calculate the various scattering cross sections, correct to second order in V, (i.e., the first Born approximation), provided the internal states of the target are known, and provided the integrals can be carried out. To obtain the correct result, one must do careful bookkeeping, keeping track of the various factors of the volume of the system, and making sure to change variables correctly when integrating over δ-functions in energy and momentum. We will not go through this here.

Galilean Invariance

In addition to translational invariance, which guarantees conservation of momentum, the Hamiltonian (12.1) has an important additional property, Galilean invariance, which arises because the kinetic energy is quadratic in the momenta. For the energy eigenstates of the target, Galilean invariance implies that the internal wave functions ψ_n in (12.2) can be chosen independent of the total momentum $\hbar\vec{K}_n$. Moreover, the energy of the state can be written in the form

$$E_n = \frac{\hbar^2 K_n^2}{2M} + E_n^{\text{int}}, \tag{12.3}$$

where the internal energy E_n^{int} is independent of $\vec{K}_n$.

For a system consisting of two particles, Galilean invariance gives a further simplification. In this case we can write the Hamiltonian as

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V_{12}(\vec{\rho}), \tag{12.4}$$

where $\mu \equiv m_1 m_2/M$ is the "reduced mass", $\vec{\rho} \equiv \vec{r}_1 - \vec{r}_2$, and $\vec{p} \equiv \frac{\hbar}{i}\frac{\partial}{\partial\vec{\rho}}$ with the center of mass position $\vec{R}$ held constant. Thus we have reduced a two body problem into a trivial problem for the center of mass motion, and an effective one-body Schrödinger equation for the relative motion. It should be noted that the relative momentum $\vec{p}$ is not simply the difference in the momenta of the two particles, but rather $\vec{p} = (m_2\vec{p}_1 - m_1\vec{p}_2)/M$.

For more on Galilean invariance, see Merzbacher pp. 75-78. For a full discussion of the reduced mass and Galilean invariance in classical as well as quantum mechanics, see Messiah volume I, Chapter IX, section 11, pp. 361 ff.

12.1.2   Time-Dependent Problems where you can't use Linear Response but which can be Solved Exactly.

Here we will discuss some problems in two level systems, specifically resonant excitations and the Landau-Zener problem, where you cannot use lowest-order time-dependent perturbation theory, but where you can solve the problem exactly. These problems have more general significance, which we shall also discuss.

Resonant Excitation

For the two level system, we first consider a Hamiltonian of the form $H = H_0 + V(t)$ where:

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \qquad V(t) = \gamma \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix} \tag{12.5}$$

where γ is real and time-independent. The wavefunction will take on the general form:

$$|\psi(t)\rangle = \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} \tag{12.6}$$

We consider the initial conditions that at $t = 0$: $c_1(0) = 1$, $c_2(0) = 0$. In other words, $|\psi\rangle = |\uparrow\rangle$ it is an eigenvector of σ_z with eigenvalue 1. We want to examine what happens to $|c^2(t)|^2$ for $t > 0$. This was solved on a problem set:

$$|c_2(t)|^2 = \frac{\frac{\gamma^2}{\hbar^2}}{\frac{\gamma^2}{\hbar^2} + \frac{(\omega - \omega_{21})^2}{4}} \sin^2\left(\frac{\Omega t}{2}\right) \tag{12.7}$$

where $\hbar\omega_{21} \equiv E_2 - E_1$ and :

$$\frac{\Omega}{2} = \sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega - \omega_{21})^2}{4}} \tag{12.8}$$

The $\sin^2$ term can be more clearly written as $\frac{1 - \cos(\Omega t)}{2}$. We can see from this that if $\omega = \omega_{21}$, the system will precess from spin up to spin down and back at a frequency $2\gamma/\hbar$. This frequency is called the **Rabi Frequency**. We can rewrite the Hamiltonian in terms of the Pauli spin matrices as:

$$H = \frac{E_2 + E_1}{2} - \frac{\hbar\omega_{21}}{2}\sigma_z + \frac{\gamma}{2}\left[(\sigma_x + i\sigma_y)e^{i\omega t} + (\sigma_x - i\sigma_y)e^{-i\omega t}\right] \tag{12.9}$$

The second term can come from a dc magnetic field $\vec{B}$ in the $\hat{z}$ direction and the third from a rotating ac $\vec{B}$ in the x-y plane. We can define $\vec{P}$, the polarization in the "Rotating Frame", as:

$$P_z = \langle\sigma_z\rangle_t \qquad P_x + iP_y = [\langle\sigma_x\rangle + i\langle\sigma_y\rangle]\, e^{i\omega t} \tag{12.10}$$

In the rotating frame, the equation of motion for the polarization will be:

$$\frac{d\vec{P}}{dt} = -\vec{\Omega} \times \vec{P} \qquad \begin{array}{c} \Omega_z = \omega_{21} - \omega\,, \qquad \Omega_y = 0\,, \\ \Omega_x = -\frac{2\gamma}{\hbar}\,. \end{array} \tag{12.11}$$

Ω is independent of time. This gives a rotation of $\vec{P}$ about some vector in the x-z plane of the rotating frame. If you are on resonance, then rotation is about the x-axis and you just get straight spin-up, spin-down precession.

The equation of motion in the rotating frame is equivalent to an effective Hamiltonian

$$H_{\text{eff}} = -\frac{\hbar}{2}(\Omega_z \sigma_z + \Omega_x \sigma_x). \tag{12.12}$$

Landau-Zener Problem and the Adiabatic Theorem.

We now consider a time-dependent Hamiltonian of the form:

$$H(t) = \alpha t \sigma_z + \beta \sigma_x \tag{12.13}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{12.14}$$

The coefficients α and β are independent of time, and could be either positive or negative. The energy eigenvalues of this at any instant of time t are:

$$E^{>}(t) = \sqrt{\beta^2 + (\alpha t)^2} \tag{12.15}$$
$$E^{<}(t) = -\sqrt{\beta^2 + (\alpha t)^2} \tag{12.16}$$

Suppose that in the limit $t = -\infty$, the system is in an pure state with $\sigma_z = 1$, which is to say that it is in an eigenstate of the the Hamiltonian H in this limit. What will be the state of the system for $t \to +\infty$? The important dimensionless parameter in this problem is

$$\Gamma \equiv \frac{\beta^2}{2\hbar|\alpha|}, \tag{12.17}$$

which is roughly the product of the "passage time" $\tau \approx |\beta/\alpha|$, during which the magnitude of the field in the z direction is smaller than the field in the x-direction , and the minimum frequency splitting between the eigenvalues of $H(t)$, which is equal to $2|\beta|/\hbar$.

In the limit where Γ is very small, the Hamiltonian describes a sudden switch from a strong field in, say, the z-direction to a strong field in the $-z$-direction. In this case, the spin does not

have any time to reorient itself during the period where there are comparable field strengths along the x and z axes, so the spin will be stuck in its initial state, and we expect that the spin will still be in a state with $\sigma_z = 1$ at $t = \infty$.

By contrast, if Γ is very large, the Hamiltonian $H(t)$ will vary very slowly in time, and it moves very slowly through the region where the field in the z-direction is small compared to the field in the x-direction. In particular, the passage rate $1/\tau$ is very small compared to the minimum frequency difference between the two eigenstates of $H(t)$. Then we expect the spin to evolve continuously and to remain in an eigenstate of $H(t)$ at all times. This is the content of the "Adiabatic Theorem" , which we mentioned earlier in the course, but did not prove except in the case of a perturbation which was assumed to be weak as well as slowly varying. Thus, in this slow limit a spin which was initially in a state $\sigma_z = 1$ at $t = -\infty$ will wind up, with 100% probability, in the state $\sigma_z = -1$ at $t = \infty$, and vice versa.

The analytic Landau-Zener solution to the problem we have just posed demonstrates the validity of the Adiabatic theorem for the case at hand, and also gives insight into when it must be true more generally. Moreover, it gives a quantitative answer for the probability that the spin does not reverse in the intermediate case, where Γ is neither 0 nor ∞.

The answer for the probability *not* to reverse the spin is given by:

$$P_{LZ} \equiv P_{\text{no-reverse}} = e^{-2\pi\Gamma}. \tag{12.18}$$

This goes to unity for small Γ, but approaches zero exponentially fast for large Γ (slow passage). The high probability of spin reversal, for large Γ means that a spin initially in the lower energy state *remains* in the lower energy state at $t = \infty$ and vice versa. **Note:** Since the normal behavior in the adiabatic limit is for the spin to reverse its direction, it is customary to say that the spin has made a "transition" when it does not reverse its spin, and so P_{LZ} is often referred to as the Landau-Zener transition probability. In the Landau-Zener problem just described, if the spin was originally in its ground state, and it does not make a transition, then it will still be in its ground state at $t = \infty$.

A derivation of the Landau-Zener formula is given in a Handout, posted on the class web site, and will not be repeated here.

We note that this formula also has important applications in **spin resonance experiments**, where the Hamiltonian has a high frequency component as well as a dc or slowly varying component. Consider a system where there is an ac field, of constant amplitude and frequency ω, and we slowly vary the magnitude of the dc field B_z. Suppose that the resonance frequency ω_{21} is initially well below the ac frequency ω, and the spin is in its ground state, aligned with the dc magnetic field. Now we ramp up the dc field linearly in time, so that the resonance frequency

passes through the value of ω, and then becomes larger than ω. We assume that the ac field is small compared to the dc field at all times, and is small compared to the detuning of the field from resonance in the initial and final states. What will be the final state of the spin?

If we transform to the frame of reference rotating at the frequency ω, we see the ac field becomes a time independent field in, say, the x-direction while the z-component of the field, proportional to $\omega - \omega_{21}$, varies slowly in time and changes its sign. Thus we have mapped this resonance problem onto the Landau-Zener problem. If the passage is slow, so that the passage rate is small compared to the Rabi frequency arising from the ac field (Γ large), then the z-component of the spin will almost certainly be reversed. On the other hand, if the passage is fast(Γ small), the spin will not be reversed. As before, the Landau-Zener transition probability P_{LZ} is the probability that the spin will not be reversed.

Now, however, for the case of spin resonance, the energy in the dc field is proportional to $B_z \sigma_z$, not to $(\omega_{21} - \omega)\sigma_z$, and B_z does not change sign during the sweep. Thus in contrast to the Landau-Zener problem discussed earlier, in the resonance problem the case of slow passage, where the spin changes direction, means that the spin has passed from a low-energy state to a high energy state. This can be very important if one wants to invert a population of spins. Note that one can equally well perform the experiment by keeping the dc field fixed and sweeping the ac frequency through the resonance. Also, the technique can be used to invert a population of spins that are in slightly different environments, so they experience slightly different magnetic fields. Then, it is not possible to choose the ac frequency to be exactly on resonance with all of the spins at once, and if the strength of the available ac source is such that the Rabi frequency is small compared to the spread in resonance frequencies, if would not be possible to turn over all the spins at once with a square "pi-pulse" of fixed frequency. However, if one slowly sweeps the field or frequencies through the resonance range, one can wind up with all the spins inverted.

Note: In the resonance literature, the case of large Γ, used for inversion of the spin population, which we refer to above as "slow passage", is often referred to as "adiabatic fast passage". This is because the passage rate, while slow compared to the Rabi frequency, is supposed to be fast compared to the rate of relaxation rate the spin caused by interactions with the environment.

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13.1   Harmonic Oscillators: 1 Oscillator, 2 Oscillators, ∞ Oscillators

We begin by examining 1 harmonic oscillator, a problem we will solve using raising and lowering operators[1]. We will then consider some problems involving two harmonic oscillators, including applications to a charged particle in a uniform magnetic field. After that, we shall use what we have learned in dealing with collections of harmonic oscillators to quantize the electromagnetic field: a problem with an infinite number of independent oscillators.

The Hamiltonian for a single 1 dimensional harmonic oscillator is:

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2 \tag{13.1}$$

The classical solution for the equation of motion for a particle in such a potential would be harmonic motion with a frequency of:

$$\omega_0 = \sqrt{\frac{k}{m}} \tag{13.2}$$

The Hamiltonian can be rewritten in terms of non-hermitian raising ($a^\dagger$) and lowering (a) operators (the nomenclature will become clear soon):

$$a = \sqrt{\frac{m\omega_0}{2\hbar}}\left(x + \frac{ip}{m\omega_0}\right) \qquad a^\dagger = \sqrt{\frac{m\omega_0}{2\hbar}}\left(x - \frac{ip}{m\omega_0}\right) \tag{13.3}$$

This definition allows for the x and p operators to be written in terms of the raising and lowering operators:

$$x = \sqrt{\frac{2\hbar}{m\omega_0}}\left(\frac{a + a^\dagger}{2}\right) \qquad p = \sqrt{2\hbar m\omega_0}\left(\frac{a - a^\dagger}{2i}\right) \tag{13.4}$$

The commutation relation for x and p: $[x, p] = i\hbar$ leads to the commutation relation for the raising and lowering operators:

$$\left[a, a^\dagger\right] = 1 \tag{13.5}$$

---

[1]The terms raising and lowering operators are used interchangeably with creation and annihilation operators respectively

This very simple commutation relation is a large motivation for the definitions of a and $a^\dagger$ given above. With the aid of this commutation relation, the Hamiltonian can be rewritten in terms of the raising and lowering operators as:

$$\boxed{\mathcal{H} = \frac{\hbar\omega_0}{2}(a^\dagger a + a a^\dagger) = \hbar\omega_0(a^\dagger a + \frac{1}{2})}$$
(13.6)

It is convenient to define the operator

$$N \equiv a^\dagger a \,.$$
(13.7)

Some helpful commutation relations are:

$$[a, N] = a a^\dagger a - a^\dagger a a = \left[a, a^\dagger\right] a = a$$
(13.8)

$$\left[a^\dagger, N\right] = -a^\dagger$$
(13.9)

Let $|n\rangle$ be an eigenstate of N with eigenvalue n:

$$N |n\rangle = n |n\rangle \,.$$
(13.10)

$N = a^\dagger a$ is a hermitian operator, since $(AB)^\dagger = B^\dagger A^\dagger$, so n will be real. We can now ask, what are the properties of the state $a|n\rangle$? We operate with N on the state $a|n\rangle$:

$$Na |n\rangle = aN |n\rangle - a |n\rangle = (n-1)(a |n\rangle)$$
(13.11)

Therefore we see that either the state $a|n\rangle$ is also an eigenstate of the operator N with eigenvalue $(n-1)$, or $a|n\rangle = 0$. To see which of these possibilities applies, we compute

$$|a |n\rangle|^2 = \langle n|a^\dagger a|n\rangle = n \langle n|n\rangle \,.$$
(13.12)

Thus we see that $a|n\rangle = 0$ only if $n = 0$. We can also see that $n \geq 0$ since a vector cannot have a negative norm. If $n \neq 0$ we must have the other option, $a|n\rangle$ is an eigenvector of N. The decrease in the value of the eigenvalue is what gives a the name of "lowering operator". If $|n\rangle$ is normalized then $\langle n|n\rangle = 1$. We can define the normalized state $|n-1\rangle$ by:

$$|n-1\rangle = \frac{a |n\rangle}{\sqrt{n}}$$
(13.13)

With this definition we can see that $\langle n-1|n-1\rangle = 1$. So $|n-1\rangle$ will be a normalized eigenstate of N with eigenvalue $n-1$. Similarly, we can look at $a^\dagger |n\rangle$ and see that:

$$N(a^\dagger |n\rangle) = (n+1)a^\dagger |n\rangle$$
(13.14)

The behavior of the two operators when acting on the base state $|n\rangle$ is therefore:

$$a\,|n\rangle \;=\; \sqrt{n}\,|n-1\rangle \tag{13.15}$$

$$a^\dagger\,|n\rangle \;=\; \sqrt{n+1}\,|n+1\rangle \tag{13.16}$$

Now since we know that either $a\,|n\rangle$ is either zero or is an eigenstate of N with eigenvalue $n-1$, and since we know that we are not allowed to have a state with $n < 0$, the only way to avoid this contradiction the following: if we keep operating on a state $|n\rangle$ with the lowering operator it must be the case that at some point $a\,|n\rangle = 0$, i.e., $n = 0$, for some $|n\rangle$ in the sequence. We also see that the only allowed values of n are integers ≥ 0. The state $|0\rangle$ is clearly the ground state of the Hamiltonian H. With these definitions we can now use the raising operator repeatedly to build an energy eigenstate for any integer n, starting from the ground state:

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}\,|0\rangle \tag{13.17}$$

We can now define matrix elements of the operators between different basis states:

$$\langle n'|a|n\rangle = \delta_{n,n'+1}\sqrt{n'+1} \tag{13.18}$$

$$\langle n|a^\dagger|n'\rangle = \delta_{n,n'+1}\sqrt{n'+1} \tag{13.19}$$

We can also obtain the matrix elements for x and p using the raising and lowering operators:

$$\langle n'|x|n\rangle = \sqrt{\frac{\hbar}{2m\omega_0}}\left(\delta_{n',n+1}\sqrt{n+1} + \delta_{n,n'+1}\sqrt{n'+1}\right) \tag{13.20}$$

$$\langle n'|p|n\rangle = i\sqrt{\frac{\hbar m\omega_0}{2}}\left(\delta_{n',n+1}\sqrt{n+1} - \delta_{n,n'+1}\sqrt{n'+1}\right) \tag{13.21}$$

This shows that x and p connect the level n with levels $n \pm 1$. We can similarly work out the matrix elements for x^2:

$$\begin{aligned}
\langle n'|x^2|n\rangle &= \frac{\hbar}{2m\omega_0}\langle n'|a^2 + aa^\dagger + a^\dagger a + a^{\dagger 2}|n\rangle \tag{13.22}\\
&= \frac{\hbar}{2m\omega_0}\left(\delta_{nn'}(2n+1) + \delta_{n',n+2}\sqrt{(n+1)(n+2)} + \delta_{n,n'+2}\sqrt{(n'+1)(n'+2)}\right)
\end{aligned}$$

So it is possible to calculate the matrix elements, expectation values of various terms (ie x^3, p^4, x^5 and so on) between eigenstates of the harmonic oscillator. It is often not necessary to have an explicit form for the wavefunctions. It is, however, also possible to use this operator method to determine the position space wavefunctions of the harmonic oscillator Hamiltonian. The wavefunctions $\psi_n(x) : \langle x|n\rangle$ can be obtained by using the fact that $a\,|0\rangle = 0$.

$$a\,|0\rangle = \left(x + \frac{ip}{m\omega_0}\right)|0\rangle = 0 \tag{13.23}$$

In the position representation (using $p = -i\frac{\partial}{\partial x}$) this translates into the differential equation:

$$\frac{\partial \psi}{\partial x} = -\frac{m\omega_0}{\hbar} x\psi(x) \tag{13.24}$$

$$\ln \psi(x) = -\frac{1}{2}\frac{m\omega_0}{\hbar}x^2 + \text{constant} \tag{13.25}$$

$$\psi(x) = \kappa e^{\frac{-x^2}{4\sigma^2}}, \tag{13.26}$$

where the constant σ has been chosen $(2\sigma^2 = \frac{\hbar}{m\omega_0})$ so that $|\psi(x)|^2$ will have standard Gaussian form with variance σ. The constant κ should be chosen as $\kappa = (2\pi\sigma^2)^{-1/4}$, if we want the wave function to be properly normalized. So we have found a unique ground state for the one-dimensional Harmonic oscillator. We could now build up any of the other states by operating on the ground state with the creation operator, obtaining the state $|n\rangle$ by the manner described in equation 13.17. Taking repeated derivatives on the ground state will lead to wave functions which are products of the Gaussian ground-state wavefunction with an nth order polynomial, for the $|n\rangle$ state. These are the Hermite Polynomials.

13.1.1 Coherent States

Coherent states are not eigenstates of the harmonic oscillator hamiltonian, but play a special role in HO physics. The definition of the coherent states are right eigenstates of the lowering operator:

$$a\left|\alpha\right\rangle = \alpha\left|\alpha\right\rangle \tag{13.27}$$

Since a is not hermitian, the eigenvalue α need not be real, and the states $|\alpha\rangle$ do not form an orthonormal set. We choose to have the states normalized such that $\langle\alpha|\alpha\rangle = 1$. [We shall eventually choose the phase such that $\langle0|\alpha\rangle > 0$.] Taking the adjoint of equation 13.27 we obtain:

$$\left\langle\alpha\right| a^\dagger = \left\langle\alpha\right| \alpha^* \tag{13.28}$$

Other quantities relating to the coherent states are:

$$\langle\alpha|a|\alpha\rangle = \alpha \qquad \langle\alpha|a^\dagger|\alpha\rangle = \alpha^* \tag{13.29}$$

$$\langle\alpha|x|\alpha\rangle = \sqrt{\frac{2\hbar}{m\omega_0}}\left(\frac{\alpha + \alpha^*}{2}\right) \propto \text{Re}\,(\alpha) \tag{13.30}$$

$$\langle\alpha|p|\alpha\rangle = \sqrt{2\hbar m\omega_0}\left(\frac{\alpha - \alpha^*}{2i}\right) \propto \text{Im}\,(\alpha) \tag{13.31}$$

Addendum: Uniqueness of Harmonic Oscillator Energy States

Our construction for the wave function of the harmonic oscillator ground state showed that it is unique except for a multiplicative constant. Uniqueness of the excited states can be established by use of the lowering operator. For example, suppose there were two orthogonal eigenstates of the number operator N, with eigenvalue $n = 1$, say $|1\rangle$ and $|1'\rangle$. Operating on these states would give two states $|0\rangle$ and $|0'\rangle$ which would be eigenstates of N with $n = 0$ and would be orthogonal to each other, since

$$\langle 0|0'\rangle = \langle 1|a^\dagger a|1'\rangle = \langle 1|1'\rangle = 0.$$

This would contradict the uniqueness of the state $|n = 0\rangle$.

More generally, however, one may show that bound states of a particle in one-dimension dimension are *never* degenerate. This follows from the fact that the differential equation of the time-independent Schrödinger equation has just two linearly independent solutions at energy given energy E, and at least one of them must go to infinity for $x \to \infty$, if E is smaller than the value of the potential $V(x)$ for $x \to \infty$.

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14.1 Coherent States of the Harmonic Oscillator (Continued)

Coherent states were defined (251b Lecture 13) as right eigenstates of the harmonic oscillator lowering operator.

$$a \left| \alpha \right\rangle = \alpha \left| \alpha \right\rangle \tag{14.1}$$

We now proceed to show that these states (1) Exist, (2) Are Unique, for any complex number α, and (3) Can be given explicit wavefunction form. Using the definition of the lowering operator from the previous lecture equation (14.1) can be rewritten:

$$\sqrt{\frac{m\omega_0}{2\hbar}} \left(x + i \frac{p}{m\omega_0} \right) \psi_\alpha(x) = \alpha \psi_\alpha(x) \tag{14.2}$$

In position space this turns into the following differential equation:

$$\frac{1}{\psi} \frac{d\psi}{dx} = -\frac{m\omega_0}{\hbar} x + \alpha \sqrt{\frac{2m\omega_0}{\hbar}} \tag{14.3}$$

The solution to this follows:

$$\ln \psi = -\frac{m\omega_0}{\hbar} \frac{x^2}{2} + \alpha x \sqrt{\frac{2m\omega_0}{\hbar}} + \text{const} \tag{14.4}$$

When we exponentiate both sides and complete the square we will arrive at the form of the wavefunction, which after normalization ($\langle \alpha | \alpha \rangle = 1$) and choice of phase such that $\psi(x = 0) > 0$, will look like:

$$\langle x | \alpha \rangle \equiv \psi(x) = \left(\frac{1}{2\pi\sigma^2} \right)^{1/4} \exp \left(-\frac{(x - \langle x \rangle)^2}{4\sigma^2} + \frac{i\langle p_x \rangle x}{\hbar} \right) \tag{14.5}$$

This is a gaussian centered around $x = \langle x \rangle$, multiplied by a phase factor which varies linearly with x. If we fourier transformed it, it would remain a gaussian and would then also be displaced in momentum space. The variance of the square of the wavefunction in position space is given by: $\sigma^2 = \frac{\hbar}{2m\omega_0}$. The expectation values as determined in p251b Lecture 13 are:

$$\langle \alpha | x | \alpha \rangle = \sqrt{\frac{2\hbar}{m\omega_0}} \left(\frac{\alpha + \alpha^*}{2} \right) \tag{14.6}$$

$$\langle \alpha | p | \alpha \rangle = \sqrt{2\hbar m\omega_0} \left(\frac{\alpha - \alpha^*}{2i} \right) \tag{14.7}$$

1

What is the overlap between two coherent states? The inner product will be:

$$\langle \beta | \alpha \rangle \;=\; \left(\frac{1}{2\pi\sigma^2} \right)^{1/2} \int dx \; e^{i[\langle p_x \rangle_\alpha - \langle p_x \rangle_\beta]\frac{x}{\hbar}} \, e^{\frac{-(x-\langle x \rangle_\alpha)^2 - (x - \langle x \rangle_\beta)^2}{4\sigma^2}} \tag{14.8}$$

$$=\; e^{-\frac{|\alpha|^2}{2} - \frac{|\beta|^2}{2} + \alpha\beta^*} \tag{14.9}$$

$$|\langle \beta | \alpha \rangle|^2 \;=\; e^{-|\alpha|^2 - |\beta|^2 + \alpha\beta^* + \beta\alpha^*} \tag{14.10}$$

$$=\; e^{-|\alpha - \beta|^2} \tag{14.11}$$

Going from equation (14.8) to (14.9) requires some integration. Eq. (14.11) makes sense. If $\alpha = \beta$ in which case the overlap squared is one. If α and β are far apart then the overlap falls off rapidly (as a Gaussian). We see that this is an overcomplete set, that is; the coherent states are not orthogonal to each other. Any function of x can be written as a combination of these states, but there are many ways to do it. The completeness can be stated by:

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\alpha_{real}\, d\alpha_{im}}{\pi} |\alpha\rangle\langle\alpha| = \mathcal{I} \; [\equiv (\delta(x - x')) \,\text{in position space}] \tag{14.12}$$

The proof is left as an exercise. It is also claimed that the coherent states can also be expressed as:

$$|\alpha\rangle = e^{\alpha a^\dagger} |0\rangle \, e^{-\frac{|\alpha|^2}{2}} \tag{14.13}$$

This can be proven by taking a Taylor expansion of the operator $e^{\alpha a^\dagger}$, which leads to an expansion of the ket vector in terms of the energy eigenstates $|n\rangle$. It is then easy to demonstrate that $a|\alpha\rangle = \alpha|\alpha\rangle$, $\langle\alpha|\alpha\rangle = 1$ and $\langle 0|\alpha\rangle > 0$.

14.2   2 Degenerate Harmonic Oscillators

We are basically talking about a 2 dimensional degenerate harmonic oscillator with circular symmetry. The Hamiltonian will be:

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2}m\omega_0^2(x^2 + y^2) \tag{14.14}$$

The only nonzero commutators in the above Hamiltonian are $[x, p_x] = [y, p_y] = i\hbar$. As we did with the single harmonic oscillator, we introduce raising and lowering operators for each oscillator:

$$a_x \;=\; \sqrt{\frac{m\omega_0}{2\hbar}} \left(x + i\frac{p_x}{m\omega_0} \right) \tag{14.15}$$

$$a_y \;=\; \sqrt{\frac{m\omega_0}{2\hbar}} \left(y + i\frac{p_y}{m\omega_0} \right) \tag{14.16}$$

The commutation relations are $\left[a_x, a_x^\dagger\right] = \left[a_y, a_y^\dagger\right] = 1$ and $[a_x, a_y] = \left[a_x, a_y^\dagger\right] = 0$. The Hamiltonian can be rewritten in term of the raising and lowering operators:

$$\boxed{H = \hbar\omega_0(a_x^\dagger a_x + a_y^\dagger a_y + 1)} \tag{14.17}$$

The energy levels for this Hamiltonian are: $E_{n_x, n_y} = \hbar\omega_0(n_x + n_y + 1)$. This can also be written as $E_n = \hbar\omega_0(n + 1)$ with $n = n_x + n_y = 0, 1, 2 \ldots etc.$

The method presented above is not the only way to quantize this system. We could have used any pair of operators b_1, b_2 related to a_1, a_2 by a unitary transformation. In other words, let

$$b_1 = U_{11}a_x + U_{12}a_y \tag{14.18}$$
$$b_2 = U_{21}a_x + U_{22}a_y \tag{14.19}$$

where U is an arbitrary unitary matrix. These new operators will have the same commutation relations as before. Using the convention of summation over repeated indices, we find:

$$[b_i, b_j^\dagger] = [U_{ik}a_k, U_{jk'}^* a_{k'}^\dagger] = U_{ik}U_{jk}^* = \delta_{ij} \tag{14.20}$$
$$[b_i, b_j] = [b_i^\dagger, b_j^\dagger] = 0 \tag{14.21}$$

Furthermore the Hamiltonian will also have the same form as before, since:

$$b_1^\dagger b_1 + b_2^\dagger b_2 = (U_{ik}^* a_k^\dagger)(U_{ik'} a_{k'}) = \delta_{kk'} a_k^\dagger a_{k'} = a_x^\dagger a_x + a_y^\dagger a_y \tag{14.22}$$

$$H = \hbar\omega_0(b_1^\dagger b_1 + b_2^\dagger b_2 + 1) \tag{14.23}$$

Since the b operators have the same commutation relations as the a operators, there will be the same overall energy eigenvalues of the Hamiltonian, however the degenerate states (with n_1, n_2 now corresponding to the states created and annihilated by b_1, b_2) will be linear superpositions of the original untransformed states.

One obvious transformation is to choose

$$b_1 = a_x \cos\theta + a_y \sin\theta \equiv a_{x'} \tag{14.24}$$
$$b_2 = -a_x \sin\theta + a_y \cos\theta \equiv a_{y'} \tag{14.25}$$

This corresponds to a rotation of coordinates by an angle θ, so that the new operators describe degrees of freedom quantized in directions

$$x' = x\cos\theta + y\sin\theta \tag{14.26}$$
$$y' = -x\sin\theta + y\cos\theta \tag{14.27}$$

.

Another, very useful choice, is the complex unitary transformation, defining operators by:

$$b_1 = \frac{a_x + ia_y}{\sqrt{2}} \qquad b_2 = \frac{a_x - ia_y}{\sqrt{2}} \tag{14.28}$$

These correspond to excitations with definite angular momentum. To see this explicitly, invert the transformations and express a_x, a_y in terms of b_1, b_2, and then express x, y, p_x, p_y in terms of $b_i, b_i^\dagger$. The results may be summarized as

$$x + iy = \sqrt{\frac{\hbar}{m\omega_0}}(b_1 + b_2^\dagger) \qquad x - iy = \sqrt{\frac{\hbar}{m\omega_0}}(b_1^\dagger + b_2) \tag{14.29}$$

$$p_x + ip_y = \sqrt{\hbar m\omega_0}\left(\frac{b_1 - b_2^\dagger}{i}\right) \qquad p_x - ip_y = \sqrt{\hbar m\omega_0}\left(\frac{b_2 - b_1^\dagger}{i}\right) \tag{14.30}$$

Using these relations, one can write the angular momentum operator $L_z = xp_y - yp_x$ in terms of the redefined operators b_1 and b_2. The final result is

$$L_z = \hbar(b_2^\dagger b_2 - b_1^\dagger b_1). \tag{14.31}$$

15.1 Charged Particle in a Circularly Symmetric Parabolic Potential and Uniform Magnetic Field

We consider a charged particle moving in two dimensions (i.e., confined to the x-y plane) and subject to a circular-symmetric two-dimensional harmonic potential. We want to explore what happens when we add a uniform magnetic field parallel to to the z direction. This discussion will have applications to (1) Ions in a trap, and (2) The Quantum Hall Effect.

The Hamiltonian for this system, following the discussion of p251a Lecture 27, will be:

$$H = \frac{\left(\vec{p} - \frac{q\vec{A}(\vec{r})}{c}\right)^2}{2m} + \frac{k_0(x^2 + y^2)}{2} \tag{15.1}$$

We consider this with $k_0 = m\omega_0^2 \geq 0, q > 0$ and $B_z = B_0 > 0$. (The situation with $k_0 = 0$ corresponds to the free particle in a uniform magnetic field.) In order to best take advantage of the circular symmetry, we choose to work in the circularly symmetric gauge, where

$$\vec{A} = \frac{1}{2}B_0(-y\hat{x} + x\hat{y}), \tag{15.2}$$

which will give back $\nabla \times A = B_0\hat{z}$. The Hamiltonian in this gauge can be written as:

$$H = \frac{p^2}{2m} + \left(\frac{k_0}{2} + \frac{q^2 B_0^2}{8mc^2}\right)(x^2 + y^2) - \frac{1}{2}\frac{qB_0}{mc}L_z \tag{15.3}$$

The middle term still looks like an oscillator potential, just with some more complicated spring constant we can call $\tilde{K}$. If we now define the following two frequencies:

$$\tilde{K} = \left(\frac{q^2 B_0^2}{4mc^2} + k_0\right) \equiv m\Omega^2 \tag{15.4}$$

$$\omega_c \equiv \frac{qB_0}{mc} \tag{15.5}$$

We can proceed to rewrite the Hamiltonian in terms of the circularly polarized lowering operators b_1 and b_2 and their adjoints, as discussed in 251b Lecture 14.

$$H = \hbar\Omega(b_1^\dagger b_1 + b_2^\dagger b_2 + 1) - \frac{\hbar\omega_c}{2}(b_2^\dagger b_2 - b_1^\dagger b_1) \tag{15.6}$$

The eigenvalues of this Hamiltonian will be:

$$E_{n_1 n_2} = \hbar\omega_1(n_1 + \frac{1}{2}) + \hbar\omega_2(n_2 + \frac{1}{2}), \tag{15.7}$$

where n_1 and n_2 are integers ≥ 0, and the new frequencies ω_1 and ω_2 are given by:

$$\omega_1 = \Omega + \frac{\omega_c}{2} \qquad \omega_2 = \Omega - \frac{\omega_c}{2} \tag{15.8}$$

So we still have two independent harmonic oscillators, one corresponding to the motion in the clockwise direction, one corresponding to the counterclockwise direction. The effect of the magnetic field is to split the frequencies which were degenerate for $B = 0$.

The operators x, y, p_x and p_y are linear combinations of the raising and lowering operators, as discussed in Lecture 14.

In 3 dimensions, we can add the term $\frac{p_z^2}{2m}$ to the Hamiltonian. It can be quickly confirmed that $[p_z, H] = 0$, therefore the x-y and z solutions are separable. The eigenstates are then products of a plane wave function in z, and the previously derived solution for motion in the x-y plane:

$$|k_z, n_1, n_2\rangle = \frac{1}{\sqrt{L_z}} e^{ik_z z} |n_1, n_2\rangle. \tag{15.9}$$

The energy is just the sum $E_{n_1 n_2} + (\hbar^2 k_z^2 / 2m)$.

15.1.1   *Free* electrons in a magnetic field

If $\omega_0 = 0$ we have the case of free electrons with:

$$\Omega = \frac{\omega_c}{2} \qquad \omega_1 = \omega_c \qquad \omega_2 = 0 \tag{15.10}$$

The Hamiltonian for the motion in the x-y plane then becomes:

$$H = \hbar\omega_c(n_1 + \frac{1}{2}) \tag{15.11}$$

We see that the Hamiltonian is independent of n_2 and therefore the energy levels are infinitely degenerate. These are known as **Landau levels**. States of different n_2 are all orthogonal to each other, but for any given n_1 they all correspond to the same energy level. In a finite system, there is a finite number of degeneracies. In a homework assignment it is found that states of increasing n_2 are distributed further out from the origin, and you will find the number of degenerate states contained in a circle of finite area.

We also want to explore what occurs for the case of $0 < \omega_0 << \omega_c$. In this case we can expand ω_1 and ω_2. Writing out the value for Ω in each case we get:

$$\omega_2 = \left(\omega_0^2 + \frac{\omega_c^2}{4}\right)^{\frac{1}{2}} - \frac{\omega_c}{2} = \frac{\omega_0^2}{\omega_c} + \mathcal{O}\left(\frac{\omega_0^4}{\omega_c^3}\right), \quad \omega_1 = \omega_c + \mathcal{O}\left(\frac{\omega_0^2}{\omega_c}\right) \tag{15.12}$$

Now ω_2 is slightly larger than zero, and is denoted the "magnetron" frequency, which describes the guiding center motion. ω_1 is still approximately equal to ω_c This is similar to a classical analysis of a charged particle in combined electric and magnetic fields. In a uniform magnetic field a classical particle will execute a circular motion about some point, If there is, in addition, a uniform electric field perpendicular to the magnetic field. the center of that cyclotron orbit will drift with a velocity given by:

$$\vec{v}_{drift} = \frac{\vec{E} \times \vec{B}}{|B|^2} c \tag{15.13}$$

If the electric field is not uniform, but is derived from a potential $V(\vec{r})$ that varies slowly in space, the center of the cyclotron orbit will move at the drift velocity along an equipotential curve of V. If V is a circularly symmetric parabolic potential, the guiding center will move around a circular orbit with the magnetron frequency computed above.

15.2   1-D Harmonic Oscillator with Forcing Terms

We now consider an oscillator with time dependent forcing terms. We add two terms to the Hamiltonian for the one dimensional oscillator.

$$
\begin{aligned}
H &= \frac{p^2}{2m} + \frac{kx^2}{2} - F(t)x - G(t)p \tag{15.14} \\
&= \hbar\omega_0 \left(a^\dagger a + \frac{1}{2} \right) + f(t)a + f^*(t)a^\dagger \tag{15.15}
\end{aligned}
$$

The Hamiltonian was rewritten by using the forms of x and p in terms of $a, a^\dagger$ from p251b lecture 13 and by defining:

$$f(t) = -\sqrt{\frac{\hbar}{2m\omega_0}} F(t) + i\sqrt{\frac{\hbar m\omega_0}{2}} G(t) \tag{15.16}$$

It is useful to work in the Heisenberg representation for this problem. The equations of motion for the Heisenberg operators $\bar{x}, \bar{p}$ will be:

$$
\begin{aligned}
\frac{d\bar{x}}{dt} &= \frac{1}{i\hbar} \left[\bar{x}, \bar{H} \right] = \frac{\bar{p}}{m} - G \tag{15.17} \\
\frac{d\bar{p}}{dt} &= \frac{1}{i\hbar} \left[\bar{p}, \bar{H} \right] = -k\bar{x} + F \tag{15.18}
\end{aligned}
$$

Combining equations (15.17) and (15.18) we can obtain a second order differential equation for $\bar{x}$

$$\frac{d^2\bar{x}}{dt^2} = -\frac{k}{m}\bar{x} + \left(\frac{F}{m} - \frac{dG}{dt}\right) \tag{15.19}$$

This corresponds to a force of $\left(F - m\frac{dG}{dt}\right)$. Instead of solving individually for the equations of motions of the various operators, we can instead calculate the time dependence of the raising and lowering operators $\bar{a}(t), \bar{a}^\dagger(t)$:

$$i\hbar\frac{d\bar{a}(t)}{dt} = \left[\bar{a}, \bar{H}\right] = \hbar\omega_0\bar{a}(t) + f^*(t) \tag{15.20}$$

This can be rewritten as:

$$\frac{d\bar{a}}{dt} + i\omega_0\bar{a} = \frac{1}{i\hbar}f^*(t) \tag{15.21}$$

If $f(t) = 0$ for $t < t_0$ then the solution to this equation is just:

$$\bar{a}(t) = \bar{a}(t_0)\exp(-i\omega_0(t - t_0)) \quad \text{(For } t < t_0\text{)} \tag{15.22}$$

For $t > t_0$ the problem can be solved by using a Green's function.

$$\bar{a}(t) = \bar{a}(t_0)\exp(-i\omega_0(t - t_0)) + \frac{1}{i\hbar}\int_{t_0}^{\infty} G_R(t, t')f^*(t')\,dt \tag{15.23}$$

where the Green's function $G_R(t, t')$ must satisfy:

$$\left(\frac{d}{dt} + i\omega_0\right)G_R(t, t') = \delta(t - t') \tag{15.24}$$

We also want G_R to satisfy the boundary condition that $G_R(t, t') = 0$ for $t < t'$. We can guess a simple such Green function:

$$G_R(t, t') = \Theta(t - t')e^{-i\omega_0(t - t')}, \tag{15.25}$$

where Θ is the step function: $\Theta = 1$ for $t > t'$, and $\Theta = 0$ otherwise.

Therefore we can summarize the motion of the Heisenberg raising and lowering operators as:

$$\boxed{\bar{a}(t) = \bar{a}(t_0)\exp(-i\omega_0(t - t')) + \alpha(t)} \tag{15.26}$$

$$\boxed{\alpha(t) = \frac{1}{i\hbar}\int_{t_0}^{t}\exp(-i\omega_0(t - t'))f^*(t')\,dt} \tag{15.27}$$

To explore the physical significance of this, the most interesting case is to look at what happens if at $t = t_0$ the system is in the ground state of the Harmonic Oscillator, so that in the Schrödinger picture we would have:

$$|\Psi(t_0)\rangle = |0\rangle \qquad a\,|\Psi(t_0)\rangle = 0 \tag{15.28}$$

In the Heisenberg picture this equation will be, at $t = t_0$:

$$\bar{a}(t_0) \left| \bar{\Psi} \right\rangle = 0 \tag{15.29}$$

Then, from Eq. (15.26), we find at time t:

$$\bar{a}(t) \left| \bar{\Psi} \right\rangle = \alpha(t) \left| \bar{\Psi} \right\rangle \tag{15.30}$$

If we transform back from the Heisenberg picture to the Schrödinger picture, we find

$$a \left| \Psi(t) \right\rangle = \alpha(t) \left| \Psi(t) \right\rangle, \tag{15.31}$$

since the unitary transformation preserves eigenvalue and eigenvector relations. This is a coherent state of the harmonic oscillator, as defined in the previous lectures. We can characterize the coherent state by the real and imaginary parts of α or, equivalently, by the expectation values of x or p. For example, if we wanted to calculate the expectation value of x, we would have:

$$\langle x \rangle_t = \frac{\alpha(t) + \alpha(t)^*}{2} \left(\frac{2\hbar}{m\omega_0} \right)^{\frac{1}{2}} \tag{15.32}$$

Using the definition of α from equation (15.27), also taking into account the definition of $f(t)$ from equation (15.16), we see that $\alpha(t) \propto \hbar^{-1/2}$. This shows that $\langle x \rangle_t$ is independent of $\hbar$. Indeed, it is the same as what one would calculate for a classical harmonic oscillator with the given forcing term.

We can think of the coherent states as being as close as you can get to a classical state of the harmonic oscillator in quantum mechanics. We will see that similar states arise in the electromagnetic field.

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16.1   Radiation Field

The first step in our analysis is to specify the "classical" currents and charges. We will quantize the field and see how it responds to the classical currents and charges. Then we will quantize the currents and charges themselves.

16.1.1   Review Classical E+M

We begin with Maxwell's equations:

$$\nabla \cdot \vec{E} = 4\pi\rho \qquad \nabla \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t} \tag{16.1}$$

$$\nabla \cdot \vec{B} = 0 \qquad \nabla \times \vec{B} = \frac{1}{c}\frac{\partial \vec{E}}{\partial t} + \frac{4\pi}{c}\vec{j} \tag{16.2}$$

The fields can be written in terms of scalar ϕ and vector $\vec{A}$ potentials as follows:

$$\vec{B} = \nabla \times \vec{A} \qquad \vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} - \nabla\phi \tag{16.3}$$

The curl equation for $\vec{B}$ and the divergence equation for $\vec{E}$ require the conservation of charge:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{j} \tag{16.4}$$

We choose to write the electric field as combination of the a longitudinal component and a transverse component:

$$\vec{E} = \vec{E}_{long} + \vec{E}_{trans} \tag{16.5}$$

The definitions of these components can be stated as:

$$\nabla \cdot \vec{E}_{trans} = 0\,, \qquad \nabla \times \vec{E}_{long} = 0 \tag{16.6}$$

If the fields do not go to zero at infinity, then the division into transverse and longitudinal parts would not be unique. For example, you could add an arbitrary constant vector to one part and subtract it from the other, without affecting the sum, and without affecting the validity of (16.6). However, if $\vec{E} \to 0$ for $r \to \infty$, we may impose the condition that $\vec{E}_{long} \to 0$ for $r \to \infty$, in which case the two fields $\vec{E}_{trans}, \vec{E}_{long}$ are uniquely determined by the total field.

If the field $\vec{E}$ is square integrable, we can construct the longitudinal and transverse parts by fourier transform. In particular, we can show that any vector field $\vec{F}(\vec{r})$ that is square integrable can be broken up into longitudinal and transverse parts by taking the Fourier transform so that

$$\vec{F}(\vec{r}) = (2\pi)^{-3/2} \int d^3\vec{k}\, \vec{F}(\vec{k}) e^{i\vec{k}\cdot\vec{r}}.$$

Then, for each value of $\vec{k}$, write $\vec{F}(\vec{k}) = \vec{F}_{long}(\vec{k}) + \vec{F}_{trans}(\vec{k})$, where the first term contains the component parallel to $\vec{k}$ and the second term the components perpendicular to $\vec{k}$. Then Fourier transform back to position space.

The reason for breaking $\vec{E}$ up this way is that $\vec{E}_{long}(t)$ depends only on what the charge distribution is at that time. $\vec{E}_{trans}$ is not so simple; it depends on the location of the charges and currents at all *previous* times. Thus we shall need to introduce a set of new dynamic variables to describe $\vec{E}_{trans}$, which we will then need to quantize, while $\vec{E}_{long}$ is entirely determined by the location of the charges.

We choose to work in the Coulomb Gauge: having the vector potential satisfy $\nabla \cdot \vec{A} = 0$. The divergence of the electric field equation in Maxwell's equations can then be simply stated in terms of the electric potential:

$$\nabla \cdot \vec{E} = -\nabla^2\phi = 4\pi\rho \qquad (16.7)$$

This is Poisson's equation. If the charge density goes to zero at infinity ($\rho \to 0$ for $r \to \infty$), and if we assume that $\vec{E}_{long} \to 0$ for $r \to \infty$, we can also require that $\phi \to 0$ at $r \to \infty$. Then there will be a unique solution to Poisson's equation:

$$\boxed{\phi(\vec{r}) = \int \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d^3\vec{r}\,'} \qquad (16.8)$$

Now taking the gradient, we arrive at Coulomb's law for a charge distribution.

$$\vec{E}_{long} = -\nabla\phi = \int \frac{\rho(\vec{r}\,')(\vec{r} - \vec{r}\,')}{|\vec{r} - \vec{r}\,'|^3} d^3\vec{r}\,'. \qquad (16.9)$$

This is the longitudinal component of the field. There will also be a transverse component of the field given by:

$$\nabla \cdot \vec{A} = 0 \qquad \vec{E}_{trans} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} \qquad (16.10)$$

We now want to look at the magnetic field. To go back to Maxwell's equations, we are interested in looking at the curl of B.

$$\nabla \times \vec{B} = \nabla \times (\nabla \times \vec{A}) = -\nabla^2\vec{A} + \nabla(\nabla \cdot \vec{A}) = -\nabla^2\vec{A} \qquad (16.11)$$

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Now using Maxwell's equations (16.2) we arrive at a wave equation with a source term $\vec{s}$ for the vector potential:

$$-\nabla^2 \vec{A} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{A} = \left(\frac{4\pi}{c}\vec{j} + \frac{1}{c}\frac{\partial \vec{E}_{long}}{\partial t}\right) \equiv \vec{s}(\vec{r},t) \tag{16.12}$$

The curl and divergence of the source term will be:

$$\nabla \times \vec{s} = \frac{4\pi}{c}\nabla \times \vec{j} \qquad \nabla \cdot \vec{s} = \left(\frac{4\pi}{c}\nabla \cdot \vec{j} + \frac{\partial}{\partial t}\frac{4\pi\rho}{c}\right) = 0 \tag{16.13}$$

By the conservation of charge, $\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0$, we see that the divergence of the source term is zero. This tells us that the source term is purely transverse. This is good, because if the source term had a longitudinal part then it would imply $\vec{A}$ had a longitudinal part, which would be inconsistent. Thus, we have

$$\vec{s} = \frac{4\pi}{c}\vec{j}_{trans} \tag{16.14}$$

Equation (16.12) is the equation of motion for the vector potential $\vec{A}$. We shall see that it is an equation for a collection of driven harmonic oscillators. To get more information, we will be interested in the Hamiltonian for the system, thus we want to know the energy.

The energy density of the electromagnetic fields is given by:

$$u(\vec{r}) = \frac{|\vec{E}|^2}{8\pi} + \frac{|\vec{B}|^2}{8\pi} \tag{16.15}$$

The total energy will be given by the integral of the density over all space.

$$U = \int u(\vec{r})d^3r \tag{16.16}$$

The energy flux will be giving by the Poynting vector (not to be confused with the above source term):

$$\vec{S} = \frac{\vec{E} \times \vec{B}}{4\pi}c \tag{16.17}$$

There exists the following relationship between the time derivative of the energy density and the divergence of the Poynting vector.

$$\frac{\partial u}{\partial t} + \nabla \cdot \vec{S} = -\vec{E}(\vec{r}) \cdot \vec{j} \tag{16.18}$$

If we integrate this over all space, assuming that the Poynting vector will vanish at infinity, then the the divergence term will vanish and we are left with:

$$\frac{\partial U}{\partial t} = -\int d^3r \vec{E} \cdot \vec{j} \tag{16.19}$$

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This tells us the total amount of work being done by the electric field on the charges in the system. As we know, the magnetic field does no work on the charges, as the Lorentz force is always perpendicular to the motion.

We now want to break up the E^2 term in U into longitudinal and transverse pieces. The integral of the cross term of these two will be zero when integrated over all space.

$$\int \vec{E}_{long} \cdot \vec{E}_{trans} d^3r = 0 \tag{16.20}$$

This can be seen by writing the longitudinal part in terms of the electric potential, and then integrating by parts, dropping the surface term under the assumption that the potential and/or transverse field falls to zero at infinity.

$$-\int \vec{E}_{trans} \cdot \nabla \phi d^3r = \int \phi \nabla \cdot \vec{E}_{trans} d^3r \tag{16.21}$$

The remaining integral is equal to zero, because by definition $\nabla \cdot \vec{E}_{trans} = 0$. The overall energy U of the fields can now be written as (since the $\vec{E}$ cross term disappears):

$$U = \int \left(\frac{|\vec{B}|^2}{8\pi} + \frac{|\vec{E}_{trans}|^2}{8\pi} + \frac{|\vec{E}_{long}|^2}{8\pi} \right) d^3r \tag{16.22}$$

The energy of the electromagnetic field can thus be written as:

$$U = \frac{1}{8\pi} \int d^3r \left(\left| \nabla \times \vec{A} \right|^2 + \frac{1}{c^2} \left| \frac{\partial \vec{A}}{\partial t} \right|^2 \right) + \left(\int d^3r \frac{|\vec{E}_{long}|^2}{8\pi} \right) \tag{16.23}$$

The second term is the Coulomb energy, which depends only on the current position of the charges. It is important for considering the motion of the charge particles and we shall eventually include it in the Hamiltonian for the motion of the particles, but we can ignore it for now. The first term can be considered to be the energy due to the transverse fields, which we will treat as new dynamic variables. For these variables, we have an energy term which looks like a harmonic oscillator, and equations of motion that look like harmonic oscillators, if no current sources are present..

To make this more precise we are interested in expanding the vector potential out into normal modes. To do this, we now want to put everything into a box. We use a cubic box with sides of length L. and with periodic boundary conditions. The vector potential $\vec{A}(\vec{r}, t)$ can now be expanded in terms of plane waves (which represent a complete orthogonal set of functions for the space). Let $\Omega = L^3$ be the volume of the box. Then we write

$$\vec{A}(\vec{r}, t) = \left(\frac{1}{\Omega} \right)^{\frac{1}{2}} \sum_k \vec{A}_k(t) e^{i\vec{k} \cdot \vec{r}} \tag{16.24}$$

The allowable values of $\vec{k}$ due to the boundary conditions will be given by:

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_x) \tag{16.25}$$

$$n_x, n_y, n_z \in \mathcal{Z}: \quad -\infty < n < \infty \tag{16.26}$$

The vector potential will also satisfy:

$$\nabla \cdot \vec{A} = 0, \ \vec{k} \cdot \vec{A}_{\vec{k}} = 0, \ \vec{A}_{\vec{k}} \perp \vec{k}. \tag{16.27}$$

For $\vec{A}(\vec{r})$ to be real the expansion coefficients must have the property that $\vec{A}_{\vec{k}} = \vec{A}^*_{-\vec{k}}$.

If we want to deal with harmonic oscillators, it is useful to deal with variables which are scalars and not vectors. To enable this, we introduce polarization vectors $\hat{\epsilon}_{\vec{k}\lambda}$ at each $\vec{k}$. The index $\lambda = 1, 2$ indicates which of the orthogonal polarization vectors perpendicular $\vec{k}$ we are referring to. The polarization vectors have the following properties:

$$\vec{k} \cdot \hat{\epsilon}_{\vec{k}\lambda} = 0 \qquad \hat{\epsilon}^*_{\vec{k}\lambda} \cdot \hat{\epsilon}_{\vec{k}\lambda'} = \delta_{\lambda\lambda'} \tag{16.28}$$

We also require that $\hat{\epsilon}_{\vec{k}\lambda} = \hat{\epsilon}^*_{-k\lambda}$. The vector potential coefficients will now be written as:

$$\vec{A}_k(t) = A_{k,1}\hat{\epsilon}_{k,1} + A_{k,2}\hat{\epsilon}_{k,2}, \tag{16.29}$$

which, with the requirement $A_{k,\lambda} = A^*_{-k,\lambda}$, does give us back the desired property of the coefficients $\vec{A}_k(t)$: $\vec{A}_{\vec{k}} = \vec{A}^*_{-\vec{k}}$, which we needed to give us a real vector potential $\vec{A}(\vec{r}, t)$.

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17.1   Classical E+M (continued)

From the last lecture, using the Coulomb gauge $(\nabla \cdot \vec{A})$ we found the following equation for the electromagnetic vector potential

$$-\nabla^2 \vec{A}(\vec{r},t) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{A}(\vec{r},t) = \frac{4\pi}{c}\vec{j}_{tr}(\vec{r},t) \tag{17.1}$$

The energy of the transverse electric and magnetic fields was given by:

$$U_{field} = \frac{1}{8\pi}\int\left(|\nabla \times \vec{A}|^2 + \left|\frac{1}{c}\frac{\partial\vec{A}}{\partial t}\right|^2\right)d^3r \tag{17.2}$$

We decided to expand the vector potential in terms of plane waves, by placing the whole system into a cubic box with periodic boundary conditions.

$$\vec{A}(\vec{r},t) = \frac{1}{\Omega^{\frac{1}{2}}}\sum_{\vec{k}}\sum_{\lambda=1}^{2}A_{\vec{k}\lambda}(t)\hat{\epsilon}_{\vec{k}\lambda}e^{i\vec{k}\cdot\vec{r}} \tag{17.3}$$

The $\vec{k}$ vectors, polarizations and vector potential coefficients satisfy:

$$\vec{k}\cdot\hat{\epsilon}_{\vec{k}\lambda} = 0 \qquad \hat{\epsilon}^*_{\vec{k}\lambda}\cdot\hat{\epsilon}_{\vec{k}\lambda'} = \delta_{\lambda\lambda'} \tag{17.4}$$

$$\hat{\epsilon}_{-\vec{k}\lambda} = \hat{\epsilon}^*_{\vec{k}\lambda} \qquad A_{\vec{k}\lambda}(t) = A^*_{-\vec{k}\lambda}(t) \tag{17.5}$$

We will also expand the transverse part of the current in the same way using plane waves.

$$\vec{j}_{trans}(\vec{r},t) = \frac{1}{\Omega^{1/2}}\sum_{\vec{k}}\sum_{\lambda=1}^{2}e^{i\vec{k}\cdot\vec{r}}\hat{\epsilon}_{\vec{k}\lambda}j_{\vec{k}\lambda} \tag{17.6}$$

If we now take our normal mode expansions for the vector potential and the transverse part of the current in equations (17.3) and (17.6) and plug them into equation (17.1 we arrive at the following relationship:

$$\boxed{\left(k^2 + \frac{1}{c^2}\frac{d^2}{dt^2}\right)A_{\vec{k}\lambda} = \frac{4\pi}{c}j_{\vec{k}\lambda}} \qquad \bigstar \tag{17.7}$$

For each value of $\vec{k}$ and λ, this is clearly the equation of motion for a driven harmonic oscillator, with frequency $\omega_{\vec{k}} = ck$, independent of λ.

The energy of the transverse electromagnetic field in Fourier space is given by:

$$U_{field} \;=\; \frac{1}{8\pi} \sum_{\vec{k}} |\vec{k} \times \vec{A}_{\vec{k}}|^2 + \left| \frac{1}{c} \frac{d\vec{A}_{\vec{k}}}{dt} \right|^2 \tag{17.8}$$

$$=\; \frac{1}{8\pi} \sum_{\vec{k}} \sum_{\lambda} \left(k^2 |A_{\vec{k}\lambda}|^2 + \left| \frac{1}{c} \frac{dA_{\vec{k}\lambda}}{dt} \right|^2 \right) \tag{17.9}$$

This is the total energy if we have no driving currents.

We want to find a Hamiltonian which will yield both this energy and the correct equations of motion. There are two related complications

1. $A_{\vec{k}\lambda}$ are complex.

2. These coefficients are not independent $A_{\vec{k}\lambda} = A^*_{-\vec{k}\lambda}$. We don't want to count these two as seperate harmonic oscillators, instead we want to group them together.

The most straightforward way to avoid this double counting is to restrict $\vec{k}$ to the upper half space $k_z > 0$ and use two real variables for the real and imaginary parts of $A_{\vec{k}\lambda}$. For example, we could define the variables $Q^\sigma_{\vec{k}\lambda}$ whenre $\sigma = 1, 2$.

$$Q^{(1)}_{\vec{k}\lambda} = \mathrm{Re}\left(A_{\vec{k}\lambda} \right) \qquad Q^{(2)}_{\vec{k}\lambda} = \mathrm{Im}\left(A_{\vec{k}\lambda} \right), \tag{17.10}$$

so that we now have a set of real harmonic oscillators. The amplitudes of these oscillators can be interpreted as amplitudes of standing waves, proportional to sines and cosines, rather than the amplitudes of traveling waves.

We discuss below the way to count these modes properly and use them to to quantize the electromagnetic field. However, we shall not discuss this method in class, but shall skip directly to the section detailing the method of quantization using traveling waves/

17.1.1   Quantization using standing wave modes

We can state the vector potential coefficients in terms of the Q variables as

$$A_{\vec{k}\lambda} = Q^{(1)}_{\vec{k}\lambda} + i Q^{(2)}_{\vec{k}\lambda} \tag{17.11}$$

$$A_{-\vec{k}\lambda} = Q^{(1)}_{\vec{k}\lambda} - i Q^{(2)}_{\vec{k}\lambda} \tag{17.12}$$

We can now substitute into the expressions for energy of the field, and we find that:

$$U_{field} = \frac{1}{2} \sum_{\alpha} \left(\frac{k^2}{2\pi} Q^2_\alpha + \frac{1}{2\pi c^2} \left(\dot{Q}_\alpha \right)^2 \right) \tag{17.13}$$

where the label α denotes the set of indices $\vec{k}, \lambda, \sigma$, with $\vec{k}$ restricted to the upper half space. These are real variables, and there is no double counting. Now these really are a set of independent harmonic oscillators.

Now to get the equations of motion, let us first assume that $j_{\vec{k}\lambda} = 0$ so that there is no driving term. The equation we expect to come out should be

$$\ddot{Q}_\alpha = -c^2 k^2 Q_\alpha \tag{17.14}$$

In analyzing equation (17.13 we can consider the term $\left(\frac{k^2}{2\pi}\right) Q_\alpha^2$ to be like the potential energy while having the term $\left(\frac{1}{2\pi c^2}\right) \dot{Q}_\alpha^2$ be the kinetic energy. We will set $(2\pi c^2)^{-1}$ to be the mass of the mode α and will take the quantity $\frac{\dot{Q}_\alpha}{2\pi c^2}$ to be the momentum P_α. Now stating the Hamiltonian as a function of Q_α and P_α we have:

$$H(\{P_\alpha, Q_\alpha\}) = U_{field} = \frac{1}{2} \sum_\alpha \left(\frac{k_\alpha}{2\pi} Q_\alpha^2 + 2\pi c^2 P_\alpha^2 \right) \tag{17.15}$$

Now from Hamilton's equations of motion we have:

$$\frac{dQ_\alpha}{dt} = \frac{\partial H}{\partial P_\alpha} = 2\pi c^2 P_\alpha \tag{17.16}$$

$$\frac{dP_\alpha}{dt} = -\frac{\partial H}{\partial Q_\alpha} = -\frac{k^2}{2\pi} Q_\alpha \tag{17.17}$$

Combining these, we do indeed reproduce the desired equation of motion .

$$\frac{d^2 Q_\alpha}{dt^2} = -k^2 c^2 Q_\alpha \tag{17.18}$$

If we now consider the presence of a driving term $j_{\vec{k}\lambda} \neq 0$ we can perform a similar analysis by decomposing the current coefficients in terms of new real variables defined on the upper half space $k_z > 0$

$$F_{\vec{k}\lambda}^{(1)} = \frac{2}{c} \text{Re}(j_{\vec{k}\lambda}) \qquad F_{\vec{k}\lambda}^{(2)} = \frac{2}{c} \text{Im}(j_{\vec{k}\lambda}) \tag{17.19}$$

Now plugging this back into equation (17.7) we arrive at a new driven set of equations of motion:

$$\boxed{\frac{1}{2\pi c^2} \frac{d^2 Q_\alpha}{dt^2} = \frac{-k^2 c^2}{2\pi c^2} Q_\alpha + F_\alpha} \tag{17.20}$$

To get the correct equations of motion, we must let the Hamiltonian be the sum of both the field and source terms.

$$H(P_\alpha, Q_\alpha) = H_{field} + H_{source} \tag{17.21}$$

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where the source Hamiltonian is given by:

$$H_{source} = -\sum_\alpha Q_\alpha F_\alpha \tag{17.22}$$

We can now recalculate the equations of motion which will be:

$$\frac{dQ_\alpha}{dt} = \frac{\partial H}{\partial P_\alpha} = 2\pi c^2 P_\alpha \tag{17.23}$$

$$\frac{dP_\alpha}{dt} = -\frac{\partial H}{\partial Q_\alpha} = \frac{-k^2}{2\pi} Q_\alpha + F_\alpha \tag{17.24}$$

This gives us the same equation of motion we saw before.

We can now write the source term as a sum over all $\vec{k}$, not just over the half plane, because the complex conjugate on the current term ensures that all terms are included. Furthermore, by the properties of Fourier transforms, this term can also be written as an integral in position space:.

$$H_{source} = -\frac{1}{c}\sum_{\vec{k}}\sum_\lambda A_{\vec{k}\lambda} j^*_{\vec{k}\lambda} \tag{17.25}$$

$$= -\frac{1}{c}\int d^3r\, \vec{A}(\vec{r})\cdot\vec{j}(\vec{r}) \tag{17.26}$$

We now have a Hamiltonian, with or without a source, which gives us the correct equation of motion. It now remains to quantize it. We treat Q_α and P_α as operators with the following commutation relations:

$$[Q_\alpha, P_\alpha] = i\hbar\delta_{\alpha\beta} \qquad [Q_\alpha, Q_\beta] = 0 = [P_\alpha, P_\beta] \tag{17.27}$$

Again, α and β stand for sets of indices $[\vec{k}, \lambda, \sigma]$, with $k_z > 0$. Now since the Hamiltonian is quadratic, the Heisenberg equations of motion (for the expectation values) will correspond to that of the classical equations of motion. If it had a more complicated dependence, then an exact correspondence would not be guaranteed to exist, but the equations would necessarily reduce to the classical equations of motion in the appropriate classical limit.

We can now proceed to introduce raising and lowering operators $a^\dagger_\alpha$ and a_α consisting of linear combinations of Q's and P's, such that we obtain operators that increase or decrease the energy in one of the modes α.

If we look at the $\sigma = 1$, the real mode, that would give us a vector potential proportional to a cosine $\vec{A}(\vec{r}) \propto \cos(\vec{k}\cdot\vec{r})$, and similarly $\sigma = 2$ would give us $\vec{A}(\vec{r}) \propto \sin(\vec{k}\cdot\vec{r})$. So this would be a method of quantizing in standing waves. It turns out however, that this is not the most convenient way to quantize this system. Instead we want to quantize in terms of travelling waves.

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17.1.2   Quantization Using Traveling Waves

Here we want quantize this system much like complex 2-D degenerate oscillator. In that case we had:

$$x + iy \quad \propto \quad (b_1 + b_2^\dagger) \tag{17.28}$$

$$x - iy \quad \propto \quad (b_2 + b_1^\dagger) \tag{17.29}$$

$$p_x + ip_y \quad \propto \quad \frac{b_1 - b_2^\dagger}{i} \tag{17.30}$$

Similarly now, rather than use Q we want to take linear combinations. We shall try to expand $\vec{A}$ in terms of harmonic oscillator operators for traveling wave modes,,which we write as $a_{\vec{k}\lambda}$, where $\vec{k}$ goes over all space. We shall require that these obey the standard commutation relations,

$$\left[a_{\vec{k}\lambda}, a_{\vec{k}',\lambda'}^\dagger \right] = \delta_{\vec{k},\vec{k}'}\delta_{\lambda,\lambda'} , \quad \left[a_{\vec{k}\lambda}, a_{\vec{k}',\lambda'} \right] = \left[a_{\vec{k}\lambda}^\dagger, a_{\vec{k}',\lambda'}^\dagger \right] = 0 \tag{17.31}$$

We are going to assume that we can write:

$$A_{\vec{k}\lambda} = C_{\vec{k}}(a_{\vec{k}\lambda} + a_{-\vec{k}\lambda}^\dagger) = A_{-\vec{k}\lambda}^\dagger \tag{17.32}$$

Similarly, we will assume that we can write the electric field coefficients as:

$$E_{\vec{k}\lambda} = iD_{\vec{k}}(a_{\vec{k}\lambda} - a_{-\vec{k}\lambda}^\dagger) = E_{-\vec{k}\lambda}^\dagger \tag{17.33}$$

The operators $a_{\vec{k}\lambda}$ and $a_{-\vec{k}\lambda}$, which are analogs of the operators b_1 and b_2 for the two-dimensional harmonic oscillator, will be orthogonal complex linear combinations of the operators a_α for the real standing-wave oscillators corresponding to $\cos \vec{k} \cdot \vec{r}$ and $\sin \vec{k} \cdot \vec{r}$, defined in the previous subsection, just as the operators b_1 and b_2 were linear combinations of the operators a_x and a_y for the two-dimensional harmonic oscillator.

The coefficients $C_{\vec{k}}$ and $D_{\vec{k}}$ have values yet to be determined. However, the requirements $A_{\vec{k}\lambda} = A_{-\vec{k}\lambda}^\dagger$, $E_{\vec{k}\lambda} = E_{-\vec{k}\lambda}^\dagger$, imply that $C_{\vec{k}} = C_{-\vec{k}}^*$ and $D_{\vec{k}} = D_{-\vec{k}}^*$.

We would like to choose the values of these constants such that the overall Hamiltonian of the field will be given by:

$$H_{field} = \sum_{\vec{k}\lambda} \hbar ck \left(a_{\vec{k}\lambda}^\dagger a_{\vec{k}\lambda} + \frac{1}{2} \right) \tag{17.34}$$

When expressed in terms of $A_{\vec{k}l}$ and $E_{\vec{k}l}$, this Hamiltonian should give the same form for field energy as we have previously derived, so we want

$$H_{field} \;=\; \frac{1}{8\pi} \sum_{\vec{k},\lambda} \left(E_{\vec{k}\lambda} E_{\vec{k}\lambda}^\dagger + k^2 A_{\vec{k}\lambda} A_{\vec{k}\lambda}^\dagger \right) \tag{17.35}$$

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Plugging in equations (17.32) and (17.33) into equation (17.35) we arrive at:

$$
\begin{aligned}
H_{field} &= \frac{1}{8\pi} \sum_{\vec{k}\lambda} \left(k^2 |C_{\vec{k}}|^2 + |D_{\vec{k}}|^2\right) \left(a_{\vec{k}\lambda} a_{\vec{k}\lambda}^{\dagger} + a_{-\vec{k}\lambda}^{\dagger} a_{-\vec{k}\lambda}\right) \\
&\quad + \frac{1}{8\pi} \sum_{\vec{k}\lambda} \left(k^2 |C_{\vec{k}}|^2 - |D_{\vec{k}}|^2\right) \left(a_{\vec{k}\lambda} a_{-\vec{k}\lambda} + a_{\vec{k}\lambda}^{\dagger} a_{-\vec{k}\lambda}^{\dagger}\right)
\end{aligned}
\tag{17.36}
$$

In the first term, since we are summing over all $\vec{k}$, the term with two $-\vec{k}$ operators can be replaced with $\vec{k}$ operators. We can then use the commutation relations to write

$$
(a_{\vec{k}\lambda} a_{\vec{k}\lambda}^{\dagger} + a_{\vec{k}\lambda}^{\dagger} a_{\vec{k}\lambda}) = (2 a_{\vec{k}\lambda}^{\dagger} a_{\vec{k}\lambda} + 1)
\tag{17.37}
$$

If we are to arrive at the desired form of the Hamiltonian specified in equation (17.34), then there should be no $a_{\vec{k}\lambda} a_{-\vec{k}\lambda}$ or $a_{\vec{k}\lambda}^{\dagger} a_{-\vec{k}\lambda}^{\dagger}$ terms remaining. This means we should pick $C_{\vec{k}}$ and $D_{\vec{k}}$ such that the second term in equation (17.36) vanishes. The condition for this is that:

$$
k^2 |C_{\vec{k}}|^2 - |D_{\vec{k}}|^2 = 0
\tag{17.38}
$$

The remaining conditions to impose on $C_{\vec{k}}$ and $D_{\vec{k}}$ are to choose them such that the remaining prefactors in (17.36) give the form in (17.34). This gives the requirement.

$$
(k^2 |C_{\vec{k}}|^2 + |D_{\vec{k}}|^2) = \frac{8\pi}{2} \hbar c k
\tag{17.39}
$$

Together, equations (17.38) and (17.39) determine the values of $C_{\vec{k}}$ and $D_{\vec{k}}$ up to a phase. We have some leeway in terms of choosing the values for these, and we choose the phase of $a_{\vec{k}\lambda}$ so that $C_{\vec{k}} > 0$ and in doing so, the phase of $D_{\vec{k}}$ will be set by the Heisenberg equation of motion.

$$
E_{\vec{k}\lambda} = -\frac{1}{c} \frac{dA_{\vec{k}\lambda}}{dt} \qquad D_{\vec{k}} > 0
\tag{17.40}
$$

With these choices, we find that the values of the coefficients depend only on the magnitude of k, and are given by:

$$
C_k = \sqrt{\frac{2\pi \hbar c}{k}} \qquad D_k = \sqrt{2\pi \hbar k c}
\tag{17.41}
$$

With that, equation (17.36) reduces to equation (17.34) as desired. We can now look at the energy eigenvalues of this system for the case where there is no current, and therefore no additional source term $H_{source} = 0$. In this situation the energy eigenvalues will be given by:

$$
E = \sum_{\vec{k}\lambda} \hbar c k \left(n_{\vec{k}\lambda} + \frac{1}{2}\right)
\tag{17.42}
$$

where $n_{\vec{k}\lambda} = 0, 1, 2, 3 \ldots$. An immediate distressing point about this field energy is that the ground state energy seems to diverge.

$$E_0 = \sum_{\vec{k}\lambda} \frac{\hbar c k}{2} = \infty \tag{17.43}$$

This is the first of several infinities that we will encounter in quantizing the electromagnetic field. Our solution for the time being is to ignore it, and redefine the field Hamiltonian as:

$$H_{field} = \sum_{\vec{k},\lambda} \hbar c k \, a^\dagger_{\vec{k}\lambda} a_{\vec{k}\lambda}, \tag{17.44}$$

so the ground state energy is zero. This should be okay, because subtracting a constant from the definition of the Hamiltonian will have no real effect on observable quantities. For example. the Heisenberg equations of motion are unchanged, and all energy differences are unchanged.

We next look at the commutation relations for $A_{\vec{k}\lambda}$ and $E_{\vec{k}\lambda}$. Plugging in the coefficients from equation (17.41) into equations (17.32) and (17.33) we arrive at:

$$A_{\vec{k}\lambda} = \sqrt{\frac{2\pi\hbar c}{k}}(a_{\vec{k}\lambda} + a^\dagger_{-\vec{k}\lambda}) \tag{17.45}$$

$$E_{\vec{k}\lambda} = i\sqrt{2\pi\hbar k c}(a_{\vec{k}\lambda} - a^\dagger_{-\vec{k}\lambda}) \tag{17.46}$$

This leads directly to the following commutation relations.

$$\left[A_{\vec{k}\lambda}, A_{\vec{k}\,'\lambda'}\right] = 0 \tag{17.47}$$

$$\left[E_{\vec{k}\lambda}, E_{\vec{k}\,'\lambda'}\right] = 0 \tag{17.48}$$

$$\left[A_{\vec{k}\lambda}, E_{-\vec{k}\,'\lambda'}\right] = -4\pi i \hbar c \, \delta_{\vec{k}\vec{k}\,'} \delta_{\lambda\lambda'} \tag{17.49}$$

To arrive at coefficients in the expansion of the magnetic field, we need only take the cross product of the coefficients of the vector potential. with the $\vec{k}$ vector.

$$\vec{B}_k = i\vec{k} \times \vec{A}_k \tag{17.50}$$

17.1.3   What is the Hilbert Space?

Now that we have defined creation and annihilation operators, we can ask what are the states of the system, and try to do some interpretation. To begin with, for $\vec{j}_{\vec{k}} = 0$ we can specify a ground state of the system $|0\rangle$, which we call the *vacuum state*, such that any annihilation operator acting on that state will return 0.

$$a_{\vec{k}\lambda}|0\rangle = 0, \ \forall \ \vec{k}, \lambda. \tag{17.51}$$

The vacuum state is clearly the ground state of the redefined field Hamiltonian (17.44), with energy 0:

$$H_{field} \left|0\right\rangle = 0. \tag{17.52}$$

We shall assume that the vacuum state is unique.

We can now define photon occupation states. The simplest single occupation state will be given by single creation operator acting on the vacuum:

$$\left|1_{\vec{k}\lambda}\right\rangle = a_{\vec{k}\lambda}^{\dagger} \left|0\right\rangle \tag{17.53}$$

This state lends itself to obvious interpretation: it is the state consisting of a single photon, with momentum $\vec{k}$ and polarization specified by λ. It will have an energy $\hbar c k$. It will also be orthogonal to other single photon states:

$$\left\langle 1_{\vec{k}\,'\lambda} | 1_{\vec{k}\,'\lambda'} \right\rangle = \delta_{\vec{k}\vec{k}\,'} \delta_{\lambda\lambda'} \tag{17.54}$$

The proof of this, in the formalism we have used so far is:

$$\langle 0| a_{\vec{k}\lambda} a_{\vec{k}\,'\lambda'}^{\dagger} |0\rangle = \langle 0| a_{\vec{k}\,'\lambda'}^{\dagger} a_{\vec{k}\lambda} |0\rangle + \langle 0| \delta_{\vec{k}\vec{k}\,'} \delta_{\lambda\lambda'} |0\rangle \tag{17.55}$$

The next set of states, two-photon states, can consist of either two photons in different modes (where either $\vec{k} \neq \vec{k}\,'$ or $\lambda \neq \lambda'$), or two photons in the same mode. In the first case, we have

$$\left|1_{\vec{k}\lambda} 1_{\vec{k}\,'\lambda'}\right\rangle = a_{\vec{k}\lambda}^{\dagger} a_{\vec{k}\,'\lambda'}^{\dagger} |0\rangle \tag{17.56}$$

The energy of this state will be given by:

$$E = \hbar c (|\vec{k}| + |\vec{k}\,'|) \tag{17.57}$$

Note that the order of labeling the states does not matter because the raising operators commute:

$$\left|1_{\vec{k}\lambda} 1_{\vec{k}\,'\lambda'}\right\rangle = \left|1_{\vec{k}\,'\lambda'} 1_{\vec{k}\lambda}\right\rangle \tag{17.58}$$

It is also the case that this state is properly normalized $\left\langle 1_{\vec{k}\lambda} 1_{\vec{k}\,'\lambda'} | 1_{\vec{k}\lambda} 1_{\vec{k}\,'\lambda'} \right\rangle = 1$ as can be verified by turning these states into creation and destruction operators acting on the ground states, and then playing around with commutation relations.

The other kind of two-photon state consists of two photons in the same mode. In this case an additional normalization factor is required, as can also be verified using the method specified in the paragraph above.

$$\left|2_{\vec{k}\lambda}\right\rangle = \frac{1}{\sqrt{2!}} (a_{\vec{k}\lambda}^{\dagger})^2 |0\rangle \tag{17.59}$$

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We can introduce a total photon number operator N_{photon} which will return the total number of photons of all momenta and polarizations :

$$N_{photon} = \sum_{\vec{k}\lambda} a_{\vec{k}\lambda}^{\dagger} a_{\vec{k}\lambda} \tag{17.60}$$

The eigenvectors of our field Hamiltonian now serves to specify a basis for the entire Hilbert space.

$$H_{field} = \sum_{\vec{k}\lambda} \hbar c k (a_{\vec{k}\lambda}^{\dagger} a_{\vec{k}\lambda}) \tag{17.61}$$

The basis states have specified photon occupation numbers, ie a set of numbers $\{n_{\vec{k}\lambda}\}$ specifying the number of photons for every momentum and polarization. In order to have a finite total energy, we require that there be at most a finite number of modes, $\{\vec{k}_i, \lambda_i\}, (i = 1, ...r)$ with nonzero occupancy. Thus we have only

$$n_{\vec{k}_1\lambda_1}, n_{\vec{k}_2,\lambda_2} \ldots n_{\vec{k}_r\lambda_r} \neq 0 \tag{17.62}$$

We now claim that we can construct a normalized state of definite photon occupation number by using creation operators on the vacuum state in the following manner:

$$|\{n_{\vec{k}\lambda}\}\rangle = \frac{(a_{\vec{k}_1\lambda_1}^{\dagger})^{n_{\vec{k}_1\lambda_1}}}{(n_{\vec{k}_1\lambda_1}!)^{1/2}} \cdots \frac{(a_{\vec{k}_r\lambda_r}^{\dagger})^{n_{\vec{k}_r\lambda_r}}}{(n_{\vec{k}_r\lambda_r}!)^{1/2}} |0\rangle \tag{17.63}$$

The corresponding energy of such a state will be:

$$E_{\{n_{\vec{k}}\}} = \sum_{\vec{k}\lambda} n_{\vec{k}\lambda} \hbar c k < \infty \tag{17.64}$$

The set of all states of the form 17.63), with a finite value of N_{photon}, will serve as a basis for the entire Hilbert Space.

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18.1   Quantization of the E+M Field (continued): Expectation Values of Field Operators.

We have quantized the electromagnetic field by introducing photon creation and annihilation operators $a^\dagger_{\vec{k}\lambda}$, $a_{\vec{k}\lambda}$ and we have expressed the fourier expansion coefficients for the vector potential and the electric field in terms of them.

$$A_{\vec{k}\lambda} = \left(\frac{2\pi c}{k}\right)^{1/2}(a_{\vec{k}\lambda} + a^\dagger_{-\vec{k}\lambda}) \tag{18.1}$$

$$E_{\vec{k}\lambda} = i(2\pi\hbar ck)^{1/2}(a_{\vec{k}\lambda} - a^\dagger_{-\vec{k}\lambda}) \tag{18.2}$$

The Hamiltonian for the field without a source term ($\vec{j} = 0$) is given by:

$$H_{field} = \sum_{\vec{k}\lambda} \hbar ck(a^\dagger_{\vec{k}\lambda} a_{\vec{k}\lambda}) \tag{18.3}$$

We also introduced the total photon number operator

$$N_{photon} = \sum_{\vec{k}\lambda} a^\dagger_{\vec{k}\lambda} a_{\vec{k}\lambda} \tag{18.4}$$

We can go on to state the full field operators for the vector potential, the electric field and the magnetic field by substituting the fourier expansion coefficients into the relevant expansions:

$$\vec{A}(\vec{r}) = \left(\frac{1}{\Omega}\right)^{1/2} \sum_{\vec{k}\lambda} \left(\frac{2\pi\hbar c}{k}\right)^{1/2} e^{i\vec{k}\cdot\vec{r}} \hat{\epsilon}_{\vec{k}\lambda}(a_{\vec{k}\lambda} + a^\dagger_{-\vec{k}\lambda}) \tag{18.5}$$

$$\vec{E}_{trans}(\vec{r}) = \left(\frac{1}{\Omega}\right)^{1/2} \sum_{\vec{k}\lambda} (2\pi\hbar ck)^{1/2} i e^{i\vec{k}\cdot\vec{r}} \hat{\epsilon}_{\vec{k}\lambda}(a_{\vec{k}\lambda} - a^\dagger_{-\vec{k}\lambda}) \tag{18.6}$$

$$\vec{B}(\vec{r}) = \nabla \times \vec{A}(\vec{r}) = \left(\frac{1}{\Omega}\right)^{1/2} \sum_{\vec{k}\lambda} i\vec{k} \times \hat{\epsilon}_{\vec{k}\lambda} \left(\frac{2\pi\hbar c}{k}\right)^{1/2} e^{i\vec{k}\cdot\vec{r}}(a_{\vec{k}\lambda} + a^\dagger_{-\vec{k}\lambda}) \tag{18.7}$$

States with Definite Photon Occupation Numbers

States labeled $|\{n_\alpha\}\rangle$ specify the number of each mode separately. These states form a basis for the Hilbert space. We can calculate expectation values. For example, what is the expectation value of the fields in the ground state $|0\rangle$. The answer is zero at any point. This can be seen by just looking at the annihilation and creation operator expectation values.

$$\langle 0|a_{\vec{k}\lambda}|0\rangle = \langle 0|a_{\vec{k}\lambda}^\dagger|0\rangle = 0 \tag{18.8}$$

Therefore it follows:

$$\langle 0|\vec{E}|0\rangle = 0 \qquad \langle 0|\vec{B}|0\rangle = 0 \tag{18.9}$$

What about the expectation value of $\langle 0|E^2(\vec{r})|0\rangle$? When we say $E^2(\vec{r})$ we really mean the square of the transverse part of the field.

$$E^2(\vec{r}) = \vec{E}_{trans}(\vec{r}) \cdot \vec{E}_{trans}(\vec{r}) \tag{18.10}$$

In the case where there are no charges, the longitudinal part is zero, so the field and the transverse component are the same. We just go ahead and calculate this:

$$\langle 0|E^2(\vec{r})|0\rangle = \frac{1}{\Omega}\sum_{\vec{k}\lambda}\sum_{\vec{k}\,'\lambda'}i^2(2\pi\hbar c)(\vec{k}\vec{k}\,')^{1/2}\hat{\epsilon}_{\vec{k}\lambda}\hat{\epsilon}_{\vec{k}\,'\lambda'}\langle 0|(a_{\vec{k}\,'\lambda'} - a_{-\vec{k}\,'\lambda'}^\dagger)(a_{\vec{k}\lambda} - a_{-\vec{k}\lambda}^\dagger)|0\rangle \tag{18.11}$$

The expectation value of the operators on the right will turn out to be a product of delta functions:

$$\langle 0|(a_{\vec{k}\,'\lambda'} - a_{-\vec{k}\,'\lambda'}^\dagger)(a_{\vec{k}\lambda} - a_{-\vec{k}\lambda}^\dagger)|0\rangle = \delta_{-\vec{k}\,'\vec{k}}\delta_{\lambda\lambda'} \tag{18.12}$$

Now placing this back into the series, we see that the expectation value goes to infinity.

$$\langle 0|E^2|0\rangle = \frac{1}{\Omega}\sum_{\vec{k}\lambda}(2\pi\hbar c)k(\hat{\epsilon}_{\vec{k}\lambda}\cdot\hat{\epsilon}_{\vec{k}\lambda}^*) = \infty \tag{18.13}$$

Similarly, if we work through the same situation for the magnetic field, we will also find an infinity.

$$\langle 0|B^2|0\rangle = \infty \tag{18.14}$$

This tells us that $\vec{E}(\vec{r})$ and $\vec{B}(\vec{r})$ are not valid operators. If you try to measure the field at a point, there will be infinite quantum fluctuations. There is an enormous amount of zero point energy in the field and if you try to measure all of the modes at some point, it will diverge. This

doesn't tell us the theory is garbage; it just means that you can't really measure the field at a point. The same argument holds for the individual components of the field.

$$\langle 0|E_x(\vec{r})E_x(\vec{r})|0\rangle = \infty \qquad \|E_x\,|0\rangle\,\|^2 = \infty \tag{18.15}$$

The problem is not just for the fields squared either, for on the right in equation(18.15) we see that the norm of the vector will also be infinity. Thus the operator $E_x(\vec{r})$ acting on the vacuum state does not give us a vector in the Hilbert space. We would find the same divergence if $E_x(\vec{r})$ acts on any state in the Hilbert space; thus $E_x(\vec{r})$ is simply not a legitimate operator.

In reality any measuring device has a finite size. So instead it makes more sense to look at operators defined over some finite spatial region. We can define a new operator

$$\vec{E}_{(f)}(\vec{r}) = \int d^3\vec{s}\,\vec{E}(\vec{r}+\vec{s})f(\vec{s}) \tag{18.16}$$

where the function $f(\vec{s})$ need only satisfy the conditions:

$$\int d^3\vec{s}\,f(\vec{s}) = 1 \qquad f(\vec{s}) \geq 0 \tag{18.17}$$

and also be peaked at $\vec{s} = 0$. In the limit where $f(\vec{s}) \to \delta(\vec{s})$ we recover our original field operator at a point (but we don't want to take that limit yet). The function f could be a gaussian of some small width. We now want to see the expectation value of this new operator squared will be.

We plug in the Fourier expansion of $\vec{E}_{trans}(\vec{r}+\vec{s})$, as given by equation (18.6), into our definition of $E_f(\vec{r})$, equation (18.16). If we now integrate over $\vec{s}$, we can see that the $e^{i\vec{k}\cdot\vec{s}}$ will combine with $f(\vec{s})$ to give us a Fourier transform $\tilde{f}(-\vec{k})$. Therefore we claim that the form we arrive at for $\vec{E}_f(\vec{r})$ will be:

$$\vec{E}_f(\vec{r}) = \left(\frac{1}{\Omega}\right)^{1/2}\sum_{\vec{k}\lambda}\tilde{f}^*(\vec{k})(2\pi)^{3/2}E_{\vec{k}\lambda}e^{i\vec{k}\cdot\vec{r}}\hat{\epsilon}_{\vec{k}\,\lambda} \tag{18.18}$$

The * on the fourier transform arises from the property that:

$$f^*(k) = f(-k), \tag{18.19}$$

which follows because $f(\vec{r})$ was assumed real. Now, to get to expectation value of $E_f^2(\vec{r})$, we have:

$$\langle 0|\vec{E}_f(\vec{r})\cdot\vec{E}_f(\vec{r})|0\rangle = \frac{1}{\Omega}\sum_{\vec{k}\lambda}(2\pi)^4\hbar c|\vec{k}||\tilde{f}(\vec{k})|^2 \tag{18.20}$$

We can deal with the sums by converting the sum over k to an integral, and recalling that summing over the λ's just gives us a factor of 2.

$$\sum_k \to \frac{\Omega}{(2\pi)^3} \int d^3k \qquad \sum_\lambda \to 2 \tag{18.21}$$

If $f(\vec{s})$ were a delta function, we would get the same infinite result as before. However, if $f(\vec{s})$ is a smooth function, so that the Fourier transform $\tilde{f}(\vec{k})$ falls off rapidly as $\vec{k} \to \infty$, then the integral will converge and the expectation value will be finite. But the left-hand side of the equation is just the sum of the expectations values of the squares of the three Cartesian components of $\vec{E}_f$. Hence, for any Cartesian component $E_{f,j}$, we have

$$\|E_{f,j}(\vec{r})|0\rangle\| < \infty. \tag{18.22}$$

So $\vec{E}_f(\vec{r})$ is a well-defined operator. We can similarly define with $\vec{B}_f(\vec{r})$ with the same result.

Another very useful quantity of the energy density. We would like to define an energy density operator $u(\vec{r})$ for the transverse electromagnetic field, such that the integral over all space gives us the total field energy H_{field}, and such that the integral over a finite volume can be interpreted as the energy in that volume. In classical E&M, we defined the energy density as $[B^2 + E^2]/8\pi$. If we were to use the same definition in quantum mechanics, we would find that the energy density is infinite, even in the vacuum, as the operator has not subtracted the infinite zero point energy of the harmonic oscillator modes. instead we define

$$u(\vec{r}) = \frac{: B^2(\vec{r}) : + : E^2(\vec{r}) :}{8\pi}, \tag{18.23}$$

where the colon represents a **normal ordered operator**, which we define as follows: First expand the operator out in terms of photon creation and annihilation operators. Then, whenever you encounter a product of photon creation and annihilation operators, reorder the product so that annihilation operators are to the right, throwing out all commutators. For example, we have

$$: a_{\vec{k}\lambda} a^\dagger_{\vec{k}'\lambda'} : \equiv a^\dagger_{\vec{k}'\lambda'} a_{\vec{k}\lambda} \tag{18.24}$$

Thus the expectation value of the normal ordered product is zero in the vacuum state, and $\langle u(\vec{r}) \rangle = 0$ in the vacuum state.

It may be readily shown that

$$: E^2(\vec{r}) := \lim_{f(s) \to \delta(s)} \left(\vec{E}_f(\vec{r}) \cdot \vec{E}_f(\vec{r}) - \langle 0| \vec{E}_f(\vec{r}) \cdot \vec{E}_f(\vec{r}) |0\rangle \right), \tag{18.25}$$

so it is appropriate to think of $: E^2(\vec{r}) :$ as being equal to $E^2(\vec{r})$ with the infinite zero-point contribution subtracted. The expectation value of $: E^2(\vec{r}) :$ is finite in most states of interest,

as is the expectation value of $u(\vec{r})$. Using these results, along with the similar results for B^2, you may readily check that our definition of u satisfies the condition that its integral over space is equal to H_{field}.

   You will see explicitly in a homework problem, for a wave packet state with one photon present, that

$$\langle \psi | : E^2(\vec{r}) : | \psi \rangle < \infty \tag{18.26}$$

Nevertheless, states such as $: E^2(\vec{r}) : | \psi \rangle$ or $u(\vec{r}) | \psi \rangle$ have infinite norm, so they are not in our Hilbert space, and the operators $: E^2(\vec{r}) :$ and $u(\vec{r})$ are not really legitimate operators. You can obtain legitimate operators, however, if you average them over a small volume, just as we did for the field operators $\vec{E}$ and $\vec{B}$. Alternatively, you may use these operators freely in expressions when you multiply by a smooth function and integrate over position.

18.2   Properties of One-Photon States.

We now want to talk about a general one-photon state. For these states $| \psi \rangle$, acting on the state with the number operator will just give the state back.

$$| \psi \rangle = N_{photon} | \psi \rangle \tag{18.27}$$

   We can express the most general one-photon state as a sum over many different one-photon basis states.

$$| \psi \rangle = \sum_{\vec{k}\lambda} c_{\vec{k}\lambda} | 1_{\vec{k}\lambda} \rangle = \sum_{\vec{k}\lambda} c_{\vec{k}\lambda} a_{\vec{k}\lambda}^{\dagger} | 0 \rangle \tag{18.28}$$

The normalization condition for such states (since the basis states are orthogonal) will be:

$$\langle \psi | \psi \rangle = \sum_{\vec{k}\lambda} |c_{\vec{k}\lambda}|^2 = 1 \tag{18.29}$$

Single-Photon Wave Packets

Let us suppose that the coefficients $c_{\vec{k}\lambda}$ are given by:

$$c_{\vec{k}\lambda} = N \exp\left(-\frac{(-\vec{k} - \vec{k}_0)^2}{2\sigma^2} \right) \exp(-i\vec{k} \cdot \vec{r}_0) \hat{\chi}_0 \cdot \hat{\epsilon}_{\vec{k}\lambda}^* \tag{18.30}$$

We suppose for simplicity that the polarization vector $\hat{\chi}_0$ is in the $\hat{x}$-direction and that:

$$\vec{k}_0 \| \hat{z} \qquad \sigma << k_0 \tag{18.31}$$

We claim that this is a Gaussian wavepacket centered at point $\vec{r} = \vec{r}_0$ with width in real space of order $\frac{1}{\sigma}$ and a width in momentum space of order σ. The wavevector will be centered at $\vec{k} = \vec{k}_0$. We also claim that the expectation value of energy density $u(\vec{r})$ will nearly zero everywhere except in the immediate vicinity of $\vec{r}_0$. (You will verify this point eventually in a homework problem.)

Now consider the time evolution of this wave packet in the absence of electric currents. For $\vec{j} = 0$, the Schrödinger picture coefficient will be:

$$c_{\vec{k}\lambda} = c_{\vec{k}\lambda}(0)e^{-ic|\vec{k}|t} \tag{18.32}$$

If $\vec{k}$ is close to $\vec{k}_0$ then we can expand (for the case of $\vec{k}_0 \| k_z$).:

$$|\vec{k}| = k_0 + (k_z - k_0) + \mathcal{O}(k - k_0)^2 \tag{18.33}$$

This means the coefficient is approximately:

$$c_{\vec{k}\lambda}(t) = c_{\vec{k}\lambda}(0)e^{-ick_z t} \tag{18.34}$$

The coefficient at time $t = 0$ is:

$$c_{\vec{k}\lambda}(0) \propto e^{-i(\vec{k}\cdot\vec{r}_0)} \tag{18.35}$$

Therefore the time evolved coefficient will be:

$$c_{\vec{k}\lambda}(t) \propto e^{-i\vec{k}\cdot(\vec{r}_0 + c\hat{z}t)} \tag{18.36}$$

This now means that we have a wave packet centered at $\vec{r}_0 + ct\hat{z}$. This is wavepacket traveling in the z direction at the speed of light, which is what we want. There will be some spreading as time goes on, but we can ignore that if the width in momentum is sufficiently small.

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19.1   General 1 Photon State (continued)

The generalized one photon state, consisting of a superposition of all one photon states is given by:

$$|\psi\rangle = \sum_{\vec{k}\lambda} c_{\vec{k}\lambda} a^{\dagger}_{\vec{k}\lambda}|0\rangle \tag{19.1}$$

The example of the coefficients given in the last lecture was:

$$c_{\vec{k}\lambda} = N e^{-\frac{|\vec{k}-\vec{k}_0|^2}{2\sigma^2}} e^{-i\vec{k}\cdot\vec{r}_0} \hat{x}\cdot\hat{\epsilon}^*_{\vec{k}\,\lambda} \tag{19.2}$$

Given the conditions:

$$\hat{k}_0\|\hat{z} \qquad \sigma << k_0 \tag{19.3}$$

we claimed that this would represent a wavepacket with width $\frac{1}{\sigma}$ in real space. Let us try to make this more precise.

What is the value of $\langle\psi|\vec{E}(\vec{r})|\psi\rangle$? The answer is zero! The electric field is proportional to $(a_{\vec{k}\lambda} - a^{\dagger}_{\vec{k}\lambda})$, so one operator raises the ket and one lowers the ket, meaning that when we take the inner product with the bra, we will get zero since all of the states are orthogonal.

Now we can look at the matrix element of the electric field between the vacuum state $|0\rangle$ and the one-photon wave packet state $|\psi\rangle$ defined above:

$$\langle 0|\vec{E}(\vec{r})|\psi\rangle = \sum_{\vec{k}\lambda\vec{k}'\lambda'} \overbrace{\langle 0|(a_{\vec{k}\lambda} - a^{\dagger}_{-\vec{k}\lambda})a^{\dagger}_{\vec{k}\,'\lambda'}|0\rangle}^{\delta_{\vec{k}\vec{k}\,'}\delta_{\lambda\lambda'}} \tag{19.4}$$

$$\times(Ne^{-|\vec{k}\,'-\vec{k}_0|^2/2\sigma^2}e^{-i\vec{k}\,'\cdot\vec{r}_0}(\hat{x}\cdot\epsilon^*_{\vec{k}\,'\lambda'})) \times \left(\left(\frac{1}{\Omega}\right)^{1/2}(2\pi\hbar kc)^{1/2}ie^{i\vec{k}\cdot\vec{r}}\hat{\epsilon}_{\vec{k}\lambda}\right)$$

$$= \sum_{\vec{k}\lambda} N\left(\frac{1}{\Omega}\right)^{1/2}(\hat{x}\cdot\hat{\epsilon}^*_{\vec{k}\lambda})\hat{\epsilon}_{\vec{k}\lambda}(2\pi\hbar kc)^{1/2}ie^{i(\vec{k}-\vec{k}_0)^2/2\sigma^2}e^{ik(\vec{r}-\vec{r}_0)} \tag{19.5}$$

Note that the symbol $\times$ indicates just a multiplication and not a cross product. Now since σ is small we will replace $\vec{k}$ by $\vec{k}_0$ except in the exponential. First we deal with the sum on λ. Each term in $\sum_\lambda \hat{\epsilon}^*_{\vec{k}\lambda}\hat{\epsilon}_{\vec{k}\lambda}$ is an outer product. If $\lambda = 1$ for example, this would be a projection onto the unit vector in the first polarization direction. For the case of the sum, we get a projection onto a 2-D plane which is perpendicular to $\vec{k}$ so this would give us the projection onto the transverse

part of the field. If we were to add to this the outer product $\hat{\vec{k}}\hat{\vec{k}}$, we would get back the identity matrix:

$$\sum_{\lambda=1}^{2} \hat{\epsilon}_{\vec{k}\lambda}^{*}\hat{\epsilon}_{\vec{k}\lambda} + \hat{k}\hat{k} = \mathbb{I} \tag{19.6}$$

Now, we set $\vec{k} = \vec{k}_0$, and carry out the inner product with $\hat{x}$:

$$\sum_{\lambda=1}^{2} (\hat{x} \cdot \hat{\epsilon}_{\vec{k}_0\lambda}^{*})\hat{\epsilon}_{\vec{k}_0\lambda} = \hat{x} - (\hat{x} \cdot \vec{k}_0)\vec{k}_0 = \hat{x} \tag{19.7}$$

So now our matrix element is:

$$\langle 0|\vec{E}(\vec{r})|\psi\rangle = \text{Const } i\hat{x} \sum_{\vec{k}} e^{i\vec{k}\cdot(\vec{r}-\vec{r}_0)}e^{-|\vec{k}-\vec{k}_0|^2/2\sigma^2} \tag{19.8}$$

If we now replace the sum over $\vec{k}$ with an integral with appropriate factors, we will essentially be taking a fourier transform. The fourier transform of a gaussian is just another gaussian:

$$\langle 0|\vec{E}(\vec{r})|\psi\rangle \propto \hat{x}\, e^{-|\vec{r}-\vec{r}_0|^2\sigma^2/2}e^{i\vec{k}_0\cdot(\vec{r}-\vec{r}_0)}. \tag{19.9}$$

This matrix element plays somewhat the same role as the wavefunction in the Schrödinger equation. It looks like a gaussian wavepacket, that is, it is just a plane wave times some gaussian envelope. We would get a similar result for the matrix element of $\vec{B}(\vec{r})$ except in that case it is proportional to $\hat{y}$.

What about the energy density $\langle\psi|u(\vec{r})|\psi\rangle$?

$$\langle\psi|u(\vec{r})|\psi\rangle = \frac{1}{8\pi}(\langle\psi| : \vec{E}(\vec{r})^2 : |\psi\rangle + \langle\psi| : \vec{B}(\vec{r})^2 : |\psi\rangle) \tag{19.10}$$

We now make the claim (it's a homework problem) that this matrix element is equivalent to:

$$\langle\psi| : \vec{E}(\vec{r})^2 : |\psi\rangle = 2|\langle 0|\vec{E}(\vec{r})|\psi\rangle|^2 \tag{19.11}$$

$$\langle\psi| : \vec{B}(\vec{r})^2 : |\psi\rangle = 2|\langle 0|\vec{B}(\vec{r})|\psi\rangle|^2 \tag{19.12}$$

This makes sense, and is not totally surprising, as the normal ordering brings the operators into an order with intermediary states that work out similarly to the matrix element for $\vec{E}(\vec{r})$. The energy density will also be a gaussian but with half the width of (19.9). Of course, the total energy will be $\approx \hbar c k_0$.

19.1.1   Forcing Terms and Coherent States

We now want to look at the situation in the presence of a non-zero current density $\vec{j}(\vec{r}, t)$. We have previously seen that the Heisenberg equations of motion in this case should give

$$\left(k^2 + \frac{1}{c^2}\frac{d^2}{dt^2}\right) A_{\vec{k}\lambda} = \frac{4\pi}{c}\vec{j}_{\vec{k}\lambda}, \tag{19.13}$$

which is the equation of a forced harmonic oscillator. From our experience with forced harmonic oscillators, we expect that we can get this equation of motion from a Hamiltonian of the form

$$H = H_{field} + H_{source}, \tag{19.14}$$

where the first term is the free-field Hamiltonian,

$$H_{field} = \sum_{\vec{k}\lambda} \hbar c k (a^\dagger_{\vec{k}\lambda} a_{\vec{k}\lambda}). \tag{19.15}$$

We may guess that the second term be linear in the current and linear in the photon creation and annihilation operators. To check this, and to get the precise coefficients, let us use the fact that $E_{\vec{k}\lambda} = -c^{-1} dA_{\vec{k}\lambda}/dt$ to write (19.13) in the form

$$\frac{dE_{\vec{k}\lambda}}{dt} = \frac{1}{i\hbar}[E_{\vec{k}\lambda}, H] = -4\pi \vec{j}_{\vec{k}\lambda} + k^2 c A_{\vec{k}\lambda}. \tag{19.16}$$

The last term on the right hand side comes from the commutator with H_{field}. The first term must come from the commutator with H_{source}. In a previous lecture we showed that the only non-vanishing commutators between the operators A and E can be written as $[E_{\vec{k}\lambda}, A_{\vec{k}'\lambda'}] = 4\pi i \hbar c \delta_{-\vec{k},\vec{k}'} \delta_{\lambda\lambda'}$. We see that we will recover (19.16) if we choose

$$H_{source} = -\frac{1}{c}\sum_{\vec{k}\lambda} j_{\vec{k}\lambda} A_{-\vec{k}\lambda} \tag{19.17}$$

$$= -\frac{1}{c}\sum_{\vec{k}\lambda} j_{\vec{k}\lambda} \left(\frac{2\pi\hbar c}{k}\right)^{1/2} (a^\dagger_{\vec{k}\lambda} + a_{-\vec{k}\lambda}) \tag{19.18}$$

$$= -\frac{1}{c}\int d^3 r\, \vec{A}(\vec{r}) \cdot \vec{j}(\vec{r}). \tag{19.19}$$

Let us now consider a situation where

$$\vec{j}(r, t) \neq 0 \qquad t > t_0 \tag{19.20}$$

$$\vec{j}(r, t) = 0 \qquad t < 0 \tag{19.21}$$

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Let us also suppose that our initial state is the vacuum state: $|\psi(t_0)\rangle = |0\rangle$. We want to know what is the time evolution of this state $|\psi(t)\rangle$ in the presence of the driving term.

The Heisenberg equations of motion for the annihilation operators are

$$\boxed{i\hbar\frac{d\bar{a}_{\vec{k}\lambda}}{dt} = \left[\bar{a}_{\vec{k}\lambda}, \bar{H}\right] = \hbar c k \bar{a}_{\vec{k}\lambda} - \frac{1}{c}j_{\vec{k}\lambda}\left(\frac{2\pi\hbar c}{k}\right)^{1/2}}, \tag{19.22}$$

which is just the equation for a forced Harmonic oscillator that we encountered previously. We can solve it by the Green's function method, to obtain

$$\bar{a}_{\vec{k}\lambda}(t) = \bar{a}_{\vec{k}\lambda}(t_0)e^{-ick(t-t_0)} + \alpha_{\vec{k}\lambda}(t) \tag{19.23}$$

where the $\alpha_{\vec{k}\lambda}$ is similar to what we found in p251b lecture 15:

$$\boxed{\alpha_{\vec{k}\lambda} = -\frac{i}{\hbar c}\int_{t_0}^{t} dt'\, e^{-ick(t-t')}j_{\vec{k}\lambda}(t')\left(\frac{2\pi\hbar c}{k}\right)^{1/2}} \tag{19.24}$$

If the initial state at $t = t_0$ is the vacuum state, then in the Heisenberg picture

$$\bar{a}_{\vec{k}\lambda}(t_0)|\bar{\psi}\rangle = 0, \tag{19.25}$$

and at a later time t we will have:

$$\bar{a}_{\vec{k}\lambda}(t)|\bar{\psi}\rangle = \alpha_{\vec{k}\lambda}|\bar{\psi}\rangle. \tag{19.26}$$

In the Schrödinger picture therefore we have:

$$\boxed{a_{\vec{k}\lambda}|\psi(t)\rangle = \alpha_{\vec{k}\lambda}|\psi(t)\rangle} \tag{19.27}$$

which is the definition of a coherent state. More precisely, the state is a product of coherent states for every one of the harmonic oscillator modes $(\vec{k}, \lambda)$. We call this a coherent state of the photon field.

We can now look into the expectation value of $\vec{E}(\vec{r})$ in a coherent state $\langle\psi|\vec{E}(\vec{r})|\psi\rangle$. The expectation values of the creation and annihilation states will be:

$$\langle\psi|a_{\vec{k}\lambda}^{\dagger}|\psi\rangle = \alpha_{\vec{k}\lambda}^{*} \qquad \langle\psi|a_{\vec{k}\lambda}|\psi\rangle = \alpha_{\vec{k}\lambda} \tag{19.28}$$

Therefore the expectation value of the field will be:

$$\langle\psi|\vec{E}(\vec{r})|\psi\rangle = \sum_{\vec{k}\lambda}\left(\frac{1}{\Omega}\right)^{1/2}i(2\pi\hbar ck)^{1/2}e^{i\vec{k}\cdot\vec{r}}\hat{\epsilon}_{\vec{k}\lambda}(\alpha_{\vec{k}\lambda} - \alpha_{-\vec{k}\lambda}^{*}) \tag{19.29}$$

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Similarly, the expectation value of the magnetic field will be given by:

$$\langle\psi|\vec{B}(\vec{r})|\psi\rangle = \sum_{\vec{k}\lambda} \left(\frac{1}{\Omega}\right)^{1/2} (i\vec{k}\times\hat{\epsilon}_{\vec{k}\lambda}) \left(\frac{2\pi\hbar c}{k}\right)^{1/2} e^{i\vec{k}\cdot\vec{r}}(\alpha_{\vec{k}\lambda} + \alpha^*_{-\vec{k}\lambda}) \tag{19.30}$$

It is now relevant to note, looking back at equation (19.24) that $\alpha_{\vec{k}\lambda} \propto \hbar^{-1/2}$ while we see that equations (19.29) and (19.30) have another $\sqrt{\hbar}$ in the numerator. These factors cancel, leaving $\langle\psi|\vec{E}(\vec{r})|\psi\rangle$ and $\langle\psi|\vec{B}(\vec{r})|\psi\rangle \propto \hbar^0$. This is what we would expect, that the expectation values of fields would only depend on classical variables. These coherent states are as close as we can get in quantum mechanics to a classical electromagnetic state. We can see, however, that these coherent states cannot have a definite photon number.

We also claim that the expectation value of the energy density in a coherent state is given by:

$$\langle\psi|u(\vec{r})|\psi\rangle = \frac{1}{8\pi}(|\langle\vec{E}_{trans}(\vec{r})\rangle|^2 + |\langle\vec{B}(\vec{r})\rangle|^2) \tag{19.31}$$

So the expectation value of the energy density in coherent states created by some current is exactly the same as in classical E+M, and the energy density of the coherent state is related to the expectation value of the electric and magnetic fields in just the same way as the energy density is related to the fields in classical E+M. This is very different than in a single photon state, where the energy density is finite but the expectation values of the fields are zero.

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20.1   Charged Particles in E+M Fields

To describe a quantum mechanical system of charged particles and electromagnetic fields, we must first enlarge the Hilbert space to include degrees of freedom for the particles as well as the fields. We shall assume a Hllbert space that is the direct product of the field space discussed in the last few lectures and the usual Hilbert space for a collection of non-relativistic charged particles. In addition to the operators for the electromagnetic field, we will have operators such as $\vec{p}_i$ and $\vec{r}_i$ for the the particles. The particle operators commute with the field operators, and obey the usual commutation rules among themselves.

Our strategy will be to find the simplest possible quantum Hamiltonian which generates the correct equations of motion in the classical limit, and then see whether (1) the Hamiltonian makes sense, and (2) its predictions agree with experiment. The Hamiltonian must correctly describe both the motion of the charged particles and of the fields. Without loss of generality, we may write the Hamiltonian as

$$H_{free\ field} + H_{source}, \tag{20.1}$$

where $H_{free\ field}$ is the Hamiltonian for the fields in the absence of current sources, and H_{source} is whatever is left over. The source term must generate the motion of the particles and also give rise to the response of the fields to the moving charges. From our work in Physics 251a, we know what should be the form of the Hamiltonian for a collection of charged particles in a classical external electromagnetic field, described by a vector potential $\vec{A}(\vec{r}, t)$ and an external scalar potential $\Phi_{ext}(\vec{r}, t)$. The simplest first guess is to use the same Hamiltonian as H_{source}, only interpreting the vector potential $\vec{A}$ as a quantum mechanical operator in the Coulomb gauge. Then ignoring any interactions with a particle's spin magnetic moment, we have

$$H_{source} = \sum_i \frac{|\vec{p}_i - \frac{q_i \vec{A}(\vec{r}, t)}{c}|^2}{2m_i} + \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} + \sum_i q_i \Phi_{ext}(\vec{r}_i) \tag{20.2}$$

Here we have allowed for the possibility of a time-independent external scalar potential that might arise from fixed external charges (such as infinitely massive ions) not included explicitly in our Hilbert space, but we have no external vector potential $\vec{A}_{ext}$.

To understand better what this Hamiltonian means, it is convenient to expand out the vector potential in terms of the mode operators $A_{\vec{k}\lambda}$:

$$\vec{A}(\vec{r}, t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}\lambda} A_{\vec{k}\lambda}(t) e^{i\vec{k}\cdot\vec{r}} \hat{\epsilon}_{\vec{k}\,\lambda} \tag{20.3}$$

1

To obtain the operator $\vec{A}(\vec{r}_i, t)$, we simply replace the factor $e^{i\vec{k}\cdot\vec{r}}$ in the equation above by the operator $e^{i\vec{k}\cdot\vec{r}_i}$. Then when we take the commutator of $\vec{A}(\vec{r}_i)$ with a particle operator such as $\vec{p}_i$, we get a contribution from the commutator with $e^{i\vec{k}\cdot\vec{r}_i}$, but there is no contribution from the commutator with $A_{\vec{k}\lambda}$, which is zero.

The Heisenberg equations of motion for $\vec{r}_i$ and $\vec{p}_i$ are obtained by taking the commutators with H_{source}. There is no contribution from the free field Hamiltonian. In Physics 251a, we calculated the relevant commutators assuming that $\vec{A}(\vec{r}, t)$ was a classical variable. We saw that these commutators lead to the correct equations of motion for the particle in the classical limit, and in fact the Heisenberg equations of motion have precisely the same form as the classical equations. In particular, one obtains

$$\frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i - \frac{q_i}{c}\vec{A}(\vec{r}_i)}{m_i} \tag{20.4}$$

$$m\ddot{\vec{r}}_i = q_i \left(\vec{E}(\vec{r}_i) + \frac{d\vec{r}_i}{dt} \times \frac{\vec{B}(\vec{r}_i)}{c} \right) \tag{20.5}$$

where

$$\vec{B}(\vec{r}, t) = \nabla \times \vec{A}(\vec{r}, t) \tag{20.6}$$

and the electric field is the sum of 3 parts.

$$\vec{E} = \vec{E}_{external} + \vec{E}_{transverse} + \vec{E}_{longitudinal}, \tag{20.7}$$

given by:

$$\vec{E}_{ext} = -\nabla\Phi_{ext}, \qquad \vec{E}_{trans} = -\frac{1}{c}\frac{\partial\vec{A}}{\partial t}, \tag{20.8}$$

$$E_{long}(\vec{r}_i) = -\sum_{j\neq i} q_j \frac{\partial}{\partial\vec{r}_i} \left(\frac{1}{|\vec{r}_i - \vec{r}_j|} \right). \tag{20.9}$$

Now if we consider the coefficients $\vec{A}_{\vec{k}\lambda}$ to be quantum mechanical operators instead of c-numbers, this will not change the form of the equations of motion for the particles, since the particle position and momentum operators commute with the field mode operators. The only difference is that the quantities $\vec{B}(\vec{r}_i)$ and $\vec{E}_{trans}(\vec{r}_i)$ are now operators, which may be expanded in terms of field mode operators and position operators $e^{i\vec{k}\cdot\vec{r}_i}$ in the same way as we did for $\vec{A}$.

To calculate the Heisenberg equations of motion for $\vec{A}_{\vec{k}\lambda}$ and $\vec{E}_{\vec{k}\lambda}$, we must take their commutators with the Hamiltonian H, given by (20.1) and (20.2). The results may be written in the form:

$$\frac{1}{c^2}\ddot{A}_{\vec{k}\lambda} + k^2 A_{\vec{k}\lambda} = \frac{4\pi}{c} j_{\vec{k}\lambda}, \tag{20.10}$$

where, now, $\vec{j}_{\vec{k}\lambda}$ will be given by:

$$j_{\vec{k}\lambda} = \sum_i q_i e^{-i\vec{k}\cdot\vec{r}_i} \left(\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \frac{d\vec{r}_i}{dt} \right) \tag{20.11}$$

where the velocity operator is given by (20.4).

In the equation (20.11), we have written the operator $\vec{k}\cdot\vec{r}_i$ (in the exponential) to the left of the operator $\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \vec{p}_i/m$, which is the first term in (20.4). The order does not matter; the terms actually commute, because $\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \vec{k} = 0$. Note that $j_{-\vec{k},\lambda} = j^\dagger_{\vec{k}\lambda}$, as we would expect for the Fourier expansion coefficients of the current density, which is a Hermitian operator:

$$\vec{j}(\vec{r}) = \sum_i \frac{q_i}{2m_i} \left\{ (\vec{p}_i - \frac{q_i}{c}\vec{A}(\vec{r}_i)),\ \delta(\vec{r} - \vec{r}_i) \right\}$$

If we want to include effects of coupling to the spin magnetic moment, we should add to H_{source} the term:

$$H_{spin} = -\sum_i \gamma_i \vec{B}(\vec{r}_i) \cdot \vec{S}_i \tag{20.12}$$

where γ_i is the gyromagnetic ratio of the ith particle. If the particle has charge $q_i \neq 0$, it is customary to write

$$\gamma_i = \frac{g_i q_i}{2 m_i c} \tag{20.13}$$

where the dimensionless constant g_i is the g factor of the particle. For the electron, the g factor is close to 2. Naive classical physics predicts a g factor of 1, the Dirac equation predicts a factor of 2, and QED gives higher order corrections to that value in terms of the fine structure constant α.

$$g \simeq 2 \qquad \frac{g-2}{2} = \frac{\alpha}{2\pi} + \mathcal{O}(\alpha^2) \tag{20.14}$$

The term H_{spin} leads to an additional force term on the right hand side of Eq. (20.5), equal to $\gamma_i \vec{S}_i \cdot \nabla \vec{B}(\vec{r}_i)$. It also changes the equation of motion for $A_{\vec{k}\lambda}$, Eq. (20.10), by adding a term in the current arising from the magnetic moment. Specifically, we now have

$$j_{\vec{k}\lambda} = \frac{1}{\Omega^{1/2}} \sum_i q_i e^{-i\vec{k}\cdot\vec{r}_i} \hat{\epsilon}_{\vec{k}\lambda} \cdot \frac{\vec{p}_i - \frac{q_i}{c}\vec{A}(\vec{r}_i)}{m_i} - \frac{1}{\Omega^{1/2}} \sum_i e^{-\vec{k}\cdot\vec{r}_i} (i\vec{k} \times \hat{\epsilon}_{\vec{k}\lambda}) \cdot (\gamma_i \vec{S}_i) \tag{20.15}$$

We can also obtain the Heisenberg equations of motion for the creation and annihilation operators. We find

$$i\hbar \frac{da_{\vec{k}\lambda}}{dt} = \left[a_{\vec{k}\lambda}, H \right] \tag{20.16}$$

$$= \hbar\omega_k a_{\vec{k}\lambda} - \frac{1}{c} \left(\frac{2\pi\hbar c}{k} \right)^{1/2} j_{\vec{k}\lambda}, \tag{20.17}$$

3

where $j_{\vec{k}\lambda}$ is the operator defined above.

The above equations are operator equations, and they are coupled together in a complicated way, so that they would be impossible to solve even in the classical limit. However, we can proceed using perturbation theory, assuming that the coupling to the transverse electromagnetic field is weak. Ultimately, it turns out that this works, and that the expansion parameter is the fine structure constant $\alpha = e^2/\hbar c \approx 1/137$.

20.1.1   Perturbation theory

We expand the source Hamiltonian, and treat all terms that have vector potential terms in them as a perturbation. We write

$$H = H_0 + H_1 \tag{20.18}$$

where the unperturbed Hamiltonian consists of:

$$H_0 = H_{free\,field} + H_{part}^0 \tag{20.19}$$

$$H_{part}^0 = \sum \frac{p_i^2}{2m} + \frac{1}{2}\sum_{j\neq i}\frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} + \sum_i q_i \Phi_{ext}(\vec{r}_i) \tag{20.20}$$

The perturbation Hamiltonian consists of the remaining terms in the source Hamiltonian:

$$H_1 = \sum_i \frac{|\vec{p}_i - \frac{q_i \vec{A}(\vec{r}_i)}{c}|^2 - p_i^2}{2m_i} \tag{20.21}$$

We can break this up into terms, one that involves products of vector potential and a momentum, and one that has terms with the vector potential squared:

$$H_1 = H_{\vec{A}\cdot\vec{p}} + H_{A^2} \tag{20.22}$$

The cross term Hamiltonian is:

$$H_{\vec{A}\cdot\vec{p}} = -\sum_i \sum_{\vec{k}\lambda} \frac{1}{\Omega^{1/2}} A_{\vec{k}\lambda}^\dagger e^{-i\vec{k}\cdot\vec{r}_i}(\hat{\epsilon}_{\vec{k}\lambda}^* \cdot \vec{p}_i)\frac{q_i}{m_i c} \tag{20.23}$$

This term doesn't present any immediate problems. The vector potential squared term will be:

$$H_{A^2} = \sum_i \frac{q_i^2}{2m_i c^2}\frac{1}{\Omega}\sum_{\vec{k}\lambda}\sum_{\vec{k}\,'\lambda'} e^{i(\vec{k}+\vec{k}\,')\cdot\vec{r}_i}(2\pi\hbar c)\frac{1}{(kk')^{1/2}}\hat{\epsilon}_{\vec{k}\lambda}\cdot\epsilon_{\vec{k}\,'\lambda'}(a_{\vec{k}\lambda}+a_{-\vec{k}\lambda}^\dagger)(a_{\vec{k}\,'\lambda'}+a_{-\vec{k}\,'\lambda'}^\dagger) \tag{20.24}$$

4

This term is not normal ordered, and the vacuum expectation value of this term would give an additional infinite contribution due to the sum over all of the modes. Therefore, let us rewrite the term as a sum of a normal ordered part and a conatant obtained from the commutators:

$$H_{A^2} =: H_{A^2} : + \sum_i \frac{q_i^2}{2m_i c^2} \left(\frac{1}{\Omega} \sum_{\vec{k}\lambda} \frac{2\pi\hbar c}{k} \right) \tag{20.25}$$

The second term is infinite, but it is just a constant, because in non-relativistic quantum mechanics, particles are not created or destroyed. If the momentum sum had an upper cutoff, the constant would be large but it would be the same for all states of the system with a given number of particles, so it would not affect the equations of motion. Therefore, we can throw it away, just as we ignored the infinite terms in the vacuum energy when there were no particles present.

This term would be a problem in relativistic quantum mechanics, where particles can be created and destroyed. However, coupling terms quadratic in A do not appear in the Dirac equation, so this particular infinity does not occur in relativistic quantum electrodynamics.

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21.1 Spontaneous Radiation, Photon Absorption and Stimulated Emission

We discuss three problems that concern the quantum mechanical description of the electromagnetic field interacting with non relativistic charged particles.

- Spontaneous radiation

- Photon absorption.

- Stimulated emission.

We will calculate all of these using perturbation theory and Fermi's Golden Rule[1]. To do this we need to split the Hamiltonian into unperturbed H_0 and perturbed H_1 components.

$$H = H_0 + H' \tag{21.1}$$

The unperturbed Hamiltonian will consist of the free field Hamiltonian (sum over the photon modes) and a second term taking into account the kinetic energy of all the charged particles and their interactions with the electrostatic coulomb field of the nuclei and the electrons themselves.

$$H_0 = H^0_{field} + H^0_{particles} \tag{21.2}$$

$$H_{field} = \sum_{\vec{k}\lambda} \hbar c k (a^\dagger_{\vec{k}\lambda} a_{\vec{k}\lambda}) \tag{21.3}$$

$$H^0_{particles} = \text{Kinetic Energy} + \text{Potential Energy of Electrons for} \, \vec{A} = 0. \tag{21.4}$$

Working out the quantum mechanics of this unperturbed system alone is a formidable task, but let us assume that we have solved this problem exactly and that we know what the allowable eigenstates of the system are.

The perturbation to this system will take the form:

$$H' = H_{AP} + H_{A^2} \tag{21.5}$$

$$H_{\vec{A}\cdot\vec{p}} = -\sum_i \sum_{\vec{k}\lambda} \frac{1}{\Omega^{1/2}} A^\dagger_{\vec{k}\lambda} e^{-i\vec{k}\cdot\vec{r}_i} (\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \vec{p}_i) \frac{q_i}{m_i c} \tag{21.6}$$

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[1]See P251b Lecture 10 for reference

$$H_{A^2} = \sum_i \frac{q_i^2}{2m_ic^2} \frac{1}{\Omega} \sum_{\vec{k}\lambda} \sum_{\vec{k}'\lambda'} e^{i(\vec{k}+\vec{k}')\cdot\vec{r}_i}(2\pi\hbar c)\frac{1}{(kk')^{1/2}}\hat{\epsilon}_{\vec{k}\lambda}\cdot\epsilon_{\vec{k}'\lambda'} : (a_{\vec{k}\lambda}+a^\dagger_{-\vec{k}\lambda})(a_{\vec{k}'\lambda'}+a^\dagger_{-\vec{k}'\lambda'}) :$$

$$(21.7)$$

In the situations we consider in this lecture, we will only be looking at matrix elements between states that differ by a photon number of one. Therefore when we use Fermi's golden rule and take a matrix element, there will not be a contribution from the H_{A^2} term. The $H_{\vec{A}\cdot\vec{p}}$ will have a contribution.

21.1.1   Spontaneous Emission from an Atom

We consider an initial state of the system where the atom is in an excited state $|n\rangle$ and the photon field is in the vacuum state $|0\rangle$ (no photons present). In the final state we have the atom in a lower energy state $|n'\rangle$ and the photon field in the state $|1_{\vec{k}\lambda}\rangle$ (one photon present with momentum $\vec{k}$ and polarization λ). We want to calculate this in perturbation theory, using Fermi's Golden rule. In the end, this will turn out to be the first term an expansion in $v_{el}/c \sim \alpha$, where v_{el} is a typical velocity of the electron.

We want to calculate the transition rate from $|n\rangle \rightarrow |n'\rangle$:

$$\gamma_{n\rightarrow n'} = \frac{2\pi}{\hbar} \sum_{\vec{k}\lambda} |\langle 1_{\vec{k}\lambda}, n'|H_{\vec{A}\cdot\vec{p}}|0, n\rangle|^2 \delta(E_{n'} + \hbar\omega_k - E_n) \qquad (21.8)$$

As mentioned above for this transition the matrix element:

$$\langle....|H_{A^2}|....\rangle = 0 \qquad (21.9)$$

In order to evaluate the matrix element in equation (21.8) we separate out the photon and particle spaces. First we look at the photon part:

$$\langle 1_{\vec{k}\lambda}|A^\dagger_{\vec{k}'\lambda'}|0\rangle = \left(\frac{2\pi\hbar c}{k}\right)^{1/2} \delta_{\vec{k}\vec{k}'}\delta_{\lambda\lambda'} \qquad (21.10)$$

This follows from the form of $A_{\vec{k}\lambda}$:

$$A_{\vec{k}\lambda} = \left(\frac{2\pi\hbar c}{k}\right)^{1/2} (a_{\vec{k}\lambda}+a^\dagger_{-\vec{k}\lambda}) \qquad (21.11)$$

Plugging this back into the matrix element from (21.8) we are left with:

$$\langle 1_{\vec{k}\lambda}, n'|H_{\vec{A}\cdot\vec{p}}|0, n\rangle = -\frac{1}{\Omega^{1/2}}\left(\frac{2\pi\hbar c}{k}\right)^{1/2}\langle n'|\sum_i \frac{q_i}{m_ic}e^{-i\vec{k}\cdot\vec{r}_i}\hat{\epsilon}^*_{\vec{k}\lambda}\cdot\vec{p}_i|n\rangle \qquad (21.12)$$

We still have to calculate the $\langle n| \, |n'\rangle$ matrix element on the right hand side of (21.12). This may be a difficult calculation, but we can at least simplify things somewhat. If we are interested in the case of a transition from one atomic state to another, the typical photon energy will be on the order of 1 eV. The wavelength of such a photon will be much greater than the Bohr radius a_H. This means we can make the dipole approximation – we set the exponential equal to one, and the matrix element becomes:

$$- \langle 1_{\vec{k}\lambda}, n'|H_{\vec{A}\cdot\vec{p}}|0, n\rangle \;\; = \;\; -\frac{1}{c}\langle n'| \sum_i \frac{q_i}{m_i}\vec{p}_i|n\rangle \cdot \hat{\epsilon}^*_{\vec{k}\lambda}\frac{1}{\sqrt{\Omega}}\left(\frac{2\pi\hbar c}{k}\right)^{1/2} \tag{21.13}$$

$$= \;\; \frac{1}{c}i\omega_{n'n}\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \vec{d}_{n'n}\frac{1}{\sqrt{\Omega}}\left(\frac{2\pi\hbar c}{k}\right)^{1/2} \tag{21.14}$$

Now looking back to equation (21.8) we need to do a sum over all the modes. We change the sum over $\vec{k}$ to an integral:

$$\sum_{\vec{k}} \rightarrow \frac{\Omega}{(2\pi)^3}\int d^3k \tag{21.15}$$

We also have the sum over λ. If we were to sum over $\lambda = 1$ to $\lambda = 3$, 3 being the unit vector in the direction of $\vec{k}$ then we would be doing a projection onto three orthogonal unit vectors, and we would just get back the length of the vector we are dotting into. However, since we are only dealing with the 2 λ's defined as orthogonal to the direction of $\vec{k}$ – when we average over all possible directions of emission we will get back 2/3 the length of the vector.

$$\sum_{\lambda=1}^{2} |\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \vec{d}_{n'n}|^2 = |\vec{d}_{n'n}|^2 - |\hat{k} \cdot \vec{d}_{n'n}|^2 \rightarrow \frac{2}{3}|\vec{d}_{n'n}|^2 \tag{21.16}$$

(Note: If $\vec{d}_{n'n}$ is real, then $|\hat{k} \cdot \vec{d}_{n'n}|^2 = |\vec{d}_{n'n}|^2 \cos^2\theta$, where θ is the angle between $\hat{k}$ and $\vec{d}_{n'n}$. On averaging over directions of $\hat{k}$, the factor $\cos^2\theta$ is replaced by 1/3. If $\vec{d}_{n'n}$ is complex, we perform the same analysis for the real and imaginary parts separately.)

Using $\omega_k = ck$, we make a variable change in the delta function:

$$\delta(E_{n'} + \hbar\omega_k - E_n) = \frac{1}{\hbar c}\delta\left(|\vec{k}| - \frac{\omega_{nn'}}{c}\right) \tag{21.17}$$

The transition rate then becomes:

$$\gamma_{nn'} = \frac{2\pi}{\hbar}\int \frac{d^3k}{(2\pi)^3} \frac{\delta\left(|\vec{k}| - \frac{\omega_{nn'}}{c}\right)}{\hbar c}\frac{1}{c^2}\omega^2_{n'n}|\vec{d}_{n'n}|^2\left(\frac{2}{3}\right)\left(\frac{2\pi\hbar c}{k}\right) \tag{21.18}$$

So the transition rate from state n to n' is:

$$\boxed{\gamma_{nn'} = \frac{4}{3\hbar}k^3|\vec{d}_{n'n}|^2} \tag{21.19}$$

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The radiation rate is proportional to $k^3 = \frac{\omega^3}{c^3}$, so it is small, down by a factor $(v_{\text{el}}/c)^3 \approx \alpha^3$ compared to a typical electronic frequency. The total decay rate Γ is given by:

$$\boxed{\Gamma = \sum_{n'} \gamma_{nn'} = \sum_{\alpha=x,y,z} \int_{-\infty}^{0} d\omega \, g_{\alpha\alpha}(\omega) \frac{4\pi}{3\hbar} \frac{|\omega|^3}{c^3}} \tag{21.20}$$

where the spectral functions (first presented in (p251b lecture 4) are defined as:

$$g_{\alpha\beta}(\omega) = \sum_{n'} \langle n|d^\alpha|n'\rangle \langle n'|d^\beta|n\rangle \delta(\omega - \omega_{n' n}) \tag{21.21}$$

This is the spontaneous emission rate, the key result of all of our efforts. It is a result we were unable to get using the semiclassical method.

21.1.2   Absorption, Stimulated and Spontaneous Emission

Now we want to consider what happens when an atom or molecule that is initially in an eigenstate of its Hamiltonian, which may or may not be its ground state, is illuminated by an incident beam of photons. We assume that the beam is sufficiently dilute that the atom interacts with at most one photon at a time in the incident beam. In principle we should describe the incident photon as a one-photon wave packet, and use time-dependent perturbation theory to see what happens.

Instead, we shall use Fermi's golden rule in this case and cheat, in the same way that we previously obtained the Born approximation for elastic or inelastic scattering of a particle from a target. Then, when we are done, we will go back and see if our results make sense.

For the initial state $|i\rangle$ we assume that have the atom in state n and N photons all in the same state $\vec{k}, \lambda$:

$$|i\rangle = |n, (N)_{\vec{k}\lambda}\rangle \qquad N > 0 \tag{21.22}$$

For the final state we consider here three possibilities:

1. $|n', (N-1)_{\vec{k}\lambda}\rangle$ – Absorption.

2. $|n', (N+1)_{\vec{k}\lambda}\rangle$ – Stimulated Emission.

3. $|n', (N)_{\vec{k}\lambda}, 1_{\vec{k}'\lambda'}\rangle$ – Spontaneous Emission.

If the atom is in the ground state, only the first case is possible. For excited states, all three can happen. We consider first the case of absorption, so the final state $|f\rangle$ will be

$$|f\rangle = |n', (N-1)_{\vec{k}\lambda}\rangle \tag{21.23}$$

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If $M_{n'n}$ is the matrix element of the operator $\sum_i \frac{q_i}{m_i c} e^{i\vec{k}' \cdot \vec{r}_i} \hat{\epsilon}_{\vec{k}' \lambda'} \cdot \vec{p}_i$ between the states $\langle n'|$ and $|n\rangle$, then we find:

$$\langle f | H_{\vec{A} \cdot \vec{p}} | i \rangle = \Omega^{-1/2} \langle (N-1)_{\vec{k}\lambda} | A_{\vec{k}'\lambda'} | N_{\vec{k}\lambda} \rangle M_{n'n}, \tag{21.24}$$

$$\langle (N-1)_{\vec{k}\lambda} | A_{\vec{k}'\lambda'} | N_{\vec{k}\lambda} \rangle = \left(\frac{2\pi \hbar c}{k} \right)^{1/2} \langle (N-1)_{\vec{k}\lambda} | a_{\vec{k}'\lambda'} + a^\dagger_{-\vec{k}'\lambda'} | N_{\vec{k}\lambda} \rangle \tag{21.25}$$

$$= \left(\frac{2\pi \hbar c}{k} \right)^{1/2} \sqrt{N} \delta_{\vec{k}\vec{k}'} \delta_{\lambda\lambda'} \tag{21.26}$$

Then, in the electric-dipole approximation, the absorption rate will be:

$$\gamma_{abs} = \frac{2\pi}{\hbar} \sum_{n'} |\langle f | H_{\vec{A} \cdot \vec{p}} | i \rangle|^2 \delta(E_{n'} - E_n - \hbar \omega_k) \tag{21.27}$$

$$= \frac{2\pi}{\hbar} \sum_{n'} \delta(\omega_k - \omega_{n'n}) |\hat{\epsilon}_{\vec{k}\lambda} \cdot \vec{d}_{nn'}|^2 \frac{N}{\Omega} 2\pi \omega_k \tag{21.28}$$

So we can see that the absorption rate will be proportional to the number of photons present, N. To obtain a cross-section, we divide by the incident flux, given by: $\frac{Nc}{\Omega}$. Therefore the cross section will be:

$$\sigma_{abs} = \frac{\gamma_{abs}}{\frac{Nc}{\Omega}} = \frac{(2\pi)^2}{\hbar} \frac{\omega_k}{c} \sum_{n'} \delta(\omega_k - \omega_{n'n}) |\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \vec{d}_{n'n}|^2 \tag{21.29}$$

This is the same as the semi-classical result we obtained previously.

For the case of stimulated emission, we use the final state:

$$|f\rangle = |n', (N+1)_{\vec{k}\lambda}\rangle \tag{21.30}$$

which will yield a rate of:

$$\gamma_{s.e.} = \frac{(2\pi)^2}{\hbar\Omega} \omega_k \sum_{n'} \delta(\omega_k + \omega_{n'n}) |\hat{\epsilon}^*_{\vec{k}\lambda} \cdot \vec{d}_{nn'}|^2 (N+1) \tag{21.31}$$

This is now proportional to $(N+1)$. The contribution of the 1 is the same as if we had $N = 0$; so we may group it together with the contributions of all the photon states with $\vec{k}', \lambda' \neq \vec{k}, \lambda$, as one small contribution to the total decay rate due to spontaneous emission, which is independent of N. The rest of the contribution to (21.31) is from the term proportional to N and it is the true stimulated emission contribution. Here the rate of decay of atoms emitting photons into a particular mode is proportional to the number of photons already in that mode. This rate leads to the same stimulated emission cross-section as we obtained previously in our semiclassical calculation.

Now, however, we should examine these problems more carefully, and ask whether we were actually justified in using the Fermi's Golden Rule, and whether our interpretation of the results was strictly correct.

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22.1   Elastic and Inelastic Scattering of a Photon

We discuss elastic or inelastic scattering of a photon off an atom or a molecule. We assume the scattering is off of the electrons, as the nucleus is too massive, and does not respond. We won't go through all the details here, but just hit the highlights of what is going on. Full details are given in the Handout on Photon Scattering, posted on the course web site.

As before we will address this problem using perturbation theory. The full Hamiltonian is split into an unperturbed and perturbed part.

$$H = H_0 + H' \tag{22.1}$$

The unperturbed part is given by:

$$H_0 = H^0_{photon} + H^0_{atom} \tag{22.2}$$

We assume that we can solve this exactly, there are no vector potential terms in H_0. The perturbation is split into two terms, one linear and one quadratic in the vector potential $\vec{A}$. The forms of these were given in lecture p251b Lecture 21

$$H' = H_{\vec{A}\cdot\vec{p}} + H_{A^2} \tag{22.3}$$

We want to calculate the scattering of a photon in a way that is similar to what we did for absorption and emission in the previous lecture. There is an important difference, however. Now, we cannot stop at lowest order perturbation theory, so we cannot simply use Fermi's golden rule. The strategy will be essentially the same though. We assume that we have a single photon in state $|\vec{k}, \lambda\rangle$ atom in a ground eigenstate state $|s\rangle$ of H_0.

We ask what is the transition to a bunch of possible final states. We will then translate this into a cross section by dividing the transition rate by the incident flux.

One possible final state is where the photon gets absorbed. This is absorption which we have covered before. There are two cases here, either (1) the final state is a continuum state and the electron is ejected from the atom, which is the case of photo-emission, or (2) the photon has the energy less than the threshold for photoemission, but it happens to be at the energy separation of the ground state and an excited state. In this case, eventually the atom will redecay and one or more photons will be emitted. Thus, strictly speaking this is not a case of absorption of a photon but of "resonant scattering." Therefore, true absorption is only relevant

in the photoemission case, where the final state has no photons and the electron in a continuum excited state:

$$|f\rangle = |0\rangle|n\rangle \qquad \omega_{ns} = \omega_k = kc \tag{22.4}$$

Now suppose we have a photon coming in that has energy below the photoemission threshold and is *not* equal to the energy separation of some transition. In this case, we can still get a scattering event where the final state of the atom is in some n and the photon comes out with some frequency ω_k. There are, again, two cases here. Either the atom remains in its ground state, and the photon is scattered with the same energy it had before. This is the case of elastic scattering. Or, the atom is in some different final state, and therefore the photon must have a different final energy. This is the case of inelastic scattering. The two cases are summarized as

$$|1_{\vec{k}\,',\lambda'}\rangle|n\rangle \left\{ \begin{array}{ll} |n\rangle = |s\rangle & |\vec{k}\,'| = |\vec{k}| \;\;(\text{elastic}) \\ |n\rangle \neq |s\rangle & |\vec{k}\,'| \neq |\vec{k}| \;\;(\text{inelastic}) \end{array} \right\} \tag{22.5}$$

In the inelastic case, eventually one or more additional phonons will come out as the excited state decays. In practice, the inelastic process is relatively unlikely, if the incident phonon energy is not in resonance with some transition between the ground state and an excited state, and we will concentrate on the elastic process.

22.1.1   Elastic scattering far from resonance

We first consider the case where the initial photon energy is not near a transition of the atom. To calculate this rate, we use the T-matrix generalization of Fermi's golden rule given on p.8 of the handout given in class. We will just give an outline of the derivation here, but the student should look at the more detailed derivation there.

At the end of derivation, we see that we are left with a formalism that requires the same conditions as Fermi's golden rule (see p251b lecture 10), for example – a continuum of final states. Using this we find that the transition rate for some initial state $|i\rangle$ to some final state $|f\rangle$

$$\gamma_{(f)} = \frac{2\pi}{\hbar}|\langle f|T(E)|i\rangle|^2 \delta(E_f - E_i) \tag{22.6}$$

This looks very similar to Fermi's Golden rule, but instead of having the perturbation Hamiltonian in the matrix element, we have this new quantity (described on page one of the handout) defined as:

$$T(E) = H' + H'GH' + H'GH'GH' + ... \tag{22.7}$$

where the operator G is given by:

$$G = \frac{1}{E - H_0 + i0^+} = \sum_j \frac{|j\rangle \langle j|}{E - E_j^0 + i0^+} \tag{22.8}$$

Equation (22.7) looks a lot like the formulas from p251a for Brillouin-Wigner perturbation theory, but now we are dealing with continuum states rather than discrete states. The final state for this elastic scattering process will be:

$$|f\rangle = |1_{\vec{k}\,'\lambda'}\rangle |s\rangle \tag{22.9}$$

The incident flux is given by $\frac{N}{\Omega} c$, where here $N = 1$. Therefore the cross section will be given by:

$$\sigma_{tot} = \frac{\Omega}{c} \sum_{\vec{k}\,'\lambda'} \gamma_{\vec{k}\,'\lambda'} \tag{22.10}$$

Now we have to calculate the quantity $\gamma_{\vec{k}\,'\lambda'}$. When we did this for the case of absorption and emission, we had initial and final photon occupation states that differed by 1. In that case we had no contribution form the H_{A^2} term. In the case of scattering, there is a contribution from the quadratic term, but not from the $H_{\vec{A}\cdot\vec{p}}$ term, in first order perturbation theory. However, the $H_{\vec{A}\cdot\vec{p}}$ term can contribute in second order perturbation theory This contribution could be important, because $H_{\vec{A}\cdot\vec{p}}$ has only one factor of c in the denominator, while the quadratic term has two. (Ultimately our perturbation calculations only make sense because the velocity of the electron is much slower than the speed of light by a factor of the fine-structure constant $\alpha = e^2/\hbar c$.) So roughly, we may guess that

$$H_{\vec{A}\cdot\vec{p}} = \mathcal{O}\left(\frac{e^2}{\hbar c}\right) \qquad H_{A^2} = \mathcal{O}\left(\frac{e^2}{\hbar c}\right)^2 . \tag{22.11}$$

Then, if we are expanding in $e^2/\hbar c$, we may guess that the first order term from H'_{A^2} will be the same order as the second order term in $H_{\vec{A}\cdot\vec{p}}$. Therefore, when we take the first order perturbation in H_{A^2} we should add to it the contribution from the second order perturbation in $H_{\vec{A}\cdot\vec{p}}$:

$$\langle f|T|i\rangle \simeq \langle f|H_{A^2}|i\rangle + \sum_j \frac{\langle f|H_{\vec{A}\cdot\vec{p}}|j\rangle \langle j|H_{\vec{A}\cdot\vec{p}}|i\rangle}{E - E_j + i0^+} \tag{22.12}$$

There are two kinds of intermediate states $|j\rangle$ where we will get a non zero contribution:

$$|j\rangle \quad \rightarrow \quad |0\rangle |n'\rangle \tag{22.13}$$
$$\rightarrow \quad |1_{\vec{k}\lambda}, 1_{\vec{k}\,'\lambda'}\rangle |n'\rangle \tag{22.14}$$

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The result for the A^2 term is given:

$$\langle f|H_{A^2}|i\rangle = \frac{1}{\Omega}\frac{2\pi c\hbar}{k}\hat{\epsilon}_{\vec{k}\lambda}\cdot\hat{\epsilon}^*_{\vec{k}'\lambda'}\sum_{l=1}^{Z}\frac{q^2}{mc^2}\langle s|e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_l}|s\rangle \tag{22.15}$$

$$\simeq \frac{1}{\Omega}\frac{2\pi c\hbar}{k}\hat{\epsilon}_{\vec{k}\lambda}\cdot\hat{\epsilon}^*_{\vec{k}'\lambda'}\frac{Zq^2}{mc^2} \tag{22.16}$$

We have assumed $(k << \frac{1}{a_H})$, therefore we set $\vec{k}' - \vec{k} = 0$ in the exponent on the first line. We see that the A^2 term has no dependence on the details of the atom. When we add in the $H_{\vec{A}\cdot\vec{p}}$ contributions, however, we find (refer to Handout pp.2-3) that there is a dependence on the dipole matrix elements of the atom. The result for the sum of the two terms is

$$\langle f|T|i\rangle = \frac{2\pi\hbar}{\Omega\omega}\hat{\epsilon}_{\vec{k}\lambda}\cdot\overset{\leftrightarrow}{M}\cdot\hat{\epsilon}^*_{\vec{k}'\lambda'} \tag{22.17}$$

where $\omega = ck = ck'$ is the photon frequency and the tensor $M_{\alpha\beta}$ is given by:

$$M_{\alpha\beta} = \frac{Zq^2}{m}\delta_{\alpha\beta} + \frac{1}{\hbar}\sum_n d^\alpha_{ns}d^\beta_{sn}\left[\omega^2_{ns}\left(\frac{1}{\omega - \omega_{ns} + i0^+} - \frac{1}{\omega + \omega_{ns} + i0^+}\right)\right] \tag{22.18}$$

Calculating this tensor is therefore the bulk of the problem. According to the f-sum rule (handout page 4, also discussed in p251b lecture):

$$\frac{\hbar Zq^2}{m}\delta_{\alpha\beta} = 2\sum_{n'}d^\alpha_{n's}d^\beta_{sn'}\omega_{n's} \tag{22.19}$$

Therefore it is possible to write the tensor as:

$$\overset{\leftrightarrow}{M} = -\omega^2\overset{\leftrightarrow}{\alpha}(\omega) \tag{22.20}$$

where $\alpha_{\alpha\beta}$ is the electric polarizability of the atom (discussed in p251b, lectures 4 and 5,) given by:

$$\alpha_{\alpha\beta}(\omega) = \frac{1}{\hbar}\sum_{n'}\vec{d}^\alpha_{n's}\vec{d}^\beta_{sn'}\left(\frac{-1}{\omega - \omega_{n's} + i0^+} + \frac{1}{\omega + \omega_{n's} + i0^+}\right) \tag{22.21}$$

As we are considering the case of non-resonant scattering, $\omega \neq \omega_{ns}$, we do not need to bother with the imaginary part placed in the denominators.

For an atom with spherical symmetry, $\alpha_{\alpha\beta}(\omega) = \alpha(\omega)\delta_{\alpha\beta}$, we get the total cross section (at the top of p.5 of the handout):

$$\boxed{\sigma_{tot} = \left(\frac{\omega}{c}\right)^4\frac{8\pi}{3}|\alpha(\omega)|^2} \tag{22.22}$$

This formula was derived by Lord Rayleigh in the 1800's not knowing anything about quantum mechanics. He just derived it in classical E&M from Maxwell's equations: the electric field

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of the incident radiation induces an electric dipole moment, proportional to the polarizability, which then acts as an antenna to reradiate the light in other directions.

This formula describes why the sky is blue. Light from the sun comes in at some angle, and is scattered in a direction to your eye. The cross section goes as ω^4 so blue light is scattered much more than red light.

Note that to derive this formula in quantum mechanics, it is essential to keep both the the H_{A^2} term and the $H_{\vec{A} \cdot \vec{p}}$ terms in (22.18). The ω^4 dependence of the scattering cross-section comes from an almost perfect cancellation of the two terms for $\omega \to 0$.

22.1.2   Resonant scattering

To examine the case of resonant scattering, consider the case where, as before, $k a_H << 1$, but now ω approaches the resonant frequency of some atomic transition. $\omega \to \omega_{n's}$

Using the formulas we have obtained so far, we would find that:

$$\lim_{\omega \to \omega_{n's}} \sigma_{tot} \quad \propto \quad \frac{1}{|\omega - \omega_{n's}|^2} \tag{22.23}$$

which would give an infinite cross section. But this is not physical. The reason is that the intermediate state has some finite decay time, and ω_{ns} is slightly broadened due to the finite life time. This effect arises from higher order terms in perturbation theory, which we have ignored so far. In fact, when we get close to a resonance, we have to sum up the most important contributions from all orders of perturbation theory. Close to a resonance, the H_{A^2} terms will not be important, but we will want to consider terms that include products of matrix elements like:

$$\langle f|H_{\vec{A} \cdot \vec{p}}|j_1\rangle \langle j_1|H_{\vec{A} \cdot \vec{p}}|j_2\rangle \langle j_2|H_{\vec{A} \cdot \vec{p}}|j_3\rangle \langle j_3|H_{\vec{A} \cdot \vec{p}}|i\rangle \tag{22.24}$$

This seems like a pain to calculate. But the only terms that matter have odd-numbered intermediate states of a simple form, where there is no photon present and the atom is in the resonant excited state $|n'\rangle$, while the even numbered intermediate states have one photon present in an arbiitrary mode and the atom in an arbitrary state:

$$|j_1\rangle = |0\rangle|n'\rangle = |j_3\rangle = |j_5\rangle \tag{22.25}$$

$$|j_{even}\rangle = |n''\rangle|1_{\vec{k}'' \lambda''}\rangle \tag{22.26}$$

Now when we sum that all up (we get the result on p.7 of the handout):

$$
\begin{aligned}
\sum_{|f\rangle} \gamma_{i\tilde{f}} &= \frac{2\pi}{\hbar} \frac{|\langle n'|H_{\vec{A}\cdot\vec{p}}|i\rangle|^2}{(\omega - \omega_{n's})^2 + \Gamma_{n'}^2/4} \frac{2\pi}{\hbar^3} \sum_f |\langle f|H'_{\vec{A}\cdot\vec{p}}|n'\rangle|^2 \delta(E_f^0 - E_i^0) \\
&= \frac{2\pi}{\hbar^2} |\langle 0, n'|H_{\vec{A}\cdot\vec{p}}|1_{\vec{k}\lambda}, s\rangle|^2 \left\{ \frac{\frac{\Gamma_{n'}}{2\pi}}{(\omega - \omega_{n's})^2 + \frac{\Gamma_{n'}^2}{4}} \right\}
\end{aligned}
\tag{22.27}
$$

where $\Gamma_{n'}$ is the decay rate of the state $|n'\rangle$ due to spontaneous emission of photons. The quantity in braces is a Lorentzian with area 1 and width $\frac{1}{2}\Gamma_{n'}$. If we had just put a delta function in place of it, we would recover the result from Fermi's golden rule.

In the special case where the only decay mode of the state n' is by emitting a photon direct to the ground state, we can relate the squared matrix element in the last line of (22.27) to $\Gamma_{n'}$. One then finds that the total cross section on resonance $(\omega = \omega_{n's})$ is given by::

$$
\begin{aligned}
\sigma_{tot} &= 6\pi \left(\frac{c}{\omega}\right)^2 \tag{22.28} \\
&= \frac{6\pi}{k^2} = \frac{3}{2\pi}\lambda_{photon}^2. \tag{22.29}
\end{aligned}
$$

This is the maximum resonant scattering cross-section for a photon. If there are other decay modes, then the peak will be broader and the maximum cross-section will be smaller, though the area of the resonant peak will be the same.

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23.1   Identical Particles, Fermions, Bosons and 2nd Quantization

Today we begin a discussion of the differences between fermions and bosons, leading into a discussion of second quantization. A number of problems are substantially easier to solve using second quantization.

To review, if we begin with a non relativistic system of N particles with no special properties or symmetries, we would talk about a Hilbert space which is a set of square integrable functions of the form:

$$\Psi(\vec{r_1}, \sigma_1, \vec{r_2}, \sigma_2, \vec{r_3}, \sigma_3, \ldots \vec{r_n}, \sigma_n,) \tag{23.1}$$

where $\vec{r_i}$ and σ_i are the position and spin of the ith particle. The equation of motion for these wavefunctions is given by the Schrödinger equation:

$$i\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi \tag{23.2}$$

H must be a self adjoint (Hermitian) operator. In the case where we have one or more indistinguishable particles, then the Hamiltonian must be invariant under interchange of the labels of these particles. That symmetry makes it natural to classify the solutions of the eigenstates under the same symmetry. This has profound effects on the nature of the universe. As an example, consider N electrons in some external position dependent potential $V(\vec{r_i})$ The Hamiltonian will therefore be, taking into account the coulomb interaction between the electrons:

$$H = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m_e} + V(\vec{r_i}) \right) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r_i} - \vec{r_j}|} \tag{23.3}$$

We could add relativistic corrections to this, the spin orbit term which mixes the spin and orbital motions of the electrons. There are also magnetic relativistic interactions. The important point is that electrons are all supposed to be identical. If I were to just change the labels of the electrons, nothing should change, as I summing over them, same for the relativistic terms.

In quantum mechanics we like to define operators to represent these symmetry transformations. Let us define the permutation operator P_{ij} that interchanges the positions and spins of particles i and j. We shall use a shorthand notation

$$\Psi \rightarrow \Psi(R_1, R_2, \ldots, R_N) \quad [R_i \equiv (\vec{r_i}, \sigma_i)] \tag{23.4}$$

where we are taking the value of R_i to indicate the combination of the position and spin of the particle. So the impact of P_{ij} acting on $\Psi(\ldots, R_i, \ldots, R_j, \ldots))$ is to interchange R_i and R_j. For example P_{12} acting on a wave function Ψ gives a new wave function Φ related to Ψ by

$$P_{12}\Psi(R_1, R_2, \ldots, R_N) = \Phi(R_1, R_2, \ldots, R_N) = \Psi(R_2, R_1, R_3, \ldots, R_N) \tag{23.5}$$

We can see quickly that using P_{ij} twice will just return the original state. Other evident properties are:

$$P_{12}^2 = 1 \qquad P_{12} = P_{21} \tag{23.6}$$

$$P_{12} = P_{12}^{-1} \qquad P_{ii} \text{ not defined} \tag{23.7}$$

So P_{ij} is a unitary, Hermitian operator with eigenvalues of ± 1.

What happens if we multiply two pair permutation operators with different labels, such as $P_{13}P_{12}$? I claim, for example, that

$$P_{13}P_{12}\Psi(R_1, R_2, R_3) = \Psi(R_2, R_3, R_1) \tag{23.8}$$

As expected, this is a cyclic permutation of the indices 1, 2 and 3. However there are two such cyclic permutations, and to get the correct one, you have to be quite careful. You can get the result (23.8) by careful application of the definition of P_{ij} and using equation (23.5) . The essential point is that the operator P_{ij} interchanges R_i and R_j, referring to the *particles* labeled i and j; it does not necessarily interchange the arguments in the places i and j of the list of arguments of a function.

Let's do this very carefully. Let $\Psi(A, B, C)$ be a function of three (position+spin) variables, and let Φ be a function such that $\Phi(A, B, C) = \Psi(B, A, C)$. Then $\Phi(R_1, R_2, R_3) = P_{12}\Psi(R_1, R_2, R_3) = \Psi(R_2, R_1, R_3)$, as defined in (23.5), and

$$P_{13}P_{12}\Psi(R_1, R_2, R_3) = P_{13}\Phi(R_1, R_2, R_3) = \Phi(R_3, R_2, R_1) = \Psi(R_2, R_3, R_1). \tag{23.9}$$

We also note that

$$P_{12}P_{13}\Psi(R_1, R_2, R_3) = \Psi(R_3, R_1, R_2). \tag{23.10}$$

So $P_{12}P_{13} \neq P_{13}P_{12}$: permutation operators do not, in general, commute.

We can now look at the impact of using the permutation operator on the position operator $\hat{\vec{r}}_i$. I claim that

$$P_{ij}\vec{r}_i P_{ij} = \vec{r}_j, \quad \text{or, equivalently} : P_{ij}\vec{r}_i = \vec{r}_j P_{ij}, \tag{23.11}$$

since $P_{ij}^2 = 1$. Similarly for the spin operator S_i and the momentum operator $\vec{p}_i$, I claim

$$P_{ij}\vec{S}_i P_{ij} = \vec{S}_j, \quad P_{ij}\vec{p}_i P_{ij} = \vec{p}_j \tag{23.12}$$

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To see this, let us consider the example of the operator S^z for a spin 1/2 particle, and let us show that $P_{1,2}S_1^z = S_2^z P_{1,2}$ For any wave function Ψ we have

$$
\begin{aligned}
P_{1,2}S_1^z \Psi(R_1, R_2) &= P_{1,2}\frac{\hbar \sigma_1}{2}\Psi(R_1, R_2) = \frac{\hbar \sigma_2}{2}\Psi(R_2, R_1) &(23.13)\\
&= S_2^z \Psi(R_2, R_1) = S_2^z P_{1,2}\Psi(R_1, R_2) &(23.14)
\end{aligned}
$$

If we sandwich the Hamilatonian in between two permutation operators, since we are summing over all the indices with equal weight, the Hamiltonian is invariant under the interchange of any two particles. Thus we have:

$$
P_{ij}HP_{ij} = H \quad\quad HP_{ij} = P_{ij}H \quad\quad [P_{ij}, H] = 0 \quad\quad (23.15)
$$

P_{ij} is a self-adjoint operator, and its a constant of the motion – it doesn't change. This is a little like angular momentum, if I start in a state with definite angular momentum, in a system in which the Hamiltonian commutes with angular momentum, then the (eigen)value of the angular momentum operator will be preserved throughout the motion. Similarly, if I start in a state that has a definite eigenvalue for the permutation operator, that value will always remain constant.

Of course, the symmetry inherent in the permutation operator is a much stronger symmetry than angular momentum. One can readily find Hamiltonians that do you not commute with angular momentum, but we have yet to find a system which is not invariant under the permutation of the labels of identical particles.

Furthermore, there is another statement to be made. Consider a system consisting of two identical particles in box. We shall see below that in general the energy levels of the system will be different depending on whether the system is a state with $P_{12} = 1$ or $P_{12} = -1$. Thus by measuring the energy levels we can find the eigenvalue of the permutation operator. If this turns out to be, say -1, for one pair of particles, it must also be -1 for all other pairs of the same identical particles, otherwise the pairs would be distinguishable and therefore not truly identical.

So if God, at the Creation, decided that there should be some small number of different types of particles, with particles within a given class truly indistinguishable from each other, he had to assign to each class an eigenvalue ± 1 for the permutation operator, and that eigenvalue would be the same today as it was at the creation. Man, in his wisdom, has given the name **bosons** to particles that have $P_{ij} = +1$ and **fermions** to particles that have $P_{ij} = -1$. The difference between fermions and bosons may seem to be innocuous, but it turns out to be of the utmost importance.

It turns out, experimentally, that Fermions are the particles which have half integer values of spin $\frac{1}{2}, \frac{3}{2}, \ldots$ (ie electrons, protons, neutrons) and Bosons (photons, hydrogen) have whole integer spins $(0, 1 \ldots)$. Non relativistic quantum mechanics has this as a coincidence. Relativistic quantum field theory has a spin and statistics theorem which explains this.

23.1.1   Hilbert Space and Bases for N Bosons and N Fermions

We will call the Hilbert space for Bosons $\mathcal{H}_N^S$ a subspace of the complete Hilbert space $\mathcal{H}_N$. The S superscript stands for symmetric. In this subspace we have $P_{ij}\Psi = \Psi \; \forall \, i, j$. Similarly, the fermions will have the space $\mathcal{H}_N^A$ subspace of $\mathcal{H}_N$, where A stands for antisymmetric. In this subspace $P_{ij}\Psi = -\Psi \; \forall \, i, j$.

We now want to go about defining a set of orthonormal basis states for these various subspaces. If we want to find the set of basis states for a single particle, we can choose any complete orthonormal set of functions $\{\phi_\alpha\{R\}\}$ where $\alpha = 1, 2, 3, \ldots$, to be a basis for $\mathcal{H}_1$, the Hilbert space for a single particle. This means any square integrable function can be expanded uniquely in terms of these basis functions.

We now claim that for $N > 1$, we can take as a basis for $\mathcal{H}_N$, the general Hamiltonian, the product states defined by $\{\phi_{\alpha_1}(R_1)\phi_{\alpha_2}(R_2)\ldots\phi_{\alpha_N}(R_N)\}$. We can see these are normalized to unity. Also, if we have two such states and any α_i is different than the corresponding α_j there inner product will be 0, showing these are orthogonal to each other. Also, any square-integrable function of $(R_1, \ldots R_N)$ function can be expanded in terms of these basis states.

Now to state a basis for the individual subspaces. We review the permutation group for N objects. There are $N!$ different permutations P_μ of N objects. All permutations can be written as products of pairwise interchanges. Half of the permutations will involve an even number of interchanges, the other half odd. For $N = 3$ we have $N! = 6$ total possible permutations.

$$\overbrace{1}^{\text{Even}}, \overbrace{P_{12}, P_{23}, P_{13}}^{\text{Odd}}, \overbrace{P_{123}, P_{321}}^{\text{Even}}, \tag{23.16}$$

where $P_{123} \equiv P_{12}P_{31} = P_{231} = P_{312}$, and $P_{321} = P_{31}P_{12}$, etc.

We now want to define two new operators:

$$\mathcal{S} = \text{Symmetrizer} = \sum_{\mu=1}^{N!} P_\mu \tag{23.17}$$

$$\mathcal{A} = \text{Antisymmetrizer} = \sum_{\mu=1}^{N!} (-1)^{\sigma_\mu} P_\mu \tag{23.18}$$

The meaning of the first term in the antisymmetrizer is:

$$(-1)^{\sigma_\mu} = -1 \text{ If } P_\mu \text{ Odd} \tag{23.19}$$
$$= 1 \text{ If } P_\mu \text{ Even} \tag{23.20}$$

For example, for $N = 3$, the antisymmetrizer operator would be:

$$\mathcal{A} = 1 + P_{123} + P_{321} - P_{12} - P_{23} - P_{31}. \tag{23.21}$$

Let us now consider a state with specified occupation numbers $\{n_\alpha\} = (n_1, n_2, ...)$, We first define a non-symmetrized reference state in the following manner:

$$|\{n_\alpha\}\rangle_0 = \overbrace{\phi_1(R_1)\phi_1(R_2)\ldots\phi_1(R_{n_1})}^{n_1 \text{ factors}} \overbrace{\phi_2(R_{n_1+1})\phi_2(R_{n_1+2})\ldots\phi_2(R_{n_1+n_2})}^{n_2 \text{ factors}} \ldots \tag{23.22}$$

The convention above is to write things in ascending order. Now, we will define the symmetric and antisymmetric sets of basis states in terms of the operators (23.17) and (23.18) operating on such a state:

$$|\{n_\alpha\}\rangle_S = \mathcal{N}\mathcal{S}|\{n_\alpha\}\rangle_0 \tag{23.23}$$
$$|\{n_\alpha\}\rangle_A = \mathcal{N}\mathcal{A}|\{n_\alpha\}\rangle_0 \tag{23.24}$$

where $\mathcal{N}$ where is an appropriate normalization factor. In doing this we have a created a set of states, which due to their reliance on the form previously discussed, are orthonormal, and also lie in the appropriate subspace as described before, as they behave the following way under the permutation operator:

$$P_{ij}|\{n_\alpha\}\rangle_S = |\{n_\alpha\}\rangle_S \tag{23.25}$$
$$P_{ij}|\{n_\alpha\}\rangle_A = -|\{n_\alpha\}\rangle_A \tag{23.26}$$

Now for the antisymmetric case, if one of the states had an occupation number greater than one, then an interchange of two of the labels would involve a negative sign, but would be a physically indistinguishable state. This would lead us to the conclusion that $|\{n_\alpha\}\rangle_A = -|\{n_\alpha\}\rangle_A$. As this would be a blatant contradiction, we see that the only allowable occupation numbers for an antisymmetric state is: $n_\alpha = 0, 1$. If the total number of particles is N, there are then N non-zero occupations numbers n_α, and there are $N!$ orthogonal terms in the antisymmetrized wave function. This tells us that for the antisymmetric states, the magnitude of the normalization factor must be $|\mathcal{N}| = \frac{1}{\sqrt{N!}}$. By convention, we shall choose $\mathcal{N} > 0$, when the reference state is occupied in ascending order, as specified above.

For the symmetric case (bosons) there is no maximum value for the occupation numbers n_α. However, the normalization factor has to be discussed more carefully.

5

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24.1 Bases for $\mathcal{H}_N^{\mathcal{S}}$ and $\mathcal{H}_N^{\mathcal{A}}$ and Second Quantization

We resume the discussion for the bases of the antisymmetric and symmetric bases of the Hilbert space for particles. The basis for a single particle consists of $\{\phi_\alpha(R)\}$ where $\langle\phi_\alpha|\phi_\beta\rangle = \delta_{\alpha\beta}$ and R is the aggregate of the position and spin of the particle $\{\vec{r}, \vec{\sigma}\}$. For multiple particles, we must define the basis states more elaborately. The general reference state that we use to construct the basis states for fermions and bosons consists of a product of single particle states:

$$|\{n_\alpha\}\rangle_0 = \overbrace{\phi_1(R_1)\phi_1(R_2)\ldots\phi_1(R_{n_1})}^{n_1 \text{ factors}} \overbrace{\phi_2(R_{n_1+1})\phi_2(R_{n_1+2})\ldots\phi_2(R_{n_1+n_2})}^{n_2 \text{ factors}} \ldots \qquad (24.1)$$

For fermions the wavefunctions must be antisymmetric, we therefore use the antisymmetrizer operator acting on the reference state to recover the desired property that $P_{ij}|n\rangle_A = -|n\rangle_A$

$$|n_1, n_2, \ldots\rangle_A = \frac{1}{\sqrt{N!}} \mathcal{A}_N |n_1, n_2, \ldots\rangle_0 \qquad (24.2)$$

where the antisymmetrizer operator is defined in terms of the permutation operator P_μ (see lecture p251 lecture 23 as:

$$\mathcal{A}_N = \sum_{\mu=1}^{N!} P_\mu (-1)^{\sigma_\mu} \qquad (24.3)$$

The states defined in equation (24.2) form an orthonormal basis for the antisymmetric subspace of the entire multiparticle Hilbert space. We now look at a different way to write such states. If we define a matrix: $M_{ij} = \phi_{\alpha_i}(R_j)$ where $1 \leq i, j \leq N$, we claim that the antisymmetric basis states (as in (24.2) can be written as:

$$|\{n_\alpha\}\rangle_A = \frac{1}{\sqrt{N!}} \det M_{ij} = \frac{1}{\sqrt{N!}} \det(\phi_{\alpha_i}(R_j)) \qquad (24.4)$$

The determinant above is called the **Slater determinant**.

The symmetric basis states can be written as:

$$|\{n_\alpha\}\rangle_S = \mathcal{N} \mathcal{S}_N |\{n_\alpha\}\rangle_0 \qquad (24.5)$$

where the symmetrizer operator $\mathcal{S}_N$ is defined as:

$$\mathcal{S}_N = \sum_{\mu=1}^{N!} P_\mu \qquad (24.6)$$

This state will be symmetric under the interchange of labels of any of the particles. Let us examine some examples. For a single particle we have:

$$|1_\alpha\rangle_S = |1_\alpha\rangle_0 = \phi_\alpha(R_1) \tag{24.7}$$

For the case of $N = 2$ we have states where two different states are occupied:

$$|1_\alpha, 1_\beta\rangle = \mathcal{N}(\phi_\alpha(R_1)\phi_\beta(R_2) + \phi_\beta(R_1)\phi_\alpha(R_2)) \tag{24.8}$$

For the case of $\alpha \neq \beta$ the normalization factor will be $\mathcal{N} = \frac{1}{\sqrt{2}}$. (We choose the normalization constant to be positive.) To avoid including the same state twice, we specify the occupation numbers of the one-particle states in ascending order of their labels; i.e. $\beta > \alpha$.

We also have states where two particles are in the same one-particle state:

$$|2_\alpha\rangle_S = \mathcal{N}\mathcal{S}_2(\phi_\alpha(R_1)\phi_\alpha(R_2)) = 2\mathcal{N}\phi_\alpha(R_1)\phi_\alpha(R_2) \tag{24.9}$$

Now the normalization is: $\mathcal{N} = \frac{1}{2}$. In general, it can be shown that the normalization factor will be given by:

$$\mathcal{N} = \frac{1}{\sqrt{N!}}\left(\prod_\alpha \sqrt{n_\alpha!}\right)^{-1} \tag{24.10}$$

To summarize, we claim that the states $|\{n_\alpha\}\rangle_S$ are a complete basis in $\mathcal{H}_N^S$ and $|\{n_\alpha\}\rangle_A$ are a complete basis in $\mathcal{H}_N^A$. How do we prove completeness? We have previously claimed that any square integrable function can be expanded uniquely in terms of the orthonormal complete set of product states. Thus we can find expansion coefficients such that

$$\Psi(R_1 \ldots R_N) = \sum_{\alpha_1 \ldots \alpha_N} c_{\alpha_1 \ldots \alpha_N} \phi_{\alpha_1}(R_1)\phi_{\alpha_2}(R_2) \ldots \phi_{\alpha_N}(R_N) \tag{24.11}$$

Two functions Ψ and Ψ' are identical if and only if all the respective expansion coefficients c and c' are equal to each other for each set of labels $(\alpha_1, \ldots \alpha_N)$, since any two product states in the basis will be orthogonal to each other unless their sets of labels are identical, and the labels appear in the same order.

If $\psi \in \mathcal{H}_N^S$ then we have $P_{ij}\Psi = \Psi \; \forall i, j$. If this is true it means we are shuffling around the indices on $c_{\alpha_1 \ldots \alpha_n}$, the coefficient must be unchanged. If all of the $N!$ coefficients with permuted indices have the same value then each of these must be $1/N!$ times the sum of all $N!$ permuted terms. But this is just a constant times what we would get if we had the symmetrizer operator (equation (24.6)) acting on a reference state, which is to say it is a constant times one of the basis states $|\{n_\alpha\}\rangle_S$ of the symmetric Hilbert space, which we discussed previously. Of course, for terms that are not related by a simple permutation of the indices, there is no relation between

the coefficients. Thus the most general symmetric state with N particles can be written as a sum over all different symmetric basis states $|\{n_\alpha\}\rangle_S$ with arbitrary coefficients. Thus the set $|\{n_\alpha\}\rangle_S$ serves as a basis for $\mathcal{H}_N^S$

Now for the case of $\Psi \in \mathcal{H}_N^A$, we have that $P_{ij}\Psi = -\Psi$. The situation is similar except that now when I permute the indices $\{\alpha\}$ on the coefficients $c_{\alpha_1 \dots \alpha_n}$ I should pick up a factor of $(-1)^{\sigma_n}$. This means that all the terms describing a similar occupation number must have the same magnitude, but may differ by a sign. In fact, they will have the same sign if they are related by by an even permutation but will have opposite sign if they are related by an odd permutation. Thus we can pull out the common factor and be left with the antisymmetrizer operator, given by (24.3) acting on the reference state specifying a particular set of occupation numbers. The states $|\{n_\alpha\}\rangle_A$ therefore serve as a basis for $\mathcal{H}_N^A$.

24.1.1   Second Quantization

Since we don't care what electron is in which state, we only care about which states are occupied. This is is a lot like the situation with photons where we can just number the occupation of a particular state. In that case it was very useful to have operators that added or subtracted a photon. We can imagine we could do a similar thing here that would add or remove a particle from a particular state. Doing this allows us to further define other operators in terms of these raising and lowering operators. The way we do it for fermions and bosons will be different from each other, but there will be similarities.

Operators that correspond to physical observables in non relativistic quantum mechanics do not include such creation or annihilation operators by themselves, as that would not conserve particle number. Therefore the creation and annihilation operators must appear in combinations with equal numbers of creation and annihilation operators in physical observables.

Formally, however, we want to add and subtract particles at will. Thus, we want to extend our definitions from a Hilbert space with a definite total particle number N to one with an arbitrary number of particles. We write such a space as the direct sum of the definite number spaces. For bosons we have:

$$\mathcal{H}_S = \mathcal{H}_0^S \oplus \mathcal{H}_1^S \oplus \mathcal{H}_2^S \oplus \dots \tag{24.12}$$

For fermions,

$$\mathcal{H}_A = \mathcal{H}_0^A \oplus \mathcal{H}_1^A \oplus \mathcal{H}_2^A \oplus \dots \tag{24.13}$$

In these equations, $\mathcal{H}_0^A = \mathcal{H}_0^S = \mathcal{H}_0$ is the vacuum state, with no particles. The vacuum state is assumed to be a unique, so $\mathcal{H}_0$ is a one-dimensional vector space, with only the vacuum state

in it. Now, the basis for $\mathcal{H}_S$ will be the states $\{|n_\alpha\rangle_S\}$ where $\sum n_\alpha < \infty$ (including $\sum n_\alpha = 0$), while the basis for $\mathcal{H}_A$ will be the states $\{|n_\alpha\rangle_A\}$.

From now on we shall **drop the scripts A and S** specifying which space a particular state belongs in. We shall infer that from context.

Number operators

We can start to define operators. We start with the number operators N_α corresponding to the basis states ϕ_α. When N_α acts on a many-body basis state with a definite occupation number n_α for the state α we should get back the occupation number of that state. That is:

$$N_{\alpha_1}|\{n_\alpha\}\rangle = n_{\alpha_1}|\{n_\alpha\}\rangle \tag{24.14}$$

The allowable eigenvalues of N_α will be:

$$
\begin{aligned}
N_\alpha &= 0,1 \quad \text{For Fermions} \tag{24.15} \\
&= 0,1,2,\ldots \quad \text{For Bosons} \tag{24.16}
\end{aligned}
$$

If we apply a second number operator N_{α_2} to both sides of Eq. (24.14) , we find

$$N_{\alpha_2}N_{\alpha_1}|\{n_\alpha\}\rangle = n_{\alpha_1}n_{\alpha_2}|\{n_\alpha\}\rangle. \tag{24.17}$$

Clearly it does not matter in which order we apply the number operators, and since this is true for an arbitrary many-body basis state $|\{n_\alpha\}\rangle$, the number operators for different states in our one-particle basis must commute with each other. Also, the sum of all number operators acting on a set specifying all occupation numbers must give back the total number of particles N. Hence

$$N_\alpha N_\beta = N_\beta N_\alpha, \qquad \sum_\alpha N_\alpha = N \tag{24.18}$$

Creation and annihilation operators

We now want to define creation $a_\alpha^\dagger$ and annihilation a_α operators, which are to be adjoints of each other. The effect of the annihilation operator acting on a state will be:

$$a_{\alpha_1}|n_1 \ldots n_{\alpha_1} \ldots\rangle = c|n_1 \ldots (n_{\alpha_1} - 1) \ldots\rangle \tag{24.19}$$

where c is a constant to be specified later. If a_α decreases the particle occupation number by 1, its adjoint must increase it by one, so we have:

$$a_{\alpha_1}^\dagger|n_1 \ldots n_{\alpha_1} \ldots\rangle = c'|n_1 \ldots (n_{\alpha_1} + 1) \ldots\rangle \tag{24.20}$$

The constants c and c' will depend on the state. We must have $c = 0$ if $n_\alpha = 0$, and we will want to have $c \neq 0$ otherwise. Several other properties follow. If $|x\rangle$ and $|y\rangle$ are basis states with specified occupation numbers, then the matrix element $\langle x|a_{\alpha_1}|y\rangle = 0$ unless $(n_{\alpha_1})_x = (n_{\alpha_1} - 1)_y$, while all the other occupation numbers are the same in the two states. Similarly $\langle x|a^\dagger_{\alpha_1}|y\rangle = \langle y|a_{\alpha_1}|x\rangle^* = 0$ unless $(n_{\alpha_1})_x = (n_{\alpha_1} + 1)_y$. The corollary of all this is:

$$[N_\alpha, a^\dagger_\beta] = \delta_{\alpha\beta}\, a^\dagger_\beta \tag{24.21}$$

$$[N_\alpha, a_\beta] = -\delta_{\alpha\beta}\, a_\beta \tag{24.22}$$

The proof is left as an exercise. We haven't yet defined these operators completely; the key will be to specify what the constant c and c' in equations (24.19) and (24.20) will be. That will depend on whether we are dealing with fermions or bosons.

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25.1 Second Quantization: Creation and Destruction Operators: Fermions and Bosons

We continue the discussion of second quantization using creation and annihilation operators for fermions on bosons, dealing with symmetric $|\{n_\alpha\}\rangle_S$ and antisymmetric states $|\{n_\alpha\}\rangle_A$ which serve as bases for the $\mathcal{H}_S$ and $\mathcal{H}_A$ Hilbert spaces respectively.

The result of the particle annihilation operator acting on such a basis state will be:

$$a_\alpha|\ldots,n_\alpha,\ldots\rangle = c\,|\ldots,(n_\alpha-1),\ldots\rangle \tag{25.1}$$

In principle, we can choose the constants c to be almost anything we want, but some choices are more convenient than others. Our choice will depend on whether we are dealing with fermions or bosons.

Regardless of the choice of c, as was left as an exercise to show in the last lecture, we have

$$[N_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta}a_\beta^\dagger \qquad [N_\alpha, a_\beta] = -\delta_{\alpha\beta}a_\beta \tag{25.2}$$

Also, from the definition of an adjoint we must have

$$\langle\phi|a_\alpha^\dagger|\psi\rangle = \langle\psi|a_\alpha|\phi\rangle^* \tag{25.3}$$

25.1.1 Bosons

Let's first explore the case of Bosons. We choose $c = \sqrt{n_\alpha}$. This is the same relation we had for photons and for harmonic oscillators. Now, of course, photons are a subset of Bosons. They don't obey the non-relativistic Schrodinger equation, but they share the same symmetry properties. So, now the commutation relations are exactly the same as they were for Harmonic oscillator. The length of the vector of a state being acted upon by the annihilation operator squared will be:

$$\|a_\alpha|\ldots,n_\alpha,\ldots\rangle\|^2 = n_\alpha \tag{25.4}$$

But this is the equivalent of taking the expectation value of $a_\alpha^\dagger a_\alpha$ in that state. Therefore we must have that:

$$a_\alpha^\dagger a_\alpha\,|\ldots,n_\alpha,\ldots\rangle = n_\alpha\,|\ldots,n_\alpha,\ldots\rangle, \qquad a_\alpha^\dagger a_\alpha = N_\alpha, \tag{25.5}$$

where N_α is the number operator. Since we know that a_α lowers the occupation number of the α state by one, for equation (25.5) to be true, it must be the case that:

$$a_\alpha^\dagger \, | \ldots, (n_\alpha - 1), \ldots \rangle = \sqrt{n_\alpha} \, | \ldots, (n_\alpha), \ldots \rangle \tag{25.6}$$

However, for bosons, the occupation n_α is an arbitrary non-negative integer. Therefore, we must have

$$a_\alpha^\dagger \, | \ldots, n_\alpha, \ldots \rangle = \sqrt{n_\alpha + 1} \, | \ldots, (n_\alpha + 1), \ldots \rangle \tag{25.7}$$

We could now repeat the process, but starting with $a_\alpha^\dagger$ in equation (25.4). We would find the following results:

$$a_\alpha a_\alpha^\dagger = N_\alpha + 1 \qquad \left[a_\alpha, a_\alpha^\dagger \right] = 1 \tag{25.8}$$

Furthermore, since, a_α only changes the occupation number for the state a_α repeating these processes would reveal that:

$$[a_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta} \qquad [a_\alpha, a_\beta] = 0 = [a_\alpha^\dagger, a_\beta^\dagger] \tag{25.9}$$

We can now construct a state of definite occupation numbers $|\{n_\alpha\}\rangle$ by having creation operators acting on the vacuum state $|0\rangle$:

$$\boxed{|\{n_\alpha\}\rangle = \prod_\alpha \left(\frac{(a_\alpha^\dagger)^{n_\alpha}}{\sqrt{n_\alpha!}} \right) |0\rangle} \tag{25.10}$$

It also follows directly from what we have done before that:

$$[N_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta} \, a_\beta^\dagger \tag{25.11}$$

It is also easy to check that:

$$\langle \ldots, (n-1)_\alpha, \ldots | a_\alpha | \ldots n_\alpha \ldots \rangle = \sqrt{n_\alpha} \tag{25.12}$$

$$\langle \ldots, n_\alpha, \ldots | a_\alpha^\dagger | \ldots (n-1)_\alpha \ldots \rangle^* = \sqrt{n_\alpha} \tag{25.13}$$

25.1.2   Fermions

It is important to emphasize that $c = \sqrt{n_\alpha}$ was a choice made out of convenience. For fermions, we would like to do something similar. However choosing $c = \sqrt{n_\alpha}$ will not be the preferable thing to do. We have shown in P251b Lecture 25 that the only allowable occupation numbers for fermion states is $n_\alpha = 0, 1$. Consider:

$$a_\alpha | \ldots, 0_\alpha, \ldots \rangle = 0 \qquad a_\alpha | \ldots, 1_\alpha, \ldots \rangle = c \, | \ldots, 0_\alpha, \ldots \rangle \tag{25.14}$$

Taking the adjoints we have:

$$\langle 0|a_\alpha^\dagger = 0 \qquad \langle \ldots, 1_\alpha, \ldots |a_\alpha^\dagger = c^* \langle \ldots, 0_\alpha, \ldots | \tag{25.15}$$

We would again like it to be the case that:

$$N_\alpha = a_\alpha^\dagger a_\alpha \tag{25.16}$$

With this requirement it must be the case that:

$$\langle \ldots, 1_\alpha, \ldots |a_\alpha^\dagger a_\alpha| \ldots, 1_\alpha, \ldots \rangle = 1 = |c|^2 \tag{25.17}$$

Therefore the value of the constant c must be determined up to a phase. We make the seemingly peculiar choice of $c = (-1)^{l_\alpha}$ where l_α is the sum of the occupations of all the states lower than α:

$$l_\alpha = \sum_{\beta=1}^{\alpha-1} n_\beta \tag{25.18}$$

It will turn out that this choice makes things much simpler later on: it allows for the definition of operators that have commutation relations that are basis independent. What about $a_\alpha^\dagger$? If we take the adjoint of the matrix element below involving a_α:

$$\langle \ldots, 0_\alpha, \ldots |a_\alpha| \ldots, 1_\alpha, \ldots \rangle = (-1)^{l_\alpha} \langle \ldots, 0_\alpha, \ldots | \ldots, 0_\alpha, \ldots \rangle \tag{25.19}$$

We can see that:

$$a_\alpha^\dagger | \ldots, 0_\alpha, \ldots \rangle = (-1)^{l_\alpha} | \ldots, 1_\alpha, \ldots \rangle \tag{25.20}$$

Since Fermion states can only have an occupation number of 1 or 0, we require that:

$$a_\alpha^\dagger | \ldots, 1_\alpha, \ldots \rangle = 0 \tag{25.21}$$

It follows now that:

$$a_\alpha^\dagger a_\alpha = N_\alpha \qquad a_\alpha a_\alpha^\dagger = 1 - N_\alpha \tag{25.22}$$

where the right hand equation simply specifies that it should return a 1 if it is operating a state with zero occupation in the α level and 0 if is it operating on an occupied state. Combining these we do not arrive at a simple relation for the commutator between the raising and lowering operators; rather we find

$$a_\alpha^\dagger a_\alpha + a_\alpha a_\alpha^\dagger = 1 \tag{25.23}$$

The left hand side of this equation is referred to as an **anti-commutator**, denoted by braces rather than by square brackets:

$$\boxed{\{A, B\} \equiv AB + BA} \tag{25.24}$$

For the anti-commutator, a value of zero indicates $AB = -BA$. Since no state can have an occupation number greater than one:

$$\{a_\alpha, a_\alpha\} = 2a_\alpha^2 = 0 \tag{25.25}$$

Similarly:

$$\{a_\alpha^\dagger, a_\alpha^\dagger\} = 0 \tag{25.26}$$

What about $\alpha \neq \beta$? We claim that:

$$\{a_\alpha, a_\beta^\dagger\} = \delta_{\alpha\beta} \tag{25.27}$$

To prove this we must show that $a_\alpha a_\beta^\dagger = -a_\beta^\dagger a_\alpha$, for $\alpha \neq \beta$. We also claim that $\{a_\alpha, a_\beta\} = 0$ and $\{a_\alpha^\dagger, a_\beta^\dagger\} = 0$. All of these can be shown in the same manner; we will only demonstrate it for the first case. Consider the following example;

$$a_1^\dagger |0, 1_2\rangle = 1|1_1, 1_2\rangle \qquad (l_1 = 0) \tag{25.28}$$

$$a_2 |1_1, 1_2\rangle = (-1)|1_1, 0\rangle \qquad (l_2 = 1) \tag{25.29}$$

$$a_2 |0_1, 1_2\rangle = 1|0_1, 0_2\rangle \qquad (l_2 = 0) \tag{25.30}$$

$$a_1^\dagger |0_1, 0_2\rangle = (1)|1_1, 0\rangle \qquad (l_1 = 0) \tag{25.31}$$

Thus

$$a_1^\dagger a_2 |0_1, 1_2\rangle = -a_2 a_1^\dagger |0_1, 1_2\rangle \tag{25.32}$$

So indeed we see for this case (and it is always true) that $a_\alpha a_\beta^\dagger = -a_\beta^\dagger a_\alpha$. As we can see (equation (25.27) and what follows), the relations for Fermions are very similar to those for Bosons and the harmonic oscillator, but they involve anti-commutators rather than commutators.

Now to create a state with definite occupation numbers for Fermions, we act with creation operators acting on the vacuum state $|0\rangle$ in the following way:

$$|\{n_\alpha\}\rangle = (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} \ldots |0\rangle \tag{25.33}$$

To get the sign to always be positive it is important to act with the highest number creation operator first (they should go in ascending order from left to right) so that the multiplicative constant $(-1)^{l_\alpha}$ is always $= 1$.

25.1.3   Changes of Basis

We can now discuss the invariance under basis changes. We define a generalization of the creation and annihilation operators. Let $f(R)$ be a wavefunction expanded as a sum of the one particle basis functions:

$$f(R) = \sum_\alpha f_\alpha \phi_\alpha(R) \tag{25.34}$$

We define a generalized creation operator $a^\dagger_{[f]}$ as follows:

$$a^\dagger_{[f]} = \sum_\alpha f_\alpha a^\dagger_\alpha \tag{25.35}$$

If the operator $a^\dagger_\alpha$ acts on the vacuum state $|0\rangle$, it gives us a state with one particle in the state $\phi_\alpha(R)$. It should now be clear that if we operate on the vacuum state $|0\rangle$ with the generalized creation operator $a^\dagger_{[f]}$ we will get back a state with one particle in state $f(R)$. This will be true for both Fermions and Bosons.

We now want to find the commutation or anticommutation relations obeyed by these new operators. Let us start with Bosons. The commutator between Bosons operators are computed as

$$[a_{[f]}, a^\dagger_{[g]}] = \sum_{\alpha\beta} f^*_\alpha g_\beta \overbrace{[a_\alpha, a^\dagger_\beta]}^{\delta_{\alpha\beta}} \tag{25.36}$$

$$= \sum_\alpha f^*_\alpha g_\alpha = \langle f|g\rangle \tag{25.37}$$

For fermions we have:

$$\{a_{[f]}, a^\dagger_{[g]}\} = \sum_{\alpha\beta} f^*_\alpha g_\beta \{a_\alpha, a^\dagger_\beta\} = \sum_{\alpha\beta} f^*_\alpha g_\beta \delta_{\alpha\beta} \tag{25.38}$$

$$= \sum_\alpha f^*_\alpha g_\alpha = \langle f|g\rangle \tag{25.39}$$

Similarly to before, for Bosons it can be shown that:

$$[a_{[f]}, a_{[g]}] = 0 = [a^\dagger_{[f]}, a^\dagger_{[g]}] \tag{25.40}$$

and for Fermions we have:

$$\{a_{[f]}, a_{[g]}\} = \{a^\dagger_{[f]}, a^\dagger_{[g]}\} = 0 \tag{25.41}$$

It follows that in general we can make a change of basis. We define a new set of creation operators $b_l^\dagger$.

$$b_l^\dagger = \sum_\alpha U_{l\alpha} a_\alpha^\dagger \tag{25.42}$$

where $U_{l\alpha}$ is a unitary operator. The commutator for Bosons will be:

$$[b_l, b_l^\dagger] = \sum_{\alpha\alpha'} U_{l\alpha}^* U_{l'\alpha'} \delta_{\alpha\alpha'} = \delta_{ll'} \tag{25.43}$$

Similarly for Fermions we would find:

$$\{b_l, b_{l'}^\dagger\} = \delta_{ll'} \tag{25.44}$$

Given these relations, we can define a number operator to measure the occupation of a state l:

$$N_l = b_l^\dagger b_l \tag{25.45}$$

From the relations above it follows that:

$$
\begin{aligned}
b_l b_l^\dagger &= & N_l + 1 && \text{For Bosons} & \tag{25.46} \\
&= & 1 - N_l && \text{For Fermions} & \tag{25.47}
\end{aligned}
$$

We shall see that the allowed eigenvalues of N_l are $n_l = 0, 1$, for fermions, and $n_l = 0, 1, 2, 3, ...$, for bosons.

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26.1 Creation and Destruction Operators for Fermions and Bosons (Continued); and General One-Body Operators

In the previous lecture we had defined creation and annihilation operators for Boson and Fermion states that obey the following commutation relation:

$$\text{Bosons} \quad \begin{cases} [a_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta} \\ [a_\alpha, a_\beta] = 0 \end{cases} \quad \text{Fermions} \quad \begin{cases} \{a_\alpha, a_\beta^\dagger\} = \delta_{\alpha\beta} \\ \{a_\alpha, a_\beta\} = 0 \end{cases} \tag{26.1}$$

For either type of particle we could define a number operator:

$$N_\alpha = a_\alpha^\dagger a_\alpha, \tag{26.2}$$

which will count the occupation number of the level α. By construction, these operators had eilgenvalues $n_\alpha = 0, 1$ for fermions, and $n_\alpha = 0, 1, 2$, for bosons.

We also saw that we could introduce operators b_l for a different set of basis states, related to the original basis by a unitary transformation of the one-particle states, and that these new operators obey the same commutation or anticommutation relations as before. We also defined number operators $N_l = b_l^\dagger b_l$ We want to know what are the allowed eigenvalues of N_l?

I claim that the allowed eigenvalues must be the same as before, $n_l = 0, 1$ for fermions, and $n_l = 0, 1, 2$, for bosons, because the eigenvalues can be deduced directly from the commutation relations. For the case of bosons, we know this, because the commutation relations are the same as for harmonic oscillators, and we saw long ago that we could obtain the eigenvalues of the operator $a^\dagger a$ in that case from the commutation rules of a and $a^\dagger$.

In the fermion case, we use the anticommutation relations, Thus. for the operators N_α, we could show:

$$\begin{aligned} N_\alpha(1 - N_\alpha) &= a_\alpha^\dagger a_\alpha (1 - a_\alpha^\dagger a_\alpha) = a_\alpha^\dagger a_\alpha (a_\alpha a_\alpha^\dagger) & (26.3) \\ &= a_\alpha^\dagger (a_\alpha)^2 a_\alpha^\dagger = 0 & (26.4) \end{aligned}$$

The last line follows because:

$$a_\alpha^2 = \frac{1}{2}\{a_\alpha, a_\alpha\} = 0 \tag{26.5}$$

So equation (26.4) tells us that $N_\alpha^2 = N_\alpha$, meaning that N_α can only have eigenvalues 0 or 1. But the operators b_l obey the same anticommutation relations as a_α. So the operators N_l must have the same eigenvalues as N_α.

26.2   One-Body Operators

26.2.1   General One-Body Operator

We want to see how general physical operators can be expressed in terms of creation and annihilation operators in the second-quantized formalism. The first type to explore are the operators that only act one particle individually. In first-quantized notation, such an operator has the form:

$$Q = \sum_{i=1}^{N} Q^{(i)} \tag{26.6}$$

where the operator $Q^{(i)}$ only acts on the particle i. These sum of one body operators are the ones that generally correspond to observables in Quantum mechanics, as we cannot distinguish identical particles, and we do not know which particular particle we are measuring. As one example, to measure kinetic energy, we would use:

$$Q^{(i)} = \frac{p_i^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \vec{r}_i^2} \equiv K^{(i)} \tag{26.7}$$

If we didn't worry about symmetry we could look at a state of many particles and form eigenstates of Q by taking a direct product of eigenstates of $Q^{(1)}$. Let f_l be eigenstates of Q^1 such that:

$$Q^{(1)} f_l(R_1) = q_l f_l(R_1) \tag{26.8}$$

We can now form product states which are eigenstates of the Q sum operator. Consider

$$\Psi = f_{l_1}(R_1) f_{l_2}(R_2) \dots f_{l_n}(R_n) \tag{26.9}$$

If we operate on this state with Q, we would recover the eigenvalue

$$q_{l_1} + q_{l_2} + \dots + q_{l_N} = \sum_{l=1}^{\infty} q_l n_l \tag{26.10}$$

where n_{l_α} is the occupation of the state described by f_{l_α}, ie the number of times the function f_{l_α} occurs in the product state.

In general, the states in equation (26.9) are not valid states for Fermions or Bosons as they are not symmetric or antisymmetric. We could however just take symmetric or antisymmetric linear combinations (by using the symmetrizer or antisymmetrizer) and we would recover states with the appropriate properties. If we have a linear combination of eigenstates all with the same eigenvalue, then that combination is also an eigenstate, with eigenvalue given by (26.10).

Now, we can obtain the value of n_l by operating on the state with the number operator N_l. So we can write the operator Q as

$$Q = \sum_{l=1}^{\infty} q_l N_l \tag{26.11}$$

But since we know that we can write the number operator for the state l in terms of creation and annihilation operators, corresponding to the f_l. we can rewrite the Q operator as:

$$Q = \sum_{l=1}^{\infty} q_l b_l^{\dagger} b_l \tag{26.12}$$

We need to be able to write this formalism in a basis independent way, since we may want to work with operators that do not commute and therefore do not have eigenstates in the same basis. Let us choose an arbitrary orthonormal basis of functions $\phi_a l(R)$, with corresponding annihilation operators a_{α}. Then the states f_l can be expanded in the new basis as

$$f_l(R) = \sum_{\alpha} U_{l\alpha} \phi_{\alpha}(R) \tag{26.13}$$

Since the f_l are also an orthonormal basis for the one-particle Hilbert space, the coefficients $U_{l\alpha}$ must form a unitary matrix. Then we can transform the creation and annihilation operators from one basis to the other by:

$$b_l^{\dagger} = \sum_{\alpha} U_{l\alpha} a_{\alpha}^{\dagger} \tag{26.14}$$

So this tells us that we can write our operator Q in the new basis as:

$$Q = \sum_{\alpha\beta} Q_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} \tag{26.15}$$

where $Q_{\alpha\beta}$ is defined by:

$$Q_{\alpha\beta} = \sum_{l} q_l U_{l\alpha} U_{l\beta}^* \tag{26.16}$$

From equation (26.15), we can also see directly that

$$Q_{\alpha\beta} = \langle 0 | a_{\alpha} Q a_{\beta}^{\dagger} | 0 \rangle = \langle \phi_{\alpha}(R_1) | Q^{(1)} | \phi_{\beta}(R_1) \rangle \tag{26.17}$$

Equations (26.15) and (26.17) therefore represent the most general form of a one body operator in terms of creation and annihilation operators. They will always involve a sum of terms involving one creation operator and one annihilation operator along with a coefficient which is actually a matrix element between one-particle basis states. In this form, it is not necessary to use basis states where Q is diagonal.

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26.2.2   Example: Kinetic Energy Operator

For kinetic energy, I will choose plane waves states as my basis states. The states also have a spin index, so the states will be of the form:

$$\phi_{\vec{k}s}(\vec{r}, \sigma) = \left(\frac{1}{\Omega}\right)^{1/2} e^{i\vec{k}\cdot\vec{r}} \delta_{\sigma s}, \tag{26.18}$$

where s is a spin index for the state, and σ is the spin variable for the particle. The single particle operator for kinetic energy will have the form:

$$K^{(1)} = \sum_{\vec{k}s} \frac{\hbar^2 k^2}{2m} \left|\phi_{\vec{k}s}(R_1)\right\rangle \left\langle\phi_{\vec{k}s}(R_1)\right| \tag{26.19}$$

Following the formulation we developed above, we therefore have that:

$$\boxed{K = \sum_{\vec{k}s} \frac{\hbar^2 k^2}{2m} a^\dagger_{\vec{k}s} a_{\vec{k}s}} \tag{26.20}$$

26.2.3   Example: Potential Energy Operator

The potential energy of a system of N particles in an external position dependent potential should be:

$$\mathcal{U} = \sum_{i=1}^{N} \mathcal{U}(\vec{r}_i) \tag{26.21}$$

How do we write this in terms of creation and annihilation operators for plane wave states? Obviously the position-dependent potential is not diagonal in the plane wave basis. Potentials of this form do not change the spin index, so we should be able to get away with a single sum for the spin indices. Then we should be able to write:

$$\mathcal{U} = \sum_{\vec{k}\vec{k}\,'s} a^\dagger_{\vec{k}s} a_{\vec{k}\,'s} \mathcal{U}_{\vec{k}\vec{k}\,'s} \tag{26.22}$$

It remains to determine the value of $\mathcal{U}_{\vec{k},\vec{k}\,'s}$. From equation (26.17) it follows that:

$$\mathcal{U}_{\vec{k}\vec{k}\,'s} = \langle\phi_{\vec{k}s}(\vec{r}_1)|\mathcal{U}(\vec{r}_1)|\phi_{\vec{k}\,'s}(\vec{r}_1)\rangle \tag{26.23}$$

$$= \frac{1}{\Omega} \int d^3r_1 \; e^{i\vec{r}_1\cdot(\vec{k}\,'-\vec{k})} \mathcal{U}(\vec{r}_1) \tag{26.24}$$

$$= \tilde{\mathcal{U}}(\vec{k} - \vec{k}\,') \frac{(2\pi)^{3/2}}{\Omega} \tag{26.25}$$

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26.2.4   Example: Total particle number operator

This one is easy:

$$N = \sum_{\vec{k}s} a_{\vec{k}s}^\dagger a_{\vec{k}s} \tag{26.26}$$

26.2.5   Example: Total Spin Operators for s=1/2

If we choose to quantize spin along the z-axis, the spin operators for a single particle may be written in terms of the Pauli spin matrices as:

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{26.27}$$

Using these to obtain the necessary matrix elements in Eq. (26.16), we find the total spin operators:

$$\boxed{S_z = \frac{\hbar}{2} \sum_k (a_{k\uparrow}^\dagger a_{k\uparrow} - a_{k\downarrow}^\dagger a_{k\downarrow})} \tag{26.28}$$

$$\boxed{S_x = \frac{\hbar}{2} \sum_k (a_{k\downarrow}^\dagger a_{k\uparrow} + a_{k\uparrow}^\dagger a_{k\downarrow})} \tag{26.29}$$

$$\boxed{S_y = \frac{i\hbar}{2} \sum_k (a_{k\downarrow}^\dagger a_{k\uparrow} - a_{k\uparrow}^\dagger a_{k\downarrow})} \tag{26.30}$$

26.3   Position Representation (Field Operators)

It is often convenient to use basis states which are eigenstates of the position operator, rather than momentum states. The complication is that there are a continuum of position states, and they are not normalizable. (The momentum states are normalizable because we work in a box of finite volume.)

If we want to use the position representation we can do that by introducing what are called the field operators. Let us define a wave function $f_{\vec{r}_0,s}(R)$:

$$f_{\vec{r}_0,s}(R) = \delta(\vec{r} - \vec{r}_0)\delta_{\sigma s} = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}_0} \phi_{\vec{k},s}(R) \tag{26.31}$$

This is an eigenfunction of the position operator with eigenvalue $\vec{r}_0$. From the definition of the generalized creation operator we defined in p251b lecture 25 we can define $a^\dagger_{[f_{\vec{r}_0},s]}$ as:

$$a^\dagger_{[f_{\vec{r}_0},s]} = \left(\frac{1}{\Omega}\right)^{1/2} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}_0} a^\dagger_{\vec{k}s} \equiv \psi^\dagger_s(\vec{r}_0) \tag{26.32}$$

We have given this a special symbol $\psi^\dagger_s(\vec{r}_0)$ for convenience as this is an operator we will use very often. This operator creates a particle with definite position $\vec{r}_0$, with definite spin s. We call this a field operator.

Such operators have the following commutation/anti-commutation relations:

$$\text{Bosons} \quad [\psi_s(\vec{r}_0), \psi^\dagger_{s'}(\vec{r}_0')] = \delta(\vec{r}_0 - \vec{r}_0')\delta_{ss'} \tag{26.33}$$

$$\text{Fermions} \quad \{\psi_s(\vec{r}_0), \psi^\dagger_{s'}(\vec{r}_0')\} = \delta(\vec{r}_0 - \vec{r}_0')\delta_{ss'} \tag{26.34}$$

These operators are not really valid operators in the Hilbert space, since if I take it the operator acting on a state I will get back a nonnormalizeable state. But if, instead, I multiply it by some function and integrate it over some range, I can get a well defined operator. This is much the same as the electric field operator we encountered earlier in the course.

We can now go about rewriting the quantities we had discussed above using the new operators. Consider the potential energy:

$$\mathcal{U} = \sum_{i=1}^N \mathcal{U}(\vec{r}_i). \tag{26.35}$$

We can express this in terms of the creation and annihilation operators for plane waves by using equation (26.21), and we can then write it in terms of the $\psi_s(\vec{r})$ operators by inverting equation (26.32):

$$a^\dagger_{\vec{k}s} = \int \frac{d^3r}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}} \psi^\dagger_s \tag{26.36}$$

When we combine these, we will find that one of the integrals over $\vec{k}$ and $\vec{k}'$ gives us a delta function in position space and we are left with:

$$\mathcal{U} = \sum_s \int d^3r \mathcal{U}(\vec{r})\psi^\dagger_s(\vec{r})\psi_s(\vec{r}) \tag{26.37}$$

$$\equiv \sum_s \int d^3r \mathcal{U}(\vec{r})\rho_s(\vec{r}) \tag{26.38}$$

This is what we would expect: the position-dependent potential is diagonal in the basis where we create particles in states of definite position. The operator $\rho_s(\vec{r})$ is the density operator for

particles of spin s at position $\vec{r}$.

$$\rho_s(\vec{r}) = \psi_s^\dagger(\vec{r})\psi_s(\vec{r}) \tag{26.39}$$

We can follow the same procedure and obtain an expression for kinetic energy operator as:

$$K = \sum_s \int d^3r \left(\frac{-\hbar^2}{2m}\right) \psi_s^\dagger(\vec{r})\nabla^2\psi_s(\vec{r}) \tag{26.40}$$

The proof is left as an exercise.

The total Hamiltonian for non-interacting particles in a potential $\mathcal{U}(\vec{r})$ will then be given by the Hamiltonian

$$H = \sum_s \int d^3r \ \psi_s^\dagger(\vec{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + \mathcal{U}(\vec{r})\right] \psi_s(\vec{r}) \tag{26.41}$$

We can now see why this is called second quantization. In the first pass of quantum mechanics, if we were to take an expectation value for the Hamiltonian, it would look just like equation (26.41) except that the $\psi_s(\vec{r})$ would just be a wave function, which gives some complex number for every value of position $\vec{r}$ and spin index s. Now, when we quantize a second time, they are operators: at each position of space we assign an operator with a creation or annihilation operator contained in it. We thus convert the expression for the expectation value of an operator for a single particle, which is just a number, into an operator in the Hilbert space of an arbitrary number of identical particles.

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27.1 Operators in Second Quantization (continued)

In the previous lecture p251b lecture 26 we covered the general one body operator involving creation and annihilation operators:

$$Q = \sum_{i=1}^{N} Q^{(i)} \rightarrow \sum_{\alpha\beta} Q_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} \tag{27.1}$$

An example of such an operator was the Hamiltonian for non interacting particles which we found to be of the form:

$$H = \sum_{s} \int d^3r \; \psi_s^{\dagger}(\vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + \mathcal{U}(\vec{r}) \right] \psi_s(\vec{r}) \tag{27.2}$$

27.1.1 2 Body Interaction

We are now interested in looking at two-body interactions using the same formalism.

$$V = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} V(\vec{r}_i, \vec{r}_j) \tag{27.3}$$

We are usually interested in a class of interactions that only depend on the spatial separation between two bodies:

$$V(\vec{r}_i, \vec{r}_j) = V(|\vec{r}_i - \vec{r}_j|) \tag{27.4}$$

But for present purposes, we will look at a larger group of interactions assuming only that $V(\vec{r}', \vec{r}) = V(\vec{r}, \vec{r}')$, which is actually no restriction at all for indistinguishable particles. We can rewrite the potential stated in equation (27.3) in the following way:

$$\begin{aligned}
V &= \frac{1}{2} \sum_{i,j} V(\vec{r}_i, \vec{r}_j) - \frac{1}{2} \sum_{i} V(\vec{r}_i, \vec{r}_i) \tag{27.5} \\
&= \frac{1}{2} \int d^3r \, d^3r' \, V(\vec{r}, \vec{r}') \left(n(\vec{r}) n(\vec{r}') - \delta(\vec{r} - \vec{r}') n(\vec{r}) \right) \tag{27.6}
\end{aligned}$$

where $n(\vec{r}) \equiv \sum_i \delta(\vec{r} - \vec{r}_i)$ measures the density of particles at point $\vec{r}$. In second quantized notation we have

$$n(\vec{r}) = \sum_s \rho_s(\vec{r}) = \sum_s \psi_s^{\dagger}(\vec{r}) \psi_{s'}(\vec{r}) \tag{27.7}$$

We can now look at the quantity $n(\vec{r})n(\vec{r}\,')$, and use the commutation rules (which were discussed at the end of p251b Lecture 26) to arrive at:

$$n(\vec{r})n(\vec{r}\,') = \sum_{ss'} \psi_s^\dagger(\vec{r})\psi_s(\vec{r})\psi_{s'}^\dagger(\vec{r}\,')\psi_{s'}(\vec{r}\,') \tag{27.8}$$

$$= \sum_{ss'} \left(\psi_s^\dagger(\vec{r})\psi_{s'}^\dagger(\vec{r}\,')\psi_{s'}(\vec{r}\,')\psi_s(\vec{r}) \right) + \delta(\vec{r}-\vec{r}\,')n(\vec{r}) \tag{27.9}$$

We claim this is true for both Fermions and Bosons. For Bosons the relevant quantity to use is the commutator so we don't need to worry about sign changes as we commute things through. For Fermions since we are using two anticommutation relations, the negative signs cancel out. For the case of $\vec{r} \neq \vec{r}\,'$ we just have the anticommutator or commutator equal to zero. For the case where they are equal we just need to insert the delta function. Written more compactly, the above is true because, for fermions or bosons:

$$[\psi_s(\vec{r}), \psi_{s'}^\dagger(\vec{r}\,')\psi_{s'}(\vec{r}\,')] = \delta_{ss'}\delta(\vec{r}-\vec{r}\,')\psi_s(\vec{r}) \tag{27.10}$$

Now if we plug the value in equation (27.9) into equation (27.6) the rightmost terms cancel and we are left with:

$$V = \frac{1}{2}\int d^3r \int d^3r' \sum_{ss'} V(\vec{r},\vec{r}\,')\psi_s^\dagger(\vec{r})\psi_{s'}^\dagger(\vec{r}\,')\psi_{s'}(\vec{r}\,')\psi_s(\vec{r}) \tag{27.11}$$

Having all of the creation operators to the left of all the annihilation operators is called the normal ordered form. The operator vanishes if there are less than two particles present, as it should. The order of $\vec{r}$ and $\vec{r}\,'$ is important for Fermions, but doesn't matter for Bosons. For Fermions we need to have the two $\vec{r}\,'$ terms on the inside and $\vec{r}$ terms on the outside or vice versa, in order to get the correct sign.

Above is the potential in terms of the field operators. If we want to express the potential in terms of the momentum operators $a_{\vec{k}s}^\dagger, a_{\vec{k}s}$ we would have:

$$V = \frac{1}{2}\sum_{\substack{\vec{k}\vec{k}\,' \\ \vec{k}''\vec{k}'''}} \sum_{ss'} V_{\vec{k}'''\vec{k}''\vec{k}\,'\vec{k}}\, a_{\vec{k}''s}^\dagger a_{\vec{k}'''s'}^\dagger a_{\vec{k}\,'s'} a_{\vec{k}s} \tag{27.12}$$

If V is only a function of $(\vec{r}-\vec{r}\,')$, the coefficient at the front of the sum will be given by:

$$V_{\vec{k}'''\vec{k}''\vec{k}\,'\vec{k}} = \frac{1}{\Omega^2}\int d^3r \int d^3r'\, e^{i(\vec{k}-\vec{k}'')\cdot\vec{r}}e^{i(\vec{k}\,'-\vec{k}''')\cdot\vec{r}\,'}V(\vec{r}-\vec{r}\,') \tag{27.13}$$

$$= \delta_{\vec{k}+\vec{k}\,',\vec{k}''+\vec{k}'''}\left(\frac{1}{\Omega}\right)(2\pi)^{3/2}\tilde{V}(\vec{k}-\vec{k}'') \tag{27.14}$$

If we now define a new quantity:

$$\vec{\mathcal{K}} = \vec{k} - \vec{k}'' = \text{momentum transfer} \tag{27.15}$$

We can rewrite the potential as:

$$V = \frac{1}{2} \sum_{\substack{s,s' \\ \vec{k},\vec{k}',\mathcal{K}}} \frac{(2\pi)^{3/2}}{\Omega} \tilde{V}(\vec{\mathcal{K}}) a^\dagger_{\vec{k}+\vec{\mathcal{K}},s} a^\dagger_{\vec{k}'-\vec{\mathcal{K}},s'} a_{\vec{k}',s'} a_{\vec{k}s} \tag{27.16}$$

This form has a very satisfying interpretation: we are destroying two particles with momentum $\vec{k}$ and $\vec{k}'$ and creating two particles with momentum $\vec{k}+\vec{\mathcal{K}}$ and $\vec{k}-\vec{\mathcal{K}}$ indicating a transfer of momentum. Since $V(\vec{r}-\vec{r}') = V(\vec{r}'-\vec{r})$ must be real, the Fourier components must be real, with $\tilde{V}(\vec{k}) = \tilde{V}(-\vec{k})$. The most general 2 body operator in a general coordinate system will be of the form:

$$V = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta}\, a^\dagger_\beta a^\dagger_\alpha a_\gamma a_\delta \tag{27.17}$$

27.1.2   Coulomb Interaction

The case we are most concerned with is where we have a two body potential whose value is determined by the difference in positions of two particles. Of particular interest is the Coulomb interaction, where the Fourier transform of the potential should take the form:

$$(2\pi)^{3/2} V(\vec{\mathcal{K}}) = \frac{4\pi e^2}{\mathcal{K}^2} \tag{27.18}$$

We could now go ahead and substitute this into equation (27.16), but there is a problem. What do we do about the $\vec{\mathcal{K}} = 0$ term, which is infinite?

We drop it. The following are the reasons why this is usually justified:

1. The $k = 0$ term is just a constant. The term will be:

$$(2\pi)^{3/2} \tilde{V}(\vec{\mathcal{K}} = 0) \frac{N(N-1)}{2\Omega} \tag{27.19}$$

   which is a constant independent of the position of all the particles. Even if the constant were very large, it wouldn't affect the dynamics or anything else, so it is okay to get rid of it, as long as we are not trying to calculate the absolute value of the ground state energy.

2. Secondly, if we have a finite number of particles with Coulomb interactions in a large volume Ω, than we would basically have:

$$(2\pi)^3 \tilde{V}(\vec{\mathcal{K}} = 0) = \int_\Omega d^3 r \, \frac{e^2}{r} \simeq \Omega^{2/3} \tag{27.20}$$

Putting this into equation (27.19), we end up with something that scales as $\frac{N^2}{\Omega^{1/3}}$, so if the volume goes to infinity while the number of particles does not, the term would die out. Thus we can drop the term even if we are interested in the absolute energy.

3. For the case of $N \to \infty$ and $\Omega \to \infty$ such that $\frac{N}{\Omega} = $ constant, if we want to have a sensible thermodynamic limit where the energy doesn't just go to infinity we require overall neutrality of the system, so the $\vec{\mathcal{K}} = 0$ term is cancelled when you sum over all the species.

So the bottom line is that for Coulomb interactions, we normally ignore the $\vec{\mathcal{K}} = 0$ terms.

27.1.3   Systems with Several Types of Particles

We want to explore systems that can involve several different types of particles, where there can be several types of fermions (e.g., protons and neutrons and electrons), or of bosons, or a mix of fermions and bosons. The Hilbert space for this situation is the direct product of the individual Hilbert spaces for the different particles.

$$\mathcal{H} = \mathcal{H}_a \otimes \mathcal{H}_b \ldots \tag{27.21}$$

We can introduce creation and annihilation operators for the different species $a_\alpha^\dagger \; b_\beta^\dagger$. We know what the commutation or anticommutation relations are between $a's$, between $b's$, etc. . But what about between different kinds of particles. We use the following conventions. If either a or b both are Bosons, then we use the following commutation relations:

$$[a_\alpha, b_\beta^\dagger] = 0 = [a_\alpha, b_\beta] = [a_\alpha^\dagger, b_\beta^\dagger] \tag{27.22}$$

If both a and b are Fermions we then have:

$$\{a_\alpha, b_\beta^\dagger\} = 0 = \{a_\alpha, b_\beta\} = \{a_\alpha^\dagger, b_\beta^\dagger\} \tag{27.23}$$

For non relativistic quantum mechanics it wouldn't matter if we were to use the Bose commutation relations for different species of Fermions. Because in NRQM particles are not created or destroyed, we always have operators for a given type of particle going together in pairs. However, we use the convention (27.23) because in relativistic quantum mechanics there can be situations where different species of Fermions get converted from one to the other, and then it is more convenient to use the convention that creation and annihilation operators for different species of fermions anticommute.

Many Electron Problem

In the many electron problem, we are interested in finding the ground state. Given a Hamiltonian:

$$H = K + U + V \tag{27.24}$$

where $K =$ kinetic energy operator, $U =$ one body potential and V is a two-body interaction, with N Fermions, we want to be able to calculate the ground state. This will require some approximations. The common approach is to consider $H_1 = K + U$ exactly and treat V as a perturbation. Later we will speak about a better approximation, called the Hartree-Fock approximation.

Let us look first at the spectrum of H_1, where $|\phi_\alpha\rangle$ are the eigenstates of H_1:

$$H_1|\phi_\alpha\rangle = \epsilon_\alpha|\phi_\alpha\rangle \tag{27.25}$$

We assume the spectrum is not degenerate, and order the energy levels: $\epsilon_1 < \epsilon_2 < \epsilon_3 < \ldots$. We then define creation and annihilation operators $c_\alpha^\dagger$ and c_α for the corresponding states $|\phi_\alpha\rangle$ (it is conventional to use $c's$ rather than $a's$ for the creation/annihilation operators for electrons). H_1 can therefore be written:

$$H_1 = \sum_\alpha \epsilon_\alpha c_\alpha^\dagger c_\alpha \tag{27.26}$$

We can now ask, what is the ground state for N particles? For Bosons, the answer is easy: all the particles will be in the lowest energy state $\alpha = 1$. Then

$$E_N^0 = N\epsilon_1, \qquad n_1 = N, \ \ n_\alpha = 0 \text{ for } \alpha > 1. \tag{27.27}$$

The situation where you have a large number of bosons in one single particle state is called Bose-Einstein condensation. Experimental realizations, where a collection of ultracold trapped bosonic atoms form a Bose-Einstein condensate, are an active subject of current research. In many cases, the atoms are far apart, and it is a good approximation to neglect the two-body interactions.

For Fermions we achieve the ground state by filling up the lowest N single particle states with one particle in each state:

$$E_N^0 = \sum_{\alpha=1}^N \epsilon_\alpha \qquad \begin{array}{ll} n_\alpha = 1 & \text{for } \alpha \leq N \\ n_\alpha = 0 & \text{for } \alpha > N \end{array} \tag{27.28}$$

The ground state will therefore be constructed by using the $c^\dagger$ operators on the ground state:

$$|\psi_0\rangle = c_1^\dagger c_2^\dagger \ldots c_N^\dagger|0\rangle \rightarrow \psi_0(R_1 \ldots R_N) = \frac{1}{\sqrt{N!}} \det(\phi_\alpha(R_j)) \tag{27.29}$$

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As is shown on the right, this can be written using the Slater determinant (see p251b lecture 25) where $\alpha, j = 1 \dots N$. To go further than this we will have to take into account the effect of of V. To lowest order in V, this will require taking matrix elements involving a two body operator in single Slater determinant states.

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28.1   Slater Determinant State − Properties

In the previous lecture we began an analysis of a multi electron system with the Hamiltonian $H = K + U + V$, with K being the kinetic energy, U being the one body potential and V denoting the two body potential. We started by looking at the spectrum of $H_1 = K + U$ and determined that:

$$H = H_1 = \sum_{\alpha=1}^{\infty} \epsilon_\alpha c_\alpha^\dagger c_\alpha \tag{28.1}$$

where $c_\alpha^\dagger$ is the creation operator for an electron in the energy eigenstate state $\phi_\alpha(R)$. We shall assume a nondegenerate energy spectrum with $\epsilon_1 < \epsilon_2 < \epsilon_3 \ldots$. For the case of fermions, the ground state has particles in the lowest N energy levels, with α from $1 \to N$, which can be colnstructed by creation operators acting on the vacuum state, or which can equivalently be written in terms of the Slater determinant.

$$c_1^\dagger c_2^\dagger \ldots c_N^\dagger |0\rangle = \frac{1}{\sqrt{N!}} \det(\phi_\alpha(R_i)) \tag{28.2}$$

where α, i run from $1 \to N$.

Example: Non Interacting Electrons in Potential U(r) = 0

For the case of $U(\vec{r}) = 0$ with N particles in a volume Ω with periodic boundary conditions, H_1 can now be written.

$$H_1 = K = \sum_{\vec{k}s} \frac{\hbar^2 k^2}{2m} c_{\vec{k}s}^\dagger c_{\vec{k}s} \tag{28.3}$$

We are interested in the limit of large N and Ω for when $\frac{N}{\Omega} = \bar{n}$ is a constant. $c_{\vec{k}s}^\dagger$ creates a particle in the state:

$$\phi_{\vec{k}s}(\vec{r}, \sigma) = \frac{1}{\Omega^{1/2}} e^{i\vec{k}\cdot\vec{r}} \delta_{s,\sigma} \tag{28.4}$$

When the system is in its ground state, because of the Pauli exclusion principle (allowing a maximum occupancy of one per energy level for Fermions), the electrons will fill up all the energy levels up to some momentum $|\vec{k}| < k_F$ known as the Fermi momentum. We can state the total number of particles (for spin 1/2 in 3-D) in terms of the Fermi momentum by performing the following integration

$$N = \sum_{\vec{k}s} n_{\vec{k}s} = 2 \frac{\Omega}{(2\pi)^3} \int_{k<k_F} d^3k = 2 \frac{\Omega}{(2\pi)^3} \frac{4\pi k_F^3}{3} \tag{28.5}$$

The number density is therefore given by:

$$\bar{n} = \frac{N}{\Omega} = \frac{k_F^3}{3\pi^2} \tag{28.6}$$

We can now also perform an energy integration yielding:

$$E = \sum_{\vec{k}s} n_{\vec{k}s}\epsilon_k = \frac{2\Omega}{(2\pi)^3}\int_0^{k_f} 4\pi k^2\,dk\,\frac{\hbar^2 k^2}{2m} = \frac{3}{5}NE_f \tag{28.7}$$

where the Fermi energy E_F is given by:

$$E_f = \frac{\hbar^2 k_F^2}{2m} \tag{28.8}$$

Expectation Value of General One Body Operator in a General Slater Determinant State

We start by considering a state of the form:

$$|\Psi\rangle = c_1^\dagger \ldots c_N^\dagger |0\rangle \tag{28.9}$$

where as before the creation operators $c_\mu^\dagger$ are associated with the creation of a particle in single state-particle states $\phi_\mu(R)$ that are properly normalized and are orthogonal to each other.

We extend the states ϕ_μ to form a basis for $\mathcal{H}$ with $\mu = 1, \ldots, \infty$. Now let M be an arbitrary one body operator. As we have done in P251b lecture 26 we can write this in the form:

$$M = \sum_{\alpha\beta} M_{\alpha\beta} c_\alpha^\dagger c_\beta \tag{28.10}$$

The expectation value of this operator in the state specified in equation (28.9) will be:

$$\langle\Psi|M|\Psi\rangle = \sum_{\mu=1}^N M_{\mu\mu} = \sum_{\mu=1}^N \langle\phi_\mu|M|\phi_\mu\rangle \tag{28.11}$$

Invariance of the Slater determinant under change of basis

There is an important property of Slater determinant states which needs emphasis. Consider the following unitary transformation, for $1 \leq \nu \leq N$:

$$\psi_\nu(R) = \sum_{\mu=1}^N U_{\nu\mu}\phi_\mu \tag{28.12}$$

I claim that the Slater determinant state I get by occupying the N single particle states ψ_ν is the same, except for a possible phase factor, as the one obtained by occupying the original states ϕ_μ.

We can write the matrix $\psi_\nu(R_j)$ as a matrix product:

$$\psi_\nu(R_j) = \text{Matrix Product of } U_{\nu\mu}\,\phi_\mu(R_j) \tag{28.13}$$

Thus if we take the determinant of both sides, we get:

$$\frac{1}{\sqrt{N!}}\det\psi_\nu(R_j) = \overbrace{\det U_{\nu\mu}}^{\text{Constant }e^{i\theta}}\ \overbrace{\frac{1}{\sqrt{N!}}\det\phi_\mu(R_j)}^{|\Psi\rangle} \tag{28.14}$$

Equation (28.11) is consistent with this. Now when I change basis $\langle\Psi|M|\Psi\rangle$ must be invariant as the $e^{i\theta}$ terms cancel and indeed $\sum\langle\phi_\mu|M|\phi_\mu\rangle$ is a trace, which is independent of basis.

In other words, the N-particle Slater determinant state formed by occupying N single particle levels depends only on the subspace spanned by those states, not on the choice on the individual states directly. This is particularly important if the energy levels for non-interacting particles are degenerate. Thus for free particles, it does not matter if we use basis states which are plane waves or are standing waves (sines and cosines) so long as all states with the same energy are occupied. Similarly, it does not matter if we use energy levels with spin quantized in the z-direction, or in some other direction, as long as both spin states are occupied.

Expectation Value of General Two Body Operator in a General Slater Determinant State

We now want to consider two body operators of the form:

$$V = \frac{1}{2}\sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta}\,c_\beta^\dagger c_\alpha^\dagger c_\gamma c_\delta \tag{28.15}$$

To tackle matrix elements involving such operators, it is convenient to employ Wick's theorem.

Wick's Theorem

There is an accompanying handout posted on the class web site – *"Wick's theorem and the Hartree Fock approximation"* which serves as a supplement to this discussion. Let A, B, C, D be linear combinations of the annihilation operators c_i. Let $|\Psi\rangle$ be any Slater determinant state. We now claim:

$$\langle A^\dagger B^\dagger C D\rangle_\Psi = \langle A^\dagger D\rangle_\Psi \langle B^\dagger C\rangle_\Psi - \langle A^\dagger C\rangle_\Psi \langle B^\dagger D\rangle_\Psi \tag{28.16}$$

Note: This result is not true for general states in the antisymmetric Hilbert space; it is only true for states that can be represented as a single Slater determinant.

To prove the result, we use a basis where $|\Psi\rangle = c_1^\dagger c_2^\dagger....c_N^\dagger|0\rangle$ and expand out the operators as $A = \sum_i A_i c_i$, *etc.* The left-hand side of Eq. (28.16) now becomes:

$$\langle A^\dagger B^\dagger C D\rangle_\Psi = \sum_{ii'i''i'''} A_i^* B_{i'}^* C_{i''} D_{i'''} \langle c_i^\dagger c_{i'}^\dagger c_{i''} c_{i'''}\rangle_\Psi \tag{28.17}$$

Recalling the anticommutation relations for Fermions, as well as our convention for the constant that appears when acting with a creation or annihilation operator (see p251b Lecture 25) we find:

$$\langle c_i^\dagger c_{i'}^\dagger c_{i''} c_{i'''}\rangle_\Psi = 1 \quad (\text{If } i = i''' \leq N \quad i' = i'' \leq N \quad i' \neq i) \tag{28.18}$$
$$= -1 \quad (\text{If } i = i'' \leq N \quad i' = i''' \leq N \quad i' \neq i) \tag{28.19}$$
$$= 0 \quad \text{Otherwise.} \tag{28.20}$$

We also know that $\langle c_i^\dagger c_{i''}\rangle_\Psi = 1$ if $i = i'' \leq N$, and $= 0$, otherwise; etc. From this, we see that

$$\langle c_i^\dagger c_{i'}^\dagger c_{i''} c_{i'''}\rangle_\Psi = \langle c_i^\dagger c_{i'''}\rangle_\Psi \langle c_{i'}^\dagger c_{i''}\rangle_\Psi - \langle c_i^\dagger c_{i''}\rangle_\Psi \langle c_{i'}^\dagger c_{i'''}\rangle_\Psi \tag{28.21}$$

Then, from this, we can readily derive equation (28.16).

We can also extend Wick's theorem to products of six or more operators. For example:

$$\langle A^\dagger B^\dagger C^\dagger D E F\rangle = \langle A^\dagger F\rangle \langle B^\dagger E\rangle \langle C^\dagger D\rangle \pm (\text{Permutations} \, (6 \, \text{Total})) \tag{28.22}$$

This example is discussed more in the handout page 2.

A general formulation of Wick's theorem is to say that to find the expectation value of a product of some number of creation and annihilation operators in a Slater-determinant state, we replace the expectation value of the product by the sum over all **contractions**, where we group the operators into pairs and replace each pair of operators by its expectation value, multiplying each term by ± 1 depending on the sign of the permutation implied by the contraction.

Wick's Theorem Applied to a 2 Body Potential

We can now return to the two body potential first given in p251b lecture 27:

$$V = \frac{1}{2} \sum_{ss'} \int d^3r \int d^3r' \, V(\vec{r} - \vec{r}') \psi_s^\dagger(\vec{r}) \psi_{s'}^\dagger(\vec{r}') \psi_s(\vec{r}') \psi_s(\vec{r}) \tag{28.23}$$

If we apply Wick's theorem, we find:

$$\langle V \rangle_\Psi = \frac{1}{2} \int d^3 r d^3 r' V(\vec{r} - \vec{r}\,') \left(\langle n(\vec{r}) \rangle_\Psi \langle n(\vec{r}\,') \rangle_\Psi - \overbrace{\sum_{ss'} |\langle \psi_s^\dagger(\vec{r}) \psi_{s'}(\vec{r}\,') \rangle|^2}^{\text{Exchange Term}} \right) \tag{28.24}$$

where:

$$n(\vec{r}) = \sum_s \psi_s^\dagger(\vec{r}) \psi_s(\vec{r}) \tag{28.25}$$

Taking the expectation value we have:

$$\langle n(\vec{r}) \rangle_\Psi = \sum_s \langle \psi_s^\dagger(\vec{r}) \psi_s(\vec{r}) \rangle_\Psi = \sum_{i=1}^N \sum_s |\phi_i(\vec{r}, s)|^2 \tag{28.26}$$

In the simplest case where:

$$\phi_i(\vec{r}, s) = \phi_i(\vec{r}) \delta_{s,s_i} \tag{28.27}$$

this yields:

$$\langle n(\vec{r}) \rangle_\Psi = \sum_{i=1}^N |\phi_i(\vec{r})|^2 \tag{28.28}$$

We also find that:

$$\langle \psi_s(\vec{r})^\dagger \psi_{s'}(\vec{r}\,') \rangle_\Psi = \sum_{i=1}^N \phi_i^*(\vec{r}, s) \phi_i(\vec{r}\,', s') \tag{28.29}$$

In the simplest case where $\phi_i \propto \delta_{s,s_0}$ only $s = s'$ contributes to the exchange term. The negative exchange term in equation (28.24) may be understood as a reflection of of the Pauli exclusion principle, which prevents two fermions of the same spin from coming close together in space.

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29.1   Hartree Fock Approximation

Note: there is an accompanying handout posted on the class web site – *"Wick's theorem and the Hartree Fock approximation"* – which serves as a supplement to this discussion.

We are interested in dealing with a Hamiltonian where we have a one body potential U and two body potential V:

$$H = K + U + V \tag{29.1}$$

where K is the kinetic energy term. The one body potential term can be written in the form: $\int d^3r\, U(\vec{r}) n(\vec{r})$, where $n(\vec{r})$ is the density of particles at the location $\vec{r}$. The two body potential V takes the form in second quantized notation as:

$$V = \frac{1}{2} \sum_{ss'} \int d^3r\, d^3r' V(\vec{r} - \vec{r}\,') \psi_s^\dagger(\vec{r}) \psi_{s'}^\dagger(\vec{r}\,') \psi_{s'}(\vec{r}\,') \psi_s(\vec{r}) \tag{29.2}$$

In general, we cannot find the ground state of such a Hamiltonian. What we can try is to find the best single Slater determinant (SSD) state approximation to the ground state. We say "best" since by the variational theorem we can find the SSD state that minimizes the expectation value of:

$$E(\Psi) = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{29.3}$$

Minimization, in turn, implies that the value of $E(\Psi)$ as written above is stationary ($\delta E = 0$) for any infinitesimal change $|\Psi\rangle \to |\Psi\rangle + \delta|\Psi\rangle$ that *preserves* the SSD form.

Let us write our trial SSD state in the form

$$|\Psi\rangle = c_1^\dagger c_2^\dagger \ldots c_N^\dagger |0\rangle \tag{29.4}$$

where c_μ annihilates a particle in the state $\phi_\mu(R)$. The *result*, which we will prove later, is that if $E(\Psi)$ is stationary to infinitesimal changes, ϕ_μ can be chosen to be eigenfunctions of a one body operator H_{eff}, which has the form (as shown on p.4 of the handout) of:

$$H_{eff} = K + U + V_{direct} + V_{exchange} \tag{29.5}$$

where V_{direct} and $V_{exchange}$ are one body operators. The functions ϕ_μ will obey: $H_{eff}\, \phi_\mu = \epsilon_\mu \phi_\mu$ and the aforementioned one body operators will be:

$$V_{direct} = \int d^3r d^3r' \sum_{ss'} V(\vec{r} - \vec{r}\,') \langle \psi_{s'}^\dagger(\vec{r}\,') \psi_{s'}(\vec{r}\,') \rangle_\Psi \; \psi_s^\dagger(\vec{r}) \psi_s(\vec{r}) \tag{29.6}$$

$$V_{exchange} = - \int d^3r d^3r' \sum_{ss'} V(\vec{r} - \vec{r}') \langle \psi_s^\dagger(\vec{r}) \psi_{s'}(\vec{r}') \rangle_\Psi \ \psi_{s'}^\dagger(\vec{r}') \psi_s(\vec{r}) \tag{29.7}$$

As we can see, by taking the expectation value of two of the four creation and annihilation operators, we have turned the two body operator into a one body operator, involving only single pairs of creation and annihilation operators, $\psi^\dagger$ and ψ.

Form in a General Basis

The Hartree-Fock equations can be written in an arbitrary basis. In arbitrary basis we would write the two body operator as:

$$V = \frac{1}{2} \sum_{lmnp} V_{lmnp} a_m^\dagger a_l^\dagger a_n a_p \tag{29.8}$$

Because Hamiltonian is Hermitian, and because the product of operators is unchanged if we interchange simultaneous the index m with l and n with p, we may assume , without loss of generality, that

$$V_{lmnp} = V_{mlpn} = V_{pnml}^*. \tag{29.9}$$

The effective one-body Hamiltonian we obtain in this case is

$$H_{eff} = K + U + V_{eff}, \tag{29.10}$$

where V_{eff} has the form

$$V_{eff} = \sum_{ln} V_{ln}^{eff} a_l^\dagger a_n, \tag{29.11}$$

and the value of the matrix element is given by:

$$V_{ln}^{eff} = \sum_{mp} \langle a_m^\dagger a_p \rangle_\Psi \ (V_{lmnp} - V_{lmpn}). \tag{29.12}$$

Here V_{lmnp} represents the direct term and V_{lmpn} the exchange term. We note that if this form is correct in one basis, it is true in any basis, as the form is invariant under unitary transformations.

The rule for constructing the effective potential may be stated as follows. Take the two body potential (29.8) and replace the product of four creation and annihilation operators by the sum over all **partial contractions**, obtained by replacing one pair of operators by its expectation value in the state Ψ, while leaving the other pair as operators, and multiplying by the appropriate sign as in Wick's theorem. The factor of 1/2 in (29.8) has disappeared in (29.11) because we only list explicitly one-half of the possible pairings in the latter equation. The omitted pairings are physically identical to the ones which have been listed except for relabeling of indices.

2

29.1.1 Physical Meaning.

Before we get to the derivation of the Hartree-Fock equations, let us say more about the meaning. Consider the case of the two body potential (29.2), with a potential $V(\vec{r} - \vec{r}\,')$. The V_{direct} term once we carry out the sum over s just has the form:

$$V_{direct} = \int d^3 r V_{dir}(\vec{r}) n(\vec{r}) \tag{29.13}$$

$$V_{dir}(\vec{r}) \equiv \int d^3 r V(\vec{r} - \vec{r}\,') \langle n(\vec{r}\,') \rangle_{\Psi} \tag{29.14}$$

This term embodies an approximation that if we pick out any particular electron in the system, then it moves in an effective potential which arises from the Coulomb interaction with the *average* charge density of all the electrons in the system (including itself).

From the direct potential, we subtract the exchange term, which is harder to interpret. We shall see that it reflects the Pauli exclusion principle, which says that two electrons of the same spin cannot exist at the same point. Thus the Slater determinant (or any valid many-body wave function) will vanish when two particle of like spin approach each other, and the Coulomb repulsion energy is thereby reduced. We shall also see that in a certain sense, the exchange term cancels the electron's interaction with itself.

Unfortunately, the exchange term (equation (29.7)) is hard to use in calculations, because it has a creation operator at one location and an annihilation operator in another location, so it is non-local. It is particularly hard to deal with in numerical calculations, because when the Hamiltonian is discretized, the exchange term leads to matrix with many more non-zero elements, compared to the direct term and kinetic energy, which are relatively sparse. This makes inversion of the matrix much more time-consuming.

Since the exchange term is relatively intractable, one often makes a further approximation called the **Hartree approximation** where one simple drops the exchange term. In many cases the direct term is the most important contribution, so it is often not such a bad approximation to use.

There are other approximations, including what is called the **local density approximation** or **LDA**. In this case the exchange term is dropped and replaced by a local term which tries to take into account correlations between the electrons. It is sometimes better than the Hartree Fock approximation and is much easier to use.

29.1.2   How to solve the Hartree-Fock equations.

Regardless of the headaches involved, we look into how to solve the Hartree Fock equations. (Similar issues will arise if you employ one of the simplified approximations such as Hartree or LDA.) To solve these equations, we make some rough guess as to what H_{eff} looks like (you could equivalently guess a set of states at first and look at the resulting form of H_{eff}), we solve the Schrödinger equation $H_{eff}\phi_\mu = \epsilon_\mu \phi_\mu$ using that guess and you get a bunch of states. Then you have to go back, fill up the proper N states and calculate self consistently what your new H_{eff} looks like. Now you will have a slightly different H_{eff} term, and you recalculate and solve the Schrödinger equation $H_{eff}\phi_\mu = \epsilon_\mu \phi_\mu$ again, getting a new set of states, filling up the first N levels, and recalculating H_{eff} until, hopefully, you get convergence. Sometimes, this process does not converge; for example if the two body-potential is sufficiently strong, you might find that the successive iterations overshoot the goal by a larger and larger amounts. In this case there are tricks for helping convergence: for example, one may be able to reach convergence by starting with a small value of V, and increasing its strength gradually, so that the Hartree-Fock state changes by only a small amount at each iteration.

Once you get convergence you have found a local minimum of the energy expectation value, but it is not necessarily an absolute minimum. As the Hartree-Fock expectation value is a non-linear function of the constituent one-body orbitals, it may have several local minima, and it is possible to get trapped in a minimum whose energy is higher than the best one. In cases where the two-particle Hamiltonian has a symmetry and the starting trial wave function respects that symmetry, the iterative Hartree-Fock procedure may lead you to a saddle point, where the energy is a minimum within the class of Slater Determinant states that respect the symmetry, but where the energy may be reduced by going in a direction which breaks the symmetry. In this case we say that the true Hartree-Fock ground state is a state with **spontaneously broken symmetry**.

This may be illustrated by the following example.

29.1.3   Fermions in a box with periodic boundary conditions.

Consider a system of identical fermions in a box with periodic boundary conditions and an external potential U which is zero inside the box. Furthermore, assume a two-body interaction V which is independent of spin and depends only on the separation between particles, as in Eq. (29.2). Then the Hamiltonian H is invariant under translations, and it commutes with the total momentum operators $\vec{P}$. It also commutes with the total spin operators $\vec{S}$, so the Hamiltonian is invariant under rotations in spin space. It is then natural to assume an SSD

trial state which is physically invariant under translations and rotations. In that case, when we take partial contractions, we would expect that the resulting effective Hamiltonian H_{eff} will be translationally and rotationally invariant; it too will commute with the momentum and spin operators. Thus H_{eff} must have a complete set of one-body eigenstates of H_{eff} which are simultaneously eigenstates of $\vec{P}$ and S_z. These states are nothing but the plane wave states $\phi_{\vec{k}s}$ of the kinetic energy operator K itself. Thus the filled Fermi sea of the noninteracting is already a self-consistent solution of the Hartree-Fock equations when the two-body interaction is turned on. The total energy of the ground state may be computed by adding to the unperturbed kinetic energy the expectation value of the two-body interaction V, which we compute exactly as we did in the previous lecture, when we calculated the energy in first order perturbation theory.

If the interaction V is sufficiently weak and non-singular, one generally finds that the translationally invariant state is the absolute ground state of the Hartree-Fock equations, so that the Hartree-Fock energy is the same as the energy computed in first-order perturbation theory. On the other hand, if the interaction is strong, there may be other solutions with lower energy. For example, we may consider a Slater determinant state which is translationally invariant but is completely spin polarized. That is, we spontaneously break the spin symmetry and only populate states with $s = 1$, or we only populate states with $s = -1$. Such a state will have a higher kinetic energy that the unpolarized state, as the Fermi wave vector must now be larger by a factor of $2^{1/3}$ in order to keep the total number of particles fixed. However, the exchange energy will be different in the two states, and if the two-body interaction is repulsive, the potential energy will generally be lower in the spin-polarized (**ferromagnetic**) state. The ferromagnetic state may win out, if the interaction is sufficiently strong.

The ferromagnetic state is only one of many competing states one should consider in the presence of strong interactions. Possible states with broken translational symmetry include states with charge-density oscillations of various types, crystalline states, spin-density-wave states and antiferromagnetic states. Various types of spontaneously-broken symmetry states can occur for electrons in the presence of a periodic external potential arising from a crystal lattice of ions. Questions of which state has the lowest energy, and whether Hartree-Fock is a qualitatively reliable guide, depend on details of the system, and are beyond the scope of the present course.

One important class of ground-states, beyond the reach of the Hartree-Fock approximation, are superconducting states. These states can be described by the Bardeen-Cooper-Schrieffer (BCS) approximation, which will be discussed briefly at the end of this Lecture, and which may be considered to be a generalization of the Hartree-Fock approximation,

29.1.4   Significance of ϵ_μ

What is the significance of the eigenvalues ϵ_μ of the Hartree-Fock effective Hamiltonian? They are in some sense the energies that make up the states in the Slater determinant. However, it is not true that the sum of the eigenvalues of the occupied states is equal to the energy $E(\Psi)$, which is the expectation value of the Hamiltonian in Slater determinant state. Rather we find that :

$$\sum_{\mu=1}^{N} \epsilon_\mu = \langle T + U \rangle_\Psi + 2\langle V \rangle_\Psi = \langle H_{eff} \rangle_\Psi \tag{29.15}$$

$$= \langle H \rangle_\Psi + \langle V \rangle_\Psi \neq \langle H \rangle_\Psi \tag{29.16}$$

The sum of one body interactions gets summed up properly. However we get an extra factor of 2 for the two body interactions. This is related to each electron seeing the potential from every other electron, so in a sense each pair gets counted twice when we add up the eigenvalues ϵ_μ for all the occupied states.

There is a theorem, however, **Koopman's theorem**, that states if you take a particle out of an occupied state μ, allowing no other changes, then amount of energy change is $-\epsilon_\mu$. Similarly if you just add an electron to an unoccupied state α, without changing the other states, then that change will be ϵ_α.

In general, if one wants to find a self-consistent Hartree-Fock solution with one additional particle or one particle removed, it is not correct to ignore effects due to the induced changes of the wave functions for the remaining particles. However, in the case of a very large system, if the Hartree Fock states are extended throughout the system, these induced changes are negligible, so that Koopman's theorem applies even when changes are taken into account. (A more complete discussion of this is given in the Handout.)

29.1.5   Derivation of the Hartree Fock Approximation Recipe

Let $\{\phi_\alpha\}$ be an orthonormal basis of wave functions for the one-particle Hilbert space, and let $c_\alpha^\dagger$ be the corresponding creation operators, chosen so that the functions ϕ_α with $1 \leq \alpha \leq N$ are the states that enter our SSD state $|\Psi\rangle$, following Eq. (29.4).

We shall construct infinitesimal changes onto our wave functions such that they are still Slater determinant states, by writing

$$|\Psi\rangle + |\delta\Psi\rangle = b_1^\dagger \ldots b_\mu^\dagger |0\rangle \tag{29.17}$$

where $\mu = 1 \ldots N$, and the $b_\mu^\dagger$ are infinitesimally shifted from the $c_\mu^\dagger$. Then we may expand the operators $b_\mu^\dagger$ in terms of the operators $c_\alpha^\dagger$ as

$$b_\mu^\dagger = c_\mu^\dagger + \sum_{\alpha=1}^{\infty} \lambda_{\mu\alpha} c_\alpha^\dagger, \tag{29.18}$$

where $\lambda_{\alpha\mu}$ are infinitesimal complex numbers. This means:

$$|\delta\Psi\rangle = \sum_{\alpha=1}^{\infty} \sum_{\mu=1}^{N} \lambda_{\mu\alpha} |\Psi_{\alpha\mu}\rangle \tag{29.19}$$

where $|\Psi_{\alpha\mu}\rangle$ is:

$$|\Psi_{\alpha\mu}\rangle = c_\alpha^\dagger c_\mu |\Psi\rangle \tag{29.20}$$

This last is the state that results if one uses the operator c_μ to remove a particle from a one-particle state μ that was occupied in the original Slater-determinant state $|\Psi\rangle$ and replaces it by a particle in another state α, using the operator $c_\alpha^\dagger$. Then, the change in energy for the Slater determinant state is,

$$\delta\langle H\rangle_\Psi = \langle\Psi|H|\delta\Psi\rangle + \langle\delta\Psi|H|\Psi\rangle - \langle H\rangle_\Psi\langle\langle\Psi|\delta\Psi\rangle + \langle\delta\Psi|\Psi\rangle\rangle \tag{29.21}$$

$$= 2\mathrm{Re}\left(\sum_{\alpha=1}^{\infty}\sum_{\mu=1}^{N} \lambda_{\mu\alpha}\right) \left(\langle\Psi|H|\Psi_{\alpha\mu}\rangle - \langle H\rangle_\Psi \langle\Psi|\Psi_{\alpha\mu}\rangle\right) \tag{29.22}$$

But $\lambda_{\mu\alpha}$ are arbitrary complex infinitesimals. For the quantity to be stationary ($\delta\langle H\rangle_\Psi = 0$) equation (29.22) must be zero for all values of the $\lambda_{\mu\alpha}$, meaning that the quantity in parentheses on the right must be zero for all terms in the sum, i.e.:

$$\langle\Psi|H|\Psi_{\alpha\mu}\rangle = \langle H\rangle_\Psi \langle\Psi|\Psi_{\alpha\mu}\rangle \quad \begin{array}{l} \forall\ \mu = 1\ldots N \\ \forall\ \alpha = 1\ldots\infty \end{array} \tag{29.23}$$

There is some algebra to be done after this step (described on pages 5-7 of the handout), but what this leads us to is that for $\mu \leq N$ and $\alpha > N$:

$$\langle\phi_\mu|H_{eff}|\phi_\alpha\rangle = 0 \tag{29.24}$$

Taking the adjoint we also have:

$$\langle\phi_\alpha|H_{eff}|\phi_\mu\rangle = 0 \tag{29.25}$$

We also see (from the handout) that if both $\alpha, \mu \leq N$, the matrix elements $\langle\phi_\alpha|H_{eff}|\phi_\nu\rangle$ are generally $\neq 0$. However, the elements of this matrix form an $N \times N$ hermitian matrix, so we

could now make a unitary transfomation to the occupied states, without changing the N body wavefunction, so that within the space of occupied states, H_{eff} is a diagonal matrix.

$$\langle \phi_\mu | H_{eff} | \phi_\nu \rangle = \epsilon_\mu \delta_{\mu\nu} \tag{29.26}$$

Once we have done this, it follows that our condition for equation (29.3) to be stationary reduces to

$$H_{eff}\phi_\mu = \epsilon_\mu \phi_\mu. \tag{29.27}$$

Finite temperatures.

There is also an extension of the Hartree Fock approximation to **finite temperatures** that we shall not discuss in class, but which is discussed in the Handout.

29.1.6　Superconductivity – the BCS approximation

The BCS approximation begins with a trial state of the form

$$|\Psi\rangle = \prod_{\vec{k}} (u_{\vec{k}} + v_{\vec{k}} c_{\vec{k}\uparrow}^\dagger c_{-\vec{k}\downarrow}^\dagger) |0\rangle, \tag{29.28}$$

where the product is over all wave vectors consistent with the periodic boundary conditions in a box, and $u_{\vec{k}}$ and $v_{\vec{k}}$ are complex numbers satisfying $|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1$. The familiar SSD state of a filled Fermi sea is a special case of this, where $v_{\vec{k}} = 1, u_{\vec{k}} = 0$ for $k < k_F$, and $v_{\vec{k}} = 0, u_{\vec{k}} = 1$ for $k > k_F$. In the general BCS state, however, one allows both $v_{\vec{k}} \neq 0, u_{\vec{k}} \neq 0$ for a range of wave vectors close to the Fermi wave vector. The BCS does not have a definite number of particles, but fluctuations in the number will be relatively small in the case of a very large system, so this may not be a cause for worry. The expectation of the Hamiltonian, including one body and two body terms, can be calculated in a BCS state using a generalization of Wick's theorem, and one can choose the coefficients $u_{\vec{k}}$ and $v_{\vec{k}}$ to minimize the energy. (More accurately, one wants to minimize the expectation value of $H - \mu N$ where μ is the chemical potential. The BCS state can have a lower energy than the ordinary Fermi sea, particularly when the two-body potential is attractive. The generalized form of Wick's theorem for a BCS state is

$$\langle A^\dagger B^\dagger C D \rangle = \langle A^\dagger D \rangle \langle B^\dagger C \rangle - \langle A^\dagger C \rangle \langle B^\dagger D \rangle + \langle A^\dagger B^\dagger \rangle \langle C D \rangle, \tag{29.29}$$

where A, B, C, and D are arbitrary linear combinations of electron annihilation operators c_α. Moreover, expectation values such as $\langle A^\dagger B^\dagger \rangle$ and $\langle C D \rangle$ can be non-zero in the BCS state.

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30.1   Symmetry in Quantum Mechanics

We now begin with a discussion of the importance of symmetry in Quantum Mechanics. We will focus on the rotation group, but a lot of what we say is demonstrative of more general principles. There is a good discussion of this material in chapter 17 of Merzbacher. You may also want to look at chapter 16 on spin.

In p251a we looked at general angular momentum operators J_x, J_y, J_z and J^2:

$$J^2 \equiv J_x^2 + J_y^2 + J_z^2 \tag{30.1}$$

The operators obeyed the commutation values of the form:

$$[J_x, J_y] = i\hbar J_z \tag{30.2}$$

and cyclic permutations. These imply that $[\vec{J}, J^2] = 0$.

From the commutation relations alone we were able to say the only possible eigenvalues of J^2 are:

$$\vec{J}^2 = \hbar^2 j(j+1) \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2} \ldots \tag{30.3}$$

Similarly the allowed values for J_z are:

$$J_z = \hbar m \qquad m = -j, -j+1, \ldots, j \tag{30.4}$$

For a fixed value of j. there are $2j+1$ allowed values for J_z, which are in fact all required. Once we have one value of m, we can apply raising and lowering operators to get the rest of them. These are the generalized angular momentum operators because we are only using the commutation rules. They could be total angular momentum, orbital angular momentum, or spin angular momentum; or they could also represent some symmetry that has nothing to do with rotation, like the isospin symmetry of strong interactions that connects protons and neutrons. They are all described by operators that obey these commutation relations.

There are many connections with symmetry. A strong one is that we can take functions of these Hermitian operators and form a unitary rotation matrix:

$$U(\lambda, \hat{n}) = e^{-i\lambda \hat{n} \cdot \vec{J}/\hbar} \tag{30.5}$$

which produces a rotation by the angle λ about an axis $\hat{n}$. This mixes states of different m but does not change j.

In general, there will be an infinite number of states in the Hilbert space corresponding to a given value of j and m. We distinguish these by another index α. For example, for the one-particle Schrödinger equation in a central potential, α may represent the radial quantum number n. More generally, we can consider some maximal set of operators which commute with each other and commute with the angular momentum operators, and let α represent the eigenvalues of these operators. Then the value of α will be invariant under rotations. We can now write the effect of the operator $U(\lambda, \hat{n})$ acting on some eigenstate $|\alpha, j, m\rangle$ as:

$$U(\lambda, \hat{n})|\alpha, j, m\rangle = \sum_{m'} |\alpha, j, m'\rangle \overbrace{D^{(j)}_{m'm}(\lambda, \hat{n})}^{(2j+1)\times(2j+1) \text{ Matrix}} \tag{30.6}$$

These matrices $D^{(j)}$ with fixed j form a group. If we take two such matrices and multiply them together we get any another matrix that corresponds to an angle which corresponds to composing to subsequent rotations. These form an **irreducible representation** of the rotation group. This means that if we have some matrix A which commutes with all the $D^{(j)}$ matrices, then the matrix must have the form $A = cI$, which is a multiple of the identity. We also say that the states $|j, \alpha, m\rangle$ with fixed j and α form a basis for the irreducible representation of the rotation group. This means there is a 2j+1 dimension space that is spanned by these vectors, which is invariant under rotations, and there is no smaller subspace that is invariant under those rotations. The last statement is equivalent to saying that within the vector space, there is no operator that can commute with all the rotation operators unless it is a multiple of the identity.

The value of the D matrices can be obtained by taking the inner product of equation (30.6) with $\langle \alpha, j, m'|$:

$$D^{(j)}_{m',m} = \langle \alpha, j, m'|e^{-i\lambda\hat{n}\cdot\vec{J}/\hbar}|\alpha, j, m\rangle \tag{30.7}$$

These expressions can be evaluated by expanding the exponential out in a Taylor series and using J_z and either J_x, J_y or the somewhat more convenient $J_\pm$ operators: defined by:

$$J_\pm = J_x + iJ_y \tag{30.8}$$

The effect of J_z is $J_z|j, \alpha, m\rangle = \hbar m|j, \alpha, m\rangle$ and the effect of $J_\pm$ is:

$$J_\pm|\alpha, j, m\rangle = \sqrt{j(j+1) - m(m \pm 1)}\ |\alpha, j, m \pm 1\rangle \tag{30.9}$$

or, equivalently,

$$J_\pm|\alpha, j, m\rangle = \sqrt{(j \mp m)(j \pm m + 1)}\ |\alpha, j, m \pm 1\rangle \tag{30.10}$$

These formulas are all independent of the additional quantum number α, so $D^{(j)}_{m',m}$ is also independent of α.

30.1.1   Addition of Angular Momentum

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We now want to explore what happens when you combine (take the direct product of) two irreducible representations. To illustrate this in concrete terms we will look at the case of addition of angular momentum. We'll look at the example of two non-interacting particles in a central potential. We have a Hamiltonian H_0 such that $H_0 = H_1 + H_2$, where:

$$H_1 = \frac{p_1^2}{2\mu_1} + V_1(|\vec{r}_1|) \qquad H_2 = \frac{p_2^2}{2\mu_2} + V_2(|\vec{r}_1|) \tag{30.11}$$

Let $\vec{J}_1 = \vec{r}_1 \times \vec{p}_1$ be the angular momentum of particle one and $\vec{J}_2 = \vec{r}_2 \times \vec{p}_2$ be the angular momentum of particle two. These operators commute with each other, as particles 1 and 2 are independent, and with the Hamiltonian H_0, since the potentials are spherically symmetric. The eigenstates of H_0 can be considered as direct products of the eigenstates of each of the subspaces:

$$\text{Eigenstates of H}_0 \rightarrow |\alpha_1, j_1, m_1\rangle \otimes |\alpha_2, j_2, m_2\rangle \tag{30.12}$$

The degeneracy of each of the states (for the different m_{j_1}, m_{j_2} values) will be $(2j_1+1)(2j_2+1)$. We can now add a distance-dependent two-body potential:

$$H_{int} = \gamma U(|\vec{r}_1 - \vec{r}_2|) \tag{30.13}$$

For this potential we now have:

$$\left[\vec{J}_1, H_{int}\right] \neq 0 \qquad \left[\vec{J}_2, H_{int}\right] \neq 0 \tag{30.14}$$

This means that we can no longer expect to find simultaneous eigenvalues of $J_1^2, J_2^2, J_1^z, J_2^z$ and the Hamiltonian. However, we claim that the total angular momentum $\vec{J}$ still commutes with the Hamiltonian

$$\vec{J} = \vec{J}_1 + \vec{J}_2 \qquad \left[\vec{J}, H_{int}\right] = 0 \tag{30.15}$$

so that we can still find simultaneous eigenfunctions of H, J^2, J_z.

The reason for this is that the operator $e^{i\lambda\hat{n}\cdot\vec{J}} = e^{i\lambda\hat{n}\cdot\vec{J}_1}e^{i\lambda\hat{n}\cdot\vec{J}_2}$ produces simultaneous rotations of both particles, and does not change the distance between them. Therefore, it should commute with H_{int}, for arbitrary λ and $\hat{n}$, which implies that H_{int} commutes with all three components of $\vec{J}$.

If we wish to treat this problem using H_{int} as a perturbation, we should be prepared to use degenerate perturbation theory, since H_0 has degenaracies, If γ is small, then to first first order

in γ we need to diagonalize H_{int} in the subspaces of the eigenstates of H_0 that are degenerate. In the present case, we have a subspace of size $(2j_1 + 1)(2j_2 + 1)$. We want to take linear combinations of those eigenstates that will be eigenstates of J^2 and J_z. We will find that there is at most a single state in this subspace with a given value of j and m, so if we use these states as basis states, we are guaranteed to have diagonalized H_{int}.

To summarize, since:

$$H = H_0 + H_{int} \qquad \left[\vec{J}, H\right] = 0, \tag{30.16}$$

we want to find linear combinations of the basis (product) states $|\alpha_1, j_1, m_1\rangle|\alpha_2, j_2, m_2\rangle$ (with fixed $j_1, j_2, \alpha_1, \alpha_2$) that are eigenstates of $H_0, J_1^2, J_2^2, J^2, J_z$. This is possible as $[J_1^2, \vec{J}] = [J_2^2, \vec{J}] = 0$. These states will be eigenstates of H correct to first order in γ. (If we go to higher order in γ, the energy eigenstates can still be chosen to be eigenstates of J^2 and J_z, but they will generally not be exact eigenstates of J_1^2 or J_2^2.)

The states we are looking for will be labeled $|\alpha_1, \alpha_2, j_1, j_2, j, m\rangle$, and we will write them as linear combinations of the basis states in the form:

$$|\alpha_1, \alpha_2, j_1, j_2, j, m\rangle = \sum_{m_1 m_2} |\alpha_1, \alpha_2, j_1, j_2, m_1, m_2\rangle \cdot \overbrace{\langle j_1, j_2, m_1, m_2 | j, m \rangle}^{\text{Clebsch Gordan Coefficient}} \tag{30.17}$$

As indicated, the proper coefficients in the linear combinations are called Clebsch Gordan coefficients, and we shall see that they are independent of α_1 and α_2. We can then ask the following questions:

1. What values of j will appear for a given value of j_1 and j_2?

2. What are the values of the CG coefficients?

3. What is the expectation value of H_{int}?

The third question relies on the form of the potential, so there is no universal symmetry answer for that. But there are answers for the first two questions. For the first question: we shall find all values of j in the interval

$$|j_1 - j_2| \leq j \leq |j_1 + j_2|, \tag{30.18}$$

subject to the constraint that j must be an integer if j_1 and j_2 are both integers or both half integers, while j must be half integer otherwise. There is a certain physical sense to this. If we think of things classically, we can think of j as the magnitude of a vector that is the sum of two

vectors of length j_1 and j_2 so by the triangle inequality we have equation (30.18). A consistency check is to verify that the number of allowed states from our formula corresponds to what we had before. We assume, for convenience, that $j_1 \geq j_2$. Then if (30.18) is correct, the number of independent states should be

$$N_{states} = \sum_{j=j_1-j_2}^{j=j_1+j_2} (2j+1) \tag{30.19}$$

This is a finite arithmetic series that will give:

$$
\begin{aligned}
N_{states} &= \frac{(2j_1 - 2j_2 + 1 + 2j_1 + 2j_2 + 1)}{2}(2j_2 + 1) \tag{30.20} \\
&= (2j_1 + 1)(2j_2 + 1) \tag{30.21}
\end{aligned}
$$

This is indeed the number of independent basis states in the direct product space we are working with.

30.1.2   Determining the Clebsch-Gordan Coefficients

We now wish to determinthe values of the CG coefficients.

To keep the notation as simple as possible, we won't write the indices j_1, j_2 in the state kets. First we note that :

$$
\begin{aligned}
J_z|j,m\rangle &= \hbar m|j,m\rangle \tag{30.22} \\
J_z|m_1,m_2\rangle &= (J_{1z} + J_{2z})|m_1,m_2\rangle = \hbar(m_1 + m_2)|m_1,m_2\rangle \tag{30.23} \\
\langle m_1,m_2|J_z|j,m\rangle &= \hbar m \langle m_1,m_2|j,m\rangle = \hbar(m_1 + m_2)\langle m_1,m_2|j,m\rangle \tag{30.24}
\end{aligned}
$$

This tells us immediately that if $\langle m_1, m_2|j,m\rangle \neq 0$ we must have $m = m_1 + m_2$.

To proceed further, we we shall look at the matrix element $\langle m_1, m_2|J_\pm|j,m\rangle$.

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31.1 Clebsch Gordan Coefficients (Continued)

We continue the discussion of addition of angular momentum. We have an angular momentum $\vec{J} = \vec{J}_1 + \vec{J}_2$ which is the sum of two angular momentum. We can express the states which have quantum numbers of total angular momentum j and m which can be expanded in terms of states with quantum numbers j_1, j_2, m_1, m_2 through the use of Clebsch Gordan coefficients.

$$|j, m\rangle = \sum_{m_1 m_2} \overbrace{\langle j_1, j_2, m_1, m_2 | j, m\rangle}^{\text{Clebsch Gordan Coefficient}} |j_1, j_2, m_1, m_2\rangle \tag{31.1}$$

We found that the CG coefficient $= 0$ unless $m = m_1 + m_2$. We are left with the issue of how to calculate these coefficients. To do this, we will use first order recursion relations using the raising and lowering operators for angular momentum $J_\pm$ that are defined as:

$$J_\mp |j, m\rangle = \sqrt{(j \pm m)(j + 1 \mp m)}|j, m \mp 1\rangle \tag{31.2}$$

It is also to note the reverse operation:

$$J_\mp |j, m \pm 1\rangle = \sqrt{(j + 1 \pm m)(j \mp m)}|j, m\rangle \tag{31.3}$$

We first get the recursion relation by breaking up equation (31.3), using $\vec{J}_\mp = \vec{J}_{1\mp} + \vec{J}_{2\mp}$ and multiplying on the left by the state $\langle m_1, m_2|$. This gives us:

$$\langle m_1, m_2 | J_{1\mp} = (J_{1\pm} | m_1, m_2\rangle)^\dagger \tag{31.4}$$

$$= \langle m_1 \pm 1, m_2 | \sqrt{(j_1 \mp m)(j_1 + 1 \pm m_1)} \tag{31.5}$$

$$\langle m_1, m_2 | J_{2\mp} = \langle m_1, m_2 \pm 1 | \sqrt{(j_2 \mp m)(j_2 + 1 \pm m_2)} \tag{31.6}$$

So now we have two methods of evaluating $\langle m_1, m_2 | J_\mp | j, m \pm 1\rangle$, first by operating to the right on the ket, and second by operating to the left on the bra. We therefore have the (unfortunately somewhat unwieldy) recursion relation:

$$\langle m_1, m_2 | J_\mp | j, m \pm 1\rangle = \sqrt{(j + 1 \pm m)(j \mp m)}\, \langle m_1, m_2 | j, m\rangle$$
$$= \langle m_1 \pm 1, m_2 | j, m \pm 1\rangle \sqrt{(j_1 \mp m_1)(j_1 + 1 \pm m_1)}$$
$$+ \langle m_1, m_2 \pm 1 | j, m \pm 1\rangle \sqrt{(j_2 \mp m_2)(j_2 + 1 \pm m_2)} \tag{31.7}$$

To make the recursion relation expressed in equation (31.7) somewhat more bearable to use, we will introduce a graphical notation to express the relations between the different coefficients.

1

We can either use equation (31.7) to connect the $|m_1, m_2\rangle$ CG coefficient to the $|m_1+1, m_2\rangle$ and $|m_1, m_2+1\rangle$ CG coefficients. We will call this the upper relation. Or, we use equation (31.7) to connect the $|m_1, m_2\rangle$ CG coefficient to the $|m_1-1, m_2\rangle$ and $|m_1, m_2-1\rangle$ CG coefficients. We will call this the lower relation. We can express both of these relationships by placing nodes on a graph with axes for m_1 and m_2. (See separate file with figures for Lecture 31 (p251b-GL31fig.pdf). The upper and lower relationships are illustrated in Fig. 2)

We can now look at more complete graph representing the basis states m_1 m_2 for the specific example of $j_1 = 3/2$, $j_2 = 2$ and $j = 3/2$. (Illustrated in Fig. 1) The allowed values of m_1 are $-3/2, -1/2, 1/2, 3/2$ and get represented on the y axis (arbitrary), the allowed values of m_2 are $-2, -1, 0, 1, 2$ and get represented on the x-axis.

There are a few additional pieces of information we can stick on our graph. First, since we know the only allowed values of $m = m_1 + m_2$ are $-3/2, -1/2, 1/2, 3/2$ (since $-j \leq m \leq j$) we can eliminate all nodes on the graph that have $|m_1 + m_2| > 3/2$. Second, we will find it very convenient to depict which nodes lie along a particular value of the total quantum number m. Nodes corresponding to the same m lie on the same diagonal line in figures 1 and 2.

Given this graphical representation as a guide, we can develop a procedure to find the values for all the Clebsch Gordan coefficients.

Procedure for Determining Clebsch Gordan Coefficients

1. Since we know that different coefficients are related to each other by linear relations, we can try to express the values of all the coefficients in terms of a single coefficient. However, it is important this coefficient not be equal to zero, or else all of our relations to the other coefficients would be useless. We claim that if we pick the coefficient c_j which has $m = j$, $m_1 = j_1$ and $m_2 = j - j_1$ it will be guaranteed not to be zero (proof left as an exercise). If we can now relate all other coefficients to c_j, we then use a normalization condition to establish the magnitude of c_j, and use a sign convention to establish its value. Note that the linear relations all involve real coefficients, so if c_j is real, we shall find that all the Clebsch Gordan coefficients will be real.

2. We now use the lower relations to determine the remainder of the coefficients on the $m = j$ diagonal. This relation is especially useful since we know that one of the nodes in the lower relation (the $m_1 = j_1$, $m_2 = j - j_2 + 1$ node, for example, at the top right of the triangle) has to be equal to zero because $m_1 + m_2 > m$.

   We can also use the upper relation now to find the values along the $m_1 = j_1$ line. The two $m_1 = j_1$ values will lie at the base of the triangle, and the upper node will have $m_1 > m$

and will thus be equal to zero.

3. We can now use the upper and lower relations to figure out the rest of the nodes in terms of c_j.

4. It remains to determine what c_j is. Now we know that $\langle mj|mj \rangle = 1$. If we now expand this in terms of the CG coefficients since all the different m_1, m_2 are orthogonal to each other, we must have:

$$\sum_{m_1} |\langle j_1, j_2, m_1, m - m_1 | j_1, j_2, j, m \rangle|^2 = 1 \tag{31.8}$$

These coefficients are all equal to known constants, multiplied by the unkonwn c_j. So this condition fixes the magnitude $|c_j|$. So we can normalize the values in terms of c_j. In principle could choose any value for the phase of c_j we want, so long as we are consistent. We shall use the standard convention, that $c_j > 0$.

We shall now will now work through the simplest possible example. Consider the case of two spin 1/2 particles, with $j_1 = j_2 = 1/2$. The total angular momentum will be $s = j$ with $s = 0, 1$. The $s = 0$ is called the singlet state, the $s = 1$ state is called the triplet state. There are four possible states, corresponding to all possible combinations of $m_{1,2} = \pm 1/2$.

Let's first consider the case of $j = 1$. Let's consider the maximum values allowed, which would be $m_1 = m_2 = 1/2$. This has $m = j = 1$. There is only state with total angular momentum quantum number $m = 1$. Therefore by normalization we must have:

$$|j = 1, m = 1\rangle = |\uparrow, \uparrow\rangle \qquad \langle \uparrow, \uparrow\, |1, 1\rangle = 1 \tag{31.9}$$

We can now use the upper relation to relate the $\langle \uparrow, \downarrow\, |1, 0\rangle$ coeficient to the $\langle \uparrow, \uparrow\, |1, 1\rangle$ coeficient, giving:

$$\sqrt{2}\, \langle \uparrow, \downarrow\, |1, 0\rangle \;=\; \sqrt{1}\, \langle \uparrow, \uparrow\, |1, 1\rangle \tag{31.10}$$

$$\langle \uparrow, \downarrow\, |1, 0\rangle \;=\; \frac{1}{\sqrt{2}} \tag{31.11}$$

We can now use the lower relation to determine the value of $\langle \downarrow, \uparrow\, |1, 0\rangle$ in terms of the ones we have already figured out.

$$\sqrt{2}\, \langle \uparrow, \uparrow\, |1, 1\rangle \;=\; \sqrt{1}\, \langle \uparrow, \downarrow\, |1, 0\rangle + \sqrt{1}\, \langle \downarrow, \uparrow\, |1, 0\rangle \tag{31.12}$$

$$\langle \downarrow, \uparrow\, |1, 0\rangle \;=\; \frac{\sqrt{2}}{2} = \frac{1}{\sqrt{2}} \tag{31.13}$$

3

So we can now answer questions of the form: how can we express the state $|j = 1, m = 0\rangle$ in terms of linear combinations of states $|m_1, m_2\rangle$. The answer is:

$$|1, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle) \tag{31.14}$$

Similarly for $|1, -1\rangle$ we have:

$$|1, -1\rangle = |\downarrow, \downarrow\rangle \tag{31.15}$$

Now what about the state $s = 0$, $m = 0$?. Since we know $m_1 + m_2 = 0$, we know the $m_1 = 1/2, m_2 = 1/2$ coefficient $= 0$. This means we can use a lower relation connecting that coefficient with the ones at $m_1 = 1/2, m_2 = -1/2$ and $m_1 = -1/2, m_2 = 1/2$ to establish that:

$$0 = \sqrt{1} \langle \uparrow, \downarrow | 0, 0 \rangle + \sqrt{1} \langle \downarrow, \uparrow | 0, 0 \rangle \tag{31.16}$$

Then by normalization, we find that up to an overall sign,

$$\langle \uparrow \downarrow | 0, 0 \rangle = \frac{1}{\sqrt{2}} \qquad \langle \downarrow \uparrow | 0, 0 \rangle = -\frac{1}{\sqrt{2}} \tag{31.17}$$

Our sign convention, $c_j > 0$ tells us to choose the first sign above to be positive, and the second sign to be negative, as we have done.

So we have:

$$|0, 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow \downarrow\rangle - |\downarrow \uparrow\rangle) \tag{31.18}$$

There's a more direct way to obtain these results, in this simple case, rather than going through the whole apparatus of the recursion relations. It is clear upon inspection that the right hand side of (31.18) has $S_z = 0$. We want to check if $S^2 = 0$. We can do this by checking that it is also annihilated by

$$S^+ = S_1^+ + S_2^+ \tag{31.19}$$

since we know that:

$$S^+ |0, 0\rangle = 0 \tag{31.20}$$

but S_+ will not annihilate a state with $S_z = 0$ if it does not also correspond to $S^2 = 0$. If youhave a state $|s, m\rangle$ and you act on it with S^+, you will get a constant times $|s, m+1\rangle$ unless $m = s$, in which case you will get zero. Indeed we see that $S_1^+ + S_2^+$ acting on the right hand side of (31.18) will give me $\frac{1}{\sqrt{2}}(|\uparrow, \uparrow\rangle - |\uparrow, \uparrow\rangle) = 0$.

To state another variant of this argument, we note that the same argument applies for S^-, which we can see annihilates the right hand side of (31.18) This shows that having the minus sign in (31.18) is the appropriate condition for satisfying $S^\pm |0, 0\rangle = 0$.

To put the argument still another way, we can rewrite S^2 as:

$$S^2 = S_z^2 + \frac{(2S^-S^+ + \hbar S_z)}{2} \tag{31.21}$$

where we need to use the commutator $[S_x, S_y] = i\hbar S_z$ to get rid of the cross terms. Now since we know that $S^+|0,0\rangle = 0$ and $S_z|0,0\rangle = 0$, it follows that $S^2|0,0\rangle = 0$.

Similarly we can check that the expression (31.14) satisfies:

$$S^+|1,0\rangle = \sqrt{2}|1,1\rangle \tag{31.22}$$

as is required. It is clear we need to have a $+$ in between the m_1, m_2 states for the expansion of $|s = 1, m = 0\rangle$ or else we will get zero. And we can also check:

$$S^-|1,-1\rangle = \text{Const}|1,0\rangle \tag{31.23}$$

Note that the $S = 1$ states are all even under interchange of the labels of the spins, while the $S = 0$ is odd under this interchange.

Note also that if we fix j_1, j_2 and we consider the set:$\langle j_1 j_2 m_1 m_2|jm\rangle$ these coefficients form a unitary real matrix that expands the states $|j, m\rangle$ in terms of $|m_1, m_2\rangle$. Therefore we could invert this matrix to obtain all the coefficients $\langle jm|j_1 j_2 m_1 m_2\rangle$ which will expand the states $|m_1, m_2\rangle$ in terms of $|j, m\rangle$. In general, the inverse of a unitary matrix is its adjoint, but if the matrix is real, the inverse is simply the transpose. This means that:

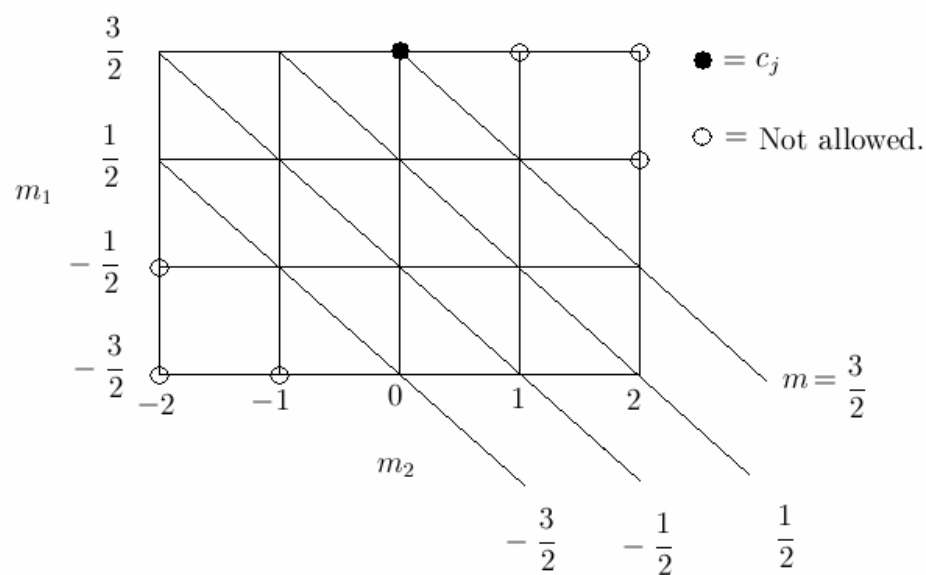$$\langle jm|j_1 j_2 m_1 m_2\rangle = \langle j_1 j_2 m_1 m_2|jm\rangle . \tag{31.24}$$
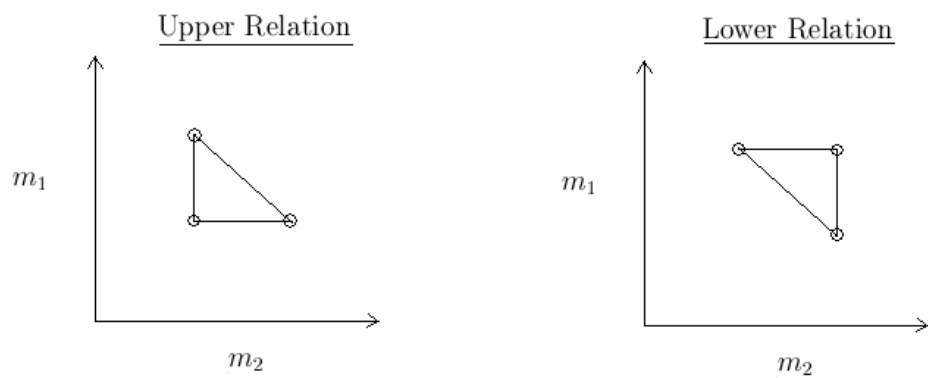
Figure 1

Figure 2

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32.1 Consequences of Rotational Symmetry

32.1.1 Vector and Tensor Operators

We begin by giving a definition of vector operators.

Definition A: A "vector operator" $\vec{A}$:

$$\vec{A} = \{A_i\} \qquad (i = \overbrace{x, y, z}^{1,2,3}) \tag{32.1}$$

is a set of three operators that transform under rotations like the operator $\vec{r}$. Specifically, if we pick an angle λ about an axis $\hat{n}$, we know that the Unitary operator in quantum mechanics that corresponds to this rotation is given by:

$$U(\lambda, \hat{n}) = e^{-i\lambda\hat{n}\cdot\vec{J}/\hbar} \tag{32.2}$$

If we want to calculate the expectation values of operators and see how they change under such a rotation, then we use perform the operation $U^{-1}A_i U$. The condition that A be a vector operator is that we can express:

$$U^{-1}(\lambda, \hat{n})A_i U(\lambda, \hat{n}) = \sum_{j=1}^{3} R_{ij}(\lambda, \hat{n})A_j \tag{32.3}$$

where R_{ij} is the 3x3 rotation matrix corresponding to the rotation of angle λ about axis $\hat{n}$. We won't write down the most general case, but for example if $\hat{n} = \hat{z}$ then we have:

$$R(\lambda, \hat{z}) = \begin{pmatrix} \cos\lambda & -\sin\lambda & 0 \\ \sin\lambda & \cos\lambda & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{32.4}$$

32.1.2 Equivalent Definition of Vector Operator

The equivalent definition to the one above, the one that is most convenient to use, is that a vector operator obeys the commutation relation:

$$[J_i, A_j] = i\hbar\epsilon_{ijk}A_k \tag{32.5}$$

where ϵ_{ijk} is the antisymmetric Levi-Cevita alternating tensor defined by:

$$
\begin{aligned}
\epsilon_{ijk} &= 1 & \text{If} \quad ijk &= xyz, yzx, zxy \ (\text{Even Permutations}) \\
&= -1 & ijk &= zyx, xzy, yxz \ (\text{Odd Permutations}) \\
&= 0 &
\end{aligned}
\tag{32.6}
$$

In equation (32.5), we are using an implied summation convention for the repeated index k. However, there is only one non-zero term in the sum.

If $\vec{A}$ were an angular momentum operator, we would just get back the angular momentum commutation relations we have established before. This is consistent and goes to show that $\vec{J}$ itself is in fact a vector operator.

We won't go through in detail as to why the definition we've given in terms of commutation relations in equation (32.5) is equivalent to the one in equation (32.3). We can sort of see how the proof goes though. Because if we expand out equation (32.3) in a Taylor series on either side we will get a bunch of terms involving the angular momentum operators. With a bit more scrutiny we would see that equation (32.3) holds true if and only if equation (32.5) is true.

Before we proceed further, we just want to note that the R matrices are real and unitary. They have the property $R^{-1} = R^{\dagger} = R^{\text{transpose}}$, so

$$
R_{ij}(-\lambda, \hat{n}) = R_{ji}(\lambda, \hat{n}),
\tag{32.7}
$$

and they form a group. We also note that the Unitary operators:

$$
U(-\lambda, \hat{n}) = U^{-1}(\lambda, \hat{n})
\tag{32.8}
$$

also form a group. Using these two equations, together with the definition (32.3) of a vector operator, we can rewrite the definition in an alternate form:

$$
U(\lambda, \hat{n}) A_i U^{-1}(\lambda, \hat{n}) = \sum_{j=1}^{3} A_j R_{ji}(\lambda, \hat{n})
\tag{32.9}
$$

32.1.3   Irreducible Tensor Operators

In much the same way as we have defined vector operators, we now proceed to define what are called irreducible tensor operators.

Definition A: An irreducible tensor operator $\{T_m^{(l)}\}$ $m = -l, -l+1, \ldots l$ is a set of $2l + 1$ operators, labelled $m = -l, -l+1, \ldots l$ (with l fixed) that transforms under rotations like the spherical harmonics $Y_m^l(\theta, \phi)$.

In other words, an irreducible tensor operator will transform under rotation like:

$$U(\lambda, \hat{n}) T_m^{(l)} U^{-1}(\lambda, \hat{n}) = \sum_{m'} T_{m'}^{(l)} D_{m'm}^l(\lambda, \hat{n}) \tag{32.10}$$

where the Matrix elements $D_{m'm}^l$ first discussed in p251b lecture 30 are defined as:

$$D_{m'm}^{(j)} = \langle \alpha, j, m' | e^{-i\lambda \hat{n} \cdot \vec{J}/\hbar} | \alpha, j, m \rangle. \tag{32.11}$$

Thus D^l is the rotation matrix in the basis $|l, m\rangle$. For the simplest case of a single particle on a shell of fixed radius r, the states $|l, m\rangle$ correspond to the spherical harmonics $Y_l^m(\theta, \phi)$.

Definition B: An equivalent definition, the one we will use below, is that an irreducible tensor operator satisfies:

$$\left[J^{(\mu)}, T_m^{(l)} \right] = \sum_{m'} T_{m'}^{(l)} \tilde{J}_{m'm}^\mu \qquad (\mu = x, y, z, \pm) \tag{32.12}$$

The definitions of $\tilde{J}_{m'm}^\mu$ are:

$$\tilde{J}_{m'm}^\mu = \langle lm' | J^{(\mu)} | lm \rangle \tag{32.13}$$

So, for example, for $\tilde{J}_{m'm}^\pm$ we have:

$$\tilde{J}_{m'm}^\pm = \hbar\sqrt{l(l+1) - m(m \pm 1)} \delta_{m', m \pm 1}, \tag{32.14}$$

while $\tilde{J}_{m'm}^z = \hbar m \delta_{m'm}$.

32.1.4   Examples of Irreducible Tensor Operators

For $l = 0$, we have a scalar operator A. This operator is invariant un derotations, and such an operator just commutes with the angular momentum operator: $[\vec{J}, A] = 0$

For $l = 1$, I have, essentially, a vector operator, since we can take linear combinations which convert $T_{m'}^{(1)} \to \vec{A}$. The three elements of this tensor operator such that will satisfy equation (32.12) will be: $T_0^1 = A_z$, and

$$T_1^1 = -\frac{A_x + iA_y}{\sqrt{2}} \qquad T_{-1}^1 = \frac{A_x - iA_y}{\sqrt{2}} \tag{32.15}$$

As another example, consider the function $P_m^l(\vec{r}) = r^l Y_m^l(\theta, \phi)$, which is a polynomial in the cartesian components of $\vec{r}$. If we treat $\vec{r}$ as operator, then P_m^l becomes an operator which simply multiplies a wave function $\psi(\vec{r})$ by the function $P_m^l(\vec{r})$. Then P_m^l transforms as an irreducible tensor operator $T_m^{(l)}$. This is also true if we multiply P_m^l by any function of the absolute value r.

3

Using the above formalism, we could also define tensor operators corresponding to half-integer l, eg., $l = 1/2$. But in fact, only integer values of l can occur for physical observables. If one were to construct an operator which obeyed the definitions of a tensor with half-integer l, one would find, according to Eq. (32.10) that the operator is multiplied by -1 under a rotation by an angle 2π about any axis. This is not allowed for physical observables.

32.2   Wigner-Eckart Theorem

Why do we bother introducing such tensor operators? One reason is to introduce the useful and powerful Wigner-Eckart theorem.

Let $\{T_m^{(l)}\}$ be a tensor operator. Let $|\alpha, j, m\rangle$ be our relevant quantum states, with $J^2 = \hbar^2 j(j+1)$ and $J_z = \hbar m$. Let α be another set of quantum numbers that commute with the angular momentum.

The Wigner Eckart theorem states that:

$$\langle \alpha, j, m | T_\mu^{(l)} | \alpha', j', m' \rangle = \text{Const} \times \langle j', l, m', \mu | j, m \rangle \, , \tag{32.16}$$

where the constant is independent of m, m', μ and is dependent only on $\alpha, \alpha', T^l, j, j'$.

It is a particular convention (Sakurai, Merzbacher) to write the constant as:

$$\text{Const} = \frac{\langle \alpha, j || T^{(l)} || \alpha', j' \rangle}{\sqrt{2j+1}}. \tag{32.17}$$

The constant $\langle \alpha, j || T^{(l)} || \alpha', j' \rangle$ is known as the reduced matrix element of the tensor operator. The factor $\sqrt{2j+1}$ is introduced in the denominator of the definition in order to make the reduced matrix element symmetric under interchange of the initial and final states. Specifically, it can be shown that for physical observables, where $T_0^{(l)} = T_0^{(l)\dagger}$, $\langle \alpha, j || T^{(l)} || \alpha', j' \rangle = \langle \alpha', j' || T^{(l)} || \alpha, j \rangle^*$.

To prove the Wigner-Eckart theorem, we use the commutation rules given in equation (32.12). First, we shall use J_z to show that in order to have a non-zero matrix element, we must have $m = m' + \mu$:

$$\langle \alpha, j, m | J^z T_\mu^l | \alpha', j', m' \rangle = \langle \alpha, j, m | T_\mu^l J^z | \alpha', j', m' \rangle + \hbar \mu \langle \alpha, j, m | T_\mu^{(l)} | \alpha', j', m' \rangle \tag{32.18}$$

$$m = m' + \mu \tag{32.19}$$

Now using $J^\pm$ in equation (32.12) and making use of (32.14) we arrive at:

$$\langle \alpha j m | J^\pm T_\mu^l | \alpha' j' m' \rangle = \langle \alpha j m | T_\mu^l J^\pm | \alpha' j' m' \rangle + \hbar \sqrt{(l \mp \mu)(l \pm \mu + 1)} \langle \alpha j m | T_{\mu \pm 1}^l | \alpha' j' m' \rangle \tag{32.20}$$

If we now let the operators $J^\pm$ in the above formula act on the adjacent bra or ket, we will get the following recursion relations:

$$\sqrt{(j \pm m)(j \mp m + 1)}\langle \alpha, j, m \mp 1|T^l_\mu|\alpha'j', m'\rangle =$$
$$\sqrt{(l \mp \mu)(l \pm \mu + 1)}\langle \alpha, j, m|T^l_{\mu \pm 1}|\alpha', j', m' \pm 1\rangle$$
$$+\sqrt{(j' \mp m)(j' \pm m' + 1)}\langle \alpha, j, m|T^l_\mu|\alpha', j', m' \pm 1\rangle \tag{32.21}$$

These recursion relations are identical to the recursion relations for the Clebsch Gordon coefficients $\langle j_1, j_2, m_1, m_2|j, m\rangle$ that we obtained previously, except for a change of labels. Specifically, you may compare Eq. (32.21) with Eq. (31.7) of Lecture 31, after replacing (j_1, j_2, m_1, m_2) by $(l.j', \mu, m')$, and m by $m \mp 1$. As before, we can solve these equations to express all the tensor matrix elements, for the different values of m, m', μ, in terms of one selected matrix element, which remains unknown. The correspondence of the recursion relations means that the matrix elements $\langle \alpha, j, m|T^l_\mu|\alpha', j', m'\rangle$ and the Clebsch Gordon coefficients of the form $\langle j', l, m', \mu|j, m\rangle$ must be proportional to each other, with the ratio being a constant independent of m, μ and m'. This proves (32.16). A more detailed discussion of the proof may be found in Sakurai.

Of course to evaluate the remaining unknown constant, or equivalently the reduced matrix element defined above, one must finally do a non-trivial quantum mechanical calculation. In some cases, the calculated constant may be zero, perhaps as a consequence of some other symmetry (such as inversion symmetry) that the system may have in addition to the rotational symmetry exploited above.

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33.1   Consequences of Rotational Symmetry: Wigner Eckart Theorem

In the last lecture we introduced the Wigner Eckart theorem:

$$\langle \alpha, j, m | T_\mu^l | \alpha', j', m' \rangle = \langle j'lm'\mu | jm \rangle \frac{\langle \alpha, j || T^{(l)} || \alpha', j' \rangle}{\sqrt{2j+1}} \tag{33.1}$$

where $\langle \alpha, j || T^{(l)} || \alpha', j' \rangle$ is a constant independent of m, m' and μ, and $\langle j'lm'\mu | jm \rangle$ are Clebsch Gordon coefficients. Some of the consequences that follow from this theorem are:

1. We can immediately see when some of the matrix elements of the form $\langle \alpha, j, m | T_\mu^l | \alpha', j', m' \rangle$ are zero just by observing when the corresponding Clebsch coefficient is zero.

2. We know that for a Clebsch Gordon coefficient of the form $\langle j'lm'\mu | jm \rangle$ to be nonzero, a necessary condition is that $m = \mu + m'$ and that $|j' - l| \le j \le j' + l$. The latter is the **Triangle Inequality**. We can rearrange this equality to yield $|j - j'| \le l \le j + j'$.

33.1.1   Example: Matrix Elements for Electric Dipole Transitions

As an example of an application of these properties, we shall look at electric dipole transitions. If we have an atom initially in some state $|\alpha', j', m'\rangle$ and we want it to make the transition to a different state $|\alpha, j, m\rangle$ by means of a photon coming in, we want to ask if this transition is possible by means of an electric dipole interaction. If it is not, then the probability of a transition will be much lower, and we will have to analyze higher order interactions. To answer this question, we want to see whether the matrix element:

$$\langle \alpha, j, m | d_i | \alpha', j', m' \rangle \overset{?}{=} 0 \tag{33.2}$$

The dipole operator is a vector, and thus can be decomposed into first rank spherical tensors, ie $d_i = \sum_m c_m^i T_m^{(l)}$ where $l = 1$. From the triangle inequality $|j - j'| \le l \le j + j'$ it follows that $j - j'$ must be either $-1, 0$ or 1 for the matrix element to be nonzero $[(j - j') = -1, 0, 1]$. It also follows that $j + j' \ge 1$ for a nonzero element, leading to the important implication that dipole matrix elements for $j = j' = 0$ are zero.

The angular momentum operator $\vec{J}$ in the above discussion refers to the total angular momentum of the electrons in the atom, including both their orbital and spin degrees of freedom.

For light atoms, where relativistic effects are weak, however, the orbital and spin portions of the angular momentum are separately conserved, and we can classify energy levels by their quantum number L of the total orbital angular momentum, as well as by the total spin quantum number S and the total angular momentum quantum number j. Then since the electric dipole operator acts on the orbital degree of freedom, not on the spin, we can apply the Wigner-Eckart theorem to the orbital quantum numbers, and we can say that electric dipole transitions are forbidden unless $|L - L'| = 1$ or 0. In addition, we see that electric dipole transitions are forbidden between two states with total orbital angular momentum $L = 0$.

For the case of polarized light; if we have light polarized in the z direction $\vec{E} \| \hat{z}$ then we have $d_z \propto Y_0^l$ which imposes the condition of $m - m' = 0$ for non zero matrix elements. For $\vec{E}$ in the x-y plane where we would have, for example, $d_x = \propto T_{-1}^1 - T_1^1$, then we would have the condition $(m - m') = \pm 1$

For the case of absorption of circularly polarized light:

$$\vec{E} \propto \mathrm{Re}\left[E_0 \frac{\hat{x} \pm i\hat{y}}{\sqrt{2}} \exp(ik_z - i\omega t)\right] \tag{33.3}$$

we can find allowed transitions from a state with quantum number m' to a state with quantum number m only if $m - m' = 1$ for the plus case, or $m - m' = -1$ for the minus case.

Diagonal Matrix Elements

By diagonal matrix elements we mean elements involving eigenstates in the same α, j manifold (ie with $\alpha = \alpha'$ and $j = j'$):

$$\langle \alpha, j, m | T_\mu^l | \alpha, j, m' \rangle = \overbrace{\mathrm{Constant}}^{\mathrm{Ind't\ of\ } m, m', \mu} \times \langle j, l, m', \mu | j, m \rangle \tag{33.4}$$

Let's consider that we have vector operators $\vec{A}$, $\vec{B}$, which will each be simple linear combinations of $l = 1$ tensor operators. It then follows immediately that:

$$\langle \alpha, j, m | \vec{A} | \alpha, j, m' \rangle = \mathrm{Const} \times \langle \alpha, j, m | \vec{B} | \alpha, j, m' \rangle \tag{33.5}$$

If we choose $\vec{B} = \vec{J}$, we have:

$$\langle \alpha, j, m | \vec{A} | \alpha, j, m' \rangle = \mathrm{Const} \times \langle \alpha, j, m | \vec{J} | \alpha, j, m' \rangle \tag{33.6}$$
$$= \mathrm{Const} \times \tilde{J}_{mm'} \tag{33.7}$$

This implies that within the manifold (with the same α and j) $\vec{A} \simeq \vec{J} \times \mathrm{Const}$.

33.1.2   Example: Magnetic Moment of a Nucleus

The magnetic moment is a vector operator. For a nucleus there are various contributions from the orbital and spin angular momentum of the protons and neutrons. If the ground state of the nucleus has an internal angular momentum j, generally referred to as the "spin" of the nucleus, there will be $(2j+1)$ degenerate ground states. According to the Wigner-Eckart theorem, within the manifold of these degenerate states, the three components of the magnetic moment operator $\vec{M}$ can be written as a multiple of the total internal angular momentum operator $\vec{J}$: $\vec{M} = \gamma \vec{J}$, where γ is the gyromagnetic ratio, found from calculation or experiment.

33.1.3   Applications to Atoms (with infinitely massive nuclei)

We begin by writing the Hamiltonian for the atom as:

$$H = H_{nr} + H_{relativistic}, \tag{33.8}$$

where H_{nr} is the non-relativistic Hamiltonian we have been dealing with thus far:

$$H_{nr} = \sum_i \frac{p_i^2}{2m} - \sum_i \frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \tag{33.9}$$

Since the relativistic corrections are generally small, at least for light atoms, we would like to solve H_{nr} completely before analyzing the relativistic corrections. This Hamiltonian does not depend on spin, and since it is also spherically symmetric it will have the following commutation relations:

$$
\begin{array}{lll}
[\vec{S}, H_{nr}] = 0 & \vec{S} = \sum_{i=1}^{Z} \vec{S}_i & [\vec{L}, H_{nr}] = 0 \\
\vec{L} = \sum_{i=1}^{Z} \vec{L}_i & \vec{J} = \vec{S} + \vec{L} & [\vec{J}, H_{nr}] = 0
\end{array} \tag{33.10}
$$

The eigenstates of H_{nr} will have a total degeneracy equal to the degeneracy associated with the spin times the degeneracy associated with the orbital angular momentum for a total degeneracy of $(2S + 1)(2L + 1)$. We can choose eigenstates to have definite values of $S_z = \hbar m_s$ $L_z = \hbar m_L$. We can denote such states as: $|L, S, m_L, m_S\rangle$.

Now we want to deal with H_{rel}. There are terms which couple the spin and orbital angular momentum. We will call the contribution due to these interactions V^{so}. The relevant commutation relations are:

$$[\vec{S}, V^{so}] \neq 0 \qquad [\vec{L}, V^{so}] \neq 0 \qquad [\vec{J}, V^{so}] = 0 \tag{33.11}$$

When V_{so} is included, eigenstates of H have definite quantum number J (but not L and S). If however, V_{so} is small, then we can treat V_{so} by first order perturbation theory, which

means that we must diagonalize the perturbation with in the manifold of degenerate states of the unperturbed Hamiltonian. We shall assume that there are no accidental degeneracies of eigenstates of H_{nr}, so that the only degeneracies are those associated with non-zero values of L or S. (This assumption is not true in the case of the hydrogen atom.)

We can find the small corrections to the eigenstates of $|L, S, m_s, m_L\rangle$, which are the good quantum numbers for H_{nr}, by changing those states into the $|j, m\rangle$ basis which diagonalizes V_{so}. We can relate the states in the two bases through the use of a linear combination involving the Clebsch Gordan coefficients:

$$|L, S, m_L, m_S\rangle = \sum_{Allowed} |L, S, j, m\rangle \langle L, S, j, m|m_L, m_S\rangle \tag{33.12}$$

The allowed values of j are those that satisfy

$$|L - S| < j < L + S \tag{33.13}$$

Since the $|j, m\rangle$ states are unique in the degenerate subspace of H_{nr}, and since V_{so} commutes with $\vec{J}$, it follows that V_{so} is diagonal in the $|j, m\rangle$ basis, and the matrix element must be independent of m. Thus to quantify the effects of V_{so}, within this subspace, it will be sufficient to calculate the matrix elements of the form: $\langle j, m|V^{so}|j, m\rangle$. If we wish, we can then use equation (33.12) to relate this back to the matrix elements: $\langle m_L, m_S|V_{so}|m'_L, m'_S\rangle$.

If we have a non-relativistic energy level with $S = 0$, then the states in the manifold have $\vec{J} = \vec{L}$ and hence $j = L$. If we have a non-relativistic energy level with $L = 0$, then the states in the manifold have $\vec{J} = \vec{S}$ and hence $j = S$. In either case the state has no residual degeneracy to be split by spin orbit interaction. In fact, it turns out that the expectation value of V_{so} is zero in these cases, so the spin-orbit coupling has no effect on the eergy of the state, to first order.

However, if S and L are both non-zero, there will be a degeneracy to be broken by spin-orbit, as there will be several vales of j corresponding to a given L, S. Spin-orbit will split this degeneracy.

This scheme is called L, S coupling. In this scheme L, S remain approximate quantum numbers, and we use a labeling scheme: $^{(2S+1)}X_j$ where:

$$
\begin{aligned}
X &= S & L &= 0 \\
&= P & L &= 1 \\
&= D & L &= 2
\end{aligned}
\tag{33.14}
$$

As an example of how this works: $^3P_2$ is the triplet P_2 state, which has $L = 1, S = 1, j = 2$.

This $L - S$ coupling scheme works reasonably well for light atoms with $Z \leq 50$. For heavy atoms $Z \geq 70$, the spin-orbit coupling is quite large, and S, L are bad quantum numbers. Instead, you diagonalize V_{so} for the one-electron states first, before taking electron-electron interactions into account. Of course, the total orbital angular momentum j is still an exact quantum number.

There is one important exception to these rules. For the Hydrogen atom there is a special degeneracy. In the absence of the relativistic correction, states with different L but the same radial quantum number are degenerate. The relativistic corrections, arising from the Dirac equation, partially lifts this degeneracy, so that states of different total j have slightly different energy, but do not otherwise split the states of different L. For example, the $P_{j=\frac{1}{2}}$ has the same energy as the $S_{j=\frac{1}{2}}$ state, but the $P_{j\frac{3}{2}}$ has a higher energy. The degeneracy between the S and P states is finally broken by the Lamb shift, which is a QED correction that is still higher order in the fine-structure constant, and is not included in the Dirac equation.

This is not the final story, as we haveso-far assumed an infinitely massive nucleus. If we consider a spherically symmetrical nucleus with a finite mass but zero nuclear spin, then we can retain the same basic quantum numbers in the center of mass frame, and there are only small renormalizations of the electronic energies due to the finite nuclear mass.

An additional effect occurs, however, if the nucleus has a non-zero spin, and thus a magnetic moment. This moment will be much smaller than that of the electron due to the fact that the gyromagnetic ratio is inversely proportional to the mass. Nevertheless, if the nucleus has a spin $\vec{I}$ there will be what are called hyperfine couplings between the spin of the electrons and the nucleus, which can have important effects.

What we find in the end, using the Wigner Eckart theorem, is that effective interaction to first order will be proportional to $\vec{I} \cdot \vec{J}$, where $\vec{J}$ is the total angular momentum of the electrons in the center of mass frame. The higher order terms are also invariant under simultaneous rotations of I, J, so the Hamiltonian commutes with the operators $\vec{F} = \vec{I} + \vec{J}$. The allowed eigenvalues of F^2 are given by $\hbar^2 f(f+1)$, where f is either integer or integer according to the sum of quantum numbers i and j for the nuclear and electronic angular momenta, and $|i - j| \leq f \leq i + j$. States with different values of f have (slightly) different energies.

Although the energies of the hyperfine splittings are very small on the scale of the the Rydberg, they can be easily measured in atomic spectroscopy, because line widths are very narrow. These splittings are of crucial importance in experiments which use lasers to trap or manipulate atoms or ions. The hyperfine coupling is also of great importance in NMR experiments, and it can be an important mechanism for relaxation of electron spins in solids.

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Consequences of Rotational Symmetry: Applications to Atoms (continued)

In this lecture we continue our discussion of the consequences of symmetry and its applications to atomic physics. Last time we spoke about a general classification of states. Now we want to look at a specific example in practice with the case of a light atom, silicon (Si) which has $Z = 14$. We shall try to understand the values of the quantum numbers L, S, j that emerge for the ground state of the atom, by solving the Hamiltonian in an approximate way

We begin by looking at the solution to the non relativistic problem, then we will proceed to look at further corrections. We write the non relativistic Hamiltonian in a slightly different manner than we have before

$$H_{non\,rel} = H_c + V^{(2)} \tag{34.1}$$

where H_c is a one-body Hamiltonian, which includes the kinetic energy of the electrons and a spherically symmetric potential $U_c(r)$ that best approximates the Coulomb attraction that an electron would see from the nucleus, after the nucleus is screened by all the other electrons, and $V^{(2)}$ is whatever is left over. Thus:

$$H_c = \sum_{i=1}^{Z} \left[\frac{p_i^2}{2m} + U_c(r_i) \right] \tag{34.2}$$

$$V^{(2)} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i=1}^{Z} \left[-\frac{Ze^2}{r_i} - U_c(r_i) \right] \tag{34.3}$$

Whatever approximation we make for $U_c(r_i)$ in H_c, we subtract it off in two body interaction term $V^{(2)}$. The reason for introducing U_c, however, despite the fact that we are both adding and subtracting it, is that it allows us to make $V^{(2)}$ as small as possible, and then treat it as a perturbation.

To treat $V^{(2)}$ as a perturbation, we begin by diagonalizing the unperturbed Hamiltonian H_c. This is a one body Hamiltonian and it is spherically symmetric, so the energy eigenstates can be labeled by their angular momentum and radial quantum numbers. We can name the states as in a hydrogen atom: $1s, 2s, 2p, 3s, 3p, 3d \ldots$. We now want to fill up the states, following the Pauli exclusion principle and using the various rules for the number of states available for a given l. For the Hydrogen atom there is a special degeneracy: states with different angular momenta l but the same principal quantum number n, have identical energies. This is not the case for a

more general spherically symmetric potential U_c. In atoms, we expect that for a given n, states with lower value of l will have lower energies, because they get in closer to the nucleus, where the nuclear potential is less screened by the other electrons.

For Si, there will be two electrons in each of the $1s$ and $2s$ states. Then there can be 6 in the $2p$ states, 2 in the $3s$ and 2 more in the $3p$ bringing us to a total of 14. The occupation can be written: $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$. In the absence of the electron electron interaction the one-electron states with the same (n, l) are all degenerate. For the closed shells, however, the many-body state, formed by taking a Slater determinant of all the states in the closed shell, is invariant under rotations, so it is non-degenerate and gives a contribution of zero to the total L and total S.

Since there are only two electrons in the six possible states of the outermost 3p shell, this part of the wavefunction is degenerate, and can contribute to the total angular momentum. Clearly, there are $(6 \times 5)/2 = 15$ different ways we can pick to occupy those $3p$ states, which will form a basis for the subspace of degenerate groundstates of the non-interacting problem. These different possibilities can be labeled by the quantum numbers m_l, m_s of the z-components of the orbital angular momentum and spin for each of the two occupied states. We can then take linear combinations of these states which have definite values of the total orbital angular momentum quantum number L and total spin quantum number S.

For the situation we are exploring our claim is that the allowed combinations are:

$$
\begin{array}{llllll}
9\,\text{States} & L = 1 & S = 1 & (2L+1)(2S+1) = 9 & {}^3P & \\
5\,\text{States} & L = 2 & S = 0 & (2L+1)(2S+1) = 5 & {}^1D & (34.4) \\
1\,\text{State} & L = 0 & S = 0 & (2L+1)(2S+1) = 1 & {}^1S &
\end{array}
$$

Let us first note that if we had two *distinguishable* particles, each with $l = 1$ and $s = 1/2$, then there would be 36 (4×9) possible states with $S = 0, 1$, $L = 0, 1, 2$.

For Fermi statistics, however, we must require that $P_{12}\Psi = -\Psi$. Looking at the case of two electrons, not concerning ourselves with the electrons on the inner shells, then specifying S and m_S will completely specify the spin state. The possible states are:

$$
S = 0 \; m_S = 0 : \qquad \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \tag{34.5}
$$

$$
S = 1 \; m_S = 1 : \qquad |\uparrow\uparrow\rangle \tag{34.6}
$$

$$
S = 1 \; m_S = 0 : \qquad \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \tag{34.7}
$$

$$S = 1 \; m_S = -1 : \qquad |\downarrow\downarrow\rangle. \tag{34.8}$$

Here we are using first quantized notation. The first arrow represents σ_1, which labels the z-component of the spin of electron 1, while the second arrow represents σ_2.

We may describe a state with a given S and m_S by a spin wave function $f_{S,m_S}(\sigma_1, \sigma_2)$, where σ_1, σ_2 are the spins of the two particles. We can see that $f_{0,0}$ is antisymmetric: $P_{12} f_{0,0} = -f_{0,0}$, while the $S = 1$ states are symmetric under permutation of the spins. Since, for two electrons, there is a unique spin wave function for each of the allowed values of (S, m_S), we can write the total wave function as a product of a spin function and position-dependent function.

$$\Psi_{S,m_S}(\vec{r}, \sigma_1, \vec{r}_2, \sigma_2) = f_{S,m_S}(\sigma_1, \sigma_2)\Phi(\vec{r}_1, \vec{r}_2) \tag{34.9}$$

(Note: For 3 or more electrons specifying S and m_S does not provide a complete description of the spin state, so the above factorization may not work. For the case of two particles, however, it does.)

To meet the antisymmetric requirement on the total wavefunction $P_{12}\Psi = -\Psi$ we can now conclude:

$$\begin{aligned} S &= 0 & P_{12}\Phi &= \Phi \\ S &= 1 & P_{12}\Phi &= -\Phi \end{aligned} \tag{34.10}$$

Moreover, if the quantum numbers L and m_L are specificied, the position-dependent part of the wavefunction is determined as

$$\Phi(\vec{r}_1, \vec{r}_2) = \sum_{m_{l_1}, m_{l_2}} g_{3p\, m_{l_1}}(\vec{r}_1) g_{3p\, m_{l_2}}(\vec{r}_2) \overbrace{\langle l_1, l_1, m_{l_1}, m_{l_2} | L, m_L \rangle}^{\text{Clebsch Gordon Coefficient}} \tag{34.11}$$

where g represents the single particle spatial wave functions, and $l_1 = l_2 = 1$.

To determine the symmetry under permutation, we need to know what will happen if we exchange the indices m_{l_1} and m_{l_2}. The claim is (proof omitted) that:

$$\langle l_1, l_1, m_{l_1}, m_{l_2} | L, m_L \rangle = \langle l_1, l_1, m_{l_2}, m_{l_1} | L, m_L \rangle (-1)^{2l_1 - L} \tag{34.12}$$

This tells us that for integer l_1, the Clebsch Gordan coefficient is even under the interchange if L is even, and odd if L is odd. Thus, in the present case

$$\begin{aligned} P_{12}\Phi &= \Phi, & L &= 0, 2 \\ P_{12}\Phi &= -\Phi, & L &= -1 \end{aligned} \tag{34.13}$$

This implies, therefore, that for fermions, the allowed combinations are

$$\begin{aligned} S &= 0, & L &= 0, 2 \\ S &= 1, & L &= 1 \end{aligned} \tag{34.14}$$

3

This is what gave us the results in (34.4). For bosons we would have had the opposite combinations of L and S, which would give rise to 21 states. Thus the 36 total states for two particles in the 3p orbitals can be divided into 15 states that are antisymmetric under P_{12} and 21 that are symmetric.

Note that formula (34.12) can also be used for half-integer l_1, though. In this case the variable l_1 cannot represent a pure orbital angular momentum. We now find that the Clebsch Gordan coefficient is odd under interchange of m_1 and m_2 if the resulting total angular momentum is even, and even if the angular momentum is odd. This is in agreement with what we have already found for the $S = 0$ and $S = 1$ states of a pair of spin-1/2 objects.

It remains to understand the ordering of energies. Here we wave our hands a bit. The first order splittings of the energy levels come from the expectation value of the two body interaction term:

$$\langle L, S, m_L, m_S| \sum \frac{e^2}{2|\vec{r}_i - \vec{r}_j|} |L, S, m_L, m_S\rangle, \tag{34.15}$$

since the one-body terms are the same for all members of the subspace we are considering. Because the non-relativistic Hamiltonian is invariant, separately, under simultaneous rotations of all electron positions, or under rotations of the spins, the energy must be independent of the quantum numbers m_L and m_S.

The wave function for the many-body state in (34.15) is, in general a superposition of several Slater determinant states, so that the expectation value cannot be evaluated directly using Wick's theorem. Nevertheless, the answer can be written down as a multiple integral, which can be evaluated numerically if the constituent one-body wave-functions are known (or estimated). We shall not discuss details of this procedure here, but rather will give a hand waving argument which suggests that the $L = 1$ state should have have the lowest energy.

We expect that $L = 1$ has the lowest energy since it is the only state which has describes an antisymmetric spatial wave part. This means that $\Phi(\vec{r}_1, \vec{r}_2) = 0$ for $r_1 = r_2$, so the wave function must tend to zero, when the two particles come close together, which is when the Coulomb repulsion will be greatest. Since the $L = 0$ and $L = 2$ wave functions do not vanish when the two electrons come together, they will have a higher potential energy.

It is not obvious how to order the $L = 0$ and $L = 2$ states, but numerical calculations, or a a detailed analysis, tell us that the $L = 2$ state has lower energy than the $L = 0$.

For more than 2 electrons in the outer shell, we would similarly like to align all the spins in the same direction if possible. For example, we see immediately that if all the electrons have the same value of m_s, then the spatial wave function will vanish when any two of them come together in space. Aligning the spins means that the value of S is as large as possible. If the outer shell is more than half full, we can no longer choose all the spins in the same direction,

but we still get the lowest interaction energy if we align as many of them as possible. Of course, we do not have to align the spins along the z-axis; aligning them in any other direction would give a state which is rotated in spin space and has the same energy and the same value of S.

There are some nice empirical rules for at least finding the lowest energy for states in a given atom.

Hund's first and second rules state that to obtain the lowest energy configuration for an atom: fill the available states in an open shell to get the largest possible S, then choose the largest possible L. We can achieve this in a simple way by filling up the single-particle orbitals in order: first fill states with $m_s = 1/2$, then those with $m_s = -1/2$, choosing always the state with the highest available value of m_l. The resulting state will be a ground state, with total spin and orbital angular momenta maximally aligned in the z-direction, i.e., $L = m_L$ and $S = m_S$, equal respectively to the sum of the occupied m_l and m_s.

Table (34.16) shows the application of Hund's rules to the ground state for all the elements with a partially full 3p shell, including Si. The m_S and m_L columns show the values of the last filled electron state.

Z	Element	$3p^n$ n	m_S	m_L	$S = \sum m_S$	$L = \sum m_L$
13	Al	1	$1/2$	1	$1/2$	1
14	Si	2	$1/2$	0	1	1
15	P	3	$1/2$	-1	$3/2$	0
16	S	4	$-1/2$	1	1	1
17	Cl	5	$-1/2$	0	$1/2$	1
18	Ar	6	$-1/2$	-1	0	0

(34.16)

Thus we see that for Si, the state of H_{nr} with lowest energy has $L = S = 1$.

As we shall discuss in the next lecture, when the spin orbit term is taken into account, one finds that the states with smaller vales of j have lower energy. Thus the ordering of states is $^3P_0 < {}^3P_1 < {}^3P_2$ (recalling that the notation is $^{2S+1}L_j$).

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35.1   Symmetry and Atoms (continued) and Molecules

35.1.1   Spin-orbit coupling

We now look at the relativistic spin-orbit correction to the energy spectrum of atoms, making use of the Wigner Eckart theorem. For light atoms, we begin by assuming we have solved the problem in the absence a nuclear spin and for an infinite nuclear mass, and for no relativisitic corrections. We have a basis set of electronic ground states, characterized by some angular momentum L and some spin S, that will combine to give:

$$\vec{J} = \vec{L} + \vec{S} \tag{35.1}$$

To begin, we will look at the dominant spin orbit correction. This, and the other relativistic corrections to the Schrödinger equation can be obtained from the fully relativistic Dirac equation by expanding it to the next-to-leading order in the fine-structure constant. The results are simplest in the case of independent electrons moving in some effective central potential $U_c(\vec{r})$ similar to the one described in the previous lecture. Then one finds an additional relativistic term in the Hamiltonian of the form:

$$V^{(so)} = \sum_{i=1}^{Z} \vec{S}_i \cdot \vec{l}_i \, g(r_i) \tag{35.2}$$

where:

$$g(r) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dU_c}{dr} \tag{35.3}$$

The central potential goes to negative infinity at the origin and goes to zero at large r, so we expect U_c to be monotonic, and the function $g(r)$ should be positive for all values of r. A heuristic explanation, which is not quite right, for the origin of this term is that if we go to the moving frame of an electron it sees an effective magnetic field in the moving frame which is equal to

$$\vec{B}' = \vec{E} \times \frac{\vec{v}}{c} \tag{35.4}$$

where $\vec{E}$ is the electric field in the laboratory frame, and $\vec{v}$ is the velocity in the laboratory frame. Then we might guess there should be an additional term in the Hamiltonian due to the Zeeman interaction between the electron spin and the effective magnetic field in the moving frame, proportional to $\vec{B}' \cdot \sigma$. However, this is wrong, it would be off by a factor of 2 from (35.2),

which is what one gets from the Dirac equation. Further corrections come from QED, but they are quite small.

If we now want to see the effect of this term on the energy levels through first order perturbation theory, we want to look at the matrix elements of this term in the manifold of degenerate states. We imagine that we have found the exact many-body wave functions in the absence of spin orbit coupling, which have definite values of L and S, but have varying values of m_L and m_S. Then the calculation would look like:

$$\sum_{i=1}^{Z} \langle m_L, m_S | \vec{S}_i \cdot \vec{l}_i g(r_i) | m'_L, m'_S \rangle \;=\; Z \sum_{\alpha,\beta=1}^{3} \delta_{\alpha\beta} \langle m_L m_S | S_i^{\alpha} l_i^{\beta} g(r_i) | m'_L m'_S \rangle \tag{35.5}$$

$$=\; Z \cdot \text{Constant} \sum_{\alpha=1}^{3} \langle m_S | S^{\alpha} | m_{S'} \rangle \langle m_L | L^{\alpha} | m_{L'} \rangle \tag{35.6}$$

We have used the Wigner Eckart theorem twice in the last line of equation (35.5), as the operator $S_i^{\alpha} l_i^{\beta} g(r_i)$ transforms as a vector under rotations of either spin or space. Clumping the terms out in front into a constant λ we can write the spin orbit term more simply, within the manifold of degenerate states, as:

$$V^{(so)} \simeq \lambda \vec{L} \cdot \vec{S} \tag{35.7}$$

Given that:

$$\vec{J}^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S} \tag{35.8}$$

We can rewrite the dot product as:

$$\vec{L} \cdot \vec{S} \;=\; \frac{J^2 - L^2 - S^2}{2} \tag{35.9}$$

$$=\; \frac{\hbar^2}{2} \left(j(j+1) - L(L+1) - S(S+1) \right) \tag{35.10}$$

There is a third Hund's rule, which states that for the ground state manifold with a shell less than half full, we have $\lambda > 0$, so the energy is minimized by choosing $j = |L - S|$, while for more than half full, we have $\lambda < 0$, and $j = |L + S|$. For a half full shell we have S at its maximum value, and L is zero, so there is only one value of j .

If there are three or more allowed values of j, Eq. (35.9) determines the relative spacing between the levels.

35.1.2   Hyperfine Correction

The hyperfine correction, involving the interaction of the nuclear and electron spins, to the Hamiltonian takes the form:

$$H_{HF} = -\vec{M}_N \cdot \vec{B}(0) \tag{35.11}$$

where

$$\vec{M}_N = \gamma_N \vec{I}_N. \tag{35.12}$$

The magnetic field $\vec{B}(0)$ is the field at the nucleus created by the orbital motion and the spin magnetic moments of the electron. It is dependent on the positions, spins and velocities of the electrons. The important point is that it is a vector operator, which transforms as a vector under simultaneous rotations of the positions and spins of the electrons. Thus we can write $\vec{B}(0) \simeq A\vec{J}$ within the manifold of the degenerate states of the electrons. Using $\vec{F} = \vec{I} + \vec{J}$, as we used $\vec{J} = \vec{L} + \vec{S}$ before, we get:

$$
\begin{aligned}
H_{HF} &\simeq A\vec{I} \cdot \vec{J}\gamma_N \tag{35.13}\\
&\simeq -\frac{A\gamma_N\hbar^2}{2}\left(f(f+1) - j(j+1) - I(I+1)\right). \tag{35.14}
\end{aligned}
$$

35.2   Molecules: Electrons and Several Nuclei with Finite Mass

We use the Born Oppenheimer separation, an adiabatic approximation for the electrons in a system with several nuclei. The nuclei are at least 2000× more massive than the electrons, so we would expect the electrons to move very fast, and we would expect them to just follow the motion of the nuclei. We shall assume that for any set of positions of interest for the nuclei, the electrons are in their many-body ground state, which we assume to be non-degenerate.

The total (non-relativistic) Hamiltonian for the system can be written as:

$$H = \sum_{i=1}^{N_e} \frac{p_i^2}{2m_e} + V\{\vec{r}_i, \vec{R}_j\} + \sum_{j=1}^{N} \frac{P_j^2}{2M_j} \tag{35.15}$$

where $\vec{p}_i$, $\vec{r}_i$ are the momentum and position of the electrons, $\vec{P}_j$, $\vec{R}_j$ are the momentum and position of the nuclei. If we wish, we may include the spin-orbit coupling for the electrons, but we shall ignore the nuclear spins. The masses are such that $M_j >> m_e$. According to the adiabatic approximation, we can break down the wavefunction into a product:

$$\Psi(r_i, \sigma_i, R_j, t) = \Psi^0_{elec}(\vec{r}_i, \sigma_i \vec{R}_j)\Phi(\vec{R}_j, t) \tag{35.16}$$

The separated wavefunction for the electrons will satisfy:

$$H_0\Psi^0_{elec} = E^0(\vec{R}_j)\Psi^0_{elec}, \tag{35.17}$$

3

where H_0 is the Hamiltonian (35.15) with the nuclear kinetic energy (final term) omitted. The ground state energy E^0 is dependent on the position of the nuclei. We also assume the following normalization:

$$\sum_{\sigma_i} \int |\Psi^0_{elec}|^2 d^{3N_e} r_i = 1 \tag{35.18}$$

If the electronic ground state is non-degenerate, then the normalized solution to (35.17) is unique up to an arbitrary phase factor $e^{i\phi}$, which may depend on the nuclear positions.

   The complete wavefunction should obey the time dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi(\vec{r}_i, \sigma_i, \vec{R}_j)}{\partial t} = H\Psi \tag{35.19}$$

If we substitute: $\Psi = \Phi(\vec{R}_j)\Psi^0_{elec}(\vec{r}_i, \sigma_i, \vec{R}_j)$, multiply by $\Psi^{0*}_{elec}(\vec{r}_i, \sigma_i, \vec{R}_j)$ and integrate over the electron coordinates and spins, I claim that the result is:

$$i\hbar \frac{\partial \Phi(\vec{R}_j)}{\partial t} = H_{eff}\Phi(\vec{R}_j) \tag{35.20}$$

$$H_{eff} = \sum_{j=1}^{N} \frac{|\vec{P}_j - \vec{A}_j^{eff}(\vec{R}_j)|^2}{2M_j} + V_{eff}(\vec{R}_j) \tag{35.21}$$

where $V_{eff}(\vec{R}_j) \approx E^0(\vec{R}_j)$, and $\vec{A}_j^{eff}$ is given by:

$$\vec{A}_j^{eff}(\vec{R}_j) = -\hbar \operatorname{Im}\left(\left\langle \Psi^0_{el} \Big| \frac{\partial \Psi^0_{el}}{\partial \vec{R}_j} \right\rangle\right) \tag{35.22}$$

This additional term is called "Berry's Connection". It should be noted that in the all of above equations, functions such as E^0 and $\vec{A}_j^{eff}$ are functions of all the R_j, not just of one.

   In general, the vector potential $\vec{A}_j^{eff}$ depends on the way that the arbitrary phase factor $e^{i\phi}$ of the electronic ground state wave function varies, as one varies the positions of the nuclei. However, if the allowed positions of the nuclei form a singly-connected space, and if the electronic ground state is non-degenerate throughout this region, then different choices of the phase ϕ will lead to vector potentials that differ only by the gradient of a scalar function. This is equivalent to a different choice of gauge, and it will have no effect on the energy eigenvalues of H_{eff} or on time-dependence of any physical quantities, as we learned in Physics 251a.

   Specifically, suppose that we have made a particular choice of phase factors such that the electronic ground state wave function Ψ^0_{el} varies continuously with the nuclear positions, and is single valued, for all nuclear positions inside some singly connected region K. Let us define a new set of wave functions $\Psi^1_{el} = e^{i\chi}\Psi^0_{el}$, where χ is a continuous, differentiable single-valued

function of the nuclear positions within the region K. The the vector potential $\vec{A}_j^{(1)eff}$ defined by the new wave functions will be related to the vector potential $\vec{A}_j^{eff}$, defined by the old wave functions, by

$$\vec{A}_j^{(1)eff} = \vec{A}_j^{eff} - i\hbar \partial \chi / \partial \vec{R}_j. \qquad (35.23)$$

We see that for any closed path in the region K, the integral $\sum_j \oint \vec{A}_j^{eff} \cdot d\vec{R}_j$ is unchanged by this transformation. Therefore, if the allowed nuclear positions are contained in the region K, the eigenvalues of H_{eff} are unchanged as well.

In many common cases, one can choose the phases of wave functions so that $\vec{A}_j^{eff} = 0$. However, there are important cases where this cannot be done, and then the Berry connection must be taken into account. In particular, if no magnetic field is present, so that the Hamiltonian is time-reversal invariant, we can choose the electronic wave functions to be real for any fixed set of nuclear positions. Moreover, if there are no degeneracies in the electronic states, we can choose the wave function to vary continuously with the nuclear positions, at least for any local region of these positions. Then, in any such region, we will find that $\vec{A}_{eff} = 0$. What is not so obvious is whether when you move the nuclear positions around some closed path in their multidimensional space, coming back to original positions, the state will necessarily have the same phase (i.e., the same overall sign) as it started with. There is a theorem in topology that if the space of allowed nuclear positions is simply connected, you can choose the sign of the of the wave function so that the wave function is always real and is a unique and continuous function of position, so you always come back to the same wave function when you come back to the same nuclear position. With this choice, then $\vec{A}_{eff} = 0$ everywhere, and there is no contribution from the Berry connection. This case includes, in particular, all diatomic molecules.

If the space is multiply connected, and if going around a closed path brings you back to the original wave function with a reversed sign, then if you want the wave function to be uniquely defined, including its sign, you will either need to introduce a discontinuity some where, or you will have allow complex phases for the wave functions. Since the definition of A_{eff} involved derivatives, we should not allow the wave function to change discontinuously, so we must choose, in this case the alternative of complex phases, and a non-zero Berry's connection. One example, where the topological space is multiply connected, and Berry's phase must be taken into account in the absence of an applied magnetic field, is the Na$_3$ molecule.

Berry's phase can also be important when one wants to understand spin systems from a semiclassical point of view, or in systems where magnetic fields are important, including the fractional quantized Hall effect. Berry's phases can also occur in optics, and show up in various exotic many body states that are the subject of current research.

For molecules, in the usual case where the Berry connection can be set equal to zero, the

effective Hamiltonian for the nuclei (35.20) is just the sum of an ordinary kinetic energy and a potential energy function E^0, which depends on the relative positions of the nuclei. This function will be invariant under simultaneous translations or simultaneous rotations of all the nuclear positions. Normally this function will have a unique configuration which minimizes the energy. The center of mass motion of the molecule may be separated out rigorously. Variations of the distances between nuclei will lead to increases in E^0, with a restoring force that leads to vibrational modes that can generally be treated in a harmonic approximation. The rotational degrees of freedom, which do not change the distances between the nuclei, which can be treated in quantum mechanics as the rotation of a rigid body, give rise to rotational excitation energies that are much lower than the vibrational energy. For a diatomic molecule of unlike atoms, such as CO, or HCl, the rotational energy levels have the simple form

$$E_{rot} = \hbar^2 \frac{l(l+1)}{2 I_{AB}}, \tag{35.24}$$

where $l = 0, 1, 2, \ldots$ is the quantum number for the rotation of the molecule, and I_{AB} is the moment of inertia of the molecule. For a diatomic molecule with two identical atoms, there may be constraints on l due to the requirements of permutation symmetry.

The effective potential V_{eff} in (35.22) also contains a correction to E^0 due to the finite nuclear mass, which may be written:

$$V_{eff}(\vec{R}_j) = E^0(\vec{R}_j) + \sum_j \frac{\hbar^2}{2 M_j} \left[\langle \partial_j \Psi^0_{elec} | \partial_j \Psi^0_{elec} \rangle - \langle \partial_j \Psi^0_{elec} | \Psi^0_{elec} \rangle \langle \Psi^0_{elec} | \partial_j \Psi^0_{elec} \rangle \right], \tag{35.25}$$

where $\partial_j \equiv \partial / \partial \vec{R}_j$. This correction is usually small and is unimportant in the limit where $M_j \gg m_e$. In the case of an atom with one electron and one nucleus, (35.25) describes the correction to the electronic energy that one obtains by replacing the electron mass by the reduced mass.

A more complete discussion of Berry's connection may be found in Shankar's book on quantum mechanics.

Berry's connection pays a very important role in current research on "topological insulators" and other "topological phases" of matter.

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36.1   Path Integral formulation of Quantum Mechanics

Discussions of this topic may be found in Shankar, Chapters 8 and 21; in Gottfried and Yan, Section 2.7; and in Stöckmann's book "Quantum Chaos", Section 7.2.

Feynman's path integral formulation gives a different way of thinking about quantum mechanics, which can be very useful for certain kinds of problems. Important applications are found in Relativitistic Quantum Field Theory, and in a variety of quantum many body problems. There are powerful numerical methods based on the path integral formulation both in field theory and in non-relativistic many body problems.

The path integral formulation can also be used to describe the semiclassical limit of quantum mechanical problems in more than one-dimension, in the general case where classical orbits are chaotic, and the simple WKB approach cannot be used. This has found important recent application in analyses of electron states in nanoscale particles at low temperatures, where the particle is large compared to the wavelength of the electron, but small enough so that the electrons can bounce around many times without losing their phase coherence.

The path integral formulation is based on the Lagrangian, rather than the Hamiltonian formulation of classical mechanics. The Lagrangian is a function of the positions and velocities of the particles, rather than of positions and momenta. For a set of M particles in zero magnetic field, we may write

$$L = \sum_{j=1}^{M} \frac{m_j}{2} \left| \frac{d\vec{x}_j}{dt} \right|^2 - V(\{\vec{x}_j\}) \tag{36.1}$$

For charged particles in the presence of a vector potential $\vec{A}(\vec{x})$, we add to the Lagrangian a term

$$L_A = \sum_{j} (q_j/c) \vec{A}(\vec{x}_j) \cdot \frac{d\vec{x}_j}{dt}.$$

Below, we shall use X to represent the set of all position variables, which is to say $D = Md$ variables, if space has d dimensions.

We may define the action integral S for a path from a specified initial point X_0 at time t_0 to a final point X_f at a later time t_f by

$$S \equiv \int_{t_0}^{t_f} dt' L[X(t'), \dot{X}(t')] \tag{36.2}$$

In classical mechanics, the allowed trajectories between the initial and final points are those which lead to a local minimum of S.

In Quantum Mechanics, we are interested in the time translation operator $T(t_f, t_0) = \exp[-i(t_f - t_0)H/\hbar]$ which takes a wave function from time t_0 to time t_f. In particular we may want to calculate the matrix elements of T in the position representation, which we write as:

$$U(X_f, t_f; X_0, t_0) \equiv \langle X_f | T(t_f, t_0) | X_0 \rangle$$

We claim that

$$U = A \sum_P \exp[iS(P)/\hbar],$$

where A is a constant, $\sum_P$ represents a sum over *all* possible paths P from the initial point X_0, t_0 to the final point X_f, t_f, and $S(P)$ is the action integral for path P. In the limit of $\hbar \to 0$, the sum is dominated by the shortest path and classical trajectory is recovered.

In class, we shall make more precise what we mean by the sum over all paths, and we shall prove that the result for U is identical to what one would obtain in the usual Hamiltonian formulation of quantum mechanics.

Precise definition of $\sum_P$ is as follows:

1. Divide the time interval into N equal steps.

2. Define $t_k = t_0 + k\tau$, $k = 1, \ldots, N$, , $\tau \equiv \frac{t_f - t_0}{N}$.

3. Choose arbitary values of $X_k \equiv X(t_k)$.

4. Use straight line interpolation of $X(t)$ within the intervals $t_k < t' < t_{k+1}$.

5. Calculate $e^{iS(P)/\hbar}$ for each path thus defined.

6. We may now calculate the sum over all discretized paths of N steps by integrating over all possible positions for the variables X_k. Thus we obtain an approximation to U of the form

$$U_N(X_f, t_f; X_0, t_0) = A \sum_P \exp[iS(P)/\hbar] = \left(\frac{m}{2\pi i\hbar\tau}\right)^{DN/2} \int \int \ldots \int dX_{N-1} dX_{N-2} \ldots dX_1 \, e^{iS/\hbar},$$

   where the prefactor in front of the integration is the most convenient normalization factor.

7. Take the limit of $N \to \infty$. It is common to write the sum over paths, in the limit of $N \to \infty$, as $\int \mathcal{D}[x(t')]$.

How do we calculate S ? We shall illustrate it here for the case of one particle in dimension $d = 1$.

- We write the total S as the sum over the contribution from each interval $t_{k-1} < t' < t_k$:

$$S = \sum_{k=1}^{N} s_k \quad , \quad s_k = \int_{t_{k-1}}^{t_k} dt' \left(\frac{m\dot{x}^2}{2} - V \right).$$

- With the straight-line interpolation, $\dot{x} = \frac{x_k - x_{k-1}}{\tau}$,

$$s_k = \frac{m(x_k - x_{k-1})^2}{2\tau} - \tau \left[\frac{V(x_k) + V(x_{k-1})}{2} \right] \quad ,$$

assuming that $|x_k - x_{k-1}|$ is small. This assumption is not completely obvious since $(x_k - x_{k-1})$ could be anything. However, since $\exp\left[\frac{im(x_k - x_{k-1})^2}{2\tau\hbar} \right]$ is very rapidly oscillating when $|x_k - x_{k-1}|$ gets too large, it is reasonable to estimate that the dominant contributions come from $|x_k - x_{k-1}| \ll \sqrt{\frac{\hbar\tau}{m}}$. So, this is fine when $\tau \to 0$, in which case $|x_k - x_{k-1}|$ is small.

36.1.1   Proof of Equivalence between Path Integral and standard Schrödinger Quantum Mechanics

For Schrödinger picture, we write time evolution operator as (assuming V is time independent)

$$\begin{aligned} T(t_f - t_0) &= T(t_f - t_{N-1})T(t_{N-1} - t_{N-2})\ldots T(t_1 - t_0) \\ &= [W(\tau)]^N \quad , \quad W(\tau) \equiv e^{-i\tau H/\hbar} \ . \end{aligned}$$

Using Baker-Hausdorff Theorem:

$$e^{\tau A} e^{\tau B} = \exp\left[\tau(A + B) + \frac{\tau^2}{2}[A, B] + \mathcal{O}(\tau^3) \right]$$

$$\Rightarrow \exp\left(\frac{\tau}{2}A \right) \exp\left(\tau B \right) \exp\left(\frac{\tau}{2}A \right) = e^{\tau(A+B)} \left[1 + \mathcal{O}(\tau^3) \right] \ .$$

Let $A = \frac{iV(x)}{\hbar}$ and $B = \frac{ip^2}{2m\hbar}$. Now, we can evaluate the product of N factors of W by inserting a complete set of eigenstates $|x_k\rangle \langle x_k|$ between each factor, and integrating over the vales x_k. Then, we need to evaluate the matrix elements,

$$\langle x | W(\tau) | x' \rangle \approx \exp\left[\frac{iV(x)\tau}{2\hbar} \right] \cdot G_0\left(\tau, x - x' \right) \cdot \exp\left[\frac{iV(x')\tau}{2\hbar} \right]$$

where $G_0\left(\tau, x - x' \right) \equiv \langle x | e^{\tau B} | x' \rangle$.

In 1-d:

$$
\begin{aligned}
G_0 &= \sum_k \langle x|k\rangle \langle k|x'\rangle \, e^{-i\tau \frac{\hbar k^2}{2m}} \\
&= \int dk \left[\frac{L}{2\pi}\right] \left[\frac{e^{ik(x-x')}}{L}\right] \left[e^{-i\tau \frac{\hbar k^2}{2m}}\right] \\
&= \sqrt{\frac{m}{2\pi i \hbar \tau}} \, \exp\left[\frac{i}{\hbar} \frac{m(x-x')^2}{2\tau}\right] .
\end{aligned}
$$

In D dimensions:

$$
G_0 = \left(\sqrt{\frac{m}{2\pi i \hbar \tau}}\right)^{D/2} \exp\left[\frac{i}{\hbar}\frac{m(x-x')^2}{2\tau}\right] .
$$

Thus, we arrive at

$$
\boxed{\langle x_k | \, W(\tau) \, | x_{k-1}\rangle = e^{is_k/\hbar},}
$$

up to a constant normalization factor. Multiplying the N factors together, for a given choice of the set of positions $\{x_k\}$ gives a constant times $e^{iS_P/\hbar}$ for the equivalent path P. Finally, summing over all choices for $\{x_k\}$ is the same as summing over all paths. QED.

36.1.2   Application: Aharonov Bohm effect Interference

See the figure for this problem, on page 5.

The action S_P for any path is the sum of the part which is independent of Φ and the part $\frac{q}{c}\int \vec{A}\cdot d\vec{r}$ along the path. The second term is the same for any two paths on the same side of the hole, but if one path is on the top and one is on the bottom, the difference is

$$
\frac{q}{c}\oint \vec{A}\cdot d\vec{r} = \frac{q}{c}\Phi .
$$

Thus when the two sets of paths interfere with each other, they have a field-dependent interference phase, due to the flux Φ, given by

$$
e^{i\frac{q}{\hbar c}\Phi} = e^{2\pi i \Phi/\Phi_0}
$$

where $\Phi_0 = 2\pi \hbar c/q$.
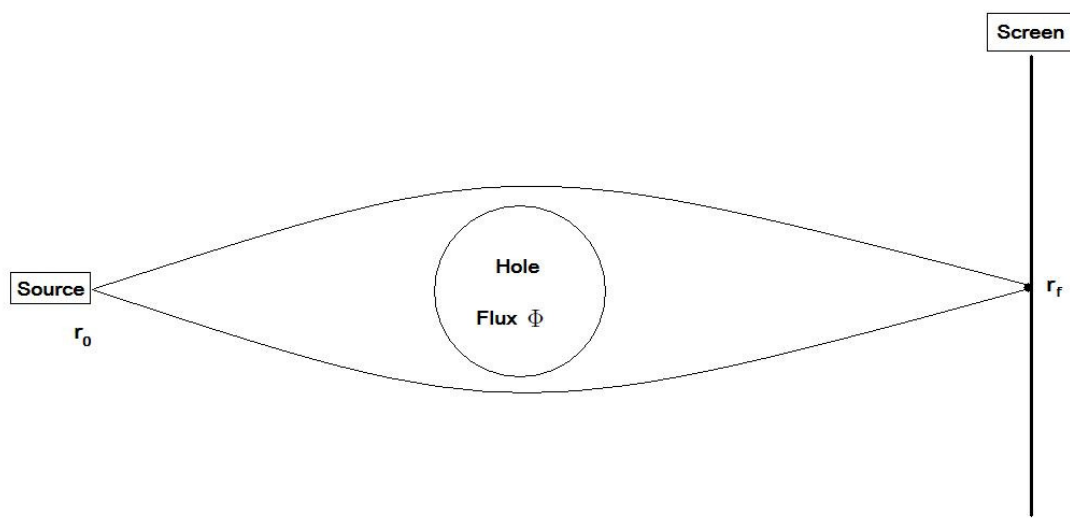
Pages printed to pdf April 24, 2012.

37.1 Assorted Topics and Course Wrap-up

Complete notes for this lecture are not currently available.

37.1.1 Scattering of identical particles

Please see the handout on this topic in the Handout folder of the course web site.

37.1.2 Additional remarks on Berry's connection and Na$_3$.

Please see the handout on this topic in the Handaout folder of the course web site.