Chapter 6

Perturbation Theory

6.1 Time independent perturbation theory

In this chapter we will assume that the Hamiltonian $H$ of a quantum mechanical system can be written as a small perturbation of a simple Hamiltonian $H_0$, i.e.

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \cdots \equiv H(\lambda) = H_0 + V(\lambda) \quad (6.1)$$

We will also assume that $H_0$ has an eigenvalue $E_0$ which is $n_0$-fold degenerate. Under rather general assumptions (e.g. Messiah) the perturbation $V(\lambda)$ will resolve $E_0$ analytically in maximally $n_0$ different Eigenvalues $E_k(\lambda)$, with corresponding eigenvectors $|\psi_k(\lambda)\rangle$ which are also analytic in $\lambda$,

$$H(\lambda)|\psi_k(\lambda)\rangle = E_k(\lambda)|\psi_k(\lambda)\rangle$$
$$E_k(\lambda) = E_0 + \lambda E_1^k + \lambda^2 E_2^k + \cdots \quad (6.2)$$
$$|\psi_k(\lambda)\rangle = |\psi_0^k\rangle + \lambda|\psi_1^k\rangle + \lambda^2|\psi_2^k\rangle + \cdots$$

with normalization condition

$$<\psi_0^k|\psi_k(\lambda)> = 1 \iff <\psi_0^k|\psi_l^k> = 0, \quad l > 0 \quad (6.3)$$

In physical applications one usually stops at the second order in $\lambda$, i.e.

$$(H_0 - E_0)|\psi_0^k\rangle = 0 \quad (6.4)$$
$$(H_0 - E_0)|\psi_1^k\rangle + (H_1 - E_1^k)|\psi_0^k\rangle = 0 \quad (6.5)$$
$$(H_0 - E_0)|\psi_2^k\rangle + (H_1 - E_1^k)|\psi_1^k\rangle + (H_2 - E_2^k)|\psi_0^k\rangle = 0 \quad (6.6)$$
Let $\mathcal{M}_0$ be the eigenspace to $H_0$ with eigenvalue $E_0$ and $\hat{P}_0$ the projection operator onto $\mathcal{M}_0$. In addition let $\hat{Q}_0 = (1 - \hat{P}_0)$ be the projection operator onto the orthogonal complement $\mathcal{M}_0^c$. Since $\hat{P}_0 H_0 = H_0 \hat{P}_0 = E_0 \hat{P}_0$, the subspace $\mathcal{M}_0$ and its complement are invariant under $H_0$ and $H_0 - E_0$ is invertible on $\mathcal{M}_0^c$. In other words the resolvent

$$\hat{R}_0 = -\hat{Q}_0 (H_0 - E_0)^{-1} \hat{Q}_0$$

(6.7)

is well defined on $\mathcal{H}$.

If $E_0$ is non-degenerate, $n_0 = 1$, then $|\psi_0 >$ is uniquely fixed by (6.4) up to normalization. Taking the scalar product of (6.5) with $<\psi_0 |$ we get

$$E_1 = <\psi_0 | H_1 | \psi_0 >$$

(6.8)

On the other hand acting on (6.5) by $\hat{Q}_0$ we obtain

$$(H_0 - E_0) \hat{Q}_0 |\psi_1 > + \hat{Q}_0 H_1 |\psi_0 >= 0$$

(6.9)

Taking

$$|\psi_1 > = \hat{Q}_0 |\psi_1 > = \hat{R}_0 H_1 |\psi_0 >$$

(6.10)

we have satisfied all components of equation (6.5). Finally we act on (6.6) by $\hat{P}_0$ to obtain

$$\hat{P}_0 H_1 |\psi_1 > + \hat{P}_0 (H_2 - E_2) |\psi_0 >= 0$$

(6.11)

Upon substitution of $|\psi_1 >$ from (6.19) and taking the scalar product with $<\psi_0 |$ we get

$$E_2 = <\psi_0 | H_1 \hat{R}_0 H_1 |\psi_0 > + <\psi_0 | H_2 |\psi_0 >$$

$$= \sum_{\epsilon_n \neq E_0} \frac{| <\phi_n | H_1 |\psi_0 > |^2}{E_0 - E_n} + <\psi_0 | H_2 |\psi_0 >$$

(6.12)

where

$$H_0 |\phi_n > = \epsilon_n |\phi_n >$$

(6.13)

on $\mathcal{M}_0^c$. Similarly acting on (6.6) by $\hat{Q}_0$ we obtain

$$(H_0 - E_0) \hat{Q}_0 |\psi_2 > + \hat{Q}_0 (H_1 - E_1) |\psi_1 > + \hat{Q}_0 H_2 |\psi_0 >= 0$$

(6.14)
and thus by taking
\[ |\psi_2> = \hat{Q}_0|\psi_2> = \hat{R}_0 H_2|\psi_0> + \hat{R}_0 (H_1 - E_1) \hat{R}_0 H_1|\psi_0> \] (6.15)
we have satisfied all components of equation (6.6).

If \( E_0 \) is degenerate, then (6.5) together \( \hat{P}_0 (H_0 - E_0) = 0 \) leads to the \( n_0 \)-dimensional eigenvalue problem
\[ (\hat{P}_0 H_1 \hat{P}_0 - E_1)|\psi_0^k> = 0 \] (6.16)
which determines the first order correction to the energy \( E_1^k \) and the corresponding eigenvectors \( |\psi_0^k> \) up to degeneracy. We then consider for a given solution \( E_1 \) of (6.16) with degeneracy \( n_1 \), \( 1 \leq n_1 \leq n_0 \) the eigenspace \( M_1 \subset M_0 \) of \( \hat{P}_0 H_1 \hat{P}_0 \) with corresponding projector \( \hat{P}_1 = \hat{P}_1 \hat{P}_0 = \hat{P}_0 \hat{P}_1 \) and \( \hat{P}_1 (H_0 - E_0) = \hat{P}_1 (\hat{P}_0 H_1 \hat{P}_0 - E_1) = 0 \). The family of vectors \( \{|\psi_1^k>\}, \) \( \hat{k} = 1, \ldots, n_1 \), is then found from (6.5)
\[ \hat{Q}_0 |\psi_1^k> = \hat{R}_0 H_1 |\psi_1^k> \] (6.17)
with \( |\psi_0^k> \in M_1 \). Taking \( \hat{Q}_0 |\psi_1^k> = |\psi_1^k> \) eqn (6.17) determines \( |\psi_1^k> \) uniquely. Alternatively we may write
\[ |\psi_1^k> = \hat{R}_0 H_1 |\psi_1^k> \] (6.18)
of which only \( n_1 \) vectors can be non-vanishing and distinct (question: what is the role of \( \hat{P}_1 \) on the r.h.s. of (6.19)??). Acting with \( \hat{P}_1 \) on (6.6) we get
\[ \hat{P}_1 H_1 |\psi_1^k> + (\hat{P}_1 H_2 \hat{P}_1 - E_2^2)|\psi_0^k> = 0 \] (6.19)
which upon substitution of (6.17) leads to a \( n_1 \)-dimensional eigenvalue problem of \( E_2 \), etc.

### 6.2 Time dependent perturbation theory

Time dependent perturbation theory is relevant for the time-evolution of transition probabilities. We will assume that the Hamiltonian is of the form \( H(t) = H_0 + \lambda H_1(t) \) with \( H_1(t) = H_1^*(t) \) bounded in \( \mathcal{H} \) and (piecewise) continuous in \( t \). We work in the interaction picture:
\[ \hat{U}(t,s) = \hat{U}_0(t,0) \hat{U}_W(t,s) \hat{U}_0^*(s,0), \quad \hat{U}_0(t,0) \equiv \hat{U}_0(t) = e^{-\frac{i}{\hbar} H_0 t} \] (6.20)
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with

\[ i\hbar \frac{d}{dt} \hat{U}_W(t, s) = H_W(t)\hat{U}_W(t, s), \quad \hat{U}_W(s, s) = 1 \]  
(6.21)

\[ H_W(t) = \hat{U}_0^*(t, 0)H_1(t)\hat{U}_0(t, 0) \]

The solution for the evolution operator \( \hat{U}_W(t, s) \) can then be expanded as

\[ \hat{U}_W(t, s) = 1 + \sum_{n=1}^{\infty} \hat{U}_W^{(n)}(t, s) \]  
(6.22)

\[ = 1 + \sum_{n=1}^{\infty} \left( \frac{-i}{\hbar} \right)^n \int_s^t \int_{r_{n-1}}^{r_n} H_W(r_1) \cdots H_W(r_n) \right) dr \]  

We now consider the special case of a time-independent perturbation, \( H_1 \neq H_1(t) \). Let \( |\psi_0>\) be the normalized eigenvector of \( H_0 \) for the non-degenerate eigenvalue \( E_0 \). we shall also assume that \( H_0 \) has the spectral representation

\[ H_0 = E_0|\psi_0><\psi_0| + \sum_n E_n \hat{P}_n + \int E \, d\hat{P}(E) \]  
(6.23)

with projection operators \( \hat{P}_n \) for the discrete eigenvalues \( E_n \) and \( d\hat{P}(E) \) for the continuous spectrum.

6.2.1 Transition from \( |\psi_0> \) to the discrete spectrum

Using that \([\hat{P}_n, \hat{U}_0(t, 0)] = 0\) we find for the transition probability

\[ w_n(t) = <\psi_0|\hat{U}(0, t)\hat{P}_n\hat{U}(t, 0)|\psi_0> \]  
(6.24)

\[ = <\psi_0|\hat{U}_w(0, t)\hat{P}_n\hat{U}_w(t, 0)|\psi_0> \leq 1 \]  
(6.25)

Upon substitution of (6.22) we obtain (using \( \hat{P}_n|\psi_0> = 0 \))

\[ w_n(t) = w_n^{(2)}(t) + O(H_1^3) \]  
(6.26)
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with

\[ w_n^{(2)}(t) = < \psi_0 | \hat{U}_w(0,t) \hat{P}_n \hat{U}_w(t,0) | \psi_0 > \]

\[ = < \psi_0 | H_1 \hat{P}_n H_1 | \psi_0 > | \frac{i}{\hbar} \int_0^t dt' e^{i(E_n-E_0)t'/\hbar} |^2 \]  

\[ = 4 < \psi_0 | H_1 \hat{P}_n H_1 | \psi_0 > \sin^2 \left( \frac{E_n-E_0}{2\hbar} t \right) \]  

(6.27)

(6.28)

The transition probability \( w_n^{(2)}(t) \) thus shows oscillatory behavior and is small for \( ||H_1||/|E_n - E_0| \ll 1 \).

6.2.2 Transition from \( |\psi_0> \) to the continuous spectrum

Let \( \Delta = [a, b] \) be a closed interval in the continuous spectrum and

\[ \hat{P}_\Delta = \int_\Delta d\hat{P}(E) \]  

(6.29)

be the projector on the corresponding subspace of \( \mathcal{H} \). The transition probability from \( |\psi_0> \), at \( t = 0 \), to \( \hat{P}_\Delta \mathcal{H} \) at time \( t \) is then (\( \hat{P}_\Delta |\psi_0> = 0 \))

\[ w_\Delta(t) = w_\Delta^{(2)}(t) + O(H_1^3) \]  

(6.30)

\[ w_\Delta^{(2)}(t) = < \psi_0 | \hat{U}_w(0,t) \hat{P}_\Delta \hat{U}_w(t,0) | \psi_0 > \]

\[ = 4 \int_\Delta \frac{\sin^2 \left( \frac{E-E_0}{2\hbar} t \right)}{(E_n-E_0)^2} < \psi_0 | H_1 d\hat{P}(E) H_1 | \psi_0 > \]  

(6.31)

If \( E_0 \notin \Delta \) then we have for \( 0 < \frac{\hbar}{t} \ll |\Delta| \)

\[ w_\Delta^{(2)}(t) \simeq 2 \int_\Delta \frac{\chi(E)dE}{(E_n-E_0)^2} \]  

(6.32)

with

\[ \chi(E)dE := < \psi_0 | H_1 d\hat{P}(E) H_1 | \psi_0 > \]  

(6.33)

(what is the dimension of \( \chi(E) \)?) so that \( w_\Delta^{(2)}(t) \) approaches a constant (\( t \)-independent) value provided \( \chi(E) \) is integrable, ie. \( \int |\chi(E)|dE < \infty \).
If \( \Delta(\epsilon) = [E_0 - \epsilon, E_0 + \epsilon] \) for \( \epsilon > 0 \), small and \( \chi(E) \) continuous in \( \Delta(\epsilon) \) then we have for late times \( 0 < \frac{t}{\hbar} << \epsilon \):

\[
p^{(2)}_{\Delta(\epsilon)} = \frac{w^{(2)}_\Delta(t)}{t} \simeq \frac{2\chi(E_0)}{\hbar} \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} \, dx = \frac{2\pi}{\hbar} \chi(E_0)
\]

Thus, the transition rate \( p^{(2)}_{\Delta(\epsilon)} \) in second order perturbation theory approaches a constant \( p^{(2)}_{E_0} \) independent of \( \epsilon \).

Suppose now that \( H_0 \) has an almost continuous spectrum around \( E_0 \) with normalized eigenvectors \( |\psi_n> \), such that

\[
<\psi_n|H_1|\psi_0><\psi_n|H_1|\psi_0> \approx \sum_{n \neq 0} \frac{\sin^2 \left( \frac{E_n - E_0}{2\hbar} t \right)}{(E_n - E_0)^2 t} |<\psi_n|H_1|\psi_0>|^2
\]

for \( E \approx E_0 \) and \( <\psi_n|H_1|\psi_0> \) is a “typical” matrix element. Then we have

\[
\frac{w^{(2)}_\Delta(t)}{t} = 4 \sum_{\{n \neq 0, |E_n - E_0| < \epsilon\}} \frac{\sin^2 \left( \frac{E_n - E_0}{2\hbar} t \right)}{(E_n - E_0)^2 t} |<\psi_n|H_1|\psi_0>|^2
\]

\[
\simeq 4 \frac{1}{t} |<\psi_n|H_1|\psi_0>|^2 \int_{\Delta_\epsilon} \frac{\sin^2 \left( \frac{E_n - E_0}{2\hbar} t \right)}{(E - E_0)^2} \rho(E) \, dE
\]

\[
\simeq \frac{2\pi}{\hbar} |<\psi_n|H_1|\psi_0>|^2 \rho(E_0)
\]

where \( \rho(E) \) is the density of states of \( H_0 \) around \( E_0 \). This is Fermi’s golden rule.

### 6.3 Atom in the radiation field

We consider an atom with Hamiltonian

\[
H_0^A = \sum_i \frac{\hat{p}_i^2}{2m_e} + V(\tilde{q}_i) + \sum_{i<j} W(\tilde{q}_i - \tilde{q}_j)
\]

We will be interested in the transition rate between two bound states \( |\phi_i^A> \) with

\[
H_0^A|\phi_i^A> = \epsilon_i|\phi_i^A>, \quad \epsilon_i \neq \epsilon_j, \quad <\phi_i^A|\phi_j^A> = \delta_{ij}
\]
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In the dipole approximation the minimal coupling to the quantized radiation field (2.40) in Coulomb gauge (2.32) with Hamiltonian (2.44) to first order in $\varepsilon$ is given by

$$H_1 = \sum_i \frac{e}{m_c} \vec{p}_i \cdot \hat{A}(\vec{q}_0)$$  \hspace{1cm} (6.39)

where $\vec{q}_0$ is the position of the atom. The Hilbert space of the combined system is given by $\mathcal{H}^A \otimes \mathcal{H}^{rad}$ with $\mathcal{H}^{rad}$ as in (2.29). We take the initial state of the combined system at $t = 0$ to be

$$|\psi_1> = |\phi_1^A> \otimes |n_1> =: |\phi_1^A, n_1>$$  \hspace{1cm} (6.40)

where $n_1 = n_{k_1}, \ldots, n_{k_j}, \ldots$ are the photon occupation numbers for the wave vectors $\vec{k}_1, \ldots, \vec{k}_j, \ldots$.

Let us now compute the transition probability at time $t$, in lowest order in time-dependent perturbation theory

$$w_{21}(t) = \langle \psi_1(t) | \hat{P}_2 | \psi_1(t) > = \sum_{n_2} \langle \psi_1(t) | \phi_2^A, n_2 > < n_2, \phi_2^A | \psi_1(t) >$$  \hspace{1cm} (6.41)

into the subspace $\mathcal{H}_2^A \otimes \mathcal{H}^{rad}$ where the atom is in the state $|\phi_2^A>$. We have

$$w_{21}(t) = \frac{2}{\hbar^2} |< n_2, \phi_2^A | H_1 | \psi_1(t) >|^2 \frac{1 - \cos \left( \frac{E_2 - E_1}{\hbar} t \right)}{(E_2 - E_1)^2 / \hbar^2}$$  \hspace{1cm} (6.42)

with

$$H_0 |\phi_i^A, n_i> = (\varepsilon_i + \sum_{\vec{k}, \lambda} n(\vec{k}, \lambda) \hbar \omega(\vec{k})) |\phi_i^A, n_i>$$  \hspace{1cm} (6.43)

It is clear from (2.40) that $H_1$ changes the photon number by $\pm 1$ corresponding to a photon emission/absorption by the atom. We will treat these two cases separately.

During an absorption of a $\vec{k}, \lambda$-photon we have

$$n_2(\vec{k}', \lambda') = n_1(\vec{k}', \lambda'), \hspace{1cm} (\vec{k}, \lambda) \neq (\vec{k}', \lambda')$$  \hspace{1cm} (6.44)

and

$$n_2(\vec{k}, \lambda) = n_1(\vec{k}, \lambda) - 1$$  \hspace{1cm} (6.45)
and hence
\[ \frac{1}{\hbar^2}(E_2 - E_1) = \frac{1}{\hbar}(\epsilon_2 - \epsilon_1) - \omega(\vec{k}, \lambda) =: \omega_{21} - \omega(\vec{k}, \lambda) \tag{6.46} \]

In $\mathcal{H}_{\text{rad}}$ eqn. (2.40) leads to the transition amplitude
\[ < n_2 | \hat{A}(\vec{q}) | n_1 > = \left( n_1(\vec{k}, \lambda) \frac{\hbar c^2 2\pi}{\omega(\vec{k}) L^3} \right)^{\frac{1}{2}} \hat{c}(\vec{k}, \lambda) e^{i\vec{k} \cdot \vec{q}_0} =: \sqrt{n_1(\vec{k}, \lambda)} \tilde{A}_{\vec{k}, \lambda} \tag{6.47} \]

In $\mathcal{H}^A$ we have with $\hat{D} = \sum_i e \vec{q}_i$ (see worksheet 9)
\[ < \phi_2^A | \sum_i e \frac{\vec{p}_i}{m_e} | \phi_1^A >= \frac{i}{\hbar} < \phi_2^A | [H^A_0, \hat{D}] | \phi_1^A >=: i\omega_{21} \hat{D}_{21} \tag{6.48} \]

Altogether we get for the probability to absorb a $(\vec{k}, \lambda)$-photon
\[ w_{21}^a((\vec{k}, \lambda), t) = \frac{2}{\hbar^2} \frac{n_1(\vec{k}, \lambda) \omega_{21}^2}{c^2} |\hat{D}_{21} \cdot \tilde{A}_{\vec{k}, \lambda}|^2 \frac{1 - \cos(E_2 - E_1) t}{(E_2 - E_1)^2 / \hbar^2} \tag{6.49} \]

and hence for the total absorption rate
\[ \frac{dw_{21}^a}{dt} = \sum_{\vec{k}, \lambda} \frac{dw_{21}^a((\vec{k}, \lambda), t)}{dt} = \frac{2\omega_{21}^2}{\hbar^2 c^2} \sum_{\vec{k}, \lambda} n_1(\vec{k}, \lambda) |\hat{D}_{21} \cdot \tilde{A}_{\vec{k}, \lambda}|^2 \frac{\sin((\omega_{21} - \omega(\vec{k})) t)}{\omega_{21} - \omega(\vec{k})} \tag{6.50} \]

We note in passing that one can obtain this last result for the "absorption" rate by treating the electro-magnetic field as a classical external field $\tilde{A}_{\vec{k}, \lambda}^{\text{class}}$ provided we set
\[ \tilde{A}_{\vec{k}, \lambda}^{\text{class}} := \tilde{A}_{\vec{k}, \lambda} \sqrt{n_1(\vec{k}, \lambda)} \tag{6.51} \]

If we consider an ensemble of atoms with $\vec{q}_0$ arbitrary in $V$ and arbitrary orientation of $\hat{D}_{21}$ we take the average
\[ |\hat{D}_{21} \cdot \tilde{A}_{\vec{k}, \lambda}|^2 \rightarrow \frac{1}{3} |\hat{D}_{21}|^2 |\tilde{A}_{\vec{k}, \lambda}|^2 \rightarrow \frac{1}{3} |\hat{D}_{21}|^2 \frac{1}{V} \int d^3q |\tilde{A}_{\vec{k}, \lambda}(\vec{q})|^2 = \frac{1}{3} |\hat{D}_{21}|^2 \frac{\hbar c^2 2\pi}{\omega(\vec{k}) V} \tag{6.52} \]
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With this the total absorption rate per atom becomes

$$\frac{dw_{a21}}{dt} = \frac{4\pi\omega_{21}^2}{3\hbar^2} |\vec{D}_{21}|^2 \frac{1}{V} \sum_{\vec{k},\lambda} n_1(\vec{k}, \lambda) \hbar \omega(\vec{k}) \frac{1}{\omega(\vec{k})^2} \frac{\sin((\omega_{21} - \omega(\vec{k})))t}{\omega_{21} - \omega(\vec{k})}$$

(6.53)

For large volume $V \to \infty$ we may assume a quasi continuous occupation number of photons and then

$$\frac{1}{V} \sum_{\vec{k},\lambda} n_1(\vec{k}, \lambda) \hbar \omega(\vec{k}) f(\omega(\vec{k})) \simeq \int_0^\infty d\omega \ u(\omega) f(\omega)$$

(6.54)

where $u(\omega)$ is the spectral energy density of the radiation field. Suppose now that $t >> \frac{2\pi}{\omega}$ for $\omega$ in the support of $u(\omega)$. Then we have

$$\int_0^\infty d\omega \ u(\omega) f(\omega) \frac{\sin((\omega_{21} - \omega)t)}{\omega_{21} - \omega} \simeq \begin{cases} \pi u(\omega) f(\omega_{21}) & \omega_{21} > 0 \\ 0 & \omega_{21} < 0 \end{cases}$$

(6.55)

Thus for $\epsilon_2 - \epsilon_1 = \hbar \omega_{21} > 0$ we find a constant transition rate for stimulated absorption

$$\frac{dw_{a21}}{dt} = \frac{4\pi^2}{3\hbar^2} u(\omega_{21}) |\vec{D}_{21}|^2$$

(6.56)

in agreement with Fermi’s golden rule with $\rho(E) = u(\omega)/\hbar \omega$ (why?). For $\epsilon_2 - \epsilon_1 = \hbar \omega_{21} < 0$ there is no absorption but instead we have emission of a $(\vec{k}, \lambda)$-photon, ie.

$$n_2(\vec{k}', \lambda') = n_1(\vec{k'}, \lambda'), \quad (\vec{k}, \lambda) \neq (\vec{k}', \lambda')$$

(6.57)

and

$$n_2(\vec{k}, \lambda) = n_1(\vec{k}, \lambda) + 1$$

(6.58)

Then using

$$< n_2 | \hat{A}(\vec{q}) | n_1 > = \sqrt{n_1(\vec{k}, \lambda) + 1} \hat{A}_{\vec{k},\lambda}^*$$

(6.59)
and
\[
\frac{1}{V} \sum_{k} f(\omega(k)) \simeq \int_{0}^{\infty} d\omega \frac{\omega^2}{\pi^2 c^3} f(\omega)
\]  

we and up with
\[
\frac{dw_{21}^{\sigma}}{dt} = \frac{4\pi^2}{3\hbar^2} \left[ u(\omega_{21}) + \frac{\hbar|\omega_{21}|^3}{\pi^2 c^3} \right] |\vec{D}_{21}|^2
\]

for the sum of stimulated and spontaneous emission. In particular, an excited atomic state can be relaxed even in the absence of a radiation field.

### Historical Notes

In a 1905 paper Einstein postulated that light itself consists of localized particles (quanta). Einsteins light quanta were nearly universally rejected by all physicists, including Max Planck and Niels Bohr. This idea only became universally accepted in 1919, with Robert Millikans detailed experiments on the photoelectric effect, and with the measurement of Compton scattering. Einsteins paper on the light particles was almost entirely motivated by thermodynamic considerations. He was not at all motivated by the detailed experiments on the photoelectric effect, which did not confirm his theory until fifteen years later. Einstein considers the entropy of light at temperature T, and decomposes it into a low-frequency part and a high-frequency part. The high-frequency part, where the light is described by Wiens law, has an entropy which looks exactly the same as the entropy of a gas of classical particles. Since the entropy is the logarithm of the number of possible states, Einstein concludes that the number of states of short wavelength light waves in a box with volume V is equal to the number of states of a group of localizable particles in the same box. Since (unlike others) he was comfortable with the statistical interpretation, he confidently postulates that the light itself is made up of localized particles, as this is the only reasonable interpretation of the entropy. This leads him to conclude that each wave of frequency f is associated with a collection of photons with energy hf each, where h is Plancks constant. He does not say much more, because he is not sure how the particles are related to the wave. But he does suggest that this idea would explain certain experimental results, notably the photoelectric effect.
Further Reading

For a more detailed treatment of time-independent perturbation theory see e.g. Messiah, Quantum mechanics I+II. Absorption and emission of photons by atoms can be found eg. in Sakurai, "Advanced Quantum Mechanics". Einstein’s original derivation of Plank’s radiation law can be found in C. Kittel “Elementary Statistical Physics” (1958).
Chapter 7

Scattering Theory

In many experiments, especially in particle physics, interactions between two initially widely separated systems are investigated. Generically the projectile and the target have a complicated structure and inelastic processes are common, including particle production. In other cases such as structure analysis via neutron scattering processes with repeated scattering are of relevance. Here we will consider the simple case of elastic scattering off a central potential spinless particles.

7.1 Central Potential

For potentials that vanish sufficiently fast \( V(r) \propto \frac{1}{r^{1+\epsilon}}, \epsilon > 0 \) one looks for stationary solutions with the asymptotic form

\[
\psi(k, q) \simeq e^{ik \cdot q} + f(k, \theta) \frac{e^{ikr}}{r}
\]  

(7.1)

The differential cross section is then given by (see QMI or my German notes)

\[
\frac{d\sigma}{d\Omega} = |f(k, \theta)|^2
\]  

(7.2)

In analogy to the free particle we should be able to write \( \psi(k, q) \) as a partial wave decomposition

\[
\psi(k, q) = \sum_{l=0}^{\infty} b_l f_l(r) P_l(\cos \theta)
\]  

(7.3)
where $P_l(x)$ are the Legendre polynomials and $f_l(r) = g_l(r)/r$ satisfies the radial equation

$$g''_l(r) + \left( k^2 - \frac{l(l + 1)}{r^2} - \frac{2mV(r)}{\hbar^2} \right) g_l(r) = 0 \quad (7.4)$$

A classical result by Weyl and Kodaira shows that for $V(r) \propto \frac{1}{r^{1+\epsilon}}$, $\epsilon > 0$ at large $r$ and $V(r) = O(r^{-2+\epsilon})$ for small $r$ the scattering solutions have the asymptotic behaviour

$$f_l(r) \simeq \sqrt{\frac{2}{\pi}} \frac{\sin(kr - \frac{\epsilon}{2} + \delta_l)}{r} \quad (7.5)$$

In particular, the plane wave $e^{i\vec{k} \cdot \vec{r}}$ has the following expansion (see eg. Sakurai, p.398)

$$e^{i\vec{k} \cdot \vec{q}} = \sum_{l=0}^{\infty} i^l (2l + 1) j_l(kr) P_l(\cos \theta) \quad (7.6)$$

and therefore

$$\psi(\vec{k}, \vec{q}) \simeq e^{i\vec{k} \cdot \vec{q}} + f(\theta) \frac{e^{ikr}}{r} \quad (7.7)$$

$$= \sum_{l=0}^{\infty} b_l \sqrt{\frac{2}{\pi}} \frac{1}{2ikr} \left( e^{i(kr - \frac{\epsilon}{2} + \delta_l)} - e^{-i(kr - \frac{\epsilon}{2} + \delta_l)} \right) P_l(\cos \theta)$$

implies

$$b_l \sqrt{\frac{2}{\pi}} e^{-i\delta_l} = \frac{i^l (2l + 1)}{k} \quad (7.8)$$

Upon substitution into (7.7) and using (7.6) we then find

$$f(k, \theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l + 1) e^{i\delta_l(k)} \sin(\delta_l(k)) P_l(\cos \theta) \quad (7.9)$$
7.2. SHORT RANGED POTENTIALS

so that \( f(k, \theta) \) and therefore the cross section is uniquely determined in terms of the scattering phases \( \delta_l(k) \). Furthermore due to the orthogonality condition

\[
\int_{-1}^{1} P_l(x) P_{l'}(x) = \frac{2\delta_{ll'}}{2l + 1}
\]

(7.10)

the total cross section satisfies the optical theorem

\[
\sigma_T = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l + 1) \sin^2 \delta_l(k) = \frac{4\pi}{k} \text{Im} f(k, 0)
\]

(7.11)

In words: The total cross section is the sum of the partial wave cross sections \( \sigma_l = \frac{4\pi}{k^2} (2l + 1) \sin^2 \delta_l(k) \) and the sum equals the imaginary part of the forward scattering amplitude just like in classical optics (e.g. J. Jackson, class. ED, page 453). For each \( l \) we have \( \sigma_l \leq \frac{4\pi}{k^2} (2l + 1) \) with maximum for resonances, \( \delta_l(k) = \left( n + \frac{1}{2} \right) \pi \). The partial wave expansion is useful if either most of the \( \delta_l(k) \) are negligible or if one partial wave dominates. The first case arises at low energies or short ranged potentials whereas the latter situation arises for example in pion-nucleon scattering at \( E \simeq 189 \text{ Mev} \) in the laboratory frame due to the \( N^* \) resonance.

7.2 Short ranged potentials

Suppose that \( V(r) = 0 \) for \( r > R \) and let \( f_l(k, r) \) be the regular solution of the radial equations (7.4). For \( r > R \) we then have

\[
f_l = f_l^> = \sqrt{\frac{2}{\pi}} \left( j_l(kr) \cos(\delta_l) - n_l(kr) \sin(\delta_l) \right)
\]

(7.12)

where \( j_l(x) \) and \( n_l(x) \equiv y_l(x) \) are the spherical Bessel functions of the first and second kind respectively (see eg. http://www.phys.ufl.edu/ lex/pdfs/sphericalbessel.pdf). If we let

\[
\chi_l(k) = \frac{d \log f_l^< (r)}{dr}
\]

(7.13)

then the matching condition

\[
\chi_l(k) = \frac{d \log f_l^> (r)}{dr}
\]

(7.14)
implies
\[ \tan(\delta_l(k)) = \frac{k j_l'(kR) - \chi_l(k) j_l(kR)}{kn_l'(kR) - \chi_l(k) n_l(kR)} \tag{7.15} \]
and thus the logarithmic derivative of \( f_l \) at \( r = R \) completely determines the scattering phases for all \( l \). Measuring the \( \delta'_l \) therefore provides little information about the wave function.

### 7.2.1 Threshold behaviour

For small energies or small range \( R \) we can expand \( j_l(x) \) and \( n_l(x) \) leading to
\[
\tan(\delta_l(k)) \approx \frac{kl(kR)^{l-1} - (kR)^l \chi_l}{(2l+1)!!(2l-1)!! \left[ \frac{k^{l+1}}{(kR)^{l+2}} + \frac{\chi_l}{(kR)^{l+1}} \right]} \\
= \frac{(kR)^{l+2}[l - R\chi_l]}{(2l+1)!!(2l-1)!![l + 1 + R\chi_l]} 
\tag{7.16}
\]
For \( l + 1 + R\chi_l(k) \neq 0 \) we have \( \sin(\delta_l) \propto k^{2l+1} \) for \( k \to 0 \) and the scattering amplitude \( f(k, \theta) \) is isotropic at \( k \approx 0 \).

### 7.2.2 Application: Hard sphere scattering

Suppose the potential is of the form
\[ V(r) = \begin{cases} \infty & r \leq R \\ 0 & r > R \end{cases} \tag{7.17} \]
and thus
\[ \tan(\delta_l(k)) = \frac{j_l(kR)}{n_l(kR)} \overset{t=0}{=} - \tan(kR) \tag{7.18} \]
In particular \( \delta_0 \approx -kR \). For more general short range potential \( \delta_0 \approx -ka_s \) still holds where \( a_s \) is the scattering length which can differ considerably from the range of the potential. For small \( kR \) where the total cross section is dominated by the s-wave we have with (7.11)
\[ \sigma_T \approx \frac{4\pi}{k^2} \sin^2 \delta_0(k) = 4\pi R^2 \tag{7.19} \]
which is four times the geometric cross section.
7.3 Born approximation for phase shifts

Let \( g_l(k, r) \) be the regular solution of (7.4) with \( g_l(k, 0) = 0 \) (why?) and asymptotic behaviour from (7.5). Furthermore let \( g^0_l(k, r) = \sqrt{\frac{2}{\pi}} kr j_l(kr) \) be the regular solution for \( V \equiv 0 \). Then we have

\[
\frac{2m}{\hbar^2} \int_0^\bar{R} V(r)g^0_l(r)g(r)dr = \int_0^\bar{R} (g^0_l(r)g''(r) - g(r)g''^0(r))dr
\]

\[
= \left[ g^0_l(\bar{R})g'(\bar{R}) - g(\bar{R})g''^0(\bar{R}) \right]
\]

\[
\overset{R \to \infty}{=} \frac{2k}{\pi} \sin(k\bar{R} - \frac{l\pi}{2})\cos(k\bar{R} - \frac{l\pi}{2} + \delta_l) - \frac{2k}{\pi} \cos(k\bar{R} - \frac{l\pi}{2})\sin(k\bar{R} - \frac{l\pi}{2} + \delta_l)
\]

\[
= -\frac{2k}{\pi} \sin(\delta_l(k)) \quad (7.20)
\]

This then leads the exact relation for \( \bar{R} \to \infty \),

\[
\sin(\delta_l(k)) = -\frac{\sqrt{2\pi m}}{\hbar^2} \int_0^\infty V(r)g_l(r, k)j_l(kr)dr 
\]

\[
(7.21)
\]

In analogy with the **Born approximation** for the scattering amplitude (see QMI or my German notes) we then obtain the first Born approximation for the phase shifts by writing \( g_l(r, k) = g^0_l(r, k) + O(V) \) and therefore

\[
\sin(\delta_l(k)) = \sin(\delta_l^{(1)}(k)) + O(V^2) \quad (7.22)
\]

with

\[
\sin(\delta_l^{(1)}(k)) = -\frac{\sqrt{2\pi m}}{\hbar^2 k} \int_0^\infty V(r)[kr j_l(kr)]^2 dr \quad (7.23)
\]

For large \( k \) and integrable potential (\( \int |V(r)|dr < \infty \) the boundedness of \( |\rho j_l(\rho)| \leq a_l \) for \( 0 \leq \rho \leq \infty \) the implies

\[
\sin(\delta_l^{(1)}(k)) = O(1/k), \quad k \to \infty \quad (7.24)
\]

and the successive Born approximations for the phase shifts converge for large \( k \) (Taylor, page 143).
For integrable potential with compact support we can be more precise about the $l$-dependence. For this we first recall that in classical mechanics there is no scattering for impact parameter $b > R$ on a potential with support in $[0, R]$. Furthermore, if $p$ is the momentum of the in-falling particle, then $bp$ is its angular momentum. If we then identify $b \approx \frac{h \sqrt{l(l+1)}}{b_0}$, this suggests that the phase shift are small for $\sqrt{l(l+1)} \geq kR$. Indeed the radial component $g_l^0(\rho)$, $\rho = kr$, of the free particle wave function changes qualitatively from a growing function to an oscillatory behaviour for $\rho \approx \sqrt{l(l+1)}$. For $kR << \sqrt{l(l+1)}$ the function $r_{jl}(kr)$ is small in the support of the potential $V(r)$ and therefore $\sin(\delta_l^{(1)}(k))$ should be small unless $g_l(kR)$ is large. This happens typically for resonances (see next subsection).

In order to emphasize the importance of integrability we consider again the hard sphere scattering but now at high energy. According to the above discussion we should have

$$\sigma_T \approx \frac{4\pi}{k^2} \sum_{l=0}^{(l=kR)} (2l + 1) \sin^2 \delta_l(k)$$

(7.25)

with

$$\sin^2 \delta_l(k) = \frac{\tan^2 \delta_l(k)}{1 + \tan^2 \delta_l(k)} = \frac{j_l(kR)^2}{j_l(kR)^2 + n_l(kR)^2} \approx \sin^2(kR - \frac{\pi l}{2}), \quad kR >> 1$$

(7.26)

In particular the scattering phase does not decay for large $k$. Noting that $\sin^2 \delta_{l+1}(k) = \cos^2 \delta_l(k)$ we can approximate $\sin^2 \delta_l(k) \approx \frac{1}{2}$. Then

$$\sigma_T \approx \frac{2\pi}{k^2} \sum_{l=0}^{(l=kR)} (2l + 1) \approx 2\pi R^2$$

(7.27)

which is twice the geometric cross section.
7.4 Resonances

In the absence of resonance we have seen that partial wave cross sections \( \sigma_l \) show the simple \textit{threshold behaviour}

\[
\sigma_l = \frac{4\pi}{k^2} (2l + 1) \sin^2(\delta_l) \propto k^{2l}
\] (7.28)

On the other hand for \( E \approx E_r \) with \( l + 1 + R\chi_l(E_r) = 0 \) we have to be more careful and expand

\[
l + 1 + R\chi_l(E) \approx (E - E_r)\chi'_l(E_r)
\]
\[
l - R\chi_l(E) \approx 2l + 1
\] (7.29)

We then have for \( E \approx E_r \),

\[
\cot(\delta_l) \approx -\frac{2(E - E_r)}{\Gamma_r}
\] (7.30)
\[
\Gamma_r = -\frac{2k^{2l+1}R^{2l}}{((2l + 1)!!)^2\chi'_l(E_r)}
\]

If we then write

\[
\sin^2(\delta_l) = \frac{1}{1 + \cot^2(\delta_l)}
\] (7.31)

obtain for the resonant partial wave cross section the \textbf{Breit-Wigner Formula}

\[
\sigma_l = \frac{4\pi}{k^2} (2l + 1) \frac{\Gamma_r^2}{4(E - E_r)^2 + \Gamma_r^2}
\] (7.32)

For \( E = E_r \) the partial wave cross sections \( \sigma_l \) then saturates the \textbf{unitarity limit} \( \frac{4\pi}{k^2} (2l + 1) \). The \textbf{with at half maximum}, \( \Gamma_r \) decreases with growing angular momentum \( l \). This can be interpreted as a suppression of the tunneling probability through the increasing potential barrier.

To better understand the resonant behaviour of \( \delta_l \) we first show that \( \Gamma_r \) is always positive. In deed let \( g_l(r) := g_l(k_i, r) \). The we have

\[
\frac{(k_1^2 - k_2^2)}{g_1(R)g_2(R)} \int_0^R g_1(r)g_2(r)dr = \frac{g'_2(R)}{g_2(R)} - \frac{g'_1(R)}{g_1(R)}
\]
\[
= \chi_l(E_2) - \chi_l(E_1)
\] (7.33)
and thus

\[
\chi_i'(E) = \lim_{E_2 \neq E_1 \to E} \frac{\chi_i(E_2) - \chi_i(E_1)}{E_2 - E_1}
\]

\[
= -\frac{2m}{\hbar^2 g_i^2(k, R)} \int_0^R g_i(k, r)^2 \, dr < 0
\]

(7.34)

for \( R > 0 \) and thus \( \Gamma_r \geq 0 \). Now using that \( \cot(\delta_l - \frac{\pi}{2}) = -\tan(\delta_l) \) we get

\[
\delta_l = \frac{\pi}{2} + \arctan\left(\frac{E - E_r}{\Gamma_r/2}\right) \quad \text{mod } n\pi
\]

(7.35)

and

\[
\left. \frac{d\delta_l}{dE} \right|_{E=E_r} = \frac{2}{\Gamma_r}
\]

(7.36)

**Historical Notes**

**Further Reading**

The partial wave expansion described in this section can be found in Sakurai’s *Modern Quantum Mechanics*, section 7.6. An in depth discussion of scattering theory in quantum mechanics can be found in J. Taylor, *scattering theory*. Resonant behaviour in low energy scattering in nuclear physics can be found e.g. in Blatt and Weisskopf, *theoretische Kernphysik.*