Quantum Mechanics II

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1 Time-independent perturbation theory

1.1 Solving a Quantum Mechanical System

We have a standard QM system: given H, $|\psi(t_0)\rangle$, we want to find $|\psi(t)\rangle = U(t,t_0)\,|\psi(t_0)\rangle$, we then get the time-evolution operator for H time independent

$$U(t,t_0) = \exp\left(-\frac{i}{\hbar}H\cdot(t-t_0)\right)$$

We have $H = H^\dagger$, $UU^\dagger = \mathbb{I}$. H is self-adjoint, U is unitary.
"solution": find all eigenvalues and eigenvectors $|n\rangle$ of H, such that $H\,|n\rangle = E_n\,|n\rangle$. We have furthermore

$$H = \sum_n E_n\,|n\rangle\langle n| \text{ and } U(t,t_0) = \sum_n e^{-\frac{i}{\hbar}E_n(t-t_0)}\,|n\rangle\langle n|$$

These are the spectral representations. We have the problem that only a small number of systems can be solved exactly (e.g. Coulomb potential, harmonic oscillator, infinite well,...). We therefore want to find approximate solutions. We can use perturbation theory and the variational method for that.

1.2 Non-degenerate case

We assume that H can be written as

$$H = \underbrace{H_0}_{\substack{\text{"free" Hamiltonian}}} + \underbrace{\lambda V}_{\text{perturbation}}$$

The "free" Hamiltonian can be solved exactly. We know all the $\left|n^{(0)}\right\rangle$, $E_n^{(0)}$ with $H_0\left|n^{(0)}\right\rangle = E_n^{(0)}\left|n^{(0)}\right\rangle$ and $\left\langle m^{(0)}\middle|n^{(0)}\right\rangle = \delta_{mn}$
The perturbation is comparably "small", for $\lambda \to 0$ we get the free Hamiltonian, for $\lambda \to 1$ we get the full Hamiltonian.
In section 1.2 we assume no degeneracy, i.e. $E_n^{(0)} \neq E_m^{(0)} \quad \forall m \neq n$.
We want $|n\rangle$, E_n, such that $H\,|n\rangle = E_n\,|n\rangle$
Let

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... + \mathcal{O}(\lambda^3)$$
$$|n\rangle = \left|n^{(0)}\right\rangle + \lambda\left|n^{(1)}\right\rangle + \lambda^2\left|n^{(2)}\right\rangle + ... + \mathcal{O}(\lambda^3)$$

When doing perturbation theory, we always have to check in posteriori wether we get reasonable results. If the perturbation terms are bigger than the initial result, we might have to throw them away! Always take care to check well!

We then have to plug this expansion into the Schrödinger equation:

$$(H_0 - E_n^{(0)})\left|n^{(0)}\right\rangle + \lambda((H_0 - E_n^{(0)})\left|n^{(1)}\right\rangle + (V - E_n^{(1)})\left|n^{(0)}\right\rangle)$$
$$+\lambda^2\left((H_0 - E_n^{(0)})\left|n^{(2)}\right\rangle + (V - E_n^{(1)})\left|n^{(1)}\right\rangle - E_n^2\left|n^{(0)}\right\rangle\right)$$
$$+\lambda^3\left((H_0 - E_n^{(0)})\left|n^{(3)}\right\rangle + (V - E_n^{(1)})\left|n^{(2)}\right\rangle - E_n^{(2)}\left|n^{(1)}\right\rangle - E_n^{(3)}\left|n^{(0)}\right\rangle\right)$$
$$+\mathcal{O}(\lambda^4) = 0$$

We now look at the case of non-degenerate perturbation theory:
Let's first calculate the terms of order λ:

$$\left\langle m^{(0)}\middle|H_0 - E_n^{(0)}\middle|n^{(1)}\right\rangle + \left\langle m^{(0)}\middle|V - E_n^{(1)}\middle|n^{(0)}\right\rangle = 0$$
$$= \left\langle m^{(0)}\middle|\left(E_m^{(0)} - E_n^{(0)}\right)\middle|n^{(1)}\right\rangle + \left\langle m^{(0)}\middle|V\middle|n^{(0)}\right\rangle - E_n^{(1)}\underbrace{\left\langle m^{(0)}\middle|n^{(0)}\right\rangle}_{\delta_{mn}} = 0$$

We now have two cases:

- $m = n$:

$$\implies E_n^{(1)} = \left\langle n^{(0)}\middle|V\middle|n^{(0)}\right\rangle = \langle V\rangle_{n^{(0)}} \qquad \boxed{\text{Eq1.2}}$$
$$\left|n^{(1)}\right\rangle = \underbrace{\sum_m \left|m^{(0)}\right\rangle\left\langle m^{(0)}\right|}_{\mathbb{I}} n^{(1)}\rangle = \sum_{m\neq n}\left|m^{(0)}\right\rangle\left\langle m^{(0)}\middle|n^{(1)}\right\rangle + \underbrace{\left|n^{(0)}\right\rangle\left\langle n^{(0)}\middle|n^{(1)}\right\rangle}_{=0 \text{ see below}}$$
$$= \sum_{m\neq n}\left|m^{(0)}\right\rangle\frac{\left\langle m^{(0)}\middle|V\middle|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}$$

- $m \neq n$:

$$1 = \langle n|n\rangle = \underbrace{\left\langle n^{(0)}\middle|n^{(0)}\right\rangle}_{1} + \lambda\underbrace{\left(\left\langle n^{(0)}\middle|n^{(1)}\right\rangle + \left\langle n^{(1)}\middle|n^{(0)}\right\rangle\right)}_{=0} \implies \left\langle n^{(0)}\middle|n^{(1)}\right\rangle = 0$$
$$\left|n^{(1)}\right\rangle = \sum_{m\neq n}\left|m^{(0)}\right\rangle\frac{\left\langle m^{(0)}\middle|V\middle|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} \qquad \boxed{\text{Eq1.3}}$$

  - $E_n^{(0)} = E_m^{(0)}$: degenerate case
  - $E_n^{(0)} \sim E_m^{(0)}$: quasi-degenerate case

Now to the terms of order λ^2:
We now multiply with $\left\langle k^{(0)}\right|$:

$$\boxed{\text{Eq1.4}} \qquad \left(E_k^{(0)} - E_n^{(0)}\right)\left\langle k^{(0)}\middle|n^{(2)}\right\rangle + \left\langle k^{(0)}\middle|V\middle|n^{(1)}\right\rangle - E_n^{(1)}\underbrace{\left\langle k^{(0)}\middle|n^{(1)}\right\rangle}_{\to 0} = E_n^{(2)}\underbrace{\delta_{kn}}_{\to 1}$$
$$E_n^{(2)} = \left\langle n^{(0)}\middle|V\middle|n^{(1)}\right\rangle = \sum_{m\neq n}\frac{\left\langle n^{(0)}\middle|V\middle|m^{(0)}\right\rangle\left\langle m^{(0)}\middle|V\middle|n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}$$
$$= \sum_{m\neq n}\frac{\left|\left\langle n^{(0)}\middle|V\middle|m^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} \equiv \sum_{m\neq n}\frac{|V_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

for the ground state ($n=0$), the 2^{nd} order correction will always be negative $E_n^{(2)} < 0$

$$\left|n^{(2)}\right\rangle = \sum_{k\neq n} \left|k^{(0)}\right\rangle \left\langle k^{(0)}\middle|n^{(2)}\right\rangle + \left|n^{(0)}\right\rangle \left\langle n^{(0)}\middle|n^{(2)}\right\rangle$$

The normalization of the wave function is then:

$$\left\langle n^{(0)}\middle|n^{(2)}\right\rangle = -\frac{1}{2}\left\langle n^{(1)}\middle|n^{(1)}\right\rangle = -\frac{1}{2}\sum_{k\neq n}\frac{|V_{kn}|^2}{\left(E_n^{(0)}-E_k^{(0)}\right)^2}$$

$$\left\langle k^{(0)}\middle|n^{(2)}\right\rangle = \left(\frac{\left\langle k^{(0)}\middle|V\middle|n^{(1)}\right\rangle}{E_n^{(0)}-E_k^{(0)}} - \frac{E_n^{(1)}\left\langle k^{(0)}\middle|n^{(1)}\right\rangle}{E_n^{(0)}-E_k^{(0)}}\right)$$

$$\left|n^{(2)}\right\rangle = \sum_{k\neq n}\sum_{m\neq n}\left|n^{(0)}\right\rangle \frac{V_{kn}V_{mn}}{\left(E_n^{(0)}-E_k^{(0)}\right)\left(E_n^{(0)}-E_m^{(0)}\right)}$$

$$-\sum_{k\neq n}\left(\left|k^{(0)}\right\rangle \frac{V_{mn}V_{kn}}{\left(E_n^{(0)}-E_k^{(0)}\right)^2} + \frac{1}{2}\left|n^{(0)}\right\rangle \frac{|V_{kn}|^2}{\left(E_n^{(0)}-E_k^{(0)}\right)^2}\right) \qquad \boxed{\text{Eq1.5}}$$

Step j: Look at $(O)(\lambda^j)$ of Eq1.1:

- get E_n^j
- get $\left|n^{(j)}\right\rangle$

1.3 Degenerate perturbation theory

In this case, the energy level $E_n^{(0)}$ of H_0 is α-fold degenerate:

$$H_0\left|n_i^{(0)}\right\rangle = E_n\left|n_i^0\right\rangle \qquad\qquad i=1,...,\alpha$$

where $\left|n_i^{(0)}\right\rangle$ is an orthonormal basis of eigenvectors of H_0 with eigenvalue E_n and $\left\langle n_i^{(0)}\middle|n_j^{(0)}\right\rangle \sim \delta_{ij}$.
any linear combination

$$\left|\chi_n^{(0)}\right\rangle = \sum_{i=1}^{\alpha} c_{n_{k,i}}\left|n_i^{(0)}\right\rangle$$

is an eigenstate of H_0 with eigenvalue $E_n^{(0)}$.
Typically, the perturbation V lifts the degeneracy (partially or completely) since usually $[H_0, V] \neq 0$.
Take E_{n_k} and $|n_k\rangle$ with $H|n_k\rangle = E_{n_k}|n_k\rangle$. For $\lambda \to 0$, $E_{n_k} \to E_n^{(0)}$ and $|n_k\rangle \to \left|\chi_{n_k}^{(0)}\right\rangle = \sum_{i=1}^{\alpha} c_{n_k,i}\left|n_i^{(0)}\right\rangle$.
We then ask ourselves, which linear combination is the "good" one? We therefore have to find the coefficients $c_{n_k,i} \forall n_k, k=1,...,\alpha$.

$$|n_k\rangle = \left|\chi_{n_k}^{(0)}\right\rangle + \lambda\left|n_k^{(1)}\right\rangle + \lambda^2\left|n_k^{(2)}\right\rangle + \mathcal{O}(\lambda^3)$$

$$E_{n_k} = E_n^{(0)} + \lambda E_{n_k}^{(1)} + \lambda^2 E_{n_k}^{(2)} + \mathcal{O}(\lambda^3)$$

- $$\left(H_0 - E_n^{(0)}\right)\left|n_k^{(1)}\right\rangle + \left(V - E_{n_k}^{(1)}\right)\left|\chi_{n_k}^{(0)}\right\rangle = 0$$

- multiply with $\left\langle m_j^{(0)}\right|$:

$$0 = \left(E_m^{(0)} - E_n^{(0)}\right)\left\langle m_j^{(0)}\middle|n_k^{(1)}\right\rangle + \sum_{i=1}^{\alpha} c_{n_k,i}\left(\left\langle m_j^{(0)}\middle|V\middle|n_i^{(0)}\right\rangle - E_{n_k}^1\left\langle m_j^{(0)}\middle|n_i^{(0)}\right\rangle\right)$$

- $n = m$ then one needs to solve:

$$0 = \sum_{i=1}^{\alpha} c_{n_k,i}\left(\left\langle n_j^{(0)}\middle|V\middle|n_i^{(0)}\right\rangle - E_{n_k}^{(1)}\delta_{ij}\right) = \sum_{i=1}^{\alpha} c_{n_k,i}\left(V_{ji} - E_{n_k}^{(1)}\delta_{ij}\right) \sim A\vec{x} = 0$$

- only non-trivial solution when

$$\text{Det}\begin{pmatrix} V_{11} - E_{n_k}^{(1)} & V_{12} & \dots & V_{1\alpha} \\ V_{21} & & & \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ V_{\alpha 1} & & & V_{\alpha\alpha} - E_{n_k}^{(1)} \end{pmatrix} = 0$$

  This is an equation of order α in the energies $E_{n_k}^{(1)}$, so we will get α solutions.

- if all the solutions are different: degeneracy completely lifted
- if some of the solutions are the same: we still have partial (complete) degeneracy.

Once all the $E_{n_k}^{(1)}$ are known, we can find the $c_{n_k,i}$ (using linear algebra).
if $V_{ij} = 0$ if $i \neq j$:
solutions $E_{n_i}^{(1)} = \left\langle n_i^{(0)}\middle|V\middle|n_i^{(0)}\right\rangle$ (as in non-degenerate case)
$\rightarrow$ try to find $\chi_{n_k}^{(0)}$ such that $\left\langle \chi_{n_i}^{(0)}\middle|V\middle|\chi_{n_j}^{(0)}\right\rangle = 0$ for $i \neq j$.
if there is an operator A with $[A, V] = 0$ and eigenvectors/eigenvalues

$$A\left|\psi_{n_k}\right\rangle = a_{n_k}\left|\psi_{n_k}\right\rangle \text{ with } a_{n_k} \neq a_{n_i} \text{ for } i \neq k$$

then $\left|\chi_{n_k}^{(0)}\right\rangle = \left|\psi_{n_k}\right\rangle$ does the job.
Proof:

$$\left\langle\psi_{n_i}\middle|[A,V]\middle|\psi_{n_j}\right\rangle = 0 = \underbrace{\left(a_{n_i} - a_{n_j}\right)}_{\neq 0}\underbrace{\left\langle\psi_{n_i}\middle|V\middle|\psi_{n_j}\right\rangle}_{\Longrightarrow\ =0}$$

1.4 The Variational Method

Given a time-independent Hamiltonian H with a set of eigenvalues E_n and eigenvectors $|\psi_n\rangle$

$$H\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle$$

the for any arbitrary $|\psi\rangle$ in the Hilbert space,

$$\langle H\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

Proof of Ritz theorem
We expand $|\psi\rangle$ in eigenstates of H:

$$\left|\psi\right\rangle = \sum_n c_n\left|\psi_n\right\rangle$$

$$\langle\psi|\psi\rangle = \sum_{m,n} c_n^* c_m \underbrace{\langle\psi_n|\psi_m\rangle}_{\delta_{mn}} = \sum_n c_n^* c_n = \sum_n |c_n|^2$$

$$\langle\psi|H|\psi\rangle = \sum_{m,n} c_n^* c_m \underbrace{\langle\psi_n|H|\psi_m\rangle}_{E_m\langle\psi_n|\psi_m\rangle = E_m\delta_{mn}} = \sum_n |c_n|^2 E_m$$

$$\implies \langle H\rangle = \frac{\sum_n E_n |c_n|^2}{\sum_n |c_n|^2}$$

- Since $|c_n|^2 \geq 0$ and $E_n \geq E_0 \implies$

$$\langle H\rangle \geq E_0 \frac{\sum_n |c_n|^2}{\sum_n |c_n|^2} = E_0$$

- E_0 is a lower bound on $\langle H\rangle$
- approximate E_0 by minimizing of $\langle H\rangle$ with respect to any parameter $|\psi\rangle$ might depend on.

2 Hydrogen Atom

2.1 Coulomb potential (QMI)

General 2-body-problem $(m_1, \vec{r}_1)$, $(m_2, \vec{r}_2) \to V(\vec{r}_1 - \vec{r}_2)$ (with no external interactions).
We then write down the Hamiltonian:

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r}_1 - \vec{r}_2)$$

∇_1 acts on $\vec{r}_1$, ∇_2 acts on $\vec{r}_2$. We have a wave function $\Psi(\vec{r}_1, \vec{r}_2)$($\otimes$ spin degrees of freedom) as in classical mechanics, separate centre-of-mass variables. We introduce

$$\vec{r}_1, \vec{r}_2 \to \vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \text{ and } \vec{r} = \vec{r}_1 - \vec{r}_2$$

We then rewrite the Hamiltonian:

$$H = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + V(\vec{r}) \text{ with } M = m_1 + m_2 \text{ and } m = \frac{m_1 m_2}{m_1 + m_2}$$

We then want to find the eigenstates:

$$H|\Psi(\vec{R}, \vec{r})\rangle = E_{\text{tot}}|\Psi(\vec{R}, \vec{r})\rangle$$

we separate the variables: $\Psi(\vec{R}, \vec{r}) = \phi(\vec{R})\psi(\vec{r})$ in order to get two separate differential equations:

$$-\frac{\hbar^2}{2M}\nabla_R^2\phi(\vec{R}) = E_R\phi(\vec{R}) \qquad \text{free particle (“boring”)}$$

We are looking for bound states.

$$-\frac{\hbar^2}{2m}\nabla_r^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E_r\psi(\vec{r}) \qquad \text{particle in potential } V(\vec{r})$$

Only the relative motion is interesting. The nice thing about the Coulomb potential is that $V(\vec{r}) = V(r)$, the potential only depends on the absolute value of $\vec{r}$. In the hydrogen atom we have:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\psi(\vec{r}) = E\psi(\vec{r})$$

We have $V(r) = -\frac{Ze^2}{r}$ in Gauss units. From QMI we know we can write

$$\psi(\vec{r}) = R_{El}(r)Y_l^m(\theta,\varphi) = \frac{u_{El}(r)}{r}Y_l^m(\theta,\varphi)$$

We then get by applying the differential equation:

$$u''_{El} - \left(\frac{l(l+1)}{r^2} + \frac{2m(V(r)-E)}{\hbar^2}\right)u_{El} = 0$$

We then get the possible eigenvalues for bound states:

$$E_n = -\left(\frac{Ze^2}{\hbar^2}\right)^2 \frac{m}{2n^2} = -\frac{(Ze)^2}{2n^2}\frac{1}{a} = -\frac{(Z\alpha)^2}{2n^2}mc^2 \text{ with } \alpha = \frac{e^2}{\hbar c} \sim \frac{1}{137} \text{ and } a = \frac{\hbar^2}{me^2}$$

We know that this system is very degenerate. The degeneracy for one particular value of n is:

$$l : 0, 1, ..., n-1$$

$$m_l : -l, -l+1, ..., 0, ..., l-1, l$$

For a fixed n we get:

$$\underbrace{2}_{\text{spin}} \sum_{l=0}^{n-1}(2l+1) = 2n^2$$

The wave functions are:

$$\Psi_{nlm_l} = |n,l,m\rangle \sim (\text{ Laguerre polynomial }) \cdot Y_l^{m_l}$$

Now we include further effects:

- relativistic effects
- spin of electron
- spin of proton
- (QFT effects)

These effects will partially lift the n^2 degeneracy.
Warning: in this section we will cheat in the derivation of the Hamiltonian → do properly at end of the course (hopefully)

2.2 Relativistic corrections

We use the non-relativistic Schrödinger equation.
Is this justified? Look at expectation value of velocity:

$$\langle v\rangle = \langle n,l,m|\,\frac{p}{m}\,|n,l,m\rangle = ... = \frac{Z\alpha}{n^2}$$

This shows that the non-relativistic approach is ok. $(Z\alpha) \ll 1 \implies$ non-relativistic system.
The kinetic energy is

$$T = \frac{p^2}{2m} \to \sqrt{p^2c^2 + m^2c^4} - mc^2 = \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{small}\to\text{use perturbation theory}} + \underbrace{...}_{\text{neglected}} \text{ relativistic energy}$$

We are interested in the shift of the energy levels due to the perturbation. This can be calculated as follows:

$$\Delta E_{\text{rel}} = -\langle n,l,m_l| \frac{p^4}{8m^3c^2} |n,l,m_l\rangle = -\frac{1}{2mc^2} \langle n,l,m_l| \underbrace{\left(\frac{p^2}{2m}\right)^2}_{\left(H_0+\frac{Ze^2}{r}\right)^2} |n,l,m_l\rangle$$

$$= \frac{1}{2mc^2} \left\langle n,l,m_l \middle| \left(H_0 + \frac{Ze^2}{r}\right)\left(H_0 + \frac{Ze^2}{r}\right) \middle| n,l,m_l \right\rangle$$

$$= -\frac{1}{2mc^2}\left((E_n^{(0)})^2 + 2E_n^{(0)} Ze^2 \left\langle \frac{1}{r} \right\rangle_{nlm} + (Ze^2)^2 \left\langle \frac{1}{r^2} \right\rangle_{nlm}\right)$$

or all $\left\langle \frac{1}{r^n} \right\rangle$ in the exercises
Results for this are:

$$\left\langle \frac{1}{r} \right\rangle_{nlm_l} = \frac{Z}{an^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{nlm_l} = \frac{Z^2}{a^2n^3\left(l+\frac{1}{2}\right)}$$

$$\left\langle \frac{1}{r^3} \right\rangle_{nlm_l} = \frac{Z^3}{a^3n^2l\left(l+\frac{1}{2}\right)(l+1)} \text{ with } l \neq 0$$

This can then be used to calculate ΔE_{rel}:

$$\Delta E_{\text{rel}} = -E_n^{(0)} \underbrace{Z^2\alpha^2}_{\text{small} \to :)} \frac{1}{n^2}\left(\frac{3}{4} - \underbrace{\frac{n}{l+\frac{1}{2}}}_{\text{dependence on } l}\right)$$

This whole thing we are calculating here is part of the fine structure. So they are proportional to the fine structure constant.

2.3 Spin-Orbit term

Now: naive and rough "derivation" of the perturbation term in the Hamiltonian. Argumentation: in the rest frame of the electron, the moving proton induces a magnetic field. This field acts on the spin of the electron.

- e^- with spin $\to$ magnetic moment : $\vec{\mu} = \frac{e}{2m} g\vec{s}$ with $g \approx 2$ (from Dirac equation, or better, from QED)
- The magnetic field is roughly

$$\vec{B} \sim -\frac{1}{c^2}\vec{v} \wedge \underbrace{\vec{E}}_{e\frac{\vec{r}}{r^3}} \sim -\frac{1}{mc^2r^3}\vec{p} \wedge \vec{r} \sim -\frac{\vec{L}}{mc^2r^3}$$

The correct result for the Hamiltonian is then

$$H_{SO} = \frac{Ze^2}{2m^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S} \qquad \left(\sim -\vec{\mu}\cdot\vec{B}\right)$$

To describe the spin of the electron

$$|n,l,m_l,(s),m_s\rangle = \Psi_{nlm_lm_s} = \underbrace{\Psi_{nlm_l}(r,\theta,\varphi)}_{L^2[\mathbb{R}^2]} \otimes \underbrace{\chi_{s=\frac{1}{2},m_s}}_{\mathbb{C}^2}$$

1^{st} order perturbation theory:

$$\Delta E_{SO} = \langle n, l, m_l, m_s | \, H_{SO} \, | n, l', m_l', m_s \rangle$$

$$\Delta E_{SO} = 0 \text{ for } l' \neq l, \text{ because } \left[\vec{L}^2, H_{SO}\right] \sim \left[\vec{L}^2, \vec{L} \cdot \vec{S}\right] = 0$$

for fixed n, l: $2 \cdot (2l+1)$-dimensional subspace of Hilbert Space n, l, m_l and m_s are not ideal quantum numbers, we change quantum numbers because of this. We take instead j, m_j

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

$j : l \pm \frac{1}{2}, \qquad m_j : -j, -j+1, ..., j, \ \left(j = \frac{1}{2} \text{ for } l = 0\right)$
from

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

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

"good" eigenstates in which $\vec{L} \cdot \vec{S}$ is diagonal:

$$|n, l, (s), j, m_j\rangle = \sum \underbrace{\langle l, s, m_l, m_s | \, j, m_j \rangle}_{\text{Clebsh-Gordan coefficients}} \cdot |n, l, m_l, (s), m_s\rangle$$

We can then again use perturbation theory: evaluate:

$$\Delta E_{SO} = \langle n, l, j, m_j | \, \frac{\vec{L} \cdot \vec{S}}{r^3} \, | n, l, j, m_j \rangle \, \frac{Ze^2}{2m^3c^2} = \left\langle \frac{1}{r^3} \right\rangle \frac{Ze^2}{2m^3c^2} \frac{1}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right)$$

$$H_{rel} : \qquad\qquad : \langle n, l, m_l, ... | \, H_{Rel} \, | n, l', m', ... \rangle$$

In principle it is degenerate perturbaton theory but already diagonal.

$$H_{SO} : \qquad\qquad : \langle n, l, m_l, ... | \, H_{SO} \, | n, l, m_l', ... \rangle$$

use "good" basis $\rightarrow$ diagonalize

$$\rightarrow \Delta E_{SO} = \frac{Ze^2}{2mc^2} \left\langle n, l, j, m_j \left| \frac{1}{r^3} \frac{1}{2} \left(\underbrace{\vec{J}^2 - \vec{L}^2 - \vec{S}^2}_{\vec{J} = \vec{L} + \vec{S} = \vec{L} \otimes \mathbb{I} + \mathbb{I} \otimes \vec{S}} \right) \right| n, l, j, m_j \right\rangle$$

$$= \frac{Ze^2\hbar^2}{4mc^2} \left\langle \frac{1}{r^3} \right\rangle_{nl} \left(j(j+1) - l(l+1) - \frac{3}{4}\right)$$

This then gives us the following result:

$$\Delta E_{SO} = \begin{cases} 0, & l = 0 \\ E_n^{(0)} \frac{(Z\alpha)^2}{2n\left(l+\frac{1}{2}\right)} \cdot \frac{1}{l+1}, & j = l + \frac{1}{2} \\ E_n^{(0)} \frac{(Z\alpha)^2}{2n\left(l+\frac{1}{2}\right)} \cdot \frac{-1}{l}, & j = l - \frac{1}{2} \end{cases}$$

2.4 Darwin term

The position of the electron fluctuates in the order of magnitude of the Compton wavelength $\lambda_C \sim \frac{\hbar}{mc}$. The electron feels the average potential $\langle V(r + \delta r)\rangle = \langle V(r)\rangle + \frac{1}{2}\langle (\delta r)(\nabla \delta r)\nabla V(r)\rangle = \langle V(r)\rangle + \frac{1}{2}\left\langle (\delta \vec{r})^2 \Delta V(r)\right\rangle \sim \langle V(r)\rangle + \frac{1}{2}\left\langle \frac{\hbar^2}{m^2c^2}\left(4\pi\delta(r)\right) Ze^2 \right\rangle$

$$\Longrightarrow \boxed{H_D = \frac{\pi\hbar^2 Ze^2}{2m^2c^2}\delta(r)}$$

This term picks the wave function at the origin. It is therefore only relevant for $l = 0$, otherwise it is zero, because for $l \geq 1$, the probability amplitude at the origin is zero.

$$\Delta E_D = \langle n, l, j, m_j | H_D | n, l, j, m_j \rangle = \frac{\pi \hbar^2 Z e^2}{2m^2 c^2} |\Psi_{nl}(0)|^2 = -E_n^{(0)} \frac{(Z\alpha)^2}{n} \delta_{l0}$$

2.5 Fine structure of hydrogen

We now want to combine all the terms we have calculated:

$$\Delta E^{(1)} = \Delta E_{rel} + \Delta E_{SO} + \Delta E_D$$

$$\rightarrow \Delta E_{nj}^{(1)} = -E_n^{(0)} \frac{(Z\alpha)^2}{n^2} \left(\frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right)$$

This formula is valid for $l = 0$, $j = l \pm \frac{1}{2}$, $\forall l$. So the degeneracy is partially lifted.

Spectrum: notation for states: ${}_nL_J$ with $n = 1, ...,\ l = 0, 1, .., n-1,\ L = S, P, D, ...,\ J$: total angular momentum

Symbol (degeneracy)

	l=0	l=1	l=2	number of states $= 2 \times n^2$
n=1	${}_1S_{1/2}$ (2)	×	×	$2 = 2 \times 1^2$
n=2	${}_2S_{1/2}$ (2)	${}_2P_{3/2}$ (4), ${}_2P_{1/2}$ (2)	×	$8 = 2 \times 2^2$
n=3	${}_3S_{1/2}$ (2)	${}_3P_{3/2}$ (4), ${}_3P_{1/2}$ (2)	${}_3D_{5/2}$ (6), ${}_3D_{3/2}$ (4)	$18 = 2 \times 3^2$

$({}_2S_{1/2}) \leftrightarrow ({}_2P_{1/2})$ is, if we look precisely at the experiment, still degenerate after taking in to account the fine structure. This is because of smaller effects that lift this degeneracy:

- hyperfine structure (spin-spin)
- QFT effects

Now we stop QM1 and start QM2.

3 Many electron atoms

We now consider an atom with N electrons.

$$H\Psi(\underbrace{1}_{\vec{r}_1, \vec{s}_1, \text{other quantum numbers}}, 2, ..., N) = E\Psi(1, 2, ..., N)$$

We can now easily write down the Hamiltonian:

$$H = \underbrace{\sum_{i=1}^{N} \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right)}_{\text{easy}} + \underbrace{\sum_{i>j} \frac{e^2}{|r_i - r_j|}}_{\text{killer}}$$

This is a complicated problem which cannot be solved exactly even for $N = 2$. We therefore have to use approximations.

3.1 Identical particles

Consider N identical particles $H(1,2,...,N)$, $\Psi(1,2,...,N)$ In Classical Mechanics you can always distinguish the N particles.
In Quantum Mechanics you cannot keep track of individual particles, because the wave function might overlap.
We now define the permutation operator P_{ij} that interchanges the two particles i and j.

$$P_{ij}\Psi(1,...,i,...,j,...,N) = \Psi(1,...,j,...,i,...,N) \qquad P_{ij}^2 = \mathbb{I}$$

P_{ij} has the eigenvalues ± 1.
H must be invariant under P_{ij}: $[H, P_{ij}] = 0$.
There are $N!$ permutations of the arguments of $\Psi(1,2,...,N)$. The permutations fall into two classes: even and odd. The signum of P is $(-1)^{\text{number of interchanges needed}}$.

$$\begin{cases} \text{sgn}(P) = +1 = (-1)^P, & P \text{ even (number of interchanges)} P_{ij} \\ \text{sgn}(P) = -1 = (-1)^P, & P \text{ odd (number of interchanges)} P_{ij} \end{cases}$$

We know certain things about P:

- we have $[P, H] = 0$
- P is unitary: $\langle\chi|\Psi\rangle = \langle P\chi|P\Psi\rangle = \left\langle \chi \middle| \underbrace{P^\dagger P}_{\mathbb{I}} \middle| \Psi \right\rangle$
- for any observable A: $[A, P] = 0$: $\langle P\chi|A|P\Psi\rangle = \langle\chi|P^\dagger A P|\Psi\rangle = \langle\chi|P^\dagger P A|\Psi\rangle = \langle\chi|A|\Psi\rangle$
- since $[P_{ij}, P_{ik}] \neq 0$: An eigenstate of A is <u>not</u> in general an eigenstate of all P_{ij}.

There are 2 special cases: the totally symmetric combination: $|\Psi_s\rangle$, with $P|\Psi_s\rangle = |\Psi_s\rangle$ and the totally antisymmetric combination: $|\Psi_A\rangle$, with $P_{ij}|\Psi_A\rangle = -|\Psi_A\rangle$ and $P|\Psi_A\rangle = \text{sgn}(P)|\Psi_A\rangle$ e.g. N=3:

$$|\Psi_S\rangle = \frac{1}{\sqrt{3!}}\left(\Psi(1,2,3) + \Psi(1,3,2) + \Psi(2,1,3) + \Psi(2,3,1) + \Psi(3,1,2) + \Psi(3,2,1)\right)$$

$$|\Psi_A\rangle = \frac{1}{\sqrt{3!}}\left(\Psi(1,2,3) + \Psi(2,3,1) + \Psi(3,1,2) - \Psi(3,2,1) - \Psi(2,1,3) - \Psi(1,3,2)\right)$$

<u>Spin-statistics theorem</u>: particles with <u>integer</u> spin (bosons) are described by symmetric wave <u>functions</u> $|\Psi_S\rangle$, particles with <u>half-integer</u> spin (fermions) are described by antisymmetric wave functions $|\Psi_A\rangle$.

We now look at a Hamiltonian

$$H = \sum_{i=1}^{N} H_i \qquad \text{(non-interacting idential particles)}$$

We now write $\Psi(1,2,...,N) = \prod_{i=1}^{N}\Psi_i(i)$ with $H_i\Psi_i = E_i\Psi_i$ and $H\Psi(1,...,N) = (\sum E_i)\,\Psi(1,...,N)$
Then we have: Bosonic case:

$$\Psi_S(1,...,N) = \frac{1}{\sqrt{N!}}\sum_P \Psi_1(\vec{r}_{P(1)}, \vec{s}_{P(1)})\ldots\Psi_n(\vec{r}_{P(N)}\vec{s}_{P(N)})$$

Fermionic case:

$$\Psi_A(1,...,N) = \frac{1}{\sqrt{N!}}\sum_P (-1)^P \Psi_1(P(1))\ldots\Psi_N(P(N))$$

This can then be written as Slater determinant

$$\Psi_A(1,...,N) = \frac{1}{\sqrt{N!}}\text{Det}\begin{pmatrix} \Psi_1(1) & ... & \Psi_1(N) \\ & & \\ \Psi_N(1) & ... & \Psi_N(N) \end{pmatrix}$$

We then get the : Pauli exclusion principle: Two identical fermions cannot be in the same state. Application: Fermi gas with the Fermi energy and its other properties.

3.2 Thomas-Fermi approximation

The Thomas-Fermi approximation is a semi-classical approximation for large Z. Each electron feels the average spherically symmetrical potential $\Phi(r)$, created by the nucleus and the other electrons. The potential then changes as follows:

$$V(r) = -\frac{Ze^2}{r} \to -e\Phi(r)$$

We now look at the Poisson equation for this $\Phi(r)$:

$$\nabla^2\Phi(r) = -4\pi\tilde{\rho} \underbrace{=}_{r>0} 4\pi e\rho \qquad \text{with } \tilde{\rho}(r) = \underbrace{-e\rho(r)}_{\text{all } e^-} + Ze\delta(r)$$

Φ and ρ are related. Let n be the number of e^- states in a particular energy range (per Momentum per Volume)

$$n = \frac{2}{(2\pi\hbar)^3} \qquad \text{if } E = \frac{p_F^2}{2m} - e\Phi < 0$$
$$n = 0 \qquad \text{if } E > 0$$

The 2 comes from the spin of the electron.
We then write ρ:

$$\rho = \int_{|\rho|<\sqrt{2me\phi}} n d^3p = \frac{2\cdot 4\pi}{(2\pi\hbar)^3}\int_0^{\sqrt{2me\Phi}} p^2 dp = \frac{8\pi}{3(2\pi\hbar)^3}(2me\Phi)^{3/2}$$

We plug this into the Poisson equation, in order to get an equation for Φ:

$$\nabla^2\Phi(r) = \frac{1}{r}\frac{d^2}{dr^2}r\Phi(r) = \frac{32\pi^2 e}{3(2\pi\hbar)^3}\left(2me\Phi(r)\right)^{3/2}$$

We have assumed that Z is large, so this approximation only works reasonable for the case of big atoms. Furthermore we have to carefully look at the boundary conditions of this differential equation:

$$\text{Nucleus: } \Phi(r) \to \frac{Ze}{r} \text{ for } r \to 0$$
$$\text{Normalization: } 4\pi\int \rho(r)r^2 dr = Z$$

The differential solution can be solved numerically. [Plot, $\Phi(r)$ looks roughly like something $r^{-\alpha}$]. This plot shows that using this approximation the electron density stretches until infinity (a failure of the model). For small r we get:

$$\Phi(r) \sim \frac{Ze}{r} - \underbrace{\text{cst.}}_{\sim 2}\cdot Z^{4/3}\frac{e}{a}$$

We can define a radius $R(\eta)$, which is the radius that contains all but the fraction η of the electrons:

$$(1-\eta)Z = \int^{R(\eta)} 4\pi\rho(r)r^2 dr$$

If you ask for the radius within which all but one e^- are:

$$R\left(\frac{1}{Z}\right) \sim \text{const.} \cdot Z^{-1/3}a$$

3.3 The Hartree approximation

Assume $\Psi(1,...,N) = \varphi_1(1)\cdot\varphi_2(2)\cdots\varphi_N(N)$ as a solution to $H = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i}\right) + \sum_{i>j}\frac{e^2}{|r_i - r_j|}$.
Note: this contradicts Fermi statistics. The statistics is partially taken into account by forcing $\varphi_i(i)$ to be distinct (orthogonal). Furthermore there is a normalization condition: $\int d^3r_i|\varphi_i(i)|^2 = 1$
We now want to find a stationary state w.r.t. to variation in $\varphi_i(i)$. $\rightarrow$ functional derivative

$$\langle H\rangle = \sum_i \int d^3\vec{r_i}\left(\varphi_i^*(\vec{r_i})\left(-\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{|r_i|}\right)\varphi_i(r_i)\right) + \sum_{i>j}\int d^3\vec{r_i}\int d^3\vec{r_j}\varphi_i^*(\vec{r_i})\varphi_j^*(\vec{r_j})\frac{e^2}{|\vec{r_i}-\vec{r_j}|}\varphi_i(\vec{r_i})\varphi_j(\vec{r_j})$$

We now want to minimize this under constraints $0 = \int d^3\vec{r_i}\,|\varphi_i(r_i)|^2 - 1$. We do this with Lagrange multipliers. We call our Lagrange multipliers ε_i. We want to minimize

$$\langle H\rangle - \sum_j \varepsilon_j\left(|\varphi_j|^2 - 1\right)$$

$$= \sum_i \int d^3\vec{r}\left(\varphi_i^*(\vec{r_i})\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{|r_i|} - \varepsilon_i\right)\varphi_i(\vec{r_i}) + \varepsilon_i\right) + \sum_{i>j}\int d^3\vec{r_i}\int d^3\vec{r_j}\varphi_i^*(\vec{r_i})\varphi_j^*(\vec{r_j})\frac{e^2}{|\vec{r_i}-\vec{r_j}|}\varphi_i(\vec{r_i})\varphi_j(\vec{r_j})$$

This is an MMP problem. This whole thing is a functional, so we have to use the appropriate techniques to minimize it. This is done by using functional derivatives with respect to $\frac{\delta}{\delta\varphi_i^*(\vec{r_i})}$.
This will then give us an equation for the function $\varphi_i(\vec{r_i})$.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{|r_i|} + V_i(\vec{r_i})\right)\varphi_i(r_i) = \varepsilon_i\varphi_i(r_i)$$

$$V_i(\vec{r_i}) = \sum_{j\neq i}\int d^3\vec{r_j}\frac{e^2}{|\vec{r_i}-\vec{r_j}|}\,|\varphi_j(r_j)|^2$$

These equations are hard to solve, since $V_i(\vec{r_i})$, the potential acting on the electron i, depends on all the other electrons.
These equations are usually solved iteratively.
We first assume $\varphi_i^{(0)}$,...,$\varphi_N^{(0)} \rightarrow V^{(0)}$
$\varphi_i^{(1)}$,...,$\varphi_N^{(1)} \rightarrow V^{(1)}$
With each iteration, we get a better approximation.
Note: ε_i is the ionisation energy of the i-th electron, assuming the other electrons do not change.

$$\varepsilon_i = \int d^3\vec{r}\left(-\frac{\hbar^2}{2m}|\nabla\varphi_i|^2 - \frac{Ze^2}{r}|\varphi_i|^2\right) + \sum_{j\neq i}\int d^3r_i\int d^3r_j\,|\varphi_i|^2\,|\varphi_j|^2\,\frac{e^2}{|r_i - r_j|}$$

3.4 Hartree-Fock approximation

In this approximation, we take the antisymmetry property into account:

$$\Psi(1,...,N) = \frac{1}{\sqrt{N!}}\left|\begin{pmatrix}\varphi_1(1) & \cdots & \varphi_N(1)\\ & & \\ \varphi_1(N) & \cdots & \varphi_N(N)\end{pmatrix}\right|$$

This then leads to changes:

$$\langle H\rangle = \sum_I \int d^3\vec{r}_i \left(\varphi_i^*(r_i)\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r_i}\right)\varphi_i(r_i)\right)$$

$$+\frac{1}{2}\sum_{i\neq j}\int d^3\vec{r}_i \int d^3\vec{r}_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|}\left(\underbrace{\varphi_i^*(\vec{r}_i)\varphi_j^*(\vec{r}_j)\varphi_i(\vec{r}_i)\varphi_j(\vec{r}_j)}_{\text{same as before}} - \underbrace{\varphi_i^*(\vec{r}_i)\varphi_j^*(\vec{r}_j)\varphi_i(\vec{r}_j)\varphi_j(\vec{r}_i)}_{\text{exchange term}}\right)$$

To understand the exchange term, we consider $N = 2$:

$$\Psi(1,2) = \frac{1}{\sqrt{2!}}\left(\varphi_1(1)\varphi_2(2) - \varphi_1(2)\varphi_2(1)\right)$$

We then plug this into the equation:

$$\left\langle\Psi\left|\frac{1}{\vec{r}_1 - \vec{r}_2}\right|\Psi\right\rangle = \frac{1}{2!}\int d^3r_1 \int d^3r_2\Big(\varphi_1^*(1)\varphi_2^*(2)\varphi_1(1)\varphi_2(2) + \underbrace{\varphi_1^*(2)\varphi_2^*(1)\varphi_1(2)\varphi_2(1)}_{\vec{r}_1\leftrightarrow\vec{r}_2\text{: the same}}$$

$$-\varphi_1^*(1)\varphi_2^*(2)\varphi_1(2)\varphi_2(1) - \varphi_1^*(2)\varphi_2^*(1)\varphi_1(1)\varphi_2(2)\Big)$$

From this place on, one has to continue as in the Hartree approximation. The difference is roughly 10%.

3.5 The periodic table and Hund's rules

Hartree(-Fock) gives us the result that the electrons are in the field of the nucleus and the other electrons. The other electrons, to some extent, shield the nucleus. So the i-th electron lives in an effective potential given by the nucleus and all the other electrons. The effective potential V_{eff} is still spherically symmetric, so the wave function of the i-th electron will have the following form:

$$\Psi_i = \underbrace{R_{nl}(r_i)}_{\text{radial part}} \;/\; \underbrace{Y_l^{m_l}(\theta,\varphi)}_{\text{angular part: } l=0,\ldots,n-1} \;/\; \underbrace{\chi_{m_s}}_{\text{spin}}$$

The general rules for the electrons are:

- n smaller $\rightarrow$ E smaller (stronger binding)
- l smaller $\rightarrow$ E smaller (electrons closer to nucleus $\rightarrow$ stronger binding)
- Those two things compete to some extent.

For each n, we have a name:

l=	0,	1,	2,	3,	...	$n-1$
name	s	p	d	f	...	
degenerady	2	6	10	14	$2\cdot(2l+1)$	

There are the following shells to surround the nucleus with electrons:

K shell	$n=1$	$l=0$	2 elements	H, He	(1s)
L shell	$n=2$	$l=0$	2 elements	Li, Be	(2s)
		$l=1$	6 elements	B,...,Ne	(2p)
M shell	$n=3$	$l=0$	2 elements	Na, Mg	(3s)
		$l=1$	6 elements	Al,...Ar	(3p)
N shell	$n=4$	$l=0$	2 elements	K, Ca	(4s)
	$n=3$	$l=2$	10 elements	Sc,...Zn	(3d)
	$n=4$	$l=1$	6 elements	Ga,...,Kr	(4p)

The configuarion of the electrons defines the chemical properties of the elements. If a shell is

completely filled, we have an inert gas.
What is the configuration of the total spin S, the total orbital angular momentum L, and the total angular momentum $\vec{J}$ of the electrons? Here we get Hund's rules. Hund's rules are empirical rules, there are examples where they fail.
Example Carbon (C: $Z = 6$):
In carbon we have: $(1s)^2(2s)^2(2p)^2$
Each of the $(2p)$-electrons can have $m_l = -1, 0, +1$, $m_s = -\frac{1}{2}, +\frac{1}{2} \to 6$ possibilities. This then gives in total $15 = \frac{1}{2}6 \cdot 5$ possibilities:

L	S	J	$^{(2S+1)}L_J$	deg
0	0	0	$^1S_0$	1
1	1	0,1,2	$^3P_0$, $^3P_1$, $^3P_2$	1,3,5
2	0	2	$^1D_2$	5

The total degeneracy is 15.
For L, 0 and 2 are symmetric, 1 is antisymmetric. In order for the whole state to be antisymmetric, for $L = 0, 2$, S has to be antisymmetric, therefore $S = 0$. If $L = 1$, is antisymmetric, then S has to be symmetric, therefore $S = 1$.
Which one is the ground state?
Rules we use:

- S maximal
  S large, spin wave function more symmetric $\to$ space wave function less symmetric/more antisymmetric $\to$ wave function overlap (of electrons) minimal, therefore we have minimal repulsion.
  For our case: $S = 1$ (for C)

- L maximal
  This is the case because for large L, the electrons are further away from the nucleus, hence further away from each other. Therefore we have less repulsion.
  For our case: $L = 1$ (for C), but that is already defined by S, so this rule does not help us.

- $\Delta E_{SO} = \underbrace{\text{cst.}}_{\begin{cases}\text{cst} > 0 \text{ if the shell is no more than half filled} \to J = |L - S| \\ \text{cst} < 0 \text{ if shell more than half filled} \to J = |L + S|\end{cases}} (J(J+1) - L(L+1) - S(S+1))$
  This comes from the fact that $V \sim \text{cst} \cdot \vec{L} \cdot \vec{S}$
  In our case we therefore want that $J = 0$. Our ground state is therefore $^3P_0$

4 Approximation methods for time-dependent problems

We are now looking at time-dependent problems. We want to know their time evolution $|\Psi(t)\rangle = U(t, t_0)\,|\Psi(t_0)\rangle$ given a Hamiltonian $H(t)$ and the Schrödinger equation $i\hbar\frac{d}{dt}\,|\Psi(t)\rangle = H(t)\,|\Psi(t)\rangle$, where $H(t)$ might depend on t.

4.1 Time-dependent perturbation theory

We will now assume that $H = H_0 + \lambda V(t)$, where we assume that H_0 is time-independent and known (we know $H_0 \left|\Psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\Psi_n^{(0)}\right\rangle$. Since the $\left|\Psi_n^{(0)}\right\rangle$ form a basis we can expand $|\Psi(t)\rangle$ in this basis

$$\forall t : |\Psi(t)\rangle = \sum_n c_n(t) \exp\left(-\frac{i}{\hbar}E_n^{(0)}t\right)\left|\Psi_n^{(0)}\right\rangle$$

We furthermore know the normalization condition for all times:

$$\langle\Psi(t)|\Psi(t)\rangle = 1 \implies \sum_n |c_n(t)|^2 = 1$$

We can also write

$$V(t)\left|\Psi_n^{(0)}\right\rangle = \sum_m \left|\Psi_m^{(0)}\right\rangle \left\langle\Psi_m^{(0)}\middle|V(t)\middle|\Psi_n^{(0)}\right\rangle$$

Where we used that $\sum_m \left|\Psi_m^{(0)}\right\rangle\left\langle\Psi_m^{(0)}\right| = \mathbb{I}$ and set $\left\langle\Psi_m^{(0)}\middle|V(t)\middle|\Psi_n^{(0)}\right\rangle = V_{mn}(t)$. We then use the Schrödinger equation:

$$i\hbar\frac{d}{dt}\left|\Psi(t)\right\rangle = \left(H_0 + \lambda V(t)\right)\left|\Psi(t)\right\rangle$$

$$\sum_n \left(i\hbar\dot{c}_n + E_n^{(0)}c_n\right)e^{-\frac{i}{\hbar}E_n^{(0)}t}\left|\Psi_n^{(0)}\right\rangle = \sum_n c_n e^{-\frac{i}{\hbar}E_n^{(0)}t}\left(E_n^{(0)}\left|\Psi_n^{(0)}\right\rangle + \lambda\sum_m V_{mn}(t)\left|\Psi_m^{(0)}\right\rangle\right)$$

where the term with $E_n^{(0)}c_n$ drops and we can swap the labels m and n:

$$\sum_n i\hbar\dot{c}_n e^{\frac{-i}{\hbar}E_n^{(0)}t}\left|\Psi_n^{(0)}\right\rangle = \sum_{n,m}\lambda e^{-\frac{i}{\hbar}E_m^{(0)}t}V_{nm}(t)c_m\left|\Psi_n^{(0)}\right\rangle$$

We therefore get equations for c_n:

$$\implies \dot{c}_n(t) = (i\hbar)^{-1}\lambda\sum_m V_{nm}c_m(t)\underbrace{\exp\left(\frac{i}{\hbar}(E_n^{(0)} - E_m^{(0)})t\right)}_{e^{i\omega_{nm}t}} \qquad \text{with } \omega_{nm} = \frac{E_n^{(0)} - E_m^{(0)}}{\hbar}$$

We here have a set of coupled differential equations which are equivalent to the Schrödinger equation. We can now do an expansion in λ: $c_n(t) = c_n^{(0)} + \lambda c_n^{(1)} + \lambda^2 c_n^{(2)} + ...$ We look at this equation order by order.

$$\mathcal{O}(\lambda^0) : \dot{c}_n^{(0)} = 0 \qquad \leftarrow \text{ trivial}$$

$$\mathcal{O}(\lambda^1) : \dot{c}_n^{(1)} = (i\hbar)^{-1}\sum_m V_{nm}c_m^{(0)}e^{i\omega_{nm}t} \qquad \leftarrow \text{focus at the moment}$$

$$\mathcal{O}(\lambda^j) : \dot{c}_n^{(j)} = (i\hbar)^{-1}\sum_m V_{nm}c_m^{(j-1)}e^{i\omega_{nm}t} \qquad \leftarrow \text{Section 4.4}$$

If the system is in state $\left|\Psi_i^{(0)}\right\rangle$ at the time $t_0(=0)$ (initial state), then we have the initial conditions $c_m^{(0)} = \delta_{mi}$. Then we get the following differential equation:

$$\dot{c}_f^{(1)} = (i\hbar)^{-1}V_{fi}e^{i\omega_{fi}t} \implies c_f(t) = (i\hbar)^{-1}\int_{t_0}^{t} V_{fi}(t')e^{i\omega_{fi}t'}dt'$$

The transition probability is then

$$P_{i\to f} = |c_f(t)|^2 = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} V_{fi}(t')e^{i\omega_{fi}t'}dt'\right|^2 + \mathcal{O}(\lambda^2)$$

This approximation is only valid if $|c_f|^2 \ll 1$.

4.2 Constant perturbation

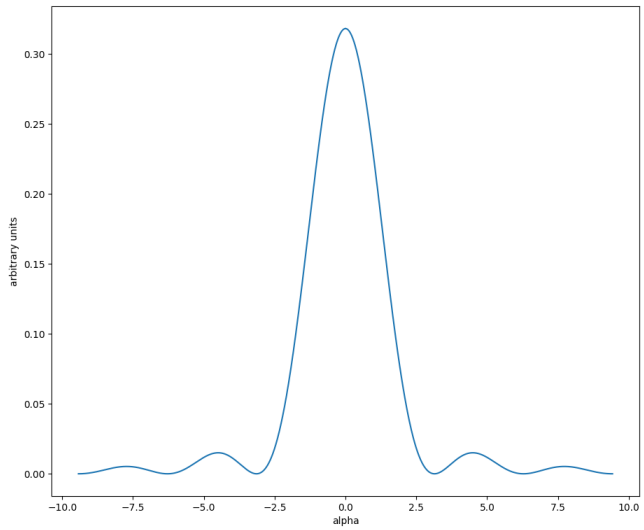
Let $V(t) = 0$ for $t < t_0(=0)$ and $V(t) = V$ (constant) for $t \geq t_0$.

$$P_{if}(t) = \frac{1}{\hbar^2}|V_{fi}|^2\underbrace{\left|\int_{t_0}^{t} e^{i\omega_{fi}t'}dt'\right|^2}_{\frac{4\sin^2(\omega_{fi}t/2)}{\omega_{fi}^2}} = \frac{\pi t}{\hbar^2}|V_{fi}|^2\underbrace{\frac{\sin^2\left(\frac{\omega_{fi}t}{2}\right)}{\pi t\left(\frac{\omega_{fi}}{2}\right)^2}}_{\delta_t(\alpha)\text{ with }\alpha=\frac{\omega_{fi}}{2}}$$

We now look at $\delta_t(\alpha)$ a bit in detail:

$$\delta_t(\alpha) = \frac{\sin^2(\alpha t)}{\pi \alpha^2 t} = \begin{cases} \frac{t}{\pi} & \alpha = 0 \\ \leq \frac{1}{\pi t \alpha^2} & \alpha \neq 0 \end{cases}$$

A plot of the function $\delta_t(\alpha)$ for $t = 1$:



$$P_{i\to f}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} V_{fi}(t')e^{-i\omega t'}dt'\right|^2 \to \frac{\pi t}{\hbar^2}\left|V_{fi}\right|^2 \underbrace{\frac{\sin^2\left(\omega_{fi}t/2\right)}{\pi t(\omega_{fi}/2)^2}}_{\delta_t(\omega_{fi}/2)}$$

We can then take the limit of $P_{i\to f}$:

$$\lim P_{i\to f}(t) = \frac{\pi t}{\hbar^2}\left|V_{fi}\right|^2 \delta\left(\frac{E_f - E_i}{2\hbar}\right) = \frac{2\pi t}{\hbar}\left|V_{fi}\right|^2 \delta(E_f - E_i)$$

This is the probability in first order to go from the ith to the fth state. It increases linearly in time and will reach more than 1 after a sufficient amount of time. The transition rate is the transition probability per time:

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}\left|V_{fi}\right|^2 \delta(E_f - E_i)$$

We will now consider a transition into a continuum of states: $\int_{E_1}^{E_2}\rho(E)dE$ is the number of states with $E_1 \leq E \leq E_2$, $\rho(E)$ is the density of states (DOS). We will now transform a sum into an integral:

$$\sum_f \Gamma_{i\to f} \to \int \rho(E)\Gamma_{i\to f}dE = \frac{2\pi}{\hbar}\rho(E_f)\left|V_{fi}\right|^2$$

This formula is called Fermi's "golden rule".

4.3 Periodic perturbation

Let $V(t) = (Ve^{-i\omega t} + V^* e^{i\omega t})$ for $t > t_0$ ($V(t) = 0$ for $t < t_0$).
We can then look at $P_{i\to f}$:

$$P_{i\to f}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t}\left(V_{fi}e^{i(\omega_{fi}-\omega)t'} + V_{fi}^{\dagger}e^{i(\omega_f+\omega)t'}\right)dt'\right|^2$$

we then get, using the result from before:

$$= \frac{\pi t}{\hbar^2}\left(|V_{fi}|^2 \frac{\sin^2\left(\frac{t}{2}(\omega_{fi}-\omega)\right)}{\pi t\left(\frac{\omega_{fi}-\omega}{2}\right)^2} + \left|V_{fi}^\dagger\right|^2 \frac{\sin^2\left(\frac{t}{2}(\omega_{fi}+\omega)\right)}{\pi t\left(\frac{\omega_{fi}+\omega}{2}\right)^2} \right.$$

$$\left. +2\mathrm{Re}(V_{fi}V_{fi}^\dagger)\frac{2\cos(\omega t)\sin\left(\frac{t}{2}(\omega_{fi}-\omega)\right)\sin\left(\frac{t}{2}(\omega_{fi}+\omega)\right)}{\pi t(\omega_{fi}-\omega)(\omega_{fi}+\omega)} \right)$$

The second term, proportional to $\mathrm{Re}(V_{fi}V_{fi}^\dagger)$ is the interference term, it drops out for $t > \frac{2\pi}{\omega}$. We now look again at the transition probability per time Γ:

$$\Gamma_{fi} = \frac{2\pi}{\hbar}\left(|V_{fi}|^2 \delta\left(E_f - E_i - \hbar\omega\right) + \left|V_{fi}^\dagger\right|^2 \delta\left(E_f - E_i + \hbar\omega\right)\right)$$

The left term is the absorption of a photon, the right term the emission of a photon.

4.4 The interaction picture

We will in this section look at the interaction picture. The goal of the interaction picture is to separate the evolution of the free Hamiltonian (without perturbation or interaction terms) from the time evolution due to the interaction / the perturbation. We therefore consider the time evolution operator:

$$|\Psi(t)\rangle = U(t,t_0)\,|\Psi(t_0)\rangle$$

U is an unitary operator which does preserve the norm. It has the following properties:

- $U(t,t) = \mathbb{I}$
- $U(t,t_1)U(t_1,t_0) = U(t,t_0)$
- $i\hbar\partial_t\,|\Psi(t)\rangle = H\,|\Psi(t)\rangle = HU(t,t_0)\,|\Psi(t_0)\rangle = i\hbar\partial_t U(t,t_0)\,|\Psi(t_0)\rangle \implies$

$$i\hbar\frac{\partial U(t,t_0)}{\partial t} = H(t)U(t,t_0)$$

The formal solution of the latter equation is:

$$U(t,t_0) = 1 + \frac{1}{i\hbar}\int_{t_0}^{t} H(t')U(t',t_0)dt'$$

The conditions for this to be the time evolution operator can be proved easily, one just has to plug it into the equation. We now want to write $U(t,t_0)$ as a sum over many terms:

$$U(t,t_0) = \sum_{n=0}^{\infty} U^{(n)}(t,t_0) \qquad \text{with } U^{(0)} = 1$$

The other terms look as follows:

$$U^{(1)}(t,t_0) = \frac{1}{i\hbar}\int_{t_0}^{t} H(t_1)dt_1$$

$$U^{(2)}(t,t_0) = \frac{1}{i\hbar}\int_{t_0}^{t_2} H(t_2)U^{(1)}(t_2,t_0)dt_2 = \frac{1}{(i\hbar)^2}\int_{t_0}^{t} dt_2 H(t_2)\int_{t_0}^{t_2} dt_1 H(t_1)$$

$$\cdots$$

$$U^{(n)}(t,t_0) = \frac{1}{(i\hbar)^n}\int_{t_0}^{t} dt_n H(t_n)\int_{t_0}^{t_n} dt_{n-1}H(t_{n-1})....\int_{t_0}^{t_2} dt_1 H(t_1)$$

$$= \frac{1}{n!}\frac{1}{(i\hbar)^n}\int_{t_0}^{t} T\left(H(t_n)\cdots H(t_1)\right) dt_1 \ldots t_n$$

In this equation, T represents the time ordering, which means that $t_n > t_{n-1} > \cdots > t_1 > t_0$. The operators inside T are always ordered in such a way, such that the earliest one is at the right and the latest is at the left. The term $1/n!$ compensates for the changed boundaries. We can now use the results from before in order to rewrite the time evolution operator:

$$U(t,t_0) = T\left[\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} H(t')dt'\right)\right]$$

This equation looks very simple, but is in fact very complicated to evaluate. The T can be avoided, if $[H(t_1), H(t_2)] = 0 \forall t_1 \neq t_2$. Furthermore we get that if H does not depend on time:

$$U(t,t_0) = \exp\left(-\frac{i}{\hbar}H(t-t_0)\right) \qquad H \text{ time-independent}$$

To make an approximation of the complicated expression with the exponential possible, we will use the interaction picture. In the Schrödinger picture, all the time dependence is in the bras and kets, while the operators are time-independent: $|\Psi(t)\rangle$ time-dependent, but A time-independent. On the other hand, in the Heisenberg picture, the kets and bras are time-independent, and only the operators depend on time. $|\Psi\rangle_H = |\Psi(t_0)\rangle = U(t_0,t)\,|\Psi(t)\rangle$ is time-independent, the operator on the other is time-dependent: $A_H(t) = U(t_0,t)AU(t,t_0)$. The matrix elements are independent of the picture used:

$${}_H\langle\Psi|A_H(t)|\Psi\rangle_H = \langle\Psi(t)|U(t,t_0)U(t_0,t)AU(t,t_0)U(t_0,t)|\Psi(t)\rangle = \langle\Psi(t)|A|\Psi(t)\rangle$$

We now look at the interaction picture, for which we split up the Hamiltonian into a time-independent and a time-dependent part: $H = H_0 + V(t)$. For the time-independent part H_0 we then have the time-evolution operator $U_0(t,t_0) = \exp\left(-\frac{i}{\hbar}H_0(t-t_0)\right)$. We then define

$$|\Psi(t)\rangle_I \equiv U_0(t_0,t)\,|\Psi(t)\rangle$$

$$A_I(t) \equiv U_0(t_0,t)AU_0(t,t_0)$$

Both the kets and the operators are time-dependent. We then have:

$$|\Psi(t)\rangle_I = U_0(t_0,t)\,\overbrace{U(t,t_1)\overbrace{U_0(t_1,t_0)U_0(t_0,t_1)}^{\mathbb{I}}}^{|\Psi(t)\rangle}\,|\Psi(t_1)\rangle$$

In this equation, $U_0(t_0,t)U(t,t_1)U_0(t_1,t_0)$, the first part of the term on the right hand side, is $U_I(t,t_1)$. Furthermore, $U_0(t_0,t_1)\,|\Psi(t_1)\rangle = |\Psi(t_1)\rangle_I$. Hence the above equation is nothing but

$$|\Psi(t)\rangle_I = U_I(t,t_1)\,|\Psi(t_1)\rangle_I \text{ with } U_I(t,t_1) = U_0(t_0,t)U(t,t_1)U_0(t_1,t_0)$$

We therefore get a differential equation for U_I:

$$\begin{aligned} i\hbar\partial_t U_I(t,t_1) &= i\hbar U_0(t_0,t)\left(\frac{i}{\hbar}H_0 - \frac{i}{\hbar}H\right)U(t,t_1)U(t_1,t_0) \\ &= U_0(t_0,t)V(t)U_0(t,t_0)U_0(t_0,t)U(t,t_1)U(t_1,t_0) \\ \Longrightarrow \boxed{i\hbar\frac{\partial}{\partial t}U_I(t,t_1) = V_I(t)U_I(t,t_1)} &\qquad \text{“solution as before”} \end{aligned}$$

We can therefore then write the time-evolution operator as a time-ordered exponential, completely analogous to the previous case:

$$U_I(t,t_0) = T\left[\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} V_I(t')dt'\right)\right]$$

If the V is a "small" perturbation, an expansion in V (in λ) might be meaningful.

$$|\Psi(t)\rangle_I = U_0(t_0,t)\,|\Psi(t)\rangle$$
$$U_I(t,t_1) = U_0(t_0,t)U(t,t_1)U_0(t_1,t_0)$$

$$\to U_I(t,t_0) = T\left[\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} V_I(t')dt'\right)\right]$$

If V is "small" (relative to H_0), we can use the perturbation theory, for example we can expand exponential in $U_I(t,t_0)$. As in Section 4.1. we compute the amplitude for $|i\rangle \to |f\rangle$ (we assume that $V_I(t) = 0 \quad t < t_0$, system in $\left|\Psi_i^{(0)}\right\rangle$ at the time t_0.
The amplitude for the system to be in the state $\left\langle\Psi_f^{(0)}\right|$ at a later time t.

$$\left\langle\Psi_f^{(0)}\middle|\Psi_i(t)\right\rangle = \left\langle\Psi_f^{(0)}\middle|U_I(t,t_0)\middle|\Psi_i^{(0)}\right\rangle$$

$$= \left\langle\Psi_f^{(0)}\middle|\Psi_i^{(0)}\right\rangle + \frac{1}{(i\hbar)}\left\langle\Psi_f^{(0)}\middle|\underbrace{\int_{t_0}^{t} dt' \exp\left(-\frac{i}{\hbar}\underbrace{H_0}_{E_f}(t_0-t')\right) V(t') \exp\left(+\frac{i}{\hbar}\underbrace{H_0}_{E_i}(t'-t_0)\right)}_{\int dt' V_{fi}(t') e^{\frac{i}{\hbar}(E_f-E_i)t'}}\middle|\Psi_i^{(0)}\right\rangle + ...$$

We therefore get the following thing:

$$P_{i\to f} = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} V_{fi}(t')e^{i\omega_{fi}t'}dt'\right|^2 + ... \text{ as in Section 4.1.}$$

4.5 The adiabatic approximation

We again look at a system with a time-dependent Hamiltonian. Here the time-dependence need not be small, but it is slow. The easiest example to show this is the following: We start with with an infinitely high potential well, with $V(x) = 0$ for $x \in [0,1]$ and $V(x) = \infty$ otherwise. The wave functions are then $\Psi_1 = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)$. We then double the width of this potential well, one time abruptly, within an instant from a width of a to a width of $2a$, the other time very slowly (adiabatically). In the case of the abrupt change, the wave function directly after the change will the same as before, while in the adiabatic case, the wave function slowly adapts to the new size. In the adiabatic case we therefore have the new wave function $\Psi = \sqrt{\frac{2}{2a}}\sin\left(\frac{\pi x}{2a}\right)$. In the adiabatic case, the system stays in the "same" eigenstate as before.
Theorem: for an adiabatic change of the initial Hamiltonian $H_i(t)$ to the final Hamiltonian $H_f(t)$, a system that is in the n-th eigenstate of H_i willl evolve to the n-th eigenstate of H_f (no level crossing).
"Proof": Let $H(t)\,|\Psi_n(t)\rangle = E_n(t)\,|\Psi_n(t)\rangle$, where the $|\Psi_n(t)\rangle$ form an orthonormal basis for all t. We can therefore write $|\Psi(t)\rangle$ in this basis:

$$|\Psi(t)\rangle = \sum_n c_n(t)\exp\left(\frac{1}{i\hbar}\int_{t_0}^{t} E_n(t')dt'\right)|\Psi_n(t)\rangle = \sum_n c_n(t)e^{i\varepsilon_n(t)}\,|\Psi_n(t)\rangle$$

where in the last step $\varepsilon(t)$ has been defined. We now plug this expansion into the Schrödinger equation:

$$i\hbar\sum_n\left(\dot{c}_n\,|\Psi_n\rangle + c_n\left|\dot{\Psi}_n\right\rangle + ic_n\dot{\varepsilon}_n\,|\Psi_n\rangle\right)e^{i\varepsilon_n(t)} = \sum_n c_n e^{i\varepsilon_n}H\,|\Psi_n(t)\rangle$$

We now see that the rightmost term on the left and the term on the right cancel. This then allows us to write our equation in a more convenient way:

$$\sum_n \dot{c}_n \left|\Psi_n\right\rangle e^{i\varepsilon_n} = -\sum_n c_n \left|\dot{\Psi}_n\right\rangle e^{i\varepsilon_n}$$

We then multiply with $\langle\Psi_m|$ from the left. We then get:

$$\rightarrow \dot{c}_m = -\sum_n \left\langle\Psi_m\middle|\dot{\Psi}_n\right\rangle c_n e^{i(\varepsilon_n-\varepsilon_m)}$$

Our next task is to calculate $\left\langle\Psi_m\middle|\dot{\Psi}_n\right\rangle$:

$$H\left|\Psi_n\right\rangle = E_n\left|\Psi_n\right\rangle \implies \dot{H}\left|\Psi_n\right\rangle + H\left|\dot{\Psi}_n\right\rangle = E_n\left|\dot{\Psi}_n\right\rangle + \dot{E}_n\left|\Psi_n\right\rangle$$

By multiplying from the left with $\langle\Psi_m|$ we get:

$$\left\langle\Psi_m\middle|\dot{H}\middle|\Psi_n\right\rangle = \left\langle\Psi_m\middle|E_n\middle|\dot{\Psi}_n\right\rangle - \left\langle\Psi_m\middle|H\middle|\dot{\Psi}_n\right\rangle + \left\langle\Psi_m\middle|\dot{E}_n\middle|\Psi_n\right\rangle = (E_n-E_m)\left\langle\Psi_m\middle|\dot{\Psi}_n\right\rangle + \delta_{mn}\dot{E}_n$$

We then use this equation in the result for $\dot{c}_m$ we had before:

$$\dot{c}_m = -c_m\left\langle\Psi_m\middle|\dot{\Psi}_m\right\rangle - \sum_{n\neq m} c_n \frac{\left\langle\Psi_m\middle|\dot{H}\middle|\Psi_n\right\rangle}{E_n-E_m} e^{i(\varepsilon_n-\varepsilon_m)}$$

What we mean with the adiabatic approximation is that $E_n - E_m$ is <u>not</u> small or zero and $\dot{H}$ is small. We can therefore drop the later part of the equation above:

$$\boxed{\dot{c}_m = -c_m\left\langle\Psi_m\middle|\dot{\Psi}_m\right\rangle}$$

We have no mixing between $|\Psi_m\rangle$ and $|\Psi_n\rangle$.
We can now solve this differential equation:

$$c_m(t) = c_m(t_0)e^{i\gamma_m(t)} \text{ with } \gamma_m(t) = i\int_{t_0}^{t}\left\langle\Psi_m(t')\middle|\dot{\Psi}_m(t')\right\rangle dt'$$

If the system is in the state $|\Psi_m\rangle$ at t_0, it remains in there. Furthermore:

$$|\Psi(t)\rangle = c_m(t)e^{i\varepsilon_m(t)}|\Psi_m(t)\rangle = e^{i\gamma_m(t)}e^{i\varepsilon_m(t)}|\Psi_m(t)\rangle$$

$\gamma_m(t)$ is called the geometric phase (Berry phase) and $\varepsilon_m(t)$ is called the dynamic phase.

5 Interaction of Matter with the Classical Radiation Field

In this section, we will look at the interaction of matter with a classical radiation field. The classical field is an external field that is not quantized. We will then take electrons and atoms, and put them into this external field. Later, in chapter 8, we will quantize this field.

5.1 Basics of QM I

The external fields are $\vec{B} = \nabla\wedge\vec{A}$ and $\vec{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}$. In relativity, we know that Φ and $\vec{A}$ belong together and form A^μ, but we will not use this here.
The physics of these fields is invariant under gauge transformations:

$$A^\mu \rightarrow A^\mu + \partial^\mu\chi(r^\mu) \;=\; \begin{cases}\vec{A}\rightarrow\vec{A}+\nabla\chi\\ \Phi\rightarrow\Phi-\frac{1}{c}\frac{\partial\chi}{\partial t}\end{cases}$$

We can therefore use this freedom to choose a particular gauge. Here, we will use the Coulomb gauge: $\nabla \cdot \vec{A} = 0$.
Maxwell's equations in free space give us a wave equation for $\vec{A}$:

$$\Box \vec{A} \equiv \left(\frac{1}{c^2} \frac{\partial^2 \vec{A}(t,\vec{r})}{\partial t^2} - \nabla^2 \vec{A}(t,\vec{r}) \right) = 0$$

The structure of the solution of this equation is

$$\vec{A} = \int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda \alpha(k,\lambda)\vec{\varepsilon}(\vec{k},\lambda) e^{i\vec{k}\cdot\vec{r} - i\omega_k t} + \alpha^*(k,\lambda)\vec{\varepsilon}^*(k,\lambda) e^{-i\vec{k}\cdot\vec{r} + i\omega_k t}$$

For this to satisfy $\Box \vec{A} = 0$ we need $\omega_k = c\left|\vec{k}\right|$. The general solution is a linear combination of all solutions, so we sum over all $\vec{k}$: $\sum_{\vec{k}} \to \int d^3\vec{k}$. The $\alpha(k,\lambda)$ are just the coefficients for fixed $\vec{k}$ and λ. From $\nabla \cdot \vec{A} = 0$, we get $\vec{k} \cdot \vec{\varepsilon} = 0$. $\lambda = \{1,2\}$ is the polarization, $\vec{\varepsilon}$ is the polarization vector.
We now plug this into the Hamiltonian, for that we recall QM I. We have

$$H = \frac{1}{2m}\left(-i\hbar\nabla - \frac{q}{c}\vec{A}\right)^2 + q\Phi + V_0 = \underbrace{\frac{\vec{p}^2}{2m} + V_0}_{H_0} \underbrace{- \frac{q}{2mc}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right) + \frac{q^2}{2mc^2}\vec{A}^2 + q\Phi}_{V(t)}$$

We look at this Hamiltonian for the case of many electrons ($q = -e$):

$$V(t,\vec{r}_i) = \sum_i \left[\frac{e}{2mc}\left(\vec{p}_i \cdot \vec{A}(\vec{r}_i,t) + \vec{A}(\vec{r}_i,t)\cdot\vec{p}\right) + \frac{e^2}{2mc}\vec{A}^2(\vec{r}_i,t) - e\Phi(\vec{r}_i,t) \right]$$

We now introduce the number density $\rho(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i)$ and the current density $\vec{j}(\vec{r}) = \frac{1}{2m}\sum_i (\vec{p}_i\delta(\vec{r}-\vec{r}_i) + \delta(\vec{r}-\vec{r}_i)\vec{p}_i)$. We use this to rewrite the time-dependent part of the potential

$$V(t,\vec{r}) = \int d^3\vec{r} \Bigg[\underbrace{\frac{e}{c}\vec{j}(\vec{r})\cdot\vec{A}(\vec{r},t)}_{\text{keep } \vec{j}\cdot\vec{A}} + \underbrace{\frac{e^2}{2mc^2}\rho(\vec{r})\vec{A}^2(\vec{r},t)}_{\text{drop} \propto e^2} - \underbrace{e\rho(\vec{r})\Phi(\vec{r},t)}_{\text{assume no charges} \to \Phi = 0} \Bigg]$$

We will only keep the term with $\vec{j}\cdot\vec{A}$, we will drop the other terms, the second term because it is proportional to e^2 (small), and the third because we assume that there are no external changes.
We will now write $V(t,\vec{r}_i)$ for a single electron in terms of the Fourier transform of the current:

$$\vec{j}(\vec{k}) = \int d^3\vec{r} e^{-i\vec{k}\cdot\vec{r}}\vec{j}(\vec{r}) = \frac{\vec{p}_i}{2m}e^{-i\vec{k}\cdot\vec{r}_i} + e^{-i\vec{k}\cdot\vec{r}_i}\frac{\vec{p}_i}{2m}$$

The potential is then

$$V(t,\vec{r}_i) = \frac{e}{c}\int \frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda \left(\alpha(k,\lambda)\vec{\varepsilon}(\vec{r},\lambda)\cdot\vec{j}(-\vec{k})e^{-i\omega_k t} + \alpha^*\vec{\varepsilon}^*\cdot\vec{j}(\vec{k})e^{i\omega_k t}\right)$$

This potential has harmonic time dependence! We can therefore use Section 4.3.

5.2 Induced emission and absorption

Consider an atom in an external electromagnetic field, we want to compute transition probabilities and transition rates of a state (e.g. ψ_i ground state) to another state (e.g. ψ_f, excited state).
From Section 4.3, for one particular $\vec{k}$, λ:

$$\Gamma_{fi}(\vec{k},\lambda) = \frac{2\pi}{\hbar}\delta(E_f - E_i - \hbar\omega)\underbrace{\frac{e^2}{c^2}\left|\alpha(\vec{k},\lambda)\right|^2\left|\left\langle\psi_f\middle|\vec{j}(-\vec{k})\cdot\vec{\varepsilon}\middle|\psi_i\right\rangle\right|^2}_{|V_{fi}|^2}$$

What "happens" is that the initial state ψ_i absorbs the energy $\hbar\omega$ from the field and jumps to ψ_f. The total transition rate (for all $\vec{k}, \lambda$) is then

$$\Gamma_{fi} = \int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda \Gamma_{fi}(\vec{k},\lambda) = \int \frac{d\omega\omega^2}{(2\pi c)^3} \int d\Omega \sum_\lambda \Gamma_{fi}(\vec{k},\lambda)$$

$$= \frac{2\pi e^2}{(\hbar c)^2} \cdot \frac{\omega_{fi}^2}{(2\pi c)^3} \int d\Omega(\vec{e}_k) \sum_\lambda \left|\alpha(\vec{k},\lambda)\right|^2 \left|\left\langle \psi_f \middle| \vec{j}(-\vec{k}) \cdot \vec{\varepsilon}(\vec{k},\lambda) \middle| \psi_i \right\rangle\right|^2$$

$\vec{e}_k$ is the direction of the vector $\vec{k}$, $\omega_{fi} = \frac{E_f - E_i}{\hbar}$.
For induced emission we must change $\vec{j}(-\vec{k})$ to $\vec{j}(+\vec{k})$ and ω to $-\omega$. We then get the following for the induced emission:

$$\Gamma_{if} = ...$$

At the moment, we cannot yet describe spontaneous emission (without external electromagnetic field), since we do not have yet quantized the electromagnetic field. We will wait with this until chapter 8.

5.3 The Dipole Approximation and Selection Rules

The transition rules for $\psi_i \to \psi_f$ governed by the matrix element $\left\langle \psi_f \middle| \vec{j} \cdot \vec{\varepsilon} \middle| \psi_i \right\rangle$:

$$\vec{j}(\vec{k}) = \frac{1}{2m}\left(\vec{p}\, e^{-i\vec{k}\cdot\vec{r}} + e^{-i\vec{k}\cdot\vec{r}}\,\vec{p}\right) \approx \frac{1}{2m}\left(\vec{p}(1 - i\vec{k}\cdot\vec{r} + ...) + (1 - i\vec{k}\cdot\vec{r} + ...)\,\vec{p}\right)$$

For atomic transitions we have an r with the size of a few Bohr radii, a few 10^{-10} meters. Furthermore for visible light $k \sim \frac{1}{\lambda} \sim$ (a few 100nm)$^{-1}$. So we get $\vec{k}\cdot\vec{r} \ll 1$

A little aside: This approximation is equivalent to having a term $e\,\vec{r}\cdot\vec{E} = -\vec{d}\cdot\vec{E}$ where $\vec{d} = -e\vec{r}$ is the electric dipole moment. We will proof this in two ways:
Proof 1:

$$[r_x, H_0] = \left[r_x, \frac{p^2}{2m}\right] = \frac{1}{2m}\left(\underbrace{[r_x,\vec{p}]}_{i\hbar p_x}\vec{p} + \vec{p}\,[r_x,\vec{p}]\right) = \frac{i\hbar p_x}{m} \implies [\vec{r}, H_0] = \frac{i\hbar\vec{p}}{m}$$

We can now look at the matrix element

$$\left\langle \psi_i \middle| e\vec{r}\cdot\vec{E} \middle| \psi_f \right\rangle = -\frac{e}{c}\left\langle \psi_i \middle| \vec{r}\cdot\dot{\vec{A}} \middle| \psi_f \right\rangle = -\frac{e}{c}(i\omega_e)\left\langle \psi_i \middle| \vec{r}\cdot\vec{A} \middle| \psi_f \right\rangle$$

$$= -\frac{e}{c}\frac{i}{\hbar}(E_f - E_i)\left\langle \psi_i \middle| \vec{r}\cdot\vec{A} \middle| \psi_f \right\rangle = -\frac{e}{c}\frac{i}{\hbar}\left\langle \psi_i \middle| \underbrace{[\vec{r}, H_0]}_{i\hbar\vec{p}/m}\vec{A} \middle| \psi_f \right\rangle$$

$$= \frac{e}{c}\left\langle \psi_i \middle| \vec{j}\cdot\vec{A} \middle| \psi_f \right\rangle$$

Proof 2: make a gauge transformation with $\chi(\vec{r},t) = -\vec{A}(t)\cdot\vec{r}$. Therefore we have under this transformation

$$\begin{cases} \vec{A} \to \vec{A}' = \vec{A} + \nabla\chi = 0 \\ \Phi \to \Phi' = \Phi - \frac{1}{c}\cdot\chi = 0 + \frac{1}{c}\dot{\vec{A}}\cdot\vec{r} = -\vec{E}\cdot\vec{r} \end{cases}$$

So now we turn back to the atomic transition:
The atomic transition is only non-zero if $\langle\psi_f|\vec{r}|\psi_i\rangle \neq 0$.

$$\to \text{i.e. } \langle\psi_{n',l',m'}|\vec{r}|\psi_{n,l,m}\rangle$$

To see whether this matrix element is zero, one can use the Wigner-Eckart-Theorem, or do this calculation in the pedestrian (explicit) way:

$$\int dr\, r^2 \int d\Omega\, Y_{l'}^{m_l'}(\theta,\varphi) \begin{Bmatrix} \sin\theta e^{i\varphi} \\ \sin\theta e^{-i\varphi} \\ \cos\theta \end{Bmatrix} Y_l^{m_l}(\theta,\varphi) = \left\langle \psi_{n',l',m_l'} \middle| \begin{matrix} x+iy \\ x-iy \\ z \end{matrix} \middle| \psi_{n,l,m} \right\rangle$$

$$\left\langle \psi_{n',l',m_l'} \middle| z \middle| \psi_{n,l,m} \right\rangle \neq 0 \text{ if } l' = l \pm 1 \text{ and } m_l' = m_l$$

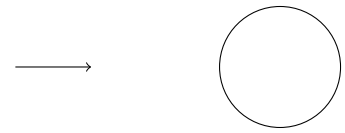
$$\left\langle \psi_{n',l',m_l'} \middle| x \pm iy \middle| \psi_{n,l,m} \right\rangle \neq 0 \text{ if } l' = l \pm 1 \text{ and } m_l' = m_l \pm 1$$

Here are the (E1) selection rules: $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$.

6 Potential Scattering

We look again at the Hamiltonian $H_0 + V$, and we look at what we call static scattering states. We have an incoming plane wave, a potential, and the incoming plane wave will be scattered in some way. Consider $H = H_0 + V(\vec{r})$ with V is restricted to a small region, more precisely $\lim_{r\to\infty} rV(r) = 0$. We look for a stationary solution $\Psi(\vec{r},t) = \psi(r)\exp\left(-\frac{i}{\hbar}Et\right)$ and are interested only in the region $r \to \infty$.

6.1 Elastic scattering & cross section



We have at some point a scattering centre, that represents $V(r)$. Furthermore, we have a incoming static beam of particles with small transverse size dA. The beam is directed in z-direction, the angle w.r.t. the z-axis is θ, the other angle is φ. We then look at a small piece of solid angle $d\Omega$ far away from the scattering centre and determine the flux of particles arriving there. These are the scattered, outgoing particles. In beam direction we will have furthermore the outgoing beam that was not scattered. We are not in interested in details for small r.

The incoming and the outgoing non-scattered beams are represented bv a plane wave, the outgoing scattered particles by a spherical wave.
We look for solutions $(H_0 + V)\,|\psi\rangle = E\,|\psi\rangle$.
For $r \to \infty$, we have

$$\psi_{\vec{k}}(r) = \psi_{in} + \psi_{sc} = \underbrace{e^{-i\vec{k}\cdot\vec{r}}}_{e^{-ik_z z}} + \underbrace{f(\theta,\varphi)}_{\text{scattering amplitude}} \underbrace{\frac{e^{+ikr}}{r}}_{\text{outgoing spherical wave}}$$

We have elastic scattering, therefore $E_{in} = E_{out} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$.
The differential cross section:

$$\frac{d\sigma}{d\Omega} = \frac{N}{F} = \frac{\#\text{ scattered particles, per time, per } d\Omega}{\text{flux of incoming particles} = \text{nr. of particles per are per time}}$$

The total cross section:

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega.$$

For $|\psi_{in}|^2 = 1$ (1 particle / volume): $F = \frac{V}{t\,dA} = v = \frac{p}{m} = \frac{\hbar k}{m}$.
for N: probability current density

$$\vec{j} = \frac{\hbar}{2mi}\left(\Psi^*\nabla\Psi - (\nabla\Psi^*)\Psi\right) = ... = \frac{\hbar k}{m}\left|f(\theta,\varphi)\right|^2 \frac{\vec{e}_r}{r^2} + \mathcal{O}\left(\frac{1}{r^3}\right)$$

This result we got from an exercise. We now look at N:

$$N d\Omega = \frac{\hbar k}{m} |f(\theta,\varphi)|^2 \, d\Omega \to \boxed{\frac{d\sigma}{d\Omega} = |f(\theta,\varphi)|^2}$$

We have no interference between ψ_{in} and ψ_{sc}. There is often no φ-dependence: f depends only on θ. Now we go to the gory details:

6.2 Partial-wave analysis

We look at a central potential $V(r)$. We therefore have no φ dependence in ψ_k.

$$\psi_k(r,\theta) = e^{i\vec{k}\cdot\vec{r}} + f(\theta)\frac{e^{ikr}}{r} = \sum_{l=0}^{\infty} R_l(k,r) P_l(\cos\theta) \tag{1}$$

$$f(\theta) = \sum_{l=0}^{\infty} f_l(k) P_l(\cos\theta)$$

Recall hydrogen atom: $R_l \sim \frac{u_l}{r}$. We then get an equation:

$$\to \left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2m}{\hbar^2}(V(r) - E)\right] R_l(r) = 0$$

or equivalent

$$u_l'' + \left(k^2 - \frac{2m}{\hbar}V(r) - \frac{l(l+1)}{r^2}\right) u_l = 0$$

Aside: For the moment, we assume that $V(r) = V_0$ is constant

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + \underbrace{\frac{2m}{\hbar^2}(V_0 - E)}_{\equiv k^2}\right] R_l(r) = 0.$$

Setting $\rho \equiv kr$ we then get the spherical Bessel functions as solutions:

$$j_l(\rho) = (-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \frac{\sin\rho}{\rho} \quad \text{and} \quad \eta_l(\rho) = -(-\rho)^l \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l \frac{\cos\rho}{\rho}$$

We have a second order differential equation, therefore we have 2 linearly independent solutions j_l and η_l, they behave as follows:
For $\rho \to 0$: $j_l(\rho) \sim \rho^l$ and $\eta_l(\rho) \sim \frac{1}{\rho^{l+1}}$,
for $\rho \to \infty$, $j_l(\rho) \sim \frac{1}{\rho}\sin\left(\rho - \frac{\pi l}{2}\right)$ and $\eta_l(\rho) \sim -\frac{1}{\rho}\cos\left(\rho - \frac{\pi l}{2}\right)$.
This then shows that e.g. for j_l we have $\int d^3\vec{r}\,|\psi|^2 \sim \int dr r^2 \frac{1}{r^2} |\sin(..)|^2$. Thus $\rho_l, \eta_l \notin L^2(\mathbb{R}^3)$ and these solutions correspond to scattering states.
For $-V_0 \leq E < 0$, we get bound states with Hankel functions: $h_l^{1,2} = j_l \pm i\eta_l \sim e^{\pm \sin\rho}$, which for $-$ is in $L^2(\mathbb{R}^3)$. This solution corresponds to a bound state. This is the end of the aside.

Now to the general solution for $V(r)$ in the limit $r \to 0$: $\frac{l(l+1)}{r^2}$ dominant if $V(r)$ is less singular than $\frac{1}{r^2}$. Thus $R_{kl}(r) \sim j_l(kr)$ (regular for $r \to 0$).
In the limit $r \to \infty$, $V(r) \to 0$.
The general solution is then

$$R_{kl}(r) = B_l(k) j_l(kr) + C_l(k)\eta_l(kr)$$

B_l and C_l are the coefficients of the general linear combination of j_l and η_l. For $r \to \infty$

$$\to \frac{1}{kr}\left(B_l \sin\left(kr - \frac{\pi l}{2}\right) - C_l \cos\left(kr - \frac{\pi l}{2}\right)\right) = \frac{1}{kr} A_l \sin\left(kr - \frac{\pi l}{2} + \delta_l(k)\right)$$

$$\text{with the phase shift } \tan\delta_l = -\frac{C_l(k)}{B_l(k)} \text{ and a new constant } A_l = \sqrt{B_l^2 + C_l^2}$$

Note: for $V \to 0$, $R_l \sim j_l$, $\delta_l = 0$.
for generic V: solution (for $r \to \infty$) are characterised by phase shifts.
Next: find relation between phase shifts $\delta_l(k)$ and $f(\theta)$, from which we then get $\frac{d\sigma}{d\Omega}$.
For this we will need a thing we did in MMP: Aside: We expand the plane wave in spherical harmonics → Legendre polynomials: (we assume no φ-dependence)

$$e^{i\vec{k}\cdot\vec{r}} = e^{ikr\cos\theta} = \sum_l a_l j_l(kr) P_l(\cos\theta)$$

where the a_l are the expansion coefficients and the $j_l P_l$ form a basis.
We then want to find the a_l. The solution is :

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

We then expand Eq.(1) in $P_l(\cos\theta)$ and consider $r \to \infty$:

$$\frac{1}{kr} A_l(k) \sin\left(kr - \frac{\pi l}{2} + \delta_l\right) = (2l+1) i^l \frac{1}{kr} \sin\left(kr - \frac{\pi l}{2}\right) + f_l \frac{e^{ikr}}{r}$$

$$\to \frac{A_l}{2i} e^{ikr} e^{-il\pi/2} e^{i\delta_l} - \frac{A_l}{2i} e^{-ikr} e^{+il\pi/2} e^{-i\delta_l} = (2l+1) i^l \frac{1}{2i} e^{ikr} e^{-il\pi/2} - (2l+1) i^l \frac{1}{2i} e^{-ikr} e^{+il\pi/2} + k f_l e^{ikr}$$

The terms in e^{ikr} and e^{-ikr} must be separately equal. $A_l = (2l+1) i^l e^{i\delta_l}$ and

$$f_l = \frac{2l+1}{2ik}\left(e^{2i\delta_l} - 1\right) = \frac{2l+1}{k} e^{i\delta_l} \sin\delta_l. \tag{2}$$

The δ_l determine f_l and thus on $f(\theta)$ and thus on $\frac{d\sigma}{d\Omega}$. The full information on the scattering is in δ_l.
We then get

$$f(\theta) = \sum_{l=0}^{\infty} \frac{2l+1}{k} e^{i\delta_l} \sin\delta_l P_l(\cos\theta)$$

The total cross section is then

$$\sigma_{\text{tot}} = \int d\Omega\, |f(\theta)|^2 = \int d\Omega \left|\sum_l f_l P_l(\cos(\theta))\right|^2 = 2\pi \int_{-1}^{+1} d(\cos(\theta)) \sum_{ll'} f_l f_{l'}^* \underbrace{P_l(\cos\theta) P_{l'}^*(\cos(\theta))}_{\int d(\cos\theta) P_l P_{l'} = \frac{2}{2l+1}\delta_{ll'}}$$

$$= \boxed{4\pi \sum_l \frac{|f_l|^2}{2l+1} = \sigma_{\text{tot}}} = 4\pi \sum_l \frac{2l+1}{k^2} \sin^2\delta_l \equiv \sum_l \sigma_l$$

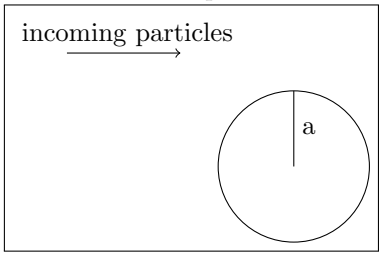
Optical theorem

$$\text{Im}(f(\theta=0)) = \text{Im}\left(\sum_l f_l P_l(\cos 0)\right) = \text{Im} \sum_l \frac{2l+1}{k} e^{i\delta_l} \sin\delta_l = \sum_l \frac{2l+1}{k} \sin^2\delta_l$$

$$\to \sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im}\left(f(0)\right)$$

This theorem is more general than the partial wave analysis, $f(0)$ is the forward scattering amplitude.

The partial wave analysis is useful if only a "few" σ_l are important. Typically, for l large, $\frac{l(l+1)}{r^2}$ becomes more important than $V(r)$ thus $\sim \delta_l \rightsquigarrow 0$



Another way to see that small l are usually more important is to consider $V(r)$ with range a, $V(r) = 0, r > a$. Semiclassical: no scattering if impact parameter $b > a$: $L = \sqrt{l(l+1)}\hbar \sim l\hbar = bp = b\hbar k$, so no scattering if $b = \frac{l\hbar}{k\hbar} = \frac{l}{k} > a \to \sigma_l \rightsquigarrow 0$ for $l > ak$

6.3 Coulomb scattering

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_1 Z_2 e^2}{r}\right)\psi(\vec{r}) = E\psi(\vec{r})$$

This potential violates $\lim_{r\to\infty} rV(r) = 0$. We are here not interested in the bound state solutions, but only in the scattering states. We will not do the derivation here, but the exact solution is known.

$$\psi_c(r) \propto e^{i(kz+\gamma \ln 2k(r-z))} - \frac{\gamma}{2k\sin^2(\theta/2)} \exp\left(-i\gamma \ln \sin^2\frac{\theta}{2} + i\pi + 2i\eta_0\right) \frac{e^{i(kr-\gamma \ln 2kr)}}{r}$$

$$\text{with } \gamma = \frac{mZ_1 Z_2 e^2}{\hbar^2 k} \text{ and } \eta_0 : e^{2i\eta_0} = \frac{\Gamma(1+i\gamma)}{\Gamma(1-i\gamma)}$$

What we expected was $e^{i\vec{k}\cdot\vec{r}} + f(\theta)\frac{e^{ikr}}{r}$, but there are additional phases (for example $\gamma \ln 2k(r-z)$), we therefore have distorted incoming and outgoing plane waves. The additional phases appear because $\lim_{r\to\infty} rV(r) \not\to 0$.
The cross section

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \frac{\gamma^2}{4k^2\left(\sin\frac{\theta}{2}\right)^4} = \left(\frac{Z_1 Z_2 e^2}{4E}\right)^2 \frac{1}{\sin^4\frac{\theta}{2}}$$

So when doing the calculation of the Rutherford cross section, the additional phases drop out, BUT they matter in other cases: They are important in the scattering of identical particles. In this case, we can't know which result of the scattering process we measure at $r = \infty$. We cannot distinguish the particles. The total wave function is then symmetric or antisymmetric (bosons, fermions).

$$\psi_{\text{sym/asym}} = \left(e^{i\vec{k}\cdot\vec{r}} \pm e^{-i\vec{k}\cdot\vec{r}}\right) + \left(f(\theta) \pm f(\pi-\theta)\right)\frac{e^{ikr}}{r}$$

Example: scattering of 2 protons (unpolarized):
probability $\frac{1}{4}$ in singlett: $\sigma_{\text{sing}} = |f(\theta) + f(\pi-\theta)|^2$
probability $\frac{3}{4}$ in triplett: $\sigma_{\text{trip}} = |f(\theta) - f(\pi-\theta)|^2$
We then get:

$$\begin{aligned}\sigma_{\text{unpol}} &= \frac{1}{4}|f(\theta) + f(\pi-\theta)|^2 + \frac{3}{4}|f(\theta) - f(\pi-\theta)|^2 \\ &= |f(\theta)|^2 + |f(\pi-\theta)|^2 - \frac{1}{2}\left(f(\theta)f^*(\pi-\theta) + f^*(\theta)f(\pi-\theta)\right)\end{aligned}$$

for $Z_1 = Z_2 = 1$:

$$= \left(\frac{e^2}{4E}\right)^2 \left(\frac{1}{\sin^4\frac{\theta}{2}} + \frac{1}{\cos^4\frac{\theta}{2}} - \frac{\cos\left(\gamma \ln\tan^2\frac{\theta}{2}\right)}{\sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2}}\right)$$

19.4.18:

6.4 Lippmann-Schwinger equation and Green function

This will be an integral equation. We start with the Schrödinger equation:

$$\left(\frac{\hbar^2}{2m}\nabla^2 + E_k\right)\psi_k(\vec{r}) = V(r)\psi_k(\vec{r}) \qquad (1) \qquad \text{with } E_k = \frac{\hbar^2 k^2}{2m}$$

$$\text{with the requirement } \lim_{r\to\infty} rV(r) \to 0$$

The Green's function is defined in the following way for the case of the Schrödinger equation. Given the Green's function, we can arrive at a general solution for our partial differential equation.

$$\left(\frac{\hbar^2}{2m}\nabla^2 + E_k\right) g_k(\vec{r}) = \delta(\vec{r})$$

$$\implies \psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \int d^3\vec{r}' g_k(\vec{r}-\vec{r}')V(r')\psi_k(r') \qquad (3)$$

Math addition about Green's function: The Dirac's delta is a distribution, so Green's function is in general also a distribution. A general differential equation would be

$$Lu(x) = f(x)$$

where L is a combination of derivatives, partial derivatives, ... and f is the inhomogeneous part. The Green's function is then defined as the impulse response of the differential operator:

$$LG(x,y) = \delta(y-x)$$

G can also be seen as the right-handed inverse of the differential operator: $G = L^{-1}$. Now if we integrate:

$$L\int G(x,y)f(y)dy = \int LG(x,y)f(y)dy = f(x) = Lu(x)$$

Now we have a solution:

$$u(x) = \int G(x,y)f(y)dy$$

End of the math addition.
The obvious problem with the equation for $\psi_k(\vec{r})$ is that ψ_k appears on both sides of the equal sign. But we have seen a similar equation before in 4.4: $U(t,t_0) = 1 + (i\hbar)^{-1}\int_{t_0}^{t} H(t')U(t',t_0)dt'$. Before we can solve our equation by iteration, we have to calculate the Green's function $g_k(\vec{r})$.
First, we will write down the Green's function in momentum space, using the Fourier transform of it:

$$g_k(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}} g_k(\vec{q})$$

$$\int \frac{d^3\vec{q}}{(2\pi)^3}\left(-\frac{\hbar^2}{2m}q^2 + \frac{\hbar^2}{2m}k^2\right)e^{i\vec{q}\cdot\vec{r}} g_k(\vec{r}) = \delta(\vec{r}) = \int \frac{d^3\vec{q}}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}}$$

$$\implies \tilde{g}_k(\vec{q}) = \frac{2m}{\hbar^2}\frac{1}{k^2-q^2} = \left(E_k - \frac{\hbar^2 q^2}{2m}\right)^{-1} \qquad (4)$$

Now we do the backwards Fourier transform:

$$g_k(\vec{r}) = \frac{1}{(2\pi)^3}\int_0^\infty q^2 dq \int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos(\theta)) e^{iqr\cos\theta}\frac{2m}{\hbar^2}\frac{1}{k^2-q^2}$$

The integration over the angels is rather easy and results in

$$= \frac{2m}{\hbar^2}\frac{1}{(2\pi)^2}\int_0^\infty dq \frac{q^2}{iqr}\frac{1}{k^2-q^2}\left(e^{iqr}-e^{-iqr}\right) = \frac{m}{2\pi^2\hbar^2}\frac{1}{ir}\int_{-\infty}^{+\infty} dq \frac{q}{k^2-q^2}e^{iqr}$$

We have two poles at $-k$ and k in the complex plane. We shift those poles by an infinitesimal amound $\pm i\epsilon$. We shift the two poles: The one at $-k$ to $-k-i\epsilon$ and the pole at $+k$ to $+k+i\epsilon$. Furthermore, we will close our contour at $+i\infty$. We will use the Residue Theorem, which states that

$$\oint f(z)dz = 2\pi i \mathrm{Res}(f,z_0) = \frac{1}{(n-1)!}\lim_{z\to z_0}\frac{d^{n-1}}{dz^{n-1}}\left((z-z_0)^n f(z)\right).$$

For the special case that $f(z) = \frac{g(z)}{h(z)}$ with $h(z_0)=0$ and $h'(z_0)\neq 0$, then $\mathrm{Res}(f,z_0) = \frac{g(z_0)}{h'(z_0)}$
In our case we then get, after applying the Residue theorem

$$g_k^+ = -\frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}$$

$$g_k^- = -\frac{m}{2\pi\hbar^2}\frac{e^{-ikr}}{r} \text{ for only pole at } -k \text{ in contour}$$

$$g_k^+ + g_k^- \text{ for both poles in contour}$$

$$0 \text{ for no pole in contour}$$

We can now write again the equation for ψ_k, Eq.(3), using the Green's function we have found:

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \int d^3\vec{r}' \frac{m}{2\pi\hbar^2}\frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}V(r')\psi_k(r')$$

We now want to look at what happens after the scattering. For that we look at $r\to\infty$: $|\vec{r}-\vec{r}'| = \sqrt{r^2+r'^2-2rr'\cos\theta} \to r\left(1-\frac{r'}{r}\cos\theta+\mathcal{O}\left(\left(\frac{r'}{r}\right)^2\right)\right) = r-\frac{\vec{r}\cdot\vec{r}'}{r} = r-\vec{e}_r\cdot\vec{r}'$. We now use this:

$$\psi_k(r) = e^{i\vec{k}\cdot\vec{r}} - \frac{m}{2\pi\hbar^2}\int d^3\vec{r}'\frac{e^{ikr}e^{-ik\vec{e}_r\cdot\vec{r}'}}{r}V(r')\psi_k(\vec{r}') = e^{i\vec{k}\cdot\vec{r}} + f\frac{e^{ikr}}{r}$$

$$\text{where } f(\theta) = -\frac{m}{2\pi\hbar^2}\int d^3\vec{r}' e^{-ik\vec{r}'\cdot\vec{e}_r}V(r')\psi_k(\vec{r}')$$

has no φ dependence for a spherical potential.

6.5 Born approximation

We now want to solve equation (3) iteratively with an ansatz

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \sum_{n=1}^{\infty}\int d^3\vec{r}' K_n(\vec{r},\vec{r}')e^{i\vec{k}\cdot\vec{r}'}$$

with K_n:

$$K_1(\vec{r},\vec{r}') = g_k^+(\vec{r}-\vec{r}')V(\vec{r}')$$

$$K_n(\vec{r},\vec{r}') = \int d^3r'' K_{n-1}(\vec{r}'',\vec{r}')K_1(\vec{r},\vec{r}'') + \mathcal{O}(V^{m>n})$$

This can then be used to evaluate $f(\theta)$:

$$f^{(1)}(\theta) = -\frac{m}{2\pi\hbar^2}\int_0^{2\pi} d\phi \int_{-1}^{+1} d(\cos\vartheta) \int_0^{\infty} dr' r'^2 V(r') e^{iqr'\cos\vartheta}$$

Here ϑ is an integration variable and θ is the scattering angle, i.e. the angle between the vector $\vec{k}' = k\vec{e}_r$ and $\vec{k} = k\vec{e}_z$, where $\vec{k}' + \vec{q} = \vec{k}$ and $q = 2k\sin\frac{\theta}{2}$

$$f^{(1)}(\theta) = -\frac{m}{\hbar^2}\int_0^{\infty} r'^2 V(r')\frac{2\sin(qr')}{qr'}dr' = -\frac{2m}{\hbar^2}\frac{1}{q}\int_0^{\infty} dr' V(r') r' \sin(qr')$$

Yukawa potential: $V(r) = \frac{V_0}{\mu}\frac{e^{-\mu r}}{r}$ where μ gives the order of magnitude of the range of interaction.

$$f^{(1)}(\theta) = -\frac{2m}{\hbar^2}\frac{1}{q}\frac{V_0}{\mu}\int_0^{\infty} dr' e^{-\mu r'}\sin(qr') = -\frac{2m}{\hbar^2}\frac{V_0}{\mu}\frac{1}{\mu^2+q^2}$$

$$\implies \frac{d\sigma}{d\Omega} \approx \left|f^{(1)}(\theta)\right|^2 = \left(\frac{2mV_0}{\mu\hbar^2}\right)^2 \frac{1}{(\mu^2 + 2k^2(1-\cos\theta))^2}$$

7 General scattering theory

Here we work in any representaion $|\Psi(t)\rangle$ in some Hilbert space (not necesarily wave function $\Psi(\vec{r}, t)$)

7.1 Dynamics of scattering

We start with the time-dependent Schrödinger equation:

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

with $H = H_0 + V$, where we assume that V is time independent. Now we get an equation:

$$\left(i\hbar\frac{\partial}{\partial t} - H_0\right)|\Psi(t)\rangle = V|\Psi(t)\rangle \equiv |\alpha(t)\rangle$$

This can be seen as an inhomogeneous differential equation in t.
Definition: The free Green operator $G_0^{\pm}(t,t')$ is defined through

$$\left(i\hbar\frac{\partial}{\partial t} - H_0\right)G_0(t,t') = \delta(t-t')\mathbb{I} \qquad \text{(all operators!!)} \tag{5}$$

Solutions:

$$G_0^+(t,t') = -\frac{i}{\hbar}\theta(t-t')\exp\left(-\frac{i}{\hbar}H_0(t-t')\right)$$

This object is called the retarded Green operator. There is also an advanced Green operator:

$$G_0^-(t,t') = +\frac{i}{\hbar}\theta(t'-t)\exp\left(-\frac{i}{\hbar}H_0(t-t')\right)$$

Proof:

$$i\hbar\frac{\partial}{\partial t}G_0^+(t,t') = \frac{\partial}{\partial t}\theta(t-t')\exp\left(-\frac{i}{\hbar}H_0(t-t')\right)$$

$$= \delta(t-t')\exp\left(-\frac{i}{\hbar}H_0(t-t')\right) + \theta(t-t')\frac{-i}{\hbar}H_0\exp\left(-\frac{i}{\hbar}H_0(t-t')\right)$$

$$= \delta(t-t') + H_0 G_0^+(t,t')$$

- The + and − are "the same" as in Section 6 (to be confirmed)
- $G_0^{\pm}(t,t') = G_0^{\pm}(t-t')$

The (formal) solution to the time-dependent Schrödinger equation is

$$\left|\Psi^{\pm}(t)\right\rangle = |\Psi_0(t)\rangle + \int dt' G_0^{\pm}(t-t') V \left|\Psi^{\pm}(t')\right\rangle \tag{6}$$

$|\Psi^+(t)\rangle$ goes for $t \to -\infty$ into the free state $|\Psi_0(t)\rangle$.
$|\Psi^-(t)\rangle$ goes for $t \to +\infty$ into the free state $|\Psi_0(t)\rangle$.
Connection to Section 6: recall $\lim_{r\to\infty} rV(r) = 0$.
To make contact with Section 6, we make a Fourier transform ($t \to E$).

$$G_0^+(E) = \int_{-\infty}^{+\infty} dt e^{\frac{i}{\hbar}Et} G_0^{\pm}(t,t') = -\frac{i}{\hbar}\int_0^{\infty} dt e^{\frac{i}{\hbar}Et} e^{-\frac{i}{\hbar}H_0 t}$$

We replace E by $E + i0^+$ with $0^+ > 0$ to ensure converence of the t integration

$$\lim_{0^+\searrow 0}\left(-\frac{i}{\hbar}\int_0^{\infty} dt e^{\frac{i}{\hbar}(E+i0^+)t} e^{-\frac{i}{\hbar}H_0 t}\right) = \frac{1}{E - H_0 + i0^+} \equiv (E - H_0 + i0^+)^{-1}$$

$$G_0^-(E) = \frac{1}{E - H_0 - i0^+}$$

In an exercise, we will compare this to Section 6: $\tilde{G}_k = \left(E - \frac{\hbar q^2}{2m}\right)^{-1}$, Eq. (4).
Let α be a set of quantum numbers of H_0 (includes energy E_α). We now make the Fourier transform of Eq. (6):

$$\int dt e^{\frac{i}{\hbar}Et}\left|\Psi_\alpha^+(t)\right\rangle = \int dt e^{\frac{i}{\hbar}Et}\left|\Psi_\alpha^0(t)\right\rangle + \int dt e^{\frac{i}{\hbar}Et}\int dt' G_0(t,t') V \left|\Psi_\alpha^+(t)\right\rangle$$

Which implies that

$$\boxed{\left|\Psi_\alpha^+(E)\right\rangle = \left|\Psi_\alpha^0(E)\right\rangle + G_0(E) V \left|\Psi_\alpha^+(E)\right\rangle} \tag{7}$$

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$$\left|\Psi^{\pm}(t)\right\rangle = \left|\Psi^0(t)\right\rangle + \int dt' G_0^{\pm}(t-t') V \left|\Psi^{\pm}(t')\right\rangle$$

$$\to \left|\Psi_\alpha^{\pm}(E)\right\rangle = \left|\Psi_\alpha^0(E)\right\rangle + G_0^{\pm}(E) V \left|\Psi^{\pm}(E)\right\rangle \leftarrow \Psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \int dr' G(\vec{r}-\vec{r}') V \Psi_k(\vec{r}')$$

α are the quantum numbers of the operator H_0. $\left|\Psi_\alpha^0(E)\right\rangle$ is a well-defined eigenstate of H_0, $|\Psi_\alpha^{\pm}(E)\rangle$ is a well-defined eigenstate of H. In a way, we now have a generalized Lippmann-Schwinger equation. $G_0^{\pm}(E)$ is, from a functional point of view, the resolvent of H_0:

$$G_0^{\pm}(E) = \lim_{0^+\searrow 0} \frac{1}{E - H_0 \pm i0^+}.$$

What is always understood is that we should really work with normalizable states (wave packets or put system in a box): $|\Psi_f(t)\rangle = \int d^3\vec{k} f(k) e^{-\frac{i\hbar}{2m}\vec{k}^2} |\Psi^{\pm}\rangle$ where $f(k)$ is peaked at $k \sim E_\alpha$ or put system in a box. The "solution" to the equation is

$$\left|\Psi_\alpha^{\pm}\right\rangle = \underbrace{\frac{1}{1 - G_0^{\pm} V}}_{(1-G_0^{\pm}V)^{-1}} \left|\Psi_\alpha^0\right\rangle$$

$$(1-G_0^{\pm}V)^{-1} = (1-G_0^{\pm}V)^{-1}G_0^{\pm}(G_0^{\pm})^{-1} = \left[\left(G_0^{\pm}\right)^{-1}(1-G_0^{\pm}V)\right]^{-1}\left(G_0^{\pm}\right)^{-1}$$
$$= \left(\left(G_0^{\pm}\right)^{-1} - V\right)^{-1}\left(G_0^{\pm}\right)^{-1} = \frac{1}{E_\alpha - H_0 \pm i0^+ - V}(E_\alpha - H_0 \pm i0^+)$$

We then get

$$\left|\Psi_\alpha^{\pm}\right\rangle = \frac{1}{E_\alpha - H_0 \pm i0^+ - V}(E_\alpha - H_0 \pm i0^+)\left|\Psi_\alpha^0\right\rangle = \frac{1}{E_\alpha - H \pm i0^+}\left(E_\alpha - H_0 - V \pm i0^+ + V\right)\left|\Psi_\alpha^0\right\rangle$$

$$\left|\Psi_\alpha^{\pm}\right\rangle = \left(1 + G^{\pm}(E)V\right)\left|\Psi_\alpha^0\right\rangle \tag{8}$$

This is a relation between a full state $|\Psi_\alpha^{\pm}(t)\rangle$ and a free state $\left|\Psi_\alpha^0\right\rangle$. It is a 'solution' to Eq. (7) at the price of having to know the full Green operator $G^{\pm}(E)$.

This can also be obtained starting from

$$\left|\Psi^{\pm}(t)\right\rangle = \lim_{t'\to\mp\infty} i\hbar G^{\pm}(t-t')\left|\Psi_0(t')\right\rangle$$

with

$$G^{+}(t-t') = -\frac{i}{\hbar}\theta(t-t')e^{-\frac{i}{\hbar}H(t-t')}$$
$$G^{-}(t-t') = +\frac{i}{\hbar}\theta(t'-t)e^{-\frac{i}{\hbar}H(t-t')}$$

which do satisfy

$$(i\hbar\frac{\partial}{\partial t} - H)G^{\pm}(t-t') = \delta(t-t')\cdot\mathbb{I}$$

(compare to Eq. (5)) $|\Psi^{+}(t)\rangle$ evolves with the full Hamiltonian H but is equal to the free state $|\Psi_0\rangle$ for $t\to-\infty$. $|\Psi^{-}(t)\rangle$ is a full state, is equal to free state for $\left|\Psi^0\right\rangle$ for $t\to+\infty$. Exercise: Show:

$$\left|\Psi^{\pm}(t)\right\rangle = \left|\Psi^0(t)\right\rangle + \int dt' G^{\pm}(t-t')V\left|\Psi_0(t')\right\rangle$$

WARNING: many subtle issues: it is not clear whether these operators exist, it is not clear whether there is always a unique connection $|\Psi^{\pm}\rangle$ and $\left|\Psi^0\right\rangle$, but it is still the basic assumption of scattering theory. (not always the case: Coulomb scattering, strong interaction, many more).

7.2 Möller operators & scattering operator

α is a complete set of quantum numbers:

$$H_0\left|\Psi_\alpha^0\right\rangle = E_\alpha\left|\Psi_\alpha^0\right\rangle \qquad\qquad H_\alpha\left|\Psi_\alpha^{\pm}\right\rangle = E\left|\Psi_\alpha^{\pm}\right\rangle$$

We then consider again

$$\left|\Psi_\alpha^{\pm}\right\rangle = \left|\Psi_\alpha^0\right\rangle + \underbrace{(E_\alpha - H_0 \pm i0^+)^{-1}\mathbb{I}V\left|\Psi_\alpha^{\pm}\right\rangle}_{\text{expand in basis }\left|\Psi_\alpha^0\right\rangle}$$

we then set $\mathbb{I} = \int d\beta \left|\Psi_\beta^0\right\rangle\left\langle\Psi_\beta^0\right|$. This then leads to

$$\left|\Psi_\alpha^{\pm}\right\rangle = \left|\Psi_\alpha^0\right\rangle + \int d\beta \frac{T_{\beta\alpha}^{\pm}\left|\Psi_\beta^0\right\rangle}{E_\alpha - E_\beta \pm i0^+} \qquad \text{with transfer matrix } T_{\beta\alpha}^{\pm} = \left\langle\Psi_\beta^0\right|V\left|\Psi_\alpha^{\pm}\right\rangle$$

This state satisfies

$$e^{-\frac{i}{\hbar}E_\alpha\tau}\left|\Psi_\alpha^{\pm}\right\rangle \to^{\tau\to\mp\infty} e^{-\frac{i}{\hbar}E_\alpha\tau}\left|\Psi_\alpha^0\right\rangle$$

$$e^{-\frac{i}{\hbar}H\tau}\left|\Psi_\alpha^\pm\right\rangle \leftrightarrow e^{-\frac{i}{\hbar}H_0\tau}\left|\Psi_\alpha^0\right\rangle$$

$$\left|\Psi_\alpha^\pm\right\rangle = \lim_{\tau\to\mp\infty} e^{\frac{i}{\hbar}H\tau}e^{-\frac{i}{\hbar}H_0\tau}\left|\Psi_\alpha^0\right\rangle = \Omega^\pm\left|\Psi_\alpha^0\right\rangle$$

where $\Omega^\pm$ is the Møller operator. Now we turn to a typical scattering experiment. At $t=-\infty$ prepare an eigenstate (or a superposition of eigenstates) of H_0 with quantum numbers α
Q: What is the amplitude for this state to evolve (scatter) into an eigenstate of H_0 with quantum numbers β (at $t\to+\infty$)
The Answer:

$$\left\langle\Psi_\beta^-\middle|\Psi_\alpha^+\right\rangle = \left\langle\Psi_\beta^0\middle|\underbrace{\left(\Omega^-\right)^\dagger\Omega^+}_{\equiv S:\ \text{scattering operator}}\middle|\Psi_\alpha^0\right\rangle = \left\langle\Psi_\beta^0\middle|S\middle|\Psi_\alpha^0\right\rangle$$

with

$$S = \lim_{\tau\to\infty\&\tau_0\to-\infty} e^{\frac{i}{\hbar}H_0\tau}e^{-\frac{i}{\hbar}H(\tau-\tau_0)}e^{-\frac{i}{\hbar}H_0\tau_0} = \lim_{\tau\to\infty\&\tau_0\to-\infty} U(\tau,\tau_0) = U(\infty,-\infty)$$

This is the evolution operator in the interaction picture (Section 4) and

$$i\hbar\frac{dU(\tau,\tau_0)}{d\tau} = e^{\frac{i}{\hbar}H_0\tau}(H-H_0)e^{\frac{i}{\hbar}H(\tau_0-\tau)}e^{-\frac{i}{\hbar}H_0\tau} = V(\tau)U(\tau,\tau_0)$$

where $V(\tau)$ is the interaction in the interaction picture. The solution of the differential equation can be looked up in Section 4:

$$U(\tau,\tau_0) = T\left(\exp-\frac{i}{\hbar}\int_{\tau_0}^{\tau}d\tau' V(\tau')\right)$$

$$S = U(\infty,-\infty) = 1 - \frac{i}{\hbar}\int_{-\infty}^{+\infty}dt_1 V(t_1) + \left(-\frac{i}{\hbar}\right)^2\int_{-\infty}^{+\infty}dt_1\int_{-\infty}^{t_1}dt_2 V(t_1)V(t_2) + ...$$

If the perturbation V is small (whatever this means) the terms in this series become smaller and smaller.
$SS^\dagger = \mathbb{I}$ is unitary
S-matrix:

$$S_{\beta\alpha} = \left\langle\Psi_\beta^0\middle|S\middle|\Psi_\alpha^0\right\rangle = \left\langle\Psi_\beta^-\middle|\Psi_\alpha^+\right\rangle$$

either: insert S

$$1^{\text{st}}\text{ term: }\left\langle\Psi_\beta^0\middle|1\middle|\Psi_\alpha^0\right\rangle = \delta(\beta-\alpha) \qquad \text{orthogonality of } \left|\Psi_\alpha^0\right\rangle$$

$$2^{\text{nd}}\text{ term: } -\frac{i}{\hbar}\int_{-\infty}^{\infty}dt_1\left\langle\Psi_\beta^0\middle|e^{\frac{i}{\hbar}H_0t_1}Ve^{-\frac{i}{\hbar}H_0t}\middle|\Psi_\alpha^0\right\rangle = -\frac{i}{\hbar}\int_{-\infty}^{+\infty}dt_1 e^{-\frac{i}{\hbar}(E_\alpha-E_\beta)t_1}\left\langle\Psi_\beta^0\middle|V\middle|\Psi_\alpha^0\right\rangle$$
$$= -2i\pi\delta(E_\alpha-E_\beta)V_{\beta\alpha}$$

The 3rd and the 4th term will be covered in the exercises.
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$$\left|\Psi_\alpha^\pm\right\rangle = (1+G^\pm V)\left|\Psi_\alpha^0\right\rangle$$

$$\left|\Psi_\alpha^\pm\right\rangle = \lim_{\tau\to\mp\infty} e^{\frac{i}{\hbar}H\tau}e^{-\frac{i}{\hbar}H_0\tau}\left|\Psi_\alpha^0\right\rangle = \Omega^\pm\left|\Psi_\alpha^0\right\rangle$$

$$\left\langle\Psi_\beta^-\middle|\Psi_\alpha^+\right\rangle = \left\langle\Psi_\beta^0\middle|S\middle|\Psi_\alpha^0\right\rangle \propto \delta(E_\alpha-E_\beta) \qquad \text{with } S=U(\infty,-\infty)$$

either: $\delta(\beta-\alpha) - 2i\pi\delta(E_\alpha-E_\beta)V_{\beta\alpha} +$ higher order
or: $H\left|\Psi_\alpha^+\right\rangle = (H_0+V)\left|\Psi_\alpha^0\right\rangle + (H-E_\alpha+E_\alpha)G^+V\left|\Psi_\alpha^0\right\rangle = E_\alpha\left|\Psi_\alpha^0\right\rangle + V\left|\Psi_\alpha^0\right\rangle + E_\alpha G^+V\left|\Psi_\alpha^0\right\rangle -$

$V\left|\Psi_\alpha^0\right\rangle = E_\alpha(\left|\Psi_\alpha^0\right\rangle + G^+V\left|\Psi_\alpha^0\right\rangle) = E_\alpha\left|\Psi_\alpha^+\right\rangle$, where we remember that $G^+ = (E_\alpha - H + i0^+)^{-1}$.

$$\left|\Psi_\alpha^-\right\rangle - \left|\Psi_\alpha^+\right\rangle = (G^-(E_\alpha) - G^+(E_\alpha))V\left|\Psi_\alpha^0\right\rangle$$
$$\left\langle\Psi_\alpha^-\right| - \left\langle\Psi_\alpha^+\right| = \left\langle\Psi_\alpha^0\right| V(G^+ - G^-)$$

$$S_{\beta\alpha} = \left\langle\Psi_\beta^-\middle|\Psi_\alpha^+\right\rangle = \left(\left\langle\Psi_\beta^+\right| + \left\langle\Psi_\beta^0\right| V(G^+ - G^-(E_\beta))\right)\left|\Psi_\alpha^+\right\rangle = \delta(\alpha-\beta) - 2i\pi\delta(E_\alpha - E_\beta)\left\langle\Psi_\beta^0\middle|V\middle|\Psi_\alpha^+\right\rangle$$

For the last step we use $G^+(E_\beta) - G^-(E_\beta)$:

$$G^+ - G^- = \frac{1}{E_\beta - H + i0^+} - \frac{1}{E_\beta - H - i0^+} = \frac{1}{E_\beta - E_\alpha + i0^+} - \frac{1}{E_\beta - E_\alpha - i0^+}$$

$$= \frac{-2i0^+}{(E_\beta - E_\alpha)^2 + (0^+)^2} = -2i\pi\delta(E_\alpha - E_\beta) \text{ using } \lim_{\epsilon\to 0}\frac{1}{\pi}\frac{\epsilon^2}{x^2+\epsilon^2} = \delta(x)$$

We then get:

$$S_{\beta\alpha} = \delta(\beta - \alpha) - 2i\pi\delta(E_\alpha - E_\beta)\left\langle\Psi_\beta^0\middle|V\middle|\Psi_\alpha^+\right\rangle$$

8 Quantisation of the radiation field

8.1 Quantisation of the free photon field

We will here do all the details of this. We recall Section 5.1. This will start with a bit of repetition.

$$\vec{A}(\vec{r},t) = \int \frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda \left(\alpha(k,\lambda)\vec{\epsilon}(\vec{k},\lambda)e^{i\vec{k}\cdot\vec{r}-i\omega_k t} + \alpha^*(\vec{k},\lambda)\vec{\epsilon}^*(\vec{k},\lambda)e^{-i\vec{k}\cdot\vec{r}+i\omega_k t}\right)$$

$$\text{with } \omega_k = c\left|\vec{k}\right| \text{ and 2 polarizations}$$

For each fixed $\vec{k}$ and λ: $q(t) = \alpha(k,\lambda)e^{-i\omega_k t}$ with $\ddot{q} = -\omega_k^2 q$. So for each choice of $\vec{k}$ and λ we get an harmonic oscillator, so we have a two times infinitely many harmonic oscillators sum. So let's quantize these harmonic oscillators.
Now we recall the quantization of the harmonic oscillator: $\hat{H} = \frac{\hbar\omega}{2}\left(\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\right)$. In the next few formulae, operators will be written with a hat. The states of the harmonic oscillator are $|0\rangle$ and $|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle$. This then gives us a basis of our Hilbert space. Furthermore we get the counting operator $\hat{N} = \hat{a}^\dagger\hat{a}$ with $\hat{N}|n\rangle = n|n\rangle$. Outlook: Take classical field $\vec{A}$ and make it an operator: $\hat{\vec{A}}$. The Hilbert space in which the $\hat{\vec{A}}$ lives is the Fock space. (see Section 8.2)
We want an interpretation of $\vec{A}$ as a collection of independent harmonic oscillators.
Cross-checks: $\boxed{1}$: compute energy:

$$H = \frac{1}{8\pi}\int d^3\vec{r}\left(\vec{E}^2 + \vec{B}^2\right)$$

$$\vec{E} = -\frac{1}{c}\frac{d\vec{A}}{dt} = \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda\left(\alpha\vec{\epsilon}\frac{i\omega}{c}e^{-i\omega t+i\vec{k}\cdot\vec{r}} - \alpha^*\vec{\epsilon}^*\frac{i\omega}{c}e^{+i\omega t-i\vec{k}\cdot\vec{r}}\right)$$

Now:

$$\int d^3\vec{r}\left|\vec{E}\right|^2 = \int d^3\vec{r}\int\frac{d^3\vec{k}}{(2\pi)^3}\int\frac{d^3\vec{k}'}{(2\pi)^3}\sum_{\lambda\lambda'}\left(\alpha\alpha'\vec{\epsilon}\cdot\vec{\epsilon}'\frac{-\omega\omega'}{c^2}e^{-i(\omega+\omega')t}e^{i(\vec{k}+\vec{k}')\cdot r}\right.$$

$$\left.+\alpha^*\alpha'^*\vec{\epsilon}^*\cdot\vec{\epsilon}'^*\frac{-\omega\omega'}{c^2}e^{+i(\omega+\omega')t}e^{-i(\vec{k}+\vec{k}')\cdot\vec{r}} - \alpha^*\alpha'\vec{\epsilon}^*\cdot\vec{\epsilon}'\frac{-\omega\omega'}{c^2}e^{-i(\omega'-\omega)t}e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}\right.$$

$$-\alpha\alpha'^{*}\vec{\epsilon}\cdot\vec{\epsilon}'^{*}\frac{-\omega\omega'}{c^2}e^{-i(\omega-\omega')t}e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\Bigg)$$

In this integration, the $\vec{r}$-dependences lead to δ-functions: $\int d^3\vec{r}e^{i(\vec{k}-\vec{k}')\cdot r} = (2\pi)^3\delta(\vec{k}-\vec{k}')$ and $\int d^3\vec{r}e^{i(\vec{k}+\vec{k}')\cdot r} = (2\pi)^3\delta(\vec{k}+\vec{k}')$. Furthermore with the δ, we can simplify the $\vec{\epsilon}$: $\vec{\epsilon}(\vec{k},\lambda)\cdot\vec{\epsilon}(\vec{k}',\lambda') = \delta_{\lambda\lambda'}$.We then use this to integrate out $\vec{k}'$:

$$\int d^3\vec{r}\left|\vec{E}\right|^2 = \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda\frac{\omega^2}{c^2}\left(\alpha(k,\lambda)\alpha^*(k,\lambda)+\alpha^*(k,\lambda)\alpha(k,\lambda)+\ \text{2 more terms }\right)$$

$$\int d^3\vec{r}\left|\vec{B}\right|^2 = \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda\frac{\omega^2}{c^2}\left(\underbrace{\alpha\alpha^*+\alpha^*\alpha}_{=2\alpha\alpha^*}-\text{ 2 more terms}\right)\ \text{(exercise)}$$

Then we plug everything together (exercise):

$$H = \frac{1}{8\pi}\int d^3\vec{r}\left(\left|\vec{E}\right|^2+\left|\vec{B}\right|^2\right) = \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda\frac{\omega^2}{4\pi c^2}\left(\alpha(\vec{k},\lambda)\alpha^*(\vec{k},\lambda)+\alpha^*(\vec{k},\lambda)\alpha(\vec{k},\lambda)\right)$$

We then define $a(\vec{k},\lambda) = \sqrt{\frac{\omega}{2\pi\hbar c^2}}\alpha(\vec{k},\lambda)$ and $a^*(\vec{k},\lambda) = \sqrt{\frac{\omega}{2\pi\hbar c^2}}\alpha^*(\vec{k},\lambda)$ We use this to rewrite the vector potential $\vec{A}$:

$$\vec{A}(\vec{r},t) = \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda\frac{2\pi\hbar c^2}{\omega}\left(a(\vec{k},\lambda)\vec{\epsilon}(\vec{k},\lambda)e^{i\vec{k}\cdot\vec{r}-i\omega t}+a^*\vec{\epsilon}^{*}e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right)$$

$$H = \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda\frac{\hbar\omega}{2}\left(a(\vec{k},\lambda)a^*(\vec{k},\lambda)+a^*(\vec{k},\lambda)a(\vec{k},\lambda)\right)$$

H is a sum of (infinitely many) harmonic oscillators (for each $\vec{k}$, λ). In case you are bothered by the fact that we have more than countable infinitely many oscillators, put the system into a box $\to$ discretized momentum $\to$ countably many oscillators.
Also:

$$\vec{P} = \frac{1}{4\pi c}\int d^3\vec{r}\left(\vec{E}\wedge\vec{B}\right) = ... = \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda\hbar k a^*(\vec{k},\lambda)a(\vec{k},\lambda)$$

2^{nd} Quantization
So far, $\vec{A}$, H, a, a^* are (classical) functions. Now we promote them to operators in Fock space. Now we interpret:

$$\text{Now interpret }\begin{cases}a(\vec{k},\lambda)\to\hat{a}(\vec{k},\lambda)=\hat{a}_{k\lambda}\\ a^*(\vec{k},\lambda)\to\hat{a}^\dagger(\vec{k},\lambda)=\hat{a}^\dagger_{k\lambda}\end{cases}\quad\text{as operators: ladder/creation ops.}$$

The commutation relations for these operators are:

$$\left[\hat{a}_{k\lambda},\hat{a}^\dagger_{k'\lambda'}\right] = (2\pi)^3\delta(\vec{k}-\vec{k}')\delta_{\lambda\lambda'}$$

$$[\hat{a}_{k\lambda},\hat{a}_{k'\lambda'}] = \left[\hat{a}^\dagger_{k\lambda},\hat{a}^\dagger_{k'\lambda'}\right] = 0$$

We have a $\delta(\vec{k}-\vec{k}')$ because $\vec{k}$ is continuous, if we put the system into a box, we get a $\delta_{\vec{k},\vec{k}'}$.
We have infinitely many harmonic oscillators. The classical field has now become a quantum field.

$$\vec{A}(\vec{r},t)\to\hat{\vec{A}}(\vec{r},t)$$

$$V(\vec{r},t) \to \hat{V}(\vec{r},t)$$

These are operators in the Fock space.
Now, we do a few more cross-checks to find out whether the thing we have written down makes sense. To do this we do a bit of classical field theory. We start with the Lagrangian:

$$\mathcal{L} = \frac{1}{16\pi} F_{\mu\nu}F^{\mu\nu} = \frac{1}{8\pi}\left(\left|\vec{E}\right|^2 - \left|\vec{B}\right|^2\right) \qquad \text{with } F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$$

Then we calculate the conjugate momentum field

$$\vec{\pi} = \frac{\partial \mathcal{L}}{\partial \dot{\vec{A}}} = ... = -\frac{1}{4\pi}\vec{E}$$

After 2nd quantization, $\vec{A}$ and $\vec{\pi}$ become operators: $\hat{\vec{A}}$ and $\hat{\vec{\pi}}$. In a exercise, we will calculate what is called the "equal time commutation relations".

$$\left[\hat{A}_i(\vec{r},t), \hat{A}_j(\vec{r}',t)\right] = [\hat{\pi}_i(\vec{r},t), \hat{\pi}_j(\vec{r}',t)] = 0$$

$$\left[\hat{A}_i(\vec{r},t), \hat{\pi}_j(\vec{r}',t)\right] \underbrace{=}_{\uparrow} \delta_{ij} i\hbar\delta(\vec{r}-\vec{r}')$$

Exercise subltety: $i\hbar \int \frac{d^3\vec{k}}{(2\pi)^3} \left(\delta_{ij} - \underbrace{\frac{k_i k_j}{k^2}}_{\vec{k}\cdot\vec{A}=0 \Leftrightarrow \nabla\cdot\vec{A}=0}\right) e^{i(\vec{r}-\vec{r}')\cdot\vec{k}} \equiv \delta^{\text{tr}}(\vec{r}-\vec{r}')$
remminiscent of $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$ and $[\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0$.

8.2 Fock space

After 2nd quantization, $\hat{\vec{A}}$ (and $\hat{H}$) are operators given in terms of the creation ($\hat{a}^\dagger_{k\lambda}$) and annihilation ($\hat{a}_{k\lambda}$) operators (ladder operators). We now construct a Hilbert space where they act. Start with state $|0\rangle$, defined by $\hat{a}_{\vec{k}\lambda}|0\rangle = 0\ \forall \vec{k},\lambda$. $|0\rangle$ is a state with no photon. The one photon state is then given by $\left|1(\vec{k},\lambda)\right\rangle = \hat{a}^\dagger_{\vec{k},\lambda}|0\rangle$, which then contains one photon of momentum $\hbar\vec{k}$ and polarization λ. A general state is given by:

$$\left|n_1(\vec{k}_1,\lambda_1)n_2(\vec{k}_2,\lambda_2)...n_m(\vec{k}_m,\lambda_m)\right\rangle = \frac{\left(\hat{a}^\dagger_{\vec{k}_1,\lambda_1}\right)^{n_1}\left(\hat{a}^\dagger_{\vec{k}_2,\lambda_2}\right)^{n_2}...\left(\hat{a}^\dagger_{\vec{k}_m,\lambda_m}\right)^{n_m}}{\sqrt{n_1!n_2!\cdots n_m!}}|0\rangle$$

Furthermore we can increase the number of photons in a certain state:

$$\hat{a}^\dagger_{\vec{k}_j\lambda_j}\left|n_1(\vec{k}_1,\lambda_1)....n_j(\vec{k}_j\lambda_j)...\right\rangle = \sqrt{n_j+1}\left|n_1(\vec{k}_1,\lambda_1)....(n_j+1)(\vec{k}_j,\lambda_j)...\right\rangle$$

Now look at:

$$\int \frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda \hat{a}_{\vec{k},\lambda}\left|n_1(\vec{k}_1,\lambda_1\right\rangle = \frac{1}{\sqrt{n_1!}}\int \frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda \hat{a}_{k,\lambda}\left(\hat{a}^\dagger_{k_1,\lambda_1}\right)^{n_1}|0\rangle$$

Aside: $a(a^\dagger)^n = aa^\dagger(a^\dagger)^{n-1} = [a,a^\dagger](a^\dagger)^{n-1} + a^\dagger a(a^\dagger)^{n-1} = [a,a^\dagger](a^\dagger)^{n-1} + a^\dagger[a,a^\dagger](a^\dagger)^{n-2} + (a^\dagger)^2 a(a^\dagger)^{n-2} = 2[a,a^\dagger](a^\dagger)^{n-1} + (a^\dagger)^2 a(a^\dagger)^{n-2} = ... = n[a,a^\dagger](a^\dagger)^{n-1} + (a^\dagger)^n a$

$$= \frac{1}{\sqrt{n_1!}}\int \frac{d^3\vec{k}}{(2\pi)^3}\sum_\lambda \left(n_1(2\pi)^3\delta_{\lambda\lambda_1}\delta(\vec{k}-\vec{k}_1)\right)\left(a^\dagger_{k_1,\lambda_1}\right)^{n-1}|0\rangle$$

$$= \frac{n_1}{\sqrt{n_1!}} \left(a^\dagger_{k_1\lambda_1}\right)^{n-1} |0\rangle = \sqrt{n_1} \left|(n_1-1)(\vec{k}_1,\lambda_1)\right\rangle$$

$$\int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda a_{\vec{k}\lambda} \left|1(\vec{k}_1,\lambda_1)1(\vec{k}_2,\lambda_2)\right\rangle = \int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda a_{k\lambda} a^\dagger_{k_1\lambda_1} a^\dagger_{k_2\lambda_2} |0\rangle$$

Aside: $(aa^\dagger\tilde{a}^\dagger = [a,a^\dagger]\tilde{a}^\dagger + a^\dagger a\tilde{a}^\dagger = [a,a^\dagger]\tilde{a}^\dagger + a^\dagger[a,\tilde{a}^\dagger] + a^\dagger\tilde{a}^\dagger a)$ We then use this

$$\int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda (2\pi)^3 \left(\delta(\vec{k}-\vec{k}_1)\delta_{\lambda\lambda_1}\hat{a}^\dagger_{k_2\lambda_2} + \delta(\vec{k}-\vec{k}_2)\delta_{\lambda\lambda_2}\hat{a}^\dagger_{k_1\lambda_1}\right)|0\rangle = |1(k_1,\lambda_1)\rangle + |1(k_2,\lambda_2)\rangle$$

In general we get the formula :

$$\int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda \hat{a}_{k\lambda} |n_1, n_2, ..., n_m\rangle = \sum_{i=1}^m \sqrt{n_i} |n_1, ..., n_i - 1, ..., n_m\rangle$$

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$$\left[\hat{a}_{k\lambda}, \hat{a}^\dagger_{k'\lambda'}\right] = (2\pi)^3 \delta_{\lambda,\lambda'} \delta(\vec{k}-\vec{k}')$$

$$a^\dagger_{k\lambda} |n_1(k_1,\lambda_1)...n_m(k_m,\lambda_m)\rangle = \sqrt{n+1}\, |n_1(k_1,\lambda_1)...(n+1)(k,\lambda)...n_m(k_m,\lambda_m)\rangle$$

$$\int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda a_{k,\lambda} |n_1...n_m\rangle = \sum_{i=1}^m \sqrt{n_1} |n_1, ..., n_i - 1, ...n_m\rangle$$

Consider now the expectation value of $\hat{H}$ in a particular state: $\left|n_1(\vec{k}_1,\lambda_1)\right\rangle$

$$\left\langle n_1 \middle| \hat{H} \middle| n_1 \right\rangle = \int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda \frac{\hbar\omega_k}{2} \left\langle n_1(\vec{k}_1,\lambda_1) \middle| \underbrace{\hat{a}_{k,\lambda}\hat{a}^\dagger_{k,\lambda}}_{\hat{a}^\dagger_{k\lambda}\hat{a}_{k\lambda}+\sim\delta(0)} + \hat{a}^\dagger_{k,\lambda}\hat{a}_{k,\lambda} \middle| n_1(\vec{k}_1,\lambda_1 \right\rangle$$

In this formula, the $\delta(0)$ represents the ground state energy. What we want to calculate is the difference to the ground state.

$$\to \int \frac{d^3\vec{k}}{(2\pi)^3} \sum_\lambda \hbar\omega \left\langle n_1 \middle| \hat{a}^\dagger_{k\lambda}\hat{a}_{k\lambda} \middle| n_1 \right\rangle = \hbar\omega_1 \sqrt{n_1} \left\langle n_1 \middle| \hat{a}^\dagger_{k\lambda_1} \middle| n_1 - 1 \right\rangle$$

$$= \hbar\omega_1 \sqrt{n_1}^2 \langle n_1 | n_1 \rangle = n_1 \hbar\omega_1 = \left\langle : \hat{H} : \right\rangle \text{ with } \omega(\vec{k}_1) = c\left|\vec{k}_1\right|$$

$$\left\langle n_1, n_2, ..., n_m \middle| \hat{H} \middle| n_1, n_2, ..., n_m \right\rangle = \sum_{j=1}^m \hbar\omega_j n_j + \infty(\text{Ground state})$$

Interaction of the 2nd quantized electromagnetic field $\hat{A}$ with matter (compare Section 5).
The potential

$$\hat{V} = -\frac{q}{2mc}(\underbrace{p\hat{A} + \hat{A}p}_{\text{in Coulomb gauge: } p\hat{A} = \hat{A}p}) + \frac{q^2}{2mc^2}\hat{A}^2$$

$\hat{V}$ is an operator in the Fock space. The matter fields are still described by "wave functions". The quantization of the matter will be treated in QFT. When computing S matrix elements:

$$V_{\beta\alpha} = \left\langle \Psi^0_\beta \middle| \hat{V} \middle| \Psi^0_\alpha \right\rangle \qquad \text{(Section 7.2)}$$

The photon part of Ψ^0_α lives in the Fock space.

8.3 Photon emission and absorption

Compare with 5.2.

$$\hat{H} = H_0 + \hat{V} + \hat{H}_{em} \text{ with } H_0 = \frac{p^2}{2m} + ... \text{ and } V : \text{Interaction with electromagnetic field}$$

$$\hat{H}_{em} = \frac{1}{8\pi} \int d^3\vec{r} \left(\left| \hat{\vec{E}} \right|^2 + \left| \hat{\vec{B}} \right|^2 \right)$$

The eigenstates $\left|\Psi_\alpha^0\right\rangle$ are eigenstates of $H_0 + \hat{H}_{em}$: $|\text{matter}\rangle \otimes |\text{photons}\rangle = |I; n_1, n_2, ..., n_m\rangle$, where the I-part belong to H_0 and the $n_1, ..., n_m$ belong to $\hat{H}_{em}$.
Absorption of a photon

$$\left\langle F; (n-1)(\vec{k}, \lambda) \middle| \hat{V} \middle| I; n(\vec{k}, \lambda) \right\rangle$$

The system loses one photon, the initial state has n photons with $\vec{k}$, λ, the final state has $(n-1)$ photons. For this to happen we need exactly one $\hat{a}$ in $\hat{V}$. The Fock space part is:

$$\left\langle (n-1)(\vec{k}, \lambda) \middle| \hat{V} \middle| n(\vec{k}, \lambda) \right\rangle$$

$$= \frac{e}{mc} \int \frac{d^3\vec{k}'}{(2\pi)^3} \sum_{\lambda'} \sqrt{\frac{2\pi\hbar c^2}{\omega'}} \left\langle F; (n-1)(\vec{k}, \lambda) \middle| \hat{a}(\vec{k}', \lambda') \vec{p} \cdot \vec{\epsilon}(\vec{k}', \lambda') e^{i\vec{k}' \cdot \vec{r}} \middle| I; n(\vec{k}, \lambda) \right\rangle$$

Note that $\hat{a}^\dagger$-part yields zero and use that $\left\langle (n-1) \middle| \hat{a}(\vec{k}', \lambda') \middle| n(\vec{k}, \lambda) \right\rangle = \sqrt{n}(2\pi)^3 \delta_{\lambda\lambda'} \delta(\vec{k} - \vec{k}')$. Then we get:

$$= \frac{e}{m} \sqrt{\frac{2\pi\hbar}{\omega}} \sqrt{n} \, \langle F | \vec{p} \cdot \vec{\epsilon} | I \rangle$$

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We are looking at :

$$\langle F, (n-1)(k, \lambda) | V | I, n(k, \lambda) \rangle \text{ with } V = \frac{e}{mc} \vec{p} \cdot \hat{\vec{A}} + \frac{e^2}{2mc^2} \hat{\vec{A}}^2$$

where V is our perturbation. In the $\hat{\vec{A}}$, a single $\hat{a}_{k\lambda}$ sits.

$$\frac{e}{m} \sqrt{\frac{2\pi\hbar}{\omega}} \sqrt{n} \, \langle F | \vec{p} \cdot \vec{\epsilon}(k, \lambda) | I \rangle \, e^{i\vec{k} \cdot \vec{r} - i\omega t} \approx \frac{e}{m} \sqrt{\frac{2\pi\hbar}{\omega}} \sqrt{n} \, \langle F | \vec{p} \cdot \vec{\epsilon}(k, \lambda) | I \rangle \, e^{-i\omega t}$$

where we use the dipole approximation: $e^{i\vec{k} \cdot \vec{r}} \to 1$.
Emission of photon:
Again we have to calculate the matrix element $V_{\beta\alpha}$:

$$V_{\beta\alpha} = \langle F, (n+1)(k, \lambda) | V | I; n(k, \lambda) \rangle$$

From the V we will only get the contribution with a single $\hat{a}_{k,\lambda}^\dagger$. This then leads to:

$$V_{\beta\alpha} = ... = \frac{e}{m} \sqrt{\frac{2\pi\hbar}{\omega}} \sqrt{n+1} \, \langle F | \vec{p} \cdot \vec{\epsilon}^*(k, \lambda) | I \rangle \, e^{+i\omega t}$$

Now the wonder has happenend: in Section 5 we had that a atom not object to an external EM-field could not emit electromagnetic radiation. Now we see that spontaneous emission is possible (difference to Section 5). Now atoms can simply create photons, because this also works for $n = 0$! In section 5.2. (classical), the absorption-rate Γ_{n0} and the emission-rate Γ_{0n} were the same. Now, treated quantum mechanically, the fraction $\Gamma_{n0}/\Gamma_{0n} = \frac{n}{n+1}$. If you have a "proper" electromagnetic field, with a lot of photons, then $n \to \infty$ and $\Gamma_{n0} \to \Gamma_{0n}$

8.4 Scattering of photons by atoms

The initial state consists of an atom in the intitial state $|I\rangle$ and photon $\vec{k}_i\lambda_i$. For $t \to \infty$, we get the atom in the final state $|F\rangle$ and a photon in the final state $\vec{k}_f, \lambda_f$.
We have to compute

$$\left\langle F, 1(\vec{k}_f, \lambda_f)\right|V\left|I, 1(\vec{k}_i, \lambda_i\right\rangle \text{ with } V = \frac{e}{mc}\vec{p}\cdot\hat{\vec{A}} + \frac{e^2}{2mc^2}\hat{\vec{A}}^2$$

The only nonzero term is the one that creates the final photon and annihilates the inital photon: V must contain $\hat{a}(\vec{k}_i, \lambda_i)\hat{a}^\dagger(\vec{k}_f, \lambda_f)$. So the part $\propto \vec{p}\cdot\vec{A}$ does not contribute at first order, since it contains either $\hat{a}$ or $\hat{a}^\dagger$. But the term $\propto \hat{\vec{A}}^2$ does contribute at first order, since it contains term $\propto \hat{a}\hat{a}^\dagger$, so the term $\frac{e^2}{2mc^2}\hat{\vec{A}}^2$ contributes. The first order contribution is:

$$V^{(1)}_{\beta\alpha} = \left\langle F; 1(\vec{k}_f, \lambda_f)\right|\frac{e^2}{2mc^2}\vec{A}^2\left|I, 1(\vec{k}_i, \lambda_i)\right\rangle =$$

$$\frac{e^2}{2mc^2}\left\langle F; 1(\vec{k}_f, \lambda_f)\right|\int\frac{d^3\vec{k}}{(2\pi)^3}\int\frac{d^3\vec{k}'}{(2\pi)^3}\sum_{\lambda\lambda'}\left(a_k\vec{\epsilon}e^{i\vec{k}\cdot\vec{r}-i\omega t} + a^\dagger_k\vec{\epsilon}^* e^{-i\vec{k}\cdot\vec{r}+i\omega t}\right)$$

$$\left(a_{k'}\vec{\epsilon}e^{i\vec{k}'\cdot\vec{r}-i\omega' t} + a^\dagger_{k'}\vec{\epsilon}^* e^{-i\vec{k}'\cdot\vec{r}+i\omega' t}\right)\left|I, 1(\vec{k}_i, \lambda_i)\right\rangle\frac{2\pi\hbar c^2}{\sqrt{\omega\omega'}}$$

we need an $\hat{a}$ and an $\hat{a}^\dagger$. So we use e.g.:

$$\int\frac{d^3\vec{k}}{(2\pi)^3}\int\frac{d^3\vec{k}'}{(2\pi)^3}\sum_{\lambda\lambda'}\left\langle 1_f\left|a^\dagger_{k,\lambda}a_{k',\lambda'}\right|1_i\right\rangle F(k, k', \lambda, \lambda')$$

where F is a function of ks and λs, that contains the exponentials,....

$$= \int\frac{d^3\vec{k}}{(2\pi)^3}\sum_{\lambda}\left\langle 1_f\left|\hat{a}^\dagger_{k\lambda}\right|0\right\rangle F(k, k_i, \lambda, \lambda_i) = F(k_f, k_i, \lambda_f, \lambda_i)$$

We now use this for $V^{(1)}_{\beta\alpha}$:

$$V^{(1)}_{\beta\alpha} = \frac{e^2\hbar\pi}{m\sqrt{\omega_i\omega_f}}\left\langle F\left|\vec{\epsilon}(\vec{k}_i\lambda_i)\cdot\vec{\epsilon}^*(\vec{k}_f, \lambda_f)e^{i\vec{r}(\vec{k}_i-\vec{k}_f)}e^{-it(\omega_i-\omega_f)}\right|I\right\rangle \times 2 =$$

$$= \frac{2e^2\hbar\pi}{m\sqrt{\omega_i\omega_f}}\epsilon(\vec{k}_i\lambda_i)\cdot\vec{\epsilon}^*(\vec{k}_f, \lambda_f)e^{-it(\omega_i-\omega_f)}\left\langle F\left|e^{i\vec{r}(\vec{k}_i-\vec{k}_f)}\right|I\right\rangle$$

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We again look at the same process:

$$V^{(1)}_{\beta\alpha} = \frac{2e^2\hbar\pi}{m\sqrt{\omega_i\omega_f}}\epsilon(\vec{k}_i\lambda_i)\cdot\vec{\epsilon}^*(\vec{k}_f, \lambda_f)e^{-it(\omega_i-\omega_f)}\left\langle F\left|e^{i\vec{r}(\vec{k}_i-\vec{k}_f)}\right|I\right\rangle$$

We recall from section 7.2: $H = H_0 + V$,

$$S_{\beta\alpha} = \delta(\beta-\alpha) - \frac{i}{\hbar}\int_{-\infty}^{+\infty}dt_1 e^{-\frac{i}{\hbar}t_1(E_\alpha - E_\beta)}\left\langle\Psi^0_\beta\right|V\left|\Psi^0_\alpha\right\rangle$$

in our case we get for S at first order:

$$\to -\frac{i}{\hbar}\int dt_1 e^{-\frac{i}{\hbar}t_1(E_I+\hbar\omega_i-E_F-\hbar\omega_f)}\underbrace{\left(\frac{2e^2\hbar\pi}{m\sqrt{\omega_i\omega_f}}\vec{\epsilon}\cdot\vec{\epsilon}^*\left\langle F\right|...\left|I\right\rangle\right)}_{T^{(1)}}$$

in principle there are infinitely many more terms on the right, but for the moment we will not look at them. the integral over the first part (the exponential with the t_1) will result in a energy-conserving δ-function: $-2i\pi\delta(E_I + \hbar\omega_i - E_F - \hbar\omega_f)$. Now we use Fermi's Golden Rule (Section 4.2/3) and we calculate the transition rate in terms of T: The transition rate is then

$$\frac{2\pi}{\hbar} |T|^2 \rho$$

where ρ is the density of states of the continuum of states.
for $\frac{d\sigma}{d\Omega}$ within a certain energy range $\hbar\omega_f ....\hbar\omega_f + d(\hbar\omega_f)$.
The number of states $\frac{d^3\vec{k}_f}{(2\pi)^3} = \frac{k_f^2 dk_f d\Omega}{(2\pi)^3} = \frac{\omega_f^2 d\Omega}{(2\pi)^3 c^3 \hbar} d(\omega_f \hbar)$
$\rho(\omega_f) = \frac{\omega_f^2 d\Omega}{(2\pi)^3 c^3 \hbar}$. When we now assemble everything, we get:

$$\frac{d\sigma}{d\Omega} = \frac{1}{c}\frac{2\pi}{\hbar}|T|^2 \frac{\omega_f^2}{(2\pi)^3 c^3 \hbar} = \frac{e^4}{m^2c^4}\frac{\omega_f}{\omega_i}\left|\vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \langle F|...1....|I\rangle\right|^2 = \left(\frac{\alpha\hbar}{mc}\right)^2 \frac{\omega_f}{\omega_i}\left|\vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \langle F|...1....|I\rangle\right|^2$$

The one in the expectation value appears in the dipole approximation. We now want to express everything in terms of the fine structure constant, using that $\frac{e^4}{m^2c^4} = \left(\frac{\alpha\hbar}{mc}\right)^2$.
However, what we have found now, is NOT the full answer. Other terms, that are also proportional to $e^4 \propto \alpha^2$ are missing. We can also have "second order" contributions with $e\vec{p}\cdot\vec{A}$. So we will have to do second order perturbation theory.
<u>2nd order contributions</u>

$$S_{\beta\alpha} = ... + \left(\frac{-i}{\hbar}\right)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_\gamma e^{-\frac{i}{\hbar}(E_\gamma - E_\beta)t_1} e^{+\frac{i}{\hbar}(E_\gamma - E_\alpha)t_2} V_{\beta\gamma} V_{\gamma\alpha}$$

To do this we have to recall exercise sheet 9.

$$\left(\frac{-i}{\hbar}\right)^2 \int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_N e^{-\frac{i}{\hbar}(E_N - E_F)t_1} e^{-\frac{i}{\hbar}(E_I - E_N)t_2} \left(\frac{e}{mc}\right)^2$$

$$\times \int \frac{d^3\vec{k}}{(2\pi)^3} \int \frac{d^3\vec{k}'}{(2\pi)^3} \sum_{\lambda\lambda'} \frac{2\pi\hbar c^2}{\sqrt{\omega\omega'}} \left\langle F, 1(\vec{k}_f\lambda_f)\middle| a_k \vec{p}\cdot\vec{\epsilon}_k e^{\cdots} + a_k^\dagger \vec{p}\cdot\vec{\epsilon}_k e^{\cdots}\middle| N, n\right\rangle$$

$$\times \left\langle N, n\middle| a_{k'} \vec{p}\cdot\vec{\epsilon}_k e^{\cdots} + a_{k'}^\dagger \vec{p}\cdot\vec{\epsilon}_{k'} e^{\cdots}\middle| I, 1(k_i)\right\rangle$$

This only gives non-zero contribution if we have one $a^\dagger$ and one a. So we get only the contributions

- $\left\langle 1(\vec{k}_f)\middle| a_k^\dagger \middle| 0\right\rangle \left\langle 0\middle| a_{k'} \middle| 1(\vec{k}_i)\right\rangle$: 0 photons in the intermediate state γ
- $\left\langle 1(\vec{k}_f)\middle| a_k \middle| 1(\vec{k}_i)1(\vec{k}')\right\rangle \left\langle 1(\vec{k}_i)1(\vec{k}')\middle| a_{k'}^\dagger \middle| 1(\vec{k}_i)\right\rangle$: 2 photons in the intermediate state γ

We can draw diagrams of these two cases.
After putting everything together, you get (where we use the dipole approximation):

$$\left(\frac{-i}{\hbar}\right)^2 \int dt_1 \int dt_2 \sum_N \frac{2\pi\hbar c^2}{\sqrt{\omega_i\omega_f}} \cdot \Big(\langle F|\vec{p}\cdot\vec{\epsilon}_f^*|N_0\rangle \langle N_0|\vec{p}\cdot\vec{\epsilon}_i|I\rangle\, e^{-\frac{i}{\hbar}(...)t_1} e^{-\frac{i}{\hbar}(...)t_2}$$

$$+ \langle F|\vec{p}\cdot\vec{\epsilon}_i|N_2\rangle \langle N_2|\vec{p}\cdot\vec{\epsilon}_f^*|I\rangle\, e^{\frac{i}{\hbar}(...)t_1} e^{\cdots t_2} \Big)$$

After t_1 and t_2 integration

$$-2i\pi\delta(E_f + \hbar\omega_f - E_I - \hbar\omega_i) \frac{2\pi\hbar e^2}{m^2\sqrt{\omega_i\omega_f}} \cdot \left(\frac{\left\langle F\middle| \vec{p}\cdot\vec{\epsilon}_f^* e^{-i\vec{k}_f\cdot\vec{r}}\middle| N\right\rangle \left\langle N\middle| \vec{p}\cdot\vec{\epsilon}_i e^{i\vec{k}_i\cdot\vec{r}}\middle| I\right\rangle}{E_I + \hbar\omega_i - E_N} \right.$$

$$+\frac{\left\langle F\middle|\vec{p}\cdot\vec{\epsilon}_i e^{i\vec{k}_I\cdot\vec{r}}\middle|N\right\rangle\left\langle N\middle|\vec{p}\cdot\vec{\epsilon}_f^* e^{-i\vec{k}_f\cdot\vec{r}}\middle|I\right\rangle}{E_I-\hbar\omega_f-E_N}+m\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*\left\langle F\middle|e^{i(\vec{k}_i-\vec{k}_f)\cdot r}\middle|I\right\rangle\Bigg)$$

Here we have time-ordered perturbation theory.
If you would want to make a relativistic theory, you would feel bothered by the fact that time is a special coordinate in time-ordered treatment. In a relativistic theory, you would get rid of the time appearing explicitely, and get the Feynman diagrams.
The energy of the intermediate state is not the same as the initial state but $E_{\text{initial}} = E_{\text{final}}$ (an overall δ-function).
If you put all together, we get the marvelous Kramers Heisenberg formula:

$$\boxed{\frac{d\sigma}{d\Omega}=\left(\frac{\alpha\hbar}{mc}\right)^2\frac{\omega_f}{\omega_i}\left|\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*\langle F|I\rangle+\sum_N\frac{\left\langle F\middle|\vec{p}\cdot\vec{\epsilon}_f^*\middle|N\right\rangle\langle N|\vec{p}\cdot\vec{\epsilon}_i|I\rangle}{m(E_I-E_N+\hbar\omega_i)}+\frac{\langle F|\vec{p}\cdot\vec{\epsilon}_i|N\rangle\left\langle N\middle|\vec{p}\cdot\epsilon_f^*\middle|I\right\rangle}{m(E_f-\hbar\omega_f-E_N)}\right|^2}$$

Now we are looking at special cases:
special case 1: Rayleigh-scattering:
elastic scattering of light: $\omega_i=\omega_f$ and $|I\rangle=|F\rangle$ and $\hbar\omega\ll E_I-E_N$. What follows now is a bit of a exercise in commuting things around. What we want to do is combining the term with $\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*$ with the others:

$$\left\langle I\middle|\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*\middle|I\right\rangle=\frac{1}{i\hbar}\left\langle I\middle|\left[\vec{x}\cdot\vec{\epsilon}_f^*,\vec{p}\cdot\vec{\epsilon}_i\right]\middle|I\right\rangle=\frac{1}{i\hbar}\sum_N\left\langle I\middle|\vec{x}\cdot\vec{\epsilon}_f^*\middle|N\right\rangle\langle N|\vec{p}\cdot\vec{\epsilon}_i|I\rangle-\langle I|\vec{p}\cdot\vec{\epsilon}_i|N\rangle\left\langle N\middle|\vec{x}\cdot\vec{\epsilon}_f^*\middle|I\right\rangle$$

We then use that $\langle I|p|N\rangle=\frac{m}{i\hbar}\langle I|[x,H_0]|N\rangle=\frac{m(E_N-E_I)}{i\hbar}\langle I|x|N\rangle$

$$\left\langle I\middle|\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*\middle|I\right\rangle=\frac{1}{m}\sum_N\frac{1}{(E_N-E_I)}\left(\left\langle I\middle|\vec{p}\cdot\vec{\epsilon}_f^*\middle|N\right\rangle\langle N|\vec{p}\cdot\vec{\epsilon}_i|I\rangle+\langle I|\vec{p}\cdot\vec{\epsilon}_i|N\rangle\left\langle N\middle|\vec{p}\cdot\vec{\epsilon}_f^*\middle|I\right\rangle\right)$$

Furthermore we need a small helper calculation:

$$\frac{1}{E_N-E_I}+\frac{1}{E_I-E_N\pm\hbar\omega}=\frac{\pm\hbar\omega}{(E_I-E_N)^2}+\frac{(\hbar\omega)^2}{(E_I-E_N)^3}+...$$

from which in the Kramers Heisenberg equation the first term then cancels, since we have once a $-\hbar\omega$ and once a $+\hbar\omega$.
So we can then use this in the Kramers Heisenberg formula:

$$\left.\frac{d\sigma}{d\Omega}\right|_{\text{Rayleigh}}=r_0^2\frac{(\hbar\omega)^4}{m^2}\left|\sum_N\frac{\left\langle F\middle|\vec{p}\cdot\vec{\epsilon}_f^*\middle|N\right\rangle\langle N|\vec{p}\cdot\vec{\epsilon}_i|I\rangle+\langle F|\vec{p}\cdot\vec{\epsilon}_i|N\rangle\left\langle N\middle|\vec{p}\cdot\epsilon_f^*\middle|I\right\rangle}{(E_I-E_N)^3}\right|^2$$

special case 2: Thomson scattering: $\hbar\omega_i\gg E_I-E_N$. The photon energy is much bigger than the binding energy $\rightarrow$ free electron. We do not care about ionization. In this case the term with $\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*$ is dominant:

$$\frac{d\sigma}{d\Omega}=r_0^2\left|\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*\right|^2$$

for unpolarized photons.

$$\left|\vec{\epsilon}_i\cdot\vec{\epsilon}_f^*\right|^2=\frac{1}{2}\sum_{\lambda_i\lambda_f}\epsilon_j(k_i,\lambda_i)\epsilon_j^*(k_f,\lambda_f)\epsilon_l^*(k_i,\lambda_i)\epsilon_l(k_f,\lambda_f)=\frac{1}{2}\left(\delta_{jl}-\frac{(k_i)_j(k_i)_l}{k_i^2}\right)\left(\delta_{jl}-\frac{(k_f)_j(k_f)_l}{k_f^2}\right)$$

$$=\frac{1}{2}\left(3-1-1+\frac{(\vec{k}_i\cdot\vec{k}_f)^2}{\vec{k}_i^2\cdot\vec{k}_f^2}\right)=\frac{1}{2}\left(1+\cos^2\theta\right)$$

The total cross section is then:

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = r_0^2 \int d\Omega \frac{1}{2} \left(+ + \cos^2\theta\right) = \frac{8\pi}{3} r_0^2$$

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9 Second quantisation

We go from a classical field theory of classical fields (results of Schrödinger equation but not 2^{nd} quantized) to 2^{nd} quantised fields. (as for radiation field Chapter $5 \to 8$)

9.1 Creation and annihilation operators

Before we had for the radiation field $\hat{a}_{k,\lambda}$ and $\hat{a}^\dagger_{k,\lambda}$. We now make the index k, λ discrete (for a while): we call the new indices i and j which contain $k, \lambda, ...$: $\hat{a}_i, \hat{a}^\dagger_j$. In the case of bosons, these operators satisfy commutation relations:

$$\underline{\text{Bosons:}}\ [\hat{a}_i, \hat{a}_j] = \left[\hat{a}^\dagger_i, \hat{a}^\dagger_j\right] = 0 \text{ and } \left[\hat{a}_i, \hat{a}^\dagger_j\right] = \delta_{ij}$$

We then have states

$$|n_1, n_2, ..., n_m\rangle = \frac{\left(\hat{a}^\dagger_1\right)^{n_1} \cdots \left(\hat{a}^\dagger_m\right)^{n_m}}{\sqrt{n_1! \cdots n_m!}} |0\rangle \qquad\qquad \hat{a}_i |0\rangle = 0$$

For fermions we get anticommutation relations: we have to replace all the $[\ \ ,\ \ ] = [\ \ ,\ \ ]_-$ with $\{\ \ ,\ \ \} = [\ \ ,\ \ ]_+$: the only thing that changes, is that the minus becomes a plus: $AB - BA \to AB + BA$. For the next few minutes we will use $\hat{a}$ for bosons and $\hat{b}$ for fermions.

$$\underline{\text{Fermions}}\text{: } \left\{\hat{b}_i, \hat{b}_j\right\} = \left\{\hat{b}^\dagger_i, \hat{b}^\dagger_j\right\} = 0 \text{ e.g. } \hat{b}^\dagger_i \hat{b}^\dagger_i + \hat{b}^\dagger_i \hat{b}^\dagger_i = 0$$

$$\implies \left(\hat{b}^\dagger_i\right)^2 = 0 \implies n_i \in \{0, 1\} \text{ (Pauli principle)}$$

$$\text{and } \left\{\hat{b}_i, \hat{b}^\dagger_j\right\} = \delta_{ij}$$

for a particular i: $|1\rangle = \hat{b}^\dagger |0\rangle$ and then $\hat{b}^\dagger |1\rangle = \left(\hat{b}^\dagger\right)^2 |0\rangle = 0$

for some i and j: $|n_i = 1, n_j = 1\rangle = \hat{b}^\dagger_i \hat{b}^\dagger_j |0\rangle = -\hat{b}^\dagger_j \hat{b}^\dagger_i |0\rangle = -|n_j = 1, n_i = 1\rangle$

$$\text{cp. } \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_1(1) & \Psi_1(2) \\ \Psi_2(1) & \Psi_2(2) \end{vmatrix} \text{ for non-interacting fermions (Hartree-Fock)}$$

orthogonality of states: $\langle n_1, n_2, ..., n_m | n'_1, n'_2, ..., n'_m\rangle = \delta_{n_1, n'_1} \cdots \delta_{n_m, n'_m}$
completeness relation: $\mathbb{I} = \sum_{n_i} |n_1, ..., n_m\rangle\langle n_1, ..., n_m|$
counting operator: $n = \sum_i n_i = \sum_i \hat{b}^\dagger_i \hat{b}_i$
Second quantization: Take a "classical" wave function and make it an operator in the Fock space.

9.2 Field operators

Hats are used for operators in the Fock space. Let $\Psi_i(x)$ be a one-particle wave-function, which can be thought of as a coordinate representation of a state $|i\rangle$:

$$\Psi_i(x) = \langle x | i\rangle$$

We now take these Ψ_i as a basis of the Hilbert space:

$$\int d^3\vec{x}\;\; \Psi_j^*(x)\Psi_i(x) = \delta_{ij}$$

we can think of these Ψ_i as being something like plane waves: $\Psi_i(x) \sim e^{-i\vec{k}_i\cdot\vec{x}}$.
We now take these Ψ_i as eigenvectors of the Hamilton-operator H: $H\Psi_i(x) = E_i\Psi_i(x)$.
Now we consider a general state $|f\rangle$: $f(x) \in L^2(\mathbb{R}^3)\otimes\mathbb{C}^n$. We then expand this state in the basis Ψ_i:

$$f(x) = \sum_i c_i\Psi_i(x) = \int d^3y f(y)\sum_i \Psi_i(x)\Psi_i(y) \quad \text{with} \quad c_i = \int d^3y f(y)\Psi_i^*(y)$$

from which we conclude

$$\sum_i \Psi_i(x)\Psi_i(y) = \delta(x-y) \tag{9}$$

The Field operator (operator valued function):

$$\hat{\Psi}(x) = \sum_i \hat{a}_i\Psi_i(x) \qquad\qquad \hat{\Psi}^\dagger(x) = \sum_i \hat{a}_i^\dagger\Psi_i^*(x)$$

which is an operator in Fock space and where the $\hat{a}_i$ are fermionic or bosonic creation/annihilation operators.
Now: $\hat{\Psi}^\dagger(x)\,|0\rangle = \underbrace{\sum_j |j\rangle\langle j|}_{\mathbb{I}} \sum_i \hat{a}_i^\dagger\,|0\rangle\,\Psi_i^*(x)$. We then use $|j\rangle = \hat{a}_j^\dagger\,|0\rangle$ and $\langle j| = \langle 0|\,\hat{a}_j$. Then we get

$$\sum_{ij}|j\rangle\left\langle 0\left|\underbrace{\hat{a}_j\hat{a}_i^\dagger}_{[\hat{a}_j,\hat{a}_i^\dagger]_\pm \mp \hat{a}_i^\dagger\hat{a}_j = \delta_{ij}}\right|0\right\rangle\Psi_i^*(x) = \sum_i |i\rangle\,\Psi_i^*(x) = \sum_i |i\rangle\langle i|x\rangle = |x\rangle.$$

So this field operator creates a particle at the position x.
$\hat{\Psi}^\dagger(x)$ creates a particle localized at the position x
$\hat{\Psi}(x)$ annihilates a particle localized at the position x
Commutation realtions of field operators:

$$\left[\hat{\Psi}(x),\hat{\Psi}(y)\right]_\pm = 0 = \left[\hat{\Psi}^\dagger(x),\hat{\Psi}^\dagger(y)\right]_\pm$$

$$\left[\hat{\Psi}(x),\hat{\Psi}^\dagger(y)\right]_\pm = \sum_{ij}\Psi_i(x)\Psi_j^*(y)\underbrace{\left[\hat{a}_i,\hat{a}_j^\dagger\right]_\pm}_{\delta_{ij}} = \sum_i \Psi_i(x)\Psi_i^*(y) = \delta(x-y)$$

where we have used Eq. (9). Many particle states:

$$|x_1,x_2,...,x_n\rangle = \frac{1}{\sqrt{n!}}\hat{\Psi}^\dagger(x_1)\cdots\hat{\Psi}^\dagger(x_n)\,|0\rangle$$

Example: two non-interacting particles (bosons/fermions) at x_1, x_2:

$$\Psi_{ij}(x_1,x_2) = \langle x_1,x_2|i,j\rangle = \frac{1}{\sqrt{2}}\left\langle 0\left|\hat{\Psi}(x_2)\hat{\Psi}(x_1)\hat{a}_i^\dagger\hat{a}_j^\dagger\right|0\right\rangle = \frac{1}{\sqrt{2!}}\sum_{n,m}\left\langle 0\left|\hat{a}_m\hat{a}_n\hat{a}_i^\dagger\hat{a}_j^\dagger\right|0\right\rangle\Psi_m(x_2)\Psi_n(x_1)$$

$$\delta_{ni}\delta_{mj} \pm \delta_{nj}\delta_{mi}\begin{cases}\text{bosons}\\ \text{fermions}\end{cases}$$

$$= \frac{1}{\sqrt{2}}\left(\Psi_j(x_2)\Psi_i(x_1) \pm \Psi_i(x_2)\Psi_j(x_1)\right)\begin{cases}\text{symmetric bosons}\\ \text{antisymmetric fermions}\end{cases}$$

$$\hat{\Psi}^\dagger : \mathcal{H}_n \to \mathcal{H}_{n+1}$$
$$\hat{\Psi} : \mathcal{H}_n \to \mathcal{H}_{n-1}$$

Fock space:

$$\mathcal{F} = \bigoplus_{n=0}^{\infty} \mathcal{H}_n = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_2 \oplus ....$$

General state:

$$|f\rangle = \{|f_0\rangle, |f_1\rangle, ..., |f_n\rangle_n, 0...0...\}$$

Scalar product:

$$\langle f'|f\rangle = \sum_{i=1}^{n} \langle f_i'|f_i\rangle$$

9.3 Observables in 2^{nd} quantization

Observables are expressed in terms of fields → observables are operators in the Fock space $\mathcal{F}$
Example: particle number density
The $\rho(x) = |\Psi(x)|^2$ from QM1 becomes $\hat{\rho}(x) = \hat{\Psi}^\dagger(x)\hat{\Psi}(x) = \sum_{ij} \hat{a}_i^\dagger \Psi_i^*(x)\hat{a}_j\Psi_j(x) = \sum_{ij} \hat{a}_i^\dagger \hat{a}_j \langle x|i\rangle \langle j|x\rangle$
We then get

$$\int d^3\vec{x}\hat{\rho}(x) = \sum_{ij} \hat{a}_i^\dagger \hat{a}_j \int d^3\vec{x} \langle j|x\rangle \langle x|i\rangle = \sum_{ij} \hat{a}_i^\dagger \hat{a}_j \langle j|i\rangle = \sum_i \hat{a}_i^\dagger \hat{a}_i$$

Example: kinetic energy, free particle

$$\hat{T} = \int d^3x \hat{\Psi}^\dagger(x) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \hat{\Psi}(x) = ... = \sum_i E_i \hat{a}_i^\dagger \hat{a}_i$$

with $\hat{\Psi}(x) = \sum \hat{a}_i \Psi_i(x)$ and $E_i = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m}$ expectation value:

$$\left\langle n_1, ..., n_m \middle| \hat{T} \middle| n_1, ..., n_m \right\rangle = ... = \sum_{j=1}^{m} E_j n_j$$

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$$\hat{\Psi}(x) = \sum_i \hat{a}_i \Psi_i(x)$$
$$\hat{\Psi}^\dagger(x) = \sum_i \hat{a}_i^\dagger \Psi_i^*(x)$$
$$\hat{\Psi}(x) = \int \frac{d^3\vec{k}}{(2\pi)^3} \hat{a}_k e^{-i\vec{k}\cdot\vec{x}}$$

In case of a photon, we also have to sum over λ, not only over k

$$\hat{\Psi}^\dagger(x) = \int \frac{d^3\vec{k}}{(2\pi)^3} \hat{a}_{\vec{k}}^\dagger e^{i\vec{k}\cdot\vec{x}}$$

Kinetic energy:

$$\hat{T} = \int d^3\vec{x}\hat{\Psi}^\dagger(x) \left(-\frac{\hbar^2}{2m}\nabla^2\right) \hat{\Psi}(x) = \int \frac{d^3\vec{k}}{(2\pi)^3} \int \frac{d^3\vec{k}'}{(2\pi)^3} \underbrace{\int d^3\vec{x} e^{i\vec{x}(\vec{k}-\vec{k}')}}_{(2\pi)^3\delta(\vec{k}-\vec{k}')} \hat{a}_k^\dagger \hat{a}_{k'} \frac{+\hbar^2 k^2}{2m}$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \underbrace{\frac{\hbar^2 k^2}{2m}}_{\text{energy of 1 quantum of momentum } \vec{k}} \underbrace{\hat{a}_k^\dagger \hat{a}_k}_{\#\text{ of quanta of momentum } \vec{k}}$$

Interaction in external potential $U(x) = \int \frac{d^3\vec{q}}{(2\pi)^3} e^{-i\vec{q}\cdot\vec{x}} \tilde{U}(\vec{q})$. Then:

$$\hat{U} = \int d^3\vec{x} \hat{\Psi}^\dagger(x) U(x) \hat{\Psi}(x) = \int \frac{d^3\vec{k}}{(2\pi)^3} \int \frac{d^3\vec{k}'}{(2\pi)^3} \int \frac{d^3\vec{q}}{(2\pi)^3} \underbrace{\int d^3\vec{x} e^{i\vec{x}\cdot(\vec{k}-\vec{k}'-\vec{q})}}_{(2\pi)^3\delta(\vec{k}-\vec{k}'-\vec{q})} \hat{a}_k^\dagger \hat{a}_{k'} \tilde{U}(q)$$

$$= \int \frac{d^3\vec{k}}{(2\pi)^3} \int \frac{d^3\vec{k}'}{(2\pi)^3} \hat{a}_k^\dagger \hat{a}_{k'} \tilde{U}(\vec{k}-\vec{k}')$$

or :

$$V(x_1, x_2) = V(x_1 - x_2) = \int \frac{d^3\vec{q}}{(2\pi)^3} e^{-\vec{q}(\vec{x}_1 - \vec{x}_2)} \tilde{V}(\vec{q})$$

$$V = \frac{1}{2} \int d^3x_1 \int d^3x_2 \Psi^\dagger(x_1) \Psi^\dagger(x_2) V(x_1, x_2) \Psi(x_1) \Psi(x_2)$$

$$\to \hat{V} = \frac{1}{2} \int d^3x_1 \int d^3x_2 \hat{\Psi}^\dagger(x_1) \hat{\Psi}^\dagger(x_2) V(x_1, x_2) \hat{\Psi}(x_1) \hat{\Psi}(x_2)$$

$$= \frac{1}{2} \int \prod_{i=1}^{4} \frac{d^3k_i}{(2\pi)^3} \int \frac{d^3\vec{q}}{(2\pi)^3} \hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger \hat{a}_{k_3} \hat{a}_{k_4} \tilde{V}(\vec{q}) \int d^3\vec{x}_1 \int d^3\vec{x}_2 e^{i\vec{x}_1\cdot(\vec{k}_1 - \vec{k}_3 - \vec{q})} e^{i\vec{x}_2\cdot(\vec{k}_2 - \vec{k}_4 + \vec{q})}$$

we get two δ-functions from the exponentials: $(2\pi)^3\delta(\vec{k}_1 - \vec{k}_3 - \vec{q})$ and $(2\pi)^3\delta(\vec{k}_2 - \vec{k}_4 + \vec{q})$:

$$= \frac{1}{2} \int \frac{d\vec{k}_1}{(2\pi)^3} \frac{d\vec{k}_2}{(2\pi)^3} \frac{d\vec{q}}{(2\pi)^3} \hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger \hat{a}_{\vec{k}_1 - \vec{q}} \hat{a}_{\vec{k}_2 + \vec{q}} \tilde{V}(\vec{q})$$

If there was an exercise sheet 12, it would ask us to derive the Hartree-Fock-approximation from this. The creation-annihilation operators give you the 2 terms of the Hartree-Fock (exchange term!).
From the (anti)commutation relations of the field operators

$$\left[\hat{\Psi}(x), \hat{\Psi}^\dagger(y)\right]_\pm = \int \frac{d^3\vec{k}}{(2\pi)^3} \int \frac{d^3\vec{k}'}{(2\pi)^3} e^{-i\vec{k}\cdot\vec{x}} e^{+i\vec{k}'\cdot\vec{y}} \underbrace{\left[\hat{a}_k, \hat{a}_{k'}^\dagger\right]_\pm}_{(2\pi)^3\delta(\vec{k}-\vec{k}')} =^! \delta(x-y)$$

If the commutator of $\hat{a}_k$ and $\hat{a}_{k'}^\dagger$ has exactly this value, we get the $\delta(x-y)$ by integration over $\vec{k}$. Compare radiation field $\left[\hat{a}_k, \hat{a}_{k'}^\dagger\right]_\pm = (2\pi)^3\delta(\vec{k}-\vec{k}')$: continuum version of $\left[\hat{a}_i, \hat{a}_j^\dagger\right]_\pm = \delta_{ij}$.
<u>time dependence</u>:

$$\underbrace{\hat{\Psi}(t,x)}_{\text{Heisenberg picture (operator, } \underline{\text{not}} \text{ state)}} = \exp\left(\frac{i}{\hbar}Ht\right) \underbrace{\hat{\Psi}(x)}_{\text{Schrödinger}} \exp\left(-\frac{i}{\hbar}Ht\right)$$

This then leads to

$$i\hbar\frac{\partial}{\partial t}\hat{\Psi}(t,\vec{x}) = -\left[\hat{H}, \hat{\Psi}(t,\vec{x})\right] = \exp\left(\frac{i}{\hbar}\hat{H}t\right)\left[\hat{H}, \hat{\Psi}(x)\right]\exp\left(-\frac{i}{\hbar}\hat{H}t\right)$$

take free case $\hat{H} \to \hat{T}$:

$$\left[\hat{T}, \hat{\Psi}(x)\right] = \int d^3\vec{y} \frac{\hbar^2}{2m}\left[\nabla_{(y)}\hat{\Psi}^\dagger(x)\nabla_{(y)}\hat{\Psi}(y), \hat{\Psi}(x)\right] = \cdots = \frac{\hbar^2}{2m}\nabla^2\hat{\Psi}(x)$$

Then:

$$i\hbar\frac{\partial}{\partial t}\hat{\Psi}(t,x) = -\frac{\hbar^2}{2m}\nabla^2\hat{\Psi}(t,x)$$

31.05.18

10 Quantum statistical mechanics

This is a crash course on quantum statistical mechanics. Normally this would be 5 lectures, but this time it's shorter. Up until now we studied systems with a few particles 1,2,...10,.... Now we will study really large systems (10^{23} particles). We will look at the impact of quantum mechanics on these systems. If you want to think about something concrete: think about an ideal gas. For example, we have a box with a lot of particles in there, the box has a specific set of energy levels, and we want to find out which energy levels are likely to be occupied. We take N (large!) particles (non-interacting or very weakly interacting). We put in a box (or another system) with border length L, Volume $V = L^3$. Each particle has $\vec{p} = \frac{\hbar\pi}{L}\vec{n}$ with $\vec{n} = (n_x, n_y, n_z)$. They then have $E_{\vec{n}} = \frac{\hbar^2\pi^2}{2mL^2}\vec{n}^2$ We want to find out information about the system with total number of particles fixed, Volume fixed, we want to find out the most likely occupation numbers of the $E_{\vec{n}}$.
First we assume these particles are classical, as a reminder of the principles. Classical particles are distinguishable. Secondly, we look at the case that the particles are fermions. Thirdly we look at the case of bosons.
We look at this in the microcanonical ensemble, which means we fix V, N, and the energy is in the range $[E, E + dE]$. It is assumed we already know that every state with same total energy is equally probable. The only information about QM comes in when we start counting how many states there are and how they are occupied.
We classify the states: $|N_{\vec{n}_1}, N_{\vec{n}_2}, N_{\vec{n}_3}, ...\rangle = |N_1, N_2, ...\rangle$. The sum of all these N_i is N: $\sum N_i = N$. $N_{\vec{n}_1} = N_1$ is the number of particles in the state with $E_{\vec{n}_1}(E_1)$. The total energy of this state is $E = \sum_i N_i E_i$ and $N = \sum_i N_i$. We will now count how many states there are, given $E + dE$. When we are counting, QM enters.
In general we have a system with one-particle energies E_i, degeneracy d_i. We denote by $W(N_1, N_2, ...)$ the number states with N_i particles of energy E_i.

Classical/Distinguishable case
This will then give us the Maxwell-Boltzmann-Distribution.

$$W_{\text{cl}}(N_1, N_2, ...) = \binom{N}{N_1} d_1^{N_1} \cdot \binom{N - N_1}{N_2} d_2^{N_2} \cdots = \frac{N! d_1^{N_1}}{N_1 (N - N_1)!} \cdot \frac{(N - N_1)! d_2^{N_2}}{N_2! (N - N_1 - N_2)!} \cdots$$

The binomial coefficient represents that we pick N_1 out ouf N, put them into E_1 "box", with d_1 possibilities, and so on. Many terms cancel (for example $(N - N_1)!$), so we are then left with the following:

$$W_{\text{cl}}(N_1, N_2, ...) = N! \prod_i \frac{d_i^{N_i}}{N_i!}$$

It counts states that are produced by swapping two identical particles as distinguishable.

Fermions: not distinguishable particles, wave function completely antisymmetric. → just one completely antisymmetric combination.

$$W_{\text{f}}(N_1, N_2, ...) = \binom{d_1}{N_1}\binom{d_2}{N_2} \cdots = \prod_i \frac{d_i!}{N_i!(d_i - N_i)!}$$

The binomial coefficient represents that we pick the N_1 (out of d_1) states with E_1 that are occupied. Each occupied state is occupied only once. (fermions)

Bosons: Now each states can be occupied many times. Here we have N_1 particles in d_1 boxes: $\binom{N_1+d_1-1}{N_1}$. Because of the particles we have N_1 $\otimes$ and because of the d_1 we have $d_1 - 1$ walls $\|$

$$\otimes\otimes\|\cdots\|\otimes\cdots\|\otimes$$

So we have to arange in $(N_1 + d_1 - 1)$ objects, $N_1!$ is the possibilities to swap the $\otimes$, $(d_1 - 1)!$ is the number of possibilities to arange the $\|$. From all the places we choose the N_i places where we put the $\otimes$. We then get:

$$W_{\mathrm{b}}(N_1, N_2, ...) = \prod_i \frac{(N_i + d_i - 1)!}{N_i!(d_i - 1)!}$$

Since all the states are equally probable, the system is most likely in the state with most options.

So we have to maximize $W(N_i)$ under the constraints $\sum_i N_i = N$ and $\sum E_i N_i = E$. We will maximize $\ln W(N_i)$ instead of the function itself, since the maximum stays at the same position, but it is easier to maximize since it transform the products into sums. We will use Lagrange multipliers.

$$F = \ln W + \alpha\left(N - \sum_n N_n\right) + \beta\left(E - \sum_n E_n N_n\right) \to \frac{\partial F}{\partial N_n} = 0$$

where the α and β are the Lagrange multipliers.
We will often use Stirlings approximation: $\ln(N_n!) \approx N_n \ln N_n - N_n$. For the classical case we get:

$$\ln W_{\mathrm{cl}} = \ln N! + \sum_n (N_n \ln d_n - N_n \ln N_n + N_n)$$

$$\frac{\partial F}{\partial N_n} = \ln d_n - \ln N_n - \alpha - \beta E_n = 0$$

$$\to N_n = d_n e^{-(\alpha+\beta E_n)}$$

α, β are the Lagrange multipliers. They are given by the constraints. This is the case of classical statistical mechanics. Here we have $\alpha = \frac{1}{kT}$ and $\beta = -\frac{\mu}{kT}$, where k is the Boltzmann constant and μ is the chemical potential. Then divide by d_n:

$$\boxed{n(E) = e^{-(E-\mu)/(kT)}} \qquad \text{Maxwell-Boltzmann distribution}$$

Now we can do exactly the same thing for bosons and fermions.
Fermions:

$$W_{\mathrm{f}} = \prod_n \frac{d_n!}{N_n!(d_n - N_n)!}$$

$$\frac{\partial F}{\partial N_n} = 0 = -\ln N_n + \ln(d_n - N_n) - \alpha - \beta E_n$$

$$\to N_n = \frac{d_n}{e^{\alpha+\beta E_n} + 1} \implies \boxed{n(E) = \frac{1}{e^{\frac{E-\mu}{kT}} + 1}} \qquad \text{Fermi-Dirac-distribution}$$

For $T \to 0$, we get a step function that jumps from 1 to 0 at μ:

$$n(E) = \begin{cases} 0 & E > \mu(0) \\ 1 & E < \mu(0) \end{cases}$$

For $T = 0$, the chemical potential is equal to the Fermi energy: $E_F = \mu(0)$
Bosons:

$$W_\mathrm{b} = \prod_n \frac{(N_n + d_n - 1)!}{N_n!(d_n - 1)!}$$

$$\frac{\partial F}{\partial N_n} = \ln(N_n + d_n - 1) - \ln N_n - \alpha - \beta E_n$$

$$\to N_n = \frac{d_n - 1}{e^{\alpha+\beta E_n} - 1} \to \frac{d_n}{e^{\alpha+\beta E_n} - 1}$$

$$\implies \boxed{\frac{1}{e^{(E-\mu)/(kT)} - 1}} \qquad \text{Bose-Einstein-distribution}$$

For $T < T_\mathrm{crit}$, bosons tend to cluster in the ground state. This then leads to the Bose-Einstein condensation.
This is the end of quantum mechanics.

11 Exam

30 minutes, oral, written on sheet of paper, not on blackboard. Structure: first 2 random weekly problems. We should know how to solve the problems and show that we understood, algebraic details less important. His favourite questions are those involving slight alterations of the problems. Then after that, there are two random other topics. He wants us to show that we have understood the concepts of the topics. Short deviations are possible, long calculations unlikely.
UZH: 25.6.18 default language: English, if wanted: German, marks: the day after, or two days after
ETH: first or third week of examination period. Language: English, not a language exam. He is not allowed to tell the marks to students.