Quantum Mechanics II
Solution Sheet 4

FS 09
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Exercise 4.1 Formalism of time-dependent perturbation theory

a) Using the definition of the time-ordering in the integral we find

$$\begin{aligned}
&\frac{1}{n!}\iiint_{t_0}^{t} dt_1 dt_2 \cdots dt_n T\left\{H(t_1)H(t_2)\cdots H(t_n)\right\} = \\
=\;&\frac{1}{n!}\iiint_{t_0}^{t} dt_1 dt_2 \cdots dt_n \left\{H(t_1)H(t_2)\cdots H(t_n)\Theta(t_1 > t_2 > \cdots > t_n)+\right. \\
&+ H(t_2)H(t_1)\cdots H(t_n)\Theta(t_2 > t_1 > \cdots > t_n) \\
&+ \left.\ldots\right\}
\end{aligned}$$

where $\Theta(\ldots)$ is a generalized step-function which is 1 if the argument is true and 0 otherwise.

The integrand in the above equation contains $n!$ terms (= number of ways to order n times) and applying an appropriate transformation of coordinates one sees that they're all the same. Therefore, we can pick the first one and find

$$\begin{aligned}
\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n H(t_1)H(t_2)\cdots H(t_n)\Theta(t_1 > t_2 > \cdots > t_n) &= \\
= \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n H(t_1)H(t_2)\cdots H(t_n).&
\end{aligned}$$

This proves the first equality.

b) To show that

$$|\Psi, t\rangle = T\left\{\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')\right]\right\}|\Psi, t_0\rangle \tag{1}$$

really solves the Schrödinger equation, we need to use the definition of the time-ordered exponential:

$$\begin{aligned}
&T\left\{\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt' H(t')\right]\right\}|\Psi, t_0\rangle \\
&= \left(1 + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n \iiint_{t_0}^{t} dt_1 dt_2 \cdots dt_n \frac{T\left\{H(t_1)H(t_2)\cdots H(t_n)\right\}}{n!}\right)|\Psi, t_0\rangle \qquad (2)\\
&= \left(1 + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 H(t_1)\int_{t_0}^{t_1} dt_2 H(t_2)\cdots \int_{t_0}^{t_{n-1}} dt_n H(t_n)\right)|\Psi, t_0\rangle \qquad (3)
\end{aligned}$$

On this expression, we can now easily apply a time derivation,

$$\partial_t|\Psi, t\rangle = -\frac{i}{\hbar}\left(H(t) + \sum_{n=2}^{\infty} H(t)\left(\frac{-i}{\hbar}\right)^{n-1}\int_{t_0}^{t} dt_2 H(t_2)\int_{t_0}^{t_2} dt_3 H(t_3)\cdots\int_{t_0}^{t_{n-1}} dt_n H(t_n)\right)|\Psi, t_0\rangle. \tag{4}$$

Taking $H(t)$ out of the brackets, we end up with the Schrödinger equation,

$$i\hbar\partial_t|\Psi, t\rangle = H(t)|\Psi, t\rangle. \tag{5}$$

c) For a closed system, the Hamiltonian is time-independent, $\partial_t H = 0$. Therefore, we can drop the time-ordering in eq. 2. The integrals are thus trivial and we find

$$
\begin{aligned}
|\Psi, t\rangle &= \left(1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \frac{H^n}{n!} \iiint_{t_0}^{t} dt_1 dt_2 \cdots dt_n \right) |\Psi, t_0\rangle \\
&= \left(1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \frac{H^n}{n!} (t - t_0)^n \right) |\Psi, t_0\rangle \\
&= \exp\left[-\frac{i}{\hbar} H (t - t_0)\right] |\Psi, t_0\rangle. \qquad (6)
\end{aligned}
$$

Exercise 4.2 Hydrogen atom in an electric field

The perturbing Hamiltonian is $\delta H(t) = -e\mathcal{E}_0 e^{-t/\tau} \hat{z} \Theta(t)$ with $\Theta(t)$ the Heaviside step-function.

a) As we already saw for the Stark effect, $\delta H(t)$ commutes with the angular momentum operator L_z and thus only transitions between states with the same angular momentum are allowed. Since we are starting from the ground state, $|n = 1, l = 0, m = 0\rangle$, this means only transitions between the $m = 0$ states can occur. In addition, δH changes the parity and therefore, only states with l odd are allowed.
Note: We will see later (using the so-called 'Wigner-Eckart-Theorem') that actually only transitions are allowed that change l by 1, i.e. $l \mapsto l \pm 1$.

b) For the $n = 2$ state, this means that we can only find a transition to the state $|n = 2, l = 1, m = 0\rangle$. The first-order expression for the probability of this transition is

$$
\mathcal{P}_{1s \to 2p(t)} = \frac{e^2 \mathcal{E}_0^2}{\hbar^2} \left| \int_0^t dt' e^{i(E_2 - E_1)t'/\hbar} e^{-t'/\tau} \langle 2\ 1\ 0 | \hat{z} | 1\ 0\ 0 \rangle \right|^2 . \qquad (7)
$$

For the matrix element we find

$$
\begin{aligned}
\langle 2\ 1\ 0 | \hat{z} | 1\ 0\ 0 \rangle &= \frac{1}{\pi a_0^4 \sqrt{32}} \int_0^{\infty} dr r^4 e^{-3r/2a_0} \int d_\Omega (\cos\theta)^2 \\
&= a_0 \frac{1}{3\sqrt{2}} \left(\frac{2}{3}\right)^5 = a_0 \frac{256}{\sqrt{2} \times 243} \qquad (8)
\end{aligned}
$$

where a_0 is the Bohr radius.
Inserting this into the expression for the probability and performing the integration, we obtain

$$
\mathcal{P}_{1s \to 2p(t)} = \frac{e^2 \mathcal{E}_0^2 a_0^2}{\hbar^2} \left(\frac{256}{\sqrt{2} \times 243}\right)^2 \frac{1 - 2e^{-t/\tau} \cos\omega t + e^{-2t/\tau}}{1/\tau^2 + \omega^2} \qquad (9)
$$

with

$$
\omega = \frac{E_2 - E_1}{\hbar} = \frac{3e^2}{8\hbar a_0}. \qquad (10)
$$

For times $t \gg \tau$, the probability that a transition has happened is

$$
\mathcal{P}_{1s \to 2p(t)} \approx \frac{e^2 \mathcal{E}_0^2 a_0^2}{\hbar^2} \left(\frac{256}{\sqrt{2} \times 243}\right)^2 \frac{\tau^2}{1 + (\omega\tau)^2}. \qquad (11)
$$