Time-dependent Perturbation Theory

David Chen

November 20, 2009

Time dependent Schrödinger equation

$$\mathcal{H}(t)\left|\psi(t)\right\rangle = i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle \tag{1}$$

where $\mathcal{H}(t) \equiv \mathcal{H}_0 + W(t)$

Let us assume that we know the solution of the time independent Hamiltonian, i.e. $\mathcal{H}_0\left|n\right\rangle = E_n\left|n\right\rangle$. We can write $\left|\psi(t)\right\rangle$ in terms of this basis set $\{\left|n\right\rangle\}$

$$\left|\psi(t)\right\rangle = \sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left|n\right\rangle \tag{2}$$

Substituting eq. (2) into (1)

$$\begin{aligned}
\mathcal{H}_0\sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left|n\right\rangle + W(t)\sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left|n\right\rangle &= i\hbar\frac{\partial}{\partial t}\sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left|n\right\rangle \\
E_n\sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left|n\right\rangle + W(t)\sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left|n\right\rangle &= i\hbar\frac{\partial}{\partial t}\sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left|n\right\rangle
\end{aligned}$$

Projecting onto the state $\left\langle k\right|$

$$E_k b_k(t)e^{-i\frac{E_k}{\hbar}t} + \sum_n b_n(t)e^{-i\frac{E_n}{\hbar}t}\left\langle k\right|W(t)\left|n\right\rangle = i\hbar\frac{\partial}{\partial t}\left(b_k(t)e^{-i\frac{E_k}{\hbar}t}\right)$$

$$i\hbar\frac{\partial}{\partial t}b_k(t) = \sum_n W_{kn}(t)b_n(t)e^{i\omega_{kn}t} \tag{3}$$

where $W_{kn}(t) \equiv \left\langle k\right|W(t)\left|n\right\rangle$ and $\omega_{kn} \equiv (E_k - E_n)/\hbar$

We add a dimensionless parameter λ to keep track of the orders, and it is assumed small compared to 1. We look for a first order solution[1].

$$W_{kn}(t) \to \lambda W_{kn}(t)$$
$$b_k(t) \equiv b_k^{(0)}(t) + \lambda b_k^{(1)}(t) + \lambda^2 b_k^{(2)}(t) + ...$$

Order 0:

$$i\hbar \frac{\partial}{\partial t} b_k^{(0)}(t) = 0$$
$$b_k^{(0)}(t) = const.$$

Order 1:

$$i\hbar \frac{\partial}{\partial t} b_k^{(1)}(t) = \sum_n W_{kn}(t) b_n^{(0)}(t) e^{i\omega_{kn} t} \tag{4}$$

Order r:

$$i\hbar \frac{\partial}{\partial t} b_k^{(r)}(t) = \sum_n W_{kn}(t) b_n^{(r-1)}(t) e^{i\omega_{kn} t} \tag{5}$$

Initial conditions: let us assume that $|\psi(0)\rangle = |i\rangle$, i.e. $b_n(t=0) = \delta_{ni}$, which implies

$$b_n^{(0)}(t=0) = b_n^{(0)}(t) = \delta_{ni}$$
$$b_n^{(1)}(t=0) = 0$$
$$\vdots$$
$$b_n^{(r)}(t=0) = 0$$

Replacing the initial conditions into (6)

$$i\hbar \frac{\partial}{\partial t} b_k^{(1)}(t) = \sum_n W_{kn}(t) \delta_{ni} e^{i\omega_{kn} t}$$
$$i\hbar \frac{\partial}{\partial t} b_k^{(1)}(t) = W_{ki}(t) e^{i\omega_{ki} t}$$

[1]According to [2], this approximation can't be used for a narrow-band laser excitation, because of the large excited-state population. However, it seems to be valid for optical atomic transitions, as used in [**?**]

$$b_k^{(1)}(t) = \frac{1}{i\hbar}\int_0^t dt' W_{ki}(t') e^{i\omega_{ki}t'} \tag{6}$$

Therefore, the transition probability is

$$\boxed{\mathscr{P}_{i\to f}(t) \equiv |b_f^{(1)}(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t dt' \langle f| W(t') |i\rangle e^{i(E_f - E_i)t'/\hbar}\right|^2} \tag{7}$$

This calculation remains valid when $|b_k^{(r\geq 1)}| \ll 1$. In consequence, $\mathscr{P}_{i\to f}(t) \ll 1$

Transition to the continuum spectrum $|f >= |E, \alpha >$

$$\mathscr{P}(t) = \int dE d\alpha \mathscr{P}_{i\to\{E,\alpha\}}\rho(E) \tag{8}$$

Special Case

$W_{fi}(t) = W_{fi}e^{-i\omega t}$, where $W_{kn} \equiv \langle k| W |n\rangle$ is time-independent

$$\begin{aligned}\mathscr{P}_{i\to f}(t) &= \frac{|W_{fi}|^2}{\hbar^2}\left|\int_0^t dt' e^{-i\delta t'}\right|^2, \text{ where } \delta \equiv \omega - \omega_{fi} \\ &= \frac{|W_{fi}|^2}{\hbar^2}\left|\frac{1 - e^{-i\delta t}}{\delta}\right|^2 \\ &= \frac{4|W_{fi}|^2}{\hbar^2}\frac{\sin^2(\delta t/2)}{\delta^2}\end{aligned}$$

A necessary condition[1] for $\mathscr{P}_{i\to f}(t) \ll 1$ is $t \ll \hbar/|W_{fi}|$

$$\mathscr{P}(t) = \frac{4}{\hbar^2}\int_{-\infty}^{\infty} dE\, |\langle E| W |i\rangle|^2 \underbrace{\frac{\sin^2(\delta t/2)}{\delta^2}}_{\equiv F(\delta)} \rho(E), \text{ where } \delta = (E - E_i)/\hbar - \omega$$

The width of $F(\delta)$ is inversely proportional to t. As $t \to \infty$, $F(\delta)$ looks like a Dirac's delta. Usually $\rho(E)$ varies much slower.

$$\begin{aligned}\mathscr{P}(t) &= \frac{4}{\hbar}\left|\langle E_i + \hbar\omega| W |i\rangle\right|^2 \rho(E_i + \hbar\omega) \underbrace{\int_{-\infty}^{\infty} d\delta \frac{\sin^2(\delta t/2)}{\delta^2}}_{\pi t/2} \\ &= \frac{2\pi t}{\hbar}\left|\langle E_i + \hbar\omega| W |i\rangle\right|^2 \rho(E_i + \hbar\omega)\end{aligned}$$

where the integral $\int_{-\infty}^{\infty} d\alpha \sin^2(\alpha)/\alpha^2 = \pi$ was used.

$$\boxed{\Gamma \equiv \frac{d\mathscr{P}(t)}{dt} = \frac{2\pi}{\hbar} \left| \langle E_i + \hbar\omega | \, W \, | i \rangle \right|^2 \rho(E_i + \hbar\omega)} \tag{9}$$

References

[1] Cohen-Tannoudji, Quantum Mechanics vol. 2, Chapter XIII

[2] Metcaf & van der Straten, Laser Cooling and Trapping, p.4