Time-Dependent Perturbation

Consider a time-independent Hamiltonian $\hat{H}$, and suppose the system was in its ground state $|\Psi_0\rangle$,

$$\hat{H}|\Psi_0\rangle = E_0|\Psi_0\rangle. \tag{1}$$

Suppose that the system is perturbed by a small, time-dependent Hamiltonian, $\hat{V}(t)$, at $t > t_0$. The wave vector satisfies

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \left(\hat{H} + \hat{V}(t)\right)|\Psi(t)\rangle \tag{2}$$

We seek the solution of Eq.(2) in terms of the $\hat{S}$ matrix,

$$|\Psi(t)\rangle = e^{-i\hat{H}t/\hbar}\underbrace{\hat{S}(t,t_0)|\Psi_0\rangle}_{|\Psi_I(t)\rangle\text{ : Interaction picture}}. \tag{3}$$

Substituting Eq.(3) in (2),

$$\cancel{\hat{H}e^{-i\hat{H}t/\hbar}\hat{S}(t,t_0)|\Psi_0\rangle} + e^{-i\hat{H}t/\hbar}\left(i\hbar\frac{\partial}{\partial t}\right)\hat{S}(t,t_0)|\Psi_0\rangle$$

$$= \left(\cancel{\hat{H}} + \hat{V}(t)\right)e^{-i\hat{H}t/\hbar}\hat{S}(t,t_0)|\Psi_0\rangle$$

$e^{i\hat{H}t/\hbar} \times$ (above)

$$i\hbar\frac{\partial}{\partial t}\hat{S}(t,t_0)|\Psi_0\rangle = e^{i\hat{H}t/\hbar}\hat{V}(t)e^{-i\hat{H}t/\hbar}\hat{S}(t,t_0)|\Psi_0\rangle$$

∴ The $\hat{S}$ matrix should satisfy the differential equation

$$i\hbar \frac{\partial}{\partial t} \hat{S}(t,t_0) = \hat{V}_H(t)\, \hat{S}(t,t_0) \tag{4}$$

where

$$\hat{V}_H(t) = e^{iHt/\hbar}\, \hat{V}(t)\, e^{-i\hat{H}t/\hbar} \tag{5}$$

and the initial condition is

$$\hat{S}(t_0,t_0) = 1 \tag{6}$$

The formal solution to Eq.(4) is

$$\hat{S}(t,t_0) = T \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt'\, \hat{V}_H(t')\right) \tag{7}$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t} dt_n\, T[\hat{V}_H(t_1)\cdots\hat{V}_H(t_n)] \tag{8}$$

$$= \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n\, \hat{V}_H(t_1)\, \hat{V}_H(t_2)\cdots\hat{V}_H(t_n) \tag{9}$$

In the first order in $\hat{V}$,

$$\hat{S}(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} dt'\, \hat{V}_H(t') \;+\; O(\hat{V}^2) \tag{10}$$

or

$$|\Psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\Psi_0\rangle - \frac{i}{\hbar} e^{-i\hat{H}t/\hbar}\int_{t_0}^{t} dt'\, e^{i\hat{H}t'/\hbar}\, \hat{V}(t')\, e^{-i\hat{H}t'/\hbar}|\Psi_0\rangle \tag{11}$$

The expectation value of arbitrary operator $\hat{\theta}(t)$ is

$$\langle\hat{\theta}(t)\rangle = \langle\Psi(t)|\hat{\theta}(t)|\Psi(t)\rangle$$

$$= \left(\langle\Psi_0|e^{i\hat{H}t/\hbar} + \frac{i}{\hbar}\langle\Psi_0|\int_{t_0}^{t}dt'\, e^{i\hat{H}t'/\hbar}\hat{V}(t')e^{-i\hat{H}t'/\hbar}e^{i\hat{H}t/\hbar}\right)$$

$$\times\hat{\theta}(t)\left(e^{-i\hat{H}t/\hbar}|\Psi_0\rangle - \frac{i}{\hbar}e^{-i\hat{H}t/\hbar}\int_{t_0}^{t}dt'\, e^{i\hat{H}t'/\hbar}\hat{V}(t')e^{-i\hat{H}t'/\hbar}|\Psi_0\rangle\right)$$

$$= \langle\Psi_0|e^{i\hat{H}t/\hbar}\hat{\theta}(t)e^{-i\hat{H}t/\hbar}|\Psi_0\rangle$$

$$- \frac{i}{\hbar}\langle\Psi_0|e^{i\hat{H}t/\hbar}\hat{\theta}(t)e^{-i\hat{H}t/\hbar}\int_{t_0}^{t}dt'\,\hat{V}_H(t')|\Psi_0\rangle$$

$$+ \frac{i}{\hbar}\langle\Psi_0|\int_{t_0}^{t}dt'\,\hat{V}_H(t')e^{i\hat{H}t/\hbar}\hat{\theta}(t)e^{-i\hat{H}t/\hbar}|\Psi_0\rangle + O(\hat{V}^2)$$

$$= \langle\Psi_0|\hat{\theta}_H(t)|\Psi_0\rangle - \frac{i}{\hbar}\langle\Psi_0|\underbrace{\left[\hat{\theta}_H(t), \int_{t_0}^{t}dt'\,\hat{V}_H(t')\right]}_{\text{commutator}}|\Psi_0\rangle + O(\hat{V}^2) \qquad (11)$$

The first term in Eq. (11) is the unperturbed expectation value, and thus the linear response value is

$$\delta\langle\theta(t)\rangle = -\frac{i}{\hbar}\int_{t_0}^{t}dt'\,\langle\Psi_0|\left[\hat{\theta}_H(t), \hat{V}_H(t')\right]|\Psi_0\rangle \quad (t > t_0) \qquad (12)$$

$$= -\frac{i}{\hbar}\int_{-\infty}^{\infty}dt'\,\Theta(t-t')\langle\Psi_0|[\hat{\theta}_H(t), \hat{V}_H(t')]|\Psi_0\rangle \qquad (13)$$

– Density response function

Consider an external Hamiltonian coupling to density operator,

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) = \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r}) \tag{14}$$

,

such that

$$\hat{V}(t) = \int d\mathbf{r}\, \hat{n}(\mathbf{r})\, \varphi(\mathbf{r},t). \tag{15}$$

∴ The linear density response is

$$\delta\langle\hat{n}(\mathbf{r},t)\rangle = \frac{i}{\hbar}\int d\mathbf{r}'\int_{-\infty}^{\infty} dt'\, \Theta(t-t')\langle\Psi_0|[\hat{n}_H(\mathbf{r},t), \hat{n}_H(\mathbf{r}',t')]|\Psi_0\rangle \times \varphi(\mathbf{r}'t') \tag{16}$$

$$= \int d\mathbf{r}'\int_{-\infty}^{\infty} dt'\, \chi(\mathbf{r}-\mathbf{r}', t-t')\,\varphi(\mathbf{r}',t') \tag{17}$$

or

$$\frac{\delta\langle\hat{n}(\mathbf{r},t)\rangle}{\delta\varphi(\mathbf{r}',t)} = \chi(\mathbf{r}-\mathbf{r}', t-t') \tag{18}$$

where the density response function is

$$\chi(\mathbf{r}-\mathbf{r}', t-t') = -\frac{i}{\hbar}\Theta(t-t')\langle\Psi_0|[\hat{n}_H(\mathbf{r},t), \hat{n}_H(\mathbf{r}',t')]|\Psi_0\rangle \tag{19}$$